ARTICLE

Sustainable Preparation of Aminosilane Monomers, Oligomers, and Polymers through Si–N Dehydrocoupling Catalysis

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This article covers historical and recent efforts to catalyze the dehydrocoupling of amines and silanes, a direct method for Si–N bond formation that offers hydrogen as a byproduct. In some applications, this transformation can be used as a sustainable replacement for traditional aminosilane synthesis, which demands corrosive chlorosilanes while generating one equivalent of ammonium salt waste for each Si–N bond that is formed. These advantages have driven the development of Si–N dehydrocoupling catalysts that span the periodic table, affording mechanistic insight that has led to advances in efficiency and selectivity. Given the divergence in precursors being used, characterization methods being relied on, and applications being targeted, this article highlights the formation of monomeric aminosilanes separately from oligomeric and polymeric aminosilanes. A recent study that allowed for the manganese catalyzed synthesis of perhydropolysilazane and commercial chemical vapor deposition precursors is featured, and key opportunities for advancing the field of Si–N dehydrocoupling catalysis are discussed.

1. Introduction

Compounds that possess Si–N bonds are used for many applications. On the small molecule, or monomeric, side of the ledger, *N*-silylamines (Fig. 1, **1a**) were essential to the discovery of constrained geometry α-olefin polymerization catalysts.[1] Moreover, reagents of this type are increasingly being used to facilitate N–C[2,3] and C–C[4] bond forming reactions. Disilazanes, or *N*,*N*-disilylamines (Fig. 1, **1b**), are often employed as surface passivation agents[5,6] and are a popular ligand motif for atomic layer deposition (ALD) and chemical vapor deposition (CVD) precursors.[7,8]

While these uses are notable, monomeric silylamines are prepared on a smaller scale than their industrially important oligomeric or polymeric counterparts. Organic polysilazanes, which feature a repeating Si–N backbone (Fig. 1, **1c**), are widely used to protect automobiles and architectural installations from corrosion.[9] These polymers can exist as mixtures of liquids or solids of varying molecular weight and are highly susceptible to hydrolysis.[10,11] Controlled hydrolysis can be advantageous as it results in amine loss and the formation of a protective silicon oxide and oxynitride glass network. Inorganic polysilazane, or perhydropolysilazane (PHPS, Fig. 1, **1d**), is of interest as a precursor for silicon nitride (Si_3N_4) thin films.[12] PHPS exhibits self-curing behaviour and can readily adhere to surfaces. Importantly, Si_3N_4 films generated from PHPS pyrolysis feature impressive electrical resistivity, dielectric strength, hardness, and stability.[13,14] These properties render PHPS indispensable for the manufacturing of electronic devices including solar cells and microprocessors.[15-18]

Polymers that feature alternating silane and diamine units (Fig. 1, **1e**), represent an emerging polymer class that has yet to be fully studied. Polymers of this type have been referred to in the literature as polycarbosilazanes, although they lack the repeating C–Si–N[19] or palindromic N–Si–C–C–Si–N[20] backbones that true polycarbosilazanes feature. The preparation of these silane diamine alternating copolymers is an increasingly popular area of research that will be covered in this review.

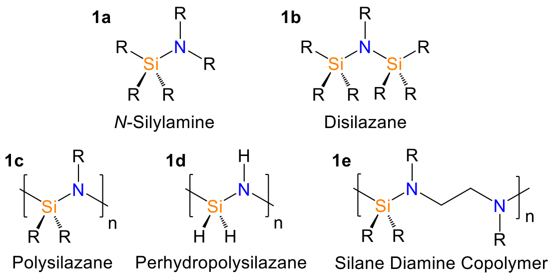

Fig. 1. Monomers and polymers commonly prepared by Si–N dehydrocoupling.

The synthesis of Si–N bonds can be achieved using a handful of methodologies.[21-23] However, chlorosilane aminolysis using ammonia or substituted amines is practiced on the largest scale (Fig. 2, a). This approach is inherently atom-inefficient since an equivalent of ammonium salt waste is generated for each Si–N bond that is formed. A promising alternative to chlorosilane aminolysis is the dehydrogenative coupling of amines and silanes in the presence of a catalyst (Fig. 2, b).[24] This method offers the added advantage of producing hydrogen as the sole by-product, regardless of the chosen amine and silane coupling partners. The release of H_2 provides an entropic driving force for Si–N bond formation and greatly simplifies product purification. It is intriguing to note that H_2 is largely produced alongside CO_2 via the steam reforming and partial oxidation of fossil fuels.[25] If Si–N dehydrocoupling catalysis were ever performed in an industrial setting at the relevant scale, this transformation would offer a green alternative to grey or brown H_2, adding value to the overall process if used for a subsequent application.

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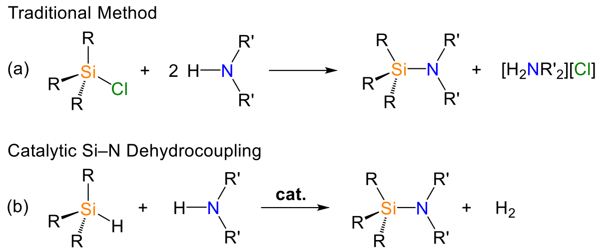


Fig. 2. Strategies for Si–N bond formation.

Catalytic dehydrogenative coupling has been achieved for several p-block element heterocoupling reactions, a topic that has been reviewed by Manners,[26] Melen,[27] and Kuciński.[28] The field is beginning to mature with the introduction of efficient catalysts capable of producing highly cross-linked inorganic polymers that are inaccessible using traditional methods.[29] Catalytic Si–N bond formation was the focus of a minireview by Waterman and co-workers highlighting catalysts from across the periodic table (including the s-, p-, d-, and f-blocks).[30] The formation and reactivity of Si–N bonds was reviewed in this journal by Schafer and co-workers last year.[22]

This article differs from prior reviews in terms of its structure and content. This contribution will *only cover Si–N formation and the release of* H_2 *from the catalytic heterodehydrocoupling of amines and silanes*. Moreover, the synthesis of aminosilane monomers will be summarized independently from oligomeric and polymeric aminosilanes. These sections are presented in chronological order to highlight how efforts to prepare common aminosilanes have overshadowed the formation of industrially relevant products in recent publications. The preparation of CVD precursors and PHPS through the dehydrocoupling of amines and silane gas (SiH_4) are applications that will be featured, and opportunities to advance Si–N dehydrocoupling catalysis and commercialization will be discussed.

2. Many Catalysts Have Been Developed to Prepare Aminosilane Monomers

To our knowledge, the first literature mention of N–H and Si–H dehydrogenative coupling catalysis came from Kraus and Nelson in 1934.[31] In this effort, the coupling of triethylsilane to ethylamine was achieved under neat conditions in the presence of lithium metal (10 mol% relative to silane). A full equivalent of H_2 was found to accompany the formation of $(C_2H_5)_3SiNHC_2H_5$. Unconsumed lithium metal was observed following the reaction and was presumed to be the catalyst.

A brief account by Saam and Speier in 1959 revealed that chloroplatinic acid acts as a catalyst for the dehydrogenative coupling of primary and secondary amines with silicon hydrides.[32] Hydrogen gas was released, and the unidentified products were presumed to be aminosilanes.

In 1967, Sommer and Citron demonstrated catalytic Si–N dehydrocoupling using palladium supported on carbon (Pd-C) and alumina ($Pd\text{-}Al_2O_3$).[33] To evaluate the stereochemistry of this transformation, they employed the chiral silane, (-) α-naphthylphenylmethylsilane (Fig. 3, left). They found that 5% $Pd\text{-}Al_2O_3$ allowed for dehydrocoupling with the complete inversion of stereochemistry when pyrrolidine or *i*-$BuNH_2$ were chosen as the coupling partner. Interestingly, it was determined that dehydrocoupling over Pd-C resulted in a racemic product.

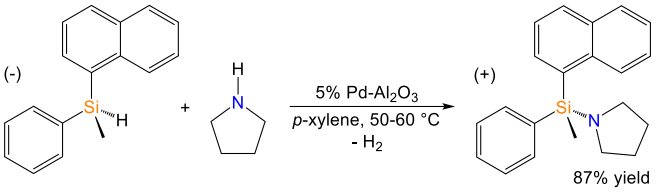


Fig. 3. Dehydrocoupling of a chiral silane with pyrrolidine using $Pd\text{-}Al_2O_3$.

Four years later, Ojima and co-workers were the first to demonstrate that efficient homogeneous Si–N dehydrocoupling could be achieved for a modest scope of primary, secondary, and tertiary silanes, even with secondary amine coupling partners.[34] Using 0.1-1.0 mol% of Wilkinson's catalyst, $(Ph_3P)_3RhCl$ (**1**), the dehydrocoupling of Et_2NH with $PhSiH_3$, Ph_2SiH_2, Et_2SiH_2, and Et_3SiH was achieved within 2-16 h at temperatures ranging from room temperature to 70 °C (Fig. 4). Additional amines were successfully coupled to both secondary silanes. Notably, these trials were run in the absence of solvent and some of the products were obtained efficiently at room temperature. For example, compound **4d** was obtained in 98% GLPC yield after only 20 min at room temperature from Ph_2SiH_2 and pyrrolidine, equating to a turnover frequency (TOF) of 5 min^{-1}. The authors were able to lower the catalyst loading for several trials; product **4f** was obtained after 2 h at room temperature using only 0.1 mol% of catalyst (TOF = 490 h^{-1}) while product **4h** was obtained in 98% yield after 40 min using 0.2 mol% of catalyst (TOF = 12.3 min^{-1}).

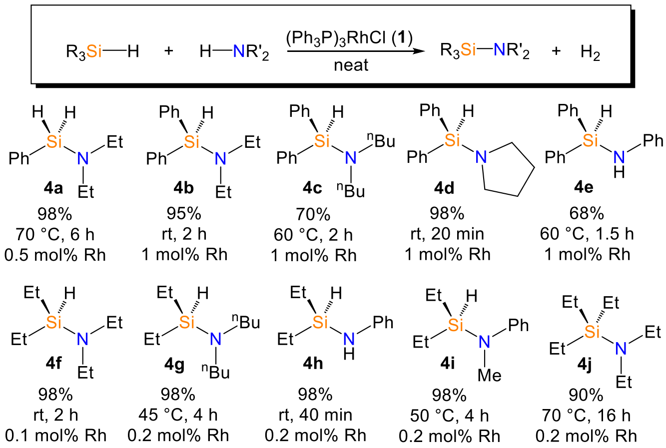


Fig. 4. Scope of Si–N dehydrocoupling reported by Ojima and co-workers.

In 1977, Sidorov and co-workers observed that $WOCl_4$ and $K_2[IrCl_6]$ mediate the non-selective dehydrogenative coupling of triethylsilane and *N*-benzylaniline at 120-130 °C for 16 h.[35] Under the same conditions, these and related catalysts including $K_2[PtCl_6]$, $[(C_{10}H_{21})_4P][PtCl_6]$, and ammonium salts $[(C_8H_{17})_3NH]_2[IrCl_6]$, $[(C_8H_{17})_3NH]_2[RuCl_6]$, $[(C_8H_{17})_3NH]_2[PtCl_6]$, and $[(C_8H_{17})_3NH]_2[PdCl_4]$ were found to promote the dehydrocoupling of triethylsilane and aniline at catalyst loadings of 2-10 mol%. Ultimately, **1** was found to be the most effective catalyst, affording *N*-triethylsilylaniline in 61% yield after 5 d at 60 °C using 0.6 mol% loading.

In 1988, Laine and co-workers presented a kinetic and mechanistic analysis of silane-amine dehydrocoupling using $Ru_3(CO)_{12}$.[36] They reacted Et_3SiH with amines (i.e., $^nBuNH_2$, $^nPrNH_2$, $^sBuNH_2$, and $^tBuNH_2$) in the presence of $Ru_3(CO)_{12}$ in THF at 70 °C. Based on kinetic observations, they proposed a set of reaction steps that were relevant for Ru-based Si–N dehydrocoupling, including N–H activation and subsequent β-hydride elimination, Si–H oxidative addition, and Si–N formation by reaction of a Ru-silyl intermediate with incoming amine. Depending on the steric demands of the amine, three different rate-limiting steps were proposed. For $^{n}PrNH_2$ and $^{n}BuNH_2$, silane oxidative addition was assumed to be rate-limiting, for $^{s}BuNH_2$, the rate-limiting step was proposed to be Si–N bond formation, and for $^{t}BuNH_2$, catalyst activation was found to be rate-limiting. Laine and co-workers also reported a turnover frequency (TOF) of 15.8 h^{-1} for $Ru_3(CO)_{12}$ catalysed Si–N dehydrocoupling in THF at 70 °C. However, $(PhCN)_2PdCl_2$, $PdCl_2$, and $Pd(OAc)_2$ were all found to catalyse this reaction with TOFs of greater than 200 h^{-1}. When these Pd catalysts were employed, the formation of Pd^0 was observed, which was believed to be the active catalyst. Carbonyl catalysts other than $Ru_3(CO)_{12}$ were found to exhibit lower activity.

In an isolated example from 1990,[37] 5 mol% of (benzene)-$Cr(CO)_2(\eta^2\text{-}HSiHPh_2)$ was found to mediate the dehydrocoupling of aniline and diphenylsilane at ambient temperature. Although $Ph_2HSiNHPh$ was characterized by ^{1}H and ^{13}C NMR spectroscopy, attempts to detect this product by mass spectrometry resulted in the observation of $(Ph_2HSi)_2O$, highlighting the susceptibility of *N*-silylamines to oxidation.

The following year, Corriu and co-workers reported that tetrabutylammonium fluoride (1M THF solution) can catalyze the dehydrogenative coupling of silanes and secondary amines.[38] Amine reactivity followed the order of $Me_2NH > (Me_3Si)_2NH > Et_2NH$, and while using an excess of Me_2NH as the coupling partner, the authors determined that $OctSiH_3$ allowed for an impressive TOF of 47.5 h^{-1} at 0 °C. The use of secondary silanes Ph_2SiH_2 and $PhMeSiH_2$ resulted in lower TOFs of 33 h^{-1} and 7.5 h^{-1}, respectively, while tertiary silane $PhMe_2SiH$ allowed for a TOF of only 1 h^{-1} under the same conditions. In the presence of excess amine, Ph_2SiH_2 and $PhMeSiH_2$ only allowed for the formation of a single Si–N bond.

In 1992, Harrod and Liu explored Cu(I) catalyzed Si–N dehydrocoupling.[39] At 100 °C, $PhMeSiH_2$ was added to (*R*) α-methylbenzylamine in the presence of 6.7 mol% CuCl, which allowed for 84% conversion to an approximate 1:1 mixture of diastereomeric silylamines after 21 h. Upon dehydrocoupling $PhMeSiH_2$ with benzylamine at different molar ratios, the authors were able to demonstrate control over the reaction selectivity. For example, when two equivalents of $PhMeSiH_2$ were added per equivalent of benzylamine, 80% conversion to the disilazane product, $BnN(SiHPhMe)_2$ was observed (Fig. 5, a). When excess amine was added (2.3 equiv. per silane), 81% conversion to PhMeHSiNHBn was observed after 6 h at 105 °C (Fig. 5, b). Allowing this reaction to heat for 67 h resulted in full conversion to diaminosilane $PhMeSi(NHBn)_2$ (Fig. 5, c). An analogous mixture of products was formed during the CuCl catalyzed dehydrocoupling of Ph_2SiH_2 and benzylamine, with preferential conversion to $Ph_2HSiNHBn$ at early reaction times (94% at 5 h). These observations highlight the selectivity challenges that researchers face when coupling primary amines to silanes that feature more than one Si–H moiety.

Based on their observations, Si–N formation likely involved σ-bond metathesis between an *in situ* generated amido intermediate and an incoming Si–H bond (Fig. 5, d).[39] Since CuCl was known to react with Si–H bonds to generate copper hydride, this hydride was proposed to react with amine to liberate H_2 and generate the amido intermediate.

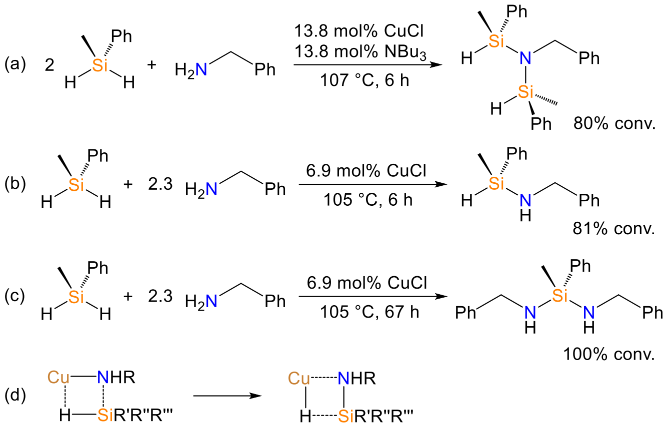
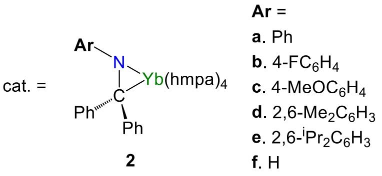


Fig. 5. (a-c) Cu(I) catalyzed Si–N dehydrocoupling product control by modifying the substrate ratio. (d) Proposed σ-bond metathesis mechanism.

In 1999, Takehira et al. demonstrated Si–N dehydrogenative coupling using ytterbium(II)-imine catalyst **2** (Fig. 6).[40] Notably, the imine aryl substituent greatly impacted amylamine and Ph_3SiH dehydrocoupling in THF at room temperature for 3 h at 3 mol% catalyst loading. Using $2,6\text{-}Me_2C_6H_3$-substituted catalyst **2d**, 93% conversion to *N*-triphenylsilylamylamine was observed. Other substituents resulted in lower conversions, from trace product generation to 61%. Other tertiary silanes Ph_2MeSiH, $PhMe_2SiH$, Et_3SiH, and $(EtO)_3SiH$, were also dehydrocoupled using **2d** with isolated yields of 90%, 93%, 21%, and 27%, respectively (lower yields for silanes without aryl groups). Other primary amines, including *sec*-pentylamine, were coupled to Ph_3SiH, though *tert*-pentylamine yielded only 16% after 20 h. For secondary alkyl secondary amines, 10 mol% loadings were required to achieve high conversion in 2-5 h, whereas aniline needed 192 h to reach 81% conversion (56% at 20 h). Reactions between Ph_2SiH_2 or $PhSiH_3$ with primary and secondary amines proceeded with modest yields in 2-20 h at room temperature using 3-5 mol% catalyst, resulting in mixtures of amino- and diaminosilanes. Very bulky secondary amines showed little to no reactivity with phenylsilane. Some control over product outcome by varying the amine and silane ratios was observed.



hmpa = hexamethylphosphoramide

Fig. 6. First f-element Si–N coupling catalysts by Takehira and co-workers.

In 2000, the dehydrogenative synthesis of silylamines using a uranium catalyst was described by Eisen. Reaction of phenylsilane with excess $^{n}PrNH_2$ in the presence of 1.7 mol% $[(Et_2N)_3U][BPh_4]$ (**3**) at 20 °C afforded a mixture of products at early reaction times, and triaminosilane $PhSi(NH^{n}Pr)_3$ selectively after 10 h.[41] Bulkier substrates $^{i}PrNH_2$ and $^{t}BuNH_2$ only afforded the corresponding diaminosilanes at extended reaction times. Notably, adding $PhSiH_3$ to $PhSiH(NH^{t}Bu)_2$ in the presence of catalyst allowed for partial conversion to $PhSiH_2(NH^{t}Bu)$ (50% after 95 h), indicating that the formation of silylamines using **3** is an equilibrium process. To explore the mechanism, an excess of $PhSiH_3$ was added to **3** and $PhSiH_2NEt_2$ was observed, suggesting that a hydride intermediate is likely to form. Moreover, the addition of excess $^{n}PrNH_2$ to **3** followed by removal of the volatiles and quenching of the uranium complex yielded only $^{n}PrNH_2$. Thus, the authors proposed the mechanism in Fig. 7, where **3** reacts with the substrate, engages in σ-bond metathesis with incoming $PhSiH_3$, and the resulting U–H bond undergoes σ-bond metathesis with amine to close the cycle.

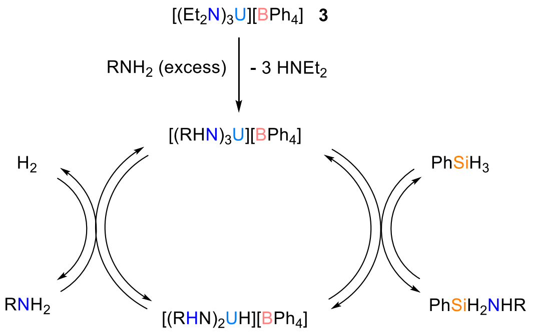


Fig. 7. Mechanism of U-catalysed Si–N dehydrocoupling by Eisen and co-workers.

Eight years after Takehira's study, Buch and Harder showed that (η^2-Ph_2CNPh)$Ca(hmpa)_3$ (**4**) also catalyses amine and silane dehydrocoupling, with similar trends in activity and selectivity.[42] Silylation of *n*-pentylamine with Ph_3SiH proceeded smoothly at room temperature with 3 mol% catalyst loading, with 98% conversion reported in THF over 0.5 h. The bulky secondary amine, *N*-methyl-*n*-butylamine required a loading of 10 mol% to reach 95% conversion at room temperature in THF. Like the Yb example, aniline coupling with Ph_3SiH proceeded very slowly. As the authors point out, Ca is much more abundant than Yb, yet the Ca catalyst offers similar activity for Si–N dehydrocoupling. The Harder group proposed a mechanism for this reaction which mirrors that of Takehira's example with Yb. Precatalyst **4** undergoes 1,2-addition with an amine to yield the catalytically active nucleophilic Ca amido species, **5** (Fig. 8). This amido reacts with silanes, generating the Si–N coupled product and calcium hydride complex **6**.

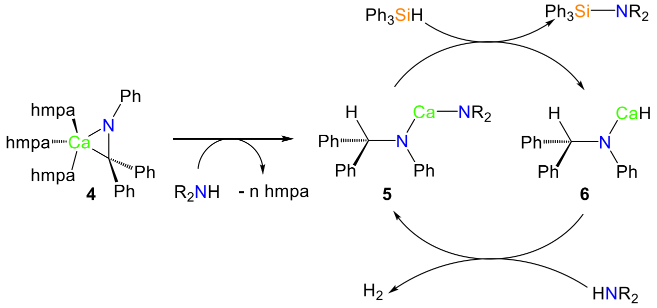


Fig. 8. Mechanism proposed by Buch and Harder.

In a 2010 paper on ruthenium silane σ-complexes, Nikonov and co-workers reported the dehydrocoupling of $PhNH_2$ and $HSiMe_2Ph$ to form $PhNHSiMe_2Ph$ using $[Cp(^{i}Pr_3P)Ru(NCMe)_2]$-$[BPh_4]$ within 10 min at room temperature in $CDCl_3$.[43]

Using the magnesium pre-catalyst $To^{M}MgMe$, where To^{M} = tris(4,4-dimethyl-2-oxazolinyl)phenylborate (**7**) (Fig. 9), Sadow and co-workers reported the dehydrogenative synthesis of aminosilanes in 2011.[44] Products were prepared efficiently with 5 mol% catalyst loading at room temperature in benzene. Primary aliphatic amines ($^{n}PrNH_2$, $^{i}PrNH_2$, $^{t}BuNH_2$) were fully converted to aminosilanes using $PhSiH_3$, $PhMeSiH_2$ and Ph_2SiH_2 within 24 h, and aniline was effectively coupled to $PhSiH_3$. Control of the silane to amine ratio generally allowed for isolation of single products in high yield with no detection of oligomers. Furthermore, the rates of the reaction were highly dependent on the steric properties of the amine and silane. For example, 3.5 equivalents of $^{n}PrNH_2$ with $PhSiH_3$ provided $(^{n}PrNH)_3SiPh$ in only 15 min whereas $^{i}PrNH_2$ gave $(^{i}PrNH)_2SiHPh$ after 45 min, never forming the respective triaminosilane even at 100 °C. Secondary amines were poorly or not converted at all, a trait noted to inhibit the formation of polysilazanes. At extended times and temperatures, the catalyst was unable to couple $BnMe_2SiH$ or Et_3SiH with primary amines.

The ligand remained coordinated to Mg even in the presence of excess amine, which allowed the authors to extend their scope to hydrazine.[44] With 10 mol% of catalyst at room temperature, N_2H_4 was selectively coupled to tertiary silanes $(C_3H_5)Me_2SiH$ (7 h, quant.), Et_3SiH (12 h, 50% conv.), and $BnMe_2SiH$ (12 h, 50% conv.) to yield the corresponding monosilylhydrazines. Mixtures were obtained with primary and secondary silanes. Impressively, in the presence of 5 mol% $To^{M}MgMe$ relative to silane, an excess of condensed ammonia in benzene was treated with $BnMe_2SiH$, resulting in the selective formation of $BnMe_2SiNH_2$ within 15 h. At 10 mol% catalyst loading, $(C_3H_5)Me_2SiH$ reacted with excess NH_3 to form $(C_3H_5)Me_2SiNH_2$ as the sole product in only 5 h. The catalyst resting state was determined to be a magnesium amido by ^{1}H NMR spectroscopy and single crystal X-ray diffraction. Notably, from their kinetic analysis, the authors opt against a concerted 4-center transition state via σ-bond metathesis due to a strong rate dependence on amine nucleophilicity, the observation of silanes with electron withdrawing groups reacting much faster, and a zeroth-order dependence on amine concentration. The nucleophilic amido is thought to attack silicon to form a five-coordinate Si center, which then undergoes β-elimination to afford a magnesium hydride (Fig. 9, right).[44]

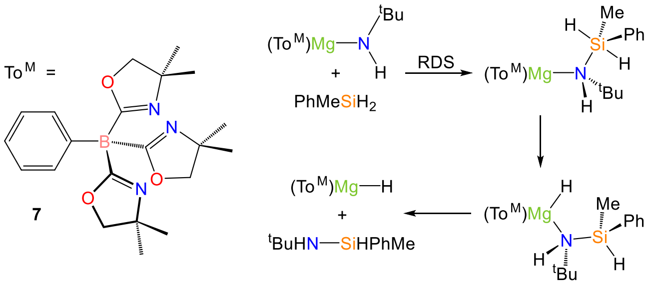


Fig. 9. Ligand for and mechanism of Mg-based Si–N dehydrocoupling by Sadow and co-workers.

In 2012, Tsuchimoto et al. published the dehydrocoupling of indoles with silanes to produce *N*-silyl indoles using Lewis acidic $Zn(OTf)_2$.[45] After initial screening, $Zn(OTf)_2$ was found to exhibit better activity than other triflate salts, operating specifically in acetonitrile with pyridine (1 eq.) as an added base. Dehydrocoupling took place between substituted indoles (featuring nitriles, halogens, boronic acids, and esters, etc.) and Ph_2MeSiH at 80-115 °C over 15-65 h using a 1 mol% catalyst loading, providing yields approaching 90%. Other tertiary alkyl silanes also performed well with lightly-substituted indoles over 24-48 h at temperatures of 80-115 °C. In a report of $Rh_2(OAc)_4$

and tungstate mediated indole *N*-silylation in acetonitrile,[46] concurrent hydrogenation of the solvent was observed. In this case, acetonitrile was believed to act as a silyl cation stabilizer.

Later that year, Cui demonstrated Si–N dehydrocoupling with ytterbium silylamide and NHC silylamide complexes.[47] Importantly, they found that NHC ligands had a powerful effect on the observed activity and reaction outcome. With a 5 mol% loading at room temperature, $Yb[N(SiMe_3)_2]_2(THF)_2$ (Fig. 10, **8**) catalysed the dehydrocoupling of 1:1 $PhSiH_3$ and $HNEt_2$ in C_6D_6 over 1 h with quantitative conversion to a mixture of $PhSiH_2NEt_2$ (11%) and $PhSiH(NR_2)_2$ (89%). With bulky amines $HN(SiMe_3)_2$ and HN^iPr_2, minimal conversion (24% and 3% respectively) to the silylated product resulted alongside Ph_2SiH_2 and SiH_4 generation. In contrast, NHC adducts **9** and **10** afforded far better results. Notably, catalyst **10** allowed for 98% conversion of $HN(SiMe_3)_2$ to $PhSiH_2N(SiMe_3)_2$. For HN^iPr_2, complete conversion to *N*-silylamine $PhSiH_2N^iPr_2$ was observed while the dehydrocoupling of $HNEt_2$ and $PhSiH_3$ resulted in quantitative conversion to diaminosilane $PhSiH(NEt)_2$. Using a 5 mol% loading of **10** in C_6D_6, a modest scope of primary and secondary amines was dehydrocoupled to $PhSiH_3$ at room temperature. Most of the examples were complete in 1 h, with bulkier amines requiring 6 h or 24 h. Catalyst **10** was also effective with $MesSiH_3$ and bulkier secondary silanes, and mono-aminated products were selectively formed and isolated after 1 h. The coupling of Ph_2SiH_2 and $^iPr_2NH$ required heating to 100 °C for 24 h with 10 mol% **10**. Polysilazanes were not detected. Catalyst **10** was proposed to react with silanes via σ-bond metathesis to generate a Yb-H intermediate, and the authors hypothesized that NHC coordination increases activity by preventing hydride oligomers from forming and precipitating from solution.

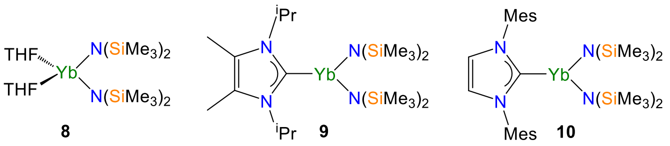


Fig. 10. Ytterbium silylamide catalysts reported by the Cui group.

In 2013, the Oestreich group described the dehydrogenative coupling of silanes to pyrroles, indoles, carbazoles, and anilines without an added base or H_2 acceptor.[48] The catalyst (Fig. 11a, **11**) features a polar Ru–S bond that can activate Si–H bonds via ligand cooperativity. Using 1 mol% of this Ru catalyst, the neat silylation of indole with Me_2PhSiH (1 equiv.) resulted in >99% conversion after 1 h at 70 °C, though the products were 76% *N*-silylated indole with an additional 24% of reduced indoline. Fascinatingly, extending the reaction time to 12 h resulted in a 92:8 *N*-silylated indole to indoline ratio, suggesting reversible dehydrogenation. 3-Methylindole and pyrrole reacted with less hindered secondary and tertiary silanes at 60 and 90 °C, respectively. No transformation occurred when attempting to dehydrocouple Et_3SiH or $^iPr_3SiH$ with 3-methylindole and $EtMe_2SiH$ or $^iPr_3SiH$ with pyrrole. Excess silane (10 equiv.) promoted the formation of doubly silylated products after 18 h at 90 °C (*N*-silylation and Friedel-Crafts C_3-silylation, Fig. 11b), without heterocycle reduction. Substituted indoles and carbazoles were dehydrogenatively coupled to Me_2PhSiH after 1 h at 60 °C using 1 mol% Ru catalyst to afford the silylated products in 76-96% isolated yield. Halogenated indoles (Cl, Br) and 2-methylindoles were also silylated. Finally, indolines and substituted anilines were coupled to Me_2PhSiH with >99% conversion to *N*-silylated products in only 5 min at room temperature in hexane (0.5 M) with 1 mol% Ru catalyst (TOF = 20 min^{-1}). For aniline, the corresponding diaminosilane product was obtained by adding a second amine equivalent and allowing the reaction to proceed for 2 h at 80 °C. *Importantly*, the catalyst was not active with alkyl amines, which coordinate and thwart Si–H bond activation.

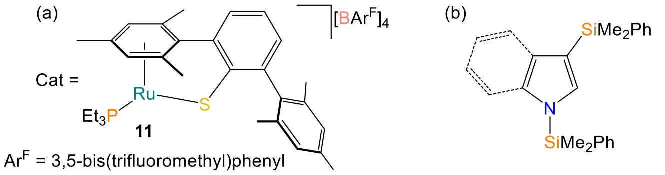


Fig. 11. (a) Ru catalyst and (b) disilylation product described by Oestreich et al.

In a 2013 contribution,[49] Hill and co-workers demonstrated that the readily available heavy group II hexamethyldisilazides of the form, $M[N(SiMe_3)_2]_2$ where M = Mg, Ca, and Sr, act as pre-catalysts for the dehydrocoupling of silanes and amines at mild temperatures. The reactions were performed using 5 mol% of catalyst at room temperature in C_6D_6 in J. Young tubes, though some combinations required heating to 60 °C. In general, the use of bulky silanes decreased conversion to *N*-silylamines. The Ca and Sr catalysts were effective in coupling bulky amines like $(Me_3Si)_2NH$ and $DippNH_2$ to afford mixtures of mono-aminated and di-aminated silanes. Like prior reports, variation of the silane and amine reactant ratios allowed for control of the product ratio. Kinetic analyses of each catalyst exposed considerable differences between them. For example, $Ca[N(SiMe_3)_2]_2$ was found to exhibit superior activity by an order of magnitude when coupling Et_2NH and Ph_2SiH_2. The Ca complex mediated Si–N dehydrocoupling with a TOF of 2822.5(54) h^{-1}, whereas the Mg and Sr analogues exhibited TOFs of 57.1(4) h^{-1} and 125.5(22) h^{-1}, respectively. A Si–H/M–N σ-bond metathesis step was proposed to be rate determining for the Mg and Ca complexes. Oligomers were detected with phenylsilane and even diphenylsilane, but were never characterized.

In 2014, the Paradies group described the dehydrocoupling of amines and silanes using $B(C_6F_5)_3$ in dichloromethane at room temperature (Fig. 12, a).[50] The strength of this catalyst was its activity for aromatic amine silylation. Using 5 mol% of $B(C_6F_5)_3$ allowed efficient coupling of bis(4-tolyl)amine and Ph_2MeSiH in 1 h with 95% yield. Although 1 mol% (73%) and 0.1 mol% (32%) of $B(C_6F_5)_3$ resulted in lower yields, several diarylamines, carbazoles, anilines, and secondary diamines were successfully dehydrocoupled to Ph_2MeSiH at 1 mol% catalyst loading. Attempts to *N*-silylate indoles were unsuccessful in that a reduction to indolines was observed. Halogenated arylamines were tolerated, although some substrates required higher temperatures of 60-70 °C and extended times of 24-48 h to reach appreciable yield. Notably, 1,1,3,3-tetramethyldisiloxane was dehydrocoupled to two equivalents of bis(4-tolyl)amine to yield the aminated siloxane product in 97% yield in 1 h at room temperature. *N*,*N'*-(Diphenyl)ethylene diamine was doubly silylated with Ph_2MeSiH to give the product in 92% yield after 24 h at 70 °C, while the dehydrocoupling of $PhSiH_3$ to the same substrate at 60 °C for 24 h yielded 83% of the cyclic bis(amino)silane rather than oligomers.

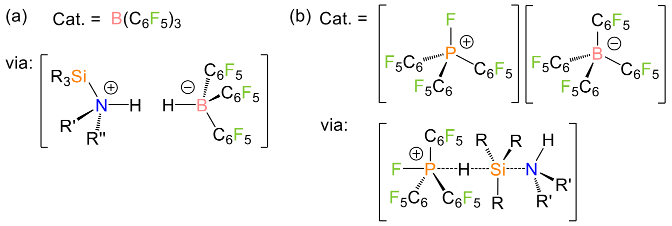


Fig. 12. Frustrated Lewis pair approaches to Si–N dehydrocoupling by (a) Paradies and (b) Stephen.

In the same year, the Stephan group reported the metal-free dehydrogenative coupling of silanes and amines using 1.5 mol% loading of the electrophilic fluorophosphonium catalyst, $[(C_6F_5)_3PF][B(C_6F_5)_4]$ at room temperature in C_6D_5Br or CD_2Cl_2.[51] Under these conditions, complete conversion (>99%) of Ph_2NH and Et_3SiH to Ph_2NSiEt_3 was observed after 10 h. The same reaction with $ClMe_2SiH$ was complete in 1 h to afford the corresponding aminochlorosilane and H_2. Impressively, Ph_3SiH and $PhMe_2SiH$ were each coupled with Ph_2NH, with complete conversion to the quaternary aminosilanes in 20 and 48 h, respectively. From theoretical insight, the authors proposed that silane binds to the phosphonium cation and then amine coordination to the phosphonium-silane adduct generates a 5-coordinate silicon intermediate (Fig. 12, b). The dehydrocoupled product is produced with the release of H_2 from an acidic N–H and hydridic P–H bond hydrogen. As a primary focus of the report, the H_2 gas generated from the Si–N dehydrocoupling was used for the transfer hydrogenation of olefins to alkanes.

In early 2015, Kaneda demonstrated that heterogeneous gold nanoparticles supported on hydroxyapatite were active for amine and silane dehydrocoupling.[52] Using a 0.83 mol% loading in THF, simple primary alkyl amines, aniline, and ammonia were dehydrogenatively coupled with secondary and tertiary silanes, typically yielding mono(amino)silane products with complete conversion at temperatures from 25-100 °C and times between 0.5 h to 20 h. Interestingly, a few examples of aryl and alkyl primary amides were dehydrocoupled with $PhMe_2SiH$ at 80 °C in 5-20 h with high isolated yields (>70%) of the respective $PhMe_2SiNHCOR$ product.

In 2015, Wright and co-workers utilized the aluminium precatalyst $Al(NMe_2)_3$ for the cross-dehydrogenative coupling of amines and silanes.[53] In the presence of 10 mol% $Al(NMe_2)_3$, $PhSiH_3$ coupled to $BnNH_2$ to generate $PhSiH(NHBn)_2$ in 94% yield after 24 h. This reaction proceeded at room temperature; however, Et_2NH reacted with $PhSiH_3$ extremely slowly at room temperature (7 d) to reach 93% conversion to a mixture of $PhSiH_2(NEt_2)$ and $PhSiH(NMe_2)(NEt_2)$ (where the NMe_2 group arises from the precatalyst). Yields rapidly diminished with bulkier primary and secondary amines. Increases in catalyst loading and the use of bulkier amines lead to higher $Si(NMe_2)$ by-product formation resulting from the amido ligands of the precatalyst. One attempt to couple Ph_2SiH_2 and Et_2NH using 100 mol% of $Al(NMe_2)_3$ resulted in the exclusive stoichiometric formation of $Ph_2SiH(NMe_2)$. In their kinetic analysis, the authors invoked a hypervalent silicon hydride mechanism.

That same year, the Crimmin group compared the activity of $Y[N(SiMe_3)_2]_3$ against a phosphonium methylide yttrium catalyst (Fig. 13, **12**) for Si–N dehydrocoupling.[54] Importantly, the catalysts showed similar activity for the dehydrocoupling of primary and non-bulky secondary amines in the presence of Ph_3SiH and Ph_2SiH_2. For example, $^nPrNH_2$ and Ph_2SiH_2 were selectively dehydrocoupled to give $^nPrNHSiHPh_2$ using a 10 mol% loading of either catalyst at room temperature in 0.5 h. With bulky primary amines major differences arose; the coupling of Ph_2SiH_2 with *t*-butylamine required 1 h using 10 mol% of the phosphonium methylide and 19 h using $Y(HMDS)_3$. A major difference in activity was noted between the catalysts when sterically bulky secondary amines were employed. In this scenario, **12** shows superior activity. For example, with 5 mol% $Y(HMDS)_3$, the reaction of $^iPr_2NH$ with $PhSiH_3$ in benzene-d_6 at room temperature showed only trace (<1%) product formation after weeks. However, **12** afforded $^iPr_2NSiH_2Ph$ in 86% yield after 26 h. This catalyst also dehydrocoupled $PhSiH_3$ with Cy_2NH, 2,6-dimethylpiperidine, and $^iPr(Cy)NH$ at 80 °C in a few hours, transformations which proceed poorly after a week of heating in the presence of $Y(HMDS)_3$. During catalysis, when sterically unhindered primary amines (e.g., $^nBuNH_2$) were used, free CH_2PPh_3 was observed by ^{31}P NMR spectroscopy, a by-product of protonolysis (Fig. 13, **13**). This was supported by stoichiometric deuterium labelling experiments where $^tBuND_2$ resulted in D incorporation into the aryl and methylide groups. Importantly, this does not occur even with an excess of the bulky secondary amine, $^iPr_2ND$. Further kinetic experiments and DFT analysis ruled against reversible activation of the ligand as a vital step of catalytic aminosilane formation.

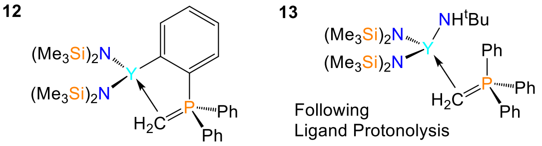


Fig. 13. Catalyst and ligand protonolysis reported by Crimmin.

Also in 2015, the Carpentier, Tobisch, and Sarazin groups demonstrated silane-amine dehydrocoupling using the alkaline Earth hexamethyldisilazide complexes, $M\{N(SiMe_3)_2\}_2(THF)_n$.[55] The dehydrocoupling of pyrrolidine and Ph_3SiH was evaluated at room temperature and the Ba analogue outperformed relative to the Ca, Sr, and Mg congeners. Using only 0.25 mol% of $Ba\{N(SiMe_3)_2\}_2(THF)_2$ and a 1:1 ratio of Ph_3SiH to $HN(CH_2)_4$ in C_6D_6, 53% conversion to $Ph_3SiN(CH_2)_4$ was observed within 5 min (TOF of 2,544 h^{-1}) and 99% conversion was noted after 15 min (TOF of 1,584 h^{-1}). The Mg, Ca, and Sr derivatives achieved TOFs of 0.5 h^{-1}, 19 h^{-1}, and 26 h^{-1} in the same transformation. Iminoanilido complexes of type $\{N^\wedge N\}M\{N(SiMe_3)_2\}(THF)_n$, where $\{N^\wedge N\}^- = [ArN(o\text{-}C_6H_4)C(H)=NAr]^-$ and Ar = 2,6-$^iPr_2$-C_6H_3 (Fig. 14a, **14**), were also prepared and tested. While less active than the bis(amido) compounds, $\{N^\wedge N\}Ba\{N(SiMe_3)_2\}(THF)_2$ was still the most active with a TOF of 512 h^{-1} at 15 min (32% conv.) or 188 h^{-1} at 120 min (94% conv.). Modification to the corresponding alkyl complex, $\{N^\wedge N\}Ba\{CH(SiMe_3)_2\}(THF)_2$ led to TOFs of 864 h^{-1} in 15 min (54% conv.). The most active catalyst was $Ba\{CH(SiMe_3)_2\}_2(THF)_3$ which had a TOF of 3,600 h^{-1} after 5 min with 75% conv. and a TOF of 1,584 h^{-1} after 15 min (99% conv.). In the presence of 0.25 mol% $Ba\{N(SiMe_3)_2\}_2(THF)_2$ or $Ba\{CH(SiMe_3)_2\}_2(THF)_3$, they demonstrated an impressive dehydrocoupling scope between primary and secondary amines with primary, secondary, and tertiary silanes. Notably, this contribution featured the coupling of substrates that feature two tertiary silane environments to secondary amines, and the coupling of primary and secondary diamines to selectively prepare *N*,*N'*-disilyldiamines (Fig. 14b). The reactions largely proceeded in 1-2 h at room temperature and chemoselectivity was observed depending on the ratio of amine to silane employed. This paper greatly expanded the scope of reported monomeric silylamines and set the authors up to prepare oligomeric and polymeric products in subsequent contributions (*vide infra*).

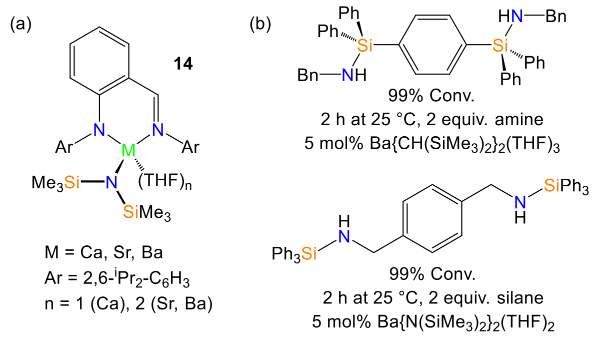


Fig. 14. (a) Alkaline Earth catalysts and (b) products obtained using Ba catalysts.

In a follow-up report, the authors continued to use Ca, Sr, and Ba precatalysts for Si–N dehydrocoupling.[56] Seven major themes were deduced from screening many alkaline Earth hexamethyldisilazide, alkyl, and iminoanilido complexes. Catalytic activity down the group proceeded as Ba>Sr>Ca, with Ba providing much more efficient catalysts (with TOFs of up to 3,600 h^{-1}). Homoleptic bis-amido and bis-alkyl complexes were found to be superior to heteroleptic derivatives. Furthermore, THF coordination did not influence activity. The alkyl complexes were found to be much more active than amido derivatives. Complexes with anionic $NSiMe_2H$ ligands hindered catalysis, even in the case of Ba. Inactivity was observed for the bis-silanido Sr complex, $Sr(SiPh_3)_2(THF)_3$; however, the heteroleptic iminoanilide strontium pyrrolido, $\{N^\wedge N\}Sr\{N(CH_2)_4\}(HN(CH_2)_4)$, was catalytically active. Even with excess Ph_3SiH, $^tBuNH_2$ was selectively silylated to $^tBuNHSiPh_3$. Overall, $Ba\{CH(SiMe_3)_2\}_2$-$(THF)_3$, which was described in the original study, was the best catalyst for dehydrocoupling. They affirmed the secondary rate law of Ba catalysed dehydrocoupling (first order in silane and catalyst), an improvement of reaction rates with electron withdrawing *p*-substituents on arylsilanes, and a kinetic isotope effect of K_{SiH}/K_{SiD} = 4.7. Along with DFT analysis, they firmly dismiss σ-bond metathesis as the mechanism and support the stepwise nucleophilic attack of silane by a metal-amido. The following hydrogen transfer from the silane to the barium centre is rate limiting. They note the accessibility in size of Ba over Sr and Ca, and that a trend of decreased M–N bond strength exists moving down the alkaline Earth metals.

In 2016, Sarazin in collaboration with Panda reported the cross-dehydrocoupling of amines and silanes using group I metal hexamethyldisilazides $MN(SiMe_3)_2$ (M = Li, Na, K).[57] Among these derivatives, the K complex was found to be the most active. General conditions included a 5 mol% loading of $KN(SiMe_3)_2$ at room temperature in neat substrate for 12 h (unoptimized) to achieve 99% silylation of primary and secondary amines. They found that $PhSiH_3$ reacts with pyrrolidine selectively to yield bis- and tris(amino)silane products depending on the initial substrate concentrations (1:2 silane:amine or 1:3 silane:amine, respectively). Hindered 2,6-diisopropylaniline was silylated at a moderate temperature of 60 °C and sterically demanding silanes allowed for the selective formation of mono-coupled products. With inconclusive mechanistic data, the authors proposed KH formation via σ-bond metathesis or through a silicate intermediate. Notably, commercial KH at a 5 mol% loading and 1:1 molar ratio of $PhSiH_3$ and pyrrolidine sluggishly afforded aminosilane due to the poor solubility of this reagent (25% conversion after 12 h at room temperature or 63% after 12 h at 60 °C).

In 2016, Sadow et al. reported the efficient dehydrocoupling of $PhSiH_3$, $PhMeSiH_2$, and Ph_2SiH_2 with primary and secondary alkylamines using $(Im^tBu)Ln\{C(SiHMe_2)_3\}_2$ where Ln = Yb (**15**) or Sm (**16**) (Fig. 15).[58] The authors observed silazane and diaminosilane mixtures using a 1:1 ratio of phenylsilane to primary amines, but using an excess of silane or amine directed product control. For example, A 5 mol% loading of **15** allowed for the dehydrocoupling of $PhSiH_3$ and 4 equivalents of $^iPrNH_2$ to afford $PhSi(NH^iPr)_3$ in 63% conversion after 0.1 h. However, 2.2 equivalents of $PhSiH_3$ reacted with 1 equivalent of $^iPrNH_2$ to form the silazane $^iPrN(SiH_2Ph)_2$ in 72% yield after 0.1 h. These products and others were successfully isolated by distillation. Using 10 mol% of **15**, dehydrocoupling was achieved for bulker silanes such as $PhMeSiH_2$ and Ph_2SiH_2, allowing for isolated yields of greater than 80%. With the exception of $PhMeSiH_2$ and $^iPrNH_2$ dehydrocoupling (which allowed for silazane formation), 1:1 amine:silane ratios were used for secondary silanes to obtain *N*-silylamines. Tertiary silane coupling was not successful. They proposed that a Yb amido amine may be the key species that reacts with silanes to generate aminosilane products in the rate determining step.

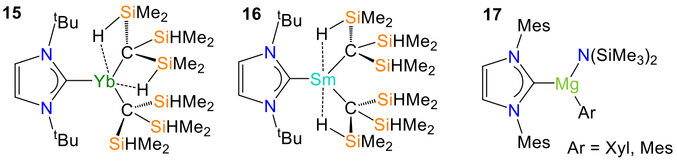


Fig. 15. Lanthanide catalysts described by Sadow in 2016 and Mg catalyst described by Nembenna in 2017.

The following year Nembenna et al. described two active Mg catalysts (**17**) for amine and silane dehydrocoupling (Fig. 15).[59] Using a 5 mol% loading, a 1:1 ratio of $PhSiH_3$ and $^tBuNH_2$ was dehydrocoupled within 1 min and the xylyl and mesityl substituted catalysts afforded $PhSiH_2NH^tBu$ in 56% and 70% yield, respectively. Heating to 60 °C for 60 min led to mixtures of *N*-silylamine, diaminosilane, and disilylamine products while adding 2.5 equivalents of amine led to selective diaminosilane formation in 85% (for xylyl catalyst) and 99% (for mesityl catalyst) after 720 min at room temperature. Since the mesityl magnesium catalyst exhibited superior activity and selectivity, it was used for the dehydrogenative coupling of primary as well as cyclic and acyclic secondary amines with primary and secondary silanes ($PhSiH_3$, Ph_2SiH_2, $PhMeSiH_2$). By optimizing the reaction temperatures, times, and amine:silane ratios, a modest range of mono- and diaminosilanes were selectively prepared with conversions of 99% and high isolated yields. Many of the reactions were completed at room temperature over 12-24 h using 5 mol% of catalyst, with bulkier aminosilanes requiring 60-100 °C over 24-72 h.

In 2017, Li and Guan synthesized chiral iminophosphonamide compounds of Ca, Mg, Sc, Y and analysed their Si–N dehydrocoupling activity.[60] With a cyclohexyl group incorporated into the ligand arm, only the Y variant was suitable for coupling *t*-butylamine and methyl(naphthalen-1-yl)silane. A 5 mol% loading of the catalyst (Fig. 16, **18**) was then found to enable quantitative $^tBuNH_2$ and $PhMeSiH_2$ coupling in 2 h at room temperature. Following distillation, the (-) aminosilane enantiomer was obtained in 89% yield. For a series of primary and secondary amines, this catalyst provided *N*-silylamines with negative optical rotation in the presence of $PhMeSiH_2$. As the authors noted, analysis of ee values proved challenging because the moisture sensitive products were incompatible with HPLC or GC. Instead, they synthesized silylamine-boron derivatives from the corresponding silylamines, which were stable enough for HPLC analysis. One product, $(C_{10}H_7)(Ph)HSiN[BCy_2]Bz$, was isolated in 70% yield with 17 % ee using the Y catalyst at 25 °C, and conducting Si–N coupling at -30 °C yielded this product with 21% ee. Kinetic resolution using a racemic axially chiral silane (Fig. 16, **19**) allowed one enantiomer to react with *t*-butylamine, *t*-amylamine, amantadine, and piperidine, and at conversions of approximately 50%, the *S* enantiomer of the starting silane was recovered with an ee of up to 80%. Although the products were largely prepared with low enantioselectivity, this contribution expanded on the efforts of Sommer and Citron[33] to prepare chiral aminosilanes.

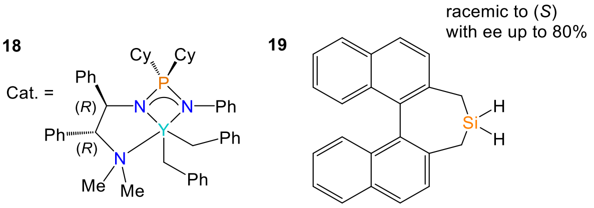


Fig. 16. The Y catalyst and axially chiral silane used by Li and Guan.

In 2017, Tsuchimoto and co-workers expanded on the zinc catalysed dehydrocoupling of indoles with silanes[61] from their original 2012 communication.[45] Employing 5 mol% $Zn(OTf)_2$ with 1 eq. of pyridine in EtCN, substituted indoles, pyrroles, and carbazoles were dehydrogenatively *N*-silylated in 15-72 h at 80-120 °C with aminosilane isolated yields approaching 90%. The indole, pyrrole, and carbazole rings remained unreduced under these conditions. As in the first report, tolerance for halogens and electron withdrawing groups was noted. For an $-NH_2$ functionalized substrate, indole *N*-silylation was selective, but disilylation occurred when excess silane was employed. Additionally, unprotected hydroxyl groups were silylated. Notably, they extended their scope to a few arylamines, including aniline, 3,5-bis(trifluoromethyl)aniline, and *N*,*N′*-diphenylamine. With a 5 mol% $Zn(OTf)_2$ loading, $HSiMePh_2$, and 1 equiv. of pyridine in EtCN, the respective *N*-silylamine products were obtained in isolated yields of 67% (80 °C, 15 h), 70% (110 °C, 48 h), and 89% (110 °C, 48 h), respectively. A detailed kinetic investigation of $Zn(OTf)_2$ catalysed Si–N dehydrocoupling was carried out. Furthermore, H_2 generated from indole Si–N dehydrocoupling was used for the Pd/C catalysed hydrogenation of *trans*-stilbene. Mechanistically, the zinc catalyst was thought to operate as an electrophile in the activation of hydrosilanes. Pyridine and the nitrile solvent were thought to function as coordinating donors (without pyridine, some examples proceed sluggishly). Pyridine is especially important for the Si–H activation step to stabilize the resulting Zn–H–Si intermediate (which the authors propose may exist as a dimer).

In 2018, the Conejero group reported the highly active electrophilic Pt(II) catalyst, $[Pt(I^tBu')(I^tBu)][BAr^F_4]$, where I^tBu = 1,3-di-*t*-butylimidazolylidene and I^tBu' is the corresponding metallacycle (Fig. 17, **20**).[62] This catalyst has been shown to mediate the dehydrocoupling of amines and silanes with the highest TONs and TOFs reported to date. For example, with a 0.5 mol% loading of catalyst in DCM, a 1:1 ratio of $PhSiH_3$ and $^tBuNH_2$ were reported to react “violently” to form the *N*-silylamine $PhSiH_2(N^tBuH)$ with complete conversion in seconds. Decreasing the catalyst loading to just 0.005 mol% in the same reaction, lead to full conversion of the silane starting material in 12 min for a TOF of 96,000 h^{-1} and a TON of 20,000. Lowering the catalyst loading to 0.003 mol% lead to a slight decrease in efficiency (57,000 h^{-1}), but an increased TON (33,000). The reaction of 1:1 $PhSiH_3$ with $HNEt_2$ using 0.005 mol% of Pt catalyst was even more impressive, with selective and complete conversion to $PhSiH_2(NEt_2)$ (88% isolated) observed within 3.6 min, equating to the highest TOF ever reported for Si–N dehydrocoupling (330,000 h^{-1} or 5,500 min^{-1}). Performing this reaction with 0.001 mol% of Pt catalyst afforded a TON of 98,000, the highest ever reported. Impressively, using a 1:2 ratio of $PhSiH_3$ to $HNEt_2$ and 0.3 mol% of catalyst selectively produced diaminosilane $PhSiH(NEt_2)_2$ with a TOF of 595 h^{-1} and TON of 666. The catalyst remained efficient across a modest scope of silanes and amines. For example, with a 0.1 mol% Pt loading, Et_2SiH_2 reacted with one equivalent of $^tBuNH_2$ to rapidly afford $Et_2SiH(^tBuNH)$ (98% isolated yield), again with a TOF of 330,000 h^{-1}. In general, $^nBuSiH_3$ was effectively coupled to amines and a significant increase in activity relative to $PhSiH_3$ was noted for the dehydrocoupling of HN^iPr_2 (35,000 h^{-1} vs. 667 h^{-1}). Other challenging amines like pyrrolidine were silylated and control of the substrate ratio led to selective mono- and diaminosilane product formation. In general, greater catalyst loadings (0.1 mol%) were employed for bulky secondary amines like HN^iPr_2 or non-nucleophilic amines like H_2NMes, and these substrates failed to form diaminosilanes regardless of the ratio. The tertiary silane, Ph_3SiH, did not allow for dehydrocoupling using the Pt catalyst. Following $PhSiH_3$ and $^tBuNH_2$ coupling, the final state of the catalyst was found to be $[PtH(I^tBu)_2][BAr^F_4]$ (**21**) (Fig. 17). The authors note an induction period, where less bulky amines must dissociate for the catalytic cycle to continue. Importantly, the addition of stoichiometric Ph_2SiH_2 and $HNEt_2$ to the Pt catalyst at -30 °C in THF-d_8 led to partial formation of the neutral platinum hydride $HPt(I^tBu')(I^tBu)$ (Fig. 17, **22**) and $[NH_2Et_2][BAr^F_4]$. Repeating this reaction with two equivalents of $HNEt_2$ resulted in complete conversion of $[Pt(I^tBu')(I^tBu)][BAr^F_4]$ to $HPt(I^tBu')(I^tBu)$ and $[NH_2Et_2][BAr^F_4]$. Overall, the Pt centre acts as a Lewis acid, much like the phosphonium catalyst described by Stephan.[51]

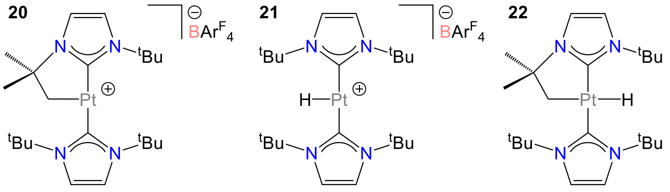


Fig. 17. Pt catalyst, post reaction hydride, and neutral intermediate described by the Conejero group.

In 2018, Waterman and co-workers reported the cross-dehydrocoupling of silanes and amines using $(N_3N)ZrNMe_2$ (N_3N = $N(CH_2CH_2NSiMe_3)_3^{3-}$; Fig. 18, **23**).[63] Heating 10 mol% of this catalyst with $PhSiH_3$ and excess Me_2NH at 80 °C in C_6D_6 revealed 60% conversion to *N*-silylamine $PhSiH_2(NMe_2)$ after 24 h, or 90% conversion after 48 h. The catalyst decomposed to a mixture of unknown products. The authors note that this poor activity contrasts with the same catalyst’s efficiency for P–Si and P–Ge dehydrocoupling. Isopropylamine in the same conditions yielded little product, but interestingly, diphenylsilane was observed (SiH_4 was not detected). The rest of the paper focused on observations suggesting that α-silylene elimination occurs during the dehydrocoupling of $PhSiH_3$ and Me_2NH. The unique reactivity of this complex explains its poor performance for the coupling of amines and silanes.

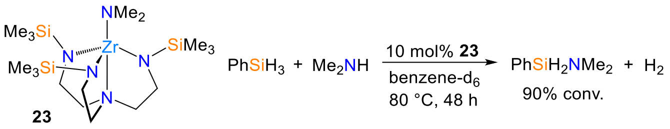


Fig. 18. Zr-mediated Si–N dehydrocoupling by Waterman.

In 2018, the Wang group employed $Ru_3(CO)_{12}$ (used by Laine originally)[36] for the coupling of indoles and related derivatives with silanes without a base.[64] For indoles, the optimized conditions were 1.5-3 mol% of catalyst with 1.5 equiv. of tertiary silane (Ph_2MeSiH, $PhMe_2SiH$, or Ph_2MeSiH) for 12-24 h at 120 °C in toluene. Indoles featuring electron donating groups were converted with a decreased catalyst loading of 1.5% while retaining yields of over 90%, but indoles with electron withdrawing groups at positions 4 and 6 required extra time. Strong electron withdrawing groups (nitrile, nitro, and ketone) at the indole 2-position shut down conversion, and methyl esters resulted in substrate decomposition. Amine, hydroxyl, and halogen substituents were tolerated with only *N*-silylation occurring. Pyrrole and carbazole were silylated with $PhMe_2SiH$ and Ph_2MeSiH, respectively.

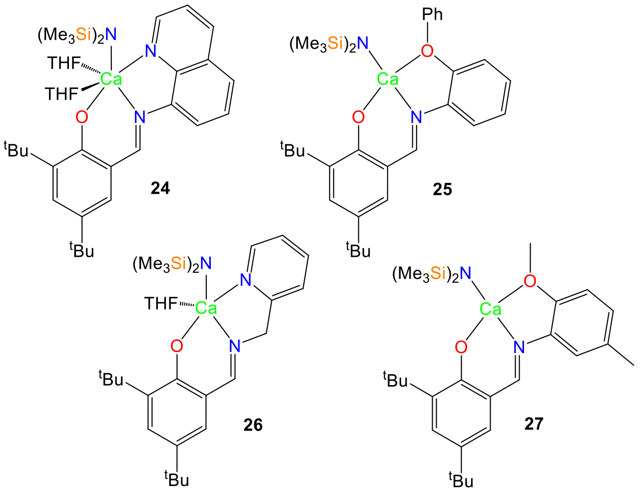


Fig. 19. Amido Ca Schiff base catalysts by Trifonov.

The same year, Trifonov demonstrated that amido Ca(II) Schiff base complexes (Fig. 19) are effective for amine and silane dehydrocoupling.[65] Using a 2 mol% loading of catalysts **24**-**27** in C_6D_6, phenylsilane was successfully coupled with aliphatic primary (e.g., $^{n}PrNH_2$, $^{i}PrNH_2$, $CyNH_2$, $^{s}BuNH_2$, $BnNH_2$) and secondary cyclic amines quantitatively in 5 min at room temperature. Aniline was much less reactive, requiring 5 h with heating to 60 °C. In comparison to earlier reports of Ca-based dehydrocoupling, the authors found moderate activity and were unable to use tertiary silanes. Despite the lower activity compared to some other reports, the catalysts tended to generate singly-aminated silanes. Donor substituted anilines were inactive for the reaction; however, $DippNH_2$ was silylated in 5 min. The catalysts exhibited similar catalytic activity, with **24** and **27** being slightly more active on average. With $PhSiH_3$ and pyrrolidine, $Ca[N(SiMe_3)_2]_2(THF)_2$ was actually found to be more active for dehydrocoupling, but less selective (forming 82:18 of mono:di products). Complicating identification of the active catalyst, calcium hydride intermediates that form upon adding $PhSiH_3$ to **24** and **27**, are prone to redistribution to form bis(phenolate)Ca species.

Also in 2018, Cibuzar and Waterman demonstrated that $La[N(SiMe_3)_2]_3(THF)_2$ efficiently catalyses the dehydrocoupling of silanes and amines at a loading of only 0.8 mol%.[66] By controlling silane and amine ratios, they were able to aminate $PhSiH_3$, $MePhSiH_2$, Ph_2SiH_2, and Ph_3SiH with n-propylamine to selectively yield the monomeric aminosilanes $PhSi(NH^{n}Pr)_3$, $MePhSi(NH^{n}Pr)_2$, $Ph_2Si(NH^{n}Pr)_2$, and $Ph_3Si(NH^{n}Pr)$, respectively in benzene-*d*$_6$ at room temperature (Ph_3SiH required 60 °C). The dehydrocoupling of silanes with an excess of $^{i}PrNH_2$, $PhNH_2$, and $^{t}BuNH_2$ largely proceeded to completion in 0.5-3 h at 25-60 °C, while the formation of quaternary silanes required extended times. The preparation of quaternary silanes via aniline dehydrocoupling was notable. The secondary amines $HNEt_2$ and $HN(SiMe_3)_2$ were successfully coupled to $PhSiH_3$ at 60 and 90 °C, respectively, while the former could also be coupled to secondary silanes. The authors reported Si–N bond formation TOFs of up to 675 h^{-1} and a maximum TON of 337.5 using $La[N(SiMe_3)_2]_3(THF)_2$. The mechanism was proposed to be consistent with the mechanism proposed by Sadow using [$To^{M}MgMe$] (Fig. 9).[44]

In 2019, Guan coupled $PhSiH_3$ and $HN^{i}Pr_2$ using 5 mol% $Ca[CH(SiMe_3)_2]_2(THF)_2$ with ligand additives in C_6D_6 at 25 °C, and *N*-alkyl NHCs were found to enable superior activity and selectivity.[67] Adding two equiv. of 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene to this alkyl precursor afforded $(NHC)_2Ca[CH(SiMe_3)_2]$, which was used as the precatalyst in subsequent experiments. At 5 mol% loading, bulky amines were coupled to $PhSiH_3$ at 25 °C with conversions between 90-99% over 3-12 h. *N*-Silylamines were obtained with no polymerization products detected. Using a 2:1 of silane:amine with phenylsilane and either *t*-butylamine or $DippNH_2$ allowed for selective formation of silazane product in excellent yield. Secondary silanes such as diphenylsilane, methylphenylsilane, and methyl(naphthalen-1-yl)silane were also coupled to bulky primary and secondary amines in nearly quantitative yield, some requiring 10-18 h. The catalyst failed to couple Ph_3SiH with H_2NBz; however, this transformation proceeded in 5 h using $Ca[CH(SiMe_3)_2]_2(THF)_2$. Finally, the scope of the reaction was also extended to chiral aminosilanes. In the presence of 5 mol% $Ca[CH(SiMe_3)_2]_2(THF)_2$ with 10 mol% of chiral alkyl NHC ligand, phenyl-(naphthalen-1-yl)silane was dehydrogenatively coupled to benzylamine at 25 °C in 7 h to yield a product with 26% ee (after borylation, the method used in 2017).[60]

In 2019, the Parkin group reported that complexes of the type, $(Tism^{iPrBenz})MgX$, where X = Me (Fig. 20, **28**) or H (**29**) and $Tism^{iPrBenz}$ = tris[(1-isopropylbenzimidazol-2-yl)dimethylsilyl]-methyl, react with secondary amines (diphenylamine and pyrrolidine) to release H_2 (or CH_4) and form the corresponding magnesium amido complex.[68] The amido complexes react with hydrosilanes to regenerate magnesium hydride **29** with release of the corresponding aminosilane at room temperature. Using 1 mol% of **28** as a precatalyst, a 1:1 mixture of Ph_2SiH_2 and

C_4H_8NH at room temperature in C_6D_6 afforded $Ph_2SiH(NC_4H_8)$ after 30 min equating to a TOF of 200 h^{-1}. Dehydrocoupling of $PhSiH_3$ and C_4H_8NH afforded a mixture of $PhSiH_2(NC_4H_8)$ and $PhSiH(NC_4H_8)_2$. In this case, 5 mol% of catalyst was required to complete the reaction in 30 min. The catalytic dehydrocoupling of $PhSiH_3$ and Ph_2NH with **28** was also carried out with 5 mol% loading in C_6D_6, and required heating to 100 °C for 21 d to generate $PhSiH_2(NPh_2)$. The same reaction using 10 mol% **29** resulted in the formation of $PhH_2Si(NPh_2)$ after 3 d at 100 °C in C_6D_6. Complex **29** was the major magnesium species observed during the reaction by ^1H NMR spectroscopy.

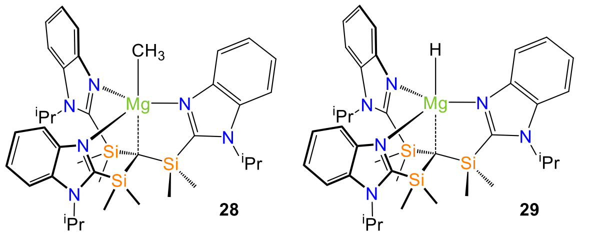


Fig. 20. (Tism^{iPrBenz})MgX catalysts for Si-N Dehydrocoupling by Parkin.

That year, the Tuttle and Murphy groups reported the coupling of simple primary and secondary amines with Et_3SiH using KO^{t}Bu at elevated temperatures.[69] The reaction took place at 130 °C, with 20 mol% catalyst and 3 equiv. of silane per amine. The amines, including piperidine, aniline, morpholine, and cyclohexylamine, required 18 h to achieve maximum yields of 75%, 87%, 80%, and 72%, respectively. The disilylation of primary amines did not occur. The mechanism was not entirely clear, but the authors concluded that ^{t}BuOK acts either as the catalyst or the initiator of a chain reaction; less ^{t}BuOK led to higher yields, and the authors argue this was due to ease of stirring. KH and ^{t}BuONa were not active for the reaction. With supplemental computational studies, *in-situ* KH generation was believed to occur from ^{t}BuOK and the respective silane. In substrate competition studies, aniline was selected for Si–N dehydrocoupling over aliphatic substrates.

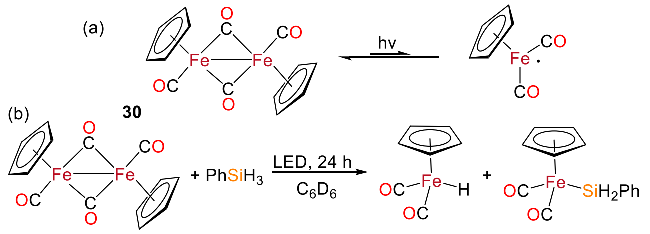


Fig. 21. Photoactivation of iron catalyst **30**.

In 2020, the Waterman group exploited the photoactivation of commercially available $[CpFe(CO)_2]_2$ (**30**) to dehydrocouple silanes and amines (they also demonstrated the formation of Si–O bonds).[70] The transformations were performed using 6-10.2 mol% of **30** with respect to silane and visible light irradiation with an LED in benzene-d_6 at room temperature. Phenylsilane was coupled to simple primary amines and Et_2NH with varied effectiveness over the course of 18-24 h (conversions were between 20-100%). $PhMeSiH_2$ was fully coupled to $^tBuNH_2$, $^iPrNH_2$, and Et_2NH after 24 h. Tertiary silane coupling with amines was not successful. As a general trend, the authors noted that more nucleophilic amines allowed for greater conversion to silylamines. Under UV or visible light, the Fe carbonyl dimer is known to dissociate to form the 17-electron monomer $CpFe(CO)_2$. However, the authors were unable to confirm its presence during catalysis (Fig. 21, a). Photolysis of **30** in the presence of $PhSiH_3$ allowed for the observation of $CpFeH(CO)_2$ and $CpFe(SiH_2Ph)(CO)_2$ in benzene-d_6 (Fig. 21, b). The silyl compound was observed during catalysis along with unreacted dimer. Amido compounds were not observed but were proposed to attack silane in a nucleophilic fashion. A flaw the authors pointed out was that full activation of catalyst was not achieved, suggesting that the active catalyst is more efficient than the loadings suggest.

In 2020, the Webster group reported an impressive scope of Si–N dehydrocoupling reactions using secondary silanes and an expanded set of primary and secondary amines using iron precatalyst ($^{2,6\text{-}iPr2Ph}$BDI)Fe(CH_2SiMe_3) (BDI = β-diketiminate; Fig. 22, **31**).[71] In C_6D_6 at room temperature using 5 mol% **31**, many reactions achieved >90% conversion in 24 h. Conversions of >99% were reported for the dehydrocoupling of secondary silanes (Ph_2SiH_2 and $PhMeSiH_2$) with simple primary amines ($BnNH_2$, $^nBuNH_2$, $PhNH_2$, *o*-methoxyaniline, and *p*-tolylaniline). Substrates containing alkenes were found to undergo Si–N dehydrocoupling with similar conversions; however, the double bonds were hydrogenated using the H_2 generated in the reaction. The dehydrocoupling of 1,4-xylylenediamine with phenyl(methyl)silane resulted in the disilylated product, but required heating to 80 °C. Even very bulky primary amines reacted to form the respective *N*-silylamine monomers at 80 °C. Secondary amines reacted with Ph_2SiH_2, Et_2SiH_2, and $PhMeSiH_2$ at room temperature to form *N*-silylamines. As a representative example, morpholine was dehydrocoupled to $PhMeSiH_2$ on a 5 mmol scale with a TON of 200, by iteratively adding substrates to the reaction over the course of 10 d.

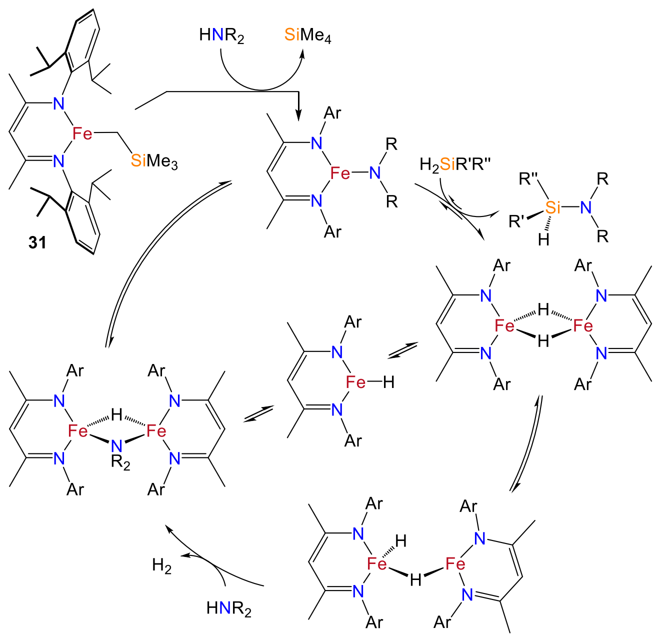


Fig. 22. Proposed catalytic cycle by Webster and co-workers.

Detailed mechanistic experiments using $MeBnNH_2$ and $MePhSiH_2$ provided evidence for the mechanism in Fig. 22. Paramagnetic ^1H NMR spectroscopy revealed the formation of an iron amido complex during the reaction, which was also synthesized and isolated. Using the amido complex directly instead of **31** circumvents the catalyst's induction period. The active species during catalysis is an iron hydride dimer. The reaction between the iron hydride dimer and *n*-BuNH$_2$ results in the release of H$_2$ and subsequent formation of a mixed hydride-amido dimer. The authors proposed that proton transfer between the amine and iron hydride to generate hydrogen is the rate limiting step in the reaction. Reversibility was inferred from amine labeling post aminosilane formation. This report also described silane dehydrocoupling with phosphines and alcohols using the same catalyst.

In 2020, the groups of Zhou and Wang demonstrated Si–N coupling with rare Earth metal dimers featuring dianionic α-iminopyridine ligands (Fig. 23, **32**).[72] For the dehydrocoupling of diphenylsilane and pyrrolidine, all 8 lanthanide compounds afforded the *N*-silylamine product within 15 min at room temperature at 1 mol% catalyst loading (97-99% NMR yield). Ligands with different substitution patterns were not effective for Si–N dehydrocoupling under these conditions. Using the Y variant, the authors were able to significantly lower the catalyst loading to 0.01 mol%, and the product was still obtained within 15 min with a 97% NMR yield (TOF = 647 min^{-1}). Under the same conditions, the secondary silanes Ph$_2$SiH$_2$ and PhMeSiH$_2$ were effectively coupled to primary and secondary alkylamines. Arylamines required higher temperatures and longer reaction times (60 °C, 8 h). Mono(amino)silanes were obtained from the dehydrocoupling of equimolar PhSiH$_3$ with pyrrolidine, Et$_2$NH, and ^{t}BuNH$_2$ in 93-96% yield. Using a 1:2 ratio of silane to amine, bis(amino)silanes were obtained in 92-95% yield. The authors propose that an α-iminopyridine yttrium hydride is formed via σ-bond metathesis of the initial amido complex with silanes.

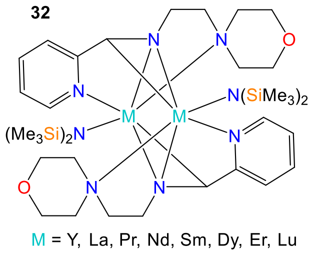


Fig. 23. Rare Earth catalysts developed by Zhou and Wang.

In 2021, Schäfer described dimethylene-, cyclohexylidene- and cycloheptylidene-bridged magnesocenophanes (Fig. 24, **33**-**35**), which they found to be active for Si–N dehydrocoupling at 5 mol% loading.[73] With each catalyst, the dehydrocoupling of PhSiH$_3$ and DippNH$_2$ required heating to 60 °C to achieve minimal conversion (13-42%) after 24 h to mono(amino)silane or a mixture of mono- and bis(amino)silane products; these ratios were solvent dependent. Toluene was chosen as the solvent for most reactions and the authors note that solvent likely had no influence on the mechanism, but rather affected solubility of the catalysts and intermediates. Higher conversion was noted using Ph$_2$SiH$_2$ as opposed to PhSiH$_3$. Phenylsilane and benzylamine were dehydrocoupled at room temperature, but afforded a mixture of mono(amino)silane, di(amino)silane, disilazane, and other products. Activities were similar to other reported magnesium catalysts, and differences between catalysts **33**-**35** were found to be small. Importantly, 5 mol% of the bis(benzylamine) adduct of **33** was a slightly more efficient for Ph$_2$SiH$_2$ dehydrocoupling than **33** itself. Higher loadings resulted in increased rates of H$_2$ formation. Isotopic labelling experiments supported N–H bond cleavage being rate determining. The authors mention the possibility of reversible Cp ring protonation by incoming N–H groups, with subsequent release of H$_2$.

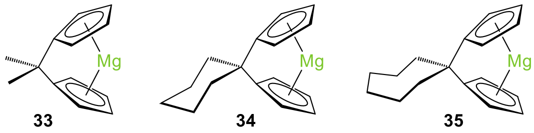


Fig. 24. Magnesocenophanes by Schäfer and co-workers.

In 2022, the Schmidt group reported a considerable amine-silane dehydrocoupling scope using the lanthanum precatalyst, La(DMBA)$_3$, where DMBA = *N*,*N*-dimethylbenzylamine.[74] Initial attempts to dehydrocouple PhSiH$_3$ and PhNH$_2$ using 2.5 mol% of La(DMBA)$_3$ found pyridine to be an optimal solvent. They proceeded to explore the scope of this reaction with 2.5 mol% of catalyst in pyridine at 50 °C for 16 h, using an optimized 1:3.3 silane:amine ratio to minimize product mixtures. With the exception of ^{t}BuNH$_2$ (mixture), primary cyclic and acyclic alkyl amines and substituted anilines were converted to quaternary tris(amino)silanes using PhSiH$_3$ in good NMR yield. Anilines featuring *para* and *meta*-substituents, including halogens and acetyl groups were effectively coupled. Unsuccessful coupling partners included 4-cyanoaniline, 4-nitroaniline, *N*,*N*-dimethyl-4-phenylenediamine, 4-aminopyridine, 2-iodoaniline, and 2-methoxyaniline. The dehydrocoupling of Ph$_2$SiH$_2$ with a modest scope of primary amines including aniline, *p*-methoxyaniline, n-propylamine, cyclohexylamine, and isopropyl amine produced quaternary silanes of type Ph$_2$Si(NHR)$_2$ at 50 °C in pyridine with 2.5 mol% La(DMBA)$_3$ loading. With Ph$_3$SiH as the silane, only ^{n}PrNH$_2$ and ^{i}PrNH$_2$ were successfully coupled at 50 °C and 80 °C respectively, using 2.5 mol% La(DMBA)$_3$ with 1:6 silane/amine ratios for 16-20 h in pyridine. The authors have not investigated whether Si–N bond formation occurs by σ-bond metathesis or silane activation.

To summarize this section in one paragraph, a large number of catalysts from across the periodic table have been found to mediate the dehydrocoupling of amines and silanes. Most of these catalysts, have been used to couple a standard set of amines (e.g., ^{n}BuNH$_2$, ^{i}PrNH$_2$, ^{t}BuNH$_2$, PhNH$_2$, Et$_2$NH, pyrrolidine) to common silanes (e.g., PhSiH$_3$, Ph$_2$SiH$_2$, PhMeSiH$_3$, Et$_2$SiH$_2$, Et$_3$SiH, Ph$_3$SiH) to generate aminosilanes that are not used in subsequent reactions. The relation of these products to important synthetic transformations are largely tenuous. Dehydrocoupling has generally been shown to occur through σ-bond metathesis (typically between M–N and H–Si bonds), electrophilic H–Si bond activation, or nucleophilic silane activation, although exceptions do exist. Historical discoveries of note include the observation of Si–N dehydrocoupling by Kraus and Nelson,[31] Ojima's initial substrate scope that included common amines and silanes,[34] and Harrod's observation that product outcome can be influenced by the substrate ratio.[39] More recent discoveries that warrant highlighting are the expansion of product scope noted by Carpentier, Tobisch, and Sarazin,[55-56] as well as the Pt catalyst described by Conejero that has been shown to mediate Si–N dehydrocoupling with leading TOFs of up to 330,000 h^{-1} (or 5,500 min^{-1}) and TONs of up to 98,000.[62]

3. Industrial Importance and Applications of Si–N Oligomers and Polymers

As reviewed by Laine et al. in 1988,[21] polysilazanes have long been valued for the synthesis of Si_3N_4 fibres, coatings, and binders. Accordingly, the dehydrocoupling of N–H and Si–H bonds represents an attractive approach to prepare higher molecular weight Si–N cyclomers, oligomers, and polymers.

In the 1960s, Fink followed up on the efforts of Kraus and Nelson[31] to use alkali metals, and ultimately alkali hydrides as catalysts for Si–N dehydrocoupling.[75,76] Reactions were carried out in ether, hydrocarbon solvents, or neat and activity in the order of Li < Na < K was observed (for the metals and their hydrides). After synthesizing *N*-silyl and *N*,*N*-disilylamines, a tetrasilyldiaminobutane was prepared along with cyclic diaminosilanes and cyclodisilazanes (Si_2N_2 rings).[75] When using aliphatic or aromatic diamines as coupling partners, polymers featuring cyclodisilazane units were obtained at 80-120 °C. This methodology was extended to the NaH-mediated preparation of several cyclodisilazane-based polymers (Fig. 25).[76] The reactions proceeded through linear polymer formation with subsequent dehydrocoupling to achieve ring formation. This approach was found to be more effective than thermolysis, which led to decomposition at 400 °C. In the same paper, cyclodisilazanes and oligomers with chlorosilane groups were used to synthesize polymers featuring silyl ether linkages.

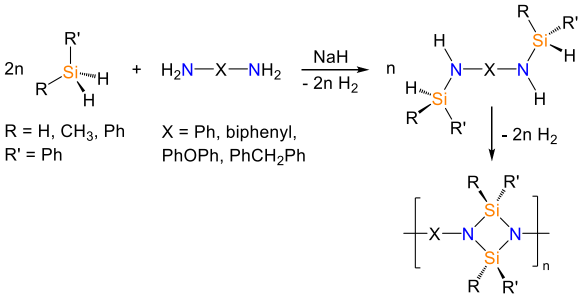


Fig. 25. Cyclodisilazane-based polymers via NaH dehydrocoupling by Fink.

In 1972, Andrianov and co-workers reported the synthesis of cyclodisilazanes by dehydrocoupling $Ph_2Si(NH_2)_2$ with Ph_2SiH_2 or $PhMeSiH_2$ in the presence of 1.3-4.3 mol% $KOSiMe_3$.[77] The reactions were initially carried out at 20 °C in anisole, at which temperature half the theoretical amount of H_2 evolved. Heating to 170 °C released the other half. Adding an excess of Ph_2SiH_2 afforded cyclodisilazanes that feature trisilylamines. In 1975, the same group dehydrocoupled organosilazanes with silanes to form monomers and 4- or 6-membered cyclic organosilazanes using 1 mol% of $KOSiMe_3$.[78] Finally, in 1977, Andrianov prepared polyorganocyclodisilazanes via the dehydrocoupling of 1,3-bis-(aminodimethylsilyl)tetramethylcyclodisilazane with $PhMeSiH_2$ at 80-300 °C using $KOSiMe_3$ (Fig. 26).[79] The resulting macromolecules were precipitated from cyclohexane with dry ethanol and found to be stable at temperatures above 400 °C.

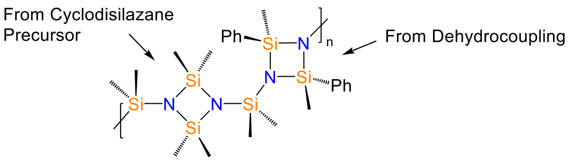


Fig. 26. Cyclodisilazane polymers prepared by the Andrianov group.

Following these early advancements, Seyferth and Wiseman employed KH to crosslink silazanes sourced from chlorosilane ammonolysis, and substantially increase ceramic yields following their pyrolysis.[80] The ammonolysis product of CH_3SiHCl_2 (average molecular weight = 280-320 g/mol) having the formula $(CH_3SiHNH)_n$ (mostly cyclic species of n = 3 and larger, with a majority of n = 4), was exposed to 3.9 mol% of KH with respect to the CH_3SiHNH unit in THF. Once H_2 gas evolution ceased, methyl iodide was used to quench any remaining basic sites and the catalyst and solvent were removed. The resulting product, which was highly soluble in organic solvents, was obtained in 99% yield, with an average molecular weight of 1,180 g/mol and composition of $(CH_3SiHNH)_{0.39}$-$(CH_3SiHNCH_3)_{0.04}(CH_3SiN)_{0.57}$ (determined by ^1H NMR spectroscopy and elemental analysis). It was proposed that Si_2N_2 bridges allow for products like the one in Fig. 27. Other experiments using distilled fractions of the CH_3SiHCl_2 ammonolysis product (225 g/mol and 490 g/mol, respectively) under the same procedure (3.5 mol% KH) resulted in distinct cross-linked polymers with molecular weights of 840 g/mol and 1800 g/mol, respectively. Their compositions were determined to be similar at $(CH_3SiHNH)_{0.37}(CH_3SiHNCH_3)_{0.03}(CH_3SiN)_{0.60}$ and $(CH_3SiHNH)_{0.41}(CH_3SiHNCH_3)_{0.02}(CH_3SiN)_{0.57}$. Pyrolysis of these oligosilazanes at 1,000 °C gave ceramic yields of 80% to 85% (a substantial upgrade from the 20% ceramic yield obtained from the unmodified ammonolysis product formed from CH_3SiHCl_2). The authors reported that other bases were effective, including NaH, $NaNH_2$, $KBH(sec\text{-}C_4H_9)_3$ (at 3.5-5 mol%) and other common organic solvents were compatible (THF, Et_2O, C_6H_6, hexane). Reaction temperatures of 0-66 °C afforded high yields and the products included viscous oils, waxy solids, and powders.

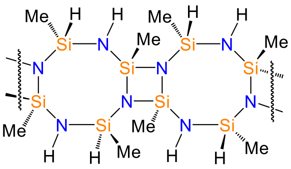


Fig. 27. Crosslinked polysilazane product proposed by Seyferth and Wiseman.

In 1986, Laine and Blum found that $Ru_3(CO)_{12}$ was as an efficient catalyst for the production of oligosilazanes.[24] They reacted tetramethyldisilazane (TMDS) with ammonia in the presence of $Ru_3(CO)_{12}$ at 60 °C and got a mixture of products with the formula $(Me_2SiNH)_n$ including cyclomers with n = 3-7, linear oligomers with n = 2-11, and a small number of branched oligomers (< 5%). These results were confirmed by GC-MS, NMR, and elemental analysis. The reaction was capable of being run at temperatures as low as 35 °C, and it was specifically pointed out that no Si–N cleavage occurs below 90 °C (meaning that the transformation is in fact dehydrogenative Si–N coupling). The outcome of the reaction largely depended on conditions. For example, performing the reaction with 13 atm of NH_3 at 90 °C afforded a 91% yield of volatile oligomers (70% tricyclomer) in 8 h with a TOF of 1,960 h^{-1} with respect to TDMS utilization and 3,438 h^{-1} with respect to Si–H bond disappearance (Fig. 28). To get a better yield of non-volatile linear and cross-linked products, they treated TMDS with 7 atm of ammonia using $Ru_3(CO)_{12}$ and heated the mixture at 135 °C. After 20 h they obtained a 68% yield of the non-volatile product with number average molecular weight (M_n) of 1,200 g/mol. In related experiments, the Laine group described the $Ru_3(CO)_{12}$ mediated cross-linking of oligomers prepared by aminolysis,[81,82] the coupling of NH_3 with Et_2SiH_2,[81] $HexSiH_3$ and $PhSiH_3$,[82,83] and the dehydrocoupling of hydride-functionalized siloxanes to NH_3 or Me_2NH to prepare polysiloxazanes that feature N-H linkages and aminated siloxanes, respectively.[82]

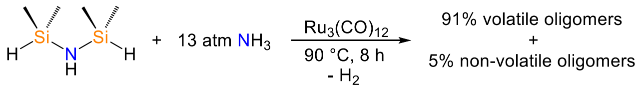


Fig. 28. Blum and Laine's Ru-catalysed oligosilazane synthesis.

In 1990, Eisenberg and co-workers reported the synthesis of several linear oligosilazanes alongside monomeric products using the dirhodium catalyst $Rh_2H_2(CO)_2(dppm)_2$ (Fig. 29, **36**).[84] Using 6 mol% of $Rh_2H_2(CO)_2(dppm)_2$ relative to silane, the coupling of $PhSiH_3$ and $^iBuNH_2$ afforded $PhSiH_2{}^iBuNH_2$ as the major non-volatile product after 1 h. In the presence of 0.15 mol% of **36** in a scaled up reaction, a mixture of products was obtained after 36 h that included $PhH_2SiN(^iBu)SiPhHNH(^iBu)$ and $(NH(^iBu)SiPhH)_2N(^iBu)$ as judged by GC-MS analysis. The length of oligomers was found to depend on the nature of the amine R group. For example, in the presence of the catalyst, treatment of $PhSiH_3$ with $MeNH_2$ afforded acyclic $H(PhHSiNMe)_2H$ at room temperature and $H(PhHSiNMe)_3H$ at 60 °C as the highest molecular weight products. However, $^iPrNH_2$ did not allow for the formation of oligomers, yielding $PhSiH(^iPrNH_2)_2$ as the highest molecular weight product. To minimize sterics, the dehydrocoupling of Me_2SiH_2 with NH_3 was performed and after 20 h at room temperature, a mixture of linear, cyclic, and branched oligosilazanes were obtained (Fig. 29). This transformation was believed to occur through the formation of a previously characterized μ-SiRR' intermediate and subsequent nucleophilic amine attack.

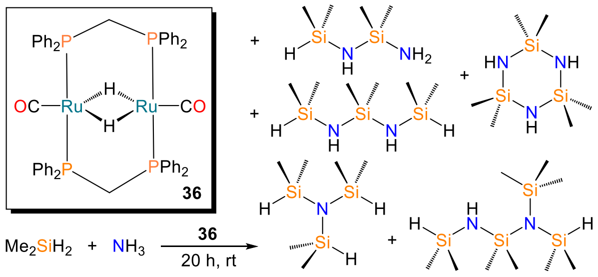


Fig. 29. Oligomers prepared by Eisenberg and co-workers.

Extending their efforts to prepare amino silane monomers, Corriu and co-workers were also interested in the synthesis of polysilazanes. $MePhSiH_2$ was reacted with ammonia in the presence of catalyst $^nBu_4NF$ in THF at room temperature to afford oligosilazane $(MePhSiNH)_n$ in 16 h with 76% yield.[38] The molecular weight was found to be 509 g/mol. They also prepared the oligosilazane $(MeHSiNH)_n$ from the ammonolysis of $MeHSiCl_2$ and were able to successfully cross-link it to ammonia using $^nBu_4NF$. This produced an insoluble non-melting product that was pyrolyzed at 1,000 °C, to generate ceramic in 48% yield.

After identifying oligomers with molecular weights of 248-592 g/mol during the Cu(I) catalysed dehydrocoupling of $PhNH_2$ and $PhSiH_3$,[39] Liu and Harrod published a second article in 1992 that focused on generating polysilazanes from NH_3 using dimethyltitanocene, Cp_2TiMe_2 (Fig. 30, **37**).[85] First, Ph_2MeSiH was reacted with NH_3 in the presence of 1.2 mol% of catalyst relative to silane and 70% conversion to the disilazane product $(Ph_2MeSi)_2NH$ was observed after 22 h at 25 °C. The same reaction was heated to 100 °C to afford $(Ph_2MeSi)_2NH$ with 60% conversion within 0.5 h. With $PhMeSiH_2$ and 0.96 mol% catalyst relative to silane, NH_3 was dehydrocoupled to give a mixture of the linear and cyclic trisilazanes, $H(PhMeSiNH)_3H$ and $(PhMeSiNH)_3$ (63%), as well as $H_2N(PhMeSiNH)_3H$ (24%) with 97% conversion over 12 h at 35 °C. In an hour or less at 100 °C, disilazane was observed with $H(PhMeSiNH)_2SiPhMeH$. The coupling of $PhSiH_3$ with NH_3 was also explored using **37**, but the reactions were slower and required heating to 90 °C. Notably, this catalyst was active for $PhSiH_3$ homocoupling and polymers with molecular weights of up to 5,000 g/mol were observed after 16 h at 95 °C. Ammonia was dehydrocoupled to *n*-hexylsilane to give a polymer with a molecular weight of 1,700 g/mol. A polymer with the predominant unit, $-MeSi(NH_2)-$, was similarly prepared from the dehydrocoupling of NH_3 and $MeSiH_3$ (Fig. 30, b), and its pyrolysis at 1,400 °C yielded a mixture of α-Si_3N_4, α-SiC, and carbon. Since Cp_2TiMe_2 was known to react with silanes in the presence of a donor ligand to form silyl complexes,[86] the authors proposed that these intermediates might undergo σ-bond metathesis with incoming NH_3 to generate aminosilane or with incoming silane to generate disilane.

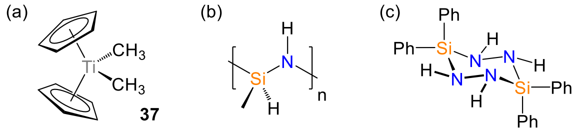


Fig. 30. (a) Dimethyltitanocene, (b) likely structure of poly(methylaminosilane), (c) cyclic product of hydrazine and Ph_2SiH_2 dehydrocoupling.

Two years later, the Harrod group described the Cp_2TiMe_2-mediated dehydrocoupling of $PhSiH_3$ and Ph_2SiH_2 to hydrazine, methylhydrazine, and dimethylhydrazine.[87] It was determined that $PhSiH_3$ and hydrazine slowly react with each other in the absence of catalyst and that heating these reagents to 90-100 °C afforded polymers with molecular weights of 780-910 in 2 h or less. Adding Cp_2TiMe_2 greatly accelerated dehydrocoupling at room temperature, leading to a reaction that was "quite violent" and which produced intractable gels that were not characterized. In the presence of 1 mol% of Cp_2TiMe_2 at room temperature, phenylsilane coupled with methylhydrazine to prepare a mixture of oligomers in 44 h (90% conversion). Disubstitution of the hydrazine with methyl groups was found to minimize polymerization; the coupling of $PhSiH_3$ with 1,1-dimethylhydrazine resulted in a low degree of polymerization with concurrent silane homocoupling while the reaction with 1,2-dimethylhydrazine resulted in *N*-silylamine formation. The dehydrocoupling of Ph_2SiH_2 with hydrazine allowed for the crystallographic characterization of $[(Ph_2Si)NHNH]_2$ (Fig. 30, c), which features a six-membered ring; however, aminosilane monomers and other oligomers were also observed. Analogous reactions between methylhydrazine or 1,1-dimethylhydrazine and Ph_2SiH_2 were similarly complex.

In 1997, Seyferth and Stewart demonstrated the KH catalyzed polymerization of cyclotetrasilazane, $(CH_3SiHNH)_4$ and $[CH_3SiHN(CH_3)CH_3SiHNH]_2$.[88] Using 1-5 mol% of catalyst KH at room temperature, cyclotetrasilazane was polymerized into polysilazanes with molecular weights of between 720-1700 g/mol in yields as high as 95% in 3 h or less. The higher molecular weight polysilazanes were white solids, soluble in common non-protic organic solvents, and their pyrolysis allowed for ceramic yields of up to 86%. When refluxed for 2.5-19 h, the KH catalyzed dehydrocoupling of $[CH_3SiHN(CH_3)CH_3SiHNH]_2$ was found to yield viscous oils and sticky solids with molecular weights of 400-700 g/mol. The best of these products provided a ceramic yield of 64%.

In 1999, Li and Kawakami reported the dehydrocoupling of a substrate containing 2 Si–H moieties and NH_3 to prepare a polycarbosilazane [or di(hydrosilane) ammonia copolymer].[89] In the presence of $Pd_2(dba)_3$, 1,4-bis(dimethylsilyl)benzene was coupled to NH_3 (0.5 M dioxane solution) over the course of 72 h at room temperature to afford a polymer with a molecular weight of 7,100 g/mol (Fig. 31). The polymer had a small quantity of siloxane linkages due to trace water in the NH_3 solution and partial decomposition was noted in MeOH. This polymer exhibited excellent thermal stability with a decomposition onset temperature (T_d) of 480 °C.

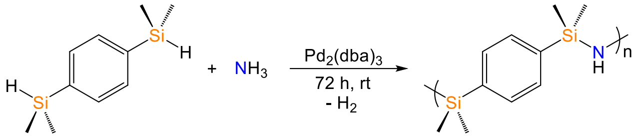


Fig. 31. Preparation of a polycarbosilazane using ammonia.

In order to study the reactivity of aminosilanes, Eisen et al. in their 2000 study reacted $PhSi(NHPr^n)_3$ with excess $PhSiH_3$ in the presence of $[(Et_2N)_3U][BPh_4]$ at 90 °C to yield a mixture of products consisting of three different 4-membered Si_2N_2 cyclodisilazanes.[41] These cyclodisilazanes were proposed to be formed by the sequential dehydrocoupling of the existing N-H bonds with $PhSiH_3$, followed by the intramolecular coupling of residual N-H and Si-H moieties.

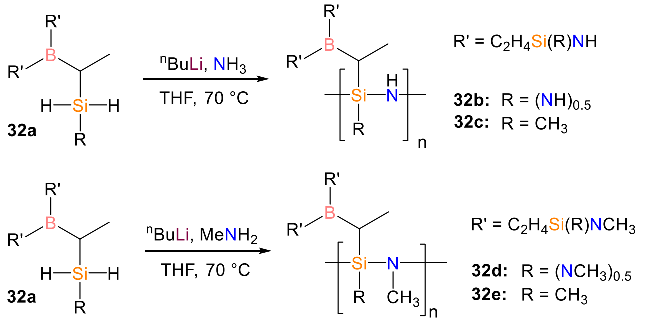


Fig. 32. Synthesis of boron-modified polysilazanes by Weinmann.

In 2001, Weinmann and co-workers reported the ⁿBuLi catalysed synthesis of highly crosslinked boron-modified polysilazanes of the type $\{B\{C_2H_4Si(R)\text{-}NR'\}_3\}_n$ as Si-B-C-N ceramic precursors (Fig. 32).[90] Tris(hydrosilylethyl)boranes, $B[C_2H_4Si(CH_3)_nH_{3\text{-}n}]_3$ (where n = 0, 1; **32a**), were reacted with NH_3 in toluene at 70 °C, in the presence of 1 mol% catalyst. In this reaction, the polymer $\{B[C_2H_4Si(NH)_{1.5}]_3\}_n$ (**32b**) precipitated in 93% yield with the evolution of H_2. And when one methyl group on Si was present, the polymer $\{B[C_2H_4Si(CH_3)NH]_3\}_n$ (**32c**) was obtained with a yield of 86%. These polysilazanes were extremely sensitive to air and moisture and insoluble in common organic solvents. Polymer **32b** did not melt or soften at temperatures as high as 250 °C whereas **32c** softened at 120 °C. Polymers **32d** and **32e** were obtained by repeating this reaction with $MeNH_2$; however, they were obtained as viscous oils rather than solids. Polymers **32b**-**32e** were slowly heated to 1,400 °C in Al_2O_3 Schlenk tubes and held at that temperature for 3 h. The highest ceramic yield of 83% was obtained for **32b**.

Efforts to aminate hydride-functionalized polysiloxanes via dehydrocoupling were described in 2016 by Ohshita.[91] Using Pd/C, the coupling of α,ω-dihydropoly(dimethylsiloxane) to pyrrolidine, piperidine, $^iPr_2NH$, and $^nBu_2NH$ was performed and the corresponding amine-functionalized siloxanes were obtained in 70-85% yield in 6-8 h at 50-70 °C. $PdCl_2$ was also used for the coupling of pyrrolidine, but a lower yield was obtained after 15 h at 50 °C. In addition, poly(dimethylsiloxane-co-hydromethylsiloxane) was dehydrocoupled to pyrrolidine using Pd/C to give the corresponding siloxane in 86% yield. The aminosiloxane products were found to be effective for the hydrophobic modification of glass surfaces.

After silylating diamines,[55-57] aminating di(hydrosilane)s,[55,56] and preparing a handful of Si_2N_2 cyclodisilazanes[55,57] in their monomer-focused studies, Sarazin and co-workers purposely set out to prepare cyclic and linear polycarbosilazanes (silane diamine copolymers) using $Ba\{CH(SiMe_3)_2\}_2(THF)_3$.[92] The contribution specifically focused on the cross-dehydrocoupling of *p*-xylylenediamine and diphenylsilane (Fig. 33) using 1 mol% of $Ba\{CH(SiMe_3)_2\}_2(THF)_3$ at 60 °C in benzene-d_6. The polymerization reactions were found to reach full conversion after only 10 min, and slight changes in substrate ratio were found to have a significant effect on the nature and M_n of the polymers. For example, a 1:1 ratio of amine to silane afforded exclusively cyclic polycarbosilazanes with M_n = 7,100 g/mol based on ^1H DOSY NMR spectroscopy. The use of a 1.25:1 or 1:1.25 ratio gave linear polymers with M_n of below 2,000 g/mol. Using a slight excess of silane (1:1.05 amine:silane) afforded a product with M_n = 10,400 g/mol and ^1H NMR analysis revealed minor quantities of disilazane and cyclodisilazane moieties. The DOSY NMR M_n values were consistent with those determined through end group analysis and running the reactions at 25 °C for 1 h gave similar results.

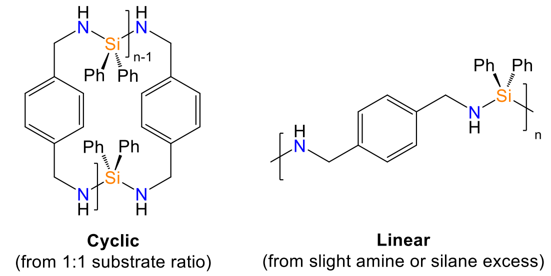


Fig. 33. Cyclic and linear polymers obtained by Carpentier and Sarazin.

In another report, these researchers explored the stepwise synthesis of oligomers with increased chain length and different compositions through the sequential dehydrocoupling of amines and hydrosilanes.[93] Triphenylsilane was reacted with aniline in the presence of 0.25 mol% of $Ba[CH(SiMe_3)_2]_2$ affording mono-coupled product $Ph_3SiNHBn$ in 2 h. This silazane was then sequentially dehydrocoupled with Ph_2SiH_2 and aniline respectively to yield $Ph_3SiNBnSiPh_2NBnH$. Further coupling with Ph_2SiH_2 did not produce the expected linear polycarbosilazane, but rather the thermodynamically stable Si_2N_2 cyclodisilazane following benzene elimination. The substrate scope was expanded to include different amines and silanes, and ring closure was not observed when an -$SiMe_3$ end group was used.

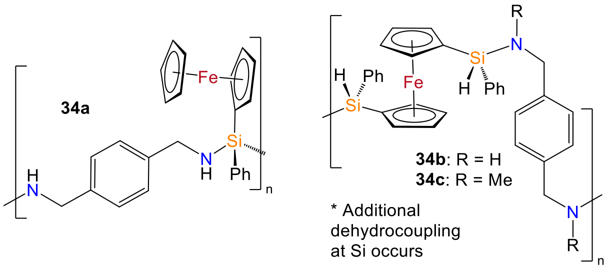


Fig. 34. Polymers incorporating ferrocene moieties by Manners and Hill.

In 2019, Manners and Hill prepared high molecular weight ferrocene-containing polycarbosilazanes (or silane diamine copolymers) using $Ba\{N(SiMe_3)_2\}_2(THF)_2$, and on one occasion $Ba\{CH(SiMe_3)_2\}_2(THF)_3$, as the dehydrocoupling catalyst.[94] The coupling of $CpFe(CpSiPhH_2)$ with *p*-xylylenediamine (1:1) in the presence of 1-5 mol% of Ba relative to the silane yielded polycarbosilazanes within 2 h at 25-60 °C. Structural analysis by ^1H NMR revealed the polymers are NH_2-terminated containing pendant ferrocene groups within the backbone (Fig. 34, **34a**). One reaction conducted at 25 °C for 3 h afforded a polymer with a M_n = 21,700 g/mol (as determined by DOSY NMR analysis). Interest in making polymers with ferrocene groups within the main chain led them to dehydrocouple $Fe[Cp(SiPhH_2)]_2$ with *p*-xylylenediamine using 3-5 mol% of $Ba\{N(SiMe_3)_2\}_2(THF)_2$ at 60 °C (Fig. 34, **34b**). One of these polymers was found to exhibit two different diffusion coefficients equating to M_n values of 19,200 and 27,800 g/mol. Interestingly, while exploring the role of sterics on polymer formation, the dehydrocoupling of *N,N′*-dimethyl-*p*-xylylenediamine with $Fe[Cp(SiPhH_2)]_2$ afforded products with M_n of 10,300 and 17,600 g/mol (Fig. 34, **34c**), while the coupling of *p*-xylylenediamine with $Fe[Cp(SiMe_2H)]_2$ allowed for the formation of a polymer with M_n of 5,500. After heating to 800 °C under a flow of nitrogen, ceramic yields of over 60% were obtained for polymers **34b** and **34c**. Notably, samples of polymers **34a** and **34b** were pyrolyzed to obtain charcoal-colored powders that were attracted to a bar magnet, and powder X-ray diffraction analysis revealed α-Fe and α-Fe_2O_3 within the matrix. These experiments are noteworthy because they showed that silane diamine copolymers can be used to prepare amorphous silicon carbonitride materials that feature metal nanoparticles, a strategy that could potentially be used to generate a wealth of new materials.

In their 2020 article, Webster and co-workers reported one example of a silane diamine copolymer by dehydrocoupling phenylsilane and 1,4-xylylenediamine at 80 °C (24 h) with a 5 mol% loading of $(^{2,6\text{-}iPr2Ph}BDI)Fe(CH_2SiMe_3)$ yielding a product with M_W = 855 g/mol, M_n = 855 g/mol, and PDI = 1.3.[71] Attempts to change the conditions (temperature and solvent dilution) resulted in no change in the polymer chain length. Reduction of catalyst loading to 1 mol % at 80 °C led to only a small increase in the chain length.

To summarize this section, researchers initially became interested in the dehydrocoupling of cyclosilazanes to prepare higher molecular weight polysilazanes that allow for improved ceramic yields of Si_3N_4. Subsequently, Laine,[24,81-83] Eisenberg,[84] Harrod[85] and others identified dehydrocoupling pathways for the synthesis of silazane oligomers and polymers, often as mixtures of cyclic and linear products. More recent advances have focused on the synthesis of silane diamine copolymers that remain underexplored, yet have the potential to be used in subsequent applications as described by Manners and Hill.[94]

4. Highlighted Work: Mn-Catalysed Si–N Dehydrocoupling

When our laboratory became interested in developing catalysts for Si–N dehydrocoupling, it was apparent that the field was unlikely to benefit from another article describing the preparation of *N*-silylamines, disilazanes, diaminosilanes, or triaminosilanes derived from common organosilanes such as $PhSiH_3$, Ph_2SiH_2, or Et_3SiH. As highlighted in Section 2, highly efficient catalysts,[62] including main group reagents,[38,50,57] had already been developed for these reactions. Moreover, while the use cases for *N*-silylamines and disilazanes have been nicely reviewed by the Schafer[22] and Kuciński[23] groups, respectively, they largely represent emerging applications for organic synthesis being performed at the bench rather than the industrial scale. Therefore, we wanted to revisit the concepts of polysilazane synthesis to prepare the industrial preceramic polymer perhydropolysilazane (PHPS) in a sustainable fashion through Si–N dehydrocoupling for the first time. We also discovered that commercial aminosilane CVD precursors that lack organic substitution on silicon had yet to be successfully prepared in this way. In order to advance the scope of Si–N dehydrocoupling along these lines, *both applications required the use of silane (SiH_4) as a coupling partner*. Although it is rarely found in academic laboratories, hundreds of tons of this gas are consumed for semiconductor production each year,[95] so it is widely available in industrial settings.

In a continuation of our efforts to develop first-row metal hydrofunctionalization catalysts,[96-108] we prepared the Mn hydride dimer (**38**) $[(^{2,6\text{-}iPr2Ph}BDI)Mn(\mu\text{-}H)]_2$ (Fig. 35) in 2018.[109] This catalyst, which features weak antiferromagnetic coupling between its manganese centres,[110] has been found to catalyse the hydrosilylation of olefins to cure silicones,[109] and the

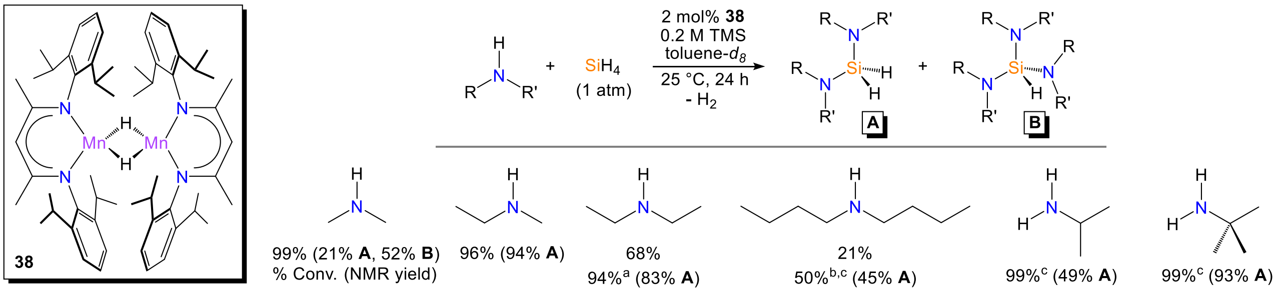


Fig. 35. Preparation of diaminosilane and triaminosilane CVD precursors through $[(^{2,6\text{-}iPr2Ph}BDI)Mn(\mu\text{-}H)]_2$ catalysed amine and silane dehydrocoupling. (a) Trial conducted for 48 h. (b) Trial conducted for 4 d. (c) Trial conducted in a 100 mL bomb since a large excess of SiH_4 prevents polymer formation.

dihydroboration of nitriles.[111] Notably, when exploring the scope of **38**-based olefin hydrosilylation, we observed that 4-aminostyrene addition to **38** resulted in the evolution of gas (presumably H_2) and that subsequent addition of $PhSiH_3$ led to polymer formation (presumably via amine silylation and olefin hydrosilylation). Therefore, this catalyst was selected for the study of SiH_4 and amine dehydrocoupling.

Initially, we focused on preparing commercial aminosilane CVD precursors.[112] To a J. Young tube charged with a toluene-*d₈* solution of $[(^{2,6\text{-}iPr2Ph}BDI)Mn(\mu\text{-}H)]_2$ and 0.2 M tetramethylsilane as an internal standard, 50 equiv. of volatile secondary amine was added, followed by 1 atm of SiH_4 gas (Fig. 35, right). ***Caution: Silane is a pyrophoric gas that requires careful handling – for detailed experimental procedures and safety considerations, please consult the original article and its Supporting Information.***[112] Once sealed, the reaction mixtures were allowed to warm to room temperature and were analysed by NMR spectroscopy after 24 h. The steric bulk of the amine was found to greatly affect the product distribution and overall effectiveness of the reaction. For example, dimethylamine allowed for the preferential formation of triaminosilane **B**, while slightly larger amines afforded the respective diaminosilane **A**. Diisopropylamine did not undergo dehydrocoupling under the reaction conditions. Importantly, $HSi(NMe_2)_3$, $H_2Si(NEt_2)_2$, and $H_2Si(NH^tBu)_2$ are used in industry to deposit Si_3N_4 films, and are currently prepared through the atom-inefficient aminolysis of halosilanes.[113,114]

In order to prepare PHPS, 1 atm of NH_3 and 1 atm of SiH_4 were condensed into to a 100 mL thick-walled glass vessel containing a benzene solution of **38** (Fig. 36).[112] After 1 h at ambient temperature, PHPS had precipitated as a yellow solid and was ultimately collected after 24 h. This product was characterized by IR spectroscopy and found to feature N–H, Si–H, and Si–N bands matching literature reports of PHPS.[115,116] CP-MAS ^{15}N NMR analysis revealed resonances at 27.26 and 42.82 ppm, corresponding to H*N*Si_2 and *N*Si_3 environments, respectively, while the CP-MAS ^{29}Si NMR spectrum featured a resonance at -37.90 ppm with spinning sidebands attributed to H_2*Si*N_2 and H*Si*N_3 moieties.[12]

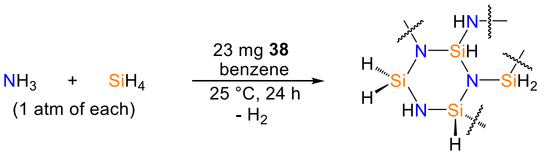


Fig. 36. Formation of perhydropolysilazane using $[(^{2,6\text{-}iPr2Ph}BDI)Mn(\mu\text{-}H)]_2$.

An analogous approach was employed to prepare SiH_4-derived silane diamine copolymers (polycarbosilazanes). Using a 2 mol% loading of **38** relative to diamine, adding 1 atm of SiH_4 afforded a variety of copolymers after 24 h at ambient temperature (Fig. 37).[112] These products were collected as off-white or tan extended solids that were insoluble in common organic solvents. Oligomers that were washed away from these polymers were found to exhibit molecular weights of up to 1,000 g/mol by MALDI-TOF mass spectrometry. Many of the products in Fig. 37, as well as the PHPS in Fig. 36, could not be characterized by elemental analysis since their combustion resulted in silicon nitride formation. Given the difficulties associated with characterizing products of this type, it is perhaps not surprising that the six compounds displayed in Fig. 37 significantly expanded the list of known silane diamine copolymers (polycarbosilazanes) that have been prepared by way of Si–N dehydrocoupling.[76,92,94] Having been prepared from SiH_4, these examples were also found to be particularly air and water sensitive.

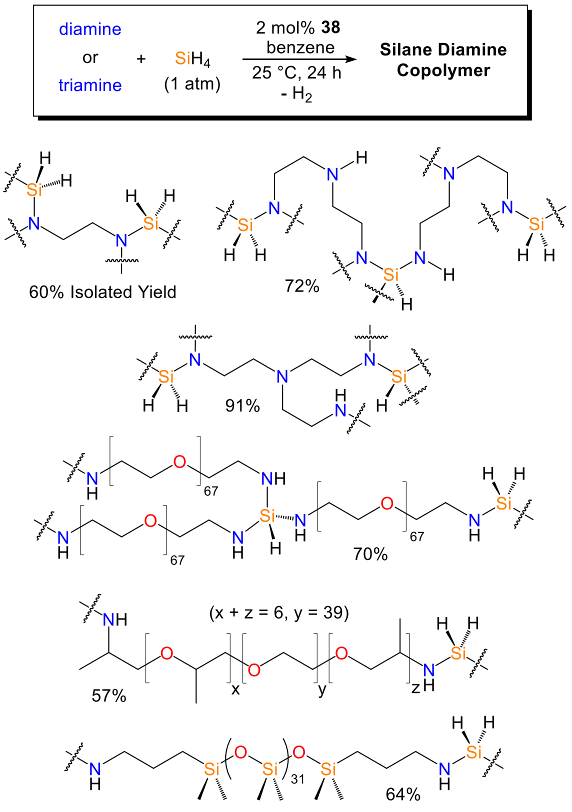


Fig. 37. Formation of SiH_4-derived silane diamine copolymers prepared using $[(^{2,6\text{-}iPr2Ph}BDI)Mn(\mu\text{-}H)]_2$.

Finally, the mechanism of $[(^{2,6\text{-}iPr2Ph}BDI)Mn(\mu\text{-}H)]_2$ catalysed Si–N dehydrocoupling was investigated.[112] When SiH_4 was added to **38**, no reaction was observed even after 24 h. However, when isopropylamine was added, complete conversion to the amido complex $[(^{2,6\text{-}iPr2Ph}BDI)Mn(\mu\text{-}NH^iPr)]_2$ was observed and this intermediate was characterized by single crystal X-ray diffraction. Knowing that **38** dissociates into monomeric hydrides with a barrier of only 1.5 kcal/mol, and that the addition of sterically unencumbered amines results in the loss of hydrogen and formation of the respective amido complex, a step-wise σ-bond metathesis mechanism was proposed (Fig. 38). Following dissociation, Mn–H and N–H σ-bond metathesis gives rise to the amido intermediate, which can then dimerize as a resting state or undergo σ-bond metathesis with an incoming Si–H bond to eliminate the aminosilane product and regenerate the catalyst.

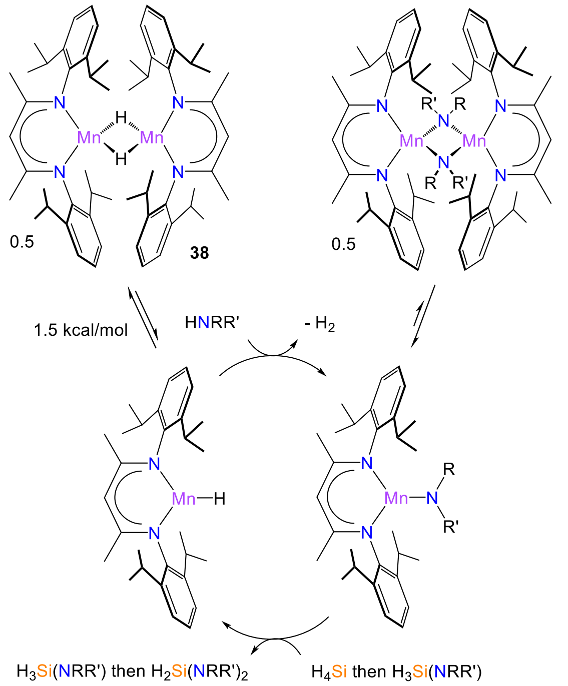


Fig. 38. Mechanism of Si–N dehydrocoupling using $[(^{2,6\text{-}iPr2Ph}BDI)Mn(\mu\text{-}H)]_2$.

5. Summary and Outlook

This article summarized catalytic Si–N dehydrocoupling in the context of the product classes that have been targeted, aminosilane monomers, oligomers and polymers. By focusing on products of industrial importance, we expanded the scope of Si–N dehydrocoupling to include commercial aminosilane CVD precursors derived from SiH_4. This study also featured the first examples of manganese-catalysed Si–N dehydrocoupling and atom-efficient perhydropolysilazane synthesis by way of SiH_4 and NH_3 dehydrocoupling.

Considering the advances in Si–N dehydrocoupling catalysis discussed herein, we believe there are a few key points that can be taken away from this article:

1. A *significant* number of catalysts have been developed for Si–N dehydrocoupling, and they have overwhelmingly been used to synthesize monomeric aminosilanes from common primary and secondary amines and organosilanes.
2. Unless a significant expansion of substrate scope, new applications, or an improvement in activity is noted, there may be limited value in developing new catalysts for the coupling of common primary and secondary amines and organosilanes to generate monomers.
3. While yet to be explored, existing Si–N dehydrocoupling catalysts are likely to show activity for the amination of SiH_4, which can be obtained from easy to handle SiH_4 surrogates.[117] This may prove valuable for aminosilane CVD precursor formation, since the steric bulk of the catalyst appears to control product selectivity.
4. The dehydrocoupling of silanes to ammonia to generate organic polysilazanes or perhydropolysilazane remains underexplored given the industrial importance of these polymers, and the fact that they are currently prepared using a method that generates a large quantity of waste.
5. Silane diamine copolymers (polycarbosilazanes) represent a promising product class that has not been widely studied by chemists and the materials science communities.

Major advancements in Si–N dehydrocoupling catalysis have been reported since the pioneering breakthroughs described in the latter half of the 20th century by Ojima, Laine, Harrod, and others. The atom-economy of this transformation relative to traditional methods of aminosilane synthesis has attracted the attention of scientists for over 50 years and new applications are still being uncovered. In addition to the discovery of new applications for aminosilane polymers, the development of Si–N dehydrocoupling catalysts that are exceptionally active, capable of preparing new polymer classes, or tailored for reactions of industrial interest represent the next frontiers of this expanding field.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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