

[(NHC)Yb{N(SiMe₃)₂}]₂-Catalyzed Cross-Dehydrogenative Coupling of Silanes with Amines**

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Silylamines are important silicon compounds that have been used as silylation and coupling agents, ligands for organometallic compounds, and precursors for Si, N polymeric materials.^[1] Catalytic cross-dehydrogenative coupling [CDC; Eq. (1)] of amines with silanes presents the most attractive and atom-economic synthetic approach for silylamines because the only by-product is hydrogen. Several well-defined metal complexes including metal carbonyls,^[2] f-element, early-transition-metal,^[3] and magnesium complexes^[4] have been successfully employed for catalytic Si–N coupling reactions. However, the control of the selectivity for Si–N coupling has proved to be problematic because the reactions can lead to several products with different Si/N ratios, including polysilazanes, as a result of multiple dehydrogenative-coupling steps; this issue is especially common for the coupling of primary silanes and amines. Thus, the development of highly reactive and selective catalytic systems for reactions of various amines and silanes is highly desirable.



Homoleptic rare-earth-metal silylamides [Ln{N(SiMe₃)₂}]_n (*n* = 2, 3) are readily available in large amounts and feature reactive Ln–N bonds for σ -bond metathesis and insertion reactions.^[5] Therefore, they are ideal choice for catalytic applications and have been successfully employed as catalysts for ring-opening polymerization reactions of lactones, intramolecular hydroamination, hydroxylation reactions of unsaturated hydrocarbons, as well as several others.^[6] To modify the catalytic performance and extend the catalytic applications of rare-earth-metal amides, various bulky anionic ligands have been designed for the preparation of ligand-supported amides.^[7] Immobilization of these amide catalysts has also been studied by the research groups of Anwander and Montreux.^[8] Given the excellent catalytic performance of ubiquitous N-heterocyclic carbenes (NHCs) in transition metal catalysis,^[9] it is surprising that the catalytic applications of NHC adducts of rare-earth amides have been virtually unexplored. Despite the fact that a large number of rare-earth complexes having NHC-functionalized anionic ligands have

been reported,^[10] there are only a couple of reports on NHC adducts of rare-earth amides.^[11] We recently reported the dehydrosilylation reaction of [(thf)₂Yb{N(SiMe₃)₂}] (1) with an aminosilane ArNHSiH₃; in this reaction the Yb–N bond undergoes σ -bond metathesis with the silane under mild reaction conditions, thus leading to the Si–N coupling and the formation of the first ytterbium silimine complex.^[12] The results suggested that ytterbium silylamide 1 might be a suitable catalyst for Si–N coupling reactions. Herein, we report the catalytic cross-dehydrogenative-coupling reactions of silanes with amines by [(NHC)Yb{N(SiMe₃)₂}] adducts. Remarkably, the catalytic activity and selectivity can be modulated by NHCs.

Initially, the stoichiometric reaction of 1 with PhSiH₃ in C₆D₆ at room temperature was investigated. ¹H NMR analysis disclosed the almost quantitative formation of PhSiH₂N(SiMe₃)₂, thus indicating a clean Si–N coupling. Therefore, we conducted the reactions of PhSiH₃ with equimolar amounts of three secondary amines (HN(SiMe₃)₂, HN(*i*Pr)₂, and HNEt₂) and 5 mol % loading of catalyst 1. However, the reactions of the two bulky amines yielded the expected 1:1 coupling products only in very low conversions of 24 % and 3 %, respectively, whereas the reaction of HNEt₂ gave the two products PhSiH₂NEt₂ and PhSiH(NEt₂)₂ with an almost quantitative conversion. These preliminary studies indicate that 1 is not a satisfactory catalyst for the coupling reactions and some modifications to the catalyst should be made to improve the activity and selectivity. It was found that the combination of 1 with a suitable N-heterocyclic carbene constitutes an efficient catalytic system for the Si–N coupling reactions. Thus, it was essential to study the reactions of 1 with NHCs to probe the roles of NHCs in the catalytic reaction. As we expected, the reactions of 1 with one equivalent of 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene (IiPr) and 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes) yielded the NHC adducts 2 and 3, respectively, in high yield (Scheme 1). Adducts 2 and 3 were fully characterized by ¹H NMR, ¹³C NMR, and IR spectroscopy, and elemental analysis. The ³¹C NMR spectra of 2 and 3 display C_{NHC} resonances at δ = 197.9 and 205.4 ppm, respectively, which are very similar to those for the reported NHC adducts of cyclopentadienyl ytterbium complexes.^[13] The molecular structure of 3 was determined by single-crystal X-ray analysis.

Single crystals of 3 suitable for X-ray single-crystal analysis were obtained from toluene solution at –40 °C, and the structure is shown in Figure 1 together with selected bond distances and angles. Complex 3 is monomeric with a three-coordinate ytterbium atom. The Yb–C_{NHC} bond length of 2.600(3) Å in 3 is only marginally longer than those observed in NHC adducts of substituted ytterbocenes (2.552(4) and

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reaction can be catalyzed by **2** at 40 °C in C₆D₆ (NMR scale) to give the aminosilane Ph₂NSiH₂Ph in 61 % yield in 15 h.

The reactions of the secondary silanes Ph₂SiH₂ and PhMeSiH₂ with primary amines and secondary amines catalyzed by **3** (5 mol %) gave 1:1 coupling products, exclusively, in high yields (Table 3). The reaction of the bulky primary silane MesSiH₃ (Mes = 2,4,6-Me₃C₆H₂) with *t*BuNH₂ gave the 1:1 coupling product MesSiH₂(NH*t*Bu) (Table 3, entry 9). However, **3** is not an effective catalyst for the coupling reactions of the secondary silanes with the bulky amines, that is, (SiMe₃)₂NH and *i*Pr₂NH. Interestingly, the reaction of Ph₂SiH₂ with the bulky secondary amine *i*Pr₂NH

Table 3: Reactions of bulky silanes with amines catalyzed by **3** (5 mol %).^[a]

Entry	Silane	Amine	Product	Yield [%] ^[b]
1	Ph ₂ SiH ₂	Et ₂ NH	Ph ₂ Si(H)NEt ₂	100 (85)
2	PhMeSiH ₂	Et ₂ NH	PhMeSi(H)NEt ₂	87 (86)
3 ^[c]	Ph ₂ SiH ₂	<i>i</i> Pr ₂ NH	Ph ₂ Si(H)N <i>i</i> Pr ₂	82 (73)
4	Ph ₂ SiH ₂	<i>i</i> PrNH ₂	Ph ₂ SiH(NH <i>i</i> Pr)	100 (87)
5	PhMeSiH ₂	<i>i</i> PrNH ₂	PhMeSiH(NH <i>i</i> Pr)	100 (84)
6	Ph ₂ SiH ₂	<i>t</i> BuNH ₂	Ph ₂ SiH(NH <i>t</i> Bu)	100 (78)
7	PhMeSiH ₂	<i>t</i> BuNH ₂	PhMeSiH(NH <i>t</i> Bu)	100 (90)
8 ^[d]	Ph ₂ SiH ₂	DippNH ₂	Ph ₂ SiH(NHDipp)	99 (64)
9	MesSiH ₃	<i>t</i> BuNH ₂	MesSiH ₂ (NH <i>t</i> Bu)	100 (86)

[a] Reaction conditions: **3** (5 mol %) in benzene or C₆D₆. [b] NMR yields, the values in parentheses refer to the yields of isolated product. [c] **2** (10 mol %), 100 °C, 24 h. [d] Reaction time: 12 h.

can catalyzed by **2** to give the 1:1 coupling product in high yield (Table 3, entry 3). The results indicated that the steric factors of both substrates and the NHCs have significant effects on the coupling products and reaction conditions that were required. The coupling of PhSiH₃ with primary amines proved to be complicated, and yielded a mixture if the ratios of the two reactants were not optimized. However, polymeric silazanes were not detected in these reactions.

The experimental results demonstrated that **2** and **3** are efficient catalysts for reactions of a wide range of amines and silanes, even for bulky secondary amines, thus indicating that the coordination of NHCs to the ytterbium effectively modulates the catalytic activity. To isolate possible intermediates, the reaction of **3** with PhSiH₃ was investigated under various reaction conditions. Unfortunately, attempts to isolate the putative (NHC)YbH₂ have been unsuccessful to date. As the reaction of PhSiH₃ with (SiMe₃)₂NH catalyzed by **3** is clean and yielded PhSiH₂N(SiMe₃)₂ as the sole product when a range amine/silane ratios were used, the influence of the amount of **3** on the reaction rate and conversions was studied by NMR spectroscopy in C₆D₆ at room temperature. The amount of the catalyst has a substantial influence on the reaction rate and conversions. The reaction rate increases linearly with an increase of the amount of catalyst (Figure 2), and the conversions also increased when the amount of the catalyst was increased (see the Supporting Information, Table S1). The use of an excess of PhSiH₃ (Si/N ratios from 1:1 to 6:1; see the Supporting Information, Table S2) has a very limited effect on the conversions in 30 minutes, whereas the use of a large excess amount of amine HN-

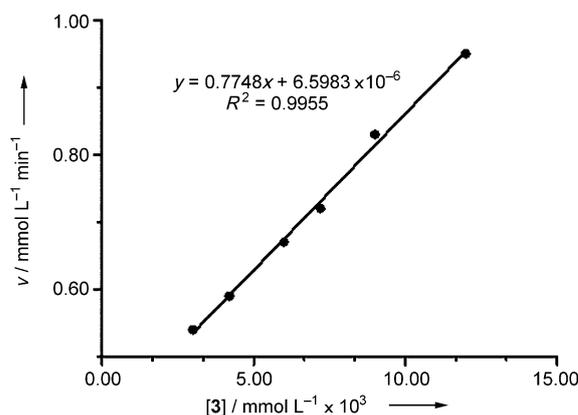


Figure 2. Rate of the formation of silylamine (v) versus the concentration of the catalyst **3**. This plot shows the first-order dependence of the reaction on the concentration of **3** (C₆D₆, 298 K).

(SiMe₃)₂ (Si/N ratios 1: ≥ 6, Table S3) significantly suppresses the reaction to give very low or no conversions within 30 minutes.

The mechanism of the reaction has yet to be investigated. However, it is possible that the key intermediate for the coupling reaction might be a NHC-stabilized ytterbium hydride formed by σ -bond metathesis of **3** with silanes. The stoichiometric reaction of **3** with PhSiH₃ at different concentrations in C₆D₆ was monitored by ¹H NMR analysis and the formation of PhSiH₂N(SiMe₃)₂ was observed. However, the ¹¹⁷Yb NMR spectra showed no peaks corresponding to a new product in these cases probably because of the instability of the intermediate under the experimental conditions. The reactions shown in Table 2 (entries 1, 2 and 3) were performed with catalyst by **1** in the presence two equivalents of IMes, and similar results were obtained as with **3** as the catalyst. The reaction of (SiMe₃)₂NH with PhSiH₃ catalyzed by **1** in the presence of the bidentate donor Me₂NCH₂CH₂NMe₂ resulted in a very low conversion (ca. 4 %) in 1 h. These experiments indicate that the NHC plays a key role in the catalytic reactions probably as a result of the strong σ -donor properties of NHC ligands. It is known that homoleptic rare-earth-metal hydrides tend to oligomerize as precipitates in solution.^[14] The presence of an NHC on the ytterbium center may prevent rapid oligomerization of the hydride in solution and allow it survive for a long enough time for the subsequent hydrogen elimination reaction with amines to occur, thus significantly improve the catalytic performance. The steric effects of NHCs on the catalytic reactions shown in Table 1 further demonstrated the important role of NHCs in the catalytic reactions.

In summary, we have shown that NHC adducts of a ytterbium amide catalyze cross-dehydrogenative-coupling of amines and silanes to yield various coupling products. The rare-earth-metal NHC silylamide complexes are highly reactive catalysts for the coupling reactions, as indicated by the unprecedented high yielding coupling of several bulky amines with silanes. In addition, the selective formation of a single coupling product can be realized by changing the molar ratios of the two substrates in the case of the primary silane PhSiH₃.

The experimental results indicated that NHCs can significantly improve and modulate catalytic performances of rare-earth-metal silylamides. Efforts to characterize the reaction intermediates and to expand the catalytic applications of the rare-earth NHC silylamide adducts are currently in progress.

Experimental Section

Preparation of **3**: A solution of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (0.91 g, 3.0 mmol) in toluene (30 mL) was added to a solution of Yb[N(SiMe₃)₂](THF)₂ (1.91 g, 3.0 mmol) in toluene. The resulting solution was stirred for 12 h at room temperature and then concentrated under vacuum. After storage at -40 °C overnight **3** was obtained as reddish black crystals (2.1 g, 88%). m.p.: 248 °C. ¹H NMR (C₆D₆, 400 MHz): δ = 0.21 (s, 36H, SiMe₃), 2.01 (s, 12H, Ar-Me), 2.12 (s, 6H, Ar-Me), 6.05 (s, 2H, NCH=CHN), 6.81 ppm (s, 4H, Ar-H); ¹³C NMR (C₆D₆, 100.64 MHz): δ = 5.69 (SiMe₃), 12.28 (Ar-Me), 20.88 (Ar-Me), 122.0 (NCH=CHN), 130.2, 134.9, 135.4, 139.7 (aromatic carbons), 205.4 ppm (NCN). Elemental anal. calcd for C₃₃H₆₀N₄Si₄Yb: C 49.65, H 7.58, N 7.02; found: C 50.21, H 7.52, N, 6.31.

Further details of the synthesis and characterization of **2** and **3**, catalytic processes, and characterization of the resulting silylamines are given in the Supporting Information.

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- [15] CCDC 890130 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.