Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Solvent-free Anhydrous Li^+, Na^+ and K^+ salts of $[B(3,5–(CF_3)_2C_6H_3)_4]^–$, $[BAr^F{}_4]^–$. Improved Synthesis and Solid-State Structures

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EXPERIMENTAL DETAILS

General considerations

All manipulations (unless otherwise stated) were performed under an atmosphere of argon at room temperature, using standard Schlenk techniques on a dual vacuum/inlet grease-free J. Young tap manifold fitted with a vacuum gauge with display (vacuum < 10^{-2} mbar). Glassware was cleaned first by placing it in a 2-propanol/KOH bath (~ 1 M) overnight and rinsed with distilled water, then in an HCl (~ 1 M) for 4 h and rinsed with distilled water, and finally dried in an oven at 140 °C overnight prior to use. Solution NMR data were collected on either a Bruker Avance III NMR spectrometer (equipped with a 11.75 T magnet) or a Bruker Avance III HD nanobay NMR spectrometer (equipped with a 9.4 T magnet) at 298 K unless otherwise started. Residual protio solvent resonances were used as a reference for ^{1}H NMR spectra. ^{19}F{^{1}H} NMR spectra were referenced externally to a 1% $CFCl_3$ sample in $CHCl_3$. ^{11}B{^{1}H} NMR spectra were referenced externally to a 5% $BF_3{\cdot}OEt_2$ sample in C_6D_6. All chemical shifts (δ) are quoted in ppm and coupling constants (J) in Hz. Isolated compounds were stored in a MBraun glovebox under an atmosphere of argon. Electrospray ionization mass spectrometry (ESI-MS) was carried out using a Bruker MicrOTOF instrument directly connected to a modified Innovative Technology glovebox.[1] Typical acquisition parameters were used (sample flow rate: 4 μL min^{-1}, nebulizer gas pressure: 0.4 bar, drying gas: argon at 333 K flowing at 4 L min^{-1}, capillary voltage: 4.5 kV, exit voltage: either 15 or 60 V). The spectrometer was calibrated using a mixture of tetra alkyl ammonium bromides $[N(C_nH_{2n+1})_4]Br$ (n = 2-8, 12, 16 and 18) in dichloromethane. Samples were diluted to a concentration of *ca.* < 1×10^{-6} M in fluorobenzene before sampling by ESI-MS. Elemental analyses were conducted by Mr Stephen Boyer at London Metropolitan University (United Kingdom).

Reagents

Mg turnings were purchased from Alfa Aesar and used as received. Iodine was purchased from Sigma-Aldrich and used as received. 3,5-bis(trifluoromethyl)bromobenzene was purchased from Fluorochem and used as received. Iodine, boron trifluoride diethyl ethearate $BF_3{\cdot}Et_2O$ (≥46% BF_3 basis), carbonates (M_2CO_3, M = lithium, sodium and potassium), and anhydrous magnesium sulfate ($MgSO_4$) were purchased from Sigma-Aldrich and used as received. Deuterated dichloromethane (CD_2Cl_2) and deuterated benzene (C_6D_6) were purchased from Cambridge Isotope Laboratories Inc, dried by stirring over CaH_2 overnight before being vacuum distilled, subsequently degassed by three freeze-pump-thaw cycles and then stored over activated 3 Å molecular sieves. Deuterated tetrahydrofuran (THF-d_8) was purchased from Cambridge Isotope Laboratories Inc, stirred over CaH_2 overnight before being vacuum distilled, subsequently degassed by three freeze-pump-thaw cycles and stored over activated 3 Å molecular sieves. *n*-pentane and dichloromethane (CH_2Cl_2, DCM) were dried using an MBraun SPS-800 solvent purification system and degassed by three freeze-pump-thaw cycles. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled over sodium benzophenone and stored over a potassium mirror. Fluorobenzene was purchased from

Fluorochem, stirred over aluminum oxide (Al_2O_3) for two hours, filtered and then stirred over CaH_2 overnight before being vacuum distilled, subsequently degassed by three freeze-pump-thaw cycles and stored over 3 Å molecular sieves. Cp_2ZrMe_2 was purchased from Strem, kept in a glove box under an atmosphere or argon at –23 °C and used without further purification.

SYNTHETHIC PROCEDURES AND CHARACTERISATION DATA

Preparation and characterization of solvent-free anhydrous Li, Na and K salts of $BAr^F{}_4$.

Glassware and set-up

A pre-dried three-neck round-bottom flask (500 mL) containing a stirrer bar was fitted with (i) a Findenser air condenser[2] with a single J. Young tap on top of it, (ii) a dropping funnel (250 mL) with pressure compensation with a rubber septum (or glass stopper) on top of it, and (iii) a single J. Young tap. The system was connected to a Schlenk line using the J. Young taps, flame dried under vacuum ($< 10^{-2}$ mbar) and argon refilled (three times) to remove traces of water, and then fitted into a stirrer hot plate over a heat-on block system (see Figure S1B).

<u>Note:</u> A silicone oil bath and a circulating cooling water condenser can alternatively be used instead a Findenser air condenser and a heat-on block. However, the latter set-up is safer and highly energy efficient. An independent running cost study done in our laboratories (in collaboration with Radleys and Green Light Laboratories Ltd)[3] for two $Na[BAr^F{}_4]$ preparations done in parallel (Figure S1) using the cooling water condenser and the silicone oil bath *versus* a Findenser air condenser and a heat-on block showed that the latter benefits in: (i) considerably decreasing energy consumption (~ 60% less energy), (ii) net zero water consumption during reflux, and (iii) lowering the risk of oil and water spillages.

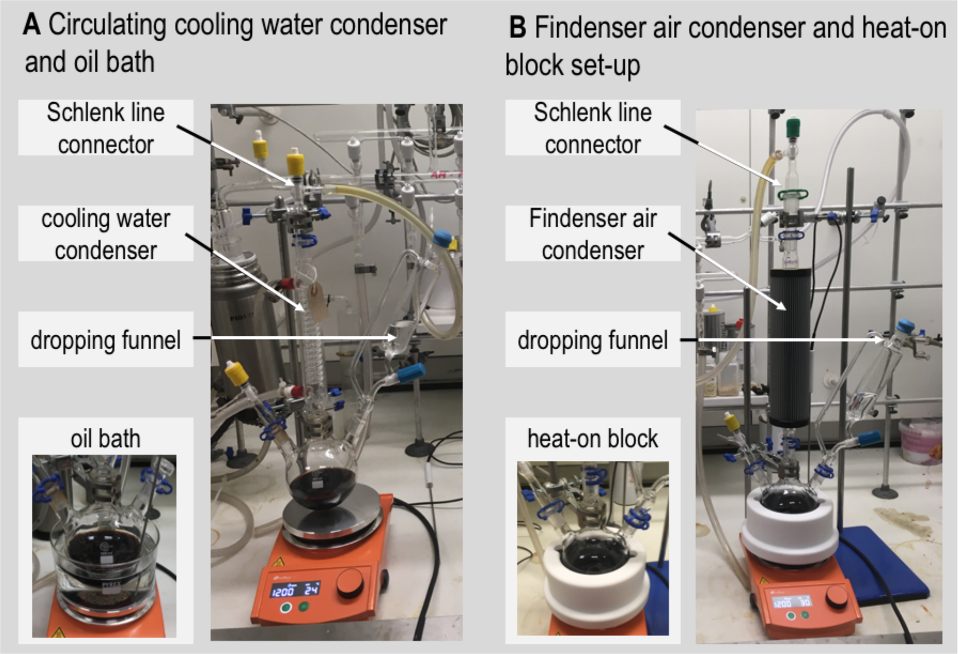

Figure S1: Comparing the two systems: (**A**) Silicone oil bath and circulating water cooling condenser set-up and (**B**) heat-on block and Findenser air condenser set-up.

Synthetic protocol

Mg turnings (10 g, 411 mmol) and I_2 (1 g, 3.75 mmol) were added to the round-bottom flask under argon. The system was placed under static vacuum and the solids were slowly heated with the help of a hair dryer until vapours of I_2 were produced, then it was immediately allowed to cool to room temperature. Dry diethyl ether (50 mL) was slowly added to the mixture. The mixture became colourless upon vigorous stirring for 20 mins. Then, the dropping funnel was charged with a solution of 1,3-bis(trifluoromethyl)-5-bromobenzene (28 mL, 162 mmol) in dry diethyl ether (50 mL) which was added dropwise to the mixture at room temperature over a minimum period of 1 h. *Caution!* This addition caused an exothermic reaction; therefore, the addition should be slow. The mixture turned brown-coffee colour. Stirring for 4 h at room temperature yielded a solution of the Grignard reagent 1,3-bis(trifluoromethyl)-5-magnesium(bromide)-benzene in diethyl ether. Then, the dropping funnel was charged with a solution of $BF_3{\cdot}Et_2O$ (4 mL, 32.5 mmol) in dry diethyl ether (25 mL) which was added dropwise to the mixture at room temperature over a period of 1 h. The mixture was then refluxed under an atmosphere of argon at 40 °C for 12 h. The contents of the mixture were added dropwise (cannula transferred) into a solution of the corresponding alkali metal carbonate salt (Li_2CO_3: 60 g; Na_2CO_3: 80 g; K_2CO_3: 80 g) in water (500 mL). Work-up protocols are not are sensitive, thus they were carried out in air. The mixture was stirred vigorously for 1 h and then filtered using a fritted glass filter. The filtrate was extracted with undried diethyl ether (3 x 75 mL). The combined organic extracts were dried by stirring over anhydrous $MgSO_4$ for 30 min and then filtered. The solvent was removed in a rotary evaporator to yield a brown-honey oily crude of the corresponding alkali metal tetra aryl borate salt.

Isolation and drying method

For **Li[BAr^F$_4$]** (**1**), dissolving the resulting oily crude in undried diethyl ether (20 mL) and layering with undried *n*-pentane (40 mL) at −23 °C for 48 h resulted in a crystalline solid, which was then recrystallised again by dissolving it in a 1:1 mixture of undried dichloromethane and undried fluorobenzene (15 mL) and layering with undried *n*-pentane (40 mL) at −23 °C for 48 h. These two crystallisation steps were done in air and yielded $[Li(H_2O)_4][BAr^F_4]$[4] as an off-white solid, as confirmed by NMR spectroscopy and single-crystal X-ray diffraction crystallography. Solvent-free **anhydrous Li[BAr^F$_4$]** (**1**) was obtained as a pale brown solid by drying the resulting $[Li(H_2O)_4][BAr^F_4]$ at 80 °C under dynamic vacuum using a Schlenk line fitted with a vacuum gauge with display ($< 10^{-2}$ mbar) for 72 h. Anhydrous $Li[BAr^F_4]$ was then transferred and stored in a glove box under an atmosphere of argon. Yield: 18.1 g, 20.8 mmol, 64%. Elemental analysis found (calculated) for $C_{32}H_{12}BF_{24}Li$: C, 43.99 (44.17); H, 1.28 (1.39)%.

Note: **$[Li(H_2O)][BAr^F_4]$** (**4**) was obtained when drying $[Li(H_2O)_4][BAr^F_4]$ at 80 °C under dynamic vacuum using a Schlenk line fitted with a vacuum gauge with display ($< 10^{-2}$ mbar) for only 24 h, as confirmed by ^1H NMR spectroscopy and elemental analyses. Drying under these conditions for longer times (72 h) are needed to ensure anhydrous

Li[BAr$^{F}_{4}$]. [Li(H_2O)][BAr$^{F}_{4}$] was then transferred and stored in a glove box under an atmosphere of argon. Elemental analysis found (calculated) for [Li(H_2O)][BAr$^{F}_{4}$] $C_{32}H_{14}BF_{24}LiO$: C, 43.15 (43.27); H, 1.66 (1.59)%.

For **Na[BAr$^{F}_{4}$]** (**2**), dissolving the resulting oily crude in a 1:1 mixture of undried dichloromethane and undried tetrahydrofuran (30 mL) and placing the mixture at –23 °C for 48 h yielded [Na(THF)$_6$][BAr$^{F}_{4}$] as an off white crystalline solid, which was then recrystallised again from a 1:1 mixture of undried dichloromethane and undried tetrahydrofuran (30 mL) at –23 °C for 48 h. These crystallisation steps were done in air. Solvent-free **anhydrous Na[BAr$^{F}_{4}$]** (**2**) was obtained as white solid by drying the resulting crystalline solid at 80 °C under dynamic vacuum using a Schlenk line fitted with a vacuum gauge with display (< 10^{-2} mbar) for 48 h. Anhydrous Na[BAr$^{F}_{4}$] was then transferred and stored in a glove box under an atmosphere of argon. Yield: 19.6 g, 22.1 mmol; 68%. Elemental analysis found (calculated) for $C_{32}H_{12}BF_2Na$: C, 43.31 (43.37); H, 1.27 (1.36)%.

Anhydrous Na[BAr$^{F}_{4}$] (**2**) was also obtained following Bergman's synthesis,[5] and recrystallising the crude (two times, in air) from a 1:1 mixture of undried dichloromethane and undried tetrahydrofuran (30 mL) at –23 °C for 48 h, and drying the resulting crystalline solid at 80 °C under dynamic vacuum using a Schlenk line fitted with a vacuum gauge with display (< 10^{-2} mbar) for 48 h. Na[BAr$^{F}_{4}$] was then transferred and stored in a glove box under an atmosphere of argon Yield: 12.3 g, 12.9 mmol, 58%.

For **K[BAr$^{F}_{4}$]** (**3**), dissolving the resulting oily crude in a 1:1 mixture of undried dichloromethane and undried tetrahydrofuran (20 mL) and placing the mixture at –23 °C for 48 h yielded [K(THF)$_6$][BAr$^{F}_{4}$] as an off white crystalline solid, which was then recrystallised again from a 1:1 mixture of undried dichloromethane and undried tetrahydrofuran (20 mL) at –23 °C for 48 h. These crystallisation steps were done in air. Solvent-free **anhydrous K[BAr$^{F}_{4}$]** (**3**) was obtained as an off white solid by drying the resulting crystalline solid at 80 °C dynamic vacuum using a Schlenk line fitted with a vacuum gauge with display (< 10^{-2} mbar) for 48 h. Anhydrous K[BAr$^{F}_{4}$] was then transferred and stored in a glove box under an atmosphere of argon. Yield: 17.0 g, 18.9 mol, 58%. Elemental analysis found (calculated) for $C_{32}H_{12}BF_{24}K$: C, 42.48 (42.60); H, 1.23 (1.34)%.

Note: For **Na[BAr$^{F}_{4}$]** (**2**) and **K[BAr$^{F}_{4}$]** (**3**), the two consecutive recrystallisation steps (prior to drying) ensure high purity of the resulting solvent-free anhydrous salts after drying the corresponding crystalline solids at 80 °C dynamic vacuum (< 10^{-2} mbar) for 48 h. NMR data for the unidentified major contaminants observed after only one crystallisation step: ^{11}B{^{1}H} NMR (128.4 MHz, THF-d_8, 298 K): δ, –7.4, –8.2; ^{19}F{^{1}H} NMR (376.5 MHz, THF-d_8, 298 K): δ, –62.8, –63.2.

Li[BAr$^{F}_{4}$] (**1**), **Na[BAr$^{F}_{4}$]** (**2**) and **K[BAr$^{F}_{4}$]** (**3**) were isolated as highly hygroscopic compounds (typical yields 60–70%) and stored in a glove box under an atmosphere of argon. The H_2O contents for these isolated salts are below the limits of detection (ppm) of NMR spectroscopic titration with Cp_2ZrMe_2 (see Figure S11 for Li[BAr^F_4], Figure S13 and S14 for Na[BAr^F_4], and Figure S15 for K[BAr^F_4]).

Single crystals

Solvent-free anhydrous **Na[BAr^F_4]** (**2**) and **K[BAr^F_4]** (**3**) suitable for X-ray diffraction studies can be obtained by slow diffusion of dry *n*-pentane into a concentrated solution of the corresponding isolated anhydrous salt in a 1:1 mixture of dry fluorobenzene and dry dichloromethane. The presence of inevitable adventitious water during the single crystal growing process from the solvents using the isolated solvent-free anhydrous **Li[BAr^F_4]** (**1**) (*highly hygroscopic solid!*) resulted in the crystallisation of single crystals the mono aquo complex **[Li(H_2O)][BAr^F_4]** (**4**).

Characterisation data

In general, solution ^{1}H, ^{11}B, ^{19}F and ^{13}C NMR resonances corresponding the [BAr^F_4]$^-$ anion for all the compounds are identical in dry THF-*d*$_8$. In addition, supporting ^{1}H and ^{7}Li NMR data in dry THF-*d*$_8$ for solvent-free anhydrous **Li[BAr^F_4]** (**1**) and **[Li(H_2O)][BAr^F_4]** (**4**) are included here. Supporting ^{1}H NMR data for the determination of H_2O content by titration with Cp_2ZrMe_2 for all the salts is also included (Figures S11-S15).

^{1}H NMR (400.2 MHz, THF-*d*$_8$, 298 K, BAr^F_4): δ, 7.79 (br s, 8 H, *ortho*-BAr^F_4), 7.58 (s, 4 H, *para*-BAr^F_4); 4.02 (br s, 2 H, H_2O, resonance only present in the isolated crystalline sample for **[Li(H_2O)][BAr^F_4]** (**4**), absent in anhydrous compounds, see Figure S2 for anhydrous **Li[BAr^F_4]** (**1**) *vs* Figure S3 for **[Li(H_2O)][BAr^F_4]** (**4**)).

^{7}Li NMR (155.5 MHz, THF-*d*$_8$, 298 K, Li[BAr^F_4]): δ, –0.54.

^{7}Li NMR (155.5 MHz, THF-*d*$_8$, 298 K, [Li(H_2O)][BAr^F_4]: δ, –0.38.

^{11}B{^{1}H} NMR (128.4 MHz, THF-*d*$_8$, 298 K, BAr^F_4): δ, –6.5.

^{13}C {^{1}H} NMR (100.6 MHz, THF-*d*$_8$, 298 K, BAr^F_4): δ, 162.8 (q, ^{1}J(C–B) = 49.9 Hz, *ipso*-C), 135.6 (br s, *ortho*-C), 130.0 (qq, ^{3}J(C–B) = 2.9 Hz, ^{2}J(C–F) = 31.8 Hz, *meta*-C), 125.5 (q, ^{1}J(C–F) = 270.8 Hz, CF_3), 118.2 (br sept, ^{3}J(C–F) = 4.2 Hz, *para*-C).

^{19}F{^{1}H} NMR (376.5 MHz, THF-*d*$_8$, 298 K, BAr^F_4): δ, –63.4.

HRMS (ESI) m/z found (calculated) for $C_{32}H_{12}BF_{24}$ [BAr^F_4]$^-$: 863.0551 (863.0654).

Procedure to determine the content of H_2O by ^1H NMR titration with Cp_2ZrMe_2[5]

A solution of Cp_2ZrMe_2 (16.5 mg, 65.6 μmol) and hexamethylbenzene (3 mg, 18.3 μmol, internal standard) in freshly distilled dry THF-d_8 (0.5 mL) was prepared in a J. Young NMR tube. A ^1H NMR spectrum (400 MHz) was acquired before titrating the corresponding alkali metal BAr^F_4 derivative: δ; 6.13 (s, 10 H, Cp), 2.21 (s, internal standard), -0.38 (s, 6 H, Me). This mixture was transferred via cannula under an atmosphere of argon to a second J. Young NMR tube containing the corresponding alkali metal BAr^F_4 salt (Li[BAr^F_4] (**1**): 10 mg, 11.5 μmol; Na[BAr^F_4] (**2**): 12 mg, 13.5 μmol; K[BAr^F_4] (**3**): 8 mg, 8.9 μmol; and [Li(H_2O)][BAr^F_4] (**4**): 11 mg, 12.4 μmol) and a second ^1H NMR spectrum (400 MHz) was acquired after 3 h: δ; 7.79 (br s, *ortho*-BAr^F_4), 7.58 (br s, *para*–BAr^F_4), 6.13 (s, 10 H, Cp), 2.21 (s, internal standard), –0.38 (s, 6 H, Me). No evidences of the formation of $[Cp_2ZrMe]_2O$ (δ, 5.97 (s, Cp), –0.02 (s, Me)) and CH_4 (δ, 0.21 (s, CH_4)) resulting from reaction of Cp_2ZrMe_2 with H_2O (attributed to traces of moisture in the BAr^F_4 salts)[5] were observed for anhydrous Li[BAr^F_4] (**1**), Na[BAr^F_4] (**2**) and K[BAr^F_4] (**3**). For [Li(H_2O)][BAr^F_4] (**4**) evolution of CH_4 gas was immediately observed upon titration and integration of the newly formed resonances for $[Cp_2ZrMe]_2O$ against the internal standard and remaining Cp_2ZrMe_2 gave a content of 0.96:1 H_2O:BAr^F_4. No further change in integration in the titrations was evident after longer periods of time.

NMR spectra for Li[BAr$^F_4$], [Li(H$_2$O)][BAr$^F_4$], Na[BAr$^F_4$] and K[BAr$^F_4$]

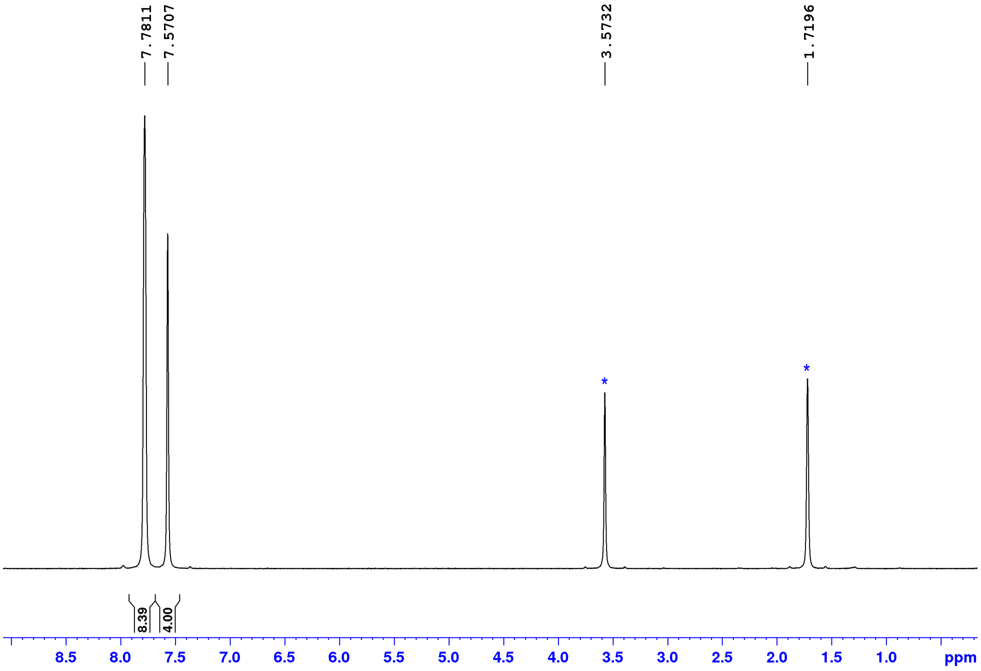

Figure S2: ^{1}H NMR (400.2 MHz, THF-d_8, 298 K) spectrum of anhydrous **Li[BAr$^F_4$]** (**1**). Residual protio solvent resonances are marked with *.

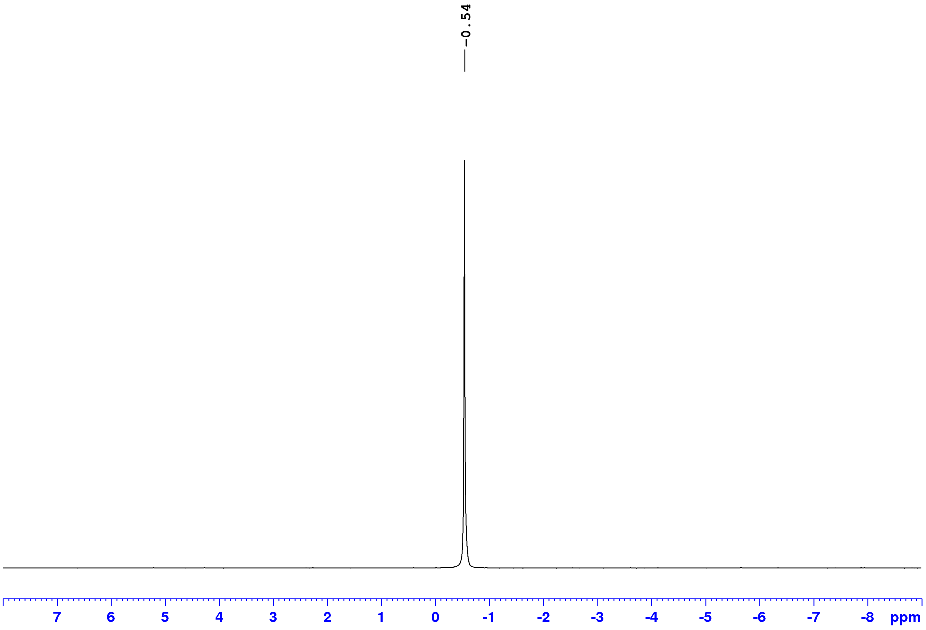

Figure S3: ^{7}Li NMR (155.5 MHz, THF-d_8, 298 K) spectrum of anhydrous **Li[BAr$^F_4$]** (**1**).

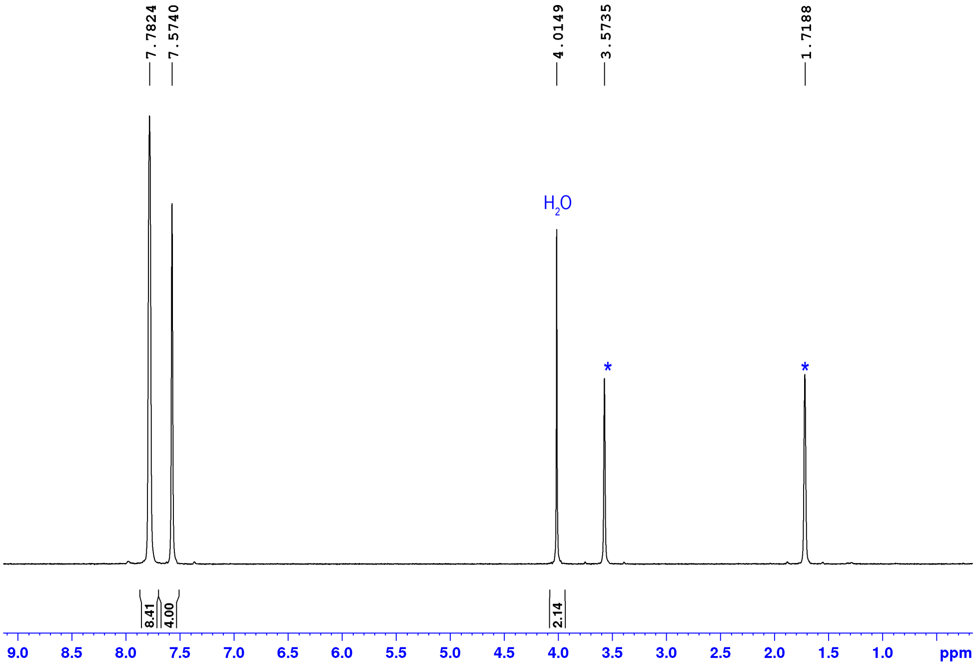

Figure S4: ^{1}H NMR (400.2 MHz, THF-d_8, 298 K) spectrum of isolated crystals of **[Li(H$_2$O)][BAr^F$_4$]** (**4**).

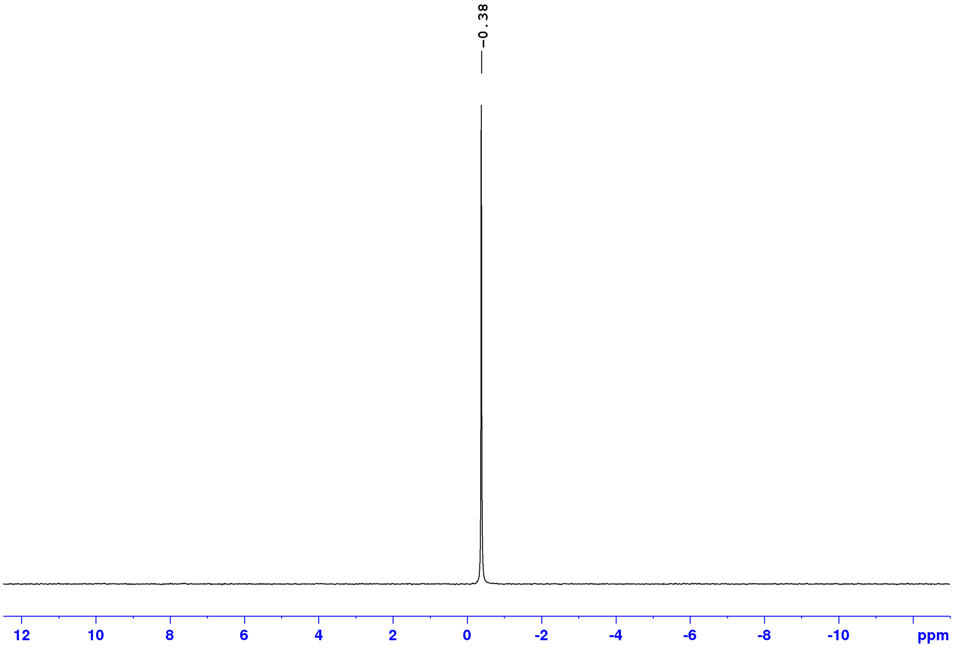

Figure S5: ^{7}Li NMR (155.5 MHz, THF-d_8, 298 K) spectrum of isolated crystals of **[Li(H$_2$O)][BAr^F$_4$]** (**4**).

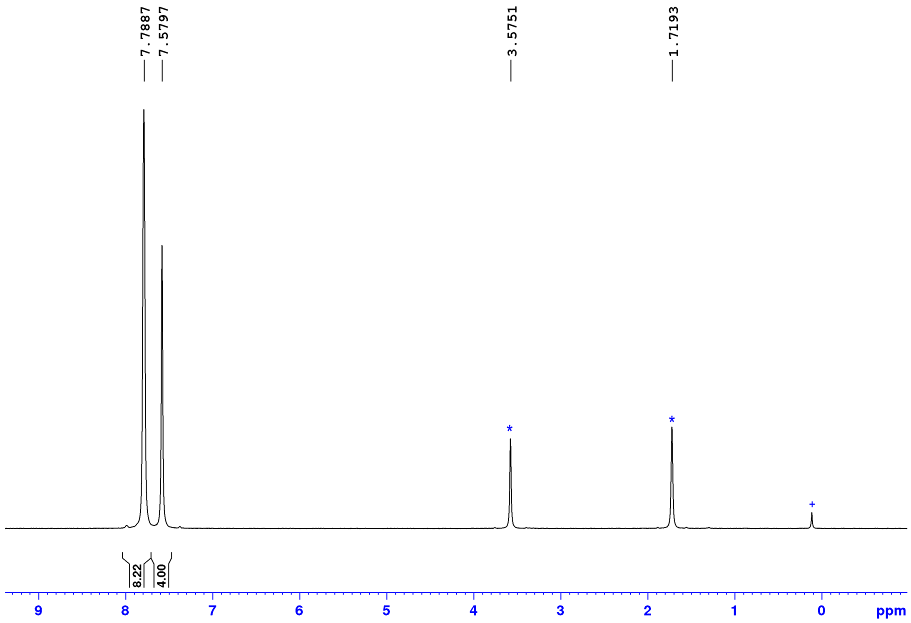

Figure S6: ^{1}H NMR (400.2 MHz, THF-d_8, 298 K) spectrum of anhydrous **Na[BAr^F$_4$]** (**2**). Residual protio solvent resonances and traces of silicone grease from THF-d_8 are marked with * and + respectively.

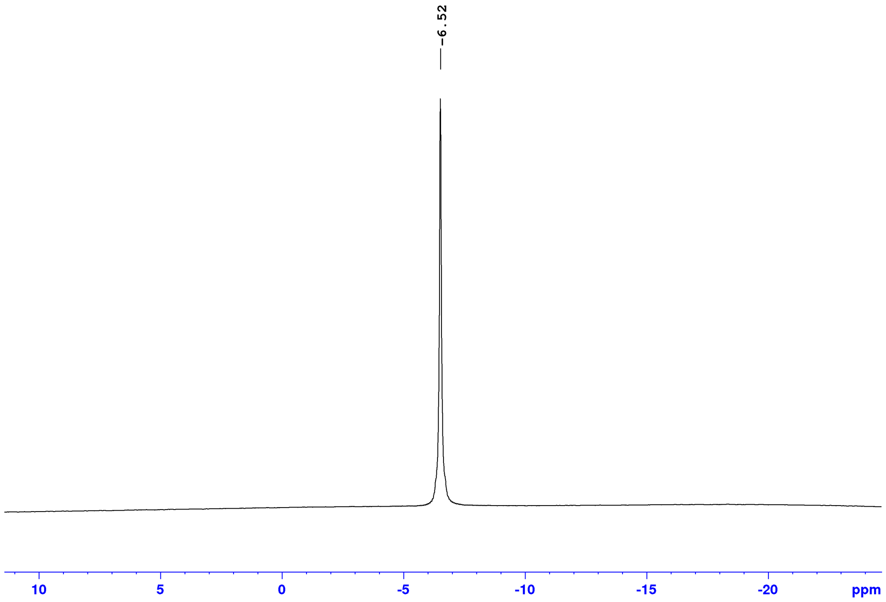

Figure S7: ^{11}B{^{1}H} NMR (128.4 MHz, THF-d_8, 298 K) spectrum of anhydrous **Na[BAr^F$_4$]** (**2**) as a representative example of anhydrous alkali metal BAr^F$_4$ salt (anhydrous Li[BAr^F$_4$] and anhydrous K[BAr^F$_4$] gave identical spectra).

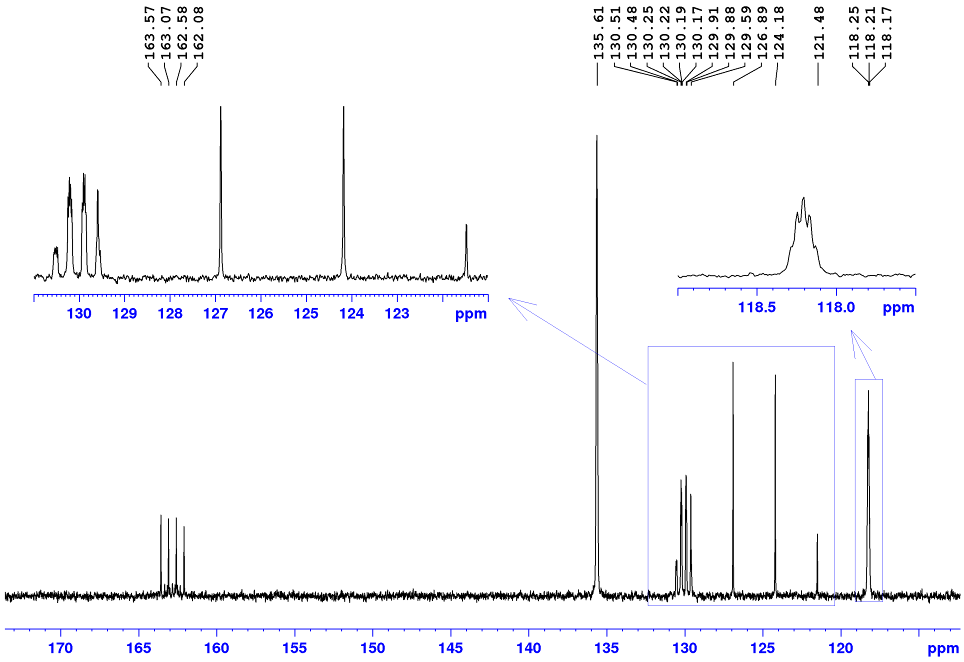

Figure S8: $^{13}C\{^{1}H\}$ NMR (100.6 MHz, THF-d_8, 298 K) spectrum of anhydrous **Na[BAr$^{F}_{4}$] (2)** as a representative example of anhydrous alkali metal BAr$^{F}_{4}$ salt (anhydrous Li[BAr$^{F}_{4}$] and anhydrous K[BAr$^{F}_{4}$] gave identical spectra).

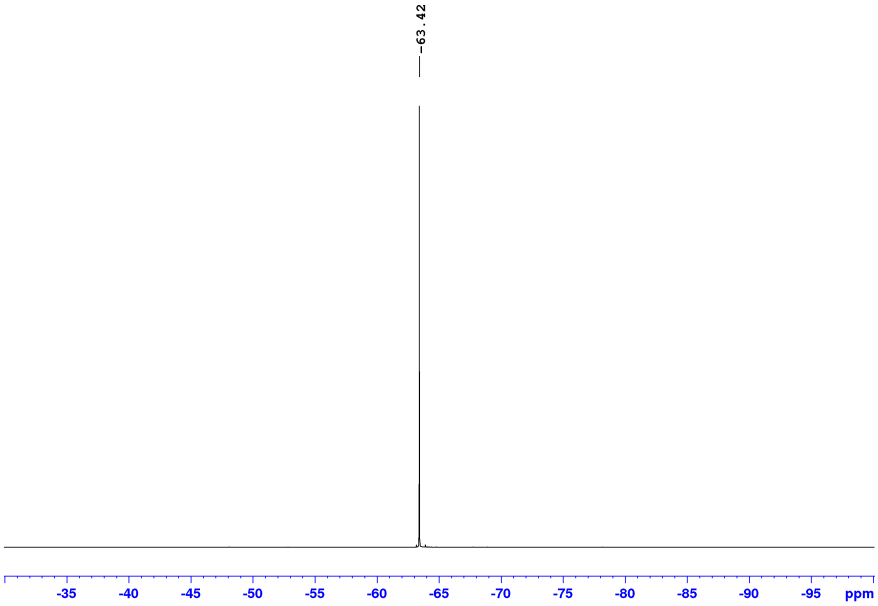

Figure S9: $^{19}F\{^{1}H\}$ NMR (376.5 MHz, THF-d_8, 298 K) spectrum of anhydrous **Na[BAr$^{F}_{4}$] (2)** as a representative example of anhydrous alkali metal BAr$^{F}_{4}$ salt (anhydrous Li[BAr$^{F}_{4}$] and anhydrous K[BAr$^{F}_{4}$] gave identical spectra).

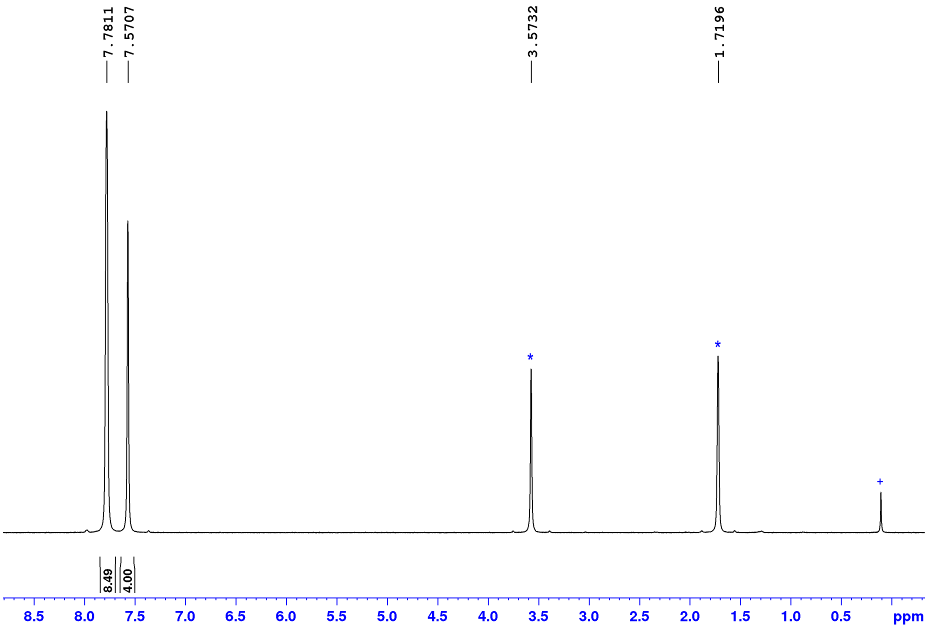

Figure S10: ^{1}H NMR (400.2 MHz, THF-d_8, 298 K) spectrum of anhydrous **K[BAr^F$_4$]** (**3**). Residual protio solvent resonances and traces of silicone grease from THF-d_8 are marked with * and + respectively.

NMR spectra for H_2O titrations of Li[BAr$^F_4$] (1), [Li(H_2O)][BAr$^F_4$] (4), Na[BAr$^F_4$] (2) and K[BAr$^F_4$] (3) with Cp_2ZrMe_2

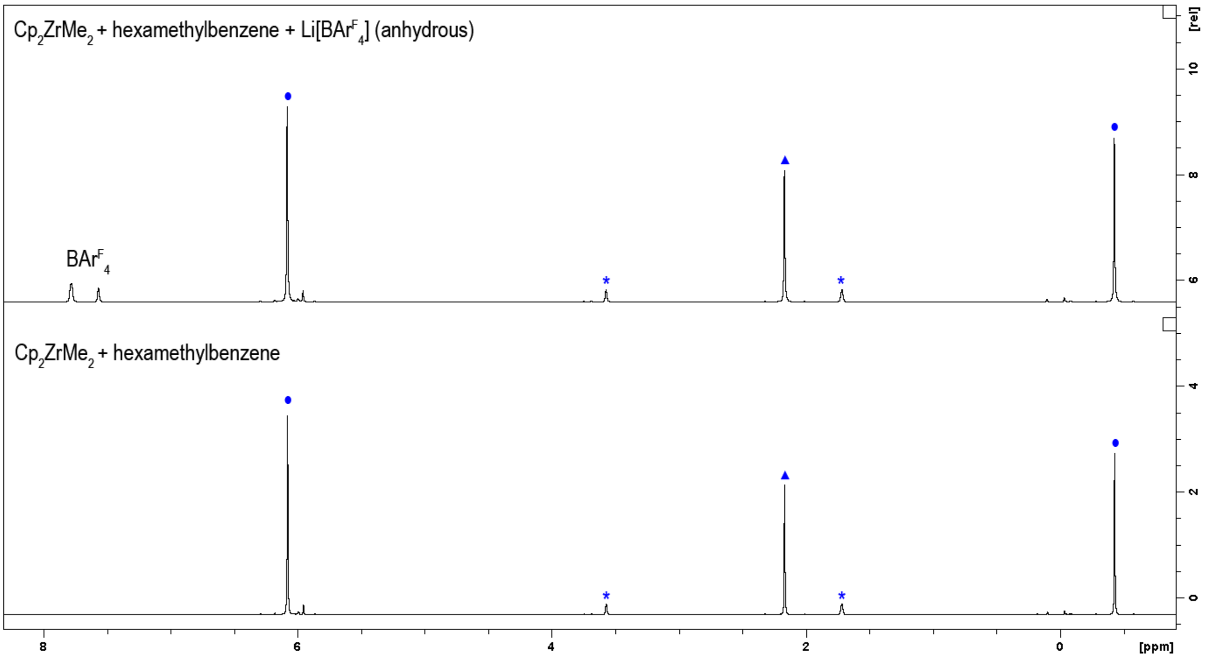

Figure S11: ^{1}H NMR (400.2 MHz, THF-d_8, 298 K) spectra for the H_2O titration of anhydrous **Li[BAr$^F_4$] (1)** with Cp_2ZrMe_2 using hexamethylbenzene as internal standard. Bottom: ^{1}H NMR spectrum corresponding to a dry THF-d_8 solution of Cp_2ZrMe_2 (16.5 mg, 65.6 μmol, marked with •) and hexamethylbenzene (3 mg, 18.3 μmol, internal standard, marked with ▲) in freshly distilled dry THF-d_8 (0.5 mL) prepared in a dry J. Young NMR tube. Top: ^{1}H NMR spectrum corresponding to a dry THF-d_8 solution of a titrated sample of anhydrous Li[BAr$^F_4$] (10 mg, 11.5 μmol) with the contents of the solution showed in the bottom spectrum after 3 h. No evidences of the formation of $[Cp_2ZrMe]_2O$ (*δ*, 5.97 (s, Cp), –0.02 (s, Me)) or CH_4 (*δ*, 0.21 (s, CH_4)) attributed to traces of moisture in the LiBAr$^F_4$ salt were observed. No further change in integration in the titrations was evident after longer periods of time. Residual protio solvent resonances are marked with *.

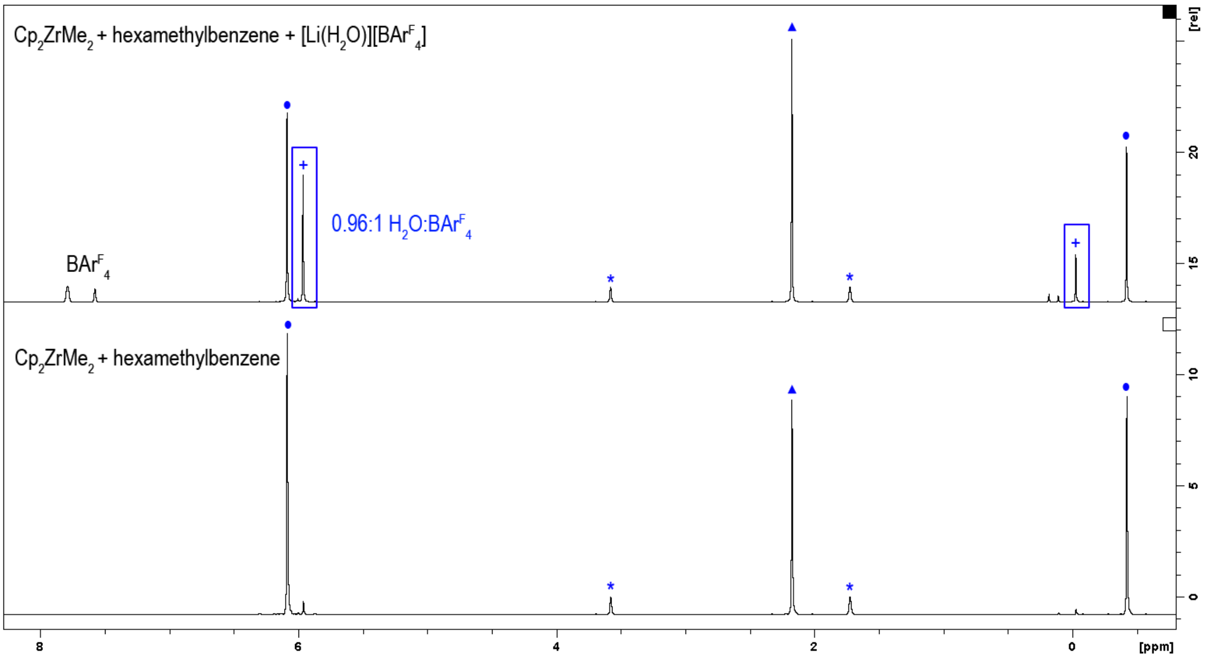

Figure S12: ^1H NMR (400.2 MHz, THF-d_8, 298 K) spectra for the H_2O titration of anhydrous **$[Li(H_2O)][BAr^F_4]$** (**4**) with Cp_2ZrMe_2 using hexamethylbenzene as internal standard. Bottom: ^1H NMR spectrum corresponding to a dry THF-d_8 solution of Cp_2ZrMe_2 (16.5 mg, 65.6 μmol, marked with •) and hexamethylbenzene (3 mg, 18.3 μmol, internal standard, marked with ▲) in freshly distilled dry THF-d_8 (0.5 mL) prepared in a dry J. Young NMR tube. Top: ^1H NMR spectrum corresponding to a dry THF-d_8 solution of a titrated sample of anhydrous $[Li(H_2O)][BAr^F_4]$ (11 mg, 12.4 μmol) with the contents of the solution showed in the bottom spectrum after 3 h. Evolution of CH_4 gas was immediately observed upon titration and the formation of $[Cp_2ZrMe]_2O$ marked with + and inside a blue box (*δ*, 5.97 (s, Cp), −0.02 (s, Me) is attributed to the water present in $[Li(H_2O)][BAr^F_4]$ salt. Integration of the resonances for $[Cp_2ZrMe]_2O$ against the internal standard and remaining Cp_2ZrMe_2 gave a content of 0.96:1 H_2O:BAr^F_4. No further change in integration in the titrations was evident after longer periods of time. Residual protio solvent resonances are marked with *.

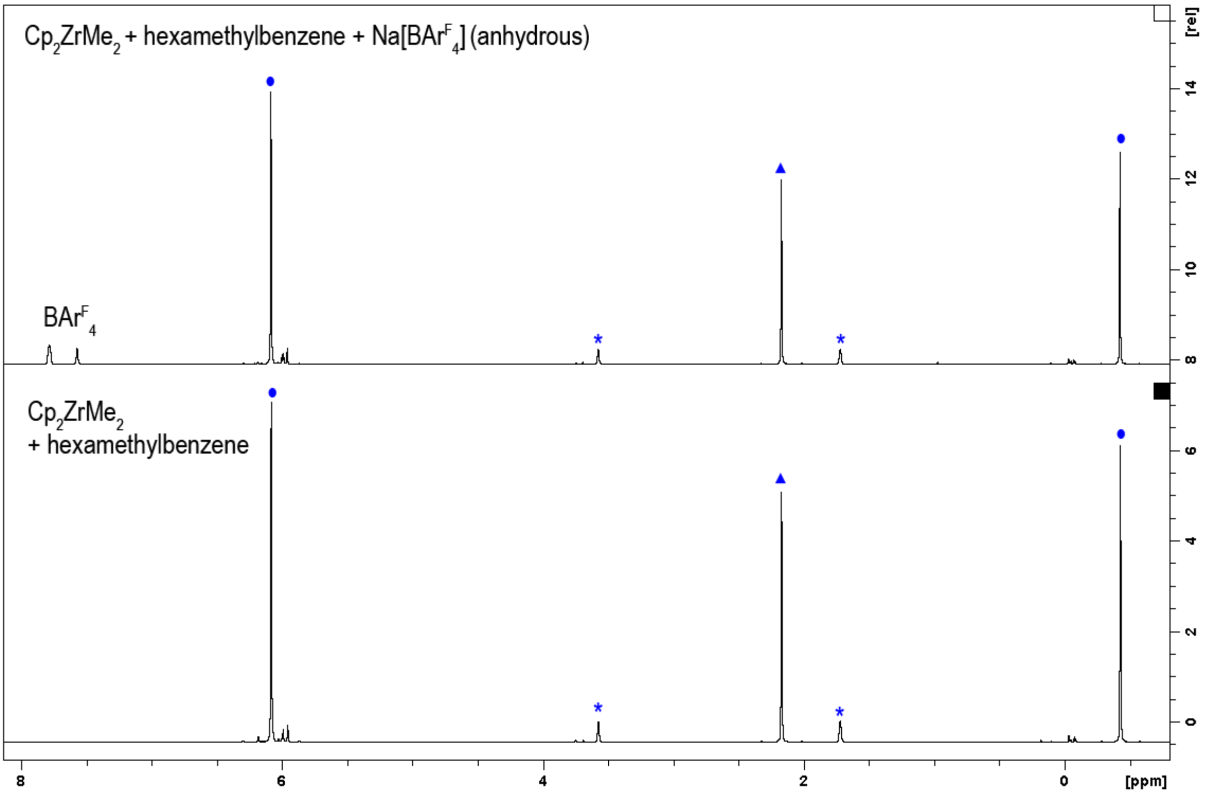

Figure S13: ^1H NMR (400.2 MHz, THF-d_8, 298 K) spectra for the H_2O titration of anhydrous **Na[BAr^F$_4$]** (**2**) with Cp_2ZrMe_2 using hexamethylbenzene as internal standard. Bottom: ^1H NMR spectrum corresponding to a dry THF-d_8 solution of Cp_2ZrMe_2 (16.5 mg, 65.6 µmol, marked with •) and hexamethylbenzene (3 mg, 18.3 µmol, internal standard, marked with ▲) in freshly distilled dry THF-d_8 (0.5 mL) was prepared in a J. Young NMR tube. Top: ^1H NMR spectrum corresponding to a dry THF-d_8 solution of a titrated sample of anhydrous Na[BAr^F_4] (12 mg, 13.5 µmol) with the contents of the solution showed in the bottom for 3 h. No evidences of the formation of $[Cp_2ZrMe]_2O$ (*δ,* 5.97 (s, Cp), −0.02 (s, Me)) and CH_4 (*δ,* 0.21 (s, CH_4)) attributed to traces of moisture in the Li[BAr^F_4] salt were observed. No further change in integration in the titrations was evident after longer periods of time. Residual protio solvent resonances are marked with *.

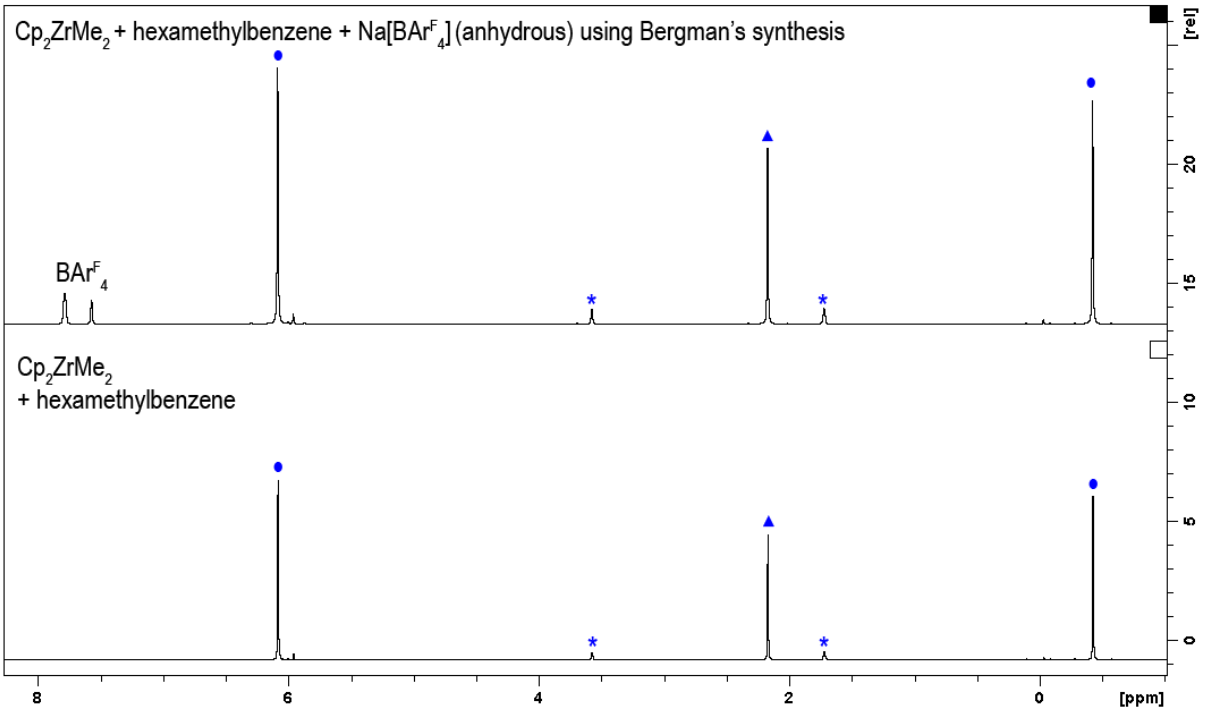

Figure S14: ^1H NMR (400.2 MHz, THF-d_8, 298 K) spectra for the H_2O titration with Cp_2ZrMe_2 using hexamethylbenzene as internal standard of anhydrous **$Na[BAr^F_4]$ (2)** obtained following Bergman's synthesis[5] and recrystallising (two times) the crude from a 1:1 mixture of undried dichloromethane and undried tetrahydrofuran (30 mL) at –23 °C (48 h), and drying the solid at 80 °C (48 h) under dynamic vacuum using a Schlenk line fitted with a vacuum gauge with a display ($< 10^{-2}$ mbar) –as per our method reported here. Bottom: ^1H NMR spectrum corresponding to a dry THF-d_8 solution of Cp_2ZrMe_2 (16.5 mg, 65.6 μmol, marked with •) and hexamethylbenzene (3 mg, 18.3 μmol, internal standard, marked with ▲) in freshly distilled dry THF-d_8 (0.5 mL) was prepared in a J. Young NMR tube. Top: ^1H NMR spectrum corresponding to a dry THF-d_8 solution of a titrated sample of anhydrous $Na[BAr^F_4]$ (14.5 mg, 16.4 μmol) with the contents of the solution showed in the bottom for 3 h. No evidences of the formation of $[Cp_2ZrMe]_2O$ (*δ,* 5.97 (s, Cp), –0.02 (s, Me)) and CH_4 (*δ,* 0.21 (s, CH_4)) attributed to traces of moisture in the $Li[BAr^F_4]$ salt were observed. No further change in integration in the titrations was evident after longer periods of time. Residual protio solvent resonances are marked with *.

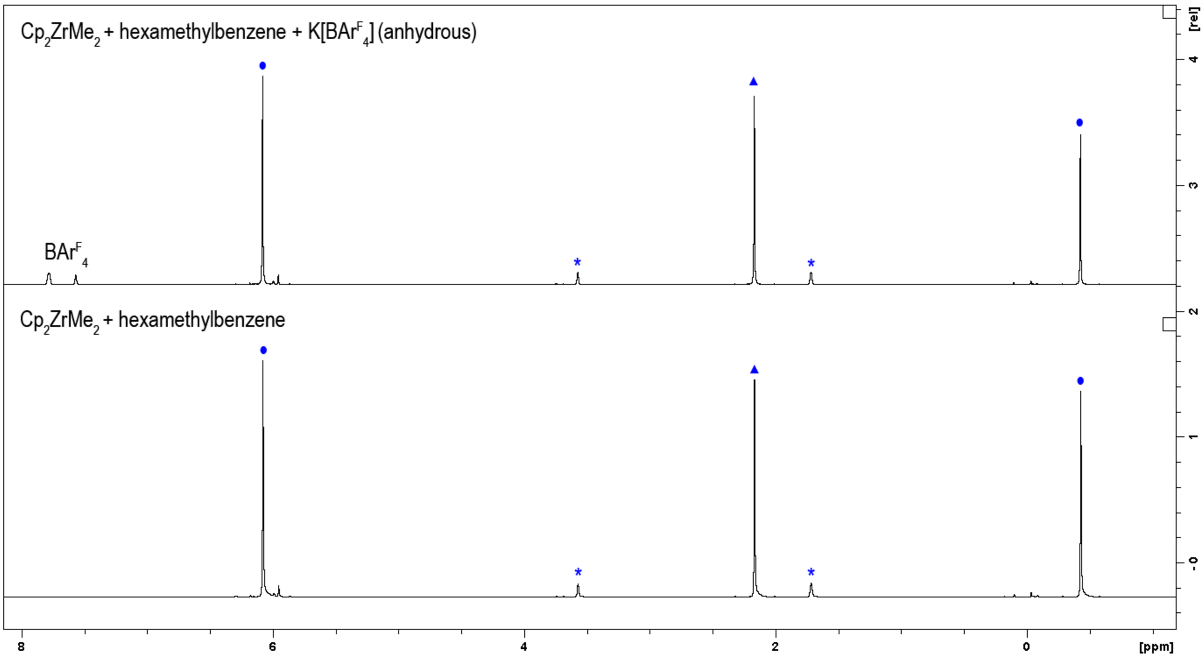

Figure S15: ^1H NMR (400.2 MHz, THF-d_8, 298 K) spectra for the H_2O titration of anhydrous **K[BAr$^F_4$]** (**3**) with Cp_2ZrMe_2. Bottom: ^1H NMR spectrum corresponding to a dry THF-d_8 solution of Cp_2ZrMe_2 (16.5 mg, 65.6 µmol, marked with •) and hexamethylbenzene (3 mg, 18.3 µmol, internal standard, marked with ▲) in freshly distilled dry THF-d_8 (0.5 mL) was prepared in a J. Young NMR tube. Top: ^1H NMR spectrum corresponding to a dry THF-d_8 solution of a titrated sample of anhydrous K[BAr$^F_4$] (8 mg, 8.9 µmol) with the contents of the solution showed in the bottom for 3 h. No evidences of the formation of $[Cp_2ZrMe]_2O$ (δ, 5.97 (s, Cp), –0.02 (s, Me)) and CH_4 (δ, 0.21 (s, CH_4)) attributed to traces of moisture in the Li[BAr$^F_4$] salt were observed. No further change in integration in the titrations was evident after longer periods of time. Residual protio solvent resonances are marked with *.

X-RAY CRYSTALLOGRAPHY

Crystal structure determinations

Single-crystal X-ray diffraction data for **$[Li(H_2O)][BAr^F_4]$** (**4**), **$Na[BAr^F_4]$** (**2**) and **$K[BAr^F_4]$** (**3**) were collected (ω-scans) on an Oxford Diffraction/Agilent SuperNova diffractometer with Cu-$K\alpha$ radiation (λ = 1.54184 Å) equipped with nitrogen gas Oxford Cryosystems Cryostream unit[6] at the Oxford Chemical Crystallography Service from the University of Oxford. Diffraction data was reduced and processed using CrysAlisPro package.[7] The structures were solved using SHELXT[8] and refined to convergence on F^2 and against all independent reflections by full-matrix least-squares using SHELXL[9] (version 2018/3) in combination with the GUI OLEX2[10] program. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were geometrically placed unless otherwise stated (see specific details for each molecular structure in the text) and allowed to ride on their parent atoms. CF_3 groups on the $BAr^F_4{}^-$ anion were necessarily modelled as disordered over two main domains, and restrained to maintain sensible geometries. Distances and angles were calculated using the full covariance matrix. Selected crystallographic data are summarized in the text and full details are given in the supplementary deposited CIF files (CCDC 1886445, 1886446 and 1886447). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://optimized.ccdc.cam.ac.uk/data_request/cif.

Selected crystallographic and refinement data

X-ray crystal structure of $[Li(H_2O)][BAr^F_4]$ (4) (CCDC 1886445)

Crystal data for **$[Li(H_2O)][BAr^F_4]$** (**4**): $C_{32}H_{14}BF_{24}LiO$, M = 888.18 g/mol, tetragonal, $P4/n$, a = 13.45985(14), b = 13.45985(14), c = 9.66072(16) Å, α = β = γ = 90°, V = 1750.21(5) Å^3, Z = 2, λ(Cu-Kα) = 1.54184 Å, T = 150 (1) K, colourless prim, ρ(calcd, g cm^{-3}) = 1.685, μ (mm^{-1}) = 1.736, 22082 reflections collected, 1826 independent measured reflections (R_{int} = 0.0207), F^2 refinement, R_1(obs, $I > 2\sigma(I)$) = 0.0523, wR_2(all data) = 0.1390, 1744 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 152.44°], 231 restrains, 192 parameters, GOF = 1.088 and residual electron density (e Å^{-3}) = 0.430/–0.333.

Additional details for **$[Li(H_2O)][BAr^F_4]$** (**4**): This compound crystallized in the tetragonal space group $P4/n$. Both trifluoromethyl group from the asymmetric unit for the borate anion were modelled as disordered (rotational). The symmetry operations used to generate the atoms labelled with ', " and "' in Figure 3 (manuscript) are -x+1,y+1/2,-z+1, -x+1,-y+1,-z+1 and -x+1/2,-y+3/2,+z.

X-ray crystal structure of $Na[BAr^F_4]$ (2) (CCDC 1886446)

Crystal data for **$Na[BAr^F_4]$** (**2**): $C_{32}H_{12}BF_{24}Na$, M = 886.22 g/mol, tetragonal, $P4/n$, a = 13.3508(2), b = 13.3508(2), c = 9.3819(2) Å, α = β = γ = 90°, V = 1672.27(7) Å^3, Z = 2, λ(Cu-Kα) = 1.54184 Å, T = 150 (1) K, colourless prim, ρ(calcd, g cm^{-3}) = 1.760, μ (mm^{-1}) = 1.916, 15966 reflections collected, 1772 independent measured reflections (R_{int} =

0.0381), F^2 refinement, R_1(obs, $I > 2\sigma(I)$) = 0.0610, wR_2(all data) = 0.1541, 1693 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 148.7°], 138 restrains, 160 parameters, GOF = 1.085 and residual electron density (e Å^{-3}) = 0.536/−0.474.

***Additional details for* Na[BAr^F$_4$] (2)**: This compound crystallized in the tetragonal space group *P*4/*n*. Only one trifluoromethyl group from the asymmetric unit was modelled as disordered (rotational). Fhe symmetry operations used to generate the atoms labelled with ’, ” and ”’ in Figure 3 (manuscript) are -x+1,-y+1,-z+1, x-1/2,-y+1,-z+2 and -x+1,y+1/2,-z+2.

X-ray crystal structure of K[BAr^F$_4$] (3) (CCDC 1886447)

***Crystal data for* K[BAr^F$_4$] (3)**: $C_{32}H_{12}BF_{24}K$, M = 902.33 g/mol, tetragonal, *P*4/*n*, a = 13.4834(3), b = 13.4834(3), c = 9.4747(5) Å, α = β = γ = 90°, V = 1722.52(12) Å^3, Z = 2, λ(Cu-Kα) = 1.54184 Å, T = 150 (1) K, colourless prim, ρ(calcd, g cm^{-3}) = 1.740, μ (mm^{-1}) = 2.819, 4443 reflections collected, 1783 independent measured reflections (R_{int} = 0.0214), F^2 refinement, R_1(obs, $I > 2\sigma(I)$) = 0.0514, wR_2(all data) = 0.1378, 1554 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 151.62°], 224 restrains, 192 parameters, GOF = 1.051 and residual electron density (e Å^{-3}) = 0.670/−0.391.

***Additional details for* K[BAr^F$_4$] (3)**: This compound crystallized in the tetragonal space group *P*4/*n*. One trifluoromethyl group from the asymmetric unit was modelled as disordered over a rotation operation, whereas the other was modelled as positional disordered. The symmetry operations used to generate the atoms labelled with ’ and ” in Figure 3 (manuscript) are x-1/2,-y+1,-z+2 and -x+3/2,-y+1/2,z+1/2.

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