

A zwitterionic hydrocarbon-soluble borenium ion based on a β -diketiminato backbone

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Supporting Information (22 pages total)

Contents:

1.	General procedures	S2
2.	Preparation of novel compounds	S3
3.	Gutmann assays of Lewis acidity	S14
4.	Details of DFT calculations	S15
5.	DFT run file	S16
6.	Crystallography	S21
6.	References for supporting information	S22

1. General procedures

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon. With the exception of fluorobenzene and 1,2-difluorobenzene, solvents were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent using a commercially available Braun SPS. NMR spectra were measured in C_6D_6 , CD_2Cl_2 or C_4D_8O ; C_6D_6 was dried over potassium, C_4D_8O was stirred over potassium overnight and distilled, and CD_2Cl_2 was distilled from calcium hydride and stored over molecular sieves, and all were stored under argon in Teflon valve ampoules. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. 1H and ^{13}C NMR spectra were recorded on Varian Mercury-VX-300 or Bruker AVII-500 spectrometers and referenced internally to residual protio-solvent (1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta_H = 0$ ppm). ^{27}Al NMR spectra were referenced with respect to $Al(H_2O)_6^{3+}$. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. ESI-MS measurements were performed on a Bruker MicroTOF ESI mass spectrometer connected to a glove box by PEEK tubing. Elemental analyses were carried out at London Metropolitan University. $PhBCl_2$ was distilled prior to use. Starting materials $Na[BAr^f_4]$,^{S1} $C_6F_5BCl_2$,^{S2} $B(C_6F_5)_3$,^{S3} $K[CH(SiMe_3)_2]$ ^{S4} and **4-tBu**^{S5} were prepared according to literature procedures. The synthesis of **7-tBu** has been communicated previously by us.^{S5}

2. Preparation of novel compounds

[1-Ph][PhBCl₃]

(NacNac)^{Dipp}Li(OEt₂) (0.750 g, 1.50 mmol) was dissolved in toluene (15 mL) and cooled to 0 °C. PhBCl₂ (0.39 mL, 3.00 mmol) was added dropwise, and the resulting pale yellow solution stirred at 0 °C for 10 mins. The ice bath was then removed and the reaction mixture allowed to warm to room temperature, and stirred for 90 mins. The mixture was then heated to 70 °C and filtered while hot. Colourless crystals formed at room temperature and the solution was then stored at -30 °C overnight to complete crystallization. The crystals were isolated by filtration and dried *in vacuo*. Yield: 0.730 g, 69%.

Spectroscopic data: ¹H NMR (400 MHz, dichloromethane-d₂, 298 K): δ_H 0.91 (12H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.21 (12H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 2.49 (6H, s, CH₃ of β-diketiminato backbone), 2.49 (4H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 6.71 (2H, d, *o*-CH, BPh of cation), 6.89 (2H, t, *m*-CH, BPh of cation), 7.10 (3H, overlapping m, *p*-CH, BPh of cation and *o*-CH, BPh of anion), 7.20 (t, 2H, *m*-CH, BPh of anion), 7.25 (4H, d, ³J_{HH} = 7.6 Hz, *m*-CH of Dipp), 7.47 (2H, t, ³J_{HH} = 7.6 Hz, *p*-CH of Dipp), 7.70 (1H, s, γ-CH), 7.78 (d, 1H, *p*-CH, BPh of anion). ¹³C{¹H} NMR (100 MHz, dichloromethane-d₂, 298 K): δ_C 23.6, 25.1 (CH₃ of Dipp ⁱPr), 23.6 (CH₃ of β-diketiminato backbone), 29.6 (CH of Dipp ⁱPr), 115.9 (γ-CH), 125.8 (aromatic C, BPh of cation), 126.4 (aromatic C, BPh of anion), 127.1 (aromatic C, BPh of anion), 127.5 (*m*-C of Dipp), 130.8 (aromatic C, BPh of anion), 131.4 (*p*-C of Dipp), 133.9 (aromatic C, BPh of cation), 134.5 (*ipso*-C of Dipp), 134.9 (aromatic C, BPh of cation), 143.6 (*o*-C of Dipp), 172.8 (NC). ¹¹B{¹H} NMR (128 MHz, dichloromethane-d₂, 298 K): δ_B -6.5 (PhBCl₃⁻), 33.7 (Dipp₂NacNacBPh⁺). ESI-MS: *m/z* 505.4 ([M]⁺, 100%); accurate mass: calc. 505.3755, meas. 505.3757. Elemental

microanalysis: calc. for $C_{41}H_{51}N_2B_2Cl_3$: C 70.36% H 7.34% N 4.00%; meas. C 70.41% H 7.19% N 3.77%.

[1-Ph][BAR^f₄]

A solution of [1-Ph][PhBCl₃] (0.350 g, 0.50 mmol) in dichloromethane (5 mL) was added to a solution of Na[BAR^f₄] (0.445 g, 0.50 mmol) in dichloromethane (5 mL) at room temperature. A pale yellow solution formed with a colourless precipitate. The reaction mixture was stirred for 30 mins and filtered, and volatiles removed *in vacuo*. The residue was washed with pentane to yield a colourless powder. Yield: 0.550 g, 81%. The exchange of the anion was confirmed by presence of a sharp singlet in the ¹¹B NMR spectrum at δ_B -6.5 ppm, and disappearance of the peak for PhBCl₃⁻ at δ_B -6.5 ppm. ¹H, ¹³C and ¹¹B data for the cation were identical to that measured for [1-Ph][PhBCl₃].

[1-C₆F₅]/[(C₆F₅)BCl₃]

(NacNac)^{Dipp}Li(OEt₂) (0.400 g, 0.80 mmol) was dissolved in toluene (15 mL) and cooled to 0 °C. (C₆F₅)BCl₂ (0.40 g, 1.60 mmol) was added dropwise, and the resulting hazy pale yellow solution stirred at 0 °C for 10 mins. The ice bath was then removed and the reaction mixture allowed to warm to room temperature, and stirred for 90 mins. The mixture was then heated to 70 °C and filtered while hot. Removal of volatiles in vacuo yielded an oily yellow residue, which was washed with pentane to yield the product as a colourless powder. Yield: 0.373 g, 53%. Single crystals suitable for X-ray crystallography were obtained from a saturated pentane solution at room temperature.

Spectroscopic data: ¹H NMR (500 MHz, dichloromethane-d₂, 298 K): δ_H 1.17 (24H, two overlapping doublets, ³J_{HH} = 7.0 Hz, CH₃ of Dipp ⁱPr), 2.57 (4H, sept, ³J_{HH} = 7.0 Hz, CH of Dipp ⁱPr), 2.60 (6H, s, CH₃ of β-diketiminato backbone), 7.30 (4H, d, ³J_{HH} = 7.5 Hz, *m*-CH of Dipp), 7.48 (2H, t, ³J_{HH} = 7.5 Hz, *p*-CH of Dipp), 7.78 (1H, s, γ-CH). ¹³C{¹H} NMR (126 MHz, dichloromethane-d₂, 298 K): δ_C 23.9 (CH₃ of β-diketiminato backbone), 24.2, 25.8 (CH₃ of Dipp ⁱPr), 29.5 (CH of Dipp ⁱPr), 117.4 (γ-CH), 126.5 (*m*-C of Dipp), 132.0 (*p*-C of Dipp), 134.7 (*ipso*-C of Dipp), 137.6 (dm, ¹J_{CF} = 260 Hz, *m*-CF), 137.7 (dm, ¹J_{CF} = 256 Hz, *m*-CF), 140.0 (dm, ¹J_{CF} = 248 Hz, *p*-CF), 143.2 (dm, ¹J_{CF} = 244 Hz, *p*-CF), 144.3 (*o*-C of Dipp), 146.2 (dm, ¹J_{CF} = 244 Hz, *o*-CF), 147.9 (dm, ¹J_{CF} = 247 Hz, *o*-CF), 173.6 (NC). ¹⁹F NMR (376 MHz, benzene-d₆, 298 K): δ_F -124.7 (d, ³J_{FF} = 18.8 Hz, *o*-CF of C₆F₅BCl₃⁻), -131.6 (d, ³J_{FF} = 23.3 Hz, *o*-CF of Dipp₂NacNacB(C₆F₅)⁺), -147.2 (t, ³J_{FF} = 20.7 Hz, *p*-CF of C₆F₅BCl₃⁻), -159.8 (t, ³J_{FF} = 17.7 Hz, *p*-CF of Dipp₂NacNacB(C₆F₅)⁺), -160.5 (m, *m*-CF of Dipp₂NacNacB(C₆F₅)⁺), -147.2 (m, *m*-CF of C₆F₅BCl₃⁻). ¹¹B{¹H} NMR (128 MHz, dichloromethane-d₂, 298 K): δ_B -5.0 (C₆F₅BCl₃⁻), 32.0 (Dipp₂NacNacB(C₆F₅)⁺). ESI-MS (+ve): *m/z* 595.3 ([M]⁺, 100%); accurate mass: calc. 595.3282, meas. 595.3284; (-ve):

m/z 282.9 ($[M]^+$, 100%); Elemental microanalysis: calc. for $C_{41}H_{41}N_2B_2F_{10}Cl_3$: C 55.98% H 4.70% N 3.18%; meas. C 55.82% H 4.83% N 2.65%.

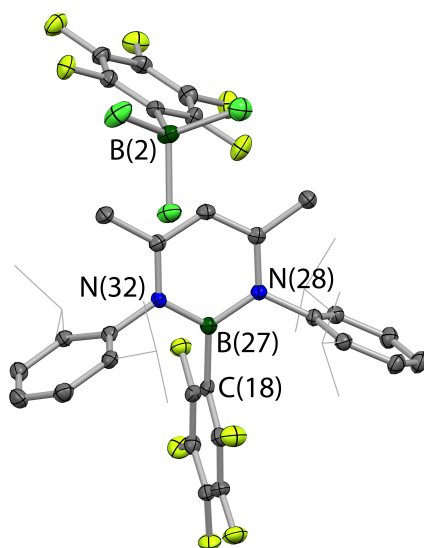


Figure S1: Molecular structure of $[1-C_6F_5][C_6F_5BCl_3]$ as determined by X-ray crystallography. Hydrogen atoms have been omitted and selected substituents shown in wireframe format for clarity; thermal ellipsoids have been depicted at the 40% probability level. Key bond lengths (\AA) and angles ($^\circ$): B-C 1.586(4), B-N 1.437(4), 1.442(4), C-N 1.368(4), 1.369(4), N-B-N 117.5(3), N-B-C 121.1(3), 122.2(3).

2-Ph

[1-Ph][BAr^f₄] (0.150 g, 0.11 mmol) was dissolved in THF (10 mL) and cooled to -78 °C. ^tBuLi (1.9M in pentane, 0.11 mL, 0.22 mmol) was added dropwise and the solution instantly turned pale brown. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. Volatiles were removed *in vacuo* and the residue extracted into toluene. Removal of the toluene *in vacuo* yielded a yellow oil, which was used without further purification. ¹H and ¹³C NMR indicated *ca.* 95% conversion to 2-Ph.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_H 0.92 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.07 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.11 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.37 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.49 (3H, s, CH₃ of β-diketiminato backbone), 3.31 (1H, s, C=CH₂), 3.40 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.55 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.98 (1H, s, C=CH₂), 5.70 (1H, s, □-CH), 6.70-7.13 (11H, m, aromatic CH). ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298 K): δ_C 20.9 (CH₃ of β-diketiminato backbone), 24.0, 24.1, 25.2, 26.5 (CH₃ of Dipp ⁱPr), 28.8, 29.1 (CH of Dipp ⁱPr), 85.1 (C=CH₂), 108.5 (γ-CH), 124.6, 125.0, 126.6, 134.6, 139.1, 140.0, 141.4, 146.4, 147.0, 148.4 (ArC and NC). ¹¹B{¹H} NMR (128 MHz, benzene-d₆, 298 K): δ_B 31.3.

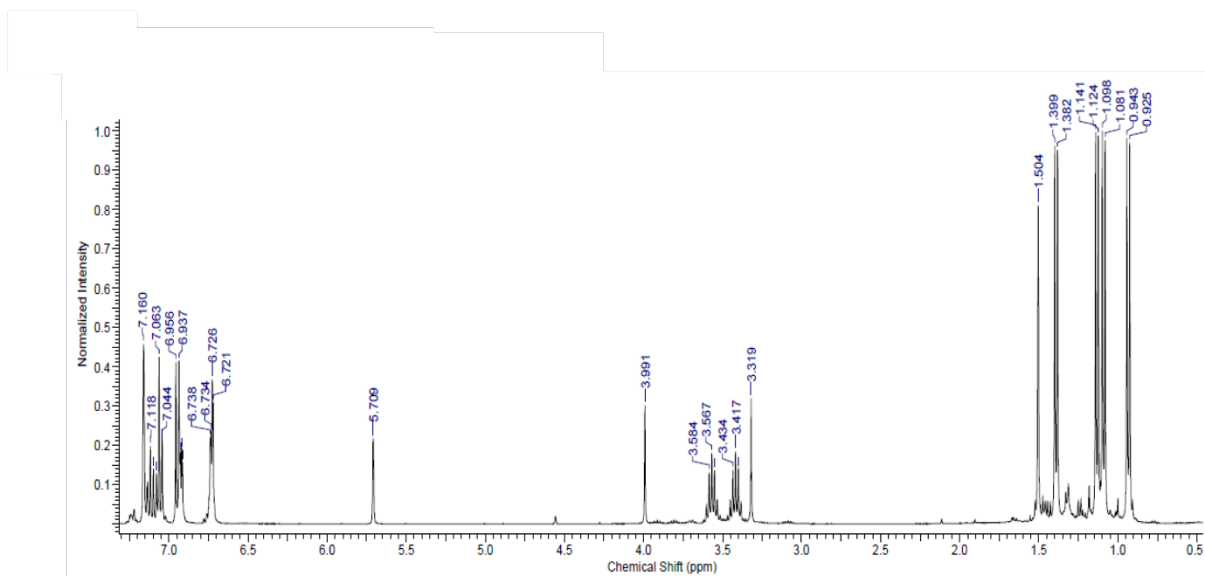


Figure S2: ^1H NMR spectrum of 2-Ph.

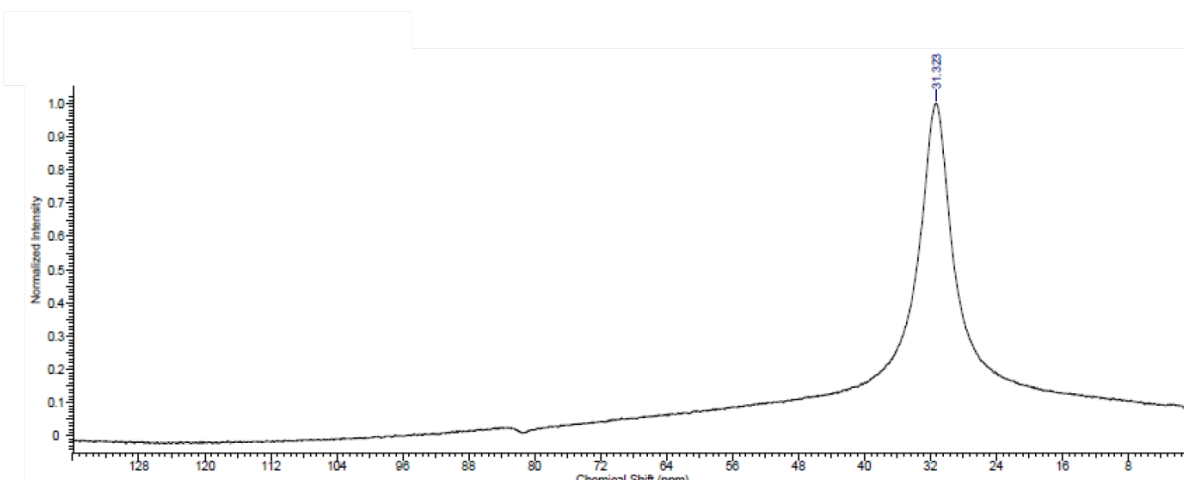


Figure S3: ^{11}B NMR spectrum of 2-Ph.

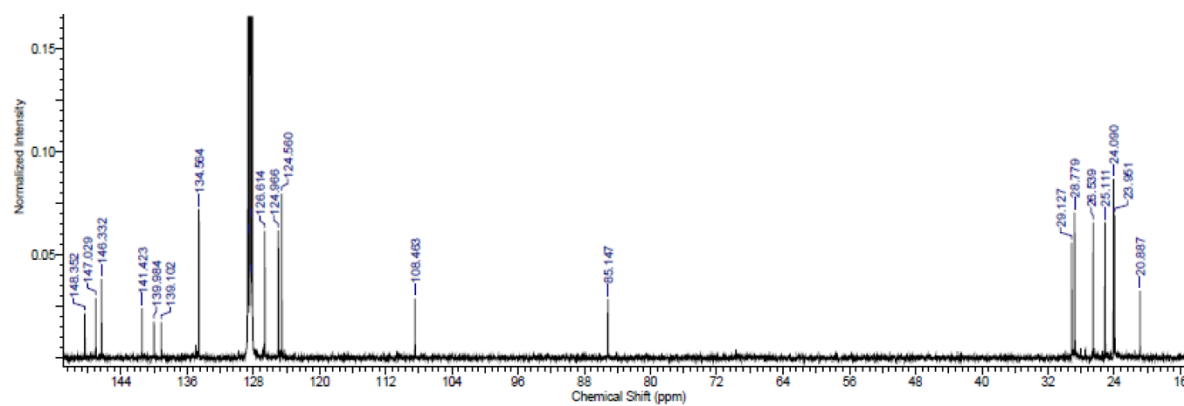


Figure S4: ^{13}C NMR spectrum of 2-Ph.

3-Ph

[1-Ph][BAr^f₄] (0.490 g, 0.36 mmol) was dissolved in THF (10 mL) and cooled to -78 °C. ^tBuLi (1.9M in pentane, 0.38 mL, 0.72 mmol) was added dropwise and the solution instantly turned pale brown. The reaction mixture was allowed to warm to room temperature and stirred overnight. Volatiles were removed *in vacuo* and the residue extracted into toluene and filtered on to solid B(C₆F₅)₃ (0.180 g, 0.36 mmol) to yield a pale yellow solution. The reaction mixture was stirred room temperature for 3 h, before being concentrated to the point of incipient crystallization. Storage overnight at -30 °C yielded the product as colourless crystals. Yield: 0.160 g, 44%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_H 0.56 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 0.58 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 0.85 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.41 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.61 (CH₃ of β-diketiminato backbone), 2.08 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 2.58 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.23 (2H, s, CH₂B), 6.40 (2H, d, ³J_{HH} = 8.0 Hz, *o*-CH of Ph), 6.48 (1H, t, ³J_{HH} = 8.0 Hz, *p*-CH of Dipp), 6.61 (1H, t, ³J_{HH} = 8.0 Hz, *p*-CH of Dipp), 6.74 (2H, d, ³J_{HH} = 8.0 Hz, *m*-CH of Dipp), 6.91 (2H, d, ³J_{HH} = 8.0 Hz, *m*-CH of Dipp), 7.05 (m, 3H, *m*-CH and *p*-CH of Ph), 7.60 (s, 1H, γ-CH). ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298 K): δ_C 22.2 (CH₃ of β-diketiminato backbone), 22.9, 23.9, 24.1, 24.7 (CH₃ of Dipp ⁱPr), 26.8 (CH₂B), 29.4, 29.5 (CH of Dipp ⁱPr), 115.4 (γ-CH), 125.8, 126.2, 127.3, 128.9, 129.7, 130.5, 131.0, 131.3, 135.5 (*ipso*-C, *m*-C and *p*-C of Dipp and ArC of Ph), 143.7, 144.1 (*o*-C of Dipp), 137.2 (dm, ¹J_{CF} = 250 Hz, *m*-CF), 139.0 (dm, ¹J_{CF} = 244 Hz, *p*-CF), 148.9 (dm, ¹J_{CF} = 250 Hz, *o*-CF), 167.6, 186.9 (NC). ¹⁹F NMR (376 MHz, benzene-d₆, 298 K): δ_F -131.4 (br s, *o*-CF), -160.1 (br s, *m*-CF), -164.9 (br s, *p*-CF). ¹¹B{¹H} NMR (128 MHz, benzene-d₆, 298 K): δ_B -14.4

(-B(C₆F₅)₃), 32.9 (-BPh). Elemental microanalysis: calc. for C₅₃H₄₅N₂B₂F₁₅: C 62.62% H 4.46% N 2.76%; meas. C 62.45% H 4.06% N 2.57%.

[K(OEt)₂][6-tBu Cl]

Benzene (10 mL) was added to 4-tBu (0.150 g, 0.28 mmol) and K[CH(SiMe₃)₂] (0.090 g, 0.45 mmol) and the resulting mixture stirred for 10 mins at room temperature. The solution was filtered onto a solution of B(C₆F₅)₃ (0.142 g, 0.28 mmol) in benzene (5 mL), and the clear, pale yellow solution stirred for 30 mins. Volatiles were removed *in vacuo* and the residue washed with toluene to yield a beige powder. Yield: 0.211 g, 61%. This solid was extracted into diethyl ether and hexane was added until the solution became cloudy. Storage at -30 °C for several days yielded colourless crystals, suitable for X-ray crystallography. Exposure to vacuum results in loss of coordinated diethyl ether – however, a small amount (*ca.* 10%) remains even after extended exposure to vacuum.

Spectroscopic data: ¹H NMR (400 MHz, thf-d₈, 298 K): δ_H 0.40 (9H, s, CH₃ of ^tBu), 0.83 (3H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.06 (3H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.10 (3H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.12 (3H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.27 (3H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.30 (3H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.33 (3H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.43 (3H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.61 (3H, s, CH₃ of β-diketiminato backbone), 1.99 (1H, d, ²J_{HH} = 19.2 Hz, CH₂B), 2.71 (1H, d, ²J_{HH} = 19.2 Hz, CH₂B), 3.09 (1H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.21 (1H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.71 (1H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.81 (1H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 5.79 (γ-CH), 7.06-7.23 (6H, m, aromatic CH). ¹³C{¹H} NMR (126 MHz, thf-d₈, 298 K): δ_C 23.8 (CH₃ of β-diketiminato backbone), 24.1, 24.6, 25.1, 25.3, 25.6, 25.8, 26.0, 28.0 (CH₃ of Dipp ⁱPr), 28.5, 28.5, 29.9, 30.2 (CH of Dipp ⁱPr), 32.4 (CH₃ of ^tBu), 101.9 (γ-CH), 124.1, 124.2, 125.6, 125.8, 127.3, 127.4, 142.4, 143.0, 143.4, 144.7, 146.8, 147.6 (ArC), 168.8, 182.8 (NC). C-F carbons not observed. ¹¹B{¹H} NMR (128 MHz, thf-d₈, 298 K): δ_B -14.4. ¹⁹F NMR (376 MHz, thf-d₈, 298 K): δ_F -129.8 (br s, *o*-F), -165.5 (br s, *p*-F),

-168.3 (br s, *m*-F). Elemental microanalysis: calc. for C₅₁H₄₉N₂AlClBF₁₅K (no coordinated diethyl ether): C 57.34% H 4.54% N 2.58%; meas. C 57.86% H 3.93% N 2.87%.

7-*t*BuNH₃

7-*t*Bu (0.300 g, 0.28 mmol) was dissolved in fluorobenzene (10 mL) and ammonia gas was bubbled through the solution for 2 min. The reaction mixture was then left to stir for 12 h, during which time it turned slightly cloudy. Volatiles were removed *in vacuo* and the residue extracted into minimal dichloromethane (ca. 15 mL). The solution was filtered and stored at -30°C for 12 h to yield a colorless, microcrystalline solid. Yield : 0.245 g, 80%. Single crystals suitable for X-ray crystallography were obtained by layering a concentrated dichloromethane solution with hexane and storing at room temperature for several days.

Spectroscopic data : ¹H NMR (500 MHz, THF-d₈, 298 K): δ_H 0.55 (9H, s, CH₃ of *t*Bu), 0.79 (3H, d, = 7.5 Hz, CH₃ of Dipp ⁱPr), 1.02 (3H, d, = 7.5 Hz, CH₃ of Dipp ⁱPr), 1.25 (3H, d, ³J_{HH} = 7.5 Hz, CH₃ of Dipp ⁱPr), 1.28 (3H, d, ³J_{HH} = 7.5 Hz, CH₃ of Dipp ⁱPr), 1.29 – 1.33 (12H, 4 overlapping doublets, ³J_{HH} = 7.5 Hz, CH₃ of Dipp ⁱPr), 1.57 (3H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.69 (3H, s, CH₃ of β-diketiminato backbone), 2.65 (1H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 2.78 – 2.92 (5H, overlapping multiplets, CH of Dipp ⁱPr and C(CH₂)B), 3.11 (1H, sept, ³J_{HH} = 7.5 Hz, CH of Dipp ⁱPr), 3.85 (3H, br s, NH₃), 5.70 (1H, s, γ-CH), 7.23 – 7.34 (6H, m, aromatic CH). ¹³C {¹H} NMR (126 MHz, THF-d₈, 298 K): δ_C 23.5 (CH₃ of β-diketiminato backbone), 24.0, 24.1, 24.7, 24.9, 24.9, 25.4, 26.0, 26.7 (CH₃ of Dipp ⁱPr), 29.2 (CH of Dipp ⁱPr), 29.3 (CH of Dipp ⁱPr), 30.3 (CH of Dipp ⁱPr), 30.8 (CH of Dipp ⁱPr), 30.9 (CH₃ of *t*Bu), 100.3 (γ-CH), 125.6, 125.6, 125.7, 125.9, 128.8, 128.9 (ArC), 137.4 (dm, ¹J_{CF} = 248 Hz, *m*-CF), 139.3 (dm, ¹J_{CF} = 219 Hz, *p*-CF), 149.4 (dm, ¹J_{CF} = 236 Hz, *o*-CF), 141.4, 141.8, 142.9, 144.3, 144.7, 144.8 (ArC), 170.2 (NC), 183.7 (NC). ¹¹B NMR (160 MHz, THF-d₈, 298 K): δ_B -14.9. ¹⁹F NMR (470 MHz, THF-d₈, 298 K): δ_F -132.2 (d, ²J_{FF} = 28.6 Hz, *ortho*-F), -163.3 (t, ³J_{FF} = 20.7 Hz, *para*-F), -168.0 (m, *meta*-F). Elemental microanalysis : calcd. for C₅₁H₅₂N₃GaBF₁₅: C 57.11%, H 4.89%, N 3.92% meas. C 56.67%, H 4.80%, N 3.89%.

3. Gutmann assay of Lewis acidity

Gutmann tests were performed on **3-Ph** and **7-tBu** by mixing the two equivalents of the compound with Et₃PO in CD₂Cl₂. A single resonance was observed in the ³¹P NMR spectrum in each case. The acceptor number was calculated as A.N. = 2.21 x ((δ_P (Lewis acid + Et₃PO) – 41).

Dipp₂NacNac^{(BC₆F₅)₃}BPh: δ_P +77.0, A.N. = 79.6.

Dipp₂NacNac^{(BC₆F₅)₃}Ga(^tBu): δ_P +71.5, A.N. = 67.6.

4. Details of DFT calculations

DFT calculations were performed using the Amsterdam Density Functional (ADF) 2014 software package. Calculations were performed using the Vosko-Wilk-Nusair local density approximation with exchange from Becke,^{S7} and correlation correction from Perdew,^{S8} and 3-dimensional dispersion effect (BP86-D3). Slater-type orbitals (STOs)^{S9} were used for the triple zeta basis set with an additional set of polarization functions (TZP). The full-electron basis set approximation was applied with no molecular symmetry. General numerical quality was good.

5. DFT run file

```
#!/bin/sh

# =====
# 3-Ph
# =====

"$ADFBIN/adf" <<eor
ATOMS
1 F      5.549435000000    10.894155000000    4.662147000000
2 C      5.268911000000    9.777248000000    3.948363000000
3 C      5.569538000000    9.846510000000    2.605531000000
4 F      6.129480000000    10.945481000000    2.073775000000
5 C      5.260980000000    8.779153000000    1.784724000000
6 F      5.489125000000    8.842199000000    0.464711000000
7 C      4.674295000000    7.665264000000    2.340714000000
8 F      4.355040000000    6.629163000000    1.546619000000
9 C      4.402993000000    7.637026000000    3.699291000000
10 C     4.675033000000    8.685559000000    4.577059000000
11 B     4.189972000000    8.805792000000    6.159942000000
12 C     5.482485000000    9.281752000000    7.097325000000
13 C     5.298973000000    9.207694000000    8.584152000000
14 N     6.377912000000    9.103977000000    9.410443000000
15 C     7.689422000000    9.432532000000    8.868604000000
16 C     8.634647000000    8.418453000000    8.633153000000
17 C     9.926791000000    8.821065000000    8.277234000000
18 C    10.254162000000    10.162278000000    8.142438000000
19 C     9.286805000000    11.133023000000    8.336849000000
20 C     7.980828000000    10.799141000000    8.704797000000
21 C     6.971052000000    11.911253000000    8.943078000000
22 C     6.926234000000    12.902600000000    7.771306000000
23 C     7.237928000000    12.649702000000    10.260438000000
24 C     8.317420000000    6.935518000000    8.717887000000
25 C     9.102187000000    6.244843000000    9.835352000000
26 C     8.624134000000    6.243778000000    7.383015000000
27 B     6.252497000000    8.814317000000    10.832880000000
28 N     4.880124000000    8.712198000000    11.311743000000
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35 C     6.420701000000    11.096261000000    14.348727000000
36 C     4.092222000000    11.638287000000    13.543842000000
37 C     4.582632000000    8.821598000000    15.014572000000
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39 C     3.961458000000    6.635379000000    14.243650000000
40 C     4.158618000000    7.008866000000    12.922576000000
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44 C     7.486545000000    8.628373000000    11.800158000000
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46 C     9.675961000000    9.292763000000    12.640600000000
47 C     9.680572000000    8.234285000000    13.536058000000
48 C     8.600157000000    7.363882000000    13.569492000000
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49 C	7.512919000000	7.572203000000	12.725865000000
50 C	2.964777000000	9.920746000000	6.033283000000
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52 F	4.046298000000	11.729571000000	7.155701000000
53 C	2.020659000000	12.180490000000	6.159411000000
54 F	2.150132000000	13.461320000000	6.558140000000
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56 F	-0.061232000000	12.691792000000	5.183642000000
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59 F	1.681485000000	8.359846000000	4.809149000000
60 F	-0.280340000000	10.094436000000	4.333293000000
61 C	3.724091000000	7.349852000000	6.780500000000
62 C	4.647737000000	6.303628000000	6.818710000000
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65 F	5.429737000000	4.188092000000	7.532848000000
66 C	3.255998000000	4.874505000000	8.121387000000
67 F	3.047772000000	3.703253000000	8.741061000000
68 C	2.291224000000	5.844540000000	8.095029000000
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71 F	1.115088000000	5.638350000000	8.703028000000
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89 H	8.194403000000	5.374085000000	7.412026000000
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99 H	7.132063000000	10.428496000000	14.351735000000
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GUIBONDS

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DISPERSION Grimme3
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GEOMETRY
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END
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SAVE TAPE21 TAPE13
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NumericalQuality Good
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NOPRINT LOGFILE
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6. Crystallography

Details of the data collection, structure solution and refinement procedures relating to the X-ray crystal structures of **[1-Ph][PhBCl₃]**, **[1-C₆F₅][(C₆F₅)BCl₃]**, **3-Ph**, **[K(OEt₂)₂][6-tBu·Cl]**, **7-tBu·NH₃** and **(Nacnac^{BCF})^{Dipp}Al(thf)Me** are included in the respective CIFs. These are included as part of the online supplementary material and are also available from the Cambridge crystallographic Data Centre (CCDC), reference numbers 1038762 and 1544787-1544791.

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