DOI: 10.1002/ejoc.200500602

Recent Advances in Silver-Catalyzed Nitrene, Carbene, and Silylene-Transfer Reactions

Zigang Li[a] and Chuan He*[a]

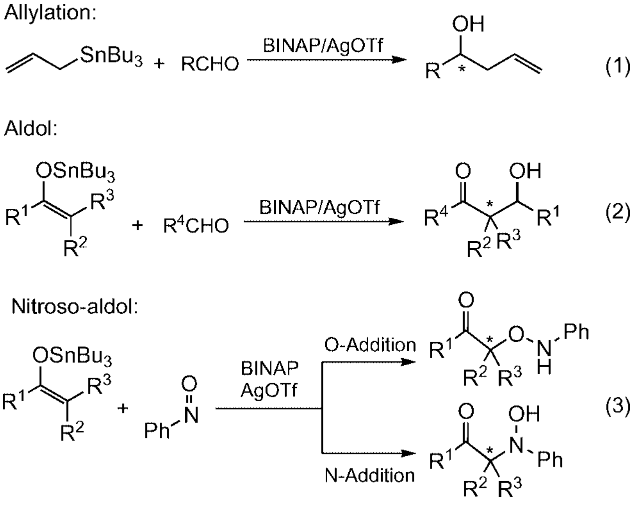
Keywords: Silver / Oxidation / Nitrene transfer / Carbene transfer / Silylene transfer / Homogeneous catalysis

Silver salts are commonly used as Lewis acids in organic synthesis. Silver complexes can also exhibit strong oxidation power due to their high oxidation potentials. This review features the recent development of nitrene, carbene and silylene-transfer reactions catalyzed by silver complexes. Interesting activity was observed in several reactions highlighting the unique redox chemistry of silver. A disilver(I) catalyst was shown to mediate efficient aziridination of simple olefins, intramolecular amidation of saturated C–H bonds and imination of sulfoxides with high regio- and stereoselectivity. Silver compounds also catalyze intermolecular carbene insertion into carbon–halogen bonds, carbon–hydrogen bonds, and aromatic systems. In addition, simple silver salts were found to mediate silylene-transfer reactions to different olefins and alkynes efficiently. Future mechanistic study of these reactions and further exploration of the redox chemistry of silver could lead to more exciting discoveries.

1. Introduction

Silver, known and utilized since ancient time, is a commonly used transition metal for catalysis in industry. The heterogeneous silver-catalyzed ethylene epoxidation has been used worldwide to produce ethylene oxide largely due to the demand in the manufacture of ethylene glycol.[1] Recently, Eastman further extended this process to epoxidize butadiene.[1b] Similar processes such as direct oxidation of alcohols, oxidative activation of olefins and also simple alkanes have attracted interests as well.[2] Other silver-based heterogeneous processes include NO_x reduction[3] and catalytic oxidation of CO to CO_2.[4,5]

Past efforts in studying homogeneous silver-catalyzed organic transformations have mostly focused on Lewis acid catalysis. For instance, Yamamoto and others have developed the Yamamoto–Yanagisawa system [BINAP + silver(I) system] in the enantioselective allylation reactions,[6] Michael addition reactions,[7] aldol-type reactions[8] including the recent nitroso-aldol reactions (Scheme 1).[9] Silver(I) salts have been used in nucleophilic addition reactions such as intramolecular nucleophilic cyclization of allenes,[10] cyclization of allenyl ketones or aldehydes,[11] cyclization of acetylenic alcohols, acids, amines, imines, or olefins,[12] and a few intermolecular nucleophilic addition to alkynes (Scheme 2).[13] We have also demonstrated that silver(I) triflate catalyzes intramolecular additions of hydroxyl or carboxyl groups to inert olefins [Equations (9) and (10), Scheme 2], a reaction that provides a simple access to cyclic ethers and lactones.[14]

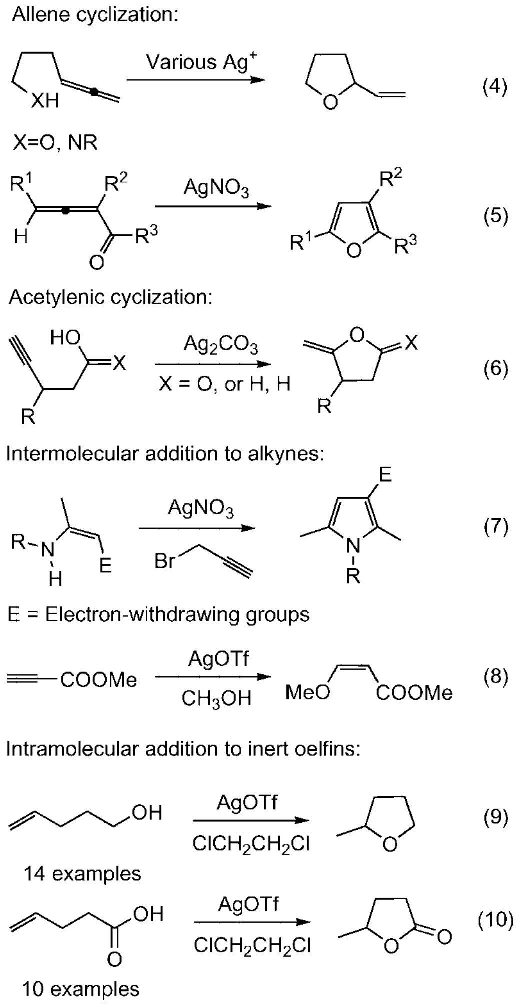


Scheme 1. Examples of the silver-catalyzed allylation, aldol and nitroso-aldol reactions.

---

[a] Department of Chemistry, The University of Chicago,
Chicago, IL 60637, USA
E-mail: chuanhe@uchicago.edu

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

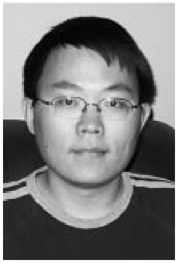


Scheme 2. Examples of silver-catalyzed nucleophilic addition reactions.

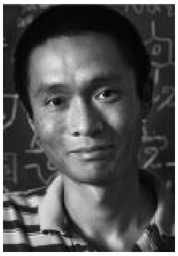
Silver has long been known to react with terminal alkynes to form silver acetylides.[15] This property has been taken advantage of by Li and others to mediate the addition of terminal alkynes to imines.[16] Similarly, the addition of electron-deficient alkynes to carbonyl groups with zirconium[17] and the use of silver acetylide in palladium-catalyzed coupling reactions[18] have been reported.

Silver catalysis has also been employed to mediate cycloaddition reactions: Zhang, Schreiber, Carreira and others reported enantioselective [3+2] cycloaddition of azomethine ylides;[19] Hoveyda and others developed an enantioselective [4+2] cycloaddition of imines with Danishefsky's diene;[20] Kozmin reported a [2+2] addition of siloxy alkyne with activated olefins.[21] Several rearrangement reactions catalyzed by silver salts were documented as well.[22]

Silver-based oxidation catalysis in solution has been less developed in the past. Homogeneous olefin epoxidation catalyzed by silver complexes remains a challenge (the heterogeneous process only works for very limited substrates so far). Silver compounds are commonly employed as stoichiometric oxidants in both organic and inorganic synthesis. But these reactions are mostly thought to go through radical pathways.[23] We started a research program to explore silver oxidation chemistry in 2002. With the high oxidation potentials associated with high-valent silver ions,[24] we wish to uncover new oxidation chemistry based on silver compounds. Practical oxidation methods may be developed from this effort. This microreview summarizes our recent efforts in developing silver-catalyzed nitrene-transfer reactions. The related carbene-transfer and silylene-transfer reactions catalyzed by silver complexes discovered in other groups are discussed as well. The purpose of this article is not to comprehensively summarize all examples in this area. We choose to focus on the recent development of the silver-based oxidation synthetic methods.



Zigang Li received his B.S. (2001) of neuroscience and biophysics from the University of Science and Technology of China, Hefei, China. He obtained his MS in organic chemistry under the guidance of Professor Chao-Jun Li from Tulane University in 2004. Then he moved to the University of Chicago to continue his Ph.D. study and his current research focuses on metal-mediated oxidation reactions.



Chuan He was born in 1972 in P. R. China and graduated with B.S. in chemistry in 1994 from the University of Science and Technology of China, Hefei, China. Then he moved to US and obtained a Ph.D. in chemistry at Massachusetts Instituted of Technology in 2000 working with Professor Stephen J. Lippard. As a Damon-Runyon Cancer Research Foundation Postdoctoral Fellow, he worked in Professor Gregory L. Verdine's group at Harvard University on DNA repair proteins. Dr. He started his independent research career as Assistant Professor in the Department of Chemistry at the University of Chicago in 2002. His research covers several different areas that include chemistry and catalysis with silver and gold, metalloregulation and development of metal ion biosensors, regulation of virulence factors in pathogens, structure, function and mechanism of direct DNA repair proteins, and proteomics on DNA repair and DNA modification proteins. He is a Searle Scholar, a G&P Foundation of Cancer Research Young Investigator, a W. M. Keck Foundation Distinguished Young Investigator, an Arnold and Mabel Beckman Foundation Young Investigator, a Cottrell Scholar from the Research Corporation, and a recipient of a Research Corporation Research Innovation Award, an Alfred P. Sloan Research Fellowship, and a National Science Foundation CAREER award.

2. Silver-Catalyzed Nitrene-Transfer Reactions

As mentioned in the Introduction, silver-catalyzed oxidation reactions are limited. We have been focusing on exploring non-radical oxidation chemistry of silver complexes and have discovered a catalytic silver-based system that mediates nitrene-transfer reactions to olefins and inert C–H groups.

2.1 Silver-Catalyzed Aziridination of Olefins

Aziridines are important intermediates that can be converted into other nitrogen-containing functional groups.[25] Their versatile reactivity leads to continuous efforts to invent new and efficient methods that can produce aziridines from simple olefins.[26] Different metals such as Rh, Cu, Ru, Co, Fe and Mn have been shown to catalyze aziridination of different olefins,[27] but no silver-mediated processes were known before our work. Out of curiosity, we first explored catalytic olefin aziridination by silver complexes. In 2003, our group successfully demonstrated the first practical silver-catalyzed olefin aziridination chemistry.

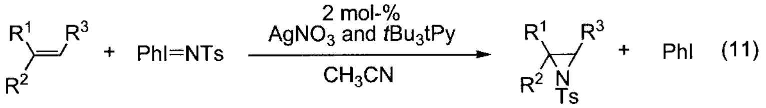
2.1.1 Aziridination of Olefins with PhI=NTs

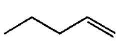
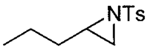
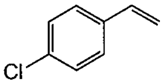
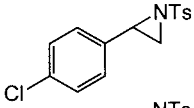
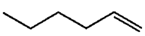
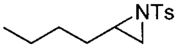
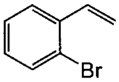
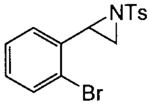
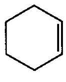
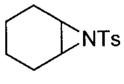
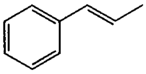
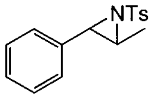
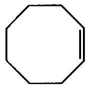
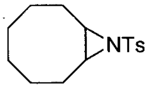
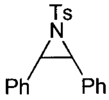
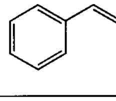
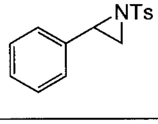
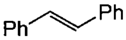
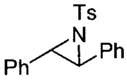
Pyridine-based ligands were employed as silver ligands in our initial studies because these ligands are known to stabilize high-valent silver ions in the presence of oxidants.[24,28] We discovered that efficient aziridination of olefins could be catalyzed by mixing a tridentate 4,4′,4′′-tri-*tert*-butyl-2,2′:6′,2′′terpyridine (*t*Bu$_3$tpy) ligand with simple silver(I) salts (1:1 ratio at 2 mol-%) and a nitrenoid source PhINTs [Equation (11), Table 1].[29] Clean production of aziridine was only observed with *t*Bu$_3$tpy but not with other nitrogen-based ligands, such as simple pyridines, bipyridines, and oxazolines. Counter anions such as NO_3^-, OTf^-, ClO_4^-, and BF_4^- did not influence the reaction much. Terminal aliphatic alkenes can be converted into aziridines in good yields and use of *cis*-stilbene at 0 °C gives the predominant *cis* aziridine product (Table 1), which may suggest a metal-mediated oxidative nitrene-transfer mechanism.[27]

The catalyst for the reaction was structurally characterized to be a dinuclear silver(I) compound [Ag$_2$(*t*Bu$_3$tpy)$_2$(NO$_3$)](NO$_3$) (**1**) (Figure 1). The Ag(1)–Ag(2) distance is 2.842(2) Å, indicating a fairly strong silver(I)–silver(I) interaction.[30] Compound **1** exhibited the same catalytic olefin aziridination activity as that of the mixture of the silver salt and the ligand. Further study with proton NMR showed the formation of the disilver complex within 5 minutes after mixing metal and ligand in CD$_3$CN, which supports compound **1** as the precatalyst for the reaction.

The structure of the disilver(I) complex **1** resembles that of a dirhodium(II) compound, Rh$_2$(OAc)$_4$, which was well known to catalyze similar olefin aziridination and other types of oxidation reactions.[26,27,31] We probed the reaction intermediates with electrospray mass spectrometry (ESI-MS). The results seems to suggest an intermediate containing a disilver core plus =NTs or =NSO$_2$Ph unit. The disilver catalyst **1** also mediates C–H amidation chemistry, as described in section 2.2. The requirement of a disilver compound to catalyze the two-electron nitrene-transfer reac-

Table 1. Silver-catalyzed aziridination of olefins.



Entry	Substrate	Product	Yield[a]	Entry	Substrate	Product	Yield[a]
1			66	6			74
2			71	7			80
3			81	8			90
4			88	9			86
5			91(89)[b]	10			88

[a] All reactions were conducted at 0 °C to r.t. in CH$_3$CN with 2 mol-% of AgNO$_3$ and *t*Bu$_3$tpy. The isolated yields are reported here (%). [b] The yield in the parentheses was obtained by using 2 mol-% compound **1** crystal as the catalyst.

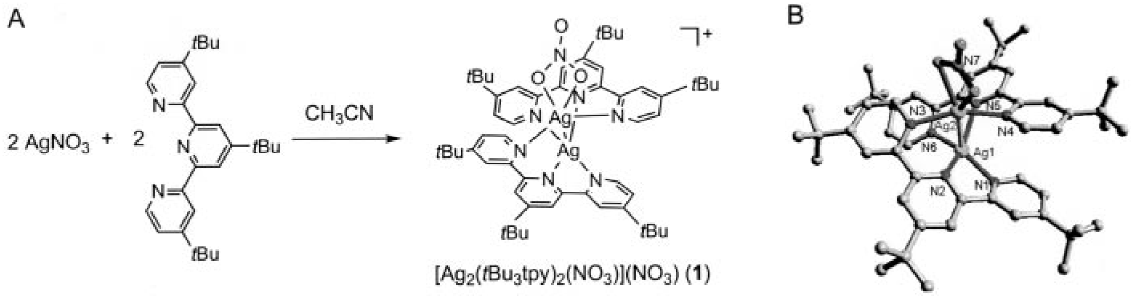
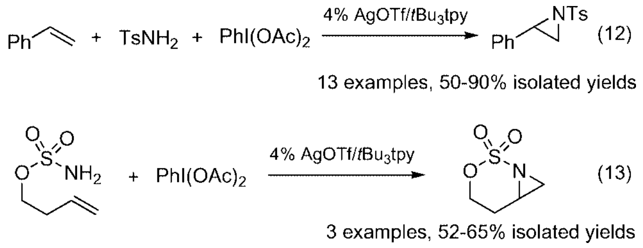


Figure 1. A) Formation of compound $[Ag_2(tBu_3tpy)_2(NO_3)](NO_3)$ (**1**). B) The molecular structure of **1**.

tion, at least from this study, has interesting implications. Perhaps, each silver(I) ion can offer one electron to avoid potential radical-based side reactions. The nitrene intermediate may also be "stabilized" by interacting with two silver(II) ions.

2.1.2 Direct Aziridination of Olefins with $TsNH_2$ and $PhI(OAc)_2$

Sulfonyliminoiodinane PhI=NTs is the most commonly used reagent in olefin aziridination; however, it has to be synthesized beforehand and the yield is not satisfying.[32] A more attractive alternative is to have an one-pot process by directly using $TsNH_2$ and an inexpensive oxidant such as $PhI(OAc)_2$. A few reports have successfully realized this strategy by using rhodium- or copper-based catalysts.[33] Complex **1** also serves as a good catalyst for the aziridination of styrenes by using the commercially available $TsNH_2$ and $PhI(OAc)_2$. The method can be applied to intramolecular aziridination of aliphatic olefins with tethered sulfamate esters in the presence of $PhI(OAc)_2$ (Scheme 3).[34]



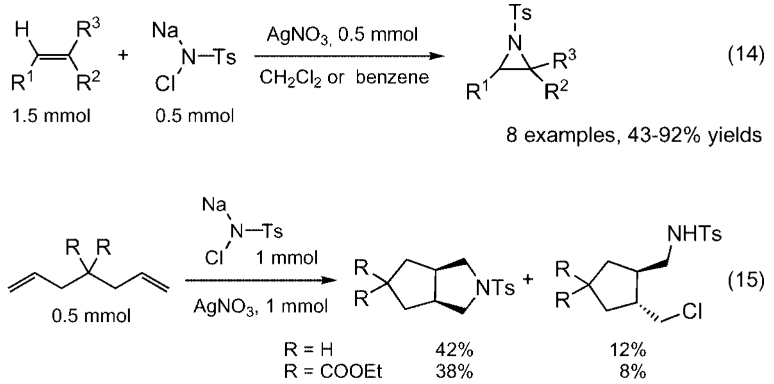
Scheme 3.

2.1.3 Aziridination of Olefins with Chloramine-T

Chloramine-T and bromamine-T are alternative nitrene sources for aziridination of olefins.[35] Rai and co-workers reported that a stoichiometric amount of $AgNO_3$ might mediate olefin aziridination with chloramine-T in aprotic solvents.[36] Komatsu and co-workers reported a similar reaction by using chloramine-T and $AgNO_3$; however, they found no activity for the system in THF. Instead, 70% conversion was observed for styrene aziridination in CH_2Cl_2 or benzene (Scheme 4).[37] In this reaction, a stoichiometric amount of $AgNO_3$ was employed to afford 43–92% yields of the corresponding products from different olefin substrates. Bicyclic pyrrolidines can be prepared starting from 1,6-dienes (Scheme 4). A nitrene radical mechanism was proposed based on the oxygen sensitivity of these reactions and the formation of bicyclic pyrrolidines. The role of silver salts in this reaction is unclear. It is possible that AgCl was produced first to help generate a nitrene radical as the reactive species.

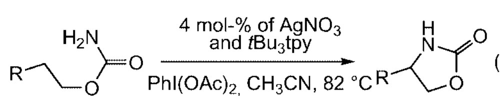
2.2 Intramolecular Amidation of Saturated C–H Groups

After the discovery of the disilver **1** as an efficient olefin aziridination catalyst, we turned our attention to the more challenging C–H amidation chemistry. Direct oxidative nitrene insertion into saturated C–H groups provides an attractive method to install amine derivatives. Only rhodium complexes and ruthenium porphyrin complexes can catalyze amidations of saturated C–H bonds in the presence of oxidants in the past.[26,27k,38] We demonstrated that the in

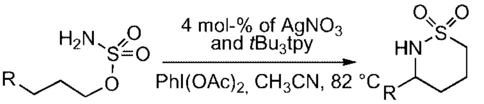


Scheme 4.

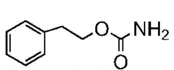
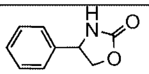
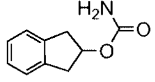
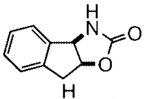
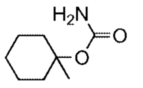
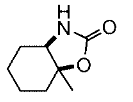
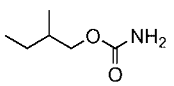
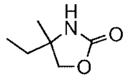
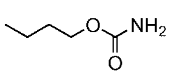
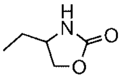
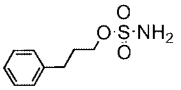
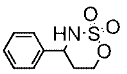
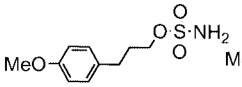
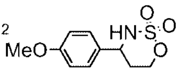
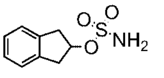
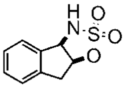
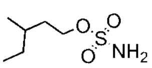
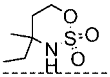
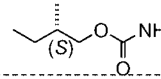
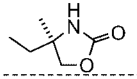
Table 2. Silver-catalyzed intramolecular amidation of saturated C–H bonds.



(16)



(17)

Entry	Substrate	Product	Yield[a]
1			81
2			83[c]
3			85[b]
4			76(68)[c]
5			58
6			87
7			78
8			65(57)[b,c]
9			90
10			73

All reactions were conducted at 82 °C in CH_3CN with 4 mol-% of $AgNO_3$ plus tBu$_3$tpy and 1.5 equiv. of $PhI(OAc)_2$. [a] The isolated yields are reported here. [b] Exclusive *cis* product was observed by NMR. [c] Reaction was run with 2 mol-% 4-*tert*-butylpyridine (the NMR yield without 4-*tert*-butylpyridine is reported in the parenthesis).

situ generated **1** could indeed catalyze an efficient intramolecular amidation of saturated C–H groups (Table 2). Other pyridine-based ligands we have tested were either completely inactive or gave low yields of the insertion products.[39] A range of carbamate and sulfamate esters were studied and showed comparable yields to the reactions using Rh- or Ru-based catalysts. The stereospecificity (Entry 10, Table 2) of the silver-catalyzed reaction provides a strong support for a metal-mediated direct nitrene-transfer mechanism. Our preliminary studies indicate that intermolecular C–H activation can be achieved by using a modified silver-based catalyst.

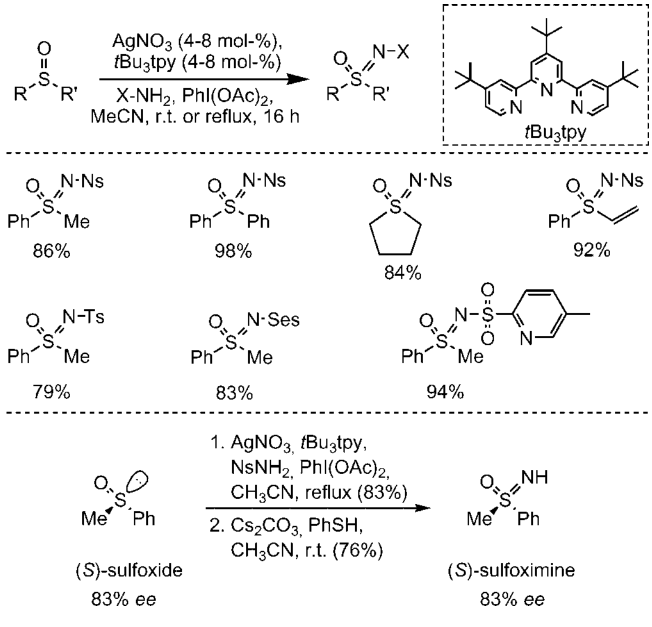


Figure 2. Silver-catalyzed imination of sulfoxides.

2.3 Silver-Catalyzed Imination of Sulfoxides

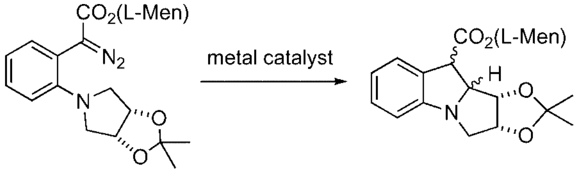
Bolm and co-worker have applied the disilver(I) **1** compound to catalyze imination of sulfoxides (Figure 2).[40] Various sulfoximines can be accessed with this simple method in good to excellent yields. If a chiral sulfoxide is employed, the corresponding sulfoximine can be prepared after oxidation and deprotection without an *ee* change. This reaction further highlights the versatile applications of the disilver(I) **1** system in catalytic nitrene-transfer chemistry.

3. Silver-Catalyzed Carbene-Transfer Reactions

3.1 Silver(I)-Catalyzed Carbene Insertion and the Wolff Rearrangement

Carbene transfers, especially those using diazo compounds as carbenoids, are important strategies in organic synthesis.[41] Silver has been known for a long time to decompose diazo compounds,[42] but the role of silver is generally considered to promote formation of free carbenes as Lewis acids.[42–46,48,49] In 1999, Jorgenson and co-workers reported an addition of trimethylsilyldiazomethane to TsN=CPh that affords the aziridine product in 88% yield.[43] When (*R*)-Tol-BINAP was employed as the ligand a 12% *ee* was obtained for the product. A silver(I)-catalyzed asymmetric carbene insertion to N–H bond with different bisoxazoline-type ligands was also reported by the same group in 2004.[44] This system resembles a earlier work by

Burgess and co-workers who screened different metal ion/ligand combinations for optimizing an intramolecular carbene insertion reaction [Equation (18)].[45] Silver with oxazoline-type ligands showed an interesting activity in this screen and gave ca. 45% yield of the desired product. Copper and rhodium were also tested which gave comparable results. It is unclear if silver-carbene is produced and responsible for the C–H insertion chemistry.

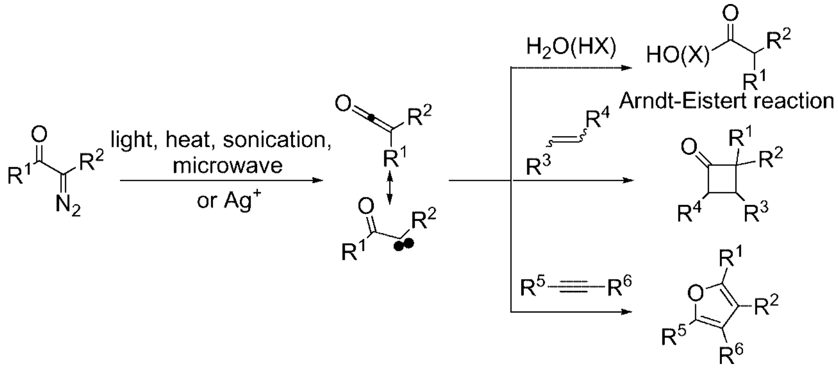


(18)

Silver and copper are known to promote the Wolff rearrangement.[46] Generally, UV light, heating, sonication or microwave irradiation are necessary to facilitate the transformation.[47] Silver(I) salts have been utilized in combination with different additives to afford more efficient and reproducible results. Commonly used additives include NH_3 solution, sodium thiosulfate and triethylamine.[48] Sudrik, Vijayamohanan and co-workers suggested that the additives may donate electrons to the silver center to help form silver nanoclusters which are involved in the rearrangement (Scheme 5).[49]

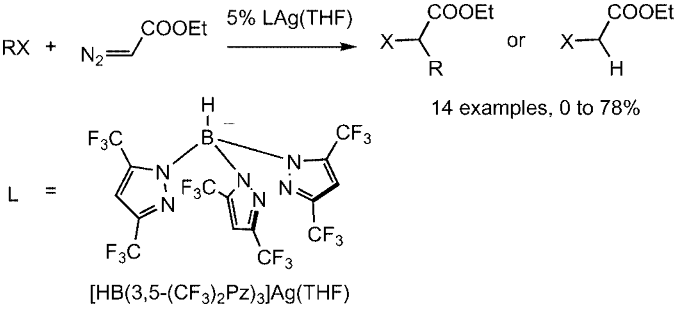
3.2 Silver-Catalyzed C–X and C–H Activation

A dimethyl diazomalonate–silver(I) complex was characterized by Dias and co-workers when [HB{3,5-$(CF_3)_2$Pz}$_3$]-Ag(THF) was mixed with dimethyl diazomalonate.[50,51] Dias and Lovely employed the more reactive ethyl diazoacetate (EDA) as the carbenoid to test potential carbene transfer to benzene in CH_2Cl_2. In this reaction, a 12% byproduct was observed from insertion of the carbenoid into the C–Cl bond of the solvent.[52] Subsequently, they showed that EDA could react with different alkyl halides to afford either C–X bond insertion products or 1,1-hydrochlorination products depending on the substrates employed (Scheme 6).



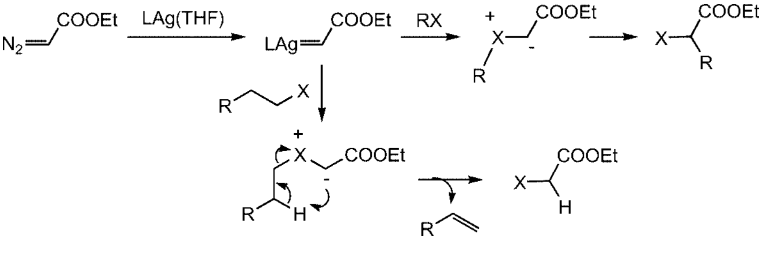
(19)
(20)
(21)

Scheme 5. Silver-catalyzed Wolff rearrangement.



(22)

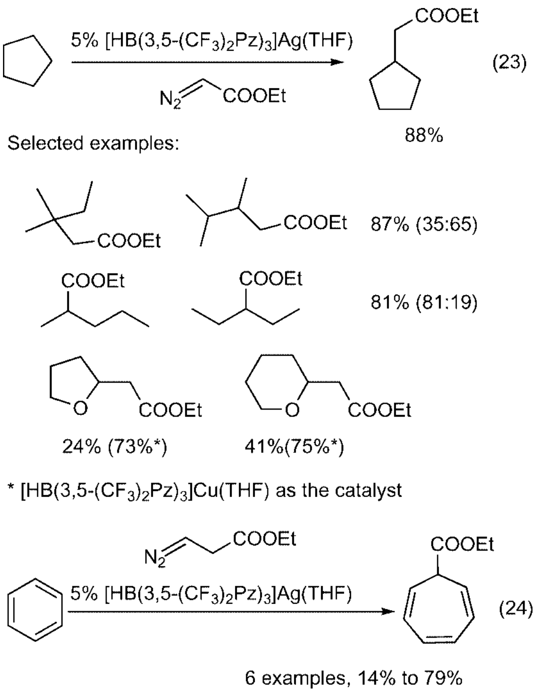
Scheme 6.



Scheme 7. A proposed mechanism for the silver-catalyzed carbene insertion into C–X bonds.

A mechanism involving formation of a silver–carbene intermediate was proposed to explain the observed results (Scheme 7).

Using the same system, Dias and Lovely also reported carbene insertion into saturated C–H bonds (Scheme 8).[53] All primary, secondary and tertiary C–H groups can undergo this transformation with the secondary and tertiary C–H groups serving as better substrates. Interestingly, ethers, which are generally good substrates for the carbene insertion reactions,[54] showed low activity; whereas the corresponding [HB{3,5-$(CF_3)_2$Pz}$_3$]Cu(THF) could give good yields with ethers. Potentially, interaction between the silver center and the ether oxygen may inhibit the C–H insertion step. Insertion of carbene into aromatics was examined as well. Both electron-rich and electron-deficient aromatics could react, but all gave lower yields than the reaction with benzene.[55] It is also found that carbene insertion into the aromatic rings is 2–7 times faster than that into the aliphatic C–H groups.



Scheme 8.

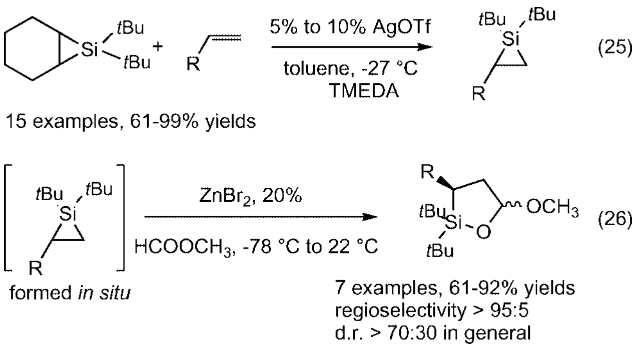
Pérez and co-workers examined the silver-catalyzed carbene insertion (with EDA) into saturated C–H bonds with their electron deficient tris(pyrazolyl)borate ligand. The difference between their ligand and the one that Dias and Lovely used is the substitution change from CF_3 to Br. This ligand system catalyzes efficient carbene transfers with both copper[54,56]and silver.[57] A mixture of benzene and cyclohexane was treated with EDA under their standard reaction conditions. Benzene insertion is 14-fold more efficient than that for cyclohexane, providing evidences to exclude a mechanism involving simple free carbene.

4. Silver-Catalyzed Silylene-Transfer Reactions

Silacyclopropanes are silicon-analogues to cyclopropanes, epoxides, and aziridines, and possess a unique reactivity to form C–C bonds.[58] The silylene-transfer reaction,[59] which involves the transfer of a silylene or a silylenoid intermediate, is analogous to the nitrene and carbene-transfer reactions. Silver complexes exhibit interesting activity to mediate silylene-transfer reactions.

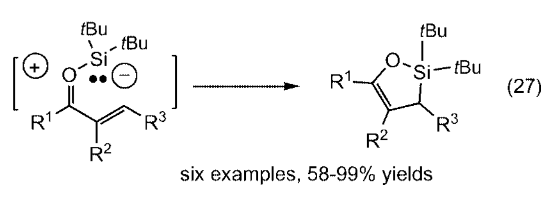
4.1 Silver-Catalyzed Silacyclopropanation of Olefins

Silylene species could be released from silacyclopropane derived from cyclohexene.[59] Woerpel and co-workers explored a silver-catalyzed silylene-transfer reaction to olefins.[60] Both mono-substituted and di-substituted alkenes serve as substrates to afford good to excellent yields (61–99%) of the final products with 5–10 mol-% of silver(I) triflate as the catalyst [Equation (25), Scheme 9]. The reaction could be followed by a tandem methyl formate insertion step with high regioselectivity and modest diastereoselectivity as shown in Equation (26), Scheme 9.



Scheme 9. Silver-catalyzed silacyclopropanation of olefins.

The method was further expanded to include α,β-unsaturated carbonyl compounds as substrates.[61] Treating these compounds with cyclohexanosilacyclopropane in the presence of 1–5 mol-% of silver(I) trifluoroacetate as the catalyst led to formation of oxasilacyclopentenes in good yields (Scheme 10). The metal silylenoid intermediate appears to attack the carbonyl group instead of the double bond due to its electrophilic nature.[62] Upon treatment with water, the oxasilacyclopentenes can be converted into the corre-



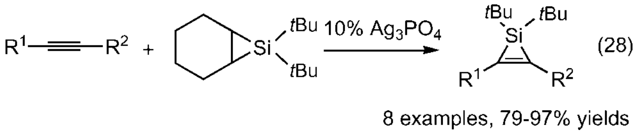
Scheme 10.

sponding silanols. With a tethered allyl group, the oxasilacyclopentene undergoes a tandem Ireland–Claisen rearrangement to give silalactone as the final product.[63]

In a mechanistic study with $Ag(PPh_3)_2OTf$ as the catalyst, a silylsilver intermediate was detected by ^{29}Si NMR at $\delta = 97$ ppm.[62a,64] The reaction order on cyclohexanosilacyclopropane was found to be one, which is the same as the thermo-promoted silylene-transfer reaction. However, an inverse saturation behavior was observed by varying the concentrations of mono-substitution alkenes, while a saturation behavior was observed in the thermo-promoted case. These results suggest a silver-mediated reversible releasing of silylene from cyclohexanosilacyclopropane, followed by an irreversible electrophilic addition of the silver-silyl intermediate to the alkene.

4.2 Silver-Catalyzed Silacyclopropenation to Alkynes

Transfer of silylene from cyclohexanosilacyclopropane to alkynes can be mediated by silver complexes as well, as reported by Woerpel and co-workers (Scheme 11).[65] Because the silacyclopropene product is a reactive intermediate, a tandem carbonyl insertion reaction could be realized with high regioselectivity.[66] This method can selectively modify the terminal alkyne in enyne-type substrates.



Scheme 11. Silver-catalyzed silacyclopropenation of alkynes.

5. Summary

In the past several years, significant progresses have been made in exploration of the silver-based homogeneous oxidation chemistry. Silver complexes have been shown to efficiently catalyze nitrene, carbene and silylene transfer to different substrates. The new chemistry enriches methods available for catalyzing such reactions. Unique activity was observed for the silver-based systems in several cases. Given the high oxidation potentials associated with silver ions, it is reasonable to expect more silver-based oxidation chemistry to be discovered and used in synthesis in the future. To introduce asymmetric control into the nitrene, carbene, and silylene transfer is another area that will see more research efforts. And lastly, the more challenging oxygen transfer mediated by silver complexes in solution still waits to be developed.

Acknowledgments

We thank Research Corporation, Petroleum Research Fund and Alfred P. Sloan Foundation for generous supports. We also want to acknowledge Dr. Y. Cui, a former member of our group who worked on the silver-nitrene chemistry presented here.

---

[1] a) Y. Kajimoto, *Kagaku Purosesu* **1998**, 121–128; b) S. Wilkinson, *Chem. Eng. News* **1999**, *77*, 27–28; c) D. F. Othmer, M. S. Thakar, *J. Ind. Eng. Chem. (Washington, D. C.)* **1958**, *50*, 1235–1244; d) G. E. Hamilton, A. B. Metzner, *J. Ind. Eng. Chem. (Washington, D. C.)* **1957**, *49*, 838–847; e) P. P. McClellan, *J. Ind. Eng. Chem. (Washington, D. C.)* **1950**, *42*, 2402–2407.

[2] For oxidation or dehydrogenation of alcohols, see: a) E. Cao, A. Gavriilidis, W. B. Motherwell, *Chem. Eng. Sci.* **2004**, *59*, 4803–4808; b) J. N. Keuler, L. Lorenzen, *Prepr. Am. Chem. Soc., Div. Pet. Chem.* **2001**, *46*, 157–160; c) W. F. Hoelderich, *Catal. Today* **2000**, *62*, 115–130; d) N. N. Jovanovic, C. Marinova, M. Stankovic, G. Tuliev, *Heterog. Catal.* **1987**, *6*, 277–282. For oxidation and/or isomerization of olefins, see; e) A. La Ginestra, P. Patrono, M. L. Berardelli, P. Galli, C. Ferragina, M. A. Massucci, *J. Catal.* **1987**, *103*, 346–356; f) E. M. Cordi, J. L. Falconer, *Appl. Catal. A* **1997**, *151*, 179–191. For activation of alkanes, see; g) M. Kralik, V. Macho, E. Jurecekova, L. Jurecl, *Chem. Pap.* **1998**, *52*, 682–691; h) S. S. Bharadwaj, C. Yokoyama, L. D. Schmidt, *Appl. Catal. A* **1996**, *140*, 73–97; i) M. J. Burk, R. H. Crabtree, *J. Am. Chem. Soc.* **1987**, *109*, 8025–8032.

[3] For recent reviews, see: a) L. E. Lindfors, K. Eraenen, F. Klingstedt, D. Y. Murzin, *Top. Catal.* **2004**, *28*, 185–189; b) R. Burch, J. P. Breen, F. C. Meunier, *Appl. Catal. B* **2002**, *39*, 283–303; c) M. C. Kung, H. H. Kung, *Top. Catal.* **2000**, *10*, 21–26.

[4] a) P. A. Wright, S. Natarajan, J. M. Thomas, P. L. Gai-Boyes, *Chem. Mater.* **1992**, *4*, 1053–1065; b) S. D. Gardner, G. B. Hoflund, B. T. Upchurch, D. R. Schryer, E. J. Kielin, J. Schryer, *J. Catal.* **1991**, *129*, 114–120; c) S. D. Gardner, G. B. Hoflund, D. R. Schryer, J. Schryer, B. T. Upchurch, E. J. Kielin, *Langmuir* **1991**, *7*, 2135–2139.

[5] For the CO caused electron poisoning, see: a) J. P. Breen, J. R. H. Ross, *Catal. Today* **1999**, *51*, 521–533; b) B. Rohland, V. Plzak, *J. Power Sources* **1999**, *84*, 183–186.

[6] For selective examples, see; a) M. Wadamoto, N. Ozasa, A. Yanagisawa, H. Yamamoto, *J. Org. Chem.* **2003**, *68*, 5593–5601; b) K. Itami, T. Kamei, M. Mineno, J.-I. Yoshida, *Chem. Lett.* **2002**, *11*, 1084–1085; c) A. Yanagisawa, H. Nakashima, Y. Nakatsuka, A. Ishiba, H. Yamamoto, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1129–1137; d) A. Yanagisawa, H. Kageyama, Y. Nakatsuka, K. Asakawa, Y. Matsumoto, H. Yamamoto, *Angew. Chem. Int. Ed.* **1999**, *38*, 3701–3703; e) A. Yanagisawa, H. Nakashima, A. Ishiba, H. Yamamoto, *J. Am. Chem. Soc.* **1996**, *118*, 4723–4724.

[7] a) M. Ohkouchi, D. Masui, M. Yamaguchi, T. Yamagishi, *Nippon Kagaku Kaishi* **2002**, *2*, 223–229; b) S. Kobayashi, K. Kakumoto, Y. Mori, K. Manabe, *Israel J. Chem.* **2001**, *41*, 247–249.

[8] a) T. Hayashi, Y. Uozumi, A. Yamazaki, M. Sawamura, H. Hamashima, Y. Ito, *Tetrahedron Lett.* **1991**, *32*, 2799–2802; b) A. Yanagisawa, Y. Matsumoto, K. Asakawa, H. Yamamoto, *Tetrahedron* **2002**, *58*, 8331–8339; c) N. Ozasa, M. Wadamoto, K. Ishihara, H. Yamamoto, *Synlett* **2003**, 2219–2221; d) A. Yanagisawa, Y. Nakatsuka, K. Asakawa, H. Kageyama, H. Yamamoto, *Synlett* **2001**, 69–72; e) A. Yanagisawa, Y. Matsumoto, K. Asakawa, H. Yamamoto, *J. Am. Chem. Soc.* **1999**, *121*, 892–893; f) A. Yanagisawa, Y. Matsumoto, H. Nakashima, K. Asakawa, H. Yamamoto, *J. Am. Chem. Soc.* **1997**, *119*, 9319–9320; g) V. A. Soloshonok, T. Hayashi, K. Ishikawa, N. Nagashima, *Tetrahedron Lett.* **1994**, *35*, 1055–1058.

[9] a) N. Momiyama, H. Yamamoto, *J. Am. Chem. Soc.* **2003**, *125*, 6038–6039; b) N. Momiyama, H. Yamamoto, *J. Am. Chem. Soc.* **2004**, *126*, 5360–5361; c) N. Momiyama, H. Torii, S. Saito, H. Yamamoto, *Proc. Natl. Acad. Sci. U. S. A* **2004**, *101*, 5374–5378; d) Y. Yamamoto, N. Momiyama, H. Yamamoto, *J. Am. Chem. Soc.* **2004**, *126*, 5962–5963.

[10] For selective examples, see; a) L.-I. Olsson, A. Claesson, *Synthesis* **1979**, 743–745; b) M. Kimura, K. Fugami, S. Tanaka, Y. Tamaru, *Tetrahedron Lett.* **1991**, *32*, 6359–6362; c) D. C. Lathbury, R. W. Shaw, P. A. Bates, M. B. Hursthouse, T. Gallagher, *J. Chem. Soc., Perkin Trans. 1* **1989**, 2415–2424; d) D. N. A. Fox, D. C. Lathbury, M. F. Mahon, K. C. Molloy, T. Gallagher, *J. Chem. Soc., Chem. Commun.* **1989**, 1073–1075; e) D. N. A. Fox, T. Gallagher, *Tetrahedron* **1990**, *46*, 4697–4710; f) I. W. Davies, T. Gallagher, R. B. Lamont, D. I. C. Scopes, *J. Chem. Soc., Chem. Commun.* **1992**, 335–337.

[11] a) J. A. Marshall, G. S. Bartley, *J. Org. Chem.* **1994**, *59*, 7169–7171; b) J. A. Marshall, X. Wang, *J. Org. Chem.* **1991**, *56*, 960–969; c) J. A. Marshall, K. G. Pinney, *J. Org. Chem.* **1993**, *58*, 7180–7184.

[12] a) P. Pale, J. Chuche, *Eur. J. Org. Chem.* **2000**, 1019–1025; b) V. Dalla, P. Pale, *New J. Chem.* **1999**, *23*, 803–805; c) J. A. Marshall, C. A. Sehon, *J. Org. Chem.* **1995**, *60*, 5966–5968; d) V. Dalla, P. Pale, *Tetrahedron Lett.* **1994**, *35*, 3525–3528; e) P. Pale, J. Chuche, *Tetrahedron Lett.* **1987**, *28*, 6447–6448; f) J. Grimaldi, A. Cormons, *Tetrahedron Lett.* **1986**, *27*, 5089–5090; g) S. Lathbury, T. Gallagher, *Tetrahedron Lett.* **1985**, *26*, 6249–6252; h) J. Grimaldi, A. Cormons, *Tetrahedron Lett.* **1986**, *27*, 825–828; i) R. Kinsman, D. Lathbury, V. Vermon, T. Gallagher, *J. Chem. Soc., Chem. Commun.* **1987**, 243–244; j) L. Anastasia, C. Xu, E.-I. Negishi, *Tetrahedron Lett.* **2002**, *43*, 5673–5676; k) Q. Huang, J. A. Hunter, R. C. Larock, *J. Org. Chem.* **2002**, *67*, 3437–3444; l) T. J. Harrison, G. R. Dake, *Org. Lett.* **2004**, *6*, 5023–5026.

[13] a) R. S. Robinson, M. C. Dovey, D. Gravestock, *Eur. J. Org. Chem.* **2005**, 505–511; b) R. S. Robinson, M. C. Dovey, D. Gravestock, *Tetrahedron Lett.* **2004**, *45*, 6787–6789; c) Y. Kataoka, O. Matsumoto, K. Tani, *Chem. Lett.* **1996**, 727–728; d) Y. Luo, Z. Li, C.-J. Li, *Org. Lett.* **2005**, *7*, 2675–2678.

[14] C. G. Yang, N. W. Reich, C. He, *Org. Lett.* **2005**, *7*, 4553–4556.

[15] a) K. Bhaduri, *Z. Anorg. Chem.* **1913**, *79*, 355–356; b) J. Eggert, *Chem. Ztg.* **1918**, *42*, 199–200; c) J. Eggert, H. Schimank, *Ber. Dtsch. Chem. Ges.* **1918**, *51*, 454–456.

[16] a) C. Wei, Z. Li, C.-J. Li, *Synlett* **2004**, 1472–1483; b) C. Wei, Z. Li, C.-J. Li, *Org. Lett.* **2003**, *5*, 4473–4475; c) Z. Li, C. Wei, L. Chen, R. S. Varma, C.-J. Li, *Tetrahedron Lett.* **2004**, *45*, 2443–2446; d) J.-X. Ji, T. T.-L. Au-Yeung, J. Wu, C. W. Yip, A. S. C. Chan, *Adv. Synth. Catal.* **2004**, *346*, 42–44.

[17] S. P. Shahi, K. Koide, *Angew. Chem. Int. Ed.* **2004**, *43*, 2525–2527.

[18] a) S. Dillinger, P. Bertus, P. Pale, *Org. Lett.* **2001**, *3*, 1661–1664; b) U. Halbes-Letinois, P. Pale, *J. Organomet. Chem.* **2003**, *687*, 420–424; c) P. Bertus, U. Halbes-Letinois, P. Pale, *Eur. J. Org. Chem.* **2001**, 4391–4393.

[19] a) J. M. Longmire, B. Wang, X. Zhang, *J. Am. Chem. Soc.* **2002**, *124*, 13400–13401; b) C. Chen, X. Li, S. L. Schreiber, *J. Am. Chem. Soc.* **2003**, *125*, 10174–10175; c) R. Grigg, *Tetrahedron: Asymmetry* **1995**, *6*, 2475–2486; d) T. F. Knopfel, P. Aschwanden, T. Ichikawa, T. Watanabe, E. M. Carreira, *Angew. Chem. Int. Ed.* **2004**, *43*, 5971–5973; e) S. Peddibhotla, J. J. Tepe, *J. Am. Chem. Soc.* **2004**, *126*, 12776–12777.

[20] a) N. S. Joesphsohm, M. L. Snapper, A. H. Hoveyda, *J. Am. Chem. Soc.* **2003**, *125*, 4018–4019; b) N. J. Patmore, C. Hague, J. H. Cotgreave, M. F. Mahon, C. G. Frost, A. S. Weller, *Chem. Eur. J.* **2002**, *8*, 2088–2098; c) C. Loncaric, K. Manabe, S. Kobayashi, *Adv. Synth. Catal.* **2003**, *345*, 475–477.

[21] R. F. Sweis, M. P. Schramm, S. A. Kozmin, *J. Am. Chem. Soc.* **2004**, *126*, 7442–7443.

[22] For an early review, see: L. A. Paquette, *Synthesis* **1975**, *6*, 347–357. For selected recent reports, see: a) K. Awano, T. Ogino, *Nippon Kagaku Kaishi* **1999**, *4*, 287–291; b) S. Usui, T. Matsumoto, K. Ohkubo, *Tetrahedron Lett.* **1998**, *39*, 9755–9758; c) W. Adam, C. P. Librera, F.-G. Klarner, F. Wurche, *J. Am. Chem. Soc.* **2003**, *125*, 995–1001; d) G. R. Krow, G. Lin, F. Yu, P. E. Sonnet, *Org. Lett.* **2003**, *5*, 2739–2741.

[23] a) W. F. Pickering, *Rev. Pure Appl. Chem.* **1966**, *16*, 185–208; b) J.-P. Taquet, O. Siri, J.-P. Collin, A. Messaoudi, P. Braunstein, *New J. Chem.* **2005**, *29*, 188–192; c) M. P. Heyward, C. F. Wells, *J. Chem. Soc., Dalton Trans.* **1982**, 2185–2189; d) R. S. Macomber, *J. Org. Chem.* **1982**, *47*, 2481–2483; e) C. Walling, D. M. Camaioni, *J. Org. Chem.* **1978**, *43*, 3266–3271.

[24] H. N. Po, *Coord. Chem. Rev.* **1976**, *20*, 171–195.

[25] a) T. B. Sim, S. H. Kang, K. S. Lee, W. K. Lee, H. Yun, Y. Dong, H.-J. Ha, *J. Org. Chem.* **2003**, *68*, 104–108; b) P. Righi, N. Scardovi, E. Marotta, P. T. Holte, B. Zwanenburg, *Org. Lett.* **2002**, *4*, 497–500; c) B. M. Kim, S. M. So, H. J. Choi, *Org. Lett.* **2002**, *4*, 949–952; d) R. J. Madhushaw, C.-C. Hu, R.-S. Liu, *Org. Lett.* **2002**, *4*, 4151–4153; e) M. T. Hancock, A. R. Pinhas, *Organometallics* **2002**, *21*, 5155–5161; f) R. D. White, J. L. Wood, *Org. Lett.* **2001**, *3*, 1825–1827; g) U. K. Syam Kumar, H. Ila, H. Junjappa, W. K. Lee, *Org. Lett.* **2001**, *3*, 4193–4196; h) D. K. Pyun, C. H. Lee, H.-J. Ha, C. S. Park, J.-W. Chang, W. K. Lee, *Org. Lett.* **2001**, *3*, 4197–4199; i) M. S. Kim, Y. W. Kim, H. S. Hahm, J. W. Jang, W. K. Lee, H. J. Ha, *Chem. Commun.* **2005**, 3062–3064; j) D. P. Galonic, N. D. Ide, W. A. van der Donk, D. Y. Gin, *J. Am. Chem. Soc.* **2005**, *127*, 7359–7369; k) B. M. Trost, D. R. Fandrick, *Org. Lett.* **2005**, *7*, 823–826.

[26] For selected reviews, see: a) J. A. Halfen, *Curr. Org. Chem.* **2005**, *9*, 657–669; b) P. Dauban, R. H. Dodd, *Synlett* **2003**, 1571–1586; c) P. Mueller, C. Fruit, *Chem. Rev.* **2003**, *103*, 2905–2919; d) G. Hilt, *Angew. Chem. Int. Ed.* **2002**, *41*, 3586–3588; e) V. K. Aggarwal, *Synlett* **1998**, 329–336.

[27] For selected reports for Rh, see: a) P. Mueller, C. Baud, Y. Jacquier, M. Moran, I. Naegeli, *J. Phys. Org. Chem.* **1996**, *9*, 341–347; b) J.-L. Liang, S.-X. Yuan, P. W. H. Chan, C.-M. Che, *Org. Lett.* **2002**, *4*, 4507–4510. For Cu, see: c) D. A. Evans, M. M. Faul, M. T. Bilodeau, *J. Org. Chem.* **1991**, *56*, 6744–6746; d) D. A. Evans, M. T. Bilodeau, M. M. Faul, *J. Am. Chem. Soc.* **1994**, *116*, 2742–2753; e) P. Dauban, R. H. Dodd, *J. Org. Chem.* **1999**, *64*, 5304–5307. For Ru, see: f) S.-M. Au, J.-S. Huang, W.-Y. Yu, W.-H. Fung, C.-M. Che, *J. Am. Chem. Soc.* **1999**, *121*, 9120–9132; g) W.-l. Man, W. W. Y. Lam, S.-M. Yiu, T.-C. Lau, S.-M. Peng, *J. Am. Chem. Soc.* **2004**, *126*, 15336–15337. For Co, see: h) G.-Y. Gao, J. D. Harden, X. P. Zhang, *Org. Lett.* **2005**, *7*, 3191–3193. For Fe, see: i) J. P. Mahy, P. Battioni, D. Mansuy, *J. Am. Chem. Soc.* **1986**, *108*, 1079–1080; j) R. Vyas, G.-Y. Gao, J. D. Harden, X. P. Zhang, *Org. Lett.* **2004**, *6*, 1907–1910. For Mn, see: k) J.-L. Liang, J.-S. Huang, X.-Q. Yu, N.-Y. Zhu, C.-M. Che, *Chem. Eur. J.* **2002**, *8*, 1563–1572; l) D. Mansuy, J. P. Mahy, A. Dureault, G. Bedi, P. Battioni, *J. Chem. Soc., Chem. Commun.* **1984**, 1161–1163.

[28] For reviews, see: a) T. Ishii, N. Aizawa, R. Kanehama, M. Yamashita, K.-I. Sugiura, H. Miyasaka, *Coord. Chem. Rev.* **2002**, *226*, 113–124; b) D. Srochinski, Y. Dziegiec, A. Grzejdziak, *Russ. J. Coord. Chem.* **1997**, *23*, 447–460; c) W. Levason, M. D. Spicer, *Coord. Chem. Rev.* **1987**, *76*, 45–120.

[29] Y. Cui, C. He, *J. Am. Chem. Soc.* **2003**, *125*, 16202–16203.

[30] S. L. Zheng, J. P. Zhang, W. T. Wong, X. M. Chen, *J. Am. Chem. Soc.* **2003**, *125*, 6882–6883 and references cited therein.

[31] M. P. Doyle, in: *Catalysis by Di- and Polynuclear Cluster Complexes* (Eds.: R. D. Adams, F. A. Cotton), Wiley-VCH, New York, **1998**; pp, 249–282.

[32] a) B. D. Heuss, M. F. Mayer, S. Dennis, M. M. Hossain, *Inorg. Chim. Acta* **2003**, *342*, 301–304; b) S. Taylor, J. Gullick, P. McMorn, D. Bethell, P. Bulman, C. Philip, F. E. Hancock, F. King, G. J. Hutchings, *Top. Catal.* **2003**, *24*, 43–50.

[33] For, Rh, see: a) K. Guthikonda, J. Du Bois, *J. Am. Chem. Soc.* **2002**, *124*, 13672–13673. For Cu, see: b) P. Dauban, L. Saniere, A. Tarrade, R. H. Dodd, *J. Am. Chem. Soc.* **2001**, *123*, 7707–7708; c) H. Han, I. Bae, E. J. Yoo, J. Lee, Y. Do, S. Chang, *Org. Lett.* **2004**, *6*, 4109–4112; d) H.-L. Kwong, D. Liu, K.-Y. Chan, C.-S. Lee, K.-H. Huang, C.-M. Che, *Tetrahedron Lett.* **2004**, *45*, 3965–3968.

[34] Z. Li, C. He, unpublished results.

[35] a) T. Ando, D. Kano, S. Minakata, I. Ryu, M. Komatsu, *Tetrahedron* **1998**, *54*, 13485–13494; b) R. Vyas, B. M. Chanda, A. V. Bedekar, *Tetrahedron Lett.* **1998**, *39*, 4715–4716; c) T. Ando, S. Minakata, I. Ryu, M. Komatsu, *Tetrahedron Lett.* **1998**, *39*, 309–312.

[36] K. A. Kumar, L. K. M. Rai, K. B. Umesha, *Tetrahedron* **2001**, *57*, 6993–6996.

[37] S. Minakaa, D. Kano, R. Fukuoka, Y. Oderaotoshi, M. Komatsu, *Heterocycles* **2003**, *60*, 289–298.

[38] a) C. G. Espino, J. Du Bois, *J. Am. Chem. Soc.* **2002**, *124*, 12950–12951; b) C. G. Espino, P. M. When, J. Chow, J. Du Bois, *J. Am. Chem. Soc.* **2001**, *123*, 6935–6936; c) P. M. When, J. Lee, J. Du Bois, *Org. Lett.* **2003**, *5*, 4823–4826; d) C. G. Espino, K. W. Fiori, M. Kim, J. Du Bois, *J. Am. Chem. Soc.* **2004**, *126*, 15378–15379; e) L. He, P. W. H. Chan, W.-M. Tsui, W.-Y. Yu, C.-M. Che, *Org. Lett.* **2004**, *6*, 2405–2408; f) J.-L. Liang, S.-X. Yuan, J.-S. Huang, C.-M. Che, *J. Org. Chem.* **2004**, *69*, 3610–3619; g) J.-L. Liang, S.-X. Yuan, J.-S. Huang, W.-Y. Yu, C.-M. Che, *Angew. Chem. Int. Ed.* **2002**, *41*, 3465–3468. Cu can mediate intermolecular amidation with PhI=NTs: h) M. M. Díaz-Requejo, T. R. Belderraíén, M. C. Nicasio, S. Trofimenko, P. J. Peréz, *J. Am. Chem. Soc.* **2003**, *125*, 12078–12079.

[39] Y. Cui, C. He, *Angew. Chem. Int. Ed.* **2004**, *43*, 4210–4212.

[40] G. Y. Cho, C. Bolm, *Org. Lett.* **2005**, *7*, 4983–4985.

[41] For selected reviews, see: a) W. Kirmse, *Eur. J. Org. Chem.* **2005**, *2*, 237–260; b) A. de Meijere, H. Schirmer, M. Duetsch, *Angew. Chem. Int. Ed.* **2000**, *39*, 3964–4002; c) S.-T. Liu, R. K. Rajender, *Chem. Soc. Rev.* **1999**, *28*, 315–322; d) M. P. Doyle, M. N. Protopopova, *Tetrahedron* **1998**, *54*, 7919–7946; e) M. P. Doyle, D. C. Forbes, *Chem. Rev.* **1998**, *98*, 911–935; f) M. P. Doyle, *Chem. Rev.* **1986**, *86*, 919–940.

[42] W. E. Bachmann, W. S. Struve, *Org. React.* **1941**, *1*, 38–62.

[43] K. Juhl, R. G. Hazell, K. A. Jorgensen, *J. Chem. Soc., Perkin Trans. 1* **1999**, 2293–2297.

[44] S. Bachmann, D. Fielenbach, K. A. Jorgenson, *Org. Biomol. Chem.* **2004**, *2*, 3044–3049.

[45] K. Burgess, H.-J. Lim, A. M. Porte, G. A. Sulikowski, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 220–222.

[46] a) M. P. Doyle, M. A. McKervey, *Chem. Commun.* **1997**, 983–989; b) T. Ye, M. A. McKervey, *Chem. Rev.* **1994**, *94*, 1091–1160; c) H. Meier, K.-P. Zeller, *Angew. Chem.* **1975**, *87*, 52–63; d) K. Wolfgang, *Eur. J. Org. Chem.* **2002**, *14*, 2193–2256; e) M. P. Doyle, M. A. McKervey, T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, John Wiley & Sons, New York, **1998**.

[47] For thermo and light condition, see ref. 46 and 48, for sonication, see: a) A. Mueller, C. Vogt, N. Sewald, *Synthesis* **1998**, 837–841. For microwave irradiation, see: b) M. R. Lindler, J. Podlech, *Org. Lett.* **2001**, *3*, 1849–1851; c) S. G. Sudrik, S. P. Chavan, K. R. S. Chandrakumar, S. Pal, S. K. Date, S. P. Chavan, H. R. Sonawane, *J. Org. Chem.* **2002**, *67*, 1574–1579.

[48] a) Y. Yukawa, Y. Tsuno, T. Ibata, *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2618–2623; b) M. Takebayashi, T. Ibata, H. Kohara, B. H. Kim, *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2392–2397; c) M. S. Newman, P. F. Beal, *J. Am. Chem. Soc.* **1950**, *72*, 5163–5165; d) J. Wang, Y. Hou, *J. Chem. Soc., Perkin Trans. 1* **1998**, 1919–1924.

[49] G. S. Surendra, M. Trupti, K. C. Nirmalya, P. C. Sambhaji, P. C. Subhash, R. S. Harikisan, K. Vijayamohanan, *Org. Lett.* **2003**, *5*, 2355–2358.

[50] a) H. V. R. Dias, W. Jin, *Inorg. Chem.* **1996**, *35*, 267–268; b) H. V. R. Dias, W. Jin, Z. Wang, *Inorg. Chem.* **1997**, *36*, 6205–6215.

[51] H. V. R. Dias, S. A. Polach, *Inorg. Chem.* **2000**, *39*, 4676–4677.

[52] H. V. R. Dias, R. G. Browning, S. A. Polach, H. V. K. Diyabalanage, C. J. Lovely, *J. Am. Chem. Soc.* **2003**, *125*, 9270–9271.

[53] H. V. R. Dias, R. G. Browning, S. A. Richey, C. J. Lovely, *Organometallics* **2004**, *23*, 1200–1202.

[54] A. Caballero, M. M. Diaz-Requejo, T. R. Belderrain, M. C. Nicasio, S. Trofimenko, P. J. Perez, *Organometallics* **2003**, *22*, 4145–4150.

[55] C. J. Lovely, R. G. Browning, V. Badarinarayana, H. V. R. Dias, *Tetrahedron Lett.* **2005**, *46*, 2453–2455.

[56] a) M. M. Dìaz-Requejo, T. R. Belderrain, M. C. Nicasio, S. Trofimenko, P. J. Pérez, *J. Am. Chem. Soc.* **2002**, *124*, 896–897; b) A. Caballero, M. M. Dìaz-Requejo, T. R. Belderrain, M. C. Nicasio, S. Trofimenko, P. J. Pérez, *J. Am. Chem. Soc.* **2003**, *125*, 1446–1447.

[57] J. Urbano, T. R. Belderrain, M. C. Nicasio, S. Trofimenko, M. M. Dìaz-Requejo, P. J. Pérez, *Organometallics* **2005**, *24*, 1528–1532. and references cited in.

[58] A. K. Franz, K. A. Woerpel, *Acc. Chem. Res.* **2000**, *33*, 813–820.

[59] a) P. Boudjouk, E. Black, R. Kumarathasan, *Organometallics* **1991**, *10*, 2095–2096; b) P. Boudjouk, U. Samaraweera, R. Sooriyakumaran, J. Chrusciel, K. R. Anderson, *Angew. Chem.* **1988**, *100*, 1406–1407; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1355–1356; c) A. Schafer, M. Weidenbruch, K. Peters, H. Schnering, *Angew. Chem.* **1984**, *96*, 311–312; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 302–303.

[60] J. Cirakovic, T. G. Driver, K. A. Woerpel, *J. Am. Chem. Soc.* **2002**, *124*, 9370–9371.

[61] S. A. Calad, K. A. Woerpel, *J. Am. Chem. Soc.* **2005**, *127*, 2046–2047.

[62] a) T. G. Driver, K. A. Woerpel, *J. Am. Chem. Soc.* **2004**, *126*, 9993–10002; b) J. Belzner, U. Dehnert, H. Ihmels, *Tetrahedron* **2001**, *57*, 511–517.

[63] R. E. Ireland, P. Wipf, J. D. Armstrong III, *J. Org. Chem.* **1991**, *56*, 650–657.

[64] T. G. Driver, K. A. Woerpel, *J. Am. Chem. Soc.* **2003**, *125*, 10659–10663.

[65] T. B. Clark, K. A. Woerpel, *J. Am. Chem. Soc.* **2004**, *126*, 9522–9523.

[66] D. Seyferth, S. C. Vick, M. L. Shannon, *Organometallics* **1984**, *3*, 1897–1905.

Received: August 7, 2005
Published Online: May 10, 2006