Earth-abundant metal complexes as catalysts for the dehydrogenative coupling of hydrosilanes and alcohols

Ana Luque-Gómez,*[a] and Manuel Iglesias*[a]

[a] Dr A. Luque-Gómez, Dr M. Iglesias
Instituto de Síntesis Química y Catálisis Homogénea
CSIC-Universidad de Zaragoza
C/Pedro Cerbuna 12, Facultad de Ciencias, 50009-Zaragoza, Spain
E-mail: analuqgom@unizar.es, miglesia@unizar.es.

Abstract: The dehydrogenative coupling of hydrosilanes with alcohols or water is a fundamental transformation in organosilicon chemistry, enabling the synthesis of alkoxysilanes, silanols, and siloxanes—key materials for coatings and adhesives. Traditionally, these reactions have relied on catalysts based on platinum-group metals (PGMs), which are costly and scarce. The development of Earth-abundant metal (EAM) catalysts offers a sustainable and cost-effective alternative. This concept article highlights recent advancements in homogeneous EAM catalysis for these transformations, focusing on mechanistic insights, reactivity trends, and catalytic efficiencies. Catalysts based on manganese, iron, cobalt, copper, or zinc, are reshaping the field by offering efficient and selective processes for the synthesis of alkoxysilanes, silanols, and siloxanes. Moreover, a key feature of these catalytic systems is their ability to generate dihydrogen as a byproduct, offering potential applications in hydrogen storage and utilization. Despite the good performances of EAM catalysts in the hydrolysis or alcoholysis of silanes, challenges remain, including improving turnover numbers, substrate scope, and catalyst stability. Future developments integrating computational and experimental approaches will be key to optimizing these systems.

Introduction

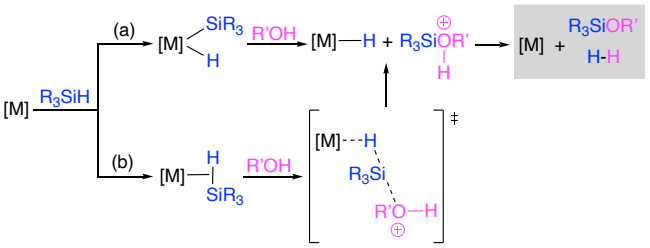
The dehydrogenative coupling of hydrosilanes and alcohols enables the synthesis of alkoxysilanes, whereas using water instead of an alcohol leads to the formation of silanols or siloxanes (Scheme 1).

R' = H, silyl, alifatic and aromatic substituents
R = alkoxy, alifatic and aromatic substituents
n = 1, 2, 3
[Cat] = PGM (eg. Ru, Rh, Ir) or EAM (eg. Mn, Fe, Co, Cu, Zn) complexes

Scheme 1. Dehydrogenative coupling of hydrosilanes with alcohols or water (R' = hydrocarbon or H).

The synthesis of these organosilicon compounds plays a crucial role in the chemical industry, as they have applications in the production of adhesives, adhesion promoters, lubricants, water repellents, etc.[1–3] Moreover, the dehydrogenative coupling of hydrosilanes and alcohols or water generate hydrogen as a byproduct, which has also led to an increasing interest in the use of hydrosilanes as hydrogen storage materials.[4–10] These reactions are primarily driven by the formation of the stable silicon-oxygen bond, which is a thermodynamically favorable process, but kinetically slow. Therefore, the design of sustainable processes for the synthesis of organosilanes entails, to a great extent, the development of efficient catalysts that are able to operate under mild conditions. In addition, the use of catalysts for the synthesis of alkoxysilanes, silanols or siloxanes circumvents the use of stoichiometric reactions, thus improving the atom economy of these processes.

Homogeneous catalysts based on precious metals have proved greatly successful for these transformations, with Ru,[11–13] Rh,[14,15] and Ir[4,9,10,16–20] catalysts being the most prominent examples. Mechanistic studies of these systems indicate that only Si–H bond activation is necessary. The splitting of the Si–H bond has been proposed to occur *via* two main pathways: (a) oxidative addition[14] or (b) heterolytic splitting[9,11,16,20] (Scheme 2). The latter, often referred to as the Luo-Crabtree mechanism, is the most widely invoked pathway for this type of reactions and entails the coordination of the silane by the Si–H bond, followed by nucleophilic attack of the alcohol on the silicon atom.



Scheme 2. Proposed types of mechanisms for the dehydrogenative coupling of hydrosilanes and alcohols.

In contrast with Platinum group metals (PGMs), there is a limited number of reports on homogeneous catalysts utilizing Earth-abundant metals (EAMs) for these processes. However, in recent years, a growing number of reports on homogeneous EAM catalysts have been published. Although PGMs have been instrumental in the advancement of modern homogeneous catalysis, EAM catalysts, in particular those based on 3d metals,

present a more attractive option regarding sustainability due to their wide availability, lower cost, and, arguably, reduced toxicity and environmental impact.[21–23] On these grounds, it appears reasonable to prioritize the development of catalysts derived from abundant metals for practical applications and industrial processes, thereby reducing dependency on limited resources. Moreover, 3d metals, instead of merely imitating their 4d and 5d counterparts, exhibit distinct reactivity that could enable the discovery of new reactions and mechanisms.

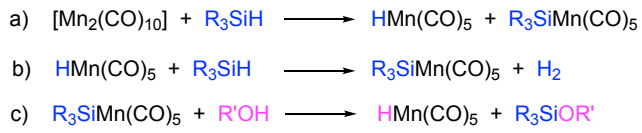
In this concept article, we will examine the most relevant examples of homogeneous EAM catalysts for the dehydrogenative coupling of hydrosilanes and alcohols or water, discussing the reaction mechanisms by which they operate.

Ana Luque-Gómez received her PhD degree from University of Zaragoza in 2024 under the supervision of Dr. Manuel Iglesias, earning the highest distinction, *Cum Laude*. Her doctoral research was supported by a competitive predoctoral fellowship funded by the Spanish Ministry of Science. During her PhD, she conducted a research stay at the University of Bern under the supervision of Prof. Martin Albrecht. Her PhD thesis was focused on the design, synthesis, characterization, and mechanistic studies of Ir(I) and Co(I) catalysts based on NHC and polydentate ligands.

Manuel Iglesias received his PhD degree from Cardiff University in 2008 under the supervision of Professor Kingsley J. Cavell. From 2008 to 2010, he was a postdoctoral fellow at the University of Fribourg and University College Dublin under the supervision of Professor Martin Albrecht. In October 2010, he joined the group of Professor Luis A. Oro at the University of Zaragoza as a research associate. Later, he was the recipient of a ''Juan de la Cierva'' and a ''Ramón y Cajal'' fellowship. Since 2018, he has been a CSIC tenured researcher at the ISQCH.

1. Manganese

The use of manganese organometallic complexes as catalysts in the dehydrogenative coupling of hydrosilanes and alcohols has been known since 1986, when Hilal's group described the activity of dimanganese decacarbonyl ([$Mn_2(CO)_{10}$]).[24] This complex was successfully used as catalyst to synthesize a variety of alkoxysilanes from tertiary silanes ($HSiEt_3$ or $HSi(OEt)_3$) and primary alcohols (ethanol of methanol) under mild reaction conditions. The reaction proposed by the authors proceeds via heterolytic Si–H hydrogen splitting, forming $R_3SiMn(CO)_5$ and $HMn(CO)_5$. Subsequently, reaction of $HMn(CO)_5$ with R_3SiH results in the formation of H_2 and $R_3SiMn(CO)_5$, which undergoes nucleophilic alcohol attack, regenerating the active species, $HMn(CO)_5$, with concomitant formation of the alkoxysilane (Scheme 3). Bulkier alcohols or the addition of PPh_3 reduce the activity due to steric and competitive effects, while electron-withdrawing silanes and non-polar solvents enhance efficiency.



Scheme 3. Proposed reaction mechanism for the synthesis of alkoxysilanes using [$Mn_2(CO)_{10}$].

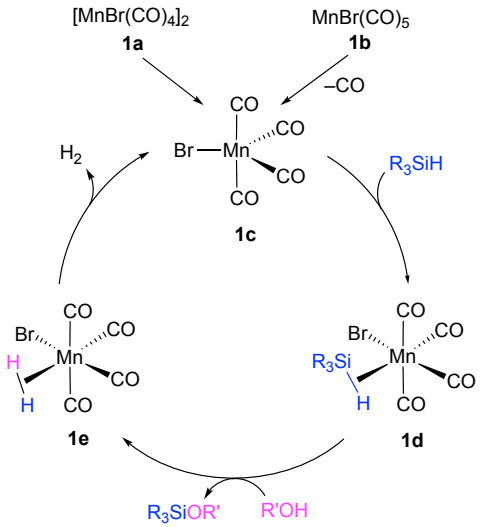
Barton and Kelly demonstrated that the dehydrogenative coupling of neopentyl alcohol with phenylsilane at room temperature using [$Mn_2(CO)_{10}$] as catalyst requires visible light to activate the dimer species, leading to turnover numbers of 3000 in the production of the corresponding alkoxysilane.[25]

A comprehensive study carried out by the group of Cutler on the reactivity of different manganese carbonyl compounds revealed that [$Mn_2(CO)_{10}$] exhibits low or no activity in dehydrogenative reactions with dimethylphenylsilane.[26] However, it was found that the reactivity of dimeric manganese tetracarbonyl bromide complex, **1a**, serves as an effective precursor for the catalytic alcoholysis of $HSiMe_2Ph$, demonstrating excellent conversions and the capability to undergo preparative-scale reactions. Additionally, it was found that $MnBr(CO)_5$ (**1b**) presents a high reactivity, but still lower than its dimeric counterpart (**1a**). Notably, complex **1a** also demonstrated chemeoselectivity in the synthesis of alkoxysilanes in a mixture 1:1:1 of 2-butanol:acetone:$HSiMe_2Ph$, without any detectable hydrosilation of the ketone, even in the presence of excess silane. A plausible reaction mechanism was proposed for **1a** and **1b** (Scheme 4).

The activation of the precatalysts can proceed via two different pathways: **1a** undergoes Mn–Mn bond cleavage, whereas **1b** is activated through CO dissociation, both reactions leading to the formation of the unsaturated active species **1c**. The coordination of the silane results in the formation of **1d**, which, after the nucleophilic attack of the alcohol on the silicon atom, yields the corresponding alkoxysilane and the dihydrogen complex **1e**. The elimination of hydrogen regenerates the active specie **1c**.

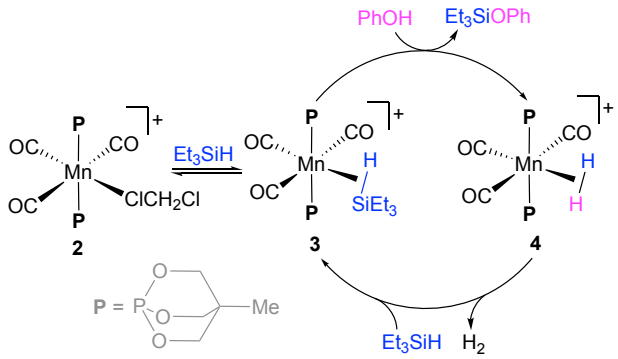
The monomer $MnBr(CO)_5$ was further studied by Scott and Wilcox in the synthesis of unsymmetrical bisalkoxysilanes by the dehydrogentative coupling of the monohydrosilane ethyl (2*S*)-2-[(diisopropylsilyl)oxy]propanoate with primary, secondary and tertiary alcohols in the presence of unsaturated C–C bonds.[27]

Kubas et al. described the dehydrogenative coupling of phenol and $HSiEt_3$ with the cationic complex [*mer*-$Mn(CO)_3\{P(OCH_2)_3CMe\}_2(CH_2Cl_2)$][$BAr^F$] (**2**).[28] The product of this catalysis, Et_3SiOPh, was obtained in a 50% yield using a 24:1 ratio silane:catalyst.



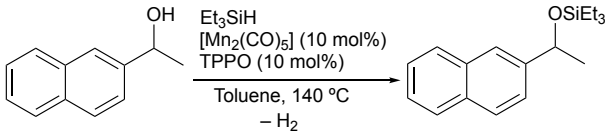
Scheme 4. Proposed reaction mechanism for the selective synthesis of alkoxysilanes employing **1a** or **1b** as precatalysts.

The proposed mechanism suggests that the first step involves a ligand exchange from dichloromethane to triethylsilane, resulting in the formation of compound **3**. This intermediate reacts with phenol to produce the alkoxysilane and the dihydrogen complex **4**, which releases H_2 to regenerate the active species **3** (Scheme 5).



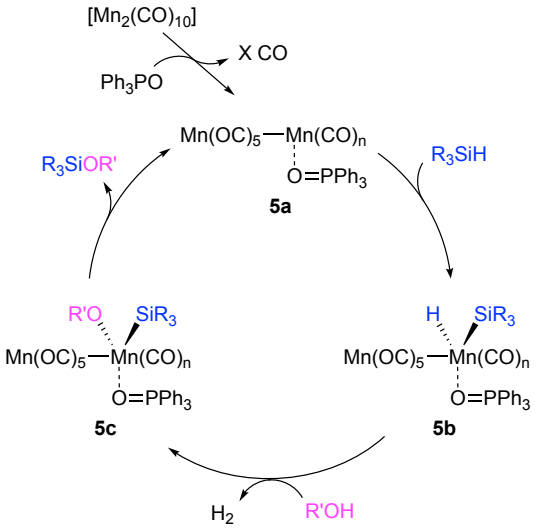
Scheme 5. Proposed reaction mechanism for the synthesis of alkoxysilanes by the cationic manganese complex **2**.

Meng and coworkers, in 2023, reported the manganese-catalyzed dehydrogenative coupling of hydroxyl compounds and silanes using 5 mol% $[Mn_2(CO)_{10}]$ as precatalyst, with a 10 mol% of phosphine oxide ligands in toluene at 140 °C.[29] The use of triphenylphosphine oxide (TPPO) results in an improved reaction yield (Scheme 6), which increases from 51% (in the a absence of ligand) to 96%. Moreover, the reaction time was reduced from 36 h to 30 minutes. The catalyst exhibited a broad substrate scope, including primary, secondary, and tertiary alcohols, as well as phenols and even water, with moderate to high conversions, enabling gram-scale synthesis. Notably, no hydrosilylation was observed in the presence of internal or terminal alkenes.



Scheme 6. Optimized reaction conditions for the selective synthesis of alkoxysilanes using $[Mn_2(CO)_{10}]$ and TPPO.

Experimental data suggest a mechanism in which, at high temperatures, CO and the phosphine oxide ligand are exchanged, forming the active species (**5a**). Subsequently, oxidative addition of the Si–H bond to one of the manganese centers, instead of breaking the Mn–Mn bond, takes place. Then, the hydride ligand in **5b** is protonated, releasing hydrogen and forming **5c**. Finally, **5c** undergoes reductive elimination, producing the silylated product and regenerating **5a** (Scheme 7).



Scheme 7. Proposed reaction mechanism for the synthesis of alkoxysilanes using $[Mn_2(CO)_{10}]$ and TPPO.

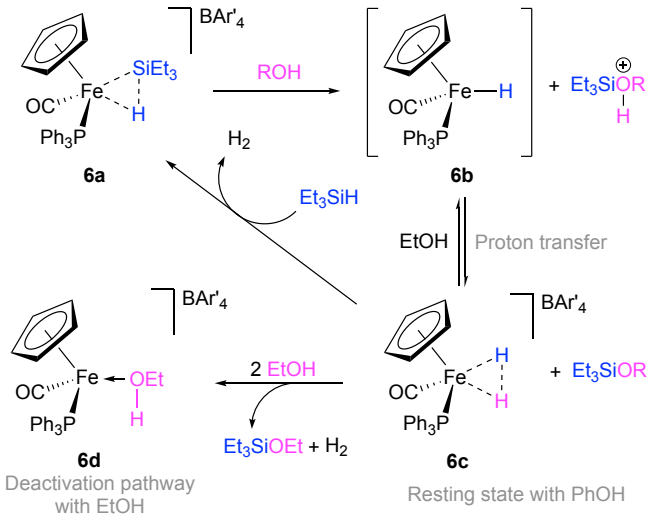
Leitner, Werlé and coworkers reported the dehydrogenative coupling of hydrosilanes and water using 1 mol% $MnBr(CO)_5$ as precatalyst, at rt-80 °C in THF (tetrahydrofurane) or 2-MTHF (2-methyltetrahydrofurane).[30] This catalytic system efficiently converts a wide range of silanes, including both mono- and dihydrosilanes, into silanols while preventing the formation of siloxanes when a 3:1 ratio H_2O:silane is employed. Notably, this system proved capable of gram-scale synthesis, selectively affording $Me_2PhSiOH$ with a 93% isolated yield. In contrast, alternative manganese compounds, such as Mn(II) ($MnBr_2$ and $MnCl_2$), Mn(III) ($Mn(OAc)_3$) or Mn(0) ($[Mn_2(CO)_{10}]$), exhibited no conversion under analogous conditions.

Mn(V) catalyst [MnN(salen-3,5-*t*Bu_2)] reported by Du and co-workers efficiently promotes the dehydrogenative coupling of alcohols and hydrosilanes.[31,32] This catalyst efficiently converts aromatic and alifatic alcohols into their corresponding silyl ethers with a variety of primary, secondary and tertiary hydrosilanes. Additionally, the reaction between diols and diphenylsilane

enables the preparation of poly(silyl ether)s. These transformations proceed at 80° C in acetonitrile employing a 0.5 mol% catalyst loading. Mechanistic investigations suggest that the Mn(V) precatalyst undergoes *in situ* reduction in the presence of excess hydrosilanes to generate a Mn(II) or Mn(III) active species, which operates by the Luo-Crabtree-type mechanism.

2. Iron

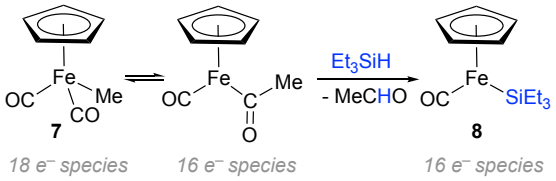
Iron has been extensively studied in homogeneous catalysis, including reactions such as hydrosilylation, hydrogenation, and dehydrogenation reactions.[33,34] However, its use in the dehydrogenative coupling of hydrosilanes remains comparatively rare. The group of Brookhart described in 1998 the first example of a cationic Fe complex (**6a**) capable of catalyzing the dehydrogenative coupling of hydrosilanes and alcohols.[35] **6a** was formed *in situ* by reaction of the hydrosilane with the parent alkylidene complex $[Cp(CO)(PPh_3)Fe{=}CHR]BF_4$ (Cp = cyclopentadienyl).[36] The identification of key reaction intermediate species (**6a-d**) in the alcohol-promoted protonation step was made by variable temperature NMR spectrometry studies. Notably, two distinct activities and mechanistic pathways were observed for **6a** depending on the alcohol (phenol or ethanol), due to their basicity and nucleophilic properties (Scheme 8).



Scheme 8. Proposed reaction mechanism for the synthesis of alkoxysilanes with **6a**.

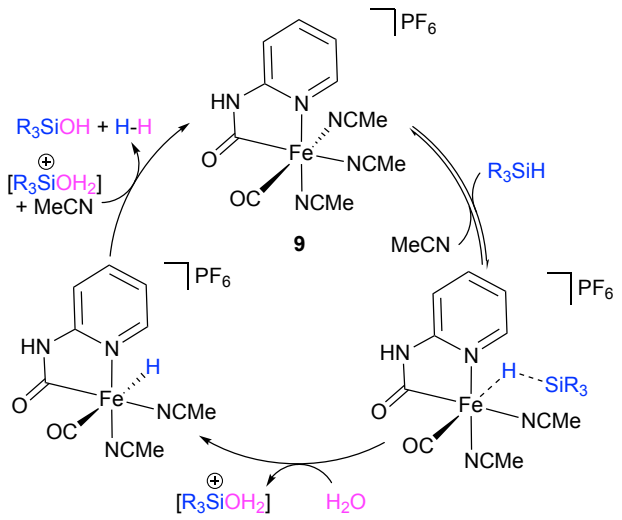
The initial steps of the reaction mechanism are common to both reactants, starting with the reaction of **6a** and the corresponding alcohol to form a neutral iron hydride complex (**6b**). This is followed by a proton transfer reaction, resulting in the formation of the corresponding alkoxysilane and a dihydrogen complex (**6c**). In the case of phenol, due to its lower basicity and nucleophilicity, the formation of Et_3SiOPh, was achieved in high yields, with concomitant displacement of H_2 by Et_3SiH. In the case of ethanol, the deprotonation of **6c** leads to the irreversible formation of an iron-ethanol complex (**6d**), resulting in the deactivation of the catalyst.

Fukumoto's group described the use of a neutral iron complex **7** as catalyst for the dehydrogenative coupling of a series of alcohols with Et_3SiH.[37] Initial studies with PhOH demonstrated that catalytic amounts of complex **7** (10 mol%) resulted in higher conversions to $PhOSiEt_3$ compared to equimolar reactions. This improvement has been ascribed to the more facile coordination of the alcohol to the active iron species during the catalytic cycle, which accelerates dehydrogenative coupling and prevents catalyst decomposition. Among the reactants tested in this work, it was found that alcohols featuring more electron-donating and less sterically hindered groups enhanced the catalytic activity. Furthermore, two potential reaction mechanisms were proposed, with experimental studies supporting the one that involves the formation of the 16-electron iron species **8**, [CpFe(CO)($SiEt_3$)], as key intermediate of the catalytic cycle. **8** has been proposed to form by initial migratory insertion of the CO ligand into de Fe–Me bond to give a 16-electron acyl complex, followed by reaction with Et_3SiH, which leads the elimination of acetaldehyde (Scheme 9).

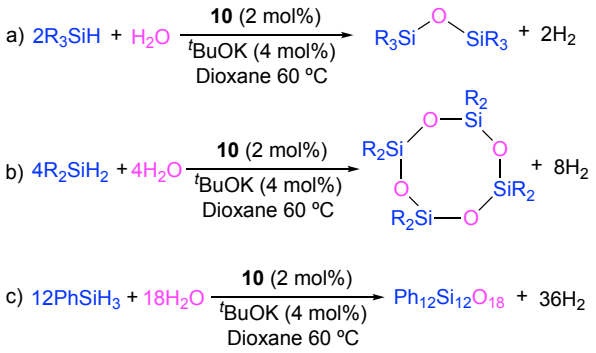


Scheme 9. Proposed reaction for the formation of the 16-electron iron active species **8**.

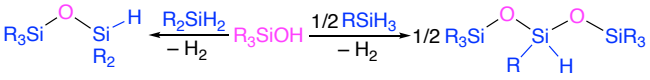
Complex **9**, developed by Fan and coworkers, represents the first example of an iron complex capable of catalyzing the hydrolysis of aliphatic and aromatic hydrosilanes.[38] This air-stable complex achieved excellent yields at room temperature, enabling the obtention of H_2 and related silanols from a variety of hydrosilanes. The study showed that less sterically hindered silanes increased the hydrolysis rate. Additionally, the use of polar solvents enhanced silane solubility in water, thereby increasing catalytic activity for silanol formation; while solvents with low dielectric constants favored the production of siloxanes. The proposed reaction mechanism for the synthesis of silanols, based on experimental data, begins with the replacement of one acetonitrile ligand in complex **9** by hydrosilane. This is followed by hydride abstraction from the η^2-coordinated silane, resulting in the concomitant formation of dihydrogen and the corresponding silanol by the reaction of the protonated silanol with the iron hydride complex (Scheme 10).



Scheme 10. Proposed reaction mechanism for the synthesis of silanols with **9.**



Scheme 12. Synthesis of siloxanes employing precatalyst **10**.



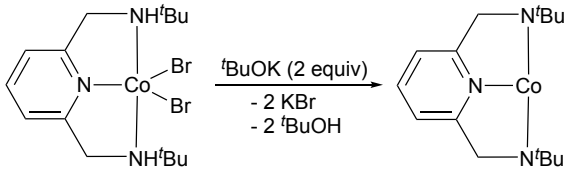
Scheme 13. Synthesis of non-symmetric hydrosiloxanes.

3. Cobalt

Cobalt complexes have shown promising results in the homogeneous dehydrogenative coupling of hydrosilanes with alcohols or water. Interestingly, mainly Co(II) precatalysts have been reported, even though Co(I) complexes are often identified as the active species in a variety of reactions, either generated *in situ* or employed as well-defined catalysts.[39–49]

Gunanathan's group reported the Co(II) precatalyst **10**, which is activated in the presence of ^{t}BuOK to give the unsaturated active species **11** (Scheme 11).[50] This catalyst is able to selectively generate symmetrical siloxanes (Scheme 12a) or cyclotetrasiloxanes (Scheme 12b) by reaction of mono- and dihydrosilanes, respectively, with water. In addition, the use of a trihydrosilane (phenylsilane) triggers the selective formation of a siloxane cage that contains 12 silicon and 18 oxygen centers (Scheme 12c).

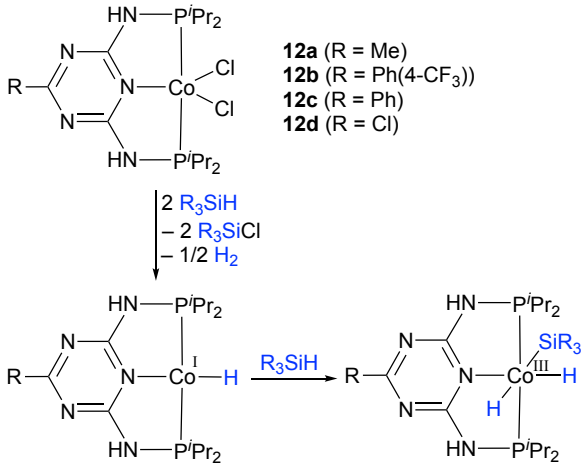
The use of **10** as catalyst also allows for the selective synthesis of non-symmetric siloxanes by reaction of silanols with di- or trihydrosilanes, affording a broad range of siloxymonohydrosiloxanes and disiloxymonohydrosilanes, respectively (Scheme 13).



Scheme 11. Activation of the Co(II) precatalyst **10**.

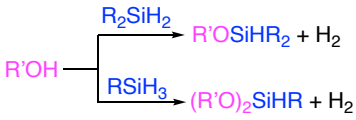
The mechanism proposed for this reaction involves the formation of the active species (**11**) upon reaction of **10** with two equivalents of ^{t}BuOK. This is followed by η^2-coordination of the silane via the Si–H bond. Next, nucleophilic attack by water (or silanol) on the silicon center occurs, according to the pathway depicted in Scheme 12b. Concomitant protonation of the resulting hydride forms a dihydrogen complex, which, upon H_2 release, regenerates **11**.

Hreczycho and coworkers also reported on the catalytic activity of well-defined Co(II) complexes (**12a-c**) in the dehydrogenative coupling of secondary and primary silanes with a variety of alcohols, under mild conditions.[51] However, in this case, *in situ* reduction to Co(I) by the silane was proposed, followed by Si–H oxidative addition to yield a Co(III) dihydride intermediate (Scheme 14).



Scheme 14. Reactivity of Co(II) complexes **12** with hydrosilanes.

Precatalysts **12a** promotes the silylation of primary, secondary, and tertiary alcohols to their corresponding monohydrosilanes selectively (Scheme 15).



Scheme 15. Dehydrogenative methanolysis of primary and secondary silanes.

The proposed catalytic cycle involves the protonation of the Co(III) dihydride complex by the alcohol to generate H_2 and the related alkoxide complex. Subsequently, reductive elimination yields the silyl ether and the monohydride species. The latter, upon reaction with the hydrosilane regenerates the Co(III) dihydride.

Ye and co-workers reported several Co(II) catalysts, prepared *in situ* from $Co(OAc)_2$ and two equivalents of functionalized 2,2'-bipyridine or 1,10-phenanthroline ligands. These systems can selectively yield silanols from monohydrosilanes and water, as well as a variety of alkoxysilanes from primary and secondary silanes.[52] Ligands **13**-**16** were tested, with ligand **15** showing the best selectivity for the synthesis of silanols, effectively preventing the formation of siloxanes (Figure 1). Remarkably, the authors proved that the presence of excess ligand is key to attain the selectivity described above. In addition, this system was also successful for the synthesis of poly(methylhydrosiloxanes) employing heptamethyl trisiloxane, bis(trimethylsiloxy), methylsilane, and tris(trimethylsiloxy)silane.

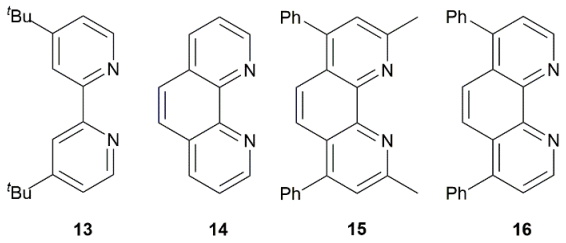
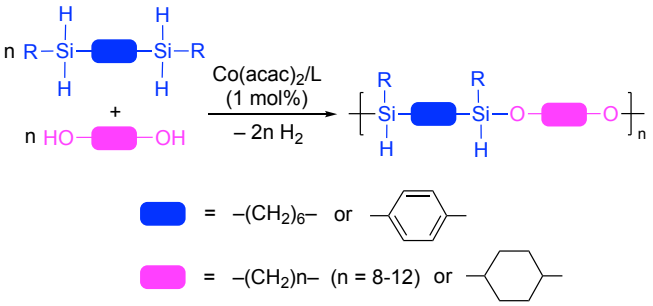


Figure 1. Depiction of ligands **13**-**16**.

The cobalt-catalyzed dehydrocoupling of diols and bis(dihydrosilanes) has also been utilized for polymer synthesis.[53] This reaction, catalyzed by $Co(acac)_2$ in the presence of several bis(phosphines), affords a variety of poly(silyl ether)s (PSEs) with pendant Si-H groups (Scheme 16). PSEs are valued for their thermal stability, biocompatibility, and degradability, making them promising materials for various applications. The best performing ligand is dppe (1,5-bis(diphenylphosphino)pentane), which allows for the preparation of polymers that show molecular weights up to 32.3 kg/mol. The asymmetric variant of this polymerization process was also explored employing (*S*)-MeO-Biphep ((*S*)-(−)-(6,6'-dimethoxybiphenyl-2,2′-diyl)bis(diphenylphosphine)) as ligand, leading to chiral PSEs with moderate enantioselectivity. Remarkably, polymers featuring bis(monohydrosilane) repeating units were reported to form selectively, which is in agreement with the selectivity described above.



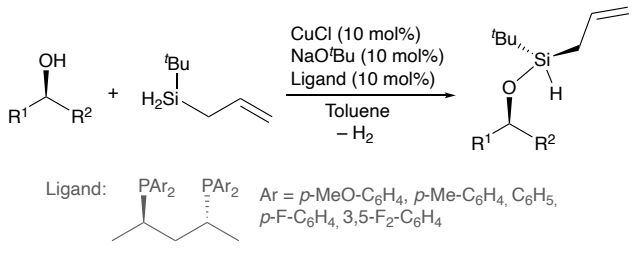
Scheme 16. Synthesis of polysilylethers by the dehydrocoupling of diols and bis(dihydrosilanes).

4. Copper

Copper-based catalysts have recently emerged as efficient alternatives to noble metals in the dehydrogenative coupling of hydrosilanes and alcohols, including asymmetric transformations involving silicon-stereogenic centers.

Seminal work by Lorentz and Schubert on copper catalyzed silane alcoholysis describes the use of the cluster $[Cu(H)(PPh_3)_3]_6$ for the preparation of a broad variety of silanols[54] and alkoxysilanes,[55] employing monohydrosilanes in the case of the former, and mono- or dihydrosilanes for the latter. The catalyst works under mild conditions for a wide range of alcohols, including tertiary alcohols. Moreover, the reaction shows excellent selectivity, even in the presence of alkene and alkyne functional groups.

Building on this work, Leighton and co-workers reported the access to chiral silanes via asymmetric silane alcoholysis catalyzed by CuCl in the presence of chiral bisphosphine ligands.[56] The authors screened various chiral phosphine ligands and found that the BDPP ligand (2,4-bis(diphenylphosphino)-pentane) provided the best reactivity and selectivity for the alcoholysis of allyl-*tert*-butylsilane (Scheme 17).

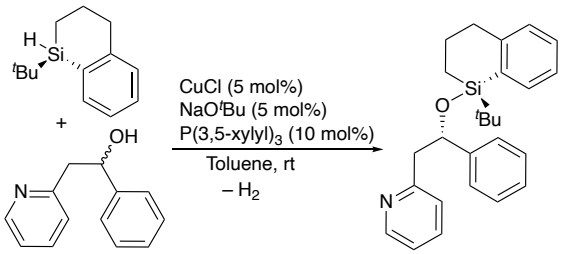


Scheme 17. Assymetric alcoholysis of allyl-*tert*-butylsilane catalyzed by CuCl/BDPP.

The use of less sterically hindered silanes, namely allyl-*tert*-phenylsilane or allyl-2,6-dimethylphenylsilane, lead to lower selectivities. Modifying the BDPP ligand with electron-deficient aryl groups has been found to improve selectivity, especially with the 3,5-difluorophenyl, which allows for a 97:3 diastereomeric ratio. The authors also demonstrated that, *via* tandem

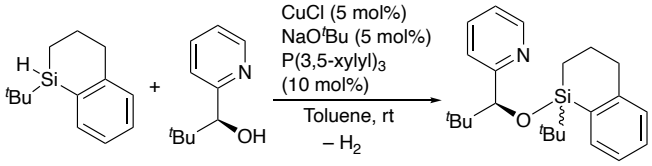
silylformylation–allylsilylation reaction, it is possible to synthesize 1,5-syn-diols and 1,5-anti-diols with moderate to good diastereoselectivity.

Oestreich's group reported the kinetic resolution of chiral secondary alcohols by dehydrogenative alcoholysis of tertiary silanes featuring a silicon-stereogenic center (Scheme 18).[57] The best results were obtained with tri(3,5-xylyl)phosphane as ligand. Treatment of the silyl ether with DIBAL-H results in the formation of the enantiomerically enriched secondary alcohol and the regeneration of the resolving reagent with no racemization.



Scheme 18. Example of kinetic resolution of secondary alcohols.

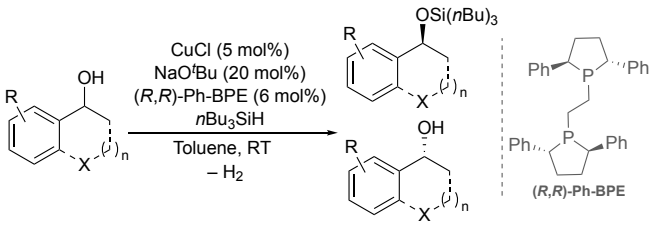
The same group also developed a practical method for preparing enantioenriched silanes through the kinetic resolution of asymmetrically substituted silanes, achieving moderate selectivity. This resolution utilizes a copper-catalyzed silane alcoholysis with recyclable chiral pyridyl alcohols as resolving agents (Scheme 19).[58] Reductive cleavage of the Si–O bond with DIBAL-H leads to the enantiomerically enriched hydrosilane.



Scheme 19. Example of kinetic resolution to obtain a diastereomerically enriched silyl ether.

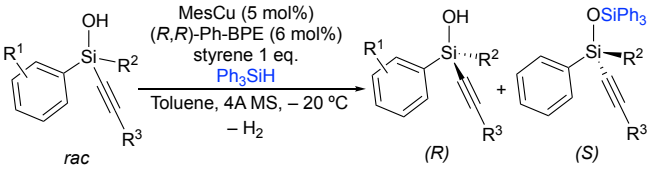
The kinetic resolution of a diverse set of alcohols has been described employing the dehydrogenative silylation reaction catalyzed by Cu(I) complexes in the presence of chiral bisphosphine ligands.

Seminal work by Oestrich employed the catalyst system CuCl/(*R*,*R*)-Ph-BPE/NaO^{t}Bu and *n*Bu$_3$SiH as hydrosilane to resolve a broad variety of benzylic and allylic alcohols (Scheme 20).[59][60]



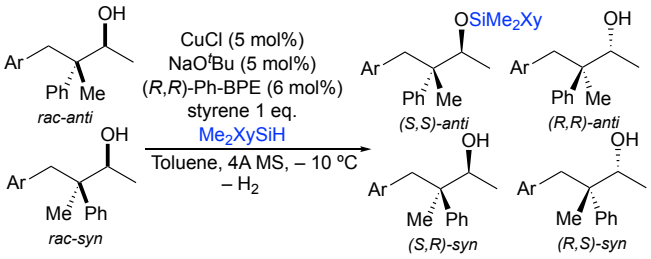
Scheme 20. Cu-catalyzed kinetic resolution of benzylic alcohols.

Tertiary propargylic alcohols can be silylated enantioselectively using the catalytic system MesCu/(*R*,*R*)-Ph-BPE (Mes = mesityl) and Ph$_3$SiH as resolving agent.[61] This method is easily scalable and leads to excellent selectivities (Scheme 21).



Scheme 21. Cu-catalyzed kinetic resolution of tertiary propargylic alcohols.

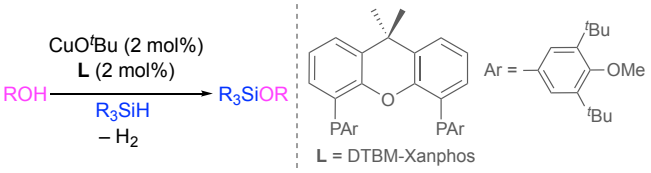
A related catalytic system enables the kinetic resolution of secondary alcohols bearing a vicinal quaternary center. Acyclic secondary alcohols with a vicinal stereocenter the selective silylation of one out of four stereoisomers was achieved (Scheme 22),[62] and acyclic or cyclic neopentylic secondary alcohols can be kinetically resolved owing to the sterically congested quaternary carbon in β-position.[63]



Scheme 22. Cu-catalyzed kinetic resolution of acyclic secondary alcohols.

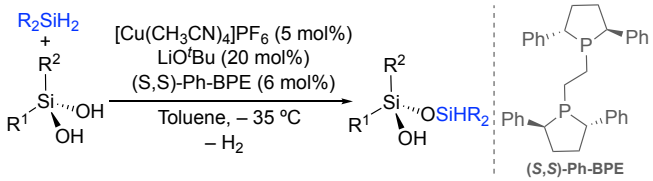
A similar system was also successfully applied to the kinetic resolution of BINOLs and Biphenols, employing PhMe$_2$SiH as hydrosilane.[64]

Sawamura and coworkers described a Cu(I)-DTBM-Xanphos system capable of catalyzing alcoholysis of tertiary silanes (Scheme 23).[65] The scope of the reaction encompasses Et$_3$SiH, Me$_2$^{t}BuSiH, and Me$_2$PhSiH, as silanes, and a broad range of aliphatic alcohols.



Scheme 23. Cu-catalyzed alcoholysis of a variety of tertiary silanes catalyzed by a Cu(I)-DTBM-Xanphos system.

Recently, Li and He described the synthesis of stereogenic silanols from prochiral silanediols by the dehydrogenative coupling of silanols and dihydrosilanes (Scheme 24).[66]



Scheme 24. Desymmetrization of prochiral silanediols.

The use of $[Cu(CH_3CN)_4]PF_6$ and chiral bisphosphine ligands as catalyst in the presence of LiO^tBu led to enantiomeric excesses of up to 96% across a range of substrates. Optimization of the reaction conditions identified (*S*,*S*)-Ph-BPE as the best performing ligand. The reaction demonstrated compatibility with various functional groups and steric environments. The method's practicality was further evidenced by successful gram-scale synthesis and subsequent transformations, including stereospecific oxidation and alkylation. Density functional theory (DFT) calculations have provided insights into the reaction mechanism and the origin of enantioselectivity, emphasizing the role of enantioselective σ-bond metathesis in the transition states to distinguish between the two hydroxyl groups in silanediols.

5. Zinc

Zn complexes have proved active catalysts for dehydrogenative coupling of hydrosilanes with alcohols (Figure 2).

The group of Sadow reported the alcoholysis of tertiary and secondary silanes employing a 10 mol% catalyst loading of **17**, $[To^MZnH]$ (To^M = tris(4,4-dimethyl-2-oxazolinyl)phenylborate).[67] The reaction was explored with several aliphatic alcohols, namely, MeOH, EtOH, ^{i}PrOH, ^{t}BuOH and ^{t}BuCH$_2$OH, leading to good conversions for the monohydrosilane when starting from secondary silanes. Diols were converted selectively into cyclic silylethers by reaction with secondary silanes, avoiding the formation of oligomers or polymers. Mechanistic studies suggest that the Si–H bond splitting is the rate-determining step in these systems. Ligand modifications of the To^M scaffold allow for the synthesis of **18**, $[To^{P^*}ZnH]$, which is capable of inducing stereoselectivity, although low, in the alcoholysis of prochiral secondary silanes.[68] The same group, also developed the related catalysts **19**, $[\{^{Ph}BOX^{Me2}\}ZnR]$, which converts $PhSiH_3$ into $PhSi(OR)_3$ by dehydrogenative coupling with MeOH and ^{i}PrOH, or into $PhSiH_2(OR)$ with ^{t}BuOH. Remarkably, secondary silanes $PhMeSiH_2$ and Ph_2SiH_2 are converted into $R_2Si(OMe)_2$ with MeOH, but into $R_2SiH(OR')_2$ with ^{i}PrOH or ^{t}BuOH.[69]

The methanolysis of primary and secondary alcohols at room temperature has been reported by Parkin[70] with 0.1 mol% of **20**, $[\{\kappa^4\text{-Tptm}\}ZnOSiMe_3]$, by Maron and Okuda[71] with 0.5 mol% of **21**, $[\{ZnH_2(NHC)_2\}_2]$, and with 0.5 mol% of **22**, $[\{ZnH_2(bisNHC)\}_2]$.[72]

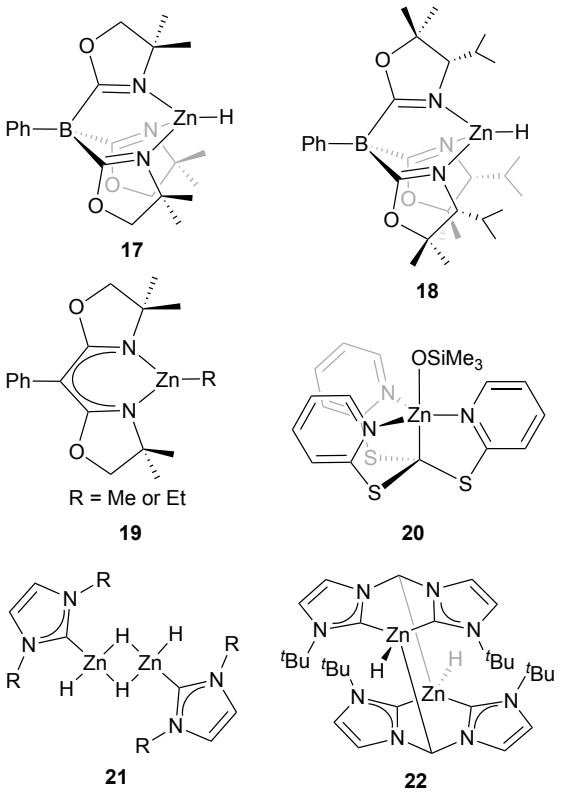


Figure 2. Depiction of Zn(II) catalysts for the dehydrogenative coupling of hydrosilanes and alcohols.

Summary and Outlook

The exploration of Earth-abundant metal catalysts for the dehydrogenative coupling of hydrosilanes and alcohols highlights their growing potential as sustainable alternatives to precious metals. Recent advances have demonstrated the versatility of manganese, iron, cobalt, copper, and zinc complexes in achieving efficient and selective transformations. These catalysts enable the selective synthesis of siloxanes or silanols, with concomitant hydrogen generation. This reactivity also enables polymerization processes, broadening the scope of accessible organosilicon compounds. Moreover, copper catalyzed asymmetric transformations provide access to silicon-stereogenic centers and allow for the kinetic resolution of alcohols via silyl ether formation. Although different reactivities are expected for Mn, Fe, Co, Cu, and Zn complexes, no clear specific reactivity or metal substrate affinities can be drawn from the examples described herein.

Regarding reaction mechanisms, most of the proposed catalytic cycles proceed by Luo-crabtree-type pathways, which involve the heterolytic splitting of the Si–H bond. However, exceptions exist; for example, in the $[Mn_2(CO)_{10}]$/TPPO system, oxidative addition of the Si–H bond has been postulated. Additionally, for the case of the Co(II) precatalysts **12**, an activation step involving reduction to generate a Co(I)–H species is required, followed by oxidative addition of the hydrosilane to form a dihydride Co(III) intermediate. Concerning metal–ancillary ligand synergies, certain patterns can be identified: Mn(I) catalysts typically feature monodentate, weakly coordinating ligands; Co catalysts appear to benefit from the use of pincer ligands; Cu(I) catalysts employed in asymmetric

transformations perform best with chiral bisphosphine ligands; and the most active Zn catalysts often incorporate polydentate nitrogen-donor ligands. Fe complexes, although less common, have demonstrated good catalytic activity when supported by the Cp ligand.

Despite these advances, several challenges remain. Many EAM-based systems require further optimization to match the efficiency and robustness of PGM catalysts. Issues such as catalyst stability, high catalyst loading in some cases, and broader substrate applicability must be addressed for practical applications. Therefore, future efforts should focus on developing more robust ligand frameworks, improving selectivity for specific silane products, and expanding the range of compatible alcohol and silane substrates. Regarding processes focused on hydrogen generation, catalyst stability and recyclability become especially important.

Additionally, deeper mechanistic insights are necessary to guide the rational design of next-generation catalysts. The integration of computational and experimental approaches will be crucial for understanding reaction mechanisms and designing new catalytic systems. By addressing these challenges, EAM-based catalysts have the potential to revolutionize silicon chemistry, promoting greener and more cost-effective processes.

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