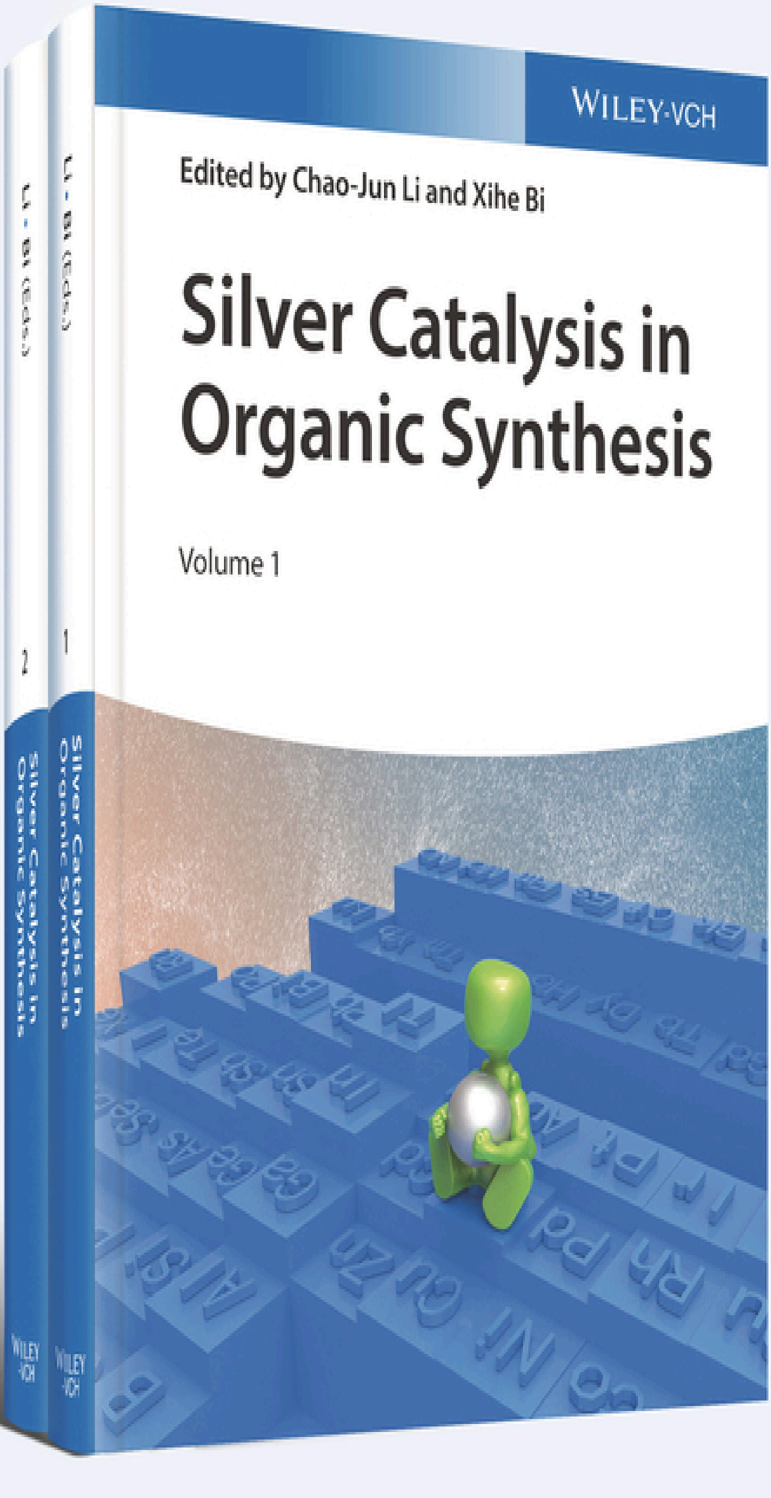

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Silver Catalysis in Organic Synthesis

Volume 1

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Volume 2

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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 σ-Lewis acid or π-Lewis acid, with preference to σ-coordination over π-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≡C, C=X, and C≡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 $C(sp^3)$—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.

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1

Introduction to Silver Chemistry

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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 [Kr] $4d^{10}5s^1$, just like copper and gold. Mostly, silver can exist in a mixture of isotopes, ^{107}Ag and ^{109}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 Ag(II) salts/complexes are less stable than that of Ag(I) and Ag(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 ($1{\cdot}59\,\mu\Omega\,cm$ at 20 °C) [4], thermal conductivity ($429\,W\,m^{-1}\,K^{-1}$) [5], and optical reflectivity than any other metal, but it has the lowest electrical contact resistance, and its specific heat capacity is $0.23\,J\,kg^{-1}\,K^{-1}$ at 25 °C. The melting and boiling point of silver is 961.9 and 2212 °C, respectively [6]. The heat of fusion of silver is $11.28\,kJ\,mol^{-1}$, 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

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(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 (AgCNO), which is a powerful touch-sensitive explosive used in percussion caps [7]. Also, silver nitrate reacts with sodium azide (NaN_3) to form silver azide (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:

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + 2H_2O + NO_3 \tag{1.1}$$

$$2Ag + 3H_2SO_4 \rightarrow 2AgHSO_4 + SO_2 + 2H_2O \tag{1.2}$$

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 $[Ag(NH_3)_2]^+$ 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]:

$$Cu(s) + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag(\downarrow) \tag{1.3}$$

$$2AgNO_3 + 2OH^- \rightarrow Ag_2O + 2NO_3{}^- + H_2O \tag{1.4}$$

$$2Ag_2O + 4NH_3 + H_2O \rightarrow 2Ag(NH_3)_2{}^+ + 2OH^- \tag{1.5}$$

$$R - CHO + 2Ag^+ + 2OH^- \rightarrow R - COOH + 2Ag + H_2O \tag{1.6}$$

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 $Ag(NH_3)_2{}^+$, $Ag(S_2O_3)_2{}^{3-}$, and $Ag(CN)_2{}^-$ with excess of respective ions. The silver thiosulfate complex is used to dissolve undeveloped 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.

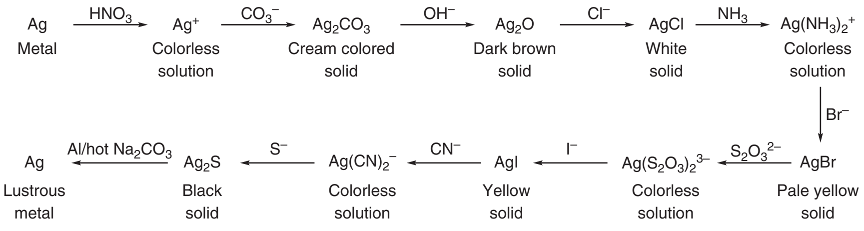


Figure 1.1 Reactions in the silver series.

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 σ-Lewis acid or π-Lewis acid, with preference to σ-coordination over π-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 (π-donors) like C=C, C≡C, C=X, and C≡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_2 [38] and reduction of NO_x [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 π-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 σ-bond is formed by the overlap of the π-system of the ligand with an empty metal orbital of suitable symmetry. A π-interaction then results through a back-donation of electron density from filled metal d orbital into an antibonding π^* 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 σ-symmetric $M \leftarrow L$ donation and $M \rightarrow L$ back-donation. The orthogonal out-of-plane $\pi_{\perp}$ orbitals can participate in $M \leftarrow L$ π-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 δ 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 π orbital into the antibonding π^* 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 σ-Lewis acid or π-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 π-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

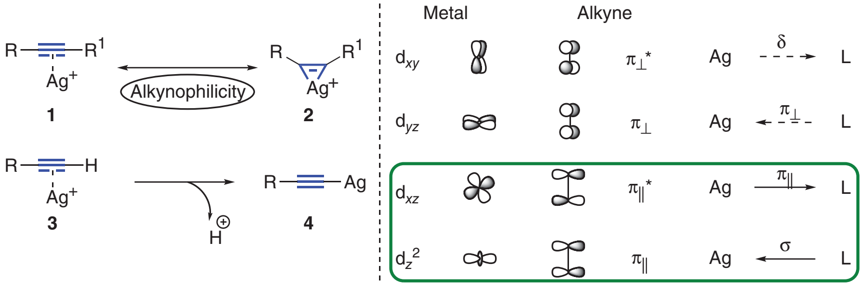
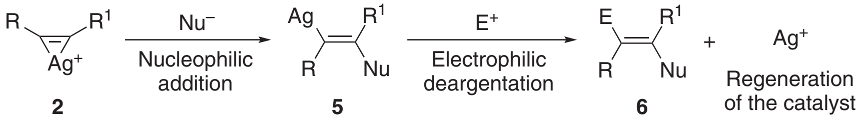


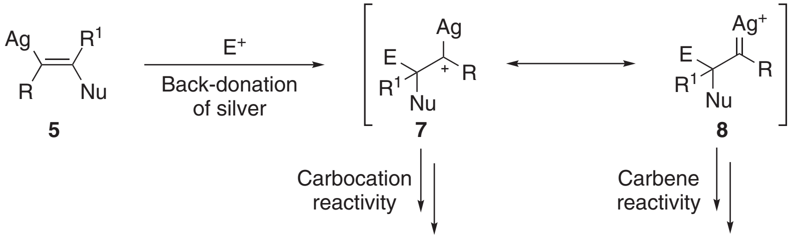
Figure 1.2 Orbital diagram. Activation of alkyne by silver catalyst.

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.



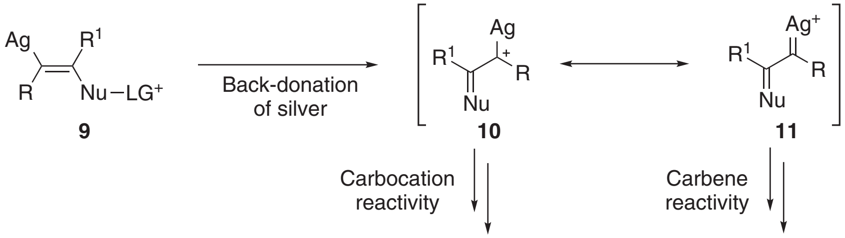
Scheme 1.1 Trapping of silver intermediate by an electrophile.

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 β-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.

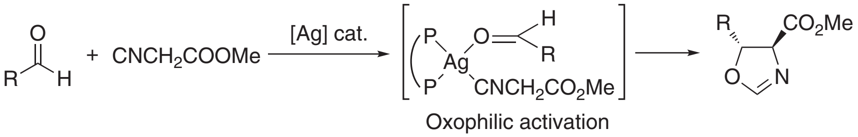
On the other hand, the nucleophilic addition of a nucleophile bearing a leaving group to a silver-activated alkyne results in a silver intermediate **9**, where, upon back-donation, extrusion of leaving group occurs to form the new silver intermediate that also exists in two limited mesomeric forms like 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.



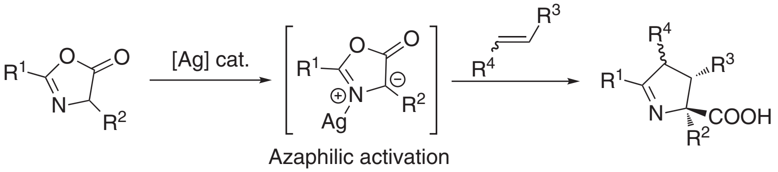
Scheme 1.3 Reaction with nucleophile bearing a leaving group via back-donation of silver.

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_π, σ^*, or π^* 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.



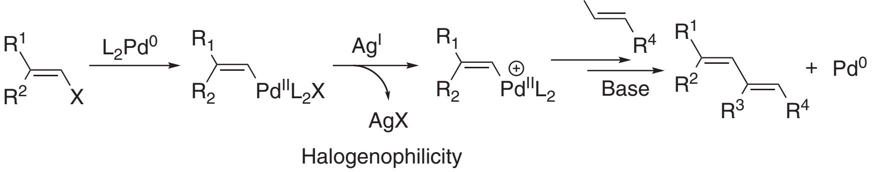
Scheme 1.4 Oxophilic activation of silver.



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 = Cl, Br, 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.