Facile Si–H Bond Activation and Hydrosilylation Catalysis Mediated by a Nickel-Borane Complex

SUPPORTING INFORMATION

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Variable temperature van't Hoff study of the equilibrium of 1 and 4

Ferrocene and **4** were dissolved in toluene-d_8 and transferred to a sealed J. Young NMR tube. The tube was inserted into a temperature controlled NMR probe and ^{1}H NMR spectra were collected at 10 K intervals from 328 K to 368 K, allowing 20 minutes for equilibration at each temperature. Concentrations of **1** and **4** were determined by integration of the mesityl aryl C-*H* resonance for the respective complexes and silane concentration was assumed to be equal to [**1**]. The equilibrium constant of the reaction was calculated according to the expression:

$$K_{obs} = \frac{[\mathbf{4}]}{[\mathbf{1}]^2}$$

The plot of $\ln(K_{obs})$ as a function of T^{-1} was fit by a line according to the expression:

$$ln(K_{obs}) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

The enthalpy and entropy of the reaction were extracted from the slope and intercept, respectively.

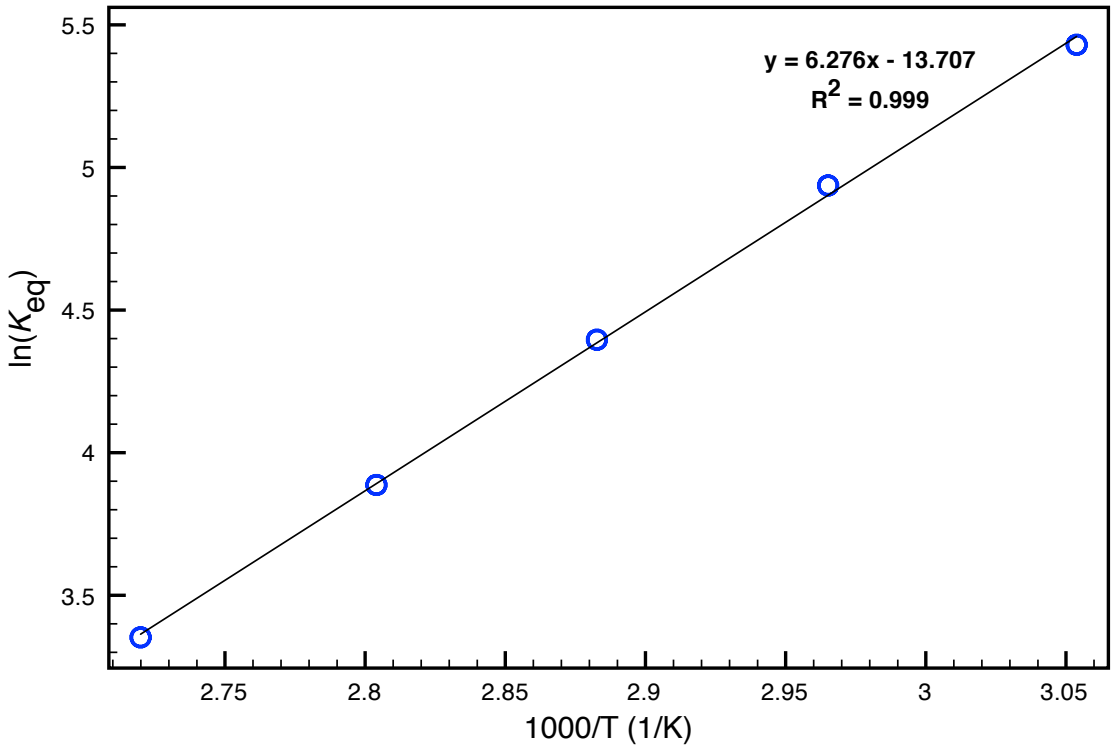


Fig. 1 Van't Hoff plot derived from variable temperature ^{1}H NMR spectra of the equilibrium between **1** and **4** from 328 K to 358 K.

Variable temperature van't Hoff study of the equilibrium of 1 and [^{Mes}DPB^{Ph}](D)NiSiDPh$_2$ (4-D)

Ferrocene, D_2SiPh_2 and **1** were dissolved in toluene-d_8 and transferred to a sealed J. Young NMR tube. The tube was inserted into a temperature controlled NMR probe and ^{1}H NMR spectra were collected at 10 K intervals from 298 K to 358 K, allowing 20 minutes for equilibration at each temperature. Concentrations of **1** and **4-D** were determined by integration of the mesityl aryl C-*H* resonance for the respective complexes and silane concentration was assumed to be equal to [**1**].

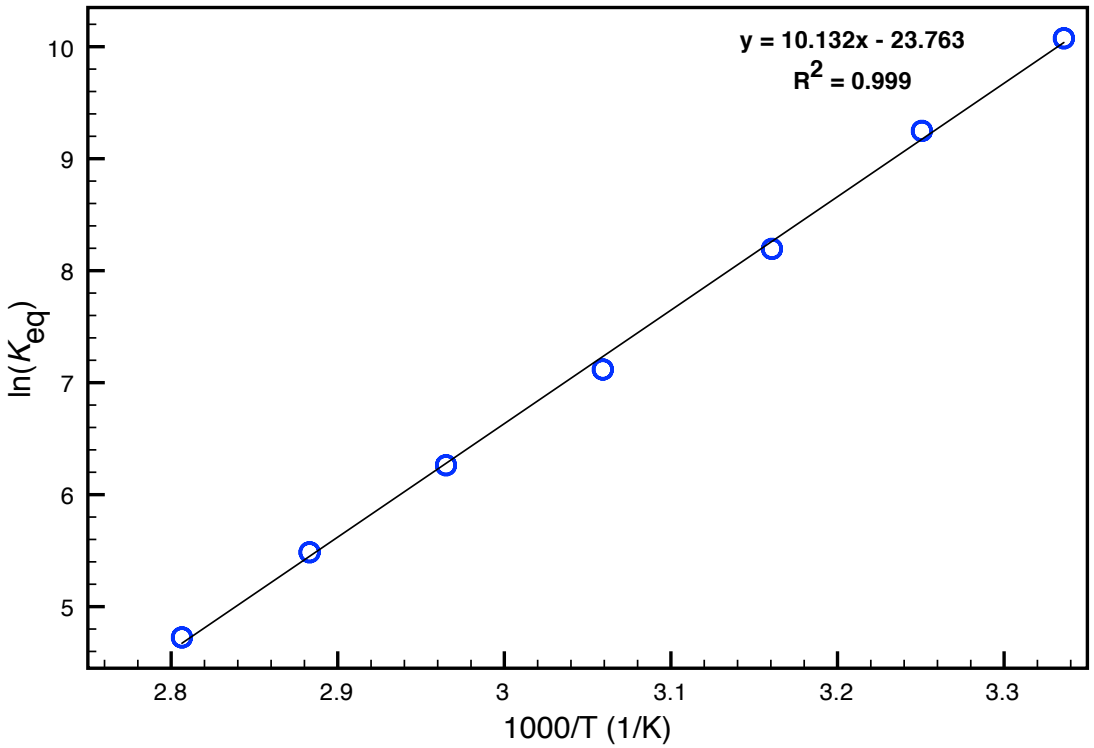


Figure 2. Van't Hoff plot derived from variable temperature ^{1}H NMR spectra of the equilibrium between **1** and **4-D** from 298 K to 358 K.

2D ^{1}H-^{1}H EXSY study of the equilibrium of 1 and 4

2D ^{1}H-^{1}H EXSY spectra were collected using the samples prepared for the variable temperature experiments outlined above. To determine the exchange rates of the equilibrium between **1** and **4**, two 2D EXSY experiments were acquired (mixing time (T_m) = 0 ms and 700 ms) at a number of temperatures. A representative example is shown below:

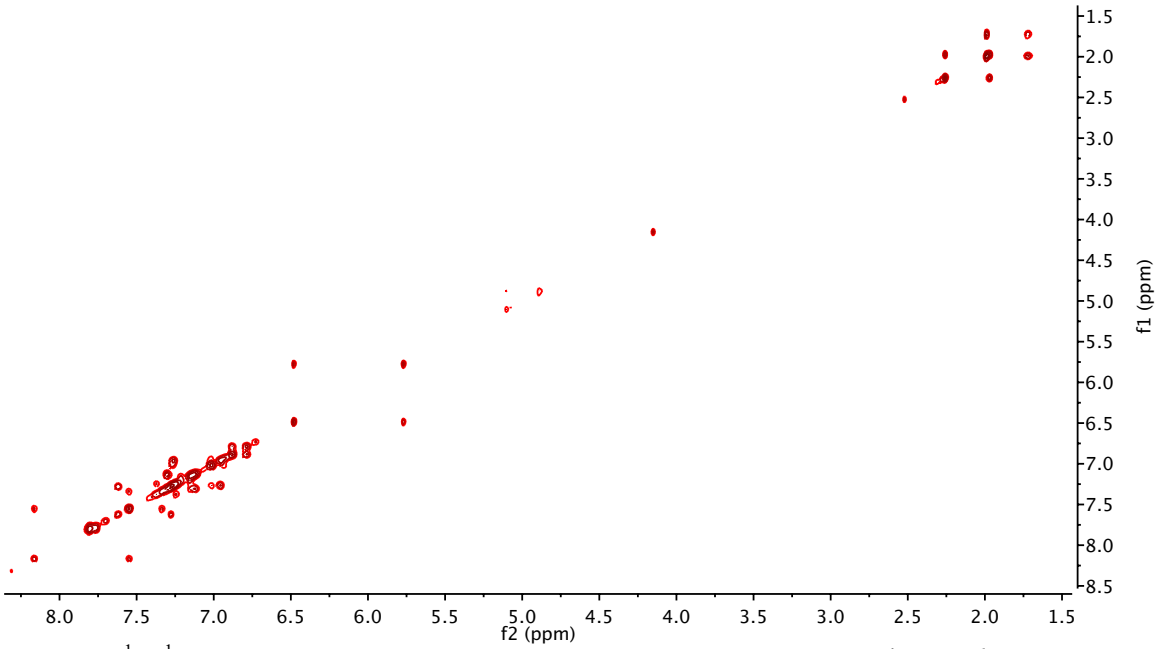


Figure 3. ^{1}H-^{1}H EXSY spectrum recorded at 348 K with T_m = 700 ms in toluene-d_8.

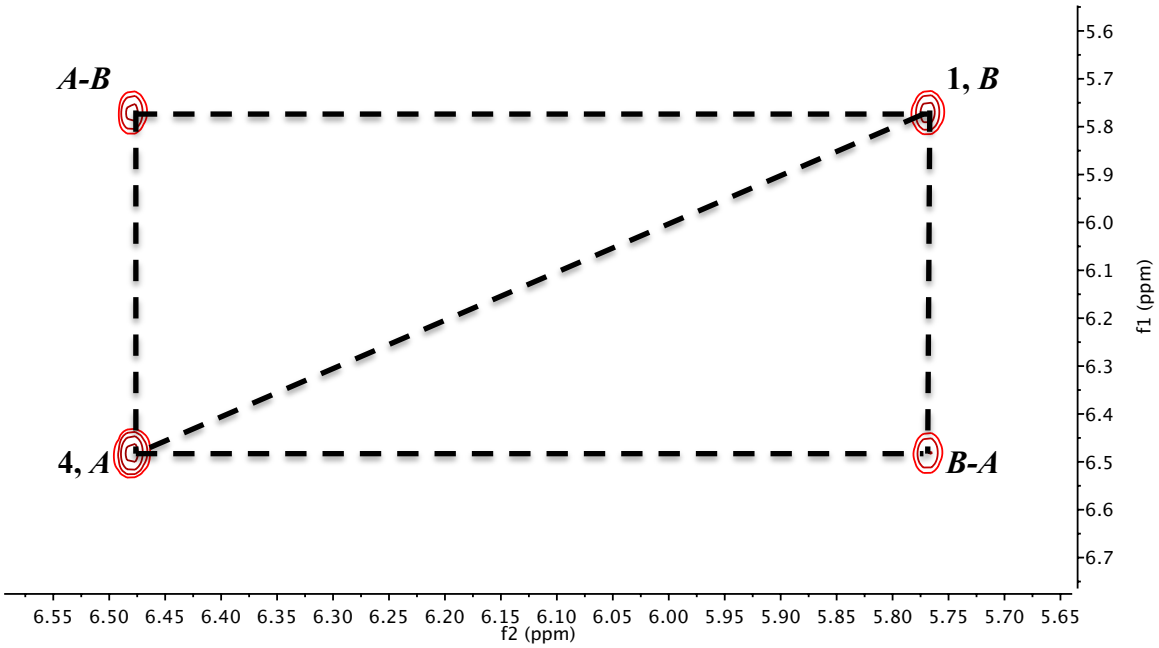


Figure 4. Expansion of the mesityl-*H* region. The peaks corresponding to **1** and **4** are labelled and dashed lines have been drawn to their cross-peaks for ease of viewing. Peaks have also been labeled with a letter code that corresponds to its position in the matrix of the EXSY CALC program.[1]

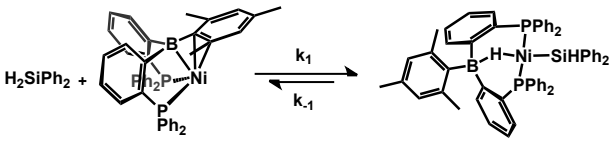
The areas of the peaks were determined by integration. These raw values were introduced to EXSY CALC, the rate exchange matrices calculated and the magnetization rates (k_1' and k_{-1}') determined.

Table 1. Raw volumes and magnetization rate constants.

	T_m = 0 ms				T_m = 700 ms					
	f2	f1	ID	Volume	f2	f1	ID	Volume	k_1' (s^{-1})	k_{-1}' (s^{-1})
328 K	6.34	6.34	A	1.00	6.34	6.34	A	7.53	0.156	0.548
	5.62	5.62	B	0.51	5.62	5.62	B	1.73		
					6.34	5.62	A-B	1.00		
					5.62	6.34	B-A	0.56		
	T_m = 0 ms				T_m = 700 ms					
	f2	f1	ID	Volume	f2	f1	ID	Volume	k_1' (s^{-1})	k_{-1}' (s^{-1})
338 K	6.34	6.34	A	1.60	6.33	6.34	A	4.24	0.357	0.742
	5.62	5.63	B	1.00	5.62	5.62	B	1.48		
					6.33	5.62	A-B	1.00		
					5.62	6.33	B-A	0.77		
	T_m = 0 ms				T_m = 700 ms					
	f2	f1	ID	Volume	f2	f1	ID	Volume	k_1' (s^{-1})	k_{-1}' (s^{-1})
348 K	6.33	6.33	A	1.00	6.34	6.33	A	2.12	0.794	1.187
	5.62	5.63	B	0.76	5.62	5.62	B	1.18		
					6.33	5.62	A-B	1.00		
					5.62	6.33	B-A	0.88		

	T_m = 0 ms				T_m = 700 ms					
	f2	f1	ID	Volume	f2	f1	ID	Volume	k_1' (s^{-1})	k_{-1}' (s^{-1})
358 K	6.33	6.33	A	0.95	6.33	6.33	A	1.28	1.459	1.459
	5.62	5.62	B	1.00	5.62	5.62	B	1.25		
					6.33	5.62	A-B	1.00		
					5.62	6.33	B-A	0.95		

Recall that the equilibrium exchange process of interest is:



The magnetization rates k_1' and k_{-1}' were converted to chemical exchange rates via the following relationships:

$$k_1 = \frac{k_1'}{[silane]} \qquad k_{-1} = k_{-1}' \qquad K_{app} = \frac{k_1}{k_{-1}}$$

Table 2. Comparison of rate data obtained from EXSY experiments and the variable temperature van't Hoff analysis.

T	k_1 ($s^{-1}M^{-1}$)	k_{-1} (s^{-1})	K_{app} (M^{-1})	K_{eq} (M^{-1}) [a]
328	43	0.16	270	230
338	51	0.36	140	130
348	67	0.79	85	80
358	73	1.40	50	49

[a] K_{eq} as determined by the variable temperature van't Hoff analysis

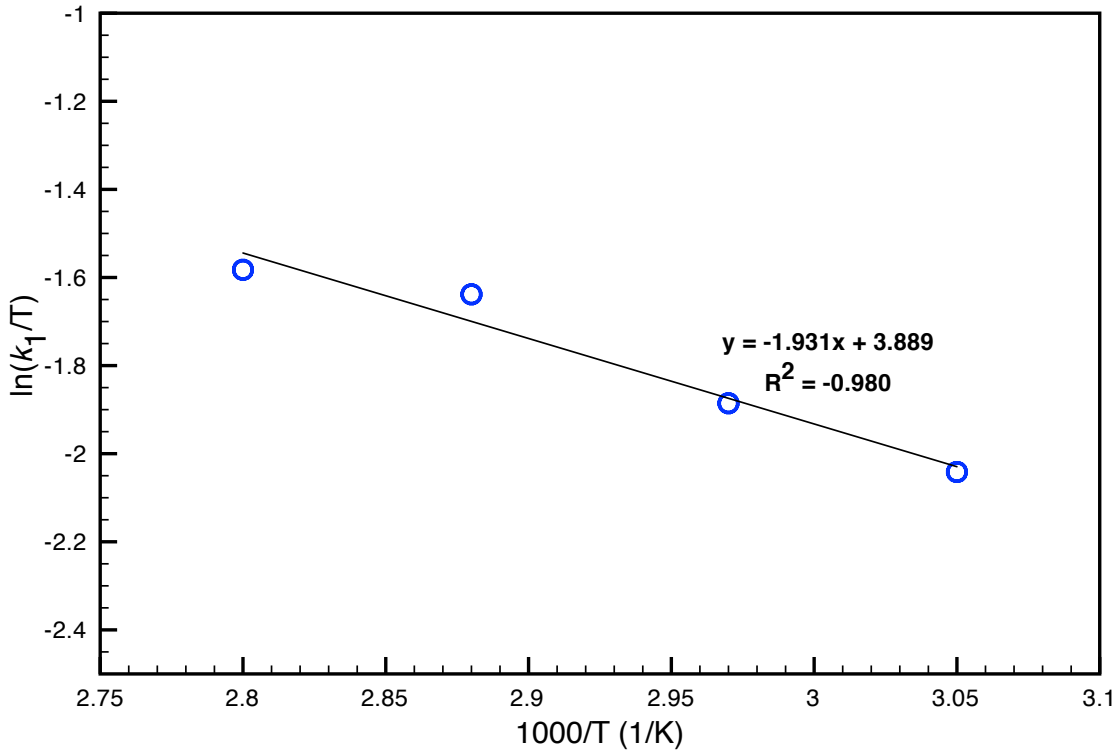


Figure 5. Eyring plot for the forward reaction derived from variable temperature ^{1}H-^{1}H EXSY NMR spectra of the equilibrium between **1** and **4** from 328 K to 358 K.

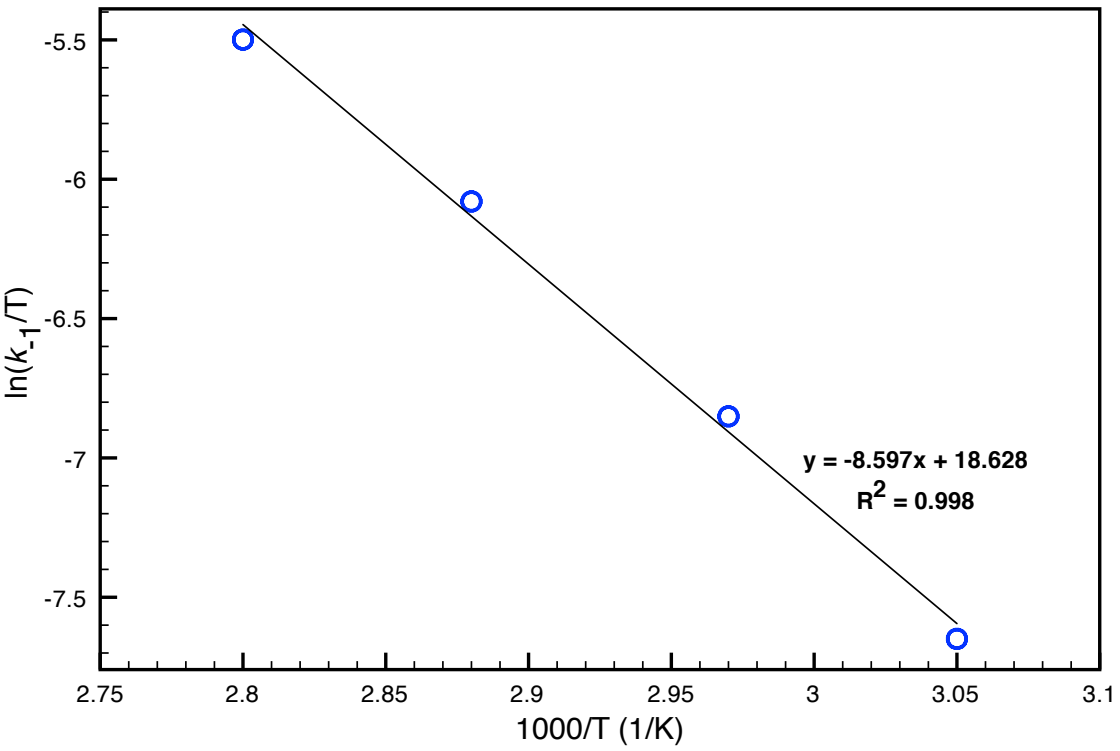


Figure 6. Eyring plot for the reverse reaction derived from variable temperature ^{1}H-^{1}H EXSY NMR spectra of the equilibrium between **1** and **4** from 328 K to 358 K.

X-ray Crystallography

Low-temperature single crystal X-ray diffraction studies were carried out at the Beckman Institute Crystallography Facility on a Bruker Kappa Apex II diffractometer with Mo Kα radiation (λ = 0.71073 Å). Crystals were coated with Paratone-N oil and mounted on glass fibers. Structures were solved by direct or Patterson methods using SHELXS[1] and refined against F^2 on all data by full-matrix least squares with SHELXL-97[2] using established refinement techniques.[3] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms (except the hydrogen atoms bound to heteroatoms in **3**-**6**) were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all calculated hydrogen atoms were fixed to 1.2 times the U values of the atoms they are linked to (1.5 times for methyl groups). Thermal ellipsoid diagrams were created using PyMOL.[4] In the structure of **3**, the OEt2 solvent molecule was disordered over two sites. The structure of **5** contained one positionally disordered toluene solvent molecule. The toluene molecule was refined anisotropically, however hydrogen atoms were not added due to the complicated nature of the positional disorder. Relevant details for individual data collections are reported in Tables 3-5.

[1] G. M. Sheldrick, *Acta Crystallogr*. 1990, **A46**, 467.
[2] G. M. Sheldrick, *Acta Crystallogr*. 2008, **A64**, 112.
[3] P. Müller, *Crystallogr*. *Rev*. 2009, **15**, 57.
[4] The PyMOL Molecular Graphics System, Version 1.5.0.4, Schrödinger, LLC.

Table 3. Crystal data and structure refinement for **3** • OEt_2

Identification code	**3** • OEt_2	
Empirical formula	$C_{26.50}\ H_{26}\ B_{0.50}\ Ni_{0.50}\ O_{0.25}\ P\ Si_{0.50}$	
Formula weight	428.25	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.6097(8) Å	α = 68.361(4)°
	b = 13.0379(9) Å	β = 72.030(4)°
	c = 17.3875(12) Å	γ = 64.875(4)°
Volume	2178.5(3) $Å^3$	
Z	4	
Density (calculated)	1.306 Mg/m^3	
Absorption coefficient	0.584 mm^{-1}	
F(000)	902	
Crystal size	0.27 x 0.18 x 0.11 mm	
Theta range for data collection	1.90 to 30.51°	
Index ranges	-16<=*h*<=16, -18<=*k*<=18, -24<=*l*<=24	
Reflections collected	105776	
Independent reflections	13243 [R_{int} = 0.0472]	
Completeness to theta = 30.51°	99.6 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9385 and 0.8577	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13243 / 0 / 564	
Goodness-of-fit on F^2	1.036	
Final *R* indices [$I>2\sigma(I)$]	*R*1 = 0.0358, *wR*2 = 0.0831	
R indices (all data)	*R*1 = 0.0467, *wR*2 = 0.0904	
Largest diff. peak and hole	0.479 and -0.544 e.$Å^{-3}$	

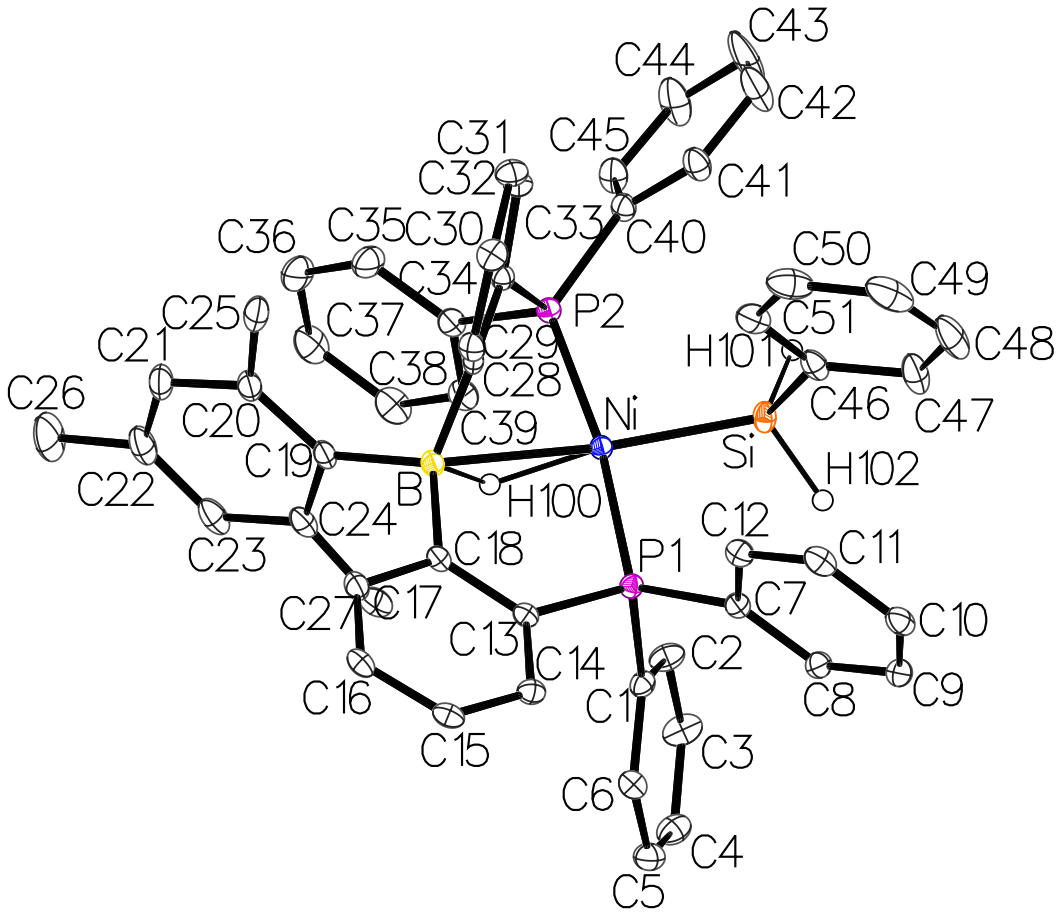


Figure 7. Fully labeled ORTEP diagram of **3**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms bound to carbon and solvent molecule are omitted for clarity.

Table 4. Crystal data and structure refinement for **4** • 0.5 C_6H_6

Identification code	**4** • 0.5 C_6H_6	
Empirical formula	C_{60} H_{54} B Ni P_2 Si	
Formula weight	934.58	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.1452(6) Å	α = 69.986(3)°
	b = 20.3316(10) Å	β = 77.017(3)°
	c = 21.4335(11) Å	γ = 82.180(3)°
Volume	4835.7(4) $Å^3$	
Z	4	
Density (calculated)	1.284 Mg/m^3	
Absorption coefficient	0.532 mm^{-1}	
F(000)	1964	
Crystal size	0.41 x 0.13 x 0.08 mm	
Theta range for data collection	1.72 to 26.02°	
Index ranges	-14<=*h*<=14, -25<=*k*<=25, -26<=*l*<=26	
Reflections collected	107064	
Independent reflections	19001 [R_{int} = 0.0675]	
Completeness to theta = 26.02°	99.8 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9607 and 0.8114	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19001 / 0 / 1193	
Goodness-of-fit on F^2	1.021	
Final *R* indices [$I>2\sigma(I)$]	*R*1 = 0.0442, *wR*2 = 0.1065	
R indices (all data)	*R*1 = 0.0686, *wR*2 = 0.1192	
Largest diff. peak and hole	1.754 and -0.610 $e.Å^{-3}$	

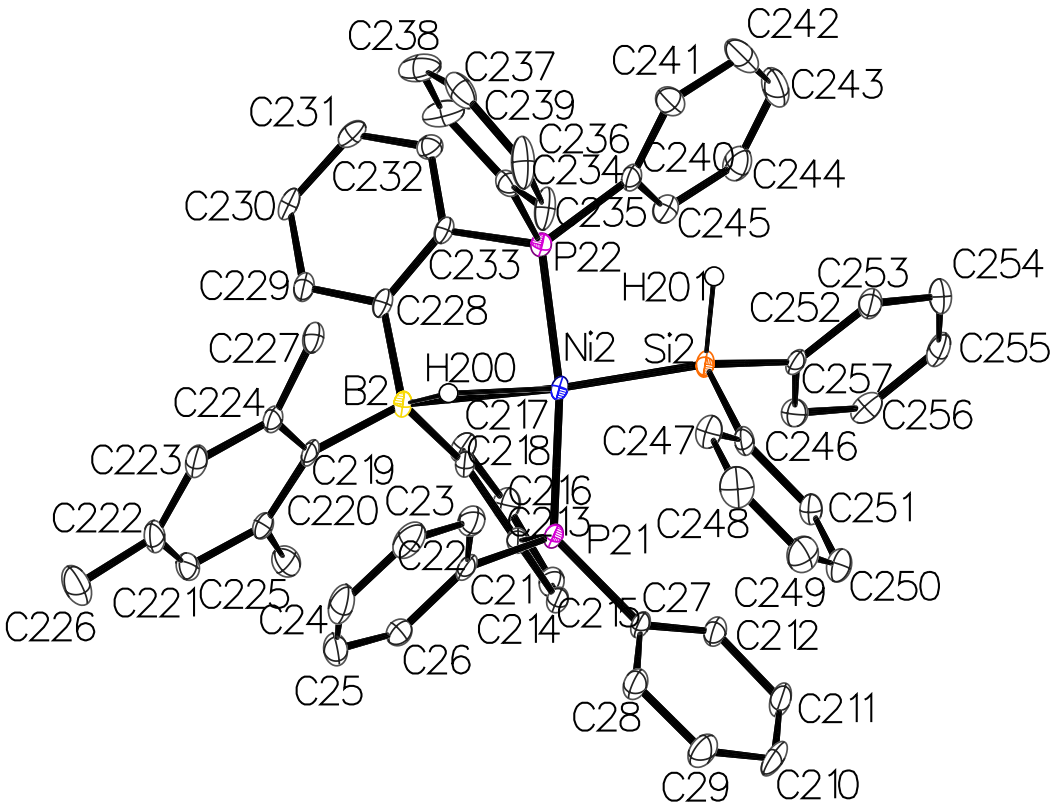


Figure 8. Fully labeled ORTEP diagram of **4**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms bound to carbon and solvent molecule are omitted for clarity. Only one of the two independent molecules is shown.

Table 5. Crystal data and structure refinement for **5** • C_7

Identification code	**5** • C_7	
Empirical formula	$C_{55.50}$ H_{45} B Ni O P_2	
Formula weight	859.38	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.9166(8) Å	α = 90°
	b = 15.2418(9) Å	β = 105.256(3)°
	c = 22.8933(15) Å	γ = 90°
Volume	4348.2(5) $Å^3$	
Z	4	
Density(calculated)	1.313 Mg/m^3	
Absorption coefficient	0.561 mm^{-1}	
F(000)	1796	
Crystal size	0.24 x 0.22 x 0.17 mm	
Theta range for data collection	2.11 to 42.16°	
Limiting indices	-24<=*h*<=24, -28<=*k*<=28, -43<=*l*<=39	
Reflections collected	250827	
Independent reflections	30670 [R_{int} = 0.0536]	
Completeness to theta = 42.16	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9132 and 0.8772	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	30670 / 0 / 585	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	*R*1 = 0.0385, *wR*2 = 0.0935	
R indices (all data)	*R*1 = 0.0710, *wR*2 = 0.1058	
Largest diff. peak and hole	0.688 and -0.445 $e.A^{-3}$	

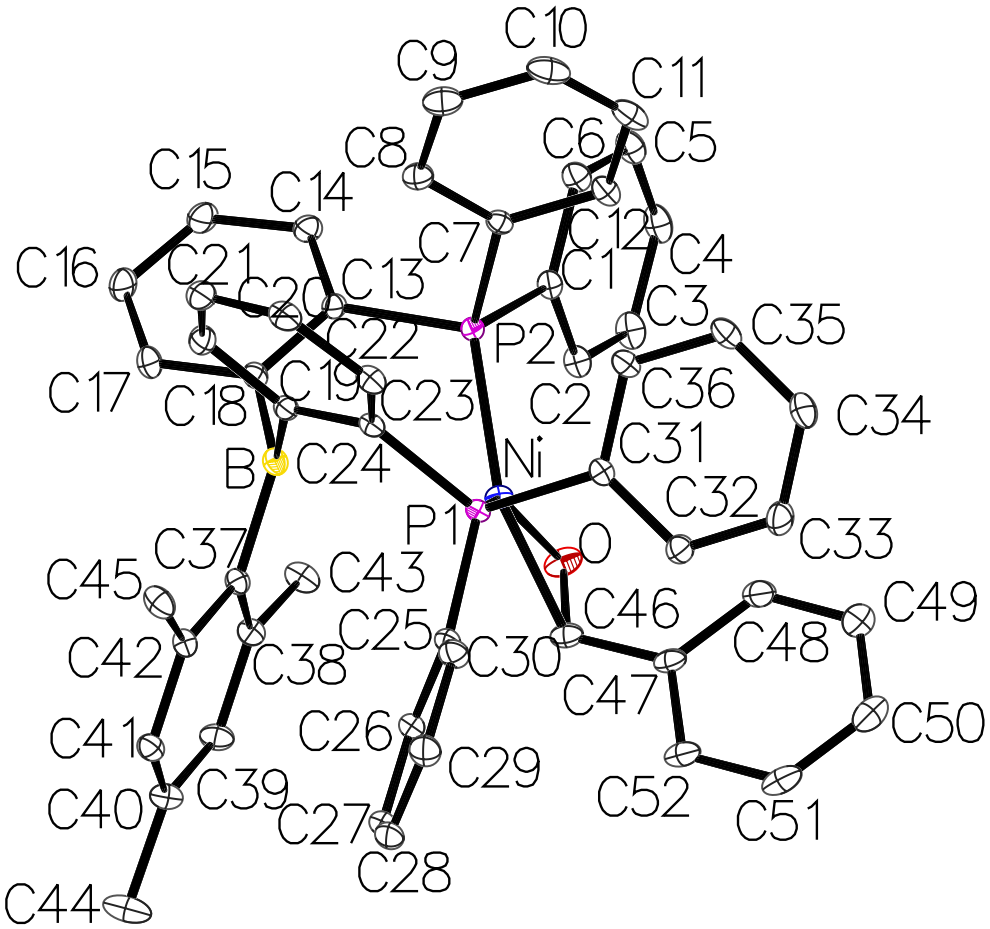


Figure 9. Fully labeled ORTEP diagram of **5**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms bound to carbon and solvent molecule are omitted for clarity.