

Supplementary Information for

Hetero-dehydrocoupling of Silanes and Amines by Heavier Alkaline Earth Catalysis[‡]

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General Synthetic Details

All manipulations were carried out under an inert atmosphere of argon utilising standard glovebox and Schlenk line techniques. J. Youngs tap NMR tubes sealed in a glovebox were utilised for NMR analysis. NMR spectroscopy was performed utilising a Bruker AV-300 spectrometer at 75.5 MHz (¹³C) or a Bruker AV-400 spectrometer and spectra were referenced to residual solvent peaks. Spectra were recorded at 298 K unless stated otherwise and calibration of temperatures was performed utilising 80% ethylene glycol in methanol. Solvents were dried utilising an Innovative Solutions Pure Solv MD SPS (hexane, toluene) or utilising potassium/benzophenone (diethyl ether, THF) and stored over 4Å molecular sieves. Hexadeuterobenzene and octadeuterotoluene were purchased from Goss Scientific Instruments Ltd. and dried over molten potassium then distilled under nitrogen. Amines, silanes and di-butylmagnesium were purchased from Sigma-Aldrich. Liquids were dried over CaH₂ then distilled while solids were subjected to vacuum overnight before use. Silylamines were identified by comparison to literature data and metal amides, [Ae{N(SiMe₃)₂}]₂, and alkyls were synthesised according to literature conditions¹ from commercial metal iodides purchased from Sigma-Aldrich.

General method for NMR Investigation into the synthesis of silylamines, Tables 1, 2.

In a glovebox, to a vial containing metal silylamide **1 - 3** (0.005 mmol) was added C₆D₆ (0.5 mL) followed by amine (0.1 mmol) and silane (0.1 mmol). The resultant solution was transferred to a NMR tube equipped with a Youngs tap which was sealed and the tube was removed from the glovebox. NMR analysis was performed at regular intervals and conversions were analysed by ratios of starting material to product, with products identified by comparison to literature values.

Synthesis of *N,N'*-2,6-di-isopropylphenyl-diamino(phenyl)silane, **7**.

In a glovebox, to a stirring 0.5 mol dm⁻³ heptanes solution of di-butylmagnesium (1 mmol, 0.2 mL) was added 2,6-diisopropylaniline (2 mmol, 0.35 g). The mixture was stirred for 1 hour after which time was added phenylsilane (1 mmol, 0.12 g). A rapid foaming was observed and the mixture was left to stir overnight during which time **7** crystallised as colourless blocks (76%). ¹H NMR ppm (*d*₈-THF) 7.71-6.95 (10H, m, ArH), 6.58 (1H, m, ArH), 5.28 (1H, s, SiH), 4.16 (2H, s, NH), 3.31 (2H, h, CH₃CHCH₃), 2.97 (2H, h, CH₃CHCH₃), 1.21 (12H, d, CH₃CHCH₃), 1.03 (12H, dd, CH₃CHCH₃). ¹³C{¹H} NMR ppm (*d*₈-THF) 144.3 (C_{Ar}), 139.3 (C_{Ar}), 138.1 (C_{Ar}), 134.8 (C_{Ar}), 130.8 (C_{Ar}), 128.6 (C_{Ar}), 124.3 (C_{Ar}), 123.8 (C_{Ar}), 29.1 (CH₃CHCH₃), 24.2 (CH₃CHCH₃), 24.1 (CH₃CHCH₃). Anal. Calcd. for C₃₀H₄₂N₂Si: C, 78.54; H, 9.23; N, 6.11%. Found: C, 78.42; H, 9.40; N, 6.15%

Synthesis of [(DiPPNH){DiPPNSi(H)Ph}Mg(THF)₂], **8**, and [{(H)PhSi(DiPPN)₂}Mg(THF)₃], **9**.

In a glovebox, to a stirring 0.5 mol dm⁻³ heptanes solution of di-butylmagnesium (1 mmol, 0.2 mL) diluted in THF (10 mL) was added 2,6-di-isopropylaniline (2 mmol, 0.35g). The mixture was stirred for 1 hour after which time was added phenylsilane (1 mmol, 0.12 g). A rapid foaming was observed and the mixture was left to stir overnight during. After this time, the THF was removed *in vacuo* and the residue taken up in toluene (10 mL). This solution was filtered, the solvent removed to incipient crystallisation and cooled to -20°C overnight yielding a powder. This suspension was submerged in hot water and allowed to cool overnight. This yielded **8** and **9** as colourless blocks (62%) which were separated under a microscope and subjected to X-ray analysis. [(DiPPNH){DiPPNSi(H)Ph}Mg(THF)₂], **8**. Owing to a rapid conversion of **8** to **9** in solution, meaningful NMR data could not be acquired.

Crystals of [{(H)PhSi(DiPPN)₂}Mg(THF)₃], **9**, separated by this method were found to be of insufficient quality for crystallographic analysis and as such a rational synthesis of this species was undertaken. To a heptanes solution of di-butylmagnesium (0.5 mol dm⁻³, 0.22 mmol) diluted in THF was added *N,N'*-2,6-diisopropylphenyl-diamino(phenyl)silane (100 mg, 0.22 mmol) and the mixture allowed to stir overnight. The solvent was then removed *in vacuo*, and the residue dissolved in toluene. The resultant solution was concentrated to incipient crystallisation and cooled to -18°C overnight yielding colourless blocks suitable for single crystal X-ray analysis (74%). ¹H NMR ppm (*d*₈-THF) 7.37-6.30 (11H, m, ArH), 5.14 (1H, s, SiH), 3.66 (2H, h, CH₃CHCH₃), 2.47 (2H, h, CH₃CHCH₃), 0.91 (24H, m,

CH_3CHCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ppm (d_8 -THF) 153.9 (C_{Ar}), 150.9 (C_{Ar}), 145.3 (C_{Ar}), 143.9 (C_{Ar}), 140.8 (C_{Ar}), 135.9 (C_{Ar}), 132.3 (C_{Ar}), 128.3 (C_{Ar}), 123.8 (C_{Ar}), 122.3 (C_{Ar}), 120.8 (C_{Ar}), 111.5 (C_{Ar}), 28.6 (CH_3CHCH_3), 28.2 (CH_3CHCH_3), 26.4 (CH_3CHCH_3), 23.9 (CH_3CHCH_3).
Anal. Calcd. for $\text{C}_{42}\text{H}_{64}\text{MgN}_2\text{O}_3\text{Si}$: C, 73.00; H, 9.03; N, 4.48%. Found: C, 72.78; H, 8.95; N, 4.56.

Synthesis $\{[(\text{H})\text{PhSi}(\text{DiPPN})_2]\text{Ca}(\text{THF})_3\}$, **10**.

In a glovebox, to a stirring solution of $[\text{Ca}(\text{CH}(\text{SiMe}_3)_2)(\text{THF})_2]$ (0.15 mmol, 75 mg) in THF (10 mL) was added 2,6-d-i-isopropylaniline (0.3 mmol, 53 mg). The mixture was stirred for 1 hour after which time was added phenylsilane (0.15 mmol, 16 mg). A rapid foaming was observed and the mixture was left to stir overnight. After this time, the THF was removed *in vacuo* and the residue taken up in toluene (5 mL). This solution was filtered, the solvent removed to incipient crystallisation and cooled to -20°C overnight. This yielded **10**, suitable for crystallographic characterisation (67%). ^1H NMR ppm (d_8 -THF) 7.66-6.48 (11H, m, ArH), 5.88 (1H, s, SiH), 4.51 (4H, h, CH_3CHCH_3), 1.23-1.16 (24H, m, CH_3CHCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ppm (d_8 -THF) 156.2 (C_{Ar}), 154.9 (C_{Ar}), 150.6 (C_{Ar}), 142.9 (C_{Ar}), 142.8 (C_{Ar}), 135.2 (C_{Ar}), 134.6 (C_{Ar}), 134.1 (C_{Ar}), 130.3 (C_{Ar}), 127.1 (C_{Ar}), 122.5 (C_{Ar}), 115.0 (C_{Ar}), 67.9 ($\text{O}(\text{CH}_2\text{CH}_2)_2$), 27.5 (CH_3CHCH_3), 26.0 ($\text{O}(\text{CH}_2\text{CH}_2)_2$), 25.9 (CH_3CHCH_3), 25.2 (CH_3CHCH_3), 23.9 (CH_3CHCH_3), 23.6 (CH_3CHCH_3). Repeated attempts to yield acceptable elemental analysis failed and the compound was observed to degrade in the solid state over time.

Synthesis $\{[(\text{H})\text{PhSi}(\text{DiPPN})_2]\text{Sr}(\text{THF})_4\}$, **11**.

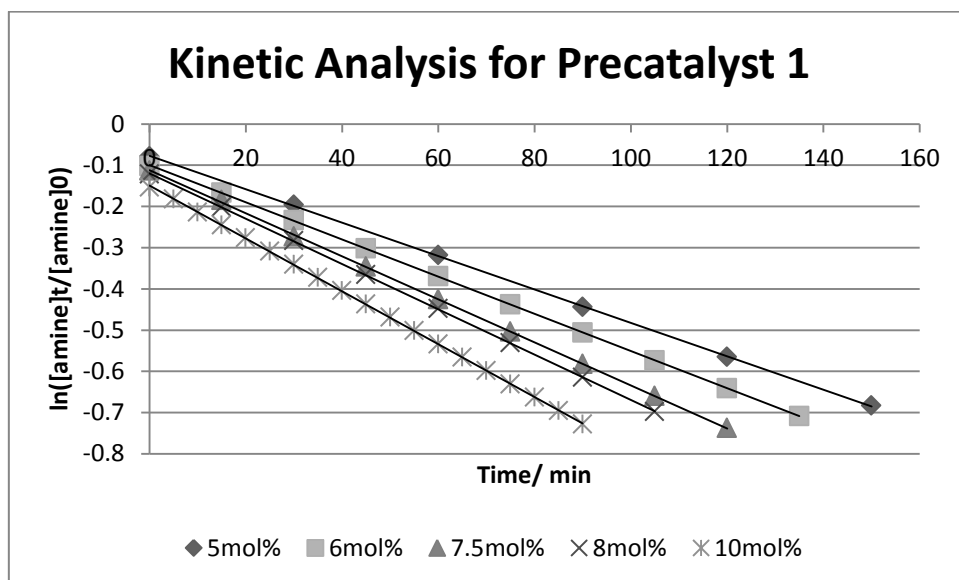
In a glovebox, to a stirring solution of $[\text{Sr}(\text{CH}(\text{SiMe}_3)_2)(\text{THF})_2]$ (0.15 mmol, 75 mg) in THF (10 mL) was added 2,6-di-isopropylaniline (0.3 mmol, 53 mg). The mixture was stirred for 1 hour after which time was added phenylsilane (0.15 mmol, 16 mg). A rapid foaming was observed and the mixture was left to stir overnight during. After this time, the THF was removed *in vacuo* and the residue taken up in toluene (5 mL). This solution was filtered, the solvent removed to incipient crystallisation and cooled to -20°C overnight. This yielded **11**, suitable for crystallographic characterisation (71%). ^1H NMR ppm (d_8 -Tol) 7.28-7.05 (11H, m, ArH), 5.60 (1H, m, SiH), 3.53 (3H, h, CH_3CHCH_3), 3.28 (16H, br. s, $\text{O}(\text{CH}_2\text{CH}_2)_2$), 2.64 (1H, h, CH_3CHCH_3), 2.12 (16H, br. s, $\text{O}(\text{CH}_2\text{CH}_2)_2$), 1.18-1.02 (24H, m, CH_3CHCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ppm (d_8 -Tol) 143.2 (C_{Ar}), 138.8 (C_{Ar}), 138.2 (C_{Ar}), 137.6 (C_{Ar}), 134.4 (C_{Ar}), 129.7 (C_{Ar}), 128.9 (C_{Ar}), 128.8 (C_{Ar}), 126.0 (C_{Ar}), 124.4 (C_{Ar}), 123.4 (C_{Ar}), 119.3 (C_{Ar}), 68.9

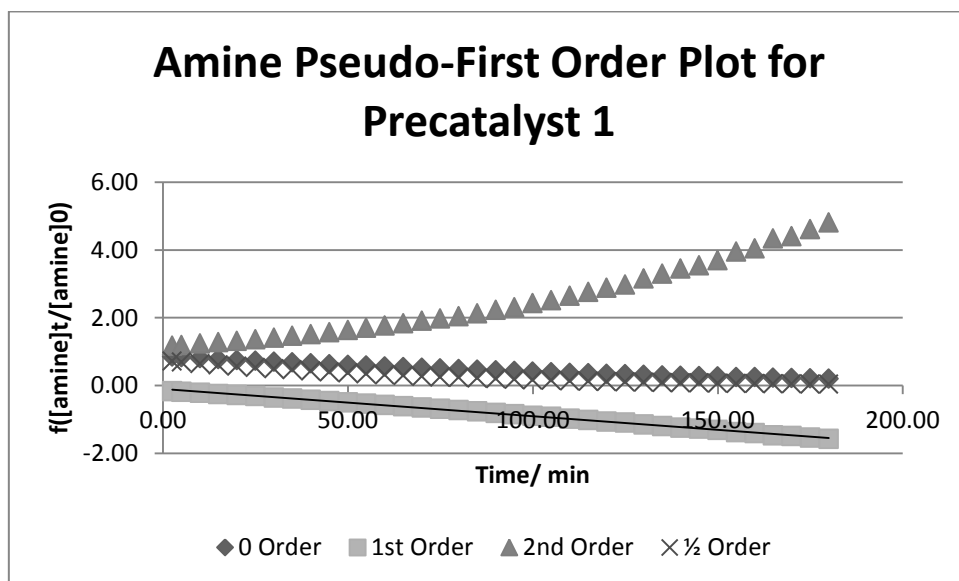
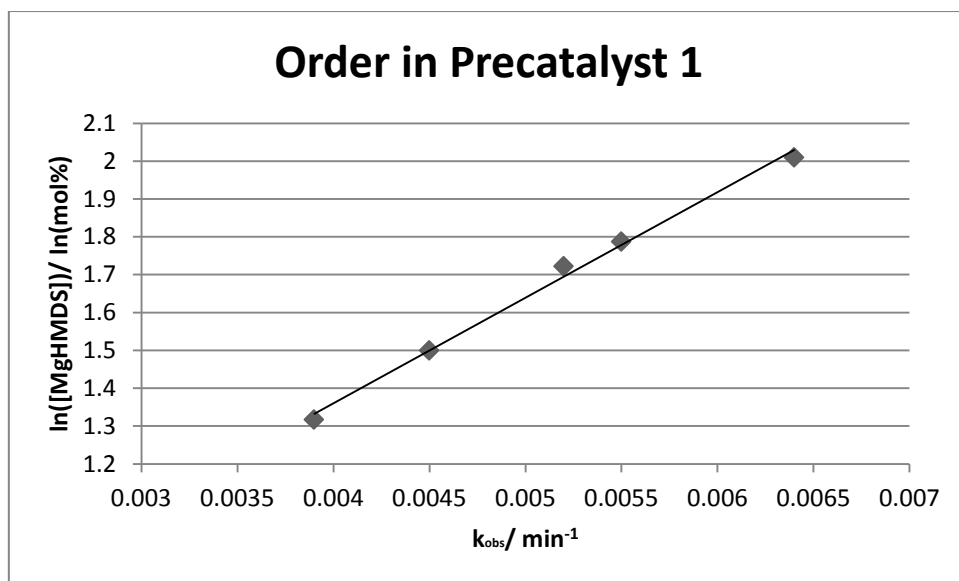
(O(CH₂CH₂)₂), 29.1 (CH₃CHCH₃), 28.6 (CH₃CHCH₃), 25.9 (O(CH₂CH₂)₂), 24.3 (CH₃CHCH₃), 22.9 (CH₃CHCH₃), 21.7 (CH₃CHCH₃). Anal. Calcd. for C₄₆H₇₂N₂O₃SiSr: C, 66.34; H, 8.71; N, 3.36%. Found: C, 66.27; H, 8.68; N, 3.42%.

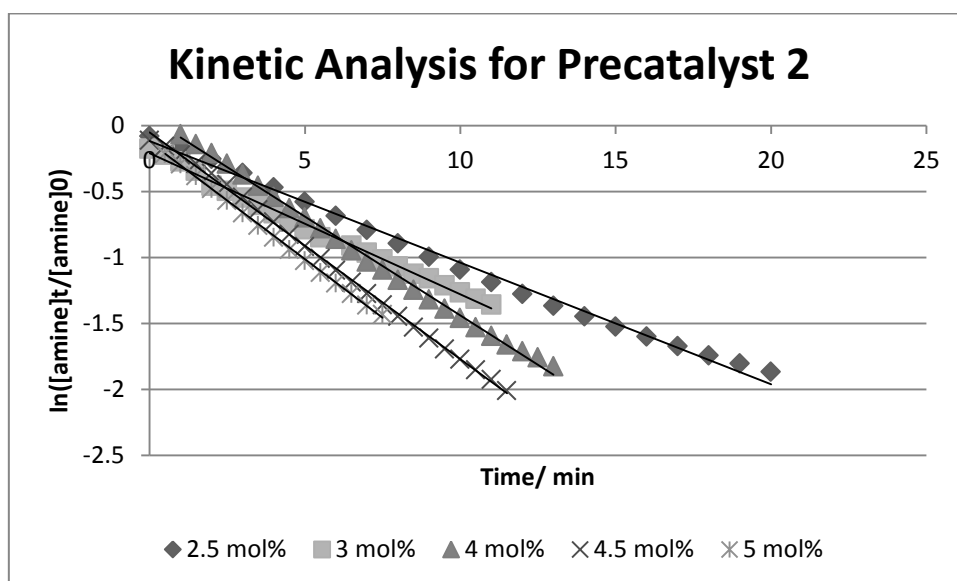
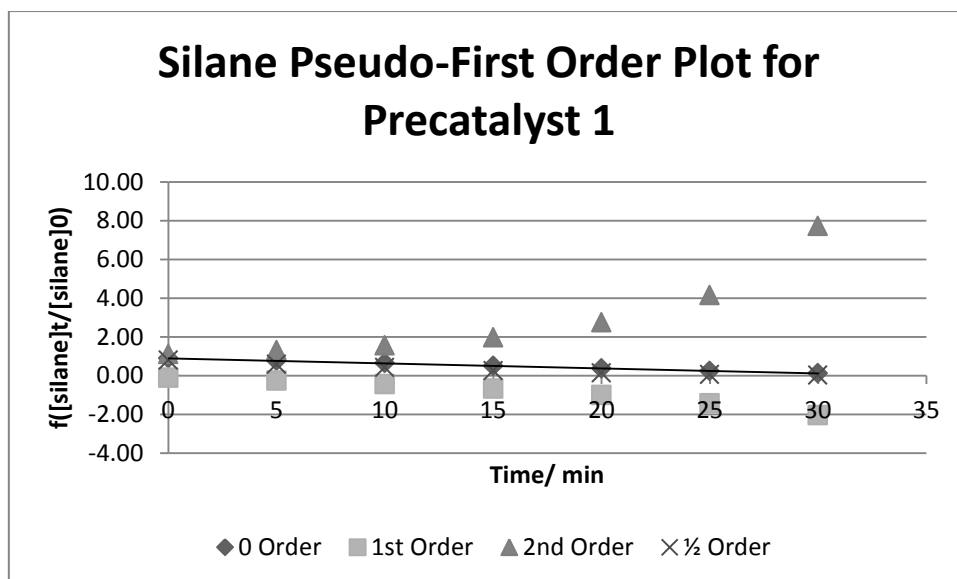
General method for kinetic investigation into the turnover frequency and order in reagents, Table 6 and equations 2 – 3.

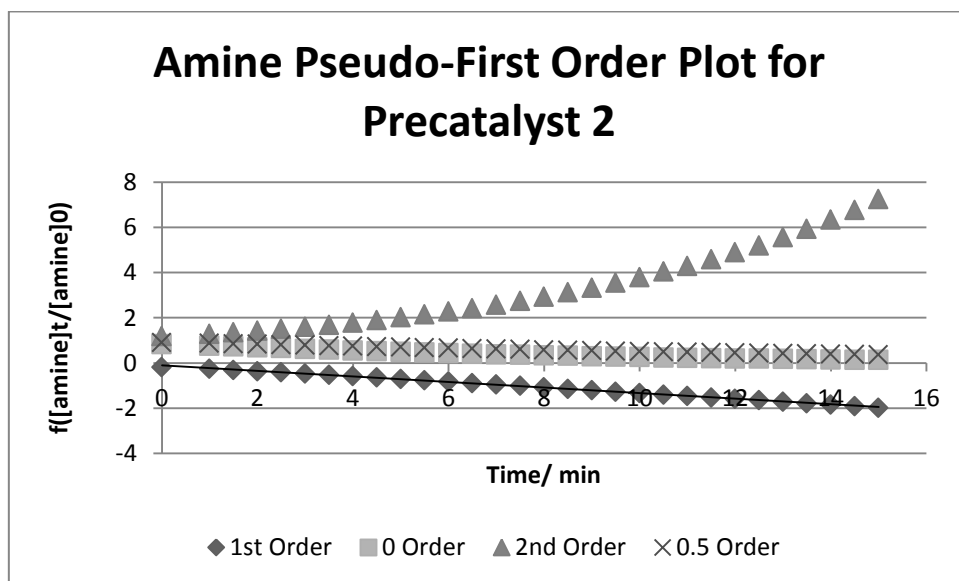
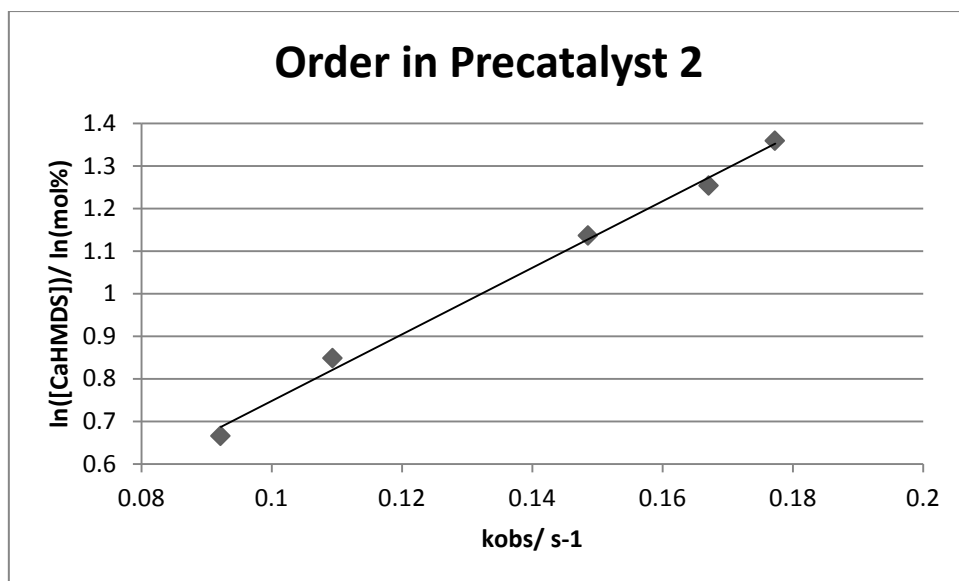
In a glovebox, to a vial containing metal silylamide **1** - **3** (concentrations noted) was added C₆D₆ (0.5 mL) followed by silane (0.1 or 1 mmol) then amine (0.1 or 1 mmol). The resultant solution was transferred to a NMR tube equipped with a Youngs tap which was sealed, removed from the glovebox and frozen in liquid nitrogen. The tube was then thawed and immediately transferred to the spectrometer and subjected to NMR analysis at regular intervals. Turnover frequencies were calculated using the least squares gradients of the catalyst loading analysis via equation A.

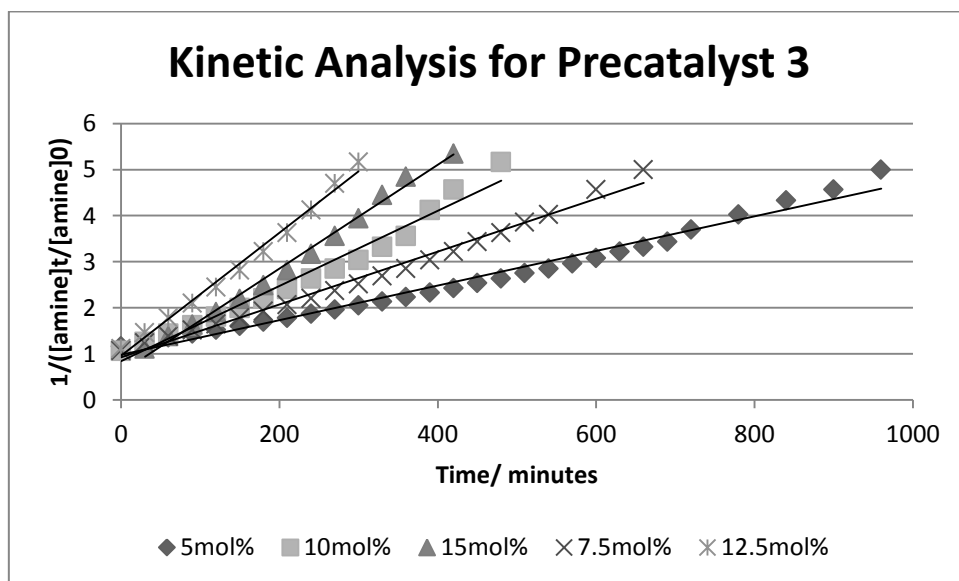
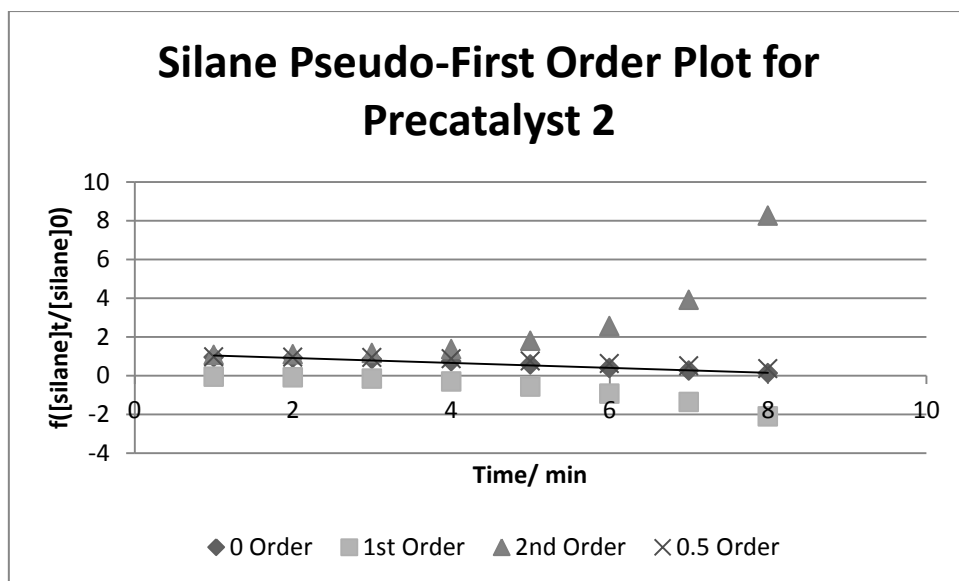
$$ToF = \frac{m}{[catalyst]} \quad (A)$$

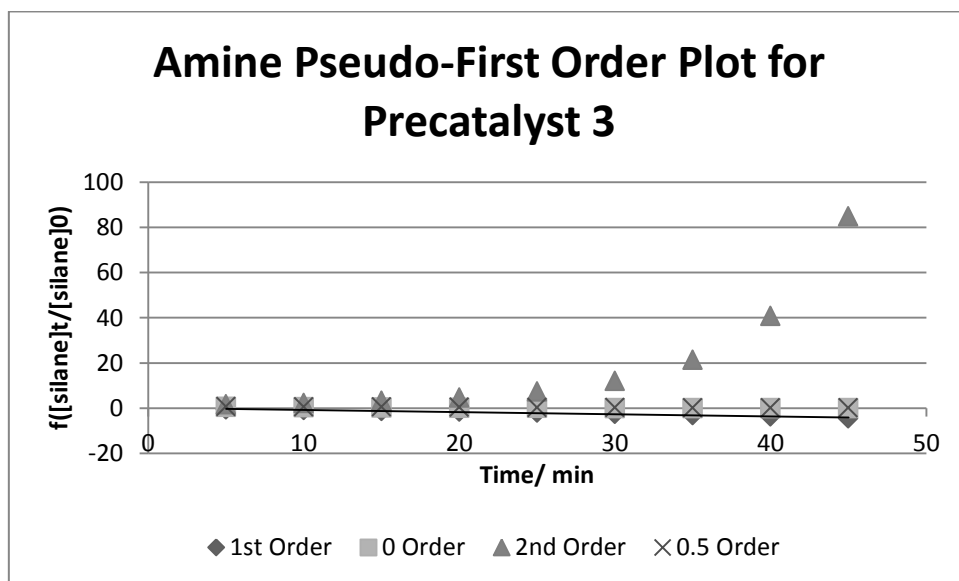
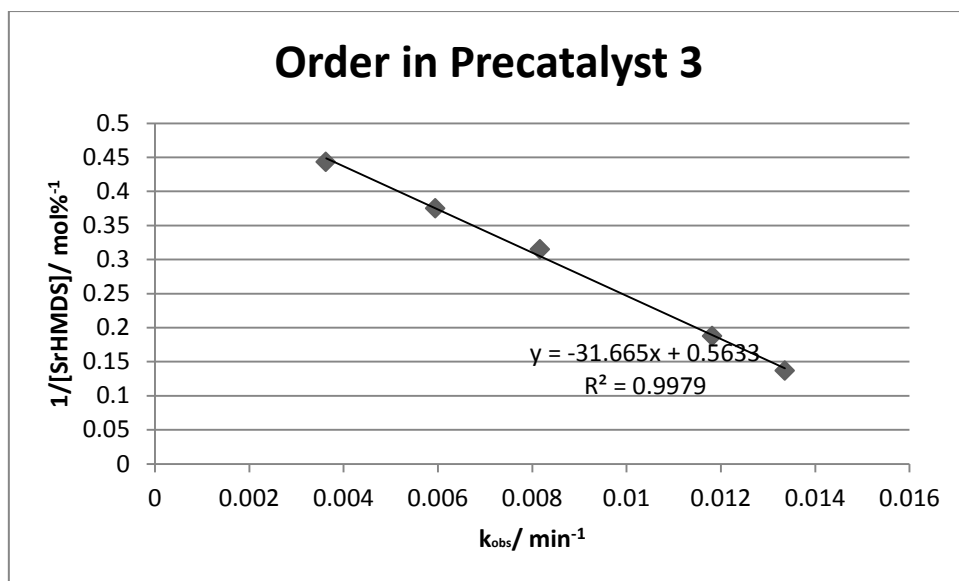


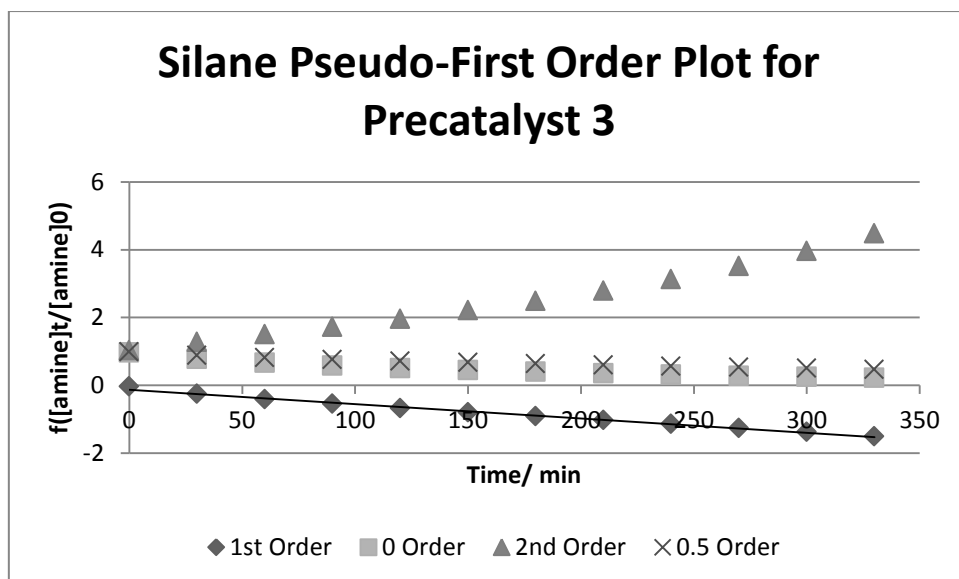






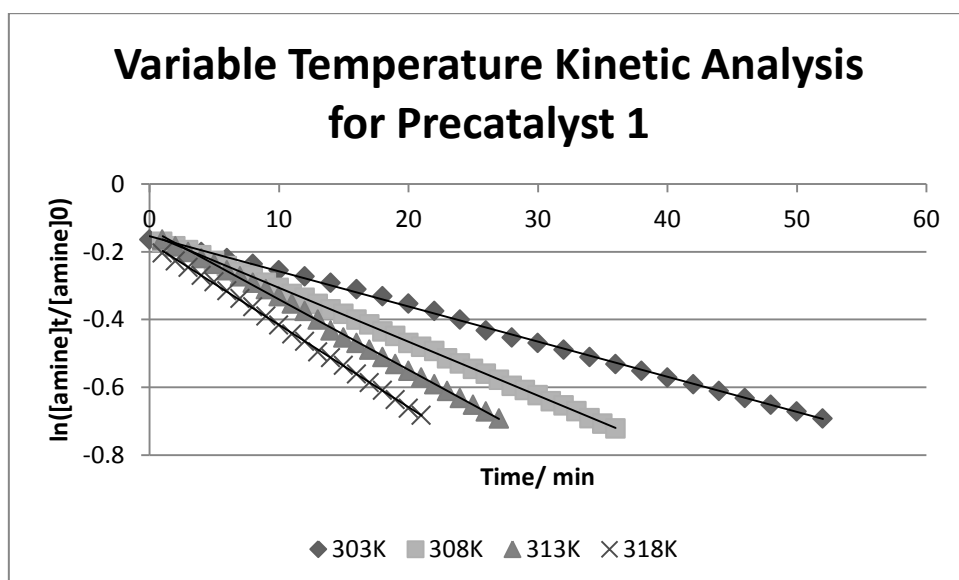


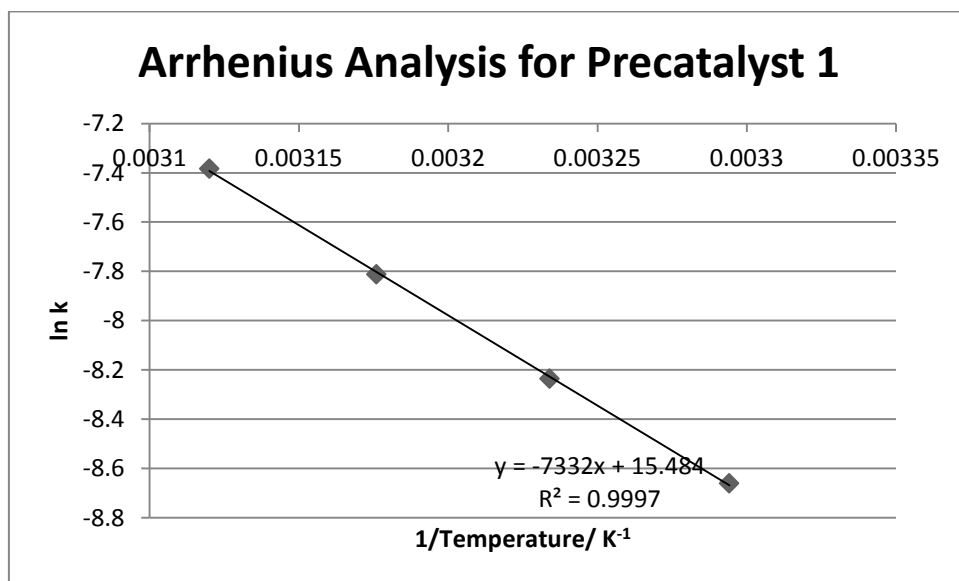
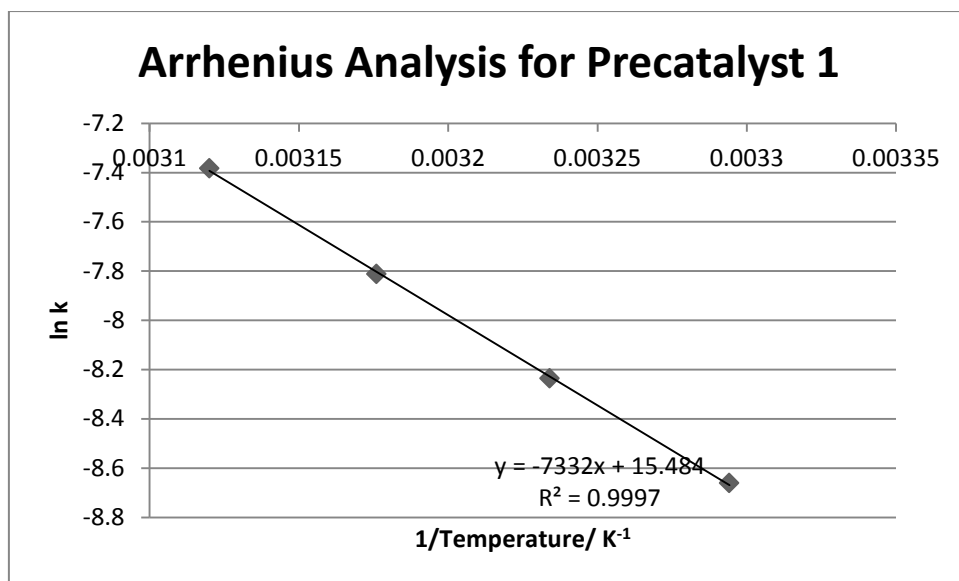


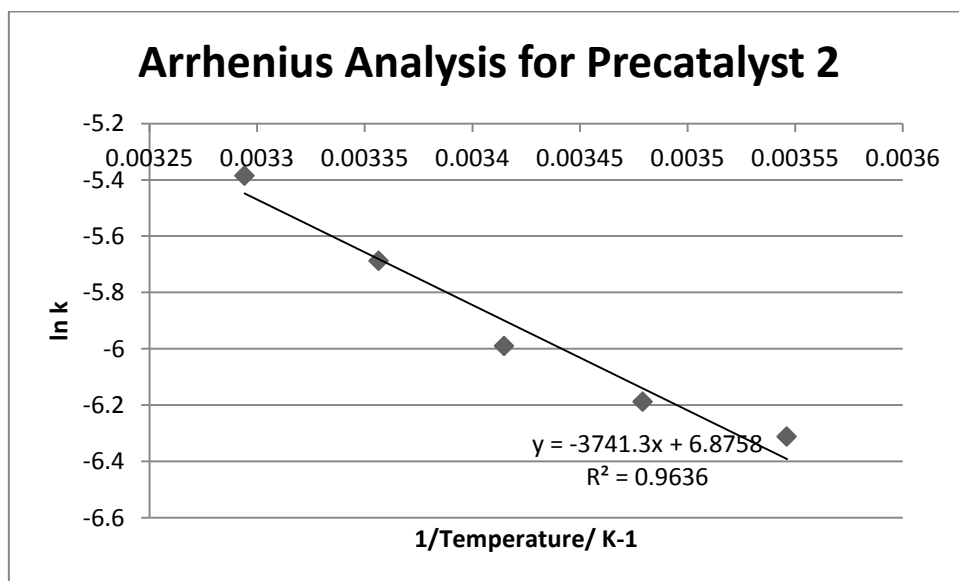
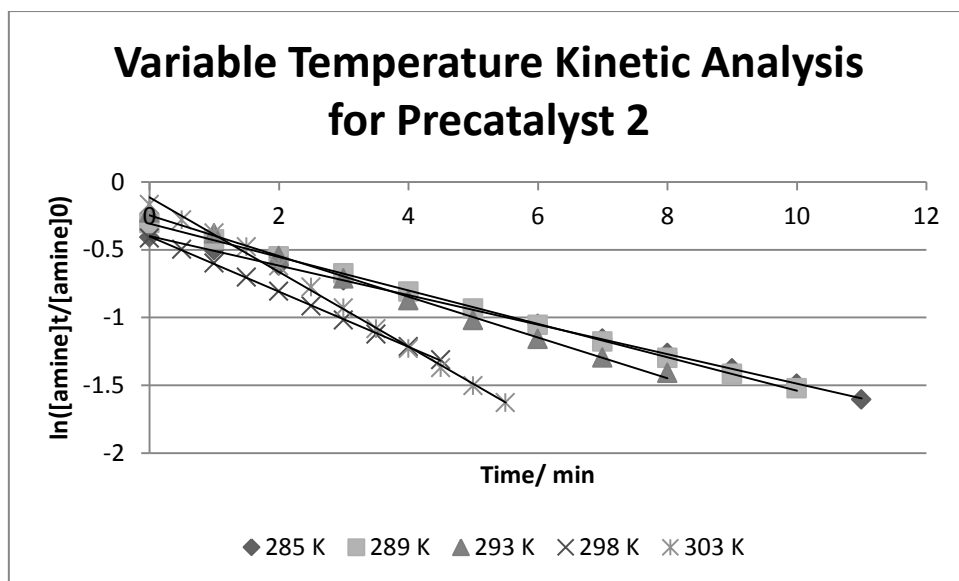


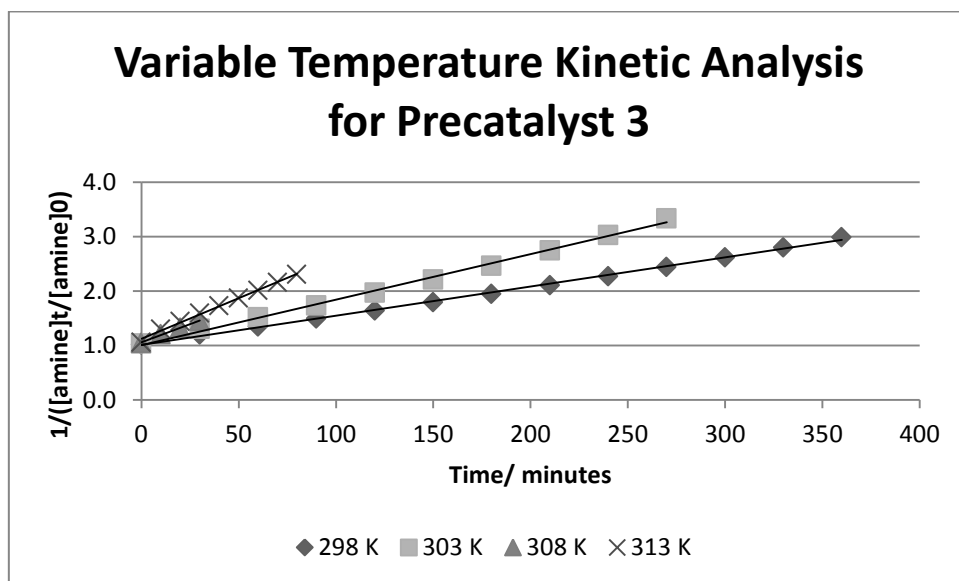
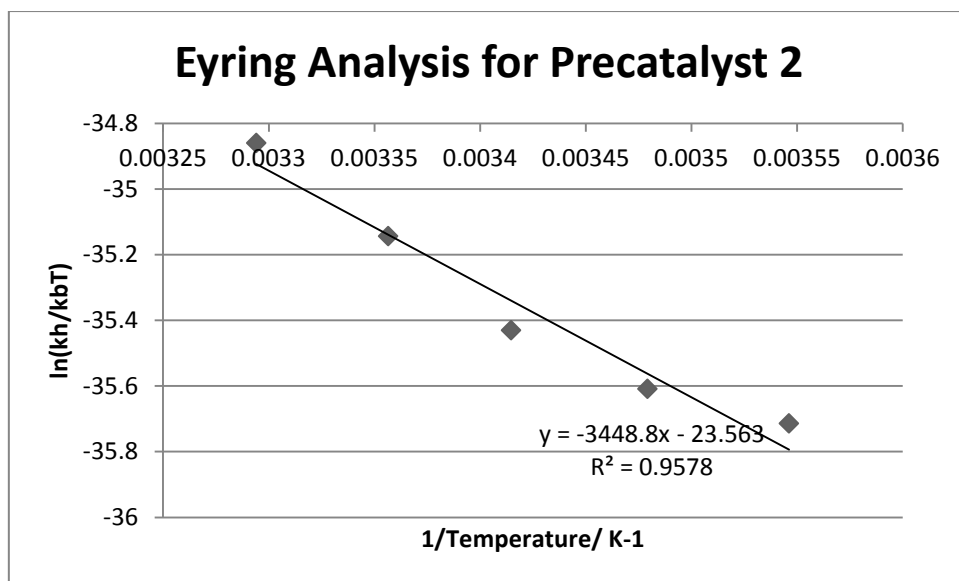
General method for Eyring and Arrhenius studies, Table 6.

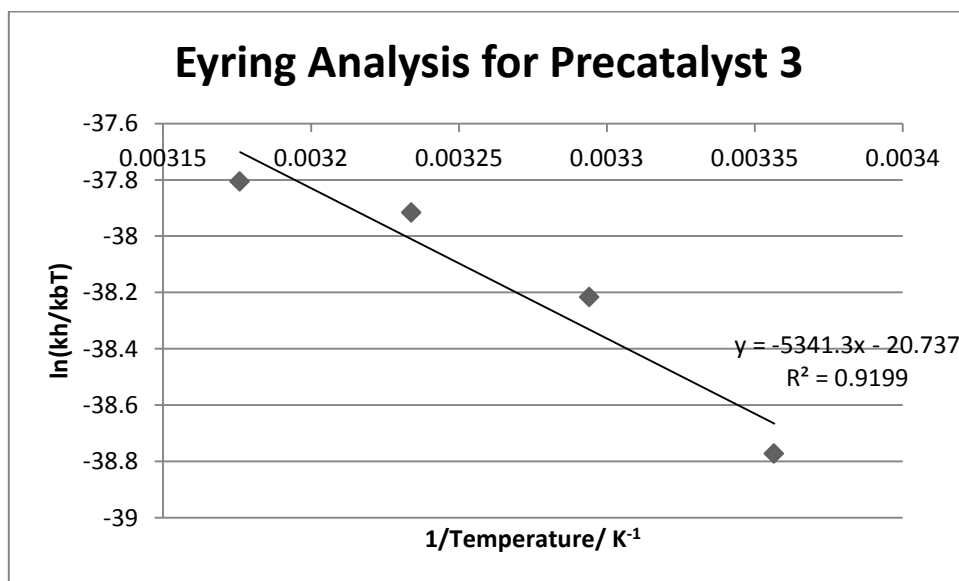
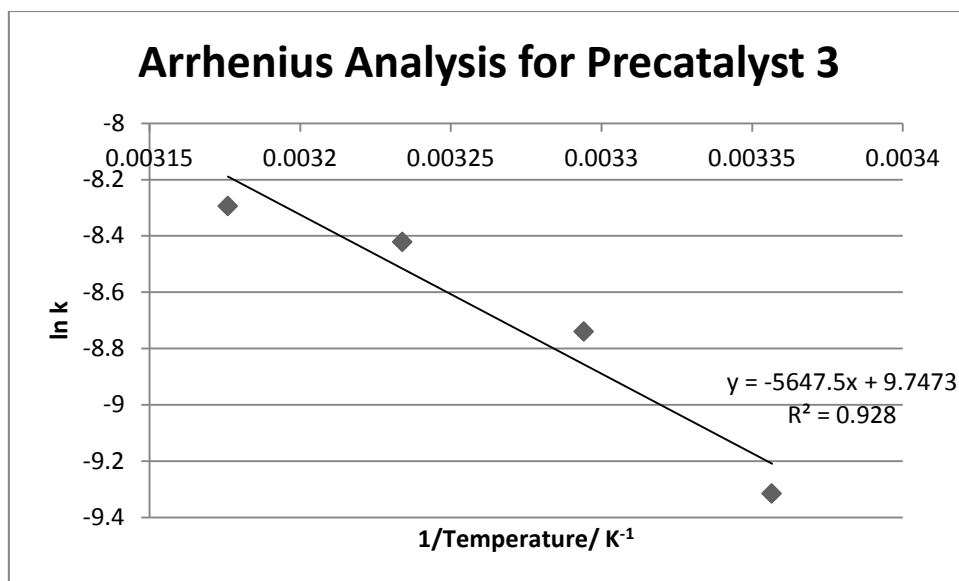
In a glovebox, to a vial containing metal silylamide **1** - **3** (concentrations noted) was added C_6D_6 (0.5 mL) followed by silane (0.1 mmol) then amine (0.1 mmol). The resultant solution was transferred to a NMR tube equipped with a Youngs tap which was sealed, removed from the glovebox and frozen in liquid nitrogen. The tube was then thawed and immediately transferred to the spectrometer and subjected to NMR analysis at regular intervals. This was then repeated at the range of temperatures noted.











Crystallographic Analysis

Diffraction data for compounds **7** - **11** were collected on a Nonius Kappa CCD with a low temperature device at 150 K, utilising Mo-K α radiation monochromated with graphite ($\lambda = 0.71070 \text{ \AA}$). Processing utilised the Nonius software,^{2,3} with structure solution and refinement using WINGX 1.6, SHELXS and SHELXL⁴ and visualised utilising Ortep 3.⁵

1. (a) P. B. Hitchcock, M. F. Lappert, G. A. Lawless, and B. Royo, *J. Am. Chem. Soc.* 1990, **30**, 96; (b) M. Westerhausen, *Inorg. Chem.* 1991, **30**, 96; (c) M. R. Crimmin, A. G. M. Barrett, M. S. Hill, D. MacDougall, M. F. Mahon and P. A. Procopiu, *Chem., Eur. J.*, 2008, **14**, 11292.
2. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *Journal of Applied Crystallography*, 1999, **32**, 115-119.
3. Z. Otwinowski and W. Minor, *DENZO-SMN Manual*, University of Texas Southwestern Medical Center, Dallas, USA, 1996.
4. G. M. Sheldrick, *SHELXL97-2, Program for Crystal Structure Refinement*, Universität Göttingen, Göttingen, Germany, 1998.
5. C. Barnes, *Journal of Applied Crystallography*, 1997, **30**, 568.