Edited by
Christian Bruneau and Pierre H. Dixneuf

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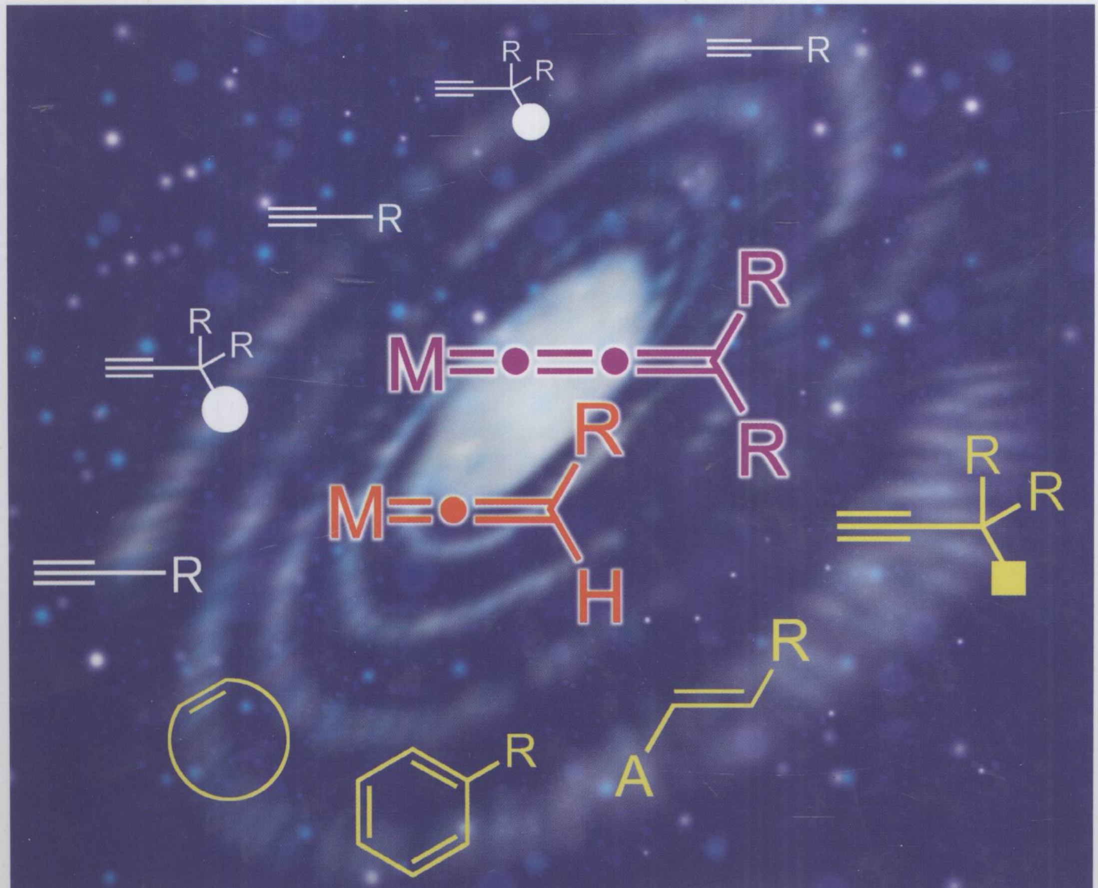
Metal Vinylidenes and Allenylidenes in Catalysis

From Reactivity to Applications in Synthesis



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Preface

Catalytic transformations of alkynes have recently led to tremendous developments of synthetic methods with useful applications in the synthesis of natural products and molecular materials. Among them, the selective activations of terminal alkynes and propargylic alcohols via vinylidene- and allenylidene-metal intermediates play an important role, and have opened new catalytic routes toward *anti*-Markovnikov additions to terminal alkynes, carbocyclizations or propargylations, in parallel to the production of new types of molecular catalysts.

After the discovery of the first terminal vinylidene-metal complex in 1972, it was established that the stoichiometric activation of terminal alkynes by a variety of suitable metal complexes led to 1,2-hydrogen transfer and the formation of metal-vinylidene species, which is now a classical organometallic reaction. A metal-vinylidene intermediate was proposed for the first time in 1986 to explain a catalytic *anti*-Markovnikov addition to terminal alkynes. Since then, possible metal-vinylidene intermediate formation has been researched to achieve catalytic regioselective formation of carbon–heteroatom and carbon–carbon bonds involving the alkyne terminal carbon.

In parallel, since the first preparation of allenylidene-metal complexes in 1976, the formation of these carbon-rich complexes developed rapidly after the discovery, in 1982, that allenylidene-metal intermediates could be easily formed directly from terminal propargylic alcohols via vinylidene-metal intermediates. This decisive step has led to regioselective catalytic transformations of propargylic derivatives via carbon(1)–atom bond formation or alternately to propargylation. Due to their rearrangement into indenylidene complexes, metal-allenylidene complexes were also found to be catalyst precursors for olefin and enyne metathesis.

Higher cumulenyl moieties stabilized by organometallic fragments were introduced in the eighties and have recently received much attention. Such linear unsaturated carbon-rich cumulenyl-metal complexes have allowed access to new molecular architectures and have revealed interesting properties in the field of electronics and molecular wires.

The activation of alkynes to metal-vinylidenes with transition metal complexes of Groups 6–9, essentially, provides reactive intermediates with an electrophilic

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terminal carbon atom, whereas allenylidene species present two electrophilic carbon centers. Advantage has been taken of this property for the rational design of new catalytic transformations, and useful atom-economical catalytic transformations have been brought to light. The new trends aim at the use of multifunctional acetylenic substrates with the objective of performing unprecedented cascade catalytic reactions.

The content of this book gathers in the same volume all aspects of vinylidene- and allenylidene-metal complexes, including the preparation of these organometallic carbon-rich systems with a metal–carbon double bond, their stoichiometric reactivity and theoretical aspects, and their applications in catalysis for the production of fine chemicals, mainly in the field of selective transformations of functional terminal alkynes. It provides essential general information on catalytic transformations of alkynes and their use in synthesis.

This book should be of interest to academic and industrial researchers involved in the fields of organometallic, coordination and bioinorganic chemistry, transition metal catalysis, and organic synthesis.

We are grateful to the team from Wiley-VCH who made this project possible and to all contributors to this book for their enthusiasm in writing a chapter on their favorite selected topic.

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Contents

Preface *XIII*
List of Contributors *XV*

1 Preparation and Stoichiometric Reactivity of Mononuclear Metal Vinylidene Complexes *1*

Michael I. Bruce

1.1 Introduction *1*
1.2 Preparative Methods *2*
1.2.1 From 1-Alkynes *2*
1.2.1.1 Migration of Other Groups (SiR_3, SnR_3, SR, SeR) *5*
1.2.2 The η^2-Alkyne → Hydrido(η^1-Alkynyl) → Vinylidene Transformation *6*
1.2.3 From Metal Alkynyls *6*
1.2.3.1 Some Specific Examples *8*
1.2.3.2 Redox Rearrangements of Metal Alkynyls and Vinylidenes *9*
1.2.4 From Metal Allenylidenes via Metal Alkynyls *11*
1.2.5 From Metal-Carbyne Complexes *11*
1.2.6 From Metal-Carbon Complexes *14*
1.2.7 From Acyl Complexes *15*
1.2.8 From Vinyls *15*
1.2.9 From Alkenes *16*
1.2.10 Miscellaneous Reactions Affording Vinylidenes *16*
1.2.11 Vinylvinylidene Complexes *17*
1.3 Stoichiometric Reactions *19*
1.3.1 Reactions at C_α *20*
1.3.1.1 Deprotonation *20*
1.3.1.2 Group 16 Nucleophiles. Oxygen *20*
1.3.1.3 Alcohols *21*
1.3.1.4 Sulfur *21*
1.3.1.5 Group 15 Nucleophiles. Nitrogen *22*
1.3.1.6 Phosphorus *22*
1.3.1.7 Halogen Nucleophiles *22*

Metal Vinylidenes and Allenylidenes in Catalysis: From Reactivity to Applications in Synthesis
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1.3.1.8 Carbon Nucleophiles *22*
1.3.1.9 Hydride *22*
1.3.2 Intramolecular Reactions *23*
1.3.2.1 Formation of Cyclopropenes *23*
1.3.2.2 Attack on Coordinated Phosphines *24*
1.3.2.3 Coupling *24*
1.3.2.4 Vinylidene/Alkyne Coupling *25*
1.3.2.5 Formation of π-Bonded Ligands *25*
1.3.3 Reactions at C_β *25*
1.3.3.1 Protonation *26*
1.3.3.2 Alkylation *27*
1.3.3.3 Other Electrophiles *27*
1.3.4 Cycloaddition Reactions *27*
1.3.5 Adducts with Other Metal Fragments *28*
1.3.6 Ligand Substitution *30*
1.3.7 Miscellaneous Reactions *31*
1.4 Chemistry of Specific Complexes *33*
1.4.1 Reactions of $Ti(=C=CH_2)Cp_2^*$ *33*
1.4.2 Complexes Derived From $Li[M(C\equiv CR)(CO)(NO)Cp]$ ($M=Cr, W$) *34*
1.4.3 Reactions of $M(=C=CRR')(CO)_5$ ($M = Cr, Mo, W$) *35*
1.4.4 Reactions of $M(=C=CRR')(CO)(L)$ Cp ($M = Mn, Re$) *37*
1.4.5 Reactions of $[M(=C=CRR')(L')(P)Cp']^+$ ($M = Fe, Ru, Os$) *39*
1.4.6 Reactions of $[Ru\{=C=C(SMe)_2\}(PMe_3)_2Cp]^+$ *39*
1.4.7 Reactions of *trans*-$MCl(=C=CRR')(L)_2$ ($M=Rh, Ir$) *41*
1.5 Reactions Supposed to Proceed via Metal Vinylidene Complexes *42*
Abbreviations *45*
References *46*

2 Preparation and Stoichiometric Reactivity of Metal Allenylidene Complexes *61*
Victorio Cadierno, Pascale Crochet, and José Gimeno
2.1 Introduction *61*
2.2 Preparation of Allenylidene Complexes *62*
2.2.1 General Methods of Synthesis *62*
2.2.2 Group 6 Metals *63*
2.2.3 Group 7 Metals *64*
2.2.4 Group 8 Metals *65*
2.2.4.1 Octahedral and Five-Coordinate Derivatives *66*
2.2.4.2 Half-Sandwich Derivatives *66*
2.2.4.3 Other Synthetic Methodologies *68*
2.2.5 Group 9 Metals *68*
2.3 Coordination Modes and Structural Features *69*
2.4 Stoichiometric Reactivity of Allenylidenes *69*
2.4.1 General Considerations of Reactivity *69*
2.4.2 Electrophilic Additions *70*

2.4.3 Nucleophilic Additions *71*
2.4.3.1 Group 6 Metal-Allenylidenes *72*
2.4.3.2 Group 7 Metal-Allenylidenes *73*
2.4.3.3 Group 8 Metal-Allenylidenes *74*
2.4.3.4 Group 9 Metal-Allenylidenes *78*
2.4.4 C–C Couplings *79*
2.4.5 Cycloaddition and Cyclization Reactions *81*
2.4.5.1 Reactions Involving the $M{=}C_\alpha$ Bond *81*
2.4.5.2 Reactions Involving the $C\alpha{=}C_\beta$ Bond *82*
2.4.5.3 Reactions Involving the $C_\beta{=}C_\gamma$ Bond *84*
2.4.5.4 Reactions Involving Both $C_\alpha{=}C_\beta$ and $C_\beta{=}C_\gamma$ Bonds (1,2,3-Heterocyclizations) *87*
2.4.6 Other Reactions *89*
2.5 Concluding Remarks *90*
References *91*

3 Preparation and Reactivity of Higher Metal Cumulenes Longer than Allenylidenes *99*
Helmut Fischer
3.1 Introduction *99*
3.2 Steric and Electronic Structure *100*
3.3 Synthesis of Cumulenylidene Complexes *103*
3.3.1 Butatrienylidene Complex Synthesis *103*
3.3.2 Pentatetraenylidene Complex Synthesis *108*
3.3.3 Hexapentaenylidene Complex Synthesis *113*
3.3.4 Heptahexaenylidene Complex Synthesis *113*
3.4 Reactions of Higher Metal Cumulenes *114*
3.4.1 Butatrienylidene Complexes *114*
3.4.2 Pentatetraenylidene Complexes *119*
3.4.3 Hexapentaenylidene Complexes *123*
3.4.4 Heptahexaenylidene Complexes *123*
3.5 Summary and Conclusion *124*
References *125*

4 Theoretical Aspects of Metal Vinylidene and Allenylidene Complexes *129*
Jun Zhu and Zhenyang Lin
4.1 Introduction *129*
4.2 Electronic Structures of Metal Vinylidene and Allenylidene Complexes *130*
4.2.1 Metal Vinylidene Complexes *130*
4.2.2 Metal Allenylidene Complexes *132*
4.3 Barrier of Rotation of Vinylidene Ligands *132*
4.4 Tautomerization Between η^2-Acetylene and Vinylidene on Transition Metal Centers *134*

4.4.1 η^2-Acetylene to Vinylidene *134*
4.4.2 Vinylidene to η^2-Acetylene *139*
4.5 Reversible C–C σ-bond Formation by Dimerization of Metal Vinylidene Complexes *141*
4.6 Metal Vinylidene Mediated Reactions *142*
4.6.1 Alkynol Cycloisomerization Promoted by Group 6 Metal Complexes *142*
4.6.2 Unusual Intramolecular [2 + 2] Cycloaddition of a Vinyl Group with a Vinylidene C=C Bond *148*
4.6.3 Intramolecular Methathesis of a Vinyl Group with a Vinylidene C=C Double Bond *149*
4.6.4 [2 + 2] Cycloaddition of Titanocene Vinylidene Complexes with Unsaturated Molecules *150*
4.7 Heavier Group 14 Analogs of Metal Vinylidene Complexes *150*
4.8 Allenylidene Complexes *151*
4.9 Summary *152*
References *153*

5 Group 6 Metal Vinylidenes in Catalysis (Cr, Mo, W) *159*
Nobuharu Iwasawa
5.1 Introduction *159*
5.2 Preparation of Fischer-type Carbene Complexes through the Generation of the Vinylidene Complexes *159*
5.3 Utilization of Pentacarbonyl Vinylidene Complexes of Group 6 Metals for Synthetic Reactions *164*
5.3.1 Catalytic Addition of Hetero-Nucleophiles *165*
5.3.2 Catalytic Addition of Carbo-Nucleophiles *172*
5.3.3 Electrocyclization and Related Reactions *178*
5.4 Utilization of Vinylidene to Alkyne Conversion *184*
5.5 Synthetic Reactions Utilizing Other Kinds of Vinylidene Complexes of Group 6 Metals *186*
5.6 Conclusion *187*
References *188*

6 Ruthenium Vinylidenes in the Catalysis of Carbocyclization *193*
Arjan Odedra and Rai-Shung Liu
6.1 Introduction *193*
6.2 Stoichiometric Carbocyclization via Ruthenium Vinylidene *193*
6.3 Catalytic Carbocyclization via Electrocyclization of Ruthenium-Vinylidene Intermediates *195*
6.3.1 Cyclization of *cis*-3-En-1-Ynes *195*
6.3.2 Cycloaromatization of 3,5-Dien-1-Ynes *196*
6.3.3 Ruthenium-Catalyzed Cyclization of 3-Azadienynes *202*
6.3.4 Cycloisomerization of *cis*-1-Ethynyl-2-Vinyloxiranes *203*

6.3.5 Catalytic Cyclization of Enynyl Epoxides *204*
6.4 Catalytic Carbocyclization via Cycloaddition of Ruthenium Vinylidene Intermediates *208*
6.4.1 Cyclocarbonylation of 1,1′-Bis(silylethynyl)ferrocene *208*
6.4.2 Dimerization of 1-Arylethynes to 1-Aryl-Substituted Naphthalenes *209*
6.4.3 Ruthenium-Catalyzed Cycloaddition Reaction between Enyne and Alkene *209*
6.5 Catalyzed Cyclization of Alkynals to Cycloalkenes *211*
6.6 Ruthenium-Catalyzed Hydrative Cyclization of 1,5-Enynes *211*
6.7 Carbocyclization Initiated by Addition of *C*-Nucleophile to Ruthenium Vinylidene *213*
6.8 Conclusion *214*
References *214*

7 Allenylidene Complexes in Catalysis *217*
Yoshiaki Nishibayashi and Sakae Uemura
7.1 Introduction *217*
7.2 Propargylic Substitution Reactions *219*
7.2.1 Propargylic Substitution Reactions with Heteroatom-Centered Nucleophiles *219*
7.2.2 Propargylic Substitution Reactions with Carbon-Centered Nucleophiles *223*
7.2.3 Reaction Pathway for Propargylic Substitution Reactions *224*
7.2.4 Asymmetric Propargylic Alkylation with Acetone *227*
7.2.5 Cycloaddition between Propargylic Alcohols and Cyclic 1,3-Dicarbonyl Compounds *231*
7.3 Propargylation of Aromatic Compounds with Propargylic Alcohols *233*
7.3.1 Propargylation of Heteroaromatic and Aromatic Compounds with Propargylic Alcohols *233*
7.3.2 Cycloaddition between Propargylic Alcohols and Phenol and Naphthol Derivatives *234*
7.4 Carbon–Carbon Bond Formation via Allenylidene-Ene Reactions *236*
7.5 Reductive Coupling Reaction via Hydroboration of Allenylidene Intermediates *238*
7.6 Selective Preparation of Conjugated Enynes *239*
7.7 Preparation of Dicationic Chalcogenolate-Bridged Diruthenium Complexes and Their Dual Catalytic Activity *241*
7.8 Other Catalytic Reactions via Allenylidene Complexes as Key Intermediates *243*
7.9 Conclusion *246*
References *247*

8 Ruthenium Allenylidenes and Indenylidenes as Catalysts in Alkene Metathesis *251*

Raluca Malacea and Pierre H. Dixneuf

8.1 Introduction *251*
8.2 Propargyl Derivatives as Alkene Metathesis Initiator Precursors: Allenylidenes, Indenylidenes and Alkenylalkylidenes *252*
8.2.1 Allenylidene-Ruthenium Complexes as Alkene Metathesis Catalyst Precursors: the First Evidence *252*
8.2.2 Allenylidene-Ruthenium Complexes in RCM, Enyne Metathesis and ROMP *254*
8.2.2.1 RCM Reactions *254*
8.2.2.2 Enyne Metathesis *254*
8.2.2.3 ROMP Promoted by Allenylidene Complexes *255*
8.2.3 Indenylidene-Ruthenium Complexes: the Alkene Metathesis Catalytic Species from Allenylidene Ruthenium Complexes *256*
8.2.3.1 The First Evidence *256*
8.2.3.2 The Intramolecular Allenylidene to Indenylidene Rearrangement Demonstration *259*
8.2.3.3 Applications of Isolated Indenylidene-Ruthenium Complexes in ROMP *261*
8.2.3.4 Indenylidene-Ruthenium(arene) Catalyst in Diene and Enyne RCM *262*
8.2.4 Propargylic Ethers as Alkene Metathesis Initiator Precursors: Generation of Alkenyl Alkylidene-Ruthenium Catalysts *262*
8.3 Indenylidene-Ruthenium Catalysts in Alkene Metathesis *265*
8.3.1 Preparation of Indenylidene-Ruthenium Catalysts *265*
8.3.2 Ruthenium Indenylidene Complexes in Alkene Metathesis *268*
8.3.3 Polymerization with Ruthenium Indenylidene Complexes *271*
8.3.4 Other Catalytic Reactions Promoted by Indenylidenes *273*
8.4 Conclusion *274*
References *274*

9 Rhodium and Group 9–11 Metal Vinylidenes in Catalysis *279*

Sean H. Wiedemann and Chulbom Lee

9.1 Introduction *279*
9.2 Rhodium and Iridium Vinylidenes in Catalysis *280*
9.2.1 Introduction *280*
9.2.2 Carbocyclization/Pericyclic Reactions *281*
9.2.3 Anti-Markovnikov Hydrofunctionalization *288*
9.2.4 Multi-Component Coupling *294*
9.3 Rhodium Alkenylidenes in Catalysis *299*
9.4 Group 10 and 11 Metal Vinylidenes in Catalysis *302*
9.4.1 Introduction *302*
9.4.2 Nickel Vinylidenes in Catalysis *302*
9.4.3 Palladium Vinylidenes in Catalysis *303*

9.4.4 Platinum Vinylidenes in Catalysis *304*
9.4.5 Copper Vinylidenes in Catalysis *306*
9.4.6 Gold Vinylidenes in Catalysis *307*
9.5 Conclusion *310*
9.6 Note Added in Proof *310*
References *311*

10 Anti-Markovnikov Additions of *O*-, *N*-, *P*-Nucleophiles to Triple Bonds with Ruthenium Catalysts *313*
Christian Bruneau
10.1 Introduction *313*
10.2 C–O Bond Formation *314*
10.2.1 Addition of Carbamic Acids: Synthesis of Vinylic Carbamates and Ureas *314*
10.2.2 Addition of Carboxylic Acids: Synthesis of Enol Esters *316*
10.2.3 Addition of Water: Synthesis of Aldehydes *318*
10.2.4 Addition of Alcohols: Synthesis of Ethers and Ketones *321*
10.2.4.1 Intermolecular Addition: Formation of Unsaturated Ethers and Furans *321*
10.2.4.2 Intermolecular Addition with Rearrangement: Formation of Unsaturated Ketones *321*
10.2.4.3 Intramolecular Addition: Formation of Cyclic Enol Ethers and Lactones from Pent-4-yn-1-ols and But-3-yn-1-ols *323*
10.3 Formation of C–N Bonds via Anti-Markovnikov Addition to Terminal Alkynes *325*
10.3.1 Addition of Amides to Terminal Alkynes *325*
10.3.2 Formation of Nitriles *via* Addition of Hydrazines to Terminal Alkynes *325*
10.4 Hydrophosphination: Synthesis of Vinylic Phosphine *326*
10.5 C–C Bond Formation: Dimerization of Terminal Alkynes *327*
10.6 Conclusion *329*
References *330*

Index *333*

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