Supporting Information for:

A Metal-Amide Dependent, Catalytic C–H Activation and Dehydrocoupling of Triphenylphosphonium Methylide

Adi E. Nako, Andrew J. P. White and Mark R. Crimmin

Department of Chemistry, Imperial College London, Exhibition Road, South Kensington, London, SW7 2AZ, U.K.

1.1 General Experimental

All manipulations were carried out under standard Schlenk-line or glovebox techniques under an inert atmosphere of dinitrogen. A Saffron 2P/O/H2O type glovebox was employed operating under an inert atmosphere of 2-8 ppm O_2. Solvents were dried over activated alumina from an SPS (solvent purification system) based upon the Grubbs design and degassed before use. Glassware was dried for 12 hours at 120 °C prior to use. Benzene, d_6-benzene and d_8-toluene were dried over molten K, distilled, and stored over molecular sieves prior to use.

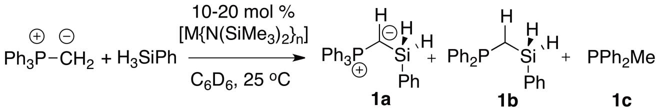
NMR spectra were obtained on Bruker 300, 400 or 500 MHz machines, all peaks are referenced against residual solvent and values are quoted in ppm. Data were processed in Topspin or MestReNova, when NMR yields have been quoted the yields were calculated against durene as an internal standard. Infrared spectra were obtained as KBr discs, pressed by a handheld dye or as a solution in *n*-hexane.

1.2 Materials

Methyl triphenylphosphonium iodide was synthesized by reaction of the methyliodide with freshly recrystallized triphenylphoshine in diethyl ether. The corresponding ylide was synthesized by deprotonation with potassium *tert*-butoxide or $[K\{N(SiMe_3)_2\}]$ in diethyl ether or toluene. The deuterium analogue Ph_3PCD_2 was synthesized from d_3-MeI in place of methyliodide in the reaction sequence. $[Li\{N(SiMe_3)_2\}]$,[1] $[Ca\{N(SiMe_3)_2\}_2]_2$, and $[Y\{N(SiMe_3)_2\}_3]$ were synthesized by literature procedures.[2-3]. Durene (1,2,4,5-tetramethylbenzene) was purchased from Sigma-Aldrich and recrystallized from toluene. $PhSiH_3$, YCl_3, $[Na\{N(SiMe_3)_2\}]$, $[K\{N(SiMe_3)_2\}]$, $[(Ph_3P)_3RhCl]$ and potassium *tert*-butoxide were purchased from Sigma-Aldrich and used without further purification. Styrene was purchased from Acros Organics, dried over CaH_2, distilled and stored in a freezer.

2.1 Catalytic Ylide/Silane Reactions

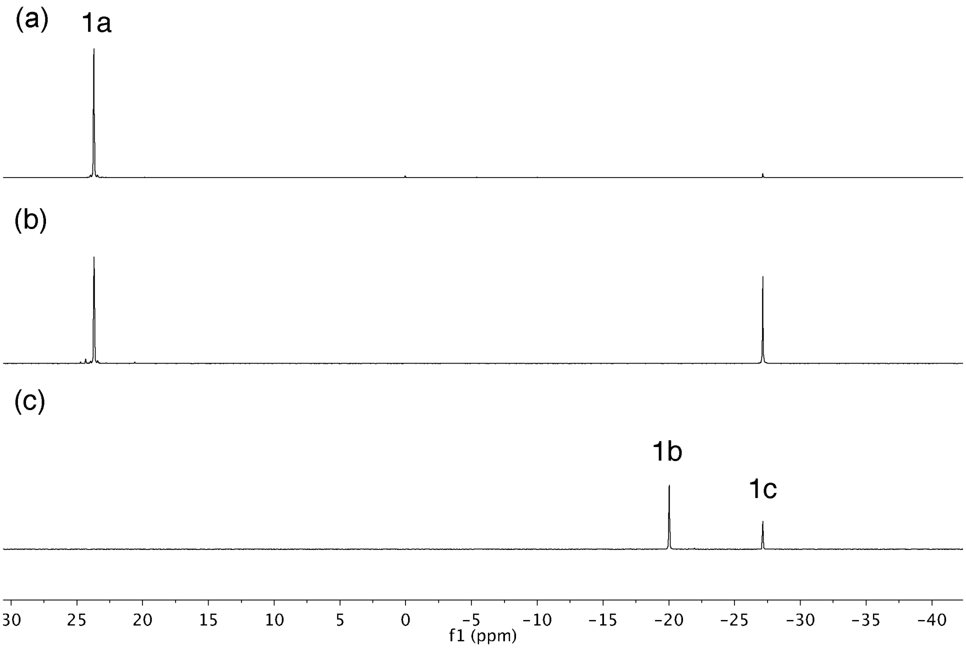
Table S1. The catalytic dehydrocoupling of Ph_3PCH_2 with $PhSiH_3$ with group 2 and 3 metal-amide catalysts

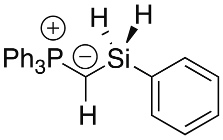


M	n	mol %	Time	Conversion	**1a** : **1b** : **1c**	Yield **1a**^{a}
–	–	–	1 h	95 %	1 : 0 : 1	47%^{b}
Li	1	20	18 h	23 %	0 : 0.3 : 1	0%
Na	1	20	22 h	19 %	0 : 0.3 : 1	0%
K	1	20	22 h	32 %	0 : 0.7 : 1	0%
Ca	2	20	5.0 h	89 %	0 : 2.1 : 1	0%
Y	3	10	2.0 h	97 %	4.5 : 0 : 1	79%
Y	3	15	0.5 h	95 %	8.4 : 0 : 1	85%
Y	3	20	0.5 h	95 %	12 : 0 : 1	88%
2c^c		30	3.5 h	97 %	7.7 : 1 : 1	77%
Lu	3	20	0.5 h	96 %	1.5 : 0 : 1	57%

a – reactions conducted at 0.22 M concentration of starting materials, yields recorded by ^1H NMR using 1,2,4,5-tetramethylbenzene and an internal standard, a – reaction conducted in triplicate in pre-silylated NMR tubes. c – conversion based on Ph_3PCH_2.

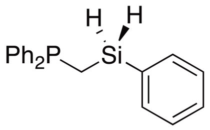
Figure S1. $^{31}P\{^1H\}$ NMR spectroscopy data for the reaction of Ph_3PCH_2 with $PhSiH_3$. (a) 20 mol % $[Y\{N(SiMe_3)_2\}_3]$ 1h at 25 °C, (b) background reaction 1h at 25 °C, (c) 20 mol % $[Ca\{N(SiMe_3)_2\}_3]$ 5h at 25 °C.



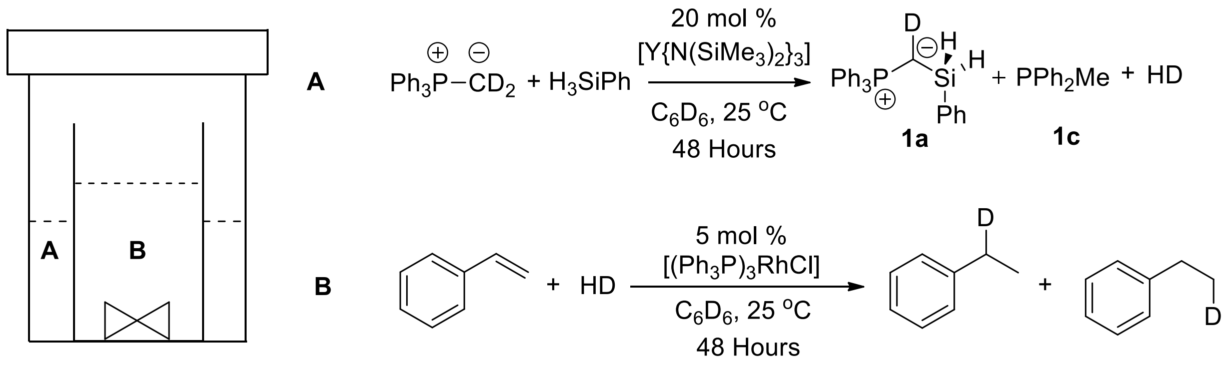


NMR scale synthesis of [$Ph_3PCHSiH_2Ph$] (**1a**): In a glovebox, $PhSiH_3$ (14.4 μL, 0.116 mmol) was dissolved in C_6D_6 (100 μL) and transferred to a Youngs tap NMR tube. [$Y\{N(SiMe_3)_2\}_3$] (0.013 g, 0.023 mmol) and durene (internal standard accurately weighed 5-10 mg) in C_6D_6 (300 μL) was added to the NMR tube followed swiftly by Ph_3PCH_2 (0.032 g, 0.116 mmol) in C_6D_6 (200 μL). The tube was left at room temperature for 30 minutes to give complete consumption of Ph_3PCH_2 and production of **1a** in an 88% NMR yield as judged by comparison to an internal standard. Triphenylphosphine and methyldiphenylphosphine were present in trace amounts and confirmed by spiking experiments with authentic samples.

Preparative scale synthesis of [$Ph_3PCHSiH_2Ph$] (**1a**): In a glovebox, [$Y\{N(SiMe_3)_2\}_3$] (0.13 g, 0.23 mmol), Ph_3PCH_2 (0.32 g, 1.16 mmol) and $PhSiH_3$ (144 μL, 1.16 mmol) were measured and transferred to separate schlenk flasks. The flasks were removed from the box, attached to a vacuum line and under a purge of argon, toluene (10 mL) was added to each flask giving homogeneous solutions. To the schlenk containing the $PhSiH_3$ solution, the toluene solution of [$Y\{N(SiMe_3)_2\}_3$] was added, followed swiftly by the toluene solution of Ph_3PCH_2. The reaction was stirred at 25 °C for 5 h during which time bubbling was observed. The toluene was removed *in vacuo* and the solid was extracted into hexane (20 mL). The solution was placed at -20 °C for 18 h to give **1a** as light yellow crystals along with a fine colourless powder. Crystals of **1a** were manually separated from the mixture. ^{1}H NMR (500MHz, C_6D_6) δ 0.56 (dt, 1H. $^{2}J_{^{1}H-^{31}P} = 7.0$ Hz, $^{3}J_{^{1}H-^{1}H} = 4.5$ Hz), 5.24 (ddd, 2H, $^{1}J_{^{29}Si-^{1}H} = 93.6$ Hz, $^{3}J_{^{1}H-^{31}P} = 4.5$ Hz, $^{3}J_{^{1}H-^{1}H} = 4.5$ Hz), 6.97-7.05 (m, 9H), 7.19-7.27 (m, 3H), 7.61-7.65 (m, 6H) 7.89 (dd, 2H, $^{3}J_{^{1}H-^{1}H} = 8.0$ Hz, $^{4}J_{^{1}H-^{1}H} = 1.5$ Hz; ^{13}C NMR (101 MHz, C_6D_6, 298 K) δ -8.55 (d, $^{1}J_{^{31}P-^{13}C} = 78.6$ Hz), 127.67, 128.17 (d, $^{2}J_{^{31}P-^{13}C} = 11.6$ Hz), 128.44, 131.04 (d, $^{4}J_{^{31}P-^{13}C} = 1.7$ Hz), 133.02 (d, $^{3}J_{^{31}P-^{13}C} = 7.9$ Hz), 133.50 (d, $^{1}J_{^{31}P-^{13}C} = 69.7$ Hz), 135.33, 140.36 (d, $^{3}J_{^{31}P-^{13}C} = 4.1$ Hz); ^{31}P NMR (162 MHz, C_6D_6) δ +23.8; ^{29}Si NMR (99MHz, C_6D_6) δ -41.8. High-resolution MS (ESI, +ve) calculated for $C_{25}H_{24}SiP$ = 383.1385 found = 383.1389.



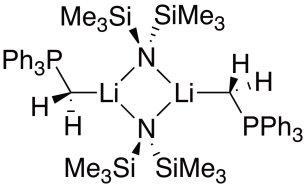
NMR scale synthesis of [Ph$_2$PCH$_2$SiH$_2$Ph] (**1b**): In a glovebox, PhSiH$_3$ (14.4 μL, 0.116 mmol) was dissolved in C$_6$D$_6$ (100 μL) and transferred to a Youngs tap NMR tube. [Ca{N(SiMe$_3$)$_2$}$_2$]$_2$ (0.008 g, 0.023 mmol) in C$_6$D$_6$ (300 μL) was added to the NMR tube followed swiftly by Ph$_3$PCH$_2$ (0.032 g, 0.116 mmol) in C$_6$D$_6$ (200 μL). The tube was left at room temperature for 5 h to give complete consumption of Ph$_3$PCH$_2$ and production of **1b** in a 60% NMR yield as judged by comparison to an internal standard. Methyldiphenylphosphine was also observed in a 28% NMR yield as judged by comparison to an internal standard. ^{1}H NMR (400MHz, C$_6$D$_6$) δ 1.48 (dt, $^3J_{^1H-^1H} = 4.0$ Hz, $^2J_{^1H-^{31}P} = 0.8$ Hz), 4.47 (dt, $^3J_{^1H-^1H} = 4.0$ Hz, $^3J_{^1H-^{31}P} = 4.0$ Hz); ^{31}P NMR (162 MHz, C$_6$D$_6$) δ -20.1; High-resolution MS (ESI, +ve) calculated for C$_{19}$H$_{20}$SiP = 307.1072 Found 307.1107. [Literature data:[3] ^{1}H NMR (CDCl$_3$) δ 1.65 ($^3J_{^1H-^1H} = 4.5$Hz), 4.25 ($^2J_{^1H-^1H} = 4.5$Hz), 7.0-7.5 (m); ^{31}P NMR (162 MHz, C$_6$D$_6$) δ -19.0].



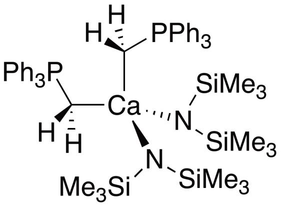
Sequestration of H–D by transfer hydrogenation: In a glovebox, [Y{N(SiMe$_3$)$_2$}$_3$] (0.039 g, 0.069 mmol) and PhSiH$_3$ (43.2 μL, 0.35 mmol) were dissolved in C$_6$D$_6$ (900 μL) and transferred to a small screw top glass vial (A). A smaller glass vial (B) containing a stirrer bar was then placed within the first container before being charged with a solution of [(Ph$_3$P)$_3$RhCl] (13.9 mg, 0.015 mmol, 5 mol%) and styrene (34.5 μL, 0.30 mmol) in C$_6$D$_6$ (600 μL). A solution of Ph$_3$PCD$_2$ (0.096 g, 0.35 mmol) in C$_6$D$_6$ (4500 μL) was then added to vial A before the cap was swiftly tightened. The system was then stirred at 20°C for 48 h to give complete consumption of both Ph$_3$PCD$_2$ and styrene as seen by ^{1}H and ^{31}P NMR spectroscopy. Selected data on *C$_8$H$_9$D:* ^{1}H NMR (400MHz, C$_6$D$_6$) δ 1.05 (t, 2.5H, $^3J_{^1H-^1H} =$

7.6 Hz), 2.42 (q, 1.5H, ${}^{3}J_{^{1}H\text{-}^{1}H}$ = 7.6 Hz), 7.02-7.05 (m, 2H), 7.12-7.15 (m, 3H); ^{2}H NMR (76.8MHz, C_6D_6) δ 1.00-1.06 (m), 2.34-2.45 (m).

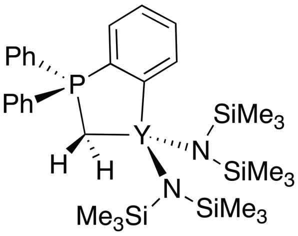
2.2 Reactions of Triphenylphosphonium Methylide with Group 1-3 Amides



Synthesis of [Li(CH$_2$PPh$_3$){N(SiMe$_3$)$_2$}] (**2a**): In a glovebox, Ph_3PCH_2 (0.30 g, 1.09 mmol) and [Li{N(SiMe$_3$)$_2$}] (0.18 g, 1.09 mmol) were weighed out separately and transferred to a schlenk flask. The schlenk was removed from the box and transferred to a vacuum line where, under a purge of argon, toluene (20 mL) was added to give a clear yellow solution. The solution was left unstirred at room temperature for one hour before the toluene was removed *in vacuo*. The resulting solid was extracted into refluxing hexane (2 x 35 mL), filtered and the volume of the solution was reduced to 35 mL. Storage of this solution at -20 °C gave a microcrystalline solid that was dried *in vacuo*, yielding [Li(CH$_2$PPh$_3$){N(SiMe$_3$)$_2$}] (**1a**) as an off-white solid (0.23 g, 0.53 mmol, 49%). Crystals suitable for X-ray diffraction were grown from a 1:1 toluene:hexane solution at -20 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K) δ 0.39 (s, 18H), 0.67 (d, 2H, ${}^{2}J_{^{31}P\text{-}^{1}H}$ = 4.8 Hz), 7.03-7.06 (m, 9H), 7.58-7.63 (m, 6H); ^{13}C NMR (101 MHz, C_6D_6, 298 K) δ -4.53 (d, ${}^{1}J_{^{31}P\text{-}^{13}C}$ = 62.3 Hz), 6.52, 128.65 (d, ${}^{2}J_{^{31}P\text{-}^{13}C}$ = 11.4 Hz), 131.19 (d, ${}^{4}J_{^{31}P\text{-}^{13}C}$ = 2.2 Hz), 132.78 (d, ${}^{3}J_{^{31}P\text{-}^{13}C}$ = 9.7 Hz), 132.81 (d, ${}^{1}J_{^{31}P\text{-}^{13}C}$ = 84.2 Hz); ^{31}P NMR (162 MHz, C_6D_6 , 298 K) δ + 27.85; ^{7}Li NMR (156 MHz, C_6D_6, 298 K) δ +2.2; Due to the air sensitive nature of this compound repeated attempts to acquire satisfactory CHN failed.



Synthesis of [Ca(CH_2PPh_3)$_2${N($SiMe_3$)$_2$}$_2$] (**2b**): In a glovebox, [Ca{N($SiMe_3$)$_2$}$_2$]$_2$ (0.18 g, 0.45 mmol) and Ph_3PCH_2 (0.25 g, 0.90 mmol, 2 equiv.) were weighed out separately and transferred to a schlenk. The schlenk was sealed, removed from the box and attached to a vacuum line where dry toluene (5 mL) was added under a purge of argon. The mixture was agitated and left to stand for one hour at 25 ^{o}C. The mixture was filtered and hexane (10 mL) added, storage of this solution at -20 ^{o}C produced colourless needles that were isolated by filtration to give the product **2b** which was dried *in vacuo* (0.25 g, 0.27 mmol, 60 %); ^{1}H (400 MHz, C_6D_6, 298 K) δ 0.46 (s, 36H), 0.54 (d, 4H, $^{2}J_{^{31}P-^{1}H}$ = 12.0 Hz), 7.00-7.06 (m, 18H), 7.42-7.48 (m, 12H); ^{31}P (162 MHz, C_6D_6 , 298 K) δ + 30.1; ^{13}C NMR (101 MHz, C_6D_6, 298 K) δ 0.3 (d, $^{1}J_{^{31}P-^{13}C}$ = 34.3 Hz), 6.9, 129.1 (d, $J_{^{31}P-^{13}C}$ = 9.1 Hz), 130.9 (d, $^{1}J_{^{31}P-^{13}C}$ = 67.7 Hz), 131.9 (d, $^{3}J_{^{31}P-^{13}C}$ = 1.1 Hz), 132.8 (d, $^{1}J_{^{31}P-^{13}C}$ = 8.1 Hz); Elemental analysis calculated for $C_{50}H_{70}CaN_2P_2Si_4$ = C: 65.74%, H: 7.72%, N: 3.07% Found = C: 65.79%, H: 7.78%, N: 2.97%.



Synthesis of $[Y\{(CH_2P(Ph)_2(C_6H_4)\}\{N(SiMe_3)_2\}_2]$ (**2c**): In a glovebox, $[Y\{N(SiMe_3)_2\}_3]$ (0.80 g, 1.40 mmol) and Ph_3PCH_2 (0.39 g, 1.40 mmol) were weighed together and transferred to a schlenck ampoule. The ampoule was removed from the box and attached to a vacuum line, under a purge of argon, toluene (10 mL) was added to give a clear yellow solution. The reaction was heated at 80 ^{o}C for three hours to give an orange solution. The toluene was removed and the solid was extracted into hexane (20 mL), left to settle for 48 hours and then filtered to remove a small amount of an unidentified fine white precipitate. Under reduced pressure, the volume of the solution was reduced to 10 mL and the mixture left at 25 ^{o}C for 14 hours at which point the product began to crystallize. The yield of this crystalline material was maximised by cooling the mixture to -78^{o}C for four hours and the product isolated by filtration, which was dried *in vacuo* to give **1c** (0.73 g, 1.06 mmol, 76%).^{1}H NMR (400 MHz, C_6D_6, 298 K) δ 0.34 (s, 38H), 1.11 (dd, 2H, $^{2}J_{^{1}H-^{31}P} = 14.0$ Hz, $^{2}J_{^{1}H-^{89}Y} = 2.4$ Hz), 6.89-7.05 (m, 8H), 7.23-7.28 (m, 5H), 8.29 (d, 1H, $^{3}J_{^{1}H-^{1}H} = 7.2$ Hz); ^{13}C NMR (101 MHz, C_6D_6, 298 K) δ 5.12, 15.56 (dd, $^{1}J_{^{31}P-^{13}C} = {}^{1}J_{^{89}Y-^{13}C} = 23.6$ Hz), 126.21 (d, $^{3}J_{^{31}P-^{13}C} = 10.5$ Hz), 129.07 (d, $^{2}J_{^{31}P-^{13}C} = 8.9$ Hz), 130.05 (d, $^{4}J_{^{31}P-^{13}C} = 1.0$ Hz), 131.24 (d, $^{1}J_{^{31}P-^{13}C} = 59.2$ Hz), 131.78 (d, $^{4}J_{^{31}P-^{13}C} = 1.3$ Hz), 132.10 (dd, $^{3}J_{^{31}P-^{13}C} = 16.0$ Hz, $^{2}J_{^{89}Y-^{13}C} = 1.8$ Hz), 132.47 (d, $^{3}J_{^{31}P-^{13}C} = 7.6$ Hz), 136.62 (dd, $^{1}J_{^{31}P-^{13}C} = 86.8$Hz, $^{2}J_{^{89}Y-^{13}C} = 2.5$ Hz), 139.58 (d, $^{1}J_{^{31}P-^{13}C} = 21.5$ Hz), 195.88 (apparent dd, $^{2}J_{^{31}P-^{13}C} = 38.5$ Hz, $^{1}J_{^{89}Y-^{13}C} = 38.5$ Hz); ^{31}P NMR (162 MHz, C_6D_6) δ +28.3 (d, $^{1}J_{^{31}P-^{89}Y} = 11.2$Hz); Elemental analysis calculated for $C_{31}H_{52}N_2PSi_4Y$ = C: 54.36%, H: 7.65%, N: 4.09% Found = C: 54.37%, H: 7.51%, N: 4.00%.

2.3 X-ray Crystallography Data

Table S1. Crystal Data, Data Collection and Refinement Parameters for the structures of **1a**, **2a**, **2b** and **2c**.

data	**1a**	**2a**	**2b**	**2c**
formula	$C_{25}H_{23}PSi$	$C_{50}H_{70}Li_2N_2P_2Si_4$	$C_{50}H_{70}CaN_2P_2Si_4$	$C_{31}H_{52}N_2PSi_4Y$
solvent	—	—	$2(C_7H_8)$	—
formula weight	382.49	887.26	1097.73	684.99
colour, habit	pale yellow blocks	colourless blocks	colourless tabular needles	colourless tablets
crystal size / mm^3	0.40 × 0.31 × 0.29	0.39 × 0.35 × 0.13	0.45 × 0.27 × 0.14	0.49 × 0.39 × 0.22
temperature / K	173	173	173	173
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	*P*-1 (no. 2)	*Cc* (no. 9)	*C*2/*c* (no. 15)	$P2_1/c$ (no. 14)
***a* / Å**	11.2823(3)	18.8666(4)	30.6079(11)	11.1459(3)
***b* / Å**	16.8988(4)	22.2888(5)	12.39475(17)	20.7732(4)
***c* / Å**	22.9869(6)	25.4992(6)	22.0579(8)	16.6276(3)
α / deg	81.236(2)	—	—	—
β / deg	79.739(2)	100.652(2)	128.948(6)	100.7824(19)
γ / deg	81.615(2)	—	—	—
***V* / Å^3**	4230.32(19)	10538.0(4)	6508.1(6)	3781.92(14)
Z	8 [a]	8 [b]	4 [c]	4
D_c / g cm^{-3}	1.201	1.118	1.120	1.203
radiation used	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα
μ / mm^{-1}	0.193	0.207	0.257	1.732
2θ max / deg	62	58	65	65
no. of unique reflns				
measured (R_{int})	22303 (0.0251)	19768 (0.0295)	10982 (0.0212)	12694 (0.0382)
obs, $\|F_o\| > 4\sigma(\|F_o\|)$	16131	16161	8561	8602
no. of variables	1002	1116	331	352
R_1(obs), wR_2(all) [d]	0.0539, 0.1390	0.0596, 0.1685	0.0458, 0.1446	0.0406, 0.0923

[a] There are four crystallographically independent molecules in the asymmetric unit. [b] There are two crystallographically independent molecules in the asymmetric unit. [c] The molecule has crystallographic C_2 symmetry. [d] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Table S1 provides a summary of the crystallographic data for the structures of **1a**, **2a**, **2b** and **2c**. Data were collected using an Oxford Diffraction Xcalibur 3 diffractometer, and the structures were refined based on F^2 using the SHELXTL and SHELX-97 program systems.[5] Compound **2a** was found to crystallise in a polar space group (*Cc*), and attempts to determine the absolute structure by using a combination of *R*-factor tests [$R_1^+ = 0.0596$, $R_1^- = 0.0596$] and the Flack parameter [$x^+ = +0.44(9)$, $x^- = +0.56(9)$] showed the crystal studied to be a partial (*ca.* 56:44) polar twin. CCDC 894051 to 894054.

The X-ray crystal structure of 1a: Compound **1a** was found to crystallise with four independent molecules (**1a-A** to **1a-D**) in the asymmetric unit. The Si(3)–Ph unit in molecule **1a-D** was found to be disordered, and two orientations of *ca.* 79 and 21% occupancy were identified. The geometries of the two orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the major occupancy non-hydrogen atoms were refined anisotropically. The Si–H hydrogen atoms of molecules **1a-A** to **1a-C** were located from ΔF maps and refined freely subject to an Si–H distance constraint of 1.45 Å. Because of the disorder in the Si(3)–Ph unit in molecule 1a-D, the Si–H hydrogen atoms in this case were added in idealised tetrahedral positions at a distance of 1.45 Å.

The X-ray crystal structure of 2a: Compound **2a** was found to crystallise with two independent molecules (**2a-A** and **2a-B**) in the asymmetric unit. The Si(4)-based $SiMe_3$ unit in molecule **2a-A**, and the Si(1)-based $SiMe_3$ unit in molecule **2a-B**, were both found to be disordered, and in each case two orientations were identified (of ca. 93 and 7% occupancy for the Si(4A) unit, and of ca. 83 and 17% occupancy for the Si(1B) unit). In both instances the geometries of the two orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the major occupancy non-hydrogen atoms were refined anisotropically. The compound was found to crystallise in a polar space group (Cc), and attempts to determine the absolute structure by using a combination of *R*-factor tests [$R_1^+ = 0.0596$, $R_1^- = 0.0596$] and the Flack parameter [$x^+ = +0.44(9)$, $x^- = +0.56(9)$] showed the crystal studied to be a partial (ca. 56:44) polar twin.

The X-ray crystal structure of 2b: The structure of **2b** showed the complex to have crystallographic C_2 symmetry about an axis that passes through the calcium centre and bisects the N(1)–Ca(1)–N(1A) and C(10)–Ca(1)–C(10A) angles.

Table S2. Comparative selected bond lengths (Å) and angles (°) for the four independent molecules present in the crystals of **1a**.

	1a-A	**1a-B**	**1a-C**	**1a-D**
P(1)–C(2)	1.6771(19)	1.6790(19)	1.6757(19)	1.672(2)
C(2)–Si(3)	1.797(2)	1.796(2)	1.804(2)	1.851(3)
Si(3)–C(22)	1.8786(19)	1.880(2)	1.885(2)	1.8833(19)
P(1)–C(2)–Si(3)	127.79(12)	126.70(12)	124.67(12)	123.84(15)
C(2)–Si(3)–C(22)	111.31(9)	111.10(10)	112.74(9)	112.93(15)

Table S3. Comparative selected bond lengths (Å) and angles (°) for the two independent molecules present in the crystals of **2a**.

	2a-A	**2a-B**
Li(1)–C(1)	2.302(8)	2.264(8)
Li(2)–C(32)	2.285(9)	2.254(8)
P(1)–C(1)	1.698(4)	1.701(4)
P(2)–C(32)	1.705(4)	1.707(4)
Li(1)–C(1)–P(1)	136.6(3)	135.0(3)
Li(2)–C(32)–P(2)	133.6(3)	136.7(3)

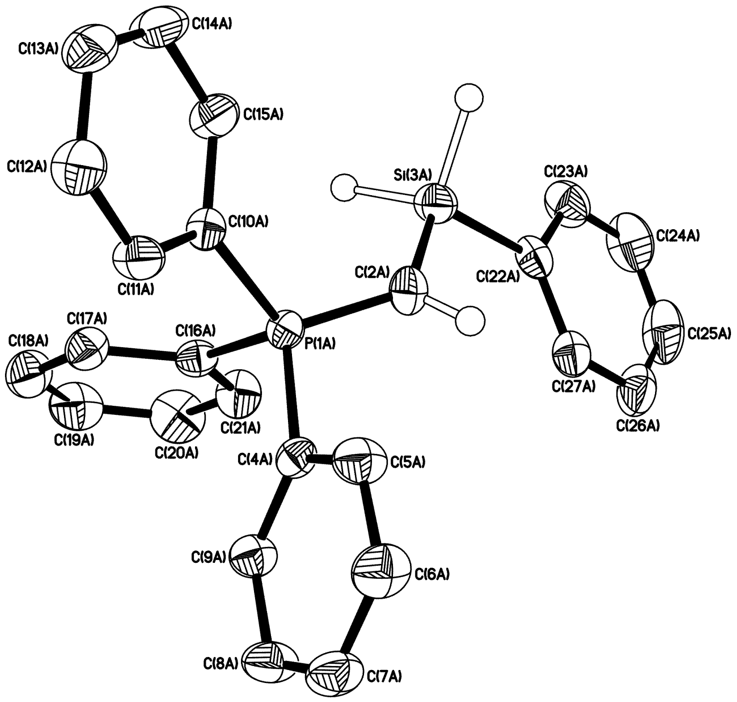


Fig. S1 The crystal structure of one (**1a-A**) of the four independent molecules present in the crystals of **1a** (50% probability ellipsoids).

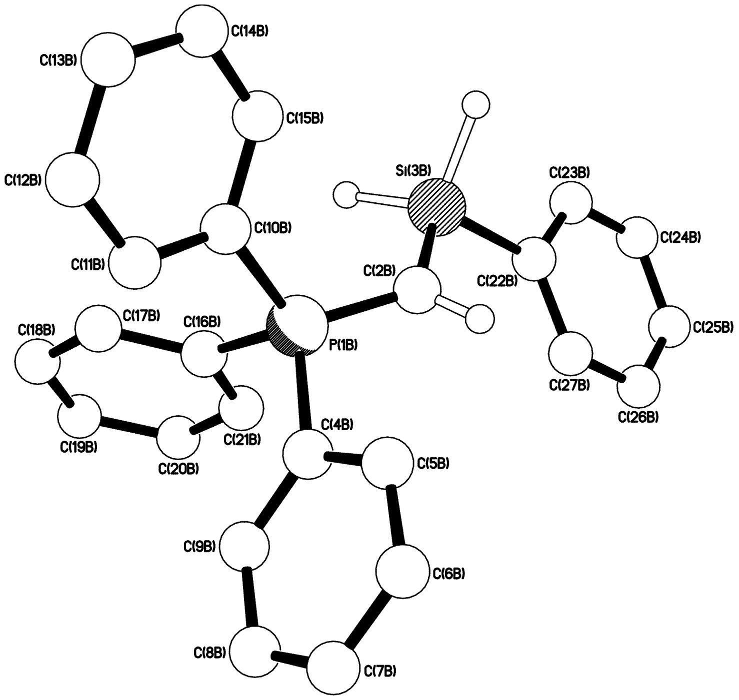


Fig. S2 The crystal structure of one (**1a-B**) of the four independent molecules present in the crystals of **1a**.

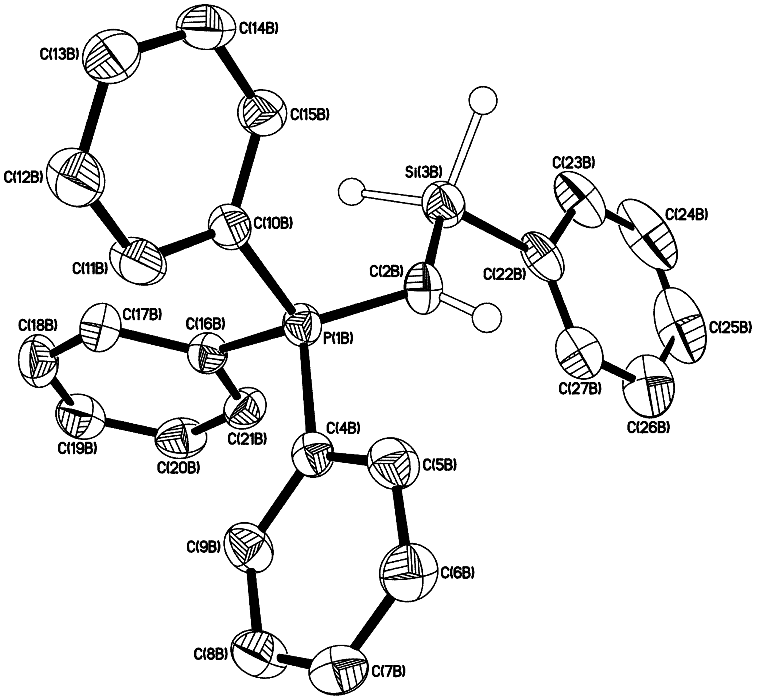


Fig. S3 The crystal structure of one (**1a-B**) of the four independent molecules present in the crystals of **1a** (50% probability ellipsoids).

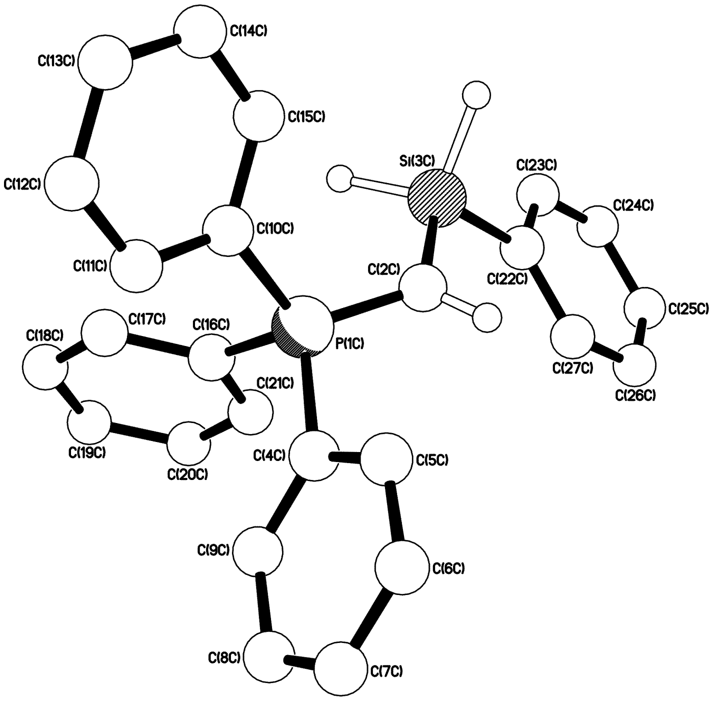


Fig. S4 The crystal structure of one (**1a-C**) of the four independent molecules present in the crystals of **1a**.

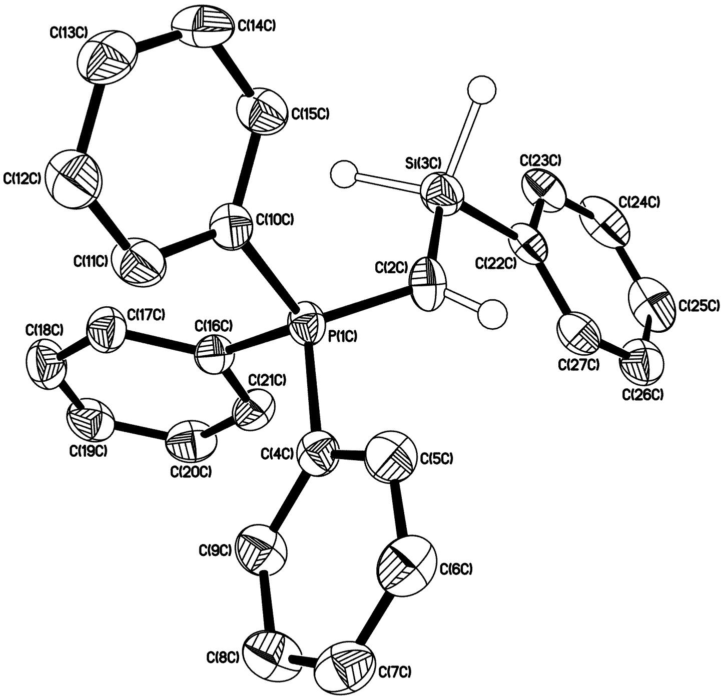


Fig. S5 The crystal structure of one (**1a-C**) of the four independent molecules present in the crystals of **1a** (50% probability ellipsoids).

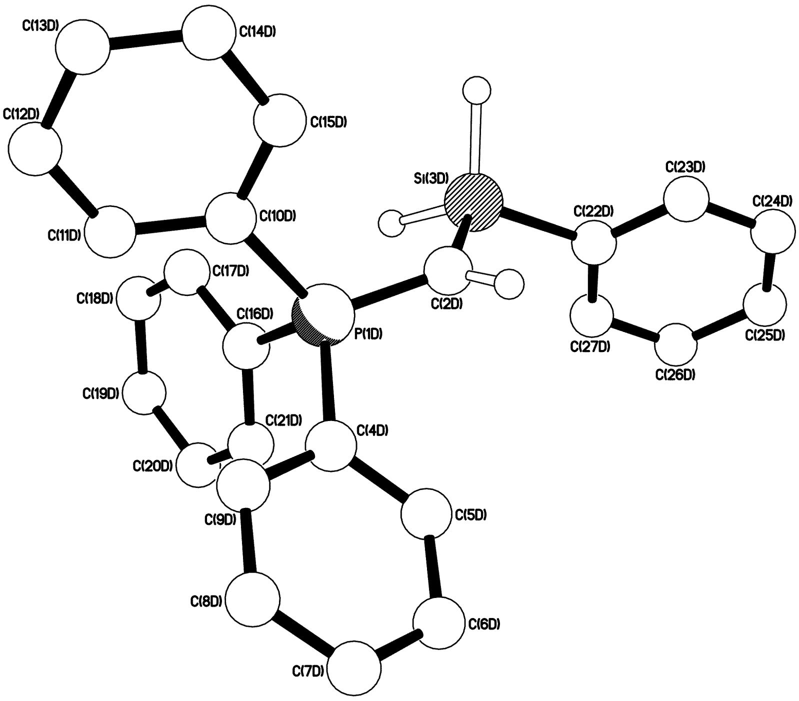


Fig. S6 The crystal structure of one (**1a-D**) of the four independent molecules present in the crystals of **1a**.

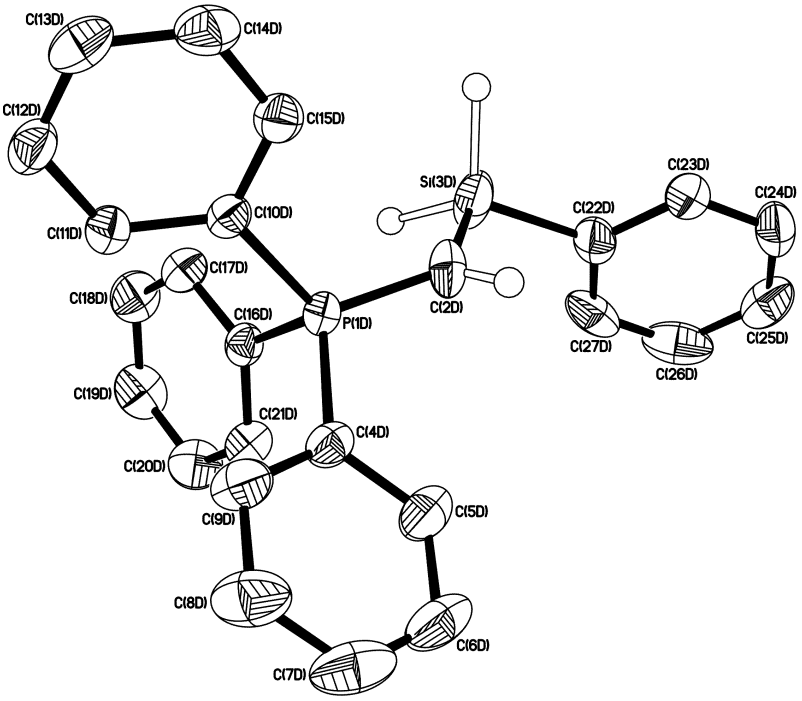


Fig. S7 The crystal structure of one (**1a-D**) of the four independent molecules present in the crystals of **1a** (50% probability ellipsoids).

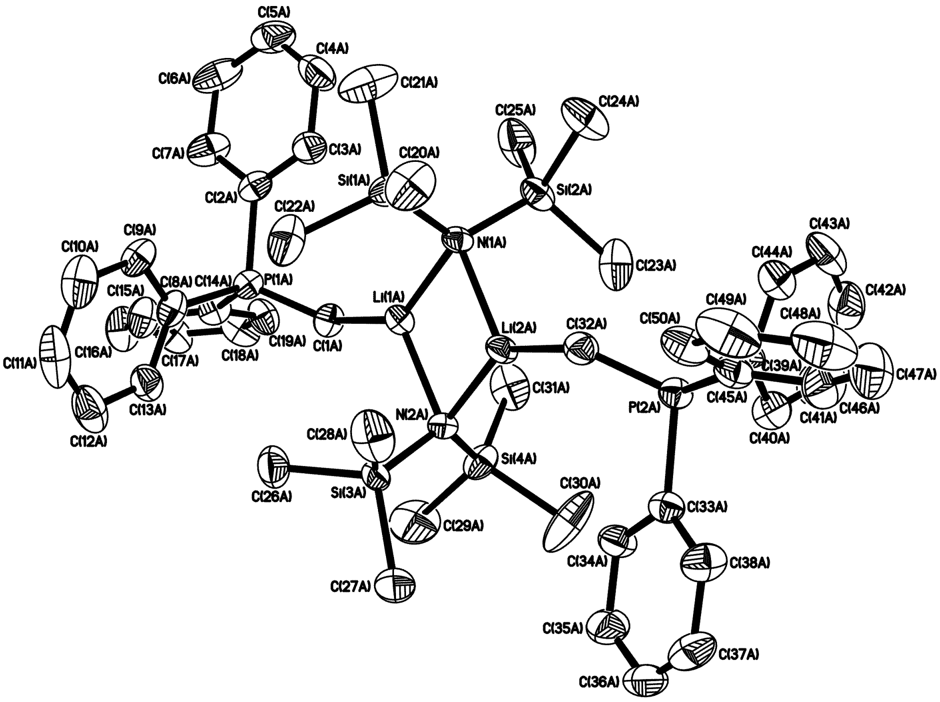


Fig. S8 The crystal structure of one (**2a-A**) of the two independent molecules present in the crystals of **2a** (50% probability ellipsoids).

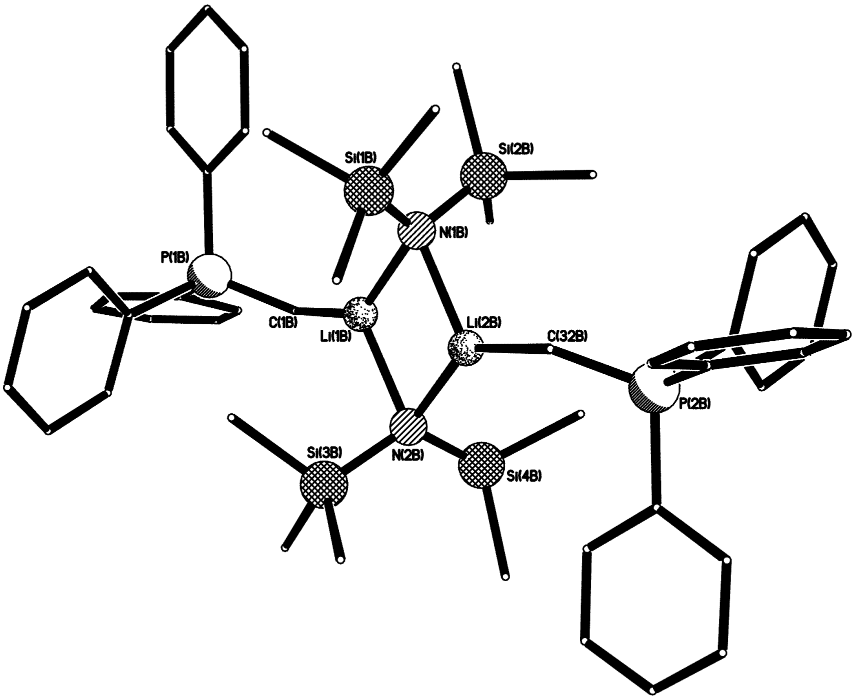


Fig. S9 The crystal structure of one (**2a-B**) of the two independent molecules present in the crystals of **2a**.

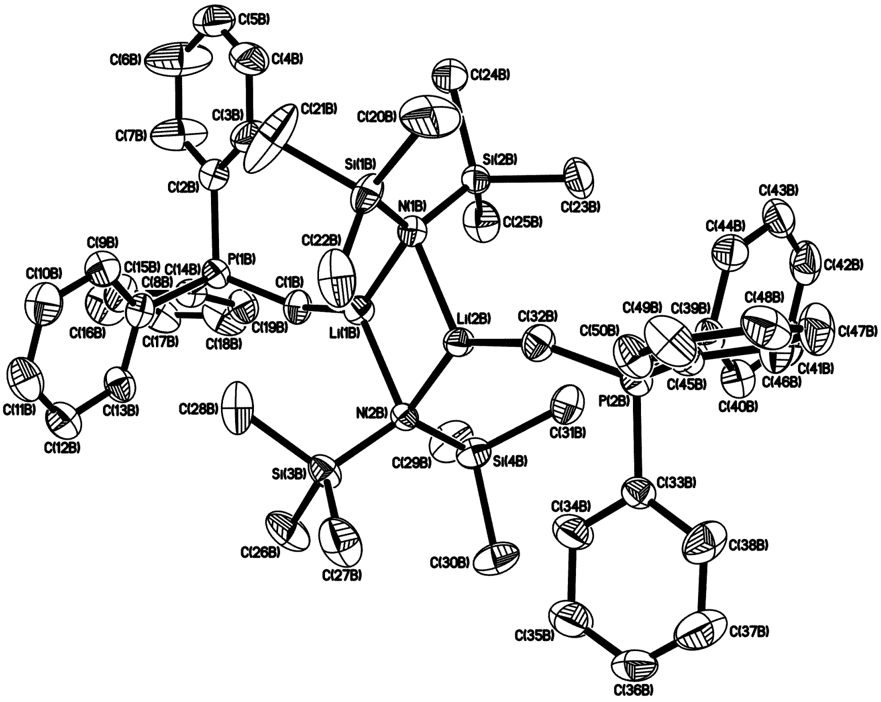


Fig. S10 The crystal structure of one (**2a-B**) of the two independent molecules present in the crystals of **2a** (50% probability ellipsoids).

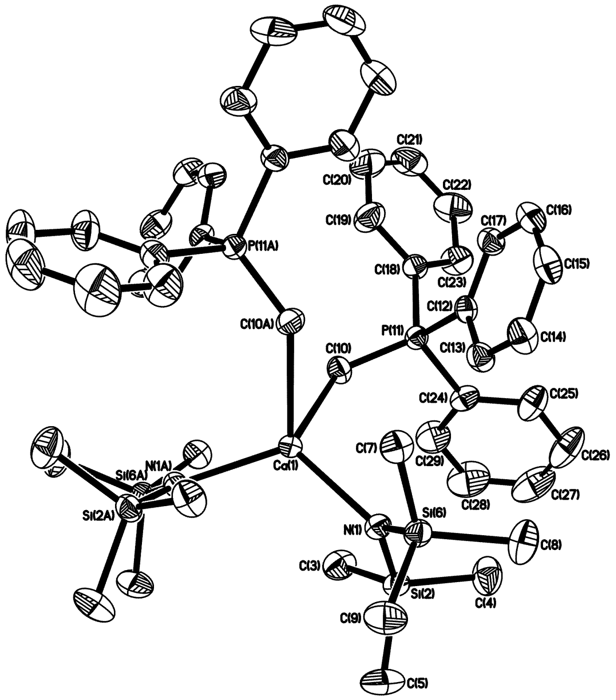


Fig. S11 The crystal structure of the C_2 symmetric complex **2b** (50% probability ellipsoids). Atoms labelled with an "A" after the number are related to their counterparts without the letter by the C_2 axis that passes through the calcium centre and bisects the N(1)–Ca(1)–N(1A) and C(10)–Ca(1)–C(10A) angles.

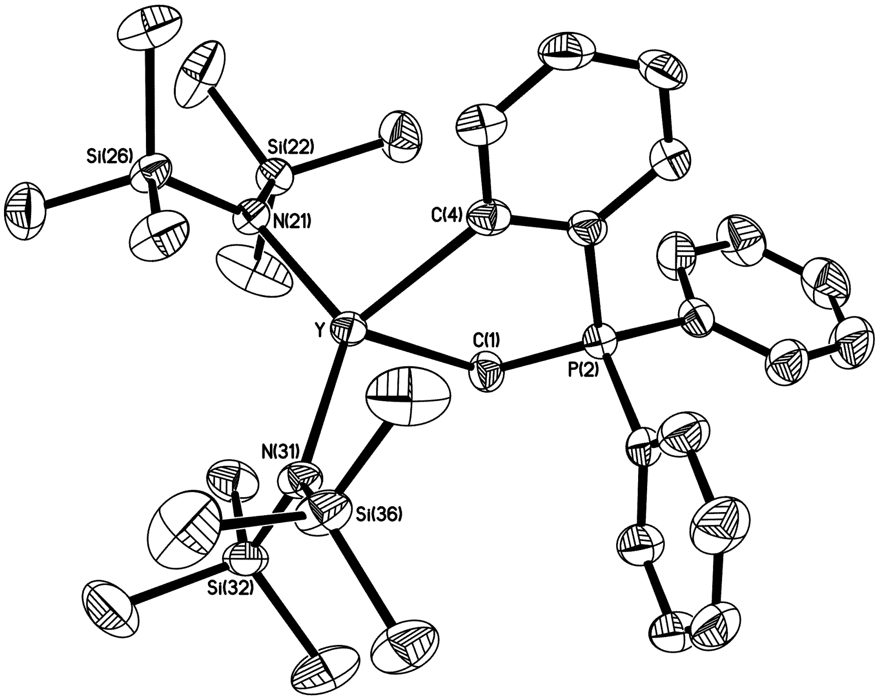


Fig. S12 The crystal structure of **2c** (50% probability ellipsoids).

2.4 DFT studies

Calculations were conducted in Gaussian09 using Gaussview5.0 as an interface. The solid-state data for **1a** was used as an initial geometry and all calculations were conducted on real systems with no truncation of the molecules. Calculations were conducted on gas phase molecules using the B3LYP functional and 6,31G+(d,p) basis-set.. Six distinct minima, all confirmed by frequency calculations, were observed on the potential energy surface, corresponding to four distinct conformers of the *ortho*-silylated phosphonium methylide (**A1-4**), a trigonal bipyramidal silicate (**B1**) and the semi-stabilised ylide **1a** (Scheme S2). Three of the isomeric conformers of **A,** display an apparent electrostatic interaction (2.46–2.91 Å) between the methylide carbon and the silicon centre which is within the sum of the mean van der Waals radii of silicon and carbon.[6] The Gibbs free energies at 298.15 K for **A1-4** vary by up to 3.3 kcal mol^{-1}. Although these data are significant, the lowest energy conformation of **A** is 12.3 kcal mol^{-1} less stable than the experimentally verified silylated ylide **1a**. Furthermore, the silicate **B1** is 8.3 kcal mol^{-1} less stable than the lowest energy conformer of **A,** and thus 20.6 kcal mol^{-1} less stable than **1a**. The silicon–carbon contact in **B1** of 2.06 Å compares reasonable well to that of 1.927(2) determined for the crystallographically characterised silicate [Ph_3SiH_2][K(18-crown-6].[7] Although these calculations imply a *thermodynamically favourable* process, the ambiguity of the mechanism of isomerisation in combination with the large number of stereoisomers has precluded us from confidentially determining the *kinetic barrier* to 1,4-silyl migration by DFT. Nevertheless, previous experimental data acquired during the synthesis of the trimethylsilyl analogue of **1a** suggest that this barrier is extremely low.[8]

Scheme S2. Located minima for the possible isomers of **1a**. Numerical values represent the Si---CH_2 interaction quoted in Angstroms.

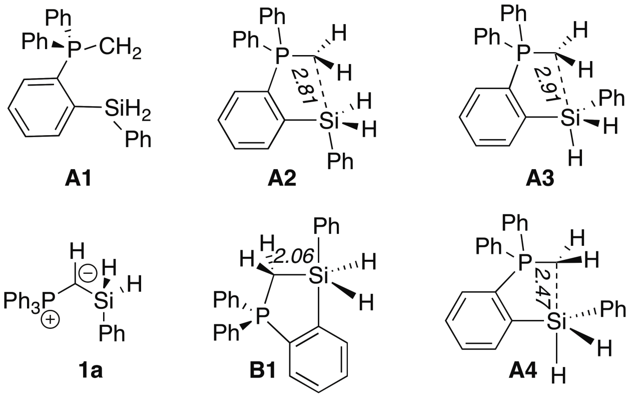


Table S4. Relative energies of **A1-A4, B1** and **1** (kcal mol^{-1})

	A1	**A2**	**A3**	**A4**	**B1**	**1a**
Zero-point energy	+13.7	+11.5	+12.3	+13.8	+18.0	0
Gibbs free energy (298.15K)	+14.0	+12.3	+13.0	+15.6	+20.7	0

3.1 References

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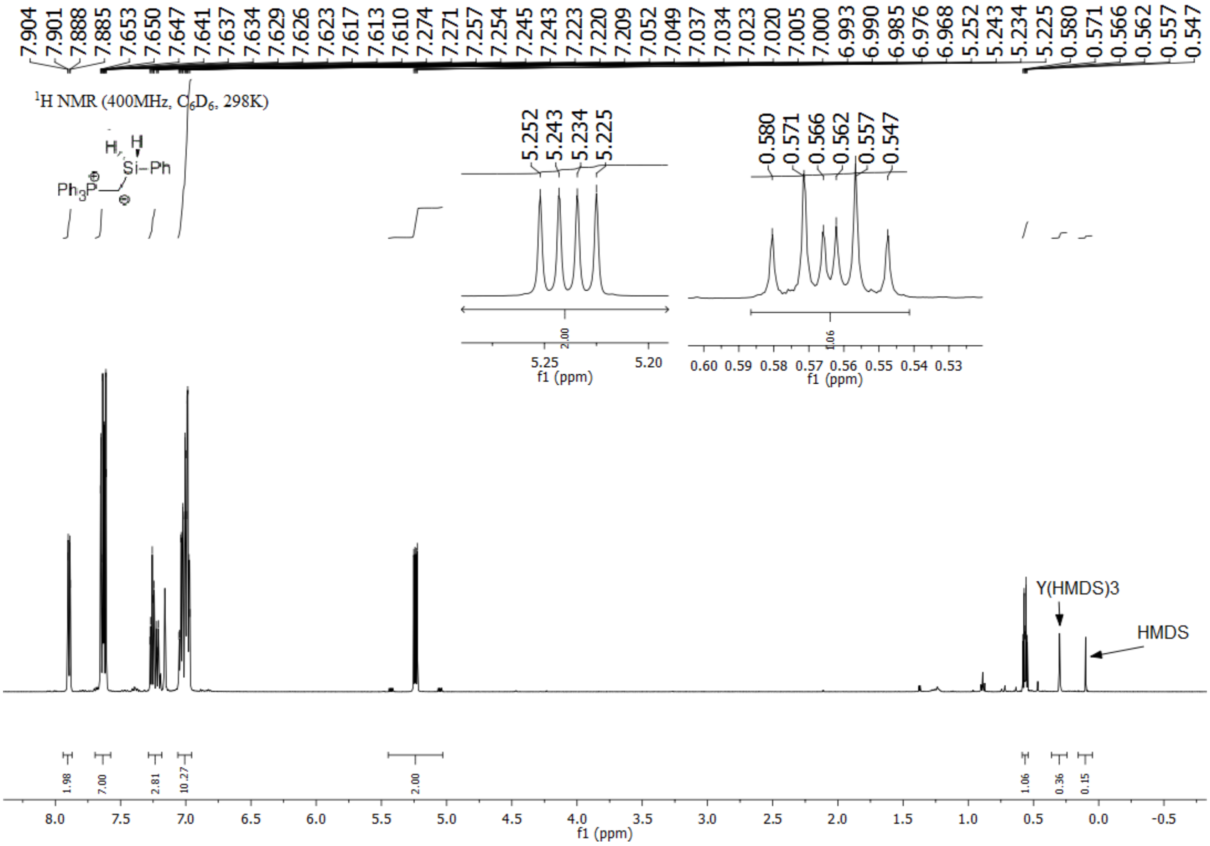
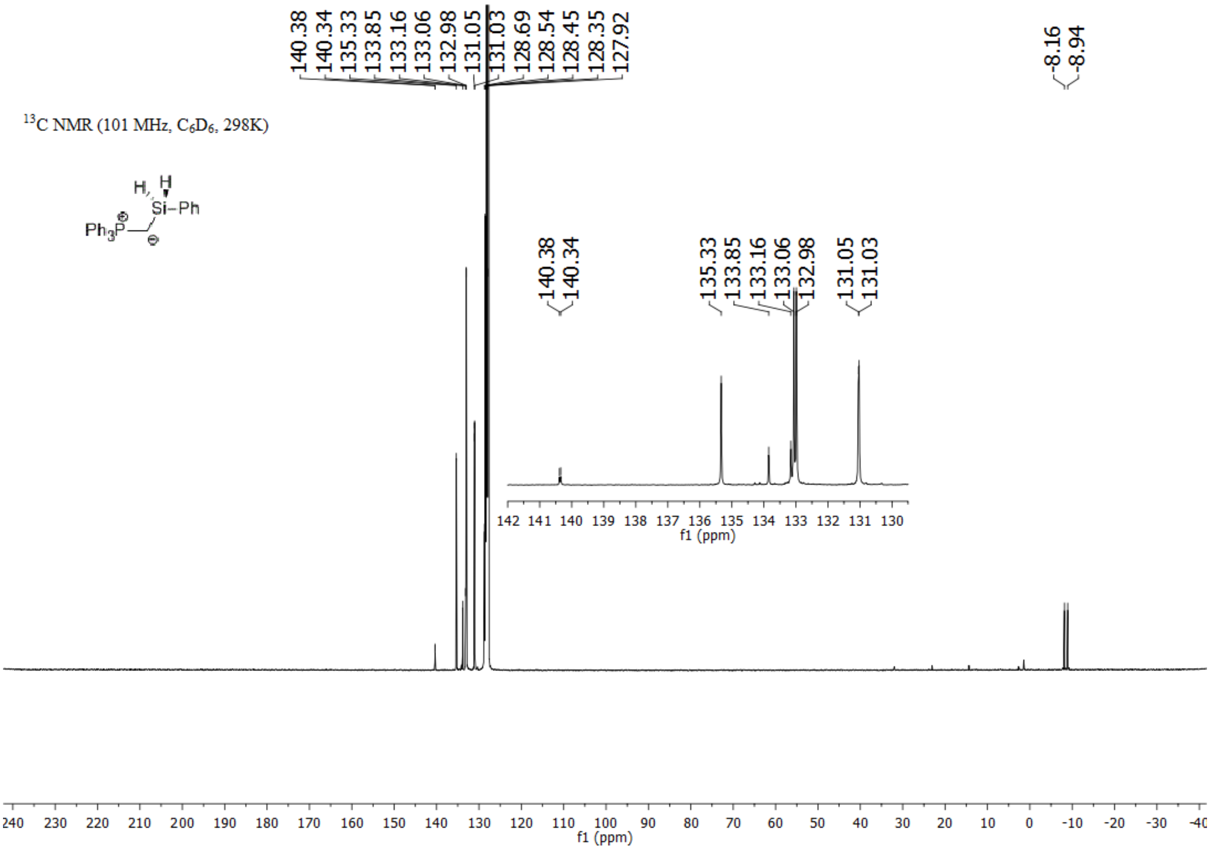
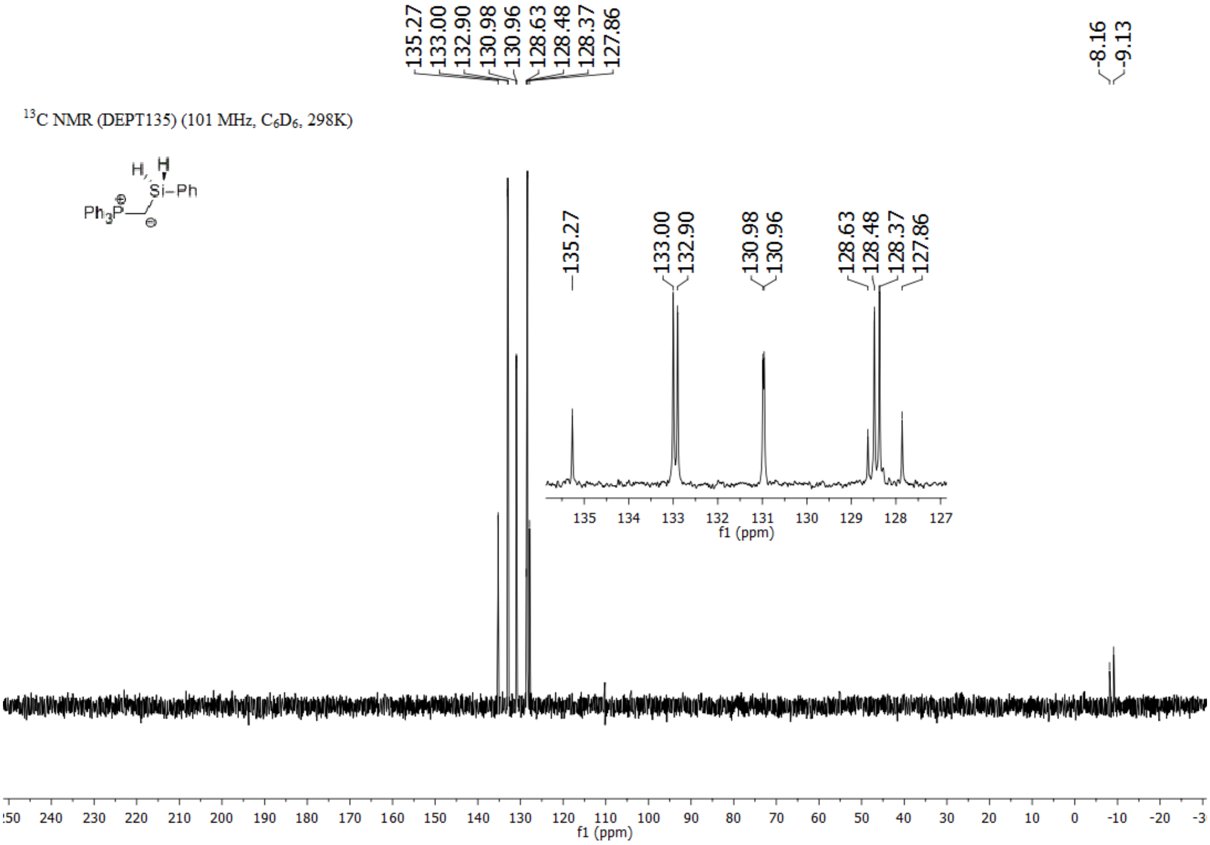
7. (a) M. J. Bearpark, G. S. McGrady, P. D. Prince, J. W. Steed, *J. Am. Chem. Soc.* 2001, **123**, 7736. (b) P. D. Prince, M. J. Bearpark, G. S. McGrady, J. W. Steed, *Dalton Trans.* 2008, 271.

8. (a) A. Kawachi, T. Yoshioka and Y. Yamamoto, *Organometallics*, 2006, **25**, 2390. (b) E. Vedejs, O. Daugulis, S. T. Diver and D. R. Powell, *J. Org. Chem.*, 1998, **63**, 2338.

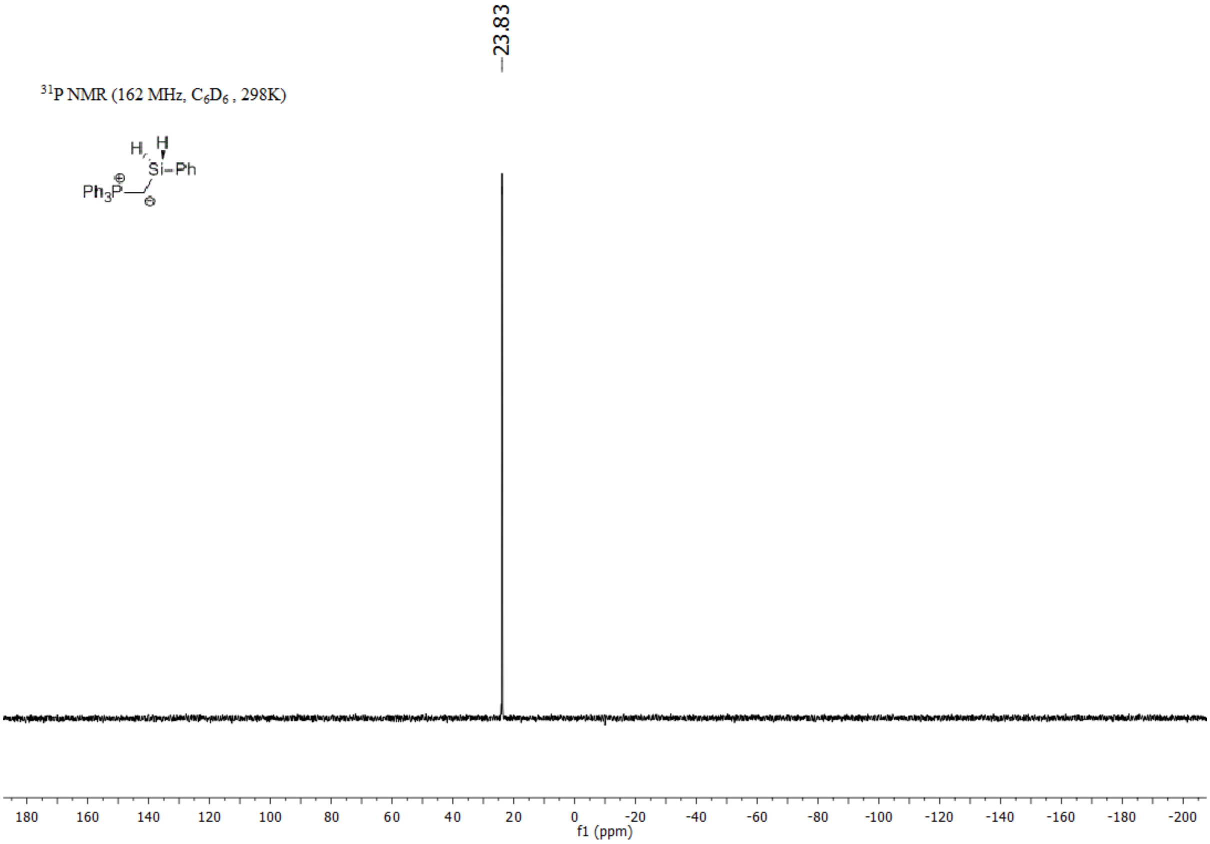
4. Multinuclear NMR data for compounds 1a and 2a-c



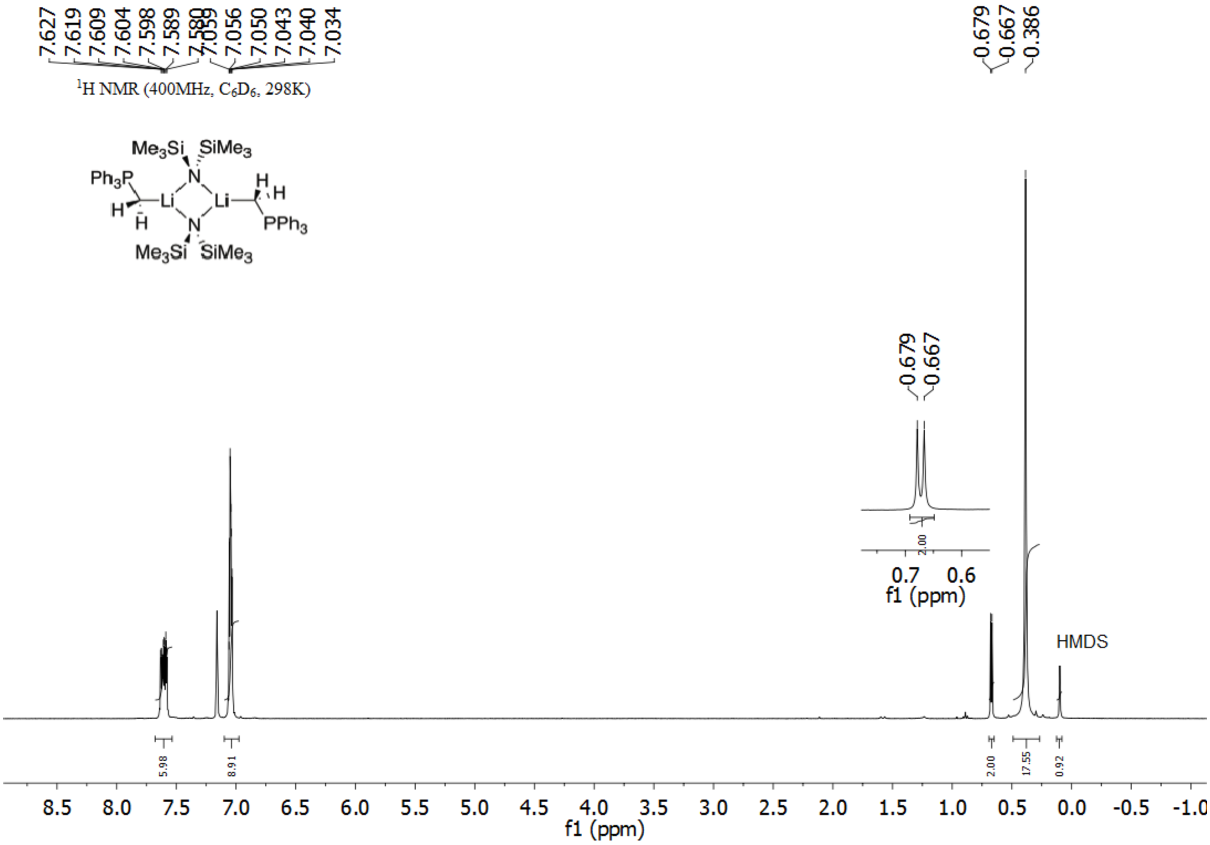


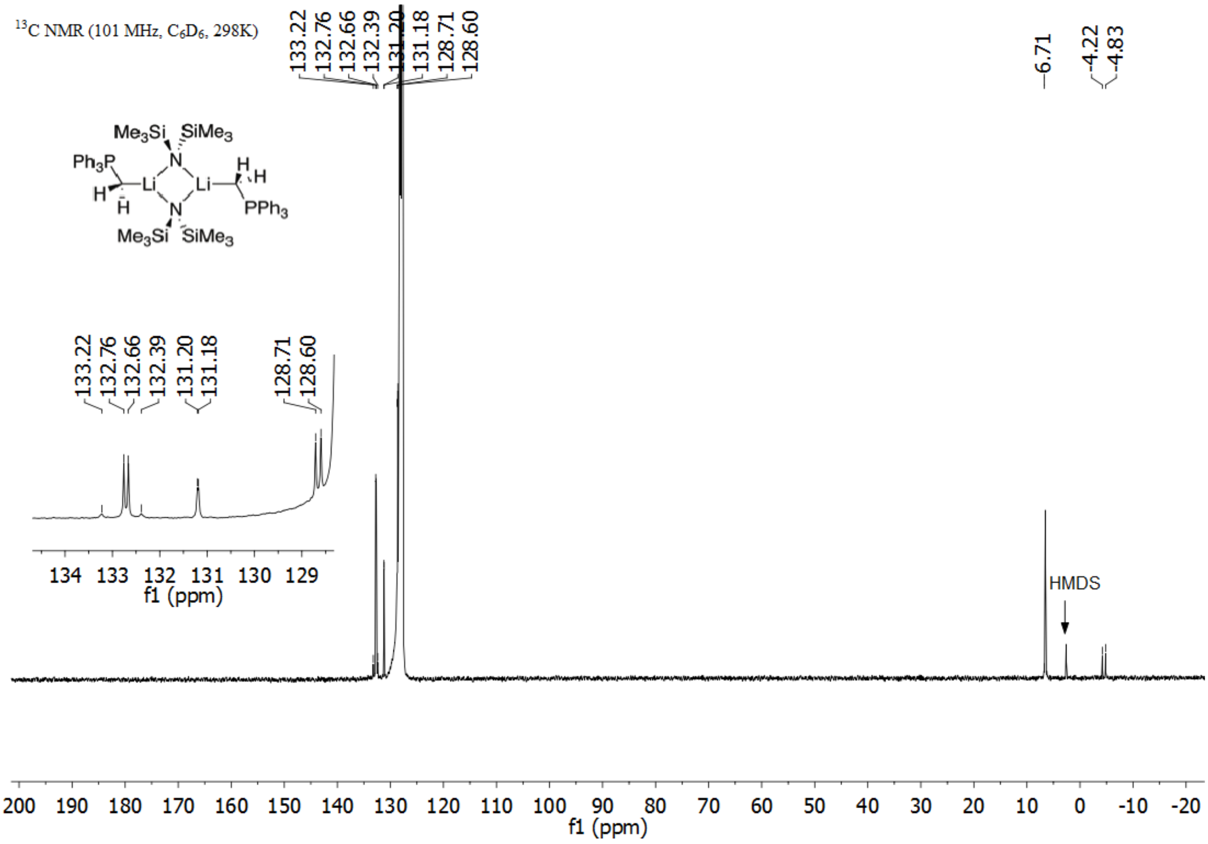


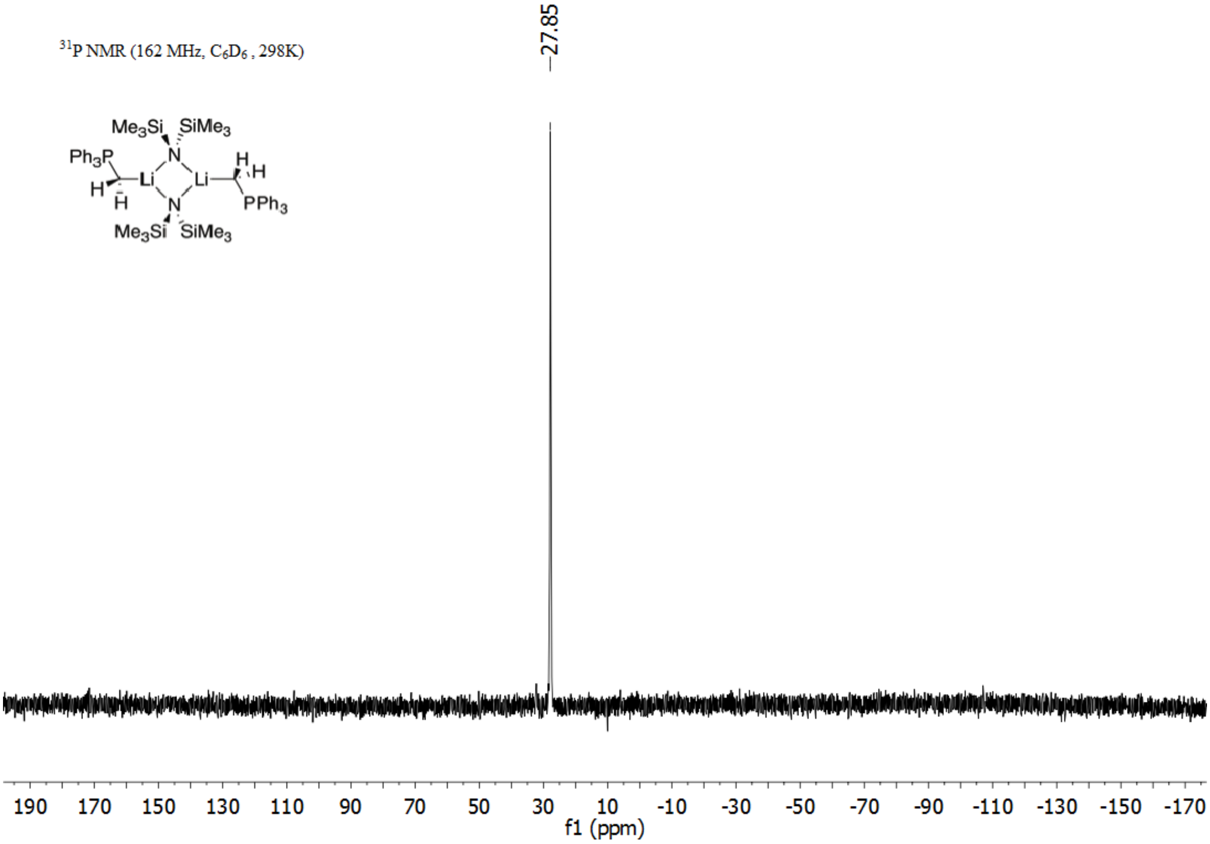
^{13}C NMR (DEPT135) (101 MHz, C_6D_6, 298K)

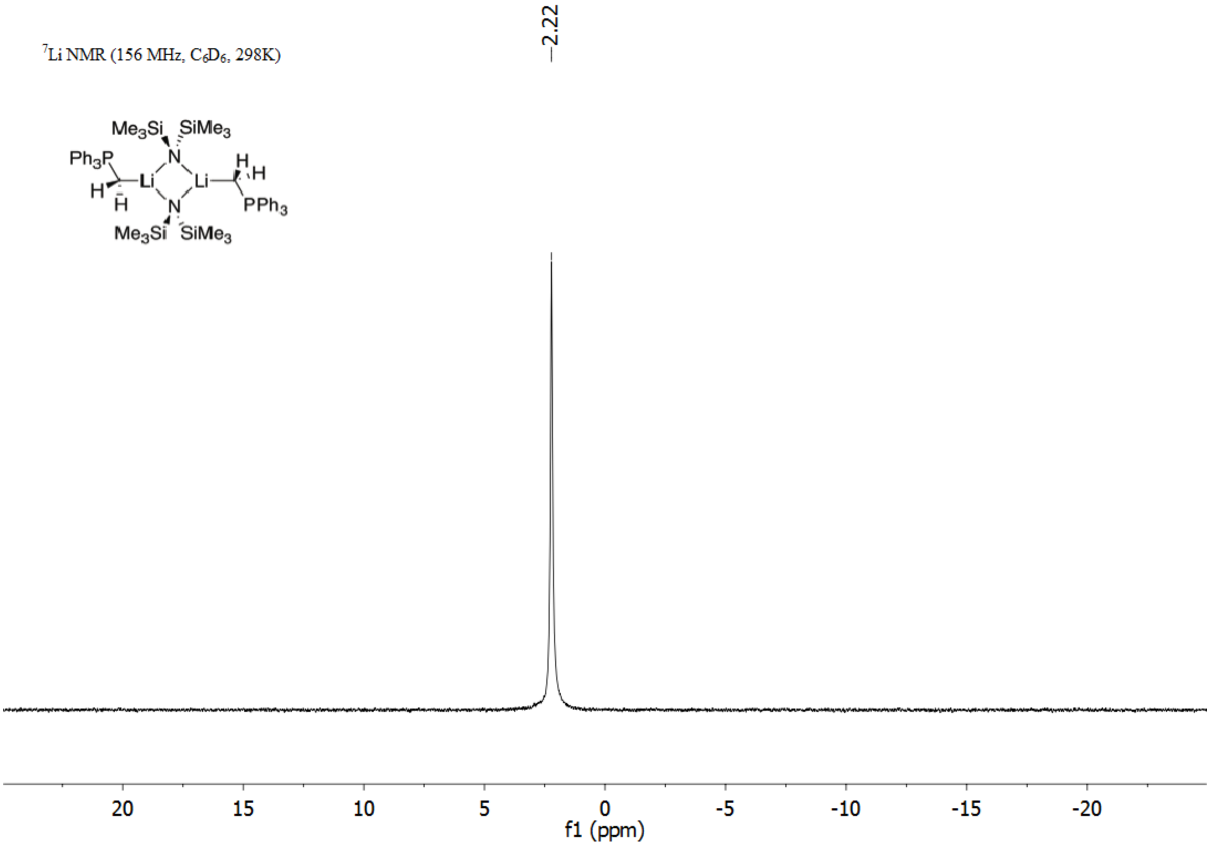


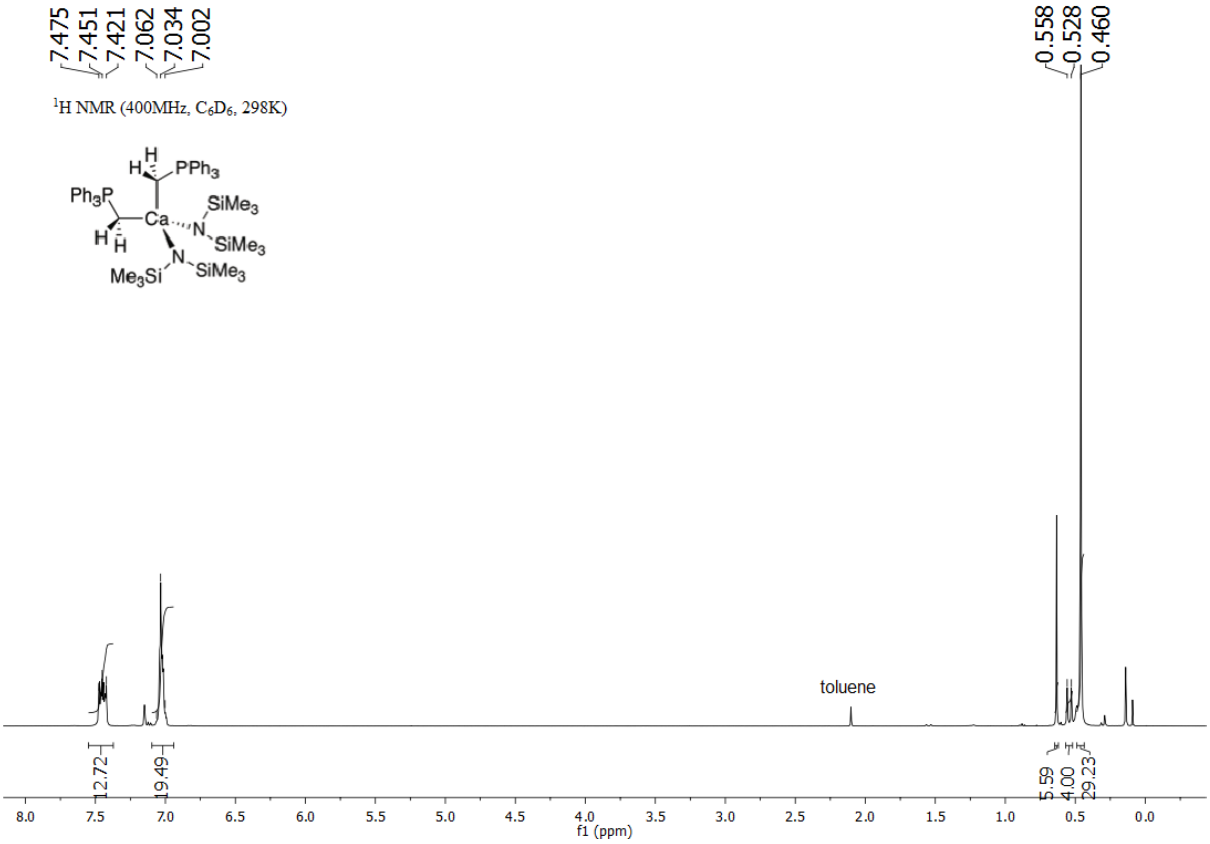
^{31}P NMR (162 MHz, C_6D_6 , 298K)

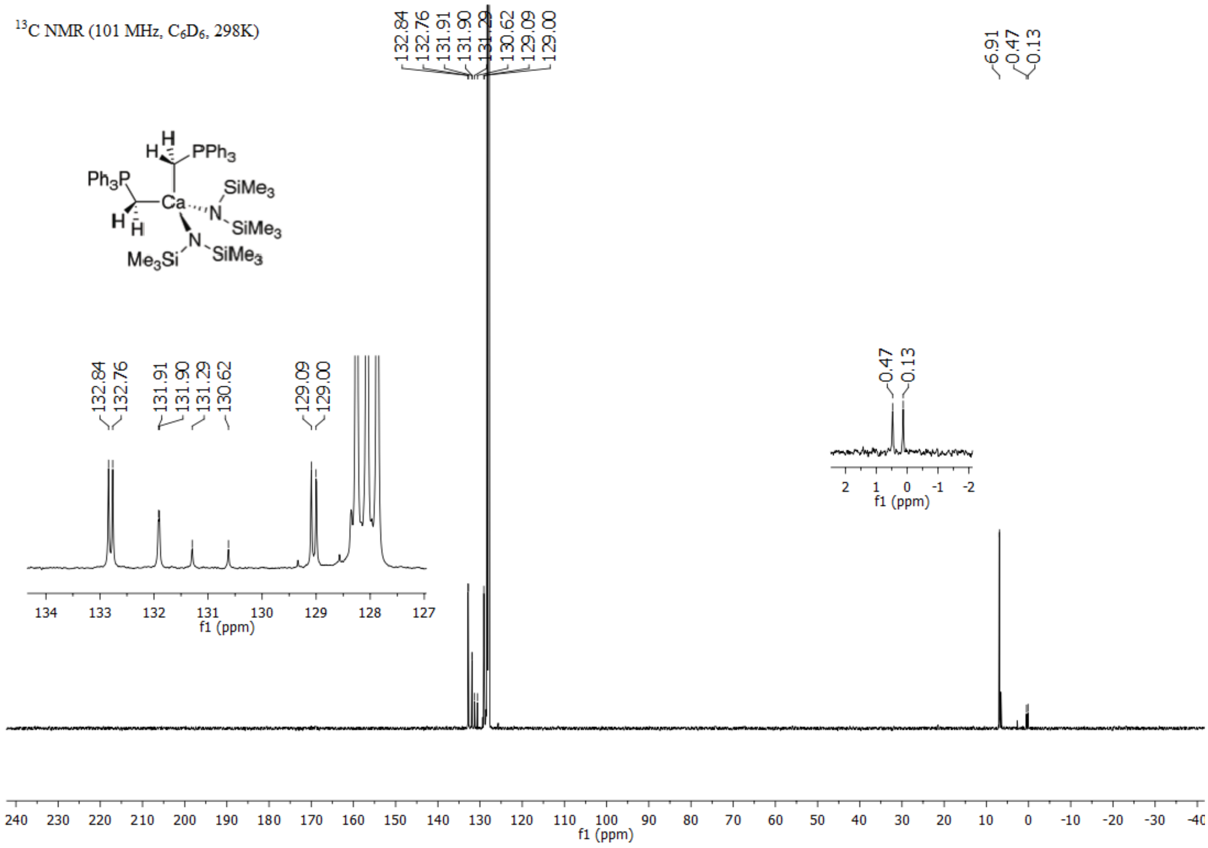

7.627
7.619
7.609
7.604
7.598
7.589
7.580
7.059
7.056
7.050
7.043
7.040
7.034
0.679
0.667
0.386
¹H NMR (400MHz, C₆D₆, 298K)
Me₃Si SiMe₃
Ph₃P
N
H
H
Li
Li
H
H
PPh₃
N
Me₃Si SiMe₃
0.679
0.667
2.00
0.7 0.6
f1 (ppm)
HMDS
5.98
8.91
2.00
17.55
0.92
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

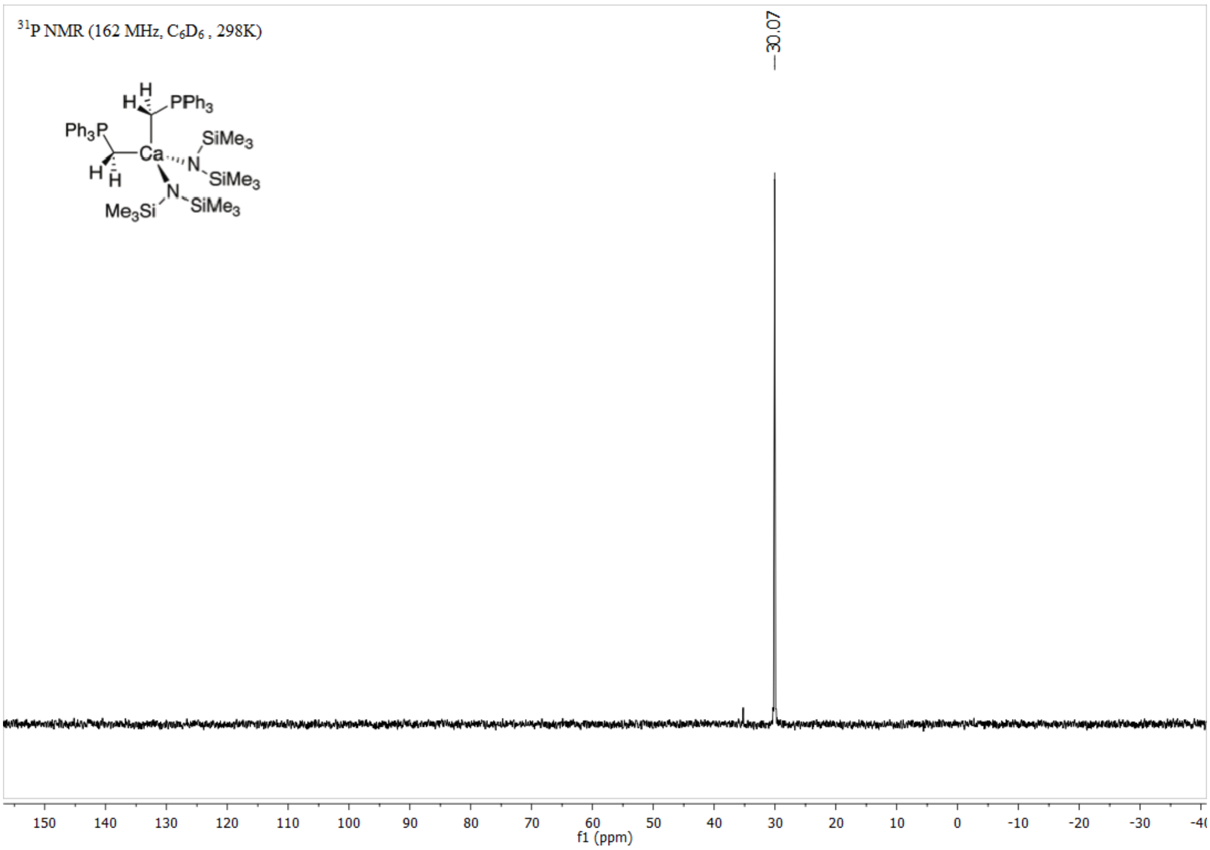

¹³C NMR (101 MHz, C₆D₆, 298K)
133.22
132.76
132.66
132.39
131.20
131.18
128.71
128.60
6.71
-4.22
-4.83
Me₃Si SiMe₃
Ph₃P
N
H
H
Li
Li
H
H
PPh₃
N
Me₃Si SiMe₃
133.22
132.76
132.66
132.39
131.20
131.18
128.71
128.60
134 133 132 131 130 129
f1 (ppm)
HMDS
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

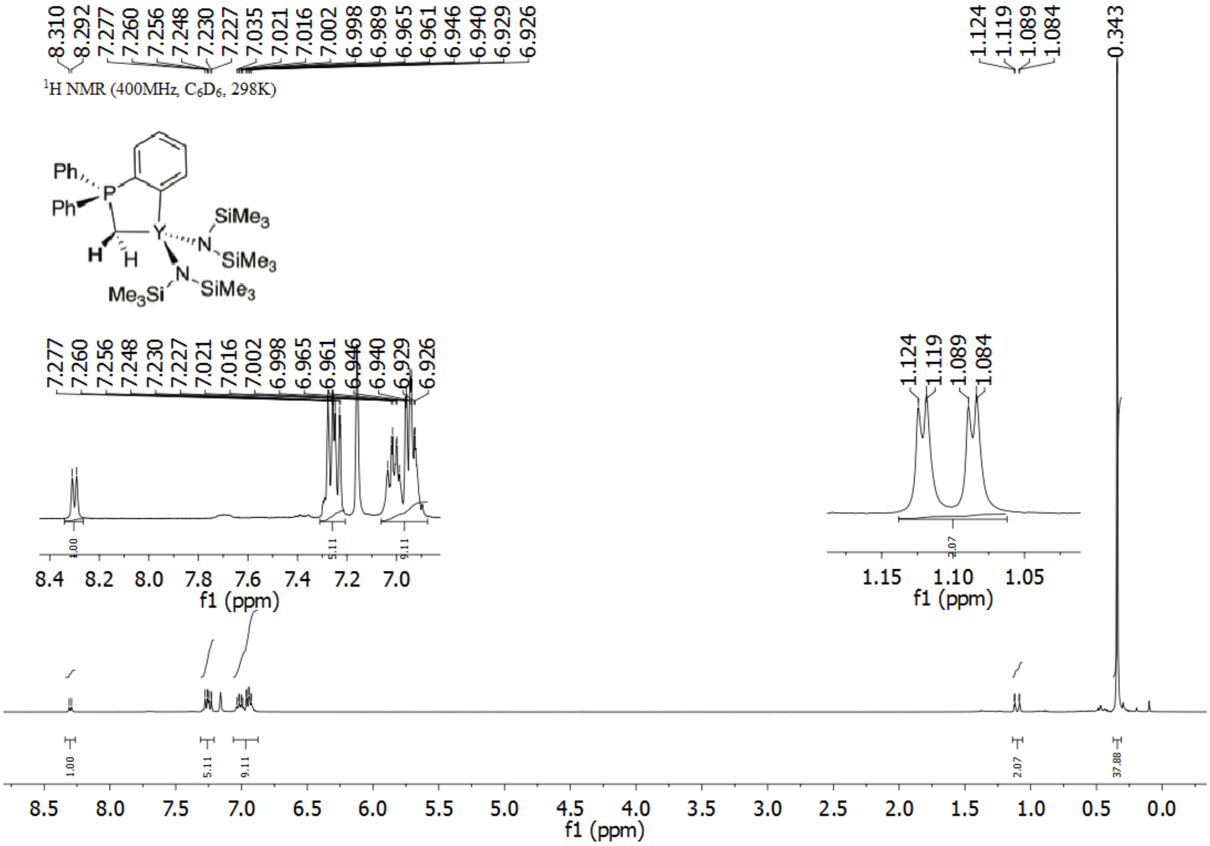

^{31}P NMR (162 MHz, C_6D_6 , 298K)
27.85
Me$_3$Si
SiMe$_3$
Ph$_3$P
H
H
Li
N
Li
H
H
PPh$_3$
Me$_3$Si
SiMe$_3$
190 170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170
f1 (ppm)

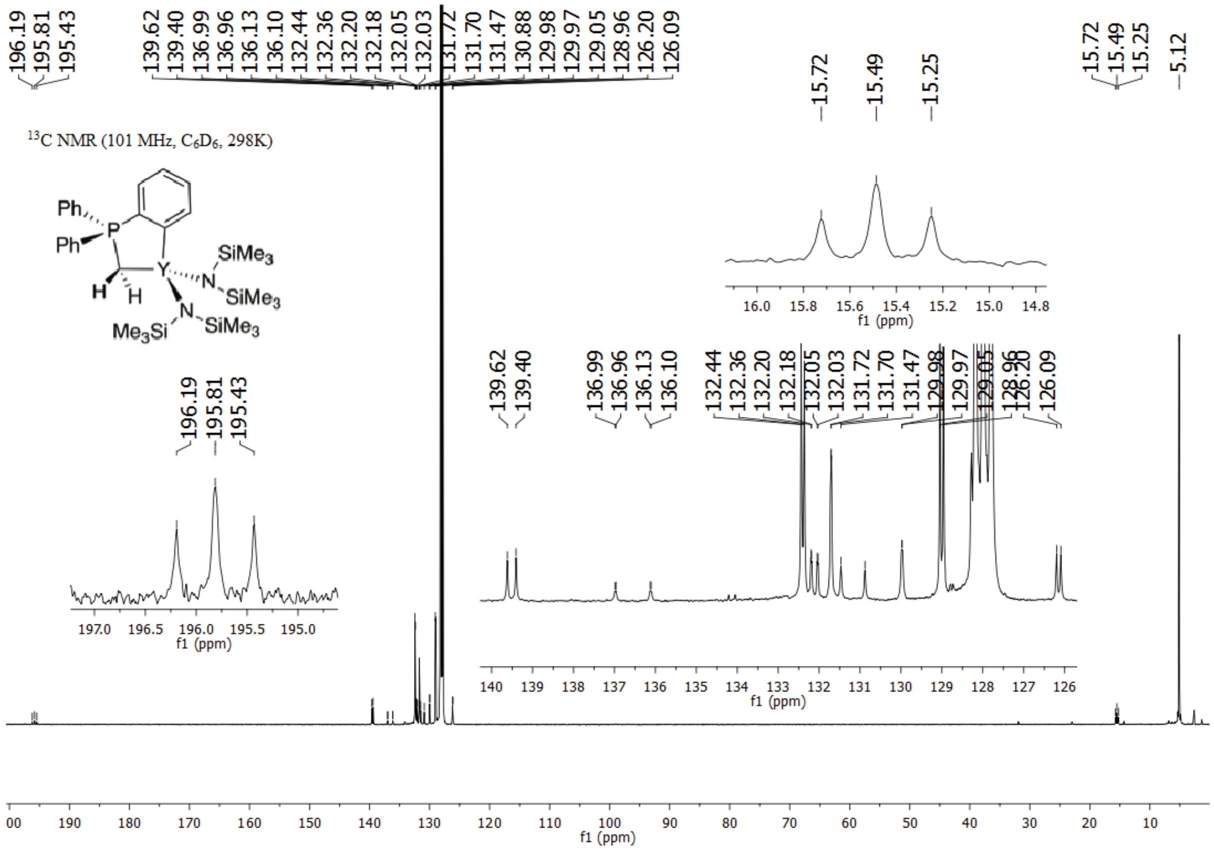

^{7}Li NMR (156 MHz, C_6D_6, 298K)
2.22
Me$_3$Si
SiMe$_3$
Ph$_3$P
H
H
Li
N
Li
H
H
PPh$_3$
Me$_3$Si
SiMe$_3$
20 15 10 5 0 -5 -10 -15 -20
f1 (ppm)

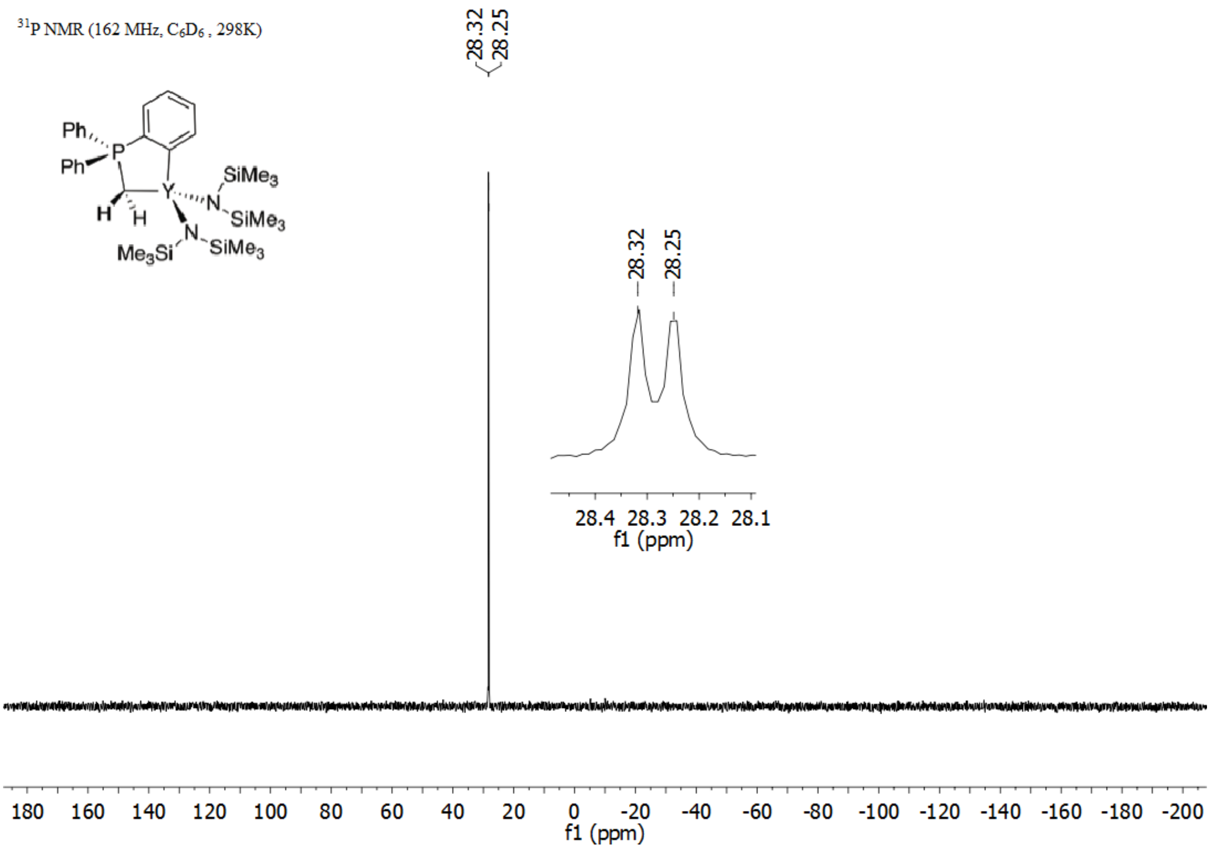

7.475
7.451
7.421
7.062
7.034
7.002
0.558
0.528
0.460
^{1}H NMR (400MHz, C_6D_6, 298K)
H
H
PPh3
Ph3P
Ca
SiMe3
N
SiMe3
H
H
N
SiMe3
Me3Si
toluene
12.72
19.49
5.59
4.00
29.23
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


^{13}C NMR (101 MHz, C_6D_6, 298K)
132.84
132.76
131.91
131.90
131.29
130.62
129.09
129.00
6.91
0.47
0.13
H
H
PPh3
Ph3P
Ca
SiMe3
N
SiMe3
H
H
N
SiMe3
Me3Si
132.84
132.76
131.91
131.90
131.29
130.62
129.09
129.00
134
133
132
131
130
129
128
127
f1 (ppm)
0.47
0.13
2
1
0
-1
-2
f1 (ppm)
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)


31P NMR (162 MHz, C6D6 , 298K)
30.07
H
H
PPh3
Ph3P
Ca
SiMe3
N
SiMe3
H
H
N
SiMe3
Me3Si
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)


8.310
8.292
7.277
7.260
7.256
7.248
7.230
7.227
7.035
7.021
7.016
7.002
6.998
6.989
6.965
6.961
6.946
6.940
6.929
6.926
1.124
1.119
1.089
1.084
0.343
1H NMR (400MHz, C6D6, 298K)
Ph
Ph
P
Y
SiMe3
N
SiMe3
H
H
N
SiMe3
Me3Si
1.00
5.11
9.11
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
f1 (ppm)
2.07
1.15
1.10
1.05
f1 (ppm)
1.00
5.11
9.11
2.07
37.88
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
f1 (ppm)


^{13}C NMR (101 MHz, C_6D_6, 298K)
Ph
Ph
P
Y
N
SiMe3
SiMe3
N
SiMe3
Me3Si
H
H
196.19
195.81
195.43
139.62
139.40
136.99
136.96
136.13
136.10
132.44
132.36
132.20
132.18
132.05
132.03
131.72
131.70
131.47
130.88
129.98
129.97
129.05
128.96
126.20
126.09
15.72
15.49
15.25
5.12
197.0 196.5 196.0 195.5 195.0
f1 (ppm)
140 139 138 137 136 135 134 133 132 131 130 129 128 127 126
f1 (ppm)
16.0 15.8 15.6 15.4 15.2 15.0 14.8
f1 (ppm)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


^{31}P NMR (162 MHz, C_6D_6 , 298K)
Ph
Ph
P
Y
N
SiMe3
SiMe3
N
SiMe3
Me3Si
H
H
28.32
28.25
28.4 28.3 28.2 28.1
f1 (ppm)
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)