Supporting Information

Activation of Si-H bonds in electron rich nickel $PC_{carbene}P$ pincer complexes

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Experimental Details

General Considerations. Storage and manipulation of all compounds were performed under an argon atmosphere either in a IT glove box or using a double manifold high vacuum line using standard techniques. Passage of argon through an OxisorBW scrubber (Matheson Gas Products) removed any residual oxygen and moisture. Toluene, hexanes, pentane and tetrahydrofuran were dried and purified using a Grubbs/Dow solvent purification system and stored in 500 mL thick-walled glass vessels over sodium/benzophenone ketal, and distilled under reduced pressure. C_6D_6 was dried over sodium/benzophenone ketal. Toluene-d8 was dried and stored over sodium. 2-MeTHF was distilled from sodium and stored over Na/K alloy. All dried solvents were degassed and vacuum distilled prior to use. ^{1}H and ^{13}C NMR spectroscopy chemical shifts were referenced to residual proteo-solvent resonances and naturally abundant ^{13}C resonances for all deuterated solvents. Chemical shift assignments are based on ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$, ^{1}H- ^{13}C-HSQC and ^{1}H- ^{13}C-HMBC NMR experiments performed on Bruker RDQ-400, Ascend-500 or Avance-600 MHz spectrometers **2,**[1] tris(*p*-tolyl)silane, tris(*p*-fluorophenyl)silane, tris(*p*-anisole)silane[2] and triphenylsilane-*d* [3] were prepared by literature methods. All other reagents were purchased from Sigma-Aldrich and used as received. All Elemental analyses were obtained by the Instrumentation Facility of the Department of Chemistry, University of Calgary. Diffraction were collected with Cu Kα radiation on a Bruker Smart diffractometer equipped with Apex II detector, fixed-CHI goniometer, and sealed-tube (Cu) source or with Mo Kα radiation on a Nonius Kappa CCD diffractometer. All calculations were carried out using Gaussian 09[4]

General Procedure for the Synthesis of Complexes $\mathbf{3_{Ph}}$, $\mathbf{3_{Ph\text{-}d}}$, $\mathbf{3_{p\text{-}Me\text{-}Ph}}$, and $\mathbf{3_{p\text{-}OMe\text{-}Ph}}$

A 25 mL round bottom flask was charged with 100 mg (0.18 mmol) of **2**, 1.1 equivalents of the appropriate silane, 40 mg (0.2 mmol) of potassium hexamethyldisilazane (KHMDS) and 2 mL THF, and left to stir under argon for 18h. Solvent was removed in vacuo, and the residue was dissolved in 5 mL toluene, and filtered through a 0.1μm PTFE syringe filter. Toluene was removed in vacuo to yield a yellow-brown oil. The oil was triturated with pentane, to yield a yellow powder. X-ray quality crystals were grown by layering a saturated toluene solution with pentane and cooling to -30 ^{o}C for two days.

3_{Ph}

Yield: 106 mg (80%)

^{1}H NMR data: ^{1}H NMR (600 MHz, Benzene-d_6) δ 7.67 (dd, J = 8.2, 1.7 Hz, 2H), 7.49 (dt, J = 6.8, 1.5 Hz, 6H), 7.14 – 7.07 (m, 5H), 7.08 – 7.05 (m, 5H), 7.05 – 7.03 (m, 1H), 7.00 – 6.94 (m, 2H), 6.94 – 6.89 (m, 2H), 2.11 – 2.02 (m, 2H), 2.00 – 1.91 (m, 2H), 1.14 (dd, J = 7.3, 5.1 Hz, 6H), 1.08 – 1.02 (m, 6H), 1.02 – 0.97 (m, 6H), 0.70 (dd, J = 7.2 Hz, 6H), -13.56 (t, J = 61.6 Hz, 1H).

^{13}C NMR data: ^{13}C NMR (151 MHz, Benzene-d_6) δ 161.03 , 140.38 (t), 140.23 , 137.95 , 132.39 (t, J = 6.7 Hz), 131.70 , 128.80 , 128.58 , 128.35 , 128.14 , 127.98 , 127.24 , 123.09 (t, J = 2.8 Hz), 26.29 (t, J = 11.4 Hz), 25.68 (t, J = 14.3 Hz), 21.17 – 21.09 (m), 20.07 (t, J = 2.9 Hz), 19.95 , 18.74

^{31}P NMR (243 MHz, Benzene-d_6) δ 56.28.

^{29}Si NMR (from ^{1}H-^{29}Si HMBC) δ -4.20

IR: 1781 cm^{-1} (Ni-H) 1260 (Ni-D)

Elemental Analysis: Calcd. (%): C 71.97% H 7.30%, Found C 72.29% H 7.58% N 0.02%

$3_{p\text{-}Me\text{-}Ph}$

Yield: 68 mg (48%)

^{1}H NMR (600 MHz, Benzene-d_6) δ 7.76 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 7.5 Hz, 8H), 7.02 (t, J = 7.5 Hz, 2H), 6.95 (dd, J = 14.3, 7.3 Hz, 8H), 2.09 (s, 9H), 1.94 (ddd, J = 10.5, 7.5, 3.8 Hz, 4H), 1.17 (q, J = 7.3 Hz, 6H), 1.07 (dq, J = 22.6, 7.6, 7.1 Hz, 12H), 0.72 (q, J = 7.1 Hz, 6H), -13.54 (t, J = 61.7 Hz, 1H).

^{13}C NMR (151 MHz, Benzene-d_6) δ 160.94 (t, J = 16.5 Hz), 140.17 (t, J = 16.8 Hz), 137.60 (d, J = 8.3 Hz), 136.49 , 132.02 (t, J = 6.7 Hz), 131.26 , 127.93 , 127.72 , 127.56 , 122.58 (t, J = 2.7 Hz), 99.96 , 59.86 , 25.76 (t, J = 11.3 Hz), 25.20 (t, J = 14.2 Hz), 20.98 , 20.88 , 19.70 (d, J = 2.9 Hz), 19.58 , 18.27 .

^{31}P NMR (203 MHz, Benzene-d_6) δ 56.65

Elemental Analysis: Calc. (%):C, 72.73; H, 7.70 Found: C 72.57% H 7.32%

$3_{p\text{-}OMe\text{-}Ph}$

Yield 69 mg (46%)

^{1}H NMR (400 MHz, Benzene-d_6) δ 7.76 (d, J = 8.2 Hz, 2H), 7.44 – 7.36 (m, 6H), 7.22 – 7.11 (m, 2H), 7.02 (q, J = 5.7, 3.6 Hz, 2H), 6.95 (s, 2H), 6.78 – 6.70 (m, 6H), 3.31 (s, 9H), 2.14 – 2.04 (m, 2H), 2.02 – 1.92 (m, 2H), 1.22 – 1.12 (m, 6H), 1.16 – 1.00 (m, 12H), 0.77 – 0.68 (m, 6H). -13.47 (t, 1H J =60 Hz).

^{13}C NMR (101 MHz, Benzene-d_6) δ 161.04 (t, J = 16.5 Hz), 160.25 , 140.22 (t, J = 16.8 Hz), 138.98 , 131.98 (t, J = 6.6 Hz), 131.26 (d, J = 11.4 Hz), 128.38 , 122.57 (d, J = 2.8 Hz), 112.70 , 60.61 , 54.13 , 25.83 (t, J = 11.6 Hz), 25.32 (t, J = 14.2 Hz), 22.33 , 20.89 (d, J = 2.6 Hz), 19.74 (t, J = 2.6 Hz), 19.62 , 18.43 .

^{31}P NMR (162 MHz, Benzene-d_6) δ 56.19 .

Elemental Analysis: Calcd. (%):C, 68.41; H, 7.24; Found: C 68.14% H 7.21%

Procedure for the Synthesis of Complex 3_{PhMe2}

A 25 mL round bottom flask was charged with 100 mg (0.18 mmol) of **2**, 1.1 equivalents of the appropriate silane, 40 mg (.20 mmol) of potassium hexamethyldisilazane (KHMDS), and 2 mL THF, and left to stir under argon for 18h. Solvent was removed in vacuo, and the residue was dissolved in 5 mL pentane, and filtered through a 0.1μm PTFE syringe filter. Pentane was removed in vacuo to yield a yellow-brown oil. The oil was dissolved in a minimal amount of pentane and left to recrystallize at -30 ^{o}C for two days.

3_{PhMe2}

Yield: 91 mg (82%)

^{1}H NMR (500 MHz, Benzene-d_6) δ 7.92 (d, J = 8.0 Hz, 2H Ar**H**), 7.47 – 7.41 (m, 2H, Ar**H**), 7.27 – 7.20 (m, 2H, Ar**H**), 7.16 (m, 3H Ar**H**), 7.11 (d, J = 7.2 Hz, 1H, Ar**H**), 6.94 (t, J = 7.3 Hz, 2H, Ar**H**), 2.24 – 2.13 (m, 2H, **CH**$(CH_3)_2$), 2.09 – 1.99 (m, 2H **CH**$(CH_3)_2$), 1.30 – 1.21 (m, 12H CH**(CH$_3$)$_2$**), 1.07 (vq, J = 7.4 Hz, 6H, CH**(CH$_3$)$_2$**), 0.70 (vq, J = 7.2 Hz, 6H, CH**(CH$_3$)$_2$**), 0.34 (s, 6H, Si**(CH$_3$)$_2$**).

^{13}C NMR (126 MHz, Benzene-d_6) δ 162.25 (vt, J = 16.9 Hz P**Ar**), 143.48 , 139.98 (vt, J = 16.6 Hz), 134.55 , 131.55 , 130.03 (vt, J = 6.9 Hz), 129.23 , 128.35 , 128.14 , 127.97 , 127.51 , 122.68 (vt, J = 2.9 Hz), 58.94 (A**r**C**A**r) , 26.20 (t, J = 11.4 Hz), 25.63 (vt, J = 13.8 Hz), 22.70 (vt, J = 3.7 Hz), 19.93 (vt, J = 2.7 Hz), 19.64 , 18.68 , 1.34 (Si**C**H$_3$) .

^{31}P NMR (203 MHz, Benzene-d_6) δ 56.55

^{29}Si NMR (From ^{1}H-^{29}Si HMBC) δ -5.58

Elemental Analysis: Calcd. (%): C 66.79% H 8.15% Found: C 66.96% H 8.47% N .06%

Synthesis of 4

A 10 mL round bottom flask was charged with 100 mg (0.18 mmol) of **2**, 50 mg (0.43 mmol) of NaOPh, and 5mL THF. The resulting suspension was stirred for 18 h, then the solvent was removed *in vacuo*. The residue was dissolved in toluene and filtered through 0.1μm PTFE syringe filter. The filtrate was concentrated *in vacuo* and triturated in pentane to yield an orange powder. The powder was dissolved in minimal hexanes and X-ray quality crystals were grown at -30 ^{o}C over two days. Yield: 24 mg (23%)

^{1}H NMR (500 MHz, Benzene-d_6) δ 7.58 (d, J = 7.8 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.16 – 7.13 (m, 4H), 7.06 – 6.98 (m, 4H), 6.89 (t, J = 7.3 Hz, 2H), 6.74 (t, J = 7.1 Hz, 1H), 4.93 (s, 1H), 2.26 – 2.15 (m, 2H), 2.12 – 2.00 (m, 2H), 1.33 – 1.19 (m, 18H), 0.96 (q, J = 6.8 Hz, 6H).

^{13}C NMR (126 MHz, Benzene-d_6) δ 169.94 , 159.18 (t, J = 17.7 Hz), 132.71 (t, J = 18.1 Hz), 130.60 , 129.11 , 128.10 , 126.03 , 123.87 (t, J = 2.9 Hz), 119.79 , 111.69 , 36.26 (t, J = 9.6 Hz), 23.90 (t, J = 9.1 Hz), 23.15 (t, J = 10.5 Hz), 17.95 (t, J = 2.6 Hz), 17.28 (t), 16.55 .

^{31}P NMR (203 MHz, Benzene-d_6) δ 38.43 .

Elemental Analysis: Calcd. (%): C, 67.54; H, 7.68 Found: C 67.86% H 7.93%

Synthesis of $\mathbf{5_{Ph}}$

200 mg of 10:90 Na/K alloy was suspended in 4 mL of THF. To this suspension, 200 mg (0.68 mmol) of $ClSiPh_3$ was added. The solution was stirred vigorously for 18h to yield a yellow-orange solution of $KSiPh_3$. The solution was filtered through a 0.1μm PTFE syringe filter. The filtrate was diluted to 15 mL THF and cooled to -30 ^{o}C. 200 mg (0.36 mmol) of **2** was added to the solution, and left to stir for 24h at -30 ^{o}C. The solution was warmed, and the solvent was removed *in vacuo*. The residue was dissolved in toluene and filtered through 0.1μm PTFE syringe filter. The filtrate was concentrated *in vacuo,* and the residue was triturated with pentane to yield an analytically pure red-brown powder. X-ray quality crystals were grown by slow evaporation of a pentane wash at ambient temperatures. Yield: 161 mg (60%)

^{1}H NMR (600 MHz, Benzene-d_6) δ 8.07 – 7.96 (m, 6H), 7.65 – 7.50 (m, 2H), 7.39 (d, J = 7.8 Hz, 2H), 7.19 – 7.07 (m, 10H), 6.86 (t, J = 7.4 Hz, 3H), 5.79 (s, 1H), 2.05 – 1.90 (m, 4H), 1.09 (m, 12H), 0.88 – 0.79 (m, 12H).

^{13}C NMR (151 MHz, Benzene-d_6) δ 159.10 (t, J = 16.2 Hz), 147.99 , 137.63 , 137.42 – 136.62 (m), 136.25 , 132.75 , 129.96 , 128.35 , 127.63 (t, J = 6.7 Hz), 127.36 , 127.19 , 123.37 (d, J = 3.1 Hz), 61.39 , 61.35 , 61.31 , 26.73 , 26.65 , 26.57 , 25.62 , 25.55 , 25.48 , 21.66 , 21.25 , 19.32 , 19.07 .

^{31}P NMR (243 MHz, Benzene-d_6) δ 52.77

^{29}Si NMR (119 MHz, Benzene-d_6) δ -0.21 (t, J = 44.8 Hz)

Elemental analysis: Calc: C 71.97%, H 7.30% Found: C 71.65%, H 7.21%

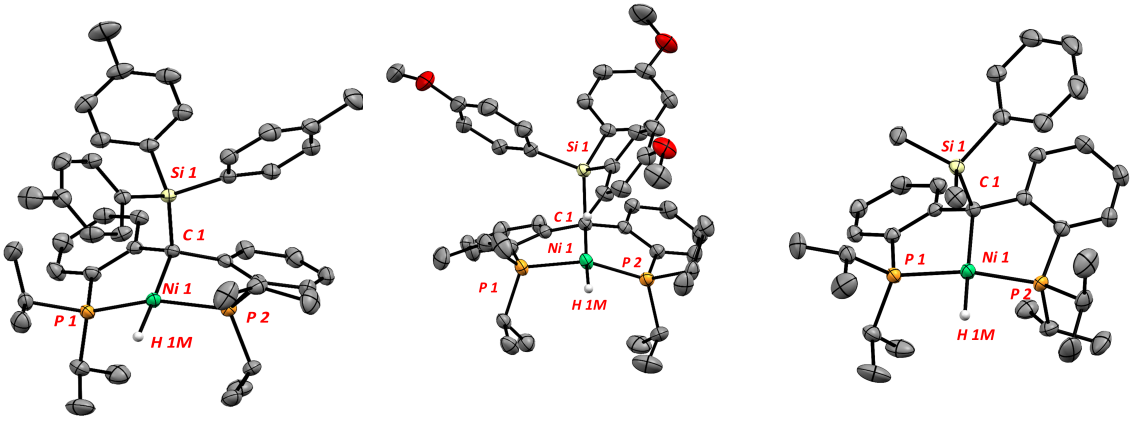


Figure S1. ORTEP diagrams for complexes $\mathbf{3}_{\mathbf{Si}}$, $\mathbf{3}_{\mathbf{p\text{-}Me\text{-}Ph}}$ (left), **$\mathbf{3}_{\mathbf{p\text{-}OMe\text{-}Ph}}$** (middle), **$\mathbf{3}_{\mathbf{PhMe2}}$** (right). Thermal ellipsoids are shown at the 50% probability level. Calculated hydrogen atoms are omitted for clarity. Selected Bond Distances and Angles for **$\mathbf{3}_{\mathbf{p\text{-}Me\text{-}Ph}}$**: Ni1-C1= 2.0559(15), Ni1-P1 = 2.1187(5), Ni1-P2 = 2.1375(5), Ni1-H1M = 1.43(3); C14-C1-Ni1 = 106.71(10), C2-C1-Ni1 = 112.05(10), Si1-C1-Ni1 = 103.97(7), C1-Ni1-P1 = 89.72(5), C1-Ni1-P2 = 90.88(5), P1-Ni1-P2 = 157.02(2), C1-Ni1-H1M = 174.5(10), P1-Ni1-H1M = 85.7(10), P2-Ni1-H1M = 92.2(10), C3-P1-Ni1 = 103.35(6), C8-P1-Ni1 = 123.06(6), C11-P1-Ni1 = 118.12(6), C15-P2-Ni1 = 99.52(6), C23-P2-Ni1 = 115.00(6), C20-P2-Ni1 = 124.24(6). Selected Bond Distances and Angles for **$\mathbf{3}_{\mathbf{p\text{-}OMe\text{-}Ph}}$**: Ni1-C1 = 2.0483(14), Ni1-P1 = 2.1220(5), Ni1-P2 = 2.1244(4), Ni1-H1M = 1.40(2); C1-Ni1-P1 = 89.91(4), C1-Ni1-P2 = 91.02(4), P1-Ni1-P2 = 154.01(2), C1-Ni1-H1M = 176.4(10), P1-Ni1-H1M = 87.1(10), P2-Ni1-H1M = 90.8(10), C15-P1-Ni1 = 103.12(5), C23B-P1-Ni1 = 105.1(2), C20-P1-Ni1 = 124.63(6), C23A-P1-Ni1 = 121.17(17), C3-P2-Ni1 = 100.50(5), C11-P2-Ni1 = 113.44(5), C8-P2-Ni1 = 124.66(7), C2-C1-Ni1 = 108.27(9), C14-C1-Ni1 = 112.28(9), Si1-C1-Ni1 = 102.67(7). Selected Bond Distances and Angles for **$\mathbf{3}_{\mathbf{PhMe2}}$**: Ni1-C1= 2.0373(16), Ni1-P2 = 2.1012(5), Ni1-P1 = 2.1244(5), Ni1-H1M = 1.44(3); C2-C1-Ni1 = 108.13(10), C14-C1-Ni1 = 113.55(11), Si1-C1-Ni1 = 97.25(7), C1-Ni1-P2 = 88.51(5), C1-Ni1-P1 = 90.21(5), P2-Ni1-P1 = 154.42(2), C1-Ni1-H1M = 179.0(10), P2-Ni1-H1M = 90.8(10), P1-Ni1-H1M = 90.7(10), C3-P1-Ni1 = 99.35(6), C11-P1-Ni1 = 116.26(6), C8-P1-Ni1 = 122.00(6), C15-P2-Ni1 = 104.42(6), C20-P2-Ni1 = 123.54(7), C23-P2-Ni1 = 110.69(6).

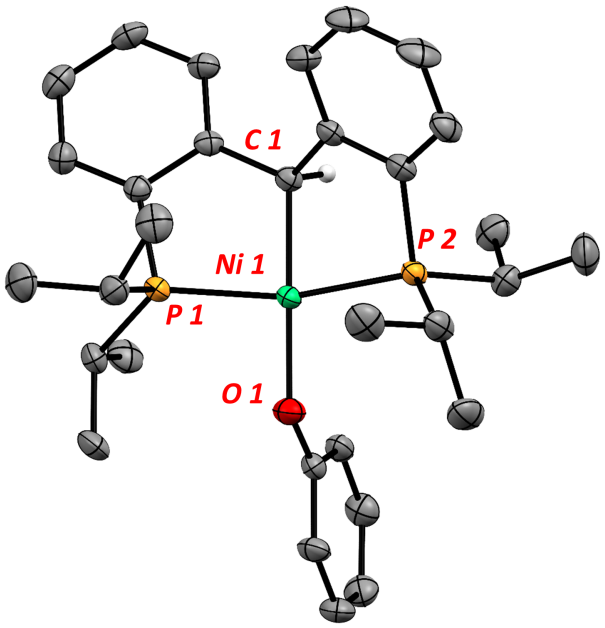


Figure S2: ORTEP diagram for complex 4. Thermal ellipsoids are shown at the 50% probability level. Calculated hydrogen atoms are omitted for clarity. Selected Bond Distances and Angles: Ni1-C1= 1.983(3), Ni1-O1 = 1.913(2), Ni1-P1 = 2.1691(8), Ni1-P2 = 2.2124(8); C14-C1-Ni1 = 109.21(18), C2-C1-Ni1 = 116.40(19), Ni1-C1-H1 = 104.9, O1-Ni1-C1 = 179.35(11), O1-Ni1-P1 = 94.12(7), C1-Ni1-P1 = 86.03(8), O1-Ni1-P2 = 95.92(7), C1-Ni1-P2 = 84.14(8), P1-Ni1-P2 = 158.43(4), C26-O1-Ni1 = 122.13(19), C3-P1-Ni1 = 104.44(10), C11-P1-Ni1 = 123.25(10), C8-P1-Ni1 = 109.82(10), C15-P2-Ni1 = 98.70(10), C20-P2-Ni1 = 113.38(10), C23-P2-Ni1 = 124.06(10)

Table S1. Crystal Data Collection and Refinement Parameters for compounds 3_{Si}.

	3_{Ph}	$3_{p\text{-}Me\text{-}Ph}$	$3_{p\text{-}OMe\text{-}Ph}$	3_{PhMe2}
formula	$C_{43}H_{52}NiP_2Si$	$C_{46}H_{58}NiP_2Si$	$C_{46}H_{57}NiO_3P_2Si$	$C_{33}H_{48}NiP_2Si$
fw	717.58	759.66	807.66	593.45
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	P21/c	P21/c	P21/c	P21/c
***a* (Å)**	20.474(4)	15.1784(2)	15.5140(4)	18.2625(12)
***b* (Å)**	22.468(4)	13.3439(2)	13.3974(3)	8.1482(5)
***c* (Å)**	17.673(3)	21.4058(3)	21.7230(5)	21.5259(18)
α (deg)	90	90	90	90
β (deg)	110.92(3)	110.7300(10)	112.905(2)	93.717(4)
γ (deg)	90	90	90	90
***V* (Å^3)**	7594(3)	4054.82(10)	4159.06(18)	3196.5(4)
Z	8	4	4	4
***T* (K)**	173(2)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	1.54178	1.54178	1.54178
ρ_{calcd} (g·cm^{-3})	1.255	1.244	1.290	1.233
***F*(000)**	3056	1624	1720	1272
μ (mm^{-1})	0.656	1.940	1.979	2.314
crystal size, mm^3	0.28×0.2×0.2	0.25×0.23×0.20	0.20×0.20×0.18	0.20×0.20×0.15
transmission factors	0.821 − 0.863	0.697 − 0.715	0.6860 − 0.7536	0.5473 − 0.7528
***θ* range (deg)**	1.593 − 24.999	3.113 − 66.495	3.092 − 72.511	2.424 − 67.007
data/restraints/param	12903/0/871	7111/0/466	7978/66/527	5623/324/348
GOF	1.109	1.043	1.064	1.029
R_1 [I > 2σ(I)]	0.0564	0.0340	0.0347	0.0316
wR_2 [all data]	0.1492	0.0925	0.0950	0.0863
residual density, e/Å^3	0.448 and -0.418	0.391 and -0.271	0.385 and -0.288	0.375 and -0.263

Table S2. Crystal Data Collection and Refinement Parameters for Complexes 4 and 5_{Ph}

	4	**5_{Ph}**
formula	$C_{31}H_{42}O1P_2Ni$	$C_{43}H_{52}NiP_2Si$
fw	551.29	717.58
crystal system	monoclinic	orthorhombic
space group	C2/c	P212121
***a* (Å)**	30.7146(4)	12.9100(5)
***b* (Å)**	10.08350(10)	15.4920(4)
***c* (Å)**	20.2840(3)	19.2540(6)
α (deg)	90	90
β (deg)	114.2950(10)	90
γ (deg)	90	90
***V* (Å^3)**	5725.82(13)	3850.8(2)
Z	8	4
***T* (K)**	173(2)	173(2)
Wavelength (Å)	1.54178	0.71073
ρ_{calcd} (g·cm^{-3})	1.279	1.238
***F*(000)**	2352	1528
μ (mm^{-1})	2.185	0.647
crystal size, mm^3	0.20×0.10×0.10	0.280×0.260×0.200
transmission factors	0.531 − 0.673	0.826 − 0.886
***θ* range (deg)**	3.157 − 66.499	1.687 − 25.427
data/restraints/param	5024/0/324	6881/0/425
GOF	1.061	1.045
R_1 [I > 2σ(I)]	0.0777	0.0601
wR_2 [all data]	0.1996	0.1314
residual density, e/Å^3	0.924 and -0.738	0.376 and -0.257

Kinetic and Mechanistic Data

Procedure for the collection of kinetic data

Sample Preparation:

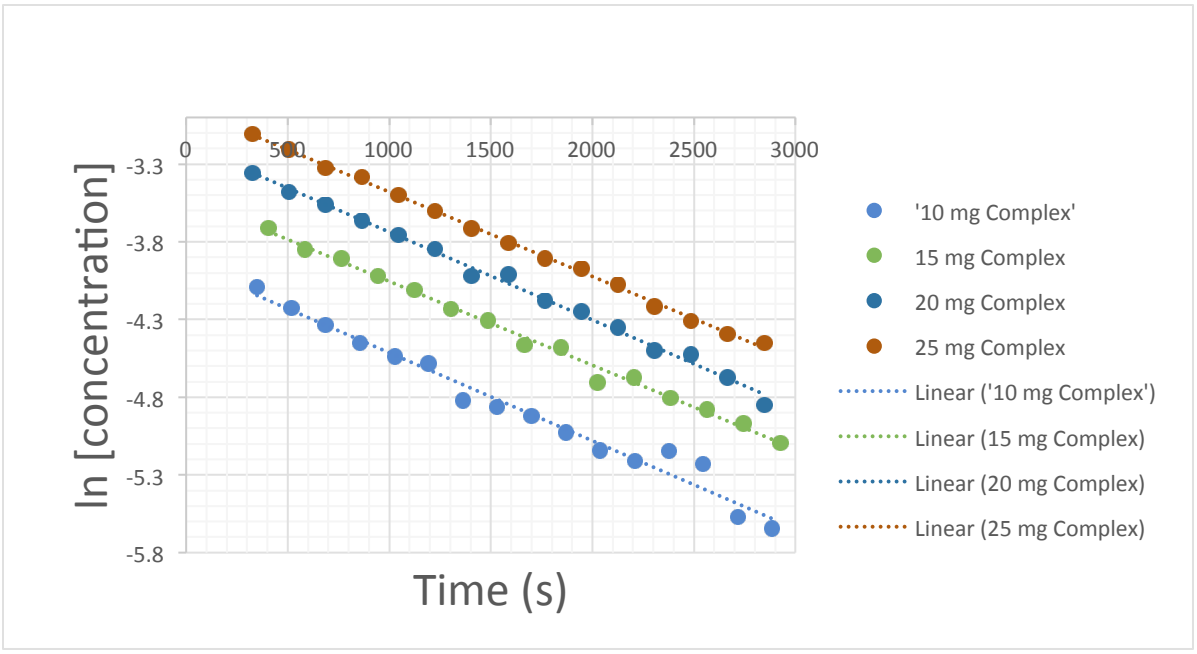
A 5 mL stock solution of PhOH (1.39 mol/L) in 95:5 THF/C_6D_6 and a separate stock solution of 0.139 mol/L $\mathbf{3_{Ph}}$ was prepared. For each experiment, appropriate amounts of each stock solution was added to J-Young NMR tube, and diluted to a total volume of 0.7 mL using 95:5 THF/C_6D_6.

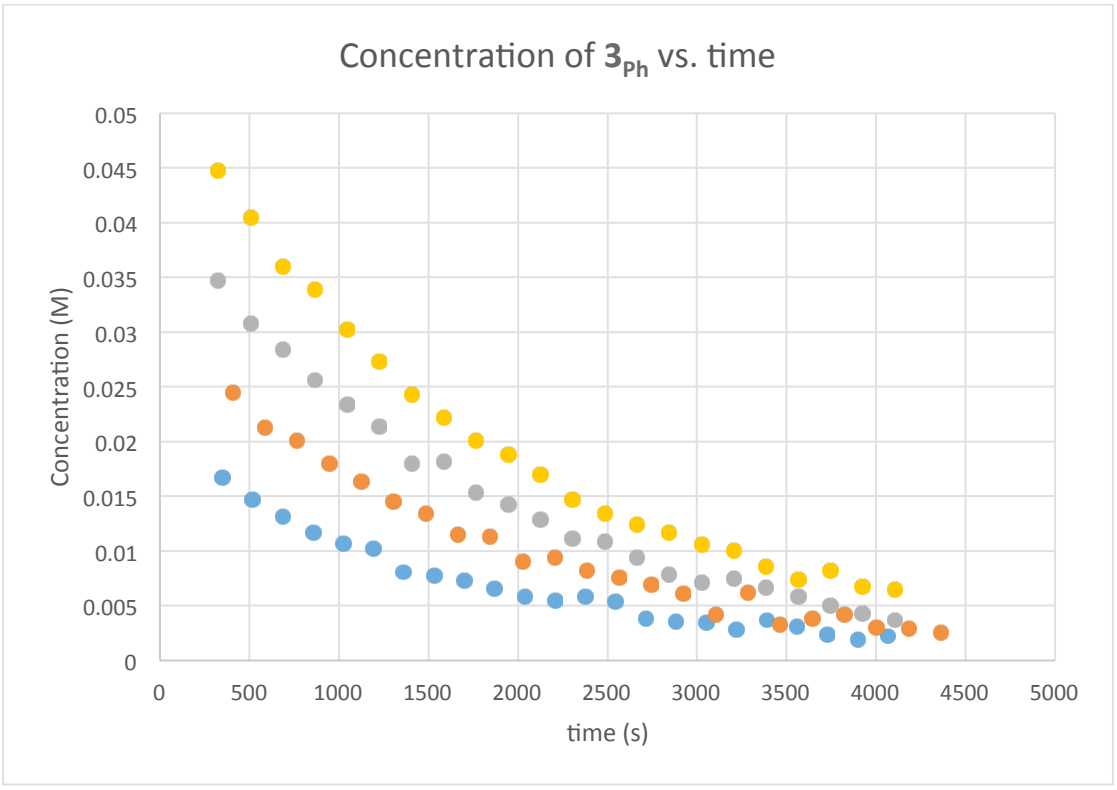
Experiment Details:

Using a 600 MHz NMR spectrometer, a control spectrum of the sample was obtained at room temperature, after which the sample was removed and the instrument was heated to the desired temperature. The sample was then introduced (time t=0) into the spectrometer and spectra were obtained every 3 minutes. The reactions were monitored by $^{31}P\{^1H\}$ NMR spectroscopy with a d1 delay time of 10 seconds and 12 scans per spectrum. The disappearance of $\mathbf{3_{Ph}}$ was followed by integration of the starting material signal, normalized against the total integral peak area in the spectrum.

Table S3: Experimental parameters and rate constants for all kinetic experiments

E	Complex	$[\mathbf{3_{Si}}]_{init}$ (M)	$[PhOH]_{init}$ (M)	$[HSiPh_3]_{init}$ (M)	k_1 (s^{-1})	T (K)
1	$\mathbf{3_{Ph}}$	0.0199	0.199	0	$5.7(2)\times10^{-4}$	338
2	$\mathbf{3_{Ph}}$	0.0299	0.299	0	$5.7(2)\times10^{-4}$	338
3	$\mathbf{3_{Ph}}$	0.0399	0.399	0	$5.7(1)\times10^{-4}$	338
4	$\mathbf{3_{Ph}}$	0.0499	0.499	0	$5.4(1)\times10^{-4}$	338
5	$\mathbf{3_{Ph}}$	0.0199	0.040	0	$5.7(1)\times10^{-4}$	338
6	$\mathbf{3_{Ph}}$	0.0199	0.060	0	$5.6(1)\times10^{-4}$	338
7	$\mathbf{3_{Ph}}$	0.0199	0.080	0	$5.6(1)\times10^{-4}$	338
8	$\mathbf{3_{Ph}}$	0.0199	0.10	0	$5.8(1)\times10^{-4}$	338
9	$\mathbf{3_{Ph}}$	0.0199	0.199	0.040	$5.6(1)\times10^{-4}$	338
10	$\mathbf{3_{Ph}}$	0.0199	0.199	.080	$5.9(1)\times10^{-4}$	338
11	$\mathbf{3_{Ph}}$	0.0199	0.199	.12	$5.7(1)\times10^{-4}$	338
12	$\mathbf{3_{Ph\text{-}D}}$	0.0299	0.299	0	$6.3(1)\times10^{-4}$	338
13	$\mathbf{3_{p\text{-}Me\text{-}Ph}}$	0.0282	0.0299	0	$5.8(1)\times10^{-4}$	338
14	$\mathbf{3_{p\text{-}OMe\text{-}Ph}}$	.0265	0.0299	0	$4.9(1)\times10^{-4}$	338
15	$\mathbf{3_{PhMe2}}$	0.0241	0.199	0	$4.0(2)\times10^{-4}$	338
16	$\mathbf{3_{Ph}}$	0.0199	0.199	0	$3.1(1)\times10^{-4}$	333
17	$\mathbf{3_{Ph}}$	0.0199	0.199	0	$1.6(1)\times10^{-4}$	328
18	$\mathbf{3_{Ph}}$	0.0199	0.199	0	$8.6(3)\times10^{-5}$	323
19	$\mathbf{3_{Ph}}$	0.0199	0.199	0	$1.7(1)\times10^{-3}$	353


ln [concentration]
Time (s)
0
500
1000
1500
2000
2500
3000
-3.3
-3.8
-4.3
-4.8
-5.3
-5.8
'10 mg Complex'
15 mg Complex
20 mg Complex
25 mg Complex
Linear ('10 mg Complex')
Linear (15 mg Complex)
Linear (20 mg Complex)
Linear (25 mg Complex)


Concentration of 3Ph vs. time
Concentration (M)
time (s)
0.05
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000

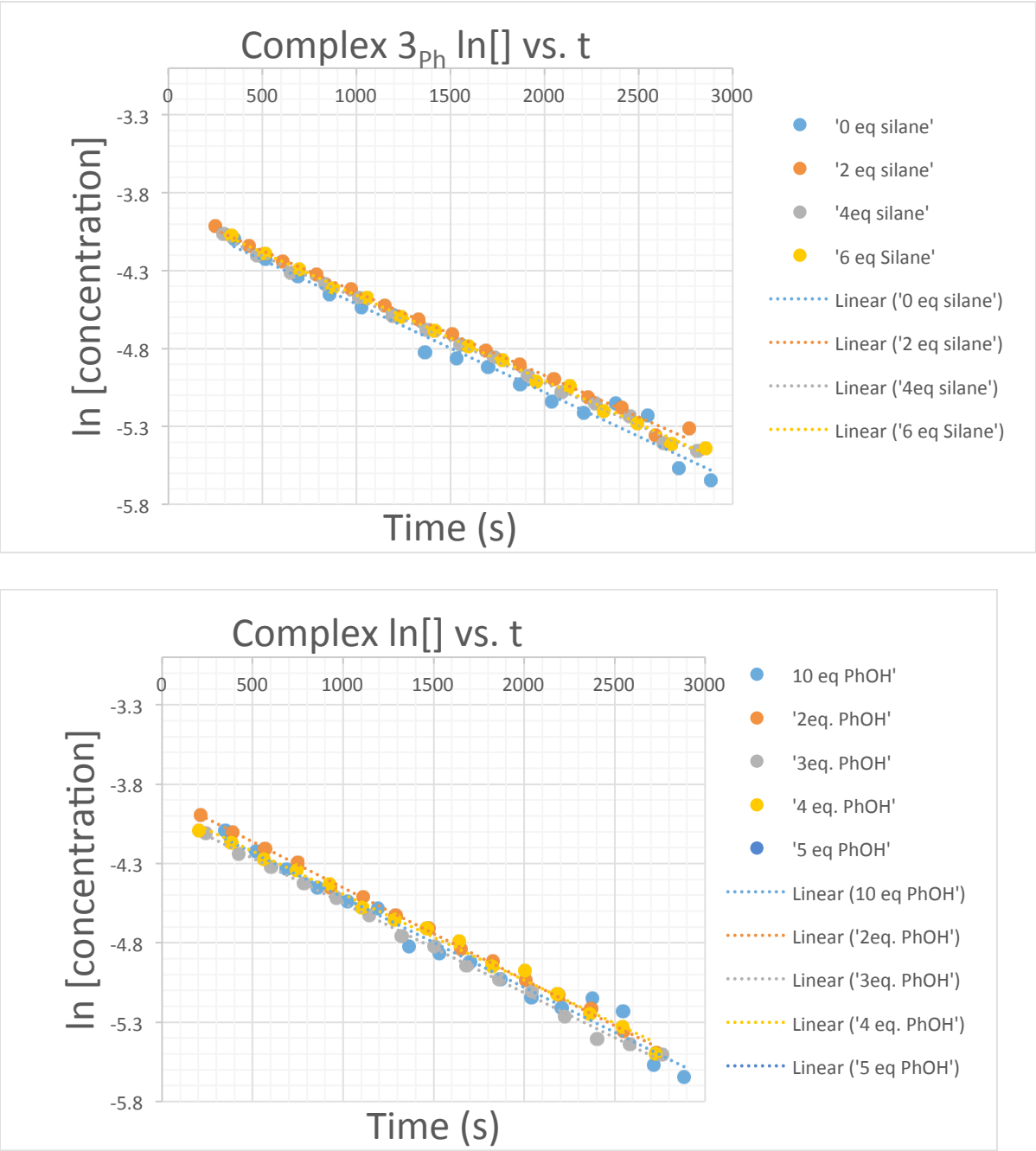
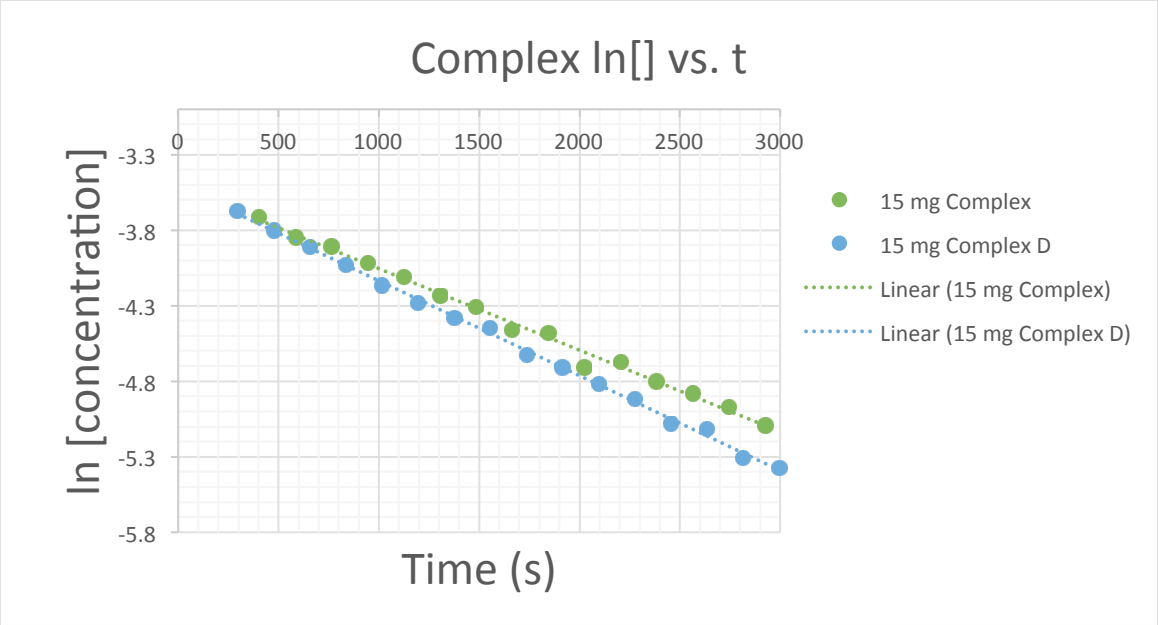
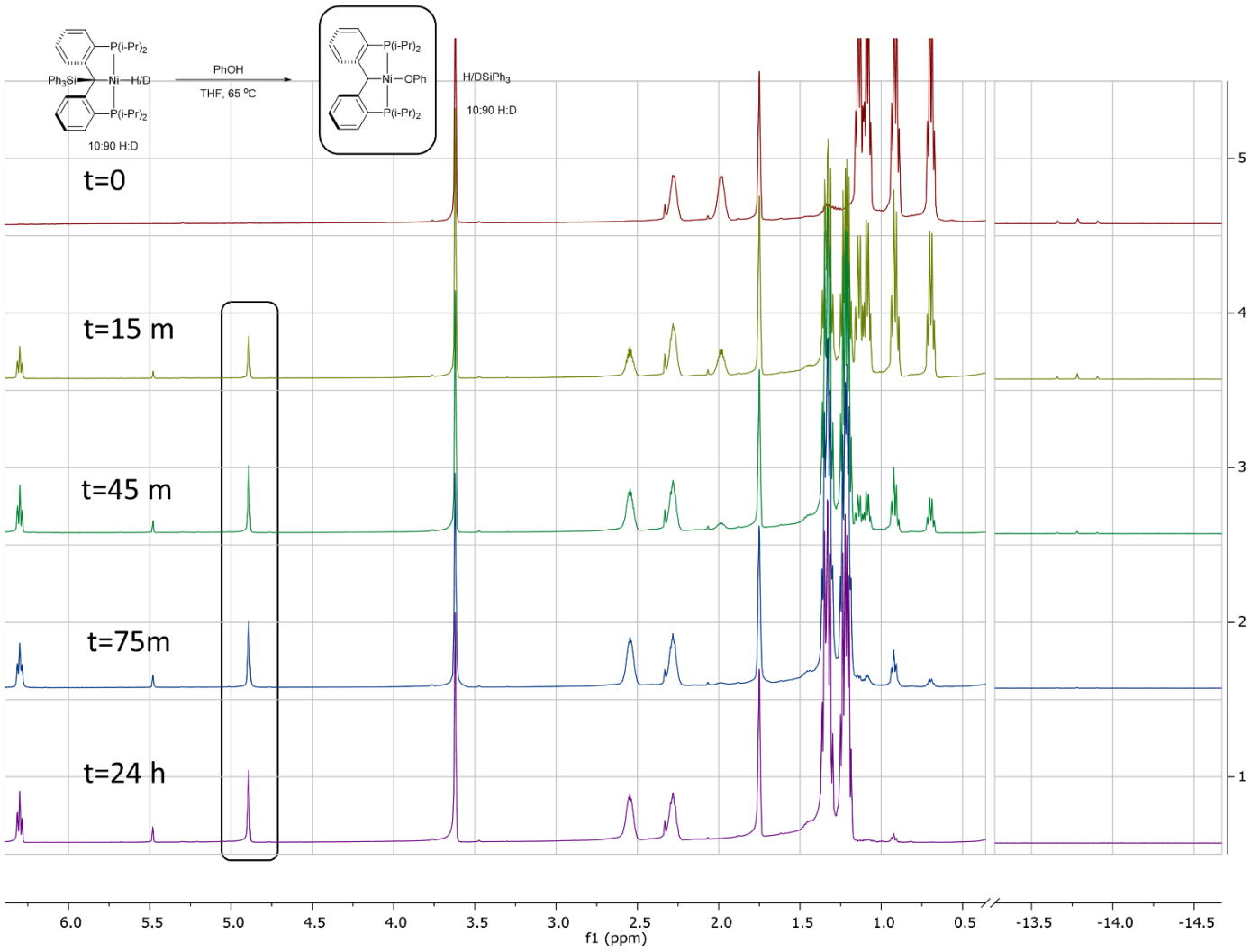


Figure S3: First order kinetics plots showing disappearance of $\mathbf{3_{Ph}}$ over time, at various concentrations of $\mathbf{3_{Ph}}$ (top two plots). Same experiments in the presence of excess Ph_3SiH and PhOH (bottom two plots).



Isotopologue	Rate
Ni-H	$5.7(2)\times10^{-4}$
Ni-D	$6.3(1)\times10^{-4}$
$k_H/k_D = 0.90(3)$	

Figure S4: First order kinetics plot showing disappearance of $\mathbf{3_{Ph}}$ and $\mathbf{3_{Ph}}$-d_1.


P(i-Pr)2
Ph3Si
Ni
H/D
P(i-Pr)2
10:90 H:D
PhOH
THF, 65 °C
P(i-Pr)2
Ni
OPh
P(i-Pr)2
H/DSiPh3
10:90 H:D
t=0
t=15 m
t=45 m
t=75m
t=24 h
5
4
3
2
1
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-13.5
-14.0
-14.5
f1 (ppm)

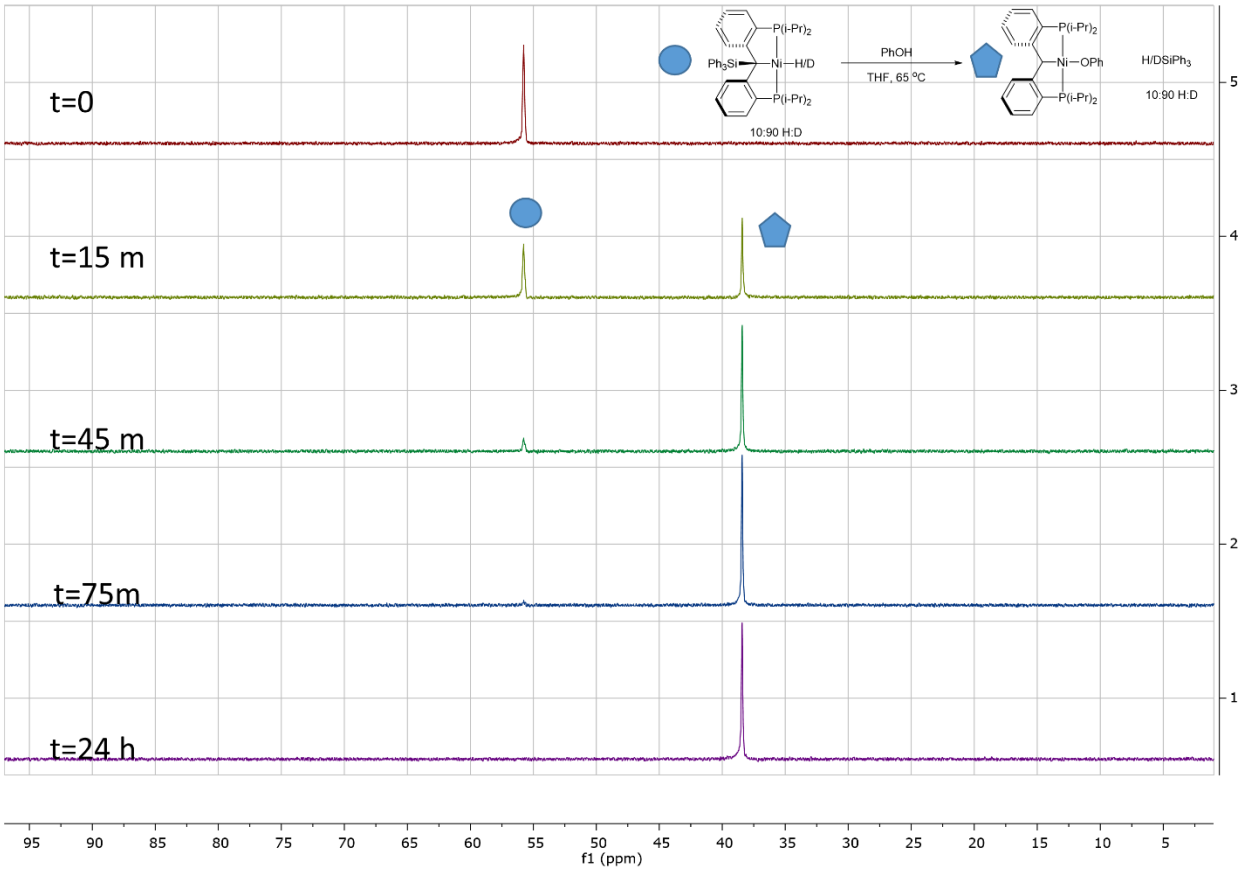
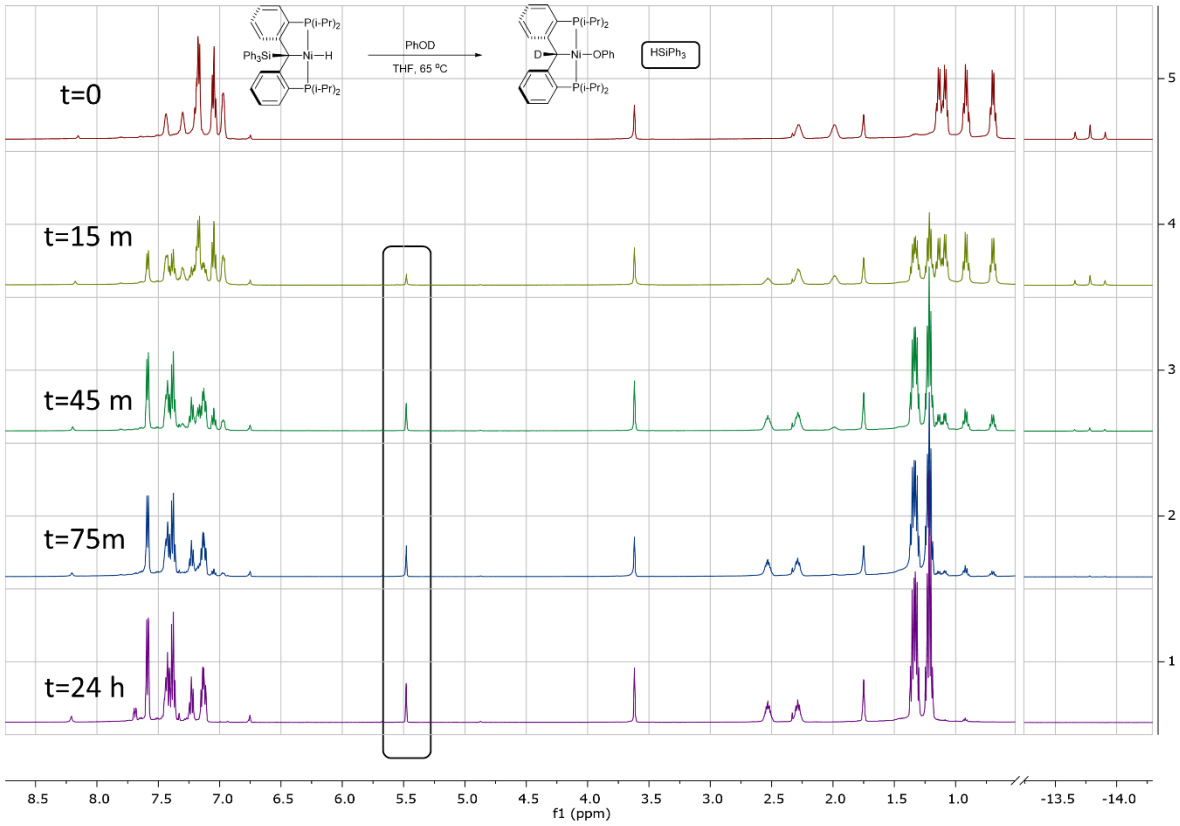


Figure S5 (top): ^{1}H NMR spectra of elimination of silane over time from $\mathbf{3_{Ph}}$-d_1 at 65°C in THF-d^8 (bottom) ^{31}P{^{1}H} NMR spectra of elimination of silane over time from $\mathbf{3_{Ph}}$-d_1 at 65°C in THF-d^8.


t=0
t=15 m
t=45 m
t=75m
t=24 h
PhOD
THF, 65 °C
HSiPh3
f1 (ppm)

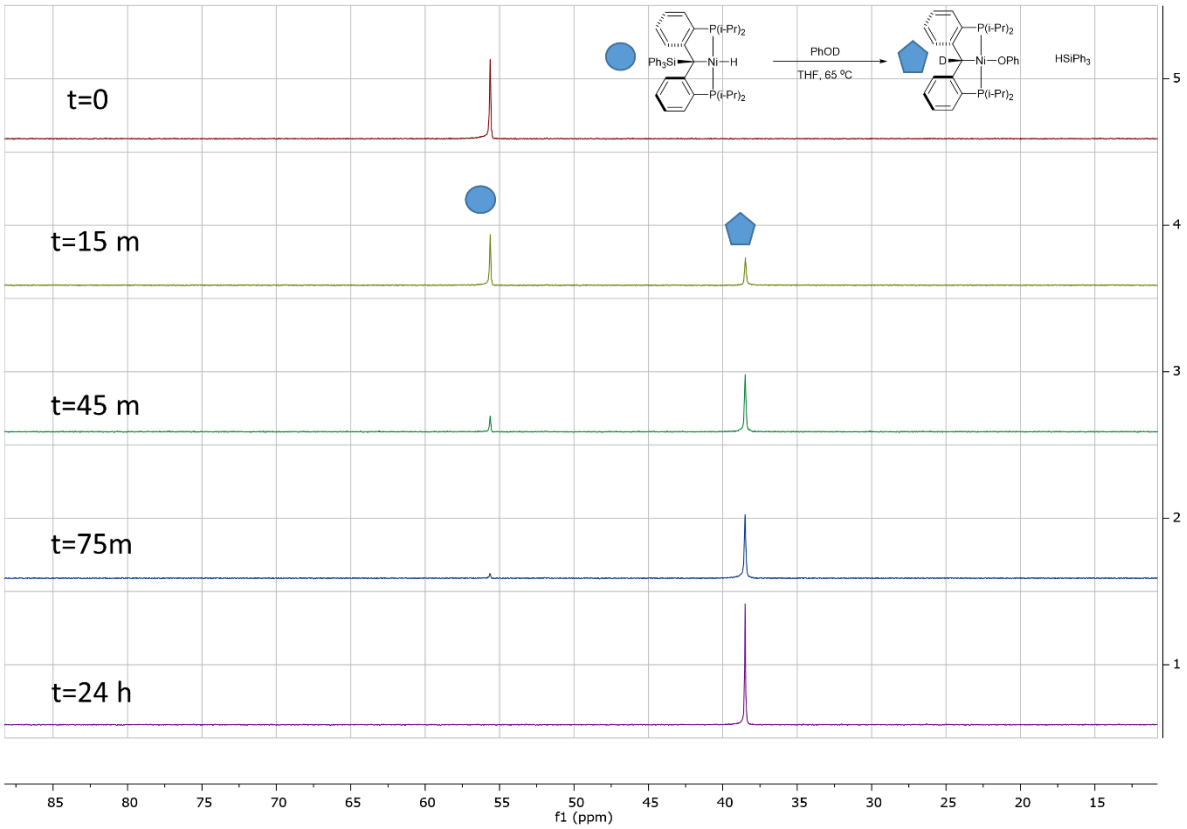


Figure S6 (top): ^{1}H NMR spectra of elimination of silane over time from $\mathbf{3_{Ph}}$, with phenol-d_6 as the trapping agent at 65°C in THF-d^8; (bottom): ^{31}P{^{1}H} spectra of elimination of silane over time from $\mathbf{3_{Ph}}$, with phenol-d_6 as the trapping agent at 65°C in THF-d^8.

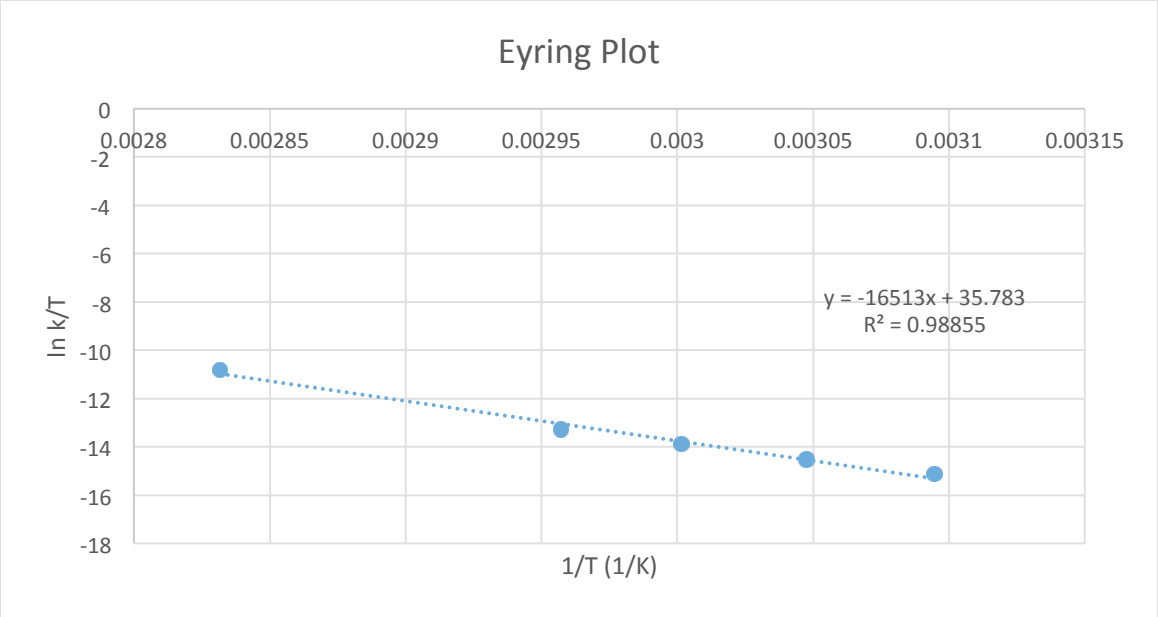


Figure S7. Eyring analysis of silane elimination from $\mathbf{3_{Ph}}$. All runs done in 95:5 THF/C_6D_6 except T = 80 °C, which was done in 2-MeTHF. $\Delta H^{\ddagger} = 33 \pm 2.0$ Kcal/mol, $\Delta S^{\ddagger} = 24 \pm 2.0$ e.u.

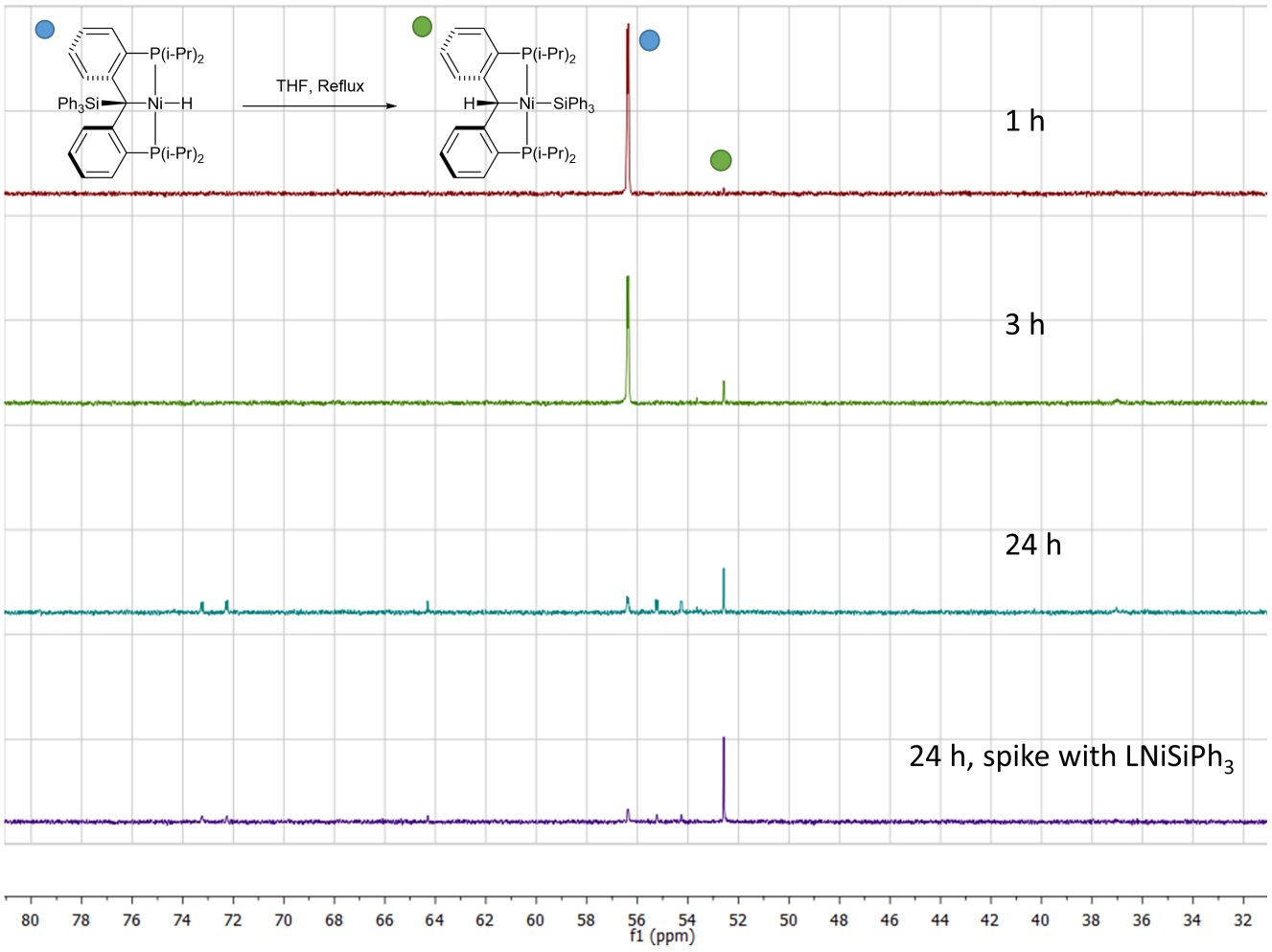


Figure S8: Thermal isomerization of $\mathbf{3_{Ph}}$ to $\mathbf{5_{Ph}}$.

Reaction performed on a 10 mg scale of $\mathbf{3_{Ph}}$ in refluxing THF-d^8 in a J-Young NMR Tube and followed by $^{31}P\{^1H\}$ NMR spectroscopy.

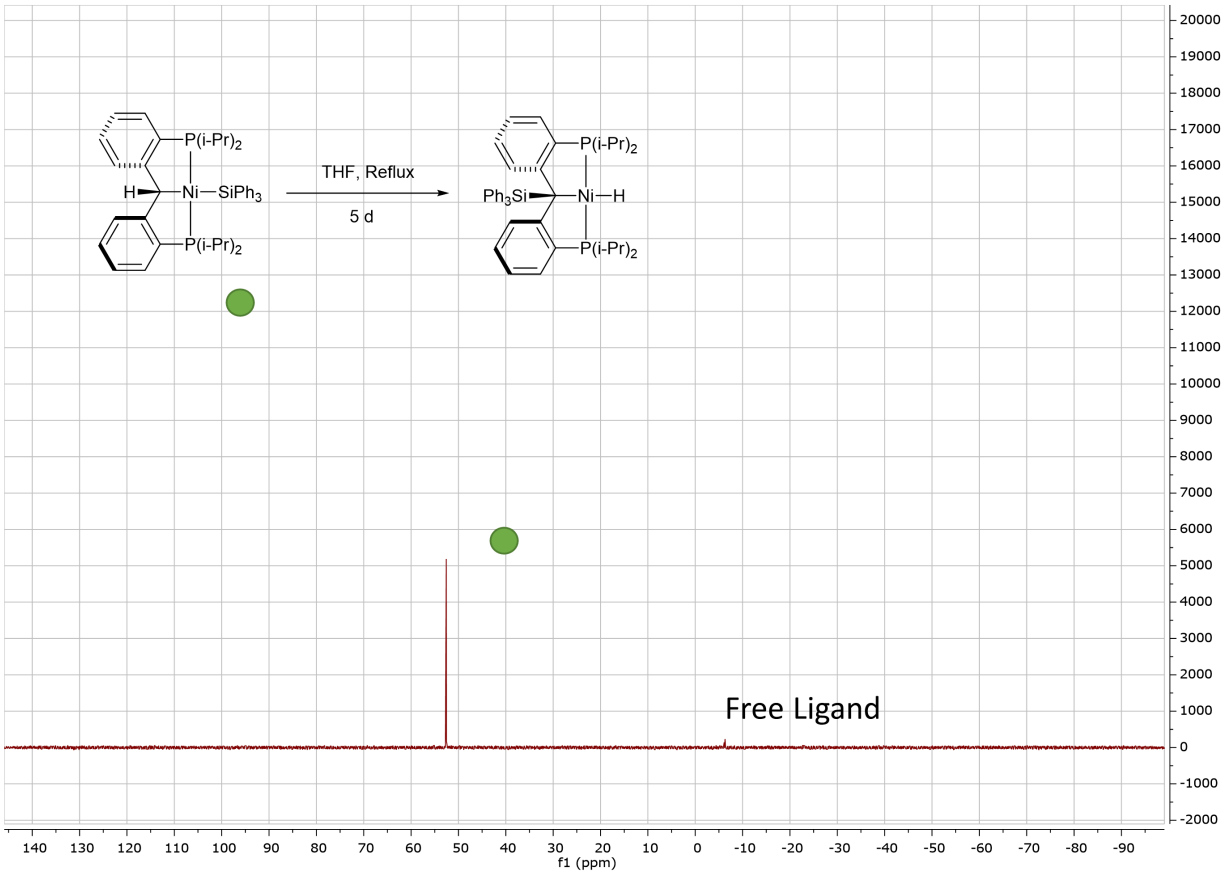
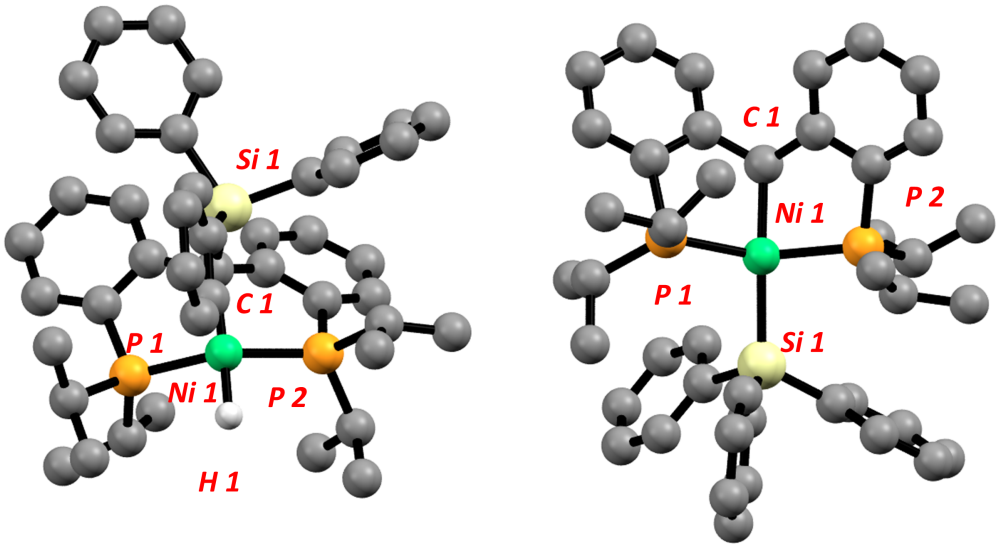


Figure S9: Attempted thermal isomerization of **5$_{Ph}$** to **3$_{Ph}$**. Reaction performed on a 10 mg scale in J-Young NMR Tube and followed by $^{31}P\{^{1}H\}$ NMR spectroscopy.

Figure S10: Computed structures of 3Ph and 5Ph with selected distances



Left: $\mathbf{3_{Ph}}$ Right: $\mathbf{5_{Ph}}$

$\mathbf{3_{Ph}}$

Bond, Angle, Contact	Experimental value (Å,°) (Solid State Structure)	Calculated Value (Å,°)
Ni(1)-C(1)	2.043(4)	2.0369
Ni(1)-P(1)	2.1344(14)	2.1386
Ni(1)-P(2)	2.1079(14)	2.1580
Ni(1)-H(1)	1.32(5)	1.4968
C(1)-Si(1)	1.916(4)	1.9570
C(39)-Ni(1)	3.051	2.902
P(1)-Ni(1)-P(2)	163.42(5)	152.70
C(1)-Ni(1)-P(1	89.99(12)	89.48
C(1)-Ni(1)-P(2)	89.94(12)	89.86
Si(1)-C(1)-Ni(1)	109.8(2)	104.56
C(1)-Si(1)-C(38)	116.49(19)	114.40

5_{Ph}

Bond, Angle, Contact	Experimental value (Solid State Structure)	Calculated Value
Ni(1)-C(13),	2.030(8)	2.0051
Ni(1)-P(1)	2.194(2)	2.2323
Ni(1)-P(2)	2.168(2)	2.2009
Ni(1)-Si(1)	2.338(2)	2.3661
P(1)-Ni(1)-P(2)	153.26(9)	152.07
C(13)-Ni(1)-Si(1)	161.7(2)	160.56
C(13)-Ni(1)-P(1),	84.1(2)	84.82
C(13)-Ni(1)-P(2)	83.6(2)	83.85
Si(1)-Ni(1)-P(1)	105.06(9)	103.62
Si(1)-Ni(1)-P(2)	93.75(7)	95.34

Table S4. Coordinates for the calculated structure of 3_{Ph}.

Ground State Energy: -4150.37486268 Hartrees, -2604400.10326035 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	28	0	-1.253181	-0.793739	0.562065
2	15	0	-2.864262	0.581026	0.265780
3	15	0	-0.188875	-2.622406	0.134217
4	14	0	1.418332	0.851325	0.184695
5	6	0	-0.150489	0.232311	-0.809336
6	6	0	1.125545	1.086491	2.064174
7	6	0	2.949739	-0.286135	0.033258
8	6	0	-1.265739	-4.142276	-0.134705
9	1	0	-0.620986	-4.893065	-0.607837
10	6	0	2.996781	5.123243	-1.178362
11	1	0	3.352704	6.102561	-1.486639
12	6	0	3.643517	3.968759	-1.618581
13	1	0	4.510232	4.044522	-2.270030
14	6	0	4.921264	-1.314651	1.065271
15	1	0	5.503285	-1.521690	1.959455
16	6	0	2.070969	2.567879	-0.370839
17	6	0	0.207760	-0.791350	-1.892494
18	6	0	1.964932	1.957768	2.789177
19	1	0	2.713690	2.542771	2.264155
20	6	0	0.172712	0.367897	2.806739
21	1	0	-0.521896	-0.317102	2.309419
22	6	0	3.187393	2.711224	-1.214475
23	1	0	3.720215	1.829422	-1.557071
24	6	0	-3.687226	1.548575	1.641659
25	1	0	-4.509670	2.112501	1.184191
26	6	0	3.414716	-0.765189	-1.208294
27	1	0	2.847555	-0.571011	-2.112453

28	6	0	-4.296509	-0.220076	-0.673064
29	1	0	-4.475812	-1.147995	-0.116275
30	6	0	1.317503	-3.261413	1.072135
31	1	0	2.071505	-2.510534	0.826788
32	6	0	1.439329	3.751239	0.061128
33	1	0	0.578521	3.691008	0.721798
34	6	0	1.863214	2.096691	4.174680
35	1	0	2.528081	2.778776	4.697742
36	6	0	-1.790449	-4.716429	1.190211
37	1	0	-2.331579	-3.953616	1.759202
38	1	0	-0.991915	-5.111641	1.822258
39	1	0	-2.483050	-5.541175	0.986105
40	6	0	-2.268379	3.806804	-2.261971
41	1	0	-2.794824	4.693717	-2.602321
42	6	0	4.595882	-1.502326	-1.313495
43	1	0	4.921383	-1.859213	-2.286883
44	6	0	1.892432	5.010098	-0.331250
45	1	0	1.383154	5.902709	0.022319
46	6	0	-3.845205	-0.584647	-2.097675
47	1	0	-4.588339	-1.237890	-2.568529
48	1	0	-2.882318	-1.099506	-2.112893
49	1	0	-3.747480	0.313238	-2.715170
50	6	0	5.353149	-1.782926	-0.175665
51	1	0	6.271477	-2.358113	-0.256181
52	6	0	-2.723488	2.556761	2.283074
53	1	0	-3.247404	3.122478	3.062296
54	1	0	-2.338746	3.271832	1.551175
55	1	0	-1.871040	2.058104	2.749336
56	6	0	0.063563	0.499096	4.193416
57	1	0	-0.687579	-0.074596	4.729616
58	6	0	0.769020	-3.111581	-2.508291
59	1	0	0.874020	-4.153751	-2.222284
60	6	0	0.981391	-2.752844	-3.837175
61	1	0	1.280590	-3.495756	-4.570349
62	6	0	0.750859	-1.429610	-4.207768
63	1	0	0.864820	-1.125358	-5.245080
64	6	0	-4.274894	0.586462	2.685707
65	1	0	-3.485673	-0.012090	3.149213
66	1	0	-5.000016	-0.108868	2.251348
67	1	0	-4.785439	1.152397	3.473034
68	6	0	3.739197	-0.577479	1.163703
69	1	0	3.425345	-0.227613	2.141814
70	6	0	-2.432942	-3.846973	-1.084604
71	1	0	-2.997394	-4.767700	-1.272677
72	1	0	-2.094185	-3.456387	-2.046923
73	1	0	-3.117359	-3.119654	-0.638382
74	6	0	0.372138	-0.479892	-3.259651
75	1	0	0.195720	0.528543	-3.605530
76	6	0	0.364236	-2.168886	-1.554610
77	6	0	0.910612	1.365033	4.884437
78	1	0	0.827983	1.470121	5.962717
79	6	0	1.862712	-4.621813	0.611125
80	1	0	2.792513	-4.838310	1.149749
81	1	0	2.100424	-4.632061	-0.455576

82	1	0	1.169351	-5.442948	0.819853
83	6	0	-2.169765	1.808883	-0.886728
84	6	0	-0.876045	1.481754	-1.353278
85	6	0	-0.312928	2.379925	-2.286048
86	1	0	0.699350	2.223729	-2.635919
87	6	0	-2.847462	2.957134	-1.324764
88	1	0	-3.831840	3.189971	-0.927965
89	6	0	-0.994569	3.505373	-2.743938
90	1	0	-0.511888	4.164480	-3.459969
91	6	0	-5.608165	0.577494	-0.722986
92	1	0	-5.475412	1.538513	-1.230232
93	1	0	-6.031129	0.766229	0.266988
94	1	0	-6.354691	0.012820	-1.293755
95	6	0	1.120025	-3.226159	2.597016
96	1	0	0.378311	-3.952673	2.939453
97	1	0	0.808926	-2.239447	2.944822
98	1	0	2.068464	-3.469196	3.090064
99	1	0	-2.118491	-1.530087	1.537308

Table S5. Coordinates for the calculated structure of 5_{Ph}

Ground State Energy: -4150.38649362 Hartrees, -2604407.40178695kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	28	0	-0.516301	0.055531	-0.141677
2	15	0	-1.453990	-1.850579	0.540809
3	15	0	-0.287618	2.244326	-0.075419
4	14	0	1.802913	-0.408694	-0.075680
5	6	0	-0.659473	-4.049337	-1.069940
6	1	0	-1.567938	-3.915988	-1.662632
7	1	0	0.143292	-3.485106	-1.543385
8	1	0	-0.388110	-5.110621	-1.108043
9	6	0	0.383692	-3.901315	1.244577
10	1	0	0.229495	-3.676201	2.303734
11	1	0	0.657122	-4.959829	1.167068
12	1	0	1.236992	-3.314042	0.904012
13	6	0	-0.863911	-3.630113	0.392821
14	1	0	-1.684353	-4.234373	0.798407
15	6	0	-2.680554	-2.975169	2.920062
16	1	0	-2.049723	-3.866683	2.906097
17	1	0	-2.963041	-2.792754	3.963374
18	1	0	-3.601696	-3.193132	2.369501
19	6	0	-1.976904	-1.728071	2.362615
20	1	0	-1.034188	-1.591799	2.904370
21	6	0	-2.857952	-0.491347	2.595234
22	1	0	-2.402514	0.427357	2.224060
23	1	0	-3.825736	-0.600878	2.096688
24	1	0	-3.047274	-0.368974	3.667695
25	6	0	-3.041516	-1.880414	-0.382285

26	6	0	-3.906883	-2.975653	-0.525580
27	1	0	-3.699613	-3.912332	-0.017372
28	6	0	-5.027125	-2.882520	-1.348916
29	1	0	-5.690677	-3.734595	-1.464014
30	6	0	-5.273185	-1.697142	-2.046176
31	1	0	-6.127635	-1.626553	-2.713719
32	6	0	-4.418269	-0.606786	-1.895535
33	1	0	-4.612092	0.307862	-2.449692
34	6	0	-3.302432	-0.670194	-1.042973
35	6	0	-2.339184	0.484156	-0.859007
36	1	0	-2.020084	0.770326	-1.877131
37	6	0	-2.939452	1.734586	-0.252360
38	6	0	-4.303509	1.954397	-0.002356
39	1	0	-5.022036	1.169957	-0.211057
40	6	0	-4.757847	3.171616	0.507924
41	1	0	-5.819881	3.309040	0.693698
42	6	0	-3.865570	4.209738	0.772814
43	1	0	-4.220389	5.158485	1.164089
44	6	0	-2.501954	4.003565	0.556151
45	1	0	-1.801447	4.798070	0.792185
46	6	0	-2.038053	2.771502	0.082412
47	6	0	-0.221397	2.480572	2.736544
48	1	0	-0.507196	1.426285	2.755349
49	1	0	0.378498	2.675283	3.632337
50	1	0	-1.133789	3.079335	2.802351
51	6	0	1.109337	4.271315	1.537076
52	1	0	1.784210	4.501405	0.709678
53	1	0	0.295239	5.002646	1.540787
54	1	0	1.674245	4.415520	2.465680
55	6	0	0.601573	2.823363	1.486286
56	1	0	1.482074	2.174861	1.490278
57	6	0	-0.016604	4.668904	-1.647194
58	1	0	0.237123	5.263221	-0.768405
59	1	0	0.480145	5.128386	-2.509617
60	1	0	-1.096054	4.744704	-1.807035
61	6	0	0.093752	2.465972	-2.844305
62	1	0	0.439194	1.430106	-2.829832
63	1	0	-0.984916	2.466041	-3.035904
64	1	0	0.579364	2.970983	-3.686488
65	6	0	0.425224	3.201101	-1.535436
66	1	0	1.508892	3.156994	-1.386775
67	6	0	3.046201	0.967248	-0.655800
68	6	0	3.732937	1.779424	0.269778
69	1	0	3.602790	1.605522	1.334343
70	6	0	4.611184	2.788886	-0.132639
71	1	0	5.122829	3.388993	0.615765
72	6	0	4.844860	3.014574	-1.489550
73	1	0	5.530405	3.794993	-1.808210
74	6	0	4.201448	2.209747	-2.431036
75	1	0	4.390365	2.356384	-3.491606
76	6	0	3.322965	1.206280	-2.016732
77	1	0	2.859756	0.584508	-2.776475
78	6	0	2.173530	-1.765398	-1.394696
79	6	0	1.576545	-1.653834	-2.667805

80	1	0	0.872315	-0.846812	-2.862485
81	6	0	1.839614	-2.563626	-3.693923
82	1	0	1.361242	-2.441533	-4.662230
83	6	0	2.704877	-3.635353	-3.469550
84	1	0	2.909985	-4.350651	-4.261145
85	6	0	3.298324	-3.781393	-2.215420
86	1	0	3.968852	-4.615832	-2.025932
87	6	0	3.037553	-2.858394	-1.199422
88	1	0	3.516222	-3.000917	-0.235424
89	6	0	2.594680	-0.910728	1.603929
90	6	0	3.951221	-1.277268	1.725894
91	1	0	4.585507	-1.287500	0.843600
92	6	0	4.516751	-1.607703	2.958405
93	1	0	5.564053	-1.893318	3.013984
94	6	0	3.743206	-1.560443	4.120359
95	1	0	4.182434	-1.812854	5.081619
96	6	0	2.406352	-1.173243	4.036807
97	1	0	1.798234	-1.115305	4.936073
98	6	0	1.849335	-0.856579	2.794672
99	1	0	0.808947	-0.547573	2.749059

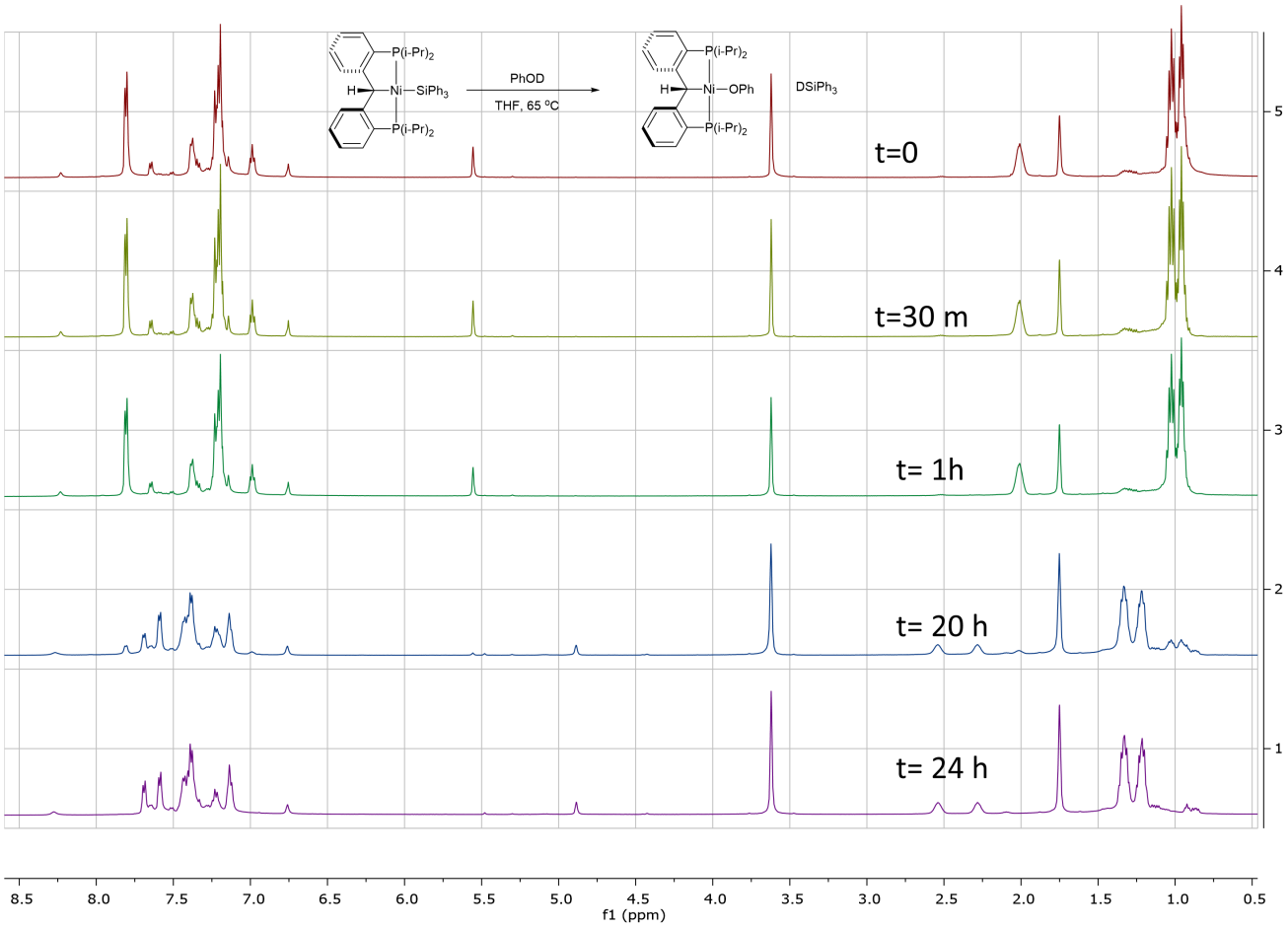


Figure S11: Protonolysis of $\mathbf{5_{Ph}}$ with phenol-d^6.

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