Flexible coordination of N,P-Donor Ligands in Aluminum Dimethyl and Dihydride Complexes

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Supporting information

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Supplementary Tables and Figures

Table S1. Selected experimental and calculated parameters for **5a-c** at two levels of theory. IR data are from solid state measurements (solution phase in parentheses).

		Al–N (Å)	Al–P (Å)	N–Al–P (º)	$\nu_{(Al–H)}$ (cm^{-1})
	experimental	-	-	-	1810, 1786 (1816)
5a	M062X/6,31G+(d,p)/LanI2DZ	1.943	2.514	84.80	1863, 1845
	M062X/Def2SVPP	-	-	-	-
	experimental	1.8972(15)	2.4442(7)	87.47(5)	1831, 1816 (1821)
5b	M062X/6,31G+(d,p)/LanI2DZ	1.944	2.509	84.78	1862, 1852
	M062X/Def2SVPP	1.918	2.478	85.89	1938, 1930
	experimental	1.892(2)	2.4790(10)	86.60(6)	1825, 1801 (1829)
5c	M062X/6,31G+(d,p)/LanI2DZ	1.943	2.514	84.80	1863, 1845
	M062X/Def2SVPP	1.916	2.486	85.72	1939, 1922

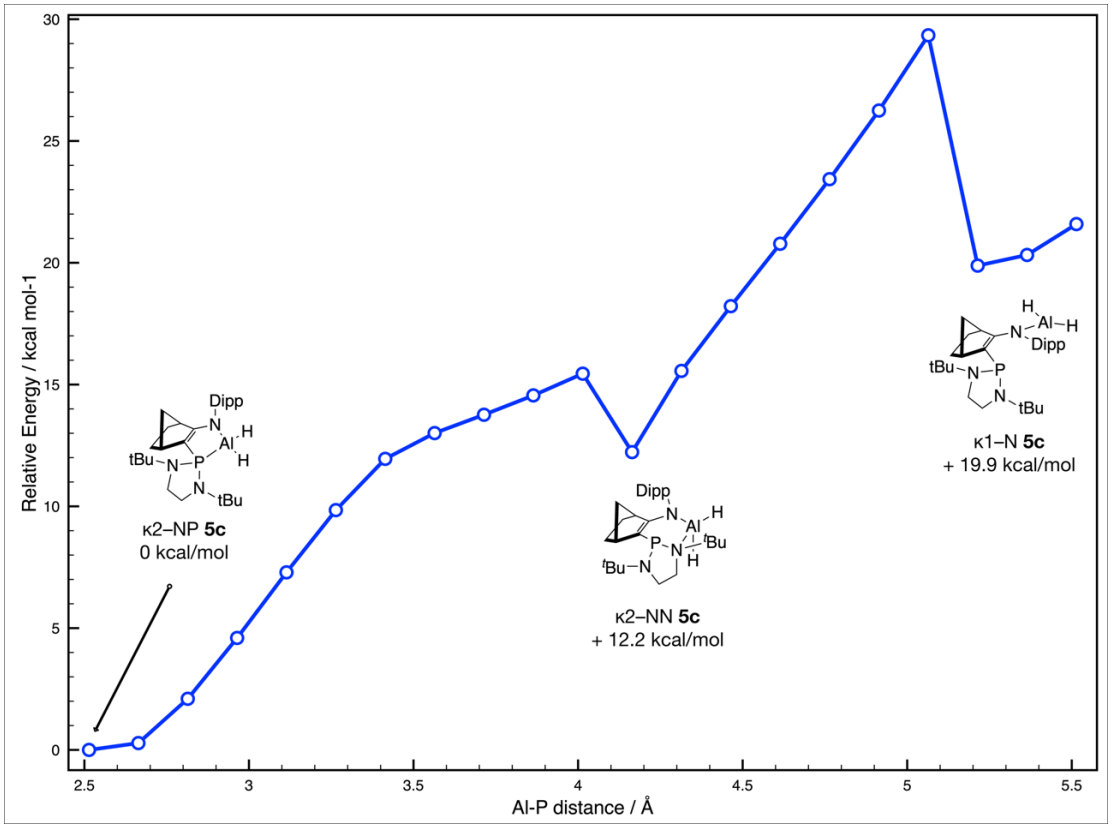


Figure S1. Relaxed potential energy surface scan of **5c** with the Al–P bond distance increased in 0.1 Å increments, using κ^2-NP **3c** as the initial geometry (at B3LYP/6,31G level).

A relaxed potential energy surface scan of κ^2-NP **5c** (at B3LYP/6,31G level for computational efficiency) in which the P–Al distance was increased in 0.15 Å increments revealed two potential isomers of **5c**, both at higher energy and both displaying no coordination to the phosphine centre (Figure S1). κ^2-*N,N* **5c** shows a 'slipped' coordination of the phosphine in which one of the P-N units coordinates to the aluminium centre through a nitrogen. κ^1-N **5c** is a high energy 3-coordinate aminoaluminum dihydride species. Both isomers were re-optimised at M062X/6,31G+(d,p)/LanI2DZ (Table S2).

Table S2. Relative energies and calculated/experimental values for $\nu_{(Al–H)}$ for isomers of **5c.** Experimental IR data are from solid state measurements (solution phase in parentheses).

		Relative energy (kcal mol^{-1})	$\nu_{(Al–H)}$ (cm^{-1})
κ^2-NP **5c**	experimental	–	1825, 1801 (1829)
	M062X/6,31G+(d,p)/LanI2DZ	0	1863, 1845
κ^2-NN **5c**	M062X/6,31G+(d,p)/LanI2DZ	−0.82	1860, 1813
κ^1-N **5c**	M062X/6,31G+(d,p)/LanI2DZ	22.58	1934, 1922

General Considerations

All manipulations were carried out under an argon atmosphere using standard Schlenk or glovebox techniques. Reactions were carried out in glass Schlenk tubes, which were dried for 16 hours at 110 °C before use. Solvents were obtained from an inert solvent purification system and stored over 4 Å molecular sieves. C_6D_6 and d_8-THF were dried over potassium then vacuum distilled and stored over 4 Å molecular sieves. Ambient temperature NMR spectra were recorded on Bruker PRO 500 MHz, AVA 400, 500 or 600MHz spectrometers. ^{1}H and ^{13}C spectra were referenced to residual solvent signals. ^{31}P NMR spectra were referenced to an external standard of 85% H_3PO_4 in H_2O. Mass spectra were acquired either using a SolariX FT-ICR MS (12 T) (Bruker UK Ltd) equipped with an APPI source (1 mM toluene solutions) or a Thermo Mat 900 XP high resolution double focussing sector mass spectrometer (solid samples, EI). Infrared spectroscopy was performed using a PerkinElmer Spectrum 65 spectrometer (hexane solutions), or a Shimadzu IRSpirit Fourier Transform Spectrometer (solid state, performed inside a glovebox) to identify the Al-H stretching frequencies.

Imine precursor **S1**[1], chlorophosphines $PCl(N^tBu)_2SiMe_2$[2] and $PCl(N^tBuCH_2)_2$,[3] ligands **1b** and **1c**[2] and $[H_3Al{\cdot}NMe_3]$[4] were synthesised according to literature procedures. $SiMe_2(NH^tBu)_2$ was synthesised according to a modified literature procedure (described below). *Tert*-butylamine was dried over calcium hydride and vacuum distilled prior to use. $LiAlH_4$ was purified by extraction with diethyl ether and filtration to afford a white solid, which was stored under an inert atmosphere. Trimethylammonium chloride was dried under vacuum at 50 °C for 3 hours prior to use. All other reagents were purchased from commercial suppliers and used without further purification.

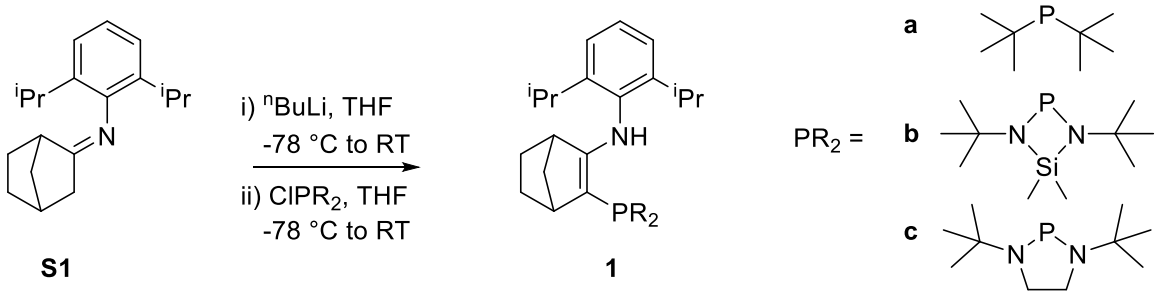
Precursor Synthesis

$SiMe_2(NH^tBu)_2$

Synthesised according to a modified literature preparation.[5] To a vigorously stirred solution of dimethylchlorosilane (3 mL, 0.025 mol) in pentane (150 mL) at 0 °C, *tert*-butylamine (12 mL, 0.114 mol, 4.6 eq.) was added dropwise. A white precipitate was formed immediately. The mixture was stirred for 16 hours at room temperature, filtered and the solvent and excess amine removed by fractional distillation to afford the product as a colourless oil (5.1 mL, 86%). ^{1}H NMR spectroscopic analysis was consistent with literature reports.

^{1}H NMR (C_6D_6, 600 MHz, 300 K): 0.18 (s, 6H, $SiCH_3$), 0.53 (br s, 2H, NH), 1.19 (s, 19H, CH_{3tBu}).

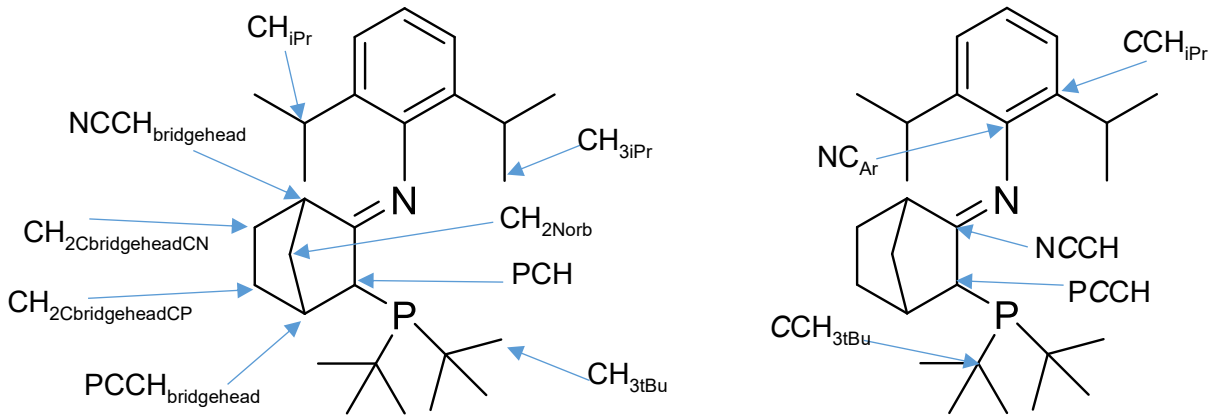
Ligand 1a-c Synthesis



1b and **1c** were synthesised according to literature procedure.[2] This procedure was also modified and applied to the synthesis of **1a**:

To a solution of imine **S1** (4.00 g, 0.015 mol) in THF (50 mL) cooled to -78 °C, ^{n}BuLi (2.5 M in hexanes, 6.0 mL, 0.015 mol, 1.0 eq) was added dropwise. The solution was warmed to room temperature and allowed to stir for 2 hours. The resultant yellow mixture was cooled to -78 °C and di-*tert*-butylchlorophosphine (2.8 mL, 0.015 mol) added dropwise. The reaction mixture was stirred at room temperature for 16 hours to afford a clear yellow solution. The solvent was removed *in vacuo* and the resultant oil washed with acetonitrile (2 x 40 mL), dried under vacuum, dissolved in pentane and filtered. The pentane was removed *in vacuo* to afford the product as a white solid (4.40 g, 72%). Multinuclear (^{1}H, ^{13}C, ^{31}P) NMR spectroscopic analysis was consistent with literature reports.[1]

1a:

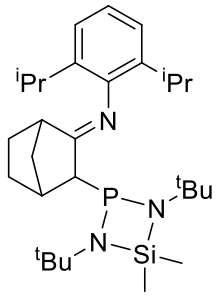


^{1}H NMR (C_6D_6, 600 MHz, 300 K): δ 1.01 (dm, $^{2}J_{HH}$ = 10.0 Hz, 1H, ½CH_{2Norb}), 1.16 (m, 1H, ½$CH_{2CbridgeheadCN}$), 1.19 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.24 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.28 (m, 1H, ½$CH_{2CbridgeheadCP}$), 1.29 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.30 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.31 (d, $^{3}J_{HP}$ = 10.9 Hz, 9H, CH_{3tBu}), 1.34 (m, 1H, ½$CH_{2CbridgeheadCN}$), 1.40 (d, $^{3}J_{HP}$ = 11.1 Hz, 9H, CH_{3tBu}), 1.47 (m, 1H, ½$CH_{2CbridgeheadCP}$), 1.93 (dm, $^{2}J_{HH}$ = 10.0 Hz, 1H, ½CH_{2Norb}), 2.56 (m, 1H, PCH), 2.63 (d, $^{2}J_{HP}$ = 3.7 Hz, 1H, $PCCH_{bridgehead}$), 2.74 (m, 1H, $NCCH_{bridgehead}$), 2.94 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.20 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 7.10-7.21 (m, 3H, $H_{aromatic}$)

^{13}C NMR (C_6D_6, 126 MHz, 300 K): δ 22.1 (s, CH_{3iPr}), 23.0 (s, CH_{3iPr}), 24.5 (s, CH_{3iPr}), 25.0 (s, CH_{3iPr}), 25.2 (s, $CH_{2CbridgeheadCN}$), 28.1 (s, CH_{iPr}), 29.1 (s, CH_{iPr}), 30.6 (d, J_{CP} = 5.6 Hz, $CH_{2CbridgeheadCP}$), 31.4 (d, J_{CP} = 14.2 Hz, CH_{3tBu}), 31.6 (d, J_{CP} = 14.9 Hz, CH_{3tBu}), 32.7 (d, J_{CP} = 29.8 Hz, C^{t}Bu), 33.4 (d, J_{CP} = 30.2 Hz, C^{t}Bu), 36.9 (s, CH_{2Norb}), 42.5 (s, PC*C*H), 43.7 (d, J_{CP} = 17.2 Hz, NC*C*H), 49.3 (d, J_{CP} = 45.2 Hz, P*C*H), 123.0 (s, C_{meta}), 123.7 (s, C_{para}), 123.8 (s, C_{meta}), 136.2 (s, *C*CH_{iPr}), 137.0 (s, *C*CH_{iPr}), 147.9 (s, NC_{Ar}), 181.7 (s, N*C*CH)

$^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz, 300K): δ 60.0 (s)

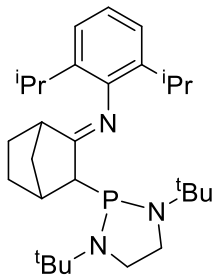
1b:



^1H NMR (C_6D_6, 600 MHz, 300 K): δ 0.39 (s, 3H, $SiCH_3$), 0.42 (s, 3H, $SiCH_3$), 1.04 (dm, $^2J_{HH}$ = 9.9 Hz, 1H, ½CH_{2Norb}), 1.22 (s, 9H, CH_{3tBu}), 1.25 (m, 1H, ½$CH_{2CbridgeheadCP}$), 1.27 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.32 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_{3iPr}), 1.33 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.36 (m, 1H, ½$CH_{2CbridgeheadCN}$), 1.40 (s, 9H, CH_{3tBu}), 1.42 (m, 1H, ½$CH_{2CbridgeheadCP}$), 1.62 (m, 1H, ½$CH_{2CbridgeheadCN}$), 1.74 (dm, $^2J_{HH}$ = 9.9 Hz, 1H, ½CH_{2Norb}), 2.57 (d, $^3J_{HH}$ = 3.9 Hz, 1H, $PCCH_{bridgehead}$), 2.62 (d, $^3J_{HH}$ = 3.9 Hz, 1H, PCH), 3.07 (m, 1H, $NCCH_{bridgehead}$), 3.08 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.44 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 7.12-7.23 (m, 3H, $H_{aromatic}$)**^{13}C NMR (C_6D_6, 126 MHz, 300 K):** δ 7.3 (s, $SiCH_3$), 7.4 (d, J_{CP} = 1.6 Hz, $SiCH_3$), 22.5 (s, CH_{3iPr}), 23.3 (s, CH_{3iPr}), 24.7 (s, CH_{3iPr}), 25.0 (s, CH_{3iPr}), 25.3 (s, $CH_{2CbridgeheadCP}$), 28.2 (d, J = 3.5 Hz, CH_{iPr}), 28.7 (s, CH_{iPr}), 30.7 (s, $CH_{2CbridgeheadCN}$), 32.5 (d, J_{CP} = 5.9 Hz, CH_{3tBu}), 32.6 (d, J_{CP} = 7.4 Hz, CH_{3tBu}), 37.5 (s, CH_{2Norb}), 40.3 (s, NC*C*H), 42.3 (s, PC*C*H), 51.1 (d, J_{CP} = 15.3 Hz, *C*^{t}Bu), 51.8 (s, J_{CP} = 8.6 Hz, *C*^{t}Bu), 66.6 (d, J_{CP} = 60.5 Hz, P*C*H), 123.0 (s, C_{meta}), 123.5 (s, C_{meta}), 123.6 (s, C_{para}), 137.0 (s, *C*CH_{iPr}), 137.1 (s, *C*CH_{iPr}), 148.2 (s, NC_{Ar}), 180.8 (d, J_{CP} = 10.6 Hz, N*C*CH)

$^{31}P\{^1H\}$ NMR (C_6D_6, 202.5 MHz, 300K): δ 147.3 (s)

1c:



^1H NMR (C_6D_6, 600 MHz, 300 K): δ 1.07 (dm, $^2J_{HH}$ = 10.1 Hz, 1H, ½CH_{2Norb}), 1.19 (s, 9H, CH_{3tBu}), 1.23 (m, 1H, ½$CH_{2CbridgeheadCP}$), 1.27 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.30 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.34 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.34 (m, 1H, ½$CH_{2CbridgeheadCN}$), 1.36 (m, 1H, ½$CH_{2CbridgeheadCP}$), 1.40 (d, $^4J_{HP}$ = 0.9 Hz, 9H, CH_{3tBu}), 1.56 (m, 1H, ½$CH_{2CbridgeheadCN}$), 1.83 (dm, $^2J_{HH}$ = 10.1 Hz, 1H, ½CH_{2Norb}), 2.36 (d, $^2J_{HP}$ = 3.4 Hz, 1H, PCH), 2.63 (d, J_{HH} = 4.5 Hz, 1H, $PCCH_{bridgehead}$), 2.75 (m, 1H, ½NCH_2), 2.78 (m, 1H, $NCCH_{bridgehead}$), 2.89 (m, 1H, ½NCH_2), 2.97 (m, 1H, ½NCH_2), 3.04 (m, 1H, ½NCH_2), 3.10 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.47 (sept, $^2J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 7.11-7.24 (m, 3H, $H_{aromatic}$)

^{13}C NMR (C_6D_6, 126 MHz, 300 K): δ 22.5 (s, CH_{3iPr}), 23.7 (s, CH_{3iPr}), 24.6 (s, CH_{3iPr}), 25.3 (s, CH_{3iPr}), 25.7 (s, $CH_{2CbridgeheadCP}$), 27.7 (d, J = 3.4 Hz, CH_{iPr}), 28.8 (s, CH_{iPr}), 29.6 (s, $CH_{2CbridgeheadCN}$), 29.8 (d, J_{CP} = 10.4 Hz, CH_{3tBu}), 30.2 (d, J_{CP} = 9.1 Hz, CH_{3tBu}), 36.6 (d, J_{CP} = 2.4 Hz, CH_{2Norb}), 40.7 (d, J_{CP} = 1.8 Hz, NC*C*H), 42.4 (s, PC*C*H), 45.4 (d, J_{CP} = 9.0 Hz, NCH_2), 47.3 (d, J_{CP} = 7.0 Hz, NCH_2), 53.5 (d, J_{CP} = 14.1 Hz, *C*^{t}Bu), 54.0 (d, J_{CP} = 19.7 Hz, *C*^{t}Bu), 55.9 (d, J_{CP} = 39.5 Hz, P*C*H), 122.9 (s, C_{meta}), 123.5 (s, C_{para}), 123.8 (s, C_{meta}), 136.7 (d, J_{CP} = 1.7 Hz, *C*CH_{iPr}), 137.5 (d, J_{CP} = 1.2 Hz, *C*CH_{iPr}), 148.2 (d, J_{CP} = 1.2 Hz, NC_{Ar}), 181.9 (d, J_{CP} = 10.3 Hz, N*C*CH)

^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz, 300K): δ 90.6 (s)

Synthesis of Dimethyl Aluminum Complexes 3a-c

General Synthesis:

To a solution of **1** in THF cooled to -78 °C, ^{n}BuLi (2.5M in hexanes, 1 equivalent) was added dropwise. The cold bath was removed and the resultant yellow solution was stirred at room temperature for 1 hour. Monitoring by ^{31}P{^{1}H} NMR spectroscopy revealed the presence of lithiated ligand **2** (see below). The reaction mixture was cooled to -78 °C and Me_2AlCl (1.0 M in hexanes) was added dropwise. The cold bath was removed and the resultant solution was stirred at room temperature for 1 hour. The solvent was removed *in vacuo*, the product extracted in hexane and dried to afford **3a-c**.

In situ characterisation of **2**:

2a:

^{31}P{^{1}H} (C_4H_8O, 202.5 MHz, 300 K): δ 10.9 (1:1:1:1 quartet, $J_{P\text{-}Li}$ = 54 Hz)

^{7}Li (C_4H_8O, 194.4 MHz, 300 K): δ 1.3 (d, $J_{Li\text{-}P}$ = 54 Hz)

2b:

^{31}P{^{1}H} (C_4H_8O, 202.5 MHz, 300 K): δ 96.4 (1:1:1:1 quartet, $J_{P\text{-}Li}$ = 63 Hz)

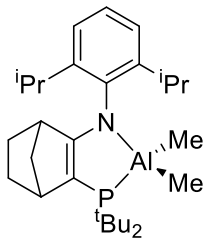
^{7}Li (C_4H_8O, 194.4 MHz, 300 K): δ 1.1 (d, $J_{Li\text{-}P}$ = 63 Hz)

2c:

^{31}P{^{1}H} (C_4H_8O, 202.5 MHz, 300 K): δ 68.6 (1:1:1:1 quartet, $J_{P\text{-}Li}$ = 54 Hz)

^{7}Li (C_4H_8O, 194.4 MHz, 300 K): δ 1.5 (d, $J_{Li\text{-}P}$ = 54 Hz)

3a:



1a (0.40 g, 0.97 mmol), THF (20 mL), ^{n}BuLi (0.39 mL, 0.97 mmol, 1.0 eq), Me_2AlCl (0.97 mL, 0.97 mmol, 1.0 eq) yielded **3a** (0.34 g, 75%) as a pale yellow solid.

Colourless crystals suitable for X-ray crystallography were grown from a saturated diethyl ether solution at 4 °C.

^{1}H (C_6D_6, 500 MHz, 300 K): δ -0.33 (d, $^{3}J_{HP}$ = 2.5 Hz, 3H, $AlCH_3$), -0.19 (d, $^{3}J_{HP}$ = 2.5 Hz, 3H, $AlCH_3$), 1.10 (m, 1H, ½CH_{2Norb}), 1.19 (d, $^{3}J_{HP}$ = 8.6 Hz, 9H, CH_{3tBu}), 1.22 (d, $^{3}J_{HP}$ = 8.6 Hz, 9H, CH_{3tBu}), 1.24 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.26 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.37 (d, $^{3}J_{HH}$ = 6.8 Hz, 6 H, CH_{3iPr}), 1.43 (m, 2H, $CH_{2CbridgeheadCP}$), 1.55 (m, 1H, ½$CH_{2CbridgeheadCN}$), 1.61 (m, 1H, ½CH_{2Norb}), 1.66 (m, 1H, ½$CH_{2CbridgeheadCN}$), 2.50 (br s, 1H, $PCCH_{bridgehead}$), 2.95 (br s, 1H, $NCCH_{bridgehead}$), 3.44 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.61 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 7.17-7.19 (m, 3H, $H_{aromatic}$)

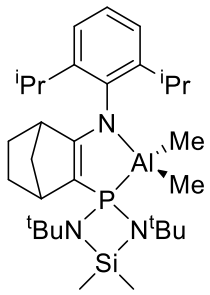
^{13}C (C_6D_6, 126 MHz, 300 K): δ -5.7 (br s, $AlCH_3$), -4.3 (br s, $AlCH_3$), 25.2 (s, CH_{3iPr}), 25.4 (s, CH_{3iPr}), 25.7 (s, CH_{3iPr}), 25.8 (s, CH_{3iPr}), 25.9 (d, J_{CP} = 2 Hz, $CH_{2CbridgeheadCP}$), 27.6 (s, CH_{iPr}), 27.7 (s, CH_{iPr}), 30.0 (s, $CH_{2CbridgeheadCN}$), 30.1 (d, J_{CP} = 5 Hz, CH_{3tBu}), 30.5 (d, J_{CP} = 5 Hz, CH_{3tBu}), 34.4 (d, J_{CP} = 30 Hz, *C*^{t}Bu), 34.8 (d, J_{CP} = 31 Hz, *C*^{t}Bu), 43.8 (d, J_{CP} = 9 Hz, PC*C*H), 44.1 (d, J_{CP} = 2 Hz, NC*C*H), 48.3 (d, J_{CP} = 3 Hz, CH_{2Norb}), 80.2 (d, J_{CP} = 42 Hz, P*C*CH), 124.2 (s, C_{meta}), 124.3 (s, C_{meta}), 126.1 (s, C_{para}), 141.7 (d, J_{CP} = 3 Hz, NC_{Ar}), 147.1 (s, *C*CH_{iPr}), 147.4 (s, *C*CH_{iPr}), 185.1 (d, J_{CP} = 21 Hz, N*C*CH)

^{31}P{^{1}H} (C_6D_6, 162 MHz, 300 K): δ 1.6 (s, $\Delta\nu_{½}$ = 21.1 Hz)

High Resolution Mass Spec (APPI): m/z = 469.341919 $[C_{29}H_{49}AlNP]^{+}$ (theoretical = 469.341252).

Elemental Analysis: Found (%): C, 74.13; H, 10.38; N, 2.85. Calc. for $C_{29}H_{49}AlNP$: C, 74.16; H, 10.52; N, 2.98.

3b:



1b (0.3 g, 0.60 mmol), THF (20 mL), ^{n}BuLi (0.24 mL, 0.60 mmol, 1.0 eq), Me_2AlCl (0.60 mL, 0.60 mmol, 1.0 eq) yielded **3b** (0.17 g, 56%) as a yellow solid. Some impurities (less than 10%) were observed by NMR spectroscopy due to reaction with water, but could not be separated since crystallisation of **3b** was not possible.

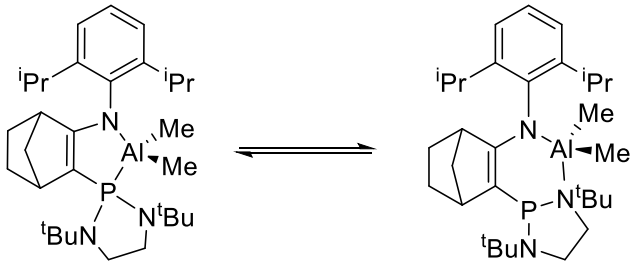
^{1}H NMR (C_6D_6, 500 MHz, 300 K): δ -0.26 (d, $^{3}J_{HP}$ = 3.9 Hz, 3H, $AlCH_3$), -0.12 (d, $^{3}J_{HP}$ = 3.9 Hz, 3H, $AlCH_3$), 0.27 (s, 3H, $SiCH_3$), 0.32 (s, 3H, $SiCH_3$), 1.12 (d, $^{2}J_{HH}$ = 8.1 Hz, 1H, ½CH_{2Norb}), 1.25 (s, 9H, CH_{3tBu}), 1.26 (s, 9H, CH_{3tBu}), 1.25 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.26 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.32 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.41 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.42 (m, 2H, $CH_{2CbridgebeadCP}$), 1.60 (d, $^{2}J_{HH}$ = 8.1 Hz, 1H, ½CH_{2Norb}), 1.69 (m, 2H, $CH_{2CbridgeheadCN}$), 2.53 (br s, 1H, $CH_{bridgeheadCP}$), 3.13 (br s, 1H, $CH_{bridgeheadCN}$), 3.51 (sept, $^{3}J_{HH}$ = 6.8 Hz, CH_{iPr}), 3.70 (sept, $^{3}J_{HH}$ = 6.8 Hz, CH_{iPr}) 7.11-7.21 (m, 3H, $H_{aromatic}$)

^{13}C NMR (C_6D_6, 126 MHz, 300 K): δ -6.3 (br d, J_{CP} = 24.8 Hz, $AlCH_3$), -5.4 (br d, J_{CP} = 19.9 Hz, $AlCH_3$), 4.6 (d, J_{CP} = 1.4 Hz, $SiCH_3$), 6.7 (d, J_{CP} = 3.7 Hz, $SiCH_3$), 25.3 (s, CH_{3iPr}), 25.4 (s, CH_{3iPr}), 25.6 (s, CH_{3iPr}), 26.0 (s, CH_{3iPr}), 26.3 (s, $CH_{2CbridgeheadCP}$), 27.6 (s, CH_{iPr}), 27.8 (s, CH_{iPr}), 29.4 (s, $CH_{2CbridgeheadCN}$), 32.3 (d, J_{CP} = 5.4 Hz, CH_{3tBu}), 32.7 (d, J_{CP} = 4.9 Hz, CH_{3tBu}), 40.6 (d, J_{CP} = 3.5, *C*HCN), 44.3 (d, J_{CP} = 43.9, *C*HCP), 46.6 (d, J_{CP} = 4.7 Hz, CH_{2Norb}), 50.8 (d, J_{CP} = 3.9 Hz, *C*^{t}Bu), 50.9 (d, J_{CP} = 2.8 Hz, *C*^{t}Bu), 99.1 (d, J_{CP} = 29.2 Hz, P*C*CH), 124.3 (s, C_{meta}), 124.3 (s, C_{meta}), 126.3 (s, C_{para}), 141.2 (d, J_{CP} = 3.1 Hz, NC_{Ar}), 146.6 (s, *C*CH_{iPr}), 147.0 (s, *C*CH_{iPr}), 186.8 (d, J_{CP} = 33.9 Hz, N*C*CH)

^{31}P{^{1}H} (C_6D_6, 162 MHz, 300 K): δ 64.0 (s, $\Delta\nu_{½}$ = 35.8 Hz)

High Resolution Mass Spec (APPI): m/z = 555.371654 $[C_{31}H_{55}AlN_3PSi]^+$ (theoretical = 555.371277).

3c:



$^{31}P\{^1H\}$ δ 49.7 ppm
κ^2-N,P **3c** (43%)

$^{31}P\{^1H\}$ δ 99.9 ppm
κ^2-N,N **5c** (57%)

1c (0.43 g, 0.92 mmol), THF (20 mL), ^{n}BuLi (0.37 mL, 0.92 mmol, 1.0 eq), Me_2AlCl (0.92 mL, 0.60 mmol, 1.0 eq). To gain analytically pure material, **3c** was further purified by recrystallization from hexanes at -20 °C to yield colourless crystals (0.23 g, 48%).

Two isomers were identified in the NMR spectra of approximate ratio of 4:3 of κ^2-N,N **3c** to κ^2-N,P **3c** at 300 K (determined from the ^{1}H NMR spectrum).

Due to the high air-sensitivity of this species, some impurities were observed in solution NMR spectra ($^{31}P\{^1H\}$ NMR spectrum, 10% unidentified impurity at 75.11 ppm).

κ^2-N,N **3c**:

^{1}H (C_6D_6, 500 MHz, 300 K): δ -0.67 (s, 3H, AlMe), -0.13 (s, 3H, AlMe), 0.89 (m, 1H, ½CH_{2Norb}), 1.18 (m, 1H, ½CH_{2Norb}), 1.21 (s, 18H, CH_{3tBu}), 1.24 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_{3iPr}), 1.27 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.45 (m, 2H, $CH_{2CbridgeheadCP}$), 1.47 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.63 (m, 1H, ½$CH_{2CbridgeheadCN}$), 1.72 (m, 1H, ½$CH_{2CbridgeheadCN}$), 2.49 (br s, 1H, $CH_{bridgeheadCP}$), 2.82 (m, 1H, ½NCH_2), 2.83 (m, 1H, ½NCH_2), 2.97 (m, $CH_{bridgeheadCN}$), 3.15 (m, 1H, ½NCH_2), 3.73 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.85 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.88 (m, 1H, ½NCH_2), 7.15-7.20 (m, 3H, $H_{aromatic}$)

^{13}C (C_6D_6, 126 MHz, 300 K): δ -5.5 (s, AlMe), -4.7 (s, AlMe), 24.3 (s, CH_{3iPr}), 24.8 (s, CH_{3iPr}), 25.75 (s, CH_{3iPr}), 25.97 (s, $CH_{2CHbridgeheadCP}$), 26.1 (s, CH_{3iPr}), 27.0 (s, CH_{iPr}), 28.2 (s, CH_{iPr}), 29.3 (s, $CH_{2CbridgeheadCN}$), 29.7 (d, J_{CP} = 9.5 Hz, CH_{3tBu}), 29.73 (d, J_{CP} = 7.7 Hz, CH_{3tBu}), 29.8 (d, J_{CP} = 5.6 Hz, CH_{3tBu}), 43.84 (s, CH_{2Norb}), 43.88 (d, J_{CP} = 12.6 Hz, NCH_2), 45.3 (s, $CH_{bridgeheadCP}$), 45.7 (d, J_{CP} = 42.0 Hz, $CH_{bridgeheadCN}$), 48.8 (d, J_{CP} = 2.8 Hz, NCH_2), 53.2 (d, J_{CP} = 6.0 Hz, *C*^{t}Bu), 63.7 (d, J_{CP} = 11.7 Hz, *C*^{t}Bu), 103.5 (d, J_{CP} = 37.7 Hz, P*C*CH), 123.9 (s, C_{meta}), 124.5 (s, C_{meta}), 125.2 (s, C_{para}), 144.1 (s, NC_{Ar}), 146.5 (s, *C*CH_{iPr}), 147.0 (s, *C*CH_{iPr}), 165.0 (d, J_{CP} = 5.0 Hz, N*C*CH)

$^{31}P\{^1H\}$ (C_6D_6, 162 MHz, 300 K): δ 99.9 (s, $\Delta\nu_{½}$ = 5.3 Hz)

κ^2-N,P **3c**:

^{1}H (C_6D_6, 500 MHz, 300 K): δ -0.27 (d, $^3J_{HP}$ = 3.1 Hz, 3H, AlMe), -0.14 (d, $^3J_{HP}$ = 3.1 Hz, 3H, AlMe), 1.06 (dm, $^2J_{HH}$ = 8.1 Hz, 1H, ½CH_{2Norb}), 1.25 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.30 (s, 9H, CH_{3tBu}), 1.32 (s, 9H, CH_{3tBu}), 1.33 (m, 1H, ½$CH_{2CbridgeheadCP}$), 1.38 (m, 1H, ½$CH_{2CbridgeheadCP}$), 1.40 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.42 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.56 (m, $^2J_{HH}$ = 8.1 Hz, 1H, ½CH_{2Norb}), 1.63 (m, 2H,

$CH_{2CbridgeheadCN}$), 2.48 (br s, 1H, $CH_{bridgeheadCP}$), 2.59 (m, 1H, ½NCH_2), 2.66 (m, 1H, ½NCH_2), 2.82 (m, 1H, ½NCH_2), 2.89 (m, 1H, NCH_2), 3.05 (br s, 1H, $CH_{bridgeheadCN}$), 3.52 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.74 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 7.15-7.20 (m, 3H, $H_{aromatic}$)

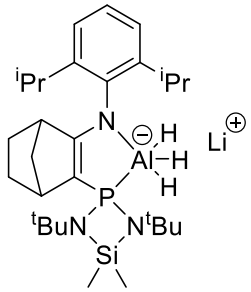
^{13}C (C_6D_6, 126 MHz, 300 K): δ -4.2 (s, AlMe), -3.5 (s, AlMe), 25.2 (s, CH_{3iPr}), 25.4 (s, CH_{3iPr}), 25.68 (s, CH_{3iPr}), 25.84 (s, $CH_{2CbridgeheadCP}$), 27.4 (s, CH_{iPr}), 27.6 (s, CH_{iPr}), 29.2 (s, CH_{3tBu}), 29.4 (d, J_{CP} = 2.2 Hz, $CH_{2CbridgeheadCN}$), 29.7 (d, J_{CP} = 7.6 Hz, CH_{3tBu}), 42.0 (d, J_{CP} = 4.2 Hz, $CH_{bridgeheadCN}$), 43.6 (s, NCH_2), 44.2 (d, J_{CP} = 9.9 Hz, $CH_{bridgeheadCP}$), 44.3 (s, NCH_2), 46.6 (d, J_{CP} = 5.3 Hz, CH_{2Norb}), 52.5 (d, J_{CP} = 11.7 Hz, C^tBu), 52.8 (d, J_{CP} = 8.8 Hz, C^tBu), 95.5 (d, J_{CP} = 33.5 Hz, P*C*CH), 124.29 (s, C_{meta}), 124.32 (C_{meta}), 126.2 (s, C_{para}), 142.0 (d, J_{CP} = 3.9 Hz, NC_{Ar}), 146.7 (s, CCH_{3iPr}), 148.0 (s, CCH_{3iPr}), 185.3 (d, J_{CP} = 34.1 Hz, N*C*CH)

^{31}P{^{1}H} (C_6D_6, 162 MHz, 300 K): δ 49.7 (s, $\Delta\nu_{½}$ = 47.5 Hz)

High Resolution Mass Spec (EI): m/z = 525.37703 $[C_{31}H_{53}AlN_3P]^+$ (theoretical = 525.37871).

Elemental Analysis: Found (%): C, 70.71; H, 10.18; N, 8.03. Calc. for $C_{31}H_{53}AlN_3P$: C, 70.82; H, 10.16; N, 7.99.

Characterisation of Aluminate Complex 4b



To a solution of **1b** (0.10 g, 0.2 mmol) in THF (20 mL) at -78 °C, ^{n}BuLi (2.5 M in hexanes, 0.08 mL, 0.2 mmol, 1 eq) was added dropwise. The cold bath was removed and the resultant yellow solution was stirred at room temperature for 1 hour. The reaction mixture was cooled to -78 °C and $H_3Al{\cdot}NMe_2Et$ (0.5 M in toluene, 0.4 mL, 1 eq) was added dropwise. The cold bath was removed and the resultant yellow solution was stirred at room temperature for 20 minutes and the solvent removed *in vacuo* to afford the product as a yellow oil. No further purification was attempted, but **4b** was characterised by NMR and mass spectrometry:

^{1}H NMR (C_4D_8O, 500 MHz, 300 K): δ 0.29 (s, 3H, $SiCH_3$), 0.33 (s, 3H, $SiCH_3$), 0.84 (m, 1H, ½CH_{2Norb}), 1.07 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.08 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.12 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.14 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.18 (m, 2H, $CH_{2CbridgeheadCP}$), 1.19 (s, 9H, CH_{3tBu}), 1.21 (s, 9H, CH_{3tBu}), 1.25 (m, 1H, ½CH_{2Norb}), 1.54 (m, 1H, ½$CH_{2CbridgeheadCN}$), 1.62 (m, 1H, ½$CH_{2CbridgheadCN}$), 2.19 (br s, 1H, $CH_{bridgeheadCP}$), 3.35 (br s, 1H, $CH_{bridgeheadCN}$), 3.54 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.63 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 6.83-6.90 (m, 3H, $H_{aromatic}$)

Note: It was not possible to locate the Al-H resonances even with the use of $^{1}H\{^{31}P\}$ NMR experiments, likely due to extremely high linewidth.

^{13}C NMR (C_4D_8O, 126 MHz, 300 K): δ 6.5 (s, $SiCH_3$), 8.3 (d, J_{CP} = 5.7 Hz, $SiCH_3$), 24.3 (d, J_{CP} = 10.2 Hz, CH_{3iPr}), 26.0 (d, J_{CP} = 15.2 Hz, CH_{3iPr}), 27.2 (s, $CH_{2CbridgeheadCP}$), 28.11 (s, CH_{iPr}), 28.13 (s, CH_{iPr}), 30.1 (s, $CH_{2CbridgeheadCN}$), 32.9 (d, J_{CP} = 5.4 Hz, CH_{3tBu}), 33.4 (d, J_{CP} = 4.8 Hz, CH_{3tBu}), 42.1 (d, J_{CP} = 1.5 Hz, $CH_{bridgeheadCN}$), 46.5 (s, CH_{2Norb}), 47.2 (d, J_{CP} = 5.5 Hz, $CH_{bridgeheadCP}$), 51.4 (d, J_{CP} = 11.5 Hz, $C^{t}Bu$), 51.6 (d, J_{CP} = 14.6 Hz, $C^{t}Bu$), 111.2 (d, J_{CP} = 43.1 Hz, P*C*CH), 123.1 (d, J_{CP} = 10.0 Hz, C_{meta}), 124.2 (s, C_{para}), 146.7 (s, *C*CH_{iPr}), 148.0 (s, *C*CH_{iPr}), 150.7 (s, NC_{Ar}), 174.2 (d, J_{CP} = 33.2 Hz, N*C*CH)

^{31}P (C_4D_8O, 162 MHz, 300 K): δ 110.8 (q, $^{2}J_{PH}$ = 34 Hz)

^{7}Li (C_4D_8O, 194.4 MHz, 300 K): δ -0.43 (s)

High Resolution Mass Spec (EI): m/z = 528.34912 $[C_{29}H_{52}N_3AlPSi]^+$ (theoretical = 528.34891).

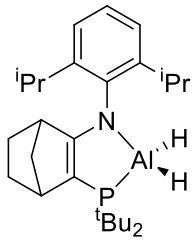
Synthesis of Aluminum Dihydride Complexes 5a-c

General Synthesis:

To a solution of ligand **1a-c** in THF cooled to -78 °C, ^{n}BuLi (2.5 M in hexanes) was added dropwise. The cold bath was removed and the resultant yellow solution was stirred at room temperature for 1 hour. The reaction mixture was cooled to -78 °C and a solution of $H_3Al{\cdot}NMe_3$ in THF was added dropwise. The cold bath was removed and the resultant colourless solution was stirred at room temperature for 1 hour. The solvent was removed *in vacuo*, the product extracted in hexane and dried to afford a white solid.

$H_3Al{\cdot}NMe_2Et$ (0.5 M in toluene) can be used in place of $H_3Al{\cdot}NMe_3$. In this work, $H_3Al{\cdot}NMe_2Et$ was used for initial test reactions to synthesise up to 0.2 g of **5** using an identical procedure to that described above.

5a:



1a (1.63 g, 0.0039 mol), THF (50 mL), ^{n}BuLi (1.6 mL, 0.0039 mol, 1.0 eq), $H_3Al{\cdot}NMe_3$ (0.84 g, 0.0037 mol, 2.4 eq) in THF (20 mL) yielded **5a** (1.57 g, 91%).

^{1}H (C_6D_6, 500 MHz, 300 K): δ 1.11 (dm, $^{2}J_{HH}$ = 8.1 Hz, 1H, ½CH_{2Norb}), 1.19 (d, $^{3}J_{HP}$ = 14.2 Hz, 9H, CH_{3tBu}), 1.22 (d, $^{3}J_{HP}$ = 14.2 Hz, 9H, CH_{3tBu}), 1.28 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.29 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.31 (m, 2H, $CH_{2CbridgeheadCP}$), 1.42 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.44 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.51 (m, 1H, ½$CH_{2CbridgeheadCN}$), 1.62 (dm, $^{2}J_{HH}$ = 8.1 Hz, 1H, ½CH_{2Norb}), 1.67 (m, 1H, ½$CH_{2CbirdgeheadCN}$), 2.53 (br s, 1H, $PCCH_{bridgehead}$), 2.94 (br s, 1H, $NCCH_{bridgehead}$), 3.42 (sept, $^{3}J_{HH}$ = 6.8 Hz, CH_{iPr}), 3.63 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 4.6 (br s, 2H, AlH_2), 7.16-7.22 (m, 3H, $H_{aromatic}$)

^{13}C (C_6D_6, 126 MHz, 300 K): δ 24.0 (s, CH_{3iPr}), 24.7 (s, CH_{3iPr}), 25.2 (d, J_{CP} = 1.8 Hz, $CH_{2CbridgeheadCP}$), 25.8 (s, CH_{3iPr}), 25.9 (s, CH_{3iPr}), 28.0 (s, CH_{iPr}), 28.1 (s, CH_{iPr}), 29.6 (d, J_{CP} = 4.5 Hz, CH_{3tBu}), 30.1 (s, $CH_{2CbridgeheadCN}$), 30.1 (d, J_{CP} = 4.0 Hz, CH_{3tBu}), 34.1 (d, J_{CP} = 18.2 Hz, C^{t}Bu), 34.3 (d, J_{CP} = 18.9 Hz, C^{t}Bu), 43.6 (d, J_{CP} = 9.1 Hz, $CH_{bridgeheadCP}$), 44.1 (d, J_{CP} = 2.1 Hz, $CH_{bridgeheadCN}$), 48.6 (d, J_{CP} = 3.9 Hz, CH_{2Norb}), 81.0 (d, J_{CP} = 44.5 Hz, P*C*CH), 124.1 (s, C_{meta}), 124.2 (s, C_{meta}), 126.3 (s, C_{para}), 141.4 (d, J_{CP} = 3.0 Hz, NC_{Ar}), 146.8 (s, *C*CH_{iPr}), 147.1 (s, *C*CH_{iPr}), 185.1 (d, J_{CP} = 20.1 Hz, N*C*CH)

^{31}P{^{1}H} (C_6D_6, 162 MHz, 300 K): δ 8.0 (s, $\Delta\nu_{½}$ = 34.7 Hz)

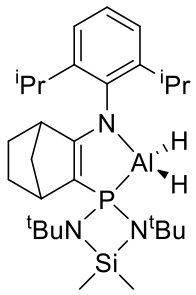
High Resolution Mass Spec (EI): m/z = 441.30855 $[C_{27}H_{45}AlNP]^{+}$ (theoretical = 441.30996).

Elemental Analysis: Found (%): C, 73.11; H, 10.39; N, 3.13. Calc. for $C_{27}H_{45}AlNP$: C, 73.43; H, 10.27; N, 3.17.

IR (solid, cm^{-1}): 1810, 1786

IR (solution, cm^{-1}): 1811

5b:



1b (3.00 g, 0.0060 mol), THF (80 mL), ^{n}BuLi (2.4 mL, 0.0060 mol, 1.0 eq), $H_3Al{\cdot}NMe_3$ (1.28 g, 0.014 mol, 2.4 eq) in THF (15 mL) yielded **5b** (2.95 g, 93%).

Colourless crystals suitable for X-ray crystallography were grown from a saturated hexane solution at -20 °C.

^{1}H NMR (C_6D_6, 500 MHz, 300 K): δ 0.24 (s, 3H, $SiCH_3$), 0.29 (s, 3H, $SiCH_3$), 1.13 (d, $^{2}J_{HH}$ = 8.1 Hz, 1H, ½CH_{2Norb}), 1.28 (d, $^{4}J_{HP}$ = 0.8 Hz, 9H, CH_{3tBu}), 1.29 (d, $^{4}J_{HP}$ = 0.8 Hz, 9H, CH_{3tBu}), 1.30 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.31 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.38 (m, 2H, $CH_{2CbridgeheadCP}$), 1.44 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.45 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.62 (d, $^{2}J_{HH}$ = 8.1 Hz, ½CH_{2Norb}), 1.67 (m, 2H, $CH_{2CbridgeheadCN}$), 2.57 (br s, 1H, $CH_{bridgeheadCP}$), 3.12 (br s, 1H, $CH_{bridgeheadCN}$), 3.53 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.74 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 4.6 (br s, 2H, Al-H), 7.17-7.23 (m, 3H, $H_{aromatic}$)

^{13}C NMR (C_6D_6, 126 MHz, 300 K): δ 4.4 (d, J_{CP} = 1.6 Hz, $SiCH_3$), 6.3 (d, J_{CP} = 3.2 Hz, $SiCH_3$), 24.1 (s, CH_{3iPr}), 24.6 (s, CH_{3iPr}), 25.6 (d, J_{CP} = 1.0 Hz, $CH_{2CbridgeheadCP}$), 25.8 (s, CH_{3iPr}), 25.9 (s, CH_{3iPr}), 28.0 (s, CH_{iPr}), 28.3 (s, CH_{iPr}), 29.3 (s, $CH_{2CHbridgheadCN}$), 32.3 (d, J_{CP} = 5.4 Hz, CH_{3tBu}), 32.7 (d, J_{CP} = 5.2, CH_{3tBu}), 40.7 (d, J_{CP} = 3.9 Hz, $CH_{bridgheadCN}$), 43.9 (d, J_{CP} = 9.7 Hz, $CH_{bridgheadCP}$), 46.8 (d, J_{CP} = 4.9 Hz, CH_{2Norb}), 51.4 (d, J_{CP} = 2.5 Hz, C^{t}Bu), 51.5 (d, J_{CP} = 3.6 Hz, C^{t}Bu), 99.7 (d, J_{CP} = 32.6 Hz, P*C*CH), 124.1 (s, C_{meta}), 124.2 (s, C_{meta}), 126.5 (s, C_{para}), 140.8 (d, J_{CP} = 3.5 Hz, NC_{Ar}), 146.4 (s, $C_{Ar}CH_{iPr}$), 146.5 (s, $C_{Ar}CH_{iPr}$), 187.6 (d, J_{CP} = 33.9 Hz, N*C*CH)

^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 300 K): δ 61.3 (s, $\Delta\nu_{½}$ = 65.4 Hz)

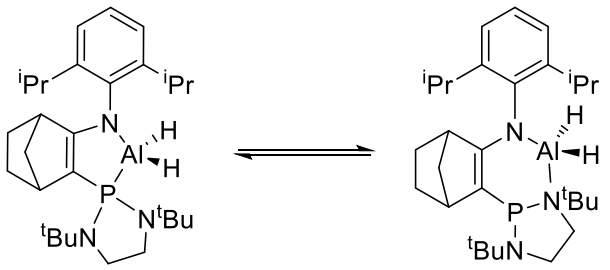
High Resolution Mass Spec (EI): m/z = 527.33886 $[C_{29}H_{51}AlN_3PSi]^{+}$ (theoretical = 527.33998).

Elemental Analysis: Found (%): C, 65.95; H, 9.66; N, 7.83. Calc. for $C_{29}H_{51}AlN_3PSi$: C, 66.00; H, 9.74; N, 7.96.

IR (solid, cm^{-1}): 1831, 1816

IR (solution, cm^{-1}): 1820

5c:



$^{31}P\{^1H\}$ δ 47.8 ppm
κ²-N,P **5c** (64%)

$^{31}P\{^1H\}$ δ 96.9 ppm
κ¹-N,N **5c** (36%)

1c (2.00 g, 0.0043 mol), THF (100 mL), ^{n}BuLi (1.7 mL, 0.0043 mol, 1.0 eq), $H_3Al{\cdot}NMe_3$ (0.91 g, 0.010 mol, 2.4 eq) in THF (15 mL). The final product was further purified by recrystallization from hexanes at -20 °C to yield **5c** as colourless crystals(1.68 g, 79%).

Two isomers were identifiable in the solution phase NMR spectra in a ratio of 4:7 for κ²-N,N **5c** to κ²-N,P **5c** at 300 K (determined from the ^{1}H NMR spectrum).

κ²-N,N **5c**

^{1}H (C_6D_6, 500 MHz, 300 K): δ 0.91 (m, 1H, ½CH_{2Norb}), 1.18 (d, $^4J_{HP}$ = 1.3 Hz, 9H, CH_{3tBu}), 1.23 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.25 (m, 1H, ½CH_{2Norb}), 1.31 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_{3iPr}), 1.32 (s, 9H, CH_{3tBu}), 1.43 (m, 2H, $CH_{2CbridgeheadCP}$), 1.60 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.65 (m, 1H, ½$CH_{2CbridgeheadCN}$), 1.71 (m, 1H, ½$CH_{2CbridgeheadCN}$), 2.56 (m, 1H, $CH_{bridgeheadCP}$), 2.70 (m, 1H, ½NCH_2), 2.78 (m, 1H, ½NCH_2), 2.97 (m, 1H, $CH_{bridgeheadCN}$), 3.33 (m, 1H, ½NCH_2), 3.56 (m, 1H, ½NCH_2), 3.85 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.98 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 4.3 (br s, 2H, AlH_2) 7.18-7.21 (m, 3H, $H_{aromatic}$)

^{13}C (C_6D_6, 126 MHz, 300 K): δ 25.4 (s, $CH_{2CbridgeheadCP}$), 25.6 (s, CH_{3iPr}), 25.7 (s, CH_{3iPr}), 25.92 (s, CH_{3iPr}), 27.5 (s, CH_{iPr}), 28.9 (s, CH_{iPr}), 29.0 (d, J_{CP} = 4.6 Hz, CH_{3tBu}), 29.6 (d, J_{CP} = 10.7 Hz, CH_{3tBu}), 29.8 (d, J_{CP} = 1.8 Hz, $CH_{2CbridgeaheadCN}$), 44.2 (s, CH_{2Norb}), 45.1 (s, $CH_{bridgeheadCN}$), 45.7 (s, NCH_2), 45.8 (d, J_{CP} = 39.1 Hz, $CH_{bridgeheadCP}$), 48.8 (d, J_{CP} = 3.3 Hz, NCH_2), 53.5 (d, J_{CP} = 5.0 Hz, C^{t}Bu), 53.8 (d, J_{CP} = 3.9 Hz, C^{t}Bu), 104.8 (d, J_{CP} = 36.9 Hz, P*C*CH), 123.9 (s, C_{meta}), 124.6 (s, C_{meta}), 125.2 (s, C_{para}), 143.22 (s, N*C*$_{Ar}$), 145.8 (*C*CH_{iPr}), 146.53 (s, *C*CH_{iPr}), 167.4 (d, J_{CP} = 2.7 Hz, N*C*CH)

$^{31}P\{^1H\}$ (C_6D_6, 162 MHz, 300 K): δ 96.9 (s, $\Delta\nu_{½}$ = 137.9 Hz)

κ²-N,P **5c**

^{1}H (C_6D_6, 500 MHz, 300 K): δ 1.07 (dm, $^2J_{HH}$ = 8.4 Hz, 1H, ½CH_{2Norb}), 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.30 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.32 (s, 9H, CH_{3tBu}), 1.35 (s, 9H, CH_{3tBu}), 1.39 (m, 2H, $CH_{2CbridgeheadCP}$), 1.42 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.45 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.56 (m, 1H, ½CH_{2Norb}), 1.63 (m, 2H, $CH_{2CbridgeheadCN}$), 2.52 (m, 1H, $CH_{bridgeheadCP}$), 2.60 (m, 1H, ½NCH_2), 2.72 (m, 1H, ½NCH_2), 2.79 (m, 1H, ½NCH_2), 2.88 (m, 1H, NCH_2), 3.02 (m, 1H, $CH_{bridgeheadCN}$), 3.54 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.76 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 4.6 (br s, 2H, AlH_2) 7.18-7.21 (m, 3H, $H_{aromatic}$)

^{13}C (C_6D_6, 126 MHz, 300 K): δ 24.0 (s, CH_{3iPr}), 24.7 (s, CH_{3iPr}), 25.3 (s, $CH_{2CbridgeheadCP}$), 25.8 (s, CH_{3iPr}), 25.86 (s, CH_{3iPr}), 27.9 (s, CH_{iPr}), 28.1 (s, CH_{iPr}), 29.0 (d, J_{CP} = 4.6 Hz, CH_{3tBu}), 29.3 (s, $CH_{2CbridgeheadCN}$), 29.9 (d, J_{CP} = 4.6 Hz, CH_{3tBu}), 42.7 (d, J_{CP} = 4.4 Hz, $CH_{bridgeheadCN}$), 43.6 (d, J_{CP} = 9.9 Hz, $CH_{bridgeheadCP}$), 43.9 (s, NCH_2), 44.2 (s, NCH_2), 46.6 (d, J_{CP} = 4.9 Hz, CH_{2Norb}), 53.4 (d, J_{CP} = 9.8 Hz, C^tBu), 53.6 (d, J_{CP} = 5.4 Hz, C^tBu), 97.0 (d, J_{CP} = 35.3 Hz, P*C*CH), 124.1 (s, C_{meta}), 124.3 (s, C_{meta}), 126.4 (s, C_{para}), 141.0 (d, J_{CP} = 4.0 Hz, NC_{Ar}), 146.51 (s, *C*CH_{iPr}), 146.8 (s, *C*CH_{iPr}), 185.4 (d, J_{CP} = 34.0 Hz, N*C*CH)

$^{31}P\{^1H\}$ (C_6D_6, 162 MHz, 300 K): δ 47.8 (s, $\Delta\nu_{½}$ = 96.6 Hz)

High Resolution Mass Spec (EI): m/z = 497.35079 $[C_{29}H_{49}AlN_3P]^+$ (theoretical = 497.34741).

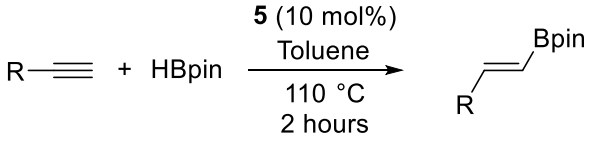
Elemental Analysis: Found (%): C, 69.80; H, 9.80; N, 8.33. Calc. for $C_{29}H_{51}AlN_3PSi$: C, 69.99; H, 9.92; N, 8.44.

IR (solid, cm^{-1}): 1825, 1801

IR (solution, cm^{-1}): 1823

Hydroboration of Alkynes Catalysed by 5a-c

The relevant alkyne (Phenylacetylene or 1-octyne, 0.15 mmol) was added to a solution of **5a-c** (10 mol%, 0.015 mmol) and HBpin (0.15 mmol, 0.022 mL) in toluene (0.5 mL) at room temperature and then heated to 110 °C for 2 hours. Yields were obtained using ^{1}H NMR spectroscopy following the addition of 1,3,5-trimethoxybenzene as an internal standard to the crude reaction mixture. The products were identified by comparison with literature.[6]



Catalyst	Substrate	Yield (%)
5a	1-octyne	40
	Phenylacetylene	79
	Phenylacetylene	24[a]
5b	1-octyne	42
	Phenylacetylene	83
5c	1-octyne	46
	Phenylacetylene	53
None	1-octyne	Trace (1%)
	Phenylacetylene	None

[a] Reaction temperature of 60 °C

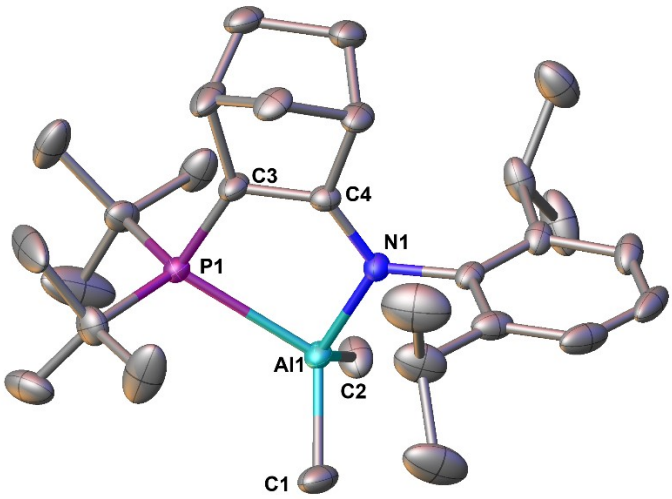
X-ray Crystallography

3a

Experimental. Single colourless block-shaped crystals of **3a** were recrystallised from diethyl ether by slow cooling. A suitable crystal 0.48×0.32×0.26 mm^3 was selected and mounted on a MITIGEN holder in Paratone oil on a Rigaku Oxford Diffraction SuperNova diffractometer. The crystal was kept at a steady T = 120.00 K during data collection. The structure was solved with the Superflip[7-9] structure solution program using the Charge Flipping methods solution method and by using **Olex2**[10] as the graphical interface. The model was refined with version 2018/3 of **ShelXL**[11] using full matrix least squares on $\mathbf{F^2}$ minimisation.

Crystal Data. $C_{29}H_{49}AlNP$, M_r = 469.64, monoclinic, $P2_1/n$ (No. 14), a = 9.18230(10) Å, b = 15.1402(3) Å, c = 21.6154(4) Å, β = 101.8270(10)°, α = γ = 90°, V = 2941.22(9) $Å^3$, T = 120.00 K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.139, 51661 reflections measured, 7623 unique (R_{int} = 0.0428) which were used in all calculations. The final wR_2 was 0.1337 (all data) and R_1 was 0.0549 (I > 2(I)).

Plot.



Hydrogen atoms and disorder omitted for clarity.
Thermal ellipsoids set to 50%

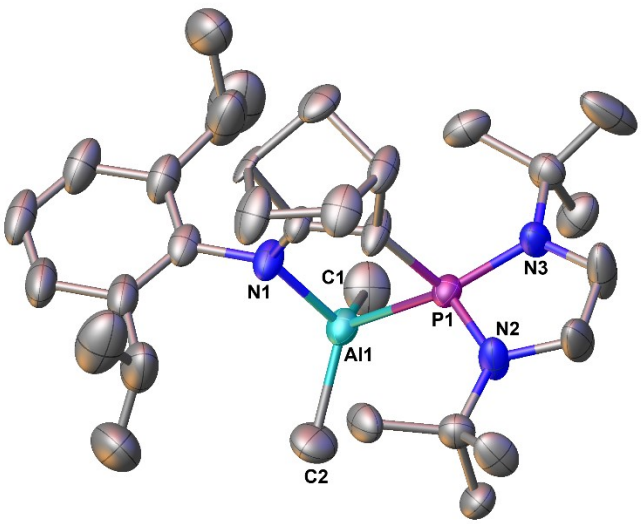
Compound	**3a**
Formula	$C_{29}H_{49}AlNP$
$D_{calc.}$/ g cm^{-3}	1.061
μ/mm^{-1}	0.139
Formula Weight	469.64
Colour	colourless
Shape	block
Size/mm^3	0.48×0.32×0.26
T/K	120.00
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	9.18230(10)
b/Å	15.1402(3)
c/Å	21.6154(4)
α/°	90
β/°	101.8270(10)
γ/°	90
V/$Å^3$	2941.22(9)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.858
Θ_{max}/°	29.738
Measured Refl.	51661
Independent Refl.	7623
Reflections with I > 2(I)	6524
R_{int}	0.0428
Parameters	360
Restraints	6
Largest Peak	0.628
Deepest Hole	-0.448
GooF	1.090
wR_2 (all data)	0.1337
wR_2	0.1277
R_1 (all data)	0.0653
R_1	0.0549

3c

Experimental. Single colourless plate-shaped crystals of **3c** were recrystallised from hexane by slow cooling. A suitable crystal 0.40×0.07×0.03 mm^3 was selected and mounted on a MITIGEN holder in Paratone oil on a Rigaku Oxford Diffraction SuperNova diffractometer. The crystal was kept at a steady T = 120.0 K during data collection. The structure was solved with the Superflip[7-9] structure solution program using the Charge Flipping methods solution method and by using **Olex2**[10] as the graphical interface. The model was refined with version 2018/3 of **ShelXL**[11] using Least Squares minimisation.

Crystal Data. $C_{31}H_{53}AlN_3P$, M_r = 525.71, monoclinic, $P2_1$ (No. 4), a = 8.87214(15) Å, b = 19.02205(19) Å, c = 10.2547(2) Å, β = 115.642(2)°, α = γ = 90°, V = 1560.21(5) Å^3, T = 120.0 K, Z = 2, Z' = 1, μ(CuK$_\alpha$) = 1.210, 25359 reflections measured, 5578 unique (R_{int} = 0.0672) which were used in all calculations. The final wR_2 was 0.1368 (all data) and R_1 was 0.0495 (I > 2(I)).

Plot.



Hydrogen atoms and disorder omitted for clarity.
Thermal ellipsoids set to 50%

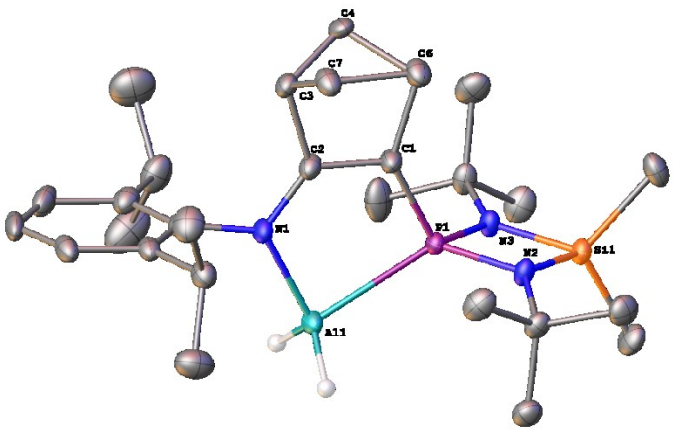
Compound	**3c**
Formula	$C_{31}H_{53}AlN_3P$
$D_{calc.}$/ g cm^{-3}	1.119
μ/mm^{-1}	1.210
Formula Weight	525.71
Colour	colourless
Shape	plate
Size/mm^3	0.40×0.07×0.03
T/K	120.0
Crystal System	monoclinic
Flack Parameter	0.068(17)
Hooft Parameter	0.074(15)
Space Group	$P2_1$
a/Å	8.87214(15)
b/Å	19.02205(19)
c/Å	10.2547(2)
α/°	90
β/°	115.642(2)
γ/°	90
V/Å^3	1560.21(5)
Z	2
Z'	1
Wavelength/Å	1.54184
Radiation type	CuK$_\alpha$
Θ_{min}/°	4.649
Θ_{max}/°	76.174
Measured Refl.	25359
Independent Refl.	5578
Reflections with I > 2(I)	5210
R_{int}	0.0672
Parameters	487
Restraints	5
Largest Peak	0.413
Deepest Hole	-0.305
GooF	1.053
wR_2 (all data)	0.1368
wR_2	0.1337
R_1 (all data)	0.0522
R_1	0.0495

5b

Experimental. Single colourless block-shaped crystals of **5b** were recrystallised from pentane by slow evaporation. A suitable crystal 0.27×0.24×0.08 mm^3 was selected and mounted on a MITIGEN holder in Paratone oil on a Rigaku Oxford Diffraction SuperNova diffractometer. The crystal was kept at a steady T = 120.0 K during data collection. The structure was solved with the **ShelXS**[12] structure solution program using the Direct Methods solution method and by using **Olex2**[10] as the graphical interface. The model was refined with version 2018/3 of **ShelXL**[11] using Least Squares minimisation.

Crystal Data. $C_{29}H_{51}AlN_3PSi$, M_r = 527.76, monoclinic, $P2_1/n$ (No. 14), a = 10.1515(4) Å, b = 12.1201(5) Å, c = 25.7328(9) Å, β = 92.986(3)°, α = γ = 90°, V = 3161.8(2) Å^3, T = 120.0 K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.174, 43426 reflections measured, 8082 unique (R_{int} = 0.0579) which were used in all calculations. The final wR_2 was 0.1113 (all data) and R_1 was 0.0521 (I > 2(I)).

Plot.



Hydrogen atoms (other than H1 and H2) and disorder omitted for clarity. Thermal ellipsoids set to 50%

Compound	**5b**
Formula	$C_{29}H_{51}AlN_3PSi$
$D_{calc.}$/ g cm^{-3}	1.109
μ/mm^{-1}	0.174
Formula Weight	527.76
Colour	colourless
Shape	block
Size/mm^3	0.27×0.24×0.08
T/K	120.0
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	10.1515(4)
b/Å	12.1201(5)
c/Å	25.7328(9)
α/°	90
β/°	92.986(3)
γ/°	90
V/Å^3	3161.8(2)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	3.116
Θ_{max}/°	29.764
Measured Refl.	43426
Independent Refl.	8082
Reflections with I > 2(I)	6872
R_{int}	0.0579
Parameters	382
Restraints	62
Largest Peak	0.432
Deepest Hole	-0.313
GooF	1.178
wR_2 (all data)	0.1113
wR_2	0.1064
R_1 (all data)	0.0661
R_1	0.0521

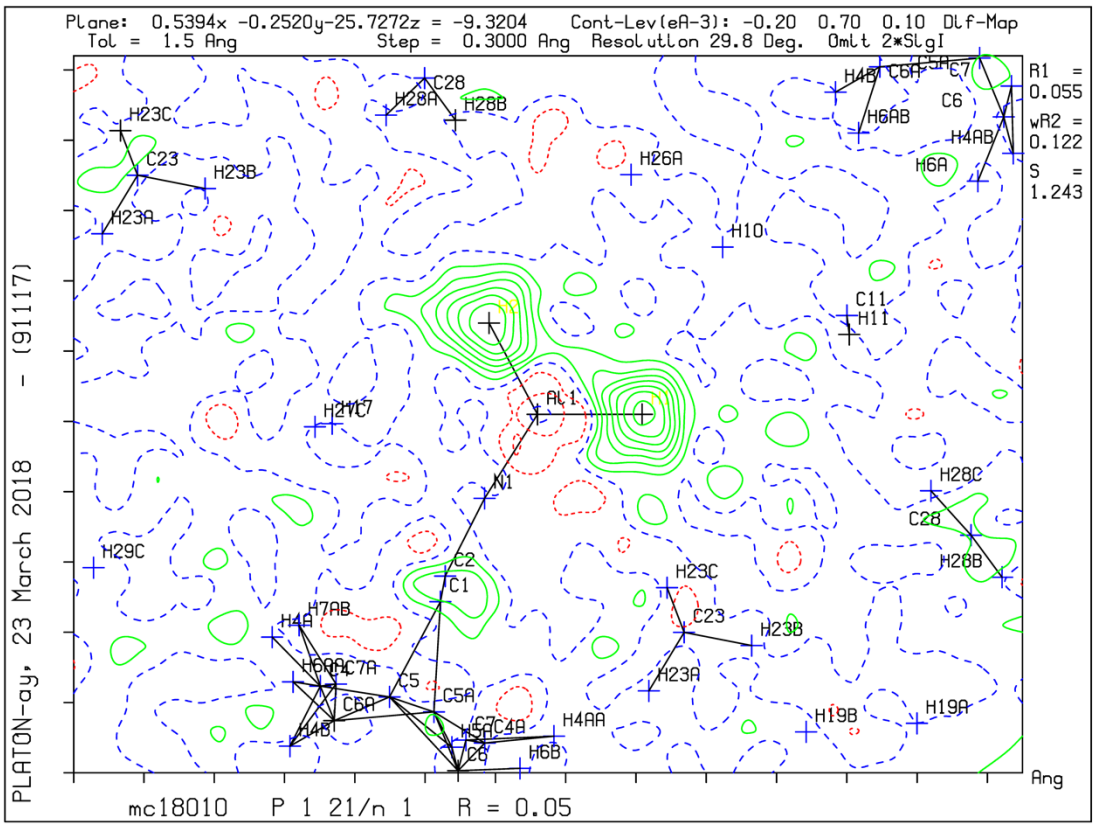


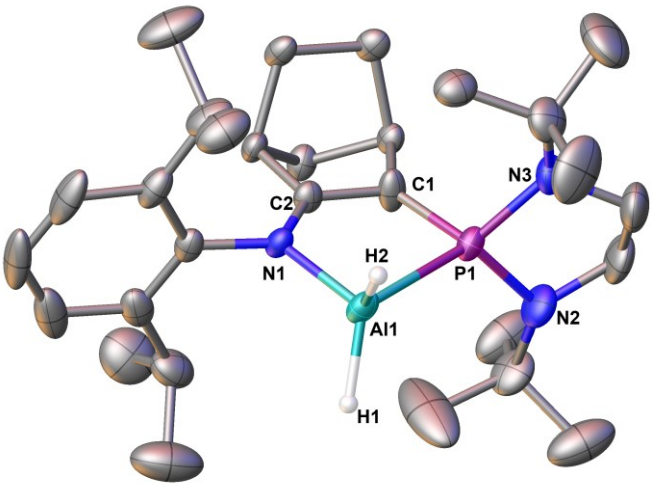
Figure 1: Electron density corresponding with H1 and H2 in 5**b**.

5c

Experimental. Single colourless plate-shaped crystals of **5c** were recrystallised from hexane by slow cooling. A suitable crystal 0.50×0.31×0.09 mm^3 was selected and mounted on a MITIGEN holder in Paratone oil on a Rigaku Oxford Diffraction SuperNova diffractometer. The crystal was kept at a steady T = 120 K during data collection. The structure was solved with the Superflip[7-9] structure solution program using the Charge Flipping solution method and by using **Olex2**[10] as the graphical interface. The model was refined with version 2018/3 of **ShelXL**[11] using Least Squares minimisation.

Crystal Data. $C_{29}H_{49}AlN_3P$, M_r = 497.66, monoclinic, $P2_1/c$ (No. 14), a = 17.2654(5) Å, b = 10.1618(4) Å, c = 17.1885(6) Å, β = 93.501(3)°, α = γ = 90°, V = 3010.05(18) Å^3, T = 120 K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.141, 49396 reflections measured, 6144 unique (R_{int} = 0.0557) which were used in all calculations. The final wR_2 was 0.1621 (all data) and R_1 was 0.0696 (I > 2(I)).

Plot.



Hydrogen atoms (other than H1 and H2) and disorder omitted for clarity. Thermal ellipsoids set to 50%

Compound	**5c**
Formula	$C_{29}H_{49}AlN_3P$
$D_{calc.}$/ g cm^{-3}	1.098
μ/mm^{-1}	0.141
Formula Weight	497.66
Colour	colourless
Shape	plate
Size/mm^3	0.50×0.31×0.09
T/K	120
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	17.2654(5)
b/Å	10.1618(4)
c/Å	17.1885(6)
α/°	90
β/°	93.501(3)
γ/°	90
V/Å^3	3010.05(18)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	3.100
Θ_{max}/°	26.371
Measured Refl.	49396
Independent Refl.	6144
Reflections with I > 2(I)	5394
R_{int}	0.0557
Parameters	371
Restraints	116
Largest Peak	0.646
Deepest Hole	-0.738
GooF	1.135
wR_2 (all data)	0.1621
wR_2	0.1571
R_1 (all data)	0.0792
R_1	0.0696

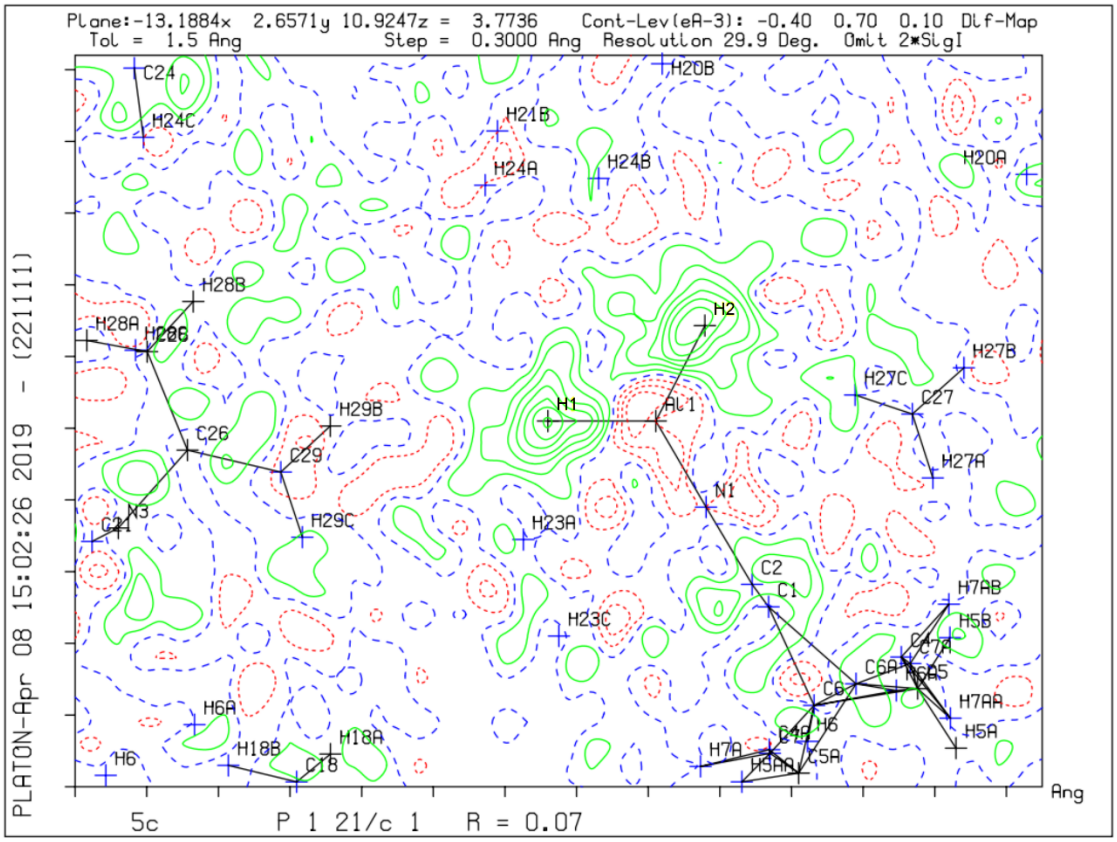
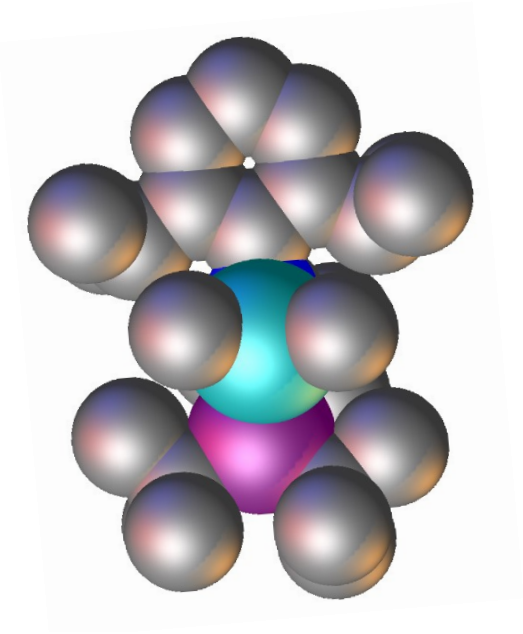


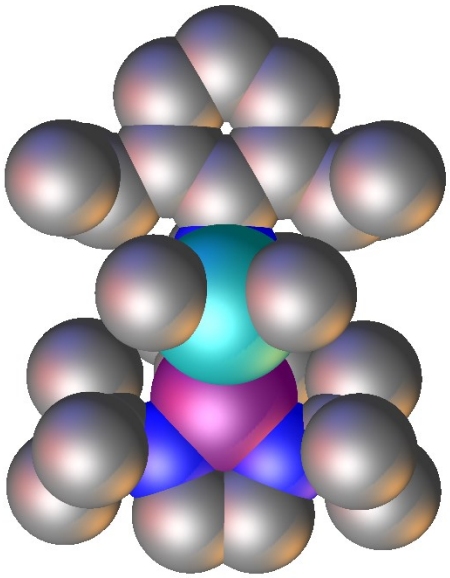
Figure 2: Electron density corresponding with H1 and H2 in **5c**.

Space Filling Diagrams

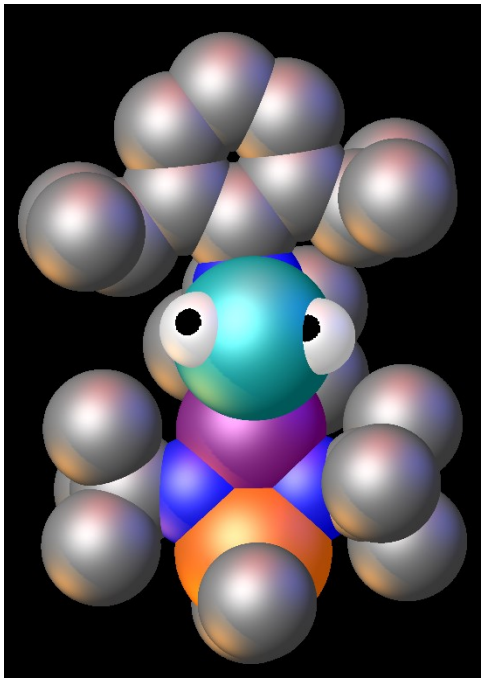
3a



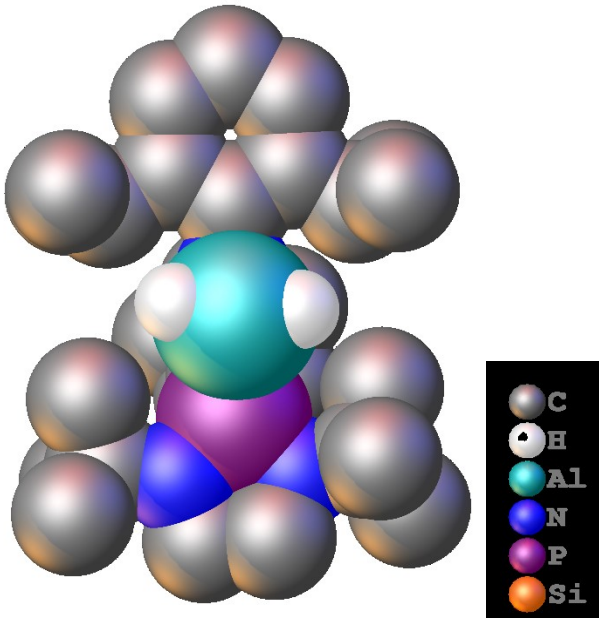
3c



5b



5c



Solid State NMR

Experimental Details:

Solid-state NMR spectra were recorded using a Bruker Avance III spectrometer equipped with a 9.4 T wide-bore superconducting magnet (Larmor frequencies of 400.1, 162.0 and 104.3 MHz for ^{1}H, ^{31}P and ^{27}Al, respectively). Samples were packed under Ar into standard 4 mm rotors and, for ^{31}P, the rotors were rotated at the magic angle at 14 kHz. ^{31}P NMR spectra were recorded with signal averaging for 8 transients with a recycle interval of 30 s. High-power ($\nu_1 \approx 90$ kHz) TPPM-15 decoupling of ^{1}H was applied during acquisition. ^{27}Al NMR spectra were recorded for static samples with signal averaging for between 128 and 512 transients with a recycle interval of 1 s. The WURST-QCPMG pulse sequence was used with optimised WURST pulses of 50 μs (1 MHz nominal bandwidth) for excitation and refocusing. The CPMG echo train comprised 100 echoes with a spacing of 250 μs, giving a spikelet separation in the spectrum of 4 kHz. High-power ($\nu_1 \approx 60$ kHz) continuous-wave decoupling of ^{1}H was applied during acquisition. Chemical shifts are reported in ppm relative to 85% H_3PO_4 and 1.1 M $Al(NO_3)_3$ using BPO_4 ($\delta = -29.6$ ppm) and $Al(acac)_3$ ($\delta_{iso} = 0.0$ ppm, $C_Q = 3.02$ MHz, $\eta_Q = 0.17$).

$^{31}P\{^{1}H\}$ MAS NMR

Figure S1 shows the $^{31}P\{^{1}H\}$ solid-state NMR spectra of the samples. Unlike in solution-state NMR, where *J* coupling to quadrupolar nuclei is rarely observed owing to motion-related relaxation effects, there is restricted molecular motion in solids and larger *J* couplings can be observed directly. The effect of coupling to ^{27}Al (spin I = 5/2, abundance = 100%) should be to split the spectrum into an equally-spaced 1:1:1:1:1:1 sextet. However, as observed below, the ^{27}Al species all have very large quadrupolar coupling constants and, as ^{31}P and ^{27}Al both have reasonably high gyromagnetic ratios, there will be a significant dipolar-quadrupolar cross term that will alter the individual spacings in the sextet. This effect can be seen most clearly for **5b**, but is present to some extent in all three samples, leading to the asymmetric lineshapes observed. In addition, minor resonances corresponding to impurities (indicated with daggers in Figure S1) are observed for **3a** (71 and 75 ppm) and **3b** (26 and 102 ppm) due to some air exposure of these samples during preparation for solid state NMR experiments.

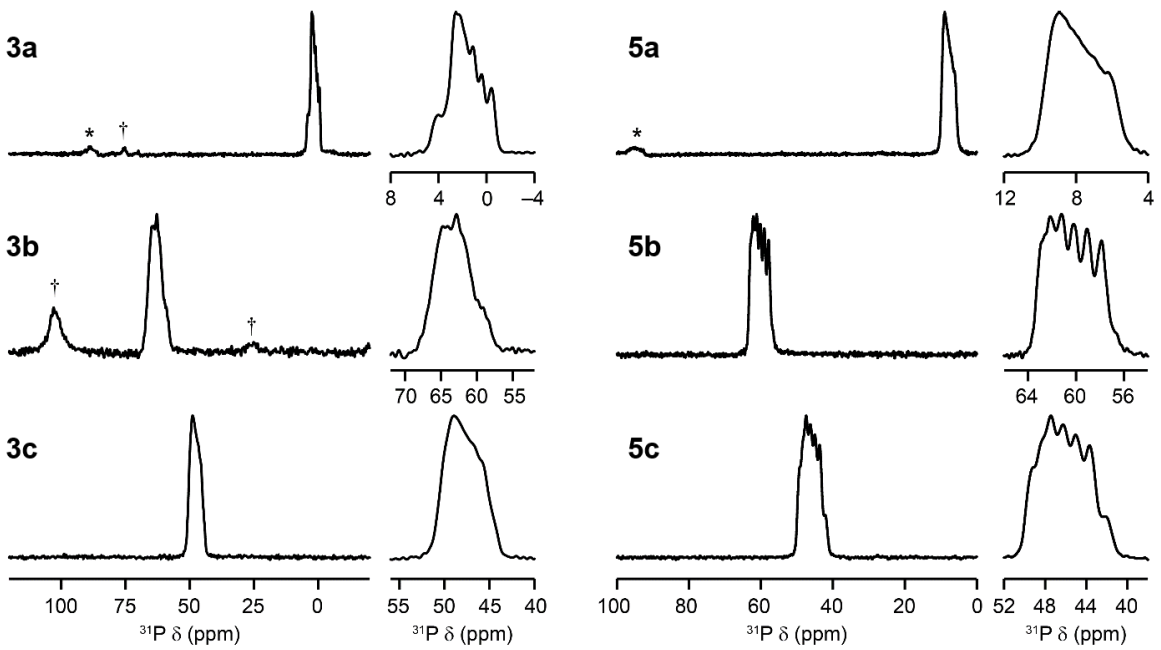


Figure S2: $^{31}P\{^{1}H\}$ (9.4 T, 14 kHz MAS) NMR spectra of the six samples. Insets show expansions of the isotropic resonances. * = spinning sideband, † = impurity.

The chemical shifts are summarised in Table S1. For **3a, 3b, 5a** and **5b** the chemical shifts are in good agreement with solution-state values. For **3c** and **5c**, only one resonance is observed in the solid state (47.8 and 47.5 ppm respectively), which is in good agreement with the upfield resonances observed in solution (49.7 and 47.8 ppm respectively). This indicates only one isomer of **3c** and **5c** is present in the solid state. The broadening of the signals indicates a direct bond between the phosphorus and aluminum, i.e. κ^2-coordination of the ligand to aluminum. This is in agreement with the solid state structures obtained by X-ray crystallography.

Table S3: ^{31}P chemical shifts observed in solution- and solid-state NMR spectra. The values for the solid state are taken as the centre of gravity of the observed resonance.

Sample	**$\delta_{(solution)}$ (ppm)**	**$\delta_{(solid)}$ (ppm)**
3a	1.6	1.9
3b	64.0	63.2
3c	99.9, 49.7	47.8
5a	8.0	8.9
5b	61.3	61.2
5c	96.9, 47.8	47.5

$^{27}Al\{^{1}H\}$ NMR

Initially, an attempt was made to record the ^{27}Al MAS NMR spectra of the hydrides, but no signal was observed, consistent with the solution-state observation. This suggested very broad resonances and, possibly, rapid relaxation owing to the directly bonded ^{1}H species. Therefore, a static wideline experiment with ^{1}H decoupling was used in a second attempt to observe the ^{27}Al species. Figure S2 shows the $^{27}Al\{^{1}H\}$ static CPMG spectra of the six samples. The CPMG experiment enhances peak height to noise at the expense of spectral resolution by forcing the signal into a series of sharp "spikelets". In this case, the spikelet spacing was selected to be 4 kHz, limiting the spectral resolution to this value (38.4 ppm at 9.4 T).

In all six spectra, a very broad resonance is observed with a shape that suggests a combination of large chemical shift anisotropy (CSA) and large quadrupolar coupling (CQ), with the lineshape depending on the relative magnitudes and orientations of the chemical shift and electric field gradient tensors. Initial analysis suggests CQ >8 MHz and CSAs of hundreds of ppm.

The spectral data are consistent with the solution-state data. While the CSA contribution to the ^{27}Al NMR spectrum will be absent in solution, the large quadrupolar contribution will remain and will lead to quadrupolar relaxation effects, which broaden the signal beyond the limit of detection in solution.

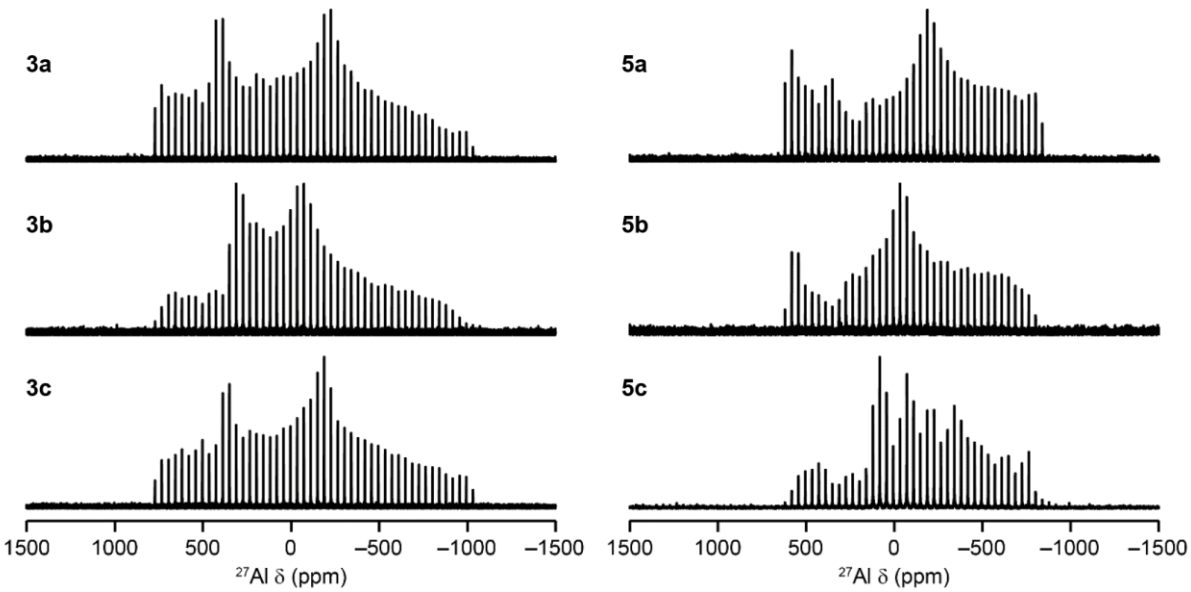


Figure S3: $^{27}Al\{^{1}H\}$ (9.4 T, static CPMG) NMR spectra of dimethyl aluminum complexes **3a-c** and aluminum dihydrides **5a-c**.

Computational methods

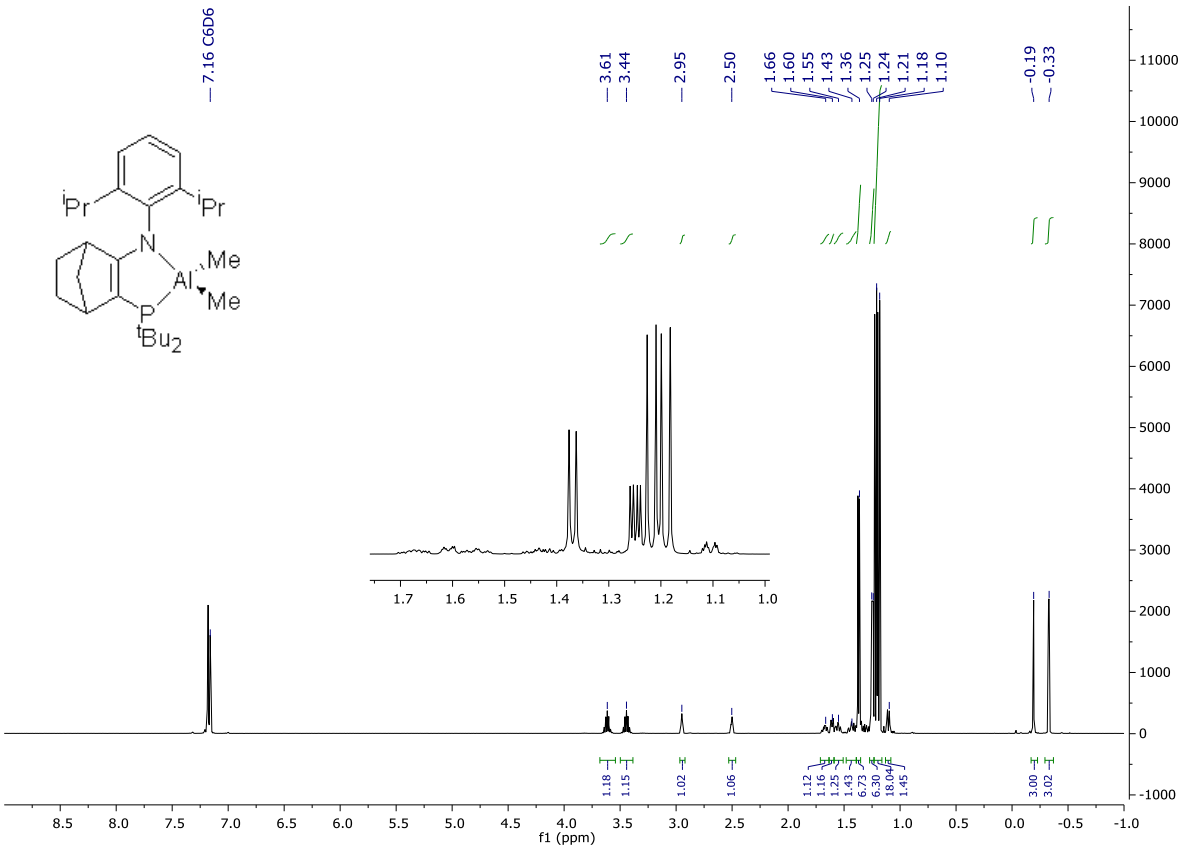
Computations were performed using the Gaussian16 program package.[13] Calculations were at the B3LYP/6,31G (PES scan), M062X/Def2SVPP,or M062X/6,31G+(d,p)/Lanl2DZ level. Use of the split basis set was essential for accurately replicating experimental Al–H stretching frequencies. Structures were optimised using crystal structures (where available) as starting points, and all stationary points were confirmed as minima by frequency analysis.

Optimised geometries

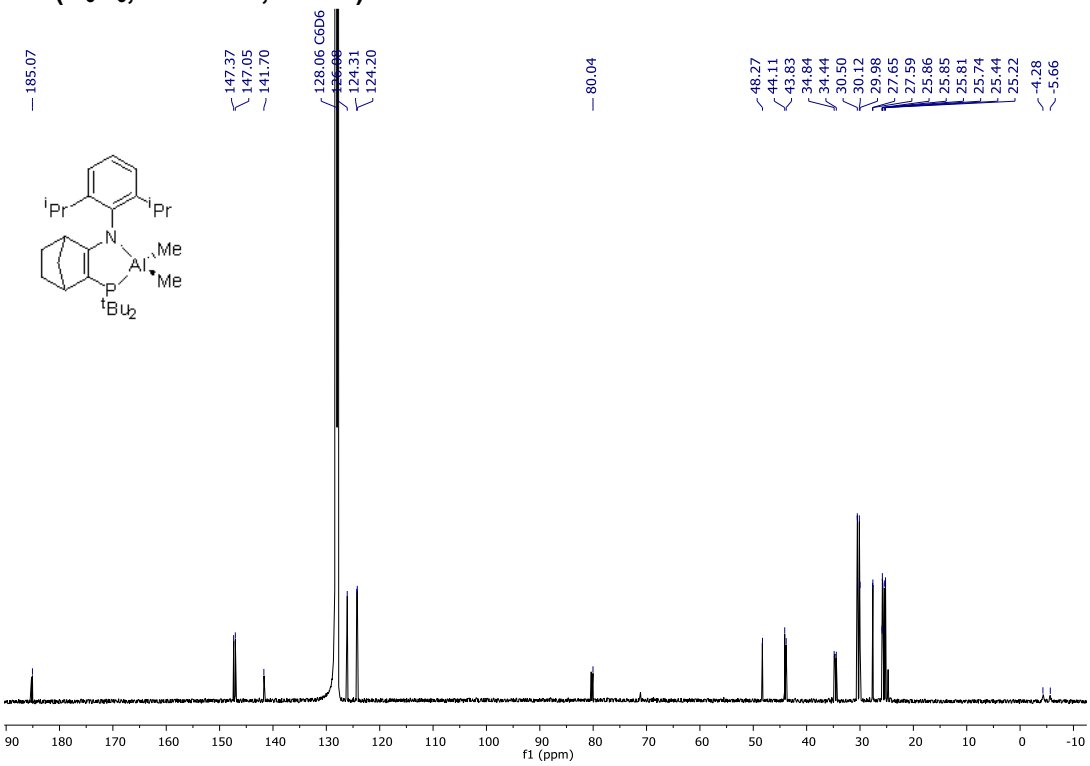
Optimised geometries for K^2-N,P-**5a**, K^2-N,P-**5b**, K^2-N,P-**5c**, K^2-N,N-**5c** and K^1-N-**5c** are supplied as .xyz files.

Solution Phase NMR Spectra for Novel Compounds:

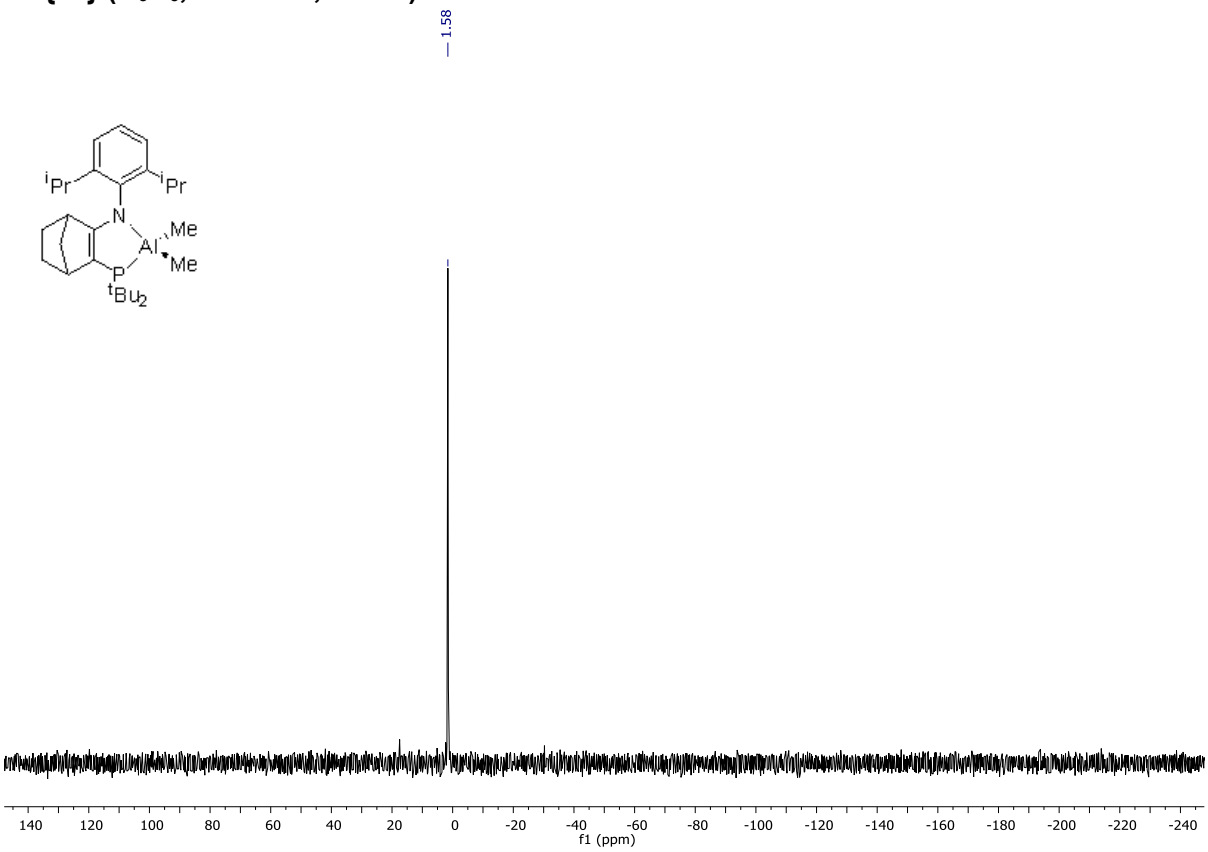
3a: ^{1}H (C_6D_6, 500 MHz, 300 K):



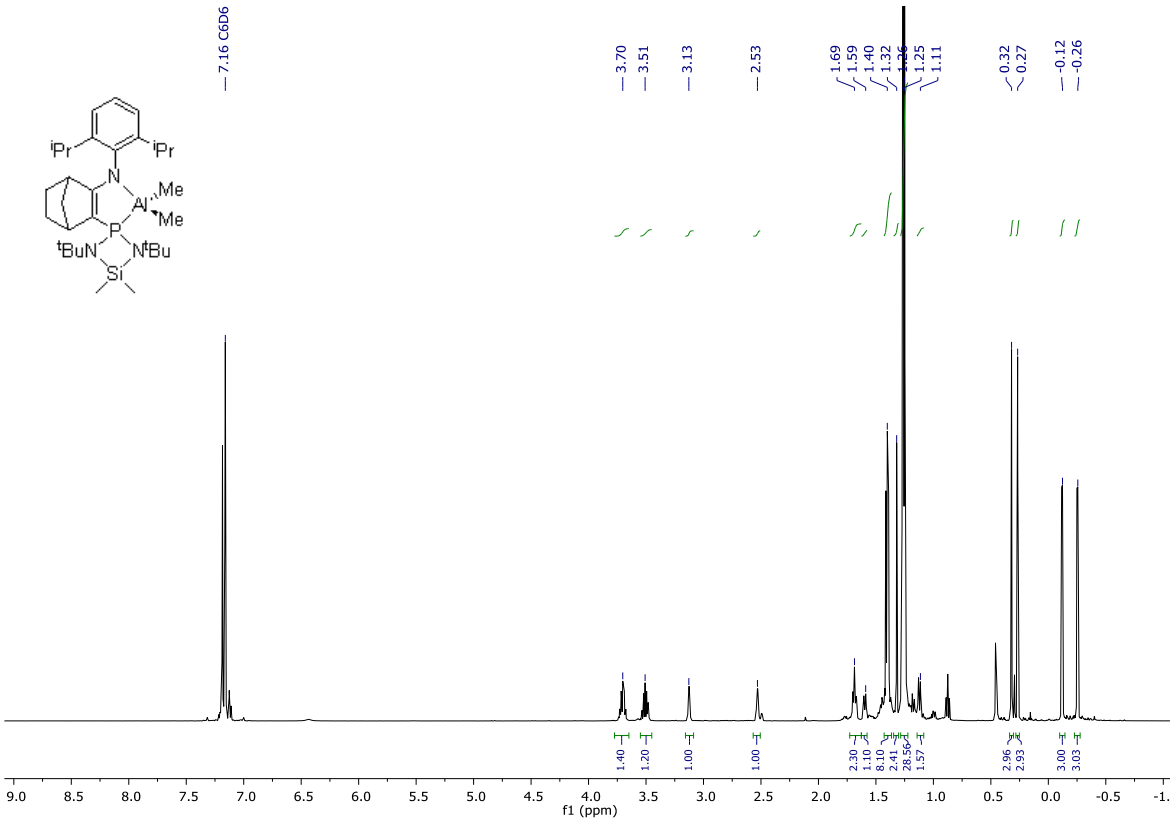
^{13}C (C_6D_6, 126 MHz, 300 K):



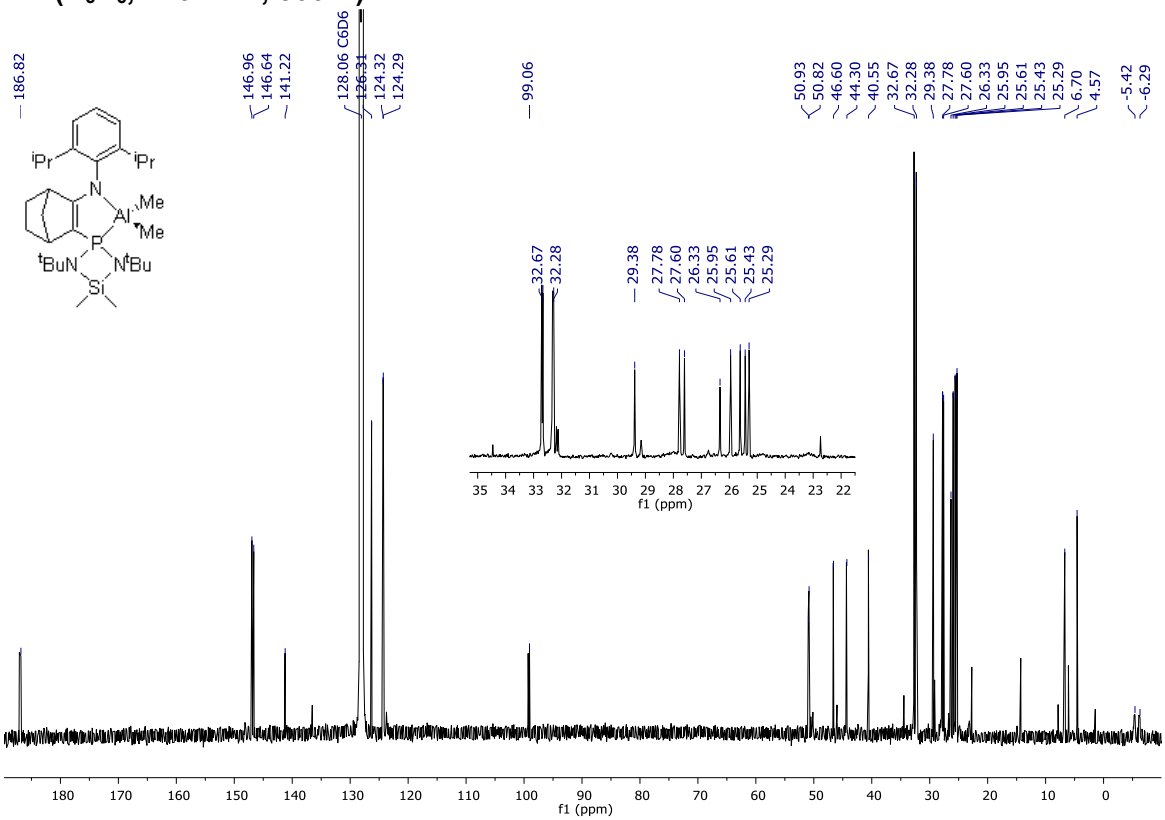
$^{31}P\{^1H\}$ (C_6D_6, 162 MHz, 300 K):



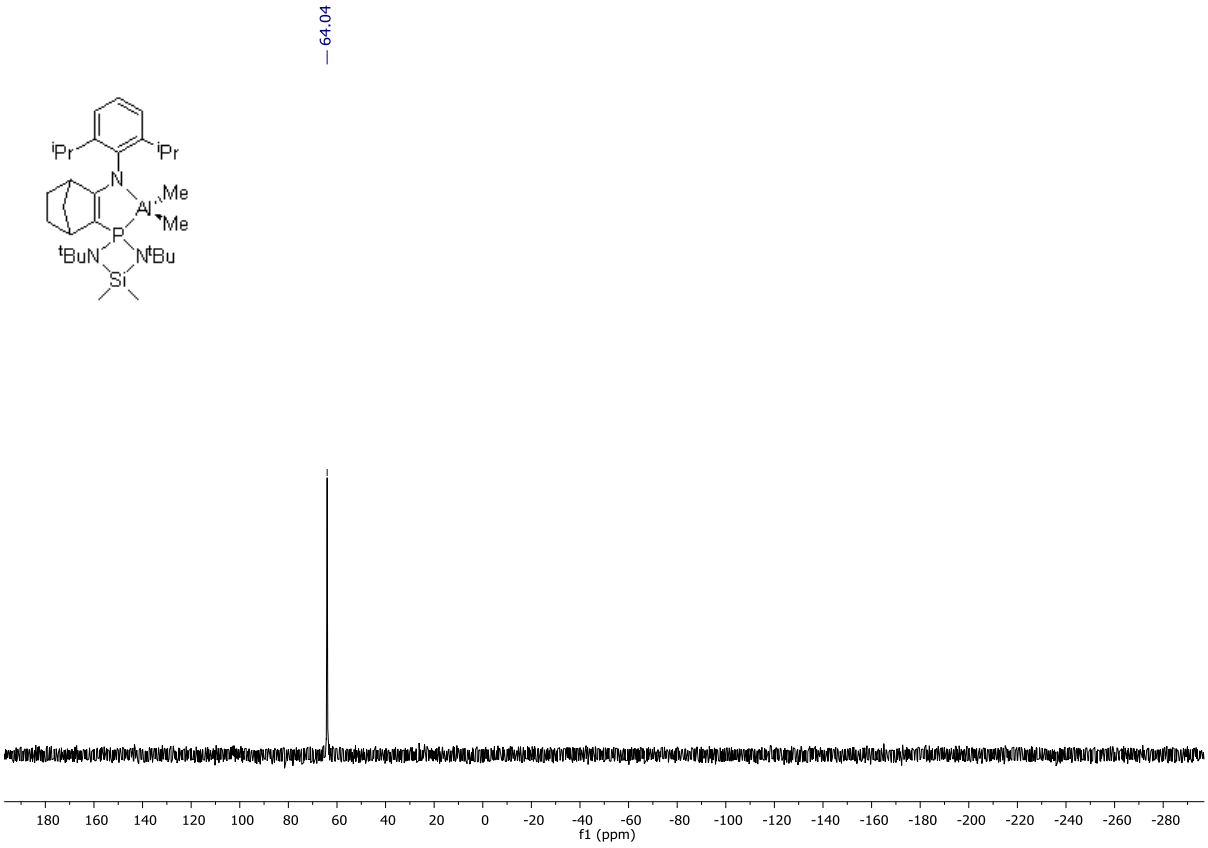
3b: ^{1}H (C_6D_6, 500 MHz, 300 K):



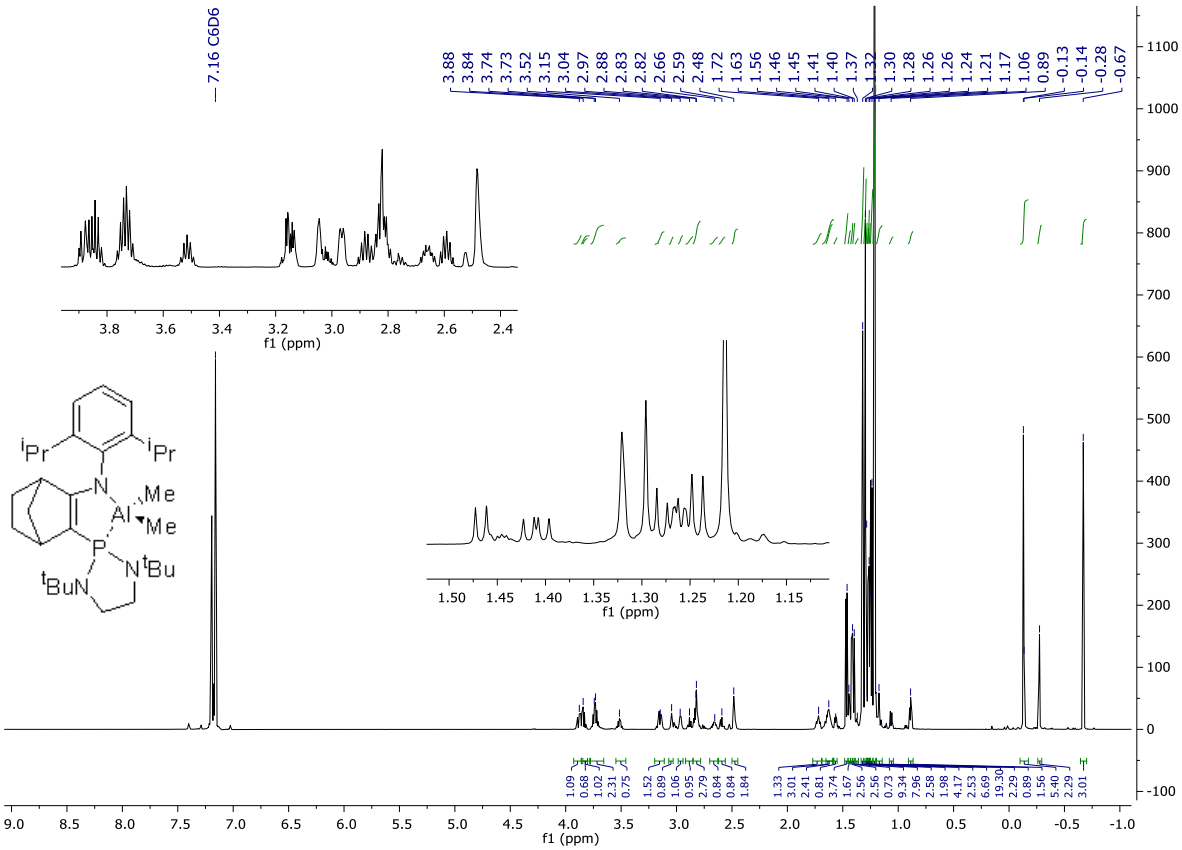
^{13}C (C_6D_6, 126 MHz, 300 K):



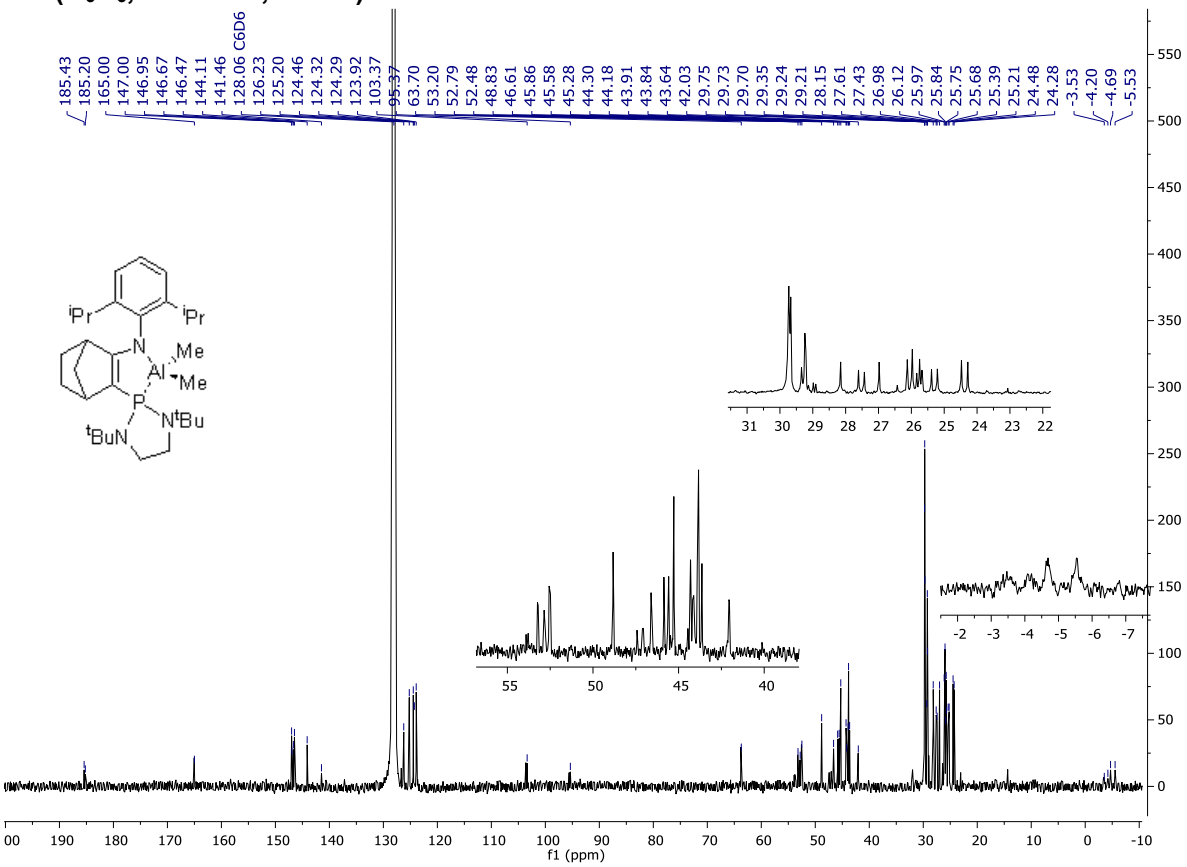
$^{31}P\{^{1}H\}$ (C_6D_6, 162 MHz, 300 K):



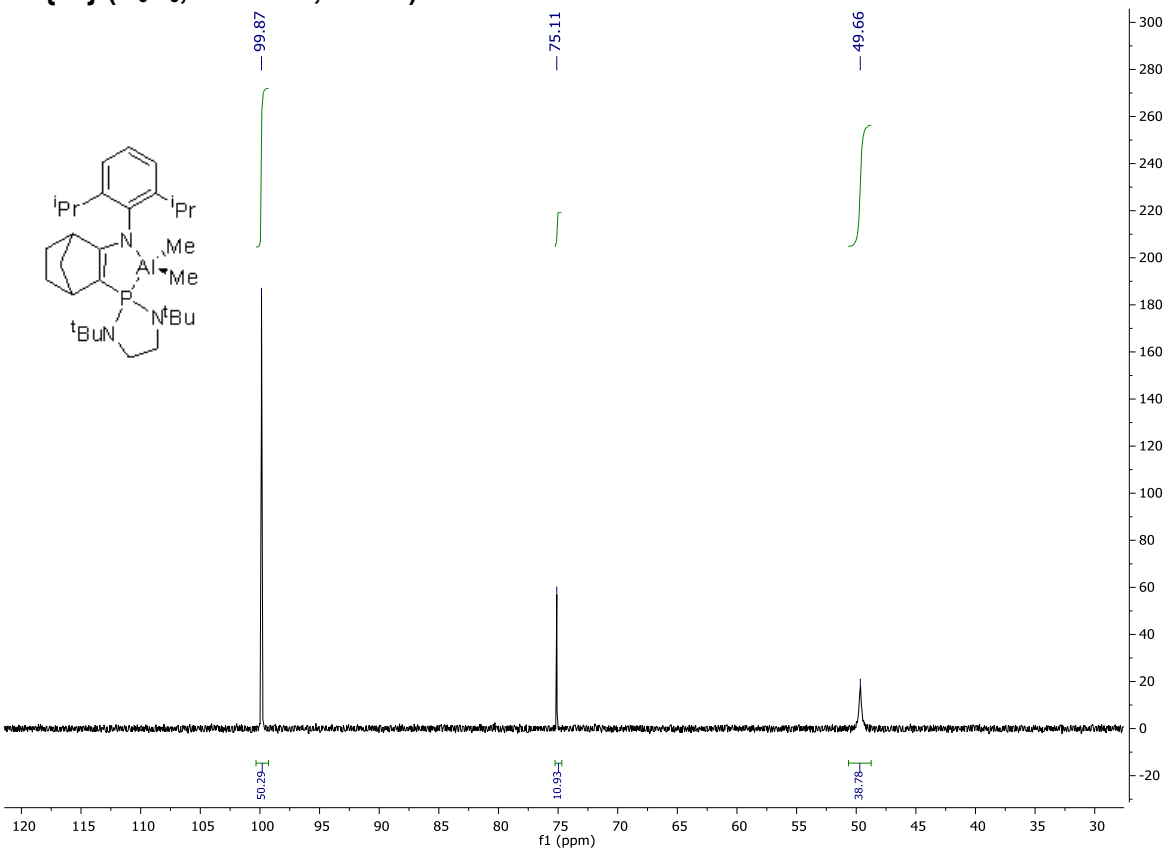
3c: ^{1}H (C_6D_6, 500 MHz, 300 K):



^{13}C (C_6D_6, 126 MHz, 300 K):

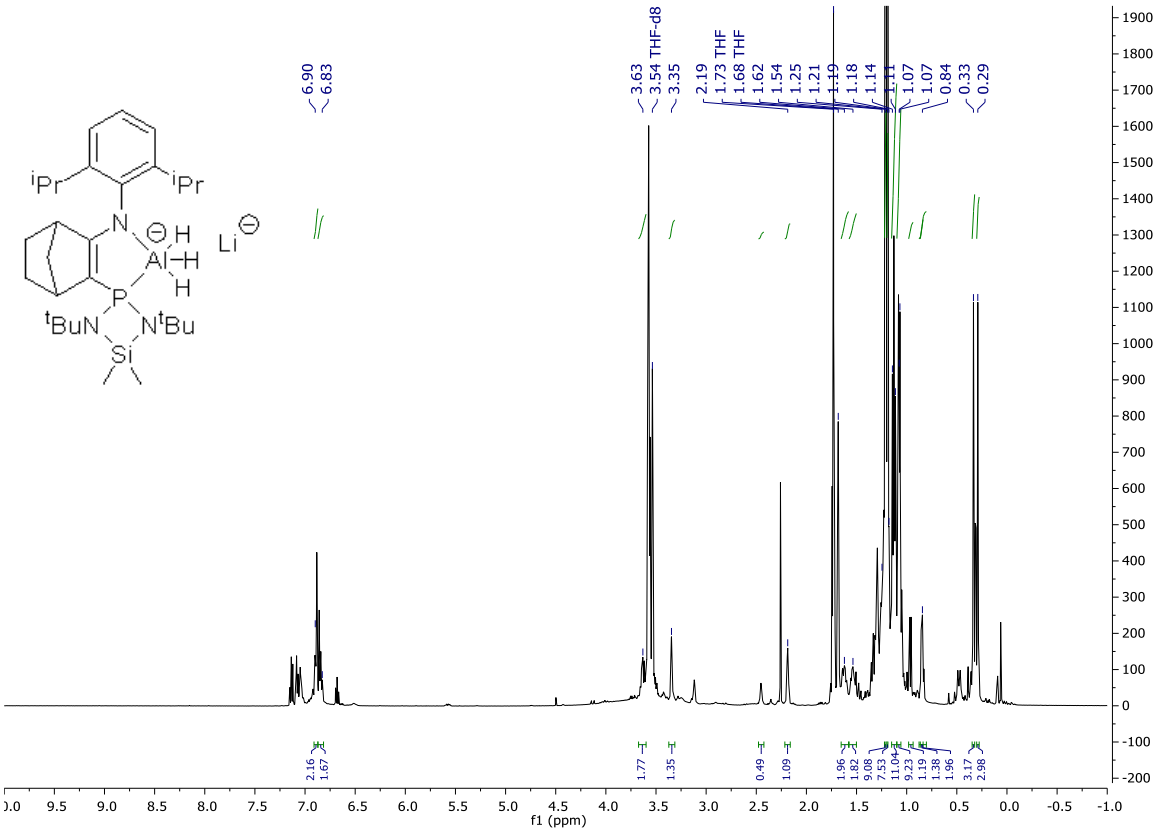


$^{31}P\{^{1}H\}$ (C_6D_6, 162 MHz, 300 K):

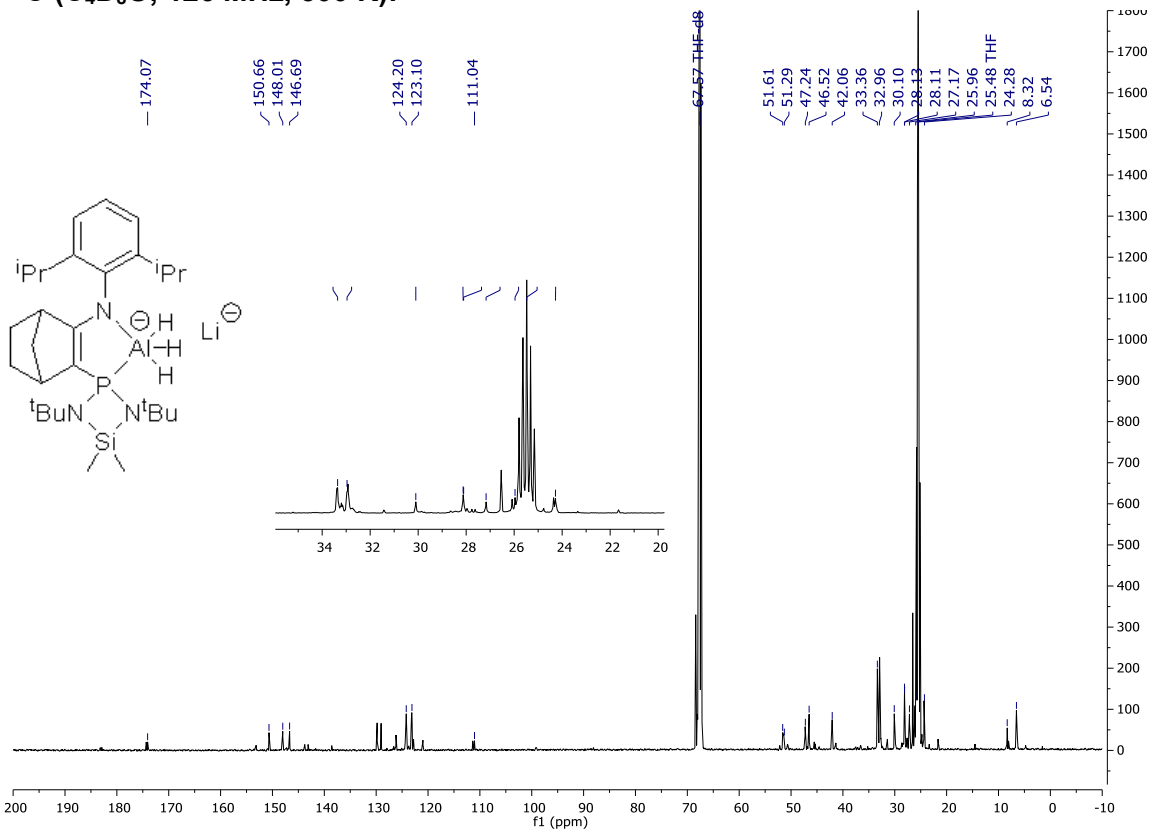


10% impurity observed at 75.1 ppm due to high sensitivity of compounds to air and moisture.

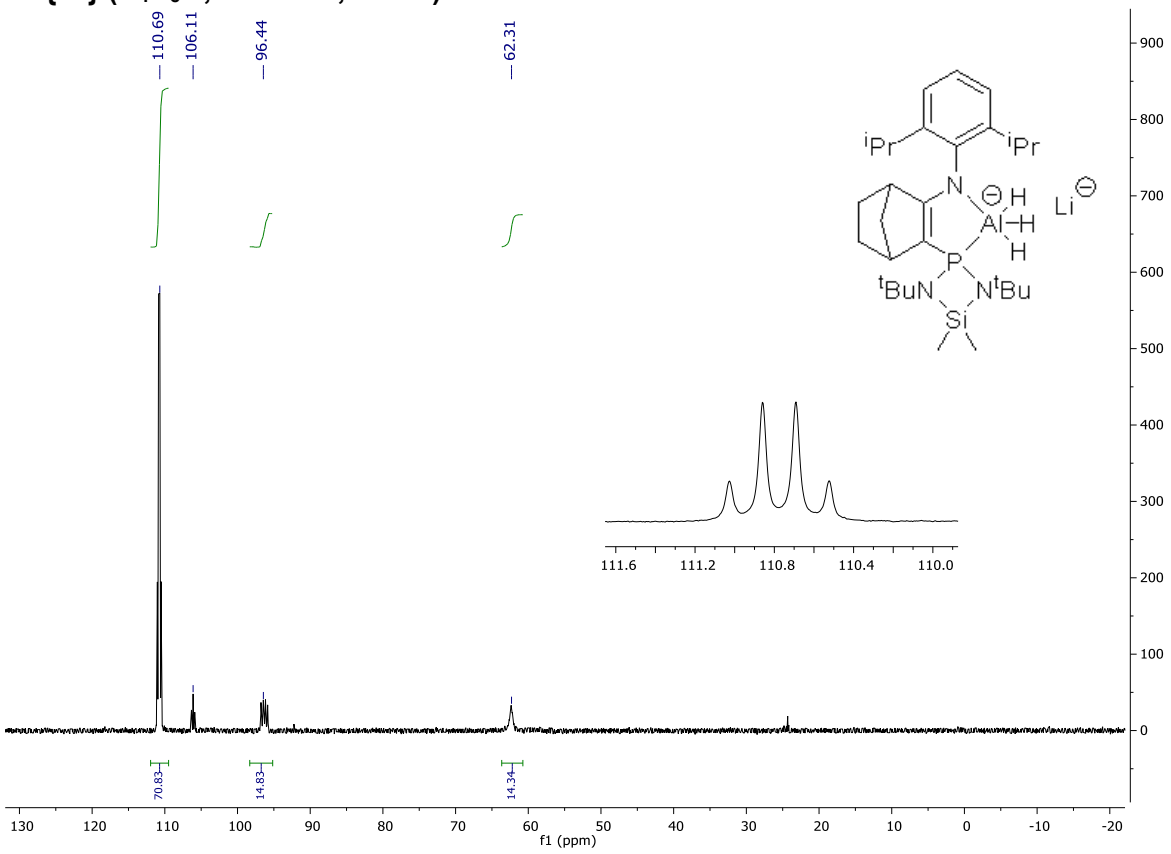
4b: ^{1}H (C_4D_8O, 500 MHz, 300 K):



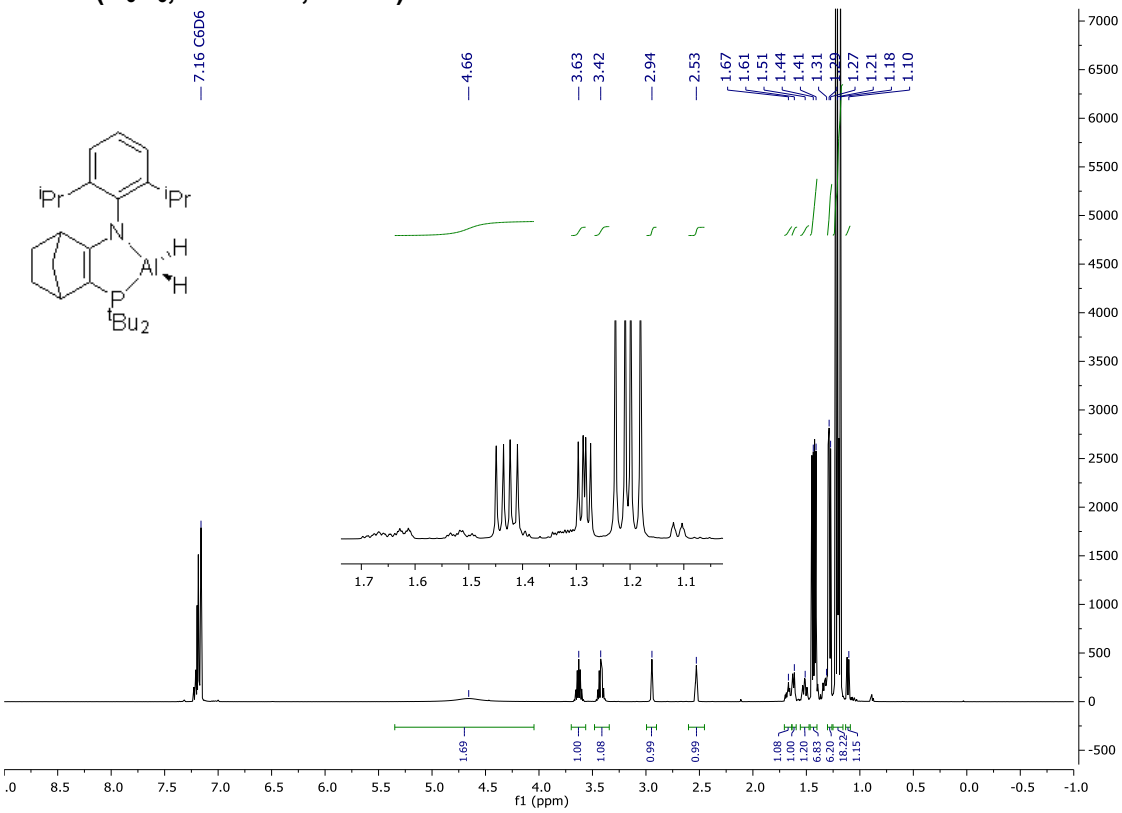
^{13}C (C_4D_8O, 126 MHz, 300 K):



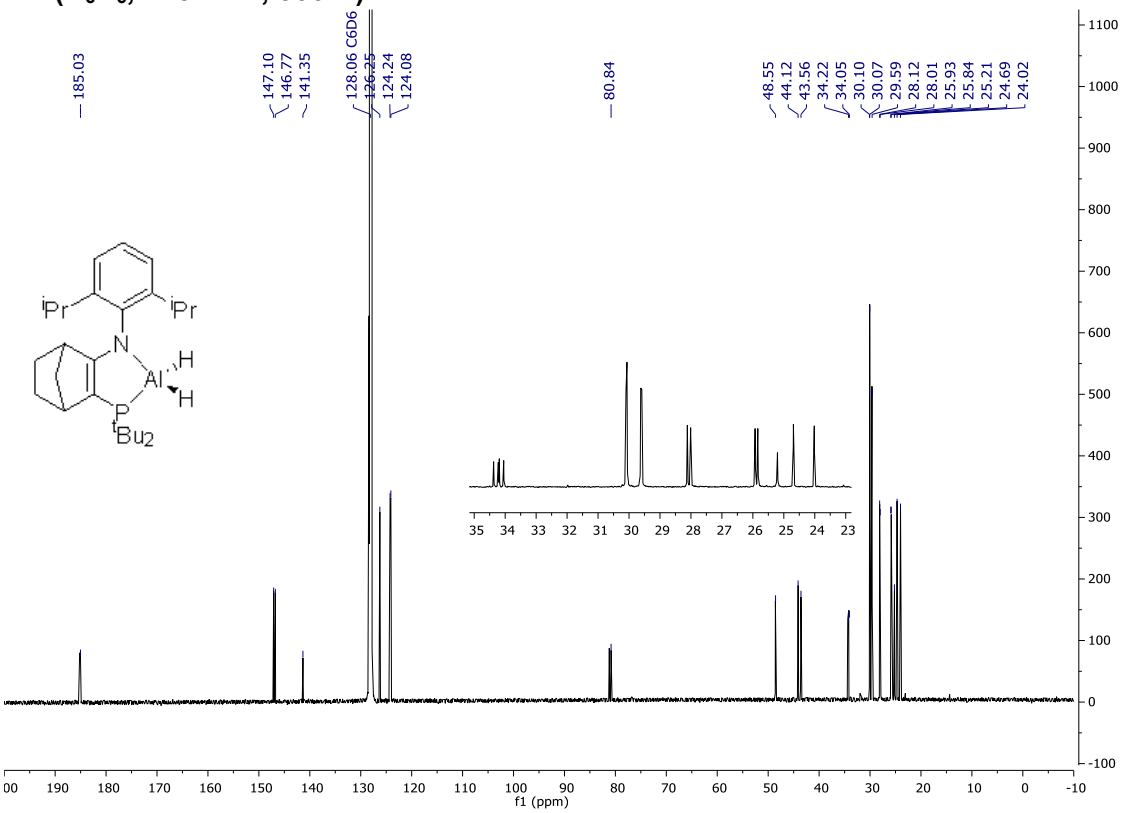
$^{31}P\{^{1}H\}$ (C_4D_8O, 162 MHz, 300 K):



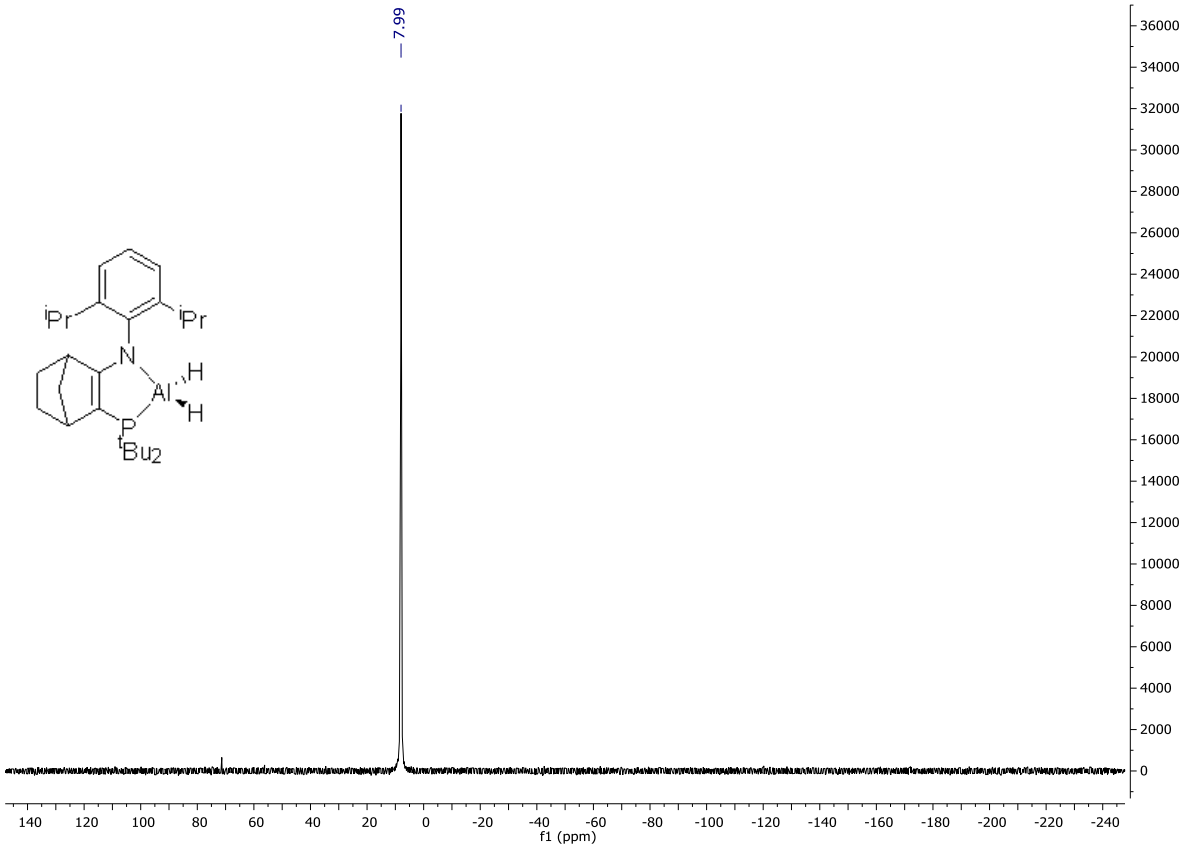
5a: ^{1}H (C_6D_6, 500 MHz, 300 K):



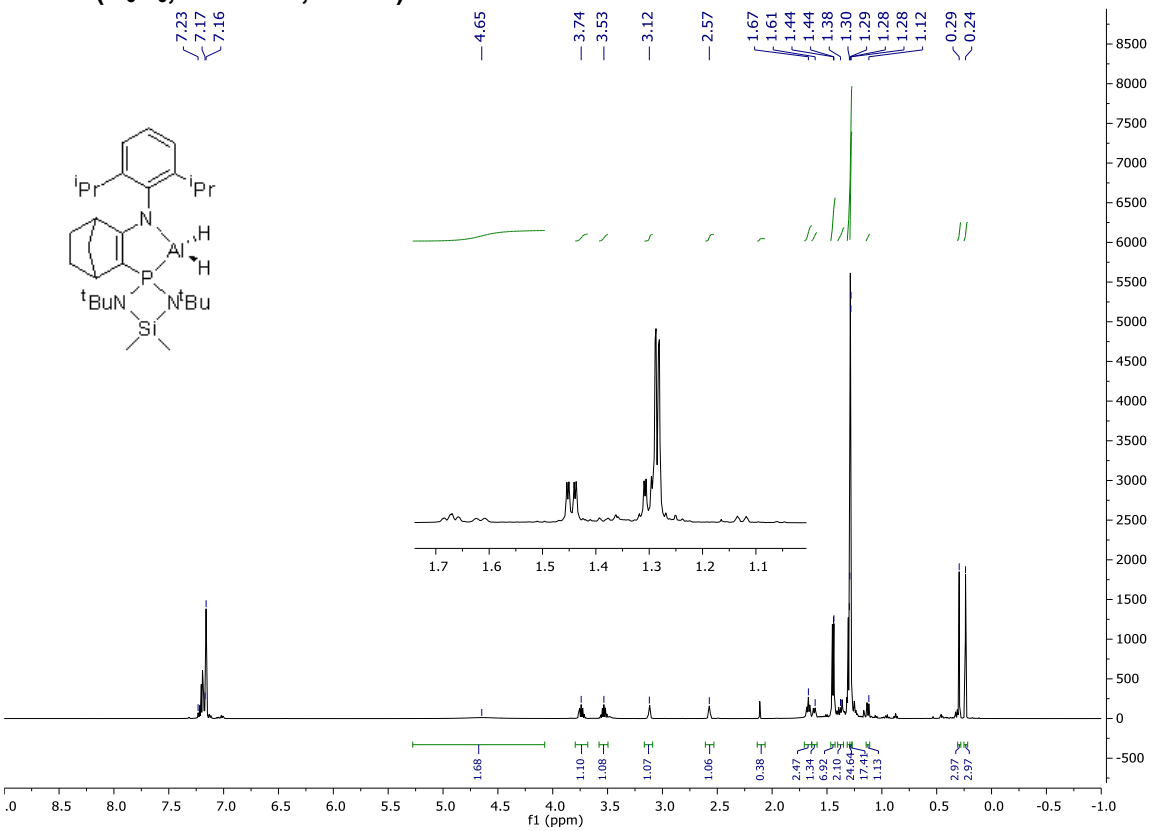
^{13}C (C_6D_6, 126 MHz, 300 K):



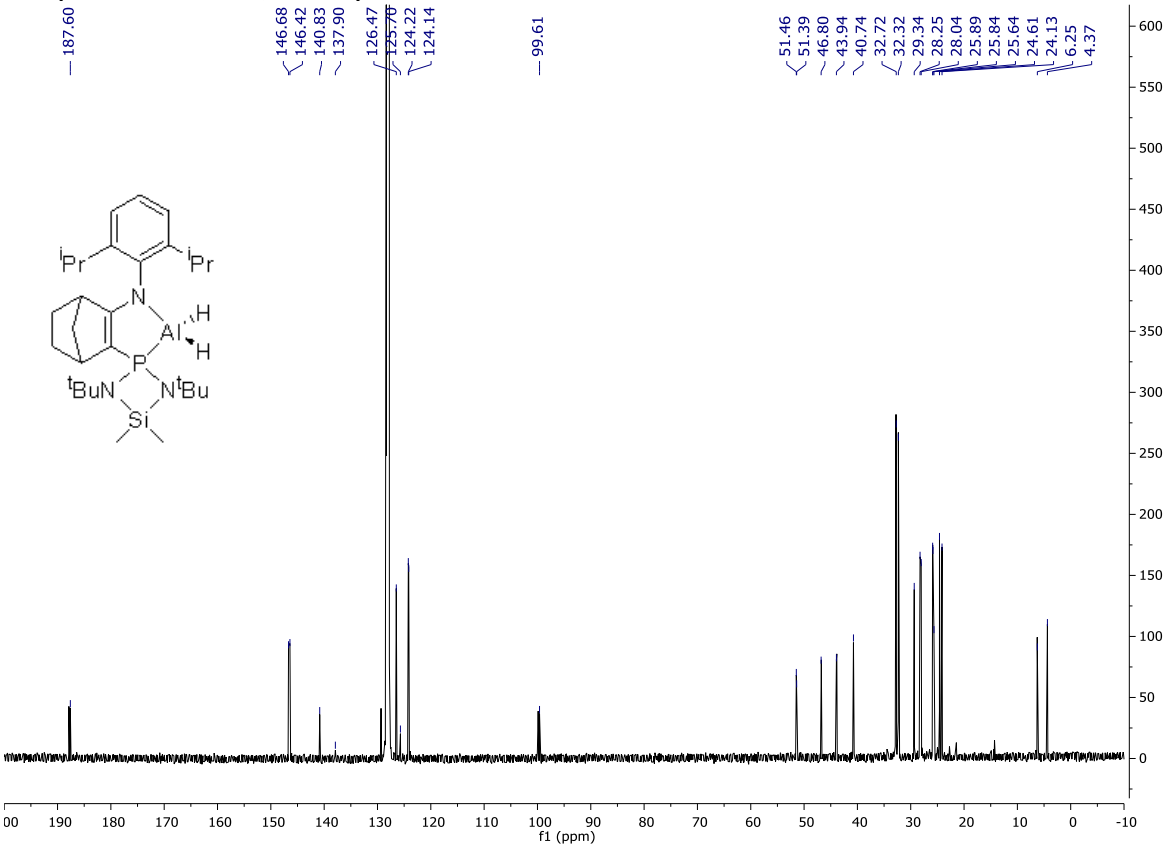
$^{31}P\{^{1}H\}$ (C_6D_6, 162 MHz, 300 K):



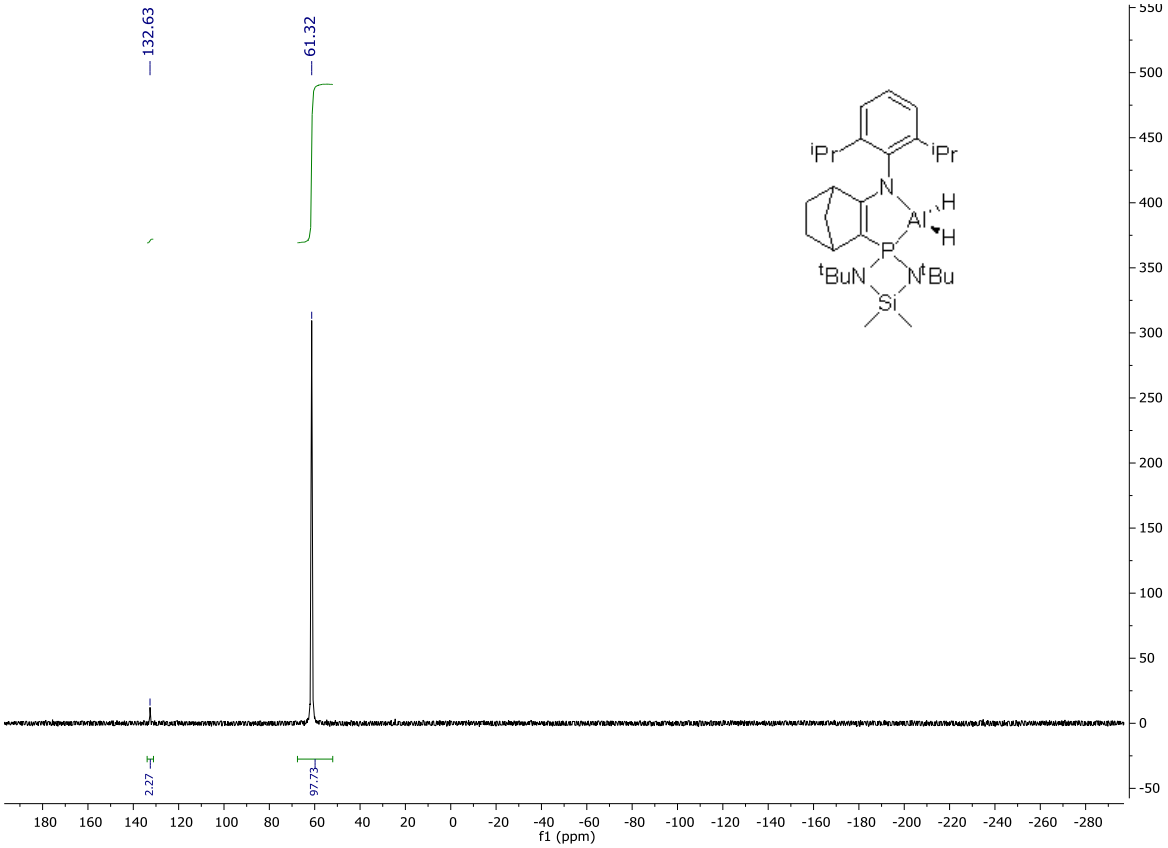
5b: ^{1}H (C_6D_6, 500 MHz, 300 K):



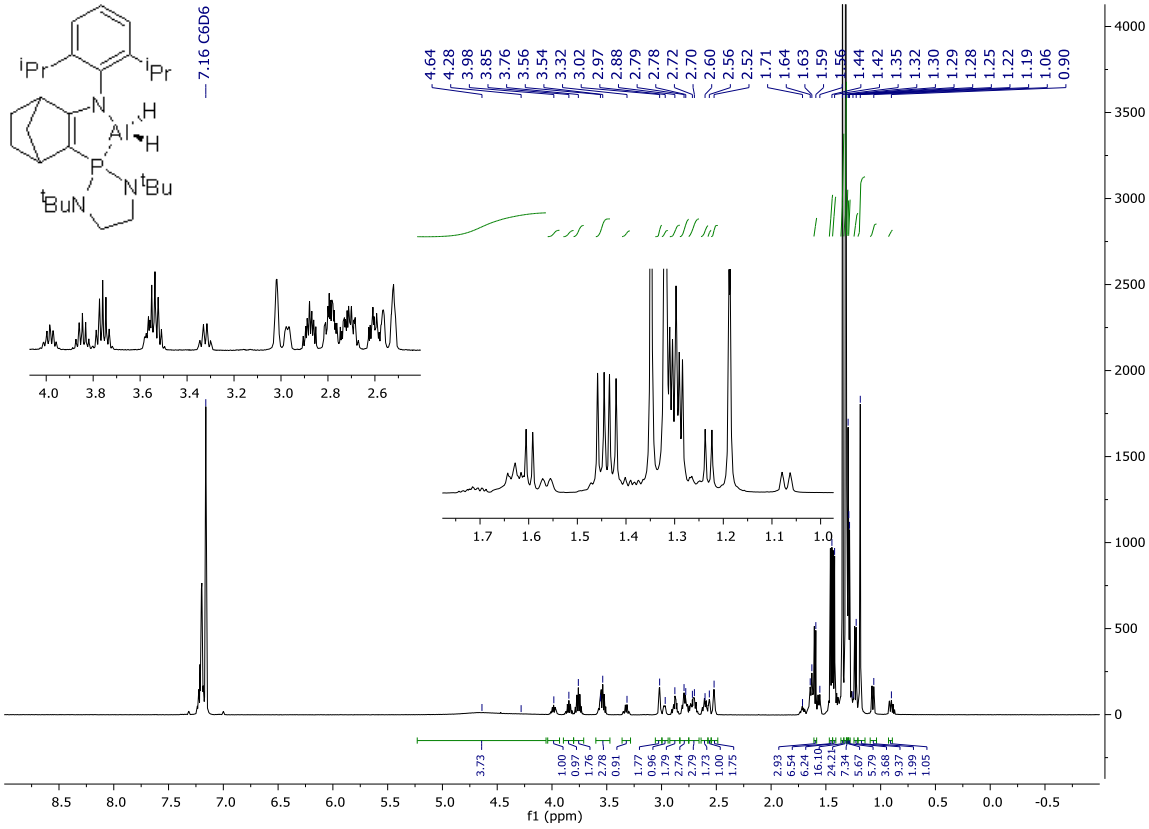
^{13}C (C_6D_6, 126 MHz, 300 K):



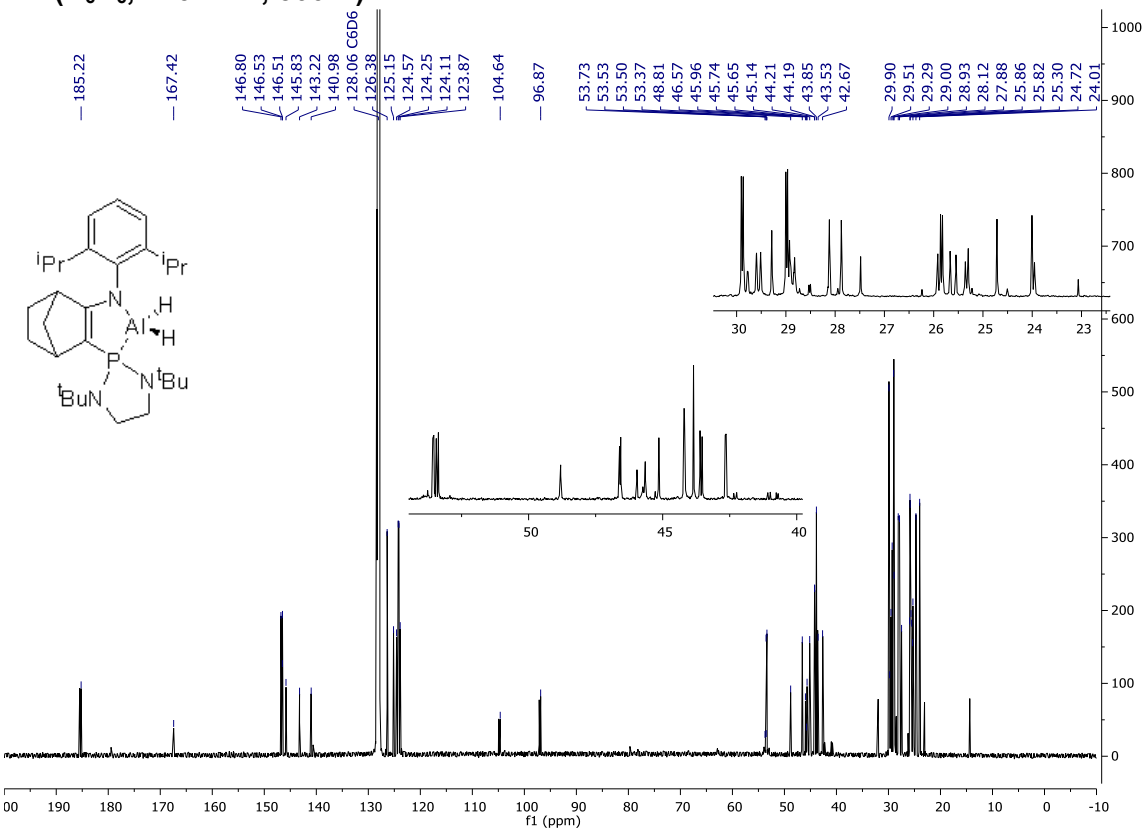
$^{31}P\{^{1}H\}$ (C_6D_6, 162 MHz, 300 K):



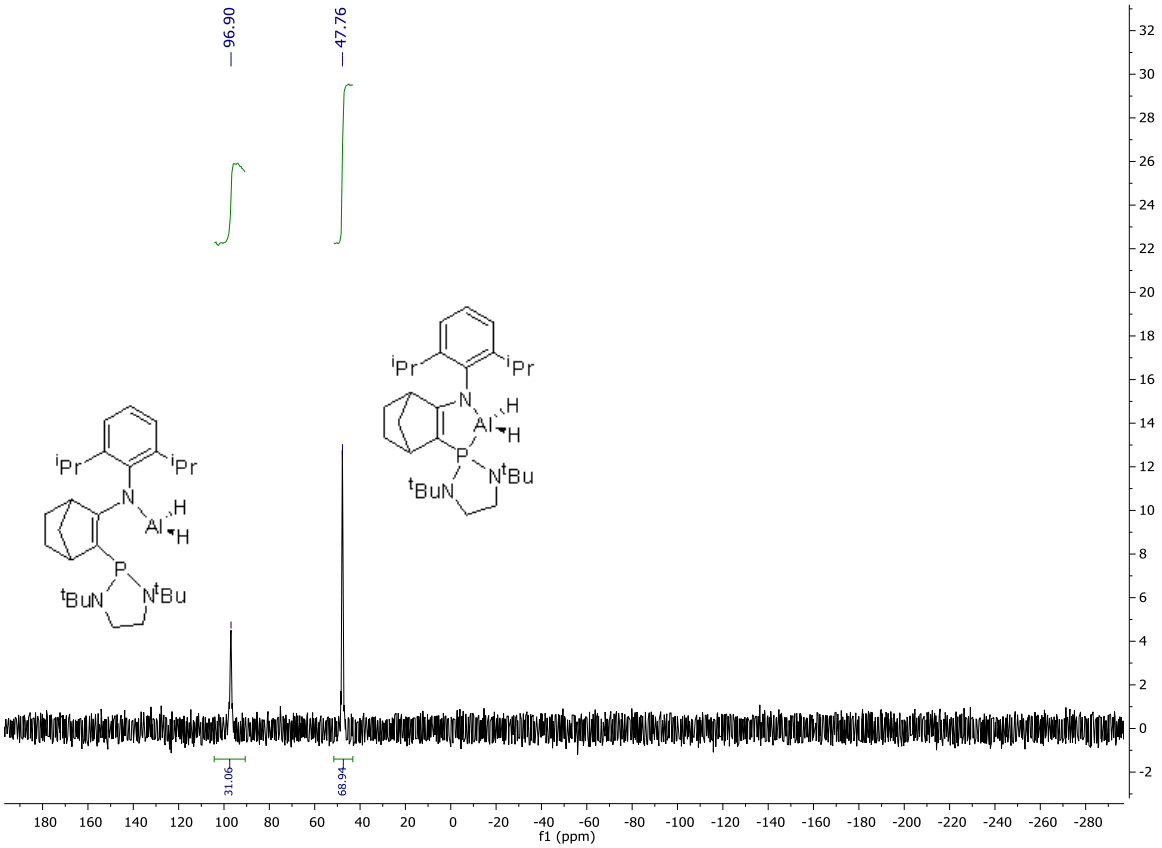
5c: ^{1}H (C_6D_6, 500 MHz, 300 K):



^{13}C (C_6D_6, 126 MHz, 300 K):



$^{31}P\{^{1}H\}$ (C_6D_6, 162 MHz, 300 K):



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