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Review

The chemistry of the carbon-transition metal double and triple bond: Annual survey covering the year 2017

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ABSTRACT

This is a review of papers published in the year 2017 that focus on the synthesis, reactivity, or properties of compounds containing a carbon-transition metal double or triple bond. Highlights for the year 2017 include: (1) significant advances in the design of new precursors to carbene complex intermediates that serve as safer alternatives to potentially hazardous diazo compounds, (2) continued vast employment of olefin metathesis for the synthesis of complex small molecules and polymers, including many examples of *Z*-selective and stereoretentive reactions, (3) design of novel transformations employing metallacumulene intermediates, (4) preparation of novel aromatic ring systems incorporating transition elements, and (5) design of reaction processes possibly invoking metal carbene complexes generated from platinum or gold complexes and alkynes.

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1. Introduction

This survey is intended to be a comprehensive summary of the synthesis, reactivity, or properties of compounds featuring a multiple bond between carbon and a transition metal (Group 3–Group 11 plus lanthanides and actinides)[1] extracted from articles published in 2017. This article represents a continuing annual survey on this topic that began publication in 1997 [3–22]. Although a determined effort has been made to include patents, in general only patents listed in the section "Organometallics and Organometallic

Abbreviations: 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); cAAC, cyclic alkyl(amino) carbene; Dipp, 2,6-diisopropylphenyl; E (as a substituent), COOMe (used only in excessively "crowded" drawings); Fc, ferrocenyl; Fur, 2-furyl; IMes, 2,5-dimesitylylimidazolylidene; IPr, 2,5-diisopropylimidazolylidene; Ind, η^5-indenyl; Mes, 2,4,6-trimethylphenyl or mesityl; MCM, mesoporous silica (Mobil Composition of Matter); mCPBA, 3-chloroperoxybenzoic acid; NHC, N-Heterocyclic Carbene; Ns, 4-nitrophenylsulfonyl (nosyl); SBA, Silica nanoparticles (Santa Barbara amorphous); SIMes, 3,4-dihydro-2,5-dimesitylylimidazolylidene; Tipp, 2,4,6-triisopropylphenyl; Tp, Tris(pyrazolyl)borate; Tp′, Tris(3,5-dimethylpyrazolyl)borate; Xyl, 2,6-dimethylphenyl.

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[1] Abbreviations see also the instructions for authors in the *Journal of Organic Chemistry* [1] and the list of ligand acronyms in the Strem Catalog [2]).

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Compounds" or "Catalysis, Reaction Kinetics, and Inorganic Reaction Mechanisms" of *Chemical Abstracts* have been included. Only compounds which feature a multiple bond between a single carbon atom and a single transition metal are featured in this survey, thus bridging carbene and carbyne complexes are not covered unless there is a multiple bond to at least one transition metal. Transition metal NHC complexes (or Arduengo carbene complexes) have not generally been included. Since the π-acceptor component of these complexes is usually minimal, there is no formal carbon-metal multiple bond [23]. The chemistry of NHC metal complexes was reviewed several times in 2017, including the following topics: (1) quantifying and understanding the steric properties of NHC ligands [24], (2) theoretical NMR spectroscopy of NHCs and their metal complexes [25], (3) recent advances in syntheses and applications of imidazole NHC metal complexes (in Chinese) [26], (4) immobilization of NHC compounds [27], (5) carbohydrate-containing NHC metal complexes [28], (6) organometallic chemistry of bis(NHC) ligands containing a heteroarene spacer [29], (7) catalytic transformations enabled by bidentate NHCs bearing anionic substituents (tethered NHCs) [30], (8) metallosupramolecular architectures obtained from poly-NHC ligands [31], (9) abnormal triazole-derived NHC complexes [32], (10) metal complexes of click-derived triazoles and mesoionic carbenes [33], (11) multidentate NHC complexes of 3d metals [34], (12) synthesis, reactivity and catalytic applications of piano-stool NHC iron complexes [35], (13) reduction reactions using iron-NHC complexes [36], (14) designing palladium–NHC complexes for high reactivity and selectivity for cross-coupling applications [37], (15) nickel and palladium N-heterocyclic carbene complexes. synthesis and application in cross-coupling reactions [38], (16) polystyrene-supported diaminocarbene complexes of palladium(II) [39], (17) use of NHC-gold/Selectfluor systems for n-bond activation [40], (18) gold carbene NHC complexes in medicine [41], (19) recent developments in medicinal applications of silver NHC complexes [42], and (20) DNA binding modes for metal-NHC complexes [43]. Every effort has been made to include NHC complex articles 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. In most cases, the Ionic Model [44] has been employed for the discussion of oxidation states and ligand electron count throughout this survey. A special section focusing on olefin 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.

1.1. Metal-carbene or metal-alkylidene complexes

1.1.1. Review articles, highlights, and comments

Many review articles focusing on some aspect of carbene complex-initiated olefin metathesis were published in 2017, including the following specific subjects: (1) recent advancements in stereoselective olefin metathesis using ruthenium catalysts [45]; (2) stereoretentive olefin metathesis [46]; (3) olefin metathesis in drug discovery [47]; (4) olefin cross metathesis and ring closing metathesis in polymer chemistry [48]; (5) ruthenium indenylidene metathesis catalysts [49]; (6) development of environmentally friendly reusable ionic-tagged ruthenium complexes and progress toward industrially relevant homogeneous catalysts [50]; (7) light-induced olefin metathesis (using catalysts that photoactivate) [51]; (8) use of vanadium alkylidene complexes as catalysts for ROMP reactions [52]; (9) remote control Grubbs catalysts that modulate ring-opening metathesis polymerizations [53]; (10) preparation of polymers of norbornenedicarboxylate ester derivatives using ROMP [54]; (11) norbornene-ethylene copolymerization (ROMP and vinyl insertion) [55]; (12) history and applications of ADMET polymerization [56]; (13) experimental considerations for ADMET polymerization [57]; (14) recent advances in the regio and stereospecific cyclopolymerization of α,ω-diynes by ruthenium and molybdenum carbene complexes [58]; (15) ruthenium-catalyzed metathesis cascade reactions in natural products synthesis [59]; (16) microwave-assisted olefin metathesis as pivotal step in the synthesis of bioactive compounds [60]; (17) preparation of heterocycles via a cross metathesis and Michael addition sequence [61]; (18) synthesis of lactams using metathesis reactions [62]; (19) synthesis of amine-containing heterocycles using metathesis reactions [63]; (20) preparation of heteroaromatic compounds using RCM and enyne metathesis reactions [64]; (21) synthesis of macrocycles other than peptides vis metathesis [65]; (22) synthesis of cyclic peptides using metathesis reactions [66]; (23) preparation of cyclic ether-containing natural and non-natural products via metathesis reactions [67]; (24) preparation of common and medium-sized lactone ring systems through metathesis [68]; (25) synthesis of P-, S-, Si-, B-, and Se-heterocycles via RCM [69]; (26) olefin cross-metathesis in polymer and polysaccharide chemistry [70]; (27) the future of ethylenolysis in bio-based chemistry [71]; (28) generation of metal-carbon double bonds from alkenes and high oxidation state metals (relevant to olefin metathesis) [72]; (29) cross-metathesis on immobilized substrates and its applications in the generation of synthetically and biologically relevant structures [73]; (30) heterogeneous olefin-metathesis using unsaturated fatty acid methyl esters [74]; and (31) olefin and alkyne metathesis in polymer chemistry (highlighting discoveries from the Moore research group at the University of Illinois) [75]. A metathesis review in Japanese was focused on industrial applications and olefin metathesis catalyst technologies for reaction injection molding of dicyclopentadiene [76].

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) six-membered ring α,β-unsaturated lactones [77]; (2) schinortriterpenoids [78]; (3) spirocyclic compounds [79]; (4) spirolactones (via metathesis or via metal-vinylidene intermediates) [80]; (5) saturated cyclic amines (emphasizing green approaches) [81]; (6) eight-membered ring amine derivatives [82]; (7) trifluoromethyl-substituted piperidine derivatives [83]; (8) epoxyquinone natural products [84]; (9) pyrrolizidines, indolizidines and quinolizidines [85]; (10) pyrroles (using α,β -unsaturated aldehyde precursors) [86]; (11) boron-substituted 1,3-dienes [87]; (12) azaborinines [88]; (13) oxaphospholenes [89]; (14) halenaquinol and xestoquinol natural products [90]; (15) prostaglandins [91]; (16) securinega alkaloids [92]; (17) cochliomycins and related resorcyclic acid lactones [93]; (18) lycopodium alkaloids [94]; (19) 19-nor type vitamin D derivatives [95]; (20) carbohydrates (via dihydropyrans) [96]; (21) humulanolides [97]; (22) strigolactones [98]; (23) macrocyclic peptidomimetics [99]; (24) highly strained para-phenylene-bridged macrocycles (from unstrained 1,4-diketo macrocycles) [100]; (25) molecular knots [101]; (26) propellanes (via either olefin metathesis or diazo-derived metal-carbene chemistry) [102]; (27) five-membered ring lactones (via RCM or carbene-mediated C-H activation) [103]; (28) carbon nanohoops [104]; (29) molecular knots [105]; (30) ladderene-derived polymers [106]; (31) macromolecules containing cobalt sandwich complexes [107]; and (32) macromolecular graph constructions [108]. Compounds often prepared by metathesis featured in reviews in Chinese include: (1) neopeltolide [109]; (2) DNA-like double-strand polymers [110]; (3) construction, self-assembly and functionalization of mesogen-jacketed liquid crystalline polymers [111]; (4) self-healing polymer materials [112,113], and (5) suprapolymers (from supramonomers) [114].

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