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Supporting Information for

Catalytic N–Si Coupling as a Method for α-Silylene Elimination: A Potential Tool for Organosilane Synthesis

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General considerations

All manipulations were performed under a nitrogen atmosphere with dry, oxygen-free solvents using an M. Braun glovebox or standard Schlenk techniques. Benzene-*d*$_6$ was purchased from Cambridge Isotope Laboratory and then degassed and dried over NaK alloy. Fluorosil was heated under vacuum to temperatures over 180 °C for 12 hours. NMR spectra were recorded with a Bruker AXR 500 MHz or Varian 500 MHz spectrometer in benzene-*d*$_6$; reported resonances are with reference to the residual solvent resonance (δ 7.16). GCMS traces were recorded using a Varian 3900 GC with a Varian Saturn 2100T GCMS. The starting materials $(N_3N)ZrNMe_2$ ($N_3N = N(CH_2CH_2NSiMe_3)_3^{3-}$) (**1**),[1] $[(Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2]Zr$ (**2**),[2] $(N_3N)ZrCl$,[2] *N,N*-dimethyl-1-phenylsilanamine, *N,N,N',N'*-tetramethyl-1-phenylsilanediamine[3] and 1,3-Bis(2,4,6-trimethylphenyl)imidazolinium chloride (IMes HCl)[4] were prepared according to the literature procedure. $(N_3N)ZrNH^iPr$ was synthesized by the addition of 1 eq of $^iPrNH_2$ to **2** in benzene, followed by removal of solvent. The dehydrohalogenation of IMes HCl to yield 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) was done by using 3 eq of sodium hydride and catalytic amounts of potassium tert-butoxide in dry THF. Phenylsilane-*d*$_3$ was prepared through reduction of trichlorophenylsilane with lithium aluminum deuteride and distillation from diglyme. All other chemicals were purchased from commercial suppliers and dried by conventional means.

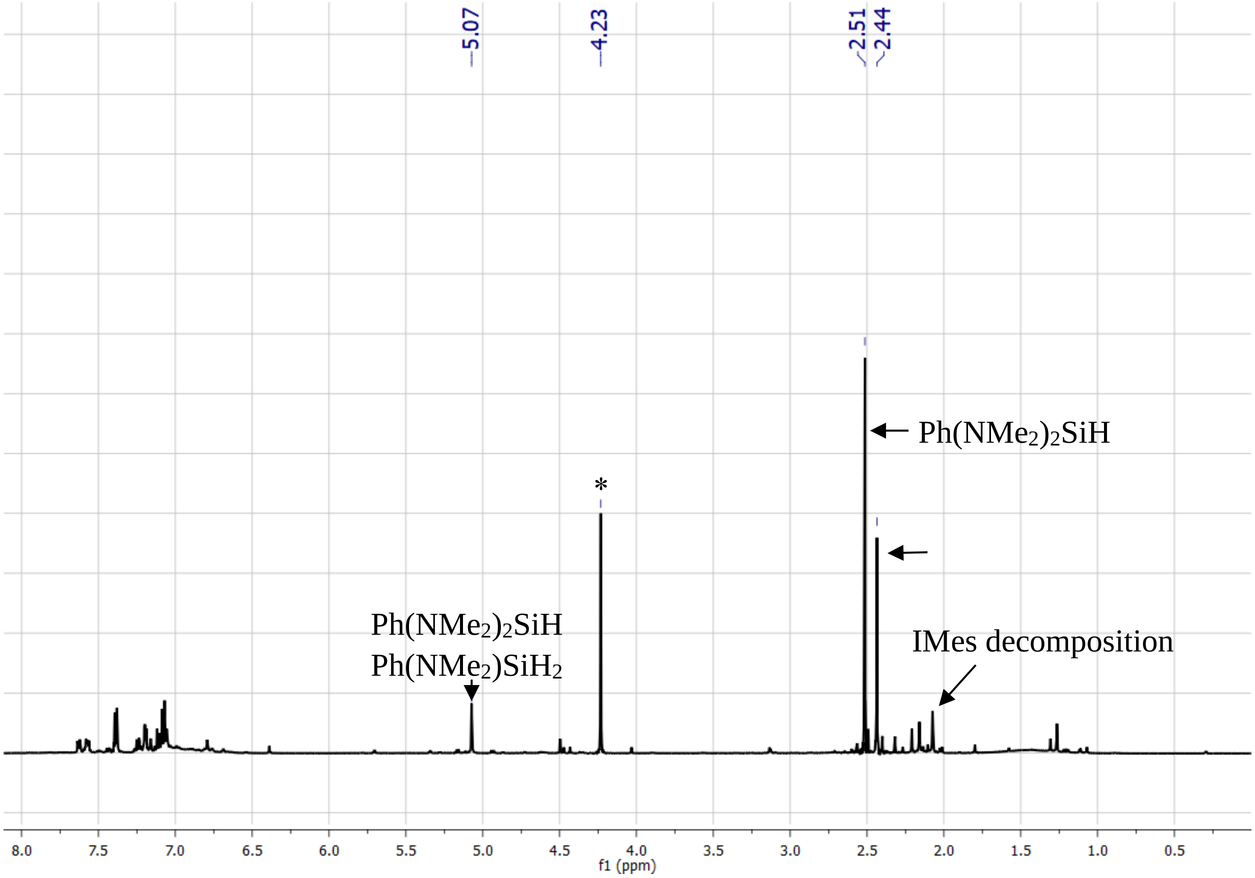
Catalytic experiments:

All reactions were conducted using a J-Young type polytetrafluoroethylene (PTFE)-valved NMR tube in benzene-*d*$_6$. Upon addition and obtaining an initial ^{1}H NMR spectrum, the solution was frozen and the headspace was evacuated. This was repeated at regular intervals during the course of the reaction. After thawing, the NMR tube was heated in an oil bath at 80 °C unless otherwise noted. ^{1}H NMR spectra were collected at 25 °C.

Compound	Pertinent δs	Symbol
Phenylsilane	4.23 (s)	⁎
1	3.21 (t), 3.02 (s), 2.31 (t), 0.24 (s)	†
2	3.61 (t), 3.13 (m), 2.40 (m), 0.42 (s), 0.28 (s)	⁋
3	5.86 (s), 2.84 (s)	⁂
Catalyst decomposition products		‡

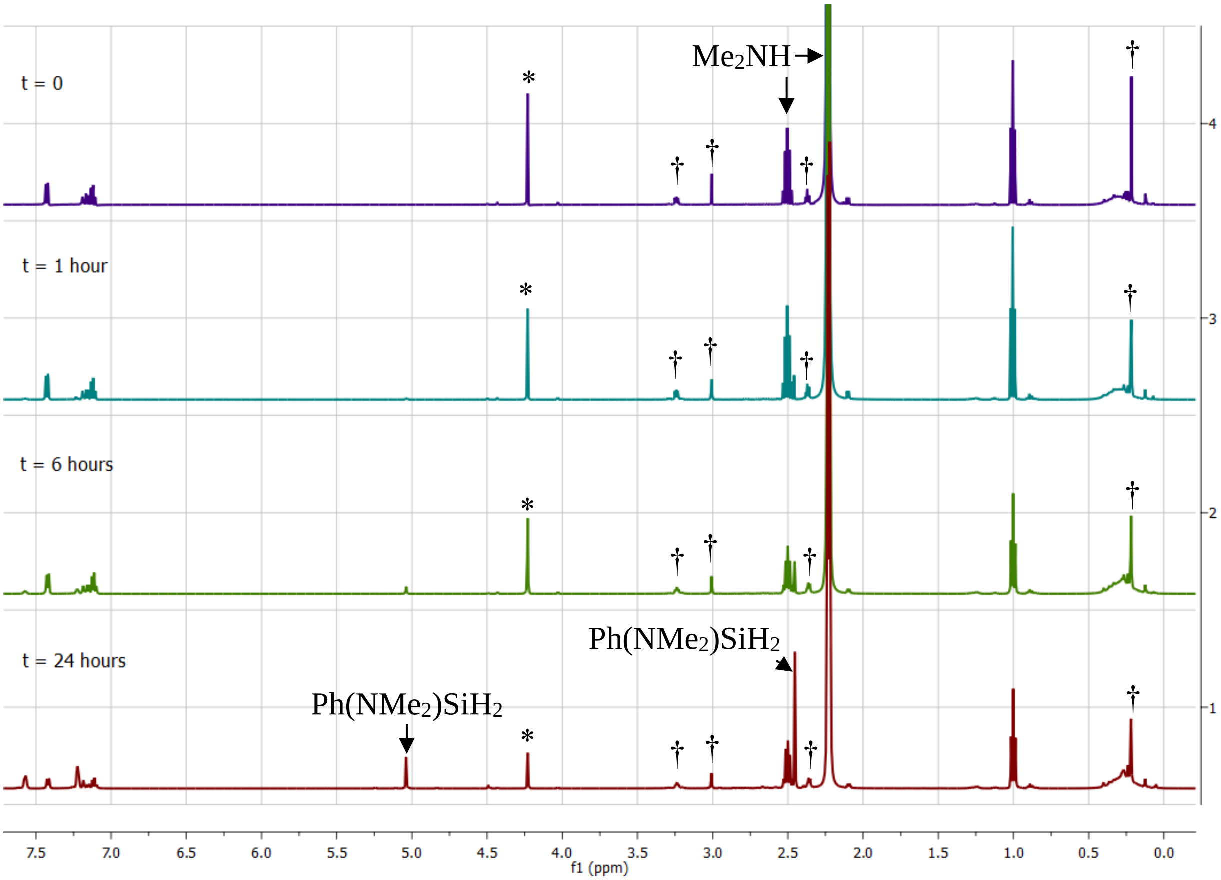
Reaction of $Zr(NMe_2)_4$ with IMes and phenylsilane

A mixture of $Zr(NMe_2)_4$ (10 mg, 3.7 x 10^{-2} mmol), IMes (11.4 mg, 3.7 x 10^{-2} mmol) and phenylsilane (44 mg, 4.1 x 10^{-1} mmol) were added in an NMR tube in ca. 0.50 mL benzene-d_6. Immediately upon addition of phenylsilane, the solution became yellow and a precipitate began to form. The formation of $[(Me_2N)_3Zr(\mu\text{-}H)(\mu\text{-}NMe_2)_2]_2Zr$ is likely, but is poorly soluble in benzene and not observed by NMR spectroscopy.[5] In addition, $Ph(NMe_2)SiH_2$ and $Ph(NMe_2)_2SiH$ are generated as seen by their overlapping Si-H resonance at 5.07 ppm and their distinctive NMe_2 resonances at 2.44 and 2.51 ppm, respectively.



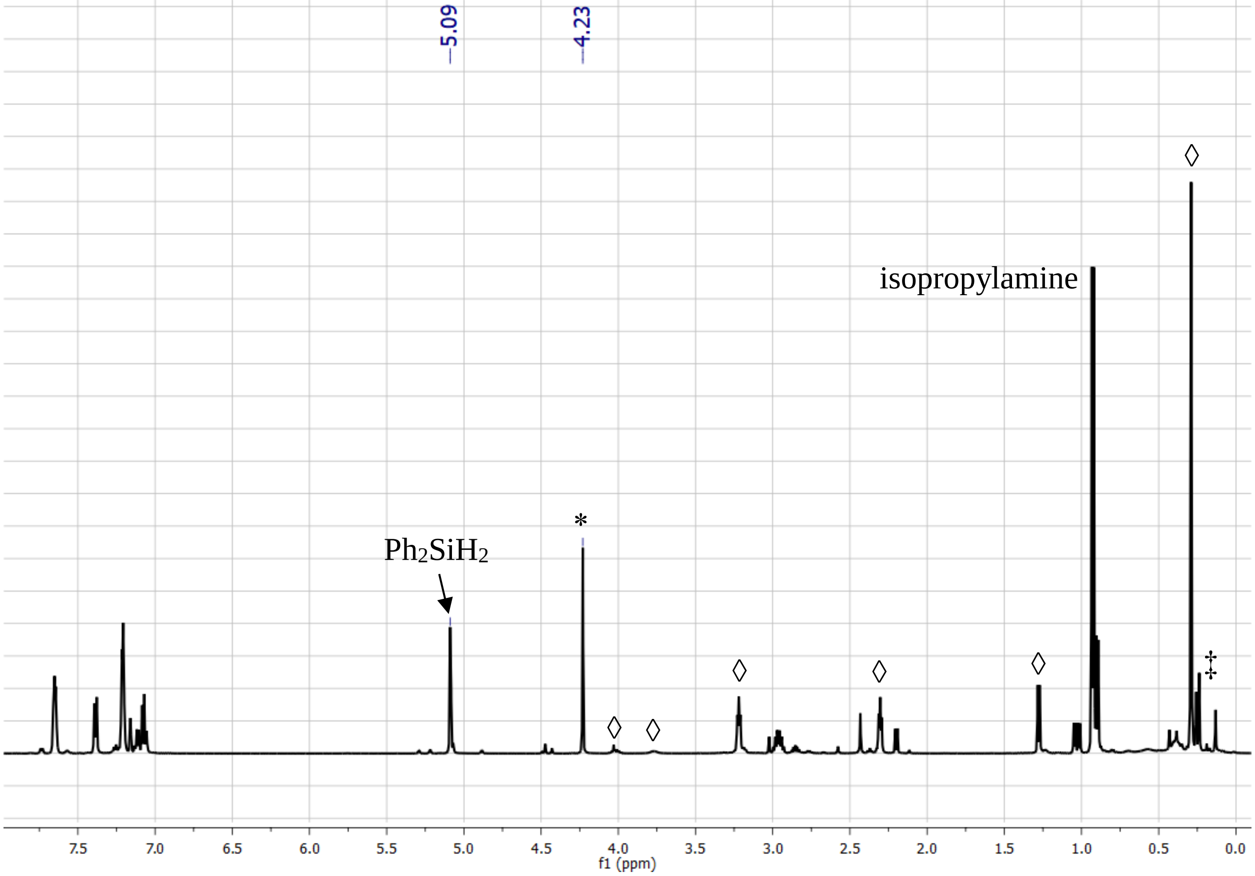
*Reaction of **1** with phenylsilane and dimethylamine:*

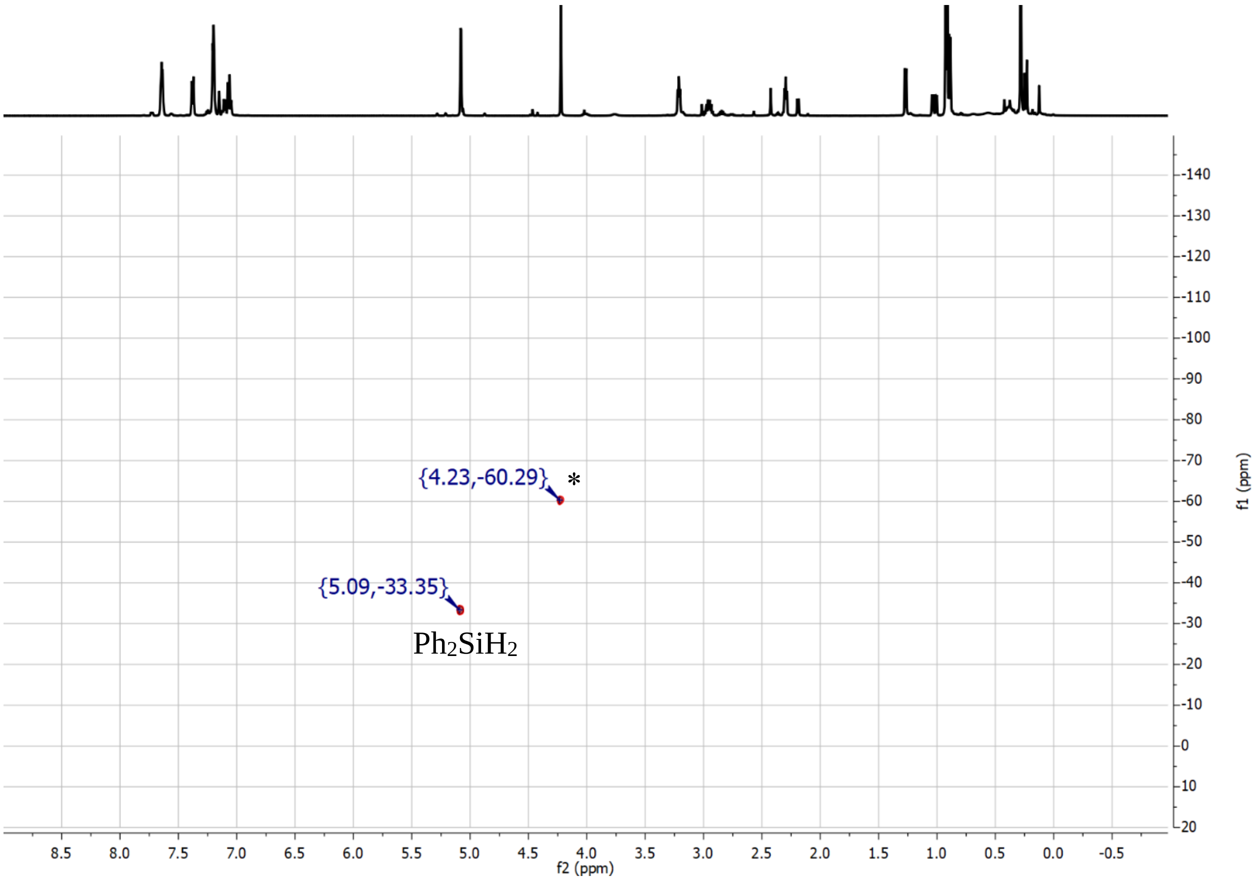
A mixture of **1** (10 mg, 2 x 10^{-2} mmol) and phenylsilane (21.9 mg, 2 x 10^{-1} mmol) were added in an NMR tube in ca. 0.50 mL benzene-*d*$_6$. The tube was frozen with liquid nitrogen and the atmosphere removed. An excess of Me_2NH was added by vacuum transfer. Formation of $Ph(NMe_2)SiH_2$ was observed by ^{1}H NMR after 6 hours. After 24 hours, there was 60% formation of $Ph(NMe_2)SiH_2$ and some catalyst decomposition. After 24 more hours, 90% of the phenylsilane had been consumed and converted into $Ph(NMe_2)SiH_2$.



*Reaction of **1** with phenylsilane and isopropylamine:*

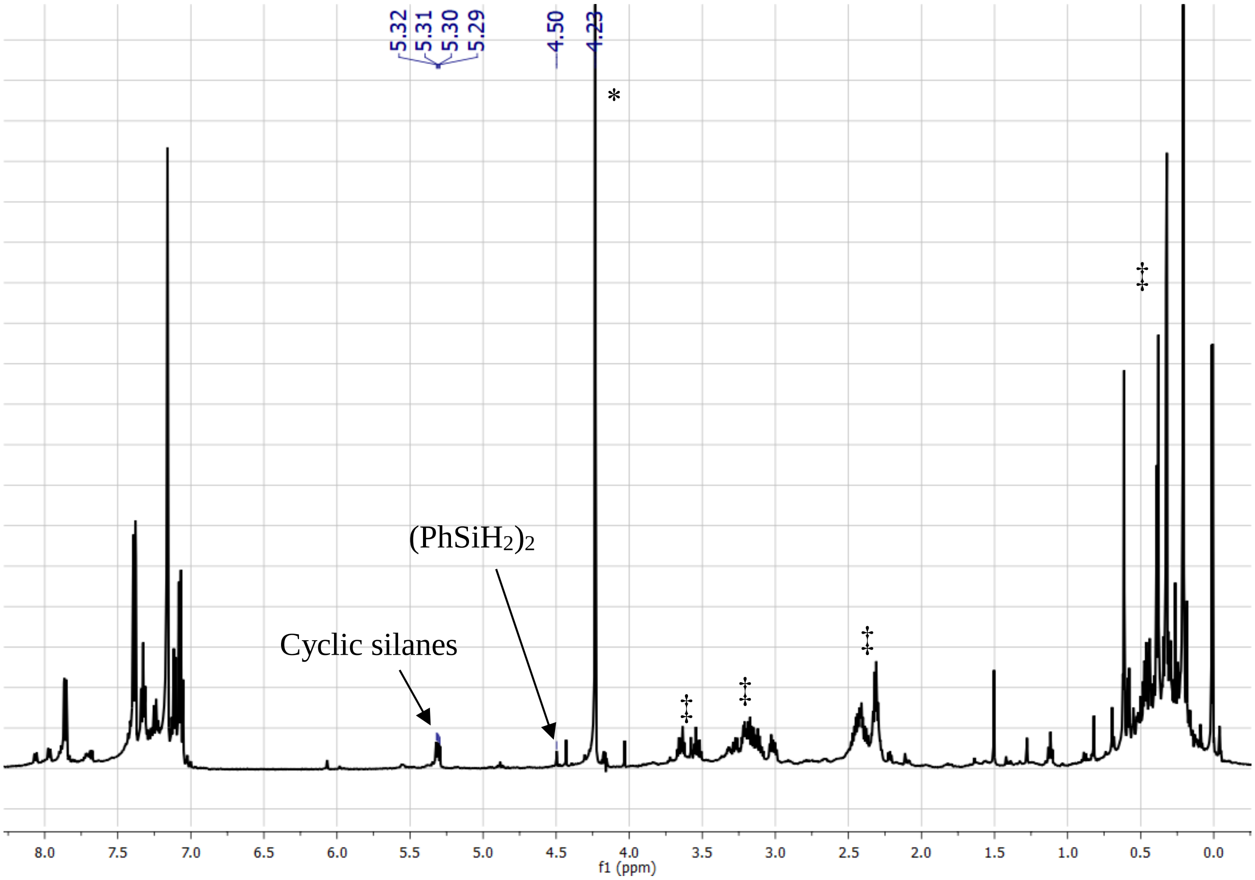
A mixture of **1** (10 mg, 2 x 10^{-2} mmol) and phenylsilane (21.9 mg, 2 x 10^{-1} mmol) and isopropylamine (60 mg, 1 mmol) were added in an NMR tube in ca. 0.50 mL benzene-d_6. After 21 hours, 62% of the phenylsilane was converted into diphenylsilane as observed by ^{1}H NMR and confirmed by ^{1}H-^{29}Si HSQC. There were no identifiable products resulting from Si–N coupling between $PhSiH_3$ and isopropylamine as seen by the ^{1}H-^{29}Si HSQC. There was a small resonance at δ 2.43, which is where $Ph(NMe_2)SiH_2$ resonates, but the corresponding Si–H wasn't observed by ^{1}H or ^{1}H-^{29}Si HSQC NMR. $(N_3N)ZrNH^iPr$ was observed (resonances denoted as ◊) ^{1}H NMR (C_6D_6): δ 4.01 (m, 1H, -C**H**CH_3), 3.77 (br. s, 1H, -NH), 3.22 (t, 6H), 2.30 (t, 6H), 1.27 (d, 6H, -CHC**H**$_3$), 0.29 (s, 27H, -Si$(CH_3)_3$).




{4.23,-60.29}
*
{5.09,-33.35}
Ph_2SiH_2
f1 (ppm)
f2 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-140
-130
-120
-110
-100
-90
-80
-70
-60
-50
-40
-30
-20
-10
0
10
20

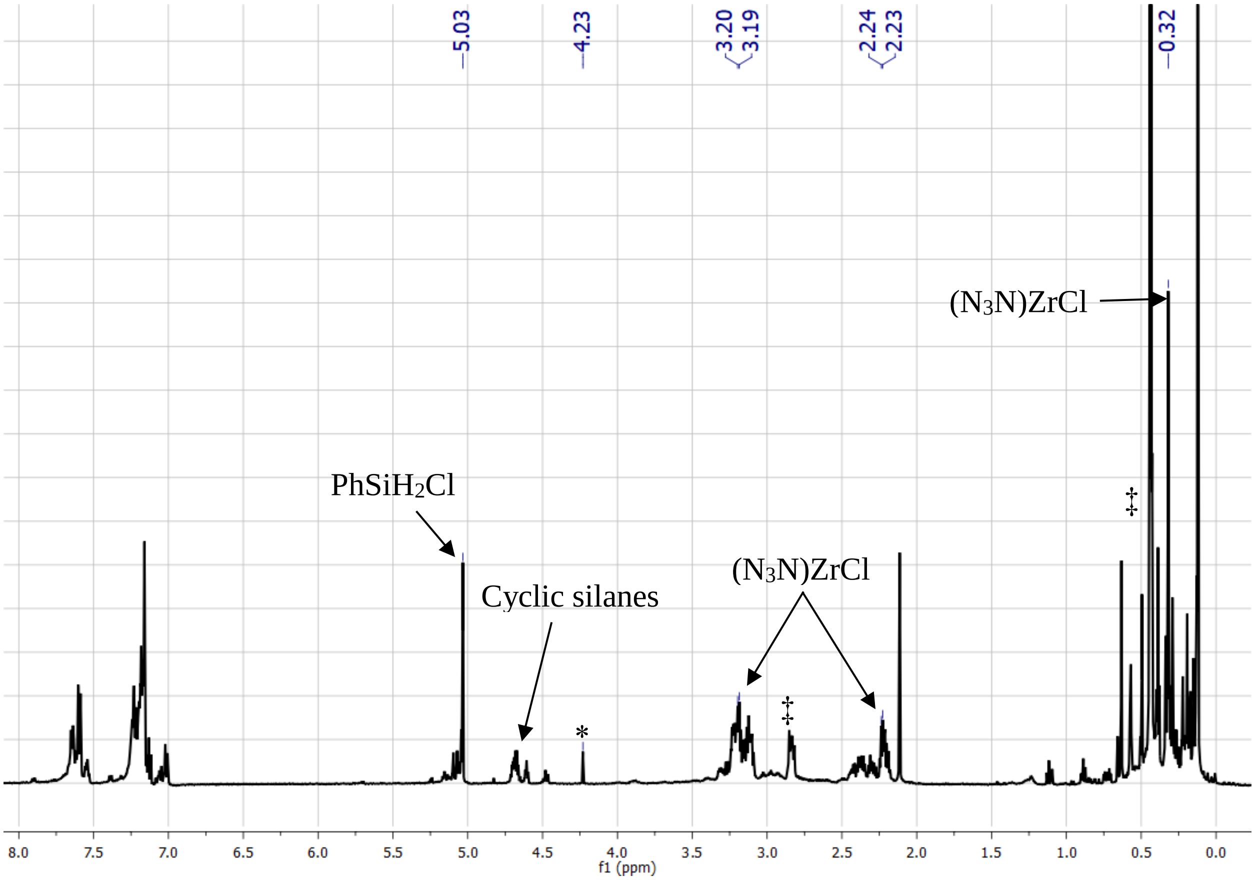
Reaction of ***2*** *with phenylsilane:*

A mixture of **2** (16 mg, 0.35 mmol) and phenylsilane (20 mg, 0.18 mmol) were added in an NMR tube in ca. 0.50 mL benzene-d_6. Trace quantities of diphenyldisilane (< 0.5%) are observed after 3 days. With time and increased heating, a multiplet corresponding to the formation of cyclic silane products is observed at ca. δ 5.3 ppm.



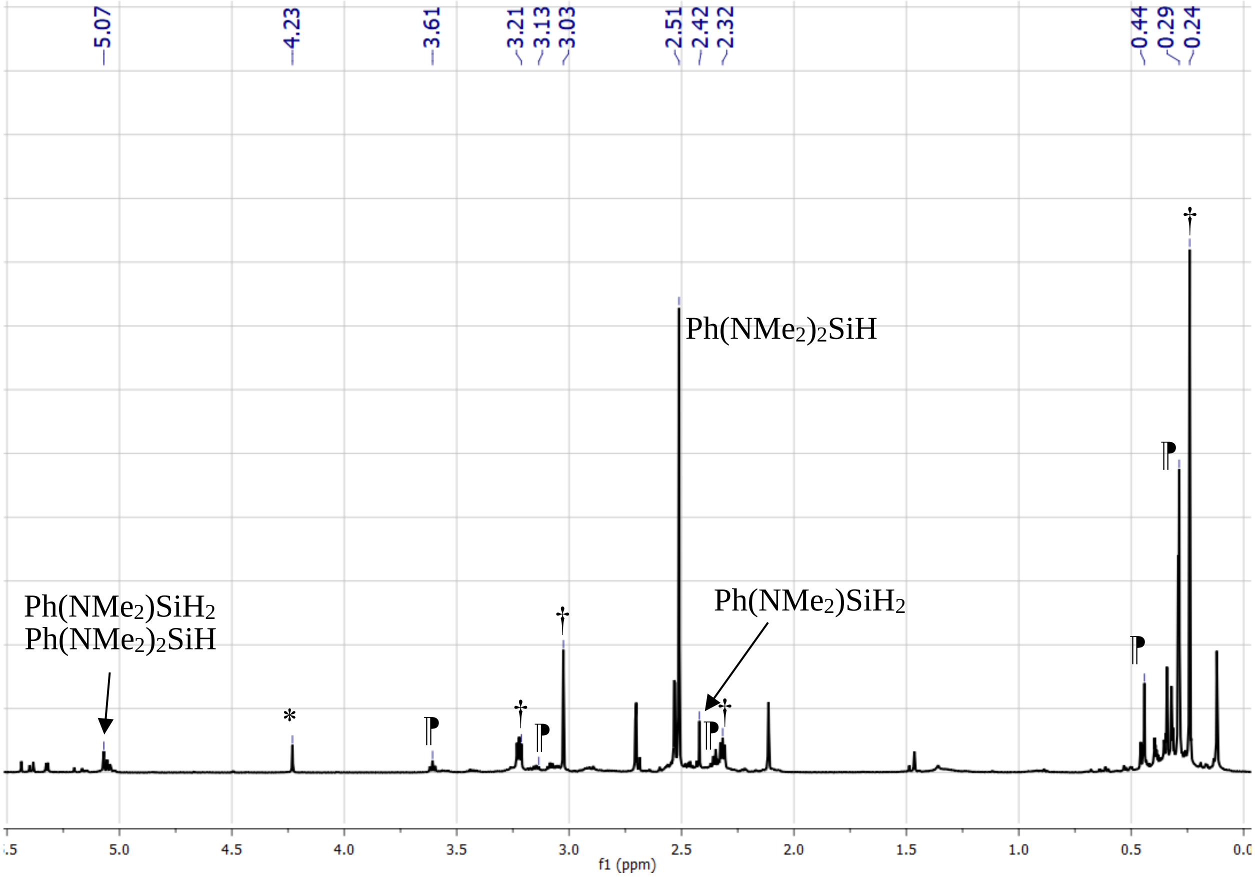
*Reaction of **2** with chlorophenylsilane:*

A mixture of **2** (25 mg, 5.2 x 10^{-2} mmol) and chlorophenylsilane (12 mg, 8.6 x 10^{-2} mmol) were added in a reaction tube in ca. 0.50 mL benzene-d_6. The reaction was allowed to stir at rt for ca. 18 hrs; after ca. 30 min, the reaction turned to a pale yellow color. The formation of $(N_3N)ZrCl$ was identified through the TMS resonances (δ = 0.32 ppm, ca. 15% conversion) while the remainder of the ^{1}H NMR spectrum was complex.



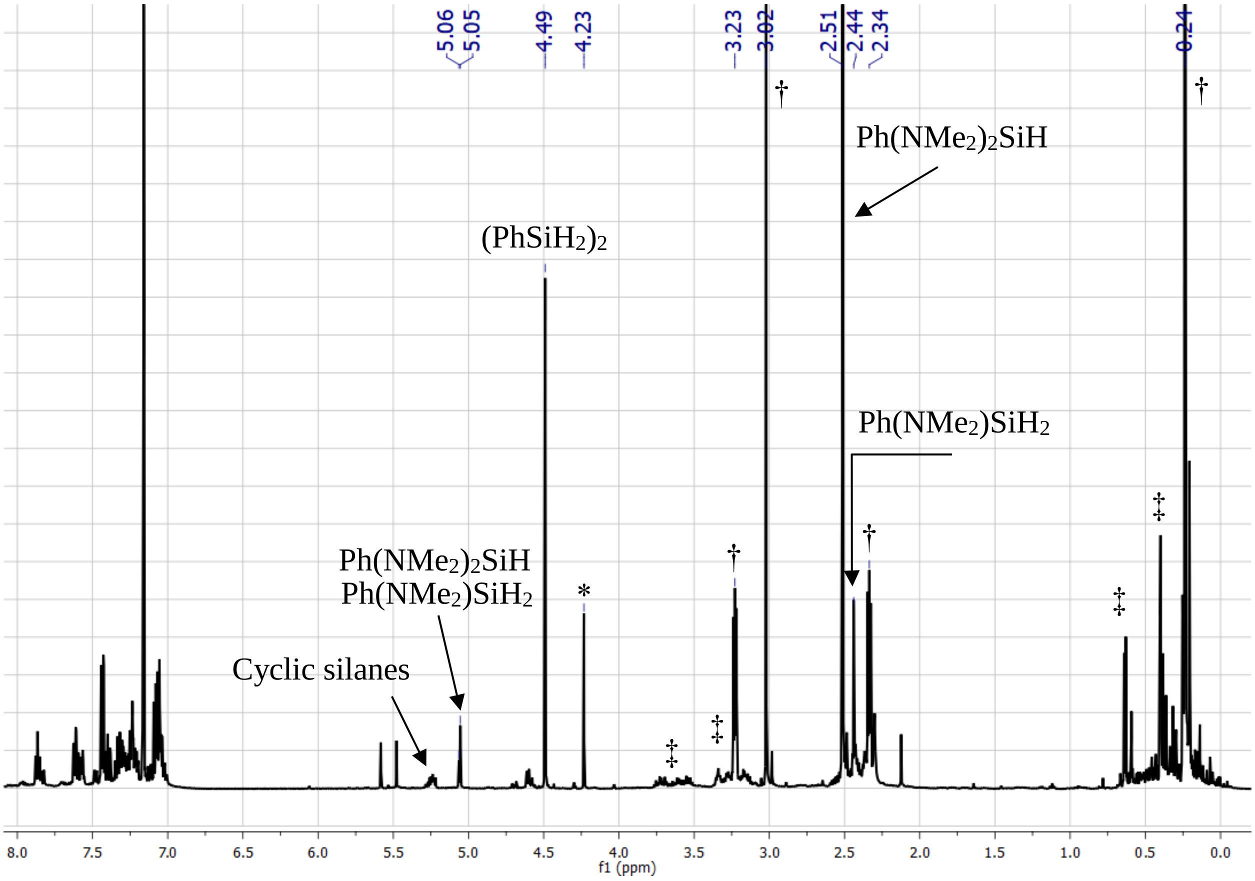
*Reaction of **2** with* Ph(NMe$_2$)SiH$_2$:

A mixture of **2** (12 mg, 2.7 x 10^{-2} mmol) and Ph(NMe$_2$)SiH$_2$ (22 mg, 0.24 mmol) were added in a reaction tube in ca. 0.50 mL benzene-*d*$_6$. After ca. 18 h the formation of phenylsilane and **1** was observed via ^{1}H NMR spectroscopy. This was confirmed through external addition of phenylsilane.



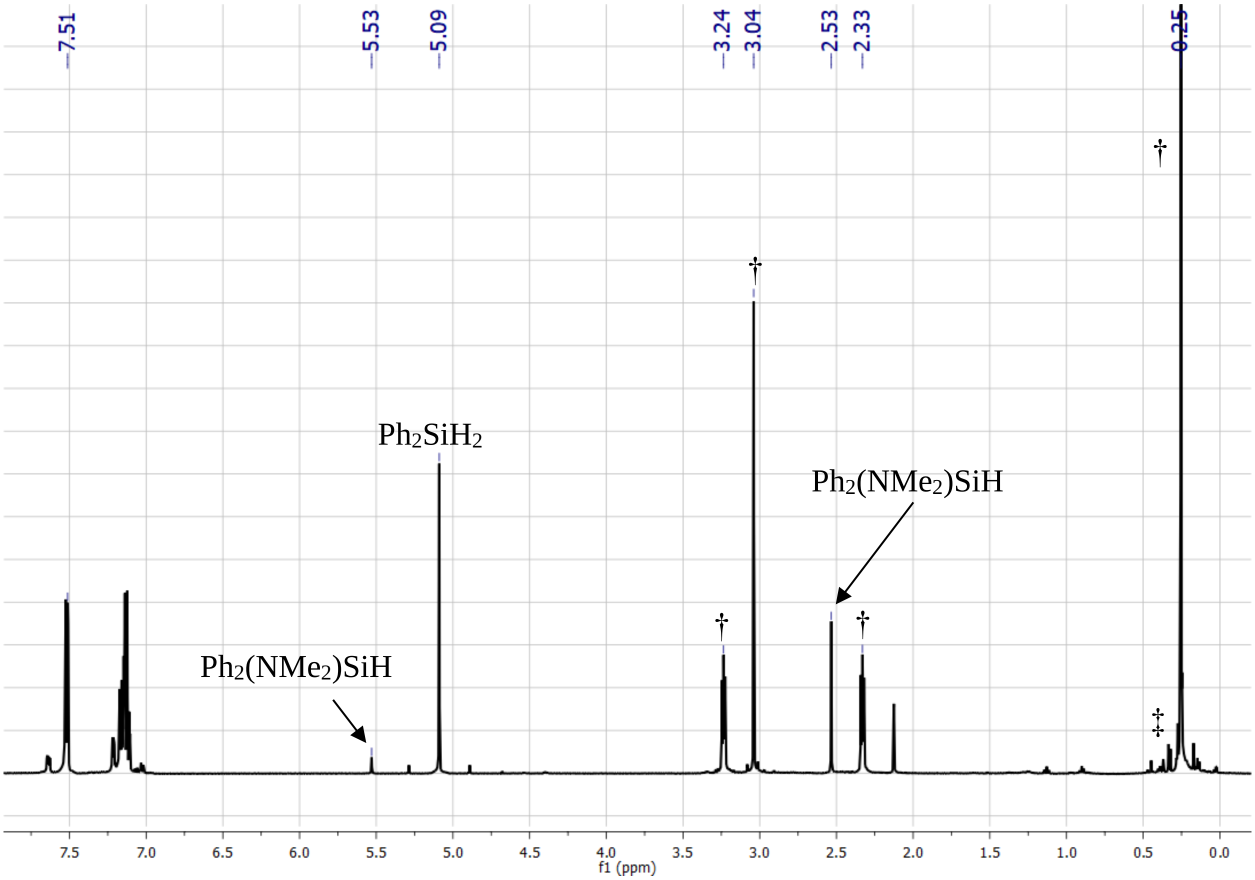
*Reaction of **1** with phenylsilane:*

A mixture of **1** (29 mg, 5.8 x 10^{-2} mmol) and phenylsilane (17 mg, 0.15 mmol) were added in an NMR tube in ca. 0.50 mL benzene-d_6. Initial formation of $Ph(NMe_2)SiH_2$was observed by ^{1}H NMR followed by increasing amounts of diphenyldisilane (49% relative yield), $Ph(NMe_2)SiH_2$ (5%) and $Ph(NMe_2)_2SiH$ (17%). A resonance (m, ca. δ 5.3 ppm, 17% relative yield) is assigned to the formation of cyclic silane products. Higher loadings of the catalyst yielded the same products.



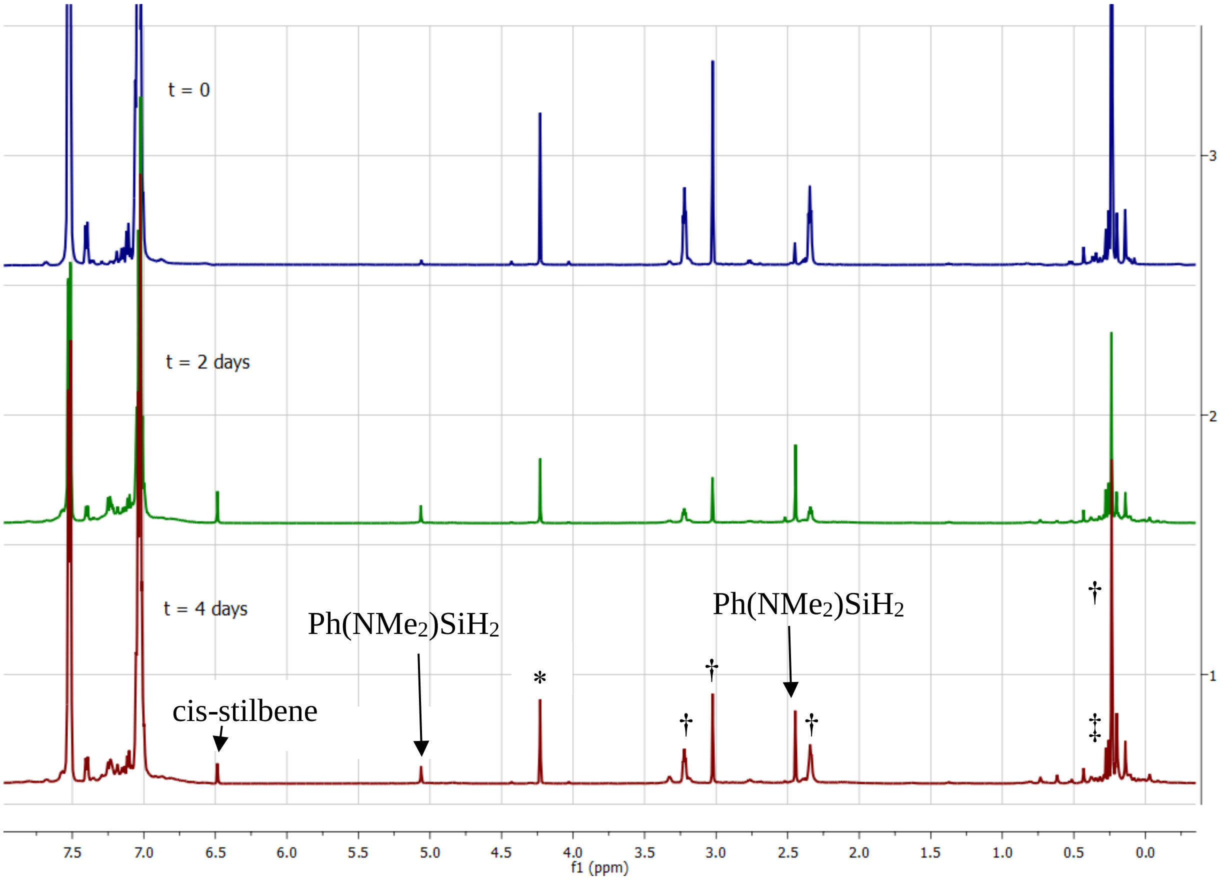
*Reaction of **1** with diphenylsilane:*

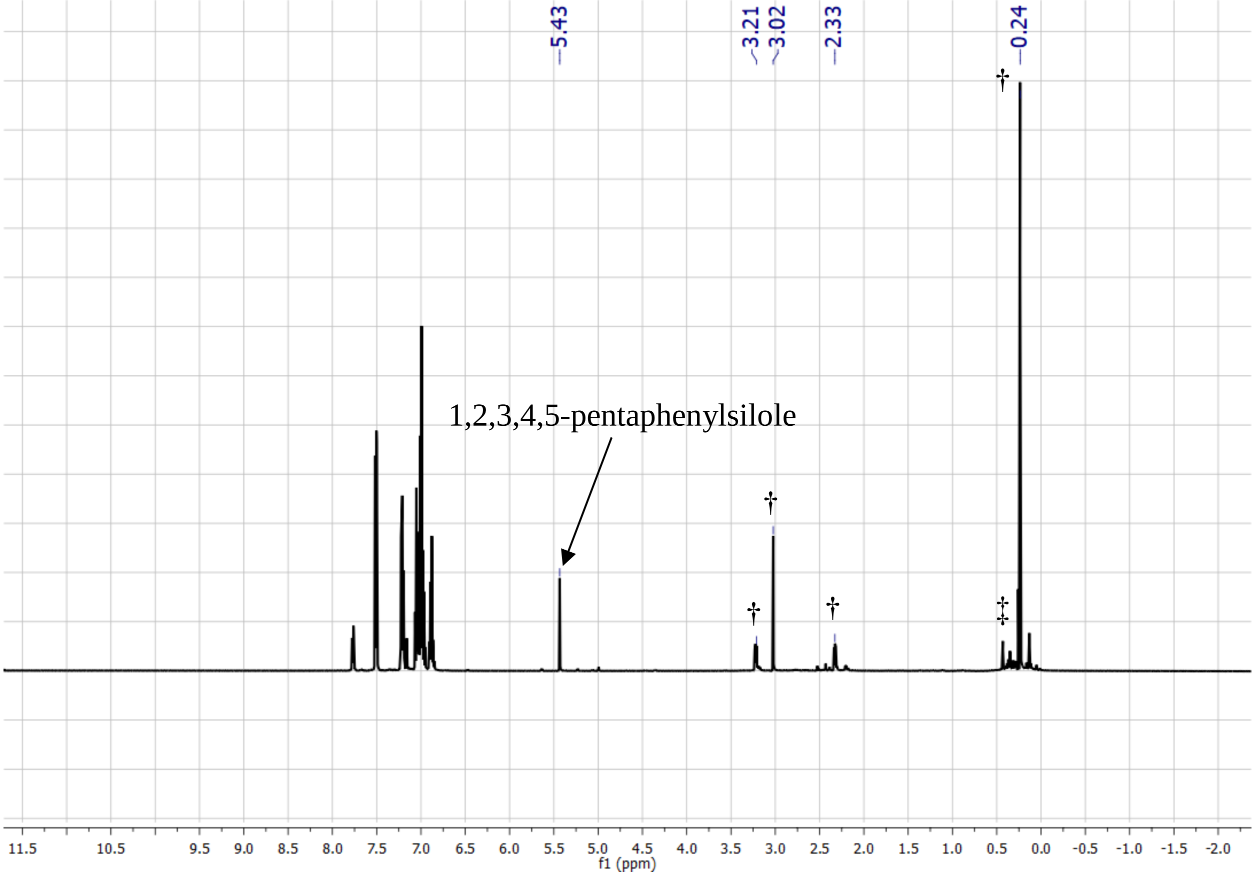
A mixture of **1** (39 mg, 7.9 x 10^{-2} mmol) and diphenylsilane (72 mg, 0.39 mmol) were added in an NMR tube in ca. 0.50 mL benzene-d_6. $Ph_2SiH(NMe_2)$ was observed by ^{1}H NMR in 10% conversion over 7 days. ^{1}H NMR (C_6D_6): δ 5.53 (s, 1H, Si-H), 2.53 (s, 6H, $-N(CH_3)_2$).



*Reaction of **1** with phenylsilane and diphenylacetylene:*

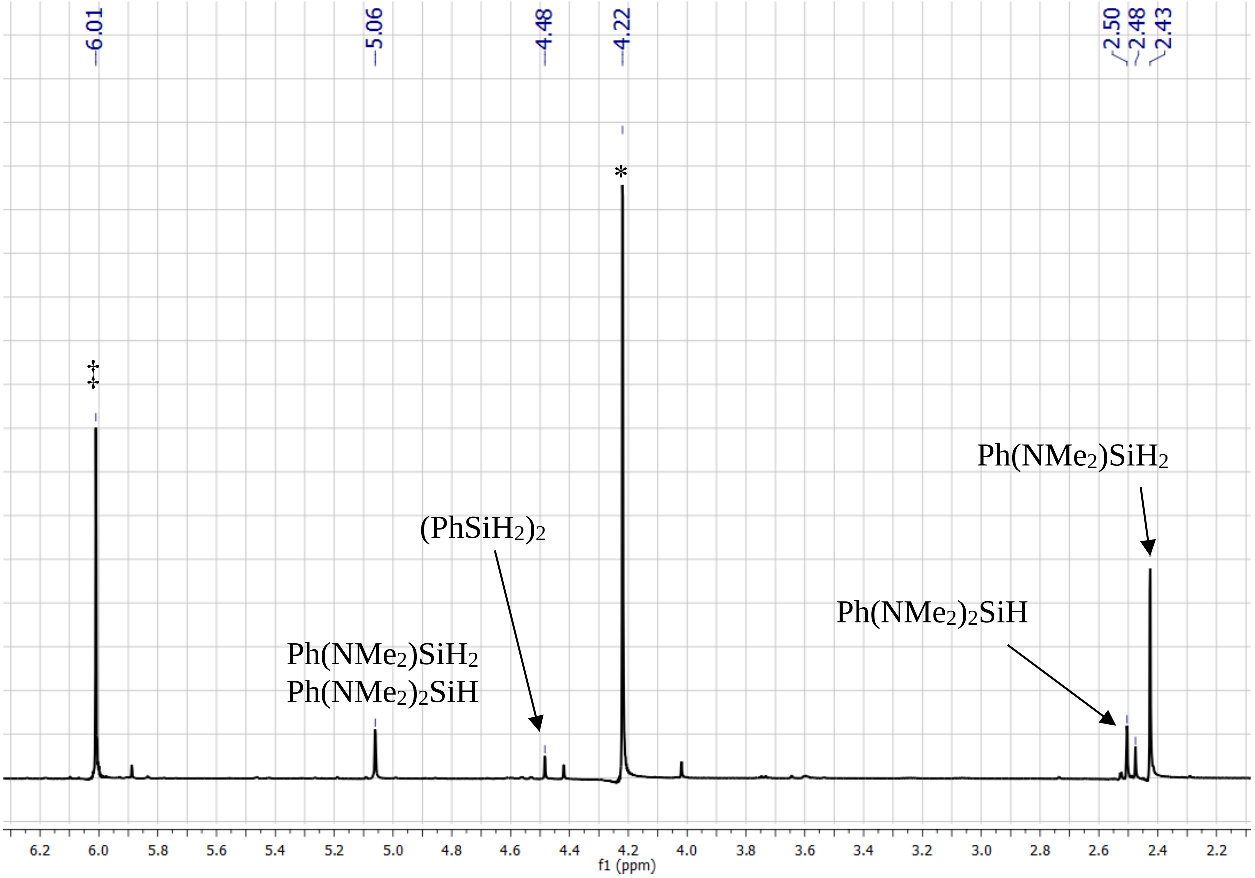
A mixture of **1** (39 mg, 7.9 x 10^{-2} mmol), phenylsilane (23 mg, 0.21 mmol), and diphenylacetylene (175 mg, 0.98 mmol) were added in an NMR tube in ca. 0.50 mL benzene-*d*$_6$. The results from this experiment were inconsistent. Cis-stilbene was observed most often as a hydrogenation product at 6.49 in ^{1}H NMR as well as $Ph(NMe_2)SiH_2$. The less frequently observed result was a new resonance in the ^{1}H NMR spectrum at δ 5.4 ppm. The reaction was filtered through fluorosil to remove the metallic species and from the resulting mixture a GCMS trace was obtained. Two chromatographic peaks were observed and identified as diphenylacetylene (MS *m/z*: 178.0) and 1,2,3,4,5-pentaphenylsilole (MS *m/z*: 464.0).




5.43
3.21
3.02
2.33
0.24
†
†
†
†
‡
1,2,3,4,5-pentaphenylsilole
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
f1 (ppm)

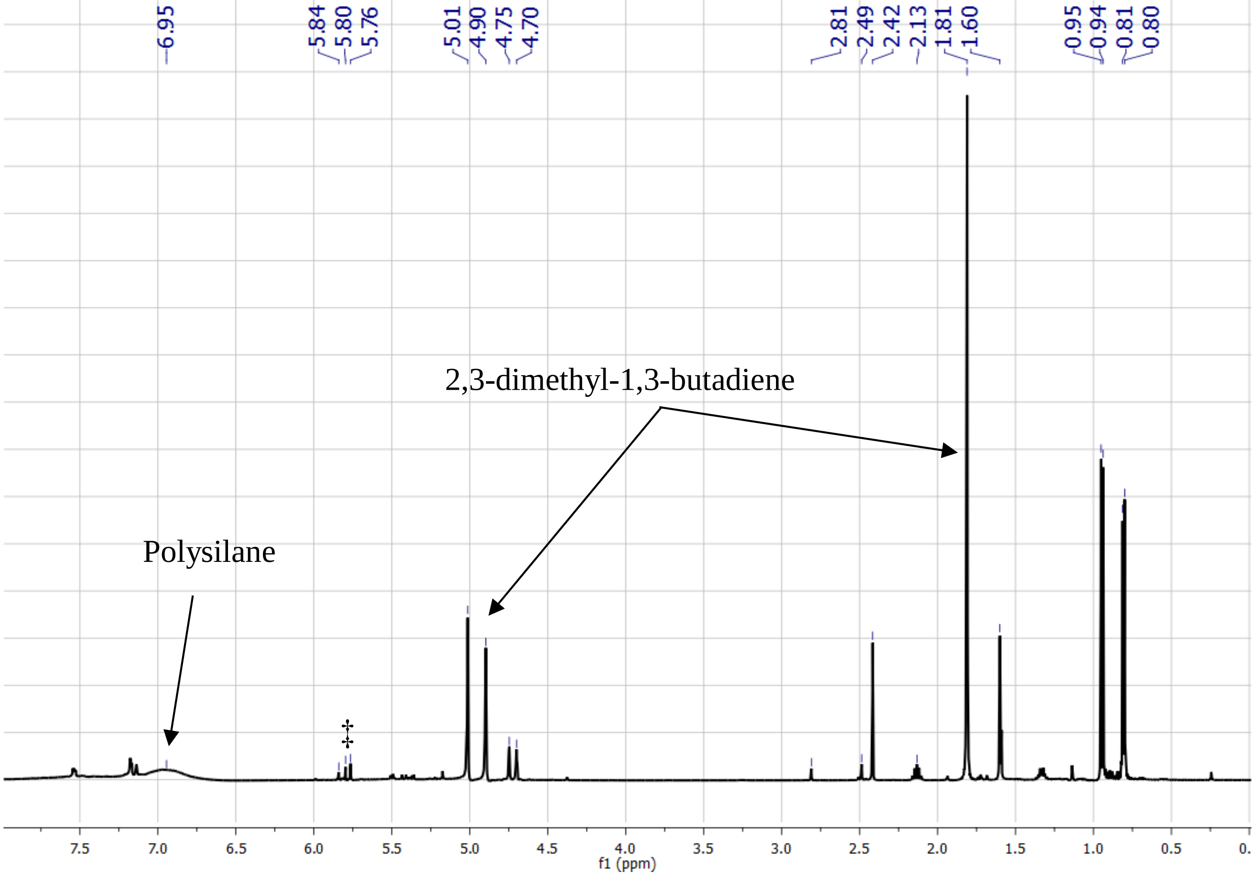
Reaction of **3** *with phenylsilane and diphenylacetylene*

A mixture of $Cp_2Zr(NMe_2)_2$ (10 mg, 3.23 x 10^{-2} mmol), phenylsilane (35 mg, 0.32 mmol), and diphenylacetylene (173 mg, 0.97 mmol) were added in an NMR tube in ca. 0.50 mL benzene-d_6. The headspace was removed; after ca 24 hours, catalyst decomposition had occurred resulting in a new resonance in the ^1H NMR spectrum at δ 6.01as well as $Ph(NMe_2)SiH_2$ and $Ph(NMe_2)_2SiH$. No trapped product was observed.



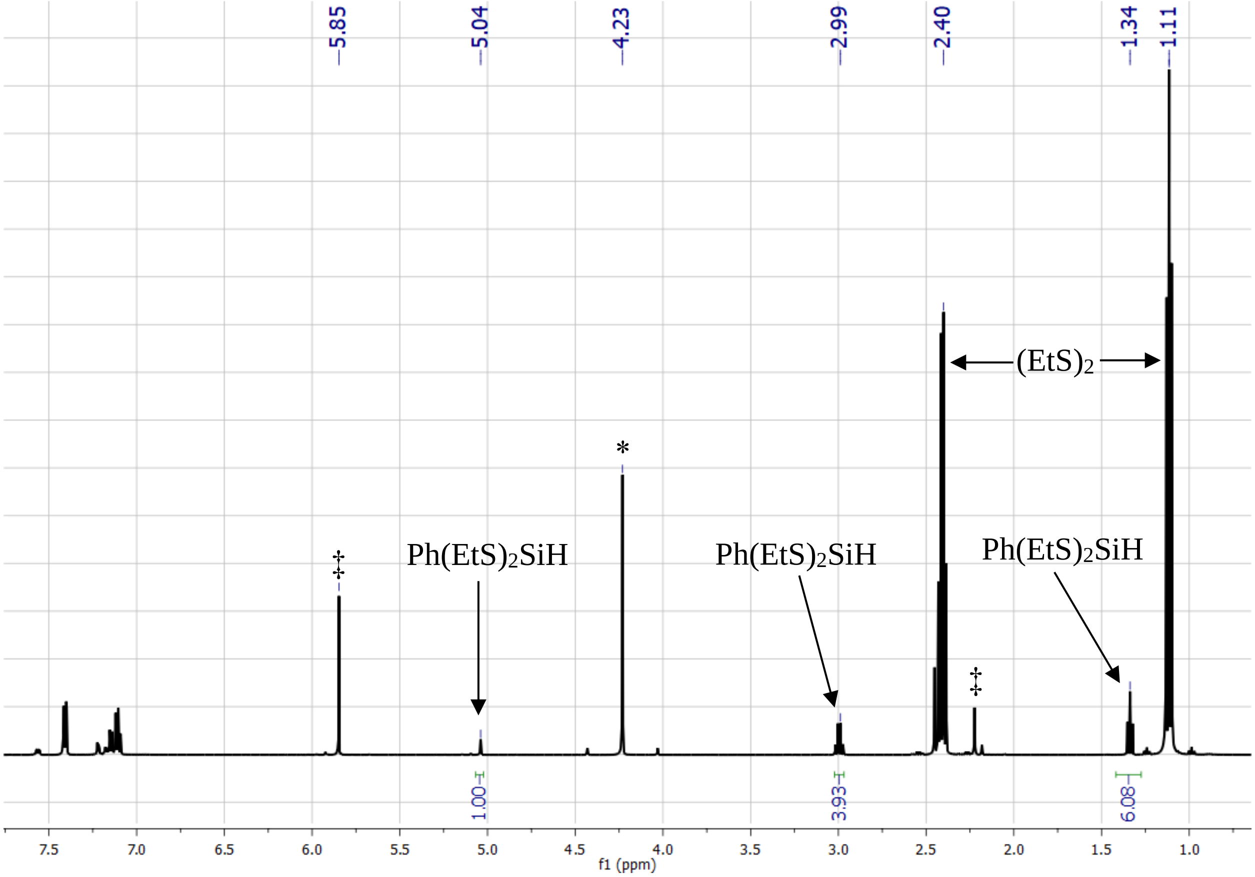
Reaction of **3** *with phenylsilane and 2,3-dimethyl-1,3-butadiene*

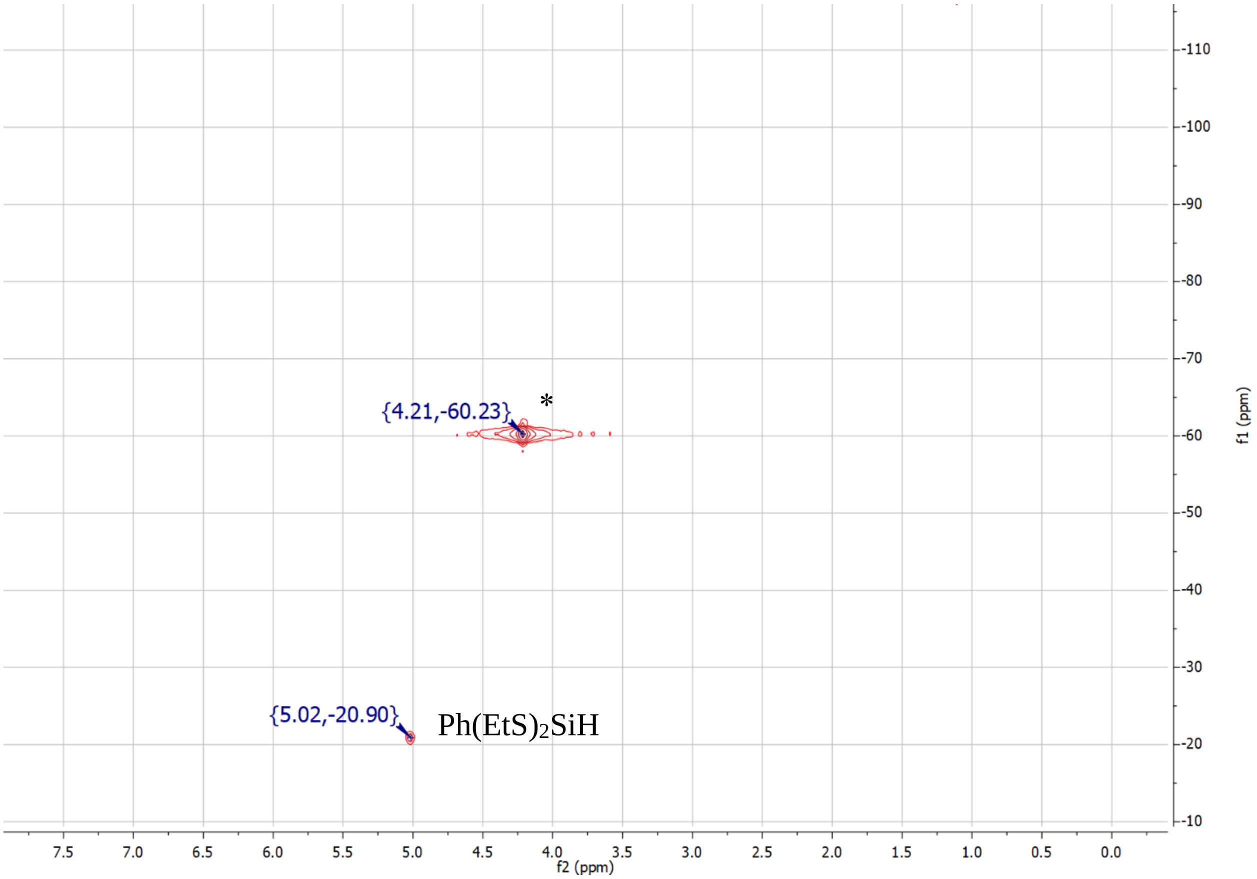
A mixture of $Cp_2Zr(NMe_2)_2$ (10 mg, 3.23×10^{-2} mmol), phenylsilane (35 mg, 0.32 mmol), and 2,3-dimethyl-1,3-butadiene (40 mg, 0.49 mmol) were added in an NMR tube in ca. 0.50 mL benzene-d_6. The headspace was removed; after ca 24 hours, complete consumption of phenylsilane had occurred. The new broad resonance at δ 6.95 is indicative of polysilane formation. There is no evidence of a trapped silylene fragment.

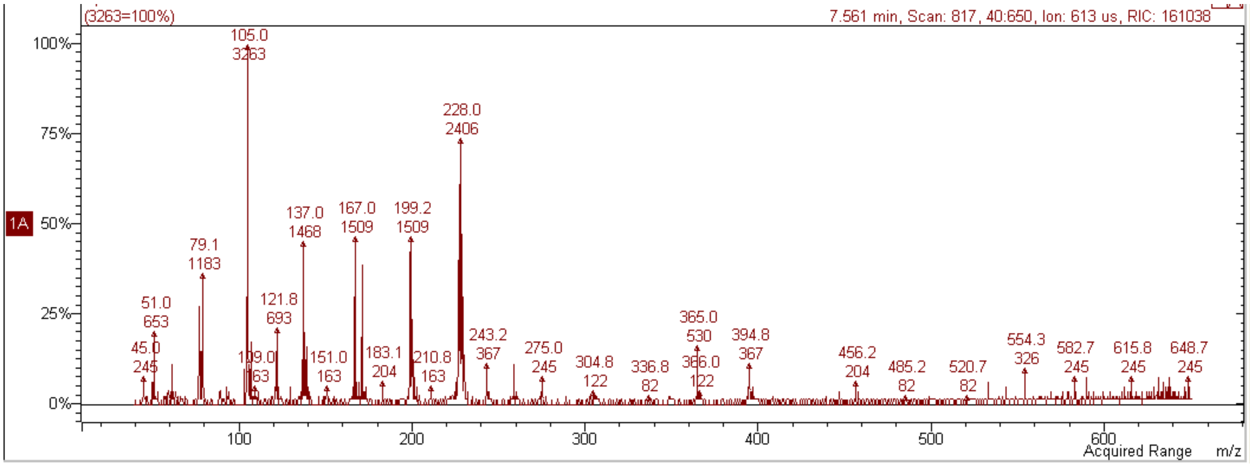


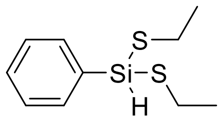
Reaction of **3** *with phenylsilane and diethyl disulfide:*

A mixture of $Cp_2Zr(NMe_2)_2$ (10 mg, 3.23 x 10^{-2} mmol), phenylsilane (35 mg, 0.32 mmol), and diethyl disulfide (79 mg, 0.64 mmol) were added in an NMR tube in ca. 0.50 mL benzene-d_6. The headspace was removed; after ca 10 minutes, a new Si–H resonance was observed. Reactivity ceased after 5 days, resulting in 15% conversion into one new Si–H containing species. By ^1H and ^1H-^{29}Si HSQC and GCMS the product was determined to be the trapped silylene, $Ph(EtS)_2SiH$. ^1H NMR (C_6D_6): δ 5.04 (s, 1H, Si–H), 2.99 (q, 4H, Et), 1.34 (t, 6H, Et). ^{29}Si NMR (C_6D_6): δ -20.90. GC/MS (Retention time = 7.56 minutes) is of reaction mixture.

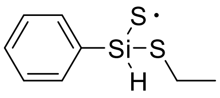




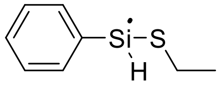




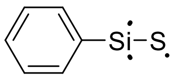
Exact Mass: 228.05



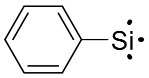
Chemical Formula: $C_8H_{11}S_2Si$
Exact Mass: 199.01



Chemical Formula: $C_8H_{11}SSi$
Exact Mass: 167.04



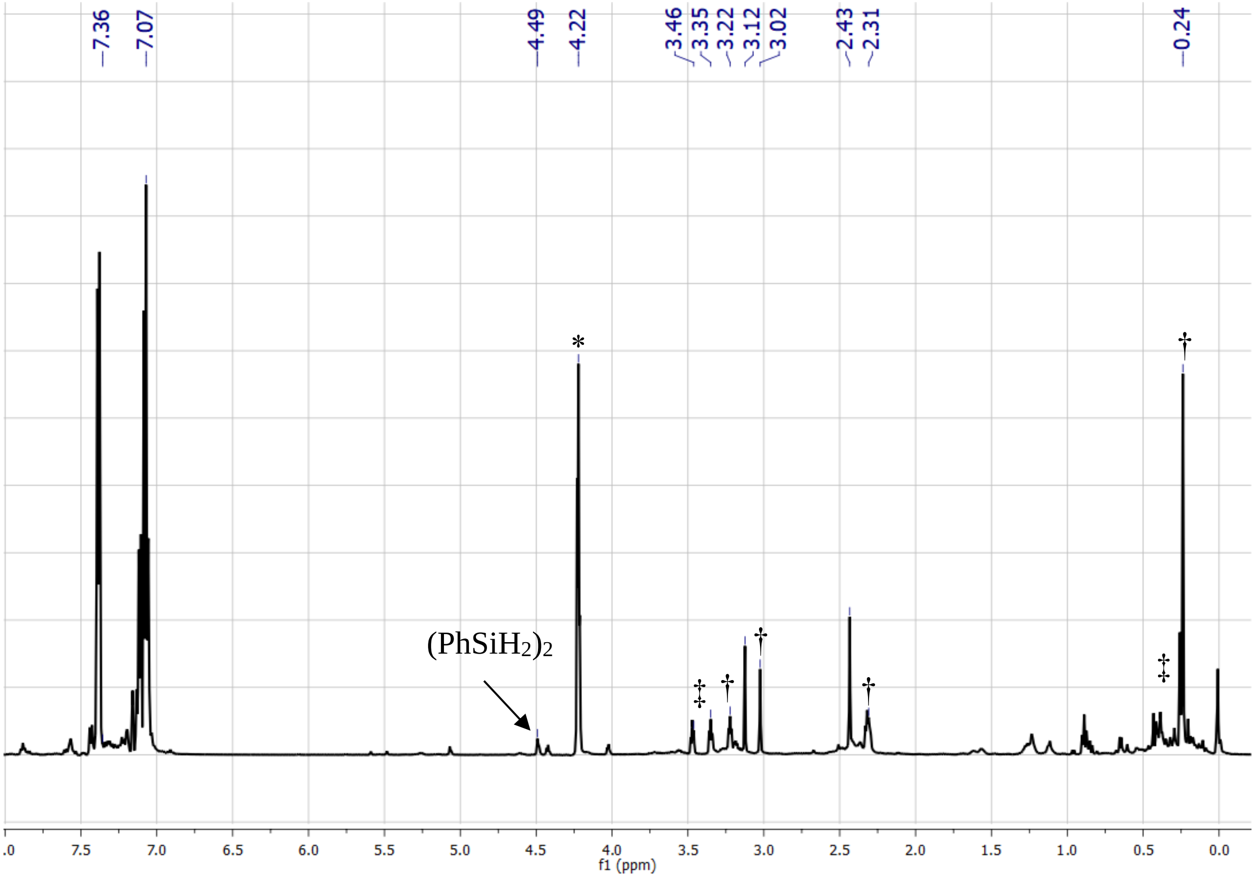
Chemical Formula: $C_6H_5SSi^{3\bullet}$
Exact Mass: 136.99

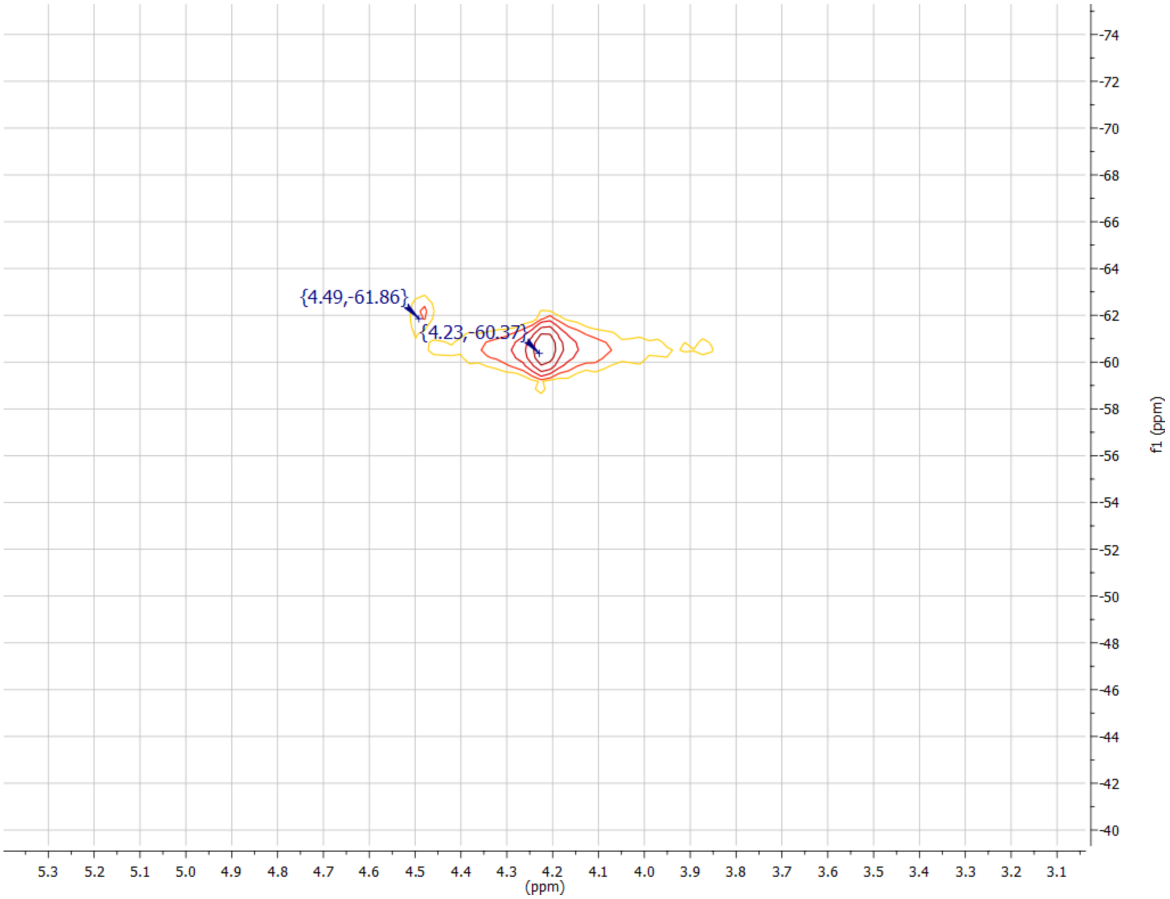


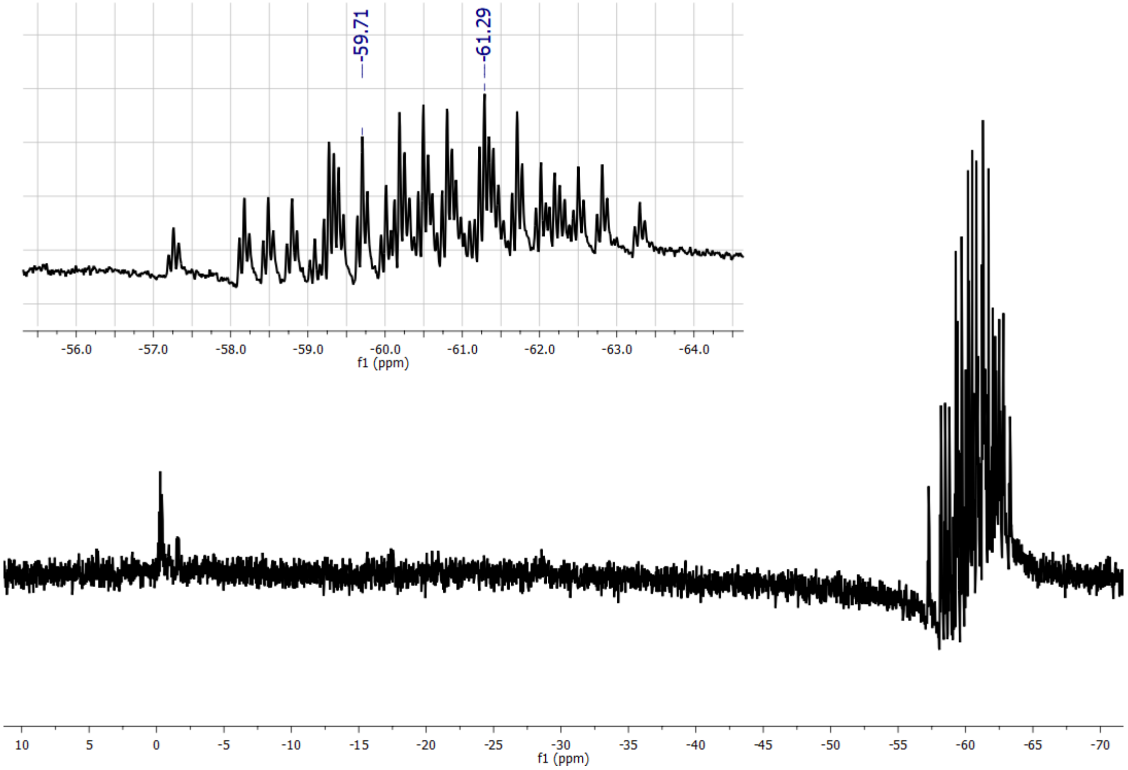
Chemical Formula: $C_6H_5Si^{4\bullet}$
Exact Mass: 105.02

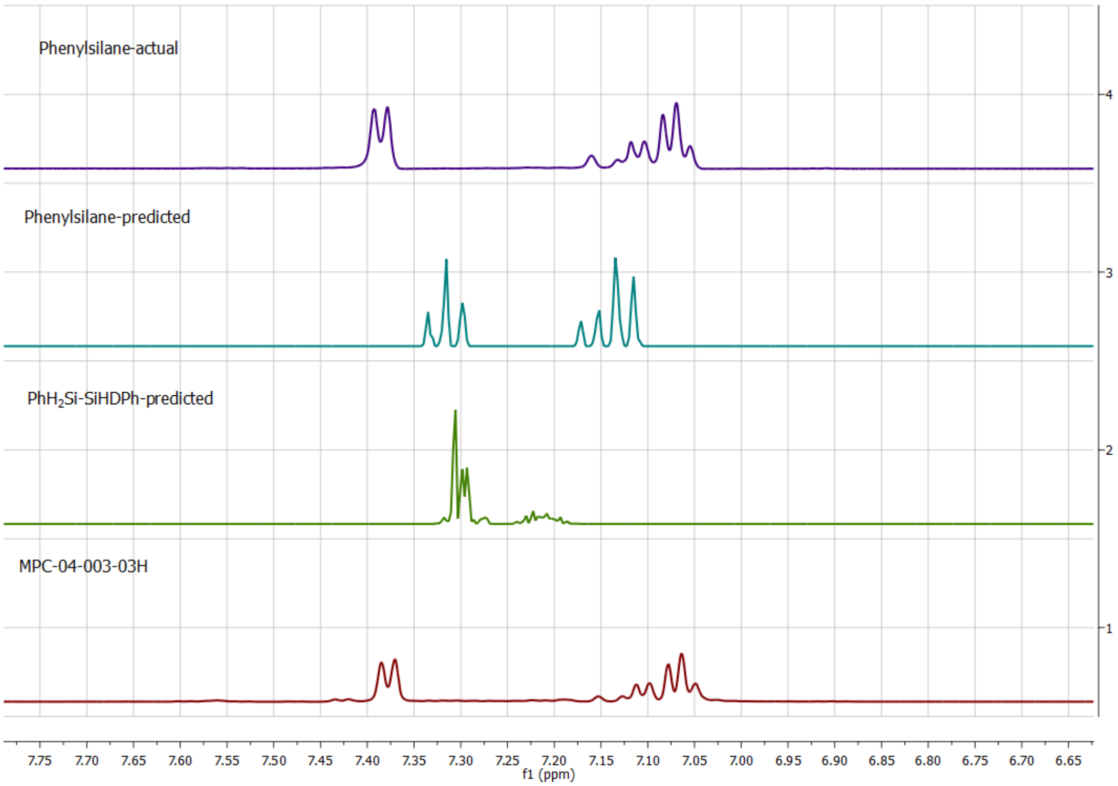
*Reaction of **1** with $PhSiH_3$ and $PhSiD_3$:*

A mixture of **1** (10 mg, 2 x 10^{-2} mmol), $PhSiH_3$ (21.9 mg, 2 x 10^{-1} mmol) and $PhSiD_3$ (24.7 mg, 2 x 10^{-1} mmol, 91% solution in diglyme) were added in an NMR tube in ca. 0.50 mL benzene-*d_6*. The headspace was removed. Over 24 hours, the Si–H resonance at indicating the presence of the dehydrocoupled product, $PhH_2Si\text{-}SiH_2Ph$, appeared. ^{29}Si NMR was run over 15 hours to try to see whether $PhH_2Si\text{-}SiHDPH$ or $PhD_2Si\text{-}SiHDPh$ was present. The spectrum was quite complex and elucidating any of these products wasn't possible. Simulating these compounds was attempted but inconclusive given that the simulated spectra of simpler compounds were inconsistent with experimental spectra (as seen with $PhSiH_3$).



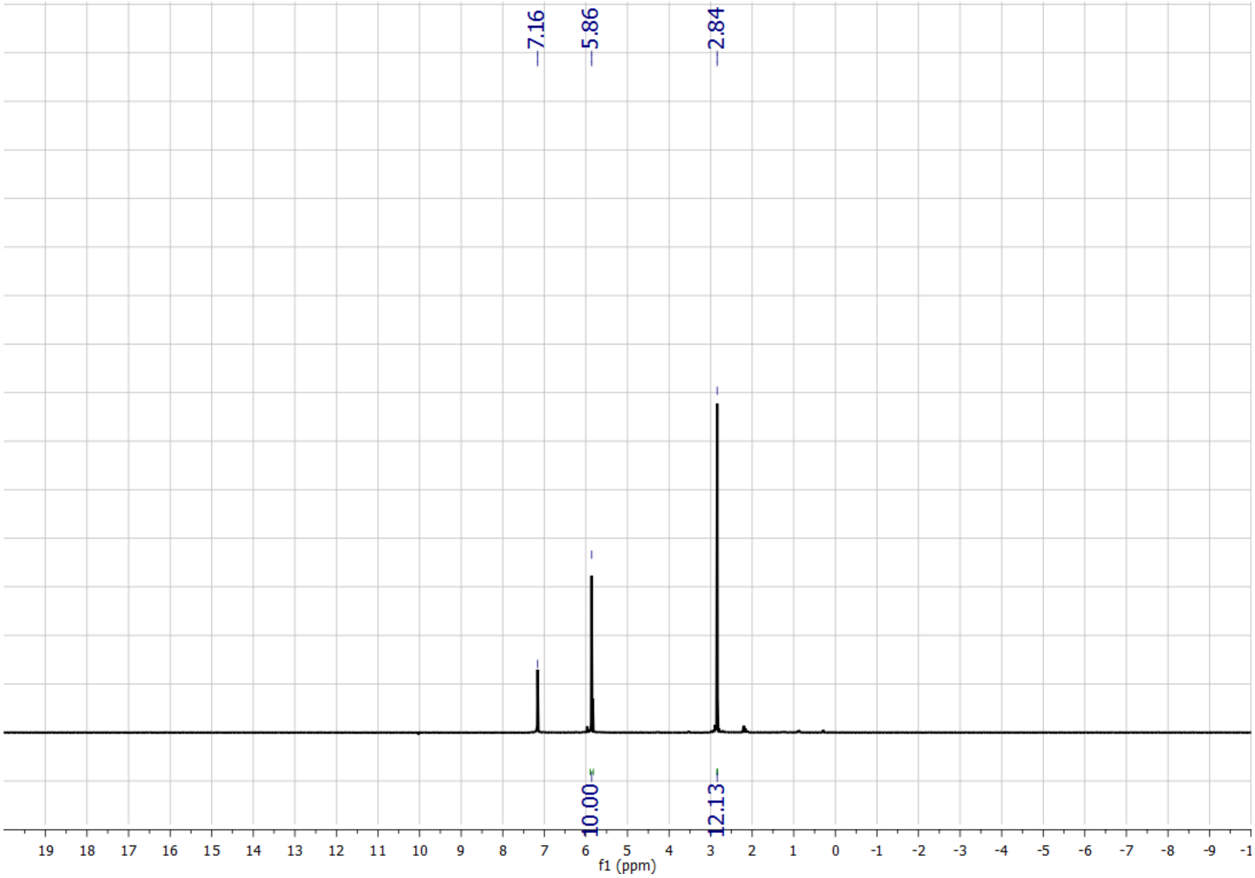

{4.49,-61.86}
{4.23,-60.37}
-74
-72
-70
-68
-66
-64
-62
-60
-58
-56
-54
-52
-50
-48
-46
-44
-42
-40
f1 (ppm)
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
(ppm)


-59.71
-61.29
-56.0
-57.0
-58.0
-59.0
-60.0
-61.0
-62.0
-63.0
-64.0
f1 (ppm)
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
f1 (ppm)


Phenylsilane-actual
Phenylsilane-predicted
PhH_2Si-SiHDPh-predicted
MPC-04-003-03H
4
3
2
1
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
7.00
6.95
6.90
6.85
6.80
6.75
6.70
6.65
f1 (ppm)

Synthesis of $Cp_2Zr(NMe_2)_2$ (**3**)

Inside a N_2 filled drybox, a vial containing Cp_2ZrCl_2 (300 mg, 1.026 mmol) was charged with 5 mL of dry THF and stirred until a homogeneous solution. Another vial containing $LiNMe_2$ (104.7 mg, 2.053 mmol) was dissolved in dry THF. Over the course of 10 minutes, the $LiNMe_2$ solution was dropwise added to the Cp_2ZrCl_2 containing solution. A color change from colorless to yellow was immediately observed upon addition of $LiNMe_2$. The reaction was stirred for one hour under ambient temperature. The solvent was then removed and extraction with dry pentane yielded a yellow solution. Removal of the pentane gave the title compound as a yellow solid in 85% yield. (269 mg, 0.87 mmol). ^1H NMR (C_6D_6): δ 5.86 (s, 10H, Cp), 2.84 (s, 12H, -$N(CH_3)_2$). $^{13}C\{^1H\}$ (C_6D_6): δ 110.10 (s), 49.58 (s). This compound has been previously synthesized by a different method[6] and used for catalytic silane dehydrocoupling.[7]



^1H NMR Spectrum of $Cp_2Zr(NMe_2)_2$

(1) Duan, Z.; Naiini, A. A.; Lee, J.-H.; Verkade, J. G. *Inorg. Chem.* **1995**, *34*, 5477.

(2) Waterman, R. *Organometallics* **2007**, *26*, 2492.

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(7) Wang, Q.; Corey, J. Y. *Canadian Journal of Chemistry* **2000**, *78*, 1434.