Electronic Supplementary Material (ESI) for Dalton Transactions.

Ligand coordination modulates reductive elimination from Aluminium(III)

Supporting Information

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Contents

1. Synthesis

General

All manipulations were carried out under an inert atmosphere of nitrogen or argon using Schlenk or glovebox techniques. Solvents were dried under nitrogen or argon over sodium dispersion and benzophenone and distilled. C_6D_6 and toluene-d_8 were dried under argon, over potassium metal and distilled. NMR spectra were recorded on Bruker PRO 500 MHz spectrometer. ^{1}H and ^{13}C spectra were referenced to residual solvent signals, and ^{27}Al spectra were referenced externally to $Al(NO_3)_3$ in D_2O (1.1 M). Cp*$_2$AlH,[1] tetramethylimidazolylidene **3a**,[2] diisopropyldimethyl imidazolylidene **3b**,[2] and were synthesised using literature procedures. Dimethylaminopyrine (DMAP) was purchased from commercial suppliers and used without further purification.

Preparation of Cp*$_2$AlH[tetramethylimidazolylidene] (4a)

A mixture of tetramethylimidazolylidene (56.0 mg, 0.45 mmol) and Cp*$_2$AlH (133.8 mg, 0.45 mmol) was dissolved in C_6H_6 (10 mL) and stirred for 2 hours at room temperature. The volatiles were removed to give an orange powder (123.3 mg, 0.29 mmol, 65.2 %). Melting point: 165-168°C. ^{1}H NMR (500.2 MHz, 298 K, C_6D_6): δ = 3.27 (s, 3H, -(NHC)CCH_3), 2.64 (s, 3H, -(NHC)CCH_3), 1.98 (s, 30H, -CCH_3), 1.29 (s, 3H, -NCH_3), 1.15 (s, 3H, -NCH_3). ^{13}C{^{1}H} NMR (125.8 MHz, 298 K, C_6D_6): δ = 124.35 (-(NHC)*C*CH$_3$), 123.15 (-(NHC)*C*CH$_3$), 118.42 (-*C*CH$_3$), 34.88 (-N*C*H$_3$), 32.89 (-N*C*H$_3$), 12.73 (-C*C*H$_3$), 7.44 (-(NHC)C*C*H$_3$) 7.34 (-(NHC)C*C*H$_3$) *(carbene NCN carbon is not observed)*. ^{27}Al NMR (130.3 MHz, 298 K, C_6D_6): δ = 136.9. High Res Mass Spec (EI): m/z = 422.32606 (calculated 422.32362 for Cp*$_2$AlH[NHC]$^+$). Despite repeated attempts, satisfactory elemental analysis of **4a** was not possible, most likely due to incomplete/poor combustion: Anal: Calcd. for $C_{27}H_{43}AlN_2$: C, 76.73; H, 10.26; N, 6.63. Found: C, 69.98; H, 8.90; N, 6.33%.

Preparation of Cp*$_2$AlH[diisopropyldimethylimidazolylidene] (4b)

A mixture of diisopropyldimethyl imidazolylidene (78.2 mg, 0.43 mmol) and Cp*$_2$AlH (127.2 mg, 0.43 mmol) were dissolved in C_6H_6 (5 mL) and stirred for 1.5 hours at room temperature. The white precipitate that formed was isolated by filtration, dried in vacuo and then washed with hexane (3 mL). The microcrystalline white solid that so obtained was dried in vacuo (98.2 mg, 0.20 mmol, 47.1 %). Melting point: 154-156 °C. ^{1}H NMR (500.2 MHz, 298 K, C_6D_6): δ = 6.08 (broad s, 1H, -C*H*(CH$_3$)$_2$), 3.59 (broad s, 1H, -C*H*(CH$_3$)$_2$), 2.04 (s, 30H, -CCH_3), 1.45 (s, 6H, -(NHC)CC*H*3). 1.12 (d, 12H, -CH(CH_3)$_2$). ^{27}Al NMR (130.3 MHz, 298 K, C_6D_6): 137.5 ppm. Due to poor solubility a ^{13}C NMR spectrum with satisfactory signal:noise ratio could not be obtained. High Res Mass Spec (EI): m/z = 298.22476 (calculated

298.22357 for $Cp^*_2AlH^+$), 180.16219 (calculated 180.16210 for NHC^+). Anal: Calcd. for $C_{31}H_4AlN_2$: C, 77.77; H, 10.74; N, 5.64. Found: C, 77.55; H, 10.62; N, 5.85%.

Preparation of Cp^*_2AlH[DMAP] (4c)

A solution of dimethylaminopyridine (50.6 mg, 0.41 mmol) in C_6H_6 was added dropwise to a solution of Cp^*_2AlH (118.9 mg, 0.39 mmol) in C_6H_6. The resulting clear yellow solution was stirred for 2.5 hours. The volatiles were removed to give a white solid (115.1 mg, 0.27 mmol, 68.8 %). Melting point: 176-177°C. ^{1}H NMR (500.2 MHz, 298 K, C_6D_6): δ = 7.52 (d, ^3J = 6.0 Hz, 2H, -Ar*H*), 5.59 (d, ^3J = 7.0 Hz, 2H, -Ar*H*), 2.01 (s, 30H, -CCH_3), 1.92 (s, 6H, -N(CH_3)$_2$). ^{13}C NMR (125.8 MHz, 298 K, C_6D_6): δ = 154.87 (quaternary *C*), 146.07 (-Ar*C*), 118.53 (-*C*CH$_3$), 103.93 (-NAr*C*H), 37.79 (-N*C*H$_3$), 12.47 (-CCH$_3$). ^{27}Al NMR (130.3 MHz, 298 K, C_6D_6): δ = 146.7 (broad). High Res Mass Spec (EI): m/z = 298.22328 (calculated 298.22357 for $Cp^*_2AlH^+$), 122.08470 (calculated 122.08385 for $DMAP^+$). Despite repeated attempts, satisfactory elemental analysis of **4c** was not possible, most likely due to incomplete/poor combustion: Anal. Calcd. for $C_{27}H_{41}AlN_2$: C, 77.10; H, 9.83; N, 6.66. Found: C, 31.38; H, 3.86; N, 2.85%.

2. NMR Spectra

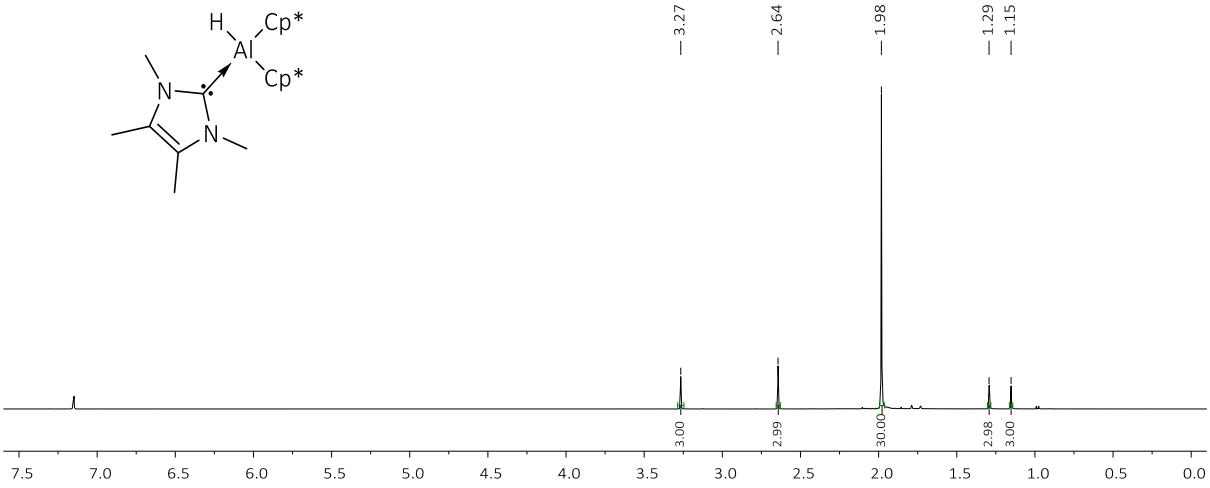


Figure S1 *^{1}H NMR (C_6D_6) of* ***4a***

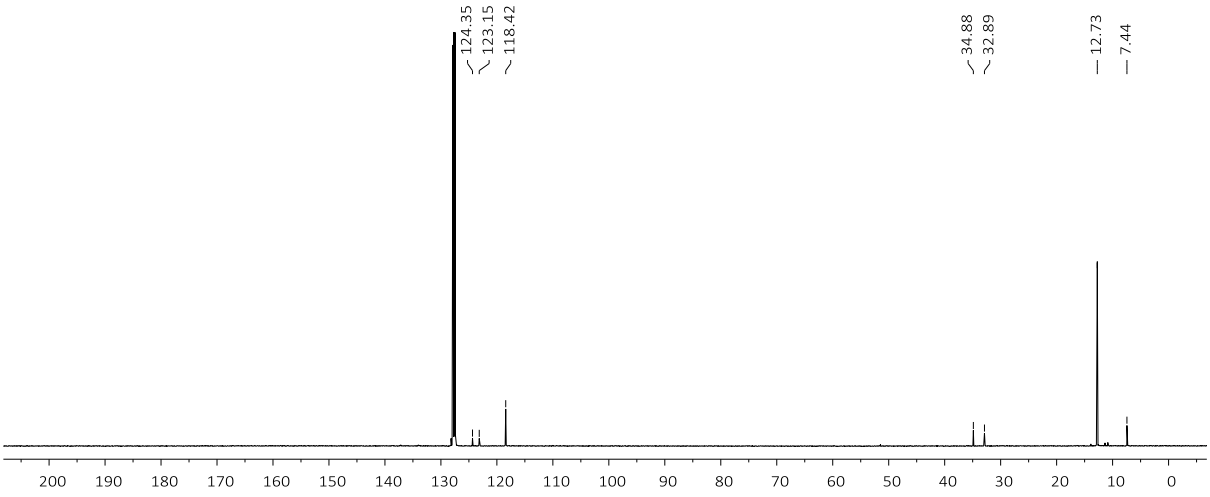


Figure S2 *^{13}C {^{1}H} NMR (C_6D_6) of* ***4a***

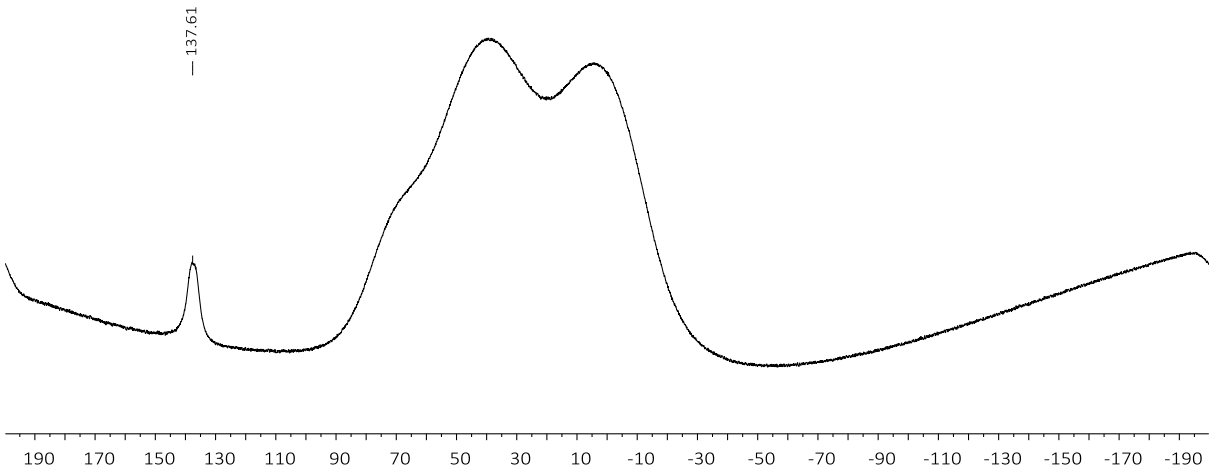


Figure S3 *^{27}Al NMR (C_6D_6) of* ***4a***

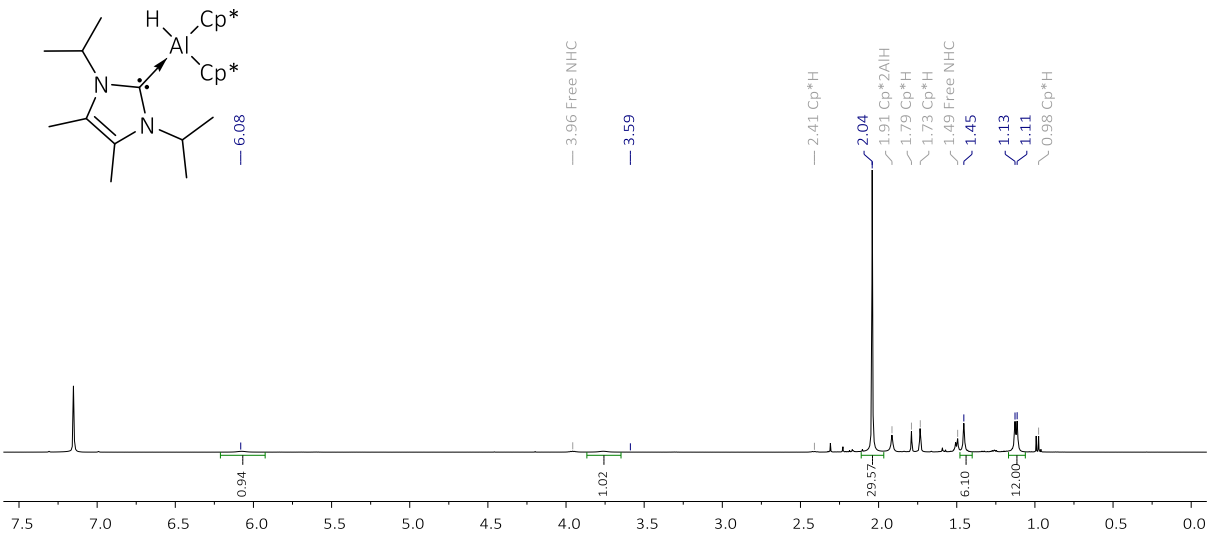


Figure S4 *^{1}H NMR (C_6D_6) of* ***4b***

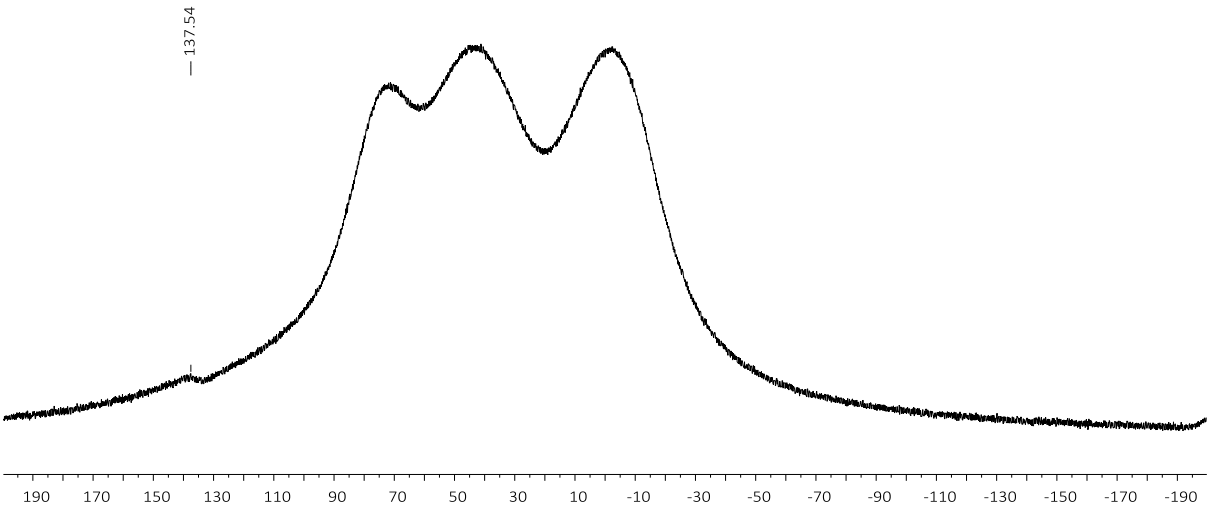


Figure S5 *^{27}Al NMR (C_6D_6) of* ***4b.*** *Sample is sparingly soluble (hence apparently high concentration of the more soluble impurities Cp*H and free NHC)*

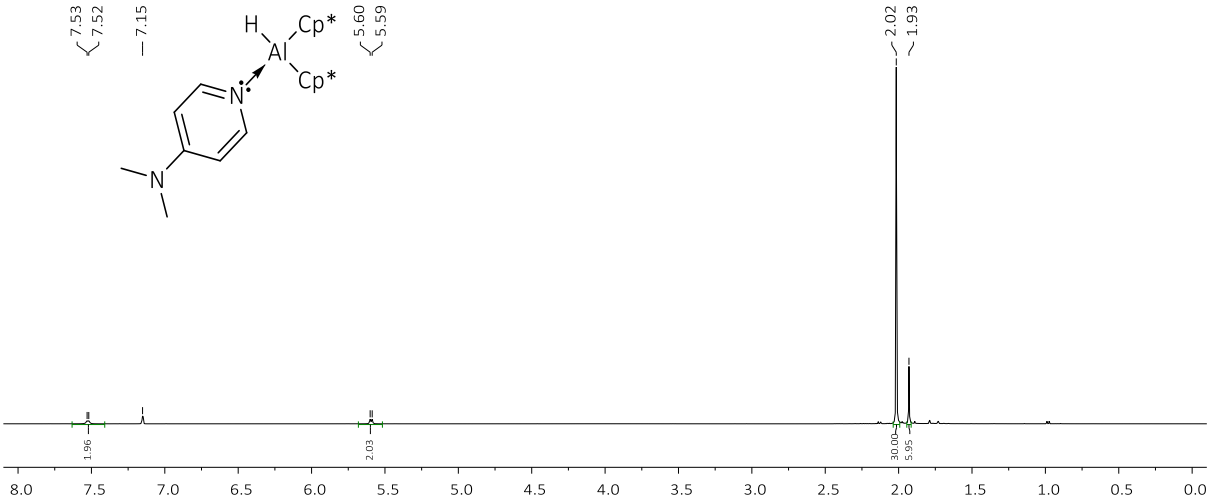


Figure S6 *^{1}H NMR (C_6D_6) of* ***4c***

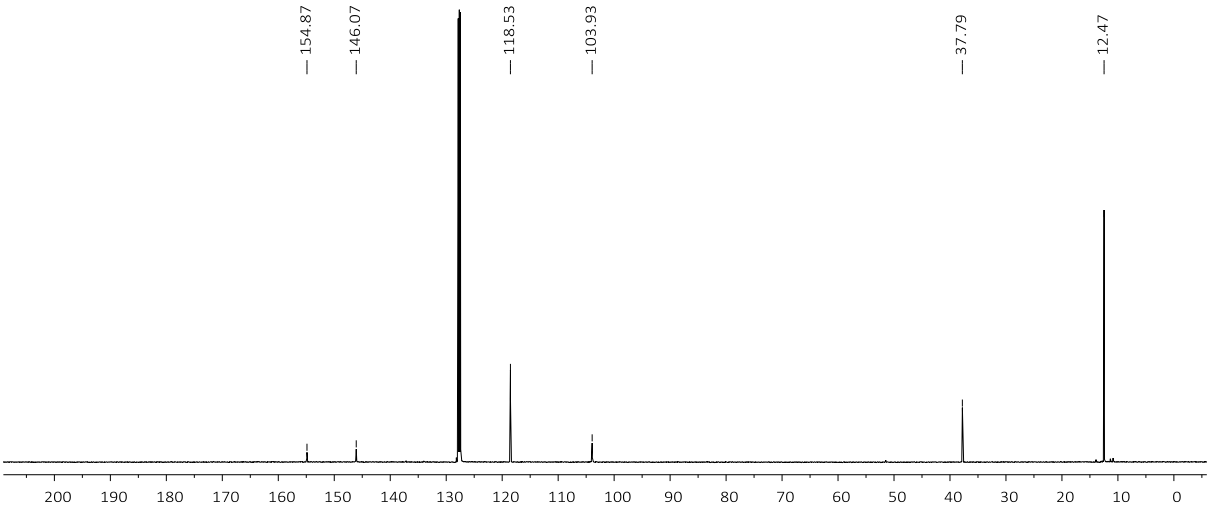


Figure S7 *^{13}C {^{1}H} NMR (C_6D_6) of* ***4c***

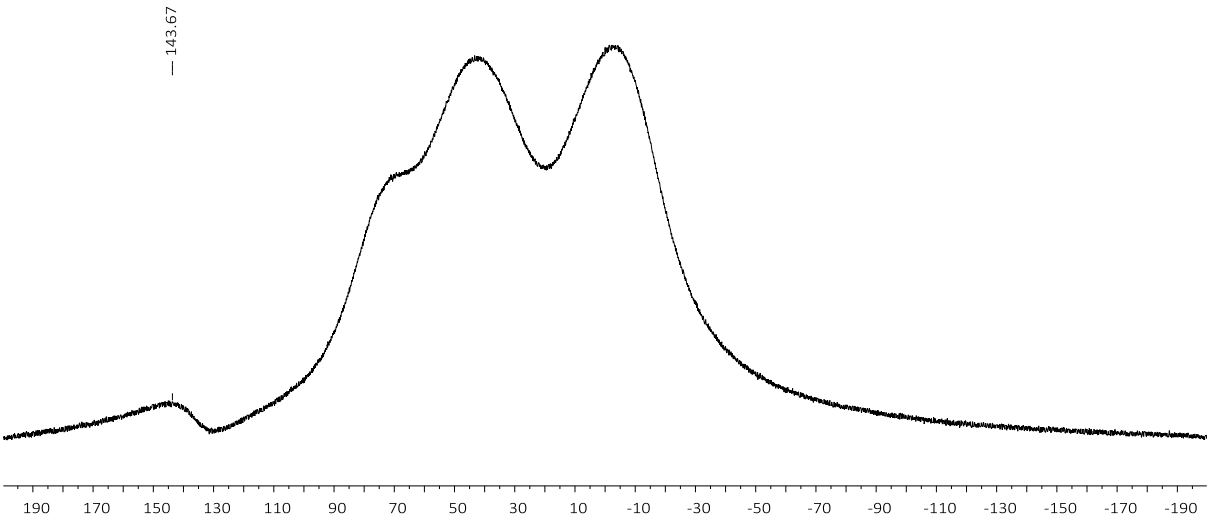


Figure S8 *^{27}Al NMR (C_6D_6) of* ***4c***

3. X-Ray Crystallographic data

Cp^*_2AlH[tetramethylimidazolylidene] (4a)

Experimental. Single colourless prism-shaped crystals were recrystallised from hexane by slow cooling. A suitable crystal (0.42×0.20×0.11) was selected and mounted on a MITIGEN holder in Paratone oil on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The crystal was kept at T = 120.00(10) K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXS** (Sheldrick, 2008) structure solution program, using the Direct Methods solution method. The model was refined with version of **ShelXL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{27}H_{43}AlN_2$, M_r = 422.61, monoclinic, $P2_1/c$ (No. 14), a = 10.7729(3) Å, b = 15.6899(4) Å, c = 16.0285(5) Å, β = 105.321(3)°, α = γ = 90°, V = 2612.93(13) Å^3, T = 120.00(10) K, Z = 4, Z' = 1, μ(MoK_α) = 0.093, 46010 reflections measured, 6853 unique (R_{int} = 0.0544) which were used in all calculations. The final wR_2 was 0.1280 (all data) and R_1 was 0.0514 (I > 2(I)).

Formula	$C_{27}H_{43}AlN_2$
$D_{calc.}$/ g cm^{-3}	1.074
μ/mm^{-1}	0.093
Formula Weight	422.61
Colour	colourless
Shape	prism
Max Size/mm	0.42
Mid Size/mm	0.20
Min Size/mm	0.11
T/K	120.00(10)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	10.7729(3)
b/Å	15.6899(4)
c/Å	16.0285(5)
α/°	90
β/°	105.321(3)
γ/°	90
V/Å^3	2612.93(13)
Z	4
Z'	1
Θ_{min}/°	3.122
Θ_{max}/°	29.719
Measured Refl.	46010
Independent Refl.	6853
Reflections Used	5373
R_{int}	0.0544
Parameters	289
Restraints	0
Largest Peak	0.296
Deepest Hole	-0.245
GooF	1.046
wR_2 (all data)	0.1280
wR_2	0.1176
R_1 (all data)	0.0724
R_1	0.0514

Cp*$_2$AlH[diisopropyldimethylimidazolylidene] (4b)

Experimental. Single colourless block-shaped crystals were recrystallised from d_6-benzene by slow evaporation. A suitable crystal (0.21×0.10×0.05) was selected and mounted on a MITIGEN holder in Paratone oil on a Rigaku Oxford Diffraction SuperNova diffractometer. The crystal was kept at T = 120 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXS** (Sheldrick, 2008) structure solution program, using the Direct Methods solution method. The model was refined with version of **ShelXL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{31}H_{51}AlN_2$, M_r = 478.71, monoclinic, $P2_1/c$ (No. 14), a = 8.8699(7) Å, b = 16.0945(13) Å, c = 20.2907(17) Å, β = 98.473(7)°, $\alpha = \gamma$ = 90°, V = 2865.0(4) Å^3, T = 120 K, Z = 4, Z' = 1, μ(MoK_α) = 0.092, 22402 reflections measured, 5441 unique (R_{int} = 0.0737) which were used in all calculations. The final wR_2 was 0.1262 (all data) and R_1 was 0.0602 (I > 2(I)).

Formula	$C_{31}H_{51}AlN_2$
$D_{calc.}$/ g cm^{-3}	1.110
μ/mm^{-1}	0.092
Formula Weight	478.71
Colour	colourless
Shape	block
Max Size/mm	0.21
Mid Size/mm	0.10
Min Size/mm	0.05
T/K	120
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	8.8699(7)
b/Å	16.0945(13)
c/Å	20.2907(17)
α/°	90
β/°	98.473(7)
γ/°	90
V/Å^3	2865.0(4)
Z	4
Z'	1
Θ_{min}/°	3.119
Θ_{max}/°	25.681
Measured Refl.	22402
Independent Refl.	5441
Reflections Used	4180
R_{int}	0.0737
Parameters	327
Restraints	0
Largest Peak	0.288
Deepest Hole	-0.305
GooF	1.072
wR_2 (all data)	0.1262
wR_2	0.1167
R_1 (all data)	0.0846
R_1	0.0602

Cp*$_2$AlH[dimethylaminopyridine] (4c)

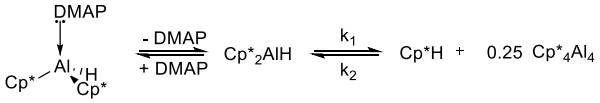
Experimental. Single colourless block-shaped crystals were recrystallised from d_6-benzene by slow evaporation. A suitable crystal (0.37×0.33×0.17) was selected and mounted on a MITIGEN holder in Paratone oil. on a Rigaku Oxford Diffraction SuperNova diffractometer. The crystal was kept at T = 120.0 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXS** (Sheldrick, 2008) structure solution program, using the Unknown solution method. The model was refined with ShelXL (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{27}H_{41}AlN_2$, M_r = 420.60, monoclinic, Ia (No. 9), a = 15.5778(7) Å, b = 11.6033(4) Å, c = 15.6858(7) Å, β = 116.418(5)°, $\alpha = \gamma = 90°$, V = 2539.2(2) Å^3, T = 120.0 K, Z = 4, Z' = 1, μ(MoK_α) = 0.095, 22186 reflections measured, 6273 unique (R_{int} = 0.0377) which were used in all calculations. The final wR_2 was 0.1010 (all data) and R_1 was 0.0437 (I > 2(I)).

Formula	$C_{27}H_{41}AlN_2$
$D_{calc.}$/ g cm^{-3}	1.100
μ/mm^{-1}	0.095
Formula Weight	420.60
Colour	colourless
Shape	block
Max Size/mm	0.37
Mid Size/mm	0.33
Min Size/mm	0.17
T/K	120.0
Crystal System	monoclinic
Flack Parameter	-0.02(6)
Hooft Parameter	-0.00(6)
Space Group	Ia
a/Å	15.5778(7)
b/Å	11.6033(4)
c/Å	15.6858(7)
α/°	90
β/°	116.418(5)
γ/°	90
V/Å^3	2539.2(2)
Z	4
Z'	1
Θ_{min}/°	3.140
Θ_{max}/°	29.651
Measured Refl.	22186
Independent Refl.	6273
Reflections Used	5769
R_{int}	0.0377
Parameters	287
Restraints	2
Largest Peak	0.210
Deepest Hole	-0.218
GooF	1.084
wR_2 (all data)	0.1010
wR_2	0.0980
R_1 (all data)	0.0495
R_1	0.0437

4. Kinetic and Thermodynamic Data

*4.1 Monitoring reductive elimination of Cp*H from the DMAP adduct **4c***



4c **1** **2**

***Scheme S1**. Equilibrium showing the fluxional association of DMAP to **1** and subsequent elimination of Cp*H to form Cp*Al*

A stock solution of tritertbutylbenzene (0.028 M) and **4c** (0.015 M) in toluene-d_8 was prepared. **4c** was found to have low solubility, so the concentration of **4c** was kept low. 0.5 mL of this solution was monitored by ^{1}H NMR at 353 K. The concentration of Cp*H was calculated by comparison to the integrals for the internal standard, tritertbutylbenzene (Figure S9). Despite heating at 353 K for over 13 hours, equilibrium was not reached in this system.

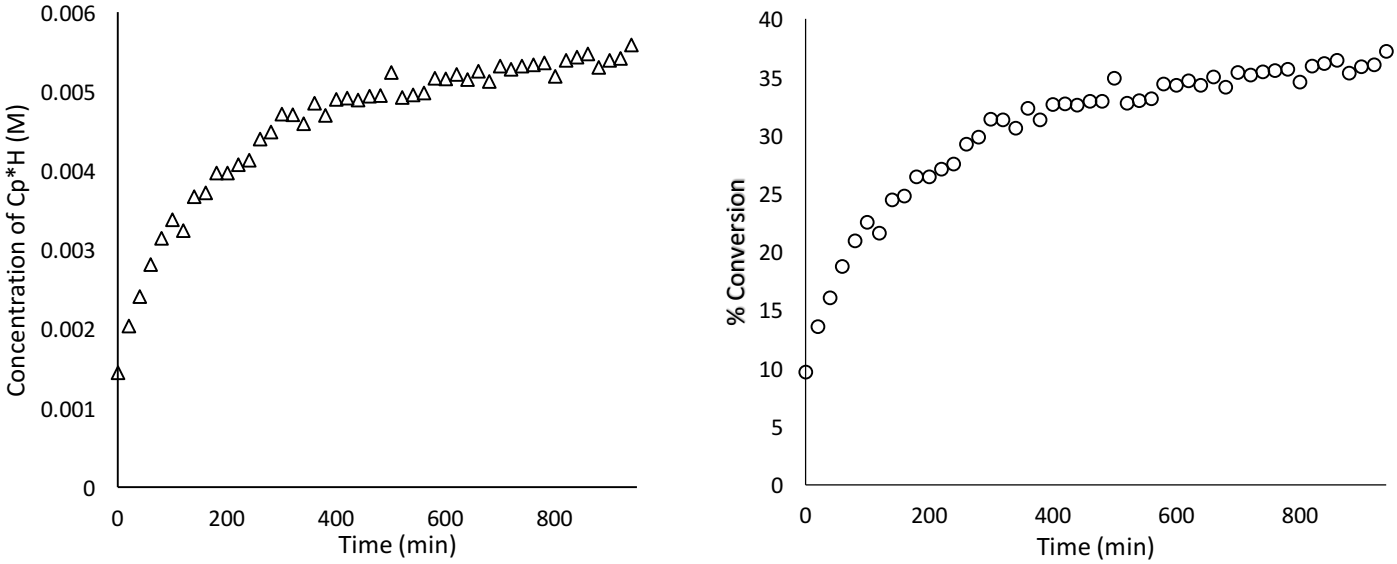


***Figure S9** Reaction profile showing the elimination of Cp*H from **4c** at 353 K*

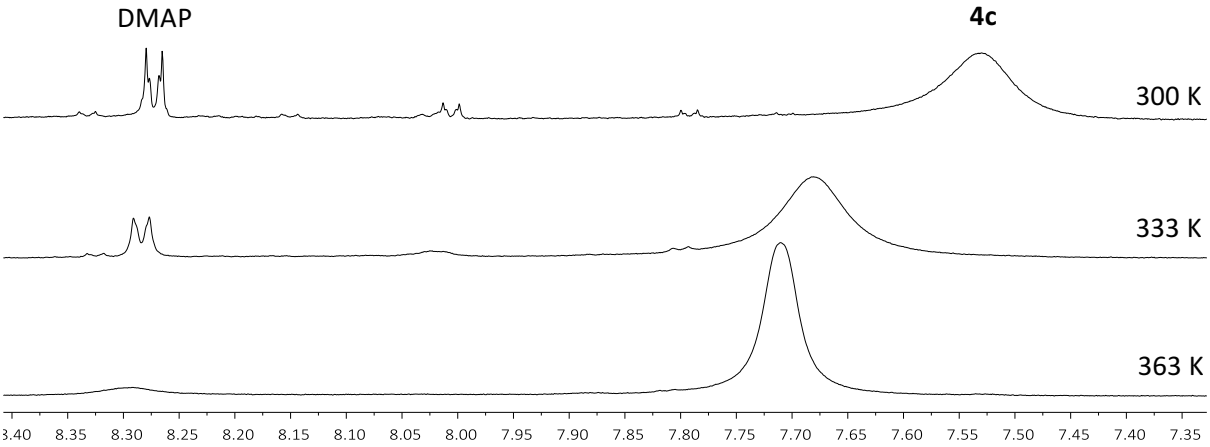


Figure S10 *Variable Temperature ^{1}H NMR of* ***4c*** *in tol-d,* showing rapid echange of free/coordinated DMAP.

*4.2 Reversible reductive elimination of Cp*H from Cp*$_2$AlH*

A solution of Cp*$_2$AlH (62.1 mg, 0.0416 M) and tritertbutylbenzene (47.2 mg, 0.0383 M) in tol-d_8 was prepared. 0.6 mL of this solution was transferred into an NMR tube and heated to 373 K in an oil bath for 1.5 hours. ^{1}H NMR spectra were recorded sequentially at 373 K, 353 K and 300 K (Figure S11). At 373 K the concentration of Cp*Al by integration was found to be equivalent to Cp*H. Upon cooling, Cp*$_2$AlH was observed to reform.

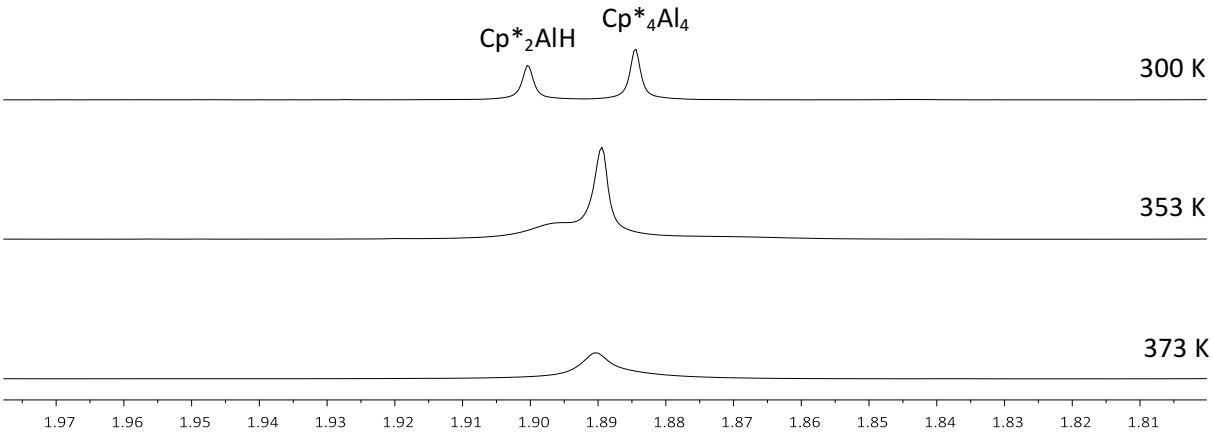


Figure S11 *Variable temperature ^{1}H NMR of Cp*$_2$AlH in tol-d_8*

*4.3 Kinetic study of reductive elimination of Cp*H from Cp*$_2$AlH*

The reductive elimination of Cp*H from Cp*$_2$AlH was followed by ^{1}H NMR at a range of temperatures, using tritertbutylbenzene as an internal standard to calculate concentrations by integration. Rate constants were obtained by fitting the experimentally determined temporal concentration data to the model shown in Scheme S2 using the software package DynaFit4[3].

$$Cp^*_2AlH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cp^*H + Cp^*Al$$

Scheme S2 *Thermal equilibrium of elimination of Cp*H from Cp*2AlH*

General Procedure: A solution of tritertbutylbenzene (0.015-0.020 M) and Cp*$_2$AlH (0.026–0.039 M) in toluene-d_8 were prepared and stored at –30 °C, and used with 48 hours. 0.5 mL of stock solution was used for each experiment. Concentrations were kept low to avoid precipitation of Cp*$_4$Al$_4$ during data collection.

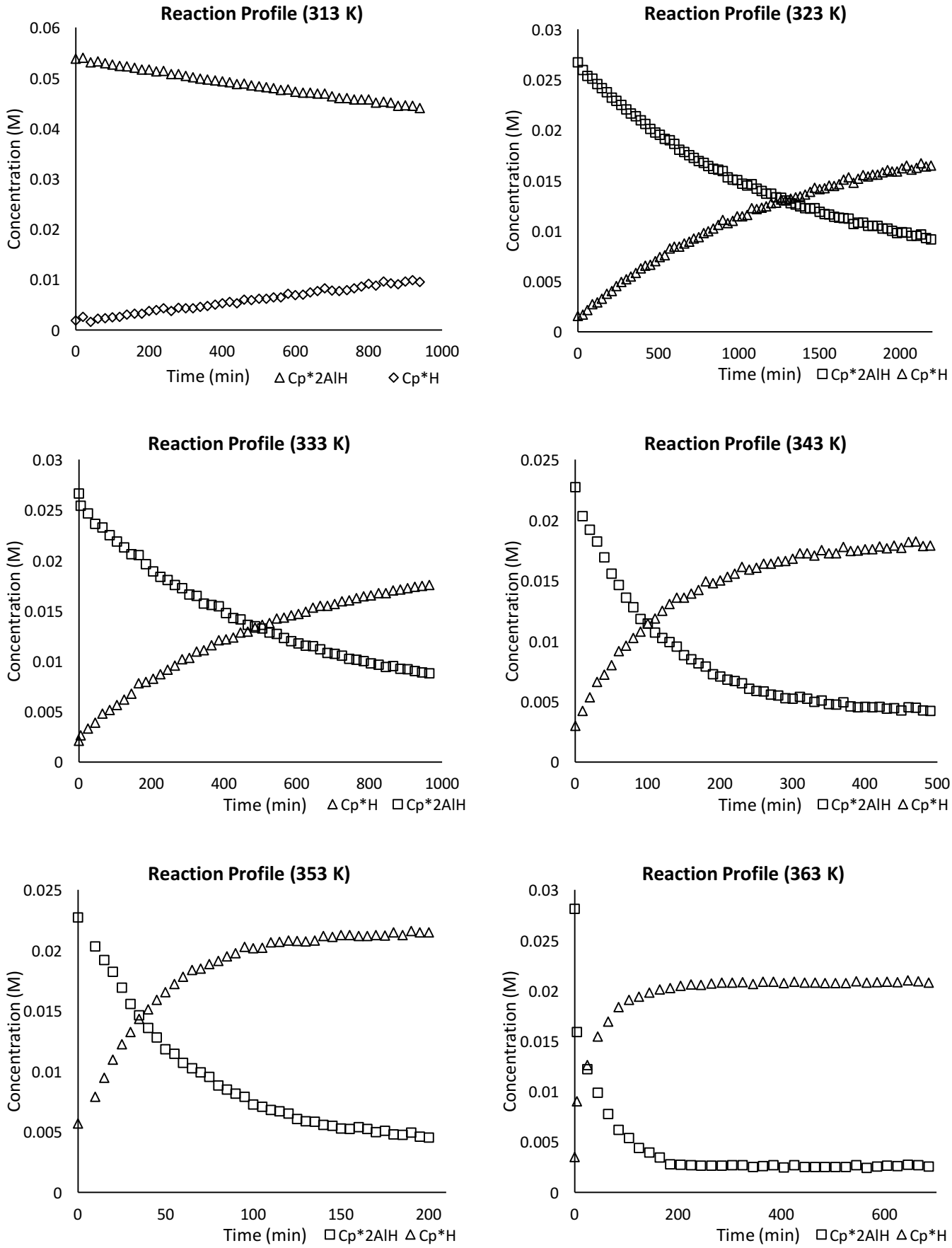


Figure S12 *Reaction profiles showing the production of Cp*H and consumption of Cp*$_2$AlH.*

Table S1 *Fitted rate constants for the reductive elimination of Cp*H from Cp*$_2$AlH*

Temperature	k_1	Standard Error	CV (%)	k_2	Standard Error	CV (%)
313 K	0.00019	0.000002	1.3		*Not Measured*	
323 K	0.00056	0.00001	2.2	0.012	0.002	14.0
333 K	0.00146	0.00004	2.8	0.035	0.004	12.8
343 K	0.006	0.0003	4.9	0.11	0.01	12.3
353 K	0.0176	0.0008	4.5	0.23	0.03	11.0

It did not prove possible to determine a value for k_2 at 313 K due to very low concentrations of Cp*Al. The obtained rate constants were used to populate an Eyring plot to determine activation parameters:

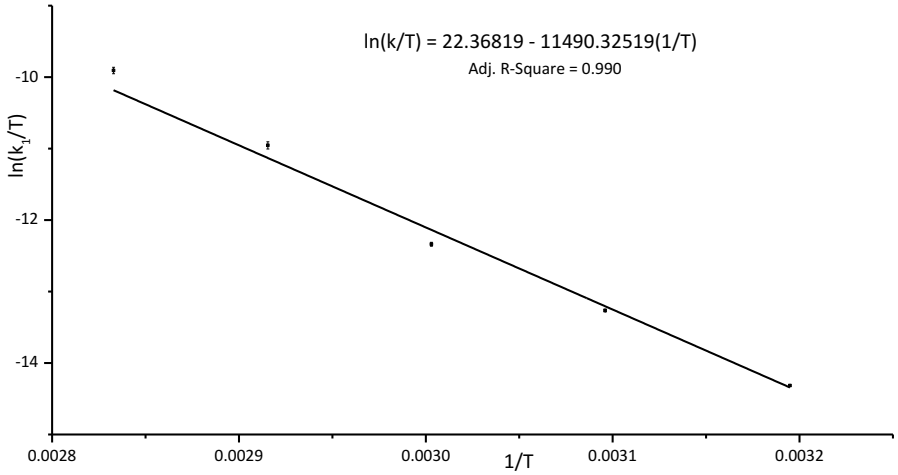


Figure S13 *Eyring plot for the reductive elimination of Cp*H from Cp*$_2$AlH in tol-d$_8$. Gradient standard error 570.51506, intercept standard error 1.7892.*

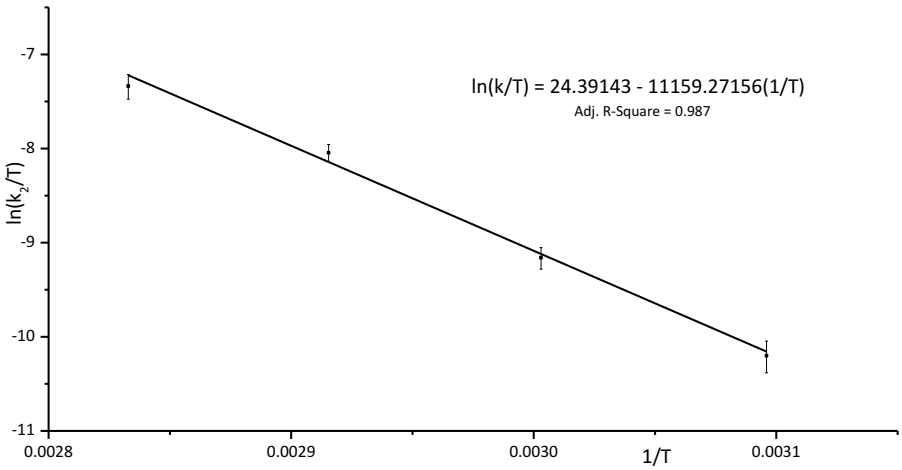


Figure S14 *Eyring plot for the oxidative addition of Cp*H to Cp*Al in tol-d$_8$.. Gradient standard error 733.13411, intercept standard error 2.15979.*

Table S2 *Summary of activation parameters*

Parameter	Reductive Elimination	Oxidative Addition
$\Delta H^{\neq}$	95.53 ± 4.74 kJ mol^{-1}	92.78 ± 6.09 kJ mol^{-1}
$\Delta S^{\neq}$	-0.167 ± 2.64 J mol^{-1}	0.0759 ± 2.59 J mol^{-1}
$\Delta G^{\neq}_{300}$	95.48 ± 3.95 kJ mol^{-1}	92.80 ± 5.32 kJ mol^{-1}

*4.4 Equilibrium Constants for reductive elimination of Cp*H from Cp*$_2$AlH*

General Procedure: Concentration data for Cp*H and Cp*Al and Cp*$_2$AlH was taken from the terminal points of the reaction profiles displayed in figure S12 (concentrations were determined by averaging the final 10 points, once the systems had reached equilibrium). The equilibrium constants calculated from these values are in Table S3. A van't Hoff plot (Figure S15) was constructed to estimate values for ΔH and ΔS, displayed in Table S4.

Table S3 *Calculated equilibrium constants for the reductive elimination equilibrium*

Temperature	K_{eq}	Error
333 K	0.040170	0.001912
343 K	0.075649	0.003856
353 K	0.145548	0.007137
363 K	0.216573	0.012833

Equilibrium constants for 323 K and 313 K are not calculated as they did not reach equilibrium even after prolonged reaction times, as seen the reaction profiles (Figure S12).

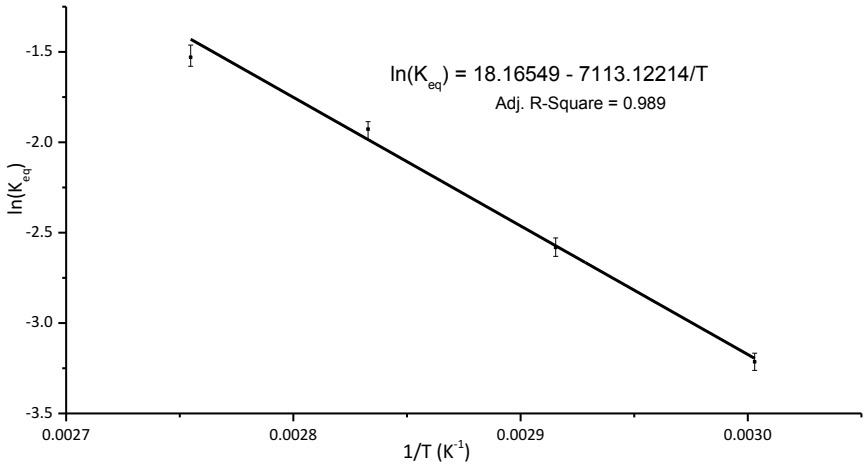


Figure S15 *Van't Hoff plot for the equilibrium of Cp*$_2$AlH with Cp*H and Cp*Al in tol-d_8 using K_{eq} from Table S2. Gradient standard error 430.32089, intercept standard error 1.24294.*

Table S4 *Thermodynamic parameters for the reductive elimination of Cp*H from Cp*$_2$AlH in tol-d$_8$*

Parameter	Value
ΔH	59.14 ± 3.58 kJ mol^{-1}
ΔS	151.04 ± 10.33 J mol^{-1}
ΔG$_{300}$	13.83 ± 0.48 kJ mol^{-1}

5. DFT Calculations

The BP86 exchange-correlation functional and def2-SVP/def2-TZVPP basis sets were employed to study the reductive elimination of Cp*H from Cp*$_2$AlH in the gas phase. Structures were optimised and confirmed as minima by performing frequency calculations. The transition states located have one imaginary frequency. Gaussian 09 Rev. A.02 was the software employed.[4]

Table S5 shows the relative energies for reactants, transition state, and products predicted for reductive elimination of Cp*H from Cp*2AlH. The transition state structure TS1-2 has an imaginary frequency of 724i at the BP/def2-SVP level of theory. A reaction barrier of 93.61 kJ/mol is predicted at the BP86/def2-SVP level, which is lowered to 89.38 kJ/mol when the zero-point-energy correction is included.

Table S6 shows the relative energetics predicted at the BP86/def2-TZVPP level of theory using the BP86/def2-SVP optimised geometries. The reaction barrier is predicted to be 91.54 kJ/mol.
The basis set superposition error (BSSE) is 2.4E-11 and -8.0E-12 au, respectively, for the BP86/def2-SVP and BP86/def2-TZVPP calculations.

Table S5 *Relative energies predicted at the BP86/def2-SVP level of theory.*

Species	Energy	Energy + ZPE correction
Cp*$_2$AlH (1)	0 kJ mol^{-1}	0 kJ mol^{-1}
TS$_{1-2}$	93.61 kJ mol^{-1}	89.38 kJ mol^{-1}
Cp*Al and Cp*H	28.12 kJ mol^{-1}	39.03 J mol^{-1}

Table S6 *Relative energies predicted at the BP86/def2-TZVPP level, with the BP86/def2-SVP optimised geometries.*

Species	Energy	Energy + ZPE correction
Cp^*_2AlH (1)	0 kJ mol^{-1}	n/a
TS_{1-2}	91.54 kJ mol^{-1}	n/a
Cp*Al and Cp*H	18.44 kJ mol^{-1}	n/a

Table S6: BP86/def2-SVP optimised geometry for Cp*2AlH, **1**:

Al	0.0012600000	-0.0019360000	-0.0836040000
C	1.8933750000	-0.9615320000	0.7280260000
C	2.4553580000	-1.0647570000	-0.5837220000
C	2.6966440000	0.2488960000	-1.0890620000
C	2.2889070000	1.1953310000	-0.1122650000
C	1.7810230000	0.4750350000	1.0407100000
C	1.7836740000	-2.0783910000	1.7391580000
H	1.0310000000	-1.8672080000	2.5237010000
H	2.7553420000	-2.2404590000	2.2590190000
H	1.5039150000	-3.0429450000	1.2676830000
C	2.6919710000	-2.3309810000	-1.3603310000
H	2.4135300000	-3.2348310000	-0.7826450000
H	3.7631740000	-2.4374420000	-1.6409430000
H	2.1138740000	-2.3495970000	-2.3106690000
C	3.1799070000	0.5430110000	-2.4827350000
H	4.1199810000	-0.0039710000	-2.7128370000
H	3.3830990000	1.6217320000	-2.6349340000
H	2.4356020000	0.2341030000	-3.2510120000
C	2.3952920000	2.6948890000	-0.2127010000
H	3.3737470000	3.0619190000	0.1727910000
H	1.6076810000	3.2081520000	0.3765410000
H	2.3064020000	3.0507380000	-1.2594480000
C	1.7143440000	1.0409600000	2.4421110000
H	1.3862830000	2.0999140000	2.4504150000
H	2.7191270000	1.0086660000	2.9219450000
H	1.0267180000	0.4743730000	3.1024150000
C	-1.7852220000	-0.4901890000	1.0424100000
C	-1.8673550000	0.9513170000	0.7370240000
C	-2.4383640000	1.0719700000	-0.5719840000
C	-2.7114300000	-0.2328350000	-1.0788700000
C	-2.3159750000	-1.1919350000	-0.1087960000
C	-2.4365500000	-2.6882080000	-0.2401330000
H	-2.1390550000	-3.0477440000	-1.2473830000
H	-3.4835840000	-3.0281640000	-0.0730030000
H	-1.8049330000	-3.2206950000	0.4994340000
C	-1.7060620000	-1.0605750000	2.4412450000
H	-1.4002640000	-2.1263410000	2.4420020000
H	-2.7001540000	-1.0072630000	2.9408110000
H	-0.9932020000	-0.5110310000	3.0889570000
C	-1.7547710000	2.0587520000	1.7588820000
H	-1.0150090000	1.8312790000	2.5509010000
H	-2.7308570000	2.2293830000	2.2676190000
H	-1.4567440000	3.0236730000	1.2991960000
C	-2.6590180000	2.3489390000	-1.3362540000
H	-2.3334700000	3.2402650000	-0.7637160000

H	-3.7349660000	2.4915270000	-1.5810000000
H	-2.1115870000	2.3545510000	-2.3044110000
C	-3.2081310000	-0.5223390000	-2.4690120000
H	-4.0682200000	0.1272200000	-2.7389410000
H	-3.5419720000	-1.5733700000	-2.5805980000
H	-2.4198600000	-0.3431020000	-3.2352570000
H	-0.0076730000	-0.0423190000	-1.6619820000

Table S7: BP86/def2-SVP optimised geometry for **$TS_{1\text{-}2}$**:

Al	-0.2812480000	-0.0031030000	-0.2498180000
C	1.9695860000	-0.7865510000	1.0132990000
C	2.4909390000	-1.1680530000	-0.2294650000
C	2.6108530000	0.0442750000	-1.0377790000
C	2.4720730000	1.1838370000	-0.1322000000
C	1.9571650000	0.6923930000	1.0744070000
C	1.7178630000	-1.6739320000	2.2075800000
H	0.8219310000	-1.3633670000	2.7838900000
H	2.5760580000	-1.6448250000	2.9174200000
H	1.5719030000	-2.7332980000	1.9150130000
C	2.6622470000	-2.5574430000	-0.7695070000
H	2.4739610000	-3.3291680000	0.0037190000
H	3.6900750000	-2.7269720000	-1.1602430000
H	1.9658630000	-2.7620090000	-1.6162620000
C	3.3189960000	0.1053580000	-2.3755080000
H	4.4242330000	0.1084880000	-2.2488460000
H	3.0489600000	1.0211330000	-2.9407620000
H	3.0624810000	-0.7642990000	-3.0149890000
C	2.6237490000	2.6155000000	-0.5549730000
H	3.6535740000	2.8350010000	-0.9146140000
H	2.4097240000	3.3182910000	0.2752620000
H	1.9360570000	2.8756460000	-1.3934410000
C	1.6937040000	1.4732010000	2.3385490000
H	1.5389440000	2.5522610000	2.1367410000
H	2.5494220000	1.3910110000	3.0471260000
H	0.7986570000	1.1066960000	2.8830790000
C	-2.1682340000	-0.1463920000	1.1106880000
C	-2.2299770000	1.1169630000	0.4165330000
C	-2.3787060000	0.8430580000	-0.9894440000
C	-2.4052520000	-0.5820730000	-1.1666760000
C	-2.2725780000	-1.1973790000	0.1276370000
C	-2.3207030000	-2.6748150000	0.4170010000
H	-1.9198830000	-3.2754460000	-0.4248340000
H	-3.3650240000	-3.0178200000	0.5926600000
H	-1.7351350000	-2.9409890000	1.3203900000
C	-2.1442740000	-0.3324600000	2.6048220000
H	-1.6727380000	-1.2921840000	2.8981730000
H	-3.1761540000	-0.3386690000	3.0230870000
H	-1.5945160000	0.4816930000	3.1196250000
C	-2.2335550000	2.4780350000	1.0617410000
H	-1.6327620000	2.4979390000	1.9936370000
H	-3.2663060000	2.7930910000	1.3325970000
H	-1.8235490000	3.2574850000	0.3877190000
C	-2.5161960000	1.8694680000	-2.0824880000
H	-2.0206020000	2.8257150000	-1.8180970000
H	-3.5851920000	2.1026410000	-2.2872690000
H	-2.0719710000	1.5197420000	-3.0369950000
C	-2.5691910000	-1.3035020000	-2.4779510000
H	-3.6437400000	-1.4370260000	-2.7359480000
H	-2.1133360000	-2.3142040000	-2.4543850000

H	-2.1004590000	-0.7492300000	-3.3169150000
H	1.1846930000	0.0460930000	-1.3564960000

Table S8: BP86/def2-SVP optimised geometry for Cp*Al and Cp*H:

Al	10.7331050000	-0.0692060000	-0.3071130000
C	-14.2855650000	0.6475990000	0.9861310000
C	-14.2577650000	1.2227560000	-0.2576060000
C	-14.2741240000	0.1193040000	-1.3045050000
C	-14.3089800000	-1.1622440000	-0.4859100000
C	-14.3172840000	-0.8327500000	0.8443300000
C	-14.2750430000	1.3339540000	2.3233270000
H	-13.3969450000	1.0281420000	2.9342820000
H	-15.1759870000	1.0756980000	2.9228650000
H	-14.2453990000	2.4373910000	2.2269100000
C	-14.2113310000	2.6771740000	-0.6193820000
H	-14.1625260000	3.3279950000	0.2766230000
H	-15.1057560000	2.9910340000	-1.2048330000
H	-13.3278890000	2.9180220000	-1.2532490000
C	-15.4226760000	0.2419630000	-2.3280910000
H	-16.4063510000	0.2138560000	-1.8141600000
H	-15.3974240000	-0.5863320000	-3.0665660000
H	-15.3591940000	1.1935060000	-2.8960570000
C	-14.3219930000	-2.5224100000	-1.1167110000
H	-15.2238660000	-2.6803550000	-1.7514260000
H	-14.3086740000	-3.3322560000	-0.3598790000
H	-13.4439320000	-2.6774140000	-1.7839380000
C	-14.3407740000	-1.7599070000	2.0272490000
H	-14.3580810000	-2.8253330000	1.7234360000
H	-15.2317830000	-1.5816630000	2.6692560000
H	-13.4523650000	-1.6130690000	2.6808490000
C	12.5294310000	0.9215740000	0.8487420000
C	12.5330940000	-0.4862640000	1.1525890000
C	12.7820850000	-1.2049020000	-0.0704910000
C	12.9323090000	-0.2411810000	-1.1302330000
C	12.7763040000	1.0730370000	-0.5620890000
C	12.9196400000	2.3781870000	-1.2998920000
H	12.6168870000	2.2895060000	-2.3630290000
H	13.9751680000	2.7313870000	-1.2901740000
H	12.3043580000	3.1815060000	-0.8461000000
C	12.3692150000	2.0406360000	1.8438930000
H	11.9218980000	2.9447330000	1.3831800000
H	13.3521200000	2.3440340000	2.2691480000
H	11.7228120000	1.7488830000	2.6964670000
C	12.3775490000	-1.0960040000	2.5209440000
H	11.7362160000	-0.4770280000	3.1807580000
H	13.3625970000	-1.2001900000	3.0287020000
H	11.9269700000	-2.1083040000	2.4757720000
C	12.9328350000	-2.6973730000	-0.2047830000
H	12.3281870000	-3.2449410000	0.5464190000
H	13.9917080000	-3.0087400000	-0.0604830000
H	12.6222830000	-3.0576790000	-1.2065800000
C	13.2662970000	-0.5502490000	-2.5659460000
H	14.3675720000	-0.5818180000	-2.7246990000
H	12.8600610000	0.2131590000	-3.2602050000
H	12.8642740000	-1.5338910000	-2.8831600000
H	-13.3066490000	0.1524340000	-1.8670540000

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