Supporting Information

Using Microcrystal Electron Diffraction, via-On Grid Solid/Gas Single-Crystal to Single-Crystal Reactivity, to Characterize a Robust σ-Alkane Complex.

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S.1 EXPERIMENTAL DETAILS

All manipulations (unless stated otherwise) were performed under an argon atmosphere, using standard Schlenk techniques on a dual vacuum/argon manifold or by using an argon filled glovebox (MBraun). Glassware was flame dried under vacuum prior to use. Pentane and dichloromethane (CH_2Cl_2) were dried using an Innovative Technology Pure-Solv™ (PS-400-3) solvent purification system and degassed by freeze-pump-thaw cycles. Deuterated solvents were dried using an appropriate drying agent: dichloromethane-d_2 (CD_2Cl_2) with CaH_2; acetonitrile-d_3 (MeCN-d_3) with 3 Å molecular sieves. After drying, these solvents were degassed by freeze-pump-thaw cycles and then stored over 3 Å molecular sieves. Hydrogen (H_2) and deuterium (D_2) gases were purchased in lecture bottles from Sigma-Aldrich and used as received. $[Rh(Cy_2P(CH_2)_2PCy_2)Cl]_2$ was prepared by a previously reported method.[1] All other chemicals were purchased from commercial vendors and used as received.

Solution NMR data were collected on either a Bruker AVIIIHD 500 MHz or 600 MHz spectrometer at 298 K unless otherwise started. Residual protio solvent resonances were used as a reference for ^{1}H NMR spectra.[2] $^{31}P\{^1H\}$ NMR spectra were referenced externally to 85 % H_3PO_4 (D_2O). All chemical shifts (δ) are quoted in ppm and coupling constants in Hz.

Solid state NMR (SSNMR) samples were prepared by packing powdered microcrystalline samples into a 4 mm zirconia solid state rotor inside an argon filled glove box. SSNMR spectra were obtained on a Bruker AVIIIHD 400 spectrometer, with a magic-angle spinning (MAS) rate of 10 kHz, referenced externally to triphenylphosphine (^{31}P: δ = –9.3) or adamantane ($^{13}C\{^1H\}$: upfield methine resonance, δ 29.5).[3]

Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) measurements were performed in a thermal analyser (Netzsch STA 449 F5 Jupiter®) using an alumina crucible. The samples were heated up to 1000 °C at a ramp rate of 10 °C min^{-1} under an atmosphere of He flowing at 20 mL min^{-1}.

The powder X-ray crystallography was performed on a Panalytical Aeris X-ray diffractometer equipped with a 600 W copper source and a PIXcel1D-Medipix3 detector. The instrument was operated in transmission mode with the sample in a 0.6mm OD borosilicate capillary.

Elemental microanalyses were carried out by Dr Graeme McAllister at the University of York using an Exeter Analytical CE-440 analyser.

S.2 SYNTHETIC PROCEDURES

S.2.1 Synthesis of [1-NBD][S-BAr$^{F}_{4}$]

Under an Ar pressure (1.2 bar), a solution of $[Rh(Cy_2P(CH_2)_2PCy_2)Cl]_2$ (70 mg, 0.062 mmol) in CH_2Cl_2 (5 mL) was quickly added to an ampoule containing a solution of $[Bu_4N][S\text{-}BArF_4]$ (188 mg, 0.120 mmol) and NBD (50 µL, 0.492 mmol) dissolved in refluxing CH_2Cl_2 (5 mL, 40 °C, 1.2 bar). After mixing, the solution was then filtered into a clean ampoule using a cannular adapted with a PTFE-wrapped glass microfiber filter pad. Bright orange microcrystals of **[1-NBD][S-BAr$^{F}_{4}$]** began forming almost immediately and the mixture was left at room temperature for a further 15 h. The supernatant was then decanted from the crystals, which were washed with additional CH_2Cl_2 (3 x 5 mL) and pentane (3 x 5 mL), then dried *in vacuo* at 10^{-3} mbar for at least 15 h. Larger crystals that were suitable for XRD measurements were obtained by keeping the above filtrate at 40 °C during crystal growth. Yield: 197 mg (0.101 mmol, 85 %).

Elemental analysis found (calculated): C 35.34 (35.19), H 3.58 (3.52).

$^{31}P\{^{1}H\}$ SSNMR (162 MHz, 10 kHz spin rate, 290 K): δ 75.67 (d, $J_{Rh\text{-}P} \approx 130$ Hz).

$^{13}C\{^{1}H\}$ SSNMR (101 MHz, 10 kHz spin rate, 290 K): δ 162.07-164.40 (br m, S-BAr$^{F}_{4}$), 155.40 (s, S-BAr$^{F}_{4}$), 154.85 (s, S-BAr$^{F}_{4}$), 135.62 (s, S-BAr$^{F}_{4}$), 133.77 (s, S-BAr$^{F}_{4}$), 121.07 (s, S-BAr$^{F}_{4}$), 91.16 (s, NBD, alkene-CH), 84.09 (s, NBD, alkene-CH), 69.48 (s, NBD, CH2 bridge), 56.28 (s, NBD, bridgehead), 39.17, 36.23, 32.67, 29.65, 28.81, 27.54, 27.01, 26.56, 23.55 (multiple overlapping aliphatic resonances).

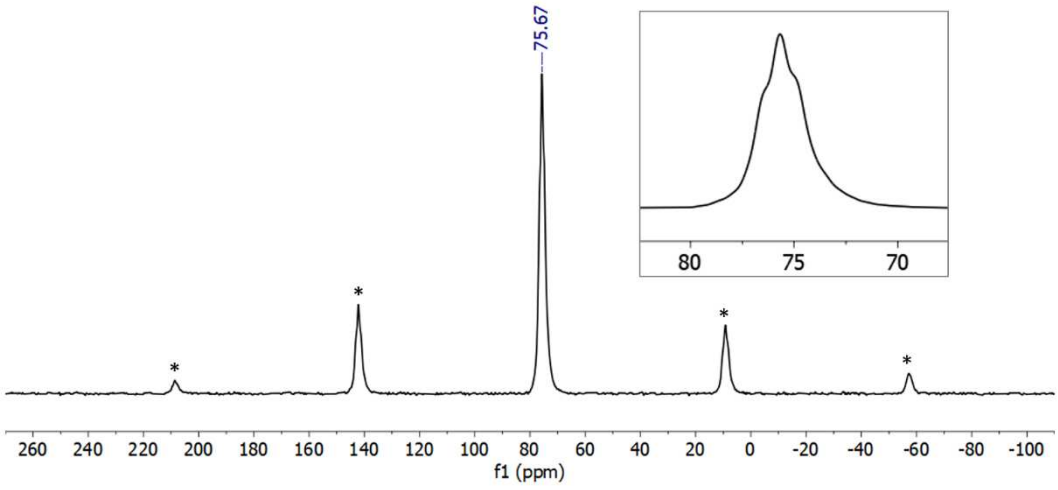


Figure S1. $^{31}P\{^{1}H\}$ SSNMR spectrum of **[1-NBD][S-BAr$^{F}_{4}$]**. Recorded at 290 K and a MAS rate of 10 KHz; * denotes spinning sidebands.

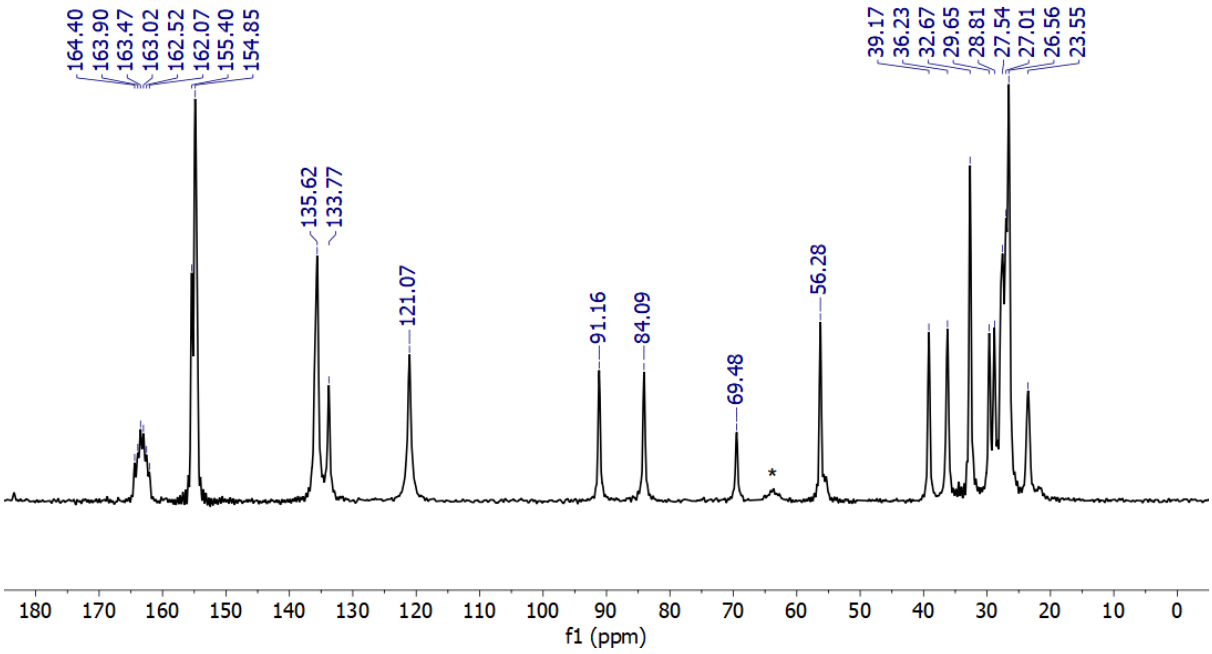


Figure S2. $^{13}C\{^{1}H\}$ SSNMR spectrum of **[1-NBD][S-BAr$^{F}_{4}$]**. Recorded at 290 K and a MAS rate of 10 KHz; * denotes a spinning sideband.

S.2.2 Synthesis of [1-NBA][S-BAr$^{F}_{4}$]

A microcrystalline sample of **[1-NBD][S-BAr$^{F}_{4}$]** (78 mg, 0.04 mmol) was hydrogenated with H_2 (20 PSI) for 30 min, resulting in quantitative conversion to reddish orange **[1-NBA][S-BAr$^{F}_{4}$]**.

Elemental analysis found (calculated): C 34.71 (35.12), H 3.90 (3.72).

$^{31}P\{^{1}H\}$ SSNMR (162 MHz, 10 kHz spin rate, 293 K): δ 110.05 (two overlapping d, $J_{Rh\text{-}P}$ = 196 Hz). 185 K: δ 110.98 (d, $J_{Rh\text{-}P}$ = 194 Hz), 107.42 (d, $J_{Rh\text{-}P}$ = 201 Hz).

$^{13}C\{^{1}H\}$ SSNMR (101 MHz, 10 kHz spin rate, 293 K): δ 163.27 (br m, S-BAr$^{F}_{4}$), 155.37 (s, S-BAr$^{F}_{4}$), 154.78 (s, S-BAr$^{F}_{4}$), 135.53 (s, S-BAr$^{F}_{4}$), 134.00 (s, S-BAr$^{F}_{4}$), 121.30 (br s, S-BAr$^{F}_{4}$), 44.51, 40.65, 37.34, 33.14, 32.23, 31.15, 27.09, 21.62 (multiple overlapping aliphatic resonances). 185 K: δ 162.56 (br m, S-BAr$^{F}_{4}$), 154.92 (s, S-BAr$^{F}_{4}$), 154.11 (s, S-BAr$^{F}_{4}$), 134.67 (br m, S-BAr$^{F}_{4}$), 121.29 (s, S-BAr$^{F}_{4}$), 120.49 (s, S-BAr$^{F}_{4}$), 44.86, 41.05, 39.81, 37.28, 36.13, 33.34, 28.97, 28.09, 27.13, 26.28, 21.88, 20.98 (multiple overlapping aliphatic resonances).

Powder XRD (298 K): a = 19.597(4) Å, b = 19.302(3) Å, c = 20.467(3) Å, α = 90°, β = 91.792(3)°, γ = 90°, volume = 7738 Å^3.

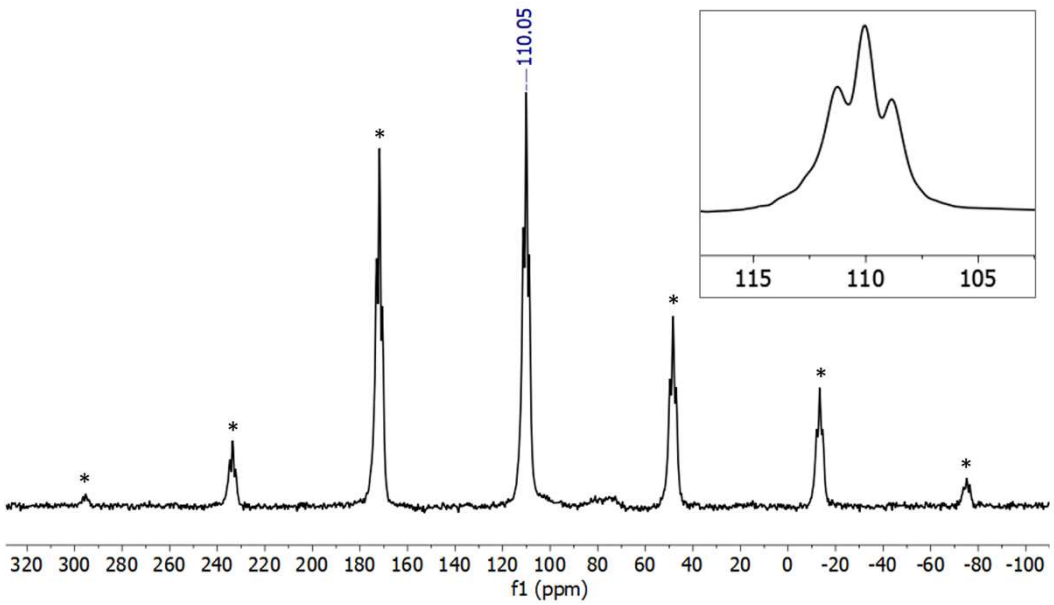


Figure S3. $^{31}P\{^{1}H\}$ SSNMR spectrum of **[1-NBA][S-BAr$^{F}_{4}$]**. Recorded at 293 K and a MAS rate of 10 KHz; * denotes spinning sidebands.

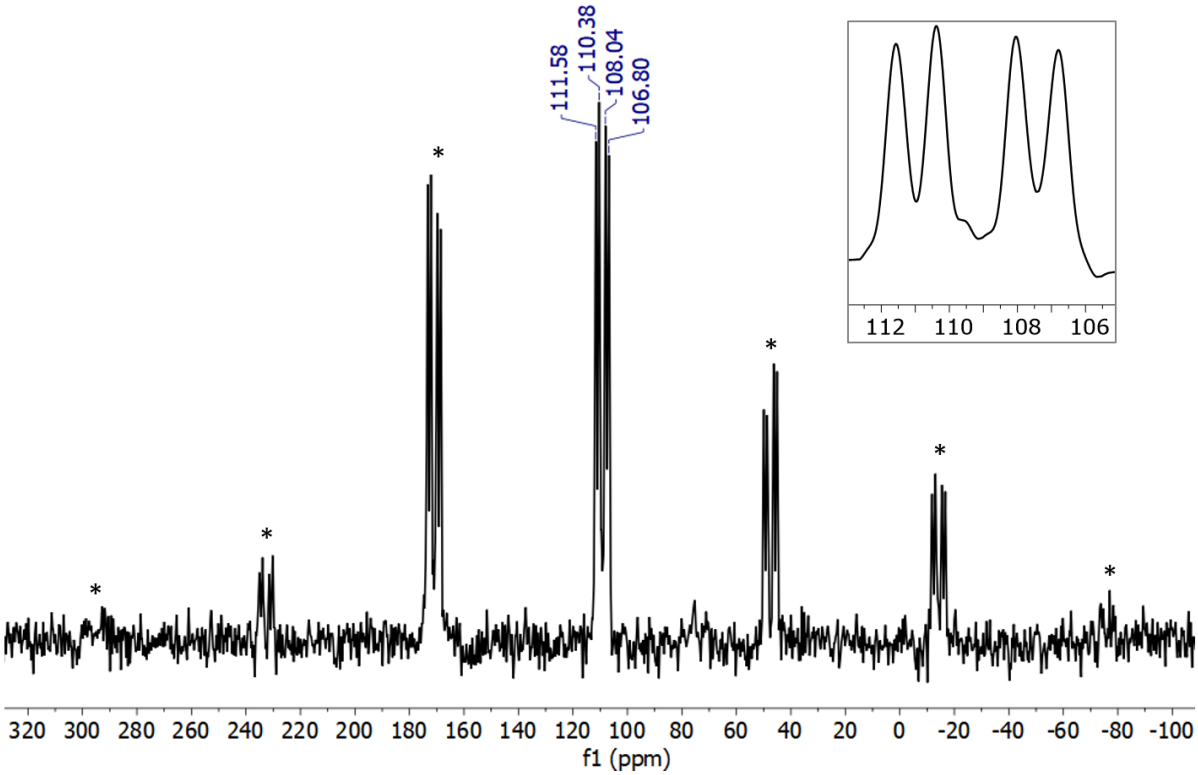


Figure S4. $^{31}P\{^{1}H\}$ SSNMR spectrum of **[1-NBA][S-BAr$^{F}_{4}$]**. Recorded at 185 K and a MAS rate of 10 KHz; * denotes spinning sidebands.

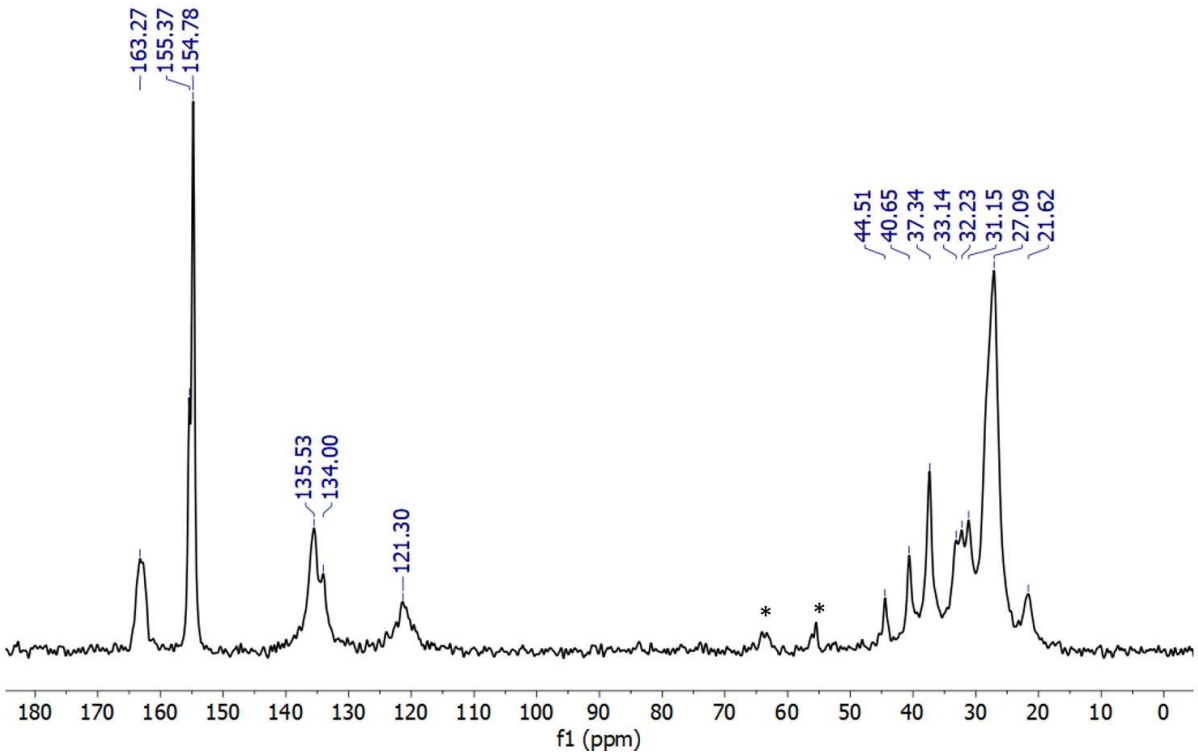


Figure S5. $^{13}C\{^{1}H\}$ SSNMR spectrum of **[1-NBA][S-BAr$^{F}_{4}$]**. Recorded at 293 K and a MAS rate of 10 KHz; * denotes spinning sidebands.

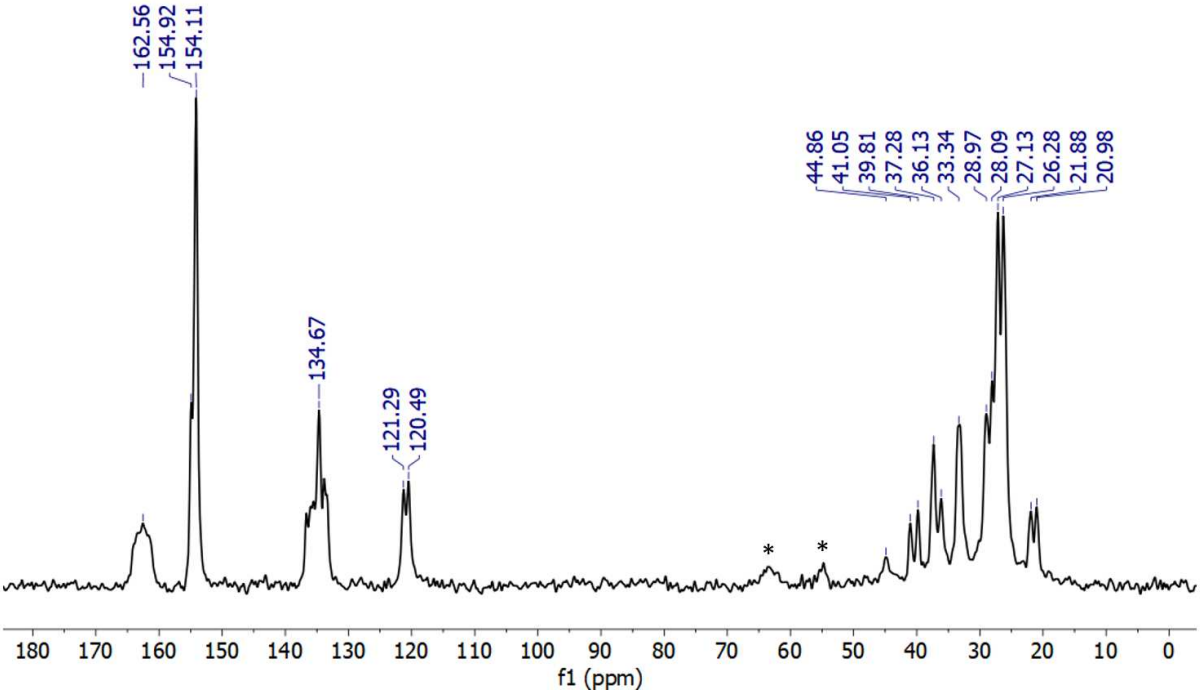


Figure S6. $^{13}C\{^{1}H\}$ SSNMR spectrum of **[1-NBA][S-BAr$^{F}_{4}$]**. Recorded at 185 K and a MAS rate of 10 KHz; * denotes spinning sidebands.

S.2.3 Synthesis of endo-d_4-[1-NBA][S-BAr$^F_4$], exo-d_4-[1-NBA][S-BAr$^F_4$], and d_8-[1-NBA][S-BAr$^F_4$]

Microcrystalline samples of **[1-NBD][S-BAr$^F_4$]** (9.7 mg, 0.005 mmol) were hydrogenated with either H_2 or D_2 (20 PSI) in one or two stages as follows. **[1-NBA][S-BAr$^F_4$]** or **endo-d_4-[1-NBA][S-BAr$^F_4$]** are formed with one, 3 min hydrogenation with H_2 or D_2, respectively (Figure S7). These species undergo H/D exchange with additional D_2 exposure over 20 hr to form **exo-d_4-[1-NBA][S-BAr$^F_4$]** and **d_8-[1-NBA][S-BAr$^F_4$]**, respectively.

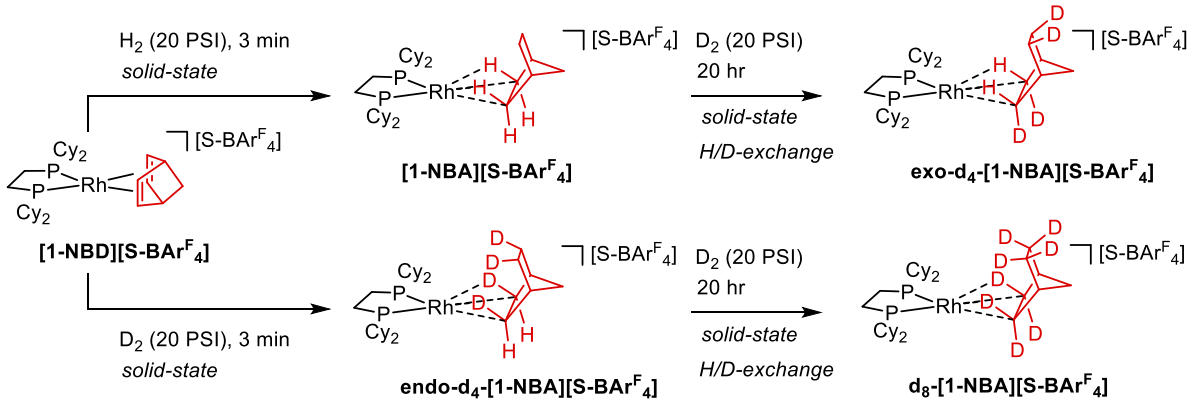


Figure S7. Syntheses of of **d_x-[1-NBA][S-BAr$^F_4$]** (x=0, 4, 8).

Volatile trapping of displaced d_x-NBA

Microcrystalline samples (0.005 mmol) of **d_x-[1-NBA][S-BAr$^F_4$]** were treated with CD_2Cl_2 (0.5 mL) and MeCN-d_3 (10.6 µL, 40 eq.), immediately resulting in a yellow solution, from which a yellow solid precipitated. The volatiles containing liberated d_x-NBA were vacuum transferred to an empty NMR tube, then sealed under an Ar atmosphere for subsequent NMR analysis.

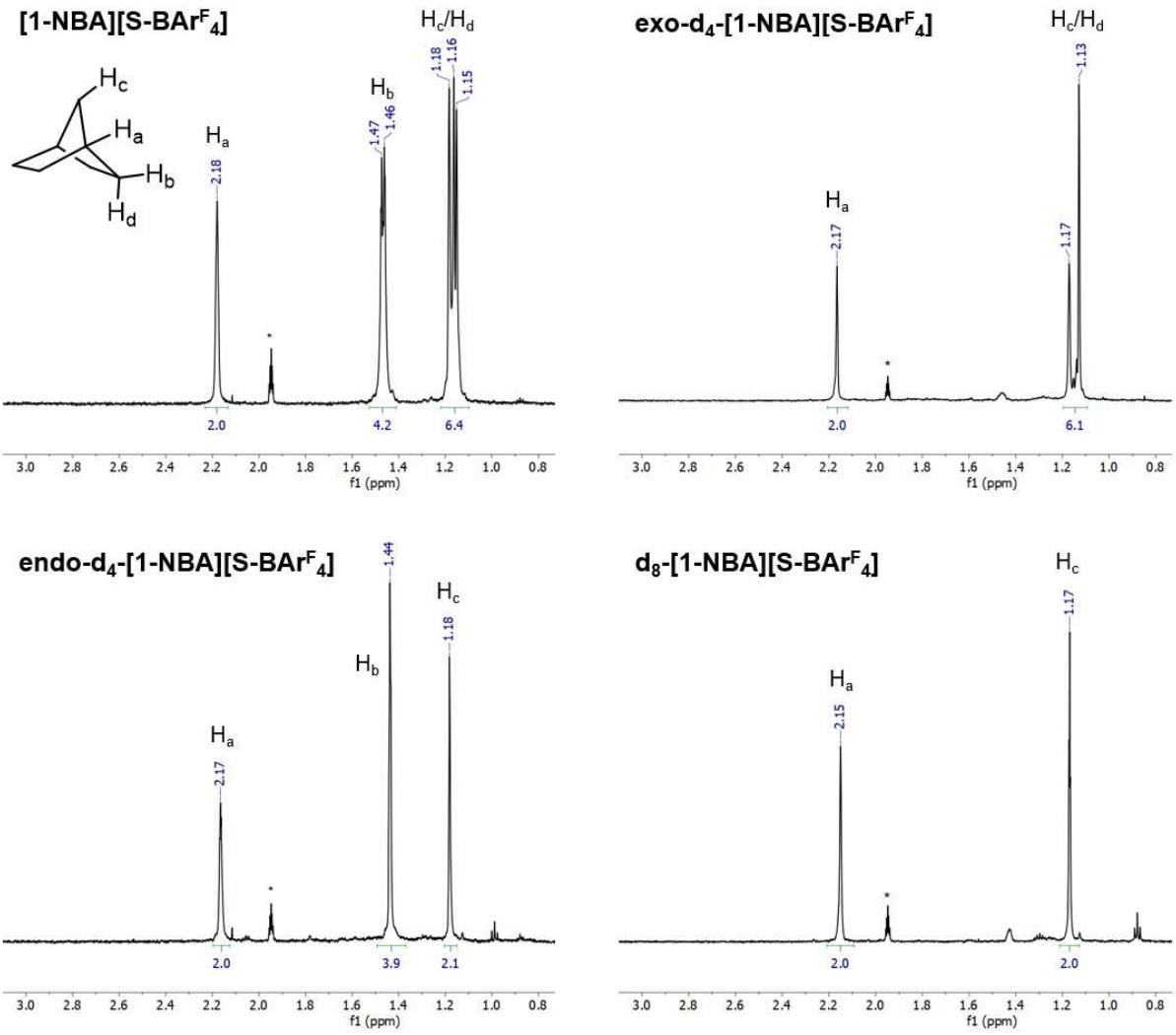


Figure S8. ^{1}H NMR spectra of **d_x-NBA** liberated from **d_x-[1-NBA][S-BAr$^F_4$]** by dissolution in MeCN-d_3 (10.6 µL) and CD_2Cl_2 (0.5 mL) followed by vacuum distillation.

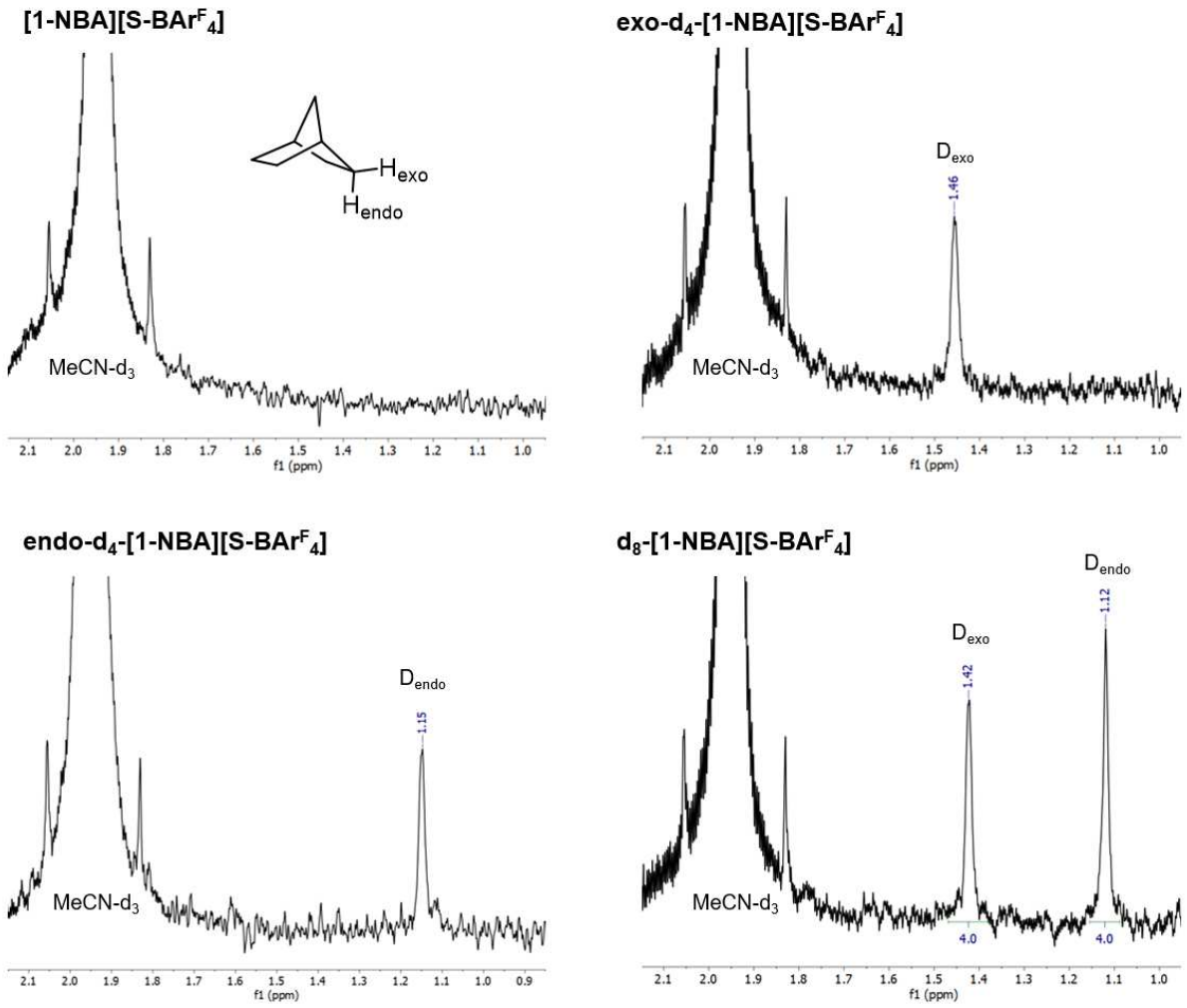


Figure S9. $^{2}H\{^{1}H\}$ NMR spectra of **d_x-NBA** liberated from **d_x-[1-NBA][S-BAr$^F_4$]** by dissolution in MeCN-d_3 (10.6 µL) and CD_2Cl_2 (0.5 mL) followed by vacuum distillation.

S.2.4 Stability of [1-NBA][S-BAr$^F_4$] and [1-NBA][BAr$^F_4$] in pentane

Separately, ground samples of **[1-NBD][S-BAr$^F_4$]** (60 mg, 0.031 mmol) and **[1-NBD][BAr$^F_4$]** (60 mg, 0.041 mmol) were hydrogenated with H_2 (20 PSI) for 30 min to form **[1-NBA][S-BAr$^F_4$]** and **[1-NBA][BAr$^F_4$]**, respectively. Within an Ar glovebox, these were dissolved in Ar-saturated pentane (1 mL) and stirred for 2 hrs. **[1-NBA][S-BAr$^F_4$]** remained as a fine suspension throughout, whereas **[1-NBA][BAr$^F_4$]** formed an orange oil at the solid-liquid interface, which initially prevented stirring; after physically dislodging the stuck stirrer bar, the stirred mixture formed a fine suspension of pale yellow **1-BAr$^F_4$** within 2 hrs. After removing all volatiles in vacuo (0.01 mbar), the remaining solids were analysed by $^{31}P\{^{1}H\}$ SSNMR.

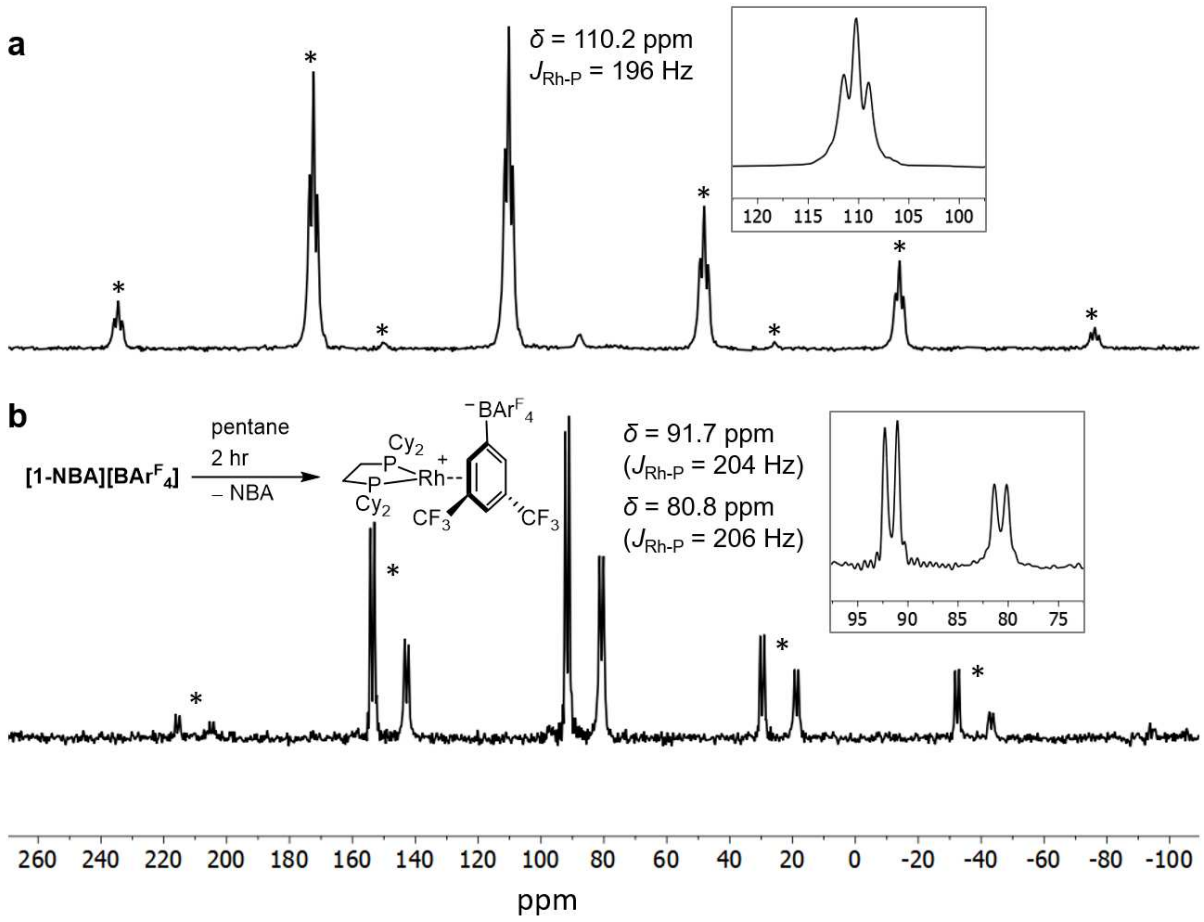


Figure S10. $^{31}P\{^{1}H\}$ SSNMR spectra of (a) **[1-NBA][S-BAr$^{F}_{4}$]** and (b) **[1-NBA][BAr$^{F}_{4}$]** after stirring in pentane for 2 hr. Recorded at 290 K and a MAS rate of 10 KHz; * denotes spinning sidebands.

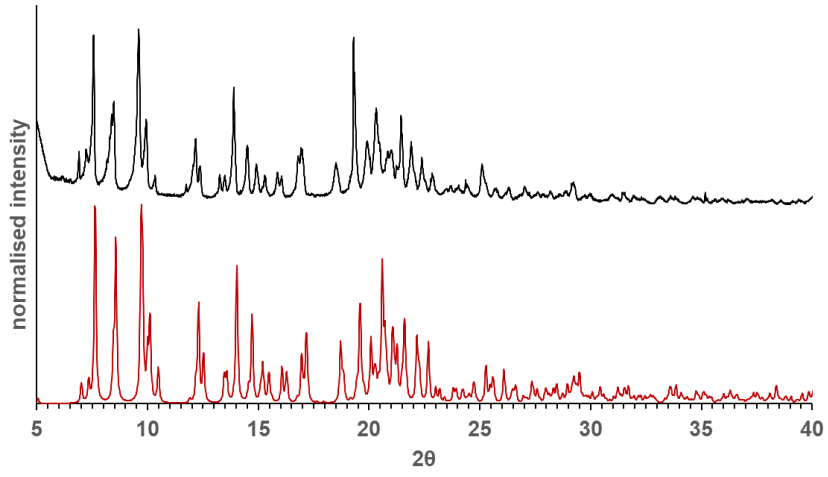


Figure S11. Powder diffraction pattern of **1-BAr$^{F}_{4}$** measured at 298 K (top, black) versus simulated diffraction pattern (bottom, red) generated using single crystal data for this complex measured at 150 K (CCDC no. 1022727).[2]

S.2.5 Solid-gas synthesis of [1-(ethene)$_2$][S-BAr$^F{}_4$]

In a ca 15 cm^3 Rotaflo® ampoule, a microcrystalline sample of **[1-NBD][S-BAr$^F{}_4$]** (78 mg, 0.04 mmol) was hydrogenated with H_2 (1.4 bar) for 30 min to form reddish orange **[1-NBA][S-BAr$^F{}_4$]**. The H_2 headspace was removed in vacuo (0.01 mbar) then replaced with ethene (4 bar) and left sealed for 24 hr to form orange **[1-(ethene)$_2$][S-BAr$^F{}_4$]**. The $^{31}P\{^1H\}$ SSNMR shows impurities that likely correspond to the butene and butadiene complexes, and are similar to those observed previously in the solid-gas synthesis of **[1-(ethene)$_2$][BAr$^F{}_4$]**, reported previously.[3]

$^{31}P\{^1H\}$ SSNMR (162 MHz, 10 kHz spin rate, 298 K): δ 75.57 (br s, fwhm ≈ 530 Hz).

$^{13}C\{^1H\}$ SSNMR (101 MHz, 10 kHz spin rate, 298 K): δ 163.48 (br s, S-BAr$^F{}_4$), 155.35 (s, S-BAr$^F{}_4$), 135.60 (s, S-BAr$^F{}_4$), 121.12 (s, S-BAr$^F{}_4$), 84.36 (br s, C_2H_4), 47.53 (s, S-BAr$^F{}_4$), 40.75, 39.80, 37.87, 32.37, 31.21, 28.10, 27.07, 23.15 (multiple overlapping aliphatic resonances). 198 K: 163.06 (br s, S-BAr$^F{}_4$), 154.81 (s, S-BAr$^F{}_4$), 135.45 (s, S-BAr$^F{}_4$), 121.01 (s, S-BAr$^F{}_4$), 83.86 (br s, C_2H_4), 47.20 (s, S-BAr$^F{}_4$), 39.59, 37.84, 37.17, 31.09, 27.77, 27.02, 19.22, 16.71 (multiple overlapping aliphatic resonances).

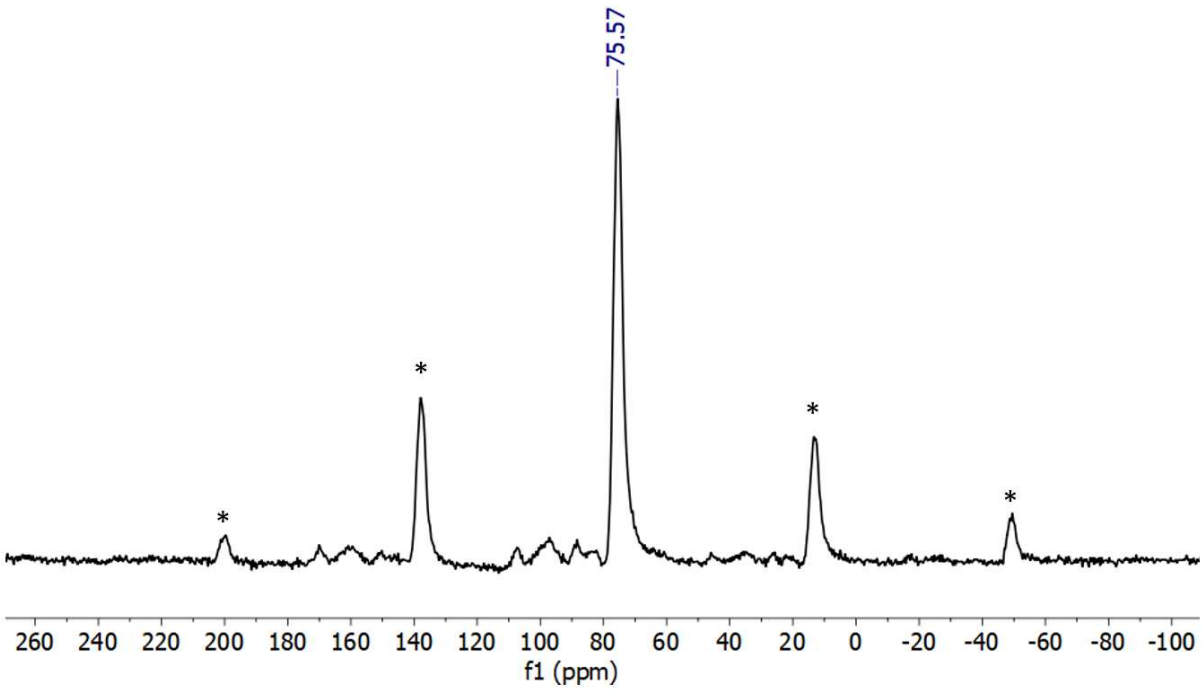


Figure S12. $^{31}P\{^1H\}$ SSNMR spectrum of **[1-(ethene)$_2$][S-BAr$^F{}_4$]** synthesised by the solid-gas method. Recorded at 298 K and a MAS rate of 10 KHz; * denotes spinning sidebands for the major resonance at 75.57 ppm.

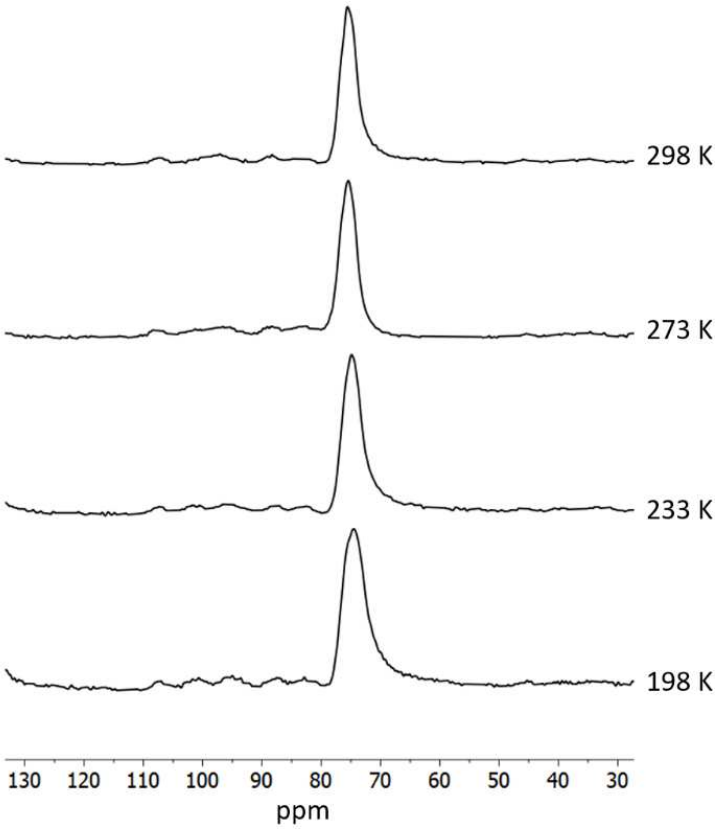


Figure S13. $^{31}P\{^{1}H\}$ VT-SSNMR spectra of **[1-(ethene)$_2$][S-BAr$^F_4$]** synthesised by the solid-gas method. Recorded at 298-198 K and a MAS rate of 10 KHz.

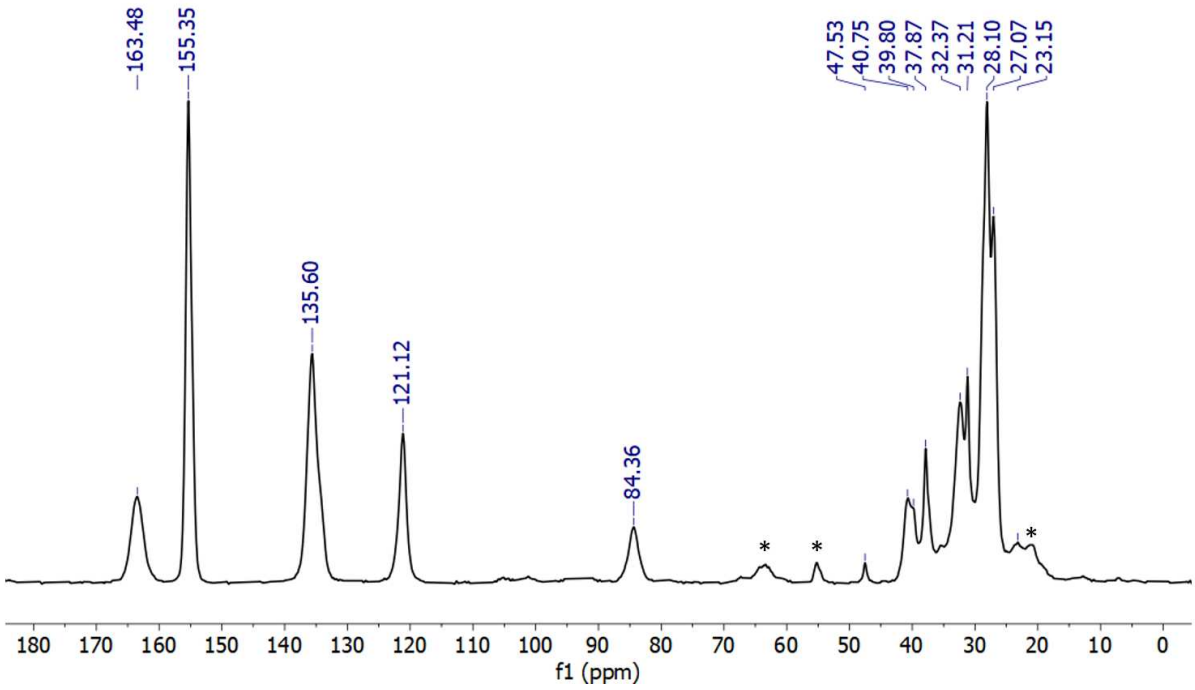


Figure S14. $^{13}C\{^{1}H\}$ SSNMR spectrum of **[1-NBA][S-BAr$^F_4$]** synthesised by the solid-gas method. Recorded at 298 K and a MAS rate of 10 KHz; * denotes spinning sidebands.

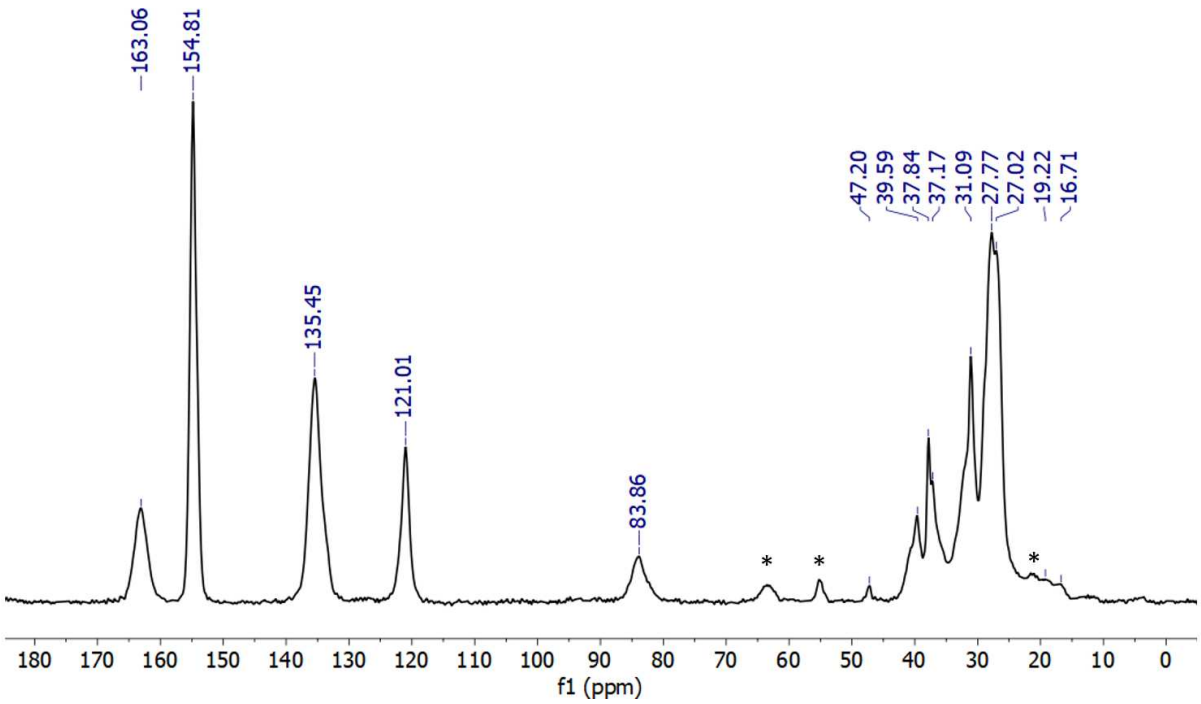


Figure S15. $^{13}C\{^{1}H\}$ SSNMR spectrum of **[1-NBA][S-BAr$^{F}_{4}$]** synthesised by the solid-gas method. Recorded at 198 K and a MAS rate of 10 KHz; * denotes spinning sidebands.

S.2.6 Synthesis of [1-(ethene)$_2$][S-BAr$^{F}_{4}$] in pentane suspension

A microcrystalline sample of **[1-NBD][S-BAr$^{F}_{4}$]** (60 mg, 0.031 mmol) was suspended in pentane (1 mL) in a 10 cm^3 ampoule with a J. Young valve and fitted with a magnetic stirrer bar. After three freeze-pump-thaw degassing cycles, the ampoule was placed under a H_2 (20 PSI) atmosphere and the mixture was stirred for 30 min, forming a suspension of reddish orange **[1-NBA][S-BAr$^{F}_{4}$]**. After three freeze-pump-thaw degassing cycles, the ampoule was recharged and sealed under an atmosphere of ethene (20 PSI). After stirring for 20 hr, a 0.5 mL aliquot was taken (see below), then all volatiles were removed in vacuo (0.01 mbar, 30 min) to isolate **[1-(ethene)$_2$][S-BAr$^{F}_{4}$]** as an orange solid.

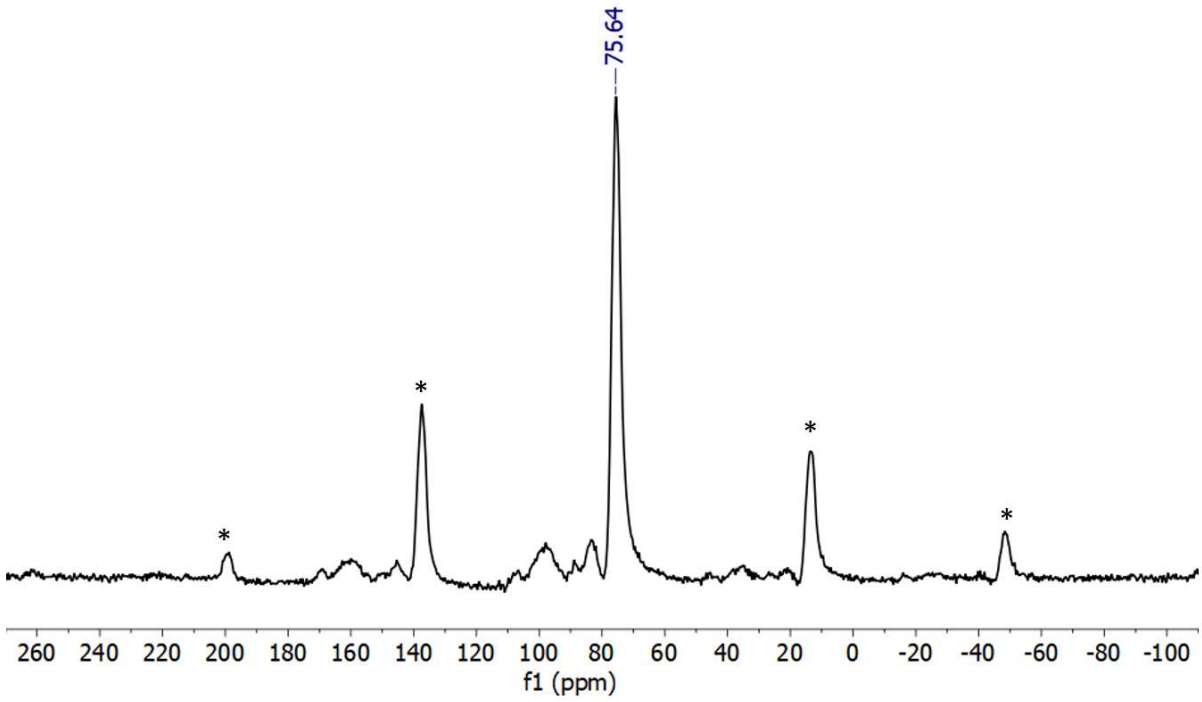


Figure S16. $^{31}P\{^{1}H\}$ SSNMR spectrum of **[1-(ethene)$_2$][S-BAr$^F_4$]** synthesised by the pentane slurry method. Recorded at 298 K and a MAS rate of 10 KHz; * denotes spinning sidebands for the major resonance at 75.64 ppm.

S.2.7 Ethene coupling to 2-butene catalysed by [1-NBA][S-BAr$^F_4$] in pentane suspension

Experiment 1: A microcrystalline sample of **[1-NBD][S-BAr$^F_4$]** (15 mg, 0.0077 mmol) was weighed into a 10 cm^3 J. Young ampoule fitted with a magnetic stirrer bar. The sample was hydrogenated with H_2 (20 PSI, 10 min) to form **[1-NBA][S-BAr$^F_4$]**, then suspended in pentane (1 mL). After three freeze-pump-thaw degassing cycles, the ampoule was charged and sealed under an atmosphere of ethene (20 PSI, ~9 cm^3, ~66 eq. per Rh) and stirred at 500 rpm. After 20 hr, an internal reference, adamantane (15 mg, 0.11 mmol), was added to the mixture, which was then filtered through a 0.2 µm pore PTFE syringe filter into a J. Young NMR tube. ^{1}H NMR analysis of this pentane solution, integrated relative to the adamantane reference, revealed liberated NBA, 2-butenes, 1-butene and unreacted ethene (Table 1). The ampoule containing the remaining solids was subsequently recharged with pentane (1 mL) and ethene (20 PSI) as before. The mixture was stirred for a further 20 hr, then quantified once more by ^{1}H NMR, relative to additional adamantane. To examine whether any trace, unobservable but active, soluble species were present, the filtered solution taken after the first 20 hr was recharged with ethene, stirred for 20 hr, then reanalysed by ^{1}H NMR: no additional 2-butenes or 1-butene had formed over this time. The analogous reaction with **[1-NBA][BAr$^F_4$]** yielded less than 0.1 equivalents of 2-butene per Rh.

Table 1. [1-NBA][S-BAr$^F_4$] catalysed ethene coupling in pentane suspension: quantification by ^{1}H NMR.

	1st cycle (20 hr)	2nd cycle (+20 hr)	Total (40 hr)
NBA (eq. per Rh)	0.93	0.07	1.0
2-butenes (eq. per Rh)	6.9	7.4	14.3
1-butene (eq. per Rh)	0.21	0.21	0.42

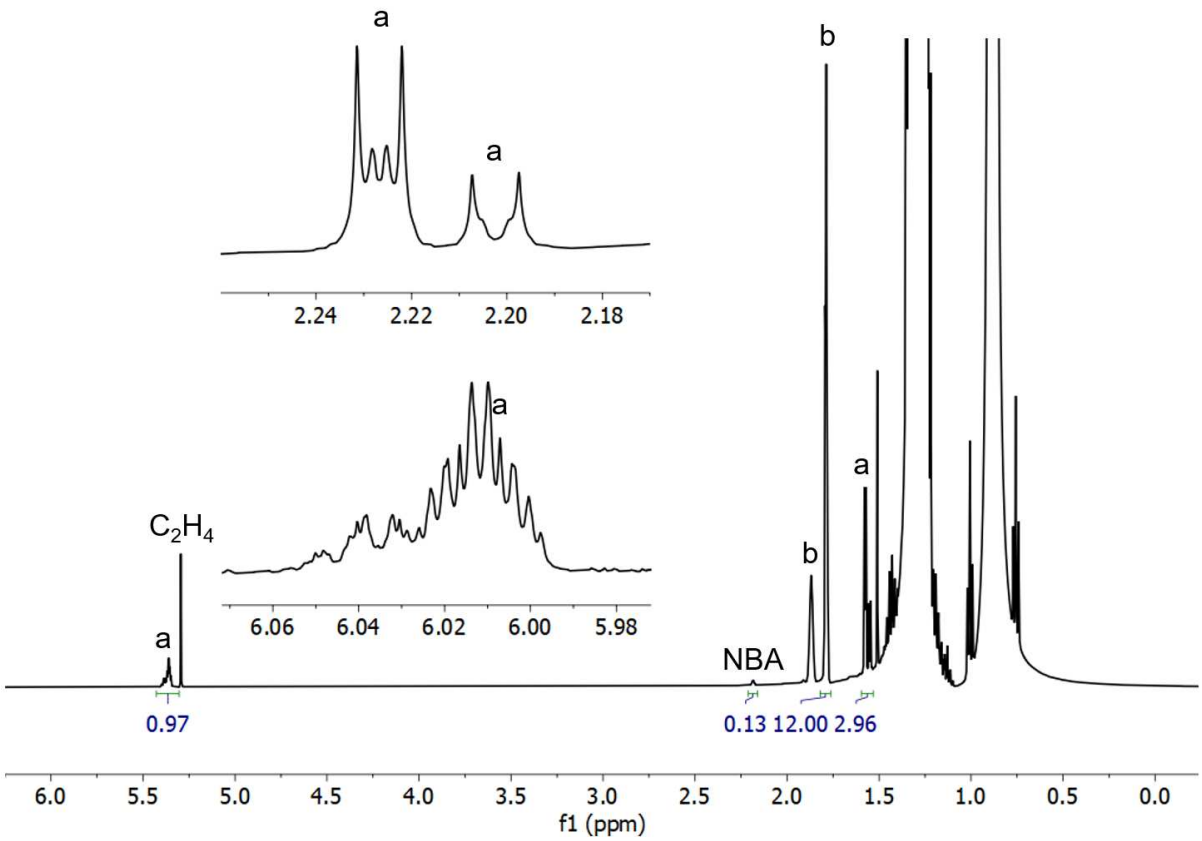


Figure S17. Exemplar ^{1}H NMR spectrum of the reaction of ethene with a pentane suspension of **[1-NBA][S-BAr$^F_4$]**, extracted after the first 20 hr cycle; a = 2-butenes, b = adamantane reference.

Experiment 2: The above synthesis of **[1-(ethene)$_2$][S-BAr$^F_4$]** from **[1-NBD][S-BAr$^F_4$]** (60 mg, 0.031 mmol) via **[1-NBA][S-BAr$^F_4$]** in a pentane suspension was conducted primarily to assess the solid reaction product by SS NMR analysis, however, the mixture was also assessed for 2-butenes and 1-butene by ^{1}H NMR analysis of the pentane supernatant, using the quantitatively displaced NBA (1 eq. per Rh) as an internal reference. After 20 hr, a 0.5 mL aliquot was removed prior to isolation of the solids for SS NMR characterisation (Table 2). The solids – predominantly **[1-(ethene)$_2$][S-BAr$^F_4$]** – were resuspended in pentane (1 mL), after

which the ampoule headspace was recharged with ethene (20 PSI). After stirring for a further 20 hr, a second aliquot was taken (total: 2 cycles, 40 hr).

Table 2. [1-NBA][S-BAr$^F_4$] (formed in situ) catalysed ethene coupling in pentane suspension: quantification by ^{1}H NMR.

	Aliquot 1 (20 hr)	**Aliquot 2 (+20 hr)**	**Total (40 hr)**
2-butenes (eq. per Rh)	7.5	7.2	14.7
1-butene (eq. per Rh)	0.2	0.2	0.4

S.2.8 1-butene isomerisation catalysed by [1-NBA][S-BAr$^F_4$] in pentane suspension

The method described in Experiment 1 above was repeated using a 15 cm^3 J. Young ampoule and 1-butene (20 PSI, 14 cm^3, ~100 eq.) instead of ethene. An aliquot taken after 20 hr was analysed by quantitative ^{1}H NMR (versus an internal adamantane reference), which found 2-butenes (~98 eq. per Rh) and 1-butene (~2 eq. per Rh).

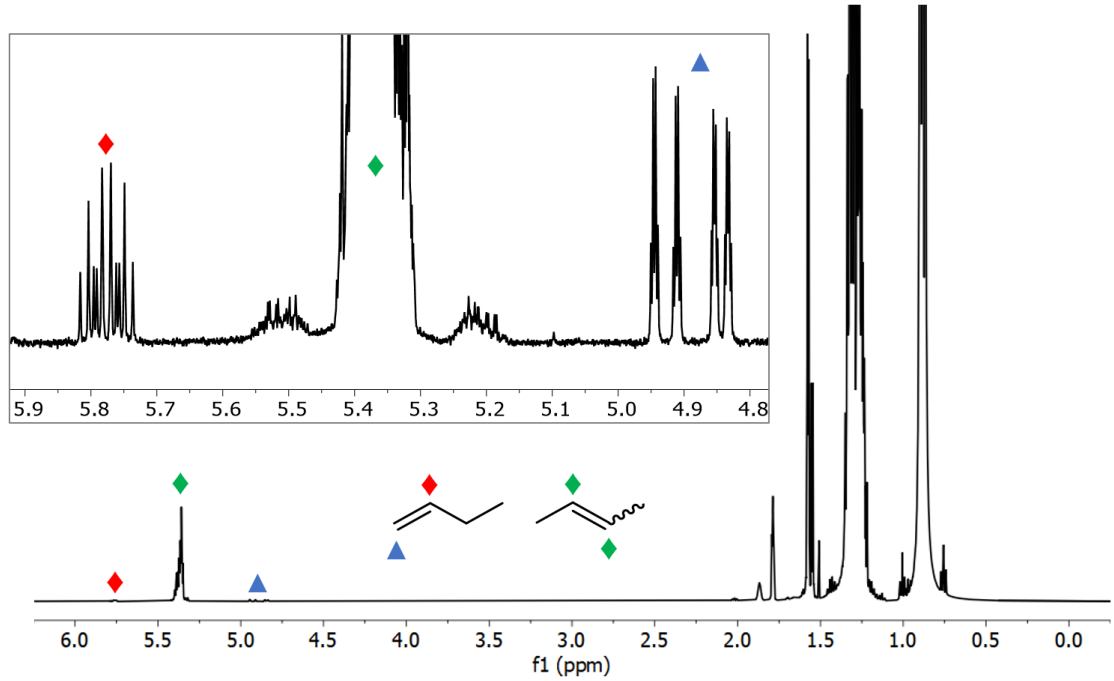


Figure S18. ^{1}H NMR spectrum of the reaction of 1-butene with a pentane suspension of **[1-NBA][S-BAr$^F_4$]**, recorded after 20 hr.

S.3 CRYSTALLOGRAPHIC AND REFINEMENT DATA

Selected crystallographic data are summarized in the text and full details are given in the supplementary deposited CIF files. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Electron diffraction data are also available from Zenodo (doi:10.5281/zenodo.5760938).

S.3.1 Single-crystal X-ray diffraction methods

Single-crystal X-ray diffraction data for **[1-NBD][S-BAr$^{F}_{4}$]**, **[1-NBA][S-BAr$^{F}_{4}$]**, and **[1-(ethene)$_2$][S-BAr$^{F}_{4}$]** were collected on an Oxford Diffraction SuperNova diffractometer with Cu-*Kα* (λ = 1.54184 Å) radiation equipped with a nitrogen gas Oxford Instruments Cryojet cooler. Raw frame data was reduced using CrysAlisPro, solved using Superflip[4], and refined using full-matrix least squares refinement on all F^2 data using SHELXL-18[5] within the OLEX2 program.[6] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were geometrically placed unless otherwise stated and allowed to ride on their parent atoms. Distances and angles were calculated using the full covariance matrix.

S.3.2 MicroED methods

Micro-crystalline **[1-NBD][S-BAr$^{F}_{4}$]** was finely ground and deposited onto Quantifoil Cu R1/4 grids that had been assembled into autogrid cartridges. These grids were then treated with H_2 (1.3 atm for 5 minutes) then placed into a grid box and transported to the microscope under an Ar atmosphere. The grids were then transferred to the cassette under a blanket of N_2 vapour and conductively cooled to liquid nitrogen temperature before loading into the TEM.

MicroED data were collected using a Thermo Fisher Glacios microscope operated at 200 kV and equipped with a Ceta-D camera. A low flux of of ~0.01 $e^{-}Å^{-2}\,s^{-1}$ was achieved using the following illumination conditions: gun lens 4, spot size 11, 30 µm C2 aperture. This resulted in an illuminated area of 4 µm. Crystals were isolated using a 40 µm selected area aperture (1.4 µm on the sample plane). Data were acquired using EPU-D with the following settings: 2x binning, a rotation speed of 0.5°/s and an exposure time of 2 s. For **[1-NBD][S-BAr$^{F}_{4}$]** datasets were collected from 28 crystals over a rotation range of 60-90° between minimum and maximum tilt angles of -45°/+55°. **[1-NBA][S-BAr$^{F}_{4}$]** crystals were highly radiation sensitive and it was only possible to collect 20-30° of data before visible loss of diffraction quality occurred. Over the course of this work 111 datasets were collected from this sample but the

highest quality data were recorded from 29 crystals across 2 duplicate grids from the same microscope session.

All data were processed using DIALS[7]. The images recorded on Ceta-D camera show mean negative background values at high resolution which hampers background modelling so a pedestal of 64 ADU was added to every pixel value. Initially the detector distance was fixed to 958.5 mm (determined using powder diffraction from an aluminium powder calibration grid). For **[1-NBD][S-BAr$^{F}_{4}$]**, 4 datasets from 4 crystals were combined to give 96.6% complete data to 0.95Å resolution. For **[1-NBA][S-BAr$^{F}_{4}$]**, 9 datasets from 9 crystals could be combined resulting in 94.0% complete data to 0.95Å resolution. The strong reflections from each of the combined datasets were used to post-refine the detector distance and unit cell parameters of each dataset. The mean refined detector distances for both datasets (**[1-NBD][S-BAr$^{F}_{4}$]**: 956.87(22) mm, **[1-NBA][S-BAr$^{F}_{4}$]:** 958.33(24) were within 0.2% of the initial estimate. The unit cell parameters for each of the combined datasets were then refined by fitting calculated to observed 2θ values.

The structures were solved *ab initio* using SHELXT.[8] Structure refinement was performed using SHELXL.[5] Electron scattering factors from Peng[9] were used in refinement. Anisotropic ADPs were refined for all non-hydrogen atoms and all hydrogen atoms were geometrically placed using the idealised (inter-nuclear) X-H distances used in refinement of structures against neutron diffraction data with SHELXL[10] and allowed to ride on their parent atoms. For **[1-NBA][S-BAr$^{F}_{4}$]**, the isotropic ADPs of hydrogens attached to C1, C2, C4 and C5 were set to 5x that of the attached carbon atom to reflect any uncertainty in the modelled position. S-F distances in the SF_5 groups were restrained to be equal, these were the only distance restraints applied. A combination of rigid-body restraints where the components of the ADPs in the direction of the bond are restrained to be equal (DELU instruction), thermal similarity restraints where the ADPs of spatially close atoms are restrained to have the same U(ij) components (SIMU instruction) and enhanced rigid-body restraints where the relative motion of a bonded pair of atoms is restrained to be perpendicular to the bond between them (RIGU instruction[11]) were applied to fragments of the structure. These restraints, together with refinement of an extinction parameter (EXTI instruction), enabled anisotropic refinement of all non-hydrogen atoms without resorting to use of ISOR or XNDP instructions to prevent ADPs of some atoms becoming non-positive definite during refinement.

S.3.3 [1-(NBD)][S-BAr$^F_4$]

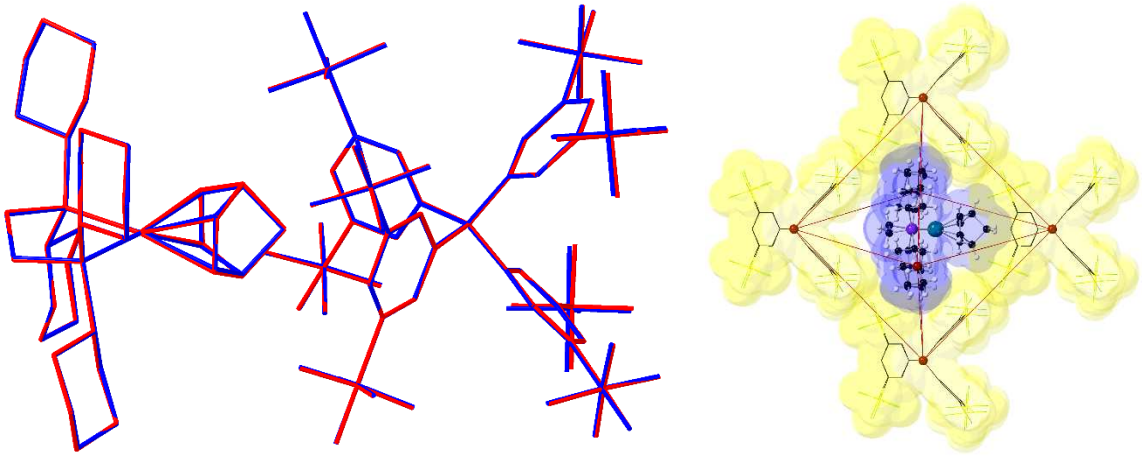


Figure S19. Left: overlay of the single-crystal X-ray (blue) and microED (red) structures of **[1-(NBD)][S-BAr$^F_4$]**. Right (X-ray): octahedral arrangement of anions around a single cation.

Table S3: Selected crystallographic and refinement data for [1-(NBD)][S-BAr$^F_4$].

Method	XRD	microED
Empirical formula	$C_{57}H_{68}BF_{40}P_2RhS_8$	$C_{57}H_{68}BF_{40}P_2S_8Rh$
Formula weight	1945.25	1945.25
Temperature/K	110(2)	80(2)
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
a/Å	19.5793(9)	19.603(3)
b/Å	18.3333(6)	18.393(3)
c/Å	20.4528(7)	20.438(2)
α/°	90	90
β/°	92.460(4)	92.355(12)
γ/°	90	90
Volume/Å^3	7334.8(5)	7362.8(18)
Z	4	4
ρ_{calc}g/cm^3	1.762	1.755
μ/mm^{-1}	5.723	-
F(000)	3912.0	1261.0

Crystal size	0.071 × 0.055 × 0.041 mm^3	microcrystals < ~1-2 μm
Radiation	Cu Kα (λ = 1.54184)	200 keV electron
Index ranges	-23 ≤ h ≤ 22, -13 ≤ k ≤ 22, -24 ≤ l ≤ 20	-20 ≤ h ≤ 20, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21
Reflections collected	13332	19560
Independent reflections	6921 [R_{int} = 0.0554, R_{sigma} = 0.0880]	4380 [R_{int} = 0.2348, R_{sigma} = 0.1680]
Data/restraints/parameters	6921/402/548	4380/585/494
Goodness-of-fit on F^2	1.025	1.718
Final R indexes [I>=2σ (I)]	R_1 = 0.0660, wR_2 = 0.1627	R_1 = 0.1565, wR_2 = 0.3421
Final R indexes [all data]	R_1 = 0.1024, wR_2 = 0.1834	R_1 = 0.2194, wR_2 = 0.3584
Largest diff. peak/hole	1.36/-1.14 e $Å^{-3}$	0.25/-0.19 e $Å^{-1}$
CCDC no.	2126936	2126160

S.3.4 [1-(NBA)][S-BAr^F_4]

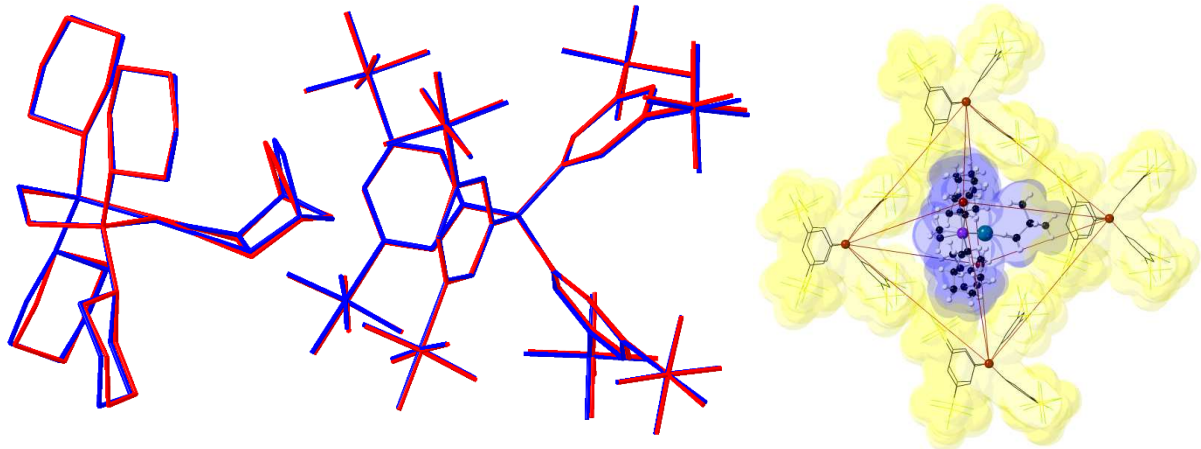


Figure S20. Left: overlay of the single-crystal X-ray (blue) and microED (red) structures of **[1-(NBA)][S-BAr^F_4]**. Right (X-ray): octahedral arrangement of anions around a single cation.

NBA binding pockets within **[1-(NBA)][S-BAr^F_4]** and **[1-(NBA)][BAr^F_4]** were estimated in the Olex2[6] program by calculating the solvent accessible void space (1.41 Å probe radius) within

the NBA-subtracted "[(dcpe)Rh]$^{+}$"[S-BAr$^{F}_{4}$]$^{-}$ and "[(dcpe)Rh]$^{+}$"[BAr$^{F}_{4}$]$^{-}$ structures, using Van der Waal radii taken from Alvarez.[12] Accordingly, for **[1-(NBA)][S-BAr$^{F}_{4}$]** and **[1-(NBA)][BAr$^{F}_{4}$]**, the pocket volumes were calculated to be 82 Å^3 and 140 Å^3, respectively. Visual representations of the binding pockets were made using the CrystalMaker® program[13] (Figure S21).

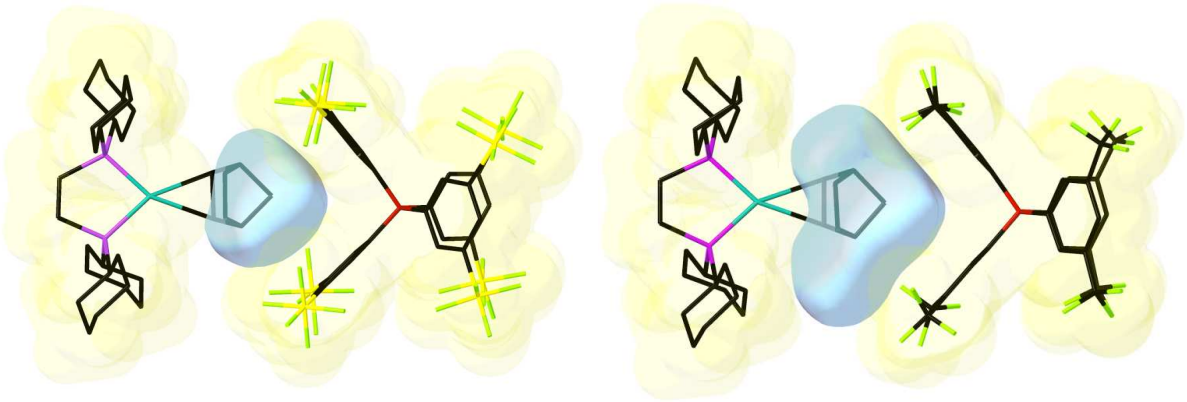


Figure S21. NBA binding pocket (blue surface) within the Van der Waal surfaces (yellow) of "[(dcpe)Rh]$^{+}$"[anion]$^{-}$ within **[1-(NBA)][S-BAr$^{F}_{4}$]** (left) and **[1-(NBA)][BAr$^{F}_{4}$]** (right).

Table S4: Selected crystallographic and refinement data for [1-(NBA)][S-BAr$^{F}_{4}$].

Method	XRD	microED
Empirical formula	$C_{57}H_{72}BF_{40}P_2S_8Rh$	$C_{57}H_{72}BF_{40}P_2S_8Rh$
Formula weight	1949.28	1949.29
Temperature/K	110(2)	80(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	19.4479(9)	19.5339(11)
b/Å	19.0194(10)	19.0160(14)
c/Å	20.1725(7)	20.3007(9)
α/°	90	90
β/°	91.572(4)	91.727(5)
γ/°	90	90
Volume/Å^3	7458.7(6)	7537.4(8)
Z	4	4

ρ_{calc}g/cm^3	1.736	1.718
μ/mm^{-1}	5.628	-
F(000)	3928.0	1269.0
Crystal size/mm^3	0.13 × 0.123 × 0.112	microcrystals < ~1-2 μm
Radiation	Cu Kα (λ = 1.54184)	200 keV electron
Index ranges	-22 ≤ h ≤ 23, -22 ≤ k ≤ 23, -24 ≤ l ≤ 15	-20 ≤ h ≤ 20, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21
Reflections collected	26754	35027
Independent reflections	13926 [R_{int} = 0.0599, R_{sigma} = 0.0851]	8652 [R_{int} = 0.1906, R_{sigma} = 0.1786]
Data/restraints/parameters	13926/0/982	8652/1470/983
Goodness-of-fit on F^2	1.070	1.671
Final R indexes [I>=2σ (I)]	R_1 = 0.0865, wR_2 = 0.2273	R_1 = 0.1640, wR_2 = 0.3631
Final R indexes [all data]	R_1 = 0.1385, wR_2 = 0.2587	R_1 = 0.2369, wR_2 = 0.3800
Largest diff. peak/hole	1.68/-0.65 e Å^{-3}	0.25/-0.23 e Å^{-1}
CCDC no.	2126937	2126161

S.3.5 [1-(ethene)$_2$][S-BAr$^F_4$]

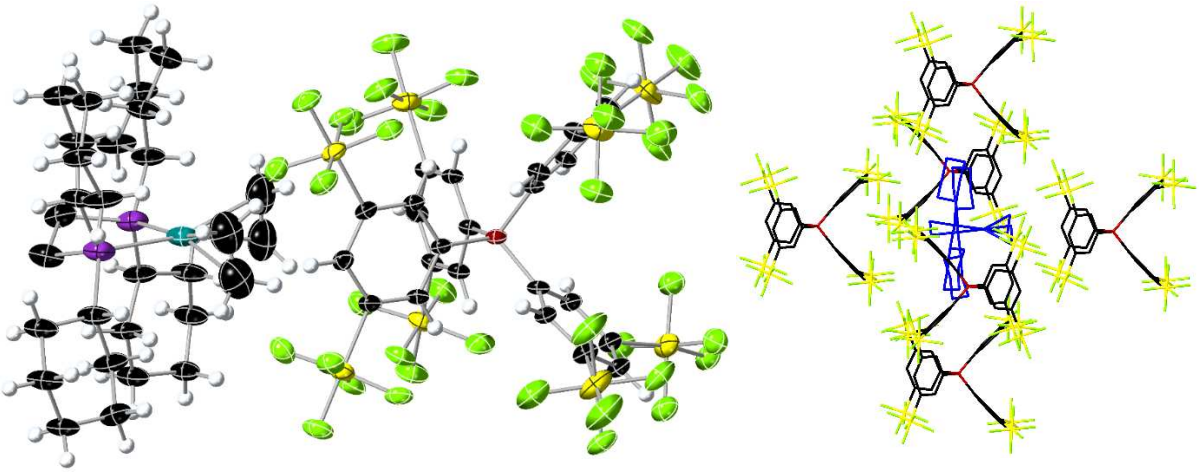


Figure S22. Structure and octahedral anion framework of **[1-(ethene)$_2$][S-BAr$^F_4$]**. Recorded at 110 K; ellipsoids at 25% probability. Selected bond distances (Å): Rh1-C1, 2.248(16); Rh1-C2, 2.256(16); R1-P1, 2.312(3); C1-C2, 1.25(3).

In the model, the cation is disordered over two positions, centred on Rh1 and Rh1A, which are related by a 180 degree rotation of the cation in the Rh1-P1-P2 plane; their respective occupancies were allowed to freely refine, converging at a final ratio of 0.844(4):0.156(4). The P(cyclohexyl)$_2$ groups are shared between the two orientations, however the ethene and diphosphine ligand $(CH_2)_2$ backbone could only be located for the major orientation. The residual electron density from the minor orientation has therefore been accounted for by incorporation into the major orientation.

Table S5: Selected crystallographic and refinement data for [1-(ethene)$_2$][S-BAr$^F_4$].

Method	XRD
Empirical formula	$C_{54}H_{64}BF_{40}P_2RhS_8$
Formula weight	1905.19
Temperature/K	110(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	19.5254(8)
b/Å	18.4417(19)

c/Å	20.4850(10)
α/°	90
β/°	92.333(4)
γ/°	90
Volume/Å^3	7370.2(9)
Z	4
ρ_{calc}g/cm^3	1.717
μ/mm^{-1}	5.681
F(000)	3824.0
Crystal size/mm^3	0.22 × 0.214 × 0.117
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.784 to 141.576
Index ranges	-14 ≤ h ≤ 23, -22 ≤ k ≤ 21, -24 ≤ l ≤ 24
Reflections collected	13346
Independent reflections	6905 [R_{int} = 0.0351, R_{sigma} = 0.0431]
Data/restraints/parameters	6905/858/648
Goodness-of-fit on F^2	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0946, wR_2 = 0.2460
Final R indexes [all data]	R_1 = 0.1319, wR_2 = 0.2755
Largest diff. peak/hole / e Å^{-3}	1.58/-0.64
CCDC no.	2126935

S.4 COMPUTATIONAL METHODS

Periodic DFT calculations on **[1-NBA][S-BAr$^F_4$]** employed the CP2K program suite (Version 5.0).[14] Initial coordinates were obtained from the experimental crystallographic data, with the

hydrogen positions normalised with Mercury.[15] Calculations employed the Gaussian Plane Wave (GPW) formalism as implemented in the QUICKSTEP[16] module with basis sets for all atoms of double-ζ plus polarization quality in their short-range variant (DZVP-MOLOPT-SR-GTH).[17] The interaction between the core electrons and the valence shell (Rh: 17, B: 3, C: 4, P: 5, F: 7, H: 1 electrons) was described by Goedecker-Teter-Hutter (GTH) pseudo potentials.[18] The generalized gradient approximation (GGA) to the exchange-correlation functional according to Perdew-Burke-Ernzerhof (PBE)[19] was used in combination with Grimme's D3-correction for dispersion interactions.[20] The auxiliary plane wave basis set was truncated at a cutoff of 500 Ry. The maximum force convergence criterion was set to 10^{-4} Eh·Bohr^{-1}, whilst default values were used for the remaining criteria. The convergence criterion for the self-consistent field (SCF) accuracy was set to 10^{-7} Eh and 10^{-8} Eh for geometry optimizations and vibrational analysis, respectively.

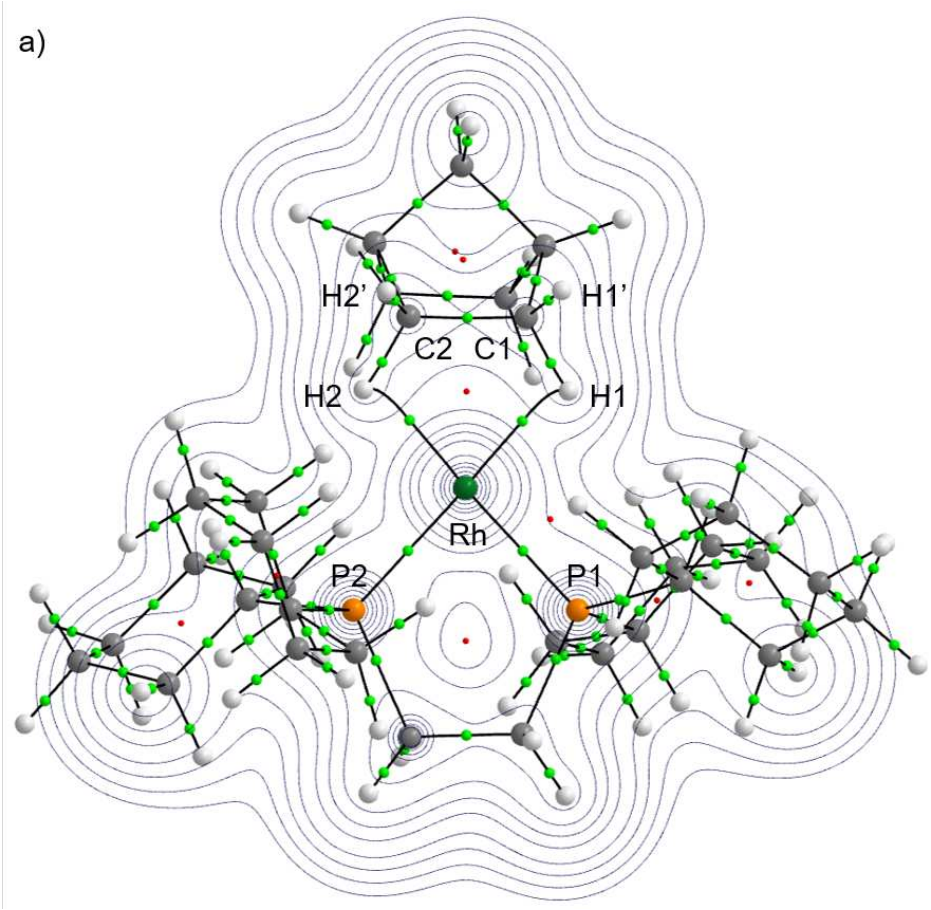
The Brillouin zone was sampled using the Γ-point. Periodic boundary conditions (PBC) were applied throughout in combination with fixed unit cell parameters obtained from experiment. All geometries were first partially relaxed, keeping the heavy atoms (non-H, F) fixed, then fully relaxed without imposing any constraints, whilst keeping unit cell parameters constant in all cases. The fully optimised geometry was further characterized by analysis of the numerical second derivatives with a displacement of 0.01 Bohr and found to have no imaginary eigenvalues. Cartesian coordinates of computed structure are included below.

All interaction energy calculations were performed in a periodic box of the same dimension as the **[1-NBA][S-BAr$^{F}_{4}$]** unit cell. Test calculations showed that increasing the size of the periodic box did not significantly affect the energies. For the lattice energies, geometries for the **[1-NBA]$^{+}$** cation and **[S-BAr$^{F}_{4}$]$^{-}$** anion were taken from the fully optimised unit cell. The normalised lattice energy quoted in the main text is the total lattice energy divided by Z, the number of formula units in the unit cell (here 4). Incorporation energies, ΔE_1, were calculated by removing one NBA ligand from the full unit cell and recomputing the electronic energy. Molecular interaction energies, ΔE_2, correspond to the change in electronic energy upon removing the NBA ligand from **[1-NBA]$^{+}$**.

Geometries for the electronic structure analyses were extracted from the optimised CP2K geometry. The topology of the electron density of the **[1-NBA]$^{+}$** cation was analysed by means of QTAIM (Quantum Theory of Atoms in Molecules),[21] as implemented in the AIMALL package.[22] Inner shell electrons on Rh and P modelled by ECPs were represented by core density functions (extended wavefunction format). NBO calculations were performed using the NBO 6.0 program.[23] NCI calculations on the nearest neighbour [1-NBA][S-BAr$^{F}_{4}$] ion-pair were performed using the NCIPLOT program.[24] The promolecular electron density was employed. Orbital plots were created with Chemcraft[25] with an outer contour value of 0.07465.

Short inter-ion contacts were analysed using the Crystal Explorer package,[26] using a central cation and the six nearest neighbour anions.

S.4.1 QTAIM study of [1-NBA]$^+$



(b)

Bond	Distance/Å	ρ(r)	∇^2(r)	ε	H(r)
Rh–H1	1.882	0.060	0.246	1.208	-0.008
Rh–H2	1.882	0.060	0.246	1.229	-0.008
C1–H1	1.153	0.233	-0.615	0.013	-0.203
C1–H1'	1.097	0.277	-0.946	0.003	-0.279
C2–H2	1.153	0.234	-0.619	0.014	-0.204
C2–H2'	1.095	0.278	-0.957	0.002	-0.282
Rh–P1	2.209	0.119	0.077	0.014	-0.059
Rh–P2	2.207	0.119	0.078	0.005	-0.099
C1–C2	1.562	0.228	-0.457	0.011	-0.172

Figure S23. (a) Molecular graph for the **[1-NBA]$^+$** cation with bond critical bonds (BCPs) in green and ring critical points (RCPs) in red. Electron density contours are shown in the plane containing Rh, H1 and H2 (b) Selected metrics for key BCPs (atomic units unless otherwise stated).

S.4.2 Non-covalent interaction (NCI) study of the [1-NBA][S-BAr$^{F}_{4}$] ion-pair

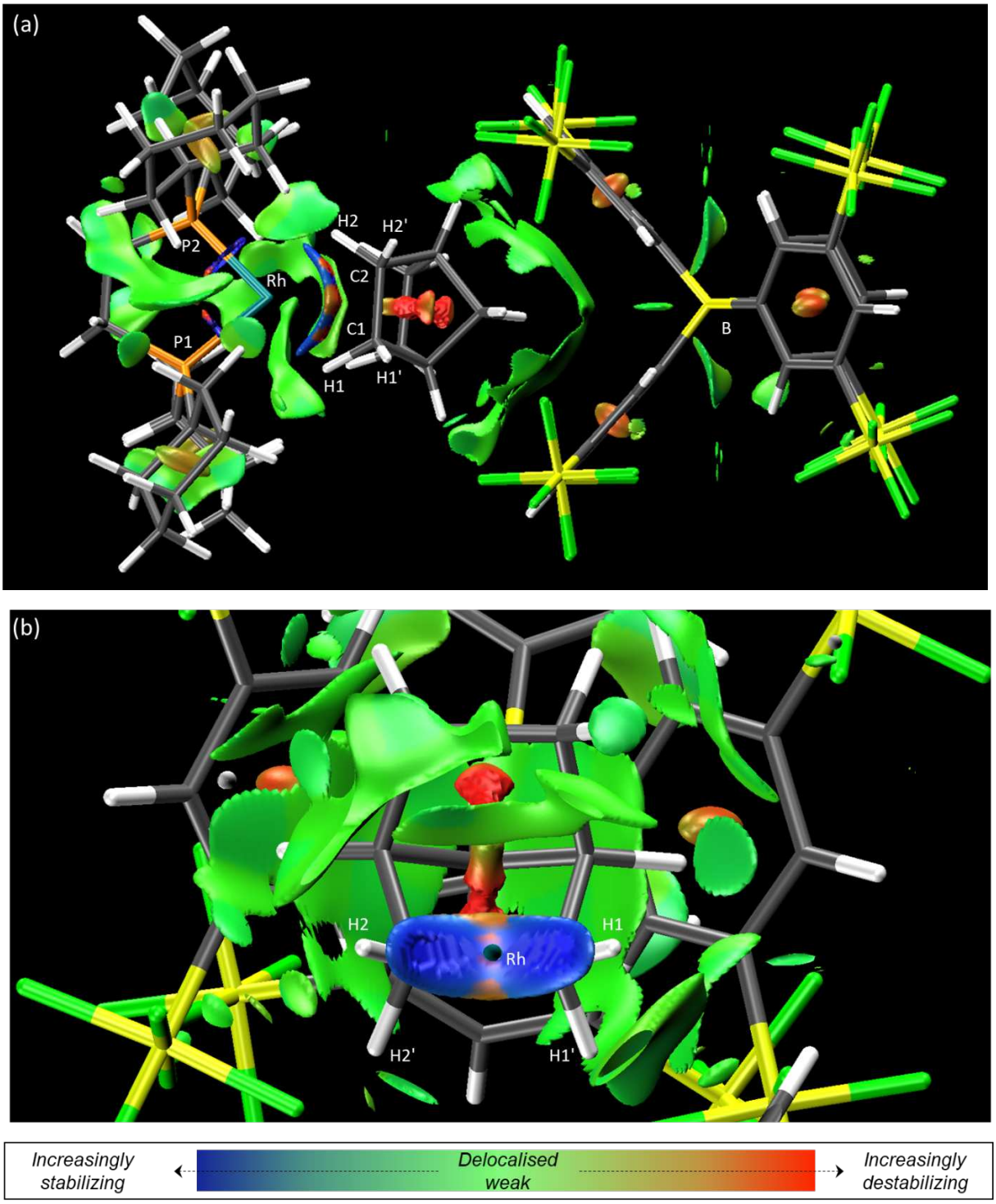


Figure S24. Two views of the NCI plots for the [1-NBA][S-BAr$^{F}_{4}$] ion-pair (a) View from above the NBA ligand showing both the cation and anion (b) Detail viewed from the Rh center looking down an axis passing through the center of the C1-C1' bond. Isosurfaces are generated for σ = 0.3 au and −0.07 < ρ < 0.07 au; a key showing the color scheme employed is also provided.

S.4.3 Natural bond orbital analysis of the [1-NBA]$^{+}$ cation

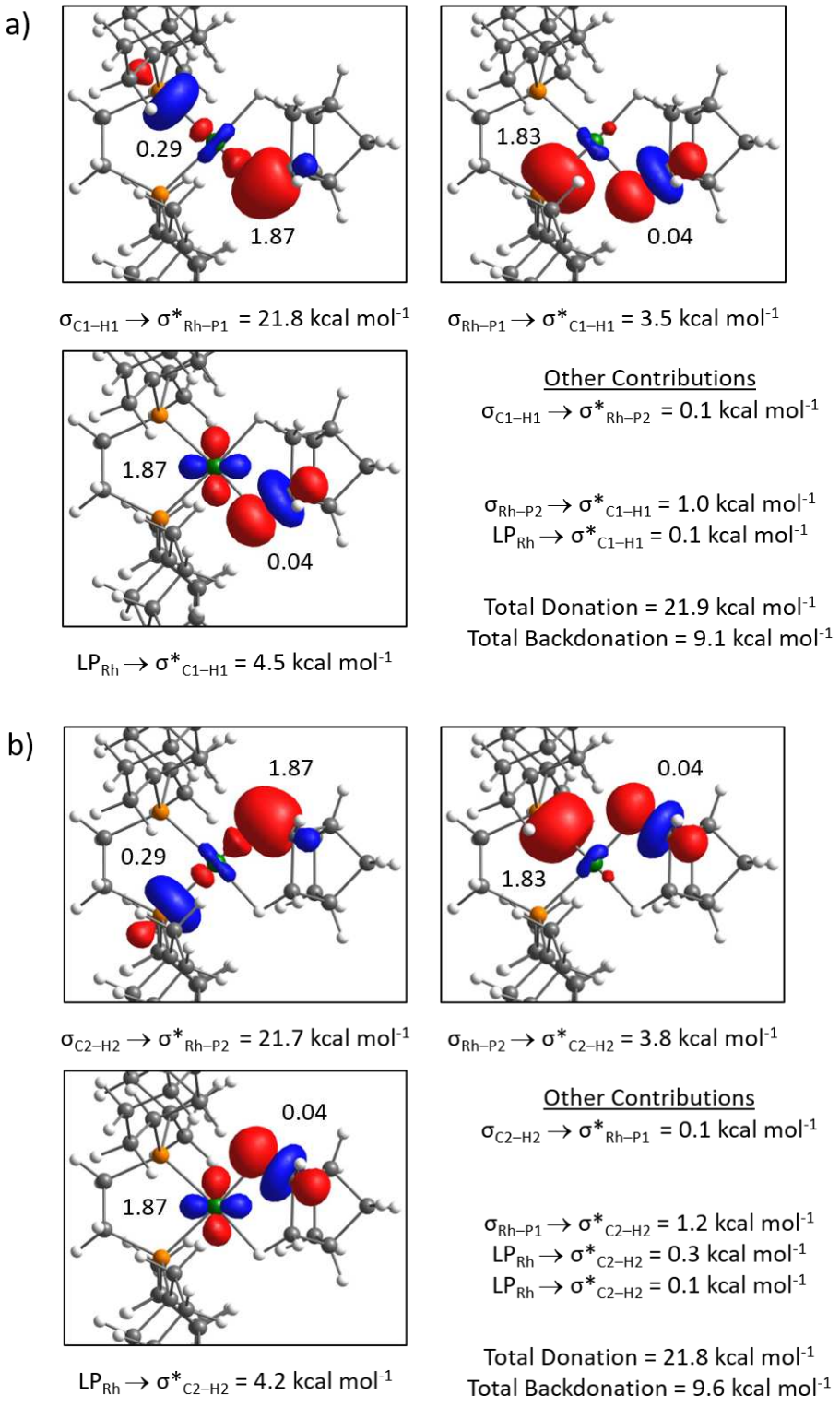


Figure S25. Major donor−acceptor interactions in **[1-NBA]$^{+}$** derived from the second-order perturbation NBO analysis (kcal/mol); (a) involving C1-H1; (b) involving C2-H2. NBO occupations are also indicated and well as other minor contributions to the back donations.

S.4.4 CrystalExplorer analysis of [1-NBA][S-BAr$^{F}_{4}$] and [1-NBA][BAr$^{F}_{4}$]

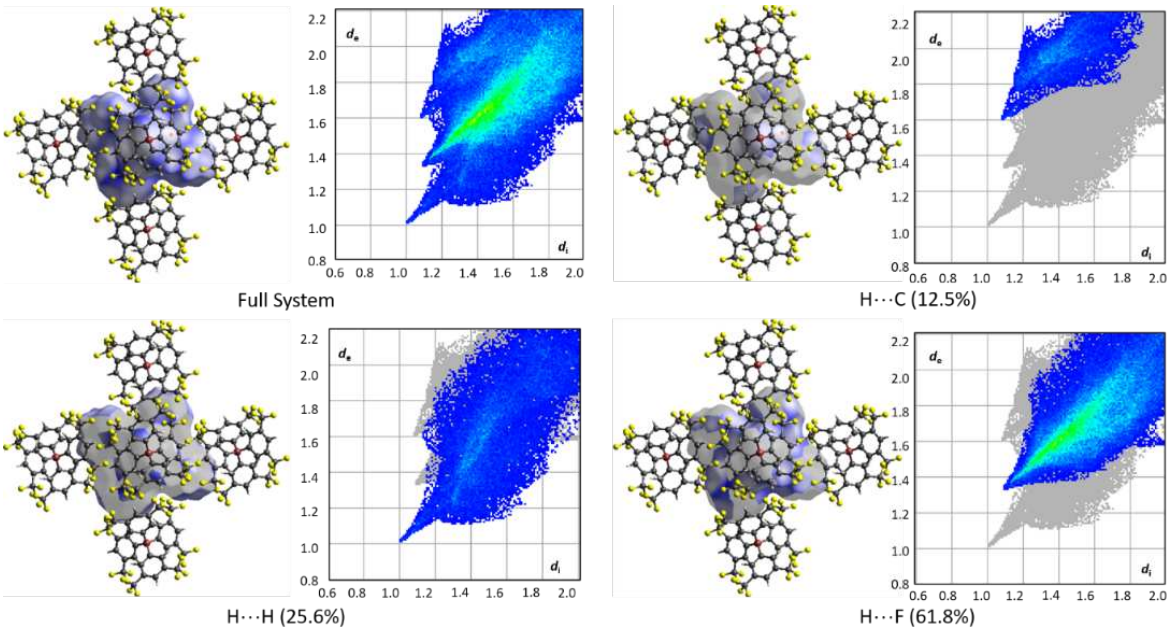


Figure S26. Hirshfeld surfaces plotted around **[1-NBA]$^{+}$** in **[1-NBA][BAr$^{F}_{4}$]** with accompanying fingerprint plots broken down into the three types of anion-cation contacts.

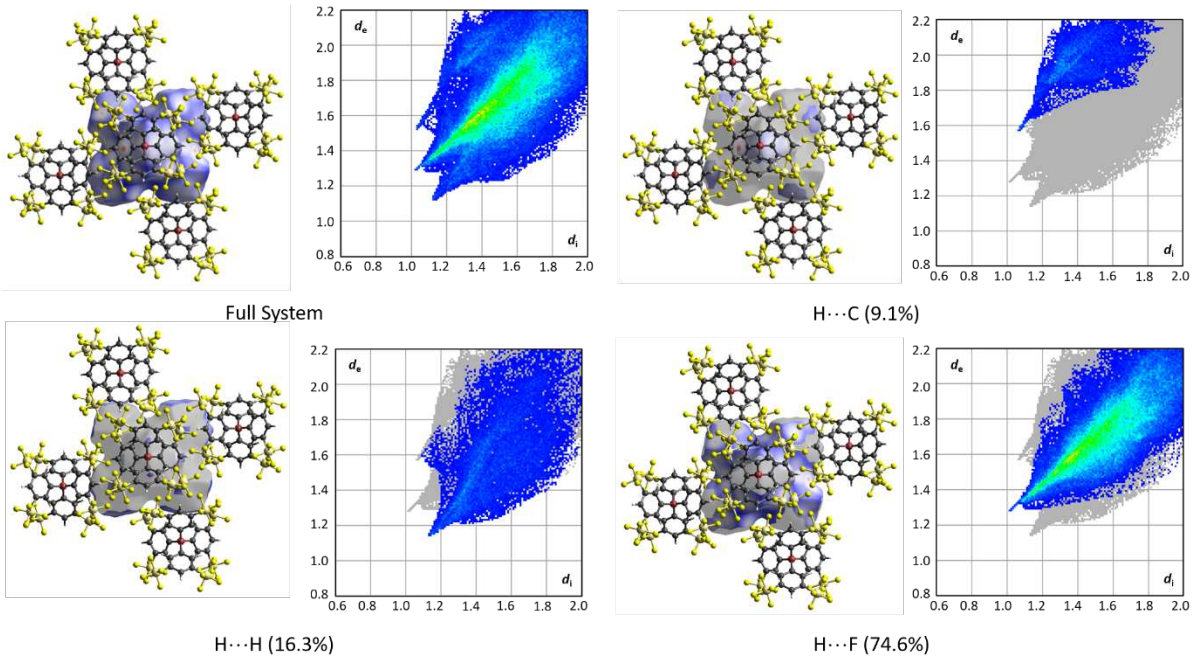


Figure S27. Hirshfeld surfaces plotted around **[1-NBA]$^{+}$** in **[1-NBA][S-BAr$^{F}_{4}$]** with accompanying fingerprint plots broken down into the three types of anion-cation contacts.

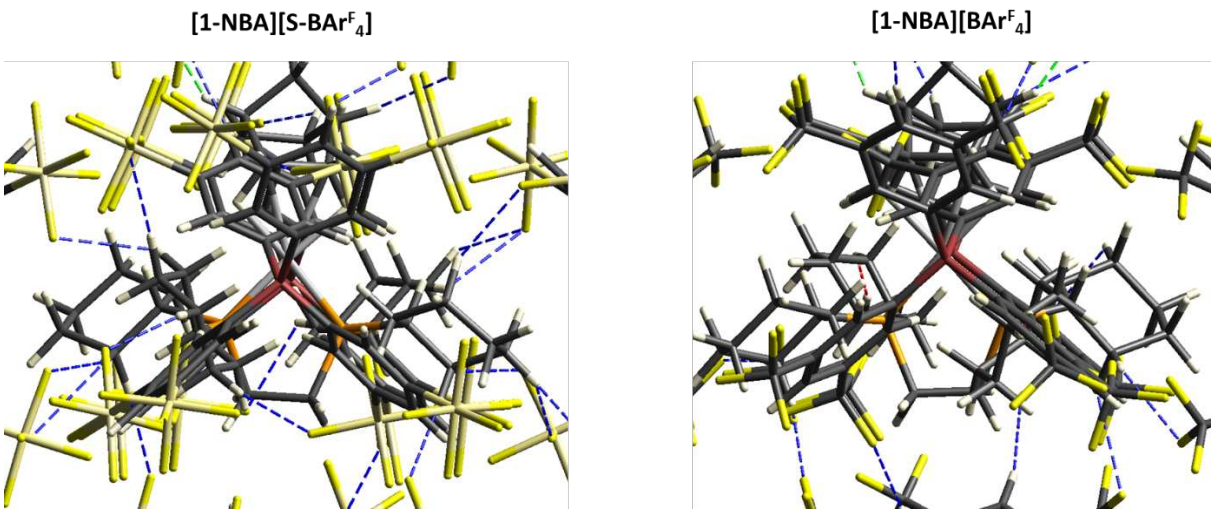


Figure S28. Close up of the **[1-NBA]$^+$** environments in **[1-NBA][S-BAr$^F_4$]** and **[1-NBA][BAr$^F_4$]** highlighting short contacts at or below the sum of the van der Waals radii (blue: C–H···F–C; red: C–H···H–C; green: C–H···C).

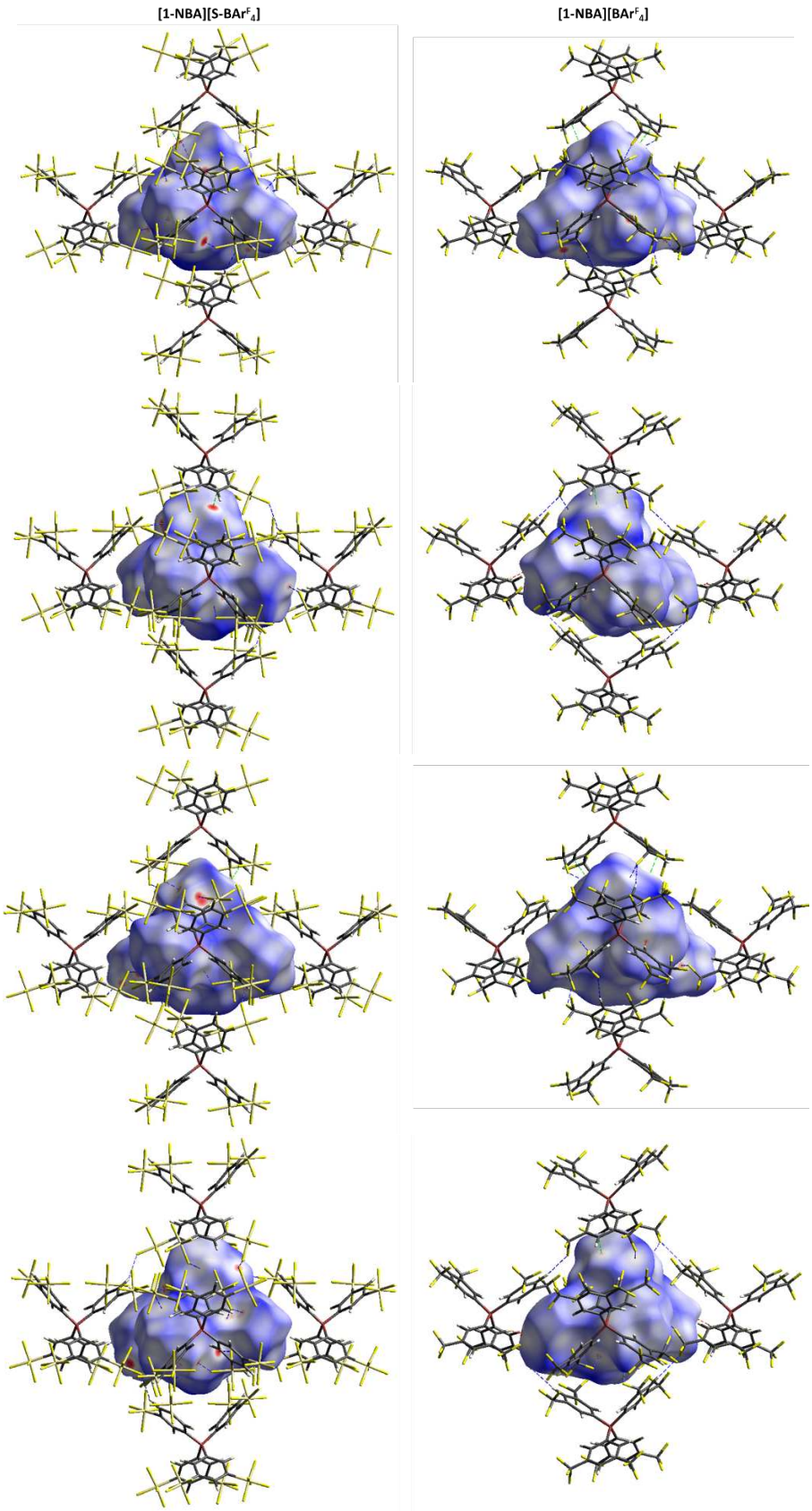


Figure S29. Hirshfeld surfaces of the **[1-NBA]$^+$** cation within the pseudo-octahedral anion environments in **[1-NBA][S-BAr$^F_4$]** and **[1-NBA][BAr$^F_4$]**; a view from behind each equatorial anion is presented. Red areas are contacts below, white at, and blue greater than the sum of the van der Waals radii.

S.4.5 Computed cartesian coordinates (Å) and energy for [1-NBA][S-BAr$^{F}_{4}$]

```
SCF Energy = -6178.989205
Rh    18.832286    13.501740    15.023018
 P    19.385817    15.175488    13.692151
 P    18.648607    15.044944    16.590486
 C    19.040509    16.826705    14.481895
 H    19.689586    17.600330    14.048299
 H    18.003548    17.080246    14.219920
 C    19.205768    16.723177    16.008228
 H    18.658339    17.514164    16.540017
 H    20.262506    16.816488    16.294244
 C    18.368535    15.041992    12.149548
 H    18.696954    14.065724    11.750326
 C    16.862147    14.920144    12.457613
 H    16.697299    14.179132    13.255904
 H    16.483699    15.881877    12.836214
 C    16.095343    14.530835    11.185145
 H    16.408972    13.523102    10.875731
 H    15.020986    14.463671    11.401532
 C    16.350749    15.523896    10.044101
 H    15.904990    16.497197    10.297738
 H    15.846713    15.183275     9.128461
 C    17.852390    15.709732     9.782232
 H    18.007150    16.479337     9.015196
 H    18.275780    14.772251     9.386210
 C    18.617676    16.098927    11.062367
 H    19.686920    16.194570    10.847675
 H    18.275620    17.081455    11.414436
 C    21.168987    15.248010    13.140349
 H    21.293337    16.228442    12.650189
 C    21.498216    14.139538    12.121980
 H    20.875464    14.245864    11.226556
 H    21.253633    13.158700    12.558874
 C    22.983665    14.155096    11.718458
 H    23.179821    13.336016    11.013948
 H    23.204725    15.088926    11.180577
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H	19.875906	15.702320	7.439567
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