Electronic Supporting Information

Stoichiometric and catalytic Si-N bond formation using the p-block base $Al(NMe_2)_3$

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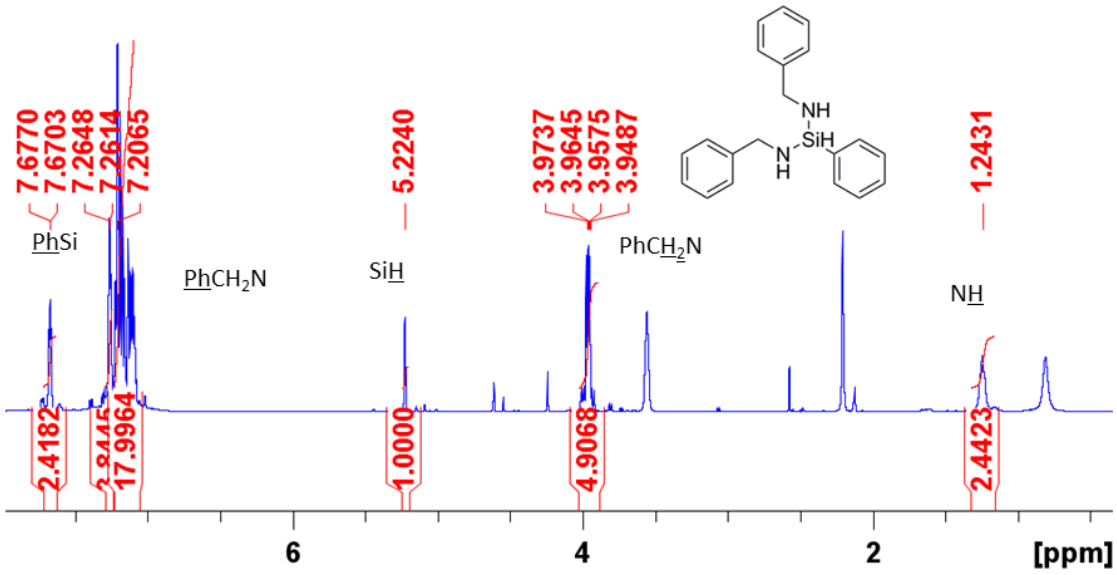
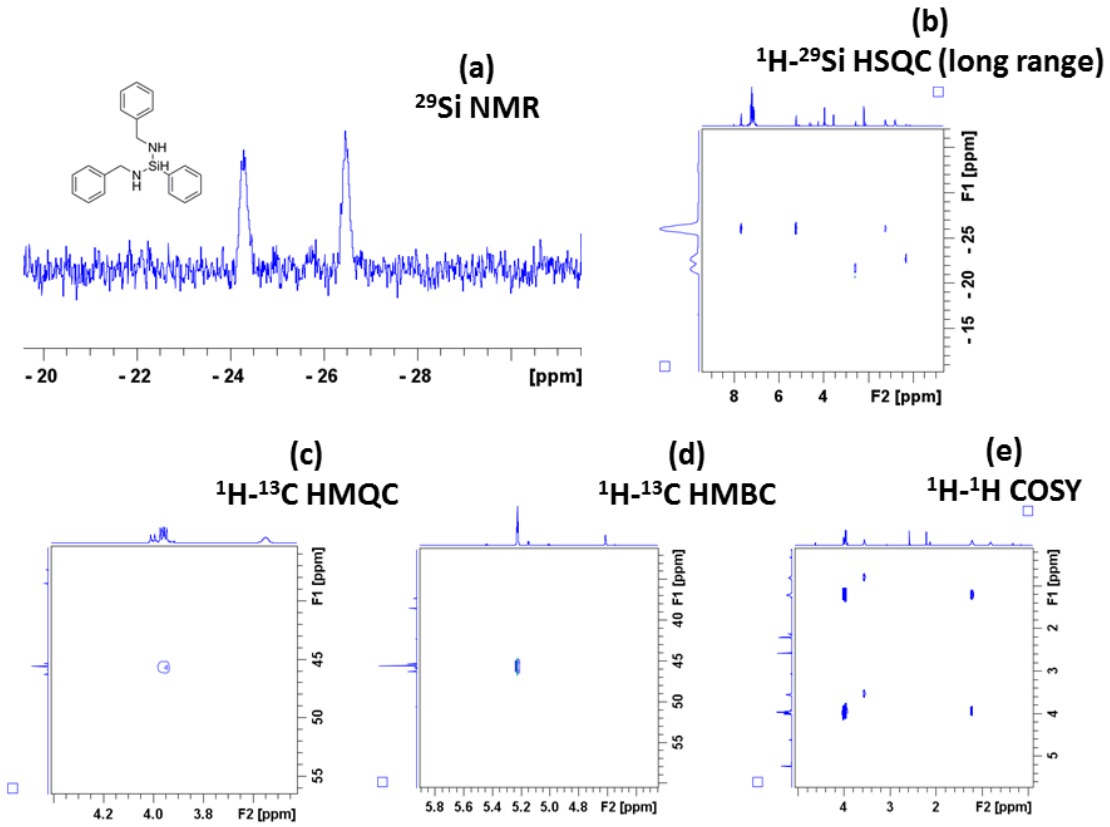
General Experimental Details of NMR Spectroscopic Studies

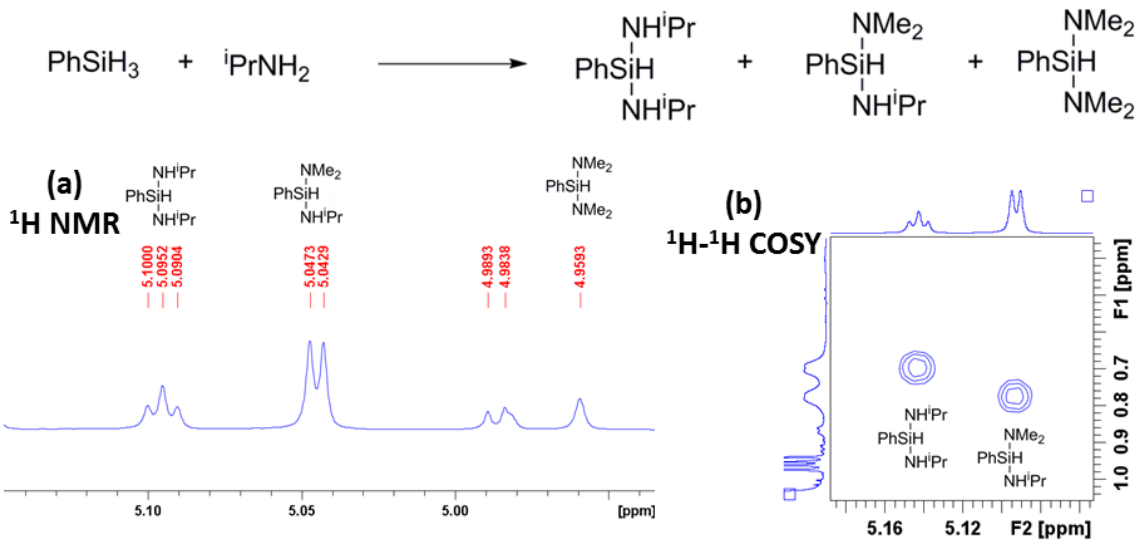
NMR spectra were acquired using a Bruker Avance BB500 MHz TCI Cryoprobe Spectrometer. Samples were dissolved in d_8-toluene or d_8-THF which had been dried over a sodium mirror. ^{29}Si NMR spectra were referenced to an internal standard of TMS (δ = 0ppm). ^{27}Al NMR spectra were referenced to an internal standard of $AlCl_3.6H_2O$ (δ = 0 ppm).



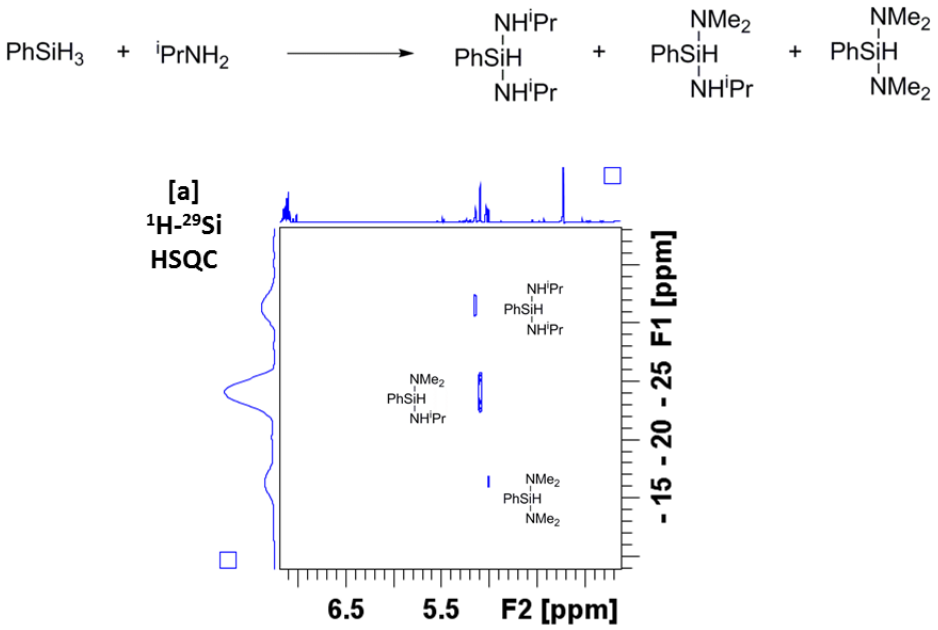
ESI 1a ^1H NMR spectrum (d_8-toluene) of the reaction between $PhSiH_3$ (1 equiv) and $BnNH_2$ (3 equiv) catalysed by $Al(NMe_2)_3$ (10 mol%) showing the formation of $PhSiH(BnNH)_2$.



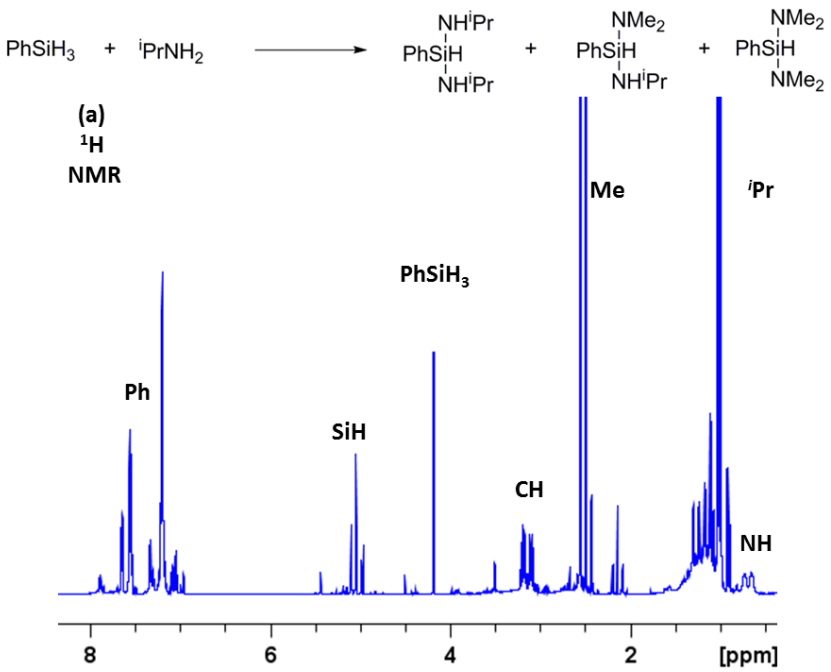
ESI 1b (a) ^{29}Si proton coupled NMR spectrum showing doublet of novel product PhSiH(BnNH)$_2$. (b) ^{1}H-^{29}Si HSQC long range spectrum correlating the silicon signal bonded to Ph, H and NH groups. (c) ^{1}H-^{13}C HMQC spectrum correlating the signals for the benzyl CH_2 group with a ^{13}C signal at δ = 45 ppm. (d) ^{1}H-^{13}C HMBC spectrum correlating the CH_2 ^{13}C signal (δ = 45 ppm) to the SiH (see ESI 1c). (e) ^{1}H-^{1}H COSY spectrum showing the correlation between the CH_2 and NH groups.



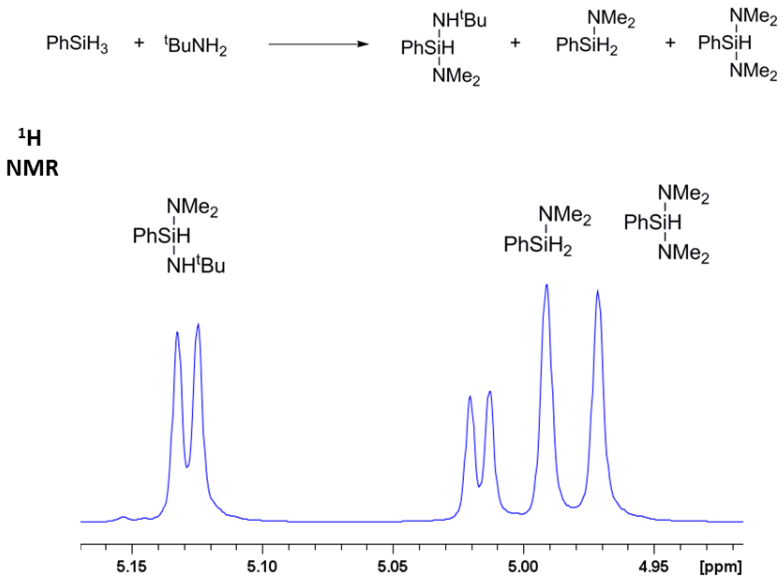
ESI 2a (a) ^{1}H NMR spectrum (d_8-toluene) showing the silyl hydride region for the products PhSiH(HN^{i}Pr)$_2$, PHSiH(HN^{i}Pr)(NMe$_2$) and PhSiH(NMe$_2$)$_2$ formed by the reaction between PhSiH$_3$ (1 equiv) and ^{i}PrNH$_2$ (1.5 equiv) catalysed by Al(NMe$_2$)$_3$ (10 mol%). (b) ^{1}H-^{1}H COSY spectrum correlating the Si-H and N-H resonances.



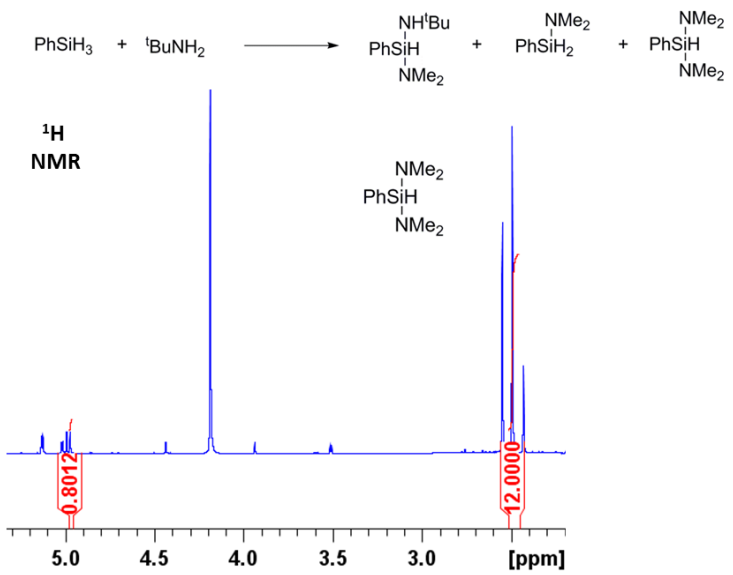
ESI 2b (a) ^{1}H-^{29}Si HSQC NMR spectrum (d_8-toluene) showing the three silyl hydride (SiH) signals correlating with the three ^{29}Si environments of the products PhSiH(HN^{i}Pr)$_2$, PHSiH(HN^{i}Pr)(NMe$_2$) and PhSiH(NMe$_2$)$_2$ formed by the reaction between PhSiH$_3$ (1 equiv) and ^{i}PrNH$_2$ (1.5 equiv) catalysed by Al(NMe$_2$)$_3$ (10 mol%).



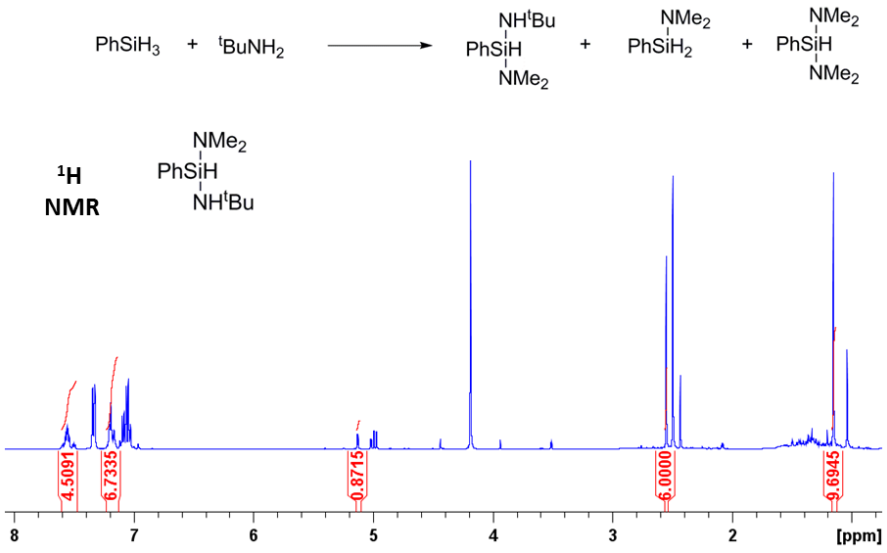
ESI 2c (a) ^{1}H NMR spectrum (d_8-toluene) showing the different regions of the products formed by the reaction between $PhSiH_3$ (1 equiv) and $^{i}PrNH_2$ (1.5 equiv) catalysed by $Al(NMe_2)_3$ (10 mol%).



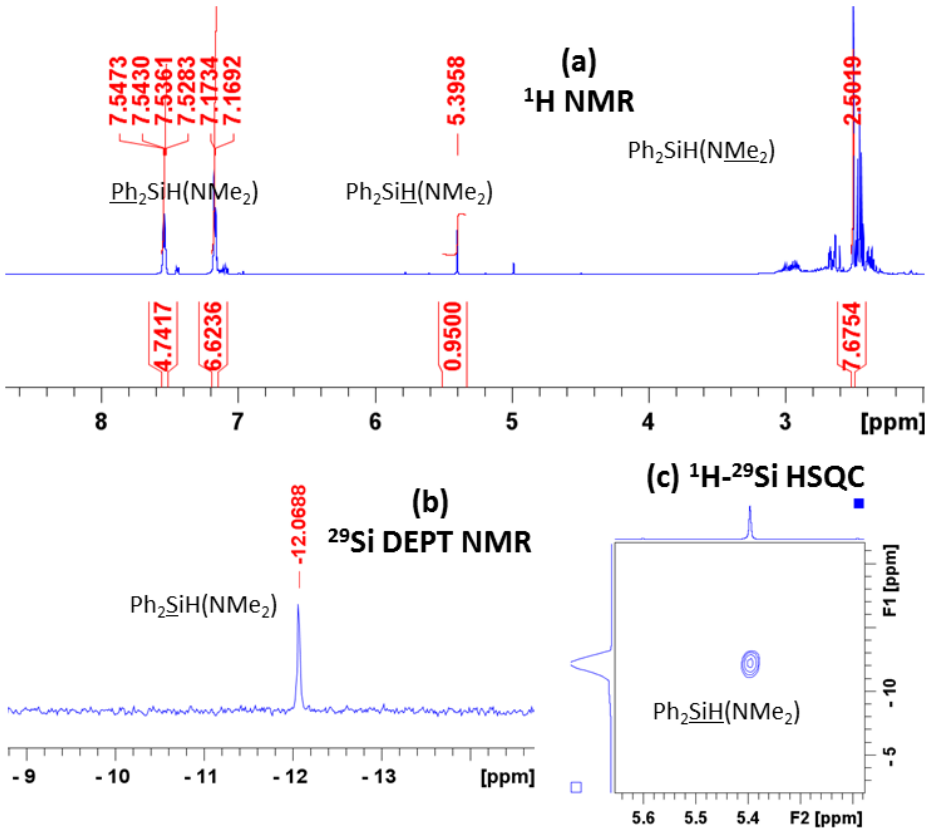
ESI 3a ^{1}H NMR spectrum (d_8-toluene) showing the silyl hydride region for the products $PhSiH(HN^{t}Bu)(NMe_2)$, $PhSiH_2(NMe_2)$ and $PhSiH(NMe_2)_2$ formed by the reaction between $PhSiH_3$ (1 equiv) and $^{t}BuNH_2$ (2 equiv) catalysed by $Al(NMe_2)_3$ (10 mol%).



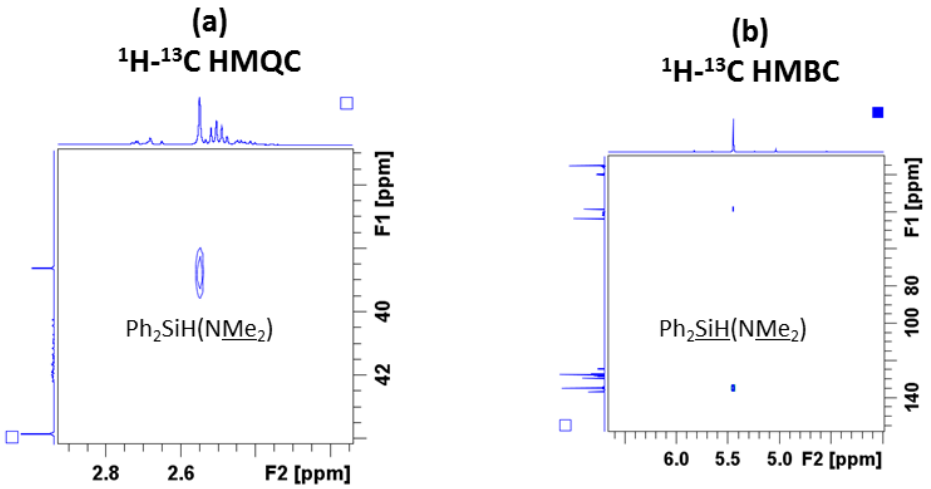
ESI 3b ^{1}H NMR spectrum (d_8-toluene) showing the product $PhSiH(NMe_2)_2$ from the reaction between $PhSiH_3$ (1 equiv) and ^{t}BuNH$_2$ (2 equiv) catalysed by $Al(NMe_2)_3$ (10 mol%).



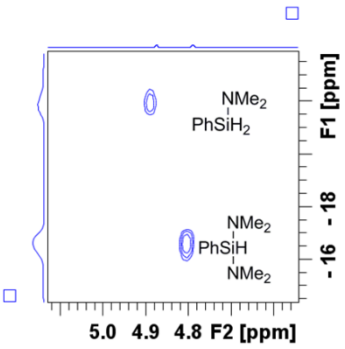
ESI 3c ^{1}H NMR spectrum (d_8-toluene) showing the product $PhSiH(HN^tBu)(NMe_2)$ from the reaction between $PhSiH_3$ (1 equiv) and ^{t}BuNH$_2$ (2 equiv) catalysed by $Al(NMe_2)_3$ (10 mol%).



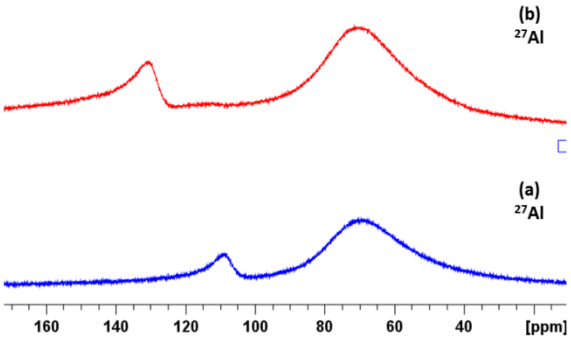
ESI 4a (a) ^{1}H NMR spectra (d_8-toluene) of the reaction between Ph_2SiH_2, Et_2NH and $Al(NMe_2)_3$ showing the formation of $Ph_2SiH(NMe_2)$. (b) ^{29}Si DEPT45 spectrum showing diagnostic peak for $Ph_2SiH(NMe_2)$ at -12ppm . (c) ^{1}H-^{29}Si HSQC spectrum correlating the diagnostic Si-H resonance at δ = 5.40 ppm with the ^{29}Si signal at δ = -12 ppm bond in $Ph_2SiH(NMe_2)$.



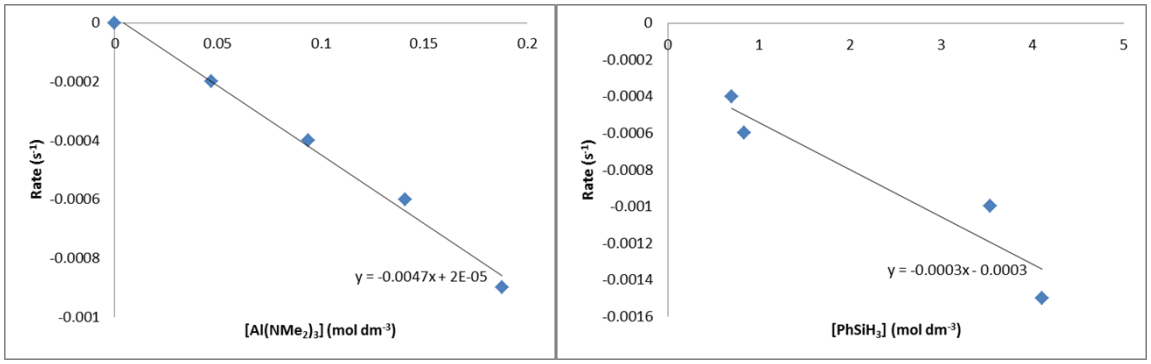
ESI 4b (a) ^{1}H-^{13}C HMQC correlating the CH_3 (^{1}H δ= 2.55 ppm) with the ^{13}C signal (δ = 38.4 ppm) in $Ph_2SiH(NMe_2)$. (b) ^{1}H-^{13}C HMBC correlating the Si-H proton (δ = 5.40 ppm) and the NMe_2 ^{13}C signal (38.4 ppm) in $Ph_2SiH(NMe_2)$.



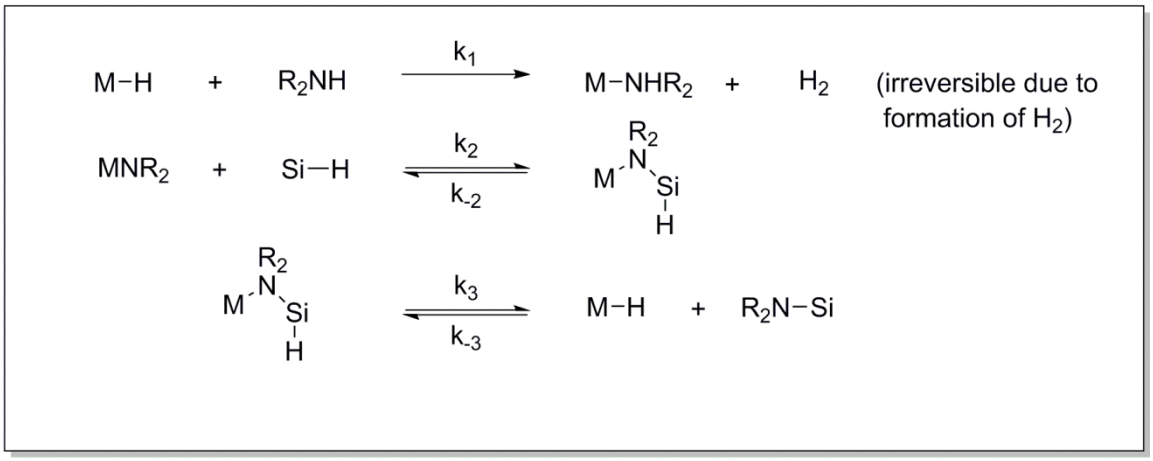
ESI 5a ^{1}H-^{29}Si HSQC NMR spectrum (d_8-toluene) showing the correlation of two ^{1}H silyl hydride (Si-H) signals and the ^{29}Si signals of the two products $PhSiH(NMe_2)_2$ and $PHSiH(NMe_2)$ (δ = -22 ppm and -17 ppm respectively) formed by the stoichiometric reaction between $PhSiH_3$ and $Al(NMe_2)_3$.



ESI 5b Overlay of ^{27}Al spectra (toluene-d_8) (a) $Al(NMe_2)_3$ (b) $Al(NMe_2)_3$ and $PhSiH_3$. The broad signal (δ = 70 ppm) arises from the probe.



ESI 6 (a) Initial rates of loss of $PhSiH_3$ *vs*. pre-catalyst loading for the 1 : 2 reaction of $PhSiH_3$ with Et_2NH, and (b) initial rates of loss of $PhSiH_3$ vs. silane concentration with 10 mol % loading of pre-catalyst. The straight lines drawn are the best-fit ones.



$$\frac{+d}{dt}\left[R_2N{-}Si\right] = k_3\left[\,M{-}\mathrm{N}(R_2){-}\mathrm{Si}(H)\,\right] - k_{-3}\left[M{-}H\right]\left[R_2N{-}Si\right] \qquad \textbf{eqn.ESI 1}$$

$\left[M{-}H\right]$ concentration (Steady State)

$$k_1\left[M{-}H\right]\left[R_2NH\right] + k_{-3}\left[M{-}H\right]\left[R_2N{-}Si\right] = k_3\left[\,M{-}\mathrm{N}(R_2){-}\mathrm{Si}(H)\,\right] \qquad \textbf{eqn.ESI 2}$$

$$\Longrightarrow \quad \frac{+d}{dt}\left[R_2N{-}Si\right] = k_1\left[M{-}H\right]\left[R_2NH\right]$$ by combining equations **ESI 1** and **ESI 2**

ESI 7a Steady-state analysis of M-H reaction

Asssuming the second step in **ESI 1a** is rate determining

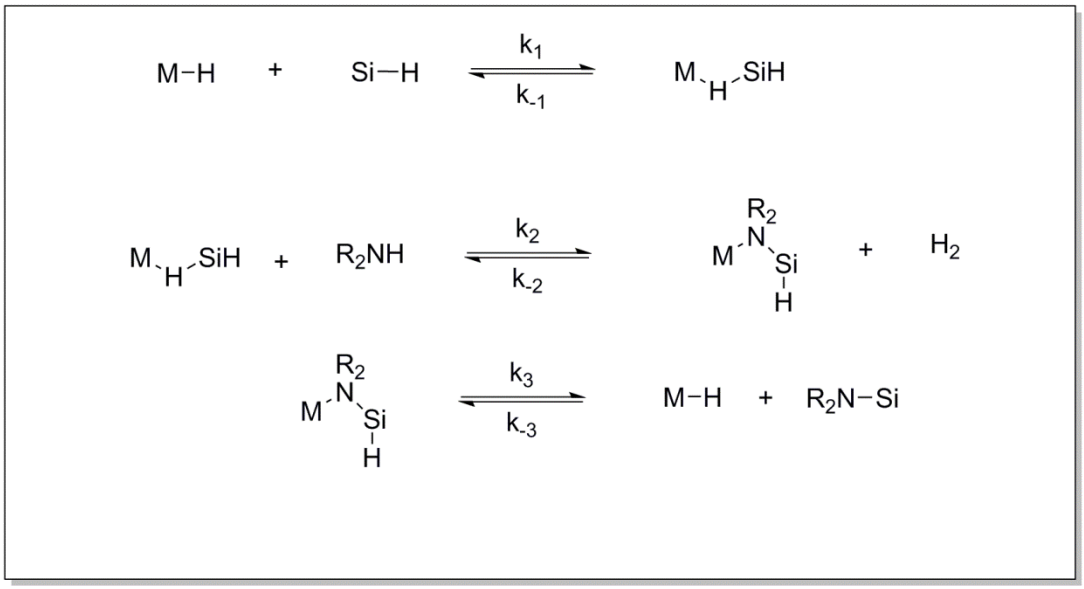
$$\Longrightarrow \quad \frac{+d}{dt}\left[R_2N{-}Si\right] = k_2\left[MNR_2\right]\left[Si{-}H\right] - k_{-2}\left[\begin{array}{c} R_2 \\ | \\ M{-}N \\ | \\ Si \\ | \\ H \end{array}\right] \qquad \textbf{eqn.ESI 3}$$

$\left[MNR_2\right]$ concentration (Steady State)

$$k_1\left[M{-}H\right]\left[R_2NH\right] + k_{-2}\left[\begin{array}{c} R_2 \\ | \\ M{-}N \\ | \\ Si \\ | \\ H \end{array}\right] = k_2\left[MNR_2\right]\left[Si{-}H\right] \qquad \textbf{eqn.ESI 4}$$

$$\Longrightarrow \quad \frac{+d}{dt}\left[R_2N{-}Si\right] = k_1\left[M{-}H\right]\left[R_2NH\right]$$ by combining equations **ESI 3** and **ESI 4**

ESI 7b Steady-state analysis assuming the second step is rate determining.



$$\frac{+d}{dt}\left[R_2N-Si\right] = k_3\left[\begin{array}{c} R_2 \\ | \\ M-N \\ | \\ Si \\ | \\ H \end{array}\right] - k_{-3}\left[M-H\right]\left[R_2N-Si\right] \qquad \textbf{eqn.ESI 5}$$

$\left[M-H\right]$ concentration (Steady State)

$$k_1\left[M-H\right]\left[Si-H\right] = k_3\left[\begin{array}{c} R_2 \\ | \\ M-N \\ | \\ Si \\ | \\ H \end{array}\right] - k_{-3}\left[M-H\right]\left[R_2N-Si\right] \qquad \textbf{eqn.ESI 6}$$

$$\Longrightarrow \quad \frac{+d}{dt}\left[R_2N-Si\right] = k_1\left[M-H\right]\left[Si-H\right]$$ by combining equations **ESI 5** and **ESI 6**

ESI 8 Steady-state analysis of silyl mechanism.