

WILEY-VCH

Edited by Chao-Jun Li and Xihe Bi

# Silver Catalysis in Organic Synthesis

Volume 1

U - M (eds.)

U - M (eds.)

2

1

Silver Catalysis in Organic Synthesis

WILEY-VCH

WILEY-VCH





## Silver Catalysis in Organic Synthesis



# Silver Catalysis in Organic Synthesis

*Edited by Chao-Jun Li and Xihe Bi*

*Volume 1*

**WILEY-VCH**

# Silver Catalysis in Organic Synthesis

*Edited by Chao-Jun Li and Xihe Bi*

*Volume 2*

**WILEY-VCH**

## Editors

### *Chao-Jun Li*

McGill University  
Department of Chemistry  
801 Sherbrooke Street West  
Montreal, QC H3A 0B4  
Canada

### *Xihe Bi*

Northeast Normal University  
Department of Chemistry  
5268 Renmin Street  
Changchun 130024  
China

## Cover

Cover image kindly provided by  
Dr. Dingyi Tong (Ningbo Institute of  
Industrial Technology (CNITECH),  
Chinese Academy of Sciences (CAS))

■ All books published by **Wiley-VCH** are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

**Library of Congress Card No.:** applied for

## **British Library Cataloguing-in-Publication Data**

A catalogue record for this book is available from the British Library.

## **Bibliographic information published by the Deutsche Nationalbibliothek**

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <<http://dnb.d-nb.de>>.

© 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Boschstr. 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

**Print ISBN:** 978-3-527-34281-5

**ePDF ISBN:** 978-3-527-80769-7

**ePub ISBN:** 978-3-527-80768-0

**oBook ISBN:** 978-3-527-34282-2

**Typesetting** SPi Global, Chennai, India  
**Printing and Binding**

Printed on acid-free paper

10 9 8 7 6 5 4 3 2 1

## Contents to Volume I

### Preface *xi*

<b>1</b>	<b>Introduction to Silver Chemistry</b>	<b>1</b>
	<i>Paramasivam Sivaguru and Xihe Bi</i>	
1.1	History and Features of Silver	1
1.1.1	Chemistry of Silver	1
1.1.2	Silver Nanoparticles	3
1.1.3	Silver Applications	3
1.2	Silver Catalysis	4
1.2.1	Alkynophilicity/Carbophilic Nature of Silver	4
1.2.2	Oxo- and Azaphilic Character of Silver	7
1.2.3	Halogenophilicity of Silver	7
1.2.4	Redox Chemistry of Silver	8
1.2.4.1	One-electron Ag(I)/Ag(II) Redox Cycles	8
1.2.4.2	Two-electron Ag(I)/Ag(III) Redox Cycle	8
1.3	Representative Examples of Silver Catalysis in the Organic Transformations	9
1.3.1	Protodecarboxylation of Carboxylic Acids	9
1.3.2	A <sup>3</sup> Coupling Reaction	10
1.3.3	Incorporation of CO <sub>2</sub>	11
1.3.4	Enantioselective Nitroso-aldol Reaction	12
1.3.5	Chemoselective Cyclopropanation Using Donor–Acceptor Diazo Compounds	13
1.3.6	Homocoupling of Alkyl Grignard Reagents	14
1.3.7	Oxidative Arene Cross-coupling	15
1.3.8	Hydroazidation of Alkynes	16
1.3.9	Isocyanide–alkyne Cycloaddition	17
1.3.10	Nitrogenation of Terminal Alkynes	18
1.3.11	Decarboxylative Alkynylation	19
1.3.12	Nitrene Transfer Reactions	20
1.3.13	Fluorination Reactions	22
1.4	Summary	23
	References	23



<b>2</b>	<b>Silver-catalyzed Cycloaddition Reactions</b>	<b>33</b>
	<i>Daesung Lee and Sourav Ghorai</i>	
2.1	Introduction	33
2.2	[3+2] Cycloadditions	34
2.2.1	Cycloaddition of Azomethine Ylides	34
2.2.2	Cycloaddition of 2-Isocyanoacetates	47
2.2.3	Cycloaddition of Azides	53
2.3	[2+2] Cycloadditions	59
2.4	[3+3] Cycloadditions	60
2.5	[4+2] Cycloadditions	63
2.5.1	Diels–Alder Reactions	63
2.5.2	Oxa- and Aza-Diels–Alder Reactions	67
2.5.3	Hexadehydro Diels–Alder Reactions	72
2.6	[2+2+1] Cycloadditions	73
2.7	Miscellaneous Reactions	74
2.7.1	[2+1] Cycloaddition	74
2.7.2	[4+1] Cycloaddition	77
2.7.3	[4+2] Cycloaddition	77
2.8	Conclusion	78
	References	79
<b>3</b>	<b>Silver-Catalyzed Cyclizations</b>	<b>85</b>
	<i>Valerie H. L. Wong and King Kuok (Mimi) Hii</i>	
3.1	Introduction	85
3.2	Cyclization by the Formation of C—C Bonds (Cycloisomerization Reactions)	86
3.2.1	Conia-ene Reaction	86
3.2.2	Cycloisomerization	89
3.2.2.1	Cycloisomerization of Enynes	90
3.2.2.2	Cycloisomerization of 1, <i>n</i> -Allenynes	94
3.2.2.3	Cycloisomerization of 1, <i>n</i> -Diyne Compounds	95
3.2.2.4	Cycloisomerization Reactions of Propargyl Compounds	96
3.2.3	Electrocyclic Reactions	99
3.2.4	Miscellaneous Reactions	100
3.3	Formation of C—N Bonds	102
3.3.1	Intramolecular Hydroamination	102
3.3.1.1	Alkynes	102
3.3.1.2	Allenes	116
3.3.1.3	Alkenes	122
3.3.2	Cycloisomerization Reactions of Alkynes	122
3.3.2.1	Imines as Nucleophiles	123
3.3.2.2	Oximes	129
3.3.2.3	Hydrazones	134
3.3.2.4	Aromatic <i>N</i> -Heterocycles	141
3.3.2.5	Other Nucleophiles	143
3.4	Formation of C—O Bonds	144
3.4.1	Hydroalkoxylation	144

- 3.4.1.1 Alkynes 144
- 3.4.1.2 Allenes 149
- 3.4.1.3 Alkenes 154
- 3.4.2 Hydrocarboxylation 155
  - 3.4.2.1 Alkynes 155
  - 3.4.2.2 Allenes 157
  - 3.4.2.3 Alkenes 158
- 3.4.3 Cycloisomerization of C=O 159
  - 3.4.3.1 Alkynes as Partners 159
  - 3.4.3.2 Allenes as Partners 168
- 3.4.4 Miscellaneous Reactions 169
  - References 173
  
- 4 Silver-Mediated Radical Reactions 183**  
*Lin Zhu and Chaozhong Li*
  - 4.1 Introduction 183
  - 4.2 Protodecarboxylation 184
  - 4.3 Radical Coupling 187
    - 4.3.1 Formation of C—C Bonds 187
    - 4.3.2 Formation of C—O/S/Se Bonds 202
    - 4.3.3 Formation of C—N/P Bonds 209
    - 4.3.4 Formation of C—Halogen Bonds 216
  - 4.4 Radical Addition 222
    - 4.4.1 Formation of C—C Bonds 222
    - 4.4.2 Formation of C—Heteroatom Bonds 228
  - 4.5 Cascade Radical Cyclizations 233
    - 4.5.1 Formation of C—C Bonds 233
    - 4.5.2 Formation of C—O/S/Se Bonds 241
    - 4.5.3 Formation of C—N/P Bonds 244
  - 4.6 Rearrangement/Migration/C—C Bond Cleavage 249
    - 4.6.1 Aryl Migration 249
    - 4.6.2 Radical C—C Bond Cleavage of Cycloalkanols 255
  - 4.7 Conclusion and Perspective 259
    - Acknowledgment 260
    - References 261
  
- 5 Silver-Mediated Fluorination, Perfluoroalkylation, and Trifluoromethylthiolation Reactions 271**  
*Vanessa Koch, Andreas Hafner, and Stefan Bräse*
  - 5.1 Introduction 271
  - 5.2 Silver-Mediated Fluorinations 273
    - 5.2.1 Nucleophilic Silver-Catalyzed Fluorination 274
    - 5.2.2 Electrophilic Silver-Catalyzed Fluorination 279
    - 5.2.3 Radical Silver-Catalyzed Fluorination 287
      - 5.2.3.1 Fluorination via Addition to Alkenes 287
      - 5.2.3.2 Decarboxylative Fluorination 294
      - 5.2.3.3 C—C Bond Activation 296

5.2.3.4	C—H Bond Activation	297
5.3	Silver-Mediated Trifluoromethylations and Perfluoroalkylations	298
5.3.1	Syntheses and Properties of Perfluoroorgano Silver Compounds	300
5.3.2	Silver-Mediated Perfluoroalkylations	301
5.3.2.1	Perfluoroorgano Silver Compounds in Copper-Mediated Perfluoroalkylations	301
5.3.2.2	Perfluoroorgano Silver Compounds as Precursors for Radicals	304
5.3.2.3	Perfluoroorgano Silver Compounds as Nucleophilic Reagents	309
5.3.3	Silver-Catalyzed Perfluoroalkylations	313
5.4	Silver-Mediated and Silver-Catalyzed Trifluoromethylthiolations	314
5.5	Conclusion and Outlook	324
	References	324
<b>6</b>	<b>Coupling Reactions and C—H Functionalization</b>	<b>331</b>
	<i>Qing-Zhong Zheng and Ning Jiao</i>	
6.1	Introduction	331
6.2	Formation of Carbon–Carbon Bonds	332
6.2.1	Glaser Coupling	332
6.2.2	A <sup>3</sup> Coupling	332
6.2.3	Oxidative Cross-coupling and Oxidative-Induced C—H Functionalization	335
6.2.3.1	Oxidative-Induced C—H Functionalization	335
6.2.3.2	Oxidative Cross-coupling	340
6.2.4	Oxidative Coupling/Cyclization Reactions	344
6.2.5	Synthesis of Biaryls	356
6.2.6	Miscellaneous Reactions	362
6.2.6.1	Isocyanide-Involved Reactions	362
6.2.6.2	Diazo-compound-Involved Reactions	364
6.2.6.3	Synthesis of Perfluoroalkylated Compounds	367
6.2.6.4	C—H Carboxylation	368
6.2.6.5	Arylation and Alkylation Reactions	370
6.3	Formation of C–Heteroatom Bonds	371
6.3.1	Formation of C–Halogen Bonds	371
6.3.1.1	C–F Bond Formation	371
6.3.1.2	C–Cl Bond Formation	374
6.3.1.3	C–Br Bond Formation	377
6.3.2	Formation of C–N/P Bonds	378
6.3.2.1	C–N Bond Formation	378
6.3.2.2	C–P Bond Formation	387
6.3.3	Formation of C–O/S Bonds	392
6.3.3.1	C–O Bond Formation	392
6.3.3.2	C–S Bond Formation	392
6.3.4	Formation of C–B Bonds	397
6.3.5	Miscellaneous Reactions	397
6.4	Conclusion	398
	References	399

## Contents to Volume II

- Preface** *xi*
- 7 Silver-Catalyzed CO<sub>2</sub> Incorporation** *407*  
*Tohru Yamada, Kohei Sekine, Yuta Sadamitsu, and Kodai Saito*
- 8 Silver-Catalyzed Carbene, Nitrene, and Silylene Transfer Reactions** *439*  
*Mahzad Dehghany, Josephine Eshon, Jessica M. Roberts, and Jennifer M. Schomaker*
- 9 Asymmetric Silver-Catalyzed Reactions** *533*  
*Hélène Pellissier*
- 10 Silver-Catalyzed Reduction and Oxidation of Aldehydes and Their Derivatives** *645*  
*Zhenhua Jia, Mingxin Liu, and Chao-Jun Li*
- 11 Silver Complexes in Organic Transformations** *661*  
*Guichun Fang and Xihe Bi*
- 12 Silver Nanoparticles in Organic Transformations** *723*  
*Alain Y. Li, Alexandra Gellé, Andreanne Segalla, and Audrey Moores*
- Index** *795*



## Contents to Volume I

- Preface** *xi*
- 1 Introduction to Silver Chemistry** *1*  
*Paramasivam Sivaguru and Xihe Bi*
- 2 Silver-catalyzed Cycloaddition Reactions** *33*  
*Daesung Lee and Sourav Ghorai*
- 3 Silver-Catalyzed Cyclizations** *85*  
*Valerie H. L. Wong and King Kuok (Mimi) Hii*
- 4 Silver-Mediated Radical Reactions** *183*  
*Lin Zhu and Chaozhong Li*
- 5 Silver-Mediated Fluorination, Perfluoroalkylation, and Trifluoromethylthiolation Reactions** *271*  
*Vanessa Koch, Andreas Hafner, and Stefan Bräse*
- 6 Coupling Reactions and C—H Functionalization** *331*  
*Qing-Zhong Zheng and Ning Jiao*

## Contents to Volume II

- Preface** *xi*
- 7 Silver-Catalyzed CO<sub>2</sub> Incorporation** *407*  
*Tohru Yamada, Kohei Sekine, Yuta Sadamitsu, and Kodai Saito*
- 7.1 Introduction *407*
- 7.2 Carboxylation of Terminal Alkynes *408*
- 7.3 Carboxylation of Aryl Boronic Esters *413*
- 7.4 Functionalization of Terminal Epoxides *414*
- 7.5 Cascade Carboxylation and Cyclization *416*
- 7.5.1 Silver-Catalyzed Sequential Carboxylation and Cyclization of Propargyl Alcohols *417*

- 7.5.1.1 Synthesis of Cyclic Carbonate 417
- 7.5.1.2 Catalytic Asymmetric Synthesis of Cyclic Carbonate 420
- 7.5.1.3 Three-Component Reaction of Propargyl Alcohols, Carbon Dioxide, and Nucleophiles 421
- 7.5.1.4 CO<sub>2</sub>-Mediated Transformation of Propargyl Alcohols 422
- 7.5.1.5 Transformation of Amine Derivatives 424
- 7.5.1.6 Cascade Carboxylation and Cyclization of Unsaturated Amine Derivatives 424
- 7.5.1.7 Benzoxazine-2-one from o-Alkynylaniline and Carbon Dioxide 426
- 7.5.1.8 Allenylamine 427
- 7.5.1.9 Domino Carboxylation–Cyclization–Migration of Unsaturated Amines 428
- 7.5.1.10 Carboxylation Involving C–C Bond Formation: Sequential Cyclization 431
- 7.5.1.11 Carboxylation of Enolate: Sequential Cyclization 431
- 7.5.1.12 Carbon Dioxide Incorporation Reaction Using Other Carbanions 435
- 7.6 Conclusion 435
- References 436

## 8 Silver-Catalyzed Carbene, Nitrene, and Silylene Transfer Reactions 439

*Mahzad Dehghany, Josephine Eshon, Jessica M. Roberts, and Jennifer M. Schomaker*

- 8.1 Introduction to Silver-Mediated Carbene Transfer Reactions 439
- 8.2 Introduction to Cyclopropanation 440
  - 8.2.1 General Catalysts for Cyclopropanation 440
  - 8.2.2 Recent Advances in Silver-Catalyzed Cyclopropanation 441
  - 8.2.3 Recent Advances in Silver-Catalyzed Cyclopropanation 441
- 8.3 Introduction to C–H Insertion 443
  - 8.3.1 General Mechanism of C–H Functionalization via Transition Metal-catalyzed Carbene Transfer 443
  - 8.3.2 General Catalysts for C–H Functionalization via Carbene Transfer 447
  - 8.3.3 Recent Advances in Silver-Catalyzed Alkane C–H Functionalization via Carbene Transfer 450
  - 8.3.4 Advances in Silver-Catalyzed Carbene Insertion into Alkene or Aromatic C(sp<sup>2</sup>)–H Bonds 450
- 8.4 Silver-Catalyzed Carbene Insertion into N–H Bonds 452
- 8.5 Silver-Catalyzed Carbene Insertion into O–H Bonds 458
- 8.6 Silver-Catalyzed Functionalization of Esters 458
- 8.7 Silver-Catalyzed Si–H Functionalization 461
- 8.8 Summary 461
- 8.9 Introduction to Transition Metal-Catalyzed Nitrene Transfer 464
  - 8.9.1 General Catalysts for Silver-Catalyzed Nitrene Transfer 468
  - 8.9.2 Typical Nitrogen Sources for Silver-Catalyzed Nitrene Transfer 470
  - 8.9.3 General Mechanistic Features of Metal-Catalyzed Nitrene Transfer 470

- 8.10 Aziridination 471
  - 8.10.1 Intramolecular Aziridination 471
  - 8.10.2 Intermolecular Aziridination 474
  - 8.10.3 Mechanistic Insights into Silver-Catalyzed Aziridination 477
- 8.11 C—H Bond Amidation 484
  - 8.11.1 Intramolecular C—H Bond Amidations 484
  - 8.11.2 Intermolecular C—H Bond Amidation 494
  - 8.11.3 Mechanistic Aspects of Site-selective C—H Bond Amidation 498
- 8.12 Silver-Catalyzed N—N Bond Formation 502
- 8.13 Summary 503
- 8.14 Introduction to Transition Metal-Catalyzed Silylene Transfer 504
- 8.15 Silver-Mediated Silylene Transfer Reactions 508
  - 8.15.1 Olefins 508
  - 8.15.2 Carbonyl Compounds 513
  - 8.15.3 C—O Bonds 518
  - 8.15.4 Allenes 522
  - 8.15.5 Allylic Silanes 522
  - 8.15.6 Allylic Sulfides 522
- 8.16 Summary 525
  - References 525
- 9 Asymmetric Silver-Catalyzed Reactions 533**  
*Hélène Pellissier*
  - 9.1 Introduction 533
  - 9.2 Silver-Catalyzed Mannich Reactions 534
    - 9.2.1 Vinylogous Mukaiyama–Mannich Reactions 534
      - 9.2.1.1 With Hoveyda–Snapper Catalysts 534
      - 9.2.1.2 With Other Catalysts 541
    - 9.2.2 Other Mannich-Type Reactions 546
  - 9.3 Silver-Catalyzed 1,3-Dipolar Cycloadditions 554
    - 9.3.1 Formal 1,3-Dipolar Cycloadditions of Glycine Imino Esters and  $\alpha,\beta$ -Unsaturated Carbonyl Compounds 555
    - 9.3.2 Formal 1,3-Dipolar Cycloadditions of Glycine Imino Esters and Nitroalkenes 564
    - 9.3.3 Formal 1,3-Dipolar Cycloadditions of Isocyanoacetates and  $\alpha,\beta$ -Unsaturated Carbonyl Compounds 568
    - 9.3.4 Other 1,3-Dipolar Cycloadditions 573
  - 9.4 Silver-Catalyzed Domino and Tandem Reactions 574
    - 9.4.1 Domino and Tandem Reactions Initiated by a Michael Addition 574
    - 9.4.2 Domino Reactions Initiated by an Aldol Reaction 579
    - 9.4.3 Domino Reactions Initiated by a Cyclization 583
    - 9.4.4 Domino Reactions Initiated by a Mannich Reaction 589
    - 9.4.5 Miscellaneous Domino Reactions 592
  - 9.5 Silver-Catalyzed Michael Reactions 595
    - 9.5.1  $\alpha,\beta$ -Unsaturated Carbonyl Compounds as Acceptors 595
    - 9.5.2 Nitroalkenes as Acceptors 598
    - 9.5.3 Other Acceptors 599



- 9.6 Silver-Catalyzed Aldol-Type Reactions 601
  - 9.6.1 Aldol Reactions 601
  - 9.6.2 Nitroso-aldol Reactions 606
- 9.7 Silver-Catalyzed Alkynylations 610
- 9.8 Silver-Catalyzed Allylations 616
- 9.9 Silver-Catalyzed Cyclizations of Allenes 619
- 9.10 Silver-Catalyzed Aminations 623
- 9.11 Silver-Catalyzed Miscellaneous Reactions 624
- 9.12 Conclusions 633
  - References 634
  
- 10 Silver-Catalyzed Reduction and Oxidation of Aldehydes and Their Derivatives 645**  
*Zhenhua Jia, Mingxin Liu, and Chao-Jun Li*
  - 10.1 Homogeneous Silver-Catalyzed Reduction of Aldehyde 645
    - 10.1.1 Silver-Catalyzed Hydrosilylation of Aldehyde 647
    - 10.1.2 Silver-Catalyzed Hydrogenation of Aldehyde 649
    - 10.1.3 Silver-Catalyzed Transfer Hydrogenation of Aldehyde 651
  - 10.2 Silver-Catalyzed Oxidation of Alcohol, Aldehyde, and Their Derivatives 652
  - 10.3 Conclusion 657
    - Acknowledgment 658
    - References 658
  
- 11 Silver Complexes in Organic Transformations 661**  
*Guichun Fang and Xihe Bi*
  - 11.1 Introduction 661
  - 11.2 NHC–Silver(I) Complexes 662
    - 11.2.1 A<sup>3</sup> Coupling Reaction 663
    - 11.2.2 CO<sub>2</sub> Insertions 665
    - 11.2.3 Borylation Reactions 667
    - 11.2.4 Hydroborylation 668
    - 11.2.5 Carbene Transfer with Diazo Compounds 668
    - 11.2.6 Cyclization Reactions 670
    - 11.2.7 Oxidation of Alcohols 672
    - 11.2.8 Semi-hydrogenation of Alkynes 672
    - 11.2.9 Synthesis and Application of Organosilver Complexes 673
  - 11.3 Chiral Silver Phosphates 674
    - 11.3.1 Alkynylation 675
    - 11.3.2 Mannich Reaction 675
    - 11.3.3 Intramolecular Annulation 677
    - 11.3.4 Cycloisomerization 678
    - 11.3.5 Enantioselective Semipinacol Rearrangement 683
    - 11.3.6 Asymmetric Hetero-Diels–Alder Reaction 685
    - 11.3.7 Miscellaneous Reaction 686

11.4	P,O-type Silver Complexes	688
11.5	TP <sup>x</sup> -silver Complexes (Trispyrazolylborate Ligands)	690
11.5.1	Carbene Transfer Reactions	690
11.5.2	Nitrene Transfer Reactions	694
11.6	Silver Complexes with Pyridine-Containing Ligands	696
11.6.1	Silver-Catalyzed Nitrene Transfer (Aziridination vs C–H Amination)	698
11.6.2	Carbene Insertion	706
11.6.3	Hydrofunctionalization	707
11.6.4	Hunsdiecker Reaction	709
11.6.5	Twelve-membered Pyridine-containing Ligands (Pc-Ls)	710
11.6.6	Miscellaneous Reactions	711
11.7	Summary	713
	References	714
<b>12</b>	<b>Silver Nanoparticles in Organic Transformations</b>	<b>723</b>
	<i>Alain Y. Li, Alexandra Gellé, Andreanne Segalla, and Audrey Moores</i>	
12.1	Introduction	723
12.2	Epoxidation of Alkenes	724
12.2.1	Epoxidation of Ethylene	724
12.2.2	Epoxidation of Propylene	727
12.2.3	Epoxidation of Styrene and Other Alkenes	729
12.3	Alcohol Oxidation	733
12.3.1	Aerobic Alcohol Oxidation	735
12.3.2	Alcohol Dehydrogenation	737
12.3.3	Silver Alloys in Alcohol Oxidation	739
12.3.4	Alcohol–Amine Coupling	742
12.3.5	Alcohol–Alcohol Coupling	748
12.4	Reduction	750
12.4.1	Carbonyl Reduction	750
12.4.2	Reduction of Alkynes	754
12.4.3	Reduction of Epoxides	755
12.4.4	Nitro Compound Reduction	757
12.5	Alkynylations	759
12.5.1	Cyclizations	759
12.5.2	A <sup>3</sup> Coupling	761
12.5.3	Alkyne Coupling to Carbon Dioxide	765
12.5.4	Alkyne Cross-coupling	767
12.6	Plasmon-Mediated Ag NP Catalysis	768
12.6.1	Localized Surface Plasmon Resonance (LSPR) in Coinage Metal Nanoparticles	768
12.6.2	Plasmon-Mediated Oxidations Using Ag NPs	770
12.6.3	Reduction Catalyzed by Ag PNPs	771
12.6.4	Silver Halides for Photocatalysis	772

12.7	Oxidative Coupling	772
12.7.1	C–H Oxidation	772
12.7.2	Azo Coupling	775
12.8	Miscellaneous Applications	776
12.8.1	Nitrile Hydrolysis	776
12.8.2	Silanol Chemistry	778
12.8.3	Silver as a Lewis Acid	780
12.9	Conclusion	781
	References	782

<b>Index</b>	<b>795</b>
--------------	------------

## Preface

Recently, coinage metal (copper, silver, and gold) salts and complexes are being increasingly used as homogeneous catalysts in organic synthesis. Among them, an important methodology is catalysis by silver, owing to its relatively lower cost than other expensive transition metals, excellent selectivity, and stability. However, in comparison with other transition metals, silver catalysts have long been believed to have low catalytic efficiency, and the rapid development of silver chemistry was achieved only in the past few decades. Generally, silver salts are mostly utilized as either  $\sigma$ -Lewis acid or  $\pi$ -Lewis acid, with preference to  $\sigma$ -coordination over  $\pi$ -coordination due to the ready availability of empty  $f$  orbitals and relativistic contraction of the electron cloud. Apart from the Lewis acid character, silver salts are also employed as cocatalysts, halophiles, general oxidants, SET oxidants (single electron transfer), weak bases, and radical initiators in numerous transformations. In addition, the distinctive  $d^{10}$  electronic configuration of silver allows to easily coordinate with most unsaturated bonds such as  $C=C$ ,  $C\equiv C$ ,  $C=X$ , and  $C\equiv X$  bonds ( $X =$  heteroatom), which facilitates the formation of new  $C-C$  or  $C-X$  bonds. Because of these aforementioned advantages, silver catalysis has provided a distinctive opportunity in organic synthesis.

The first silver-catalyzed reaction was reported in 1933, in which ethylene was oxidized into ethylene oxide, and has been used on preparative and industrial scales for decades. Since then, a number of silver-catalyzed reactions have been developed and even applied in the synthesis of complex natural products and functional materials. As a record of these early developments, a topical book entitled *Silver in Organic Chemistry* edited by M. Harmata was published in 2010, which covered the literature up to 2008. Thereafter, there has been no book devoted to the catalysis by silver in the chemistry literature, although such a collection would be of great interest to the chemical community. Therefore, we have been privileged to invite our colleagues, who are leading scientists in this field, to contribute to this new book that emphasizes on the importance of silver catalysis in various organic transformations, covering the literature up to 2017. The present book consists of 12 chapters. It begins with a brief history

and applications of silver and mainly emphasizes the fundamental reactions involved in silver catalysis by Prof. X. Bi, which laid the foundation for further discovery of catalytic reactions. The following chapter from Prof. D. Lee focuses on the silver-catalyzed/silver-mediated different types of cycloaddition reactions {[3+2], [2+2], [3+3], [4+2], [2+2+1], [2+1], [4+1]}. Major developments in the silver-catalyzed cyclization reactions are described in Chapter 3 by Prof. K. K. M. Hii. These reactions are particularly important for the production of either carbocyclic or heterocyclic rings, through the formation of C—C, C—N, and C—O bonds. Chapter 4 by Prof. C. Li provides critical and comprehensive insights into the roles of silver in radical transformations, including the protodecarboxylation, radical coupling, addition, cascade cyclization, and rearrangement reactions. Chapter 5 from Prof. S. Bräse highlights the recent progress in the silver-catalyzed various fluorination, perfluoroalkylation, and perfluorothiolation reactions.

In Chapter 6, Prof. N. Jiao discusses the important advances in the silver-catalyzed/silver-mediated coupling reactions and C—H functionalization reactions. Prof. T. Yamada in Chapter 7 describes the recent developments in the silver-catalyzed utilization of carbon dioxide in organic synthesis, for instance, the carboxylation reactions of terminal alkynes, boronic esters, and terminal epoxides, as well as tandem cyclization reactions involving nucleophilic additions into carbon dioxide. The focus of Chapter 8 by Prof. J. M. Schomaker is devoted to carbene transfer (cyclopropanation, cyclopropenation, and C(sp<sup>3</sup>)—H and X—H [X = heteroatom] bond insertion), nitrene transfer (aziridination, C—H amidation, and N—N bond formations), and silylene transfer (C—Si and Si—O bond formation) reactions. Chapter 9 by Prof. H. Pellissier exemplifies the major progresses in the silver-catalyzed enantioselective reactions. The silver-mediated oxidation and reduction of aldehydes are deliberated in Chapter 10 by Prof. C.-J. Li. Particularly, hydrogenation, transfer hydrogenation, and aerobic oxidation of aldehydes are discussed.

Chapter 11 summarizes the catalysis of silver complexes by Prof. X. Bi. Special attention is given to the use of NHC—silver(I) complexes, chiral silver phosphates, P,O-type ligand silver(I) complexes, trispyrazolylborate—silver(I) complex, and silver complexes with pyridine-containing ligands as the catalysts. The last chapter of this book showcases the applications of silver nanoparticles in catalytic organic transformations by Prof. A. Moores. Especially, the epoxidation of alkenes, oxidation of alcohols, reduction reactions, and alkynylation reactions are deliberated.

As the editors, we believe that this book will be very useful to those who are working (such as chemistry researchers, graduate students, and university/college professors) or will work in either the fundamental or applied sectors of this field, as a source of basic knowledge and convenient reference, and it will also inspire new ideas for the reader's own research endeavors.

Finally, we wish to express our sincere thanks to all the contributors for their cooperation. We also wish to express our sincere gratitude to all the people who gave valuable help in different ways during the process of gathering materials, writing, and publishing this book. We also appreciate the staff of the editorial team of Wiley-VCH for their continuous help.

September 2018

*Chao-Jun Li*

Department of Chemistry and FQRNT  
Center for Green Chemistry and Catalysis  
McGill University, 801 Sherbrooke Street West  
Montreal, QC H3A 0B8, Canada

*Xihe Bi*

Jilin Province Key Laboratory of Organic  
Functional Molecular Design & Synthesis  
Department of Chemistry  
Northeast Normal University  
Changchun 130024, China



## 1

## Introduction to Silver Chemistry

*Paramasivam Sivaguru and Xihe Bi*

*Department of Chemistry, Northeast Normal University, 5268 Renmin Street, Changchun 130024, China*

### 1.1 History and Features of Silver

Silver is a malleable, ductile, and precious metal that has been known since ancient times (its first debut around 5000 BCE) and is located in group 11 (Ib) and period 5 of the periodic table, between the coinage metal copper (period 4) and gold (period 6). Silver is widely distributed in nature. But its abundance in the earth's crust is very low (0.05 ppm) than other metals [1]. It occurs both naturally in its pure form and in ores, particularly derived from all the sulfur bearing lead, copper, gold, tellurides, and zinc, which is extracted through refining [2]. Silver has the atomic number 47 and atomic weight of 107.880, and its ground state electronic configuration is  $[\text{Kr}] 4d^{10}5s^1$ , just like copper and gold. Mostly, silver can exist in a mixture of isotopes,  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$ , approximately occurring in the equal proportions. The most common oxidation states of silver are 0 and +1, although some other oxidation states (+2 and +3) are also known [3]. Among these  $\text{Ag}(\text{II})$  salts/complexes are less stable than that of  $\text{Ag}(\text{I})$  and  $\text{Ag}(\text{III})$  salts/complexes. Silver is noticeably diamagnetic, and its magnetic susceptibility is almost independent of temperature from room temperature to just below the melting point.

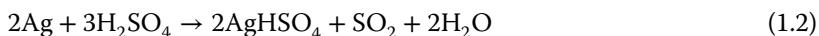
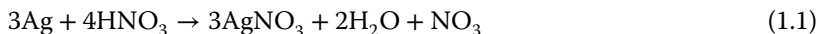
The elemental silver has the highest electrical conductivity ( $1.59 \mu\Omega \text{ cm}$  at  $20^\circ\text{C}$ ) [4], thermal conductivity ( $429 \text{ W m}^{-1} \text{ K}^{-1}$ ) [5], and optical reflectivity than any other metal, but it has the lowest electrical contact resistance, and its specific heat capacity is  $0.23 \text{ J kg}^{-1} \text{ K}^{-1}$  at  $25^\circ\text{C}$ . The melting and boiling point of silver is  $961.9$  and  $2212^\circ\text{C}$ , respectively [6]. The heat of fusion of silver is  $11.28 \text{ kJ mol}^{-1}$ , and its hardness is 2.7 on the Mohs scale.

#### 1.1.1 Chemistry of Silver

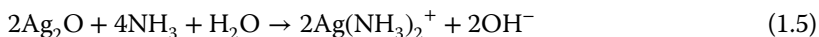
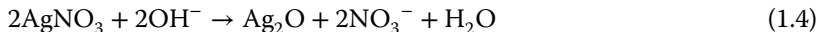
It has been recognized that the outer orbital  $5s^1$  electronic configuration of silver allowed to form numerous silver(I) salts/complexes with a wide variety of counterions (halide, sulfide, nitrate, oxide, acetylide compounds, cyano-derivatives, and olefin complexes). Silver dissolves readily in nitric acid to form silver nitrate



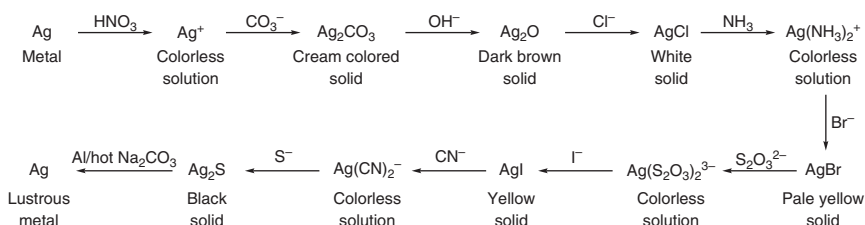
(Eq. (1.1)), which is a transparent crystalline solid that is readily soluble in water, and is a photosensitive. In addition, it is a precursor for the preparation of various other silver compounds. Silver could also dissolve rapidly with hot concentrated sulfuric acid (Eq. (1.2)). However, in the presence of ethanol, silver reacts with nitric acid to give the silver fulminate ( $\text{AgCNO}$ ), which is a powerful touch-sensitive explosive used in percussion caps [7]. Also, silver nitrate reacts with sodium azide ( $\text{NaN}_3$ ) to form silver azide ( $\text{AgN}_3$ ), which is also used as an explosive [8]. Silver or silver nitrates simply precipitate as silver chloride in the presence of chlorides, which are used in the photographic emulsion:



Furthermore, silver nitrate could easily react with copper to produce the silver crystals (Eq. (1.3)). The alkaline solution of copper also reduces the silver nitrate into silver in the presence of reducing sugars. Tollens' test/silver mirror test is a qualitative test to distinguish between an aldehyde and ketone. The Tollens' reagent  $[\text{Ag}(\text{NH}_3)_2]^+$  is prepared from silver nitrate by two-step process. In the first step, under basic conditions silver nitrate forms an insoluble silver oxide (Eq. (1.4)), and it dissolves readily with the addition of sufficient aqueous ammonia (Eq. (1.5)), which oxidizes an aldehyde into corresponding carboxylic acid (Eq. (1.6)) [9]:



Silver is stable in oxygen and water, but it is tarnishing in the presence of ozone or hydrogen sulfide or sulfur in air/water owing to the formation of a black silver sulfide layer. Besides, silver readily forms soluble silver complexes such as  $\text{Ag}(\text{NH}_3)_2^+$ ,  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ , and  $\text{Ag}(\text{CN})_2^-$  with excess of respective ions. The silver thiosulfate complex is used to dissolve undeveloped  $\text{AgBr}$  and fix the photography [10]. The silver cyanide complex is frequently used in electroplating [11]. A systematic sequence of reactions outlined in Figure 1.1 illustrated the chemistry of silver.



**Figure 1.1** Reactions in the silver series.

### 1.1.2 Silver Nanoparticles

Nanoparticulates (colloidal) of silver are fine particles of metallic silver that has been known for about 120 years [12]. Usually, these are synthesized by the reduction of soluble silver with reducing agents such as citrate, glucose, ethyl alcohol, and sodium borohydride as well as an appropriate stabilizing agent. The added stabilizing agent plays a crucial role to prevent the growth and aggregation of the formed silver nanoparticles. The reduction process can be carried out in both aqueous and organic solvents. However, a practical and reproducible synthesis of silver nanoparticle is very difficult than that of expected [13]. This might be due to its different morphologies and crystal sizes when changing reaction conditions such as concentrations, reducing agents, temperature, and additives [13, 14]. Depending on the reaction conditions, there are numerous kinds of silver nanoparticles that have been documented in the literature, including spherical [15], bipyramids [16], discs [17], rods [14, 18], cubes [19], prisms [20], rings [21], platelets [22], triangular prisms [23], and octahedral particles [19c]. Because of the different sizes and morphologies, nanosilver possesses the unique chemical, physical, and optical properties compared with the parent metallic silver. The unique properties of nanosilver are mainly attributed to the high surface area to volume ratio, leading many industrial sectors to incorporate silver nanoparticles into their products. Two main factors such as surface effects and quantum effects to cause nanomaterial behave significantly different than bulk materials [24]. These factors affect the chemical reactivity of materials as well as their mechanical, optical, electrical, and magnetic properties. Due to the unique chemical and biological properties of nanosilver, which are appealing to the consumer products, food technology, textiles/fabrics, catalysis, and medical industries.

### 1.1.3 Silver Applications

In the earlier years, silver has been used as a precious commodity in currencies, ornaments, jewelry, food decoration, solar cells, and photography [25]. Silver and its compounds have extensive applications in the twentieth century including electrical conductors, electrical contacts, catalysis, electronics, mirrors, assembly of chemical equipment and brazing alloys, drinking water filtration system, swimming pool filtration systems, healthcare products, and medical tools [26]. Silver paints are used for making printed circuits. Silver threads are woven into the fingertips of gloves so that it can be used with touch screen phones. Most importantly, silver/silver nanoparticles have long been used as an effective antibacterial agent against a broad spectrum of gram-negative (*Acinetobacter*, *Escherichia*, *Pseudomonas*, *Salmonella*, and *Vibrio*) and gram-positive (*Bacillus*, *Clostridium*, *Enterococcus*, *Listeria*, *Staphylococcus*, and *Streptococcus*) bacteria, which means silver is toxic to bacteria [27]. In addition to this, silver/silver nanoparticles are also found to have antifungal, antiviral, anti-inflammatory, antibiofilm, antiglycoprotein film, surface plasmon resonance, plasmonic heating, and metal-enhanced fluorescence properties [28]. Silver and silver nanoparticles are broadly used in urinary catheters and endotracheal breathing tubes [29]. The silver diammine

fluoride complex is a topical drug used to treat and prevent dental caries and relieve dentinal hypersensitivity [30]. One of the most beneficial uses of silver has been as a disinfectant, perhaps, which is routinely used in treating wounds and burns owing to its broad spectrum of toxicity to bacteria as well as its reputation of limited toxicity to humans [31]. Moreover, silver can easily bind with human body proteins (albumins and metallothioneins) and also interact with trace metals in metabolic process [32].

## 1.2 Silver Catalysis

Recently, catalysis by silver is an important methodology in organic synthesis owing to its more economical than other expensive transition metals (TM), excellent selectivity and stability, and environmentally benign nature. But, in comparison with other TM, silver catalysts have long been believed to have low catalytic efficiency, and the rapid development of silver chemistry was achieved only in the past few decades [33]. Generally, silver salts are mostly utilized as either  $\sigma$ -Lewis acid or  $\pi$ -Lewis acid, with preference to  $\sigma$ -coordination over  $\pi$ -coordination due to the ready availability of empty *f* orbitals and relativistic contraction of the electron cloud [34]. In addition to the Lewis acid character, which are also employed as cocatalysts, halophiles, general oxidants, SET oxidants (SET = single electron transfer), weak bases, and radical precursors. In addition, the typical  $d^{10}$  electronic configuration of silver salts could easily coordinate with most of the unsaturated bonds ( $\pi$ -donors) like C=C, C $\equiv$ C, C=X, and C $\equiv$ X bonds (X = heteroatom) and *n*-donors such as (thio)ethers, amines, and phosphine than other metals [35]. Because of these aforementioned advantages, silver catalysis has provided a unique opportunity in organic synthesis.

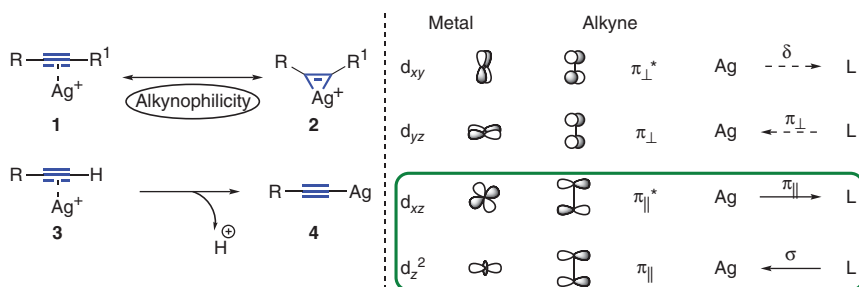
In the earlier year, the utilization of silver in organic chemistry can be classified into two prime distinct areas: (i) heterogeneous oxidation processes and (ii) homogeneous silver-mediated or silver-catalyzed reactions. The first silver-catalyzed reaction appeared in 1933, in which silver oxidizes the ethylene into ethylene oxide, and has been used on preparative and industrial scales for decades [36]. Further advancement of this protocol was also extended to other substrate, butadiene [37]. In addition to the olefin and alcohol oxidation, other examples of catalytic oxidation of CO to CO<sub>2</sub> [38] and reduction of NO<sub>x</sub> [39] by silver-based heterogeneous catalysts have also been reported. Besides, a number of silver-catalyzed transformations have been developed and even applied to the synthesis of complex natural products and functional materials, which include cycloadditions, allylations of carbonyl and imine groups, and aldol reactions along with their asymmetric versions using chiral ligands, Michael and Mannich reactions, intramolecular heterocyclizations, silver-catalyzed functionalization of C—H/C—C bonds, and C—H bond activations of terminal or silylated alkynes applied to C—C and/or C—X bond constructions [33, 35].

### 1.2.1 Alkynophilicity/Carbophilic Nature of Silver

Generally, the bonding of TM complexes with alkyne or alkene as  $\pi$ -ligands is explained on the basis of the Dewar–Chatt–Duncanson (DCD) model [40],

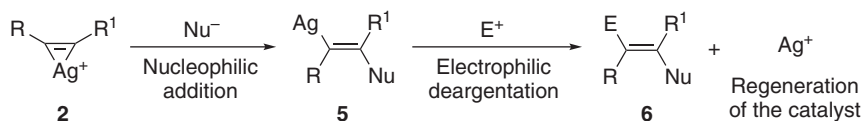
which reflects the bond as a donor–acceptor interaction between two closed-shell fragments [41]. The reason for the reputation of the donor–acceptor bonding model in TM chemistry is partly due to the fact that coordination chemistry plays a much bigger role for the TM than for main-group elements. Another reason is the success of ligand field theory (LFT) in explaining chemical bonding even in TM compounds that are not coordination compounds. According to the DCD model, a  $\sigma$ -bond is formed by the overlap of the  $\pi$ -system of the ligand with an empty metal orbital of suitable symmetry. A  $\pi$ -interaction then results through a back-donation of electron density from filled metal d orbital into an antibonding  $\pi^*$  orbital of alkyne or alkene. A TM can contribute four principal components to the bonding with alkynes as ligands (Figure 1.2) in which the in-plane  $\pi_{||}$  orbitals are responsible for a  $\sigma$ -symmetric  $M \leftarrow L$  donation and  $M \rightarrow L$  back-donation. The orthogonal out-of-plane  $\pi_{\perp}$  orbitals can participate in  $M \leftarrow L$   $\pi$ -donation, while mixing an occupied d orbital of the metal with the empty  $\pi_{\perp}^*$  orbital of alkyne can result in the addition of  $M \rightarrow L$  back-donation. However, which has the  $\delta$  symmetry and provide a weak overlap that leads to the minute contribution to the bonding. Thus, alkynes may be considered as 2- or 4-electron donor. As a result of DCD model, an elongation of triple (bending) or double (pyramidalization) bond observed as a magnitude of the net shift of electron density from bonding  $\pi$  orbital into the antibonding  $\pi^*$  orbitals. Therefore, the degree of distortion from the geometry of the unbound ligand may be reserved for the indication of the degree of back-bonding [42]. It was observed from the literature that the silver(I) salts act as a  $\sigma$ -Lewis acid or  $\pi$ -Lewis acid in homogeneous catalysis [34]. The  $d^{10}$  electronic configuration makes silver(I) cation favoring to interact with most of the unsaturated system, particularly carbon–carbon  $\pi$ -bond of alkynes **1**, so-called alkynophilicity. Upon coordination with silver(I) salts, alkyne moiety **2** is more prone to nucleophilic attack by a relatively weak nucleophile, i.e. during coordination more electron density is lost than is gained through back-donation, rendering the alkyne becomes electrophilic. But, in the case of terminal alkyne **3**, silver acetylide **4** can be formed in the presence of a suitable base and then react with carbon nucleophile (Figure 1.2). On the basis of the above characteristics features of silver(I) salts, which can be considered as one of the effective catalyst for alkyne activation [33c, 43].

The resulting silver intermediate **5** undergoes various pathways. The first potential pathway is the trapping of such a silver intermediate by an electrophile



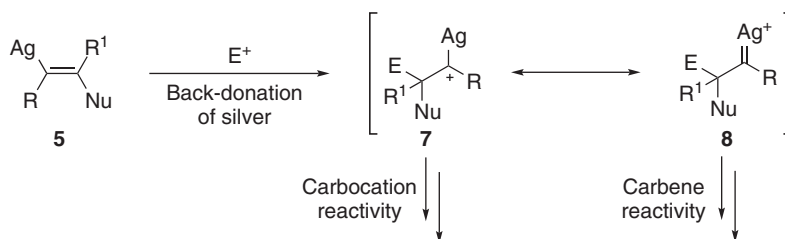
**Figure 1.2** Orbital diagram. Activation of alkyne by silver catalyst.

where the deargentation process takes place and the carbon–silver bond is replaced by carbon–electrophile bond **6** (Scheme 1.1). If the electrophile is a simple proton, this step is termed as protodeargentation.



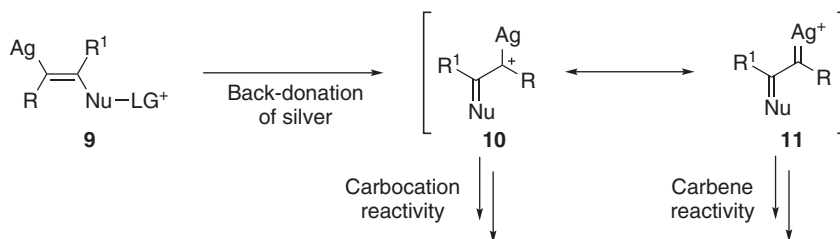
**Scheme 1.1** Trapping of silver intermediate by an electrophile.

Due to the delocalization ability of 4d electron of silver to the nonbonding electron of a carbocation, the silver intermediate **5** undergoes another kind of trapping reaction with external electrophile, where the electrophilic trapping occurs at the  $\beta$ -position to silver to generate the new silver intermediate via back-donation silver, which exists as two mesomeric forms, namely, silver-stabilized carbocation **7** and carbenes **8** (Scheme 1.2). Then, depending on its nature, the new silver intermediate can be trapped following a carbocation or carbene reactivity.



**Scheme 1.2** Trapping of silver intermediate by back-donation of silver.

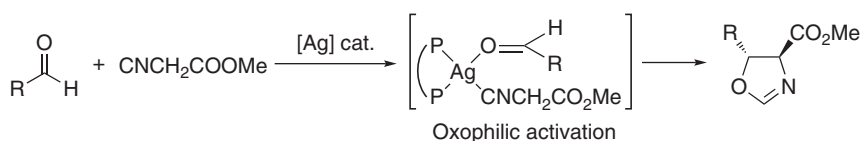
On the other hand, the nucleophilic addition of a nucleophile bearing a leaving group to a silver-activated alkyne results in a silver intermediate **9**, where, upon back-donation, extrusion of leaving group occurs to form the new silver intermediate that also exists in two limited mesomeric forms like silver-stabilized carbocation **10** and carbene **11** (Scheme 1.3). These silver intermediates can also be trapped following the carbocation and carbene reactivity, according to its nature. These three kinds of silver-catalyzed/silver-mediated alkyne activation reactions are completely described in the forthcoming chapters of this book.



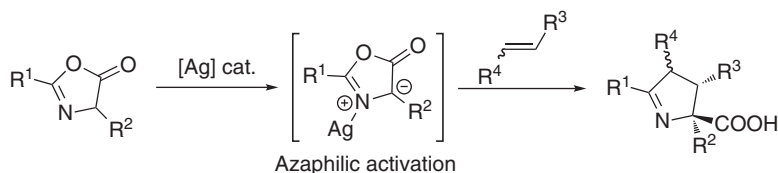
**Scheme 1.3** Reaction with nucleophile bearing a leaving group via back-donation of silver.

### 1.2.2 Oxo- and Azaphilic Character of Silver

Apart from the carbophilic character of silver, silver(I) can also form strong bonds with oxo groups, so-called oxophilicity (Scheme 1.4). This may be due to the donation of lone pairs on O into an empty orbital of silver, which might be in  $d_{\pi}$ ,  $\sigma^*$ , or  $\pi^*$  character. However, the oxophilic Lewis acid character of Ag(I) has been poorly investigated [44]; such an oxophilic character of Ag(I) has been ascribed on the basis of analogous gold(I)-catalyzed reactions [45]. However, the donation of lone pair electrons on N into an empty orbital of silver form a new strong bond, which inhibited the N-nucleophilicity; this process can be termed as azaphilicity (Scheme 1.5) [46]. Generally, the oxo- and azaphilic character of silver(I) salts has been exploited in reactions such as various cycloaddition reactions, allylation of carbonyl compounds, aldol-type reactions, Michael and Mannich reactions, and others.



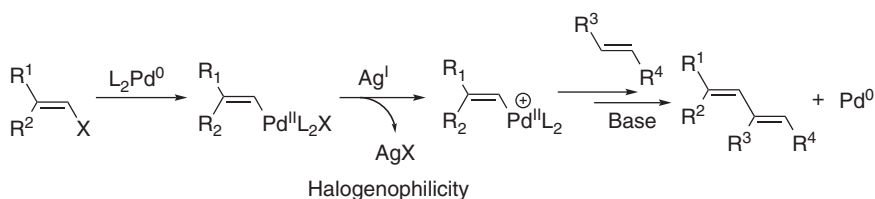
Scheme 1.4 Oxophilic activation of silver.



Scheme 1.5 Azaphilic activation of silver.

### 1.2.3 Halogenophilicity of Silver

Another important characteristic feature of silver(I) chemistry is the insolubility of its corresponding halogen salts (halogenophilicity). Generally, several TM-catalyzed transformations are led in the presence of Ag(I) salts to elicit the precipitation of AgX salts ( $X = \text{Cl}, \text{Br}, \text{I}$ ) from coordinatively saturated metal centers, for example, in the palladium-catalyzed cross-coupling reactions involving aryl or alkyl halides (Scheme 1.6) [47].



Scheme 1.6 Halogenophilicity of silver in the Pd-catalyzed cross-coupling reaction.