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Synthesis and Characterization of Lewis Base stabilized Mono- and Di-Organo Aluminum Radicals

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Content:

(S1) Synthesis

Experimental Section

All manipulations were carried out under a dry argon or nitrogen atmosphere using Schlenk line and glovebox techniques. Toluene or diethyl ether were dried by refluxing with sodium/potassium under N_2 prior to use. Commercial reagents were purchased from Sigma Aldrich and used as received. cAAC (cyclic alkyl amino carbene) was prepared according to the literature.[1] Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker E500 spectrometer equipped with an X-band microwave source (~9.445 GHz).

(cAAC)$_2$AlClEt (1): A mixture of cAAC (285 mg; 1.0 mmol) and KC_8 (75 mg; 0.055 mmol) was placed in a 100 mL Schlenk flask and 40 mL of diethyl ether was added at -78 °C. To this mixture $EtAlCl_2$ [0.5 mL (1(M) solution in hexane), 0.5 mmol] was added at -78 °C and the reaction mixture was slowly warmed to -40 °C in three hours to give a red solution. The reaction was continued for one hour at -40 °C. Then the solvent was removed by high vacuum at -30 °C and the product was quickly extracted using 30 mL of toluene at 0 °C. After filtration of the

insoluble residue, the solution was concentrated to 10 mL in vacuum, which gave single crystals of **1** at -32 °C (Yield: 24 %).

Elemental analysis (%) for $C_{42}H_{67}AlClN_2$: calcd. C, 76.15; H, 10.19; N, 4.23; found C, 76.02; H, 10.13; N, 4.18. **1** decomposes at 132 °C.

(cAAC)$_2$AlEt$_2$ (2): A mixture of cAAC: (285 mg; 1.0 mmol) and KC_8 (75 mg; 0.055 mmol) was placed in a 100 mL Schlenk flask and 40 mL of diethyl ether were added at -78 °C. To this mixture Et_2AlCl [0.5 mL (1(M) solution in hexane), 0.5 mmol] was added at -78 °C and the reaction mixture was slowly warmed to -40 °C in three hours to give a red solution. The reaction was continued for one hour at -40 °C. Then the solvent was removed in vacuum at -30 °C and the product was quickly extracted using 30 mL of toluene at 0 °C. After filtration of the insoluble residue, the solution was concentrated to 10 mL in vacuum, to result in a crystalline product of **2** at -32 °C (Yield: 22 %).

Elemental analysis (%) for $C_{44}H_{72}AlN_2$: calcd. C, 80.55; H, 11.06; N, 4.27; found C, 80.21; H, 10.97; N, 4.24. **2** decomposes at 126 °C.

(S2) **Theoretical calculations**

Computational Details: All theoretical calculations are performed by density functional theory (DFT) methods using Gaussian 09[2] and ADF2017.106[3] program packages. Geometries of all the complexes are optimized with the global-hybrid meta-GGA U-M06-2X functional[4] in conjugation with def2-SVP[5] basis set for all the atoms without symmetry constraints. The vibrational frequency calculations were accomplished at the optimized geometries to determine the nature of stationary points (minima or saddle point on the potential energy surface). The geometries were verified as true minima by the absence of imaginary frequency. Single point calculations were performed on optimized geometries using higher basis set def2-TZVP[6] for all atoms. Solvation energies in diethyl ether ($\varepsilon = 4.24$) were evaluated by a self-consistent reaction field (SCRF) approach using the SMD continuum solvation model.[7] All energy values reported in the manuscript are at U-M06-2X/def2-TZVP/SMD//U-M06-2X/def2-SVP level of theory. Within ADF2013.01, Natural bond orbital (NBO) analysis is performed by using the NBO 6.0[8] program at the BP86[9] functional in combination with a triple-ζ-quality basis set using uncontracted slater-type orbital (STO)[10] augmented with two set of polarization functions for all atoms without any frozen core approximation. This level of theory is denoted as U-BP86/TZ2P//U-M06-2X/def2-SVP. Wiberg bond indices (WBI)[11] and Mulliken spin density calculations were accomplished at the same level of theory. QTAIM[12] analysis in the AIMALL program is also performed in the wave function generated file at U-

M06-2X/def2-TZVP//U-M06-2X/def2-SVP level of theory. Any bonded pair of atoms has a bond path, i.e. a connecting line with maximum electron density. The bond critical point (BCP) is a point on this line where the gradient $\nabla\rho(r)$ of the density is equal to zero. The magnitude of the electron density, $\rho(r)$ and its Laplacian, $\nabla^2\rho(r)$ at the BCP provide information about the strength and type of bond. The Laplacian indicates whether the density is locally concentrated ($\nabla^2\rho<0$) or depleted ($\nabla^2\rho>0$). The ellipticity (ε) measures the deviation of the bonding density from cylindrical symmetry.

Furthermore, to gain insight into the bonding scenario of the complexes, ETS-NOCV[13] calculations were performed at BP86/TZ2P level without any frozen core approximation using ADF2017.106 program package on the BP86/def2-SVP optimized geometries. In extended transition state (ETS) analysis, the instantaneous interaction energy is partitioned into three chemically meaningful terms:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb}$$

where ΔE_{elstat} denotes the quasiclassical coulomb interaction energy between the fragments. ΔE_{Pauli} accounts for destabilizing interaction between the occupied orbitals. The stabilizing orbital interaction term ΔE_{orb} represents the interaction between the occupied and virtual orbitals of the two fragments. ETS-NOCV analysis is an extension of ETS analysis in which ΔE_{orb} term is decomposed into the contributions from different natural orbitals of chemical valence (NOCV). The contours of deformation densities were plotted using the ADF-GUI interface. Scalar relativistic effects were considered using the zeroth-order regular approximation (ZORA) in all ADF calculations.[14] EPR parameters including the Landé splitting factors (g) and hyperfine coupling constants (A) were computed at UB3LYP/def2-TZVP[15] level of theory. Optimized geometries and orbital diagrams are rendered in the Chemcraft[16] and CYLview[17] visualization softwares.

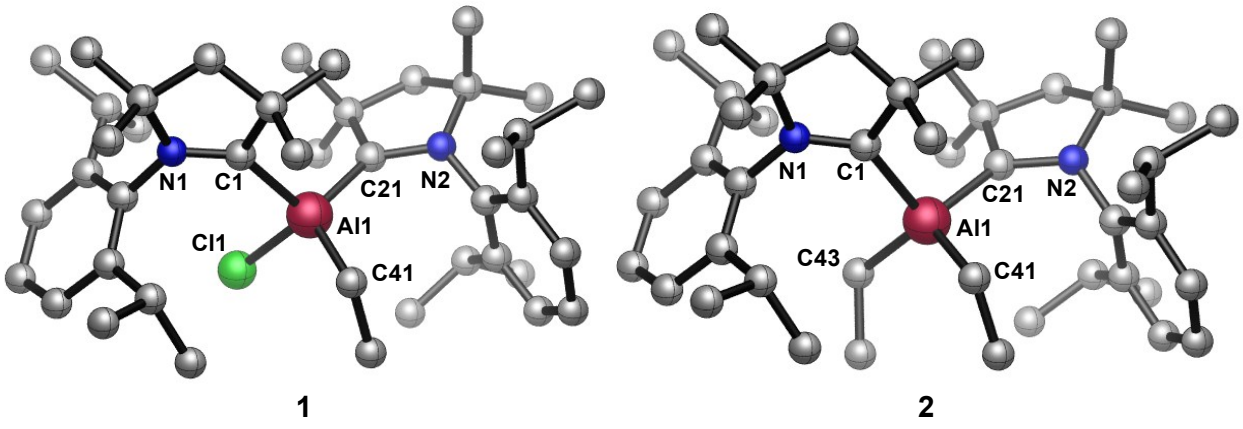

Fig. S1 Optimized geometries of the compounds **1** and **2** in doublet ground electronic states at U-M06-2X/def2-SVP level.

Table S1 Selected geometrical parameters of the compounds **1** and **2** in doublet ground electronic states at U-M06-2X/def2-SVP level. Bond distances (d) are in angstroms (Å) and bond angles (A) are in degrees (°).

Geometrical Parameter	**1**	**2**
d (Al1−C1)	2.156	2.221
d (Al1−C21)	1.987	2.028
d (Al1−C41)	1.994	2.011
d (Al1−C43)	-	2.033
d (Al1−Cl1)	2.206	-
d (C1−N1)	1.308	1.311
d (C21−N2)	1.405	1.417
A (C1−Al1−C21)	112.8	108.6
A (Cl1−Al1−C41)	108.8	-
A (C43−Al1−C41)	-	116.6

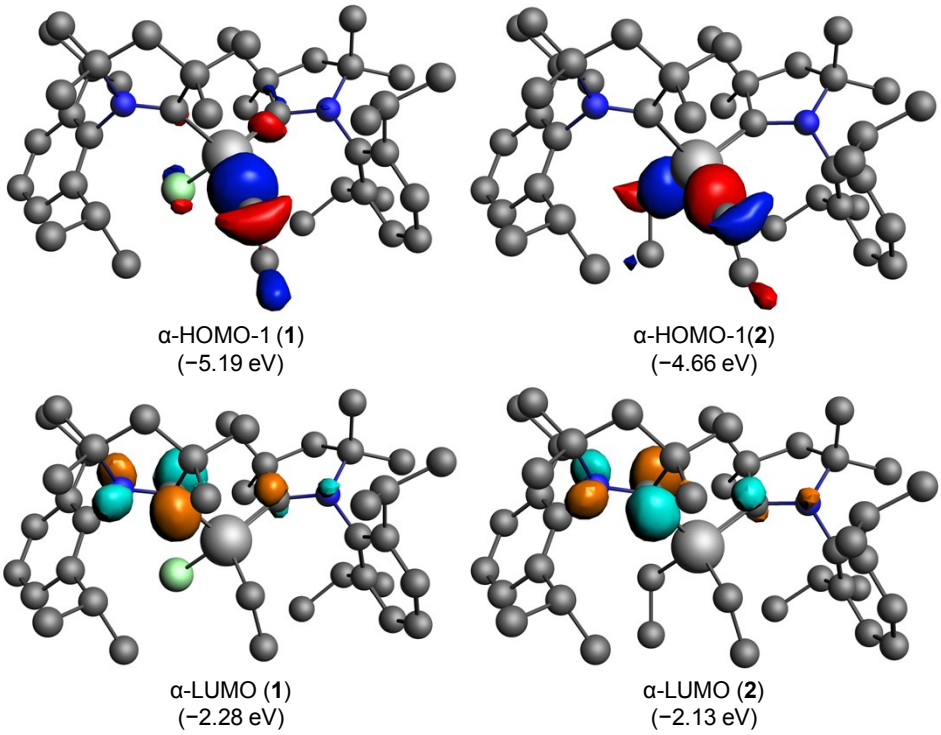

Fig. S2 KS-MOs of **1** and **2** (isosurface = 0.065 a.u.). Hydrogen atoms are omitted for clarity. The orbital energies are shown in parentheses.

Table S2 Topological parameters of selected bonds in the compounds **1** and **2** using AIMAll calculations at U-M06-2X/def2-TZVP//U-M06-2X/def2-SVP level.

Compound	Bond	$\rho(r)^{a}$	$[\nabla^2\rho(r)]^{b}$	Ellipticity $(\varepsilon)^{c}$
1	Al1−C1	0.052	+0.194	0.047
	Al1−C21	0.074	+0.307	0.133
	C1−N1	0.339	-0.529	0.112
	C21−N2	0.277	-0.617	0.095
2	Al1−C1	0.045	+0.160	0.066
	Al1−C21	0.068	+0.273	0.111
	C1−N1	0.337	-0.519	0.137
	C21−N2	0.270	-0.597	0.093

[a] Electron density at BCP (e/Å^3). [b] Laplacian at BCP (e/Å^5). [c] Ellipticity.

Table S3 Mulliken atomic spin densities (in a.u.) of selected atoms in the compounds **1** and **2**.

Atom	Compound	
	1	**2**
Al1	0.057	0.051
C1	0.152	0.152
C21	0.621	0.647
N1	0.024	0.020
N2	0.102	0.092

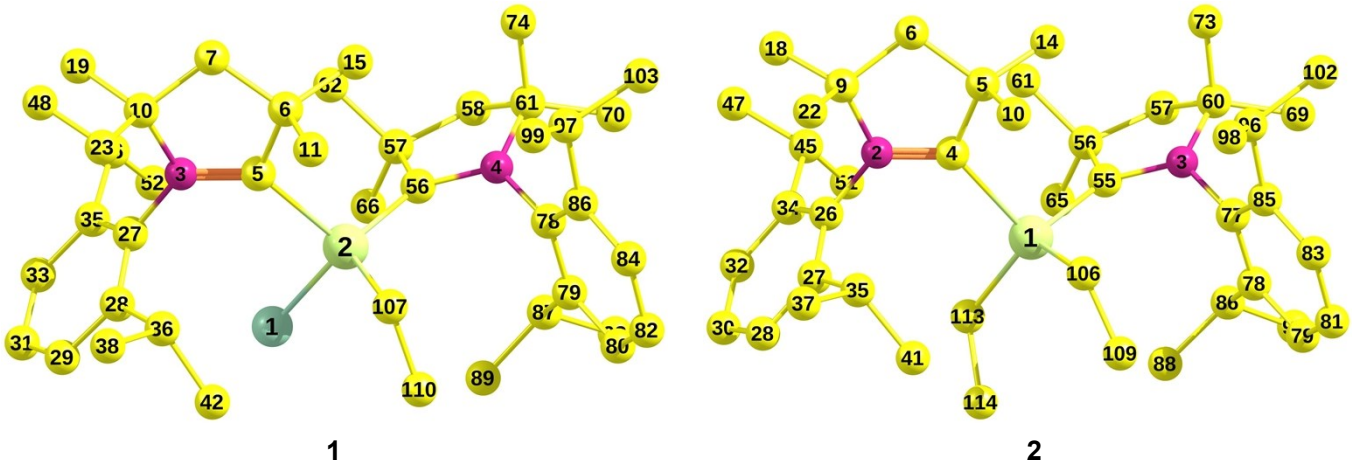

Fig. S3 Labelling of atoms for EPR calculations on **1** and **2**.

Table S4 Calculated *g*-tensors of **1** and **2** at U-B3LYP/def2-TZVP level.

Compound	g_{iso}	g_{xx}	g_{yy}	g_{zz}
1	2.0027	2.0025	2.0026	2.0031
2	2.0027	2.0023	2.0027	2.0032

Table S5 Calculated hyperfine coupling constants (A in Gauss) of **1** and **2** at U-B3LYP/def2-TZVP level.

Compound	Atom	A_{iso}	A_{xx}	A_{yy}	A_{zz}
1	Al2	-9.62	-11.45	-10.76	-6.65
	N3	0.43	0.07	0.11	1.10
	N4	2.55	-1.07	-0.81	9.53
	C5	7.82	5.28	6.32	11.86
	C6	-0.63	-0.77	-0.68	-0.46
	C27	0.04	-0.03	-0.01	0.17
	C56	17.44	-1.65	-1.24	55.2
	C57	-5.74	-6.23	-5.85	-5.15
	C78	3.14	1.97	2.78	4.66
2	Al1	-5.32	-6.79	-5.89	-3.29
	N2	0.42	0.14	0.16	0.96
	N3	2.51	-0.88	-0.62	9.04

	C4	9.30	6.68	7.90	13.32
	C5	-0.64	0.77	-0.67	-0.46
	C26	0.06	-0.01	0.01	0.18
	C55	19.77	-0.36	0.10	59.56
	C56	-6.12	-6.61	-6.28	-5.46
	C77	4.86	3.67	4.41	6.49

Table S6 ETS calculations of **1**/**2** at BP86/TZ2P level of theory using the fragments $(cAAC)_2$ and $AlClEt/AlEt_2$ in different electronic states.[a] Energy values are given in kcal/mol.

	1	**2**
	$(cAAC)_2$ (S) + AlClEt (D)	$(cAAC)_2$ (S) + $AlEt_2$ (D)
ΔE_{int}	-95.3	-86.1
ΔE_{pauli}	384.5	367.5
ΔE_{elstat}[b]	-234.5 (48.9%)	-217.6 (48.0%)
ΔE_{orb}[b]	-245.3 (51.1%)	-236.0 (52.0%)

[a] S=singlet, D=doublet. [b] Percentage contribution to the total attractive interactions $\Delta E_{elstat}+\Delta E_{orb}$.

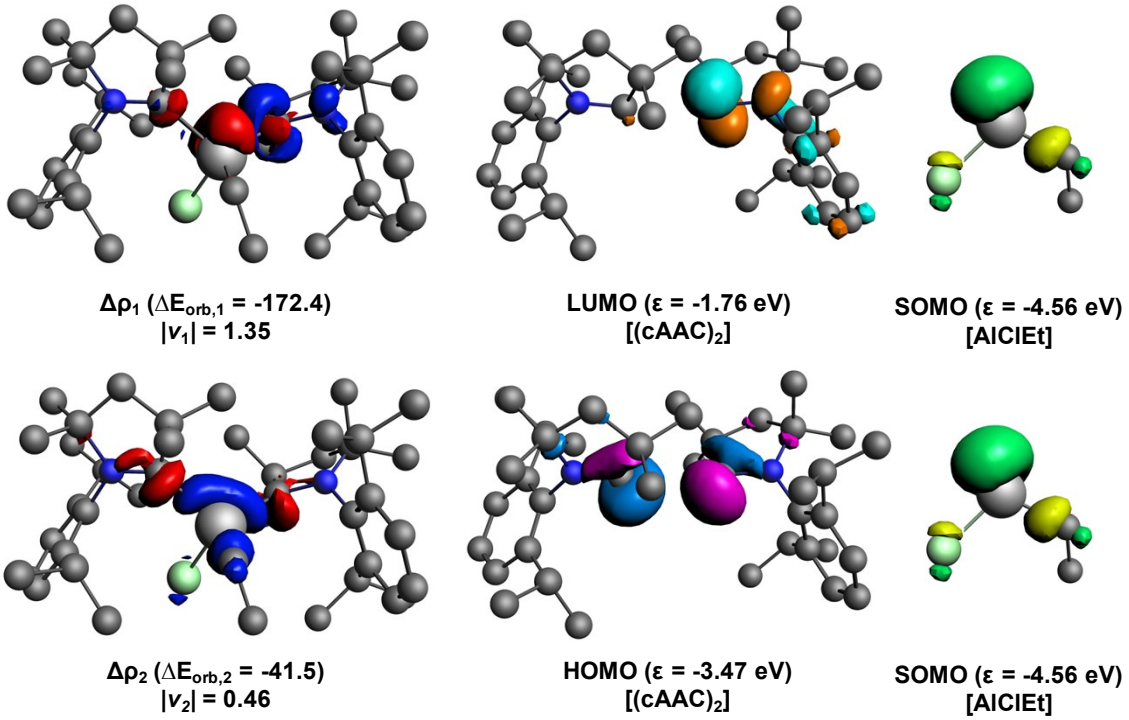

Fig. S4 Plot of deformation densities Δρ of the pairwise orbital interactions in **1** between the fragments $(cAAC)_2$ and AlClEt in singlet and doublet electronic states, respectively. The associated energies $\Delta E_{orb,n}$ (in kcal/mol) are given in parentheses. The charge eigen values v (in e) are also provided. The charge flow is color coded red→blue. The most important interacting occupied and vacant orbitals of the fragments are shown.

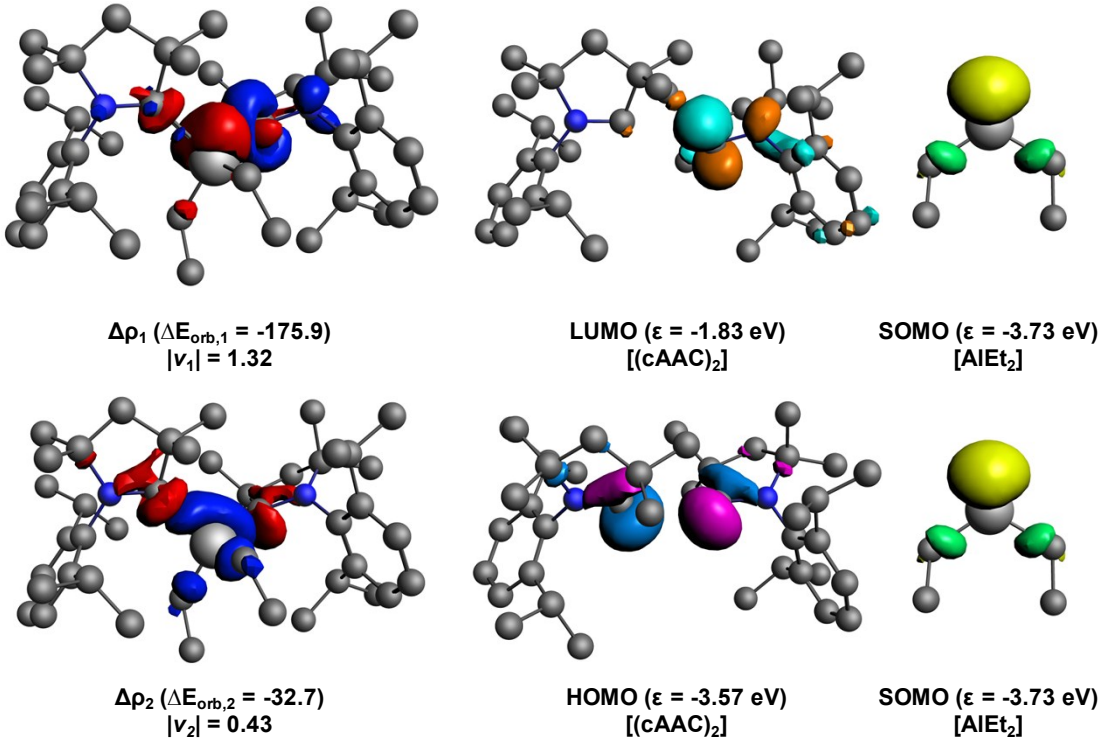

Fig. S5 Plot of deformation densities Δρ of the pairwise orbital interactions in **2** between the fragments $(cAAC)_2$ and $AlEt_2$ in singlet and doublet electronic states, respectively. The associated energies $\Delta E_{orb,n}$ (in kcal/mol) are given in parentheses. The charge eigen values *v* (in *e*) are also provided. The charge flow is color coded red→blue. The most important interacting occupied and vacant orbitals of the fragments are shown.

Table S7 Cartesian coordinates (in Å) of the optimized structures of **1** and **2** at U-M06-2X/def2-SVP level of theory. Energy terms are in kcal/mol.

1

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Energy: -1537826.0309468

XYZ

Cl	1.05879	1.35159	1.89100
Al	-0.06691	-0.01432	0.57510
N	2.78343	-0.60792	-0.74175
N	-2.76009	0.53392	-0.70085
C	1.48707	-0.77873	-0.70831
C	1.11491	-1.80043	-1.78154
C	2.35057	-1.85305	-2.69192
H	2.52678	-2.85654	-3.10453
H	2.21124	-1.16163	-3.53700
C	3.52391	-1.37509	-1.83450
C	0.87470	-3.15001	-1.07693
H	0.60482	-3.90103	-1.83462
H	0.05561	-3.07521	-0.35329
H	1.76233	-3.50899	-0.53976
C	-0.14723	-1.41881	-2.54820
H	-0.36423	-2.18160	-3.31240
H	-0.02649	-0.44635	-3.04442
H	-1.00941	-1.34329	-1.87187
C	4.46976	-0.48128	-2.62588
H	4.93244	-1.09353	-3.41340
H	5.27119	-0.08177	-1.98975
H	3.94158	0.34865	-3.11056
C	4.34800	-2.50758	-1.22340

H	4.83574	-3.06190	-2.03726
H	3.74251	-3.21356	-0.64386
H	5.13241	-2.09947	-0.57130
C	3.59420	0.08733	0.24734
C	3.93848	-0.59202	1.43678
C	4.82880	0.03648	2.31267
H	5.10339	-0.47086	3.23902
C	5.35126	1.29320	2.04154
H	6.04466	1.76238	2.74080
C	4.95896	1.96256	0.89065
H	5.33193	2.97052	0.70102
C	4.07280	1.38574	-0.02354
C	3.34941	-1.92494	1.88259
H	2.67568	-2.29388	1.09624
C	4.41917	-2.99121	2.15100
H	3.93788	-3.94680	2.40664
H	5.04577	-2.70330	3.00819
H	5.08412	-3.15958	1.29455
C	2.50815	-1.72830	3.15183
H	1.97833	-2.65853	3.40693
H	1.77270	-0.92552	3.02462
H	3.15548	-1.46404	4.00206
C	3.59403	2.25370	-1.17872
H	2.92905	1.64892	-1.81247
C	4.73451	2.80786	-2.04039
H	5.39653	2.02682	-2.43472
H	5.35339	3.50737	-1.45928
H	4.32091	3.37039	-2.89042
C	2.76866	3.42158	-0.62336
H	1.99781	3.05977	0.06641
H	2.28985	3.98078	-1.44079
H	3.41633	4.11696	-0.06790
C	-1.46146	0.99198	-0.42008
C	-1.27816	2.35289	-1.11198

C	-2.66565	2.64896	-1.72488
H	-3.21673	3.34190	-1.06965
H	-2.59539	3.12751	-2.71357
C	-3.42271	1.31071	-1.78759
C	-0.18605	2.30210	-2.19270
H	0.00359	3.30451	-2.61044
H	-0.47022	1.63906	-3.02209
H	0.75729	1.93038	-1.76101
C	-0.91439	3.46866	-0.11642
H	-0.83972	4.43627	-0.64065
H	0.03647	3.26710	0.38854
H	-1.67969	3.56169	0.66680
C	-4.91637	1.50199	-1.54170
H	-5.34107	2.11664	-2.34895
H	-5.09971	2.01035	-0.58584
H	-5.44851	0.54043	-1.52264
C	-3.21882	0.64425	-3.15823
H	-3.48084	1.34829	-3.96201
H	-3.85335	-0.24436	-3.27417
H	-2.17125	0.34037	-3.28851
C	-3.51959	-0.22753	0.24592
C	-3.92008	0.37317	1.46693
C	-4.62009	-0.39186	2.40374
H	-4.91604	0.06711	3.34956
C	-4.95081	-1.71870	2.15496
H	-5.49188	-2.30178	2.90172
C	-4.60494	-2.28659	0.93584
H	-4.88842	-3.32008	0.72426
C	-3.90178	-1.56061	-0.03177
C	-3.66797	1.83871	1.78519
H	-3.29423	2.30938	0.86833
C	-2.60699	2.02833	2.87323
H	-2.48211	3.09884	3.09933
H	-1.62678	1.63635	2.57009

H	-2.90971	1.52182	3.80376
C	-4.96234	2.55905	2.18431
H	-4.78501	3.64298	2.25032
H	-5.31993	2.22626	3.17027
H	-5.77196	2.38370	1.46093
C	-3.60965	-2.23542	-1.36042
H	-2.96174	-1.55772	-1.92751
C	-2.87413	-3.56783	-1.19778
H	-2.57610	-3.96408	-2.18097
H	-3.51326	-4.32370	-0.71687
H	-1.97202	-3.45511	-0.58284
C	-4.89800	-2.44690	-2.16475
H	-4.67265	-2.86189	-3.15943
H	-5.45313	-1.50826	-2.30175
H	-5.56580	-3.15262	-1.64695
C	-0.58954	-1.62887	1.62286
H	-1.36915	-2.19910	1.08729
H	0.28583	-2.30085	1.67893
C	-1.08408	-1.32883	3.04414
H	-1.23043	-2.24372	3.64210
H	-2.04805	-0.80230	3.02039
H	-0.38076	-0.68119	3.59212

2

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Energy: -1298729.0802301

XYZ

Al	0.01586	0.15669	0.62576
N	2.84980	-0.60039	-0.74162
N	-2.71766	0.41993	-0.76655
C	1.54395	-0.71317	-0.73147
C	1.16888	-1.72380	-1.82110
C	2.42690	-1.81321	-2.70262

H	2.57796	-2.81782	-3.12224
H	2.33097	-1.10940	-3.54350
C	3.59466	-1.38474	-1.81595
C	0.85859	-3.06789	-1.13312
H	0.76291	-3.84424	-1.90707
H	-0.08648	-3.00843	-0.58281
H	1.63876	-3.38024	-0.42506
C	-0.05433	-1.31635	-2.63255
H	-0.33077	-2.12781	-3.32465
H	0.14908	-0.41377	-3.22301
H	-0.90451	-1.10183	-1.97271
C	4.59385	-0.51352	-2.56916
H	5.07179	-1.13440	-3.34038
H	5.38083	-0.13303	-1.90263
H	4.10630	0.32955	-3.07291
C	4.36092	-2.55793	-1.20520
H	4.88861	-3.08398	-2.01281
H	3.70813	-3.28030	-0.70151
H	5.11218	-2.19508	-0.49094
C	3.63732	0.10661	0.24999
C	3.96926	-0.55413	1.45200
C	4.77818	0.12463	2.36919
H	5.03505	-0.36427	3.31052
C	5.24838	1.40572	2.11284
H	5.87959	1.91458	2.84253
C	4.89056	2.04460	0.93255
H	5.23097	3.06516	0.74875
C	4.07496	1.42023	-0.01559
C	3.44885	-1.92918	1.84845
H	2.88834	-2.34554	1.00248
C	4.57331	-2.90403	2.21652
H	4.15562	-3.90495	2.39941
H	5.07729	-2.58828	3.14209
H	5.33792	-2.98908	1.43307

C	2.46676	-1.80847	3.01695
H	2.04901	-2.79443	3.27060
H	1.63478	-1.14275	2.76121
H	2.96978	-1.40817	3.91085
C	3.61519	2.24411	-1.20927
H	3.01314	1.59843	-1.86419
C	4.77702	2.82724	-2.02029
H	5.49024	2.06071	-2.35008
H	5.33303	3.56808	-1.42683
H	4.39103	3.34613	-2.91002
C	2.70268	3.37552	-0.72360
H	1.89445	2.97941	-0.09780
H	2.26056	3.91231	-1.57586
H	3.26994	4.09858	-0.11774
C	-1.44864	0.99261	-0.50138
C	-1.34237	2.28993	-1.33061
C	-2.73712	2.44430	-1.97768
H	-3.33993	3.16124	-1.39794
H	-2.68001	2.83366	-3.00622
C	-3.40695	1.06128	-1.92639
C	-0.24021	2.22159	-2.40348
H	-0.07429	3.21297	-2.85722
H	-0.50123	1.52683	-3.21197
H	0.71103	1.88752	-1.95728
C	-1.05266	3.53206	-0.46788
H	-1.16925	4.44589	-1.07417
H	-0.02747	3.52361	-0.08047
H	-1.73490	3.59669	0.39047
C	-4.91627	1.18709	-1.72908
H	-5.34966	1.70811	-2.59536
H	-5.15481	1.76354	-0.82584
H	-5.40031	0.20493	-1.63843
C	-3.13483	0.29408	-3.22872
H	-3.55514	0.84495	-4.08385

H	-3.59038	-0.70406	-3.21158
H	-2.05748	0.17463	-3.39411
C	-3.48988	-0.24652	0.24538
C	-3.98234	0.48995	1.35351
C	-4.71413	-0.16686	2.34696
H	-5.07766	0.40318	3.20430
C	-4.99327	-1.52454	2.26188
H	-5.56141	-2.02330	3.04860
C	-4.55300	-2.23546	1.15375
H	-4.78719	-3.29879	1.07179
C	-3.81350	-1.62173	0.13681
C	-3.77430	1.98820	1.50381
H	-3.40811	2.36389	0.54209
C	-2.70837	2.29968	2.55539
H	-2.58629	3.38726	2.68136
H	-1.73923	1.88046	2.25669
H	-2.98596	1.87339	3.53288
C	-5.07709	2.72895	1.82675
H	-4.91681	3.81568	1.76208
H	-5.42449	2.51194	2.84781
H	-5.88733	2.45721	1.13432
C	-3.41915	-2.47433	-1.05833
H	-2.66707	-1.90793	-1.62318
C	-2.81387	-3.82912	-0.66546
H	-2.35181	-4.30576	-1.54367
H	-3.58834	-4.51754	-0.29471
H	-2.05281	-3.73215	0.12039
C	-4.62915	-2.72565	-1.96935
H	-4.32855	-3.27385	-2.87594
H	-5.11943	-1.79341	-2.27818
H	-5.38004	-3.33198	-1.43929
C	-0.60965	-1.55945	1.46725
H	-1.35536	-1.96650	0.76639
H	0.19669	-2.31307	1.50753

C	-1.25654	-1.43759	2.85207
H	-1.74915	-2.36986	3.17816
H	-2.02494	-0.64895	2.87473
H	-0.51267	-1.17706	3.62184
C	0.91570	1.50054	1.85710
C	0.72632	1.39027	3.38109
H	0.51698	2.48422	1.55458
H	1.99916	1.56807	1.66334
H	1.12446	2.27439	3.90704
H	-0.32950	1.29338	3.67311
H	1.24528	0.51858	3.80358

(S3) Crystal data of 1 (CCDC 1566044):

Crystals of compound **1** were selected using a polarization microscope under mounting oil and subsequently shock-frozen in liquid nitrogen and brought to the Swiss Light source (SLS) synchrotron in a storage Dewar. The structure of compound **1** was then measured at beamline X10SA at the SLS. This end station is equipped with a custom-made high-precision one axis goniometer, a DECTRIS Pilatus 6M single photon counting detector and a nitrogen gas-flow cooling device. A wavelength of 0.6358 Å (19.5 keV) and a detector distance of 165 mm were chosen. Only two phi-scans was carried out, giving a > 91 % complete coverage of reciprocal space. In total 450 plus 1800 images were collected in rotation increments of 0.2 degrees. Data integration was performed with the XDS program.[18] An empirical absorption correction, scaling and merging were performed with SADABS.[19] The structure was then solved with dual-space direct methods[20] and refined with shelxl using anisotropic displacement parameters for non-hydrogen atoms and a riding hydrogen model.[21]

Crystal data refinement parameter of 1:

$C_{42}H_{67}AlClN_2$	$F(000) = 1452$
$M_r = 662.40$	$D_x = 1.133$ Mg m^{-3}
Monoclinic, $P2_1/n$	Synchrotron radiation, $\lambda =$ 0.6358 Å

a = 14.410 (2) Å	Cell parameters from 1302 reflections
b = 17.145 (3) Å	θ = 1.4–23.0°
c = 17.2175 (5) Å	μ = 0.11 mm^{-1}
β = 114.14 (1)°	T = 100 K
V = 3881.9 (8) $Å^3$	Needle, red
Z = 4	0.06 × 0.03 × 0.03 mm

Data collection:

Microdiffractometer at the SLS Radiation source: monochromated X-rays beamline X10SA@SLS φ scans Absorption correction: multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10 T_{min} = 0.707, T_{max} = 0.745	63363 measured reflections 7291 independent reflections 6995 reflections with $I > 2\sigma(I)$ R_{int} = 0.063 θ_{max} = 23.4°, θ_{min} = 1.4° h = −18→18 k = −21→21 l = −21→21

Refinement:

Refinement on F^2 Least-squares matrix: full $R[F^2 > 2\sigma(F^2)]$ = 0.041 $wR(F^2)$ = 0.113 S = 1.06 7291 reflections 432 parameters 0 restraints 0 constraints Primary atom site location: dual	Secondary atom site location: difference Fourier map Hydrogen site location: inferred from neighbouring sites H-atom parameters constrained $w = 1/[\sigma^2(F_o^2) + (0.0647P)^2 + 1.6437P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{max} < 0.001$ $\Delta\rho_{max}$ = 0.47 e $Å^{-3}$ $\Delta\rho_{min}$ = −0.34 e $Å^{-3}$

Bond lengths (Å) and angles (deg) of 1.

Cl1—Al1	2.1967(5)	C20—H20B	0.9800
Al1—C41	1.9852(13)	C20—H20C	0.9800
Al1—C21	1.9913(13)	C21—C22	1.5395 (16)
Al1—C1	2.1507(13)	C22—C26	1.5404 (18)
N1—C1	1.3095(15)	C22—C25	1.5407 (18)
N1—C9	1.4676(16)	C22—C23	1.5483 (16)
N1—C4	1.5444(16)	C23—C24	1.5343 (17)
N2—C21	1.4138(15)	C23—H23A	0.9900
N2—C29	1.4405(16)	C23—H23B	0.9900
N2—C24	1.4996(16)	C24—C28	1.526 (2)
C1—C2	1.5381(17)	C24—C27	1.5308 (17)
C2—C6	1.5261(17)	C25—H25A	0.9800
C2—C3	1.5388(18)	C25—H25B	0.9800
C2—C5	1.5447(18)	C25—H25C	0.9800
C3—C4	1.5278(18)	C26—H26A	0.9800
C3—H3A	0.9900	C26—H26B	0.9800
C3—H3B	0.9900	C26—H26C	0.9800
C4—C7	1.5218(19)	C27—H27A	0.9800
C4—C8	1.5257(18)	C27—H27B	0.9800
C5—H5A	0.9800	C27—H27C	0.9800
C5—H5B	0.9800	C28—H28A	0.9800
C5—H5C	0.9800	C28—H28B	0.9800
C6—H6A	0.9800	C28—H28C	0.9800
C6—H6B	0.9800	C29—C34	1.4109 (17)
C6—H6C	0.9800	C29—C30	1.4151 (19)
C7—H7A	0.9800	C30—C31	1.3962 (19)
C7—H7B	0.9800	C30—C35	1.5194 (18)
C7—H7C	0.9800	C31—C32	1.383 (2)
C8—H8A	0.9800	C31—H31	0.9500
C8—H8B	0.9800	C32—C33	1.380 (2)
C8—H8C	0.9800	C32—H32	0.9500
C9—C14	1.4075(17)	C33—C34	1.3975 (19)

C9—C10	1.4084 (18)	C33—H33	0.9500
C10—C11	1.3959 (19)	C34—C38	1.5178 (19)
C10—C15	1.5228 (17)	C35—C36	1.537 (2)
C11—C12	1.378 (2)	C35—C37	1.5415 (18)
C11—H11	0.9500	C35—H35	1.0000
C12—C13	1.380 (2)	C36—H36A	0.9800
C12—H12	0.9500	C36—H36B	0.9800
C13—C14	1.3940 (18)	C36—H36C	0.9800
C13—H13	0.9500	C37—H37A	0.9800
C14—C18	1.5247 (17)	C37—H37B	0.9800
C15—C17	1.535 (2)	C37—H37C	0.9800
C15—C16	1.5419 (19)	C38—C39	1.5304 (18)
C15—H15	1.0000	C38—C40	1.5413 (17)
C16—H16A	0.9800	C38—H38	1.0000
C16—H16B	0.9800	C39—H39A	0.9800
C16—H16C	0.9800	C39—H39B	0.9800
C17—H17A	0.9800	C39—H39C	0.9800
C17—H17B	0.9800	C40—H40A	0.9800
C17—H17C	0.9800	C40—H40B	0.9800
C18—C20	1.5375 (18)	C40—H40C	0.9800
C18—C19	1.5378 (17)	C41—C42	1.526 (2)
C18—H18	1.0000	C41—H41A	0.9900
C19—H19A	0.9800	C41—H41B	0.9900
C19—H19B	0.9800	C42—H42A	0.9800
C19—H19C	0.9800	C42—H42B	0.9800
C20—H20A	0.9800	C42—H42C	0.9800
C41—Al1—C21	118.45 (5)	N2—C21—C22	107.36 (10)
C41—Al1—C1	100.39 (5)	N2—C21—Al1	126.01 (8)
C21—Al1—C1	115.19 (5)	C22—C21—Al1	126.29 (8)
C41—Al1—Cl1	108.07 (4)	C21—C22—C26	111.64 (11)
C21—Al1—Cl1	109.37 (4)	C21—C22—C25	112.27 (10)

C1—Al1—Cl1	104.14 (4)	C26—C22—C25	108.23 (10)
C1—N1—C9	126.48 (11)	C21—C22—C23	104.43 (9)
C1—N1—C4	116.04 (10)	C26—C22—C23	108.75 (10)
C9—N1—C4	117.26 (9)	C25—C22—C23	111.46 (11)
C21—N2—C29	122.09 (10)	C24—C23—C22	107.00 (10)
C21—N2—C24	112.90 (10)	C24—C23—H23A	110.3
C29—N2—C24	121.35 (9)	C22—C23—H23A	110.3
N1—C1—C2	107.41 (10)	C24—C23—H23B	110.3
N1—C1—Al1	132.60 (9)	C22—C23—H23B	110.3
C2—C1—Al1	119.79 (8)	H23A—C23—H23B	108.6
C6—C2—C1	113.86 (10)	N2—C24—C28	111.50 (10)
C6—C2—C3	111.49 (12)	N2—C24—C27	112.67 (11)
C1—C2—C3	104.02 (10)	C28—C24—C27	108.97 (11)
C6—C2—C5	108.56 (11)	N2—C24—C23	101.79 (9)
C1—C2—C5	107.72 (11)	C28—C24—C23	110.57 (11)
C3—C2—C5	111.11 (10)	C27—C24—C23	111.20 (10)
C4—C3—C2	106.13 (11)	C22—C25—H25A	109.5
C4—C3—H3A	110.5	C22—C25—H25B	109.5
C2—C3—H3A	110.5	H25A—C25—H25B	109.5
C4—C3—H3B	110.5	C22—C25—H25C	109.5
C2—C3—H3B	110.5	H25A—C25—H25C	109.5
H3A—C3—H3B	108.7	H25B—C25—H25C	109.5
C7—C4—C8	107.69 (11)	C22—C26—H26A	109.5
C7—C4—C3	111.65 (12)	C22—C26—H26B	109.5
C8—C4—C3	114.50 (11)	H26A—C26—H26B	109.5
C7—C4—N1	111.74 (10)	C22—C26—H26C	109.5
C8—C4—N1	111.13 (11)	H26A—C26—H26C	109.5
C3—C4—N1	100.10 (9)	H26B—C26—H26C	109.5
C2—C5—H5A	109.5	C24—C27—H27A	109.5
C2—C5—H5B	109.5	C24—C27—H27B	109.5
H5A—C5—H5B	109.5	H27A—C27—H27B	109.5
C2—C5—H5C	109.5	C24—C27—H27C	109.5

H5A—C5—H5C	109.5	H27A—C27—H27C	109.5
H5B—C5—H5C	109.5	H27B—C27—H27C	109.5
C2—C6—H6A	109.5	C24—C28—H28A	109.5
C2—C6—H6B	109.5	C24—C28—H28B	109.5
H6A—C6—H6B	109.5	H28A—C28—H28B	109.5
C2—C6—H6C	109.5	C24—C28—H28C	109.5
H6A—C6—H6C	109.5	H28A—C28—H28C	109.5
H6B—C6—H6C	109.5	H28B—C28—H28C	109.5
C4—C7—H7A	109.5	C34—C29—C30	119.52 (12)
C4—C7—H7B	109.5	C34—C29—N2	120.37 (12)
H7A—C7—H7B	109.5	C30—C29—N2	120.09 (11)
C4—C7—H7C	109.5	C31—C30—C29	119.09 (12)
H7A—C7—H7C	109.5	C31—C30—C35	117.81 (12)
H7B—C7—H7C	109.5	C29—C30—C35	123.10 (12)
C4—C8—H8A	109.5	C32—C31—C30	121.33 (14)
C4—C8—H8B	109.5	C32—C31—H31	119.3
H8A—C8—H8B	109.5	C30—C31—H31	119.3
C4—C8—H8C	109.5	C33—C32—C31	119.42 (13)
H8A—C8—H8C	109.5	C33—C32—H32	120.3
H8B—C8—H8C	109.5	C31—C32—H32	120.3
C14—C9—C10	121.69 (11)	C32—C33—C34	121.50 (13)
C14—C9—N1	119.48 (11)	C32—C33—H33	119.3
C10—C9—N1	118.76 (11)	C34—C33—H33	119.3
C11—C10—C9	117.46 (12)	C33—C34—C29	119.01 (13)
C11—C10—C15	116.81 (12)	C33—C34—C38	117.76 (11)
C9—C10—C15	125.59 (11)	C29—C34—C38	123.15 (12)
C12—C11—C10	121.81 (13)	C30—C35—C36	110.59 (11)
C12—C11—H11	119.1	C30—C35—C37	112.31 (11)
C10—C11—H11	119.1	C36—C35—C37	109.79 (12)
C11—C12—C13	119.67 (12)	C30—C35—H35	108.0
C11—C12—H12	120.2	C36—C35—H35	108.0
C13—C12—H12	120.2	C37—C35—H35	108.0
C12—C13—C14	121.56 (12)	C35—C36—H36A	109.5
C12—C13—H13	119.2	C35—C36—H36B	109.5

C14—C13—H13	119.2	H36A—C36—H36B	109.5
C13—C14—C9	117.76 (12)	C35—C36—H36C	109.5
C13—C14—C18	117.04 (11)	H36A—C36—H36C	109.5
C9—C14—C18	124.99 (11)	H36B—C36—H36C	109.5
C10—C15—C17	110.39 (12)	C35—C37—H37A	109.5
C10—C15—C16	112.57 (11)	C35—C37—H37B	109.5
C17—C15—C16	108.92 (12)	H37A—C37—H37B	109.5
C10—C15—H15	108.3	C35—C37—H37C	109.5
C17—C15—H15	108.3	H37A—C37—H37C	109.5
C16—C15—H15	108.3	H37B—C37—H37C	109.5
C15—C16—H16A	109.5	C34—C38—C39	113.59 (12)
C15—C16—H16B	109.5	C34—C38—C40	109.53 (10)
H16A—C16—H16B	109.5	C39—C38—C40	109.11 (10)
C15—C16—H16C	109.5	C34—C38—H38	108.2
H16A—C16—H16C	109.5	C39—C38—H38	108.2
H16B—C16—H16C	109.5	C40—C38—H38	108.2
C15—C17—H17A	109.5	C38—C39—H39A	109.5
C15—C17—H17B	109.5	C38—C39—H39B	109.5
H17A—C17—H17B	109.5	H39A—C39—H39B	109.5
C15—C17—H17C	109.5	C38—C39—H39C	109.5
H17A—C17—H17C	109.5	H39A—C39—H39C	109.5
H17B—C17—H17C	109.5	H39B—C39—H39C	109.5
C14—C18—C20	108.97 (11)	C38—C40—H40A	109.5
C14—C18—C19	113.19 (10)	C38—C40—H40B	109.5
C20—C18—C19	108.70 (10)	H40A—C40—H40B	109.5
C14—C18—H18	108.6	C38—C40—H40C	109.5
C20—C18—H18	108.6	H40A—C40—H40C	109.5
C19—C18—H18	108.6	H40B—C40—H40C	109.5
C18—C19—H19A	109.5	C42—C41—Al1	117.28 (9)
C18—C19—H19B	109.5	C42—C41—H41A	108.0
H19A—C19—H19B	109.5	Al1—C41—H41A	108.0
C18—C19—H19C	109.5	C42—C41—H41B	108.0
H19A—C19—H19C	109.5	Al1—C41—H41B	108.0
H19B—C19—H19C	109.5	H41A—C41—H41B	107.2

C18—C20—H20A	109.5	C41—C42—H42A	109.5
C18—C20—H20B	109.5	C41—C42—H42B	109.5
H20A—C20—H20B	109.5	H42A—C42—H42B	109.5
C18—C20—H20C	109.5	C41—C42—H42C	109.5
H20A—C20—H20C	109.5	H42A—C42—H42C	109.5
H20B—C20—H20C	109.5	H42B—C42—H42C	109.5

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