

# Dehydrocoupling reactions of amines with silanes catalyzed by $[(Et_2N)_3U][BPh_4]$

Jia Xi Wang<sup>a</sup>, Aswini K. Dash<sup>a</sup>, Jean Claude Berthet<sup>b</sup>, Michel Ephritikhine<sup>b</sup>,  
Moris S. Eisen<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Technion-Israel Institute of Technology, Technion City, Haifa 32000, Israel

<sup>b</sup> DSM, DRECAM, Service de Chimie Moléculaire, CNRS URA 331, CEA Saclay, F-91191 Gif sur Yvette, France

Received 20 April 2000; accepted 7 June 2000

## Abstract

Dehydrocoupling reactions of primary amines  $RNH_2$  with  $PhSiH_3$  were catalyzed by  $[(Et_2N)_3U][BPh_4]$  to give the corresponding aminosilanes  $PhSiH_{3-n}(NHR)_n$  ( $n = 1-3$ ), the relative yields of the products were found to be dependent on the experimental conditions and on the nature of R. For a primary silane ( $PhSiH_3$ ), the reactivity of  $RNH_2$  follows the order primary > secondary > tertiary. Similar dehydrocoupling reactions using secondary amines with secondary silanes were found to be less reactive. Homodehydrocoupling of the silane was found not to be a competing reaction at room temperature. The hydride  $[(RNH)_2UH][BPh_4]$ , which is plausibly formed in the reaction of  $[(RNH)_3U][BPh_4]$  with  $PhSiH_3$  is a likely intermediate in the catalytic cycle. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Dehydrocoupling; Amines; Silanes; Cationic; Uranium

## 1. Introduction

During the last decade, the chemistry of electrophilic  $d^0/f^n$  lanthanide and actinide compounds has been the source of intense investigations and has reached a high level of sophistication [1]. The broad interest in these compounds originates from their unique structure–reactivity relationships and their remarkable performances in homogeneous catalysis. For neutral organoactinides, catalyzed reactions were first limited to C–H activation [2] and hydrogenation reactions [3], although recently we have designed new processes for the hydroamination [4], oligomerization [5], selective dimerization [6] and hydrosilylation reactions of alkyne [7]. Regarding a cationic uranium amide complex,  $[(Et_2N)_3U][BPh_4]$ , it has been found to be particularly efficient in the dimerization of terminal alkynes [8] and in the hydrosilylation reactions of terminal alkynes with  $PhSiH_3$  [9], which involve the uranium amido-acetylide or the uranium amido-hydride species as the active

intermediates, respectively. A conceptual question which was raised from those studies concerned the possibility of activating the amido ancillary ligands in  $[(Et_2N)_3U][BPh_4]$  with a silane molecule producing the corresponding aminosilane and an organometallic hydride complex. The ability to transform this latter hydride, by the reaction with another amine, into the starting amido complex with the concomitant elimination of dihydrogen would allow us to perform the catalytic dehydrogenative coupling of amines and silanes. It is important to point out that theoretical thermodynamic calculations predicted that this process is plausible, but no experimental evidence has been given for this mechanistic pathway [10]. Dehydrogenative coupling of amines and silanes has been performed by either heterogeneous [11] or homogeneous [12] late transition-metal catalysts and also by the early transition metal complex  $Cp_2TiMe_2$  [13]. These reactions constitute an elegant and alternative route to silazanes, attractive precursors for important silicon nitride materials [14], which are classically prepared by the aminolysis or ammonolysis of chlorosilanes with the disadvantageous formation of large amounts of ammo-

\* Corresponding author. Tel.: +972-4-8292680; fax: +972-4-8233735.

anium halide by-products [15]. However, virtually nothing is known about the capacity of f-element complexes and, more specifically, cationic metal derivatives in the synthesis of aminosilanes. Here we report on a novel process for the selective dehydrogenative coupling of amines and silanes catalyzed by the well-defined cationic actinide complex  $[(Et_2N)_3U][BPh_4]$  [16], the influence of the structure and stoichiometry of the reactants on the course of the reaction is presented, and a plausible mechanism is proposed.

## 2. Experimental

### 2.1. Material and methods

All manipulations of air sensitive compounds were performed in a high vacuum line, or in a nitrogen-filled glove box. Deuterated solvents (from Aldrich or Cambridge Isotopes Inc.) were freeze-pump-thaw-degassed and dried over Na/K alloy for 1 h. Phenylsilane (from Aldrich) was dried on active 4 Å MS for 2 h and was freeze-pump-thaw-degassed. All amines were dried by sodium and distilled, then dried on active 4 Å MS for 2 h and freeze-pump-thaw-degassed. The catalyst  $[(Et_2N)_3U][BPh_4]$  was prepared as described in the literature [16]. The NMR assignments of the aminosilanes  $PhSiH(NHCH_2CH_2CH_3)_2$  [12d],  $PhSi(NHCH_2CH_2CH_3)_3$  [15c],  $PhSiH_2NEt_2$  [12e],  $PhSiH(NEt_2)_2$  [17],  $PhMeSi(NHCH_2CH_2CH_3)_2$  [12d], and  $PhMeSiH(NHCH_2CH_2CH_3)$  [12d], were characterized by comparison with authentic samples prepared by independent routes, as well as by comparison with the corresponding literature data.

### 2.2. Physical and analytical measurements

NMR spectra were recorded on a Bruker 400 MHz or 200 MHz instrument. Chemical shifts for  $^1H$ ,  $^{13}C$  are referenced to internal solvent resonance and to  $PhSiMeH_2$  ( $\delta = -33.6$  in  $C_6D_6$ ) for  $^{29}Si$ . NMR experiments on air-sensitive samples were conducted in Teflon valve-seal tubes.

### 2.3. Catalytic dehydrocoupling reactions

In a typical experiment, a 5 mm NMR tube equipped with a Teflon valve was charged in the glove box with  $[(Et_2N)_3U][BPh_4]$  (10 mg, 0.013 mmol). On a greaseless vacuum line, 0.33 ml of the deuterated solvent and specific amounts of phenylsilane and amine were vacuum transferred into the tube (exact measurements were performed through a Toepler Pump). The progress of the reaction was monitored by  $^1H$ -NMR spectroscopy. The products were characterized by  $^1H$ -,  $^{13}C\{H\}$ -, and  $^{29}Si\{H\}$ -NMR. Large amounts of prod-

ucts are obtained by using preparative scale, as indicated for some reaction.

### 2.4. Reaction of *n*-propylamine with phenylsilane

(a) According to the typical experimental procedure, the reaction of 0.33 ml (4.04 mmol) of  $^nPrNH_2$  with 0.09 ml (0.756 mmol) of  $PhSiH_3$  gave  $PhSi(NHCH_2CH_2CH_3)_3$  (37.2%) and  $PhSiH(NHCH_2CH_2CH_3)_2$  (62.8%) after 2 h; the relative yields of these products were 52.4: 47.8 after 4 h, respectively. After 10 h, the only product was  $PhSi(NHCH_2CH_2CH_3)_3$ , which was distilled at 100–102°C at 0.1 mmHg to another NMR tube and characterized by  $^1H$ -,  $^{13}C$ - and  $^{29}Si$ -NMR spectroscopy. When the reaction was stopped after 2 h, the compound  $PhSiH(NHCH_2CH_2CH_3)_2$  was distilled at 204–205°C at 5 mmHg producing a 60.8% yield.

(b) For large amounts, a 25 ml Schlenk flask equipped with a magnetic stir bar was charged into the glovebox with 50 mg (0.065 mmol) of  $[(Et_2N)_3U][BPh_4]$ . The flask was connected to a greaseless high vacuum line and pumped down to  $2 \times 10^{-6}$  mmHg and back filled with argon three times. Under a flash of argon, 5 ml of dry benzene, 3 ml (36.7 mmol) of *n*-propylamine and 1.1 ml (8.9 mmol) of phenylsilane were transferred by means of a syringe into the flask. The flask was connected to a reflux condenser under argon and the reaction refluxed for 10 h. The solvent and the excess of amine were removed by means of vacuum and the residue was distilled under vacuum 0.1 mmHg at 100–102°C to give 2.15 g (86.5%) of a colorless oil of  $PhSi(NHP^r)_3$ .

#### 2.4.1. $PhSiH(NHCH_2CH_2CH_3)_2$

B.p. = 204–205°C (5 mmHg).

$^1H$ -NMR ( $C_6D_6$ , 200 MHz):  $\delta$  0.85 (t,  $J = 7.2$  Hz, 6H,  $CH_3$ ), 1.05–1.25 (b, 2H,  $NH$ ), 1.45 (m, 4H,  $CH_2$ ), 2.82 (q,  $J = 7.2$  Hz, 4H,  $CH_2N$ ), 4.87 (s, 1H,  $SiH$ ), 7.15–7.30 (m, 3H, Ph), 7.50–7.70 (m, 2H, Ph).

$^{13}C$ -NMR ( $C_6D_6$ , 50 MHz):  $\delta$  11.9 ( $CH_3$ ), 28.5 ( $CH_2$ ), 44.5 ( $CH_2N$ ), 128.3 (CH), 130.0 (CH), 134.9 (CH), 138.9 (C–Si).

$^{29}Si$ -NMR ( $C_6D_6$ , 79.5 MHz):  $\delta$  –24.13 (d,  $^1J_{Si-H} = 212$  Hz, Si–H).

#### 2.4.2. $PhSi(NHCH_2CH_2CH_3)_3$

B.p. = 100–102°C (0.1 mmHg).

$^1H$ -NMR ( $C_6D_6$ , 200 MHz):  $\delta$  0.85 (t,  $J = 7.2$  Hz, 9H,  $CH_3$ ), 1.05–1.25 (b, 3H,  $NH$ ), 1.45 (m, 6H,  $CH_2$ ), 2.82 (q,  $J = 7.2$  Hz, 6H,  $CH_2N$ ), 7.15–7.30 (m, 3H, Ph), 7.50–7.70 (m, 2H, Ph).

$^{13}C$ -NMR ( $C_6D_6$ , 50 MHz):  $\delta$  11.9 ( $CH_3$ ), 28.7 ( $CH_2$ ), 44.2 ( $CH_2N$ ), 128.1 (CH), 129.3 (CH), 135.0 (CH), 139.9 (C–Si).

$^{29}\text{Si-NMR}$  ( $\text{C}_6\text{D}_6$ , 79.5 MHz):  $\delta$  – 30.59 ( $^3J_{\text{Si-H}} = 19.3$  Hz, *Si*).

## 2.5. Reaction of *i*-propylamine with phenylsilane

$i\text{-PrNH}_2$  (0.07 ml, 0.86 mmol) reacted with 0.066 ml (0.54 mmol) of  $\text{PhSiH}_3$  for 23 h at room temperature (r.t.) to yield  $\text{PhSiH}_2\text{NHPr}^i$  (33%) and  $\text{PhSiH}(\text{NHPr}^i)_2$  (56%). The conversion of  $\text{PhSiH}_3$  was 89%. When the reaction was carried out with a larger excess of  $i\text{-PrNH}_2$  (4:1 amine:silane ratio) after 56 h,  $\text{PhSiH}(\text{NHPr}^i)_2$  was the only observed product, which was distilled at 100–105°C (0.1 mmHg) to another NMR tube and characterized by  $^1\text{H}$ -,  $^{13}\text{C}$ - and  $^{29}\text{Si-NMR}$  spectroscopy. The characterization of the mono amine product  $\text{PhSiH}_2\text{NHPr}^i$  was performed by subtracting the NMR data of the clean compound,  $\text{PhSiH}(\text{NHPr}^i)_2$ , from that of the mixture obtained after 23 h.

### 2.5.1. $\text{PhSiH}_2\text{NHPr}^i$

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ , 200 MHz):  $\delta$  0.55–0.75 (b, 1H, NH), 0.89 (d,  $J = 6.4$  Hz, 6H,  $\text{CH}_3$ ), 2.80–3.00 (m, 1H, CH), 4.99 (d,  $J = 2.5$  Hz, 2H,  $\text{SiH}_2$ ), 7.05–7.25 (m, 3H, Ph), 7.50–7.60 (m, 2H, Ph).

$^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ , 50 MHz):  $\delta$  26.9 ( $\text{CH}_3$ ), 45.0 (CH), 128.2 (CH), 130.1 (CH), 134.9 (CH), 138.5 (C–Si).

$^{29}\text{Si-NMR}$  ( $\text{C}_6\text{D}_6$ , 79.5 MHz):  $\delta$  – 34.2 (t,  $^1J_{\text{Si-H}} = 203.8$  Hz, *Si–H*).

### 2.5.2. $\text{PhSiH}(\text{NHPr}^i)_2$

B.p. = 90–95°C (0.1 mmHg).

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ , 200 MHz):  $\delta$  0.55–0.75 (b, 1H, NH), 0.85–1.05 (b, 1H, NH), 0.95 (d,  $J = 6.0$  Hz, 6H,  $\text{CH}_3$ ), 0.98 (d,  $J = 6.1$  Hz, 6H,  $\text{CH}_3$ ), 3.05–3.30 (m, 2H, CH), 5.08 (t,  $J = 2$  Hz, 1H, SiH), 7.0–7.30 (m, 3H, Ph), 7.60–7.70 (m, 2H, Ph).

$^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ , 50 MHz):  $\delta$  27.6 ( $\text{CH}_3$ ), 43.1 (CH), 128.2 (CH), 129.7 (CH), 134.4 (CH), 136.0 (C–Si).

$^{29}\text{Si-NMR}$  ( $\text{C}_6\text{D}_6$ , 79.5 MHz):  $\delta$  – 31.56 (d,  $^1J_{\text{Si-H}} = 214$  Hz, *Si–H*).

## 2.6. Reaction of *t*-butylamine with phenylsilane

(a)  $t\text{-BuNH}_2$  (0.13 ml, 1.2 mmol) reacted with 0.05 ml (0.43 mmol) of  $\text{PhSiH}_3$  for 2 h to give quantitatively  $\text{PhSiH}_2\text{NHBu}^t$ . After 18 h,  $\text{PhSiH}_2\text{NHBu}^t$  was transformed into  $\text{PhSiH}(\text{NHBu}^t)_2$ .

(b) A 25 ml Schlenk flask equipped with a magnetic stir bar was charged into the glovebox with 50 mg (0.065 mmol) of  $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$ . The flask was connected to a greaseless high vacuum line and pumped down to  $2 \times 10^{-6}$  mmHg and back filled with argon three times. Under a flash of argon, 5 ml of dry benzene, 1.3 ml (12 mmol) of *t*-butylamine and 1.4 ml (11.4 mmol) of phenylsilane were syringed into the

flask. The flask was stirred under argon for 7 h. The solvent and the excess amine were removed by means of vacuum and the residue was distilled under vacuum to yield 1.93 g (94.8%) of  $\text{PhSiH}_2(\text{NHBu}^t)$ , b.p. = 65–67°C at 0.2 mmHg.

(c) In a similar manner, 3.0 ml (27.7 mmol) of *t*-butylamine reacted with 1.1 ml (8.9 mmol) of phenylsilane in 5 ml of benzene for 12 h under reflux to yield 2.0 g (90.3%) of  $\text{PhSiH}(\text{NHBu}^t)_2$ , b.p. = 90–92°C at 0.1 mmHg.

### 2.6.1. $\text{PhSiH}_2\text{NHBu}^t$

B.p. = 65–67°C (0.2 mmHg).

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ , 200 MHz):  $\delta$  0.30–0.60 (b, 1H, NH), 1.00 (s, 9H,  $\text{CH}_3$ ), 4.98 (d,  $J = 2.8$  Hz, 2H,  $\text{SiH}_2$ ), 7.00–7.20 (m, 3H, Ph), 7.50–7.65 (m, 2H, Ph).

$^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ , 50 MHz):  $\delta$  32.5 ( $\text{CH}_3$ ), 48.9 (C– $\text{CH}_3$ ), 128.1 (CH), 129.6 (CH), 135.0 (CH), 140.0 (C–Si).

$^{29}\text{Si-NMR}$  ( $\text{C}_6\text{D}_6$ , 79.5 MHz):  $\delta$  – 39.13 (t,  $^1J_{\text{Si-H}} = 202$  Hz, *Si–H*).

### 2.6.2. $\text{PhSiH}(\text{NHBu}^t)_2$

B.p. = 90–92°C (0.1 mmHg).

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ , 200 MHz):  $\delta$  0.40–0.60 (b, 2H, NH), 1.14 (s, 18H,  $\text{CH}_3$ ), 5.35 (t,  $J = 2.8$  Hz, 1H, SiH), 7.15–7.30 (m, 3H, Ph), 7.60–7.75 (m, 2H, Ph).

$^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ , 50 MHz):  $\delta$  33.6 ( $\text{CH}_3$ ), 49.4 (C– $\text{CH}_3$ ), 128.0 (CH), 129.5 (CH), 134.43 (CH), 140.4 (C–Si).

$^{29}\text{Si-NMR}$  ( $\text{C}_6\text{D}_6$ , 79.5 MHz):  $\delta$  – 38.29 (d,  $^1J_{\text{Si-H}} = 214$  Hz, *Si–H*).

## 2.7. Reaction of diethylamine with phenylsilane

The reaction of 1.86 ml (18 mmol) of  $\text{Et}_2\text{NH}$  with 0.66 ml (5.4 mmol) of  $\text{PhSiH}_3$  was found to proceed very slowly at r.t. Although at 90°C for 20 h, the reaction gave  $\text{PhSiH}_2\text{NEt}_2$  (22%) and  $\text{PhSiH}(\text{NEt}_2)_2$  (78%). The separation of the compounds was performed by fractional distillation and the full characterization is given below.

### 2.7.1. $\text{PhSiH}_2\text{NEt}_2$

B.p. = 50–55°C (0.2 mmHg).

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ , 200 MHz):  $\delta$  0.88 (t,  $J = 7.0$  Hz, 6H,  $\text{CH}_3$ ), 2.75 (q,  $J = 7.0$  Hz, 4H,  $\text{CH}_2$ ), 5.09 (s, 2H,  $\text{SiH}_2$ ), 7.05–7.20 (m, 3H, Ph), 7.50–7.60 (m, 2H, Ph).

$^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ , 50 MHz):  $\delta$  15.2 ( $\text{CH}_3$ ), 42.0 ( $\text{CH}_2$ ), 128.0 (CH), 129.4 (CH), 134.4 (CH), 138.2 (C–Si).

$^{29}\text{Si-NMR}$  ( $\text{C}_6\text{D}_6$ , 79.5 MHz):  $\delta$  – 26.16 (t,  $^1J_{\text{Si-H}} = 203$  Hz, *Si–H*).

### 2.7.2. *PhSiH(NEt<sub>2</sub>)<sub>2</sub>*

B.p. = 145–160°C ( $5 \times 10^{-4}$  mmHg).

<sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz):  $\delta$  0.93 (t,  $J = 7.2$  Hz, 12H, CH<sub>3</sub>), 2.85 (q,  $J = 7.2$  Hz, 8H, CH<sub>2</sub>), 5.02 (s, 1H, SiH), 7.05–7.20 (m, 3H, Ph), 7.60–7.70 (m, 2H, Ph).

<sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>, 50 MHz):  $\delta$  14.9 (CH<sub>3</sub>), 39.5 (CH<sub>2</sub>), 127.6 (CH), 129.1 (CH), 134.3 (CH), 137.3 (C–Si).

<sup>29</sup>Si-NMR (C<sub>6</sub>D<sub>6</sub>, 79.5 MHz):  $\delta$  –20.15 (d,  $^1J_{\text{Si-H}} = 218$  Hz Si–H).

### 2.8. Reaction of ethylenediamine with phenylsilane

According to the typical experimental procedure, the reaction of 0.226 ml (3.38 mmol) of H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> with 0.12 ml (0.97 mmol) of PhSiH<sub>3</sub> gave PhSi(NHCH<sub>2</sub>CH<sub>2</sub>NH)(NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) quantitatively (based on NMR) in about 10 min. The solution was evaporated and the solid residue was purified under vacuum ( $10^{-6}$  mmHg) for 0.5 h, in which time it eliminates ethylene diamine and forms a mixture of oligomers.

#### 2.8.1. *PhSi(NHCH<sub>2</sub>CH<sub>2</sub>NH)(NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)*

M.p. = decompose eliminating amine forming a mixture of oligomers.

<sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz):  $\delta$  0.50–1.10 (b, 3H, NH), 1.30–1.50 (b, 2H, NH<sub>2</sub>), 2.20–2.90 (b, 8H, CH<sub>2</sub>NH), 7.00–7.30 (m, 3H, Ph), 7.50–7.70 (m, 2H, Ph).

<sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>, 50 MHz):  $\delta$  44.6 (CH<sub>2</sub>), 45.7 (CH<sub>2</sub>), 127.66 (CH), 129.0 (CH), 134.6 (CH), 138.9 (C–Si).

### 2.9. Reaction of *n*-propylamine with phenylmethylsilane

The reaction of 1.3 ml (16.2 mmol) of <sup>n</sup>PrNH<sub>2</sub> with 0.53 ml (3.9 mmol) of PhMeSiH<sub>2</sub> was found to proceed slowly at r.t. Reaction for 18 h at 90°C gave a mixture of two compounds PhMeSi(NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> (35.7%) and PhMeSiH(NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>) (64.3%). The compounds were separated by fractional distillation.

#### 2.9.1. *PhMeSi(NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>*

B.p. = 115–117°C (4 mmHg).

<sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz):  $\delta$  0.21 (s, 3H, CH<sub>3</sub>Si), 0.60–0.90 (b, 2H, NH), 0.69 (t,  $J = 7.2$  Hz, 6H, CH<sub>3</sub>), 1.10–1.40 (m, 4H, CH<sub>2</sub>), 2.55 (q,  $J = 7.0$  Hz, 4H, CH<sub>2</sub>N), 7.10–7.30 (m, 3H, Ph), 7.60–7.70 (m, 2H, Ph).

<sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>, 50 MHz):  $\delta$  –2.3 (CH<sub>3</sub>Si), 11.5 (CH<sub>3</sub>), 28.0 (CH<sub>2</sub>), 43.7 (CH<sub>2</sub>N), 125.7 (C–Si), 128.5 (CH), 129.2 (CH), 135.3 (CH).

<sup>29</sup>Si-NMR (C<sub>6</sub>D<sub>6</sub>, 79.5 MHz):  $\delta$  –17.97 (Si).

#### 2.9.2. *PhMeSiH(NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)*

B.p. = 62–66°C (2 mmHg).

<sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz):  $\delta$  0.23 (d,  $J = 3.2$  Hz, 3H, CH<sub>3</sub>Si), 0.77 (t,  $J = 7.2$  Hz, 3H, CH<sub>3</sub>), 1.10–1.40 (m, 2H, CH<sub>2</sub>), 2.50–2.70 (b, 1H, NH), 2.68 (q,  $J = 7.0$

Hz, 2H, CH<sub>2</sub>N), 5.05 (s, 1H, SiH), 7.10–7.30 (m, 3H, Ph), 7.50–7.60 (m, 2H, Ph).

<sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>, 50 MHz):  $\delta$  –2.7 (CH<sub>3</sub>Si), 11.3 (CH<sub>3</sub>), 27.7 (CH<sub>2</sub>), 44.9 (CH<sub>2</sub>N), 128.0 (CH), 129.7 (CH), 134.4 (CH), 138.3 (C–Si).

<sup>29</sup>Si-NMR (C<sub>6</sub>D<sub>6</sub>, 79.5 MHz):  $\delta$  –15.14 (d,  $^1J_{\text{Si-H}} = 198$ , Si–H).

### 2.10. Reaction of *n*-propylamine with [(Et<sub>2</sub>N)<sub>3</sub>U][BPh<sub>4</sub>]

According to the typical experimental procedure, 30 mg (0.039 mmol) of [(Et<sub>2</sub>N)<sub>3</sub>U][BPh<sub>4</sub>] reacted with 0.33 ml (4.04 mmol) of <sup>n</sup>PrNH<sub>2</sub> for 5 min. After evaporating and vacuum drying for 30 min, 0.33 ml of THF-*d*<sub>8</sub> was transferred into the NMR tube. The spectrum showed two signals; one at  $\delta$  6.7 ppm corresponding to the anionic BPh<sub>4</sub> moiety and a broad signal from 0.5–3.0 ppm, corresponding to the amido moieties. Addition of 0.01 ml of water to the tube and analyses by NMR shows that only the signals corresponding to <sup>n</sup>PrNH<sub>2</sub> are present.

### 2.11. Disproportionation reaction of phenylsilane with *PhSi(NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>* promoted by [(Et<sub>2</sub>N)<sub>3</sub>U][BPh<sub>4</sub>]

According to the typical experimental procedure, a NMR tube was charged with 10 mg of [(Et<sub>2</sub>N)<sub>3</sub>U][BPh<sub>4</sub>], 0.20 g (0.75 mmol) of PhSi(NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>, 0.18 ml (1.5 mmol) of PhSiH<sub>3</sub> and 0.33 ml of C<sub>6</sub>D<sub>6</sub>. No reaction was observed at r.t. for 24 h. The tube was then heated to 90°C for 66 h forming a mixture of compounds **1–4** (conversion of 76% based on PhSi(NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>). Trace amounts of PhSiH<sub>2</sub>–SiH<sub>2</sub>Ph were also observed in the <sup>29</sup>Si-NMR spectra. Compound **4** was distilled from the reaction mixture and characterized, whereas for compounds **1–3**, fractional distillation was not possible due to decomposition. The <sup>1</sup>H-NMR of the <sup>n</sup>Pr moiety for all the compounds appeared in the following ranges: the CH<sub>3</sub> groups between 0.6 and 1.0 ppm, the central CH<sub>2</sub> between 1.2 and 1.6 ppm and the CH<sub>2</sub> attached to the nitrogen between 2.7 and 3.1 ppm. The phenyl rings for all the compounds appear between 7.0 and 7.3 ppm and from 7.5 to 7.8 ppm. The signals of the hydrogens attached to the silicon center were assigned by <sup>1</sup>H–<sup>29</sup>Si 2D Si–H correlation, INEPT, INEPTD and <sup>29</sup>Si-NMR INVGATE spectroscopy. The yields in the mixture of the compounds were measured by <sup>1</sup>H- and <sup>29</sup>Si-NMR INVGATE spectroscopy. For a full explanation of the formation and the assignments for the compounds **1–4** see below.

**1:** <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  5.75 (s, 1H, SiH).

<sup>29</sup>Si-NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –20.92 (d,  $^1J_{\text{Si-H}} = 223$  Hz, Si–H), –30.9 (Si).

**2:** <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  5.69 (s, 1H, SiH); 5.16 (s, 2H, SiH<sub>2</sub>).

$^{29}\text{Si}$ -NMR ( $\text{C}_6\text{D}_6$ , 79.5 MHz):  $\delta$  -22.42 (d,  $^1J_{\text{Si-H}} = 221$  Hz, SiH), -26.98 (t,  $^1J_{\text{Si-H}} = 209$  Hz, SiH<sub>2</sub>), -32.3 (Si).

3:  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , 400 MHz):  $\delta$  5.09 (s, 2H, SiH).

$^{29}\text{Si}$ -NMR ( $\text{C}_6\text{D}_6$ , 79.5 MHz) for *cis* and *trans* forms:  $\delta$  -23.27 (d,  $^1J_{\text{Si-H}} = 216$  Hz, Si-H), -23.43 (d,  $^1J_{\text{Si-H}} = 216$  Hz, Si-H).

4: B.p. = 70–72°C at 0.01 mmHg.

$^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , 400 MHz):  $\delta$  0.80 (t,  $J = 7.0$  Hz, 3H, CH<sub>3</sub>), 1.45 (m, 2H, CH<sub>2</sub>), 2.80 (t,  $J = 6.8$  Hz, 2H, CH<sub>2</sub>-N) 5.23 (s, 4H, SiH<sub>2</sub>), 7.10–7.40 (m, 6H, Ph) 7.5–7.8 (m, 4H, Ph).

$^{13}\text{C}$ -NMR ( $\text{C}_6\text{D}_6$ , 50 MHz):  $\delta$  11.5 (CH<sub>3</sub>), 27.5 (CH<sub>2</sub>), 43.9 (CH<sub>2</sub>N), 127.9 (CH), 130.0 (CH), 134.8 (CH), 138.4 (C-Si).

$^{29}\text{Si}$ -NMR ( $\text{C}_6\text{D}_6$ , 79.5 MHz):  $\delta$  -24.17 (t,  $^1J_{\text{Si-H}} = 206$  Hz, Si-H<sub>2</sub>).

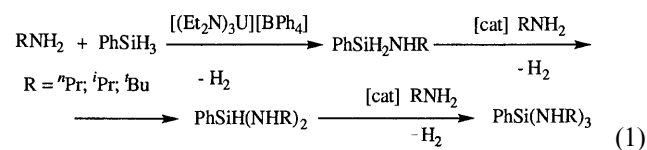
MS = 270 [M - H<sup>+</sup>, 12], 242 [M - C<sub>2</sub>H<sub>5</sub><sup>+</sup>, 100], 164 [M - SiH<sub>2</sub>Ph<sup>+</sup>, 20], 107 (PhSiH<sub>2</sub><sup>+</sup>, 50).

### 2.12. Reaction between phenylsilane and PhSiH(NHBut)<sub>2</sub>

According to the typical experimental procedure, the reaction of 0.10 g (0.43 mmol) of PhSiH(NHBut)<sub>2</sub> with 0.05 ml (0.43 mmol) of PhSiH<sub>3</sub> in 0.33 ml of benzene was stirred for 95 h at r.t. to obtain PhSiH<sub>2</sub>NHBut' in a 50% yield.

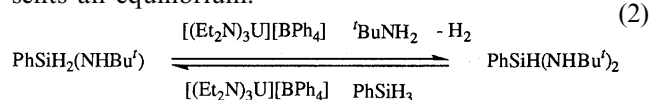
## 3. Results and discussion

The reaction of <sup>n</sup>PrNH<sub>2</sub> and PhSiH<sub>3</sub> at 20°C in THF in the presence of [(Et<sub>2</sub>N)<sub>3</sub>U][BPh<sub>4</sub>] (310:58:1 amine:silane:uranium catalyst ratio), afforded a mixture of PhSiH(NHPr<sup>n</sup>)<sub>2</sub> and PhSi(NHPr<sup>n</sup>)<sub>3</sub> with the concomitant elimination of dihydrogen (Eq. (1)). By using a large excess of amine, the silane was totally converted into products and the relative ratios of the di- and triaminosilanes were found to be 63:37, 48:52 or 0:100 after either 2, 4 or 10 h, respectively. Interestingly, the monoaminosilane, PhSiH<sub>2</sub>(NHPr<sup>n</sup>), was not detected, indicating that in this compound the Si-H hydrides are more reactive than those of the starting PhSiH<sub>3</sub> [18]. In a similar way, the same reaction catalyzed by H<sub>2</sub>PtCl<sub>6</sub> allows one to produce only the bisaminosilane, PhSiH(NHPr<sup>n</sup>)<sub>2</sub>, with no traces of the corresponding monoaminosilane, or the triaminosilane PhSi(NHPr<sup>n</sup>)<sub>3</sub>, even by heating the bisaminosilane product with a large excess of amine [12d].

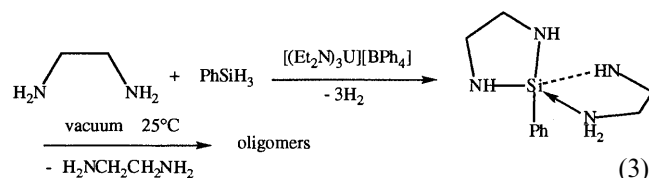


The room temperature reaction of <sup>i</sup>PrNH<sub>2</sub> and PhSiH<sub>3</sub> (66:41:1 amine:silane:uranium catalyst ratio) gave after 23 h, dihydrogen and a mixture of PhSiH<sub>2</sub>NHPr<sup>i</sup> (33%) and PhSiH(NHPr<sup>i</sup>)<sub>2</sub> (56%) with a total conversion of 89% for PhSiH<sub>3</sub>. Heating the products of the reaction mixture after the 23 h to 90°C did not cause any change in the ratio of the products. When the amine was used in greater excess (4:1 amine:silane), the bisaminosilane PhSiH(NHPr<sup>i</sup>)<sub>2</sub> was accomplished at room temperature in quantitative yield after 56 h. This same reaction could be achieved in 5 h at room temperature by removing the dihydrogen gas by means of a slight vacuum (0.1 mmHg). This result clearly indicates that the aminosilanes are in equilibrium. It is important to point out that the formation of the triaminosilane PhSi(NHPr<sup>i</sup>)<sub>3</sub> in this system was never plausible due to the bulkiness of the amine.

For the bulky <sup>t</sup>BuNH<sub>2</sub>, the sole organic product detected from the reaction with PhSiH<sub>3</sub> (100% yield) was found to be PhSiH<sub>2</sub>NHBut', which is attained quantitatively after 2 h at room temperature (90:33:1 amine:silane:uranium catalyst ratio). After 18 h, this monoaminosilane reacted further with the excess amine to produce an additional equivalent of dihydrogen and the bisaminosilane PhSiH(NHBut')<sub>2</sub> exclusively. During the first 2 h no PhSiH(NHBut')<sub>2</sub> was detected, indicating that the second coupling reaction is much slower than that of the first coupling. This latter compound could be transformed slowly into the mono aminosilane, PhSiH<sub>2</sub>NHBut', after the addition of one equivalent of PhSiH<sub>3</sub> to PhSiH(NHBut')<sub>2</sub> (50% yield after 95 h at 20°C) (Eq. (2)), again indicating that the production of aminosilanes by the complex [(Et<sub>2</sub>N)<sub>3</sub>U][BPh<sub>4</sub>] represents an equilibrium.



A primary diamine was also found to react with phenylsilane in a unique form. When ethylenediamine H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> was treated with PhSiH<sub>3</sub> in the presence of the catalyst (260:75:1 amine:silane:uranium catalyst ratio) after 10 min at room temperature, all the PhSiH<sub>3</sub> was consumed yielding dihydrogen and the spiro chelated complex PhSi(η<sup>2</sup>-NHCH<sub>2</sub>CH<sub>2</sub>NH)(η<sup>2</sup>-NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) quantitatively (yield > 99%). When the spiro product was heated at 25°C under vacuum conditions, ethylenediamine was removed and the starting spiro aminosilane PhSi(η<sup>2</sup>-NHCH<sub>2</sub>CH<sub>2</sub>NH)(η<sup>2</sup>-NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) was transformed into a mixture of oligomers (Eq. (3)).



From these results it can be concluded that the reactivity of primary amines  $\text{RNH}_2$  for the formation of aminosilanes with  $\text{PhSiH}_3$ , catalyzed by the cationic uranium complex  $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$  is strongly dependent on the steric hindrance of R, following the order primary > secondary > tertiary.

Secondary amines and secondary silanes were found to be less reactive than the corresponding primary amine and silanes. Thus, the reaction of  $\text{Et}_2\text{NH}$  with  $\text{PhSiH}_3$  (138:41:1 amine:silane:uranium catalyst ratio) was very slow when carried out at room temperature (yield < 5% after 24 h), although at  $90^\circ\text{C}$   $\text{H}_2$  and a mixture of  $\text{PhSiH}(\text{NEt}_2)_2$  (78%) and  $\text{PhSiH}_2\text{NEt}_2$  (22%), respectively, were obtained after 20 h. Interestingly, no reaction was perceived between  $(i\text{Pr})_2\text{NH}$  and  $\text{PhSiH}_3$ , presumably because of the steric hindrance of the amine. Regarding the effect of the silane, under the same conditions,  $n\text{PrNH}_2$  reacted with the secondary silane  $\text{PhSiMeH}_2$  (125:30:1 amine:silane:uranium catalyst ratio) much slower than with the primary silane; at  $90^\circ\text{C}$  and after 18 h the reaction yielded  $\text{H}_2$ ,  $\text{PhSiHMe}(\text{NHPr}^n)$  (64%) and  $\text{PhSiMe}(\text{NHPr}^n)_2$  (36%).

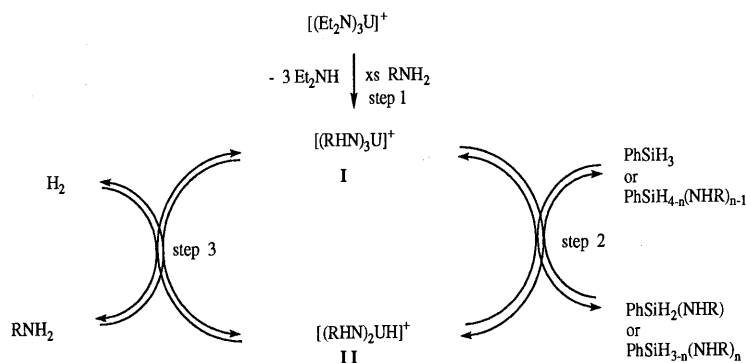
Most interestingly, the cationic complex  $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$  reacted with an excess of  $\text{PhSiH}_3$  in the absence of amine, to give only one equivalent of the corresponding aminosilane  $\text{PhSiH}_2\text{NEt}_2$ , with trace formation of the homodehydrogenative coupling product of the silane. The stoichiometric reaction of  $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$  and  $\text{PhSiH}_3$  also led to the formation of one equivalent of  $\text{PhSiH}_2\text{NEt}_2$  and a new uranium complex, presumably  $[(\text{Et}_2\text{N})\text{UH}][\text{BPh}_4]$ . These results indicate that the active intermediate should be a monohydride complex since no other amido moieties were found to react with the phenylsilane. To the best of our knowledge, such synthesis of a metal hydride by treatment of the corresponding amide with a silane has been recently reported only for a zirconium complex, while similar exchange reactions were observed with boranes, alanes and stannanes [19]. These results strongly suggested that an uranium complex with a metal–silicon bond is not an active operative intermediate in the catalytic dehydrogenative coupling reaction (only traces for the

dehydrogenative coupling products). Therefore, the mechanism operating here should be different from that proposed for the dehydrogenative coupling of ammonia with primary silanes catalyzed by  $\text{Cp}_2\text{TiMe}_2$ , in which the proposed key intermediate contains a Ti–Si bond, corroborating, for that case, the competing homodehydrocoupling of  $\text{RSiH}_3$  [13].

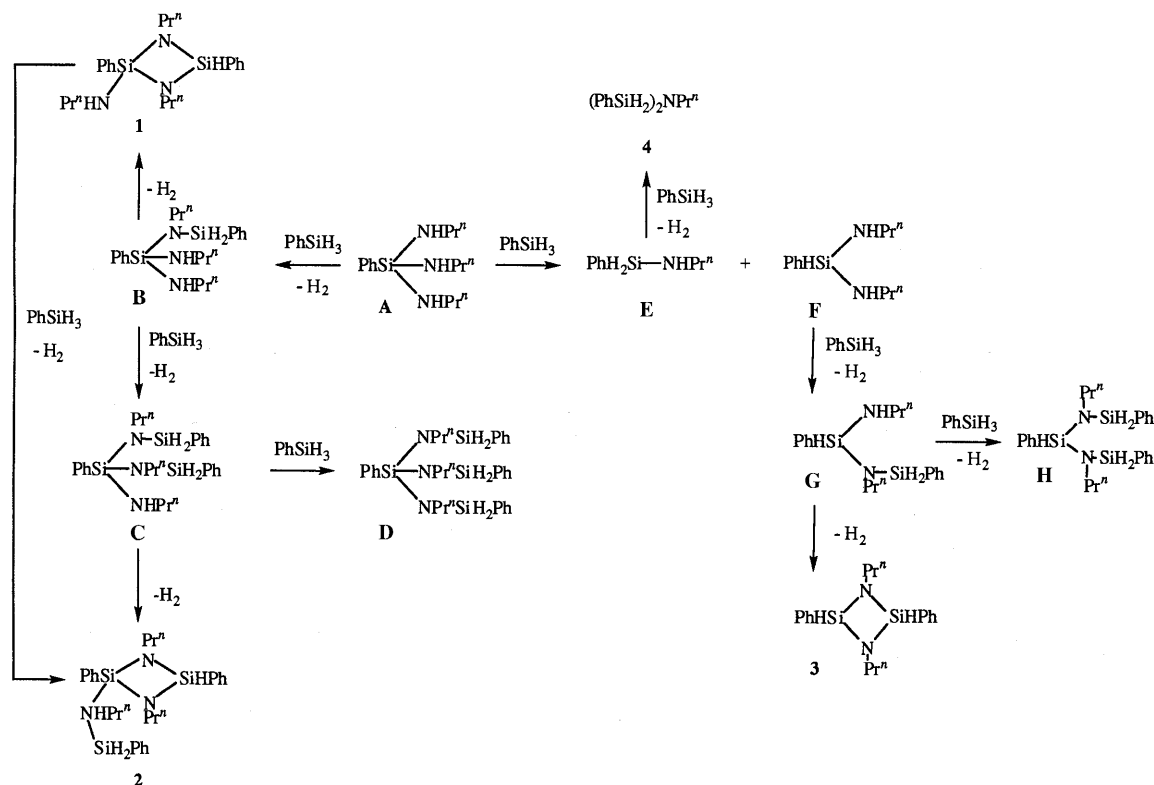
A plausible mechanism for the dehydrocoupling of amines with silanes promoted by the cationic complex  $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$  is described in Scheme 1. The first step in the proposed mechanism is the transamination reaction of  $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$  with  $\text{RNH}_2$  giving  $[(\text{NHR})_3\text{U}][\text{BPh}_4]$  (**I**) (step 1). This reaction step has been carried out (see Section 2) by reacting the cationic complex  $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$  with an excess of  $n\text{PrNH}_2$ , removing all the volatiles and quenching the product with water. We have found that only  $n\text{PrNH}_2$  is observed with no trace amounts of the corresponding  $\text{Et}_2\text{NH}$ . The  $^1\text{H-NMR}$  spectra showed that this reaction was indeed very fast at  $20^\circ\text{C}$  and that the three amido groups  $\text{NHR}$  were in rapid exchange with the free amine  $\text{RNH}_2$ . Complex **I** then reacts with  $\text{PhSiH}_3$  to afford the monoaminosilane  $\text{PhSiH}_2\text{NHR}$  and presumably the corresponding hydride  $[(\text{NHR})_2\text{UH}][\text{BPh}_4]$  (**II**) (step 2). The last step of the catalytic cycle (step 3) is the reaction of **II** and the amine, regenerating **I** with the concomitant elimination of dihydrogen.

The different polyaminosilanes  $\text{PhSiH}_{3-n}(\text{NHR})_n$  are obtained by replacing  $\text{PhSiH}_3$  with  $\text{PhSiH}_{4-n}(\text{NHR})_{n-1}$  in step 2. Steps 2 and 3 are in equilibrium, as shown by the influence of the dihydrogen pressure and the stoichiometry of the reactants on the course of the reaction.

In the presence of an excess of amine the reactive hydrogens were found to be those of the silane moiety, therefore it was interesting to study the reactivity of the aminosilane products towards the silane. Thus, the reaction of  $\text{PhSi}(\text{NHPr}^n)_3$  with an excess of  $\text{PhSiH}_3$ , in the absence of amine, was considered in order to determine a possible equilibrium and/or a tailoring approach to specific products by activation of the amine hydrogens of the aminosilane. Hence,  $\text{PhSi}(\text{NHPr}^n)_3$  (**A**) re-



Scheme 1. Plausible mechanism for the coupling of amine with silanes promoted by  $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$ .



Scheme 2. Plausible pathways for the production of compounds 1–4.

acted at 90°C with an excess of  $\text{PhSiH}_3$  in the presence of  $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$  to give a mixture of compounds 1–4.

To understand how only four compounds were obtained we should describe theoretically the formation of all possible compounds as outlined in Scheme 2. Starting from compound A, the reaction with  $\text{PhSiH}_3$  produced compound B, which reacts intramolecularly to yield 1 in 38% yield. Compound B may also react with another molecule of  $\text{PhSiH}_3$  yielding compound C that undergoes an intramolecular elimination of dihydrogen affording compound 2 in 23% yield. Compound 2 can also be acquired in one step by the reaction of 1 with  $\text{PhSiH}_3$  with the concomitant elimination of dihydrogen. The possibility that compound C reacts with another molecule of  $\text{PhSiH}_3$  to obtain compound D was found to be not operative, presumably due the bulkiness of the system. In second route compound A can react with  $\text{PhSiH}_3$ , if the organometallic hydride reacts with an amine (the reverse of step 2 in Scheme 1), to produce two compounds E and F. Compound E was not detected although its product, which is obtained by the consecutive reaction of E with another molecule of  $\text{PhSiH}_3$ , yields compound 4 in 9% yield. In a similar way, compound F reacts with another molecule of  $\text{PhSiH}_3$  producing compound G, which may react again in an intermolecular fashion with another  $\text{PhSiH}_3$  affording compound H, or may react in an intramolecu-

lar fashion resulting in compound 3 (6% yield).  $^{29}\text{Si}$ -NMR spectroscopy (INEPT, INEPTD and INVGATE) and Si–H CORRELATION is a rather simple and a straight forward methodology to account for the number of the different  $\text{SiH}_3$ ,  $\text{SiH}_2$ ,  $\text{SiH}$  and quaternary Si groups and their signal integrations (to allow a rapid recognition of what moieties belongs to what type molecule) (Fig. 1). Spectroscopically, neither compounds B, C, or D were found present at the reaction mixture. In compound B, C, and D an integration of 1:1, 2:1 and 3:1 for the corresponding  $\text{SiH}_2$ :Si (quaternary) groups are expected, whereas for compounds 1, a ratio of 1:1 for the  $\text{SiH}$ :Si groups and for compound 2 a ratio of 1:1:1 for the  $\text{SiH}_2$ : $\text{SiH}$ :Si groups are expected, respectively, as observed in the  $^{29}\text{Si}$ -NMR (Fig. 1).

Thus, in the reaction of propylamine with an excess of phenylsilane, compounds 1 and 2, that are acquired by the activation of the N–H bonds by the uranium–hydride complex, are obtained preferentially as compared with the yields obtained for compounds 3 and 4. Compounds 3 and 4 are afforded by the activation of the Si–N bond (reverse step 2 in Scheme 1). It is noteworthy to point out that the reaction of  $\text{PhSi}(\text{NHPr}^n)_3$  with  $\text{PhSiH}_3$  was found to be operative only at high temperatures in contrast to  $\text{PhSiH}(\text{NHBU}^n)_2$  (Eq. (2)), presumably due to the bulkiness of the former having three amido groups as compared with two amido groups of the latter.

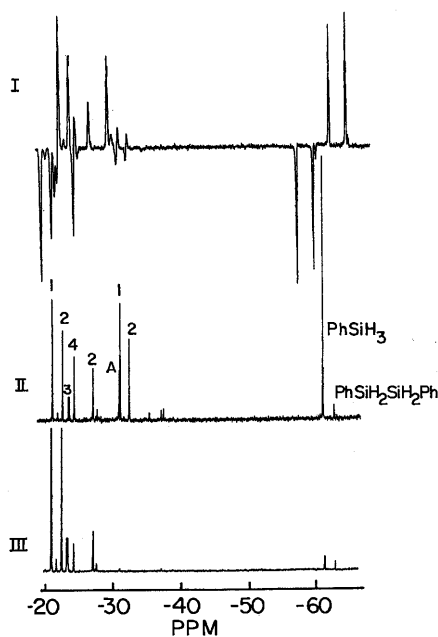


Fig. 1.  $^{29}\text{Si}$ -NMR INEPT (I), INVGATE (II) and INEPTRD (III) of the mixture of compounds 1–4. The number and letter over the signals at spectra II concur with the corresponding compounds as described in Scheme 2.  $\text{SiH}_3$ ,  $\text{SiH}_2$  and  $\text{SiH}$  groups appear as quartet, triplet and doublet, respectively, in the INEPT (I) spectra. The integration of the different compounds are obtained by the corresponding measurements in the INVGATE (II) spectra. Quaternary Si groups are not observed under INEPTRD (III) experiments.

The results here presented offer an alternative route for the dehydrogenative coupling of amines with silanes through a mechanism consisting of activation of an amido ligand by a silane, producing the aminosilane and an organometallic hydride, which can be recycled by addition of amine. This is the first time that this type of mechanism has been observed experimentally, corroborating the previous thermodynamic theoretical studies.

## Acknowledgements

A.K.D. thanks the Technion for a Postdoctoral Fellowship. M.E. and M.S.E. thanks the Israel Ministry of Sciences and the French Ministère des Affaires Étrangères for funding the Arc en Ciel/Keshet Project No 50. This research was supported by the Henri Gutwirth Fund for the Promotion of Research at the Technion and by the Technion V.P.R. Fund.

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