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Review

The chemistry of the carbon-transition metal double and triple bond: Annual survey covering the year 2013☆

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ABSTRACT

This is a review of papers published in the year 2013 that focus on the synthesis, reactivity, or properties of compounds containing a carbon-transition metal double or triple bond.

☆ For 2012, see J.W. Herndon, Coord. Chem. Rev. 272 (2014) 48.

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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 diazo decomposition are not covered, unless there is a major focus on the carbene complex intermediate. Several reviews in this area appeared in 2013 [1–3]. Although a determined effort has been made to include patents, in general only patents listed in the *Chemical Abstracts* sections titled Organometallics and Organometalloid Compounds, Inorganic Chemicals and Reactants, Physical Organic Chemistry, Organic Chemistry, Inorganic Chemistry, and Catalysis and Reaction Kinetics, have been included. Patents that appear in 2013 editions of *Chemical Abstracts* have been included. Only compounds which 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-donation component of these complexes is normally minimal, there is no formal carbon–metal multiple bond [4], however every effort has been made to include complexes where the back-bonding properties are discussed. Chemical applications and structural properties of NHC transition metal carbene complexes were reviewed several times in 2013 [5–18]. 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 [19] 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* [20] and the list of ligand acronyms in the Strem Catalog [21])

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 alkyl groups are assumed to be the straight-chain (*n*) isomer.

See also Scheme 1 for abbreviations for distinct modes of 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 2013. Many articles focusing on some aspect of carbene complex-initiated olefin metathesis were published, including the following specific subjects: (1) recent trends and challenges for metathesis reactions [22]; (2) recent advances in Z selective olefin metathesis [23,24]; (3) cationic ruthenium complexes in olefin metathesis [25]; (4) ruthenium olefin metathesis catalysts activated by electron withdrawing groups [26]; (5) stimuli-responsive olefin metathesis catalysts [27]; (6) olefin metathesis catalysts bearing unsymmetrical NHC ligands [28]; (7) ruthenium metathesis catalysts containing Schiff base ligands [29]; (8) polymer-supported ruthenium complexes for olefin metathesis [30]; (9) metal oxide (silica and alumina) supported tungsten and tantalum single-site metathesis catalysts (includes carbynes as well as carbenes) [31]; (10) mesoporous molecular sieves as supports for olefin metathesis catalysts [32]; (11) selected recent advances in the synthesis of bioactive molecules using olefin metathesis as a key step [33]; (12) formation of five- and six-membered ring heterocycles *via* RCM [34]; (13) cross metathesis in diene and polyene synthesis [35]; (14) synthesis of diverse bioactive molecules using enyne metathesis [36]; (15) the future of ADMET polymerization [37]; (16) recent advances in ADMET chemistry [38]; (17) tandem ROMP and vinyl insertion polymerization [39]; (18) ROMP of biocompatible monomers [40]; (19) ROMP using cyclobutene monomers [41]; (20) recent developments in the metathesis of unsaturated fatty acids [42]; (21) degradation of non-vulcanized natural rubber [43]; (22) olefin metathesis in aqueous media [44]; (23) olefin metathesis in a continuous flow mode [45]; (24) computational investigation of carbene complexes in homogeneous olefin metathesis [46]; (25) computational investigation of carbene complexes in heterogeneous olefin metathesis [47]; (26) research progress on metal–carbene complexes used in olefin metathesis [48]; (27) new developments in the use of metathesis for the synthesis of difficult carbon–carbon multiple bonds [49]; (28) metathesis polymerization for the synthesis of functionalized polymers for medicinal applications [50]; (29) olefin metathesis as a route to polymers with special structures [51]; and (30) synthesis of advanced functional materials through ROMP polymerization [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) synthetic α-amino acids [53]; (2) seven-membered ring carbocycles [54]; (3) furan and pyrroles [55]; (4) sultams [56]; (5) chiral perazamacrocycles [57]; (6) geldanamycin and radicicol analogs [58], (7) jasplakinolide [59]; (8) palmerolides [60]; (9) cylindrocyclophanes [61]; (10) allocolchicinoids [62]; (11) muscopyridines [63]; (12) the B ring of bryostatins [64]; (13) ripostatin B [65]; (14) carbocyclic nucleosides [66]; (15) heterocycles [67]; (16) polycyclic natural products [68]; (17) macrocyclic drugs [69]; (18) cyclic olefin derived polymers [70]; (19) ladderphanes [71]; (20) cyclic polymers [72]; (21) glycopolymer conjugates [73]; and (22) carotenoids [74].

Additional review articles include some segments on carbene complex-initiated olefin metathesis. Articles in this category focus on the following subjects: (1) non-metathesis reactions using olefin metathesis catalysts [75]; (2) the roles of step economy and function oriented synthesis in the ideal synthesis [76]; (3) strategies for the synthesis of alkaloids and novel nitrogen heterocycles [77]; (4) synthesis and applications of water-soluble NHC-transition metal complexes [78]; (5) use of strained alkenes in natural products synthesis [79]; (6) use of allenamides in organic synthesis [80]; (7) divergent pathways in natural products synthesis [81]; (8) recent developments in enantioselective multicatalyzed tandem reactions [82]; (9) a hybrid approach to new molecular scaffolds [83]; (10) transition metal-catalyzed carbon–carbon bond forming reactions using ethylene [84]; (11) diverse transformations of chiral alcohols generated by BINOL-catalyzed alkyne addition to aldehydes [85]; (12) recent development in bioorthogonal chemistry [86]; (13) polymer-supported transition metal catalysts [87]; (14) a renewable approach to thermosetting resins [88]; (15) external