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 [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 ($1\cdot59\,\mu\Omega\,cm$ at $20\,^\circ C$) [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 $25\,^\circ C$. The melting and boiling point of silver is 961.9 and $2212\,^\circ C$, respectively [6]. The heat of fusion of silver is $11.28\,kJ\,mol^{-1}$, and its hardness is 2.7 on the Mohs scale.
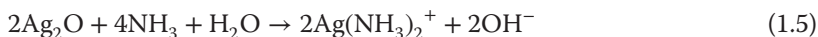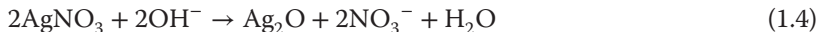
1.1.1 Chemistry of Silver

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

(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:

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

$$2Ag + 3H_2SO_4 \rightarrow 2AgHSO_4 + SO_2 + 2H_2O \tag{1.2}$$
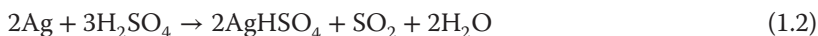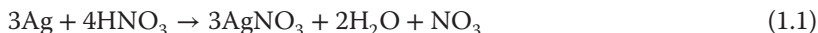
Furthermore, silver nitrate could easily react with copper to produce the silver crystals (Eq. (1.3)). The alkaline solution of copper also reduces the silver nitrate into silver in the presence of reducing sugars. Tollens' test/silver mirror test is a qualitative test to distinguish between an aldehyde 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.
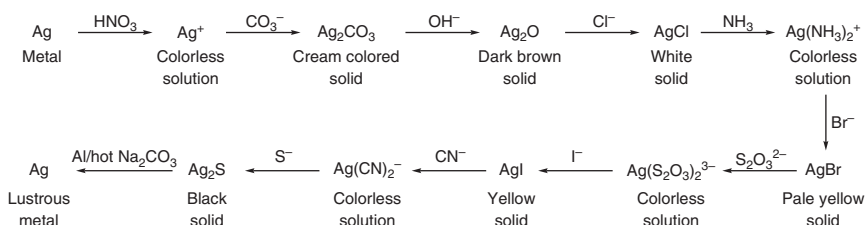

Figure 1.1 Reactions in the silver series.

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 $\pi_\parallel$ orbitals are responsible for a σ-symmetric M ← L donation and M → L back-donation. The orthogonal out-of-plane $\pi_\perp$ orbitals can participate in M ← 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 → 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
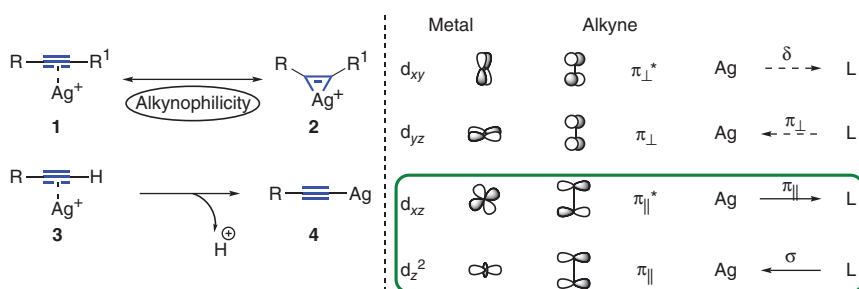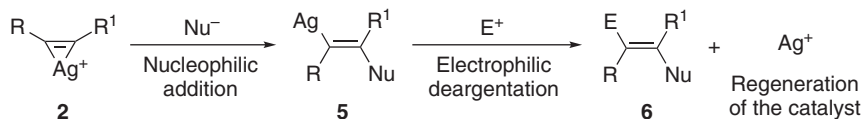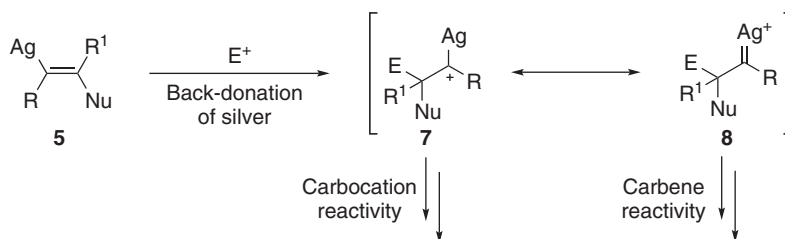

Figure 1.2 Orbital diagram. Activation of alkyne by silver catalyst.

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.
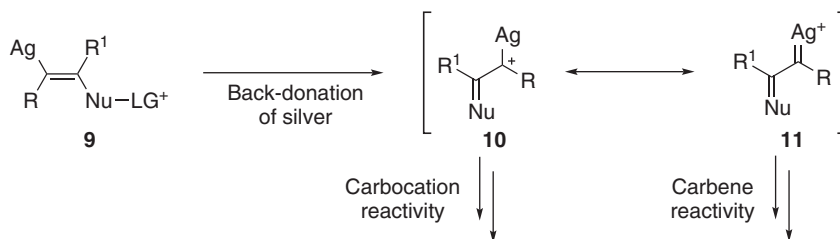

Scheme 1.1 Trapping of silver intermediate by an electrophile.

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.

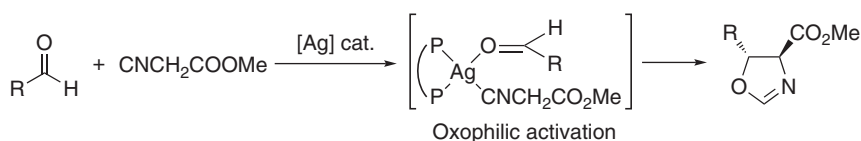**Scheme 1.2** Trapping of silver intermediate by back-donation of silver.

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.
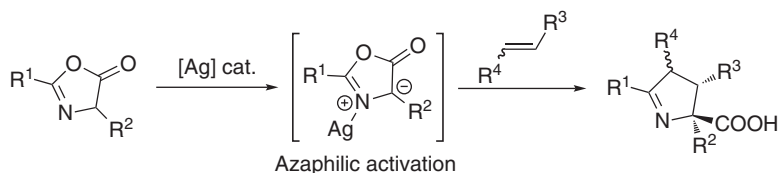

Scheme 1.3 Reaction with nucleophile bearing a leaving group via back-donation of silver.

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.

Oxophilic activation

Scheme 1.4 Oxophilic activation of silver.

Azaphilic activation

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].

Halogenophilicity

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

1.2.4 Redox Chemistry of Silver

1.2.4.1 One-electron Ag(I)/Ag(II) Redox Cycles

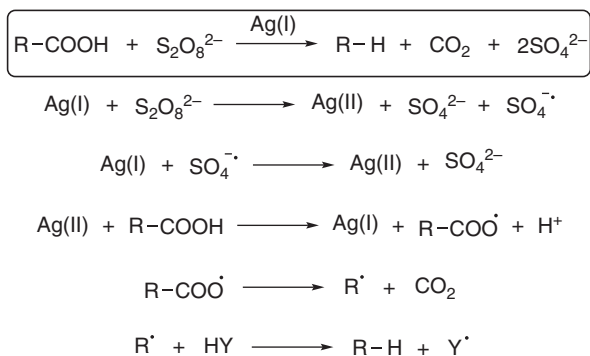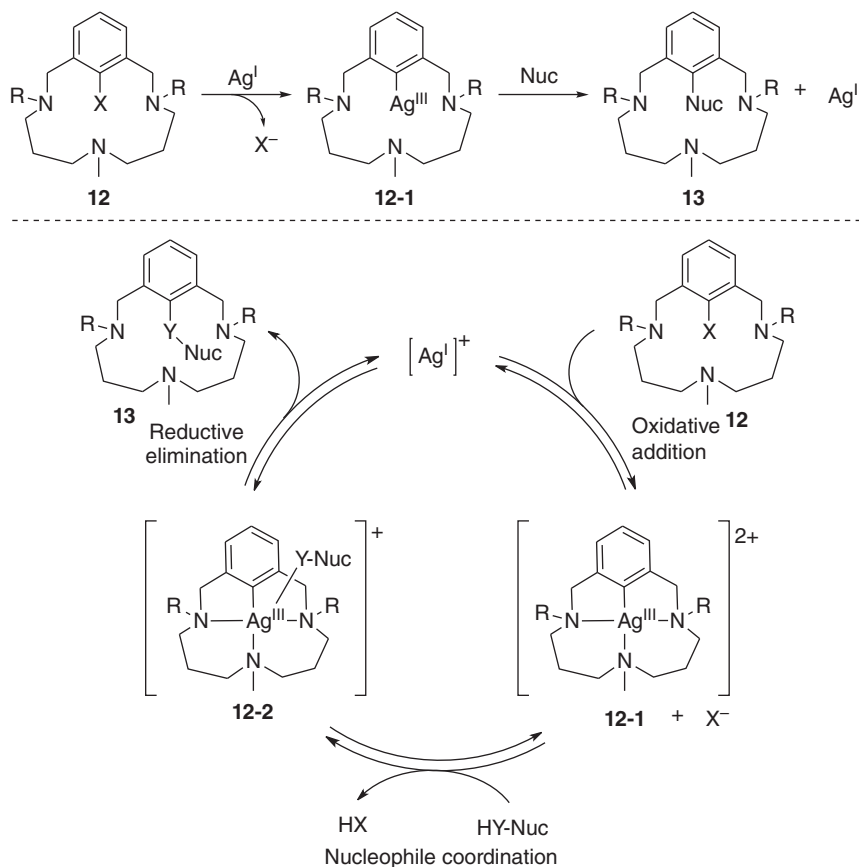It is well known that the silver(I) salts are extensively employed as one-electron oxidant as compared with other group 11 metals, copper, and gold that are involved in the two-electron redox chemistry [48], for instance, in the oxidation of alcohols into the corresponding carbonyl compounds under mild conditions [33e, 49]. Subsequently, an increasing number of oxidative C—C bond-forming and C—C bond cleavage reactions have been well documented by the use of the Ag(I) as a sacrificial outer-sphere one-electron oxidant [50]. For example, silver(I) is involved as an efficient catalyst in the oxidative decarboxylation of acids by peroxydisulfate ion in aqueous solutions [51]. Mechanistically, the *in situ* formed metastable intermediate Ag(II) species, from the rate-limiting oxidation of silver(I) by peroxydisulfate, played a crucial role in the specific and efficient decarboxylation process. The direct and facile oxidation of the carboxylic acid group by Ag(II) proceeds very fast and generates an acyloxy radical, which subsequently fragments into an alkyl radical and carbon dioxide. The final products are obtained by oxidation of the alkyl radical by silver species as well as by hydrogen transfer to solvent (Scheme 1.7).

$$R-COOH \ + \ S_2O_8{}^{2-} \ \xrightarrow{\text{Ag(I)}} \ R-H \ + \ CO_2 \ + \ 2SO_4{}^{2-}$$

$$Ag(I) \ + \ S_2O_8{}^{2-} \ \longrightarrow \ Ag(II) \ + \ SO_4{}^{2-} \ + \ SO_4{}^{-\bullet}$$

$$Ag(I) \ + \ SO_4{}^{-\bullet} \ \longrightarrow \ Ag(II) \ + \ SO_4{}^{2-}$$

$$Ag(II) \ + \ R-COOH \ \longrightarrow \ Ag(I) \ + \ R-CO\overset{\bullet}{O} \ + \ H^+$$

$$R-CO\overset{\bullet}{O} \ \longrightarrow \ R^{\bullet} \ + \ CO_2$$

$$R^{\bullet} \ + \ HY \ \longrightarrow \ R-H \ + \ Y^{\bullet}$$

Scheme 1.7 One-electron Ag(I)/Ag(II) redox cycle in Ag(I)-catalyzed oxidative cross-coupling reaction.

1.2.4.2 Two-electron Ag(I)/Ag(III) Redox Cycle

The investigation of two-electron Ag(I)/Ag(III) redox chemistry of silver is very rare, although Li and coworkers proposed in their studies on Ag(I)-catalyzed radical aminofluorinations that electrophilic fluoride sources are capable of generating monometallic Ag(III)—F intermediate species, but the C—F bond formation is proposed to occur through a one-electron redox reaction of Ag(II)—F with carbon-centered radical species [52]. Recently, the research group of Ribas studied the two-electron redox chemistry of silver in the C—O and C—C cross-coupling reactions [53], where silver can engage in two-electron oxidative addition and reductive elimination processes. More importantly, an aryl–Ag(III) **12-1** was evidently identified as a key intermediate in the catalytic cycle (Scheme 1.8) and also provided the appropriate evidence of aryl halide oxidative addition and C—N, C—O, C—S, C—C, and C—halide bond-forming

Scheme 1.8 Two-electron Ag(I)/Ag(III) redox cycle in Ag(I)-catalyzed cross-coupling reaction.

reductive elimination steps. These results exemplify a new revolution in the fundamental sympathetic of silver's redox chemistry and opens budding new opportunities for designing Ag-catalyzed synthetic tools in organic synthesis, parallel to the well-known Pd(0)/Pd(II) and Cu(I)/Cu(III) catalysis [54].

1.3 Representative Examples of Silver Catalysis in the Organic Transformations

1.3.1 Protodecarboxylation of Carboxylic Acids

Decarboxylation reactions are important transformations in synthetic organic chemistry [55], especially for the removal of carboxylate group that are employed as one of the directing groups in other transformations [56] including decarboxylative coupling reactions [57]. Consequently, significant attention has also been paid to study the protodecarboxylation of carboxylic acids. Generally, this protodecarboxylation reaction proceeds in the presence of TM such as Cu, Ag, Au, Hg, Pd, and Rh (Scheme 1.9) [58]. Among the coinage metal catalysts, silver

$$R-H \xleftarrow[\text{M = Cu, Ag, Pd, Rh}]{[M]} R-COOH \xrightarrow{[Au]} R-[Au]$$

Scheme 1.9 Transition metal-catalyzed protodecarboxylation reaction of carboxylic acid.

catalysts have been efficiently activating the decarboxylation of the variety of car-boxylic acids under mild conditions [58g] as compared with their Cu(I)-catalyzed counterparts [58c]. Notably, silver catalysts exhibited the excellent selectivity toward the monoprotodecarboxylation of dicarboxylic acids, owing to the remarkable activating effect of α-heteroatoms and ortho-electron-withdrawing groups [58g]. Mechanistically, the reaction was proposed to proceed via silver arene intermediate **14-2**, followed by protodemetalation with an aryl carboxylic acid molecule to regenerate the starting complex (Scheme 1.10). But, in the case of gold catalysis, the obtained products are not pronated because the reaction stops at the metalation (Scheme 1.9). This might be due to the high stability of C—Au bond [58k,l].
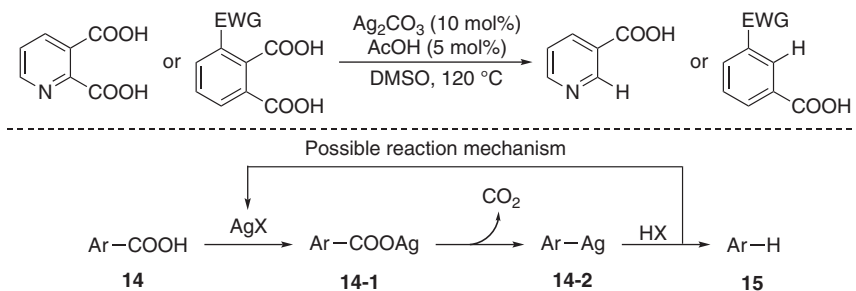
Scheme 1.10 Ag(I)-catalyzed protodecarboxylation of aromatic carboxylic acids.
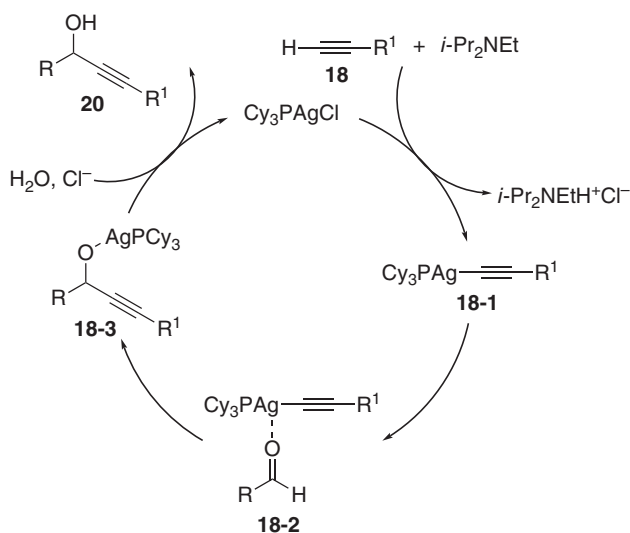
1.3.2 A³ Coupling Reaction

A³ coupling or aldehyde–alkyne–amine reaction [59] is a significant reaction as the resulting propargylamines [60] are the key building block in the synthesis of nitrogen-containing biologically active pharmaceuticals, agrochemicals, and natural products [61]. It was evident from the literature database that the silver-catalyzed A³ reaction is especially effective even with aliphatic aldehydes and more challenging coupling partners such as aniline and ketones [62]. Moreover, these silver-catalyzed approaches provided an attractive platform for developing tandem reactions, particularly for the synthesis of N-/O-containing heterocyclic compounds [63]. Besides, Li et al. observed that the phosphine ligand served as a remarkable chemo-switch in this silver-catalyzed A³ reaction in water. In the absence of phosphine ligand, exclusive aldehyde–alkyne–amine coupling product **19** was observed, whereas, in the presence of phosphine (Cy₃P) ligand, reaction provided the exclusive aldehyde–alkyne coupling product **20** (Scheme 1.11) [64].

It is well known that the simple alkynyl silver reagents are typically too reac-tive and involved in the nucleophilic addition reaction to carbonyl compounds.
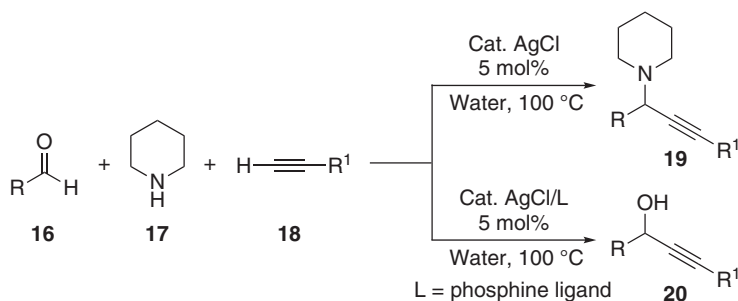
Scheme 1.11 Ligand-controlled A³ coupling reaction in water.

Mechanistically, the authors postulated that the coordination of the electron-donating P-ligand increases the electron density of silver, which results to weaken the Ag—C bond of silver acetylide **A** (Scheme 1.12).

Scheme 1.12 Catalytic cycle involved in the ligand-controlled A³ coupling reaction in water.

1.3.3 Incorporation of CO_2

The incorporation of CO_2 into propargyl alcohol is one of the frequently employed methods for the synthesis of functionalized cyclic carbonates by means of TM catalysts (Cu, Pd, Pt, Rh, Hg, and Ru). However, these reported approaches required harsh reaction conditions (high CO_2 pressure and high reaction temperature) and are only applicable to terminal alkynes, and the internal alkynes had sluggish under these catalytic conditions [65]. But, Yamada et al. discovered that, under the catalysis of silver, the CO_2 incorporation into propargyl alcohol **21** is more effective even with internal propargyl alcohols [66]. Their study revealed that the combined use of Ag(I) with DBU (1,8-Diazabicyclo(5.4.0)undec-7-ene) was found to be optimum to produce the

sole *exo*-alkenyl cyclic carbonates **22** in high to excellent yields, although other TM catalysts such as copper, gold, rhodium, mercury, platinum, and palladium were not effective at room temperature. Mechanistically, the DBU induced the deprotonation, and the silver catalyst activated the C≡C bond from the opposite side of the carbonate anion to promote anti-addition via 5-*exo*-dig cyclization as supported by DFT (density functional theory) calculations (Scheme 1.13) [67]. The backside attack is analogous to the typical reactivity of the related gold(I) catalysts [68], but only the silver catalyst is able to induce cyclization, and gold catalysis fails under these conditions [69].
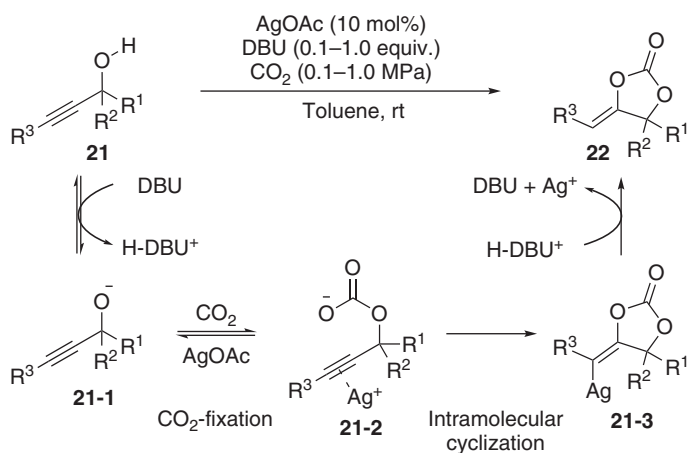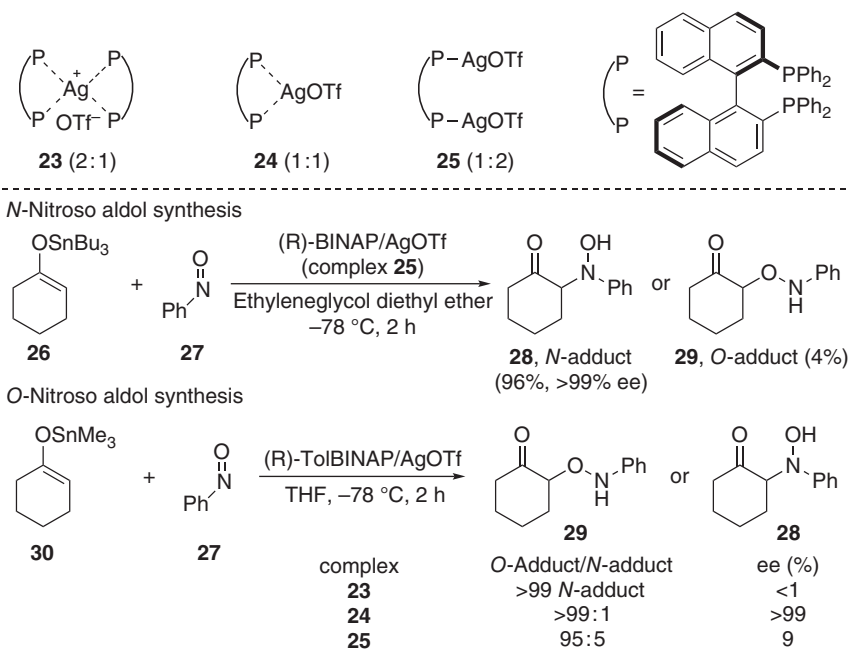

Scheme 1.13 Ag(I)-catalyzed tandem carboxylation and cyclization reaction.

1.3.4 Enantioselective Nitroso-aldol Reaction

The asymmetric nitroso-aldol-type reaction is one of the important transformations in organic synthesis that can introduce a hydroxyl group at the α-position of carbonyl compounds [70]. However, a key challenge arising in the exploitation of nitroso-aldol synthesis is controlling selectivity between *O*- and *N*-adduct owing to the high reactivity of nitroso derivatives toward nucleophiles. Generally, an organocatalyst like ʟ-proline exclusively promotes the *O*-nitroso-aldol reaction of aldehyde and ketone [71]. In sharp contrast, the selective *N*-nitroso-aldol reaction is very difficult task to achieve [72]. However, Yamamoto and coworkers selectively achieved the *N*-adduct **28** in the nitroso-aldol reaction of tributyltin enolate **26** with nitrosobenzene **27** using 10 mol% of AgOTf and (*R*)-BINAP system (Scheme 1.14) [73].

During their studies, the authors isolated the three different BINAP-silver complexes **23–25** via the systematic survey of metal-to-ligand ratio; the complex either **23** or **25** was selectively generated from 2 equiv. of (*R*)-BINAP with 1 equiv. of AgOTf or 2 equiv. of AgOTf with 1 equiv. of (*R*)-BINAP, respectively, and the complex **24** was generated from 1 : 1 ratio of (*R*)-BINAP and AgOTf. But each of the three complexes plays a different role in regio- and enantioselectivity of this nitroso-aldol reaction. Among the three complexes, the monometallic complex

N-Nitroso aldol synthesis

28, *N*-adduct
(96%, >99% ee)

29, *O*-adduct (4%)

O-Nitroso aldol synthesis

complex	*O*-Adduct/*N*-adduct	ee (%)
23	>99 *N*-adduct	<1
24	>99:1	>99
25	95:5	9

Scheme 1.14 Enantioselective *N*- and *O*-nitroso-aldol synthesis.

23 resulted the complete *N*-selectivity **29** in THF without any enantioselectivity (*O*-/*N*- = 1 :>99, 2% ee). And the enantioselectivity of *N*-adduct **29** was also very low when using the monometallic complex **24** derived from AgOAc (~20% ee). However, by using bimetallic complex **25** in ethylene glycol diethyl ether, excellent levels of enantio- and regioselectivities were observed (*O*-/*N*- = 4 : 96, >99% ee). But, in the presence of complex **24** derived from (*R*)-TolBINAP and AgOTf, the reaction of trimethyltin enolate **30** with nitrosobenzene **27** exclusively provided the *O*-adduct **28** with excellent regio- and stereoselectivity (*O*-/*N*- = >99 : 1, >99% ee) [73].

1.3.5 Chemoselective Cyclopropanation Using Donor–Acceptor Diazo Compounds

TM catalysts played a critical role on modulating the decomposition chemistry of diazo compounds. Traditional carbenoids functionalized with one- or two-electron acceptor groups (ester, ketone, phosphonate, etc.) are highly electrophilic. On the other hand, carbenoids with a donor (aryl, vinyl, alkynyl) and an acceptor group are much more chemoselective than traditional carbenoids [74] as witnessed from the myriad of reported organic transformations [75]. For instance, Davies and Thompson demonstrate that the $AgSbF_6$-catalyzed reaction of *trans*-β-methylstyrene **31** with donor–acceptor diazo compounds **32** provides a very different reactivity profile than the reaction in the presence of $Rh_2(OAc)_4$ catalyst where the silver-catalyzed reaction resulted the cyclopropane **33** in excellent yields (80%) and diastereoselectivity (>94% de) and also retained the

orientation between phenyl and methyl groups in the product. While rhodium catalysts selectively produced the C—H insertion product **34** (4%), carbene dimerization was a dominant product when using large excess of substrates (Scheme 1.15). Moreover, the silver-catalyzed cyclopropanation of a variety of alkenes including more hindered substrates can also be achieved, despite that these substrates failed to afford the cyclopropane derivatives with rhodium catalysts [76]. One the other hand, the silver-catalyzed reaction of the vinyldiazoacetate **35** with 1,3-cyclohexadiene **36** also has a major effect, in which the $AgSbF_6$ resulted in the tandem cyclopropanation and cope rearrangement to give formal [4+3] cycloadduct **37** in 67% yield. However, rhodium acetate-catalyzed reaction proceeds through the tandem C—H activation/cope rearrangement to afford 1.4 : 1 ratio of products **37** and **38** in 36% yield (Scheme 1.16).
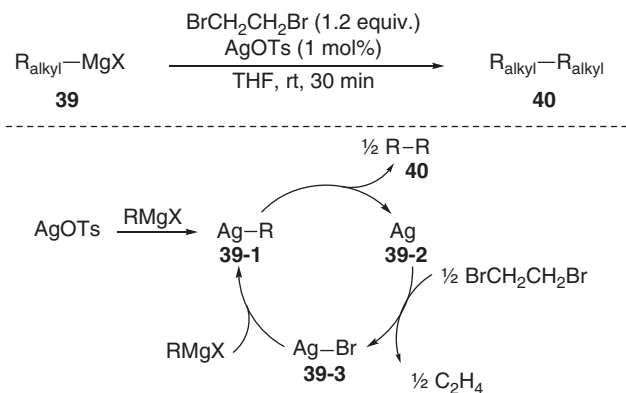

Catalyst	Yield	33 : 34	
$AgSbF_6$	80%	> 20 : 1	>94% de
$Rh_2(OAc)_4$	4%	1 : > 20	
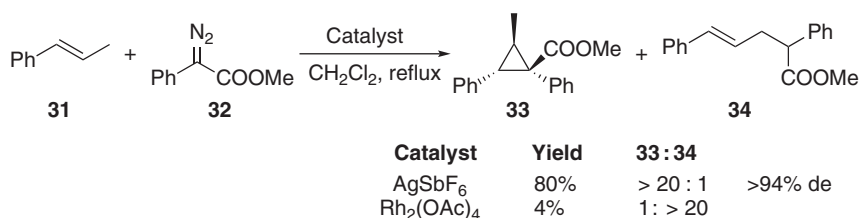
Scheme 1.15 Chemoselective reaction of styrene with donor–acceptor diazo compounds.

Catalyst	Yield	37 : 38
$AgSbF_6$	67%	5.4 : 1
$Rh_2(OAc)_4$	36%	1.4 : 1
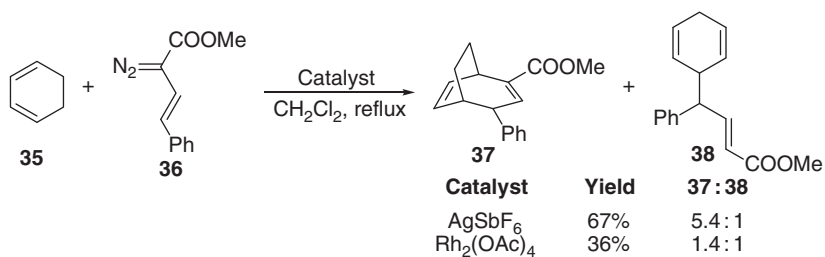
Scheme 1.16 Reaction of vinyldiazoacetate with 1,3-cyclohexadiene.

1.3.6 Homocoupling of Alkyl Grignard Reagents

TM-mediated/TM-catalyzed oxidative homocoupling of organometallic reagents is an important transformation in organic synthesis, and significant progress has been made on the several catalytic homocoupling of aryl–metal reagents [77]. However, the homocoupling of alkyl–metal reagents, especially those bearing β-hydrogens, has not been developed well, because of the difficulty in the alkyl–alkyl coupling by TM catalysis [78]. In this connection, Hayashi et al. developed a silver-catalyzed protocol to achieve the oxidative alkyl–alkyl homocoupling, where the silver tosylate (AgOTs) selectively catalyzes the homocoupling of alkylmagnesium reagents **39** in the presence of 1,2-dibromoethane as an oxidant in THF at RT to give the corresponding symmetrical alkanes **40** in excellent yields (Scheme 1.17). However, the effective aryl–aryl coupling catalyst $FeCl_3$ and other TM catalysts such as $CoCl_2$, $NiCl_2$, and $CuCl_2$ produced very

R$_{alkyl}$—MgX $\xrightarrow[\text{THF, rt, 30 min}]{\substack{\text{BrCH}_2\text{CH}_2\text{Br (1.2 equiv.)} \\ \text{AgOTs (1 mol\%)}}}$ R$_{alkyl}$—R$_{alkyl}$

39   **40**

½ R–R
40

AgOTs $\xrightarrow{\text{RMgX}}$ Ag–R   Ag
39-1   **39-2**
                             ½ BrCH$_2$CH$_2$Br

RMgX   Ag–Br
               39-3   ½ C$_2$H$_4$

Scheme 1.17 Silver-catalyzed homocoupling of alkyl Grignard reagents.

poor yields of homocoupling products along with alkene as a by-product. This may be due to the as-formed alkyl–metal intermediate more prone to undergo β-elimination to give alkene, but the alkyl silver intermediate failed to undergo β-elimination [79]. Mechanistically, the alkyl silver **39-1** species was proposed as a key intermediate in this reaction, which undergoes disproportionation to give homocoupling product **40** and silver(0) species **39-2**. Then the formed Ag(0) species **39-2** undergoes oxidation with 1,2-dibromoethane followed by transmetalation with Grignard reagents to regenerate alkyl silver species **39-1** to carry the catalytic cycle. This proposed mechanism is completely different than that of the reported one, where the alkyl bromide **41** was proposed as a crucial intermediate (Scheme 1.18) [80].
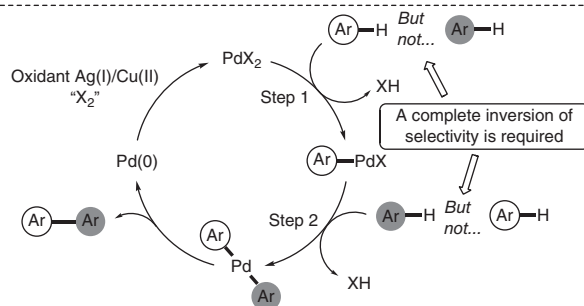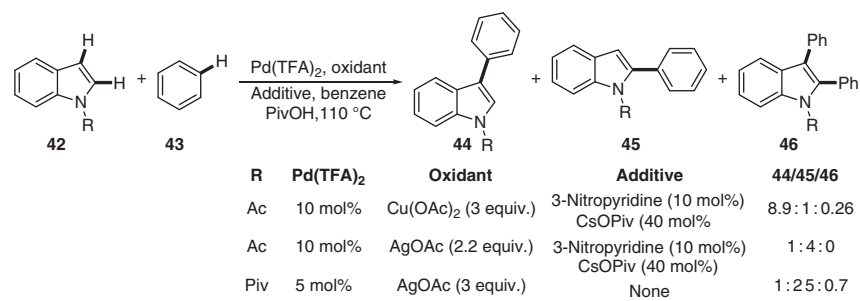
Step I   R—MgBr   +   Br$\diagdown\diagup$Br $\longrightarrow$ R—Br   +   C$_2$H$_4$ +   MgBr$_2$
          39   **41**

Step II   R—MgBr   +   R—Br $\xrightarrow{\text{[Ag] cat}}$ R—R   +   MgBr$_2$
          39   **41**   **40**
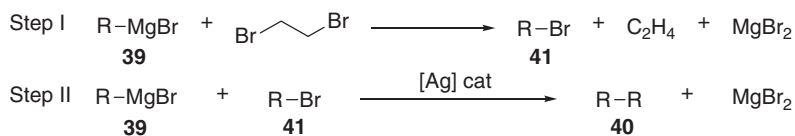
Scheme 1.18 Alternative mechanism.

1.3.7 Oxidative Arene Cross-coupling

Biaryl molecules are considered as abundant building blocks in light-emitting diodes, electron transport devices, liquid crystals, and medicinal compounds [81]. Because of the structural simplicity of biaryl compounds belies its preparative complexity, although the palladium-catalyzed cross-coupling reactions (Suzuki and Stille couplings) of alkyl halides and organometallics are the most accepted and widely used methods for the synthesis of biaryls. But these approaches required the preactivation of both aromatic coupling substrates and provided the unwanted homocoupling products that hampered the applicability of these reactions [82]. In the past few decades, some important advances have been made in the biaryl synthesis by direct cross-coupling that are devoid of any substrate preactivation [83]. For example, Fagnou group realized that the

palladium can catalyze the cross-coupling of N-substituted indoles **42** and benzenes **43** to give the C3 and C2 aryl indoles **44** and **45** in high yield over a range of indoles without recourse to any activating groups (Scheme 1.19). In this reaction, the authors found that the oxidant plays a critical role to control the product selectivity. In the presence of stoichiometric Cu(OAc)$_2$ oxidant (10 mol%), the Pd-catalyzed reaction of *N*-acetyl indoles and benzenes selectively afforded the C3 aryl indoles **44** in high yields (C3/C2 = 8.9 : 1) [84]. However, the Pd-catalyzed reaction was carried out with stoichiometric AgOAc oxidant, which delivers the C2 aryl indoles **45**. Changing the *N*-acetyl to *N*-pivalyl indole resulted in excellent C3/C2 selectivity (1 : 25) [85]. Furthermore, these standard conditions did not afford any by-products resulting from the homo-coupling of arene substrates. The reason for the inversion in C2/C3 selectivity is explained as follows: in the presence of AgOAc, the acetate behaves as a base not counterion that instructs the increased C2 selectivity to Pd catalyst, where the carboxylate-induced cleavage of higher-order Pd clusters and the formation of monomeric Pd species were occurring. While excess of Cu(OAc)$_2$ is added into the catalytic quantity of Pd(TFA)$_2$, mixed Pd—Cu clusters may be formed that exhibit pronounced C3 selectivity [86].

| R	Pd(TFA)$_2$	Oxidant	Additive	44/45/46
Ac	10 mol%	Cu(OAc)$_2$ (3 equiv.)	3-Nitropyridine (10 mol%) CsOPiv (40 mol%)	8.9 : 1 : 0.26
Ac	10 mol%	AgOAc (2.2 equiv.)	3-Nitropyridine (10 mol%) CsOPiv (40 mol%)	1 : 4 : 0
Piv	5 mol%	AgOAc (3 equiv.)	None	1 : 25 : 0.7

Scheme 1.19 Oxidative arene cross-coupling.

1.3.8 Hydroazidation of Alkynes

The hydroazidation of alkynes is one of the most straightforward pathways to access synthetically useful vinyl azides, which are versatile synthetic interme-diates in numerous organic transformations, particularly in the TM-catalyzed azaheterocyclization reactions [87]. However, the synthetic potency of vinyl

azides from unactivated alkynes remains largely unexplored [88]. In 2014, Bi's group established a silver(I)-catalyzed protocol for the chemo- and regiose-lective hydroazidation of ethynyl carbinols **47** with TMSN$_3$, affording diverse 2-azidoallyl alcohols **48** in high yields, where the hydroxyl group that is close to the alkyne unit plays a critical role in directing the regio- and chemoselectivity, and a trace amount of water in DMSO (dimethyl sulfoxide) was necessary for the reaction. But other TM catalysts such as Cu(I) and Pd(II) salts failed to yield the hydroazidation product. Mechanistically, silver acetylide **47-1** and vinyl silver **47-2** were proposed as a key intermediate in this reaction (Scheme 1.20) [89]. Later, they found that the stoichiometric amount of water has avoided the dependence of the hydroxyl group in the hydroazidation reaction. Accordingly, the numerous unactivated terminal alkynes **49** underwent the hydroazidation using TMSN$_3$ in H$_2$O with the assistance of Ag$_2$CO$_3$ to give the excellent yields of corresponding vinyl azides **50** in shorter reaction times (Scheme 1.20) [90].
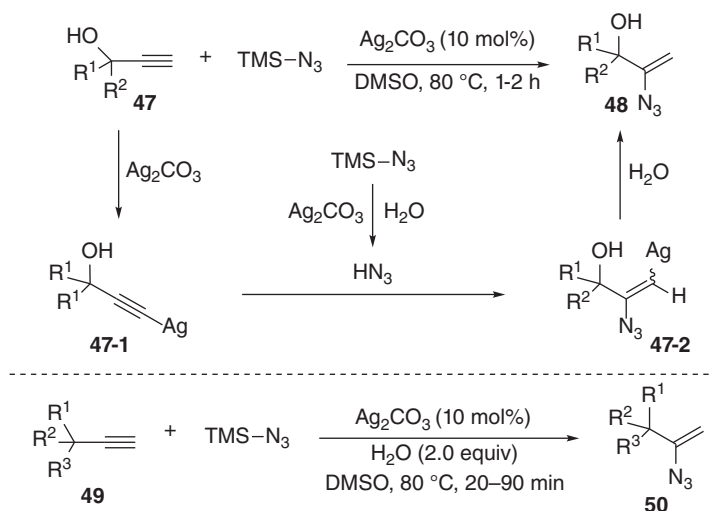
Scheme 1.20 Hydroazidation of unactivated alkynes.
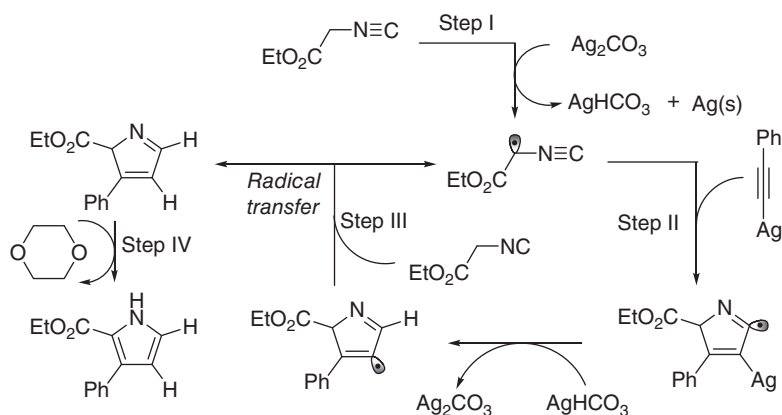
1.3.9 Isocyanide–alkyne Cycloaddition

The [3+2] cycloaddition of isocyanides and alkynes is an atom-economic and straightforward method for the synthesis of pyrroles, which are important motifs in numerous natural products, pharmaceuticals, agrochemicals, and functional materials. However, most of the reported reactions are highly limited to electron-deficient alkynes under base or copper catalysis [91]. In 2013, Bi's group [92] and Lei group [93] have addressed these challenges through a silver-catalyzed cycloaddition reaction of unactivated terminal alkynes and isocyanides (Scheme 1.21). Remarkably, Ag$_2$CO$_3$ exhibited the unique catalytic activity toward the pyrrole **51** synthesis than other silver salts such as AgNO$_3$, AgBF$_4$, AgClO$_4$, AgOAc, AgOTf, Ag$_2$O, AgF, and AgNO$_2$. In contrast, Cu(OAc)$_2$ and CuI catalysts were found to be ineffective. Also, the standard conditions did not produce any by-products derived from the homocoupling of terminal
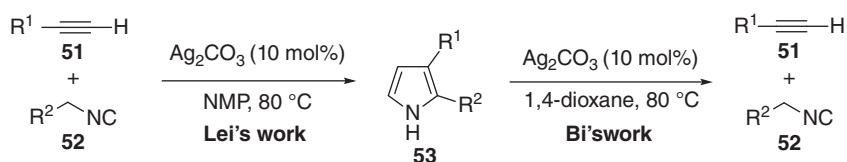
Scheme 1.21 [3+2] cycloaddition of isocyanides with terminal alkynes.

alkynes. But the reaction mechanism of this reaction proposed by both Lei's and Bi's groups remains unclear.

Later, Bi's group collaborates with Zhang group to study the precise reaction mechanism of this Ag_2CO_3-catalyzed cycloaddition of isocyanides with terminal alkynes. The combined DFT and experimental results clearly revealed that the reaction underwent through an unexpected multicatalyzed radical process, where the Ag_2CO_3 served a dual role as a base for deprotonating isocyanide and an oxidant to initiate the initial isocyanide radical formation. After the cycloaddition of isocyanide radical with silver acetylide, the substrate (isocyanide) and solvent (1,4-dioxane) replaced the role of Ag_2CO_3 and acted as a radical shuttle to regenerate the isocyanide radical for the next cycle, completing the protonation (Scheme 1.22) [94].


Scheme 1.22 Favorable radical catalytic cycle for the isocyanide–alkyne cycloaddition.

1.3.10 Nitrogenation of Terminal Alkynes

The transformation of alkynes is a fundamental method that has been widely utilized in organic synthesis. Recently, the catalytic selective cleavage of carbon–carbon triple bond has attracted significant attention, and several TM-catalyzed C≡C bond cleavage reactions have been reported for the construction of new C—C and C—heteroatom bonds, especially silver catalyst remarkable catalytic activity [95]. For example, Jiao et al. reported a novel and direct method for the nitrogenation of alkynes **54** into nitriles **55** through the selective cleavage of C≡C bonds. A range of aryl/alkyl terminal alkynes smoothly underwent this selective

nitrogenation using 10 mol% of Ag_2CO_3 as catalyst to afford the desired nitriles in high yields. However, the reaction catalyzed by other TM, such as $AuCl_3$, $NiCl_2$, $FeCl_2$, $Cu(OAc)_2$, and $Pd(OAc)_2$, either did not proceed or gave only poor yields, indicating the amazing catalytic reactivity of silver in this nitrogenation process [96]. Mechanistically, the formation of vinyl azide **54-3** is a crucial intermediate in this nitrogenation reaction, which could directly transform into corresponding nitriles **55** under standard conditions. But, in the absence of another equivalent of $TMSN_3$, corresponding nitriles obtained in very poor yields imply the pivotal role of $TMSN_3$ in C≡C bond cleavage. From these, the author concluded that the conversion of vinyl azides into nitriles does not require the silver catalyst. Then the as-formed vinyl azide **54-3** cyclizes with azide to form the unstable intermediate **54-4**, which undergoes fast rearrangement to give nitrile with the release of HN_3 and CH_2N_2 (Scheme 1.23) [96].
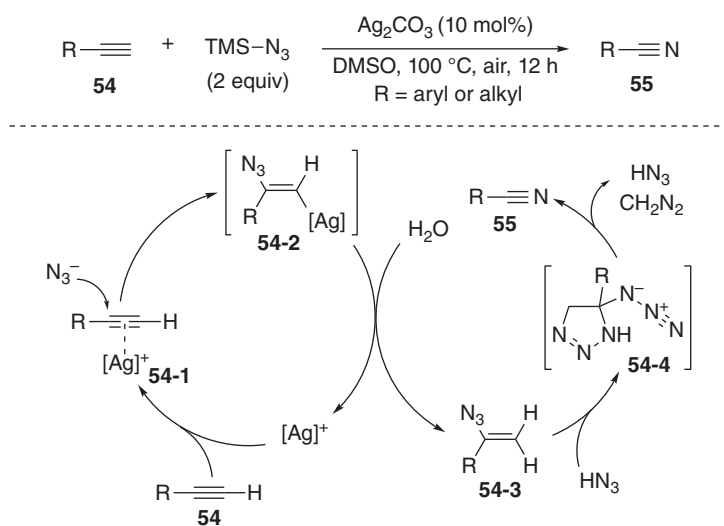
Scheme 1.23 Silver-catalyzed nitrogenation of terminal alkynes via C≡C bond cleavage.

1.3.11 Decarboxylative Alkynylation

Introduction of an alkynyl group into a molecule has drawn considerable attention not only because of its applications in materials science and chemical biology but also because of its versatile building blocks in organic synthesis [97]. Rapid progress has been made in the TM-catalyzed alkynylation via the Sonogashira reaction, which results in expedient route to $C(sp^2)$—$C(sp)$ and $C(sp^3)$—$C(sp)$ bond formations. However, these approaches are highly restricted to primary or secondary alky–alkynyl coupling, while tertiary alkyl–alkynyl coupling reaction remains a difficult task [98]. In this connection, Li group described a silver-catalyzed decarboxylative alkynylation of aliphatic carboxylic acids **56** in aqueous conditions (Scheme 1.24). Especially, in the presence of $AgNO_3$ as catalyst and $K_2S_2O_8$ as oxidant, various primary/secondary/tertiary alkyl carboxylic acids smoothly underwent the decarboxylative $C(sp)$—$C(sp^3)$
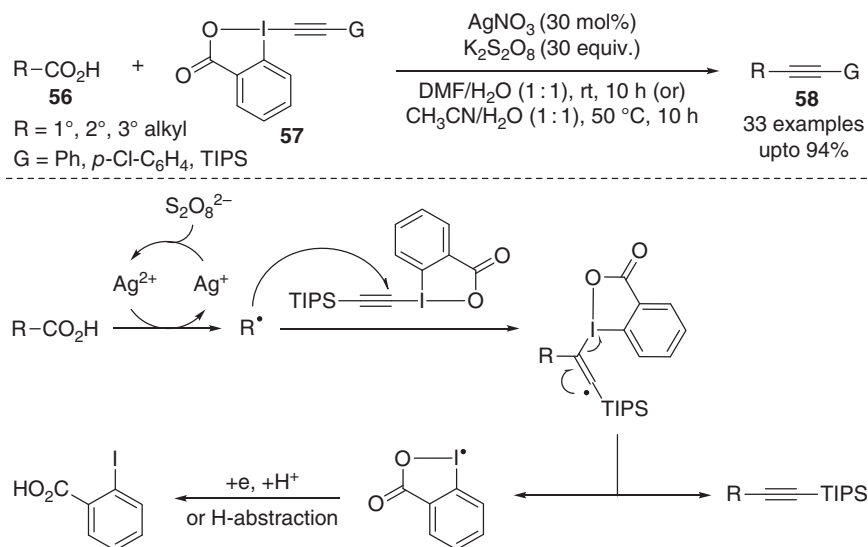
Scheme 1.24 Silver-catalyzed decarboxylative alkynylation.

coupling with various ethynylbenziodoxolones **57**, leading to the corresponding alkylated compounds **58** in high yields under mild conditions. Notably, this catalytic process exhibited the good functional group tolerance, including the more complex molecules such as N-protected amino acids or dehydrolithocholic acids. Based on their control experiments, the authors proposed a radical mechanism as shown in Scheme 1.24. Oxidation of Ag(I) by persulfate generates Ag(II), which then induces decarboxylation of aliphatic carboxylic acid into alkyl radical. The addition of alkyl radical to the C≡C triple bond of alkynyliodine(III) compound and subsequent β-elimination to afford the final product along with the benziodoxolonyl radical. The latter is transformed into 2-iodobenzoic acid either by H-abstraction or by reduction [99].

1.3.12 Nitrene Transfer Reactions

N-containing organic compounds are principal components of many biologically and pharmaceutically important molecules. Therefore, the selective introduction of N-atom into molecules is of great interest of research. The TM-catalyzed nitrene transfer into C—H or C=C bond of unsaturated substrates represents a straightforward strategy for the construction of new C—N bonds, and significant progress has been achieved in the past decades [100]. However, the chemoselective C—N bond formation via the nitrene transfer into a substrate bearing both C—H and C=C bonds is challenging task, because these substrates give rise to multiple products or exhibit substrate or catalyst controlled selectivity [101]. Thus, a novel method that can achieve both the product by means of same metal and same ligands is highly needed. In 2013, the Schomaker group has solved this problem by employing this nitrene transfer reaction of homoallenic carbamates **59** with silver catalysis. Particularly, a silver complex derived from AgOTf and

1,10-phenanthroline (phen) showed significant chemoselectivity by tuning the metal ligand ratio [102]. In the absence of an allenic C—H bond, the selective aziridination took place, and no competitive C—H amination was observed. But, in the presence of allenic C—H bonds, aziridination **60** is preferred over C—H amination **61** with a monomeric (phen)AgOTf complex derived from an equimolar ratio AgOTf and Phen, and the chemoselectivity for aziridination over C—H amination varied from 3.7 : 1 to >20 : 1. In sharp contrast, when the AgOTf/Phen ratio was increased to 1 : 3, the aziridination process was suppressed, and reactivity favored to the C—H insertion, leading to C—H aminated products **61** with excellent chemoselectivities (Scheme 1.25). Notably, trisubstituted allenes exhibited excellent selectivity under both conditions, while less substituted allenes usually gave better selectivity in C—H insertion. This result shows that Ag has the unique ability to change coordination geometry in response to changes in the metal/ligand ratio. The control experiment results support that a concerted pathway involves singlet nitrene for the C—H insertion (Scheme 1.26, Path B). But the aziridination pathway could involve either singlet
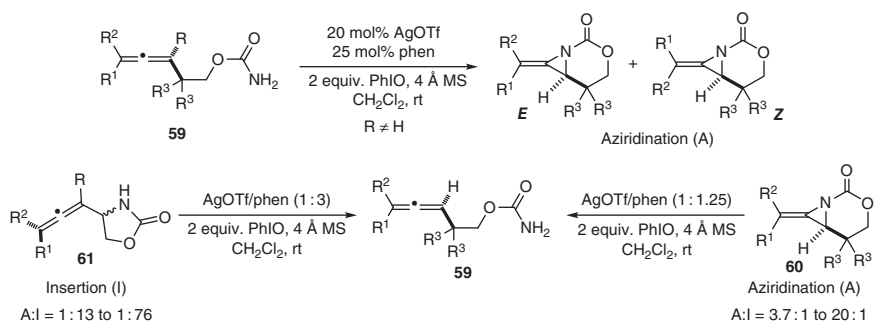
**Scheme 1.25** Silver-catalyzed nitrene transfer reaction.
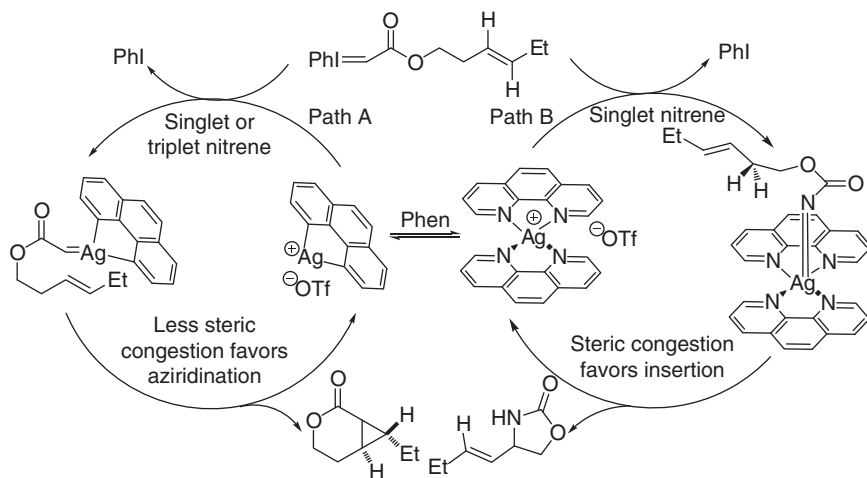
Scheme 1.26 Proposed mechanisms for Ag-catalyzed divergent chemoselective amination.

or triplet nitrene intermediate or perhaps both (Scheme 1.26, Path B) because of the energy difference between these two states are very small.
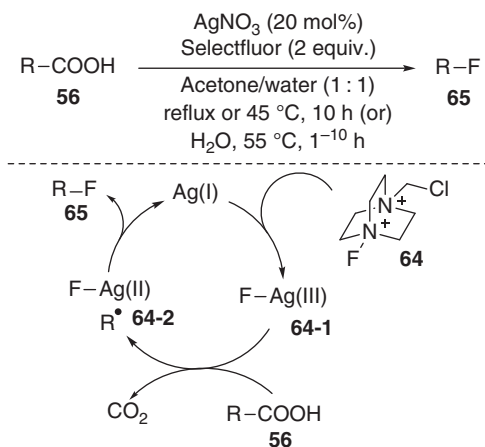
1.3.13 Fluorination Reactions

The replacement of a hydrogen by fluorine in organic molecules leads to dramatic changes in their properties such as solubility, metabolic stability, and bioavailability [103]. Thus, the efficient strategies toward fluorinated compounds have attracted significant attention. It was observed from the literature database that the silver-catalyzed/silver-mediated approaches occupied a prime position for the synthesis of fluorine-containing molecules [104]. For instance, Liu and coworkers established a novel silver-catalyzed intramolecular aminofluorination of allenes **62** for the synthesis of 4-fluoro-2,5-dihydropyrroles **63** [105]. Particularly, $AgNO_3$ resulted in remarkable catalytic reactivity in the aminofluorination of allenes using NFSI (*N*-Fluorobenzenesulfonimide) as a fluorine source. Moreover, the reaction was tolerant to various functional groups and substitution pattern. It should be noted that under the catalysis of palladium, no conversion was observed, indicating the critical role of silver(I) in the reaction outcome. The preliminary mechanistic study revealed that the reaction proposed to proceed via a vinyl silver intermediate **62-1**, which reacts with NFSI, to afford the product with the regeneration of silver catalyst (Scheme 1.27).
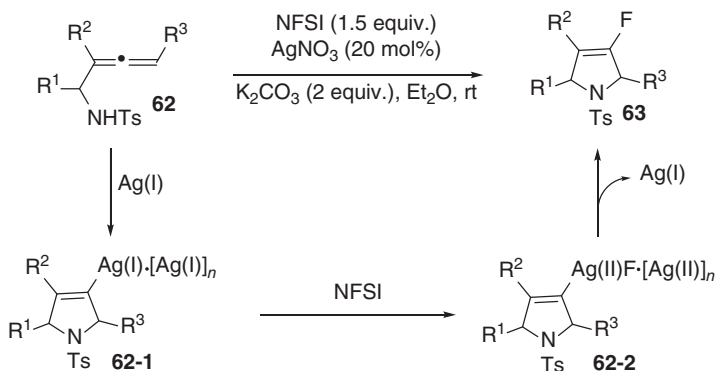
Scheme 1.27 Silver-catalyzed aminofluorination of allenes with NFSI.

In another example, Li and coworkers introduced a fluorine atom into the $C(sp^3)$ carbon via a silver-catalyzed decarboxylative fluorination of aliphatic carboxylic acids **56** using Selectfluor **64** as a fluorine source in aqueous conditions [106]. With 20 mol% of $AgNO_3$ as catalyst, various aliphatic carboxylic acids smoothly underwent the decarboxylative fluorination to afford the corresponding fluoroalkanes **65** in high yields and excellent chemoselectivity. The reactivity of carboxylic acids decreases in the order of tertiary > secondary > primary ≫ aromatics. Based on their control experiment results, the authors proposed a radical mechanism as shown in Scheme 1.28. Formation of Ag(III)—F intermediate **64-1** via the oxidation of Ag(I) by Selectfluor was proposed as

$$\text{R-COOH} \xrightarrow[\substack{\text{Acetone/water (1:1)} \\ \text{reflux or 45 °C, 10 h (or)} \\ \text{H}_2\text{O, 55 °C, 1}^{-10}\text{ h}}]{\substack{\text{AgNO}_3\text{ (20 mol\%)} \\ \text{Selectfluor (2 equiv.)}}} \text{R-F}$$

Scheme 1.28 Ag(I)-catalyzed decarboxylative fluorination of aliphatic carboxylic acids.

critical step, which then undergoes SET with carboxylate anion to produce Ag(II)—F **64-2** and carboxyl radical. The fast decarboxylation provides alkyl radical, which then abstracts fluorine atom from the Ag(II)—F to afford alkyl fluorides and regenerate the Ag(I) catalyst.

1.4 Summary

This chapter provides a collective information concerning the history, features, chemistry, and applications of silver salts/silver nanoparticles. More importantly, the fundamental reaction involved in the catalysis of silver is described on the basis of key prominent mechanistic aspects. Knowledge of these fundamental reactions would be useful to understand and develop the catalytic new multistep transformations. As the purpose of this book is the catalysis of silver in organic transformations, the remaining chapters provide an overview of various silver salts/silver complexes/silver nanoparticle-catalyzed/mediated organic transformations with the scope of reactivity, selectivity, and also reaction mechanism.

References

1 (a) Lockhart, H.B. (1983). Silver compounds. In: *Kirk-Othmer Encyclopedia of Chemical Technology*, 2e, vol. 21 (ed. M. Grayson), 16–32. New York, NY, USA: John Wiley & Sons. (b) Janes, N. and Playle, R.C. (1995). *Environ. Toxicol. Chem.* 14: 1847. (c) Purcell, T.W. and Peters, J.J. (1998). *Environ. Toxicol. Chem.* 17: 539.

2 (a) Renner, H. (1993). Silver, silver compounds and silver alloys. In: *Ullmann's Encyclopedia of Industrial Chemistry*, 5e, vol. A24 (eds. B. Elvers, S. Hawkins, W. Russey and G. Schulz), 2–19. Weinheim, Germany: VCH.

(b) Cappel, R. (1997). Silver compounds. In: *Kirk-Othmer Encyclopedia of Chemical Technology*, 4e, vol. 22 (ed. M. Howe-Grant), 179–195. New York, NY, USA: Wiley.

3 (a) Bailar, J.C. (1944). *J. Chem. Educ.* 21: 523. (b) Etris, S. (1997). Silver and silver alloys. In: *Kirk–Othmer Encyclopedia of Chemical Technology*, 4e, vol. 22 (ed. M. Howe-Grant), 163–179. New York, NY, USA: Wiley.

4 Butts, A. (1967). *Silver, Economics, Metallurgy and Use*. D. Van Nostrand Co. Inc.

5 (a) Kannulik, W.G. (1933). *Proc. R. Soc.* 141: 159. (b) Bailey, L.C. (1931). *Proc. R. Soc.* A134: 57.

6 (a) Weast, R.C. and Selby, S.M. (1968). *Handbook of Chemistry and Physics*, 49e, vol. 69. Chemical Rubber Publishing Co. (b) Brewer, L. (1977). The Cohesive Energies of the Elements. Lawrence Berkeley Laboratory Report LBL 3720 Rev. 4 May 1977.

7 Collins, P.H. and Holloway, K.J. (1978). *Propellants Explos. Pyrotech.* 3: 159.

8 Rudolf, M., Josef, K., and Axel, H. (2007). *Explosives*, vol. 284. Wiley-VCH.

9 Tollens, B. (1882). *Ber. Dtsch. Chem. Ges.* 15: 1635.

10 Pope, C.I. (1960). *J. Res. Natl. Bur. Stand., Sect. C* 64C: 65.

11 (a) Dettner, H.W., Elze, J., and Raub, E. (1966). *Handbuch der Galvanotechnik*. Munchen: C. Hanser. (b) Krusenstjern, A.V. (1970). *Edelmetallgalvanotechnik*. Saulgau: Leuze Verlag.

12 Nowack, B., Krug, H.F., and Height, M. (2011). *Environ. Sci. Technol.* 45: 1177.

13 Xia, Y., Xiong, Y., Lim, B., and Skrabalak, S.E. (2009). *Angew. Chem. Int. Ed.* 48: 60.

14 Ni, C., Hassan, A.P., and Kaler, E.W. (2005). *Langmuir* 21: 3334.

15 Schmid, G. (2004). *Nanoparticles. From Theory to Application*. Weinheim: Wiley-VCH.

16 Wiley, B.J., Xiong, Y., Li, Z.Y. et al. (2006). *Nano Lett.* 6: 765.

17 Chen, S., Fan, Z., and Carroll, D.L. (2002). *J. Phys. Chem. B* 106: 10777.

18 (a) Gao, Y., Jiang, P., Song, L. et al. (2005). *J. Phys. D: Appl. Phys.* 38: 1061. (b) Chen, C., Wang, L., Jiang, G. et al. (2006). *Nanotechnology* 17: 466. (c) Gunawidjaja, R., Jiang, C., Ko, H., and Tsukruk, V.V. (2006). *Adv. Mater.* 18: 2895. (d) Arumugam, S.K., Sastry, T.P., Sreedhar, B., and Mandal, A.B. (2007). *J. Biomed. Mater. Res. Part A* 80: 391.

19 (a) Im, S.H., Lee, Y.T., Wiley, B., and Xia, Y. (2005). *Angew. Chem. Int. Ed.* 44: 2154. (b) Rycenga, M., McLellan, J.M., and Xia, Y. (2008). *Adv. Mater.* 20: 2416. (c) Zeng, J., Zheng, Y., Rycenga, M. et al. (2010). *J. Am. Chem. Soc.* 132: 8552. (d) Zhang, Q., Li, W., Moran, C. et al. (2010). *J. Am. Chem. Soc.* 132: 11372.

20 (a) Metraux, G. and Mirkin, C.A. (2005). *Adv. Mater.* 17: 412. (b) Xue, C. and Mirkin, C.A. (2007). *Angew. Chem. Int. Ed.* 46: 2036.

21 Zinchenko, A.A., Yoshikawa, K., and Baigl, D. (2005). *Adv. Mater.* 17: 2820.

22 Xiong, Y.J., Siekkinen, A.R., Wang, J.G. et al. (2007). *J. Mater. Chem.* 17: 2600.

23 Yang, Y., Matsubara, S., Xiong, L. et al. (2007). *J. Phys. Chem. C* 111: 9095.

24 Roduner, E. (2006). *Chem. Soc. Rev.* 35: 583.

25 (a) Kerschagl, R. (1961). *Silber, Metallische Rohstoffe*, vol. 13. Stuttgart: Enke. (b) Butts, A. and Coxe, C.D. (1975). *Silver-Economics, Metallurgy, and Use*. Huntington: R. E. Krieger Publ. Comp. (c) Rompp, H. (1941). *Chemie der Metalle*. Stuttgart: Franckh'sche Verlagshandlung. (d) Degussa, A.G. (1967). *Edelmetall-Taschenbuch*. Frankfurt. (e) Degussa, A.G. (1995). *Edelmetall-Taschenbuch*, 2e. Heidelberg: Huthig-Verlag. (f) Luschin, A. and Ebengreuth, V. (1971). *Allgemeine Munzkunde und Geldgeschichte*. Munchen: R. Oldenbourg.

26 Clement, J.L. and Jarrett, P.S. (1994). *Appl. Environ. Microbiol.* 73: 1712.

27 (a) Burrell, R.E. (1997). The in vitro and in vivo antimicrobial potency of a new silver coated dressing for wound care. 51OK K955453, Washington, DC; (b) Burrell, R.E., Heggers, J.P., Davis, G.J., and Wright, J.B. (1999). *Wounds* 11: 64. (c) Wijnhoven, S.W.P., Peijnenburg, W.J.G.M., Herberts, C.A. et al. (2009). *Nanotoxicology* 3: 109. (d) Wright, J.B., Lam, K., Hansen, D., and Burrell, R.E. (1999). *Am. J. Infect. Control* 27: 344. (e) Yu, D. and Yam, V.W. (2005). *J. Phys. Chem. B* 109: 5497–5503.

28 (a) Kim, J.S., Kuk, E., Yu, K.N. et al. (2007). *Nanomedicine* 3: 95. (b) Elechiguerra, J.L., Burt, J.L., Morones, J.R. et al. (2005). *J. Nanobiotechnol.* 3: 6. (c) Sun, R.W., Chen, R., Chung, N.P. et al. (2005). *Chem. Commun.* 5059. (d) Nadworny, P.L., Wang, J., Tredget, E.E., and Burrell, R.E. (2010). *J. Inflammation* 7: 13. (e) Bhol, K.C. and Schechter, P.J. (2005). *Br. J. Dermatol.* 152: 1235. (f) Bhol, K.C. and Schechter, P.J. (2007). *Dig. Dis. Sci.* 52: 2732. (g) Tian, J., Wong, K.K., Ho, C.M. et al. (2007). *ChemMedChem* 2: 129. (h) Furno, F., Morley, K.S., Wong, B. et al. (2004). *J. Antimicrob. Chemother.* 54: 1019. (i) Schierholz, J.M., Lucas, L.J., Rump, A., and Pulverer, G. (1998). *J. Hosp. Infect.* 40: 257. (j) Percival, S.L., Bowler, P.G., and Dolman, J. (2007). *Int. Wound. J.* 4: 186. (k) Moores, A. and Goettmann, F. (2006). *New J. Chem.* 30: 1121. (l) Thomas, S., Nair, S.K., Jamal, E.M.A. et al. (2008). *Nanotechnology* 19: 075710. (m) Skirtach, A.G., Antipov, A.A., Shchukin, D.G., and Sukhorukov, G.B. (2004). *Langmuir* 20: 6988. (n) Skirtach, A.G., Oz, J.A., Kreft, O. et al. (2006). *Angew. Chem. Int. Ed.* 45: 4612. (o) Radziuk, D., Shchukin, D.G., Skirtach, A. et al. (2007). *Langmuir* 23: 4612. (p) Aslan, K., Gryczynski, I., Malicka, J. et al. (2005). *Curr. Opin. Biotechnol.* 16: 55.

29 (a) Chaiban, G., Hanna, H., Dvorak, T., and Raad, I. (2005). *J. Antimicrob. Chemother.* 55: 51. (b) Saint, S., Veenstra, D.L., Sullivan, S.D. et al. (2000). *Arch. Intern. Med.* 160: 2670. (c) Karchmer, T.B., Giannetta, E.T., Muto, C.A. et al. (2000). *Arch. Intern. Med.* 160: 3294.

30 Rosenblatt, A., Stamford, T.C.M., and Niederman, R. (2009). *J. Dent. Res.* 88: 116.

31 (a) Munteanu, A., Florescu, I.P., and Nitescu, C. (2016). *J. Med. Life* 9: 306. (b) Atiyeh, B.S., Costagliola, M., Hayek, S.N., and Dibo, S.A. (2007). *Burns* 33: 139. (c) Elliott, C. (2010). *Br. J. Nurs.* 19: S32. (d) Leaper, D.J. (2006). *Int. Wound J.* 3: 282. (e) Coutts, P. and Sibbald, R.G. (2005). *Int. Wound J.* 2: 348. (f) Cutting, K., White, R., and Edmonds, M. (2007). *Int. Wound J.* 4: 177. (g) Silverstein, P., Heimbach, D., Meites, H. et al. (2011). *J. Burn Care Rehabil.* 32: 617.

32 (a) Ahern, A.M. and Garrell, R.L. (1991). *Langmuir* 7: 254. (b) Shoeib, T., Rodriquez, C.F., Siu, K.W.M., and Hopkinson, A.C. (2001). *Phys. Chem. Chem. Phys.* 3: 853. (c) Shoeib, T. and Sharp, B.L. (2009). *Inorg. Chim. Acta* 362: 1925. (d) Ahmad, S., Hanif, M., Monim-ul-Mehboob, M. et al. (2009). *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.* 39: 45. (e) Mantion, A. and Taubert, A. (2012). *Encyclopedia of Supramolecular Chemistry: Metal-Peptide Frameworks* (eds. J. Atwood, J. Steed and K. Wallace). New York: Taylor & Francis. (f) Feng, D.-Q., Liu, G., Zheng, W. et al. (2011). *Chem. Commun.* 47: 8557.

33 (a) Zheng, Q. and Jiao, N. (2016). *Chem. Soc. Rev.* 45: 4590. (b) Pellissier, H. (2016). *Chem. Rev.* 116: 14868. (c) Fang, G. and Bi, X. (2015). *Chem. Soc. Rev.* 44: 8124. (d) Fang, G., Cong, X., Zanoni, G. et al. (2017). *Adv. Synth. Catal.* 359: 1422. (e) Yamamoto, Y. (2008). *Chem. Rev.* 108: 3199. (f) Dias, H.V.R. and Lovely, C.J. (2008). *Chem. Rev.* 108: 3223.

34 (a) Munoz, M.P. (2014). *Chem. Soc. Rev.* 43: 3164. (b) Naodovic, M. and Yamamoto, H. (2008). *Chem. Rev.* 108: 3132.

35 (a) Gorin, D.J. and Toste, F.D. (2007). *Nature* 446: 395. (b) Furstner, A. and Davies, P.W. (2007). *Angew. Chem. Int. Ed.* 46: 3410. (c) Alvarez-Corral, M., Munoz-Dorado, M., and Rodirguez-Garcia, I. (2008). *Chem. Rev.* 108: 3174. (d) Gilmore, K. and Alabugin, I.V. (2011). *Chem. Rev.* 111: 6513. (e) Halbes-Letinois, U., Pale, P., and Berger, S. (2005). *J. Organomet. Chem.* 70: 9185. (f) Patil, N.T. and Yamamoto, Y. (2008). *Chem. Rev.* 108: 3395.

36 (a) Sheldon, R.A. and Kochi, J.K. (1981). *Metal-Catalyzed Oxidation of Organic Compounds*. New York: Academic Press. (b) Othmer, D.F. and Thakar, M.S. (1958). *J. Ind. Eng. Chem.* 50: 1235. (c) Hamilton, G.E. and Metzner, A.B. (1957). *J. Ind. Eng. Chem.* 49: 838. (d) McClellan, P.P. (1950). *J. Ind. Eng. Chem.* 42: 2402. (e) Kajimoto, Y. (1998). *Kagaku Purosesu*, 121.

37 Wilkinson, S. (1999). *Chem. Eng. News* 77: 27.

38 (a) Wright, P.A., Natarajan, S., Thomas, J.M., and Gai-Boyes, J.M. (1992). *Chem. Mater.* 4: 1053. (b) Gardner, S.D., Hoflund, G.B., Schryer, D.R. et al. (1991). *Langmuir* 7: 2135.

39 Lindfors, L.E., Eraenen, K., Klingsted, F., and Murzin, D.Y. (2004). *Top. Catal.* 28: 185.

40 (a) Dewar, M.J.S. (1951). *Bull. Soc. Chim. Fr.* 18: C71–C79. (b) Chatt, J. and Duncanson, L.A. (1953). *J. Chem. Soc.* 2939.

41 (a) Mingos, D.M.P. (1982). Bonding of unsaturated organic molecules to transition molecules. In: *Comprehensive Organometallic Chemistry*, vol. 3 (eds. G. Wilkinson, F.G.A. Stone and E.W. Abel), 1–88. Oxford: Pergamon. (b) Frenking, G. and Frohlich, N. (2000). *Chem. Rev.* 100: 717. (c) Dedieu, A. (2000). *Chem. Rev.* 100: 543.

42 Fürstner, A. and Davies, P.W. (2007). *Angew. Chem. Int. Ed.* 46: 3410.

43 (a) Halbes-Letinois, U., Weibel, J.M., and Pale, P. (2007). *Chem. Soc. Rev.* 36: 759. (b) Karmakar, R. and Lee, D. (2016). *Chem. Soc. Rev.* 45: 4459. (c) Kim, S.H., Kim, K.H., and Hong, S.H. (2014). *Angew. Chem. Int. Ed.* 53: 771. (d) Gorin, D.J. and Toste, F.D. (2007). *Nature* 446: 395.

44 (a) Crist, D.R., Hsieh, Z.H., Jordan, G.J. et al. (1974). *J. Am. Chem. Soc.* 96: 4932. (b) Crist, D.R., Hsieh, Z.-H., Quicksall, C.O., and Sun, M.K. (1984). *J. Organomet. Chem.* 49: 2478. (c) Sawamura, M., Hamashima, H., and

Ito, Y. (1990). *J. Organomet. Chem.* 55: 5936. (d) Hayashi, T., Uozumi, Y., and Yamazaki, A. (1991). *Tetrahedron Lett.* 32: 2799. (e) Soloshonok, V.A. and Hayashi, T. (1994). *Tetrahedron Lett.* 7: 1055. (f) Castellino, S. and Simms, J.J. (1984). *Tetrahedron Lett.* 25: 4059.

45 Ito, Y., Sawamura, M., and Hayashi, T. (1986). *J. Am. Chem. Soc.* 108: 6405.

46 (a) Peddibhotla, S. and Tepe, J.J. (2004). *J. Am. Chem. Soc.* 126: 12776.
(b) Carswell, E.L., Snapper, M.L., and Hoveyda, A.H. (2006). *Angew. Chem. Int. Ed.* 45: 7230. (c) Nakamura, I., Nemoto, T., Yamamoto, Y., and de Meijere, A. (2006). *Angew. Chem. Int. Ed.* 45: 5176.

47 Weibel, J.-M., Blanc, A.l., and Pale, P. (2008). *Chem. Rev.* 108: 3149.

48 (a) Casitas, A., King, A.E., Parella, T. et al. (2010). *Chem. Sci.* 1: 326.
(b) Casitas, A. and Ribas, X. (2013). *Chem. Sci.* 4: 2301. (c) Hickman, A.J. and Sanford, M.S. (2012). *Nature* 484: 177. (d) Boorman, T.C. and Larrosa, I. (2011). *Chem. Soc. Rev.* 40: 1910. (e) Guenther, J., Mallet-Ladeira, S., Estevez, L. et al. (2014). *J. Am. Chem. Soc.* 136: 1778. (f) Hashmi, A.S.K., Blanco, M.C., Fischer, D., and Bats, J.W. (2006). *Eur. J. Org. Chem.* 2006: 1387.
(g) Yu, Y., Yang, W., Pflasterer, D., and Hashmi, A.S.K. (2014). *Angew. Chem. Int. Ed.* 53: 1144.

49 Mijs, W.J. and Jong, C.R.H.I.d. (1986). *Organic Synthesis by Oxidation with Metal Complexes*. Plenum Press.

50 (a) Hull, K.L. and Sanford, M.S. (2007). *J. Am. Chem. Soc.* 129: 11904.
(b) Hashmi, A.S.K. (2010). A critical comparison: copper, silver, and gold. In: *Silver in Organic Chemistry*, Ch. 12 (ed. M. Harmata), 357–379. Wiley.
(c) Tang, P., Furuya, T., and Ritter, T. (2010). *J. Am. Chem. Soc.* 132: 12150.
(d) Seo, S., Taylor, J.B., and Greaney, M.F. (2013). *Chem. Commun.* 49: 6385.
(e) Weibel, J.-M., Blanc, A., and Pale, P. (2010). Coupling reactions promoted by silver. In: *Silver in Organic Chemistry*, Ch. 10 (ed. M. Harmata), 285–327. Wiley. (f) Ghosh, S.P., Ghosh, M.C., and Gould, E.S. (1994). *Inorg. Chim. Acta* 225: 83.

51 Anderson, J.M. and Kochi, J.K. (1970). *J. Am. Chem. Soc.* 92: 1651.

52 Li, Z., Song, L., and Li, C. (2013). *J. Am. Chem. Soc.* 135: 4640.

53 Font, M., Acuna-Pares, F., Parella, T. et al. (2014). *Nat. Commun.* 5: 4373. doi: https://doi.org/10.1038/ncomms5373.

54 Hickman, A.J. and Sanford, M.S. (2012). *Nature* 484: 177.

55 Joule, J.A. and Mills, K. (2000). *Heterocyclic Chemistry*, 4e. Malden, MA: Blackwell.

56 (a) Chiong, H.A., Pham, Q.-N., and Daugulis, O. (2007). *J. Am. Chem. Soc.* 129: 9879. (b) Sonoda, M., Kakiuchi, F., Kamatani, A. et al. (1996). *Chem. Lett.* 25: 109.

57 (a) Gooßen, L.J., Rodriguez, N., and Gooßen, K. (2008). *Angew. Chem. Int. Ed.* 47: 3100. (b) Gooßen, L.J., Gooßen, K., Rodriguez, N. et al. (2008). *Pure Appl. Chem.* 80: 1725.

58 (a) Cohen, T. and Schambach, R.A. (1970). *J. Am. Chem. Soc.* 92: 3189.
(b) Cairncross, A., Roland, J.R., Henderson, R.M., and Sheppard, W.A. (1970). *J. Am. Chem. Soc.* 92: 3187. (c) Goossen, L.J., Thiel, W.R., Rodriguez, N., and Linder, C. (2007). *Adv. Synth. Catal.* 349: 2241. (d) Goossen, L.J., Manjolinho, F., Khan, B.-A., and Rodríguez, N. (2009). *J. Organomet. Chem.* 74: 2620. (e) Kolarovic, A. and Fáberová, Z. (2009). *J. Organomet. Chem.*

74: 7199. (f) Gooßen, L.J., Linder, C., Rodríguez, N. et al. (2009). *Chem. Commun.* 7173. (g) Lu, P., Sanchez, C., Cornella, J., and Larrosa, I. (2009). *Org. Lett.* 11: 5710. (h) Goossen, L.J., Rodríguez, N., Linder, C. et al. (2010). *ChemCatChem* 2: 430. (i) Dupuy, S., Lazreg, F., Slawin, A.M.Z. et al. (2011). *Chem. Commun.* 47: 5455. (j) Cornella, J., Rosillo-Lopez, M., and Larrosa, I. (2011). *Adv. Synth. Catal.* 353: 1359. (k) Dickstein, J.S., Mulrooney, C.A., O'Brien, E.M. et al. (2007). *Org. Lett.* 9: 2441. (l) Tanaka, D., Romeril, S.P., and Myers, A.G. (2005). *J. Am. Chem. Soc.* 127: 10323. (m) Sun, Z.M., Zhang, J., and Zhao, P. (2010). *Org. Lett.* 12: 992. (n) Dodd, D. and Johnson, M.D. (1970). *J. Chem. Soc. B* 1337. (o) Moseley, J.D. and Gilday, J.P. (2006). *Tetrahedron* 62: 4690. (p) Xue, L., Su, W., and Lin, Z. (2011). *Dalton Trans.* 40: 11926. (q) Toy, X.Y., Roslan, I.I.B., Chuah, G.K., and Jaenicke, S. (2014). *Catal. Sci. Technol.* 4: 516. (r) Zhan, K. and Li, Y. (2017). *Catalysts* 7: 314.

59 Sakaguchi, S., Kubo, T., and Ishii, Y. (2001). *Angew. Chem. Int. Ed.* 40: 2534.

60 (a) Akullian, L.C., Snapper, M.L., and Hoveyda, A.H. (2003). *Angew. Chem. Int. Ed.* 42: 4244. (b) Koradin, C., Gommermann, N., Polborn, K., and Knochel, P. (2003). *Chem. Eur. J.* 9: 2797.

61 (a) Huffman, M.A., Yasuda, N., DeCamp, A.E., and Grabowski, E.J.J. (1995). *J. Organomet. Chem.* 60: 1590. (b) Miura, M., Enna, M., Okuro, K., and Nomura, M. (1995). *J. Organomet. Chem.* 60: 4999. (c) Naota, T., Takaya, H., and Murahashi, S.I. (1998). *Chem. Rev.* 98: 2599. (d) Boulton, A.A., Davis, B.A., Durden, D.A. et al. (1997). *Drug Dev. Res.* 42: 150. (e) Kauffman, G.S., Harris, G.D., Dorow, R.L. et al. (2000). *Org. Lett.* 2: 3119.

62 (a) Wei, C.-M., Li, Z.-G., and Li, C.-J. (2003). *Org. Lett.* 5: 44735. (b) Zhang, Y., Santos, A.M., Herdtweck, E. et al. (2005). *New J. Chem.* 29: 366. (c) Reddy, K.M., Babu, N.S., Suryanarayana, I. et al. (2006). *Tetrahedron Lett.* 47: 7563. (d) Zhao, Y., Zhou, X., Okamura, T.-A. et al. (2012). *Dalton Trans.* 41: 5889. (e) Prakash, O., Joshi, H., Kumar, U. et al. (2015). *Dalton Trans.* 44: 1962. (f) Shao, G., He, Y., Xu, Y. et al. (2015). *Eur. J. Org. Chem.* 21: 4615. (g) Jeganathan, M., Dhakshinamoorthy, A., and Pitchumani, K. (2014). *ACS Sustainable Chem. Eng.* 2: 781. (h) Salam, N., Kundu, S.K., Molla, R.A. et al. (2014). *RSC Adv.* 4: 47593. (i) Zhou, X., Lu, Y., Zhai, L.-L. et al. (2013). *RSC Adv.* 3: 1732. (j) Trose, M., Acqua, M.D., Pedrazzini, T. et al. (2014). *J. Organomet. Chem.* 79: 7311.

63 a) Nguyen, R.-V. and Li, C.-J. (2008, 1897). *Synlett* . (b) Bai, Y.-G., Zeng, J., Ma, J.-M. et al. (2010). *J. Comb. Chem.* 12: 696. (c) Xiao, J., Chen, Y.-Y., Zhu, S. et al. (2014). *Adv. Synth. Catal.* 356: 1835. (d) Zhang, X. and Xu, X.-F. (2014). *Chem. Asian J.* 9: 3089.

64 Yao, X.-Q. and Li, C.-J. (2005). *Org. Lett.* 7: 4395.

65 (a) Laas, H., Nissen, A., and Nürrenbach, A. (1981). *Synthesis* 958. (b) Arisawa, M. and Yamaguchi, M. (2000). *J. Am. Chem. Soc.* 122: 2387. (c) Arisawa, M. and Yamaguchi, M. (2001). *Org. Lett.* 3: 763. (d) Imagawa, H., Kurisaki, T., and Nishizawa, M. (2004). *Org. Lett.* 6: 3679. (e) Matute, B.M., Nevado, C., Cardenas, D.J., and Echavarren, A.M. (2003). *J. Am. Chem. Soc.* 125: 5757. (f) Madine, J.W., Wang, X., and Widenhoefer, R.A. (2001). *Org. Lett.* 3: 385. (g) Hamze, A., Provot, O., Alami, M., and Brion, J.D. (2005). *Org. Lett.* 7: 5625. (h) Harrison, T.J. and Dake, G.R. (2004). *Org.*

Lett. 6: 5023. (i) Kadota, I., Lutete, L.M., Shibuya, A., and Yamamoto, Y. (2001). *Tetrahedron Lett.* 42: 6207. (j) Kadota, I., Shibuya, A., Lutete, L.M., and Yamamoto, Y. (1999). *J. Organomet. Chem.* 64: 4570. (k) Bajracharya, G.B., Huo, Z., and Yamamoto, Y. (2005). *J. Organomet. Chem.* 70: 4883. (l) Patil, N.T., Lutete, L.M., Wu, H. et al. (2006). *J. Organomet. Chem.* 71: 4270. (m) Zeni, G. and Larock, R.C. (2004). *Chem. Rev.* 104: 2285. (n) Cacchi, S. and Fabrizi, G. (2005). *Chem. Rev.* 105: 2873. (o) Gabriele, B., Salerno, G., and Costa, M. (2004). *Synlett* 2468.

66 Yamada, W., Sugawara, Y., Cheng, H.-M. et al. (2007). *Eur. J. Org. Chem.* 2604.

67 Kikuchi, S., Yoshida, S., Yamada, W. et al. (2011). *Bull. Chem. Soc. Jpn.* 84: 698.

68 Hashmi, A.S.K., Weyrauch, J.P., Frey, W., and Bats, J.W. (2004). *Org. Lett.* 6: 4391.

69 Hashmi, A.S.K. and Hutchings, G.J. (2006). *Angew. Chem. Int. Ed.* 45: 7896.

70 (a) Davis, F.A. and Chen, B.C. (1992). *Chem. Rev.* 92: 919. (b) Katsuki, T. (2001). *Asymmetric Oxidation Reactions*, 128–145. Oxford: Oxford University Press.

71 (a) Zhong, G. (2003). *Angew. Chem. Int. Ed.* 42: 4247. (b) Brown, S.P., Brochu, M.P., Sinz, C.J., and MacMillan, D.W.C. (2003). *J. Am. Chem. Soc.* 125: 10808. (c) Bøgevig, A., Sunden, H., and Cordova, A. (2004). *Angew. Chem. Int. Ed.* 43: 1109. (d) Hayashi, Y., Yamaguchi, J., Sumiya, T., and Shoji, M. (2004). *Angew. Chem. Int. Ed.* 43: 1112. (e) Lu, M., Zhu, D., Lu, Y. et al. (2008). *Angew. Chem. Int. Ed.* 47: 10187. (f) Lu, M., Zhu, D., Lu, Y. et al. (2009). *J. Am. Chem. Soc.* 131: 4562. (g) Kano, T., Yamamoto, A., Shirozu, F., and Maruoka, K. (2009). *Synlett* 1557. (h) Jiao, P., Kawasaki, M., and Yamamoto, H. (2009). *Angew. Chem. Int. Ed.* 48: 3333. (i) Jiao, P. and Yamamoto, H. (2009). *Synlett* 2685. (j) Bui, T., Candeias, N.R., and Barbas, C.F. III (2010). *J. Am. Chem. Soc.* 132: 5574. (k) Lu, M., Lu, Y., Zhu, D. et al. (2010). *Angew. Chem. Int. Ed.* 49: 8588.

72 (a) Kano, T., Ueda, M., Takai, J., and Maruoka, K. (2006). *J. Am. Chem. Soc.* 128: 6046. (b) Guo, H.-M., Cheng, L., Cun, L.-F. et al. (2006). *Chem. Commun.* 429. (c) Palomo, C., Vera, S., Velilla, I. et al. (2007). *Angew. Chem. Int. Ed.* 46: 8054. (d) Momiyama, N. and Yamamoto, H. (2005). *J. Am. Chem. Soc.* 127: 1080. (e) Zhang, T., Cheng, L., Liu, L. et al. (2010). *Tetrahedron: Asymmetry* 21: 2800.

73 Momiyama, N. and Yamamoto, H. (2004). *J. Am. Chem. Soc.* 126: 5360.

74 (a) Davies, H.M.L. and Walji, A.M. (2005). Rhodium(II) – stabilized carbenoids containing both donor and acceptor substituents. In: *Modern Rhodium-Catalyzed Organic Reactions* (ed. P.A. Evans), 301–340. Stamford, CT: Wiley-VCH. (b) Doyle, M.P., McKervey, M.A., and Ye, T. (1998). *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*. New York: Wiley. (c) Davies, H.M.L. and Loe, Ø. (2004). *Synthesis* 2595.

75 (a) Davies, H.M.L. and Townsend, R.J. (2001). *J. Organomet. Chem.* 66: 6595. (b) Davies, H.M.L. and Antoulinakis, E.G. (2001). *Org. React.* 57: 1. (c) Davies, H.M.L., Bruzinski, P., Hutcheson, D.K. et al. (1996). *J. Am. Chem. Soc.* 118: 6897. (d) Davies, H.M.L. and Ren, P. (2001). *J. Am. Chem.*

Soc. 123: 2070. (e) Davies, H.M.L. (1998). [3+4] annulations between rhodium-stabilized vinylcarenoids and dienes. In: *Advances in Cycloaddition*, vol. 5 (ed. M. Harmata), 119–164. Weinheim: JAI Press. (f) Davies, H.M.L., Xiang, B., Kong, N., and Stafford, D.G. (2001). *J. Am. Chem. Soc.* 123: 7461. (g) Davies, H.M.L. and Beckwith, R.E.J. (2003). *Chem. Rev.* 103: 2861.

76 Thompson, J.L. and Davies, H.M.L. (2007). *J. Am. Chem. Soc.* 129: 6090.

77 (a) Siemsen, P., Livingston, R.C., and Diederich, F. (2000). *Angew. Chem. Int. Ed.* 39: 2632. (b) Hassan, J., Sevignon, M., Gozzi, C. et al. (2002). *Chem. Rev.* 102: 1359.

78 (a) Lei, A. and Zhang, X. (2004). *Org. Lett.* 4: 2285. (b) MacKillop, A., Elsom, L.F., and Taylor, C.E. (1968). *J. Am. Chem. Soc.* 90: 2423. (c) Cardenas, D.J. (1999). *Angew. Chem. Int. Ed.* 38: 3018. (d) Luh, T.-Y., Leung, M.-K., and Wong, K.-T. (2000). *Chem. Rev.* 100: 3187. (e) Cardenas, D.J. (2003). *Angew. Chem. Int. Ed.* 72: 384. (f) Frisch, A.C. and Beller, M. (2005). *Angew. Chem. Int. Ed.* 44: 674.

79 Nagano, T. and Hayashi, T. (2005). *Chem. Lett.* 34: 1152.

80 Tamura, M. and Kochi, J. (1971). *Synthesis* 303.

81 Hassan, J., Sévignon, M., Gozzi, C. et al. (2002). *Chem. Rev.* 102: 1359.

82 Alberico, D., Scott, M.E., and Lautens, M. (2007). *Chem. Rev.* 107: 174.

83 (a) Li, R., Jiang, L., and Lu, W. (2006). *Organometallics* 25: 5973. (b) Smrčina, M., Lorenc, M., Hanus, V. et al. (1992). *J. Organomet. Chem.* 57: 1917. (c) Ding, K., Xu, Q., Wang, Y. et al. (1997). *Chem. Commun.* 693.

84 Stuart, D.R. and Fagnou, K. (2007). *Science* 317: 1172.

85 Stuart, D.R., Villemure, E., and Fagnou, K. (2007). *J. Am. Chem. Soc.* 129: 12072–12073.

86 (a) Brandon, R.W. and Claridge, D.V. (1968). *J. Chem. Soc., Chem. Commun.* 677. (b) Orito, K., Horibata, A., Nakamura, T. et al. (2004). *J. Am. Chem. Soc.* 126: 14342. (c) Chen, X., Li, J.-J., Hao, X.S. et al. (2006). *J. Am. Chem. Soc.* 128: 78.

87 Fu, J., Zanoni, G., Anderson, E.A., and Bi, X. (2017). *Chem. Soc. Rev.* 46: 7208–7228.

88 (a) Banert, K. (1989). *Chem. Ber.* 122: 1175. (b) Shen, T., Wang, T., Qin, C., and Jiao, N. (2013). *Angew. Chem. Int. Ed.* 52: 6677. (c) Qin, C., Feng, P., Ou, Y. et al. (2013). *Angew. Chem. Int. Ed.* 52: 7850. (d) Gaydou, M. and Echavarren, A.M. (2013). *Angew. Chem. Int. Ed.* 52: 13468.

89 Liu, Z., Liu, J., Zhang, L. et al. (2014). *Angew. Chem. Int. Ed.* 53: 5305.

90 Liu, Z., Liao, P., and Bi, X. (2014). *Org. Lett.* 16: 3668.

91 (a) Saikachi, H., Kitagawa, T., and Sasaki, H. (1979). *Chem. Pharm. Bull.* 27: 2857. (b) Kamijo, S., Kanazawa, C., and Yamamoto, Y. (2005). *J. Am. Chem. Soc.* 127: 9260. (c) Larionov, O.V. and de Meijere, A. (2005). *Angew. Chem. Int. Ed.* 44: 5664. (d) Cai, Q., Zhou, F., Xu, T. et al. (2011). *Org. Lett.* 13: 340. (e) Adib, M., Mohammadi, B., Sheikhi, E., and Bijanzadeh, H.R. (2011). *Chin. Chem. Lett.* 22: 314. (f) Lygin, A.V., Larionov, O.V., Korotkov, V.S., and de Meijere, A. (2009). *Chem. Eur. J.* 15: 227.

92 Liu, J., Fang, Z., Zhang, Q. et al. (2013). *Angew. Chem. Int. Ed.* 52: 6953–6957.

93 Gao, M., He, C., Chen, H. et al. (2013). *Angew. Chem. Int. Ed.* 52: 6958–6961.

94 Xiao, P., Yuan, H., Liu, J. et al. (2015). *ACS Catal.* 5: 6177–6184.

95 (a) Lee, D.-Y., Hong, B.-S., Cho, E.-G. et al. (2003). *J. Am. Chem. Soc.* 125: 6372. (b) Tanaka, K., Kamisawa, A., Suda, T. et al. (2007). *J. Am. Chem. Soc.* 129: 12078. (c) Shimada, T. and Yamamoto, Y. (2003). *J. Am. Chem. Soc.* 125: 6646. (d) Datta, S., Chang, C.-L., Yeh, K.-L., and Liu, R.-S. (2003). *J. Am. Chem. Soc.* 125: 9294. (e) Shen, H.-C., Su, H.-L., Hsueh, Y.-C., and Liu, R.-S. (2004). *Organometallics* 23: 4332. (f) Varela, J.A., Gonzalez-Rodríguez, C., Rubín, S.G. et al. (2006). *J. Am. Chem. Soc.* 128: 9576. (g) Gonzalez-Rodríguez, C., Varela, J.A., Castedo, L., and Saa, C. (2007). *J. Am. Chem. Soc.* 129: 12916. (h) Liu, Y., Song, F., and Guo, S. (2006). *J. Am. Chem. Soc.* 128: 113323. (i) Asao, N., Nogami, T., Lee, S., and Yamamoto, Y. (2003). *J. Am. Chem. Soc.* 125: 10921. (j) Okamoto, N., Ishikura, M., and Yanada, R. (2013). *Org. Lett.* 15: 2571.

96 Shen, T., Wang, T., Qin, C., and Jiao, N. (2013). *Angew. Chem. Int. Ed.* 52: 6677.

97 Diederich, F., Stang, P.J., and Tykwinski, R.R. (2005). *Acetylene Chemistry: Chemistry, Biology and Material Science*. Weinheim: Wiley-VCH.

98 (a) Chinchilla, R. and Najera, C. (2007). *Chem. Rev.* 107: 874. (b) Eckhardt, M. and Fu, G.C. (2003). *J. Am. Chem. Soc.* 125: 13642. (c) Vechorkin, O., Barmaz, D., Proust, V., and Hu, X. (2009). *J. Am. Chem. Soc.* 131: 12078. (d) Cahiez, G., Gager, O., and Buendia, J. (2010). *Angew. Chem. Int. Ed.* 49: 1278. (e) Chen, M., Zheng, X., Li, W. et al. (2010). *J. Am. Chem. Soc.* 132: 4101. (f) Nicolai, S., Piemontesi, C., and Waser, J. (2011). *Angew. Chem. Int. Ed.* 50: 4680. (g) Vechorkin, O., Godinat, A., Scopelliti, R., and Hu, X. (2011). *Angew. Chem. Int. Ed.* 50: 11777. (h) Hatakeyama, T., Okada, Y., Yoshimoto, Y., and Nakamura, M. (2011). *Angew. Chem. Int. Ed.* 50: 10973. (i) Ye, F., Ma, X., Xiao, Q. et al. (2012). *J. Am. Chem. Soc.* 134: 5742. (j) Bi, H.-P., Zhao, L., Liang, Y.-M., and Li, C.-J. (2009). *Angew. Chem. Int. Ed.* 48: 792.

99 Liu, X., Wang, Z., Cheng, X., and Li, C. (2012). *J. Am. Chem. Soc.* 134: 14330.

100 (a) Lawrence, S.A. (2004). *Amines: Synthesis, Properties and Applications*. New York, NY: Cambridge University Press. (b) Nugent, T.C. and El-Shazly, M. (2010). *Adv. Synth. Catal.* 352: 753. (c) Smith, M.B. (2009). *Compendium of Organic Synthetic Methods*, vol. 12. New York, NY: Wiley. (d) Emerson, W.S. (2004). The preparation of amines by reductive alkylation. In: *Organic Reactions* (ed.), 174–202. New York, NY: Wiley. (e) Afagh, N.A. and Yudin, A.K. (2010). *Angew. Chem. Int. Ed.* 49: 262. (f) Zalatan, D.N. and Du Bois, J. (2010). *Top. Curr. Chem.* 292: 347. (g) Roizen, J.L., Harvey, M.E., and DuBois, J. (2012). *Acc. Chem. Res.* 45: 911. (h) Müller, P. and Fruit, C. (2003). *Chem. Rev.* 103: 2905.

101 (a) Fiori, K.W. and Du Bois, J. (2007). *J. Am. Chem. Soc.* 129: 562. (b) Zalatan, D.N. and Du Bois, J. (2008). *J. Am. Chem. Soc.* 130: 9220. (c) Srivastava, R.S., Tarver, N.R., and Nicholas, K.M. (2007). *J. Am. Chem. Soc.* 129: 15250. (d) Barman, D.N. and Nicholas, K.M. (2011). *Eur. J. Org.*

Chem. 5: 908. (e) Harvey, M.E., Musaev, D.G., and Du Bois, J. (2011). *J. Am. Chem. Soc.* 133: 17207. (f) Paradine, S.M. and White, M.C. (2012). *J. Am. Chem. Soc.* 134: 2036.

102 Rigoli, J.W., Weatherly, C.D., Alderson, J.M. et al. (2013). *J. Am. Chem. Soc.* 135: 17238.

103 (a) Filler, R. and Kobayashi, Y. (1982). *Biomedicinal Aspects of Fluorine Chemistry.* Amsterdam: Elsevier. (b) Welch, J.T. and Eswarakrishman, S. (eds.) (1991). *Fluorine in Bioorganic Chemistry.* New York: Wiley.

104 (a) Liu, Q., Ni, C., and Hu, J. (2017). *Natl. Sci. Rev.* 4: 303. (b) Rong, J., Ni, C., and Hu, J. (2017). *Asian J. Org. Chem.* 6: 139. (c) Ahrens, T., Kohlmann, J., Ahrens, M., and Braun, T. (2015). *Chem. Rev.* 115: 931. (d) Campbell, M.G. and Ritter, T. (2015). *Chem. Rev.* 115: 612. (e) Champagne, P.A., Desroches, J., Hamel, J.D. et al. (2015). *Chem. Rev.* 115: 9073.

105 Xu, T., Mu, X., Peng, H.H., and Liu, G.S. (2011). *Angew. Chem. Int. Ed.* 50: 8176.

106 Yin, F., Wang, Z., Li, Z., and Li, C. (2012). *J. Am. Chem. Soc.* 134: 10401.