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Copper, Silver, and Gold Complexes in Hydrosilylation Reactions

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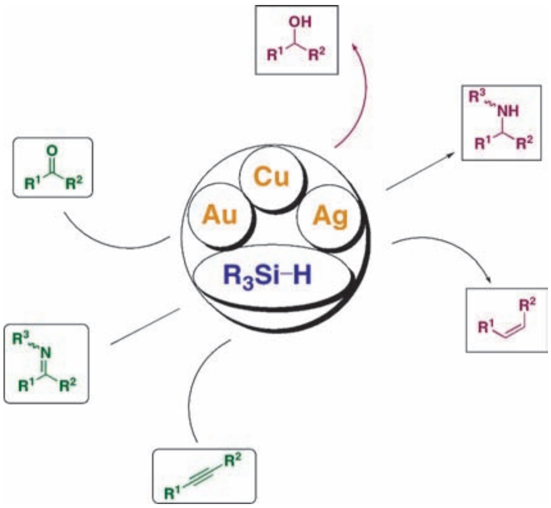

The reduction of diverse functional groups is an essential protocol in organic chemistry. Transition-metal catalysis has been successfully applied to the reduction of olefins, alkynes, and many carbonyl compounds via hydrogenation or hydrosilylation; the latter presenting several advantages over hydrogenation. Notably, hydrosilylation generally occurs under mild reaction conditions, and consequently over-reduced products are rarely detected. Moreover, the great majority of hydrosilanes employed in this reaction are easily handled, inexpensive, or both.

A large number of multiple bonds can be involved in this context, and the hydrosilylation reaction can be regarded as a useful method for the synthesis of silicon-containing organic molecules or a convenient way of reducing organic compounds. Furthermore, the silyl group can also be retained as a protecting group, a strategy that can be of great usefulness in organic synthesis.

Since the first Wilkinson's catalyst-mediated hydrosilylation of ketones in 1972, metals such as rhodium and iridium have attracted most of the attention in this area. A wide array of catalytic systems for hydrosilylation reactions is nowadays available, which has allowed for a great expansion of the synthetic scope of this transformation.

After having been overlooked in the early years, group 11 metals (Cu, Ag, and Au), especially copper, have emerged as appealing alternatives for hydrosilylation. The use of a stabilized form of copper hydride, the hexameric $[(Ph_3P)CuH]_6$, by Stryker represented a breakthrough in copper-catalyzed reduction reactions. Nowadays, several copper-based catalytic systems compare well with a variety of reported rhodium-based catalysts, which generally suffer from the high cost of the catalyst. Tertiary phosphine ligands are the most widely used in these transformations. However, other families such as N-heterocyclic carbenes (NHCs) have shown promising activities.

Compared with copper, little attention has been paid to silver- or gold-based catalysts. Silver salts have been considered inert towards hydrosilylation, and they are often employed as innocent anion exchange reagents for the *in situ* generation of cationic transition metal catalysts. Despite the rare reports available, they have already shown interesting reactivity profiles, for example, in the chemoselective reduction of aldehydes in the presence of ketones. Furthermore, 1,2-hydride delivery is favored over 1,4-reductions for α,β-unsaturated carbonyl compounds, in contrast with most copper-based systems.

Introduction

Reduction of carbonyl and pseudocarbonyl functions represents an essential protocol in organic synthesis.[1] Main group metal hydrides, especially those of boron and aluminum, can accomplish this transformation, but they are required in stoichiometric amounts, which renders them unattractive for practical, environmental, and economical reasons. Transition-metal catalysis has been successfully applied to the reduction of olefins, alkynes, and many carbonyl compounds via hydrogenation or hydrosilylation.[2] Hydrogenation reactions

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often proceed in good yields but usually only under high pressure or at elevated temperature. In contrast, since the first report of metal-catalyzed hydrosilylation of ketones in the presence of Wilkinson's catalyst,[3] smooth reaction conditions can be employed, and consequently, over-reduction products are rarely detected. Furthermore, the development of chiral ligands has also allowed for the production of optically active products under mild and simple conditions.

On the other hand, since a large number of multiple bonds may be involved, the hydrosilylation reaction can be regarded as a useful method for the synthesis of a whole family of silicon-containing organic molecules or as a convenient way of reducing organic compounds. In the hydrosilylation of carbonyl compounds or imines, a hydrosilylation/hydrolysis sequence leads to the formation of alcohols and amines, but the silyl group can also be retained as a protecting group, a strategy that can be of great usefulness in organic synthesis.

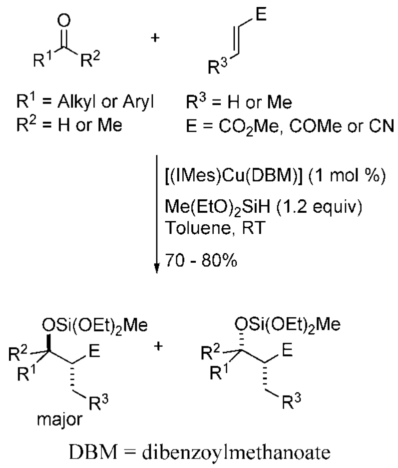
Moreover, the great majority of hydrosilanes employed in this reaction are easy to handle, inexpensive, or both. Polymethylhydrosiloxane (PMHS) must be singled out as a very convenient and most inexpensive reagent.

This Account intends to give a general overview of the possibilities that metals of group 11 (Cu, Ag, and Au) can offer to organic chemists in the context of hydrosilylation reactions.[4] Although phosphine ligands have been most widely used for these transformations, here a special focus will be made on the utilization of N-heterocyclic carbenes (NHCs).[5]

Copper-Based Catalytic Systems

a. Hydrosilylation of Carbonyl Compounds. The "Cu−H" is among the earliest metal hydrides reported in the literature,[6] but for a long time it was considered to have limited potential as a reagent in organic chemistry.[7] A stabilized form of copper hydride, the hexameric $[(Ph_3P)CuH]_6$, was first reported by Osborn,[8] and Stryker et al. demonstrated its usefulness in conjugate reductions of a number of α,β-unsaturated carbonyl derivatives with high regioselectivity.[9] The main drawback of this complex is that it is most effective as a stoichiometric reducing agent. Catalytic reactions under hydrogen atmosphere have been reported, but very careful monitoring is required in order to avoid important formation of over-reduced products.[10] Combination of Stryker's catalyst with a hydrosilane as hydride source allowed for the regioselective conjugate reduction of carbonyl compounds under mild conditions.[11] Hydrosilylation can be performed asymmetrically in the presence of a nonracemic ligand.[12] *In situ* generation of the active species from a copper salt, the ligand of choice, and a base is also an efficient and simple method.[13]

SCHEME 1. [(NHC)Copper(I)]-Catalyzed Reductive Aldol Condensation



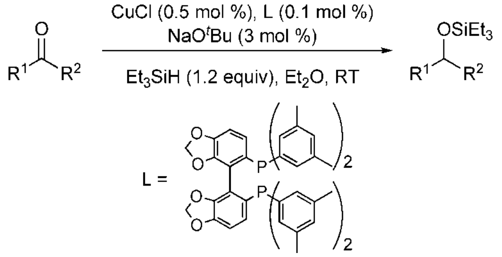
Alternatively, when using a copper hydride as reducing agent in a conjugate reduction, the copper enolate intermediate can be directly engaged in further reactions rather than quenched. The intramolecular conjugate reduction/aldol condensation tandem reaction was first explored with Stryker's reagent as a stiochiometric[14] or catalytic[15] source of hydride. The use of other ligands, mainly diphosphines, has allowed for the generalization of this methodology.[16] To date, there is a single example involving NHC ligands in this tandem reaction.[17] With an IMes (IMes = *N*,*N*′-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) ligand, the direct reduction of the electrophiles (aldehydes or ketones) was minimized, and good yields were obtained from a number of electrophilic double bonds (Scheme 1). A reasonable *anti* diastereoselectivity was obtained with this catalytic system.

Interestingly, the conjugate reduction of ketones can be catalyzed by simple copper(I) salts when 1,3-dimethylimidazolidinone (DMI) is used as solvent, which most probably also acts as a ligand.[18] This system was also the first one used for the hydrosilylation of simple ketones although the process was stoichiometric in copper.[19]

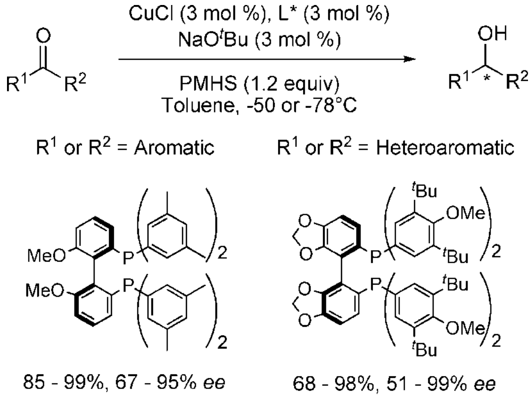
Lipshutz et al. achieved the catalytic hydrosilylation of ketones and aldehydes with Stryker's catalyst and different hydrosilanes.[20] Further studies, notably regarding the stoichiometry of the reagents and the influence of the ancillary ligand,[21] led to the effective formation of silyl ethers in high yields at room temperature (Scheme 2).

Additionally, asymmetric versions of this reaction were reported by the Lipshutz group. Aromatic ketones could be reduced by PMHS in excellent yields and optical purities using

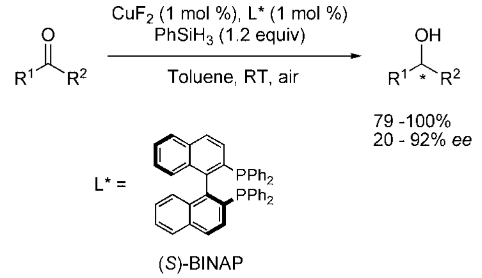
SCHEME 2. Copper-Catalyzed Hydrosilylation of Ketones



SCHEME 3. Asymmetric Copper-Catalyzed Hydrosilylation of Aromatic and Heteroaromatic Ketones



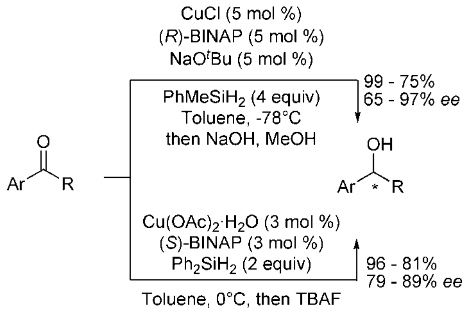
SCHEME 4. Copper-Catalyzed Asymmetric Hydrosilylation of Ketones under Aerobic Conditions



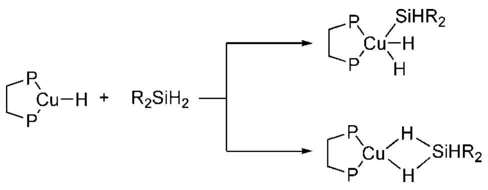
a chiral Roche BIPHEP ligand (Scheme 3).[22] In the hydrosilylation of heteroaromatic ketones, a SEGPHOS ligand was used instead, in order to ensure good asymmetric inductions.[23]

The use of Cu–F systems was first studied for the conjugate reduction of α,β-unsaturated ketones in stoichiometric conditions.[24] Concomitant with Lipshutz's work, Riant et al.[25] reported that the combination of copper(II) fluoride with a chiral phosphine catalyzed the hydrosilylation of ketones with moderate to excellent enantioselectivities (Scheme 4). Low catalyst loadings (down to 0.05 mol %) and compatibility with the presence of water are important features of this catalytic system, but above all, an interesting accelerating effect of oxygen allowed for the reactions to proceed under aerobic conditions. Similar results using a dipyridylphosphine were later reported by Wu and co-workers.[26]

SCHEME 5. BINAP-Based Asymmetric Hydrosilylation of Ketones



SCHEME 6. Postulated Intermediates for the Silane-Dependent Hydrosilylation Reactions



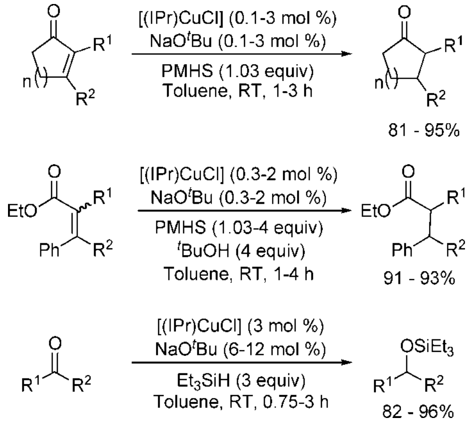
It is important to note that the beneficial effect of oxygen is not general to all Cu–F systems and oxygen inhibition rather than acceleration was observed in the conjugate reduction of nitroalkenes[27] or α,β-unsaturated dinitriles,[28] for example.

A last advantage of Riant's catalytic system is the use of BINAP, an inexpensive and readily available ligand. The use of BINAP in ketone hydrosilylation has been further studied with two different copper sources, CuCl[29] and the air and moisture stable $Cu(OAc)_2 \cdot H_2O$.[30] Both systems proved highly efficient, and the corresponding chiral secondary alcohols were obtained in good yields and ee's (Scheme 5).

Interestingly, whereas the enantioselectivity of the reaction was highly dependent on the nature of the silane in the presence of CuCl, no such effect was observed when using a copper(II) salt. This suggests two distinct mechanistic pathways. In particular, two intermediates that would account for the silane effect in the presence of copper(I) salts have been postulated: a copper(III) intermediate resulting from an oxidative addition to a copper(I) hydride or a pentacoordinate silicon species generated by the interaction of the same hydride with a molecule of silane (Scheme 6).

Although no asymmetric versions have been reported yet, N-heterocyclic carbenes have been shown to be interesting alternatives to phosphines for the copper-catalyzed hydrosilylation of carbonyl groups. [(NHC)copper(I)] complexes, [(IPr)CuCl] in particular (IPr = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), were first reported as catalysts in conjugate reduction reactions of α,β-unsaturated esters and cyclic enones.[31] High yields were obtained in both reactions in tol-

SCHEME 7. [(IPr)CuCl]-Catalyzed Hydrosilylation of Different Carbonyl Compounds



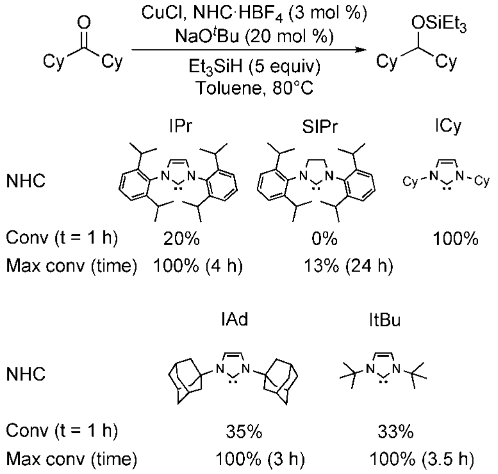
uene at room temperature (Scheme 7). Our concomitant work showed that the same complex could be used in the hydrosilylation of simple ketones to afford the corresponding silyl ethers in excellent yields.[32] For both transformations, the *in situ* generation of the active species from a copper salt, a ligand precursor, and a base was studied and represents an efficient and simple method. Related copper complexes bearing a tetrahydropyrimidin-2-ylidene have also been reported to be active in the hydrosilylation reaction of ketones and aldehydes.[33]

Despite encouraging preliminary studies, modest results were obtained for hindered ketones in the presence of [(IPr)CuCl]. Even if total conversions could be obtained at 80 °C, higher temperatures or extended reaction times were required for the most challenging substrates.[34]

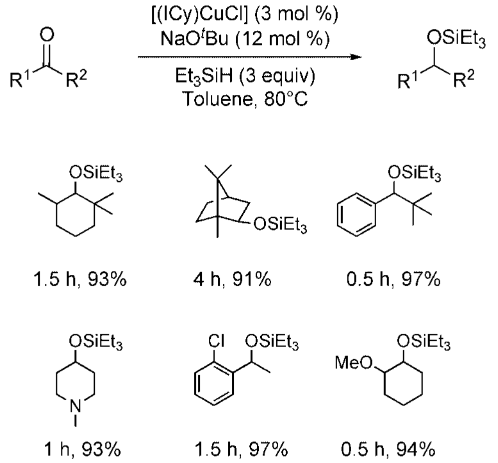
A close examination of the ligand influence on the reaction showed that ICy (ICy = *N,N′*-bis(cyclohexyl)imidazol-2-ylidene) was the most suitable ligand for encumbered substrates. It is noteworthy that the bulkiest carbenes, IAd and ItBu (IAd = *N,N′*-bis(adamantyl)imidazol-2-ylidene; ItBu = *N,N′*-bis(*tert*-butyl)imidazol-2-ylidene) yielded the hydrosilylated product in good reaction times (Scheme 8). These results imply once more that not only steric but also electronic effects are important in this reaction.[35]

With [(ICy)CuCl], a number of ketones with varying congestion around the carbonyl function could be reduced efficiently: alkyl, aromatic, aliphatic, cyclic, and bicyclic ketones (Scheme 9). Even highly congested starting materials yielded the corresponding silyl ethers in high yields and acceptable reaction times. The scope of this catalytic system was also extended to ketones bearing diverse functional groups such as amine, ether, or halogen.

SCHEME 8. NHC Screening for the Hydrosilylation of Dicyclohexyl Ketone



SCHEME 9. [(ICy)CuCl]-Catalyzed Hydrosilylation of Hindered and Functionalized Ketones

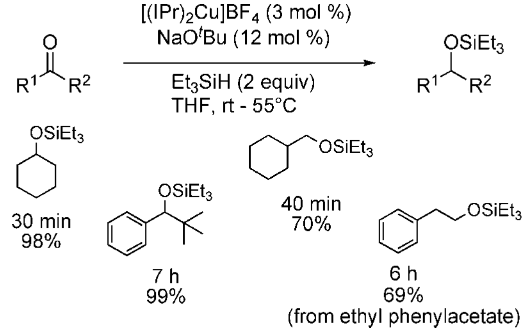


Despite the broad scope of [(ICy)CuCl], ketones containing a pyridine or a thiophene ring led to disappointing results. The reactivity of different carbene precursors in the hydrosilylation of the 2-acetylpyridine was closely examined. It was found that in the particular case of heteroaromatic ketones, the best results were obtained with SIMes as ligand (SIMes = *N,N′*-bis(2,4,6-trimethylphenyl)-2,5-dihydroimidazol-2-ylidene).

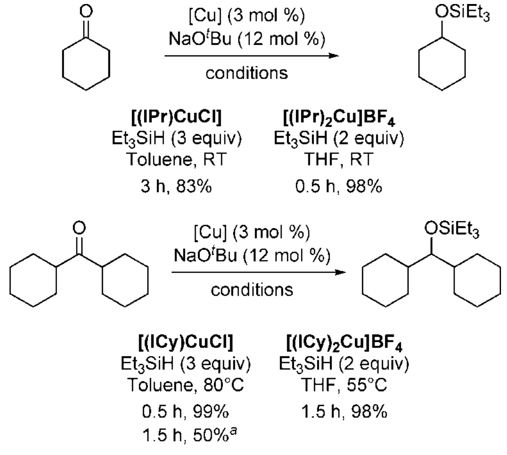
Interestingly, it was also observed that copper(II) salts could be used in this reaction. Concomitantly, Yun et al. reported that the hydrosilylation of ketones could be catalyzed by copper(II) salts in combination with an NHC ligand,[36] as it had been previously shown with a chiral phosphine.[30] For the moment, no evidence is available to unequivocally establish whether the active species is a copper(I) or a copper(II) hydride.

Another family of NHC-containing complexes of general formula [(NHC)$_2$Cu]X (X = PF$_6^-$ or BF$_4^-$), has recently been the subject of a thorough study.[37] The activity of these cationic bis-NHC complexes in the hydrosilylation of ketones was examined, and both the ligand and the counterion showed a

SCHEME 10. $[(IPr)_2Cu]BF_4$-Catalyzed Hydrosilylation of Carbonyl Compounds

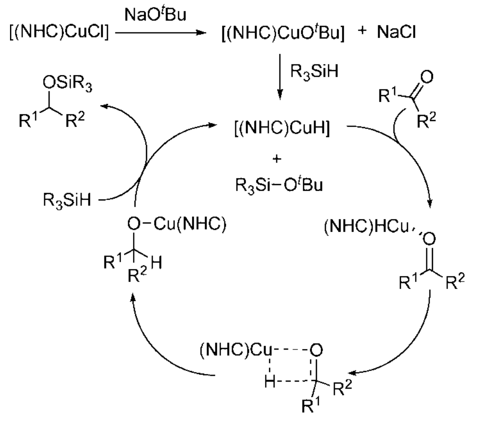


SCHEME 11. Catalysts Comparison



[a] Reaction conditions: Et_3SiH (2 equiv), toluene, 55 °C.

SCHEME 12. Proposed Mechanism for the (NHC)Copper-Catalyzed Hydrosilylation of Ketones



significant influence on the catalytic performance. Whereas the ligand influence could not be rationalized by using pure steric or electronic effect arguments, complexes with BF_4^- counterion were systematically superior to their PF_6^- analogues. For instance, under the same reaction conditions, cyclohexanone was quantitatively transformed into the corresponding silyl ether in 2 h in the presence of $[(IPr)_2Cu]PF_6$, whereas only 30 min were required with the borate analogue. Representative examples of the remarkable catalytic activity of $[(IPr)_2Cu]BF_4$ are shown in Scheme 10: ketones (hindered or not), aldehydes (also enolizable ones), and esters were suitable substrates for this copper complex.

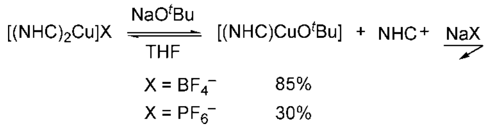
Smoother reaction temperatures and a smaller excess of hydrosilane are the obvious advantages of these cationic complexes when compared with [(NHC)CuCl]. Moreover, when submitted to comparable reaction conditions, the cationic species proved to be more efficient than their neutral analogues (Scheme 11). Cyclohexanone was more efficiently reduced in the presence of $[(IPr)_2Cu]BF_4$ than with its neutral analogue. For more hindered ketones, the activity of [(ICy)CuCl] was compared with $[(ICy)_2Cu]BF_4$ using dicyclohexyl ketone as substrate. In this case, a faster reaction was obtained with the neutral complex but under more forcing conditions. However, when comparable reaction conditions were used ($T = 55$ °C, 2 equiv of hydride source), the cationic complex was found to be the optimum catalyst.

The proposed mechanism for the [(NHC)CuCl]-catalyzed hydrosilylation of ketones is shown in Scheme 12. First, formation of [(NHC)CuO*t*Bu] from the starting complex and the base would occur. Then, the active catalyst, an NHC copper hydride species, would be formed by a σ-bond metathesis between the copper alkoxide and the hydrosilane. These steps are supported by the isolation and characterization of both complexes.[38] Hence, [(IPr)CuH] was isolated as an unstable dimeric complex that readily reacts with a terminal alkyne to provide the corresponding hydrocupration product. Addition of the copper hydride to the carbonyl would result in a copper alkoxide that would undergo another σ-bond metathesis with the hydrosilane to form the expected silyl ether and regenerate the active catalyst.[39]

This mechanism is in agreement with the experimental evidence for the phosphine–copper catalytic systems,[40] but it does not explain why an excess of base is generally required in order to complete the reaction with NHC-based catalytic systems. Because it is well-known that hydrosilanes are prone to nucleophilic attack, we proposed that the excess base that is generally required could interact with the hydrosilane and facilitate the second σ-bond metathesis.

In the case of the cationic complexes, the activation step of $[(NHC)_2Cu]X$ toward hydrosilylation was investigated by ^1H NMR to find that one of the two NHC ligands is displaced by $tBuO^-$ in the presence of NaO*t*Bu, producing the neutral [(NHC)CuO*t*Bu], direct precursor of the active species. The released NHC, being nucleophilic,[41] could then ease the σ-bond metathesis leading to the formation of the silyl ether. It has been postulated that the difference of activity between

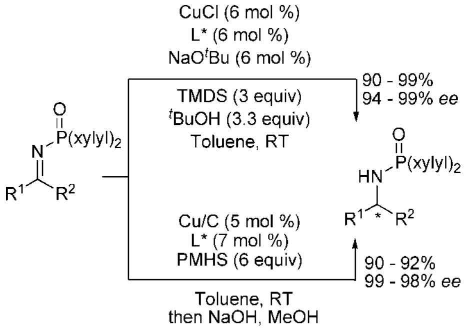
SCHEME 13. Activation of $[(NHC)_2Cu]X$ Complexes Toward Hydrosilylation



$$[(NHC)_2Cu]X \xrightleftharpoons[\text{THF}]{\text{NaO}^t\text{Bu}} [(NHC)CuO^tBu] + NHC + \underset{\swarrow}{\underline{NaX}}$$

$X = BF_4^-$ 85%
$X = PF_6^-$ 30%

SCHEME 14. Copper-Catalyzed Asymmetric Hydrosilylation of Imines



TBDS = *tert*-butyldiphenylsilane

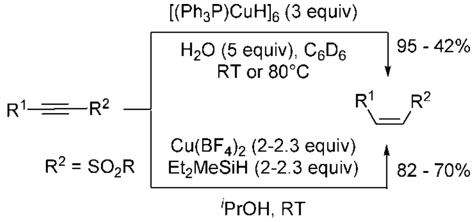
these two catalytic systems would arise from the more efficient activation of the hydrosilane by the NHC ligand than by *t*BuO$^-$.

Moreover, the previously mentioned counterion effect in the catalytic studies could be rationalized as a consequence of the difference in solubility in the reaction solvent of the inorganic salts formed (Scheme 13).

b. Hydrosilylation of Unsaturated Functions Other than Carbonyl Groups. As early as 1967, the copper-catalyzed hydrosilylation of isocyanides was reported.[42] It is therefore surprising to notice that the activity of copper hydrides toward unsaturated groups other than the carbonyl bond remains greatly unexplored.

Two catalytic systems for the copper-catalyzed hydrosilylation of imines have been reported so far. A SEGPHOS ligand has been shown optimal for the effective asymmetric hydrosilylation of aryl ketimines at room temperature. A diphenylphosphinyl moiety was introduced in the starting material to weaken the otherwise strong copper—nitrogen bond in the plausible reaction intermediate. CuCl can be used as copper source,[43] and interestingly, copper-in-charcoal is another attractive alternative (Scheme 14).[44] This heterogeneous reagent was prepared by impregnation of a copper(II) salt within a charcoal matrix using sonication to promote an even distribution of metal. A chiral copper(I) hydride would then be generated by reaction with the ligand and NaOPh in the presence of a silane. Ketones, α,β-unsaturated ketones, esters, and lactones were also good substrates for this reagent. Recycling tests showed that direct utilization of the heterogeneous reagent, after simple filtration from a reaction mixture, afforded the comparable yields and ee's. Notably, no addition of ligand or base was required for the second run, which indicates that the chiral phosphine remains most likely sequestered by the copper center.

SCHEME 15. Copper-Catalyzed Reduction of Alkynes



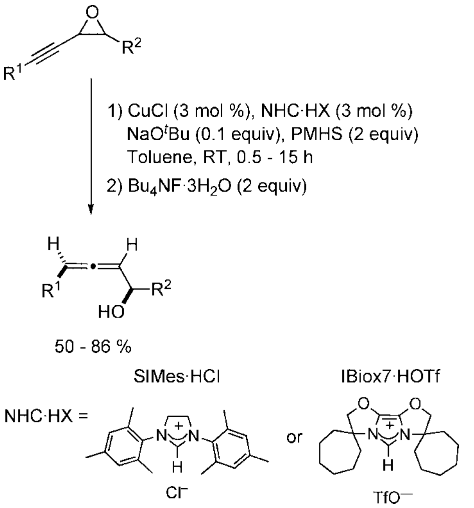
The stoichiometric reaction of alkynes with Stryker's reagent led to their selective reduction to *cis*-alkenes.[45] While terminal alkynes could be reduced at room temperature, internal alkynes only reacted at high temperatures. However, electron-withdrawing substituents can activate disubstituted alkynes toward reduction and acetylenic sulfones could be transformed into the corresponding *cis*-vinylic sulfones at room temperature (Scheme 15).[46] The postulated active species in this report, a copper(II) hydride, was generated *in situ* by the reaction of a divalent copper salt and a hydrosilane. Such a complex would be an efficient reducing agent for this kind of alkynes, but unlike most copper(I) hydride species, it would not effect conjugate reduction.

Alternatively, Sadighi and co-workers reported the hydrocupration of 3-hexyne by an isolated dimeric $[(NHC)CuH]_2$ complex.[38] Nevertheless, only a particular kind of alkynes has been thoroughly examined to date with NHC-containing catalytic systems, propargyl oxiranes, which diastereoselectively yield α-hydroxyallenes diversely functionalized (Scheme 16).[47] Of note, this study represents the only example of substoichiometric copper-catalyzed reduction of alkynes.

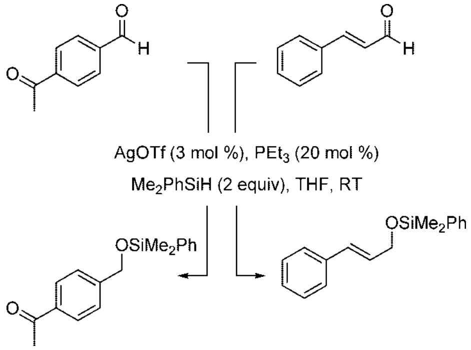
Silver-Based Catalytic Systems

Despite the efficiency of copper complexes in the hydrosilylation reactions and the growing interest in the gold-catalyzed version, little attention has been paid to silver-containing catalysts. In fact, silver salts have been considered as inert toward hydrosilylation, and they are often employed as innocent anion exchange reagents for the *in situ* generation of cationic transition metal catalysts. In this context, while studying carbonyl hydrosilylations catalyzed by $[(pybox)RhCl_3]/AgX$ systems (pybox = 2,6-bis(oxazolinyl)pyridine), Nishiyama and co-workers observed the ability of free AgX salts to mediate the hydrosilylation of acetophenone to a certain extent.[48]

SCHEME 16. Copper-Catalyzed Reduction of Propargyl Oxiranes



SCHEME 17. Silver-Mediated Chemoselective Hydrosilylation Reactions

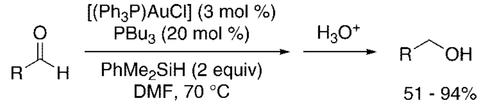


However, in the presence of the pybox ligand, the silver salts did not exhibit any catalytic activity.

The first systematic evaluation of silver salts in a hydrosilylation reaction was reported in 2006,[49] and AgOTf was shown to catalyze the hydrosilylation of aldehydes at room temperature. Lower reaction rates were obtained when a ligand was used, although cleaner reactions were obtained. PEt_3, PBu_3, and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene provided comparable high yields, whereas more sterically hindered or branched trialkylphosphines afforded significantly lower yields. The presence of a ligand had the extra advantage of rendering the transformation chemoselective; an aldehyde could be reduced in the presence of a ketone and only a 1,2-hydride delivery occurred with an α,β-unsaturated aldehyde as substrate (Scheme 17).

In a first approach, the isolation of $Me_2PhSiOTf$ as a byproduct in these reactions suggests the possible intermediacy of a "AgH" species.

SCHEME 18. Gold-Catalyzed Hydrosilylation of Aldehydes



Gold-Based Catalytic Systems

The first gold-catalyzed hydrosilylation of carbonyl compounds was reported in 2000.[50] A soluble gold(I) complex in combination with an excess of phosphine led after hydrolysis to the formation of primary alcohols from the corresponding aldehydes (Scheme 18). It is important to note that while the gold complex was inactive even in the presence of a large excess of PPh_3, the addition of PBu_3 resulted in the formation of the active species of unknown structure to date. Similarly to the silver-based catalyst, α,β-unsaturated aldehydes only reacted in a 1,2-manner with this system, and ketones were completely inert, which allowed for chemoselective reactions. The reduction of an aldimine was also achieved after a 4 day reaction at room temperature.

Since this first report, fluorine-containing phosphines[51] or alternative gold sources such as $[(Me_2S)AuCl]$[52] have been studied. In all cases, a large excess of a phosphine ligand, typically PBu_3, was required in order to achieve good catalytic activity. Rather than improving the reaction rate, the role of the ligand would be to stabilize the active gold species in the presence of the reducing hydrosilane, preventing the deactivation of the catalyst via formation of gold clusters and metallic gold.[53] Further mechanistic studies pointed out that not only the phosphine but also the starting aldehydes conferred this stabilizing effect on the gold complex or helped form the catalytically active species.[54]

Concluding Remarks

Since the first rhodium-catalyzed hydrosilylation of ketones in 1972,[3] considerable efforts have been dedicated to the development of more efficient catalysts. After having been overlooked in the early years, the use of copper-based catalysts for diverse hydrosilylation reactions is now a well-established and efficient methodology. A high level of efficiency and selectivity has been reached, and a number of user-friendly procedures are available. Several catalytic systems presented here compare well with reported rhodium-based catalysts, which generally suffer from a strong economical drawback. Notably, high turnover number (TON) and turnover frequency (TOF) values were obtained with the copper(I) fluoride–diphosphine systems reported by Riant[25] (TON = 2000, TOF = 111 h^{-1}) and Chan[26] (TON = 100, TOF = 600 h^{-1}) in the asymmetric hydrosilylation of acetophenone. These values compare favorably with the rhodium−diphosphine system reported by Imamoto[55] (TON = 86, TOF = 1 h^{-1}) or the planar P,N ligand−Rh system reported by Fu[56] (TON = 94, TOF = 5 h^{-1}). However, important improvements need to be made in order to reach the efficiency of systems like Nishiyama's pybox−Rh (TON = 8700, TOF = 4300 h^{-1}).[48] On the other hand, Lipstutz's bisphosphine−copper systems have been shown to be effective even at substrate-to-ligand ratios of 100 000.[22b] This value is of special importance since last generation ligands are usually more expensive than the common metal sources.

After an initial period of discovery, group 11 systems have several challenges to overcome. For instance, no copper-based system has been reported to date for the asymmetric reduction of dialkyl ketones. Moreover, alkynes, alkenes, or allenes have been largely ignored in the context of copper-catalyzed hydrosilylation reactions. Ultimately, the discovery of a "universal" copper catalyst that would allow for the efficient (asymmetric) reduction of different families of compounds would be highly desirable.

The study of diverse families of ligands other than phosphines, such as NHCs, or further research around other group 11 metals could be keys for surmounting these challenges. Compared with copper, silver and gold have been scarcely studied in this context, but both metals have already shown significant complementarities to their neighbor (for instance, 1,2-reductions have been shown as favored over 1,4-reductions). We believe that the success encountered so far will encourage further research into the general scope of copper, silver, and gold hydrosilylation and related reactions.

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Steven P. Nolan received his B.Sc. in chemistry from the University of West Florida and his Ph.D. from the University of Miami where he worked under the supervision of Professor Carl D. Hoff. After a postdoctoral stay with Professor Tobin J. Marks at Northwestern University, he joined the Department of Chemistry of the University of New Orleans in 1990. He is now Group Leader and ICREA Research Professor at the ICIQ in Tarragona (Spain). His research interests include organometallic chemistry and homogeneous catalysis.

FOOTNOTES

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