Electronic Supplementary Material (ESI) for ChemComm.

Supporting information for;

Cationic Aluminum Hydride Complexes: Reactions of Carbene-Alane Adducts with Trityl-Borate

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Contents

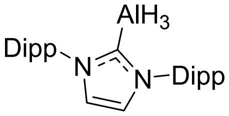
1. Syntheses

General Considerations: All manipulations were performed under an atmosphere of dry, oxygen-free N_2 by means of standard Schlenk or glovebox techniques (Innovative Technology glovebox equipped with a -38 °C freezer). Toluene and pentane were collected from a Grubbs-type column system manufactured by Innovative Technology. Pentane, bromobenzene, and toluene were stored over 4 Å molecular sieves. Molecular sieves, type 4 Å (pellets, 3.2 mm diameter) purchased from Sigma Aldrich were activated prior to usage by iteratively heating with 1050 W Haier microwave for 5 minutes and cooling under vacuum. The process was repeated until no further moisture was released upon heating. Benzene-d_6, bromobenzene-d_5, purchased from Cambridge Isotope Laboratories, and tetrahydrofuran-d_8, were degassed and stored over 4 Å molecular sieves in the glovebox for at least 8 h prior to use. Unless otherwise mentioned, chemicals were purchased from Sigma Aldrich or TCI. 1,3-Dibenzylimidazolium bromide was prepared using literature methods.[1] Combustion analyses were performed in-house employing a Flash 2000 from Thermo Instruments CHN Analyzer. Spectra were recorded on a Bruker Avance III 400 MHz or an Agilent DD2 500 MHz spectrometer and spectra were referenced to residual solvents of C_6D_5Br (^1H=7.28 ppm for meta proton; ^{13}C=122.4 ppm for ipso carbon), C_6D_6 (^1H=7.16 ppm; ^{13}C=128.06 ppm) or externally (^{11}B: $(Et_2O)BF_3$, ^{19}F: $CFCl_3$ ^{27}Al: $Al(NO_3)_3$). Chemical shifts (δ) are reported in ppm and the absolute values of the coupling constants (J) are in Hz. In some instances, signal and/or coupling assignment was derived from 2D NMR experiments. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR instrument.

Synthesis of $C_3H_2N_2(C_6H_3iPr_2)_2$ (Idipp).

This carbene was prepared according to the literature procedure wherein the synthesis and full characterization was published.[2]

Synthesis of (Idipp)AlH_3 (1).



A modified literature procedure was followed.[3] An aliquot of 0.5 M toluene solution of alane *N*,*N*-dimethylethylamine complex (0.88 mL, 0.44 mmol) was diluted in toluene (2 mL). As the solution was stirred, free Idipp (172 mg, 0.44 mmol) was added as a solid, which dissolved immediately upon addition. The resulting clear solution was allowed to stir at room temperature for 2 h. All volatiles were removed *in vacuo* to afford **1** (152 mg, 82%). Spectral data were consistent with previous literature reports.[3] **^{1}H NMR** (400 MHz, C_6D_6): δ 7.24 (t, $^3J_{HH}$ = 8 Hz, 2H, *p*-Ph), 7.11 (d, $^3J_{HH}$ = 8 Hz, 4H, *m*-Ph), 6.43 (s, 2H, NC_2H_2N), 3.68 (br. s, 3H, AlH_3), 2.68 (sept, $^3J_{HH}$ = 7 Hz, 4H, CH), 1.44 (d, $^3J_{HH}$ = 7 Hz, 12H, CH_3), 1.05 (d, $^3J_{HH}$ = 7 Hz, 12H, CH_3).

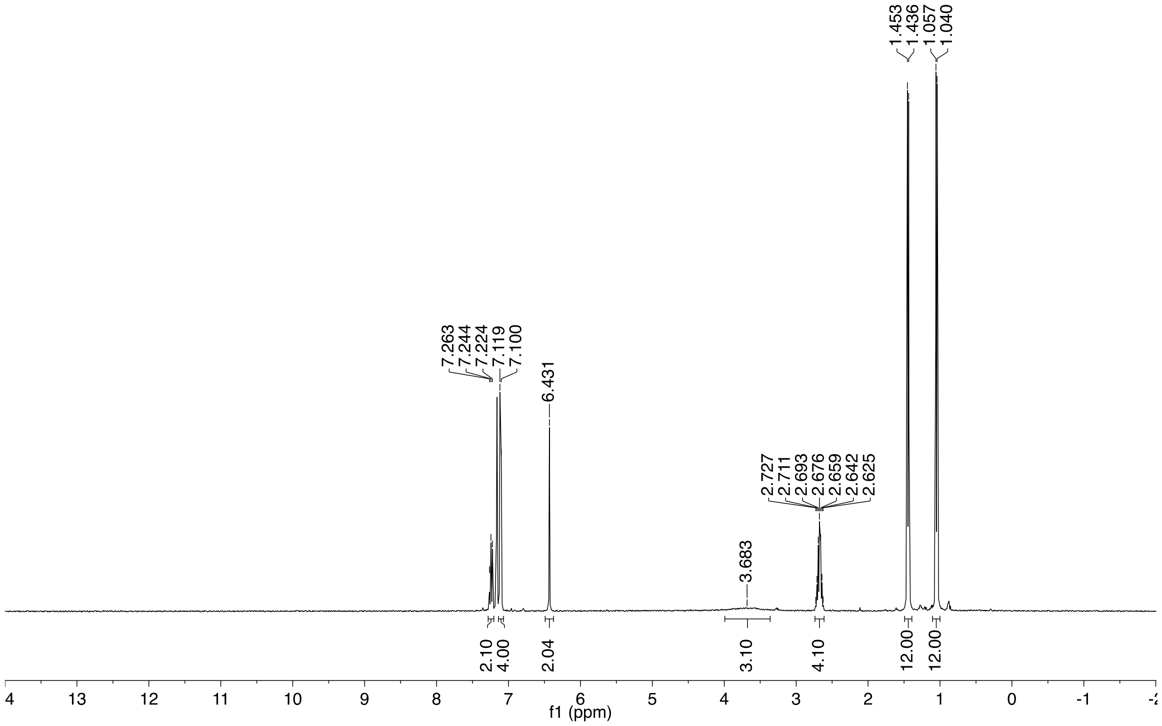
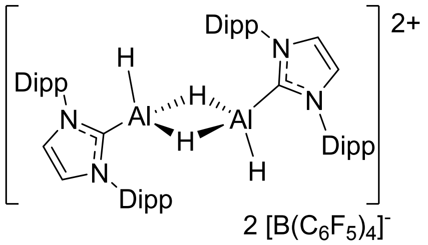


Figure S1: ^1H NMR spectrum of **1**.

Synthesis of $[((Idipp)AlH_2)_2][B(C_6F_5)_4]_2$ (2).



To a vial charged with (Idipp)AlH_3 **1** (0.096 g, 0.23 mmol) and trityl tetrakis(pentafluorophenyl)borate $[Ph_3C][B(C_6F_5)_4]$ (0.212 g, 0.23 mmol) was added C_6D_6 (0.6 mL). The vial was sealed with a cap, and then shaken vigorously for ca. 2 min. A slurry of crystals in a thick, brown oil settled from the yellow solution. The top benzene layer was decanted and crystals suitable for X-ray diffraction analysis were carefully selected, washed with cold (-35°C) benzene, and immediately coated in Paratone oil. The insolubility of **2** precluded both solution and solid state NMR characterization.

Synthesis of $C_3H_2N_2(CH_2Ph)_2)$ (IBn).

1,3-Dibenzylimidazolium bromide (2013 mg, 6.114 mmol) was suspended in 10 mL toluene and cooled to -35 °C. While stirring, solid KHMDS (1219 mg, 6.112 mmol) was then slowly added. The reaction mixture was warmed to room temperature and stirred for 4 h. The resulting mixture was passed through Celite, and volatiles were removed *in vacuo*. The obtained light yellow free carbene solid (1423 mg, Yield 93%)

was washed with pentane (3 x 5 mL) and used without further purification. **^{1}H NMR** (400 MHz, C_6D_6, 298K): δ 7.15 (d, $^3J_{HH}$ =6.9 Hz, 4H, *p*-Ph-H) 7.07 (t, $^3J_{HH}$ =7.2 Hz, 4H, *m*-Ph-H), 7.02 (d, $^3J_{HH}$ =6.9 Hz, 2H, *o*-Ph-H), 6.37 (m, 2H, NC-H), 5.09 (s, 4H, Ph-CH_2).

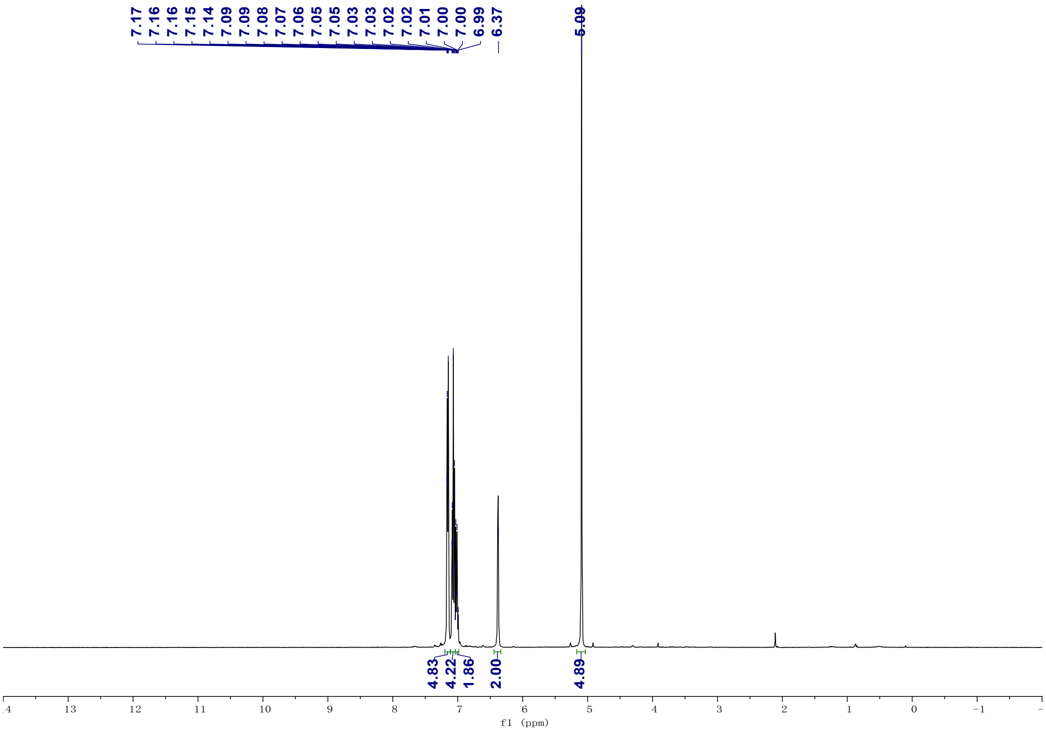
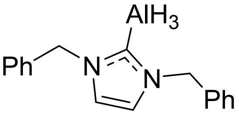


Figure S2: ^{1}H NMR spectrum of **IBn**.

Synthesis of (IBn)AlH_3 (3).



Free IBn carbene (758 mg, 3.026 mmol) was dissolved in 4 mL of toluene, and $AlH_3{\cdot}NEtMe_2$ (6.0 mL of 0.5 M solution in toluene, 3.0 mmol) was added dropwise at room temperature. The reaction was allowed to stir for another 2 h. The crude mixture was filtered through Celite and volatiles were removed *in vacuo*. The resulting residue was washed with 3 x 2 mL pentane and extracted with 3 x 5 mL toluene. The combined extracts were filtered through Celite and layered with pentane to give yellow needles (597 mg, Yield 72%) that were suitable for X-ray crystallography. **^{1}H NMR** (500 MHz, C_6D_5Br, 298K): δ 7.16-7.06 (m, 10H, Ph-H), 6.35 (s, 2H, NC-H), 5.24 (s, 4H, Ph-CH_2), 4.38 (br s, 3H, AlH_3). **$^{13}C\{^1H\}$ NMR** (126 MHz, C_6D_6, 298K): δ 136.14 (C-AlH_3), 129.11, 128.63, 128.59, 128.35, 121.10 (N-CH-CH-N), 53.67 (Ph-CH_2). **^{27}Al NMR** (130 MHz, C_6D_5Br, 298K): *δ* 108.7 (br s). Anal. Calcd. for $C_{17}H_{19}AlN_2$: C 73.36%, H 6.88%, N 10.06%. Found: C 73.04%, H 6.73%, N 9.95%.

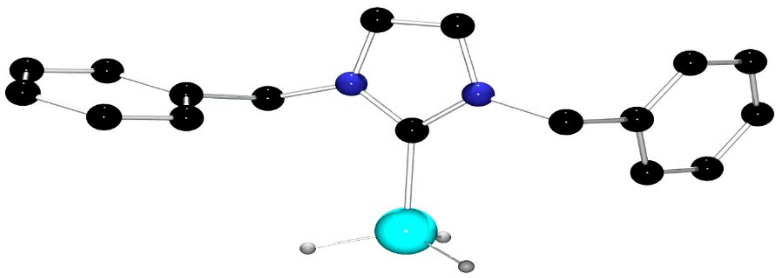


Figure S3: POV-ray depiction of **3**. C: black. Al: cyan. N: blue. H: grey. All ligand-based H atoms are omitted for clarity.

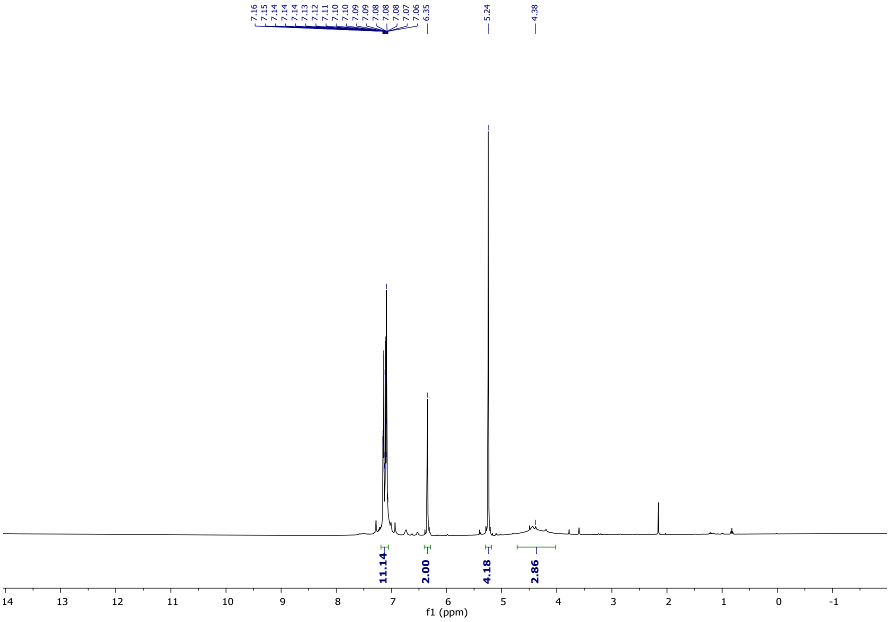


Figure S4: ^{1}H NMR spectrum of **3**

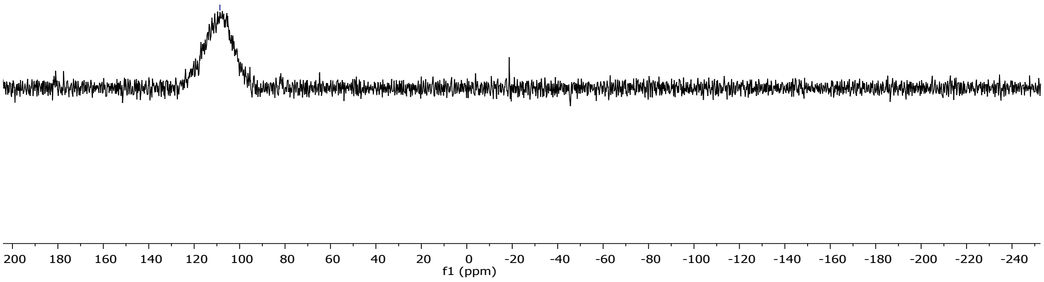


Figure S5: ^{27}Al NMR spectrum of **3**.

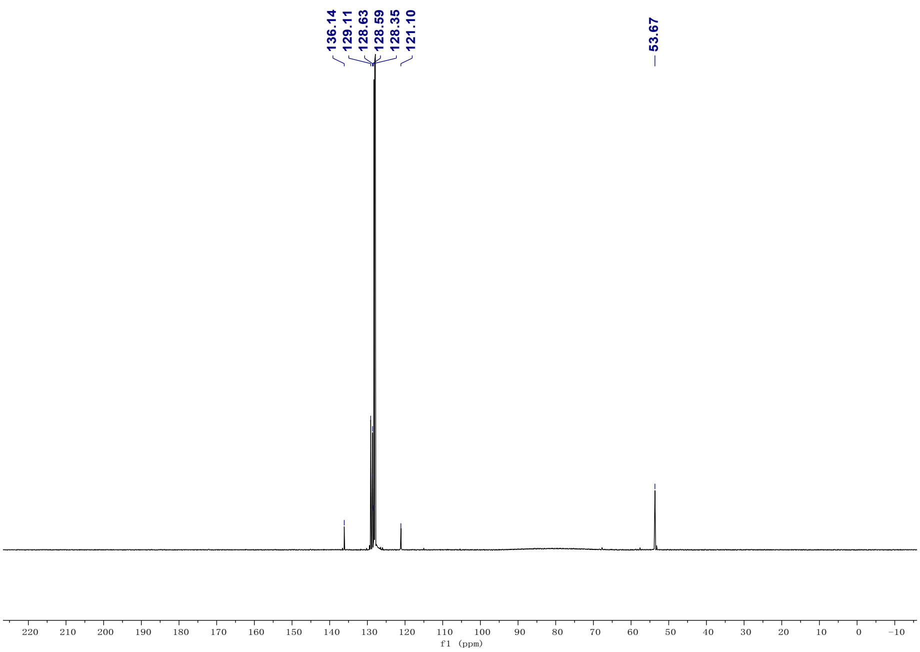
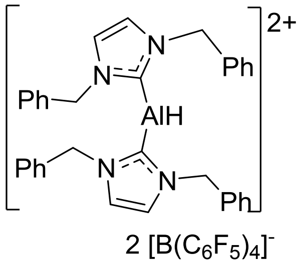


Figure S6: $^{13}C\{^1H\}$ NMR spectrum of **3**.

Synthesis of $[(IBn)_2AlH][B(C_6F_5)_4]_2$ (4)·(C_6H_5Br).



Compound **3** (363 mg 1.303 mmol) was dissolved in 1.5 mL C_6H_5Br in a vial, and trityl tetrakis(pentafluorophenyl)borate (1197 mg 1.303 mmol) in 1.5 mL of C_6H_5Br was added dropwise into the vial. The reaction mixture was allowed to sit at room temperature for 16 h. White blocky crystals formed from the solution. The supernatant was decanted and the crystals were washed with bromobenzene (3 x 1.5 mL), followed by pentane (3 x 2 mL) and subsequently dried *in vacuo* to give (**4**)·(C_6H_5Br) (614 mg, Yield 46%, calculated based on IBn). The crystals obtained were suitable for X-ray crystallography. **^{1}H NMR** (400 MHz, C_6D_5Br, 298K): δ 7.34 (s, 2H, Ph-H), 7.17-7.11 (m, 13H, Ph-H), 6.80 (dd, $^3J_{HH}$=1.7, 7.6 Hz, 7H, Ph-H), 6.41 (d, $^3J_{HH}$ =1.6 Hz, 4H, NC-H), 4.50 (s, 8H, Ph-CH_2). **^{11}B NMR** (160 MHz, C_6D_5Br, 298 K): δ -16.2 (s). **^{19}F NMR** (C_6D_5Br, 470 MHz, 298 K): δ -131.8 (br s, 16F, *o*–C_6F_5), -161.6 (t, 8F, *p*–C_6F_5, $^3J_{FF}$ = 21 Hz), -165.6 (br t, 8F, *m*–C_6F_5, $^3J_{FF}$ = 20 Hz). **$^{13}C\{^1H\}$ NMR** (125 MHz, C_6D_5Br, 298K): δ 131.32, 129.74, 128.24, 126.55, 122.14, 53.70. IR (KBr pellet, cm^{-1}): 3166 (s), 2918 (s), 1963 (s, $\nu_{Al\text{-}H}$), 1644 (s), 1515 (s), 1463 (s), 1281 (s), 1144 (s), 1086 (br), 979 (s), 775 (s), 756 (s), 714 (s), 683 (s), 661 (s); Anal. Calcd. for $C_{82}H_{33}AlB_2F_{40}N_4 \cdot C_6H_5Br$: C 51.82%, H 1.88%, N 2.75%. Found: C 51.40%, H 1.27%, N 2.61%.

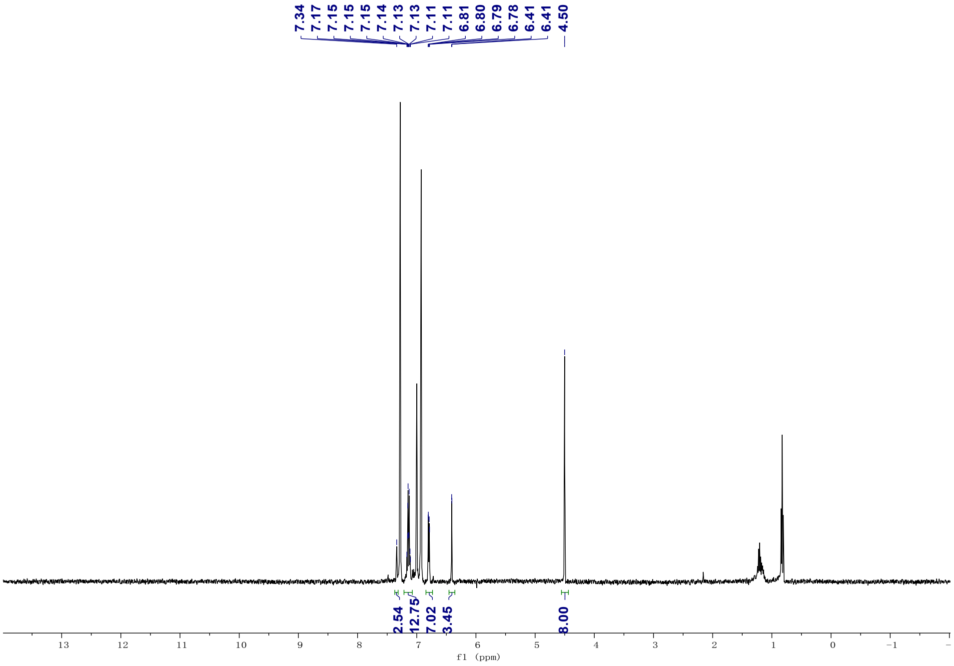


Figure S7: ^{1}H NMR spectrum of **4.**

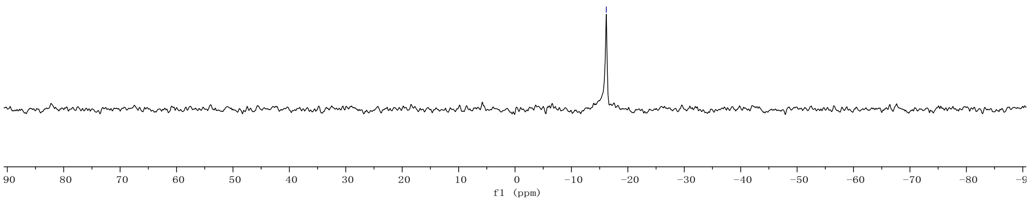


Figure S8: ^{11}B NMR spectrum of **4.**

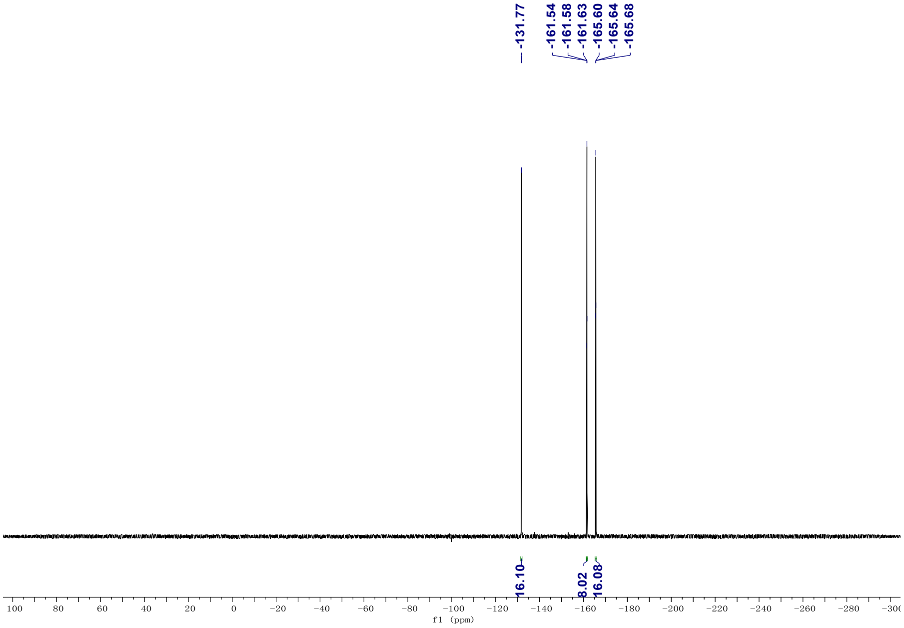


Figure S9: ^{19}F NMR spectrum of **4.**

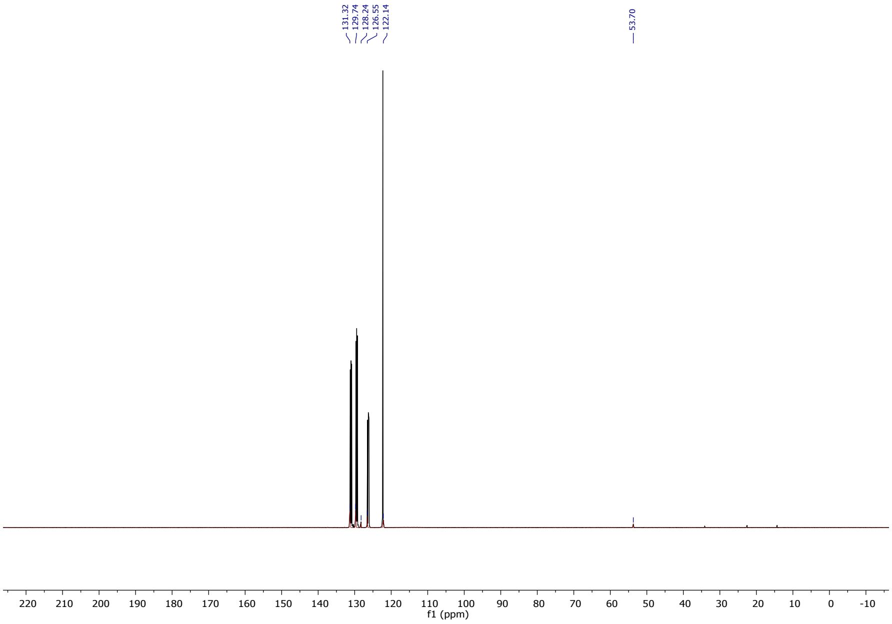


Figure S10: $^{13}C\{^1H\}$ NMR spectrum of **4.**

2. X-ray Crystallography

X-ray Data Collection and Reduction. Crystals were coated in Paratone-N oil in an N_2 filled glovebox, mounted on a MiTegen Micromount, and placed under a N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data were collected on a Bruker Apex II diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). The data were collected at 150(2) K for all crystals. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method (SADABS).

Structure Solution and Refinement. The structures were solved by direct methods using XS and subjected to full-matrix least-squares refinement on F^2 using XL as implemented in the SHELXTL suite of programs. All non-hydrogen atoms were refined with anisotropically thermal parameters, with the exception of those of the bromobenzene of crystallization in the structure of **4**·C_6H_5Br. Carbon bound hydrogen atoms were placed in geometrically calculated positions and refined using an appropriate riding model and coupled isotropic thermal parameters. The Al-bound hydrogen atoms were located in difference Fourier maps and refined in an unrestrained manner.

Table S1. Summary of crystallographic data for compounds **2**, **3**, and **4**.

	2	**3**	**4**·C_6H_5Br
empirical formula	$C_{51}H_{38}AlBF_{20}N_2$	$C_{17}H_{19}AlN_2$	$C_{88}H_{38}AlBBrF_{40}N_4$
formula weight	1096.62	278.32	2039.73
crystal system	Monoclinic	Monoclinic	Triclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a (Å)	14.3392(7)	11.8284(10)	12.4696(10)
b (Å)	22.0014(11)	11.5141(10)	13.5438(10)
c (Å)	16.1601(9)	12.6491(11)	23.9484(19)
α (deg.)			89.208(4)
β (deg.)	107.299(2)	113.135(4)	88.213(4)
γ (deg.)			79.504(4)
vol (Å^3)	4867.6(4)	1584.2(2)	3974.8(5)
Z	4	4	2
ρ (calcd) (Mg·cm^3)	1.496	1.167	1.704
μ (mm^{-1})	0.157	0.120	0.675
F(000)	2224	592	2024
T(K)	150(2)	150(2)	150(2)
reflections collected	39729	14251	65355
unique reflections	10354	3614	18261
R_{int}	0.0623	0.0564	0.0464
R1 indices [I>2σ(I)]	0.0499	0.0402	0.0740
wR2 indices (all data)	0.1118	0.1003	0.2421

CCDC No.	1453308	1453309	1453308

3. Computational Chemistry

All computations were performed using the Gaussian 09 program.[4] The geometry of the cation of **4** was performed at the B3LYP/6-311G(d,p) level of theory, using the crystallographic coordinates as the starting geometry. The stationary nature of the converged-upon geometry was confirmed by carrying out a frequency calculation and ensuring the absence of imaginary frequencies. NBO calculations were performed using the optimized geometry with NBO version 3.1 as implemented in the Gaussian 09 package.[5]

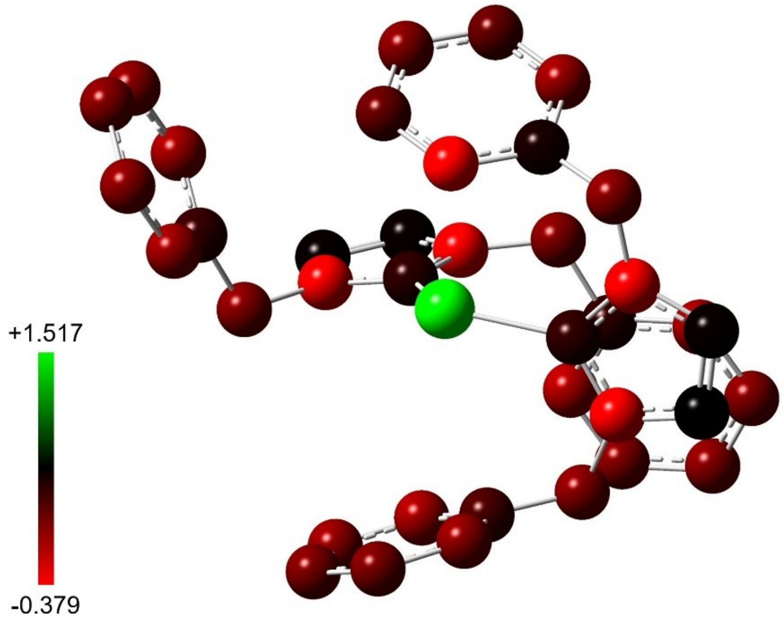
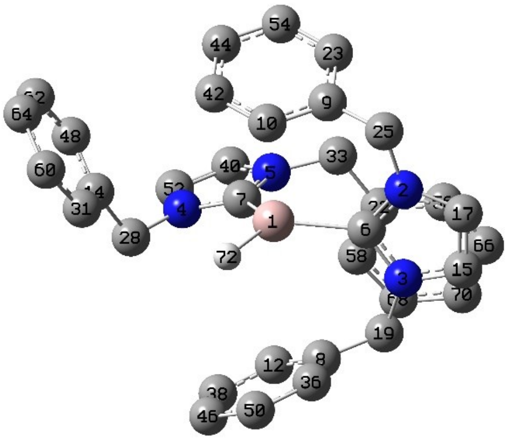


Figure S11. Charge distribution analysis from natural population analysis for $\mathbf{4}^{2+}$ (all the H atoms were omitted for clarification, the electronic charge for the Al-bound H atom is -0.379).

Table S2. Selected natural atomic charges for **4**$^{2+}$.



	Natural Atomic Charges
Al1	1.51721
C9	-0.37322
C10	-0.03685
C42	-0.13838
H72	-0.37917
Sum of Carbene [left]	0.36106
Sum of Carbene [right]	0.50090

Table S3. Selected donor-acceptor interactions from the NBO analysis of **4**$^{2+}$.

Donor	Accepter	ΔE (kcal/mol)
C10-C42 (π-Bond)	Al(3-p_z)	16.20
C6 (lone pair)	Al(3-sp)	109.24
C6 (lone pair)	Al(3-p_y)	54.16
C7 (lone pair)	Al(3-sp)	98.03
C7 (lone pair)	Al(3-p_y)	53.93

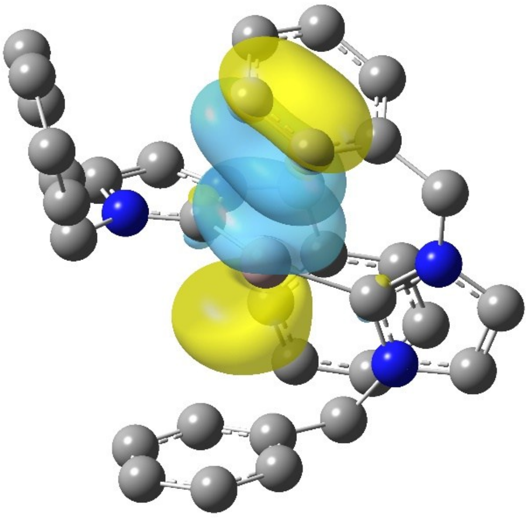


Figure S12. NBOs for the interaction between the Al(3-p_z) and the C10-C42(π-Bond).

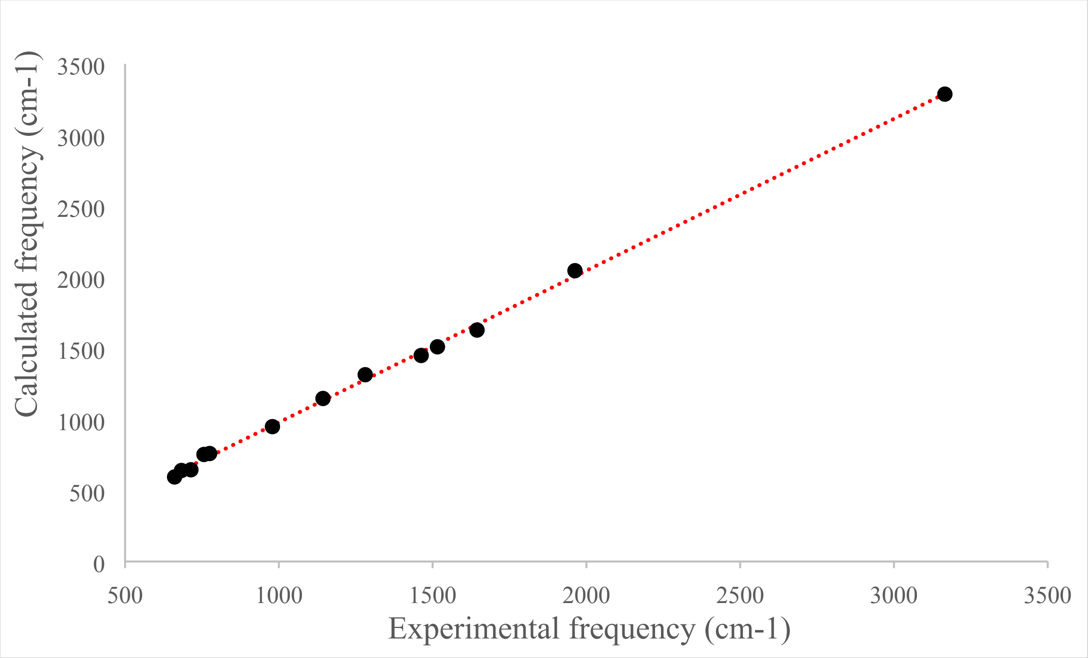


Figure S13. Calculated frequency vs. experimental frequency for **4**$^{2+}$

Table S4. Cartesian coordinates (Å) for the optimized structure of **4**$^{2+}$.

Al	-0.28993	0.17198	-0.86340

N	1.65888	-1.48381	-2.50455
N	2.63410	0.26190	-1.70163
N	-1.47393	0.61713	1.85522
N	0.11208	-0.84174	2.02957
C	1.45509	-0.40720	-1.70341
C	-0.53697	-0.05365	1.13066
C	1.82808	2.51596	-0.98721
C	-0.48649	-2.60586	-1.92381
C	-1.56960	-1.70002	-1.94984
H	-1.66342	-0.99693	-2.77396
C	1.24665	2.99569	0.19256
H	1.57192	2.60250	1.14986
C	-3.74306	1.01847	0.80874
C	3.56031	-0.38791	-2.48506
H	4.56638	-0.02539	-2.61217
C	2.94565	-1.48611	-2.99809
H	3.30920	-2.24695	-3.66836
C	2.93368	1.48840	-0.92032
H	3.85708	1.89142	-1.33925
H	3.13831	1.19136	0.10928
C	2.62561	-1.04395	1.95645
C	-0.49996	-3.65410	-1.00237
H	0.31106	-4.37405	-0.98963
C	0.63346	-2.47083	-2.92337
H	1.14480	-3.42433	-3.05366
H	0.24793	-2.16062	-3.89752
C	-2.45722	1.61145	1.34931
H	-1.96033	2.20744	0.58594
H	-2.66016	2.27440	2.19334
C	-4.23719	1.47948	-0.41496
H	-3.67646	2.21387	-0.98306
C	1.27193	-1.71065	1.76742
H	1.17258	-2.10081	0.75507
H	1.17268	-2.56524	2.44178
C	1.45393	3.08414	-2.21417
H	1.91722	2.74378	-3.13447
C	0.30728	4.02925	0.14635
H	-0.10646	4.42366	1.06724
C	-0.41341	-0.66886	3.29051
H	-0.03912	-1.20021	4.14936
C	-2.65601	-1.87073	-1.07462
H	-3.50408	-1.19956	-1.13158
C	-2.65505	-2.92595	-0.16672
H	-3.50376	-3.07224	0.48941

C	-0.06248	4.57981	-1.07678
H	-0.77614	5.39431	-1.11276
C	-4.49196	0.09043	1.54078
H	-4.14361	-0.26370	2.50522
C	0.51039	4.10278	-2.25834
H	0.23869	4.54533	-3.20908
C	-1.40797	0.25017	3.18003
H	-2.05795	0.67124	3.92823
C	-1.58261	-3.81675	-0.13681
H	-1.59832	-4.65786	0.54664
C	3.73983	-1.65031	1.36531
H	3.61563	-2.54542	0.76342
C	2.81231	0.08856	2.75295
H	1.97147	0.56743	3.24137
C	-5.45819	1.01581	-0.90445
H	-5.83853	1.39155	-1.84691
C	-5.70675	-0.37895	1.04789
H	-6.28641	-1.08692	1.62845
C	-6.19221	0.08246	-0.17638
H	-7.14528	-0.27166	-0.55055
C	5.01726	-1.13443	1.56798
H	5.87334	-1.62501	1.11996
C	4.09260	0.60846	2.95056
H	4.22586	1.48023	3.58014
C	5.19675	-0.00084	2.36038
H	6.19115	0.39484	2.52784
H	-1.15628	1.26830	-1.55259

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