Supporting Information

Tethered N-Heterocyclic Carbene-Carboranes: Unique Ligands that Exhibit Unprecedented and Versatile Coordination Modes at Rhodium.

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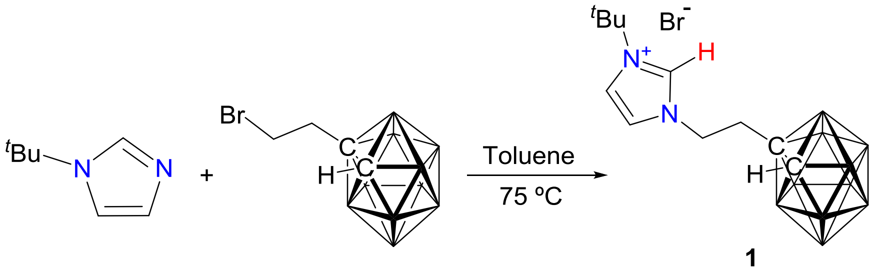
Experimental and Spectroscopic Data

General considerations

All manipulations were carried out under an inert atmosphere by means of standard Schlenk line or glovebox techniques, unless otherwise stated. Anhydrous solvents were prepared by passing over activated alumina to remove water, copper catalyst to remove oxygen and molecular sieves to remove any remaining water, *via* the Dow-Grubbs solvent system, and then freeze-pump-thaw degassed prior to use. 1-^{t}Butylimidazole[1], 6,9-bis(acetonitrile)-decaborane[2] and 1-bromoethyl-1,2-dicarba-closo-dodecaborane[3] were prepared using literature methods. Decaborane was purchased from KatChem and all other reagents were purchased from Sigma Aldrich and used without further purification. NMR spectra were recorded on a Bruker AV500 spectrometer. ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts were referenced against residual solvent peaks (^{1}H: 2.05 ppm for acetone-d_6, 2.50 ppm for dmso-d_6 and 7.26 ppm for $CDCl_3$; ^{13}C: 29.8 ppm for acetone-d_6, 39.5 ppm for dmso-d_6 and 77.2 ppm for $CDCl_3$). The ^{11}B{^{1}H} NMR spectra were referenced externally to $BF_3.OEt_2$. Assignment of ^{1}H and ^{13}C{^{1}H} NMR spectra for all rhodium complexes was aided by the use of 2D ^{1}H^{1}H COSY, ^{1}H^{13}C HMQC, ^{1}H^{13}C HMBC and ^{13}C{^{1}H} DEPT 135 experiments. Mass spectra were collected on a Bruker Daltonics (micro TOF) instrument operating in the electrospray mode. Microanalyses were performed using a Carlo Erba Elemental Analyser MOD 1106.

Synthesis of imidazolium bromide salt 1



1

To a stirred solution of bromoethyl-1,2-dicarba-*closo*-dodecaborane (4.0 g, 15.9 mmol) in toluene (20 mL) heated at 75 °C was added a toluene (20mL) solution of 1-^{t}butylimidazole (1.8 g, 14.5 mmol) dropwise over 1 hour. The reaction was kept at 75 °C for a further 18 hours. The solvent was removed *in vacuo* and hexane (10 mL) was added resulting in an off-white precipitate. This was filtered, washed with further hexane (2 × 10 mL) then diethyl ether (3 × 10 mL) and dried *in vacuo* to afford the product as a beige crystalline solid in 72 % yield (3.91 g, 10.4 mmol). Crystals suitable for X-ray diffraction analysis were grown by the slow diffusion of diethyl ether into a concentrated solution of **1** in acetonitrile.

^{1}H NMR (500 MHz, dmso-d$_6$): δ 9.41 (s, 1H, imidazolium NC*H*N), 8.03 (t, J = 1.9 Hz, 1H, imidazolium NC*H*), 7.90 (t, J = 1.9 Hz, 1H, imidazolium NC*H*), 5.38 (br. s, 1H, carborane cage C*H*), 4.33 (m, 2H, CH$_2$), 2.99 (m, 2H, CH$_2$), 1.57 (s, 9H, (CH$_3$)$_3$). ^{13}C{^{1}H} NMR (126 MHz, dmso-d$_6$): δ 134.9 (imidazolium N*C*N), 122.6 (imidazolium N*C*C), 120.2 (imidazolium NC*C*), 72.4 (carborane cage quaternary *C*), 63.2 (carborane cage *C*H), 59.6 ($\underline{C}$(CH$_3$)$_3$), 47.0 (*C*H$_2$), 35.3 (*C*H$_2$), 28.9 ((*C*H$_3$)$_3$). ^{11}B{^{1}H} NMR (161 MHz, dmso-d$_6$): δ -2.8 (1B), -5.5 (1B), -9.6 (2B), -11.8 (6B). HRMS (ESI$^+$): *m/z* 295.3188 [$C_{11}H_{27}B_{10}N_2$]$^+$, calcd. [M-Br]$^+$ 295.3177. Anal. calcd. for $C_{11}H_{27}B_{10}N_2Br$: C, 35.20; H, 7.25; N, 7.46. Found: C, 34.90; H, 7.30; N, 7.10.

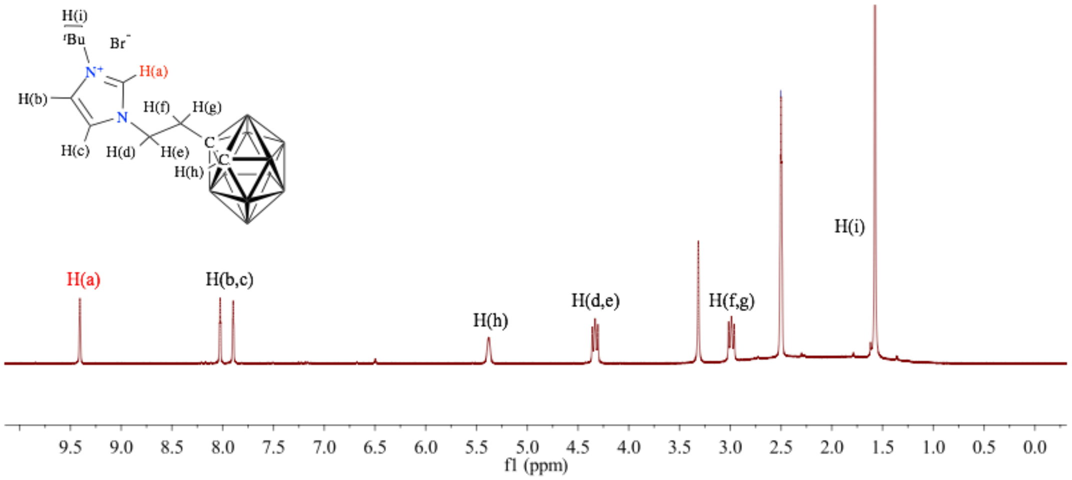


Figure S1. ^{1}H NMR spectrum (dmso-d$_6$, 500 MHz) of imidazolium bromide salt **1**.

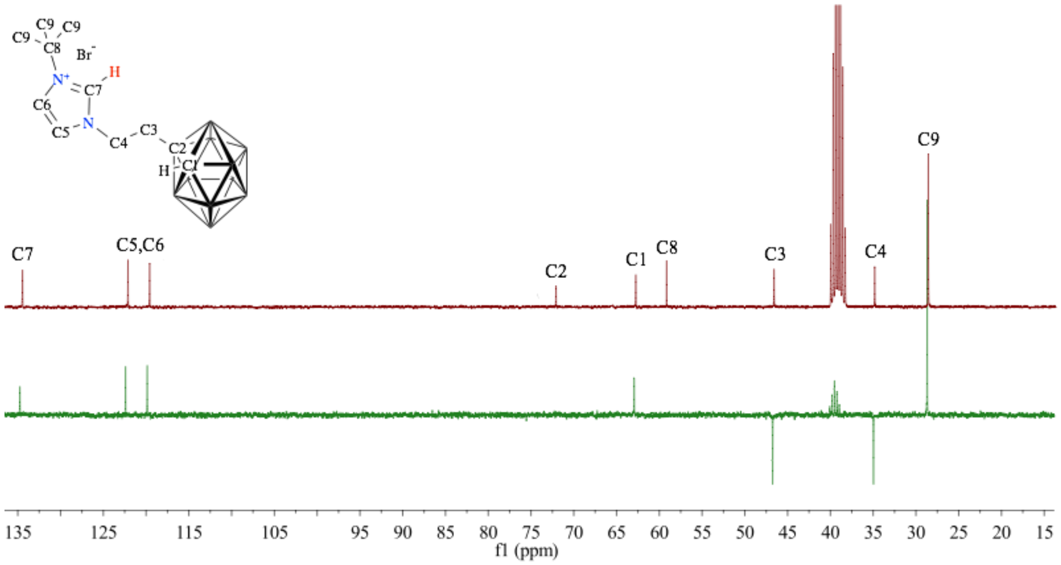


Figure S2. ^{13}C{^{1}H} (top) and ^{13}C{^{1}H}-DEPT 135 (bottom) NMR spectra (dmso-d$_6$, 126 MHz) of imidazolium bromide salt **1**.

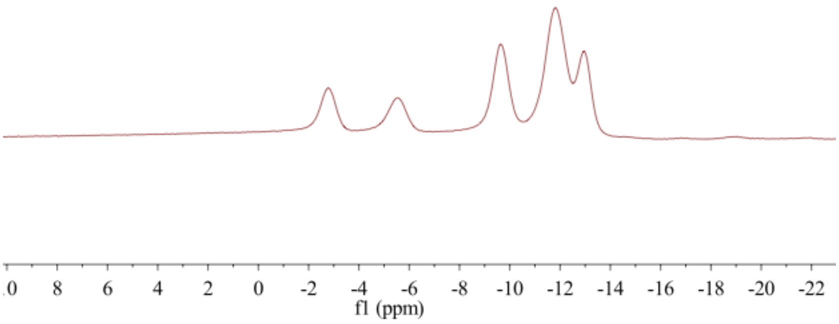


Figure S3. $^{11}B\{^1H\}$ NMR spectrum (dmso-d_6, 161 MHz) of imidazolium bromide salt **1**.

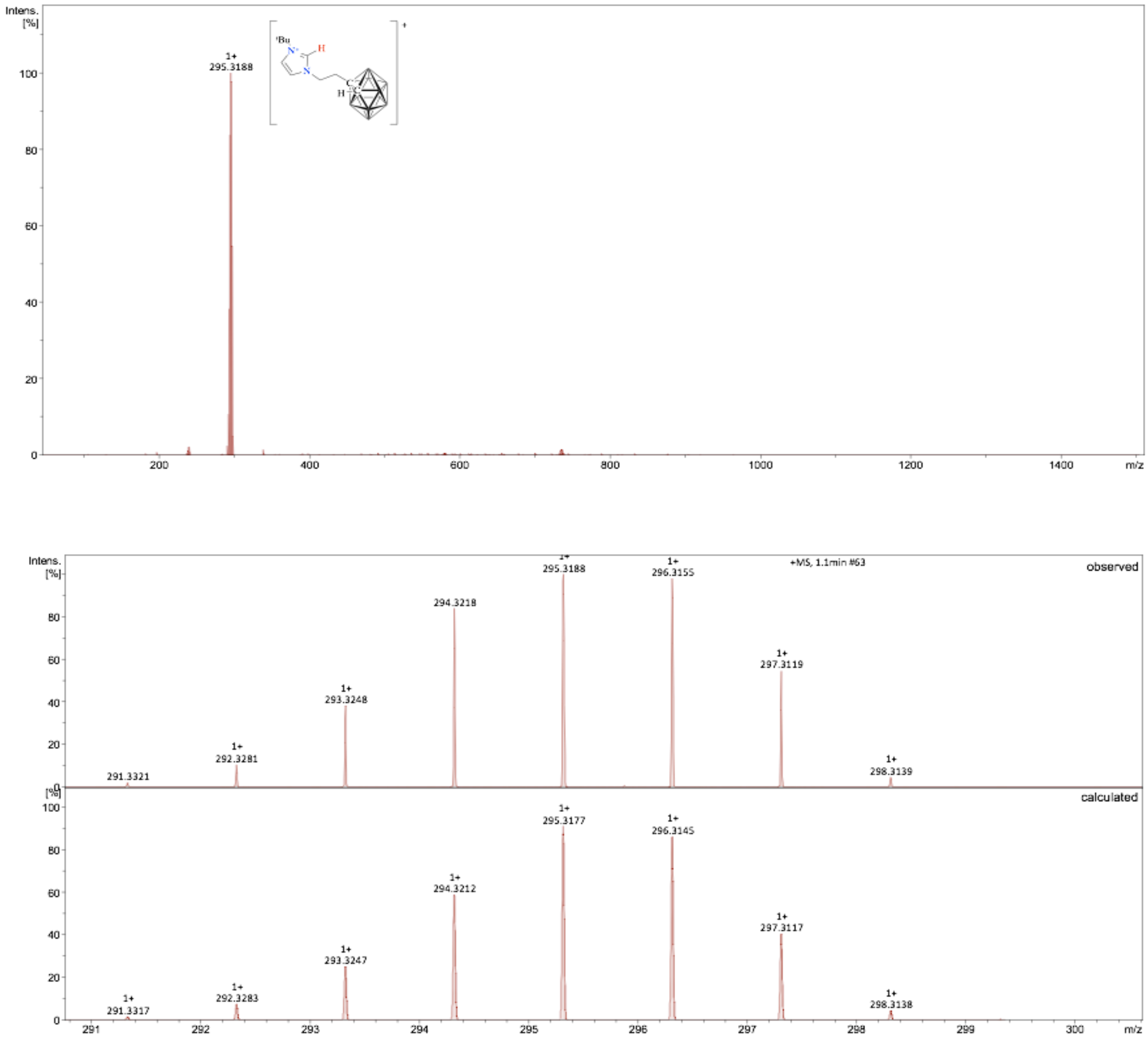
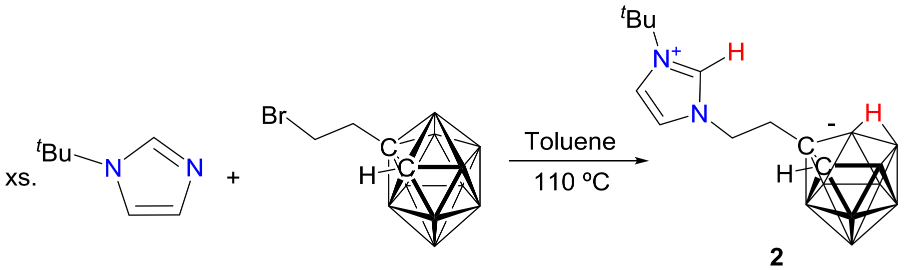


Figure S4. HRMS (ESI^+) of imidazolium-*closo*-carborane bromide **1** (top). Calculated isotope pattern (bottom) and observed (middle) for $[M-Br]^+$**.**

Synthesis of imidazolium-*nido*-carborane zwitterion 2



2

To a solution of 1-^{t}butylimidazole (4.0 g, 32.2 mmol) in toluene (10 mL) was added 1-bromoethyl-1,2-dicarba-*closo*-dodecaborane (1.6 g, 6.35 mmol), and the reaction mixture stirred at 110 °C for 24 hours. The solvent was removed *in vacuo* to afford a brown oil to which methanol (10 mL) was added to precipitate the product. This was filtered, washed with methanol (3 × 10 mL) and dried *in vacuo* to afford the product as a white solid in 65 % yield (1.2 g, 4.12 mmol). Crystals suitable for X-ray diffraction analysis were grown by slow diffusion of diethyl ether into a concentrated solution of **2** in acetonitrile.

^{1}H NMR (500 MHz, dmso-d_6): δ 9.27 (s, 1H, imidazolium NC*H*N), 8.03 (s, 1H, imidazolium NC*H*), 7.83 (s, 1H, imidazolium NC*H*), 4.17 (m, 2H, $C\mathit{H}_2$), 2.11 (m, 1H, $C\mathit{H}_2$), 1.94 (m, 1H, $C\mathit{H}_2$), 1.62 (s, 9H, $(C\mathit{H}_3)_3$), 1.55 (br. s, 1H, carborane cage CH). ^{13}C{^{1}H} NMR (126 MHz, dmso-d_6): δ 134.5 (imidazolium N*C*N), 122.8 (imidazolium N*C*C), 120.2 (imidazolium NC*C*), 59.3 ($\underline{C}(CH_3)_3$), 56.2 (carborane cage quaternary *C*), 50.01 ($\mathit{C}H_2$), 44.7 (carborane cage *C*H), 38.9 ($\mathit{C}H_2$), 29.0 ($(\mathit{C}H_3)_3$). ^{11}B{^{1}H} NMR (161 MHz, dmso-d_6): δ -11.1 (2B), -14.2 (1B), -15.9 (1B), -19.4 (2B), -21.6 (1B), -33.2 (1B), 37.3 (1B). HRMS (ESI$^+$): *m/z* 286.3131 $[C_{11}H_{28}B_9N_2]^+$, calcd. $[M+H]^+$ 286.3126. Anal. calcd. for $C_{11}H_{27}B_9N_2$: C, 46.42; H, 9.56; N, 9.84. Found: C, 46.60; H, 9.65; N, 9.80.

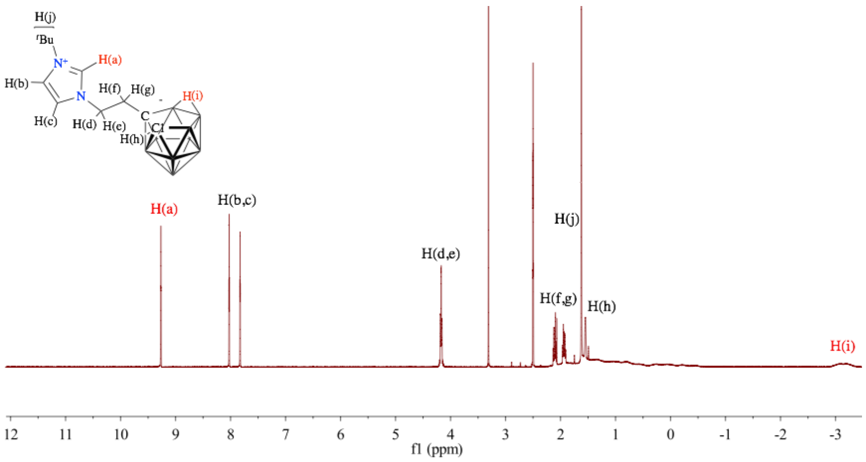


Figure S5. ^{1}H NMR spectrum (dmso-d_6, 500 MHz) of imidazolium-*nido*-carborane zwitterion **2**.

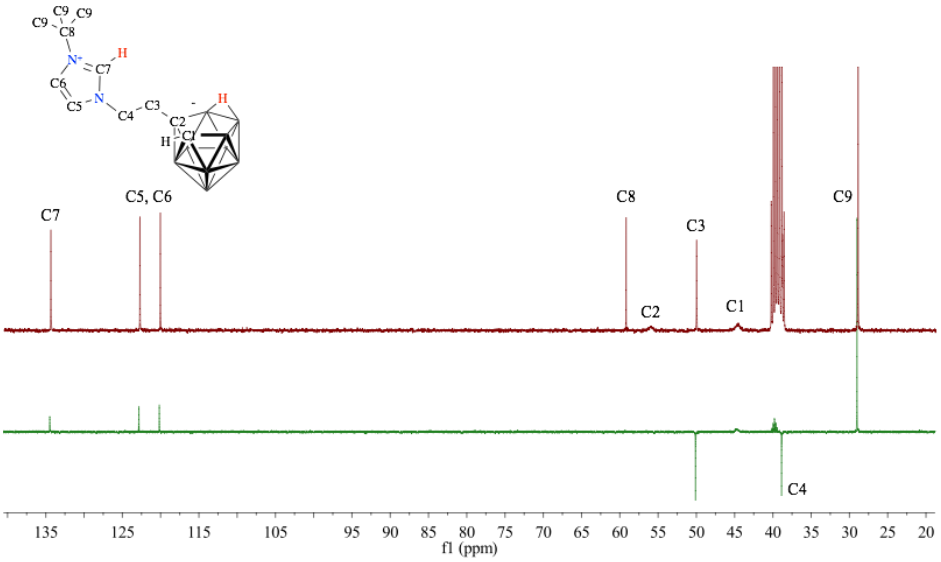


Figure S6. ^{13}C{^{1}H} NMR (top) and ^{13}C{^{1}H}-DEPT 135 (bottom) spectra (dmso-d_6, 126 MHz) of imidazolium-*nido*-carborane zwitterion **2**.

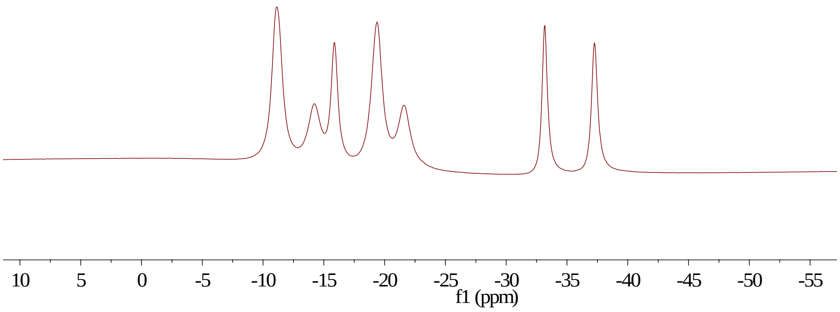


Figure S7. $^{11}B\{^{1}H\}$ NMR spectrum (dmso-d_6, 161 MHz) of imidazolium-*nido*-carborane zwitterion **2**.

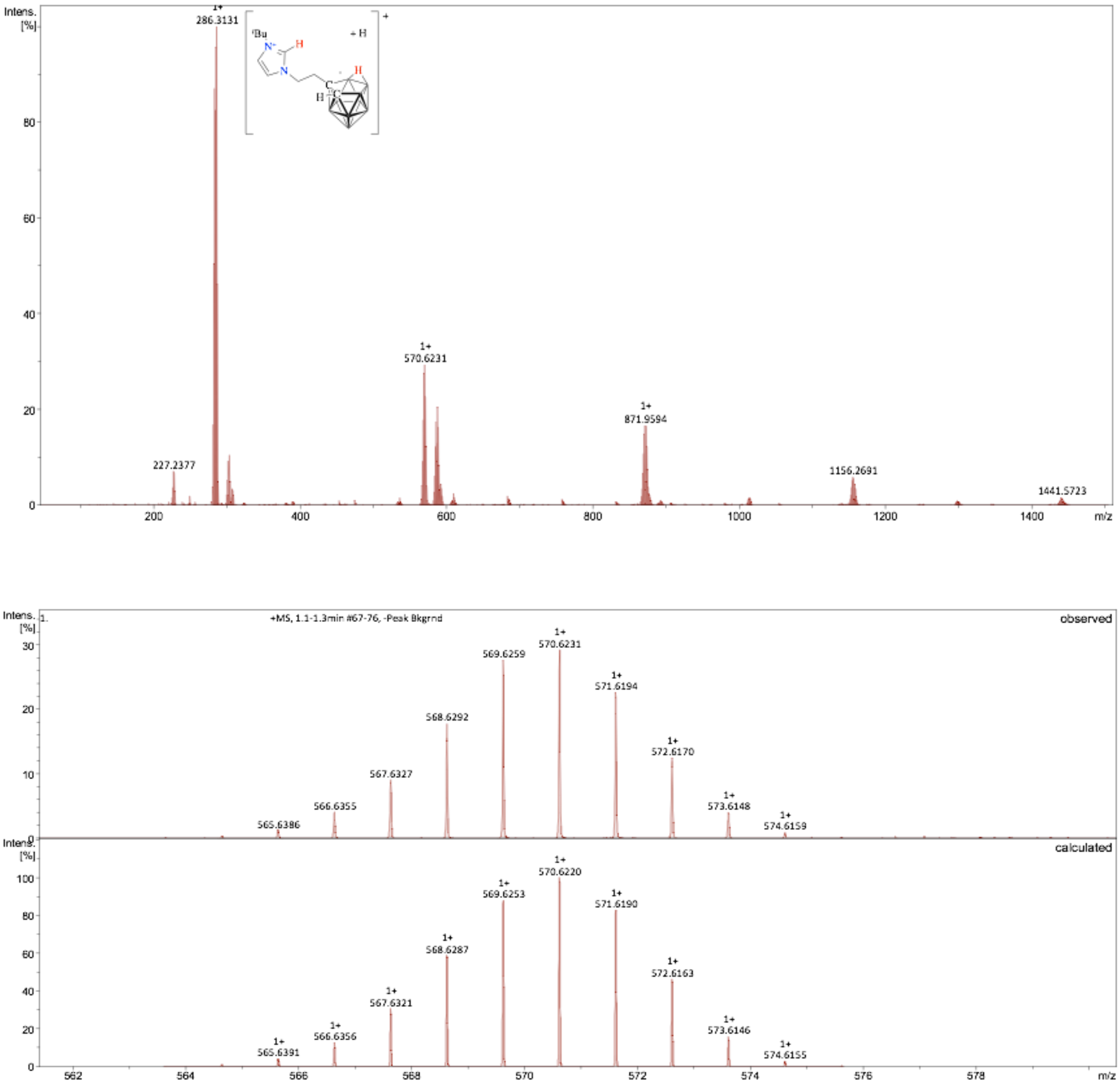
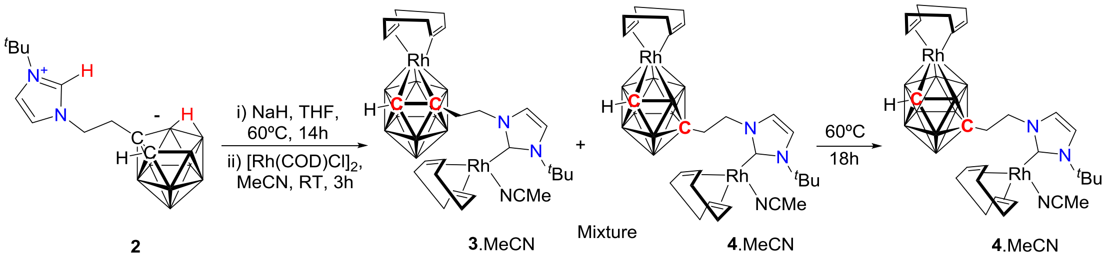


Figure S8. HRMS (ESI$^+$) of imidazolium-*nido*-carborane zwitterion **2** (top). Calculated isotope pattern (bottom) and observed (middle) for $[2M+H]^+$**.**

Synthesis of complex 4·MeCN (and crystallisation of complexes 3·MeCN and 4_2)



Imidazolium *nido*-carborane zwitterion **2** (10 mg, 0.04 mmol), NaH (1.8 mg, 0.08 mmol) and anhydrous tetrahydrofuran (0.5 mL) were added to a Young’s Tap NMR tube. The suspension was heated at 60 °C for 14 hours. The clear yellow solution was removed *via* syringe from the excess NaH. The solvent was removed *in vacuo* and $[Rh(COD)Cl]_2$ (19.1 mg, 0.04 mmol) and anhydrous acetonitrile (1 mL) were added. The reaction mixture was stirred at room temperature for 3 hours. Filtration of the mixture through celite and slow diffusion of diethyl ether into the acetonitrile solution resulted in crystals of **3**·MeCN suitable for X-ray diffraction analysis.

To obtain complex **4**·MeCN only, the reaction mixture was heated at 60 °C for 18 hours instead of room temperature for 3 hours. This was subsequently filtered through celite and slow evaporation to concentrate the solution resulted in a yellow crystalline solid. The solid was filtered, washed with anhydrous diethyl ether (3 × 5 mL) and dried *in vacuo* to afford the product as a yellow crystalline solid in 77 % yield (23 mg, 0.03 mmol). Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a concentrated solution of **4**·MeCN in acetone. Crystals of $\mathbf{4}_2$ suitable for X-ray diffraction analysis were grown by re-dissolving crystals of **4**·MeCN in the minimum amount of acetonitrile followed by the addition of anhydrous diethyl ether and hexane in a ratio of 1:3:3.

^{1}H NMR (500 MHz, acetone-d_6): δ 7.45 (d, J = 1.9 Hz, 1H, NC*H*), 7.30 (s, 1H, NC*H*), 5.36 (br. s, 1H, CH_2), 4.84 (m, 2H, COD-C*H*), 4.32 (m, 2H, COD-C*H*), 4.22 (m, 3H, COD-C*H*, C*H*$_2$), 3.81 (br. s, 1H, COD-C*H*), 3.66 (br. s, 1H, COD-C*H*), 2.45 (m, 25H, C*H*$_2$, COD-C*H*$_2$, C*H*$_3$, (C*H*$_3$)$_3$, carborane cage C*H*). ^{13}C{^{1}H} NMR (126 MHz, acetone-d$_6$): δ 174.2 (d, $^1J_{Rh\text{-}C}$ = 50.4 Hz, N*C*N), 122.3 (N*CC*N), 96.6, 93.0, 81.5 (br, COD-*C*H), 75.4 (d, $^1J_{Rh\text{-}C}$ = 10.1 Hz, COD-*C*H), 75.0 (d, $^1J_{Rh\text{-}C}$ = 11.3 Hz, COD-*C*H), 59.2 ($\underline{C}$(CH$_3$)$_3$), 53.7 (*C*H$_2$), 47.5 (carborane cage quaternary *C*), 42.6 (*C*H$_2$), 36.6 (NC$\underline{C}$H$_3$), 34.3 (COD-*C*H$_2$), 33.8 (COD-*C*H$_2$, carborane cage *C*H), 32.3 ((*C*H$_3$)$_3$), 32.0-28.9 (COD-*C*H$_2$), 3.5 (N$\underline{C}$CH$_3$). ^{11}B{^{1}H} NMR (161 MHz, dmso-d$_6$): δ -6.31 (2B), -10.70 (2B), -12.98 (2B), -22.07 (3B). HRMS (ESI$^+$): *m/z* 706.2982 [$C_{27}H_{50}B_9N_2Rh_2$]$^+$, calcd. [M-MeCN+H]$^+$ 706.2971. Anal. calcd. for $C_{29}H_{52}B_9N_3Rh_2$: C, 46.70 ; H, 7.03; N, 5.63. Found: C, 46.40; H, 7.10; N, 5.70.

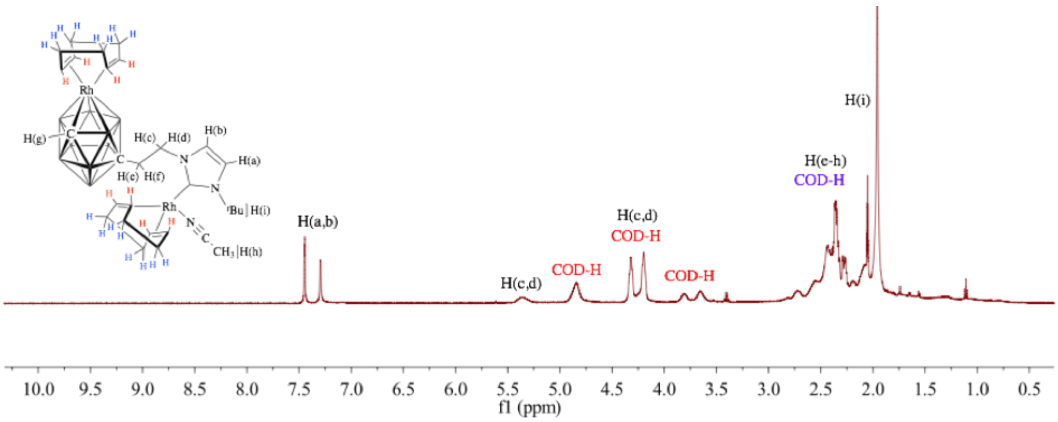


Figure S9. ^{1}H NMR spectrum (acetone-d$_6$, 500 MHz) of complex **4**·MeCN.

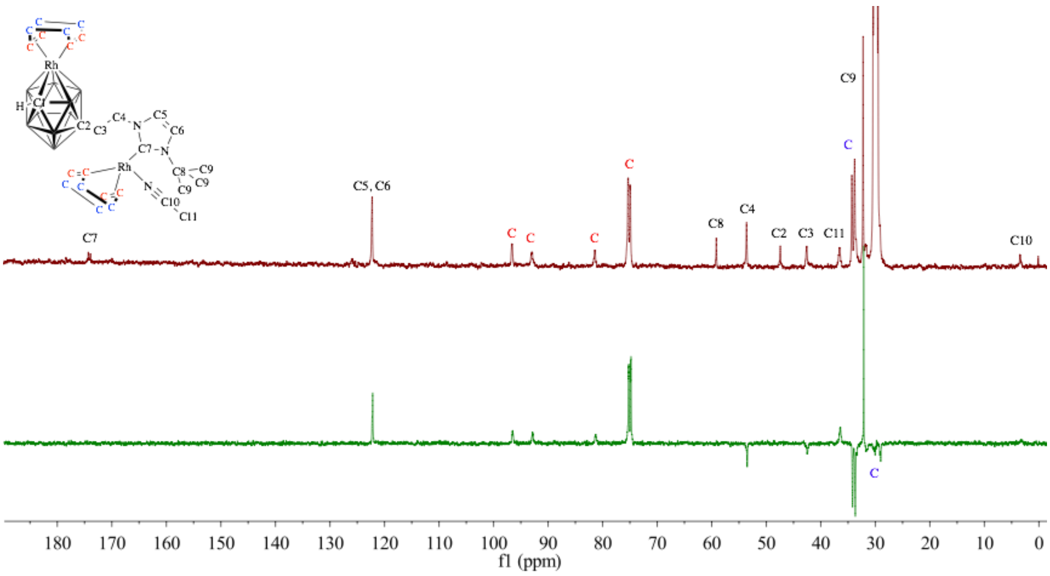


Figure S10. $^{13}C\{^{1}H\}$ NMR (top) and $^{13}C\{^{1}H\}$-DEPT 135 (bottom) spectra (acetone-d$_6$, 126 MHz) of complex **4**·MeCN.

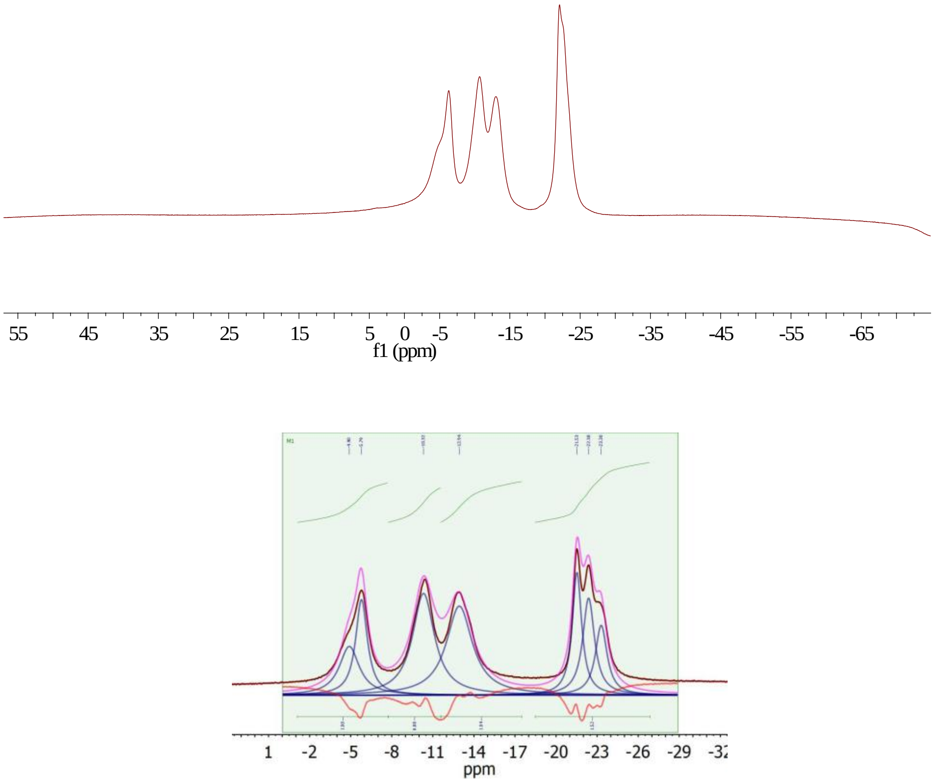


Figure S11. $^{11}B\{^{1}H\}$ NMR spectrum (acetone-d$_6$, 161 MHz) of complex **4**·MeCN.

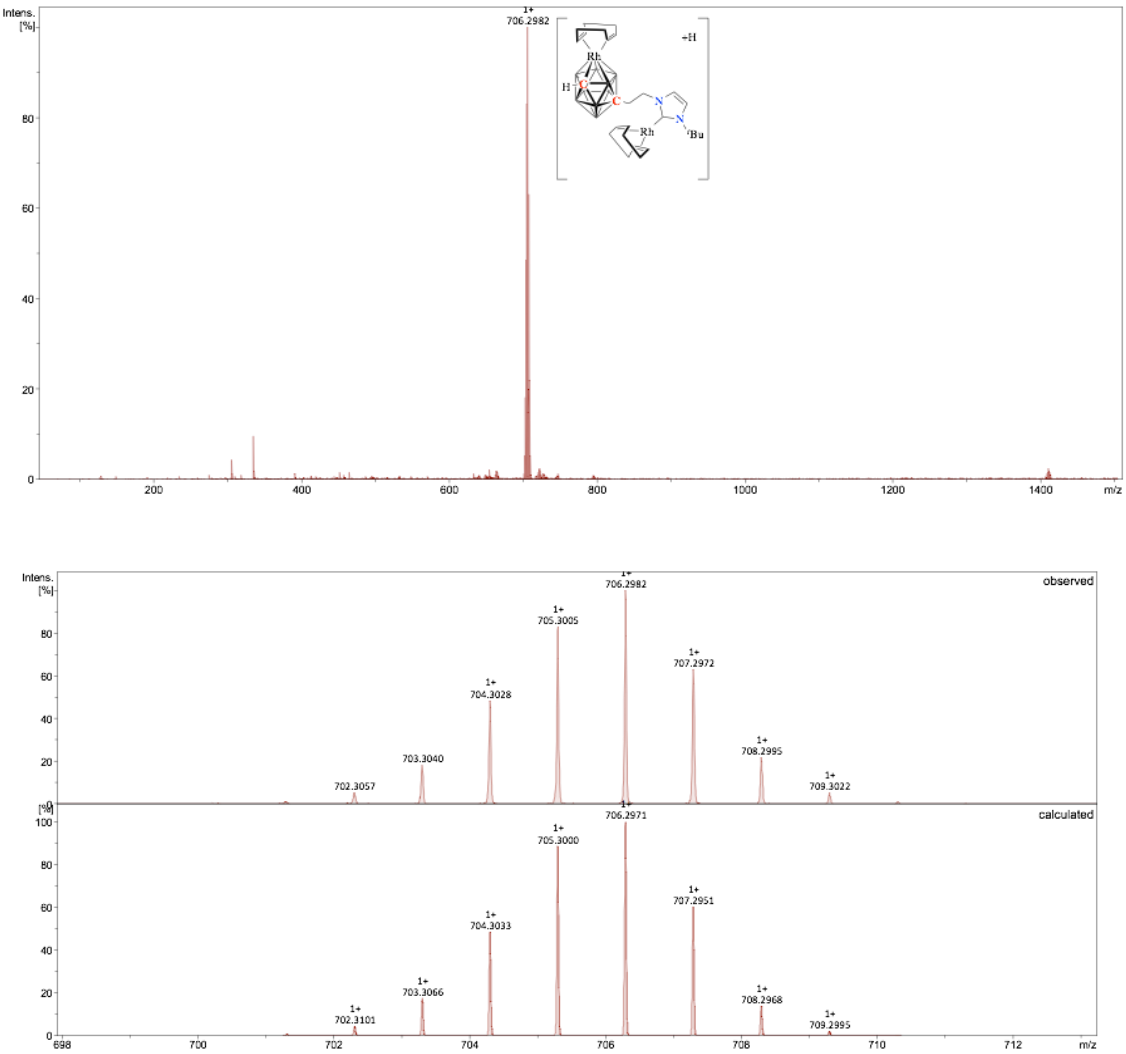
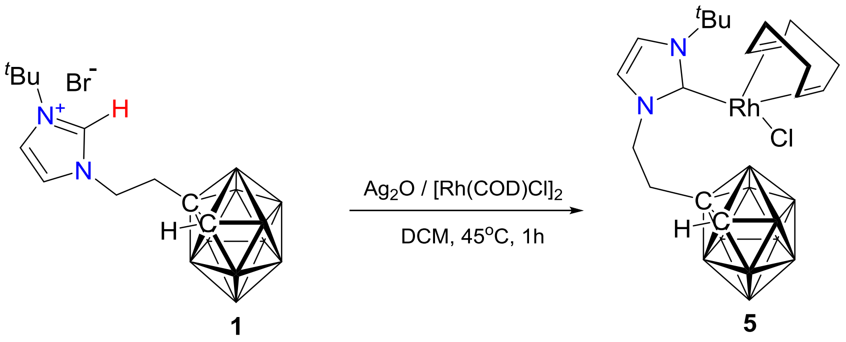


Figure S12. HRMS (ESI$^+$) of complex **4**·MeCN (top). Calculated isotope pattern (bottom) and observed (middle) for [M-MeCN+H]$^+$**.**

Synthesis of complex 5



Imidazolium *closo*-carborane bromide **1** (100 mg, 0.27 mmol), Ag$_2$O (62 mg, 0.27 mmol), [RhCODCl]$_2$ (67 mg, 0.14 mmol), several activated 4Å molecular sieves and anhydrous dichloromethane (5 mL) were added to an ampoule and heated at 45 $^{\circ}$C for 1 hour. The solution was filtered through celite and the solvent removed *in vacuo* to yield a yellow crystalline solid. The solid was washed with hexane (3 × 10 mL) and dried *in vacuo* to afford the product in 74 % yield (108 mg, 0.20 mmol). Crystals suitable for X-ray diffraction analysis were grown by the slow evaporation of a concentrated solution of the product in dichloromethane.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.02 (d, J = 2.1 Hz, 1H, NC*H*), 6.84 (d, J = 2.1 Hz, 1H, NC*H*), 5.98 (td, J = 12.6, 5.0 Hz, 1H, CH$_2$), 5.00 (td, J = 8.0, 3.4 Hz, 1H, COD-C*H*), 4.91 (dd, J = 14.2, 7.4 Hz, 1H, COD-C*H*), 4.17 (br., 1H, carborane cage C*H*), 4.11 (td, J = 12.6, 5.0 Hz, 1H, C*H*$_2$), 3.39 (m, 1H, C*H*$_2$), 3.24 (m, 2H, COD-C*H*), 2.61 (m, 1H, C*H*$_2$), 2.49 (m, 2H, COD-C*H*$_2$), 2.35 (m, 2H, COD-C*H*$_2$), 2.02 (m, 2H, COD-C*H*$_2$) 1.94 (s, 9H, C(C*H*$_3$)$_3$), 1.80 (m, 2H, COD-C*H*$_2$). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 181.7 (d, ^{1}J$_{\text{Rh-C}}$ = 50.4 Hz, N*C*N), 120.6 (N*C*C), 120.0 (NC*C*), 97.3 (d, J$_{\text{Rh-C}}$ = 7.6 Hz, COD-*C*H), 95.5 (d, ^{1}J$_{\text{Rh-C}}$ = 7.6 Hz, COD-*C*H), 73.4 (carborane cage quaternary *C*), 71.4 (d, ^{1}J$_{\text{Rh-C}}$ = 15.1 Hz, COD-*C*H), 67.4 (d, ^{1}J$_{\text{Rh-C}}$ = 15.1 Hz, COD-*C*H), 63.6 (carborane cage *C*), 58.9 (($\underline{\text{C}}$CH$_3$)$_3$), 51.5 (*C*H$_2$), 38.0 (*C*H$_2$), 34.1 (COD-

CH_2), 32.4 ((*C*H_3)$_3$), 31.5 (COD-*C*H_2), 29.8 (COD-*C*H_2), 28.2 (COD-*C*H_2). $^{11}B\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ -2.5 (1B), -5.4 (1B), -9.2 (2B), -11.0 (2B), -12.9 (4B). HRMS (ESI$^+$): *m/z* 505.3112 $[C_{19}H_{38}B_{10}N_2Rh]^+$, calcd. [M-Cl]$^+$ 505.3097. Anal. calcd. for $C_{19}H_{38}B_{10}N_2ClRh$: C, 42.18; H, 7.08; N, 5.18. Found: C, 42.40; H, 6.90; N, 5.50.

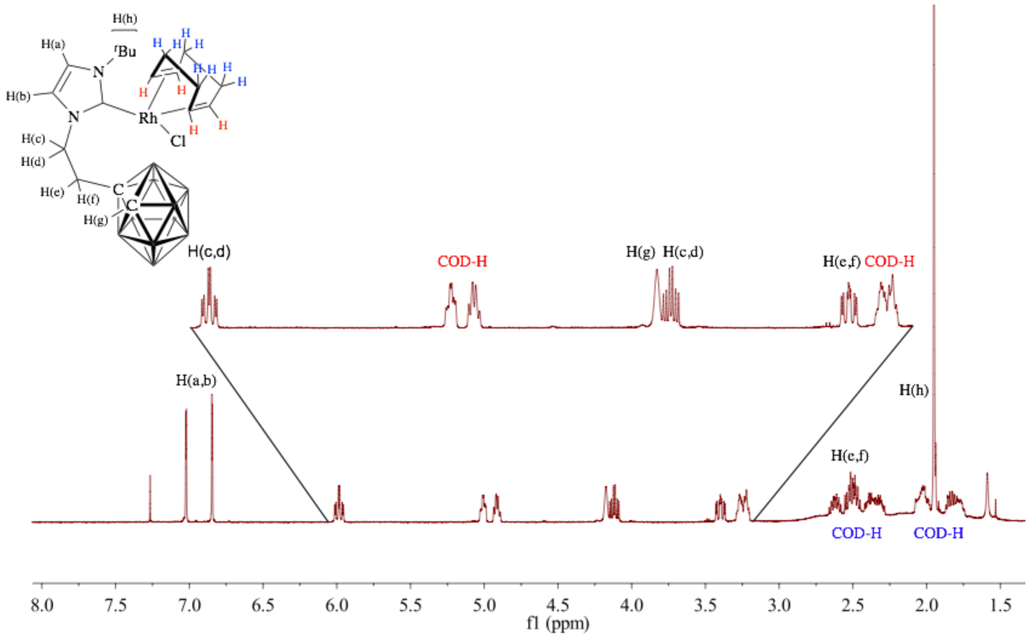


Figure S13. ^1H NMR spectrum ($CDCl_3$, 500 MHz) of complex **5**.

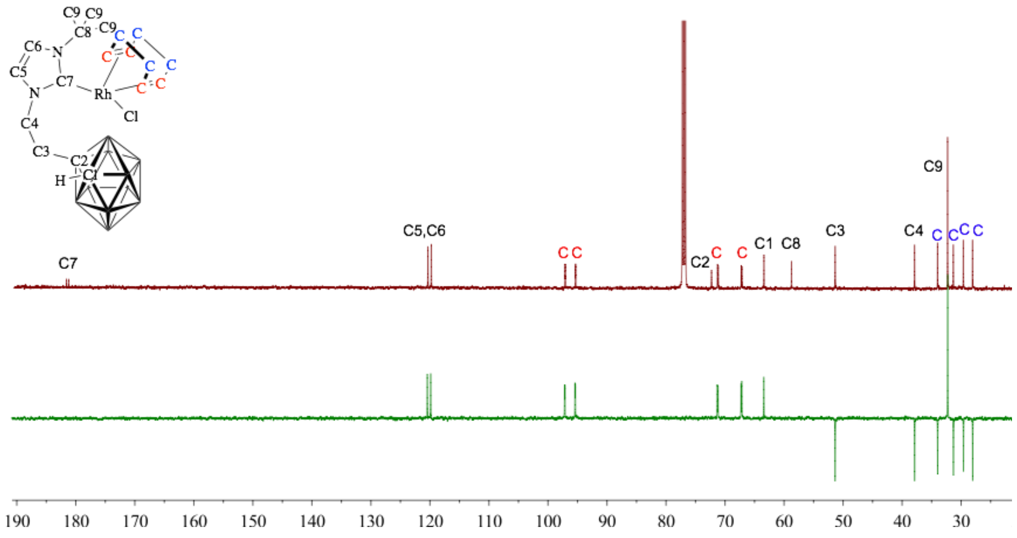


Figure S14. $^{13}C\{^1H\}$ NMR (top) and $^{13}C\{^1H\}$-DEPT 135 (bottom) spectra ($CDCl_3$, 126 MHz) of complex **5**.

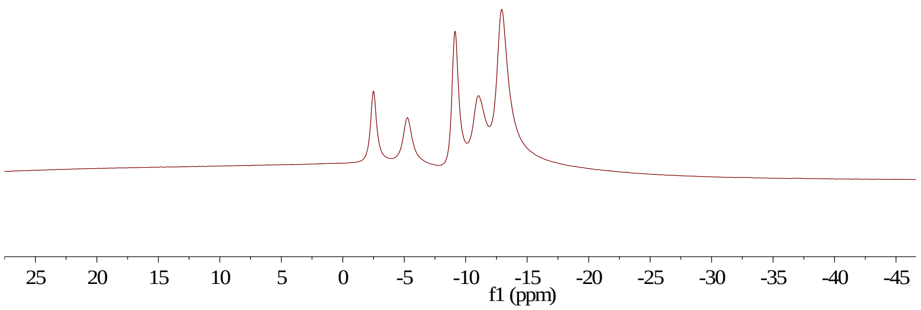


Figure S15. $^{11}B\{^{1}H\}$ NMR spectrum ($CDCl_3$, 161 MHz) of complex **5**.

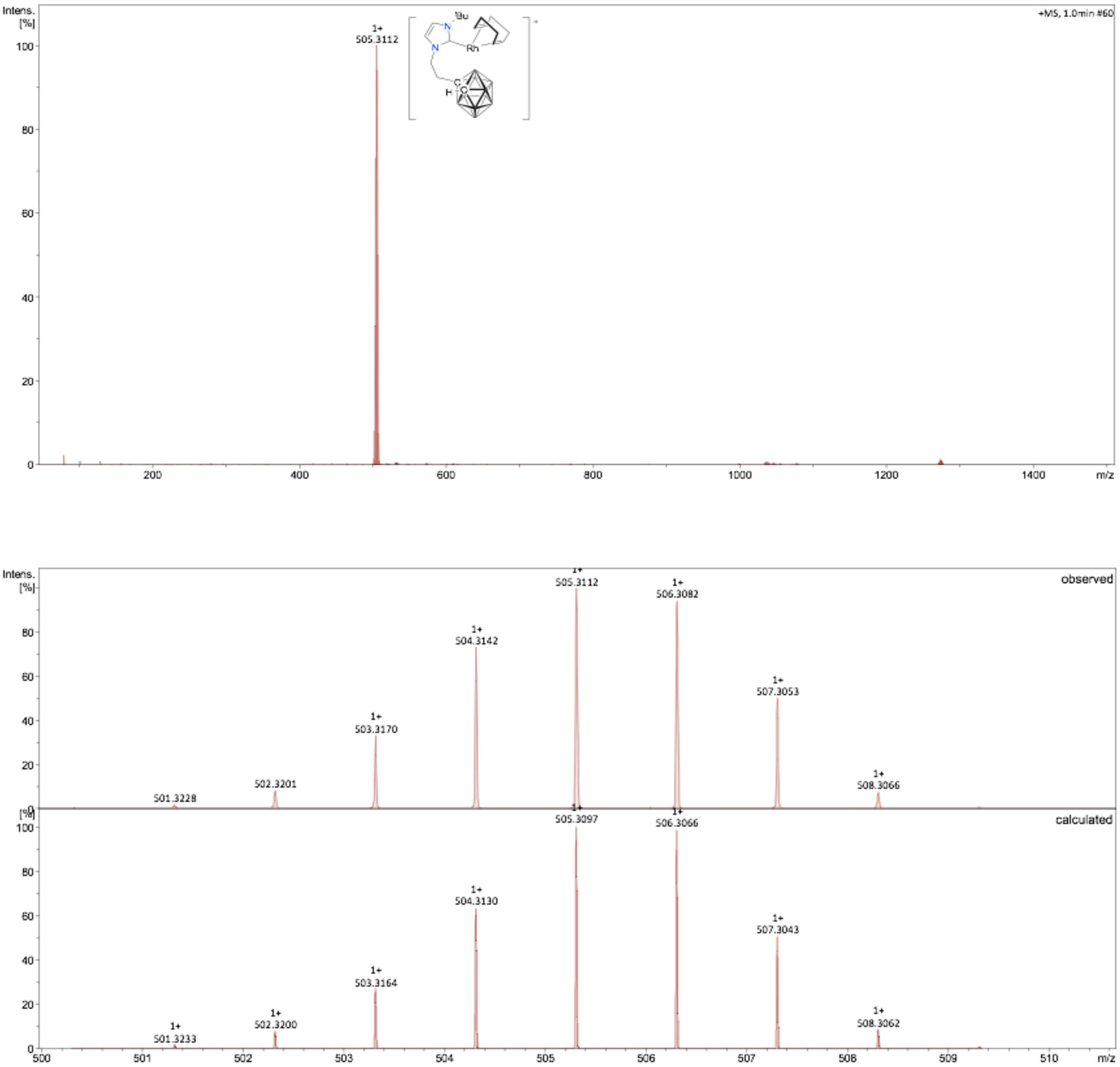
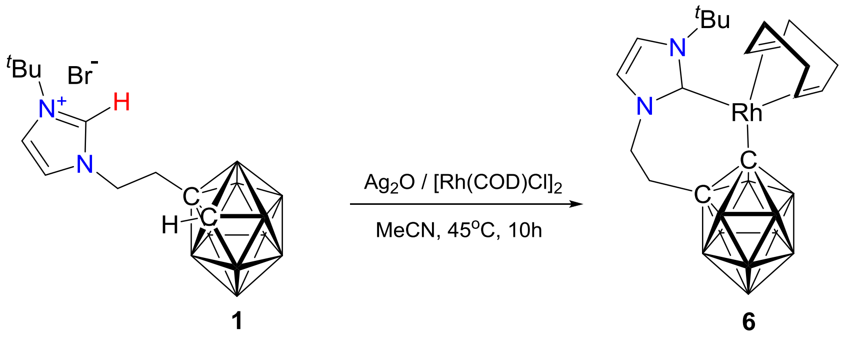


Figure S16. HRMS (ESI^{+}) of complex **5** (top). Calculated isotope pattern (bottom) and observed (middle) for $[M\text{-}Cl]^{+}$**.**

Synthesis of complex 6



Imidazolium bromide **1** (200 mg, 0.53 mmol), Ag_2O (123 mg, 0.53 mmol), $[RhCODCl]_2$ (134 mg, 0.27 mmol), several activated 4Å molecular sieves and anhydrous acetonitrile (10 mL) were added to an ampoule and heated at 45 °C for 10 hours. The solution was filtered through celite and the solvent removed *in vacuo* to yield a yellow crystalline solid. This was washed with hexane (3 × 10 mL) and dried *in vacuo* to afford the product in 79 % yield (213 mg, 0.42 mmol). Crystals suitable for X-ray diffraction analysis were grown by the slow evaporation of a concentrated solution of the product in dichloromethane.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 (d, J = 2.0 Hz, 1H, NC*H*), 6.83 (d, J = 2.0 Hz, 1H, NC*H*), 6.13 (td, J = 13.8, 1.85 Hz, 1H, CH_2), 4.83 (t, J = 7.8 Hz, 1H, COD-C*H*), 4.43 (dd, J = 15.3, 7.8 Hz, 1H, COD-C*H*), 3.90 (dt, J = 13.8, 3.45 Hz, 1H, CH_2), 3.82 (t, J = 7.2 Hz, 1H, COD-C*H*), 3.21 (m, 1H, COD-C*H*), 2.75 (m, 1H, CH_2), 2.58 (m, 1H, CH_2), 2.46 (m, 2H, COD-CH_2), 2.16 (m, 4H, COD-CH_2), 1.95 (s, 9H, $(CCH_3)_3$), 1.75 (m, 2H, COD-CH_2). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 183.2 (d, $^1J_{Rh\text{-}C}$ = 52.9 Hz, N*C*N), 121.9 (N*C*C), 119.2 (NC*C*), 95.7 (d, $^1J_{Rh\text{-}C}$ = 7.6 Hz, COD-*C*H), 95.0 (d, $^1J_{Rh\text{-}C}$ = 7.6 Hz, COD-*C*H), 84.5 (d, $^1J_{Rh\text{-}C}$ = 51.7 Hz, carborane cage C), 81.8 (d, $^1J_{Rh\text{-}C}$ = 12.6 Hz, COD-*C*H), 79.4 (carborane cage quaternary C), 70.6 (d, $^1J_{Rh\text{-}C}$ = 8.8 Hz, COD-*C*H), 58.3 ($(\underline{C}CH_3)_3$), 49.3 (*C*H_2), 41.0 (*C*H_2), 35.0 (COD-*C*H_2), 33.1 (COD-*C*H_2), 32.0 ($((CH_3)_3)$), 28.4 (COD-*C*H_2), 27.3 (COD-*C*H_2). ^{11}B{^{1}H} NMR (161 MHz,

$CDCl_3$): δ -4.2 (1B), -5.0 (1B), -6.1 (2B), -6.6 (1B), -8.3 (1B), -9.0 (1B), -9.84 (2B), -10.8 (1B). HRMS (ESI$^+$): *m/z* 505.3089 [$C_{19}H_{38}B_{10}N_2Rh$]$^+$, calcd. [M+H]$^+$ 505.3097. Anal. calcd. for $C_{19}H_{37}B_{10}N_2Rh.0.3(H_2O)$: C, 44.44; H, 7.46; N, 5.46. Found: C, 44.35 ; H, 7.47; N, 5.10.

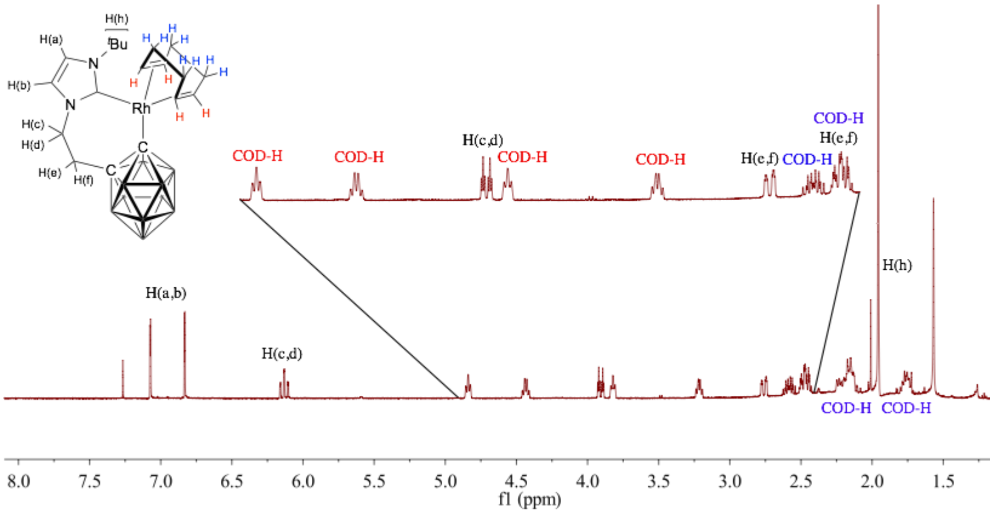


Figure S17. ^1H NMR spectrum ($CDCl_3$, 500 MHz) of complex **6**.

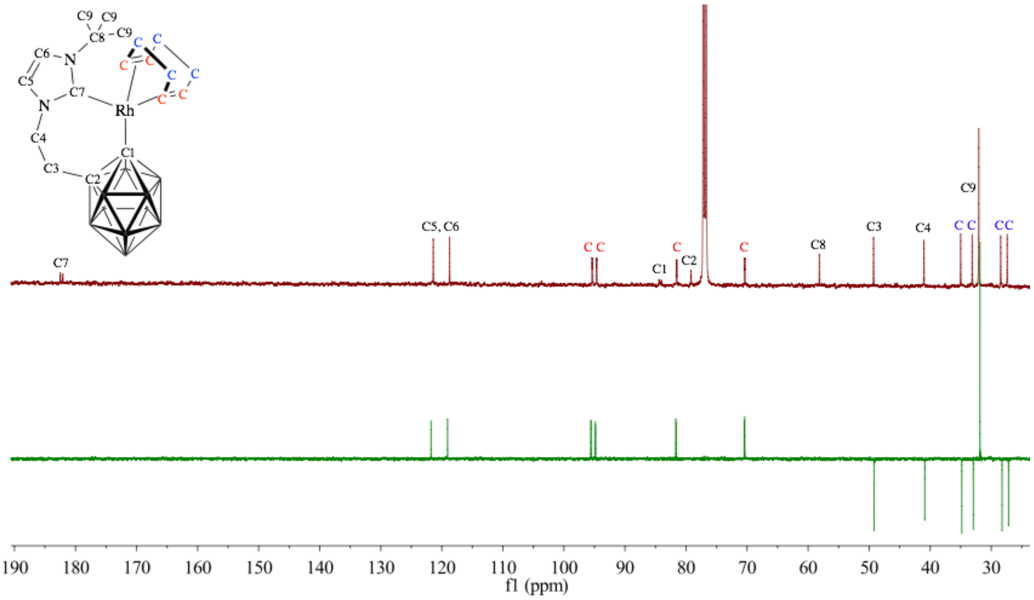


Figure S18. $^{13}C\{^1H\}$ and 135 DEPT NMR spectra ($CDCl_3$, 126 MHz) of complex **6**.

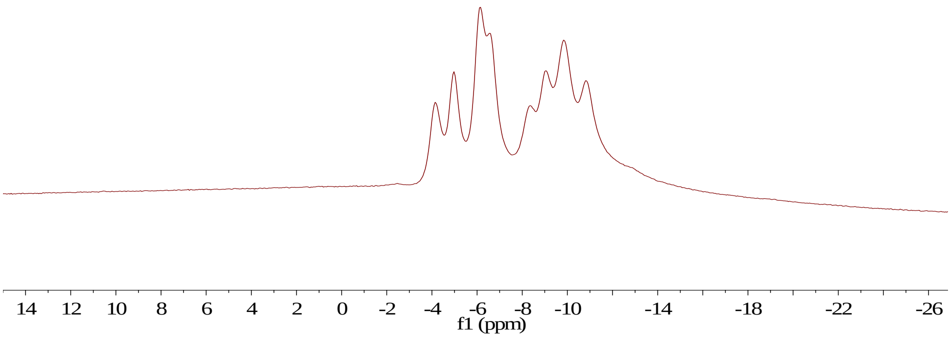


Figure S19. $^{11}B\{^{1}H\}$ NMR spectrum ($CDCl_3$, 161 MHz) of complex **6**.

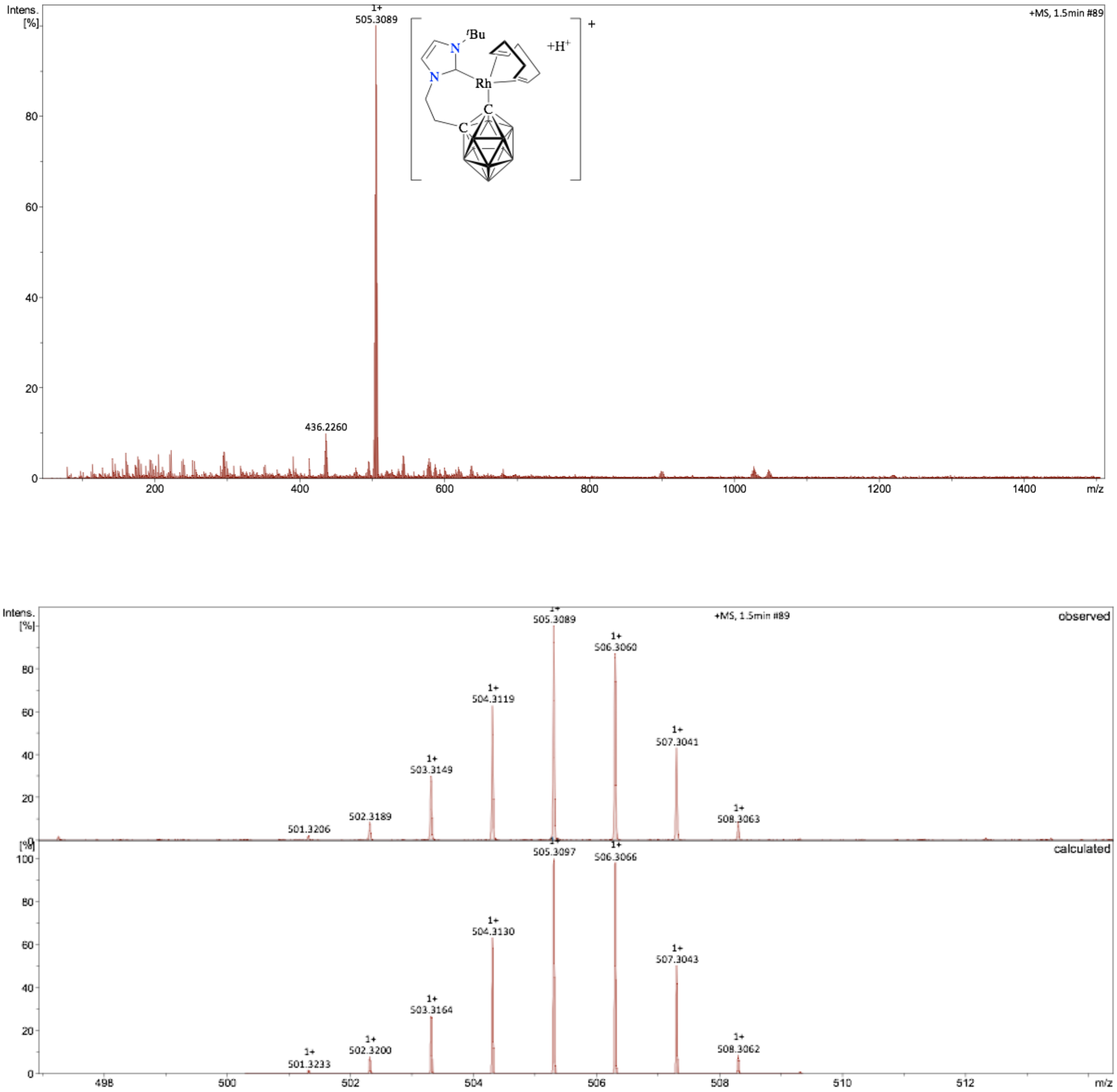


Figure S20. HRMS (ESI^+) of complex **6** (top). Calculated isotope pattern (bottom) and observed (middle) for $[M+H]^+$**.**

Crystallographic Data

General Considerations

X-ray diffraction data were collected on an Agilent SuperNova diffractometer fitted with an Atlas CCD detector with Mo- Kα radiation (λ = 0.71073 Å). Crystals were mounted under oil on nylon loops. Data sets were corrected for absorption using a multiscan method, and the structures were solved by direct methods using SHELXS-2008 and refined by full-matrix least squares on F2 using ShelXL-2008, interfaced through the program OLEX.[5,6] Molecular graphics for all structures were generated using POV-RAY in the X-Seed program. The carboranyl carbons were identified using the Vertex-to-Centroid Distance (VCD) Method.[7]

Crystallographic data has been deposited in the Cambridge Crystallographic Data Centre: CCDC 1444072-1444078.

Imidazolium bromide salt 1

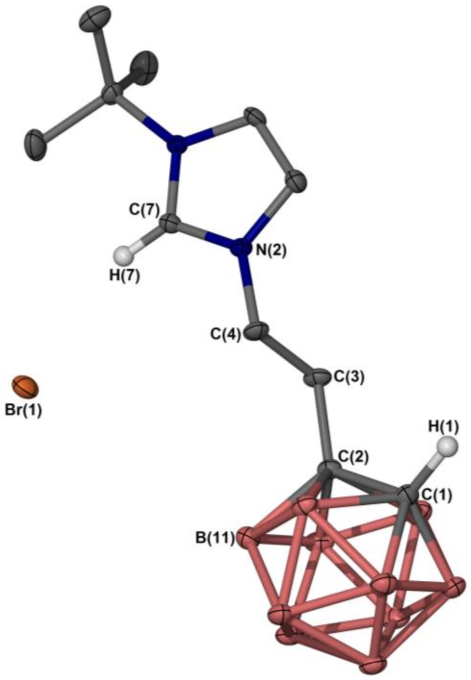


Figure S22. Molecular structure of imidazolium bromide **1**.

Table S1. Crystal data and structure refinement for imidazolium bromide salt **1**.

Identification code	Imidazolium bromide salt **1**
Empirical formula	$C_{12}H_{28.5}B_{10}BrN_{2.5}$
Formula weight	395.88
Temperature/K	119.99(14)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.6257(3)
b/Å	25.7293(10)
c/Å	10.2076(6)
α/°	90.00
β/°	92.279(4)
γ/°	90.00
Volume/Å^3	2001.19(15)
Z	4
ρ_{calc}g/cm^3	1.314
μ/mm^{-1}	2.053
F(000)	812.0
Crystal size/mm^3	0.57 × 0.13 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.22 to 56.56
Index ranges	$-10 \leq h \leq 10$, $-34 \leq k \leq 34$, $-13 \leq l \leq 13$
Reflections collected	13430
Independent reflections	4963 [R_{int} = 0.0400, R_{sigma} = 0.0517]
Data/restraints/parameters	4963/2/232
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0422, wR_2 = 0.0911
Final R indexes [all data]	R_1 = 0.0575, wR_2 = 0.0969
Largest diff. peak/hole / e Å^{-3}	0.78/-0.68

Imidazolium-*nido*-carborane zwitterion 2

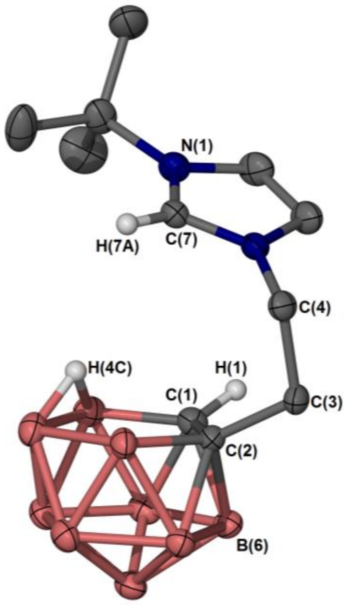


Figure S23. Molecular structure of imidazolium-*nido*-carborane zwitterion **2**.

Table S2. Crystal data and structure refinement for imidazolium-*nido*-carborane zwitterion **2**

Identification code	Imidazolium-*nido*-carborane zwitterion **2**
Empirical formula	$C_{11}H_{27}B_9N_2$
Formula weight	284.64
Temperature/K	150.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.6541(15)
b/Å	13.7503(14)
c/Å	18.3750(18)
α/°	90.00
β/°	115.101(5)
γ/°	90.00
Volume/Å^3	3581.7(6)
Z	8
ρ_{calc}g/cm^3	1.056
μ/mm^{-1}	0.054
F(000)	1216.0
Crystal size/mm^3	0.51 × 0.41 × 0.23

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.84 to 58.72
Index ranges	$-21 \leq h \leq 20$, $-18 \leq k \leq 18$, $-23 \leq l \leq 25$
Reflections collected	58101
Independent reflections	9836 [R_{int} = 0.0408, R_{sigma} = 0.0307]
Data/restraints/parameters	9836/0/613
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0462, wR_2 = 0.1191
Final R indexes [all data]	R_1 = 0.0605, wR_2 = 0.1306
Largest diff. peak/hole / e Å^{-3}	0.38/-0.20

Complex 3·MeCN

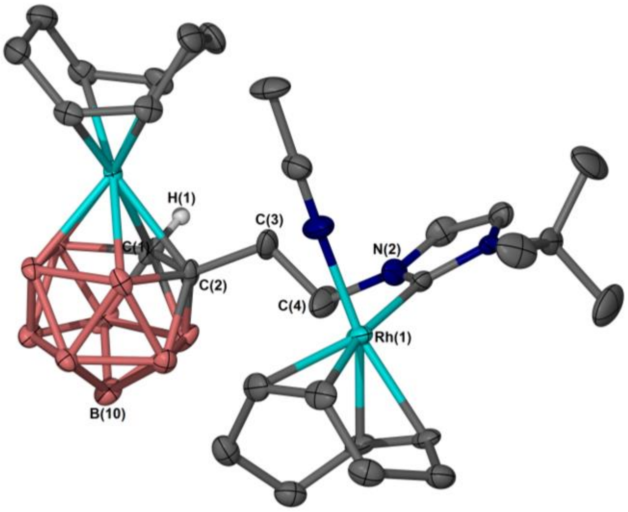


Figure S24. Molecular structure of complex **3**·MeCN.

Table S3. Crystal data and structure refinement for complex **3**·MeCN.

Identification code	Complex **3**·MeCN
Empirical formula	$C_{31}H_{55}B_9N_4Rh_2$
Formula weight	786.90
Temperature/K	120.00(11)
Crystal system	orthorhombic
Space group	Pbca
a/Å	11.9249(5)
b/Å	23.7834(11)
c/Å	25.2349(11)

α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	7157.0(6)
Z	8
ρ_{calc}g/cm^3	1.461
μ/mm^{-1}	0.951
F(000)	3232.0
Crystal size/mm^3	0.19 × 0.13 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.46 to 56.56
Index ranges	$-15 \leq h \leq 14$, $-31 \leq k \leq 30$, $-32 \leq l \leq 33$
Reflections collected	43820
Independent reflections	8855 [R_{int} = 0.0852, R_{sigma} = 0.0673]
Data/restraints/parameters	8855/0/420
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0505, wR_2 = 0.0905
Final R indexes [all data]	R_1 = 0.0741, wR_2 = 0.0997
Largest diff. peak/hole / e Å^{-3}	2.15/-1.55

Complex 4·MeCN

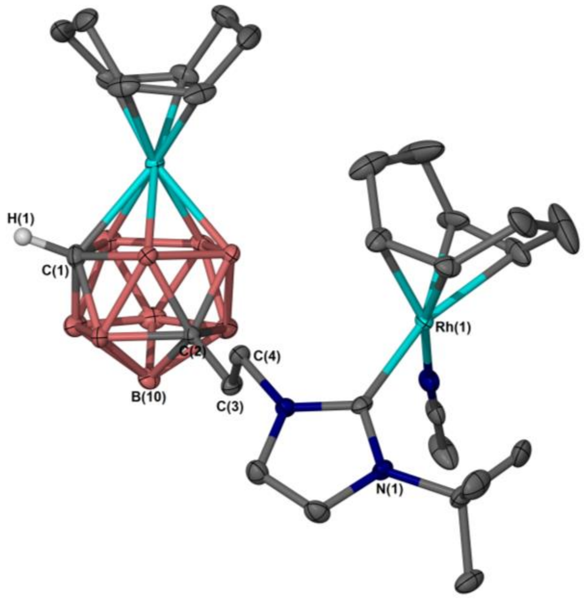


Figure S25. Molecular structure of complex **4**·MeCN.

Table S4. Crystal data and structure refinement for complex **4**·MeCN.

Identification code	Complex **4**·MeCN
Empirical formula	$C_{32}H_{58}B_9N_3ORh_2$
Formula weight	803.92
Temperature/K	120.01(11)
Crystal system	triclinic
Space group	P-1
a/Å	11.1781(5)
b/Å	12.5631(5)
c/Å	14.8258(7)
α/°	111.322(4)
β/°	92.917(4)
γ/°	105.326(4)
Volume/Å^3	1845.33(15)
Z	2
ρ_{calc}g/cm^3	1.447
μ/mm^{-1}	0.925
F(000)	828.0
Crystal size/mm^3	0.19 × 0.13 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.98 to 56.56
Index ranges	$-14 \leq h \leq 14$, $-13 \leq k \leq 16$, $-19 \leq l \leq 19$
Reflections collected	21395
Independent reflections	9142 [R_{int} = 0.0440, R_{sigma} = 0.0615]
Data/restraints/parameters	9142/0/430
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0387, wR_2 = 0.0791
Final R indexes [all data]	R_1 = 0.0490, wR_2 = 0.0855
Largest diff. peak/hole / e Å^{-3}	1.00/-0.94

Complex $\mathbf{4_2}$

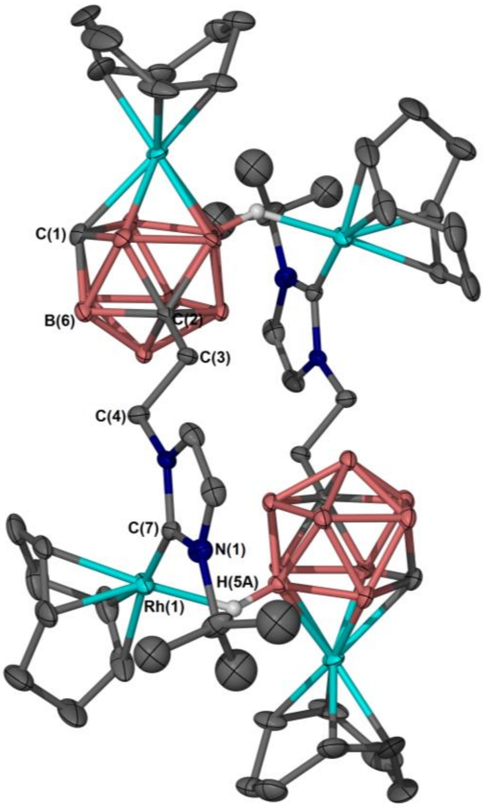


Figure S26. Molecular structure of complex $\mathbf{4_2}$.

Table S5. Crystal data and structure refinement for complex $\mathbf{4_2}$.

Identification code	Complex $\mathbf{4_2}$
Empirical formula	$C_{29}H_{54}B_9N_2O_{0.5}Rh_2$
Formula weight	741.85
Temperature/K	120.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.7898(6)
b/Å	11.4212(12)
c/Å	14.8764(14)
α/°	71.730(9)
β/°	83.274(6)
γ/°	69.415(8)
Volume/Å^3	1629.6(2)
Z	2

ρ_{calc}g/cm^3	1.512
μ/mm^{-1}	1.039
F(000)	762.0
Crystal size/mm^3	0.48 × 0.27 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.4 to 56.56
Index ranges	$-13 \leq h \leq 14$, $-13 \leq k \leq 15$, $-19 \leq l \leq 19$
Reflections collected	19367
Independent reflections	8069 [R_{int} = 0.0422, R_{sigma} = 0.0627]
Data/restraints/parameters	8069/104/400
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0511, wR_2 = 0.1046
Final R indexes [all data]	R_1 = 0.0760, wR_2 = 0.1168
Largest diff. peak/hole / e Å^{-3}	1.55/-1.40

Complex 5

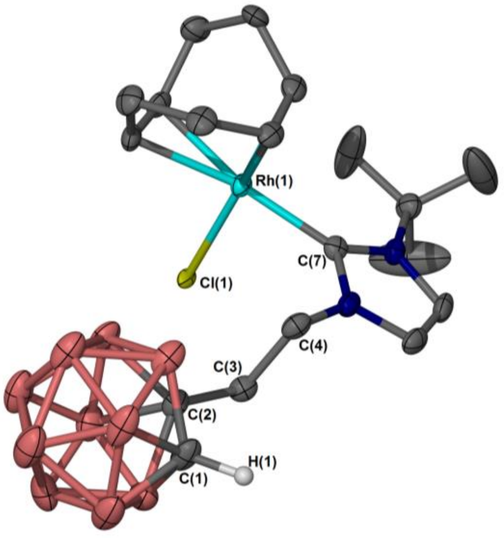


Figure S27. Molecular structure of complex **5**.

Table S6. Crystal data and structure refinement for complex **5**.

Identification code	Complex **5**
Empirical formula	$C_{19}H_{38}B_{10}ClN_2Rh$
Formula weight	540.97
Temperature/K	290.87(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.3894(4)
b/Å	15.3629(5)
c/Å	13.6908(4)
α/°	90.00
β/°	93.441(3)
γ/°	90.00
Volume/Å^3	2601.17(15)
Z	4
ρ_{calc}g/cm^3	1.381
μ/mm^{-1}	0.771
F(000)	1112.0
Crystal size/mm^3	0.14 × 0.08 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.24 to 62.42
Index ranges	$-17 \le h \le 16$, $-22 \le k \le 21$, $-19 \le l \le 19$
Reflections collected	22805
Independent reflections	7491 [R_{int} = 0.0595, R_{sigma} = 0.0762]
Data/restraints/parameters	7491/0/301
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0537, wR_2 = 0.1173
Final R indexes [all data]	R_1 = 0.0811, wR_2 = 0.1305
Largest diff. peak/hole / e Å^{-3}	1.64/-0.82

Complex 6

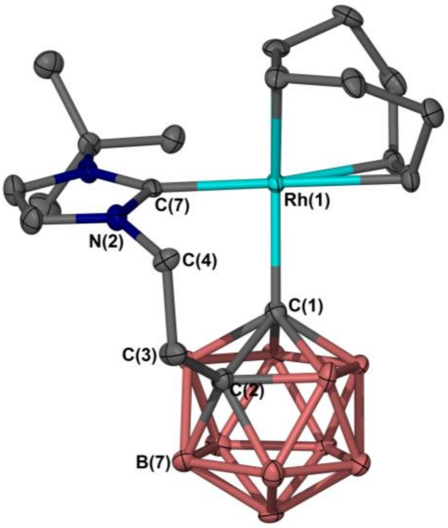


Figure S28. Molecular structure of complex **6**.

Table S7. Crystal data and structure refinement for complex **6**.

Identification code	Complex **6**
Empirical formula	$C_{19}H_{37}B_{10}N_2Rh$
Formula weight	504.52
Temperature/K	119.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.2832(5)
b/Å	10.5283(2)
c/Å	14.1775(4)
α/°	90.00
β/°	113.020(3)
γ/°	90.00
Volume/Å^3	2374.33(10)
Z	4
ρ_{calc}g/cm^3	1.411
μ/mm^{-1}	0.731
F(000)	1040.0
Crystal size/mm^3	0.65 × 0.24 × 0.11

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.12 to 56.56
Index ranges	$-23 \leq h \leq 22$, $-13 \leq k \leq 14$, $-17 \leq l \leq 18$
Reflections collected	20821
Independent reflections	5881 [R_{int} = 0.0891, R_{sigma} = 0.0773]
Data/restraints/parameters	5881/0/282
Goodness-of-fit on F^2	1.100
Final R indexes [I>=2σ (I)]	R_1 = 0.0458, wR_2 = 0.1087
Final R indexes [all data]	R_1 = 0.0581, wR_2 = 0.1230
Largest diff. peak/hole / e Å^{-3}	1.29/-0.65

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