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Selective Catalytic Synthesis of Amino-Silanes at Part-per Million Catalyst Loadings

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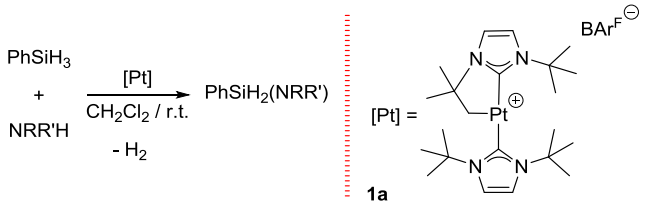
Platinum(II) complex [Pt(I^{t}Bu')(I^{t}Bu)][BAr^F] (1a) is a highly active and selective catalyst in the dehydrocoupling of amines and silanes at part-per-million catalyst loadings (up to 10 ppm), achieving the highest TON and TOF numbers reported in the literature (up to 1 mmol scale). NMR studies suggest a process taking place through electrophilic activation of the silane by the platinum species, assisted by an amine.

Catalytic dehydrocoupling processes leading to the formation of main-group E-E' bonds (E = B, Si; E' = O, N) are gaining importance as a tool for cleaner, atom economic, synthetic methods.[1] In this sense, the catalytic synthesis of Si–N bonds from silanes and amines is particularly attractive since the only by-product is dihydrogen. Amino-silanes are useful molecules for the synthesis of silicon-based bases, polymers and ceramics[1c] that have been traditionally prepared from halo-silanes, amines and bases which is less convenient than the direct dehydrocoupling. During the last years some groups have reported efficient catalytic systems based on main group elements (Li, Na, K, Mg, Ca, Sr, Al), lanthanides and actinides (Yb, U) and late transition metals.[2-4] These examples required catalyst loadings of 1-5% to achieve good conversions and reaction rates under mild reaction conditions. Most recently, it has been possible to decrease the catalyst loading (up to 0.25 mol%) by using a barium complex.[5] Another challenge associated with this type of transformations is to control the selectivity of the reaction. Particularly, primary silanes ($RSiH_3$) can produce monosilazanes ($RSiH_2(NRR')$) together with di- and trisilazanes ($RSiH(NRR')_2$ and $RSi(NRR')_3$).

Herein, we report the catalytic synthesis of amino-silanes using an electron-deficient platinum(II) catalyst, stabilized by N-heterocyclic carbenes (Scheme 1), that exhibits high efficiency at part-per million catalyst loadings with an exceptional selectivity toward the formation of mono-aminosilanes from primary silanes. Low temperature NMR studies suggest that transfer of a hydride atom from the silane to the platinum center (through σ-SiH complex intermediates) occurs during the catalytic cycle.

We have reported that the coordinatively unsaturated complex [Pt(I^{t}Bu')(I^{t}Bu)][BAr^F] (**1a**)[6] (where I^{t}Bu is 1,3-di-*tert*-butylimidazolylidene and I^{t}Bu' its cyclometalated form, (Scheme 1) is an efficient catalyst in dehydrocoupling processes leading to amino and diaminoboranes.[7] Mechanistic studies support a reaction that proceeds through nucleophilic attack of free dimethylamine to the boron atom in a σ-BH intermediate complex [Pt]←HBH_2·$NHMe_2$, exhibiting a η^1-BH coordination mode (Shimoi type). The mechanistic similarities of this process and the dehydrocoupling of silanes and alcohols by iridium species[8] prompted us to study the dehydrocoupling of silanes and amines. Recently, we have reported that complex **1a** can interact with silanes to form σ-SiH complexes[9] which, according to DFT calculations, exhibit a η^1-SiH coordination mode similar to that reported by Brookhart in an iridium complex.[10]

In this work, we first investigated the dehydrocoupling of phenylsilane ($PhSiH_3$) and *tert*-butylamine ($^tBuNH_2$) (1 to 1 ratio) using a catalyst loading of 0.5% (Scheme 1). Under these conditions a rather violent reaction led to the exclusive formation of $PhSiH_2(N^tBuH)$ within a few seconds. This selectivity is comparable to that reported using a Mg catalyst,[2a] for which longer reaction times (24 h) and higher catalyst loadings (5 mol%) were required.



Scheme 1. Catalytic dehydrocoupling of primary silanes an amines.

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Electronic Supplementary Information (ESI) available: Experimental details for the synthesis and characterization of aminosilanes. NMR spectra of aminosilanes. H_2 evolution graphics. See DOI: 10.1039/x0xx00000x

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Table1. Cross-dehydrocoupling of silanes and amines catalyzed by complex [Pt(I^{t}Bu')(I^{t}Bu)][BAr^F] (**1a**).

Entry	Silane	Amine (equiv)	mol % cat[a]	product	% yield[b] (isolated)	TON	TOF (h^{-1})
1	$PhSiH_3$	$^tBuNH_2$ (1)	0.005	$PhSiH_2(^tBuNH)$	99(90)	2×10^4	9.6×10^4
2	$PhSiH_3$	$^tBuNH_2$ (1)	0.003	$PhSiH_2(^tBuNH)$	99	3.3×10^4	5.7×10^4
3	$PhSiH_3$	$^tBuNH_2$ (2)	0.2	$PhSiH(^tBuNH)_2$	92(90)	920	540
4	$PhSiH_3$	NEt_2H (1)	0.005	$PhSiH_2(NEt_2)$	99(88)	2×10^4	3.3×10^5
5	$PhSiH_3$	NEt_2H (1)	0.001	$PhSiH_2(NEt_2)$	98	9.8×10^4	2.9×10^4
6	$PhSiH_3$	NEt_2H (2)	0.3	$PhSiH(NEt_2)_2$	99(86)	666	595
7	$PhSiH_3$	$(CH_2)_4NH$ (1)	0.01	$PhSiH_2[N(CH_2)_4]$	99[b]	1×10^4	6.4×10^4
8	$PhSiH_3$	$(CH_2)_4NH$ (1)	0.005	$PhSiH_2[N(CH_2)_4]$	99	2×10^4	3.4×10^4
9	$PhSiH_3$	$(CH_2)_4NH$ (2)	0.2	$PhSiH\ [N(CH_2)_4]_2$	99(96)	1000	8450
10	$PhSiH_3$	$^iPr_2NH$ (1)	0.3	$PhSiH_2(N^iPr_2)$	99(93)	333	1600
11	$PhSiH_3$	$^iPr_2NH$ (1)	0.1	$PhSiH_2(N^iPr_2)$	99	1000	667
12	$PhSiH_3$	$^iPr_2NH$ (4)	0.1	$PhSiH_2(N^iPr_2)$	99	1000	1.7×10^4
13	$PhSiH_3$	$MesNH_2$ (2)	0.1	$PhSiH_2(NHMes)$	95[c]	950	840
14	$PhSiH_3$	$MesNH_2$ (4)	0.1	$PhSiH_2(NHMes)$	99	1000	2300
15	Ph_2SiH_2	$^tBuNH_2$ (1)	0.1	$Ph_2SiH(^tBuNH)$	99(97)	1000	2000
16	Ph_2SiH_2	NEt_2H (1)	0.1	$Ph_2SiH(NEt_2)$	99(91)	1000	1300
17	Ph_2SiH_2	$(CH_2)_4NH$ (1)	0.1	$Ph_2SiH[N(CH_2)_4]$	99(92)	1000	1330
18	$^nBuSiH_3$	$^tBuNH_2$ (1)	0.005	$^nBuSiH_2(^tBuNH)$	99(90)	2×10^4	1.3×10^5
19	$^nBuSiH_3$	$^tBuNH_2$ (2)	0.2	$^nBuSiH(^tBuNH)_2$	96(91)	1000	1.9×10^4
20	$^nBuSiH_3$	NEt_2H (1)	0.005	$^nBuSiH_2(NEt_2)$	99(88)	2×10^4	1.2×10^5
21	$^nBuSiH_3$	NEt_2H (2)	0.2	$^nBuSiH(NEt_2)_2$	99(89)	1000	5.7×10^3
22	$^nBuSiH_3$	$(CH_2)_4NH$ (1)	0.005	$^nBuSiH_2[N(CH_2)_4]$	99(91)[c,d]	2×10^4	3×10^4
23	$^nBuSiH_3$	$(CH_2)_4NH$ (2)	0.2	$^nBuSiH[N(CH_2)_4]_2$	99(95)	1000	1.3×10^4
24	$^nBuSiH_3$	$^iPr_2NH$ (1)	0.1	$^nBuSiH_2(N^iPr_2)$	96(86)	1000	3.5×10^4
25	Et_2SiH_2	$^tBuNH_2$ (1)	0.1	$Et_2SiH(^tBuNH)$	99(98)	1000	3.3×10^5
26	Et_2SiH_2	NEt_2H (1)	0.1	$Et_2SiH(NEt_2)$	99(96)	1000	5.3×10^4
27	Et_2SiH_2	$(CH_2)_4NH$ (1)	0.1	$Et_2SiH[N(CH_2)_4]$	99(98)	1000	9.4×10^3

[a] With respect to silane. [b] Determined by NMR. [c] Not isolated. [d] ca. 5% of diaminosilane $^nBuSiH[N(CH_2)_4]_2$ has been detected in this case (see ESI).

Other main-group catalysts provide mixtures of mono- and bis(dehydrogenated) phenylsilane with, again, longer reaction times and catalyst loadings of 5 mol%.[2b] In addition, at the end of the reaction **1a** had evolved to its hydrogenated form [PtH(I^{t}Bu)$_2$][BAr^F] (**1b**).[11]

The encouraging results obtained with complex **1a** prompted us to decrease the catalyst loading. Thus, when the reaction was carried out with 0.005 mol% (50 ppm) of **1a** all the silane was consumed in about 12 min (Table 1, entry 1), whereas catalyst loadings of 30 ppm (Table 1, entry 2) required 35 min, which correspond to turnover numbers (TON) and turnover frequencies (TOF) of 2×10^4 and 3.3×10^4, and 9.6×10^4 and 5.7×10^4 h^{-1}, respectively. The reaction with NEt_2H (using 50 ppm of **1a**) is faster (Table 1, entry 4) with full conversion of the phenylsilane into the mono(amino)silane $PhSiH_2(NEt_2)$ in 3.6 min, leading to TONs and TOFs of 2×10^4 and 3.3×10^5 h^{-1} respectively, the highest reported to the best of our knowledge. In this case the amount of catalyst can be reduced to 10 ppm (Table 1, entry 5) leading to 98% conversion of the silane in 180 min. Interestingly, pyrrolidine, one of the most challenging substrates in terms of selectivity, can be converted with complete selectivity into $PhSiH_2[N(CH_2)_4]$ using 50 ppm of the catalyst (Table 1, entry 8) in 35 min. However, bulkier (HN^iPr_2) or less nucleophilic amines ($MesNH_2$) required higher catalyst loadings (0.1 mol%,

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1000 ppm) to achieve comparable reaction times (45 min) and complete conversions (see Table 1, entries 10-14).

Primary alkylsilanes such as $^{n}BuSiH_3$ are also efficiently converted into the corresponding mono(amino)silanes (Table 1, entries 18, 20, 22 and 24) using typically 50 ppm as catalyst loading. The rates of the reactions are comparable to those found for $PhSiH_3$, except when $^{i}Pr_2NH$ was used, for which an increase of the reaction rate of one order of magnitude was observed (compare table 1, entries 11 and 24). Secondary silanes can also be dehydrocoupled efficiently. Thus, Ph_2SiH_2 reacts with NEt_2NH, $^{t}BuNH_2$ and $(CH_2)_4NH$ but catalyst loadings of at least 0.1 mol% are necessary to form the desired mono(amino)silanes $Ph_2SiH(NR_2)$ at good rates (Scheme 2). The bulkier $^{i}Pr_2NH$ does not undergo reaction at room temperature, while heating at 60 °C for 4 days yields mixtures of products. Significantly, the rates at which Et_2SiH_2 is dehydrocoupled under the same reaction conditions are very high (Table 1, entries 25-27), achieving TOF numbers up to 3.3 x 10^5 h^{-1}, that is up to two orders of magnitude higher in comparison to Ph_2SiH_2 (Table 1, entries 15-17). Finally, the bulkier silane Ph_3SiH does not react at all with any of the amines.

If an amine:primary-silane molar ratio of 2:1 is used for $^{t}BuNH_2$, NEt_2H and $(CH_2)_4NH$, the bis(amino)silanes $RSiH(NR'R'')_2$ are formed but catalyst loadings above 0.2 mol% are required (Table 1, entries 3, 6, 9, 19, 21, and 23). The second dehydrogenation process is considerably faster when $^{n}BuSiH_3$ is used instead of $PhSiH_3$ (compare for example TOF numbers in Table 1, entries 19 and 23 *vs* 3 and 9, respectively). No bis(amino)silanes have been detected in reactions with $^{i}Pr_2NH$ or $MesNH_2$ even with high catalyst loadings.

At this point it should be noted that when an excess of the amine is used (up to 8 equiv) in reactions with primary silanes, working at low catalyst loadings (below 0.01 mol%),[12] the rate of the reaction increases or decreases depending on the nature of the amine (Figures S111-114). The use of an excess of $^{t}BuNH_2$, NEt_2H, $(CH_2)_4NH$ resulted in slower reaction rates, whereas a significant increase of the speed of the process takes place in the case of the bulkier $^{i}Pr_2NH$ and the less nucleophilic $MesNH_2$. This is related to the coordination ability of the less hindered amines to the platinum atom. The kinetic profile of the reaction of $PhSiH_3$ and the amines $^{t}BuNH_2$, NEt_2H and $^{i}Pr_2NH$, obtained by measuring the amount of dihydrogen released in the process in a closed system, depends on the bulkiness of the amine (Figure 1). The different kinetic profiles are probably related to a more efficient coordination of the amine to **1a** following the sequence $^{t}BuNH_2$ > NEt_2H > $^{i}Pr_2NH$. In fact, when **1a** is mixed with an excess of the less hindered amines a decrease in the PtH coupling constant of the Pt–CH_2

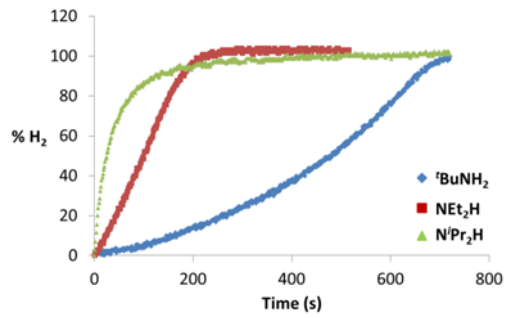
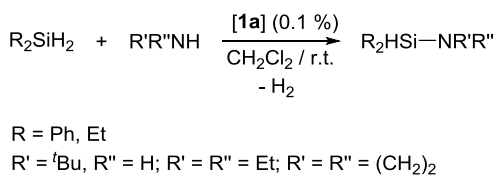


Figure 1. Kinetic profile (H_2 evolution) of the reaction of $PhSiH_3$ with $^{t}BuNH_2$, NEt_2H and $^{i}Pr_2NH$ (catalyst loadings of 0.005, 0.005 and 0.3 mol%, respectively).

in the ^{1}H NMR spectra (reduction of 15 and 7 Hz in the presence of 5 equiv of $^{t}BuNH_2$ or NEt_2H, respectively) serves as an indication of this interaction, whereas it remain unaltered with $^{i}Pr_2NH$.[13] Thus, de-coordination of the less-hindered amines is a prerequisite for the reaction to proceed, which causes the induction period observed at early reaction times[14] and as the concentration of amine decreases the reaction becomes faster (Figure S104 and comments below).

Interestingly, kinetic profiles in all reactions with Ph_2SiH_2 (and Et_2SiH_2) exhibit exponential shapes (Figures S107-109). This different behaviour might be related to a more efficient interaction of Ph_2SiH_2 with the metal compared to $PhSiH_3$ (calculated ΔE_{int} is 4.8 kcal·mol^{-1} higher for this silane).[15] An analogous result has been previously observed in the interaction of $^{n}BuSiH_3$ and Et_2SiH_2 with complexes **1a**,**b**.[9]

Low temperature (-30 °C) ^{1}H NMR studies of a stoichiometric reaction of Ph_2SiH_2, NEt_2H and **1a** conducted in THF-d[8] (a solvent in which the reaction takes place at slower reaction rates) indicate the formation of the neutral platinum hydride **3**[7a] coexisting with **1a** (Scheme 3). Very likely, complex **3** is formed through transfer of a hydride atom from Ph_2SiH_2 to the platinum atom (preceded by formation of a σ-SiH complex),[9] assisted by the amine in a similar way to the transfer of a hydride from amine-boranes during dehydrocoupling processes induced by **1a**.[7] In addition, the ^{1}H NMR spectra revealed the formation of aminosilane $Ph_2SiH(NEt_2)$ together with another species (**A**) that contains an NEt_2 fragment. This species exists in a 1:1 ratio with respect to hydride complex **3**. As the temperature increases the concentration of both **3** and **A** decreases concurrently, until they disappear completely at r. t. According to ^{1}H,^{29}Si-HMBC NMR experiments, species **A** has no silicon atom and, furthermore, we have not detected any other silicon-containing species other than Ph_2SiH_2 and aminosilane $Ph_2SiH(NEt_2)$. Additionally, the CH_2 groups of the NEt_2 fragment in species **A** correlate in a COSY experiment with another broad signal at *ca.* 7.6 ppm.[16] All this information points at species **A** being the ammonium cation $[NEt_2H_2][BAr^F]$, presumably formed by deprotonation of a transient, unobserved, silylium cation "$Ph_2SiH(NEt_2H)^+$" by free NEt_2H. Moreover, ^{1}H and ^{15}N NMR chemical shifts of **A** match those of



Scheme 2. Dehydrocoupling of secondary silanes.

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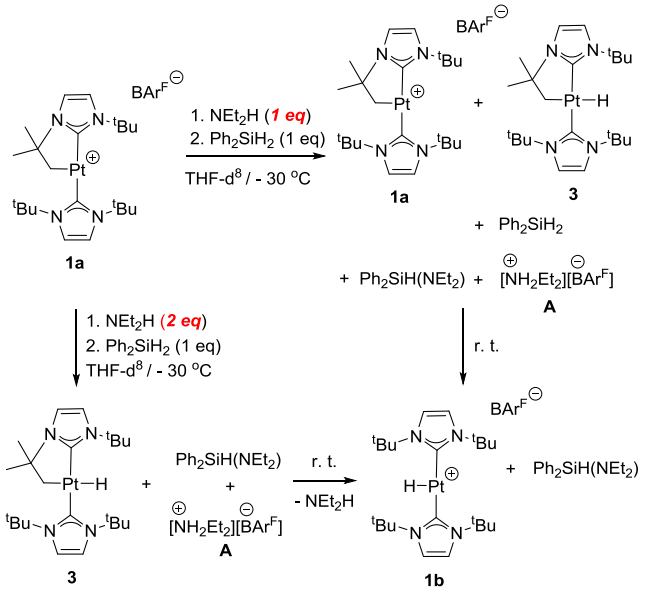

Scheme 5. Low temperature NMR studies.

the cation $[NEt_2H_2][BAr^F]$ synthesized by reaction of NEt_2H with $HBAr^F{\cdot}Et_2O$ (see ESI). In support to this, when the reaction of **1a** with Ph_2SiH_2 and NEt_2H was carried out using 2 eq of NEt_2H(**1a** : Ph_2SiH_2 : NEt_2H stoichiometry 1 : 1 : 2) under identical reactions conditions, we observed complex **3** together with $Ph_2SiH(NEt_2)$ and species **A** as major products but, importantly, no Ph_2SiH_2 nor **1a** are observed (in agreement with the need of two equiv of amine per silane). The final step of the process is the protonation of the platinum hydride **3** by the ammonium salt $[NEt_2H_2][BAr^F]$, releasing H_2 and complex **1a** that is hydrogenated leading to **1b**.[17]

In summary, we have developed a very selective and efficient catalytic system for the generation of amino-silanes (up to 1 mmol scale) using a highly electrophilic, robust, Pt(II) complex that can operate at ppm catalyst loadings. Experimental evidence hints at a process involving the transfer of a hydride from the Si–H bond to platinum *without* an oxidative addition pathway. Thus, the cationic platinum(II) complex **1a** can be viewed as a new example of Lewis acid catalyst in which their electrophilicity is transmitted to a silicon atom upon coordination of the silane leading to a σ-SiH complex.[9,18] Current work is geared at determining the mechanism of the dehydrocoupling process.

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Conflicts of interest

There are no conflicts to declare.

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