Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Addition of *in-situ* reduced amidinato-methylaluminium chloride to acetylenes

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General methods

All syntheses were performed using standard Schlenk techniques under an inert argon atmosphere. All solvents and reagents were purchased from commercial sources. Solvents were dried using the solvent purification system PureSolv MD 7 supplied by Innovative Technology, Inc., degassed and then stored under an argon atmosphere over a potassium mirror. The melting points were measured in inert perfluoroalkylether oil and were uncorrected. The elemental analyses (C, H and N) of new compounds were performed under an inert argon atmosphere on an automatic analyzer EA 1108 by FISONS Instruments. The mass spectra were measured on GC/MS configuration comprised of an Agilent Technologies - 6890N gas chromatograph (HP-5MS column, length 30 m, I.D. 0.25 mm, film 0.25 μm), equipped with a 5973 Network MS detector (EI 70 eV, mass range 33-550 Da). Deuterated benzene for NMR samples preparation was distilled, degassed and stored over a K-mirror under an argon atmosphere. NMR spectra of appropriate compounds in C_6D_6 solutions were recorded on a Bruker Avance 500 spectrometer (equipped with *Z*-gradient 5mm probe) with a resonance frequency of 500.13 MHz for ^{1}H, 125.76 MHz for ^{13}C{^{1}H}, 186.50 MHz for ^{119}Sn{^{1}H} and 129.99 MHz for ^{27}Al{^{1}H} nuclei, respectively, at 295 K. Values of ^{1}H and ^{13}C chemical shifts were calibrated to residual signals of benzene (δ(^{1}H) = 7.16 / δ(^{13}C) = 128.4) while the ^{27}Al and ^{119}Sn chemical shift values are referred to external neat of 1M solution of $Al_2(SO_4)_3$ in D_2O (δ(^{27}Al) = 0.0 ppm) and tetramethylstannane (δ(^{119}Sn) = 0.0 ppm), respectively. The preparation as well as the appropriate NMR data (for the NMR spectra see Figures S1 and S2) of the starting aluminium(III) amidinate [DippNC(Me)NDipp]AlMeCl are reported elsewhere[1].

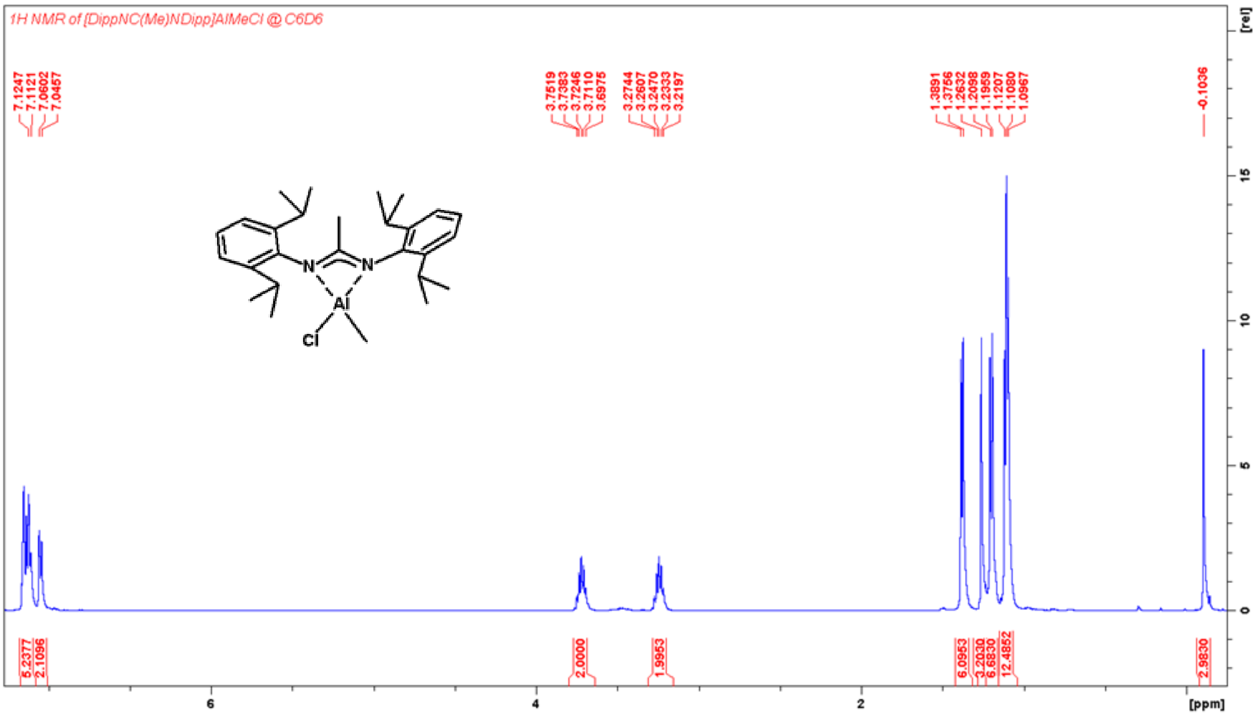


Fig. S1 ^{1}H NMR spectrum of [DippNC(Me)NDipp]AlMeCl in C_6D_6.

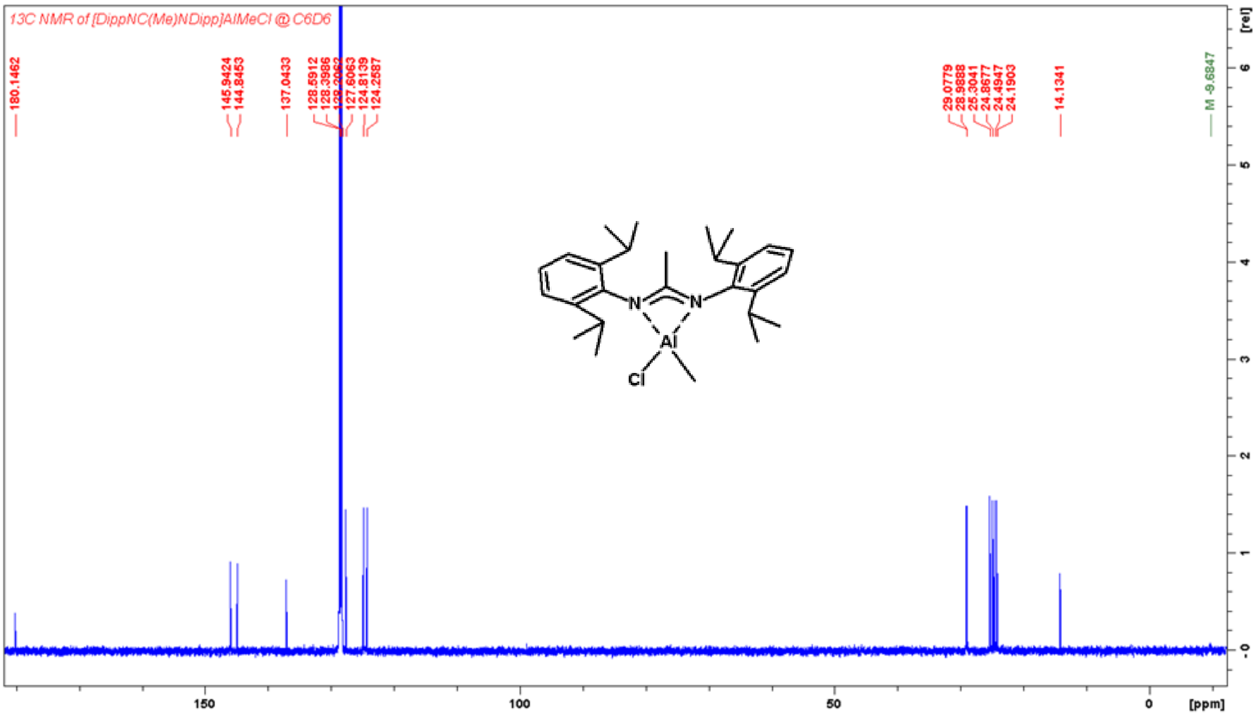


Fig. S2 $^{13}C\{^1H\}$ NMR spectrum of [DippNC(Me)NDipp]AlMeCl in C_6D_6.

Synthesis of LAlMeC(Ph)=C(Ph)AlMeL (1)

A solution of [DippNC(Me)NDipp]AlMeCl (1.465 g, 3.22 mmol) and diphenylacetylene (0.287 g, 1.61 mmol) in Et_2O (30 ml) was added into a Schlenk flask with potassium mirror (0.126 g, 3.22 mmol) and Et_2O (40 ml) at room temperature. The reaction mixture was stirred for 30 hours and then filtered with the help of celite (AW Standard Super-Cel® NF). The orange filtrate has been concentrated (ca. 10 ml) under vacuo until the white solid of **1** was precipitated. The resulting **1** was filtered off and washed with 10 ml of petroleum ether. All volatiles were evaporated under vacuo. Pure white crystalline **1** was obtained (0.508 g, 31 %). Single crystals suitable for XRD analyses were obtained from saturated solution of **1** in Et_2O at -30°C. M.p. 212 - 214 °C. ^1H NMR (C_6D_6, 500.13 MHz, 295 K, Figure S3) δ: 7.18 - 7.11 (br m, 16H, $Ar^{Dipp}+Ar^{Ph}$); 6.73 (t, 2H, ^3J = 7.3 Hz, Ph*H*); 6.36 (t, 4H, ^3J = 7.6 Hz, Ph*H*); 3.51 (br s, 4H, C*H*); 3.35 (br s, 4H, C*H*); 1.38 (s, 6H, NC(CH_3)N); 1.23 (d, ^3J = 6.6 Hz, 12H, CH_3); 1.14 (d, ^3J = 6.9 Hz, 24H, CH_3); 1.02 (br s, 12H, CH_3); -0.60 (s, 6H, AlCH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.76 MHz, 295 K, Figure S4) δ: 176.8 (N*C*N); 153.7 (*C*=*C*); 145.4 (Ar); 145.1 (Ar); 139.4 (Ar); 129.5 (Ar); 126.8 (Ar); 126.1 (Ar); 125.8 (Ar); 124.5 (Ar); 124.3 (Ar); 29.0 (*C*H); 28.7 (*C*H); 25.7 (*C*H_3); 24.7 (*C*H_3); 23.9 (*C*H_3); 15.4 (NC(*C*H_3)N); -7.6 (Al*C*H_3). Anal. Calcd for $C_{68}H_{90}Al_2N_4$: C 80.27; H 8.92; N 5.51. Found: C 79.94; H 8.83; N 5.31.

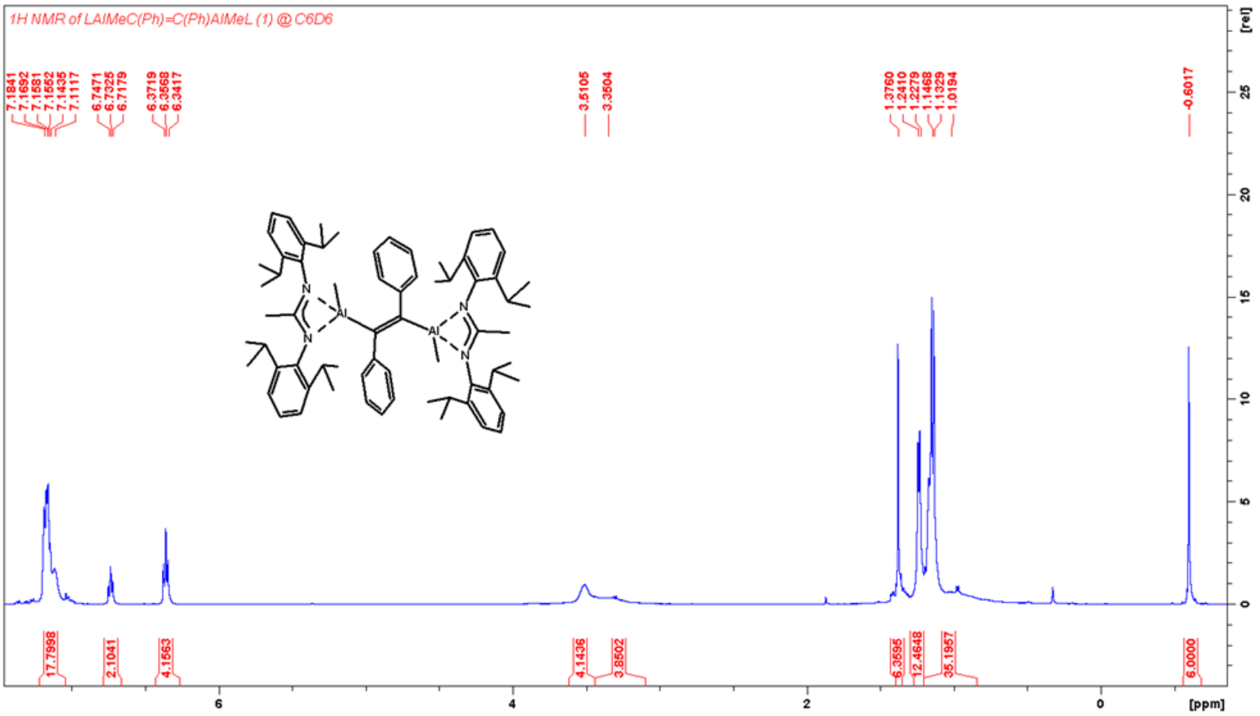


Fig. S3 ^{1}H NMR spectrum of **1** in C_6D_6.

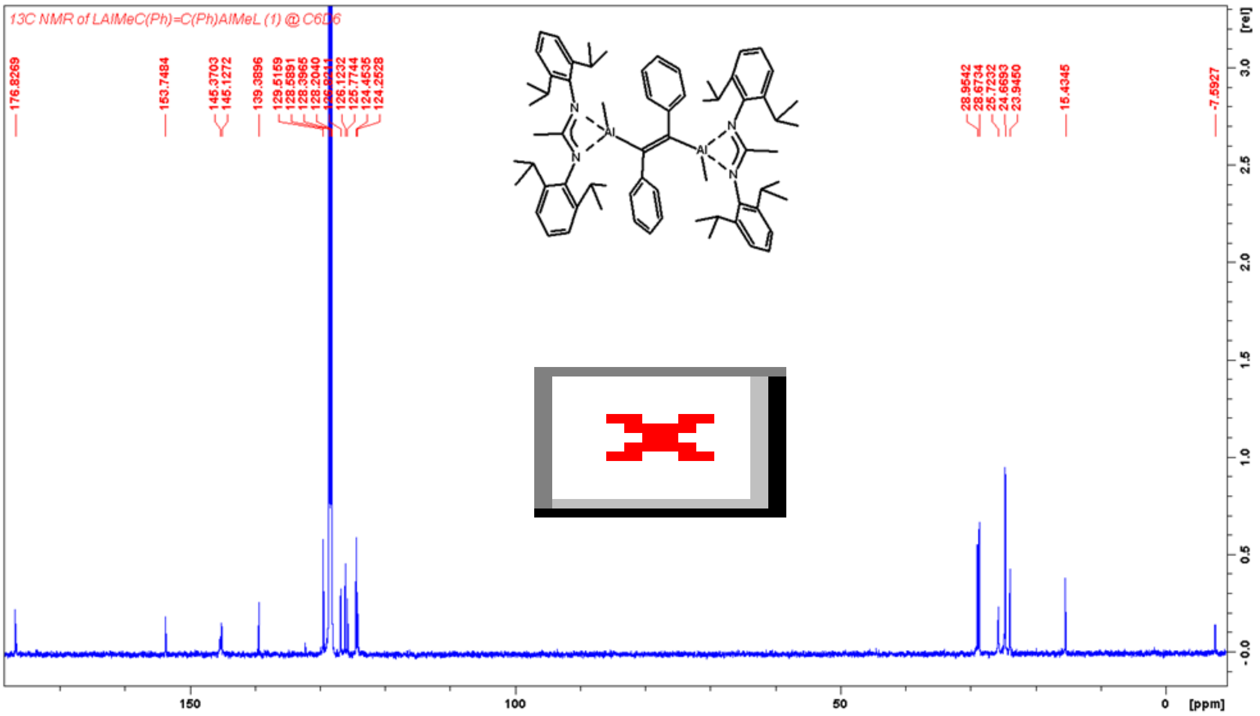


Fig. S4 $^{13}C\{^{1}H\}$ NMR spectrum of **1** in C_6D_6.

Synthesis of LAlMeC(Ph)=C(C_6H_4-4-$SiMe_3$)AlMeL (2)

A solution of [DippNC(Me)NDipp]AlMeCl (1.912 g, 4.20 mmol) and 4-(trimethylsilyl)diphenylacetylene (0.526 g, 2.10 mmol) in Et_2O (40 ml) was added into a Schlenk flask with potassium mirror (0.164 g, 4.20 mmol) and Et_2O (40 ml) at room temperature. The reaction mixture was stirred for 30 hours and then filtered with the help of celite (AW Standard Super-Cel® NF). The orange filtrate has been concentrated (ca. 15 ml) under vacuo until the white solid of **2** was precipitated. The resulting **2** was filtered off and washed with 15 ml of petroleum ether. All volatiles were evaporated under vacuo. Pure off-white crystalline **2** was obtained (0.618 g, 27 %). Single crystals suitable for XRD analyses were obtained from the saturated solution of **2** in hexane at -30°C. M.p. 205 - 207.5 °C. ^{1}H NMR (C_6D_6, 500.13 MHz, 295 K) δ: 7.14 - 7.08 (br m, 16H, Ar^{Dipp}+$Ar^{PhSiMe3}$); 6.70 (t, 1H, ^3J = 7.4 Hz, Ph*H*); 6.46 (d, 2H, ^3J = 7.8 Hz, Ph*H*); 6.33 (t, 2H, ^3J = 7.6 Hz, Ph*H*); 3.63 (br s, 1H, C*H*); 3.48 (br s, 4H, C*H*); 3.34 (br s, 3H, C*H*); 1.35 (s, 6H, NC(C*H*$_3$)N); 1.22 (d, ^3J = 6.8 Hz, 12H, C*H*$_3$); 1.17 (d, ^3J = 6.8 Hz, 12H, C*H*$_3$); 1.22 (d, ^3J = 6.8 Hz, 12H, C*H*$_3$); 1.11 (two doublets, 24H, both ^3J = 6.9 Hz, C*H*$_3$); 0.17 (s, 3H, Si(C*H*$_3$)$_3$); -0.60 (s, 3H, AlC*H*$_3$); -0.61 (s, 3H, AlC*H*$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 125.76 MHz, 295 K) δ: 176.8 (N*C*N); 176.7 (N*C*N); 153.8 (*C*=*C*); 153.7 (*C*=*C*); 145.0 (br s, Ar); 139.4 (Ar); 139.3 (Ar); 136.1 (Ar); 134.5 (Ar); 129.5 (Ar); 126.8 (br s, Ar); 126.7 (br s, Ar); 126.1 (Ar); 125.8 (Ar); 125.7 (Ar); 124.5 (Ar); 124.4 (Ar); 124.2 (br s, Ar); 124.0 (Ar); 29.0 (*C*H); 28.9 (*C*H); 28.7 (two signal, *C*H); 25.8 (br s, *C*H$_3$); 25.7 (*C*H$_3$); 24.7 (*C*H$_3$); 24.6 (*C*H$_3$); 23.9 (*C*H$_3$); 23.8 (*C*H$_3$); 15.4 (two singnal, NC(*C*H$_3$)N); -0.51 (Si(*C*H$_3$)$_3$); -7.5 (two signal, Al*C*H$_3$). Anal. Calcd for $C_{71}H_{98}Al_2N_4Si$: C 78.26; H 9.07; N 5.14. Found: C 77.86; H 8.73; N 4.92.

Synthesis of $\{[LAl^-(C{\equiv}C\text{-}SnMe_3)_3]K^+\}_2$ (3)

A solution of [DippNC(Me)NDipp]AlMeCl (1.051 g, 2.31 mmol) and bis(trimethylstannyl)acetylene (0.812 g, 2.31 mmol) in Et_2O (40 ml) was added into a Schlenk flask with potassium mirror (0.271 g, 6.93 mmol) and Et_2O (50 ml) at room temperature. The reaction mixture was stirred for 40 hours and then filtered with the help of celite (AW Standard Super-Cel® NF) affording pale yellow filtrate. The Et_2O was removed under vacuo and the residual yellow solid was dissolved in hexane (30 ml). The mixture was filtered and the colourless filtrate was stored at 7 °C for three days to give colourless single crystals of **3** (0.162 g) suitable for XRD analyses. M.p. 163 - 165.5 °C. ^{1}H NMR (C_6D_6, 500.13 MHz, 295 K) δ: 7.19 - 7.08 (br m, 12H, Ar*H*); 3.78 (m, 8H, C*H*); 1.47 (d, ^3J = 6.8 Hz, 24H, C*H*$_3$); 1.37 (s, 6H, NC(C*H*$_3$)N); 1.31 (d, ^3J = 6.9 Hz, 24H, C*H*$_3$); 0.09 (s, 36H, Sn(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 125.76 MHz, 295 K) δ: 165.9 (N*C*N); 145.5 (Ar); 144.4 (Ar); 124.8 (Ar); 124.2 (Ar); 110.1 (br s, *C*-Al); 97.2 (*C*-Sn); 28.2 (*C*H); 26.4 (*C*H$_3$); 24.8 (*C*H$_3$); 18.6 (NC(*C*H$_3$)N); -7.3 (Sn(*C*H$_3$)$_3$; ^1J ($^{119/117}$Sn,^{13}C) = 396/378 Hz). ^{119}Sn{^{1}H} NMR (C_6D_6, 186.50 MHz, 295 K) δ: -88. Anal. Calcd for $C_{82}H_{128}Al_2K_2N_4Sn_6$: C 48.89; H 6.40; N 2.78. Found: C 48.63; H 6.12; N 2.54.

X-ray structure determination

The compounds **1** (Figure S5), **2** (Figures S6 and S7) and **3** (Figure S8) have been characterized by single crystal X-ray crystallography techniques. The crystallographic details are summarized in Table S1. All diffraction experiments were performed under an inert oil using the Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with a Mo K_α radiation (λ = 0.71073 Å), a graphite monochromator, and the ϕ and χ scan mode at 150K. Data reductions were done with DENZO-SMN[2]. The absorption was corrected by integration methods[3]. Structures were solved by direct methods (Sir92)[4] and refined by a full matrix least-square based on F^2 (SHELXL97)[5]. Hydrogen atoms were mostly localized on a difference Fourier map, however, to ensure uniformity of the crystal treatment, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or of $1.5U_{eq}$ (methyl). The H atoms in methyl, methylene, methine and hydrogen atoms in aromatic rings were placed with C-H distances of 0.96, 0.97, 0.98 and 0.93 Å.

There is disordered hexane solvent in the special position of **3**, attempts were made to model this disorder or split it into two positions, but were unsuccessful. PLATON /SQUEZZE[6] was used to correct the data for the presence of disordered solvent. A potential solvent volume of 450 Å^3 was found. 90 electrons per unit cell worth of scattering were located in the void. The calculated stoichiometry of solvent was calculated to be two molecules of hexane per unit cell.

Crystallographic data for structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC no. 1406406 - 1406408 for **1** - **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table S1 Crystallographic data for **1** - **3**.

Compound reference	**1**	**2**	**3**
Formula	$C_{68}H_{90}Al_2N_4$	$C_{71}H_{98}Al_2N_4Si$	$C_{82}H_{128}Al_2K_2N_4Sn_6.(C_6H_{14})$
M_r [g.mol^{-1}]	1017.40	1089.59	2100.35
Crystal system	Monoclinic	Triclinic	Monoclinic
a [Å]	20.4820(17)	10.6230(8)	17.7131(10)
b [Å]	16.1560(7)	15.6590(8)	14.4470(12)
c [Å]	20.007(3)	22.1571(11)	25.0359(14)
α [°]	90	98.155(4)	90
β [°]	108.305(10)	99.819(5)	126.853(5)
γ [°]	90	107.948(5)	90
V [Å^3]	6285.5(12)	3379.9(4)	5126.5(6)
Space group	$P2_1/c$	$P\text{-}1$	$P2_1/c$
Crystal color	colourless	colourless	colourless
T_{min}/T_{max}	0.968/0.985	0.974/0.990	0.607/0.849
Z	4	2	2
μ/mm^{-1}	0.087	0.102	1.576
reflns measured	55909	32390	36678
independent reflns	13917	12235	11552
R_{int}[a]	0.083	0.096	0.028
GOF on F^2 (S)[b]	1.149	1.162	1.205
Final R_1 ($I > 2\sigma(I)$)[c]	0.061	0.068	0.032
Final $wR(F^2)$ ($I > 2\sigma(I)$)[c]	0.117	0.120	0.062

[a] $R_{int} = \sum |F_o^2 - F_{o,mean}^2| / \sum F_o^2$. [b] $S = [\sum(w(F_o^2 - F_c^2)^2) / (N_{diffr.} - N_{param.})]^{1/2}$. [c] Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$, $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{1/2}$

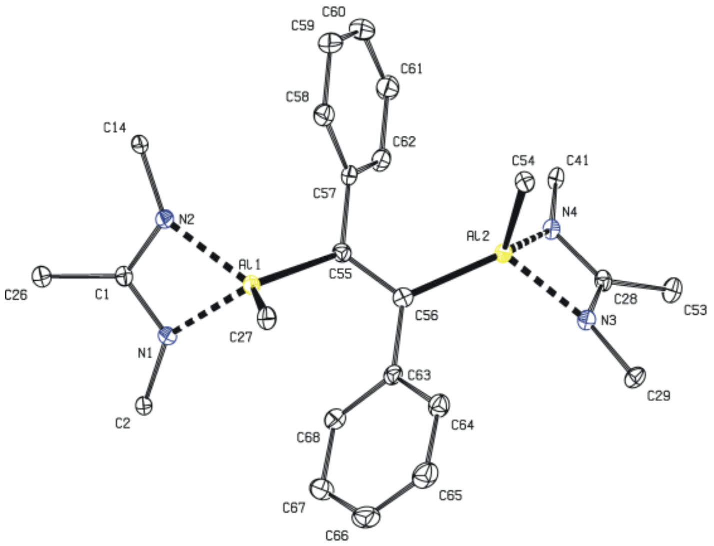


Fig. S5 The coordination sphere of aluminium atoms in **1** in detail.

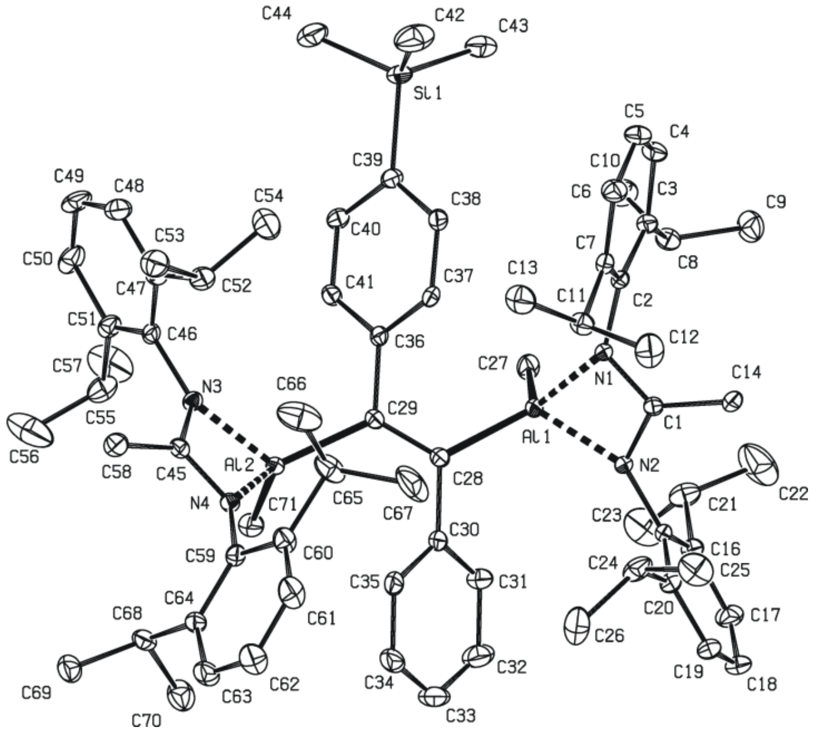


Fig. S6 The molecular structure of **2** (ORTEP view, 30% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: N1-C1 1.327(4); N2-C1 1.329(4); N4-C45 1.334(4); N3-C45 1.340(4); C1-Al1 2.378(3); C45-Al2 2.383(3); Al1-C27 1.954(4); Al2-C71 1.955(4); N1-Al1 1.965(3); N2-Al1 1.953(3); N3-Al2 1.982(3); N4-Al2 1.929(3); Al1-C28 1.984(3); C28-C29 1.364(4); C29-Al2 1.986(3); N1-C1-N2 110.4(3); N3-C45-N4 110.2(3); C1-Al1-C28 132.58(13); C45-Al2-C29 124.65(12); Al1-C28-C29 121.9(2).

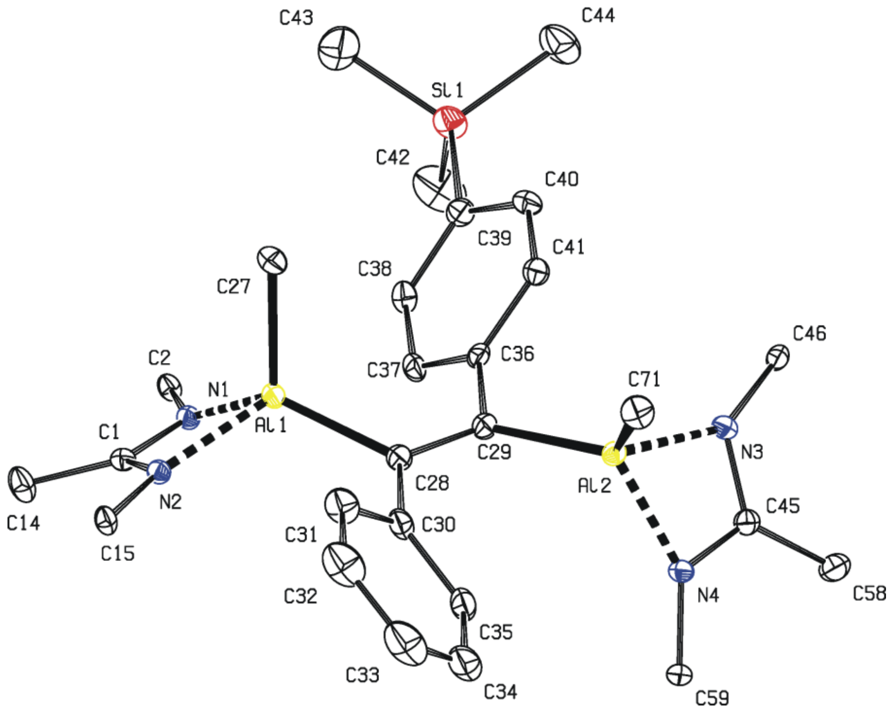


Fig. S7 The coordination sphere of aluminium atoms in **2** in detail.

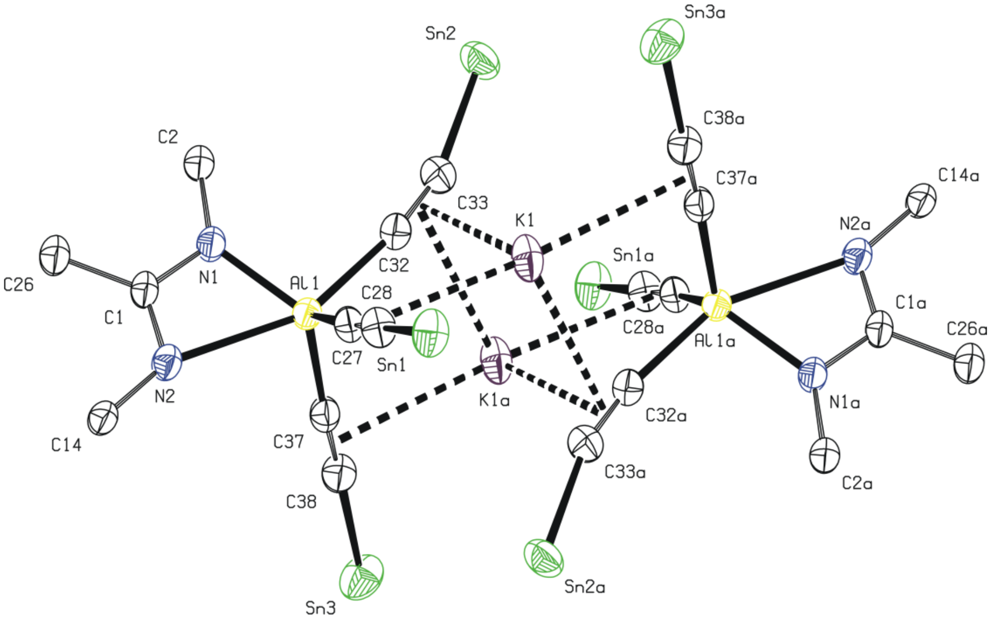
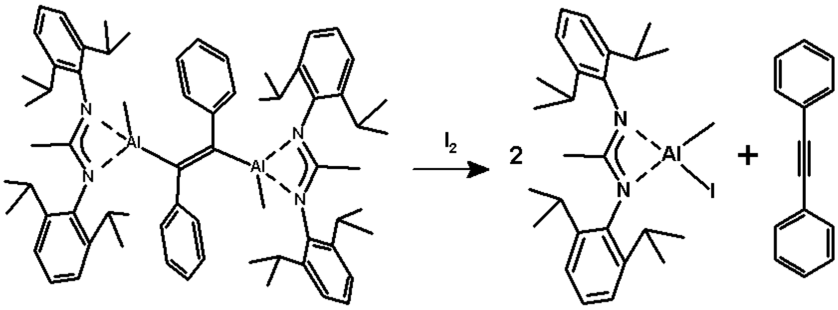


Fig. S8 The coordination sphere of aluminium and potassium atoms in **3** in detail.

Reaction of 1 with iodine



LAlMeC(Ph)=C(Ph)AlMeL (1)

LAlMeI

Scheme S1 Reaction of **1** with iodine; L = DippNC(Me)NDipp.

A colourless solution of **1** (0.436 g, 0.43 mmol) in Et_2O (30 ml) was added to a dark brown solution of iodine (0.108 g, 0.43 mmol) in Et_2O (10 ml) at room temperature (Scheme S1). The reaction mixture was stirred until it became almost colorless (*ca* 3 hours). Subsequently, the NMR spectra (Figures S9 and S10) of the reaction mixture in C_6D_6 were measured. The reaction mixture was not separated and used for a further reaction (see below) as is.

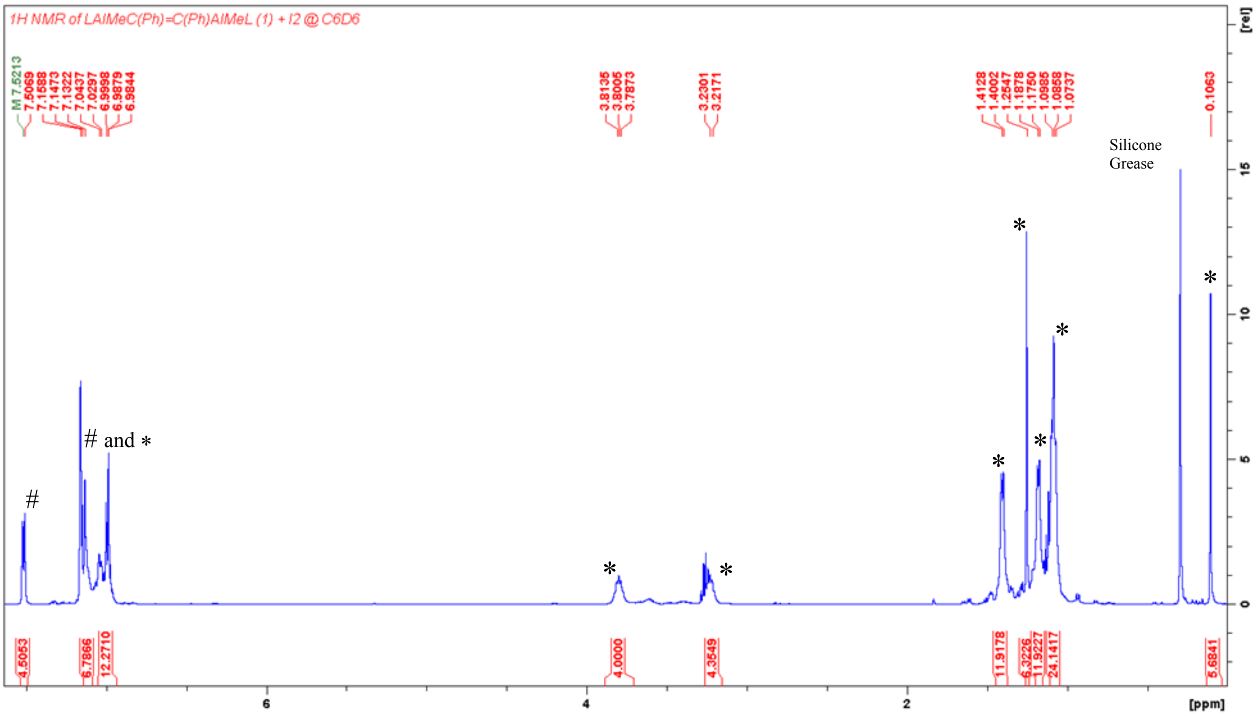


Fig. S9 ^{1}H NMR (500.13 MHz, 295 K) of the reaction mixture of **1** with iodine in C_6D_6. [DippNC(Me)NDipp]AlMeI is represented by * and diphenylacetylene is represented by #.

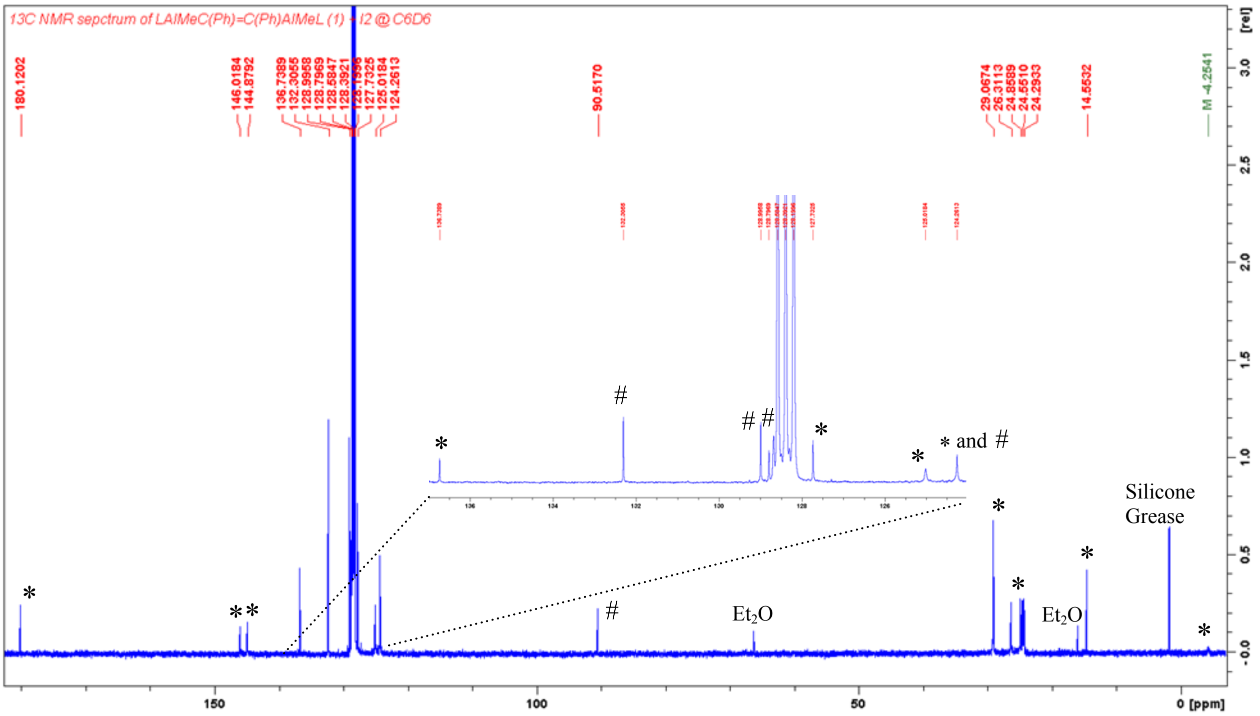
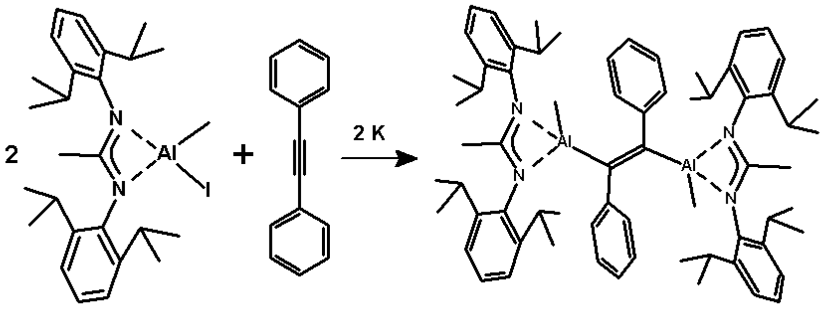


Fig. S10 ^{13}C{^{1}H} NMR (125.76 MHz, 295 K) of the reaction mixture of **1** with iodine in C_6D_6. LAlMeI is represented by * (δ: 180.1, 146.0, 144.9, 136.7, 127.7, 125.0, 124.3, 29.1, 26.3, 24.9, 24.6, 24.3, 14.6, -4.3) and diphenylacetylene is represented by # (δ: 132.3, 129.0, 128.8, 124.3, 90.5); L = DippNC(Me)NDipp.

Reaction of the LAlMeI-diphenylacetylene mixture with potassium



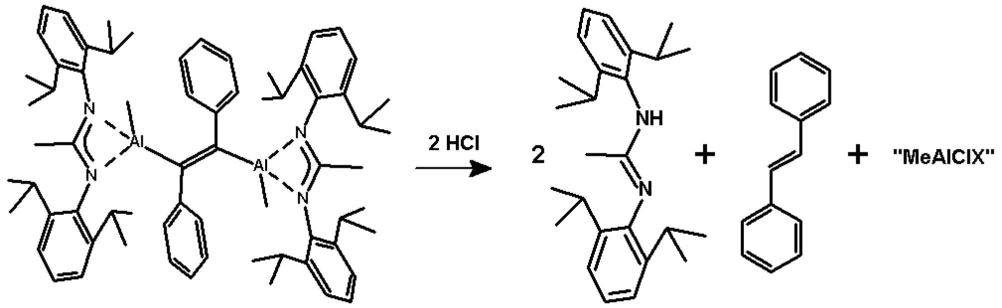
LAlMeI

LAlMeC(Ph)=C(Ph)AlMeL (1)

Scheme S2 Reaction of the LAlMeI-diphenylacetylene mixture in the presence of potassium mirror; L = DippNC(Me)NDipp.

A crude mixture (from the previous reaction; see above) of [DippNC(Me)NDipp]AlMeI (0.465 g, 0.85 mmol) and diphenylacetylene (0.076 g, 0.43 mmol) in Et_2O (30 ml) was added into a Schlenk flask with potassium mirror (0.033 g, 0.85 mmol) and Et_2O (30 ml) at room temperature (Scheme S2). The reaction mixture was stirred for 30 hours and then filtered with the help of celite (AW Standard Super-Cel® NF). The orange filtrate has been concentrated (*ca* 8 ml) under vacuo until the white solid of **1** was precipitated. The resulting **1** was filtered off and washed with 5 ml of petroleum ether. All volatiles were evaporated under vacuo. Pure white crystalline **1** was obtained (0.147 g, 34 %).

Reaction of 1 with hydrogen chloride



LAlMeC(Ph)=C(Ph)AlMeL (1)

LH

Scheme S3 Reaction of **1** with two equivalents of hydrogen chloride; L = DippNC(Me)NDipp.

2M solution of hydrogen chloride in Et_2O (1.4 ml; 1.4 mmol) was added to a solution of **1** (0.358 g, 0.35 mmol) in Et_2O (20 ml) at room temperature. The reaction mixture was stirred overnight. Subsequently, the NMR spectra (Figures S11 - S13) in C_6D_6 as well as EI-MS (Figure S14) of the reaction mixture were measured.

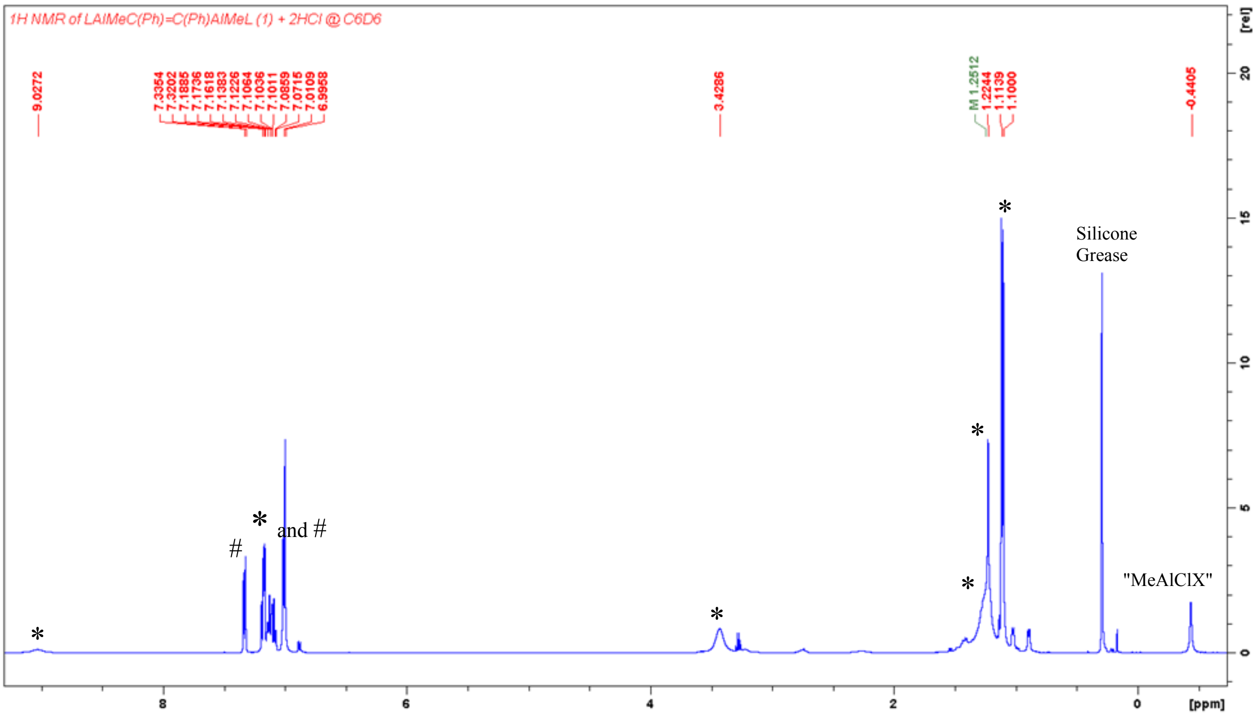


Fig. S11 ^{1}H NMR (500.13 MHz, 295 K) of the reaction mixture of **1** with HCl in C_6D_6. LH is represented by * and trans-stilbene is represented by #; L = DippNC(Me)NDipp.

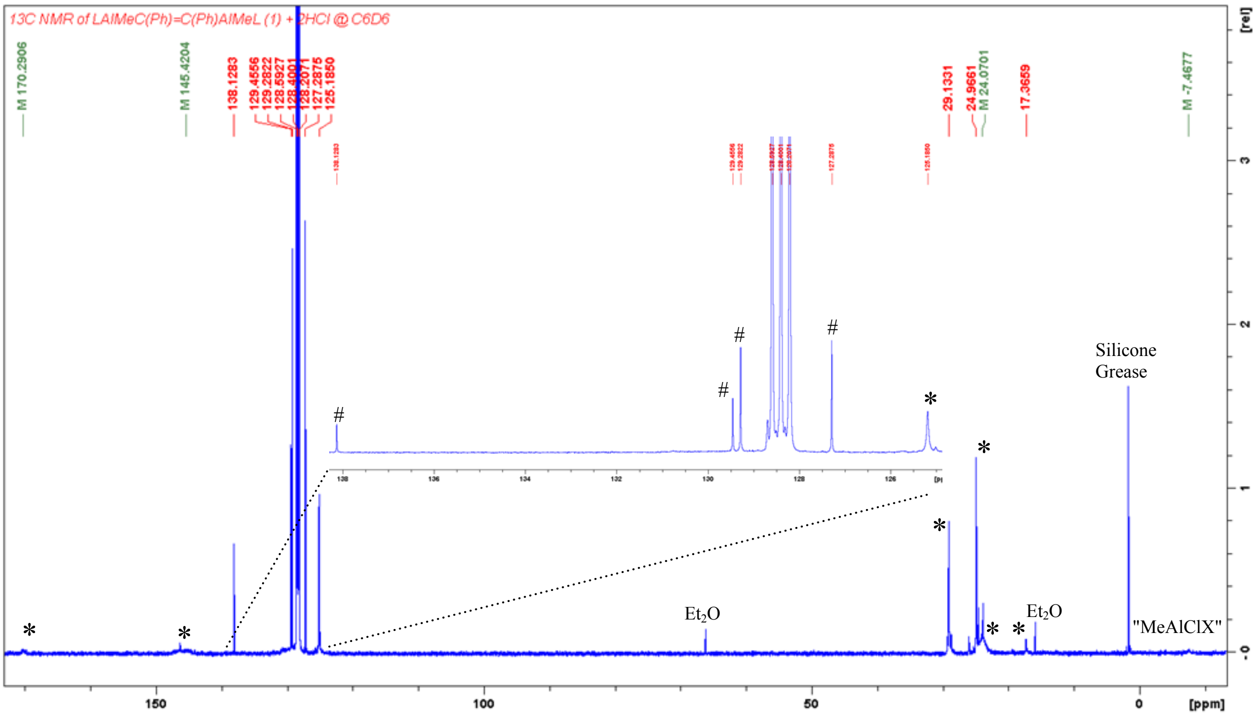


Fig. S12 $^{13}C\{^1H\}$ NMR (125.76 MHz, 295 K) of the reaction mixture of **1** with HCl in C_6D_6. LH is represented by * and trans-stilbene is represented by # (δ: 138.1, 129.5, 129.3, 127.3); L = DippNC(Me)NDipp.

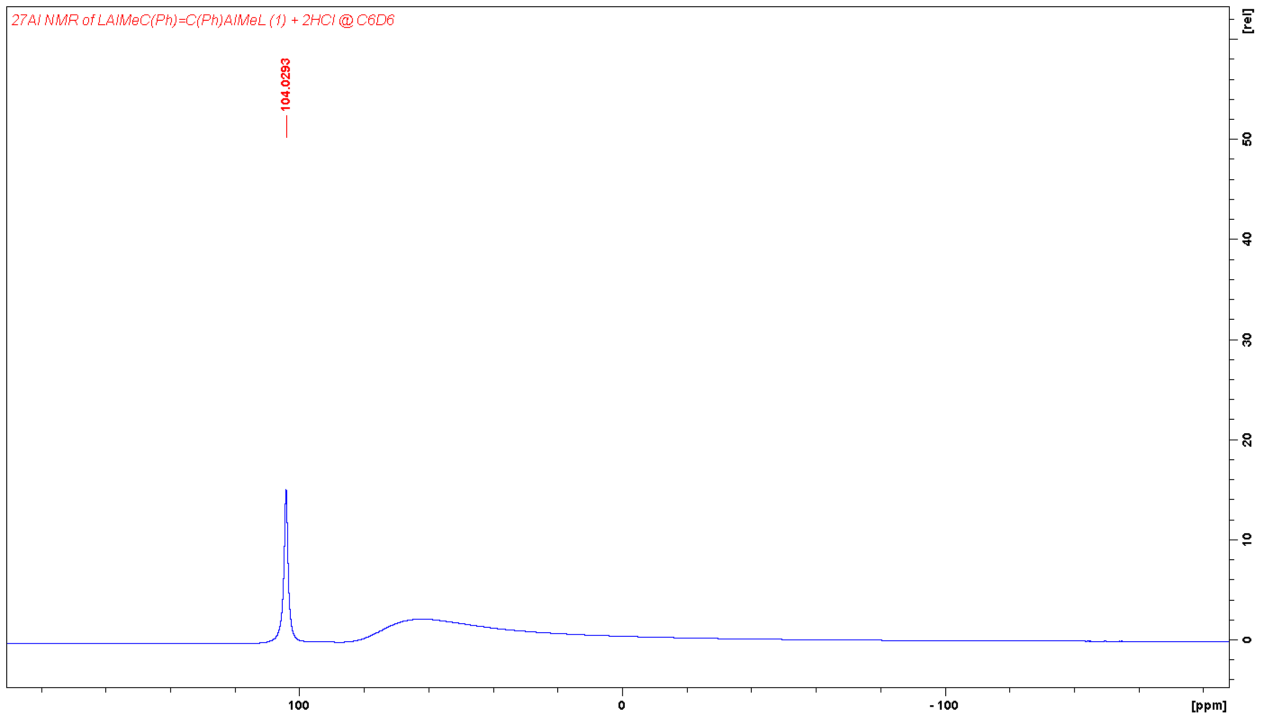


Fig. S13 ^{27}Al{^{1}H} NMR (129.99 MHz, 295 K) of the reaction mixture of **1** with HCl in C_6D_6.

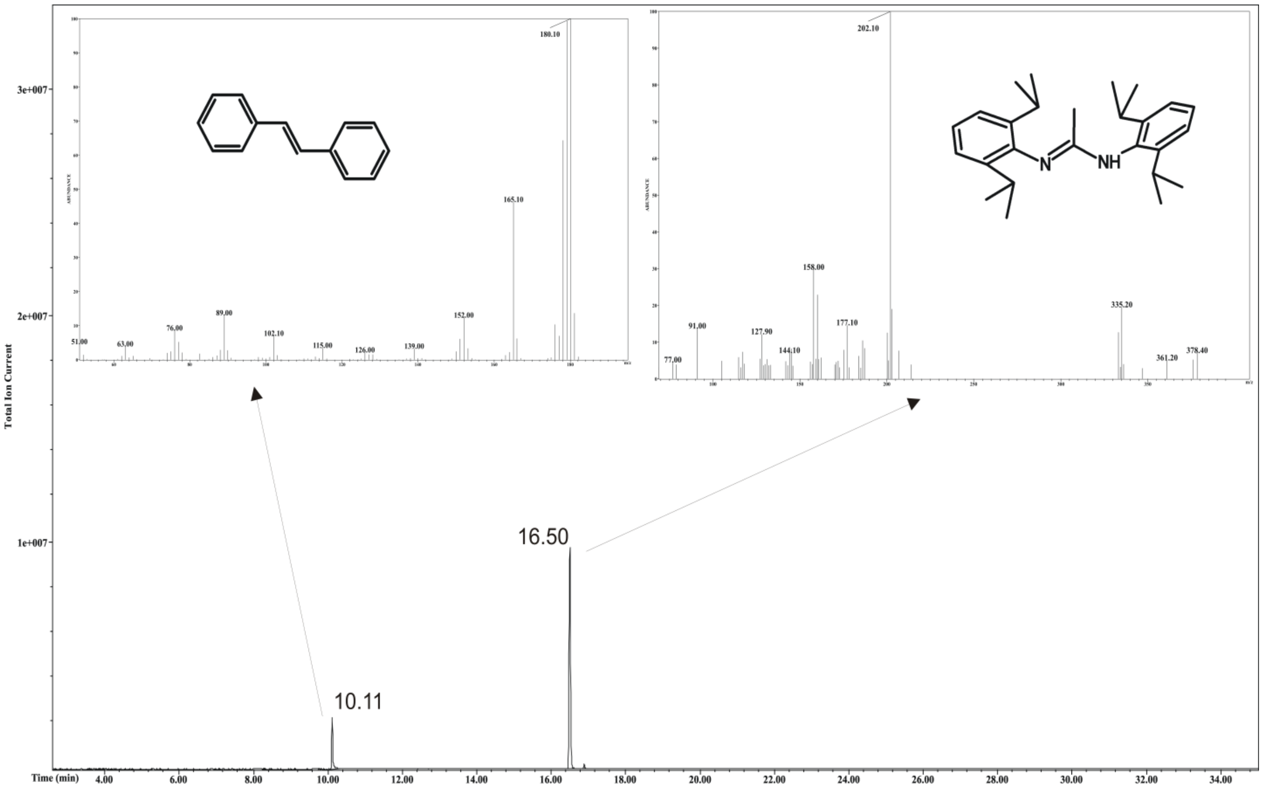


Fig. S14 EI-MS of the reaction mixture of **1** with HCl.

Computational studies

All calculations were carried out using Density Functional Theory (DFT) as implemented in the Gaussian09 quantum chemistry program.[7] Geometry optimizations were carried out at the B3LYP/cc-pVDZ level of theory and the energies of the optimized structures were re-evaluated by additional single point calculations on each of all optimized geometries using the triple-ζ-quality cc-pVTZ basis set.[8] Analytical vibrational frequencies within the harmonic approximation were computed with the cc-pVDZ basis set to confirm proper convergence to well-defined minima or saddle points on the potential energy surface. The Gibbs free energies $\mathbf{G}^{\mathbf{solv}}$(cc-pVTZ) used to calculate the energy differences reported in this article (Table S2) have been computed with the following protocol:

$$\mathbf{G}^{\mathbf{solv}}(\text{cc-pVTZ}) = \mathbf{G}(\text{cc-pVTZ}) + \mathbf{SC} \tag{1}$$

$$\mathbf{G}(\text{cc-pVTZ}) = \mathbf{E}(\text{cc-pVTZ}) + \mathbf{TC} \tag{2}$$

$$\mathbf{TC} = \mathbf{G}(\text{cc-pVDZ}) - \mathbf{E}(\text{cc-pVDZ}) \tag{3}$$

$$\mathbf{SC} = \mathbf{E}^{\mathbf{solv}}(\text{cc-pVDZ}) - \mathbf{E}(\text{cc-pVDZ}) \tag{4}$$

E(x) is the self-consistent field energy in the cc-pVDZ or cc-pVTZ basis sets respectively and **TC** is the thermal correction to the energy calculated for the cc-pVDZ basis set. **G**(cc-pVDZ) is the free energy at 298.15K for the double-ζ-quality basis set. **SC** is the solvent correction calculated using $\mathbf{E}^{\mathbf{solv}}$(cc-pVDZ), which is the self-consistent field energy in the SMD implicit solvation model using diethylether as solvent ($\varepsilon = 4.24$) in the cc-pVDZ basis set.[9]

Table S2 Energy and Gibbs free energy differences for reaction steps displayed in Fig. 1 and Fig. S16.

	ΔE (cc-pVDZ) $[\mathrm{kcal\cdot mol^{-1}}]$	$\mathbf{\Delta E^{solv}}$ (cc-pVDZ) $[\mathrm{kcal\cdot mol^{-1}}]$	**ΔE** (cc-pVTZ) $[\mathrm{kcal\cdot mol^{-1}}]$	**ΔG** (cc-pVTZ) $[\mathrm{kcal\cdot mol^{-1}}]$	$\mathbf{\Delta G^{solv}}$ (cc-pVTZ) $[\mathrm{kcal\cdot mol^{-1}}]$
INT-1→INT-2A	-54,5	-52,8	-52,5	-34,9	-31,5
INT-1→INT-2A’	-49,0	-47,2	-47,2	-28,2	-24,5
INT-1→INT-2B	-19,6	-17,8	-18,1	-4,5	-0,9
INT-1→P	-80,8	-74,1	-76,1	-42,4	-29,1
INT-1→P’	-70,8	-65,4	-65,8	-33,0	-22,2
INT-2A→INT-2A’	5,4	5,6	5,4	6,7	7,1
INT-2A→P	-26,3	-21,3	-23,6	-7,5	2,4
INT-2A→P’	-16,3	-12,6	-13,3	2,0	9,3
INT-2A’→P	-31,7	-26,9	-28,9	-14,2	-4,6
INT-2A’→P‘	-21,7	-18,2	-18,6	-4,8	2,3
INT-2B→P	-61,2	-56,3	-58,1	-38,0	-28,2
INT-2B→P’	-51,2	-47,6	-47,7	-28,5	-21,3
P→P’	10,0	8,7	10,3	9,5	6,9

As shown in Figure S15, **INT-1** is primarily aluminum-centered radical with most of the spin density located at the central metal atom (Mulliken spin densities: Al 82%, $\mathrm{C_{Me\text{-}Al}}$ 8%, $\mathrm{C_{NCN}}$ 5%, $\mathrm{N_{NCN}}$ 1%, $\mathrm{N_{NCN'}}$ 1%), while in the case of **INT-2B** the spin density is more delocalized from the ethylene carbon into the π-system of the adjacent phenyl ring (Mulliken spin densities: $\mathrm{C_{ethylene}}$ 58 %, $\mathrm{C_{C4\text{-}Ph}}$ 29 %, $\mathrm{C_{C2\text{-}Ph}}$ 24 %, $\mathrm{C_{C6\text{-}Ph}}$ 24 %, Al 7 %, $\mathrm{C_{C1\text{-}Ph'}}$ 5 %, $\mathrm{C_{C1\text{-}Ph}}$ -14%, $\mathrm{C_{C3\text{-}Ph}}$ -12%, $\mathrm{C_{C5\text{-}Ph}}$ -12%, $\mathrm{C_{ethylene'}}$ -6%, $\mathrm{C_{C2\text{-}Ph'}}$ -1%, $\mathrm{C_{C6\text{-}Ph'}}$ -1%).

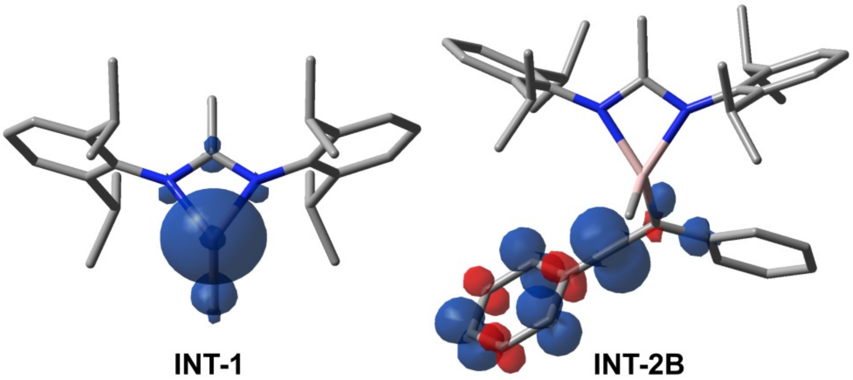


Fig. S15 Spin density plots (isovalue = 0.005 a.u.) of **INT-1** and **INT-2B**.

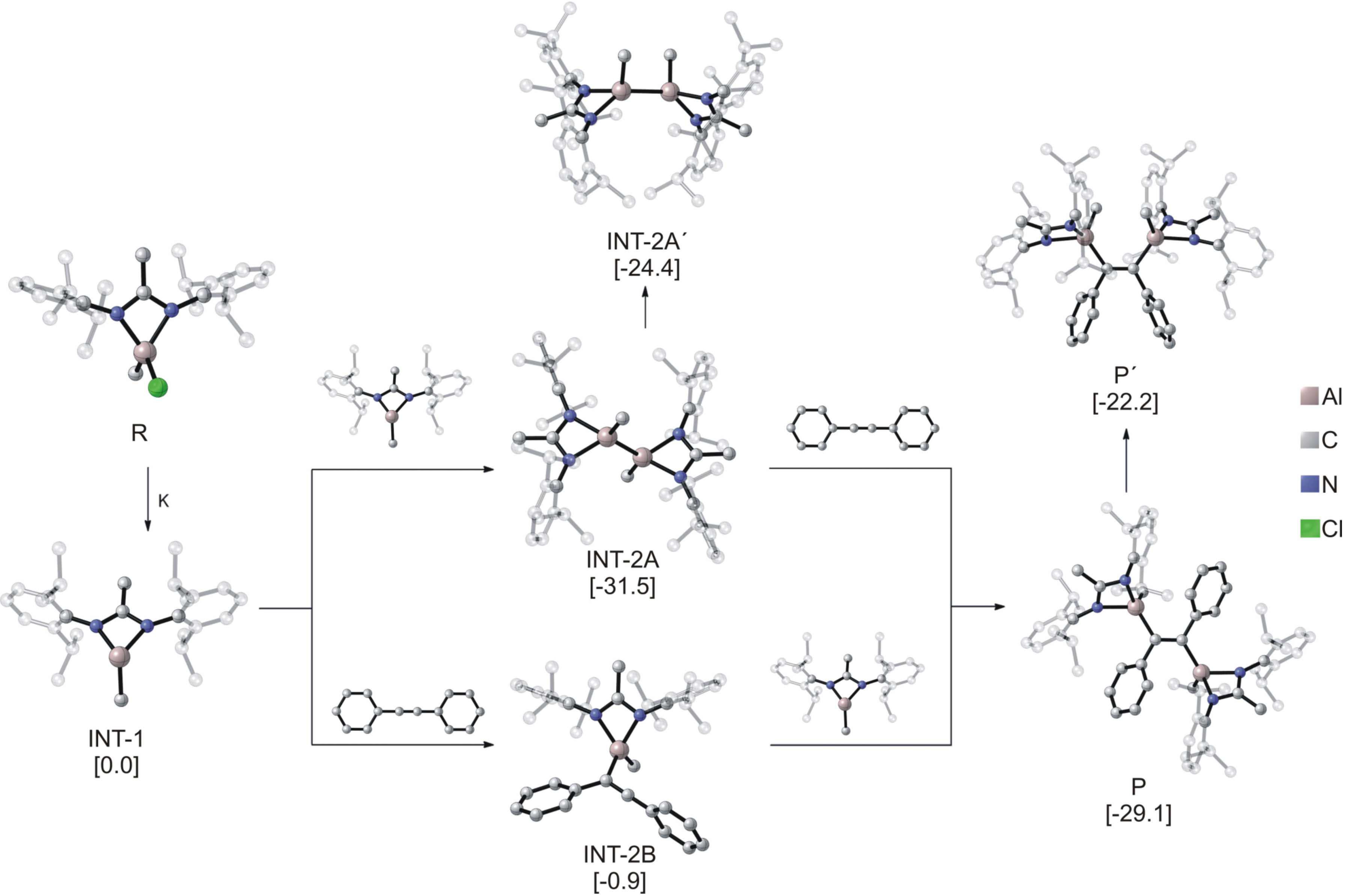


Fig. S16 Proposed reaction pathways along with Gibbs free energies (kcal mol^{-1}) for the *in-situ* interaction of [DippNC(Me)NDipp]AlMeCl (**R**) with potassium and diphenylacetylene relative to the **INT-1**. All reactants and products are represented by the B3LYP/cc-pVDZ optimized geometries.

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