Electronic Supplementary Material (ESI) for Chemical Communications
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-Supporting Information-

Reductive Elimination: A Pathway to Low-Valent Aluminium Species.

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Experimental Section

General Procedures. All manipulations were carried out in an atmosphere of purified argon using standard Schlenk and glove-box techniques. Diethylether, *n*-hexane, THF and toluene were dried using an mBraun Solvent Purification System. The final H_2O contents of all solvents were checked by Karl Fischer titration. The compounds Cp^*H and KCp^* were prepared according to the published procedures.[1] $AlCl_3$ and $LiAlH_4$ (4 M solution in Et_2O) were purchased from Aldrich chemicals and used as such.

Instrumentation. The ^1H and ^{13}C NMR (δ in ppm) spectra were recorded using a Bruker Avance DPX-200 or DPX-250 spectrometer operating at the appropriate frequencies using TMS as internal reference. Solid-state ^{27}Al MAS NMR spectrum was measured with a Bruker DSX 400 MHz instrument in ZrO_2 rotors (diameter = 2.5 mm) with a rotational frequency of 20 kHz. The sample was diluted in purified naphthalene to separate the single particle grains and avoid the magnetization effect. MAS NMR spectrum was measured by using pulse program written by H. -J. Hauswald at the Analytical Chemistry Department at the Ruhr-University Bochum. The microanalyses were performed at Mikroanalytisches Laboratorium Kolbe, Mülheim an der Ruhr. FT-IR spectra were measured in an ATR setup with a Bruker Alpha FTIR spectrometer under inert atmosphere in a glovebox. Mass spectrometry experiments were carried out in

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toluene using Jeol AccuTOF GCv instrument [Ionization method: Liquid Injection Field Desorption Ionization (LIFDI); a special ionization cell obtained from Linden CMS GmbH, Leeste, Germany, http://www.linden-cms.de]

Synthesis of Cp^*AlH_2 (1)

Diethyl ether (50 mL) was added dropwise to $AlCl_3$ (1.5 g, 11.25 mmol) at -78 °C with constant stirring. To that, $LiAlH_4$ (2.8 mL of a 4 M solution in Et_2O, 11.25 mmol) was added dropwise at -78 °C and the reaction mixture was slowly warmed to room temperature. The solution was stirred at room temperature for 1h and cannula filtered. The solvent was removed under reduced pressure to give white sticky residue of $ClAlH_2$. Thus obtained $ClAlH_2$ was used for further reaction without purification. Diethyl ether (100 mL) was added to the mixture of $ClAlH_2$ and KCp^* (3.922 g, 22.50 mmol) at room temperature. The reaction mixture was stirred at room temperature for 4 h and cannula filtered. The filtrate was concentrated under reduced pressure to give a white solid which was redissolved in *n*-hexane (150 mL) and filtered. The filtrate was concentrated to 20 mL and kept at -30° C to give analytically pure form of **1** as white crystals. Yield: 2.75 g (16.74 mmol, 74 %). Anal. Calcd. for $C_{10}H_{17}Al$: C, 73.14; H, 10.43. Found: C, 72.63; H, 10.32%. IR (neat): ν 2944 (w), 2894 (m), 2839 (w), 1814 (m), 1650 (br, m), 1424 (m), 1369 (m), 743 (s), 610 (m), 536 (m), 415 (s) cm^{-1}. ^1H NMR (C_6D_6, 250 MHz): δ 1.92 (s, 15 H, $C_5(CH_3)_5$), 3.44 (br s, 2 H, hydride). ^{13}C NMR (C_6D_6, 63 MHz): δ 10.84 (C_5Me_5), 114.15 (C_5Me_5). MS (LIFDI, *Toluene*): m/z 136.16 (Cp^*H^+), 26.89 (Al^+).

Synthesis of Cp^*_2AlH (2)

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Diethyl ether (100 mL) was added dropwise to $AlCl_3$ (2.868 g, 21.5 mmol) at -78 °C with constant stirring. To that, $LiAlH_4$ (1.8 mL of a 4 M solution in Et_2O, 7.17 mmol) was added dropwise at -78 °C and the reaction mixture was slowly warmed to room temperature. The solution was stirred at room temperature for 1h and cannula filtered. The solvent was removed under reduced pressure to give white sticky residue of Cl_2AlH which was used for further reaction without purification. Diethyl ether (200 mL) was added to the mixture of Cl_2AlH and KCp^* (10 g, 57.4 mmol) at room temperature. The reaction mixture was stirred at room temperature for 4 h and cannula filtered. The filtrate was concentrated under reduced pressure to give a white solid which was redissolved in *n*-hexane (150 mL) and filtered. The filtrate was concentrated to 15 mL and kept at -30° C for 2 days to give analytically pure form of **2** as white crystals . Yield: 7.01 g (23.5 mmol, 82 %). Anal. Calcd. for $C_{20}H_{31}Al$: C, 80.49; H, 10.47. Found: C, 79.89; H, 10.58%. IR (neat): ν 2939 (w), 2887 (m), 2838 (m), 2701 (vw), 1858 (m), 1433 (m), 1368 (m), 1252 (w), 1019 (m), 794 (m), 637 (w), 586 (w), 458 (s) cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 1.91 (s, 30 H, $C_5(CH_3)_5$). ^{13}C NMR (C_6D_6, 50 MHz): δ 11.38 ($C_5\mathit{Me}_5$), 117.17 (C_5Me_5). MS (LIFDI, *Toluene*): m/z 298.31 (M^+).

Reductive Elimination Reaction of Cp^*AlH_2 (1)

Cp^*AlH_2 (0.5 g, 3.04 mmol) in benzene (5 mL) was heated at 70° C for 2 days. The reaction mixture was brought into room temperatuere and cannula filtered to give grey precipitate. The precipitate was washed twice with 4 mL of benzene and vacuum dried. Yield: 80 % (0.066 g, 2.45 mmol). ^{27}Al MAS NMR [referenced to $Al_2(SO_4)_3$]: δ 1530 (s, Al^0). PXRD reflexes in 2θ: 38.57 (*hkl* 111), 44.77 (200), 65.19 (220), 78.36 (311), 82.56 (222).

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Reductive Elimination Reaction of Cp^*_2AlH (2)

Method 1: Cp^*_2AlH (2.6 g, 8.71 mmol) in toluene (5 mL) was heated at 110° C for 45 min. The reaction mixture was brought into room temperature and cannula filtered. The pale yellow micro crystals were washed with 10 mL of warm *n*-hexane to afford analytically pure form of Cp^*Al. The combined filtrates were dried under vacuum, redissolved in 0.8 mL of toluene and heated at 110° C for 30 min to afford additional amount of Cp^*Al. Yield: 90 % (1.267 g, 7.81 mmol). Anal. Calcd. for $C_{40}H_{60}Al_4$: C, 74.05; H, 9.32; Al, 16.63. Found: C, 72.98; H, 9.30; Al, 15.63%.

Method 2: Cp^*_2AlH (1.25 g, 4.19 mmol) was heated at 110° C for 30 min under high vacuum to afford pale yellow powder of Cp^*Al. Yield: 93 % (0.630 g, 3.88 mmol).

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Table S1. Crystallographic information for compounds **1** and **2**.

	1	**2**
Empirical formula	$C_{30}H_{51}Al_3$	$C_{20}H_{31}Al$
Fw	492.65	298.43
Cryst.system	Orthorhombic	Orthorhombic
Space group	Pna2(1)	Pbca
a, Å	15.2302(2)	12.8080(3)
b, Å	19.2003(2)	15.2538(3)
c, Å	10.43970(10)	19.2266(4)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
V, Å^3	3052.82(6)	3756.31(14)
Z	4	8
$\rho_{calc,}$ g cm^{-3}	1.072	1.055
μ (MoKa), mm^{-1}	1.230	0.860
F (000)	1080	1312
T (K)	100(2)	100(2)
2θ range, deg	3.70-74.22	5.06-74.07
Total no. reflns	44294	8666
No. of indep reflns	6063 [R_{int}=0.0422]	3706 [R_{int}=0.0194]
GOF (F^2)	1.033	1.056
R_1	0.0293	0.0637
wR_2	0.0789	0.1589
Absolute structure parameter	0.04(2)	

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Table S2. Selected bond distances and bond angles for compounds **1** and **2**.

1				**2**			
Bond distances (Å)		Bond angles (°)		Bond distances (Å)		Bond angles (°)	
Al(1)-C(2)	2.3763(15)	H(1A)-Al(1)-H(1B)	101.2(12)	Al(1)-C(11)	2.1504(16)	C(11)-Al(1)-C(5)	111.59(7)
Al(1)-C(3)	2.2634(15)	H(1A)-Al(1)-H(1C)	103.6(12)	Al(1)-C(5)	2.1715(17)	C(11)-Al(1)-C(1)	107.33(6)
Al(1)-C(4)	2.1677(15)	H(1B)-Al(1)-H(1C)	89.0(10)	Al(1)-C(1)	2.1911(17)	C(5)-Al(1)-C(1)	38.94(6)
Al(1)-C(5)	2.2381(16)	H(2A)-Al(2)-H(1B)	98.4(10)	Al(1)-C(12)	2.2753(17)	C(11)-Al(1)-C(12)	37.90(6)
Al(1)-C(6)	2.3751(15)	H(2A)-Al(2)-H(2B)	102.1(10)	Al(1)-C(15)	2.3361(17)	C(5)-Al(1)-C(12)	111.10(7)
Al(1)-H(1A)	1.46(2)	H(1B)-Al(2)-H(2B)	88.5(10)	Al(1)-H(1)	1.41(3)	C(1)-Al(1)-C(12)	132.22(6)
Al(1)-H(1B)	1.731(19)	H(3)-Al(3)-H(2B)	101.7(10)			C(11)-Al(1)-C(15)	36.99(6)
Al(1)-H(1C)	1.68(2)	H(3)-Al(3)-H(1C)	102.9(11)			C(5)-Al(1)-C(15)	142.08(7)
Al(2)-C(11)	2.2617(16)	H(2B)-Al(3)-H(1C)	85.5(11)			C(1)-Al(1)-C(15)	116.37(7)
Al(2)-C(12)	2.1975(15)					C(12)-Al(1)-C(15)	60.06(6)
Al(2)-C(13)	2.2468(15)					C(11)-Al(1)-H(1)	133.6(10)
Al(2)-C(14)	2.3332(14)					C(5)-Al(1)-H(1)	113.7(10)
Al(2)-C(15)	2.3601(15)					C(1)-Al(1)-H(1)	113.9(10)
Al(2)-H(2A)	1.48(2)					C(12)-Al(1)-H(1)	112.9(10)

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Al(2)-H(2B)	1.72(2)	C(15)-Al(1)-H(1)	102.8(10)
Al(2)-H(1B)	1.805(18)		
Al(3)-C(21)	2.3080(18)		
Al(3)-C(22)	2.2349(15)		
Al(3)-C(23)	2.2067(15)		
Al(3)-C(24)	2.2484(15)		
Al(3)-C(25)	2.3062(17)		
Al(3)-H(3)	1.58(2)		
Al(3)-H(1C)	1.68(2)		
Al(3)-H(2B)	1.66(2)		

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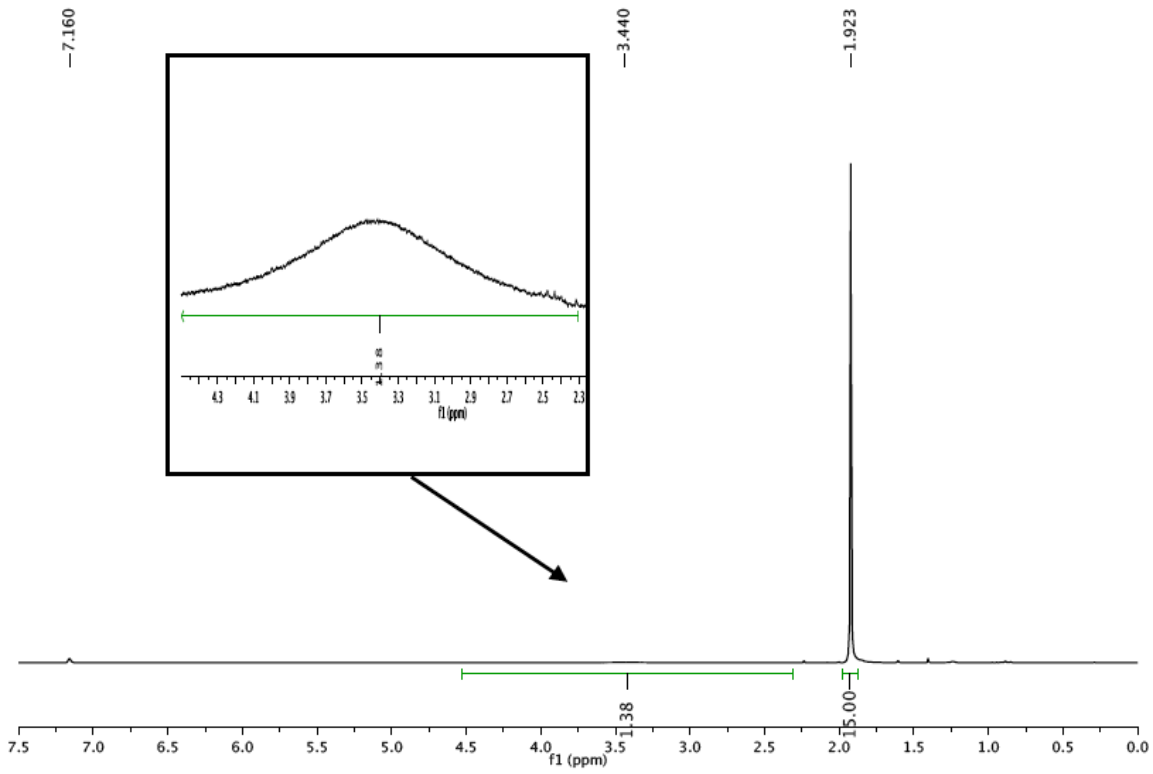

Figure S1. ^{1}H NMR spectrum of $Cp^{*}AlH_2$ (**1**) in C_6D_6.

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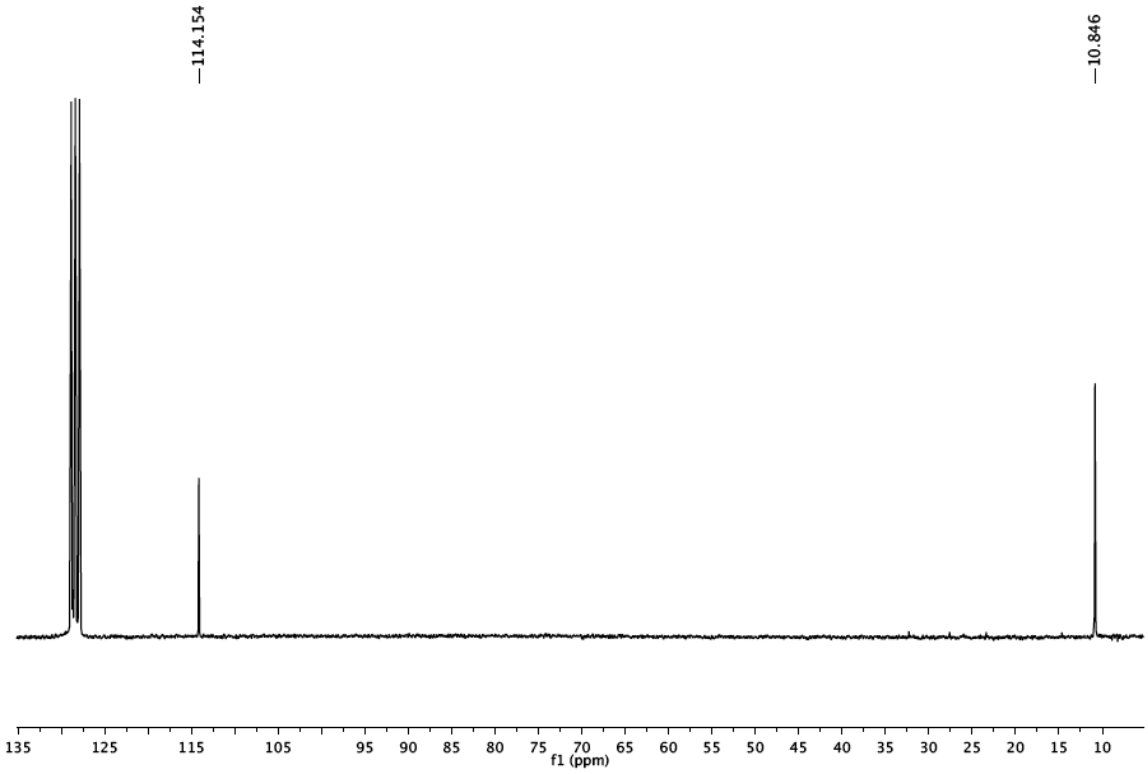

Figure S2. ^{13}C NMR spectrum of Cp^*AlH_2 (**1**) in C_6D_6.

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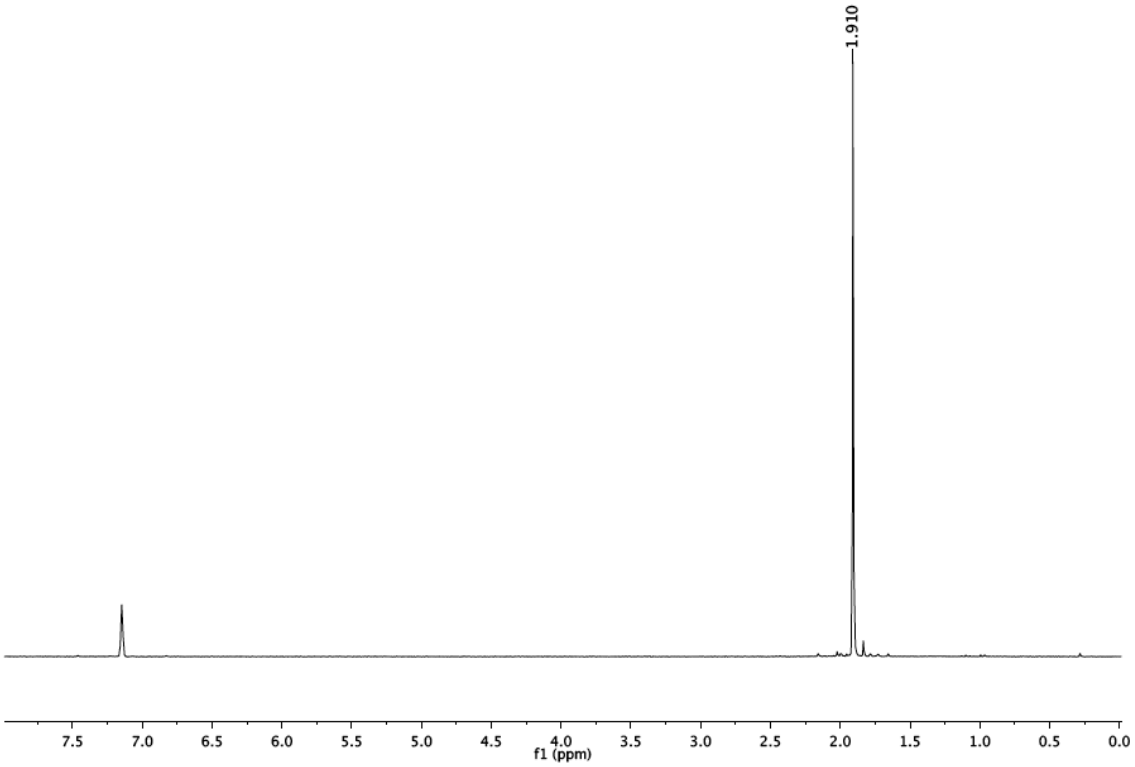

Figure S3. ^{1}H NMR spectrum of $Cp^{*}_{2}AlH$ (**2**) in C_6D_6.

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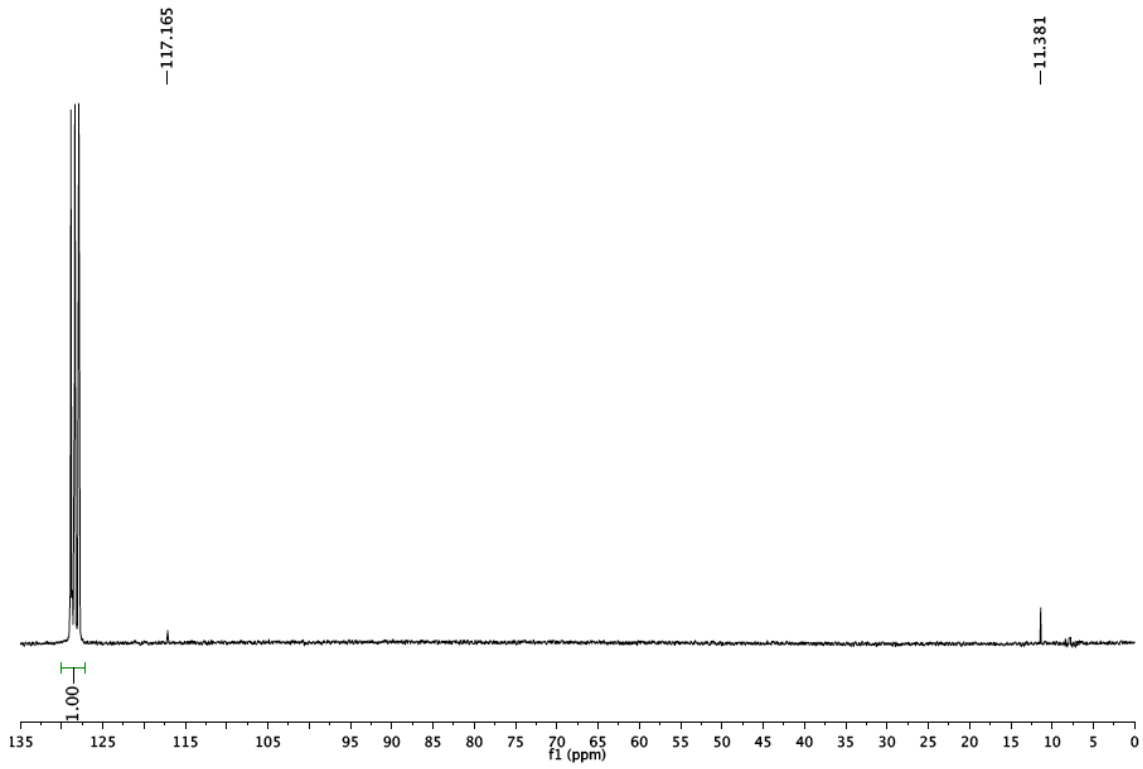

Figure S4. ^{13}C NMR spectrum of Cp^*_2AlH (**2**) in C_6D_6.

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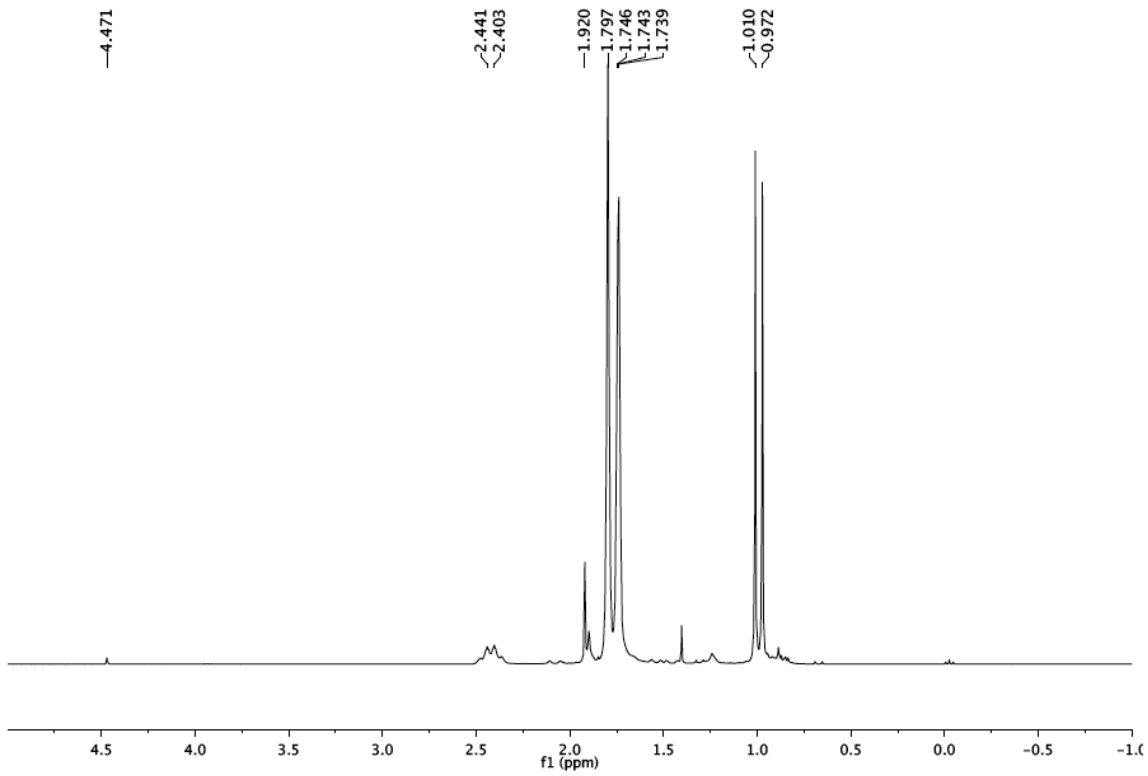

Figure S5. ^{1}H NMR spectrum of $Cp^{*}AlH_2$ (**1**) in C_6D_6 after heating it at 80 °C for 1 day.

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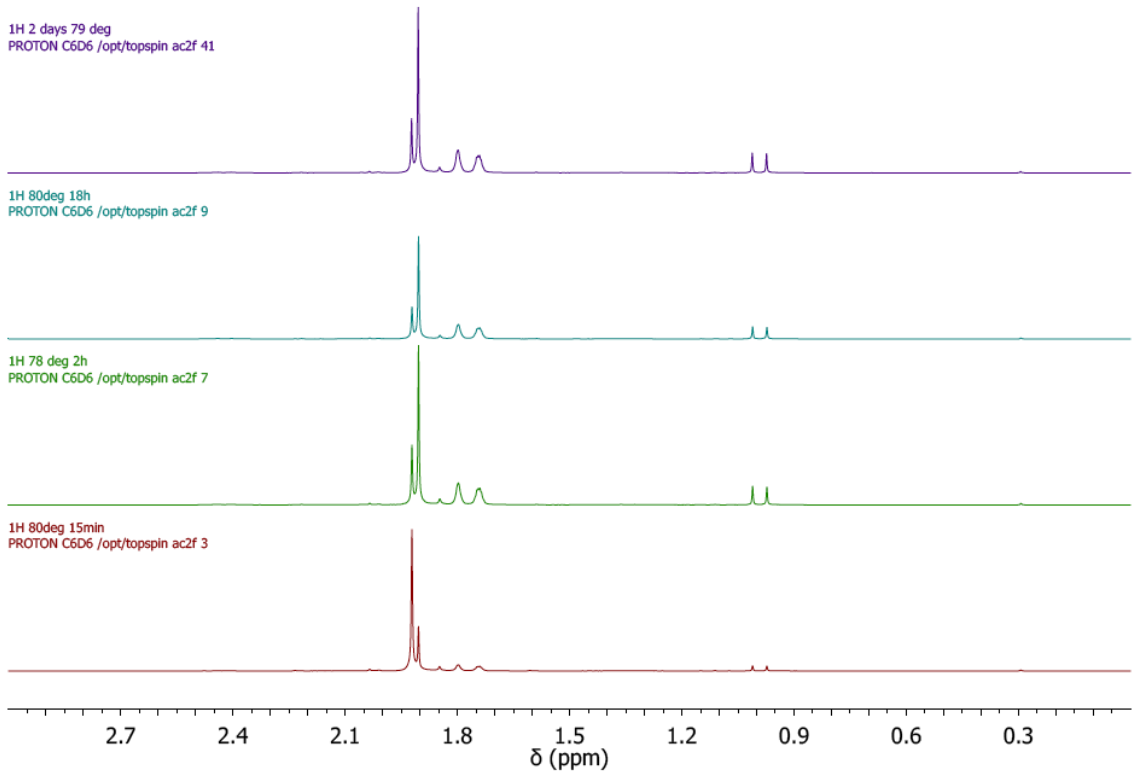

Figure S6. ^{1}H NMR spectra of $Cp^{*}_{2}AlH$ (**2**) in C_6D_6 at 80 °C. Reaction was monitored by ^{1}H NMR in regular interval. Very dilute solution of **2** was used in the measurement so as to avoid the precipitation of $AlCp^{*}$ in the reaction medium.

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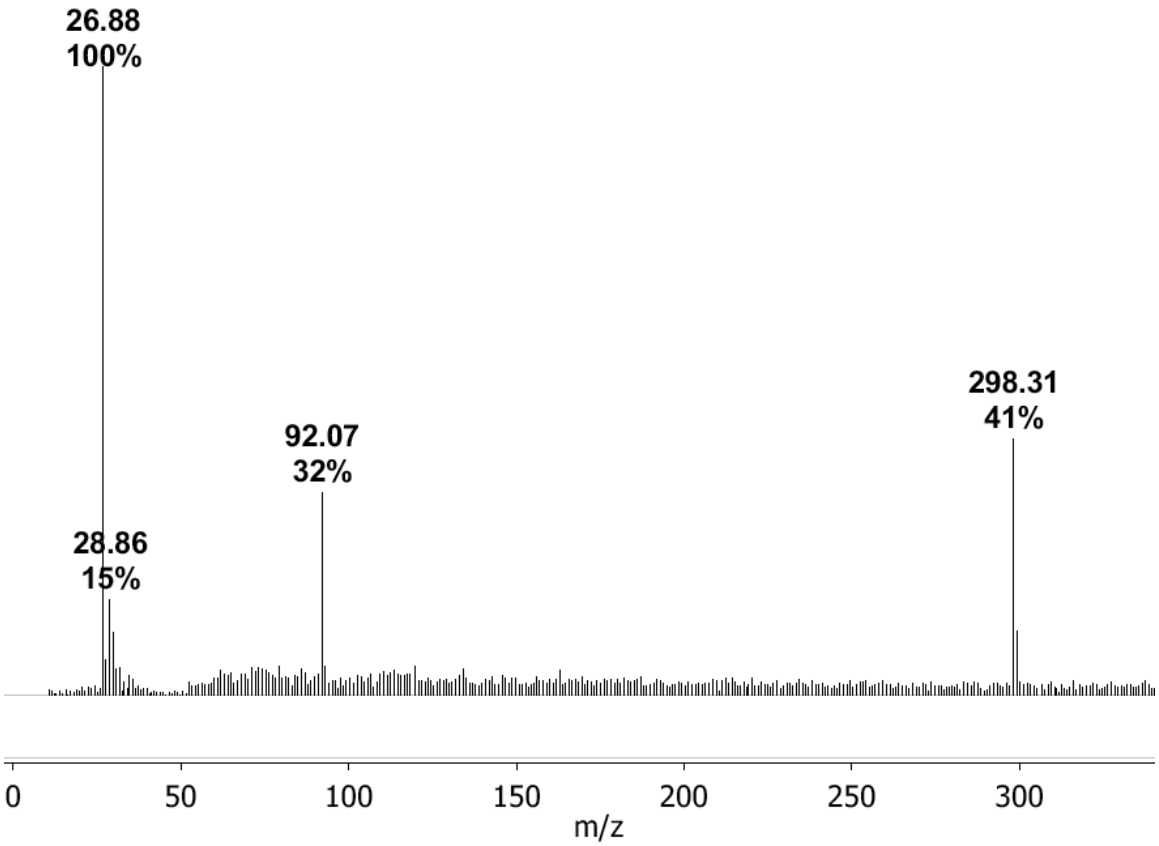

Figure S7. LIFDI-MS (*toluene*) of Cp^*_2AlH (**2**).

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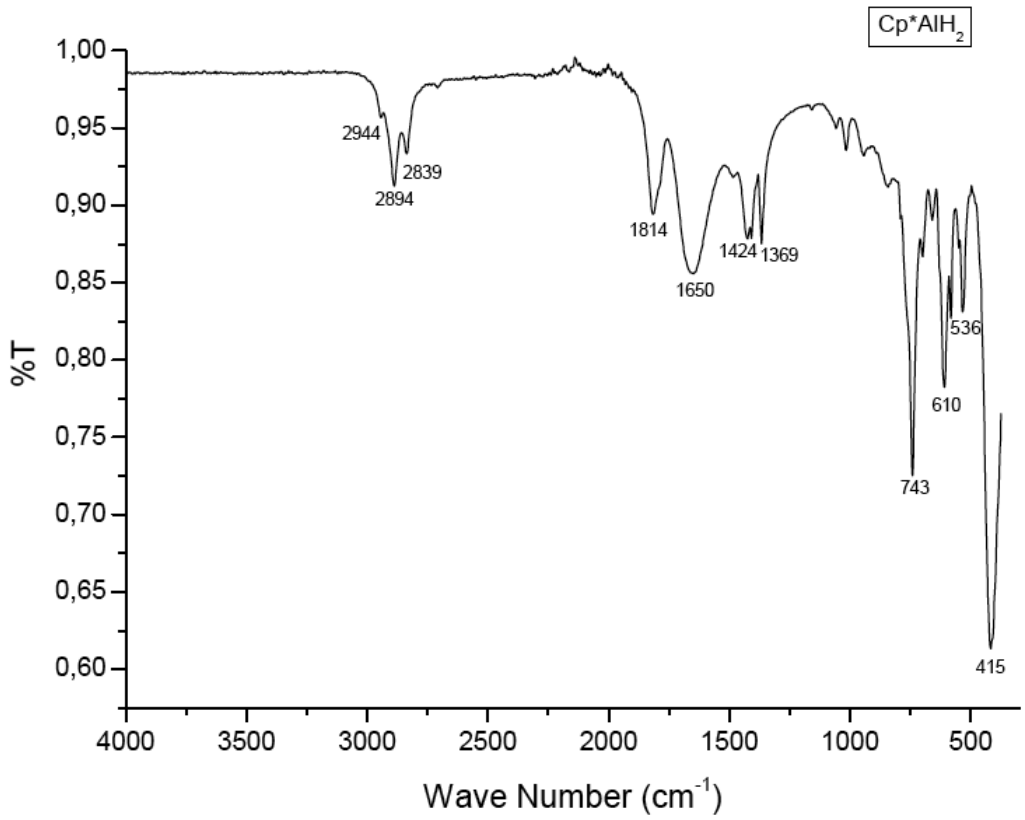

Figure S8. ATR-IR spectrum of Cp^*AlH_2 (**1**).

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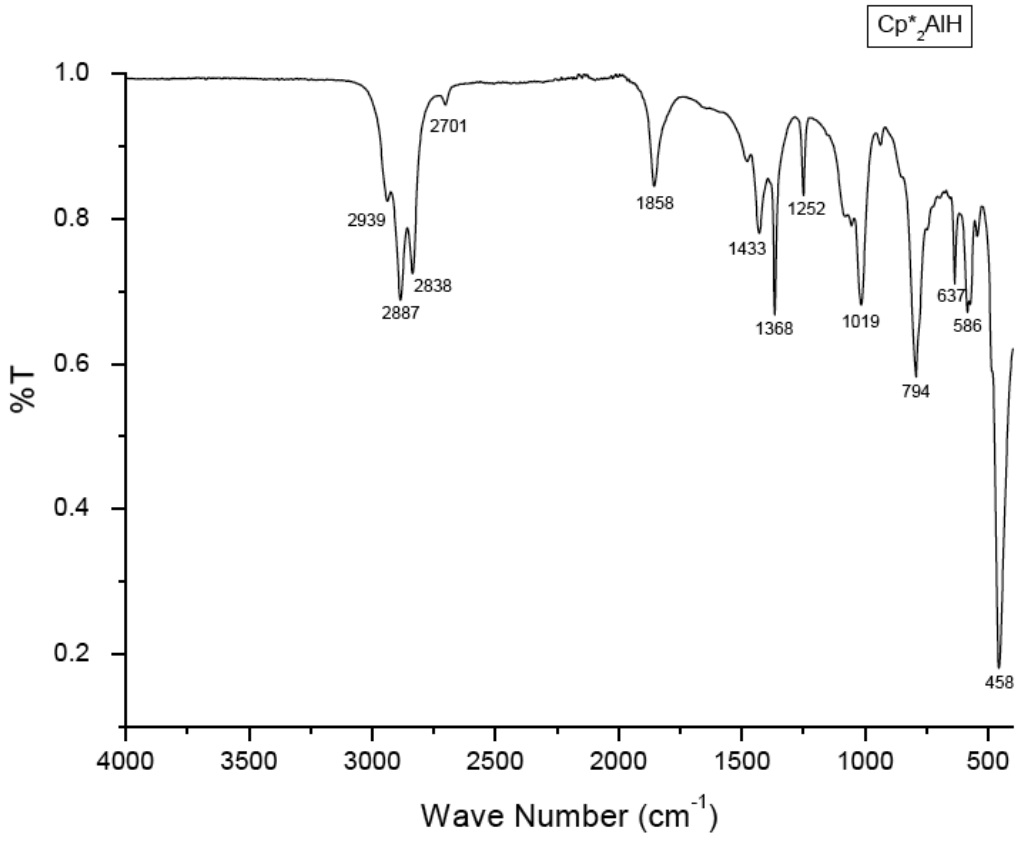

Figure S9. ATR-IR spectrum of Cp^*_2AlH (**2**).

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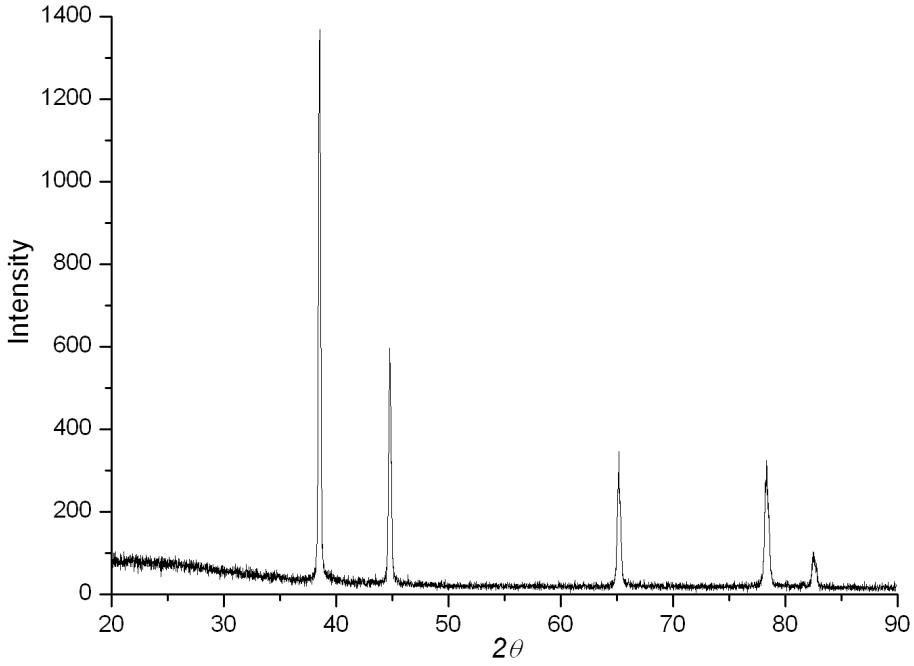

Figure S10. PXRD pattern (lines: JCPDS reference no. 4-0787) of the Al metal obtained from the reductive elimination reaction of Cp^*AlH_2 (**1**).

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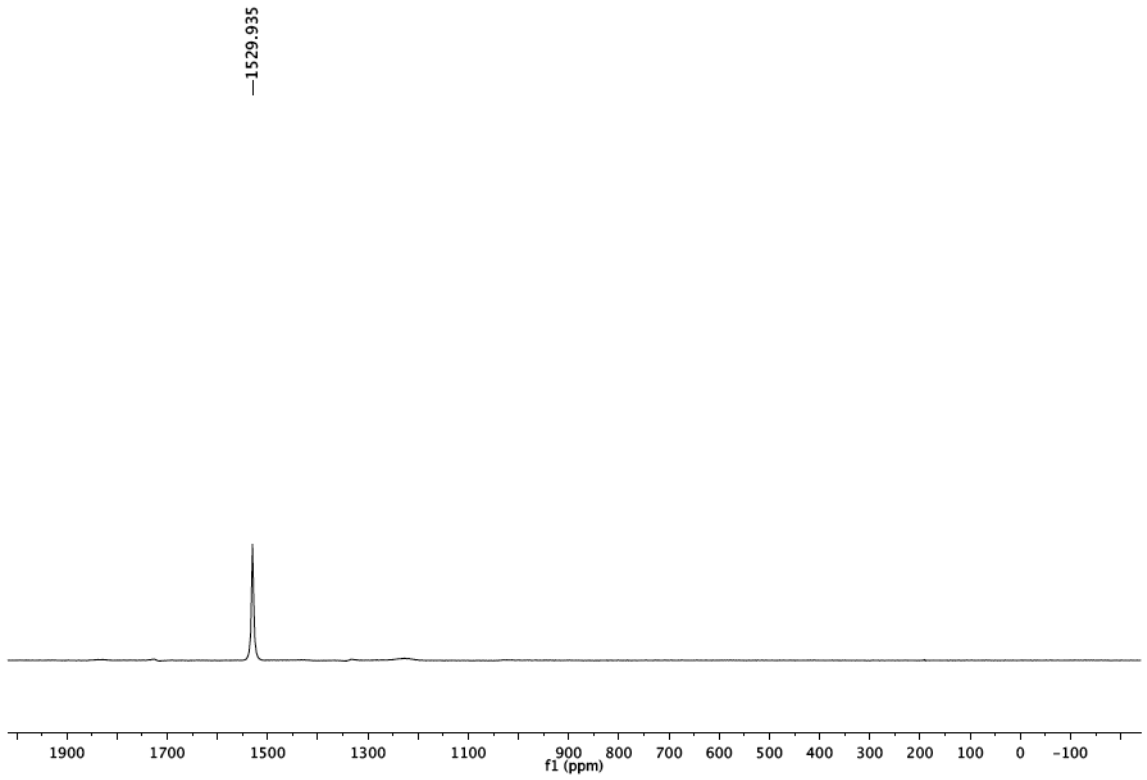

Figure S11. ^{27}Al MAS-NMR of the precipitate obtained from the reductive elimination reaction of Cp^*AlH_2 (**1**) [The NMR peak is referenced to $Al_2(SO_4)_3$].

Computational Details:

We optimized the geometries of the molecules shown below at BP86/def2-TZVPP[2-4] with the Gaussian 03, revision E.01[5] algorithm using energies calculated with the Turbomole 6.3[6] program package. The RI approximation[7] was applied using auxiliary basis functions.[8] Multipole accelerated RI-J (MARI-J)[9] was enabled. Frequencies and thermodynamic corrections were calculated with the aoforce[10] program out of the Turbomole package.

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Energy-decomposition analyses (EDA) were carried out using the ADF(2012.01) program package.[11] Uncontracted Slater-type orbitals (STOs) were employed as basis functions in self-consistent field (SCF) calculations.[12] Triple-zeta-quality basis sets were used which were augmented by two sets of polarization functions, that is, p and d functions for the hydrogen atom and d and f functions for the other atoms. An auxiliary set of s, p, d, f and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.[13]

Within the EDA, bond formation between the interacting fragments is divided into three steps: In the first step, the fragments which are calculated with the frozen geometry of the entire molecule, are superimposed without electronic relaxation to yield the quasiclassical electrostatic attraction ΔE_{elstat}. In the second step, the product wave function becomes antisymmetrized and renormalized, which gives the repulsive term ΔE_{Pauli}, named the Pauli repulsion. The third step consists of the relaxation of the molecular orbitals to their final form to yield to stabilizing orbital interaction ΔE_{orb}. The sum of the three terms $\Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}$ gives the total interaction energy ΔE_{int}. The interaction energy together with the preparation energy ΔE_{prep} (the energy necessary to promote the fragments from their equilibrium geometry to the geometry of the compounds) give the bond-dissociation energy as $-D_e = \Delta E_{\text{prep}} + \Delta E_{\text{int}}$. Because we are not concerned with the bond-dissociation energies in this paper we give only the values for ΔE_{int} and its contributing terms.

The lattice energy of aluminium was calculated with the VASP program in the version 5.2.12.[14] The used method was PBE[15]/PAW[16] (with E_{cut} = 350 eV, K-point grid: 25

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25 25 for metal; G-only for atom) together with the DFT-D3 dispersion correction including the new Becke-Johnson damping function.[17]

Coordinates and energy of the calculated species:

Cp^*AlH_2

-633.9151670961
a.u.

Al	-0.292258	-0.037775	0.132170
C	-1.072909	0.008766	-2.015391
C	-1.297674	-1.291301	-1.480899
C	-2.197125	-1.162607	-0.354676
C	-2.547240	0.216174	-0.225537
C	-1.805164	0.956654	-1.208050
C	-1.915597	2.435489	-1.462692
H	-2.097681	2.996999	-0.537632
H	-2.747489	2.656059	-2.150029
H	-1.003466	2.842466	-1.917952
C	-0.172920	0.320521	-3.172843
H	-0.037631	1.401503	-3.302207
H	-0.583323	-0.073288	-4.115279
H	0.825359	-0.124248	-3.039675
C	-0.711059	-2.562457	-2.020722
H	0.341118	-2.431370	-2.310262
H	-1.255348	-2.902465	-2.915940
H	-0.754282	-3.377308	-1.286822
C	-2.762404	-2.283944	0.471074
H	-3.747757	-2.596568	0.090412
H	-2.896213	-1.989229	1.520140
H	-2.115556	-3.170601	0.456308
C	-3.424155	0.788715	0.845592

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H	-4.330934	0.183927	0.983521
H	-3.742792	1.809754	0.601574
H	-2.901802	0.827708	1.817278
H	-0.464359	0.377736	1.675590
H	1.232809	-0.269268	-0.316373

AlH

-243.0072401973
a.u.

Al	0.000000	0.000000	-0.088076
H	0.000000	0.000000	1.588076

Cp^*H

-390.8403713521
a.u.

C	-1.730623	-0.752864	2.408037
C	-1.764174	0.729277	2.387605
C	-0.807076	1.190507	1.539170
C	-0.069353	0.006137	0.947890
C	-0.752967	-1.193615	1.572256
C	-0.469557	2.602388	1.183375
H	-0.572836	2.785336	0.101062
H	-1.115924	3.322198	1.701410
H	0.572899	2.852518	1.441470
C	-2.740021	1.527106	3.198215
H	-2.632923	1.321301	4.274935
H	-2.609676	2.606457	3.052628
H	-3.780484	1.278790	2.935646
C	-2.671438	-1.571340	3.239224
H	-2.575679	-1.332402	4.310105
H	-3.721475	-1.377180	2.968988
H	-2.492645	-2.647255	3.122706

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C	-0.354171	-2.598174	1.252917
H	0.700431	-2.793559	1.508778
H	-0.963285	-3.331543	1.796399
H	-0.457303	-2.816258	0.177078
C	1.451024	0.044020	1.192042
H	1.945198	-0.837064	0.760063
H	1.904719	0.935137	0.736962
H	1.664646	0.062898	2.269805
H	-0.239835	-0.012815	-0.146777

Cp^*_2AlH

-1023.5792634990
a.u.

Al	-0.055707	-0.062803	-0.081824
C	-1.360204	-1.705732	-0.941352
C	-1.547847	-2.286605	0.342257
C	-2.288001	-1.385143	1.152419
C	-2.574178	-0.227030	0.399001
C	-2.007908	-0.388358	-0.919332
C	-0.911958	-2.425440	-2.185561
H	-0.518057	-1.739830	-2.945774
H	-1.752305	-2.969680	-2.647657
H	-0.127280	-3.164339	-1.974210
C	-1.001319	-3.601022	0.814544
H	-0.400917	-4.097602	0.042041
H	-1.812351	-4.292407	1.092850
H	-0.366487	-3.482868	1.706383
C	-2.587487	-1.603427	2.605752
H	-3.094439	-2.566188	2.771553
H	-3.237881	-0.818117	3.011011
H	-1.667966	-1.618109	3.213272

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C	-3.361235	0.967735	0.857486
H	-4.443711	0.815951	0.713092
H	-3.089198	1.873823	0.299542
H	-3.204883	1.180012	1.923791
C	-2.480472	0.345440	-2.148996
H	-2.697090	1.401467	-1.942155
H	-3.410824	-0.107374	-2.530724
H	-1.750506	0.311143	-2.968659
C	1.520324	0.610433	-1.401928
C	0.939645	1.812899	-0.786231
C	1.598404	2.001157	0.464046
C	2.553287	0.968755	0.638523
C	2.515117	0.117202	-0.486721
C	3.367156	-1.103144	-0.689993
H	3.358153	-1.766912	0.186587
H	4.418744	-0.829083	-0.872092
H	3.035213	-1.692006	-1.554458
C	1.478526	0.312910	-2.879676
H	1.729905	-0.732941	-3.098136
H	2.206342	0.941393	-3.419383
H	0.494242	0.514214	-3.322942
C	0.132281	2.850057	-1.523119
H	-0.518565	2.407433	-2.286970
H	0.793520	3.566141	-2.039175
H	-0.507941	3.432752	-0.846884
C	1.297198	3.072095	1.471242
H	0.500155	3.743464	1.127739
H	2.184945	3.693953	1.667011
H	0.984543	2.651433	2.439297
C	3.370057	0.746740	1.876969

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H	3.660874	1.698835	2.342443
H	4.291696	0.190426	1.659619
H	2.814033	0.172926	2.636990
H	0.271071	-0.360397	1.427935

Cp^*Al

-632.7319987220
a.u.

C	-1.799292	-0.722048	2.383989
C	-1.830116	0.709420	2.343111
C	-0.611380	1.161335	1.741056
C	0.172632	0.009293	1.410090
C	-0.561721	-1.154618	1.806826
C	-0.199548	2.593088	1.553664
H	-1.063981	3.248450	1.383387
H	0.326613	2.974533	2.443518
H	0.479417	2.714462	0.699388
C	-2.916946	1.585409	2.896407
H	-2.724634	1.837752	3.951612
H	-2.997964	2.532612	2.346948
H	-3.898402	1.094988	2.854475
C	-2.848439	-1.610806	2.987461
H	-2.644703	-1.797613	4.054113
H	-3.849209	-1.163878	2.922466
H	-2.891324	-2.588909	2.490309
C	-0.087489	-2.575392	1.700839
H	0.470123	-2.875977	2.602452
H	-0.923658	-3.278123	1.588378
H	0.582413	-2.720101	0.842982
C	1.551174	0.021285	0.814983
H	1.744354	-0.876236	0.212699

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H 1.709114 0.893420 0.166903

H 2.322568 0.056813 1.600964
Al -1.792130 -0.069164 0.132970

H_2

-1.1778427895

H 0.000000 0.000000 -0.044799

H 0.000000 0.000000 0.704799

Al

-242.39180239214

Al 0.000000 0.000000 0.000000

Considered reactions:

Reaction 1: $Cp^*AlH_2 \rightarrow Al + 1/2\ H_2 + Cp^*H$

Reaction 2: $Cp^*_2AlH \rightarrow (\leftarrow)\ Cp^*Al + Cp^*H$

Reaction 3: Al (atom) → Al (metal)

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Table S3. EDA results for the breaking of the indicated bonds in the respective molecule. Energies in kcal/mol at BP86/TZ2P+. Doublet states were chosen for the electronic configuration of the fragments.

	ΔE_{int}	ΔE_{Pauli}	ΔE_{elstat}	ΔE_{orb}
$Cp^*–AlH_2$	-151.4	253.5	-185.2 (45.7%)	-219.8 (54.3%)
$Cp^*HAl–H$	-82.9	36.2	-39.9 (33.5%)	-79.1 (66.5%)
$Cp^*–AlCp^*H$	-140.5	246.4	-165.9 (42.9%)	-221.1 (57.1%)
$Cp^*_2Al–H$	-84.5	31.7	-40.3 (34.7%)	-75.9 (65.3%)
$Al–Cp^*$	-163.0	309.2	-204.1 (43.2%)	-268.1 (56.8%)
Al–H	-73.4	46.5	-40.9 (34.1%)	-79.0 (65.9%)

Table S4: Reaction energies at BP86/TZVPP level of theory in kcal/mol. ΔE are the electronic energies; ΔG include thermodynamical corrections at 298.15 K and 1.013 bar.

Reaction	ΔE	ΔG
1	59.0	60.3
2	4.3	-3.7

Table S5: Reaction energy at PBE-D3 (BJ)/PAW (E_{cut} = 350 eV, K-point grid: 25 25 25 for metal; G-only for atom) level of theory in kcal/mol.

Reaction	ΔE
3	-93.6

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X-Ray Crystallography

X-ray data for compounds **1** and **2** were collected on an Agilent SuperNova diffractometer. The crystals were coated with a perfluoropolyether, picked up with a glass fiber, and immediately mounted in the cooled nitrogen stream of the diffractometer. The structural solution and refinement were performed using the programs SHELXS-97 and SHELXL-97.[18] Molecules **1** and **2** were refined with distance restraints and restraints for the anisotropic displacement parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center (CCDC 912124 912123). The crystal data are available from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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