



Review

The chemistry of the carbon-transition metal double and triple bond: Annual survey covering the year 2012[☆]

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ABSTRACT

This is a review of papers published in the year 2012 that focus on the synthesis, reactivity, or properties of compounds containing a carbon-transition metal double or triple bond.

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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 exhibited. Several reviews in this area appeared in 2012 [1–3]. Although a determined effort has been made to include patents, in general only patents listed in the section “Organometallics and Organometallic Compounds” or “Catalysis, Reaction Kinetics, and Inorganic Reaction Mechanisms” of *Chemical Abstracts* have been included. Patents that appear in 2012 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 usually minimal, there is no formal carbon-metal multiple bond [4]. The chemistry of NHC complexes was reviewed several times in 2012 [5–15], and a review of another class of stable carbene ligands, acyclic diaminocarbenes, was also reported [16]. Every effort has been made to include NHC complexes where there is some discussion of the π -acceptor ability of the NHC ligand. 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 [17] 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. Articles from the journals *Angewandte Chemie International Edition*, *Chemistry: A European Journal*, *Tetrahedron*, and *Tetrahedron Letters* are restricted to volumes 51, 18, 68, and 53 respectively, which covers the period of December 2011–December 2012 according to some search engines.

Abbreviations (see also the instructions for authors in the *Journal of Organic Chemistry* [18] and the list of ligand acronyms in the *Strem Catalog* [19]).

NHC
Grubbs catalyst I
Grubbs catalyst II
Grubbs catalyst III
Hoveyda–Grubbs catalyst
Zhan catalyst
Schrock catalyst

N-heterocyclic carbene
Structure 1 (Fig. 1)
Structure 2 (Fig. 1)
Structure 3 (Fig. 1)
Structure 4 (Fig. 1)
Structure 5 (Fig. 1)
Structure 6 (Fig. 1)

Tp'
Dipp
Tipp
E (as a substituent)

Tris(3,5-dimethylpyrazolyl)borate
2,6-Diisopropylphenyl
2,4,6-Triisopropylphenyl
COOMe

Unless otherwise indicated, all 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 2012. Many articles focusing on some aspect of carbene complex-initiated olefin metathesis were published, including the following specific subjects: (1) strategies and tactics in olefin metathesis [20]; (2) asymmetric olefin metathesis catalysts [21]; (3) selective olefin metathesis [22]; (4) Z selective olefin metathesis [23]; (5) olefin metathesis in the synthesis of tetrasubstituted alkenes [24]; (6) the development of ruthenium carbene complexes featuring chelating alkylidene ligands as olefin metathesis catalysts [25]; (7) pseudo-halide analogs of Grubbs- and Schrock-type catalysts [26]; (8) alkane metathesis through tandem alkane dehydrogenation followed by olefin metathesis and hydrogenation [27]; (9) olefin metathesis in the total synthesis of iriomoteolides [28]; (10) olefin metathesis in the total synthesis of kendomycin [29]; (11) olefin metathesis in the synthesis of vaneprevir [30]; (12) temporary silicon-tethered RCM [31]; (13) end functionalization of living ROMP polymers [32]; (14) ROMP in the synthesis of polymeric ladderphanes [33]; (15) alkene metathesis in the synthesis of conjugated polymers [34]; (16) strategies for removal of ruthenium residues from metathesis reactions [35]; (17) olefin metathesis of renewable platform chemicals [36]; (18) conversion of plant oils to chemicals using metathesis reactions [37]; (19) synthesis of polyesters through metathesis of long-chain fatty acid esters [38]; (20) olefin metathesis for the functionalization of superparamagnetic nanoparticles [39]; (21) latest advances in olefin metathesis catalysts [40]; (22) domino metathesis reactions in India [41]; (23) E and Z selective olefin metathesis [42]; (24) ROMP as a versatile method for the synthesis of polymeric materials [43]; (25) understanding applications of olefin metathesis reactions [44]; (26) new methodology for the asymmetric construction of chiral skeletons [45]; (27) front-line polymer science (metathesis focus) [46]; (28) progress in the synthesis of Grubbs catalysts [47]; (29) mesoporous media (alumina or molecular sieves) supported metathesis catalysts [48]; (30) application of the Grubbs catalyst for self-healing polymers [49]; (31) advances in the metatheses of long-chain aliphatic olefins [50]; (32) ring closing metathesis reactions using Tebbe and Petasis reagents [51]; and (33) reaction injection molding of dicyclopentadiene [52].

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