Electronic Supporting Information (ESI)

A d^{10} Ag(I) amine–borane σ–complex and comparison with a d^8 Rh(I) analogue: structures on the η^1 to η^2:η^2 continuum.

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1. Experimental

1.1. General Procedures

All manipulations, unless otherwise stated, were performed under an argon atmosphere using standard Schlenk line and glove-box techniques. Glassware was oven dried at 130 °C overnight and flamed under vacuum prior to use. CH_2Cl_2 and pentane were dried using a Grubbs-type solvent purification system (MBraun SPS-800) and degassed by three successive freeze-pump-thaw cycles.[S1] CD_2Cl_2 and 1,2-$C_6H_4F_2$ (pre-treated with alumina) were dried over CaH_2, vacuum distilled and stored over 3 Å molecular sieves. Na[$BArF_4$],[S2] [Rh(**L1**)Cl][S3] and [$Ag(NCMe)_2$][$BAr^F{}_4$],[S4] were prepared by literature methods. $H_3B{\cdot}NMe_3$ was purchased from Aldrich and sublimed before use (5×10^{-2} Torr, 298 K). NMR spectra were recorded on a Bruker Avance III 500 MHz NMR spectrometer or a Bruker Avance III HD nanobay 400 MHz NMR spectrometer at room temperature. Residual protio solvent was used as reference for ^{1}H spectra in deuterated solvent samples. ^{31}P NMR spectra were externally referenced to 85% H_3PO_4. All chemical shifts (δ) are quoted in ppm and coupling constants (*J*) in Hz. ESI-MS were recorded on a Bruker micrOTOF instrument interfaced with a glove-box.[S5] Elemental microanalyses were performed by Stephen Boyer at London Metropolitan University.

1.2. Syntheses

1: To a solution of **4** (72.6 mg, 0.05 mmol) in dichloromethane (5 ml) was added trimethylamine-borane (3.7 mg, 0.05 mmol) and the solution stirred for 2 h. The solution was filtered through a pad of celite and concentrated under reduced pressure to approx. 1 ml. Pentane (10 ml) was added to precipitate a bright yellow solid which was collected and vacuum dried to give the product (75.1 mg, 98%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.30 (t, 1H, $^{3}J_{HH}$ = 7.7 Hz, Py), 8.22 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, Py), 7.72 (s, 8H, BAr^{F}_{4}), 7.55 (s, 4H, BAr^{F}_{4}), 7.20 (s, 6H, Ar), 2.69 (hept, $^{3}J_{HH}$ = 6.8 Hz, 4H, C*H*$(CH_3)_3$), 2.38 (s, 6H, Me), 2.10 (s, 9H, NMe_3), 1.82 (s, BH_3 observed in ^{1}H{^{11}B} spectrum) 1.18 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_3$), 1.13 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_3$). ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2) δ -6.56 (s, BAr^{F}_{4}), -16.32 (s, $H_3B{\cdot}NMe_3$). ^{19}F NMR (377 MHz, CD_2Cl_2) δ -62.88 (s, BAr^{F}_{4}). HRMS (ESI/QTOF) m/z: [M]+ Calcd for $C_{36}H_{55}BN_4Ag$ 661.3565; Found 661.3619. Elem. anal. Calcd for $C_{68}H_{67}AgB_2F_{24}N_4$: C, 53.53; H, 4.43; N, 3.67. Found C, 53.35; H, 4.28; N, 3.64.

Molecular structure:

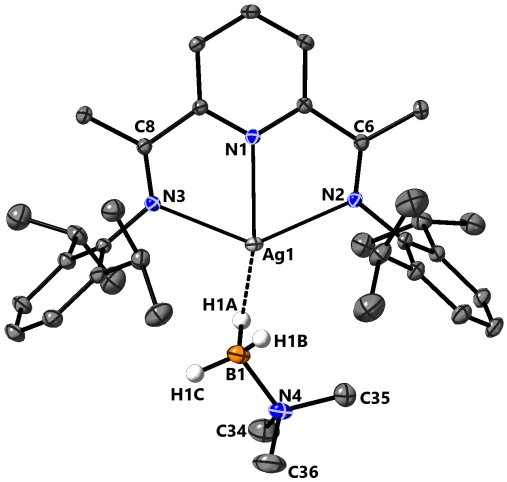


Figure S1. Molecular structure of **1** determined by single crystal X-ray diffraction. BAr^{F}_{4} anion, minor disordered component for the trimethylamino group, and hydrogen atoms are omitted for clarity with exception of H1A, H1B and H1C. Selected bond lengths [Å] and angles [°]: Ag(1)-N(1) 2.3737(13), Ag(1)-N(2) 2.4306(13), Ag(1)-N(3) 2.4303(13), Ag(1)-B(1) 2.458(3), N(4)-B(1) 1.609(3), Ag(1)-H(1A) 2.22(3), Ag(1)-H(1B) 2.01(3), N(1)-B(1) 1.609(3), B(1)-H(1A) 1.07(3), B(1)-H(1B) 1.21(3), B(1)-H(1C) 1.06(4), N(2)-C(6) 1.274(2), N(3)-C(8) 1.273(2), N(1)-Ag(1)-N(2) 66.94(4); N(1)-Ag(1)-N(3) 67.36(4), N(2)-Ag(1)-N(3) 134.14(5), N(1)-Ag(1)-B(1) 171.33(8), N(2)-Ag(1)-B(1) 121.73(8), N(3)-Ag(1)-B(1) 103.98(8), N(4)-B(1)-Ag(1) 134.24(17).

2: To a solution of **5** (31.0 mg, 0.05 mmol) in dichloromethane (10 ml) was added Na[BAr^F_4] (44.3 mg, 0.05 mmol) and $H_3B{\cdot}NMe_3$ (3.6 mg, 0.05 mmol) and the mixture stirred for 2 h. The dark green solution was filtered by cannula to remove NaCl, concentrated under reduced pressure to approx. 1 ml and pentane (20 ml) added to precipitate a dark green solid which was washed with pentane and vacuum dried to give the product (59.8 mg, 79%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.32 (t, $^3J_{HH}$ = 8.0 Hz, 1H, Py), 7.79 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Py), 7.72 (s, 8H, BAr^F_4), 7.56 (s, 4H, BAr^F_4), 7.33 – 7.16 (m, 6H, Ar), 3.02 (hept, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 2.01 (s, 9H, NMe_3), 1.93 (s, 6H, Me), 1.20 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3)_2$), 1.13 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3)_2$), -1.39 (s, 3H, BH_3 (in the ^{1}H{^{11}B} NMR spectrum this is observed as a doublet $^1J_{RhH}$ = 15.1 Hz)). ^{11}B NMR (128 MHz, CD_2Cl_2) δ -4.11 (s, BH_3), -6.61 (s, BAr^F_4). ^{19}F NMR (377 MHz, CD_2Cl_2) δ -62.88 (s, BAr^F_4). HRMS (ESI/QTOF) m/z: [M]+ Calcd for $C_{36}H_{55}BN_4Rh$ 657.3576; Found 657.3581. Elem. anal. Calcd for $C_{68}H_{67}B_2F_{24}N_4Rh$: C, 53.71; H, 4.44; N, 3.68. Found: C, 53.42; H, 4.19; N, 3.44.

Molecular structure:

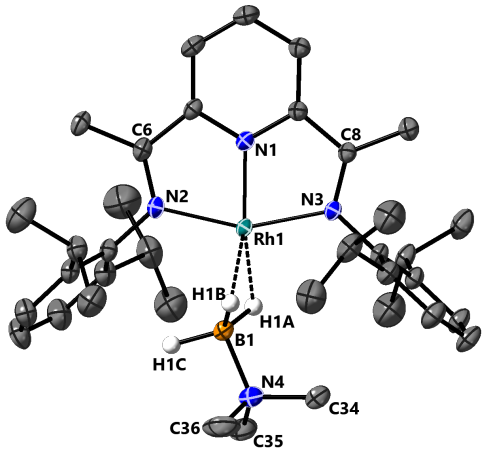


Figure S2. Molecular structure of **2** determined by single crystal X-ray diffraction. BAr^F_4 anion, disordered dichloromethane and *n*-pentane solvent molecules of crystallisation, minor disordered component for the borane trimethylamine ligand, and hydrogen atoms are omitted for clarity with exception of H1A, H1B and H1C. Selected bond lengths [Å] and angles [°]: Rh(1)-N(1) 1.910(2), Rh(1)-N(2) 2.061(2), Rh(1)-N(3) 2.050(2), Rh(1)-B(1) 2.306(5), Rh(1)-H(1A) 1.97(4), Rh(1)-H(1B) 1.93(4), N(4)-B(1) 1.588(8), B(1)-H(1A) 1.11(4), B(1)-H(1B) 1.14(4), B(1)-H(1C) 1.19(3), N(2)-C(6) 1.306(4), N(3)-C(8) 1.313(3), N(1)-Rh(1)-N(2) 78.16(9), N(1)-Rh(1)-N(3) 78.60(9), N(1)-Rh(1)-B(1) 169.12(15), N(2)-Rh(1)-B(1) 91.21(15), N(3)-Rh(1)-N(2) 156.76(9), N(3)-Rh(1)-B(1) 112.02(15).

3: To a solution of 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl]pyridine[S6] (241.0 mg, 0.5 mmol) in dichloromethane (10 ml) was added AgOTf (128.5 mg, 0.5 mmol) and the solution stirred in the dark for 1 h. The bright yellow solution was filtered through a pad of celite, concentrated under reduced pressure to approx. 1 ml and pentane (10 ml) added to precipitate a bright yellow solid which was collected and vacuum dried to give the product (339.1 mg, 92%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.36 – 8.32 (m, 1H, Py), 8.27 – 8.22 (m, 2H, Py), 7.21 (s, 6H, Ar), 2.76 (hept, $^{3}J_{HH}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_3$), 2.37 (s, 6H, Me), 1.18 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_3$), 1.14 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_3$). ^{19}F NMR (377 MHz, CD_2Cl_2) δ -78.50 (s, OTf). HRMS (ESI/QTOF) m/z: [M]+ Calcd for $C_{33}H_{43}N_3Ag$ 588.2502; Found 588.2555. Elem. anal. Calcd for $C_{34}H_{43}AgF_3N_3O_3S$: C, 55.29; H 5.87; N, 5.69. Found C, 55.15; H, 5.83; N 5.63.

Molecular structure:

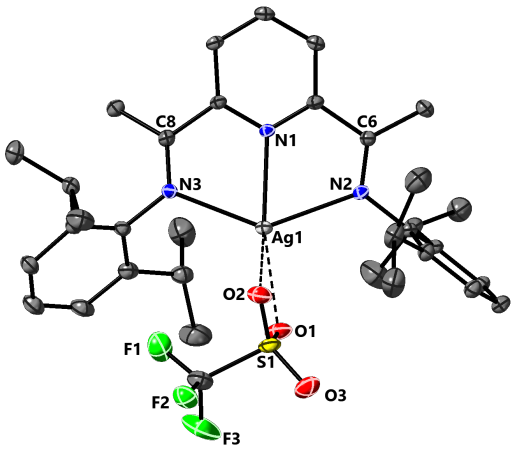


Figure S3. Molecular structure of **3** determined by single crystal X-ray diffraction. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ag(1)-O(1) 2.451(3), Ag(1)-O(2) 2.596(4), Ag(1)-N(1) 2.315(3), Ag(1)-N(2) 2.419(3), Ag(1)-N(3) 2.441(3), O(1)-Ag(1)-O(2) 56.78(11), N(1)-Ag(1)-O(1) 162.55(11), N(1)-Ag(1)-O(2) 138.38(11), N(1)-Ag(1)-N(2) 68.94(10), N(1)-Ag(1)-N(3) 68.85(10), N(2)-Ag(1)-O(1) 102.04(12), N(2)-Ag(1)-O(20 102.19(12), N(2)-Ag(1)-N(3) 137.58(10), N(3)-Ag(1)-O(1) 117.36(12), N(3)-Ag(1)-O(2) 111.90(13).

4: To a solution of **3** (73.7 mg, 0.1 mmol) in dichloromethane (10 ml) was added $NaBAr^F_4$ (88.6 mg, 0.1 mmol) and the solution stirred overnight during which time a white precipitate formed. The bright yellow solution was filtered by cannula and concentrated under reduced pressure to approx. 1 ml. Pentane was added to precipitate a bright yellow solid which was collected and vacuum dried to give the product (129.1 mg, 89%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.34 – 8.30 (m, 1H, Py), 8.25 – 8.23 (m, 2H, Py), 7.72 (s, 8H, BAr^F_4), 7.55 (s, 4H, BAr^F_4), 7.24 (s, 6H, Ar), 2.68 (hept, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*$(CH_3)_3$), 2.42 (s, 6H, Me), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_3$). ^{11}B NMR (128 MHz, CD_2Cl_2) δ -6.63 (s, BAr^F_4). ^{19}F NMR (377 MHz, CD_2Cl_2) δ -62.88 (s, BAr^F_4). HRMS (ESI/QTOF) m/z: [M]+ Calcd for $C_{33}H_{43}N_3Ag$ 588.2502; Found 588.2559. Elem. anal. Calcd for $C_{65}H_{55}AgBF_{24}N_3$: C, 53.74; H, 3.82; N, 2.89. Found C, 53.59; H, 3.74; N, 2.87.

Molecular Structure:

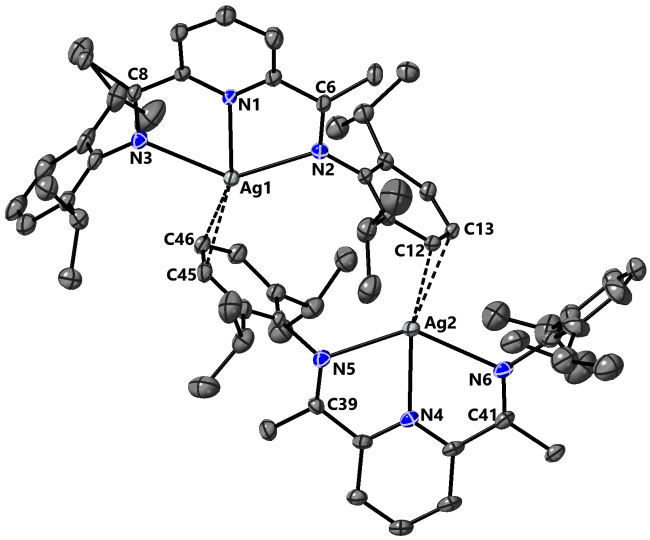


Figure S4. Molecular structure of **4** determined by single crystal X-ray diffraction showing only the dimeric arrangement containing Ag(1) and Ag(2). BAr^F_4 anions, *n*-hexane solvent molecule from crystallisation and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ag(1)-N(1) 2.347(5), Ag(1)-N(2) 2.413(5), Ag(1)-N(3) 2.511(5), Ag(1)-C(45) 2.525(7), Ag(1)-C(46) 2.571(7), Ag(2)-N(4) 2.319(5), Ag(2)-N(5) 2.421(5), Ag(2)-N(6) 2.576(5), Ag(2)-C(12) 2.439(6), Ag(2)-C(13) 2.623(6), N(1)-Ag(1)-N(2) 68.63(16), N(1)-Ag(1)-N(3) 67.37(16), N(1)-Ag(1)-C(45) 157.8(2), N(1)-Ag(1)-C(46) 155.4(2), N(2)-Ag(1)-N(3) 135.96(17), N(2)-Ag(1)-C(45) 125.19(19), N(2)-Ag(1)-C(46) 129.7(2), N(3)-Ag(1)-C(45) 97.38(19), N(3)-Ag(1)-C(46) 92.10(19), C(45)-Ag(1)-C(46) 31.2(3), N(4)-Ag(2)-N(5) 69.74(17), N(4)-Ag(2)-N(6) 66.62(17), N(4)-Ag(2)-C(12) 157.29(19), N(4)-Ag(2)-C(13) 153.94(19), N(5)-Ag(2)-N(6) 136.28(17), N(5)-Ag(2)-C(12) 125.10(18), N(5)-Ag(2)-C(13) 129.96(18), N(6)-Ag(2)-C(13) 91.28(18), C(12)-Ag(2)-N(6) 97.33(18), C(12)-Ag(2)-C(13) 31.4(2).

7: Complex **7** formed by addition of a large excess (>1000 equiv.) of MeCN to complex **1**. This complex could be prepared more practically by the following method:

To a solution of 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl]pyridine (48.1 mg, 0.1 mmol) in CH_2Cl_2 (5 ml) was added $[Ag(NCMe)_2]BAr^F{}_4$ (105.3 mg, 0.1 mmol) and the resultant bright yellow solution stirred for 2 h. The solution was concentrated under reduced pressure to approx. 1 ml and pentane (10 ml) added to precipitate a bright yellow solid which was washed with further pentane and vacuum dried to give the product (138.2 mg, 93%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.30 – 8.27 (m, 1H, Py), 8.21 (d, $^3J_{HH}$ = 7.4 Hz, 2H, Py), 7.72 (s, 8H, $BAr^F{}_4$), 7.55 (s, 4H, $BAr^F{}_4$), 7.24 (s, 6H, Ar), 2.68 (hept, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_3$), 2.37 (s, 6H, Me), 1.60 (s, 3H, NCMe), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H$_3$*)$_3$), 1.13 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H$_3$*)$_3$). ^{11}B NMR (128 MHz, CD_2Cl_2) δ -6.64 (s, $BAr^F{}_4$). ^{19}F NMR (377 MHz, CD_2Cl_2) δ -62.88 (s, $BAr^F{}_4$). Elem. anal. Calcd for $C_{67}H_{58}AgBF_{24}N_4$: C, 53.87; H, 3.91; N, 3.75. Found C, 54.03; H, 3.72; N, 3.94.

Molecular structure:

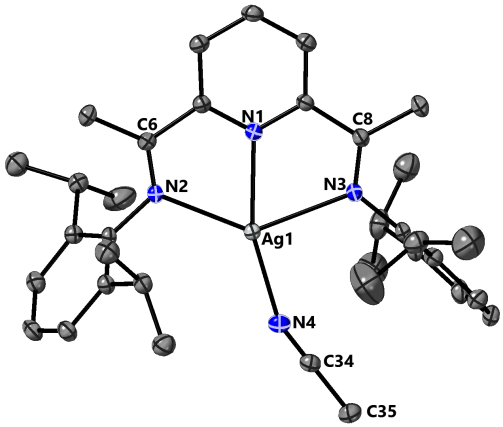


Figure S5. Molecular structure of **7** determined by single crystal X-ray diffraction. $BAr^F{}_4$ anion, disordered molecule of *n*-pentane solvent from crystallisation, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ag(1)-N(1) 2.341(2), Ag(1)-N(2) 2.3429(19), Ag(1)-N(3) 2.4692(19), Ag(1)-N(4) 2.164(2), N(2)-C(6) 1.272(3), N(3)-C(8) 1.276(3), N(1)-Ag(1)-N(2) 68.99(7), N(1)-Ag(1)-N(3) 67.45(7), N(2)-Ag(1)-N(3) 136.41(7), N(4)-Ag(1)-N(1) 160.01(9), N(4)-Ag(1)-N(2) 128.13(9), N(4)-Ag(1)-N(3) 95.02(8).

8: Complex **8** formed upon addition of 1 equiv. of MeCN to complex **2** as observed by NMR experiments. This complex could also be prepared independently by the following method:

To a solution of **7** (50 mg, 0.033 mmol) in dichloromethane (5 ml) was added $[Rh(COE)_2Cl]_2$ (12 mg, 0.0165 mmol, 0.5 equiv.) and the solution stirred for 2 h in the dark. The solution was filtered by cannula and concentrated under reduced pressure to approx. 1 ml. Pentane (10 ml) was added to precipitate a pale brown solid which was collected and vacuum dried to give the product (28.4 mg, 58%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.22 (t, $^3J_{HH}$ = 7.9 Hz, 1H, Py), 7.74 – 7.70 (m, 10H, Py+$BAr^F{}_4$), 7.56 (s, 4H, $BAr^F{}_4$), 7.38 – 7.12 (m, 6H, Ar), 3.10 (hept, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*$(CH_3)_3$), 1.97 (s, 6H, Me), 1.67 (s, 3H, MeCN), 1.17 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3)_3$), 1.11 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3)_3$). ^{11}B NMR (128 MHz, CD_2Cl_2) δ -6.65 (s, $BAr^F{}_4$). ^{19}F NMR (377 MHz, CD_2Cl_2) δ -62.88 (s, $BAr^F{}_4$). HRMS (ESI/QTOF) m/z: [M]+ Calcd for $C_{35}H_{46}N_4Rh$ 625.2772; Found 625.2853. Elem. anal. Calcd for $C_{67}H_{58}RhBF_{24}N_4$: C, 54.05; H, 3.93; N, 3.76. Found C, 54.16; H, 3.97; N, 3.57.

Molecular structure:

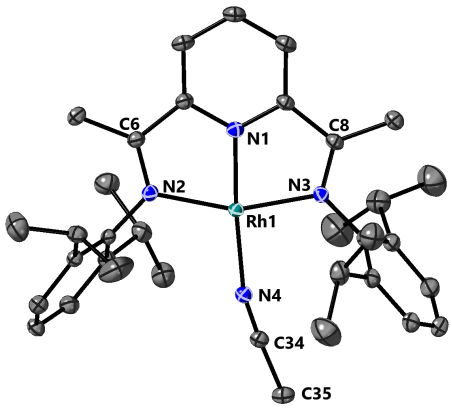


Figure S6. Molecular structure of **8** determined by single crystal X-ray diffraction. $BAr^F{}_4$ anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh(1)-N1) 1.904(2), Rh(1)-N2) 2.047(2), Rh(1)-N3) 2.026(2), Rh(1)-N(4) 2.031(3), N(2)-C(6) 1.299(4), N(3)-C(8) 1.304(4), N(1)-Rh(1)-N(2) 79.16(10), N(1)-Rh(1)-N(3) 79.44(10), N(1)-Rh(1)-N(4) 175.25(10), N(3)-Rh(1)-N(2) 158.60(10), N(3)-Rh(1)-N(4) 96.16(10), N(4)-Rh(1)-N(2) 105.20(10).

1.3. Crystallography

Structure determinations were collected on an an Oxford Diffraction/Agilent SuperNova diffractometer with Cu-$K\alpha$ radiation (λ = 1.54184 Å) equipped with nitrogen gas Oxford Cryosystems Cryostream unit[7] at the Oxford Chemical Crystallography Service from the University of Oxford. Diffraction data was reduced and processed using CrysAlisPro package.[S8] The structures were solved using SHELXT[S9] and refined to convergence on F^2 and against all independent reflections by full-matrix least-squares using SHELXL[S10] (version 2018/3) in combination with the GUI OLEX2[S11] program. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were geometrically placed unless otherwise stated and allowed to ride on their parent atoms. CF_3 groups on the BAr^F_4 anion were necessarily modelled as disordered, and restrained to maintain sensible geometries. Full crystallographic data have been deposited with the CCDC as 1895517 (**1**), 1895514 (**2**), 1895515 (**3**), 1895516 (**4**), 1895519 (**7**) and 1895518 (**8**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://optimized.ccdc.cam.ac.uk/data_request/cif.

Table S1. Selected Crystallographic Data for Complexes 1-3

Complex	**1**	**2**	**3**
Empirical formula	$C_{68}H_{67}AgB_2F_{24}N_4$	$C_{69.75}H_{71}B_2Cl_{0.50}F_{24}N_4Rh_1$	$C_{34}H_{43}AgF_3N_3O_3S$
Formula weight	1525.74	1563.56	738.64
Temperature (K)	150.00(14)	150.01(11)	150.01(10)
Wavelength (Å)	1.54184	1.54184	1.54184
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P*-1	*P*-1	$P2_1$
Unit cell dimensions			
a (Å)	14.4114(2)	12.9702(2)	9.81000(10)
b (Å)	15.6413(3)	16.6310(4)	14.6740(2)
c (Å)	16.8798(3)	17.7573(5)	12.8614(2)
α (°)	88.4148(13)	85.814(2)	90
β (°)	74.0062(14)	81.7216(18)	108.758(2)
γ (°)	78.2248(14)	81.2409(16)	90
Volume ($Å^{3)}$	3579.03(10)	3741.16(14)	1753.09(4)
Z	2	2	2
Density (calculated) (Mg/m^3)	1.416	1.388	1.399
Absorption coefficient (mm^{-1})	3.190	2.912	5.611
$2\theta_{max}$ (°)	76.319	76.343	76.736
Reflections collected	90787	40732	23626
R_{int}	0.0332	0.0383	0.0348
Data / restraints / parameters	14883 / 1176 / 1004	15487 / 1556 / 1278	7285 / 1 / 416
Goodness-of-fit on F^2	1.041	1.042	1.018
R_1 [I>2σ(I)]	0.0317	0.0465	0.0285
wR_2 (all data)	0.0847	0.1278	0.0759
Largest diff. peak and hole ($e.Å^{-3}$)	0.635 and -0.480	1.142 and -0.862	0.373 and -0.511

Table S2. Selected Crystallographic Data for Complexes 4 and 7-8

Complex	**4**	**7**	**8**
Empirical formula	$C_{263}H_{227}Ag_4B_4F_{96}N_{12}$	$C_{72}H_{70}AgBF_{24}N_4$	$C_{72}H_{70}BF_{24}N_4Rh$
Formula weight	5854.27	1566.00	1561.04
Temperature (K)	150.01(10)	150.01(12)	150.04(18)
Wavelength (Å)	1.54184	1.54184	1.54184
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*1	$P2_1/c$	$P2_1/c$
Unit cell dimensions			
a (Å)	12.0498(3)	17.4613(2)	17.49982(19)
b (Å)	19.1965(4)	17.68770(10)	18.08188(17)
c (Å)	29.6386(7)	24.9895(2)	24.0311(3)
α (°)	88.484(2)	90	90
β (°)	87.353(2)	107.0620(10)	106.9706(11)
γ (°)	80.481(2)	90	90
Volume ($Å^{3)}$	6753.0(3)	7378.32(12)	7273.01(14)
Z	1	4	4
Density (calculated) (Mg/m^3)	1.440	1.410	1.426
Absorption coefficient (mm^{-1})	3.356	3.112	2.833
$2\theta_{max}$ (°)	76.197	76.301	76.164
Reflections collected	49227	49302	47642
R_{int}	0.0337	0.0340	0.0415
Data / restraints / parameters	31300 / 2670 / 3860	15294 / 839 / 1120	15081 / 589 / 1064
Goodness-of-fit on F^2	1.022	1.031	1.024
R_1 [$I>2\sigma(I)$]	0.0442	0.0465	0.0475
wR_2 (all data)	0.1200	0.1323	0.1369
Largest diff. peak and hole ($e.Å^{-3}$)	0.781 and -0.657	0.753 and -0.742	1.205 and -0.894

Additional details for the single-crystal X-ray studies

***Additional details for* 1**: This compound crystallized in the triclinic space group *P*-1. The H atoms from the BH_3 group were located in the difference Fourier map, refined and allowed to ride in their parent B1 atom. The trimethylamine group was necessarily modelled as disordered (rotational). Two CF_3 groups from the BAr^F_4 anion were also modelled as disordered (rotational) and restrained to maintain sensible geometries.

***Additional details for* 2**: This compound crystallized in the triclinic space group *P*-1 with 0.25 molecule of dichloromethane and 0.5 molecule of *n*-hexane within the asymmetric unit (occupancies were firstly refined and then set to approximate sensible values). The borane trimethylamine ligand was necessarily modelled as disordered. H atoms from the disordered BH_3 group were located in the difference Fourier map, allowed to ride in their parent B1 and B1A atoms, and necessarily restrained to maintain sensible geometries. Seven CF_3 groups from the BAr^F_4 anion were modelled as disordered (rotational) and restrained to maintain sensible geometries.

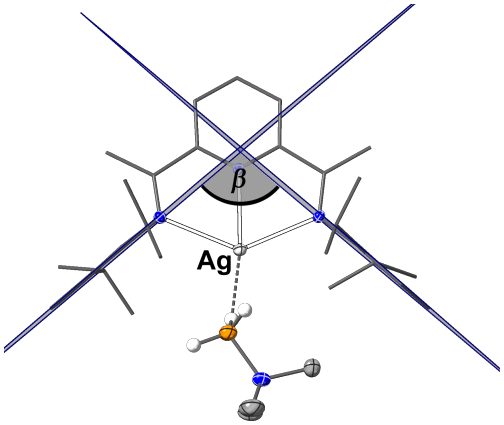
***Additional details for* 4**: This compound crystallised in the triclinic space group *P*1 with 0.5 molecule of *n*-hexane solvent from crystallisation (chemical occupancy was firstly refined and then set to approximate sensible value). Although the compound is not chiral itself, it aggregates as a dimeric species in the solid state with a chiral configuration. The Friedel pairs were not collected to full coverage as determination of its absolute configuration was meaningless. Although the Friedel pairs were not collected to full coverage, the quality and completeness of the raw data is acceptable and the Flack parameter refines to a sensible value. Some isopropyl and CF_3 groups were necessarily modelled as disordered and restrained to maintain sensible geometries.

***Additional details for* 7:** This compound crystallized in the monoclinic space group $P2_1/c$ with one molecule of *n*-pentane solvent of crystallisation in the asymmetric cell. The molecule of *n*-pentane was modelled as disordered over two main domains and constrained to maintain a sensible geometry. Five CF_3 groups from the BAr^F_4 anion were also modelled as disordered (rotational) and restrained to maintain sensible geometries.

***Additional details for* 8:** This compound crystallized in the monoclinic space group $P2_1/c$ with one molecule of *n*-pentane solvent of crystallisation in the asymmetric cell. The molecule of *n*-pentane was modelled as disordered over two main domains and constrained to maintain a sensible geometry. Three CF_3 groups from the BAr^F_4 anion were also modelled as disordered (rotational) and restrained to maintain sensible geometries.

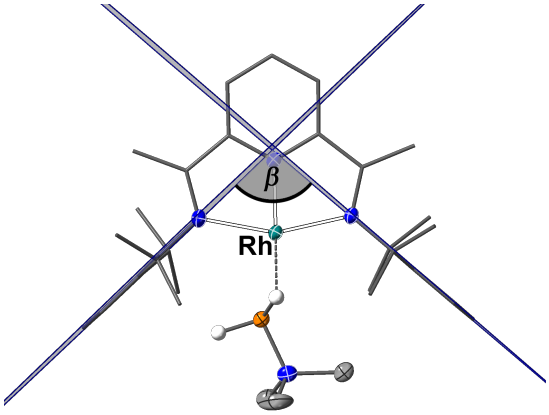
1.4. Angles between planes through Ar groups $[M(L1)(H_3B{\cdot}NMe_3)]^+$ vs. $[M(L1)(NCMe)]^+$

Complex 1



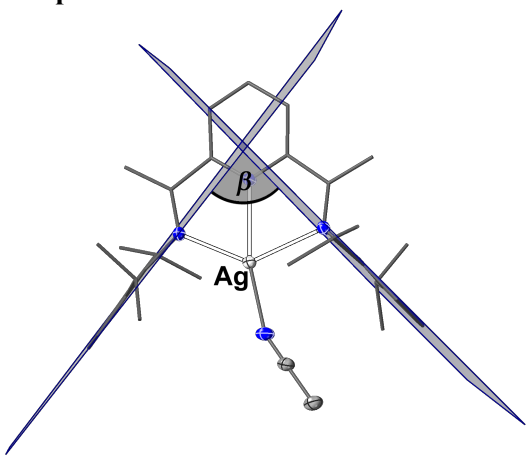
$\beta = 99.435°$

Complex 2



$\beta = 96.397°$

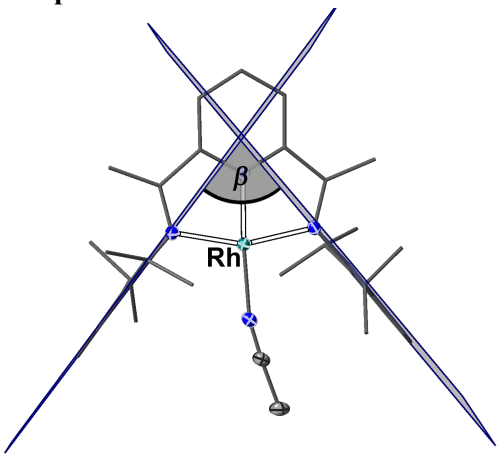
Complex 7



$\beta = 82.641°$

$\Delta\beta = 16.794°$

Complex 8



$\beta = 77.169°$

$\Delta\beta = 19.228°$

1.5. Addition of MeCN to 1

To a solution of **1** (15 mg, 0.01 mmol) in CD_2Cl_2 (0.6 ml) was added successive equivalents of MeCN. NMR studies showed the presence of an equilibrium, the position of which was far towards complex **7**. As further equivalents of MeCN were added the position of the equilibrium moved and at >1000 equiv. complex **7** could be observed by NMR.

Additionally, addition of 1 equivalent of $H_3B{\cdot}NMe_3$ to a solution of **7** led to formation of **1** and free MeCN.

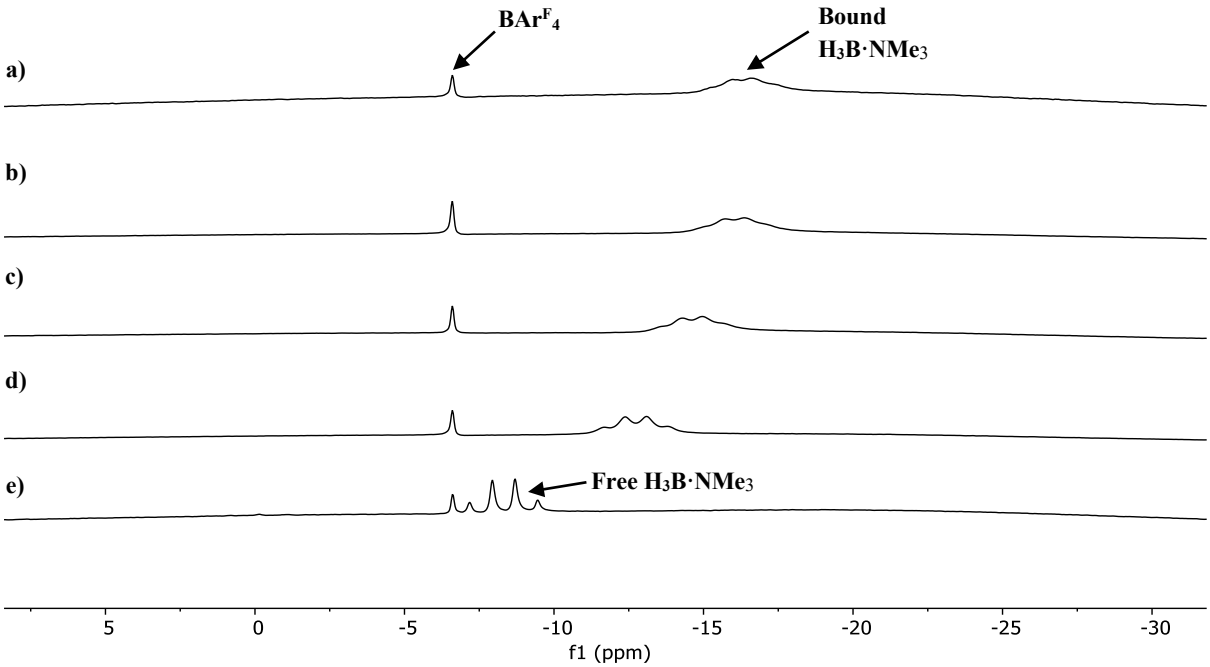


Figure S7. ^{11}B NMR spectra of complex **1** (a), complex **1** after the addition of ≈1 equiv. of MeCN (b), complex **1** after the addition of ≈3 equiv. of MeCN (c), complex **1** after the addition of ≈20 equiv. of MeCN (d), complex **1** after the addition of >1000 equiv. MeCN (e).

1.6. Addition of MeCN to 2

To a solution of **2** (15 mg, 0.01 mmol) in CD_2Cl_2 (0.6 ml) was added MeCN (≈0.5 µl, 1 equiv.). The solution immediately changed colour from dark green to dark orange. ^{1}H and ^{11}B NMR spectra showed the formation of **8** and free $H_3B{\cdot}NMe_3$. Subsequently $H_3B{\cdot}NMe_3$ (3.6 mg, 5 equiv.) was added, no reaction was observed.

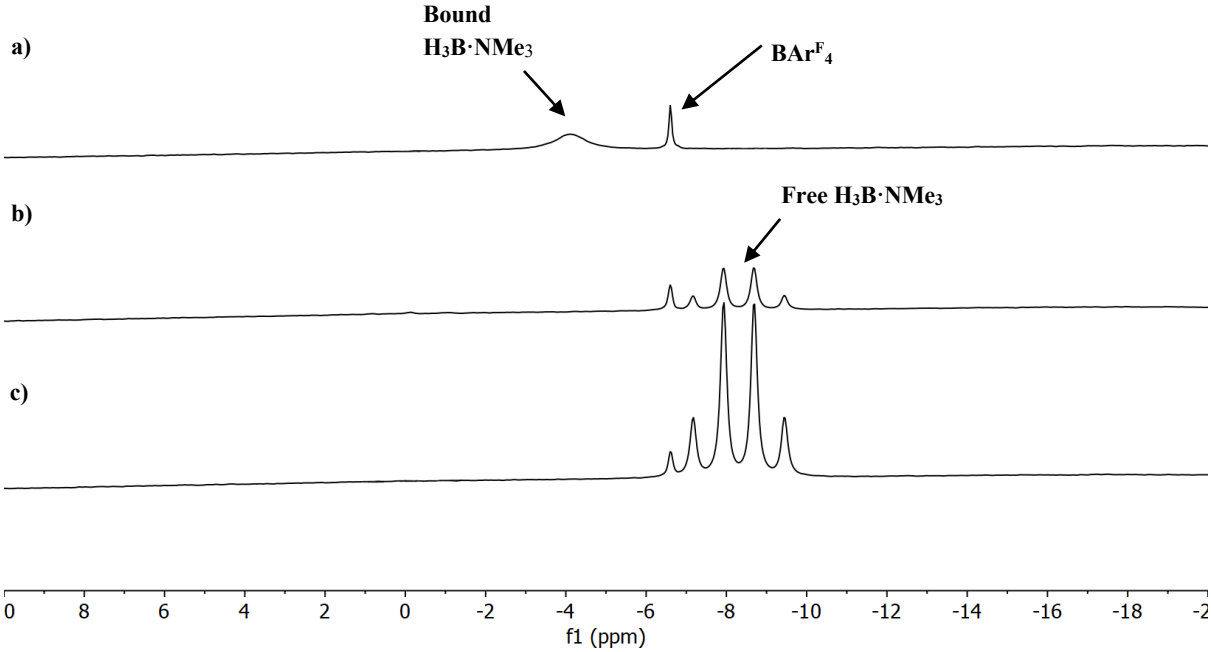
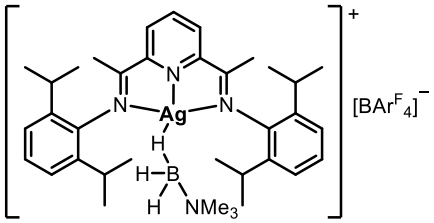


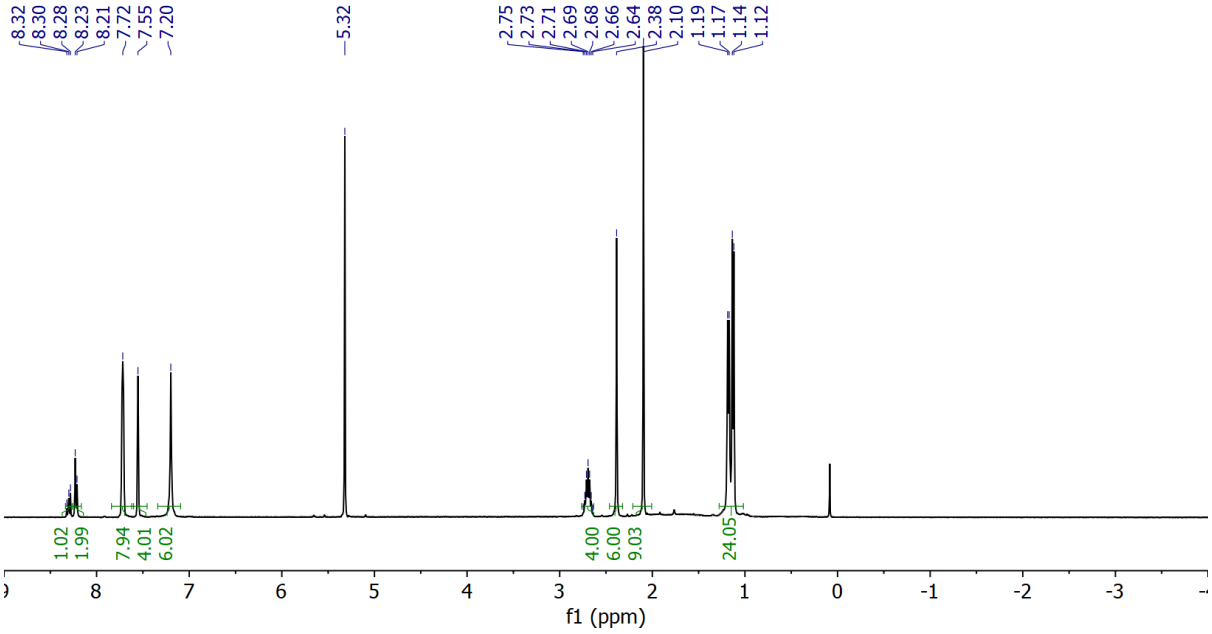
Figure S8. ^{11}B NMR spectra of complex **2** (a), complex **2** after the addition of ≈1 eq of MeCN (b) and after the addition of a further 5 eq of $H_3B{\cdot}NMe_3$ (c).

1.7. NMR Spectra for 1

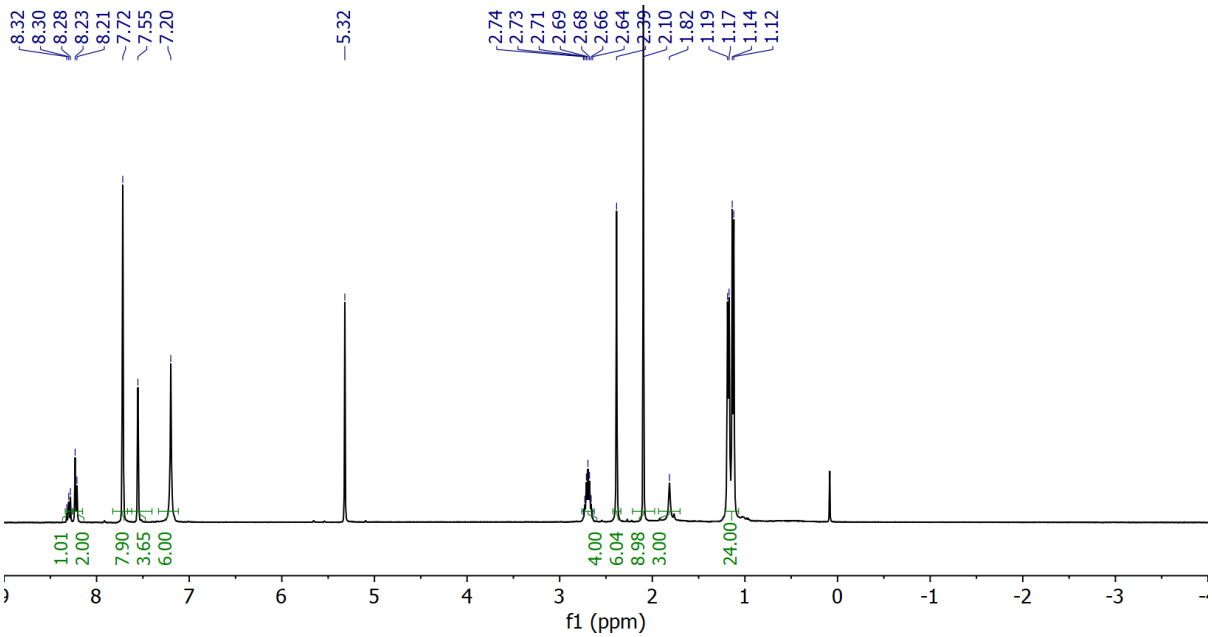


1

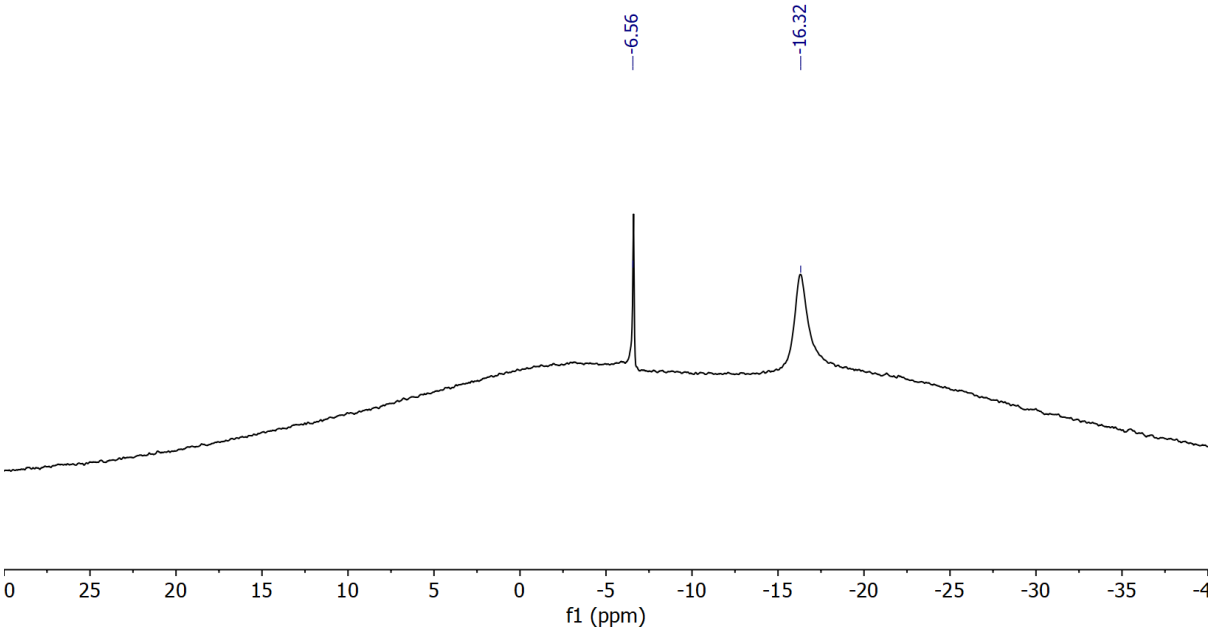
^{1}H NMR (400 MHz, CD_2Cl_2)



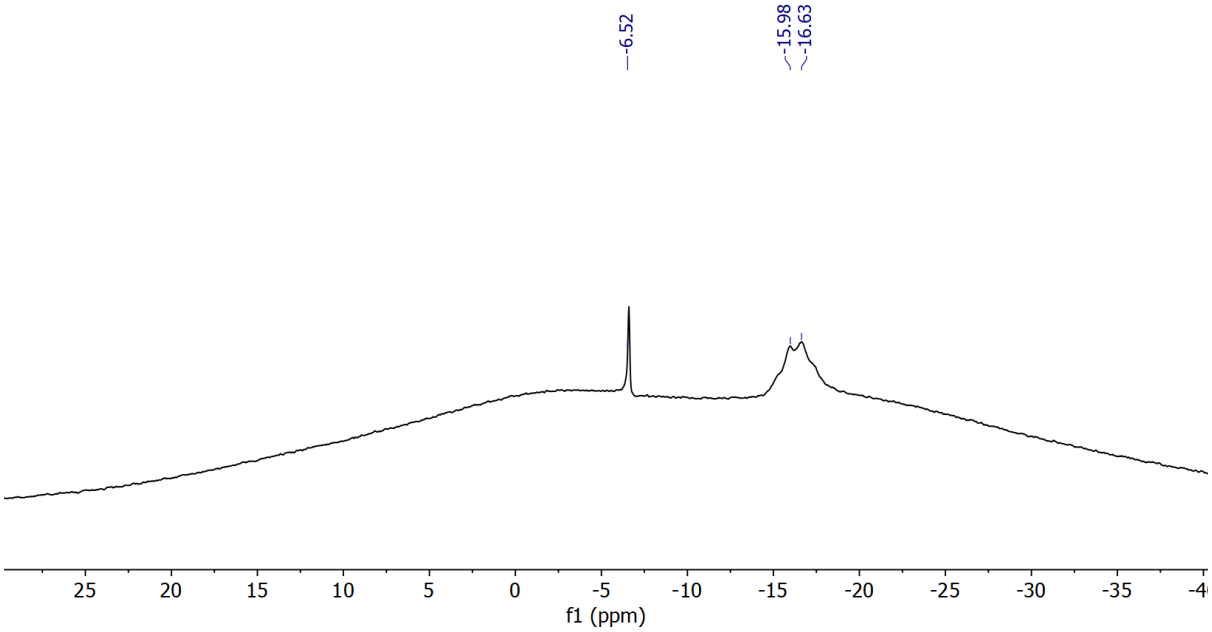
^{1}H{^{11}B} NMR (400 MHz, CD_2Cl_2)



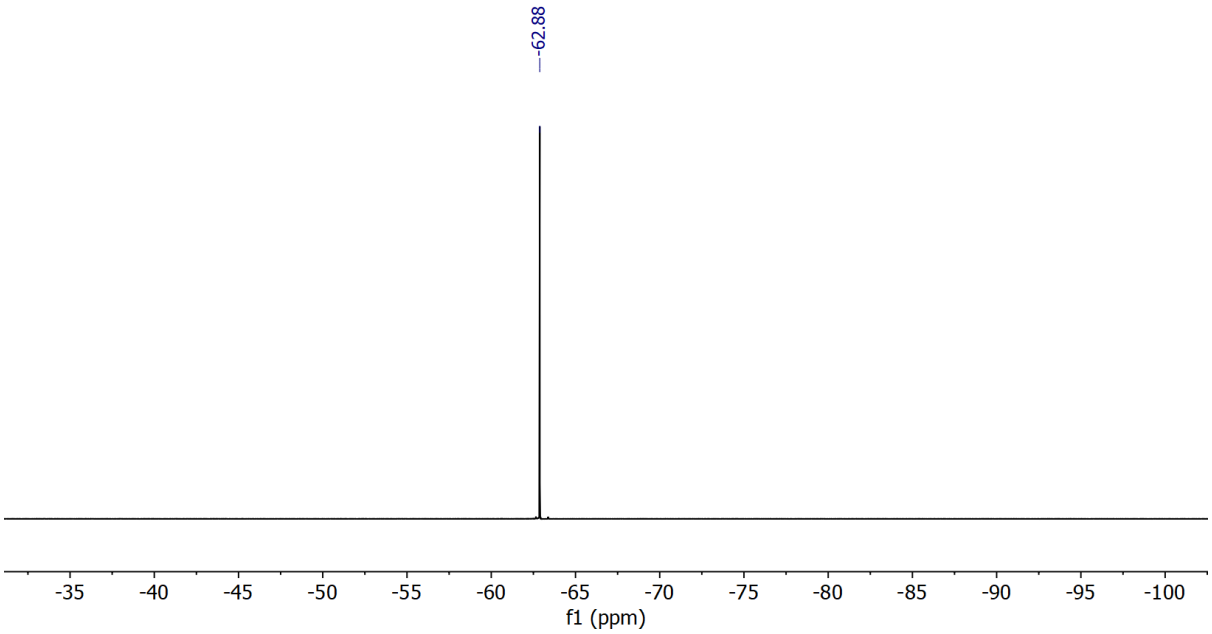
$^{11}B\{^{1}H\}$ NMR (128 MHz, CD_2Cl_2)



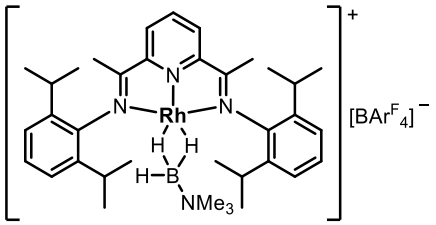
^{11}B NMR (128 MHz, CD_2Cl_2)



^{19}F NMR (377 MHz, CD_2Cl_2)

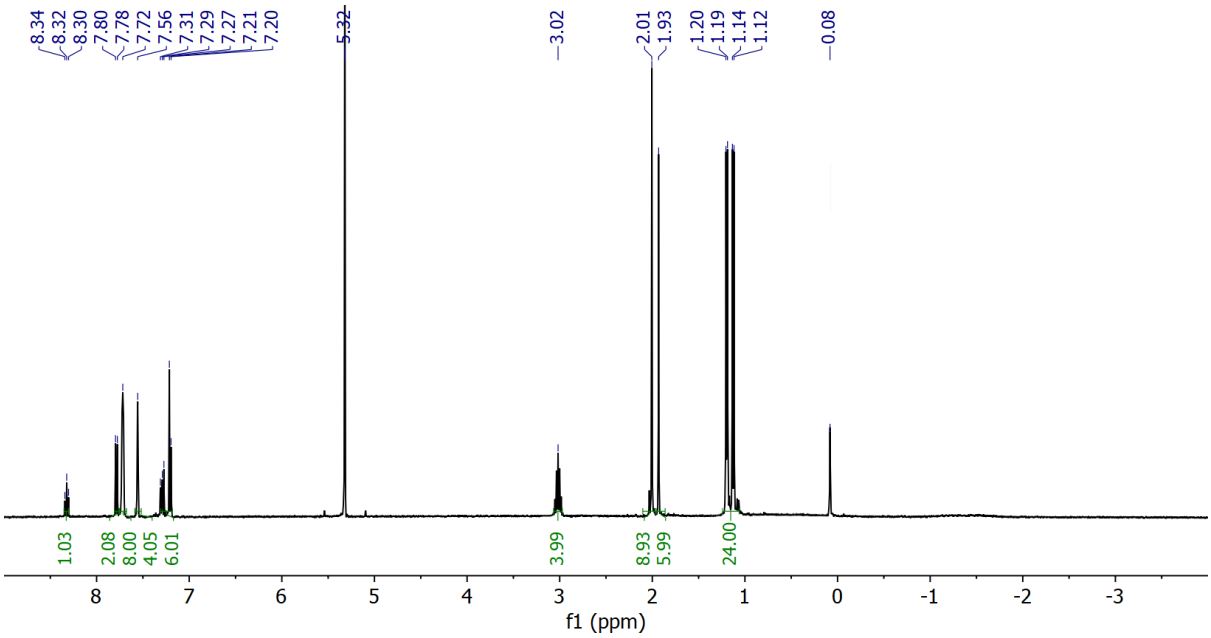


1.8. NMR Spectra for 2

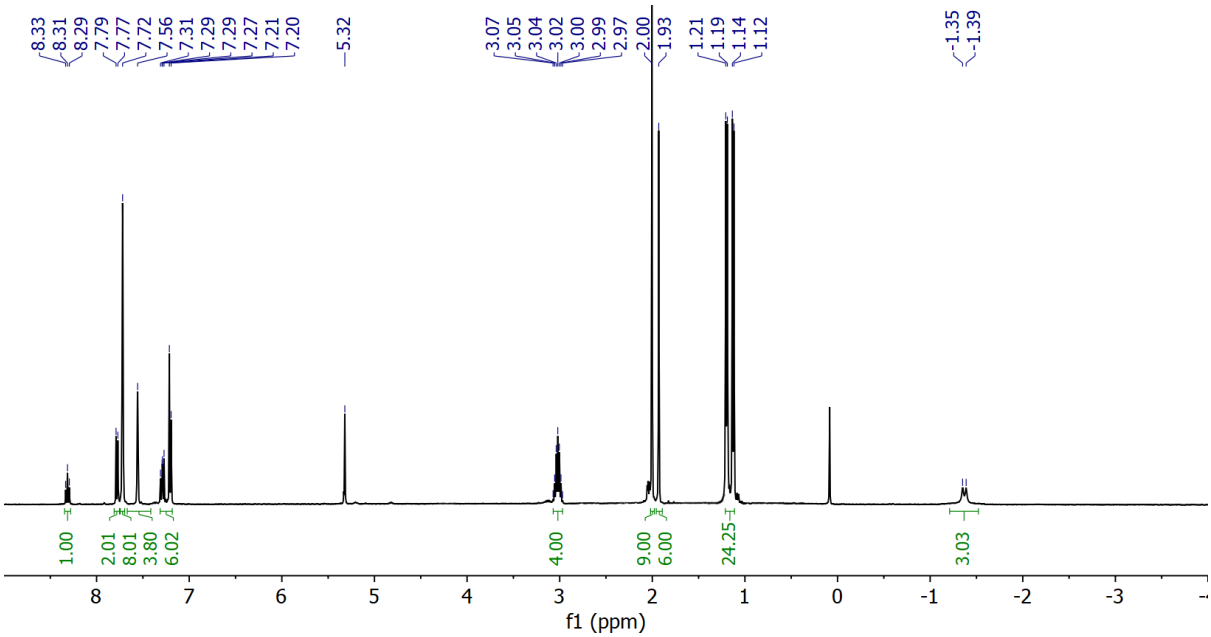


2

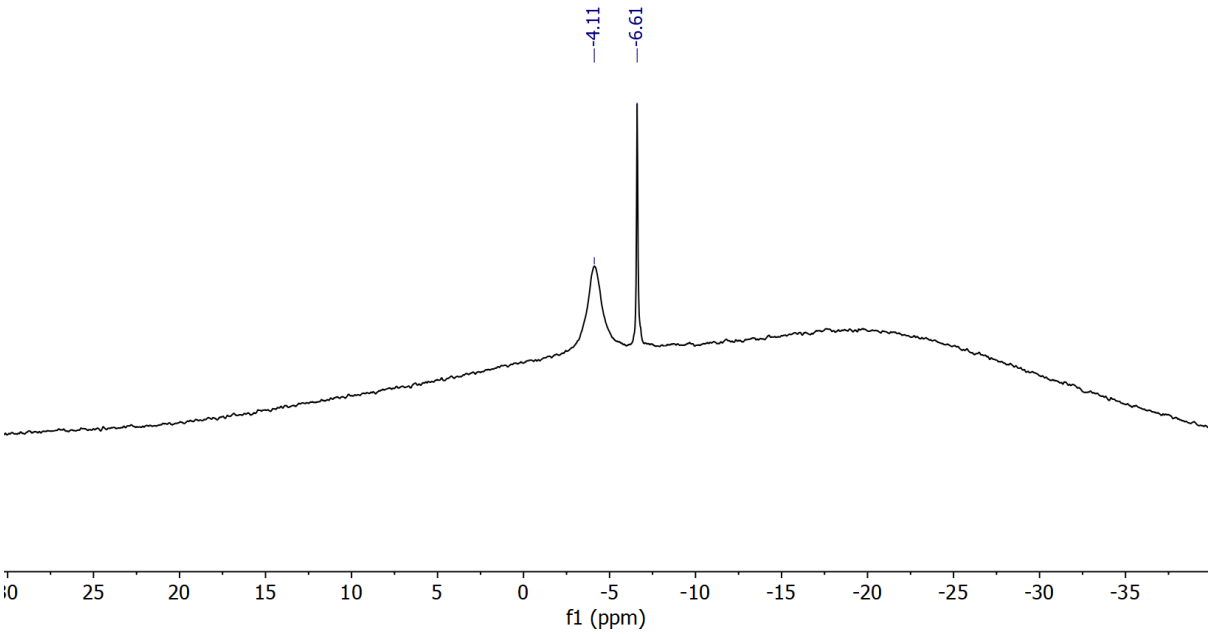
^{1}H NMR (400 MHz, CD_2Cl_2)



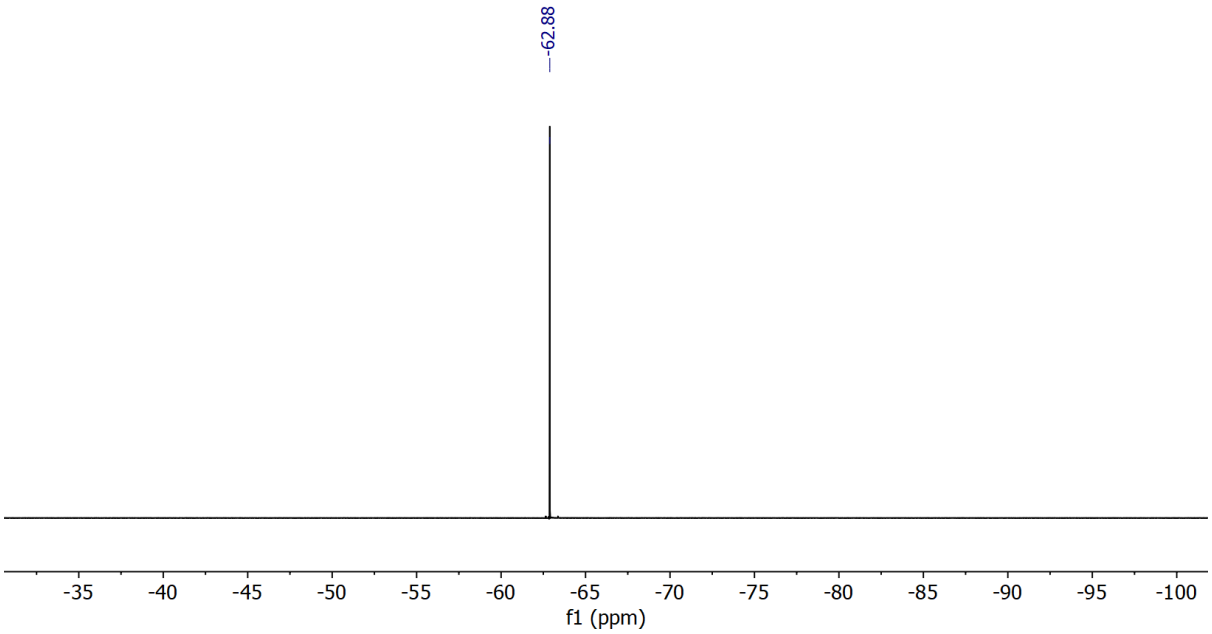
^{1}H {^{11}B} NMR (400 MHz, CD_2Cl_2)



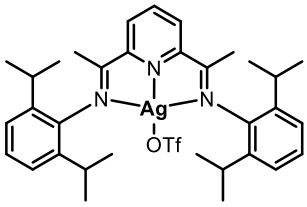
^{11}B NMR (128 MHz, CD_2Cl_2)



^{19}F NMR (377 MHz, CD_2Cl_2)

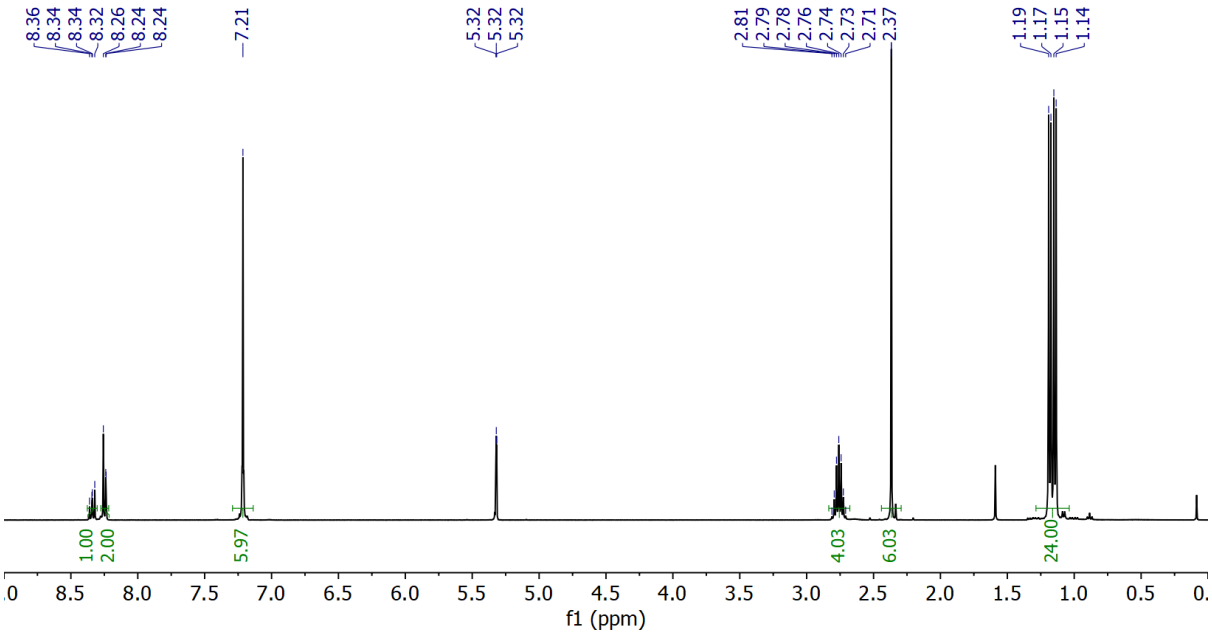


1.9. NMR Spectra for 3

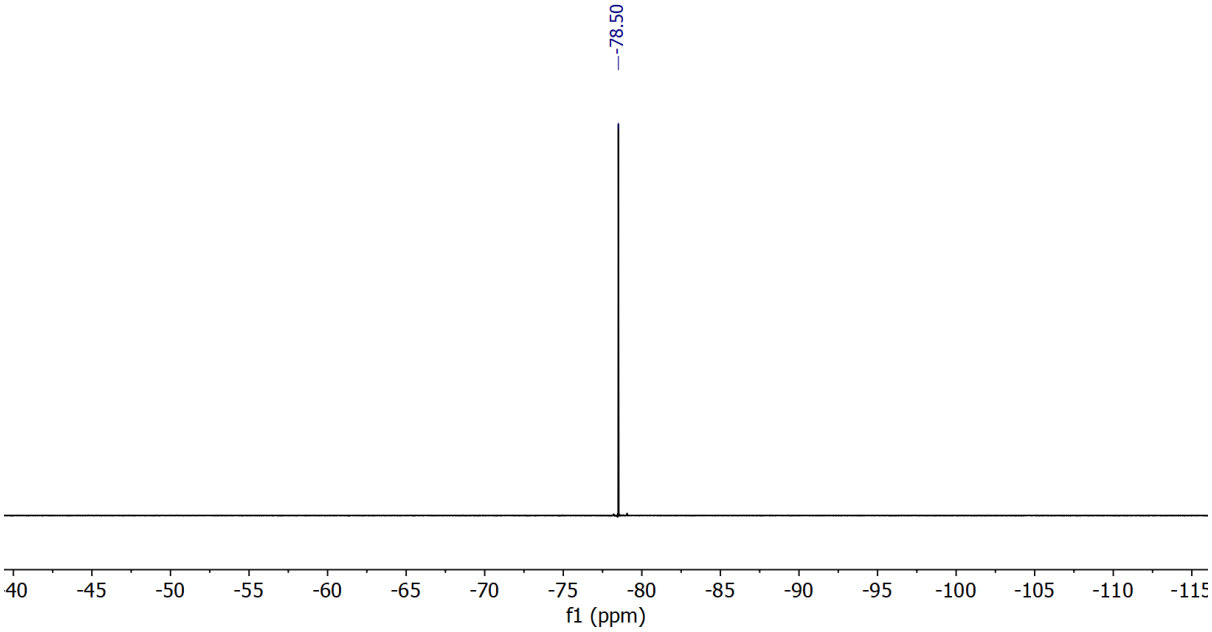


3

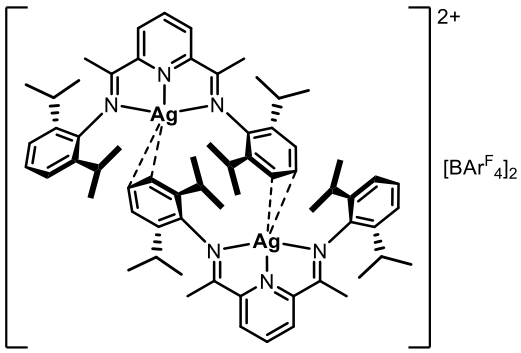
^{1}H NMR (400 MHz, CD_2Cl_2)



^{19}F NMR (377 MHz, CD_2Cl_2)

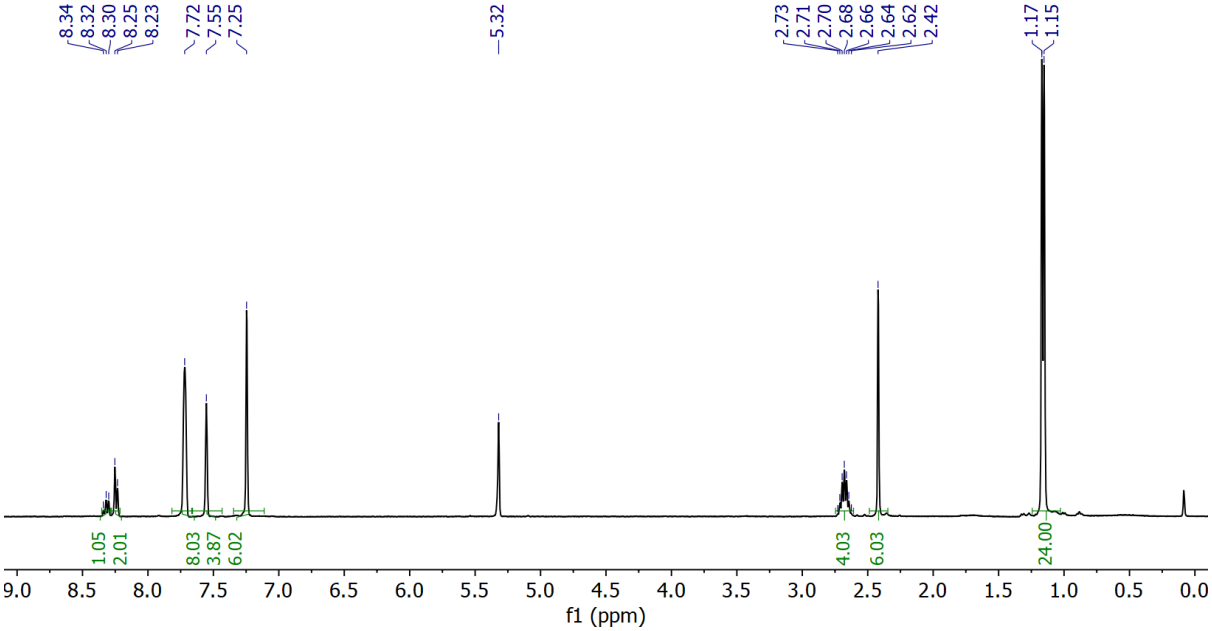


1.10. NMR Spectra for 4

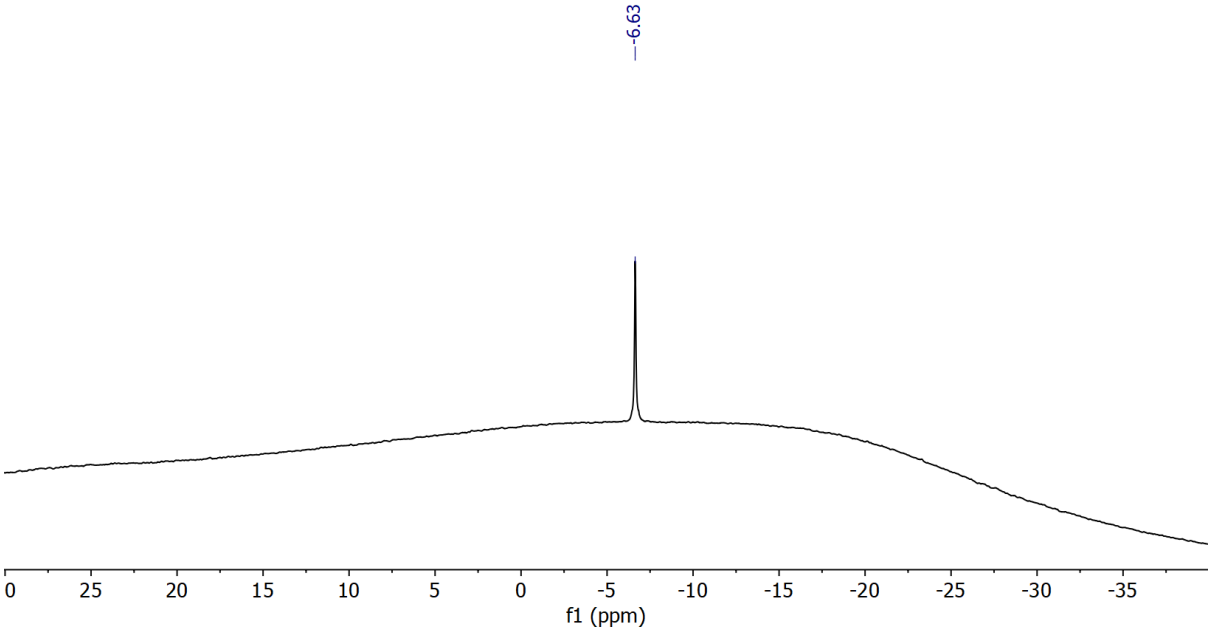


4

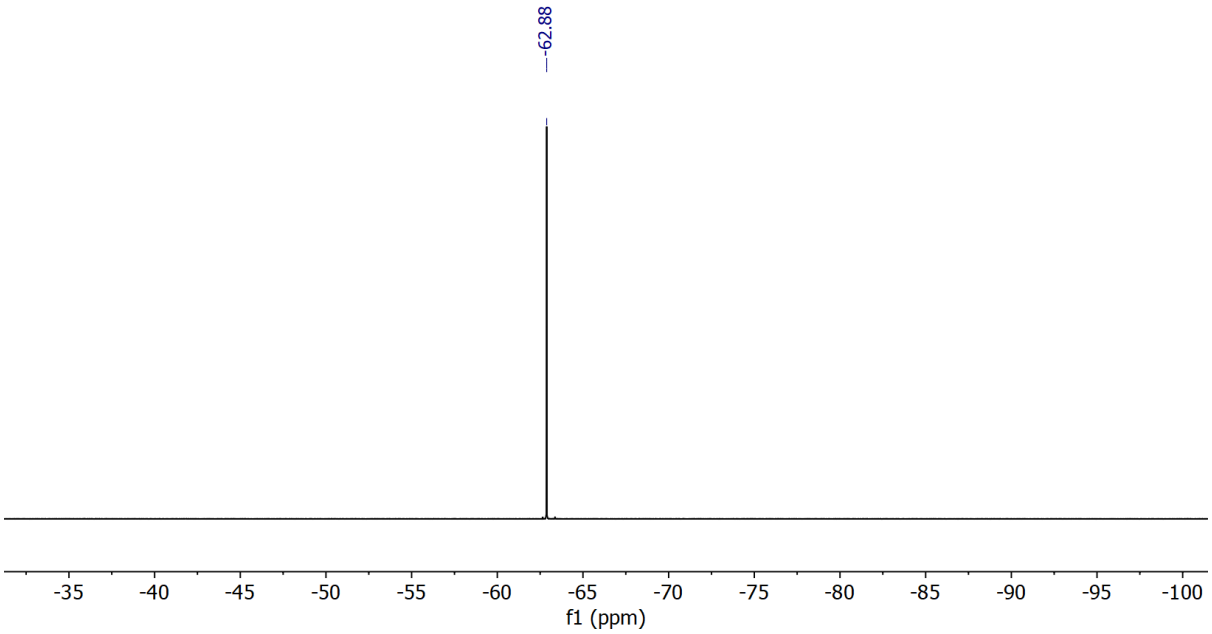
^{1}H NMR (400 MHz, CD_2Cl_2)



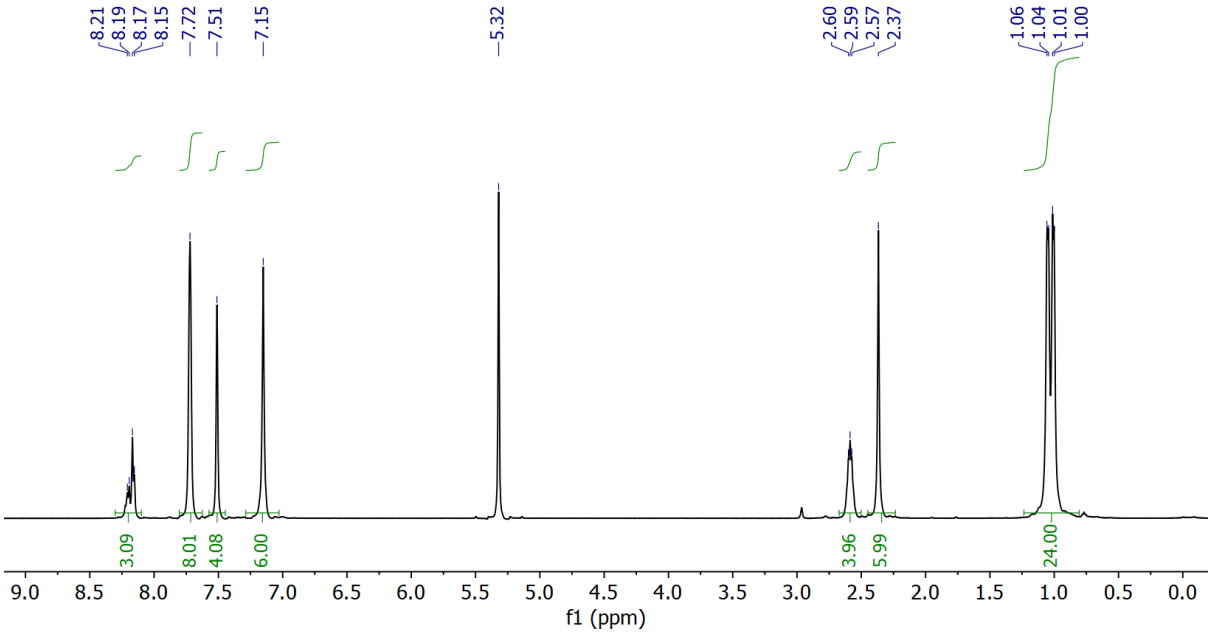
^{11}B NMR (128 MHz, CD_2Cl_2)



^{19}F NMR (377 MHz, CD_2Cl_2)

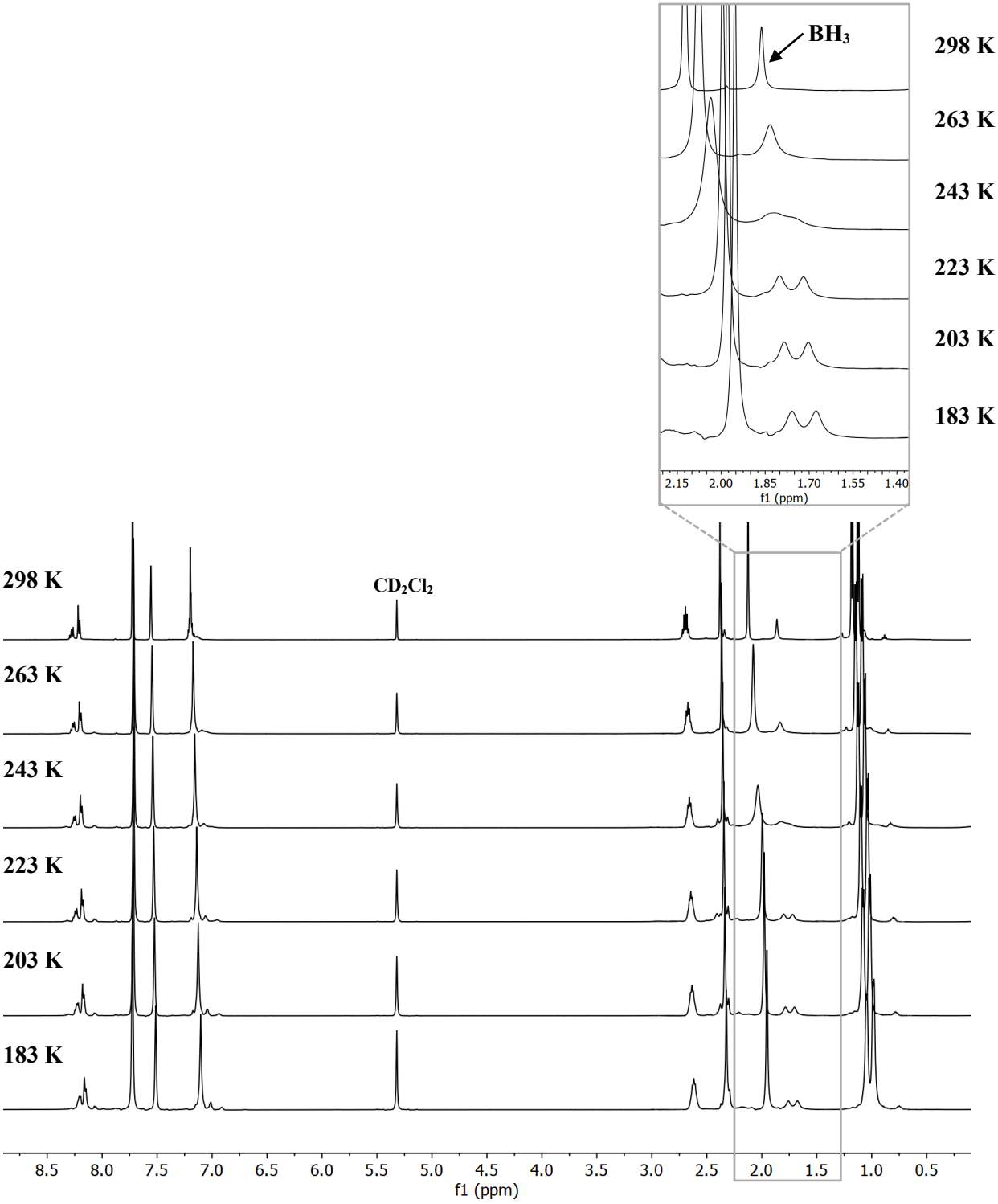


^{1}H NMR (183 K, 500 MHz, CD_2Cl_2)

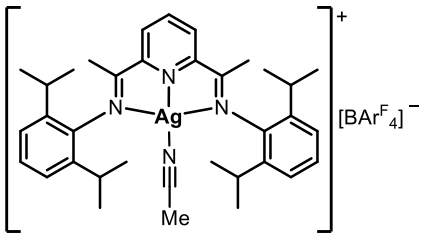


1.11. Variable Temperature NMR studies on complex 4

A solution of **4** in CD_2Cl_2 was cooled from 298 K to 183 K and NMR spectra recorded (500 MHz). The signal at 1.82 ppm corresponding to the BH_3 separates into a doublet ($^1J_{AgH}$ = 41 Hz) at low temperature due to coupling with Ag. Coupling to the different isotopes of Ag cannot be distinguished at this temperature. When recorded at 400 MHz the same coupling constant was observed.

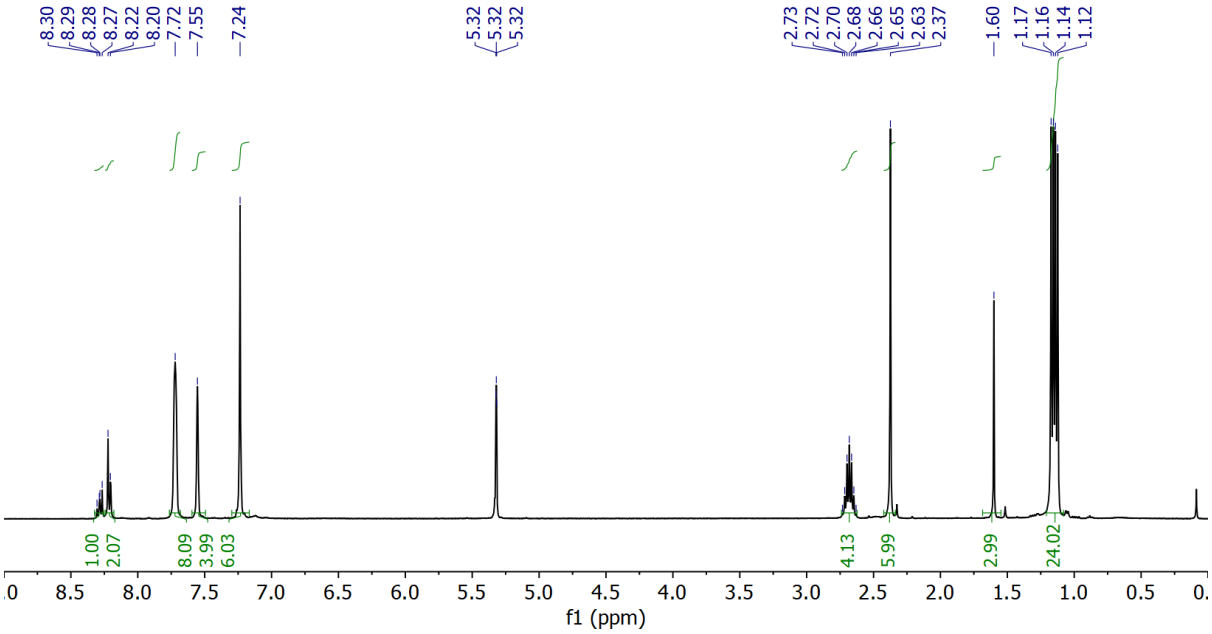


1.12. NMR Spectra for 7

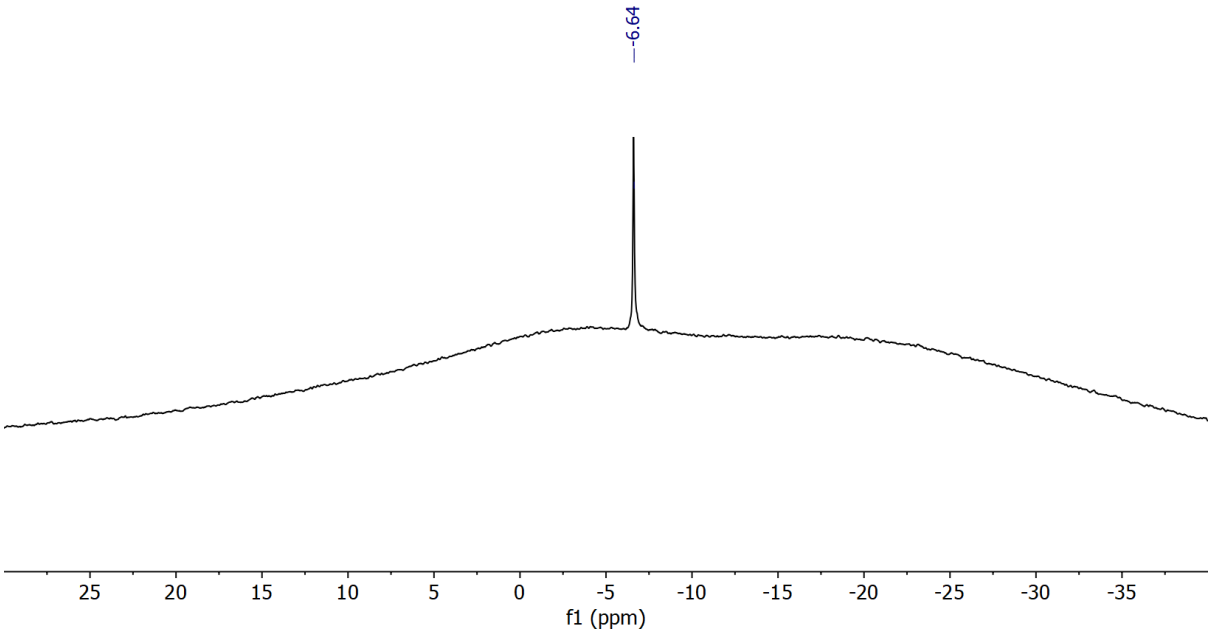


7

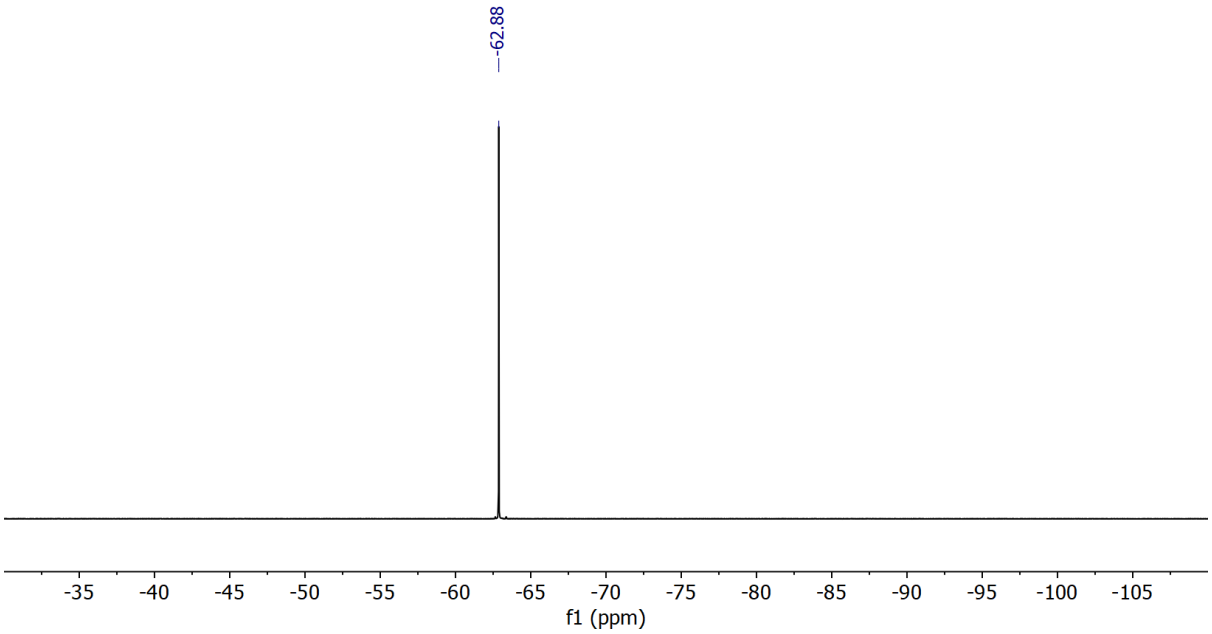
^{1}H NMR (400 MHz, CD_2Cl_2)



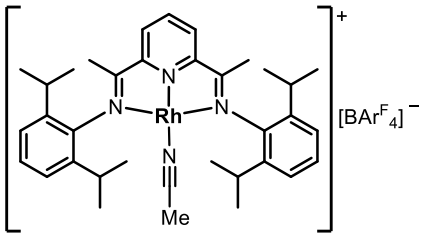
^{11}B NMR (128 MHz, CD_2Cl_2)



^{19}F NMR (377 MHz, CD_2Cl_2)

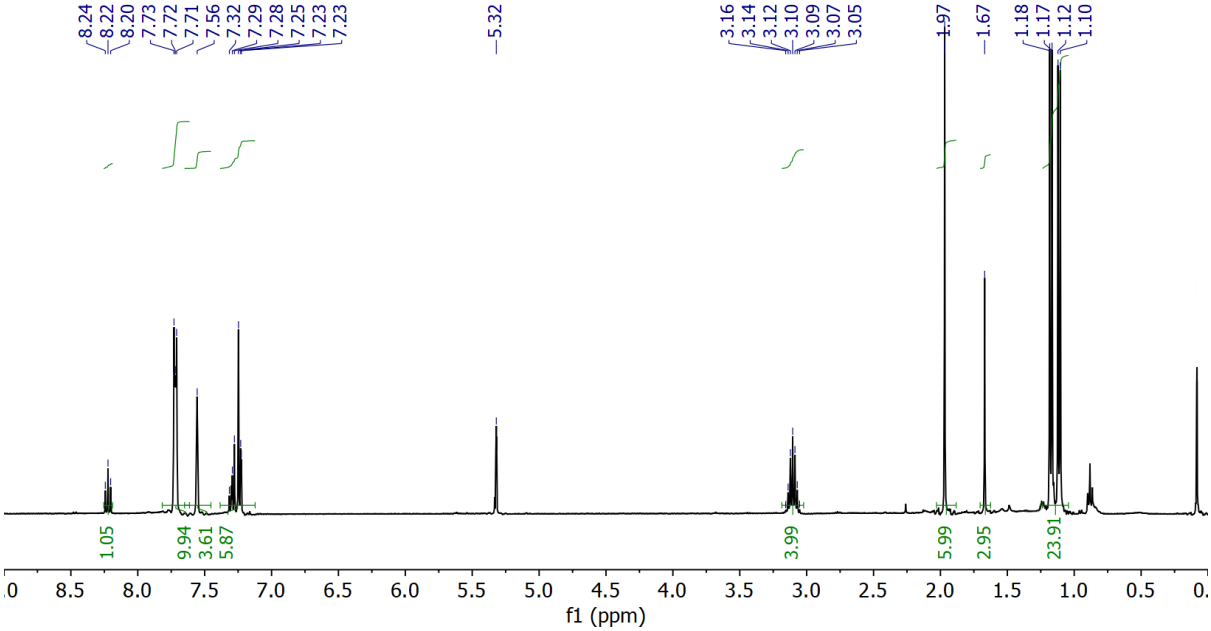


1.13. NMR Spectra for 8

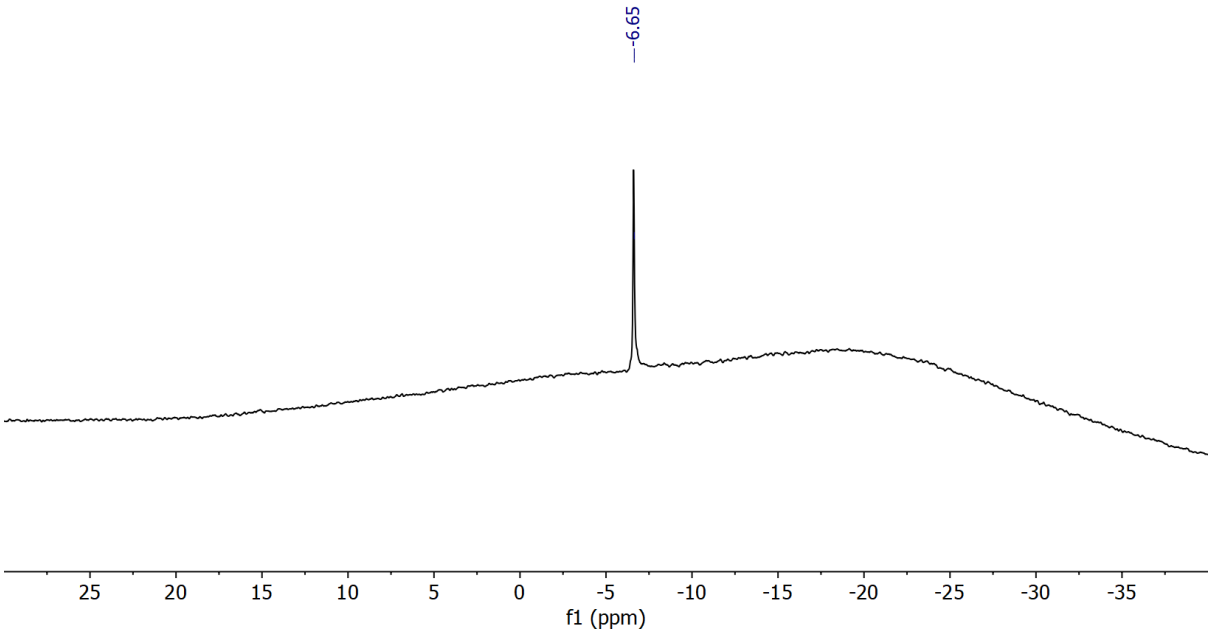


8

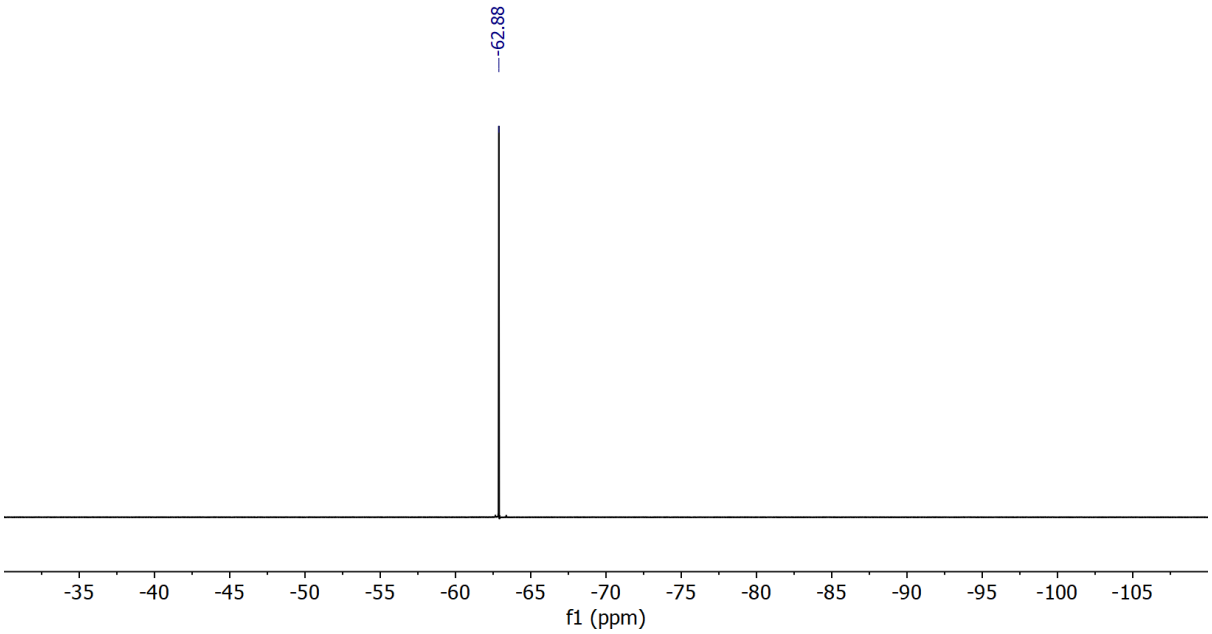
^{1}H NMR (400 MHz, CD_2Cl_2)



^{11}B NMR (128 MHz, CD_2Cl_2)

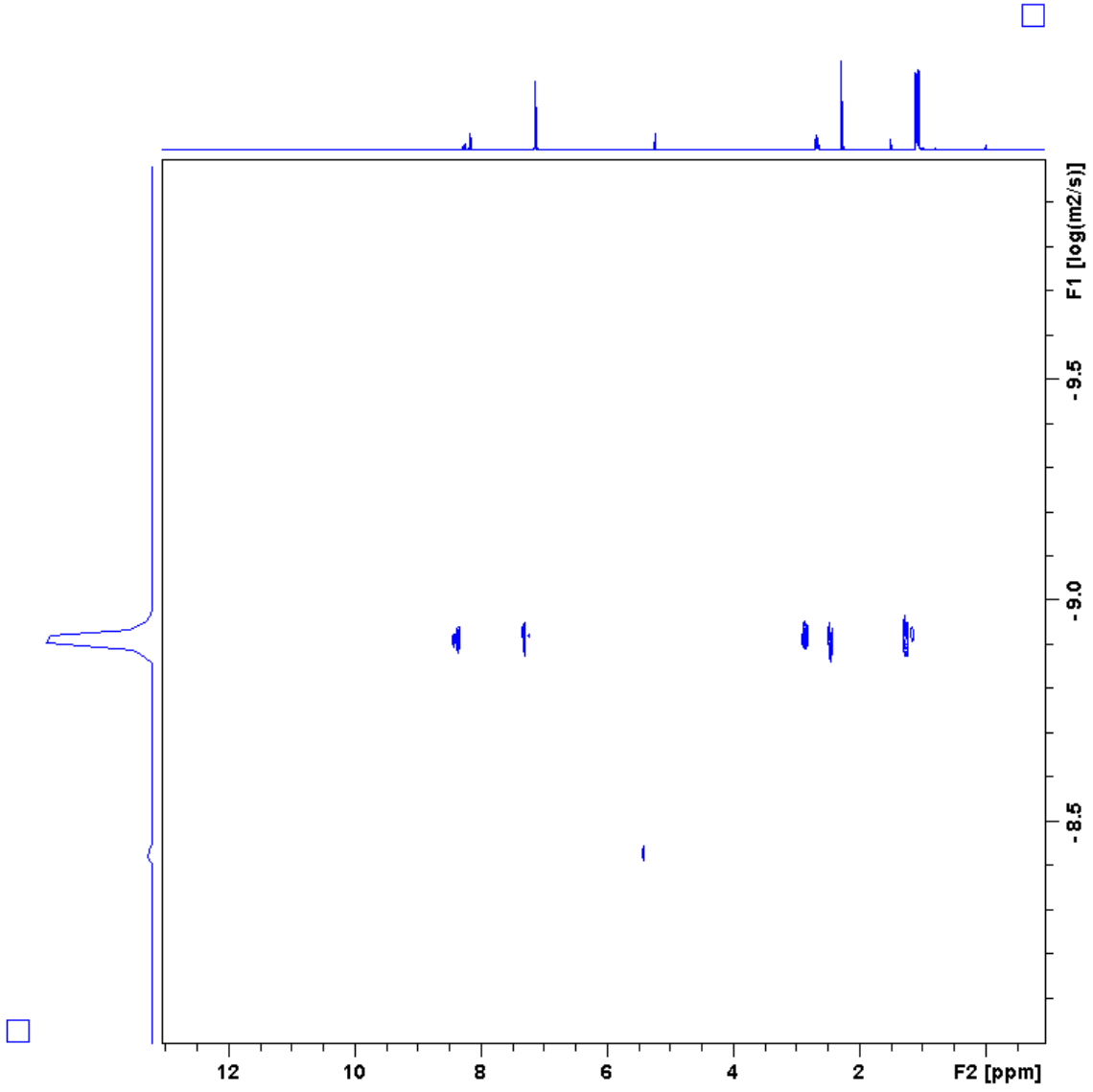


^{19}F NMR (377 MHz, CD_2Cl_2)

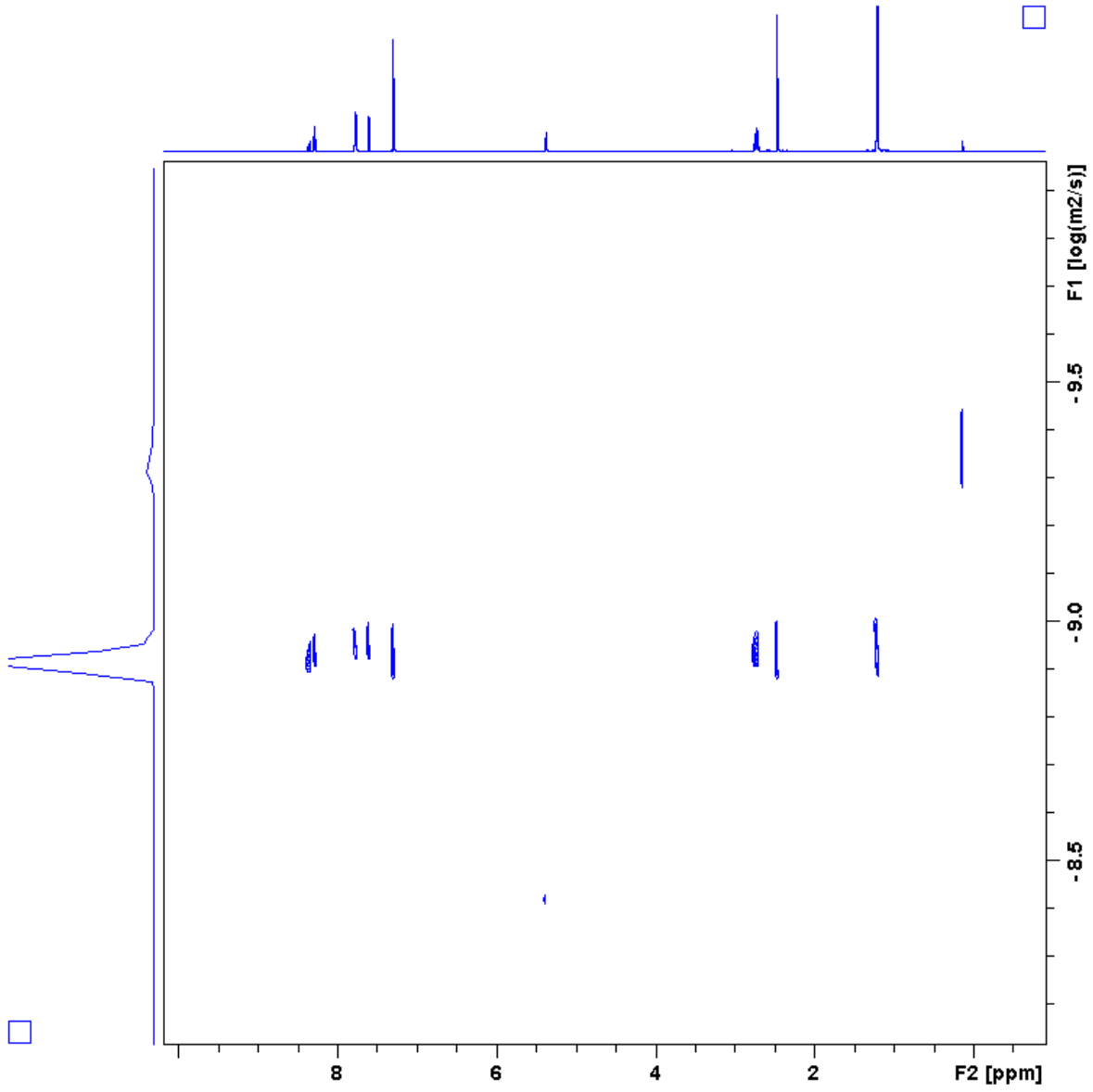


1.14. DOSY Spectra for Complexes 3 and 4

Complex 3:



Complex 4:



2. Computational Studies

2.1. Computational Details

Calculations were run with Gaussian 09 Revision D.01.[12] Geometry optimisations were performed using the BP86 functional[13-14] with Rh and Ag centres described via Stuttgart RECPs and associated basis sets[15] and 6-31G** basis sets[16-17] for all other atoms. All minima were fully characterized via analytical frequency calculations and exhibited only positive frequencies. NMR chemical shifts were calculated with the B3LYP functional[18-20] with Stuttgart RECPs and basis sets on Rh and Ag and 6-311g++** basis sets[21] on all other atoms. NMR calculations were based on the BP86-optimised geometries and included a PCM correction for dichloromethane solvent.[22] Computed chemical shifts are quoted relative to $BF_3 \cdot OEt_2$.

Quantum Theory of Atoms in Molecules (QTAIM)[23] analyses were performed with the AIMALL program,[24] Natural Bond Orbital (NBO) calculations were run with NBO 6.0[25] and NCI calculations were performed using the PLOT program and were based on the promolecular densities.[26-27] QTAIM, NBO and NCI analyses were performed on partially optimised structures based on the experimental heavy atom positions with fully optimised H atoms positions. Orbital plots were created with Chemcraft[28] with an outer contour value of 0.0622. All geometries are provided as sets of Cartesian coordinates as well as the separate xyz file readable by Chemcraft and Mercury.[29]

2.2. QTAIM Studies

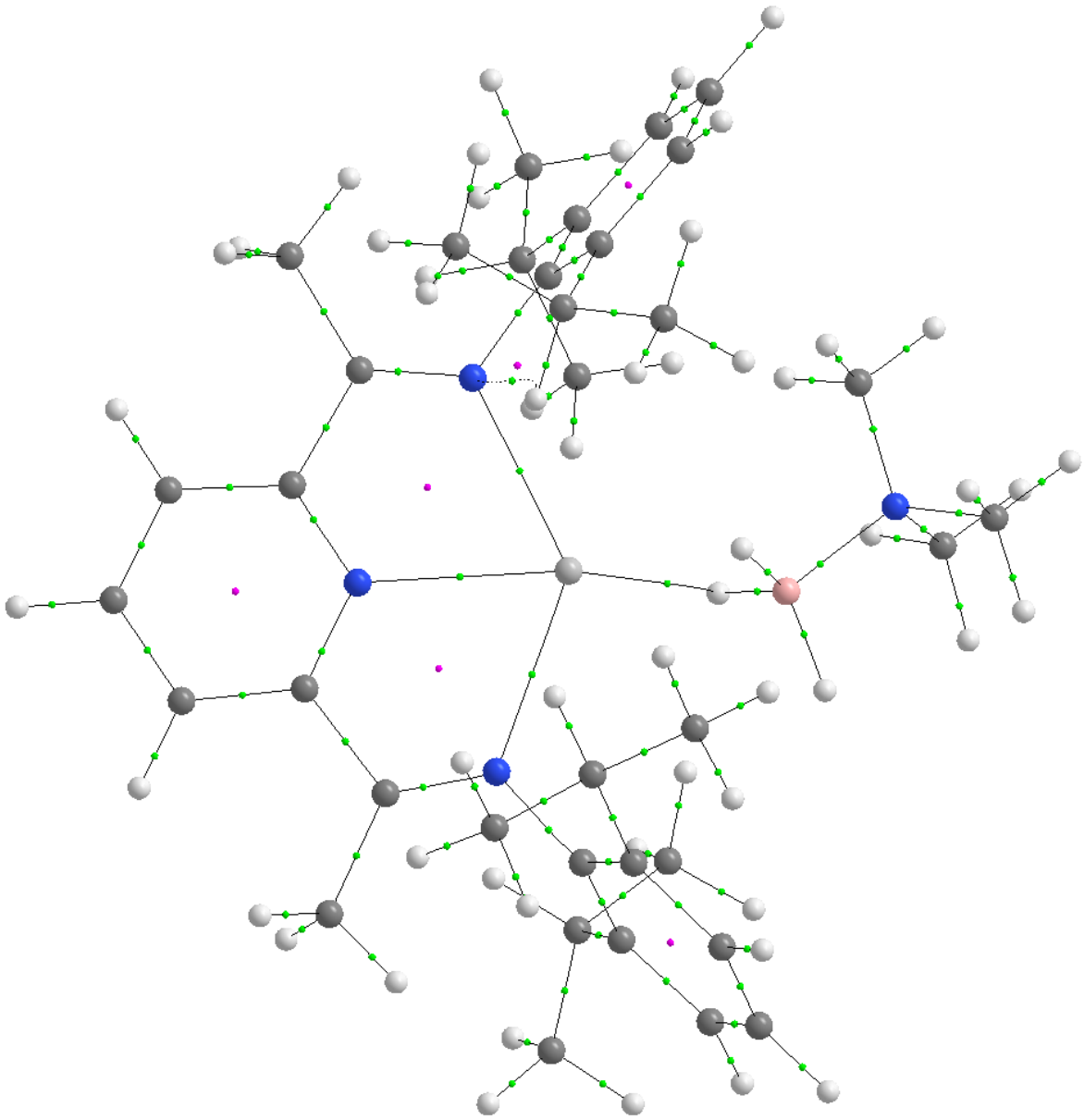


Figure S9. Full molecular graph for $\mathbf{1}^{+}$ with BCPs and RCPs indicated in green and pink, respectively.

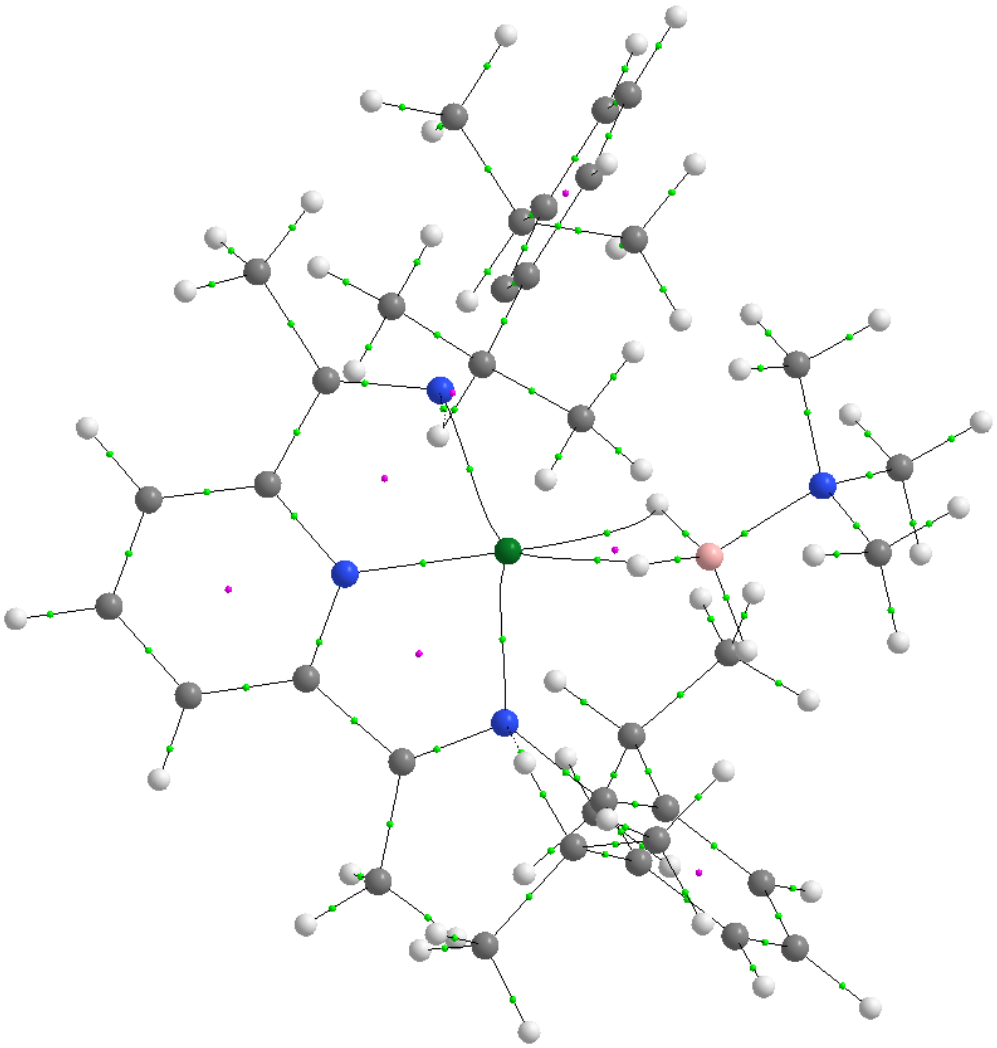


Figure S10. Full molecular graph for $\mathbf{2}^{+}$ with BCPs and RCPs indicated in green and pink, respectively.

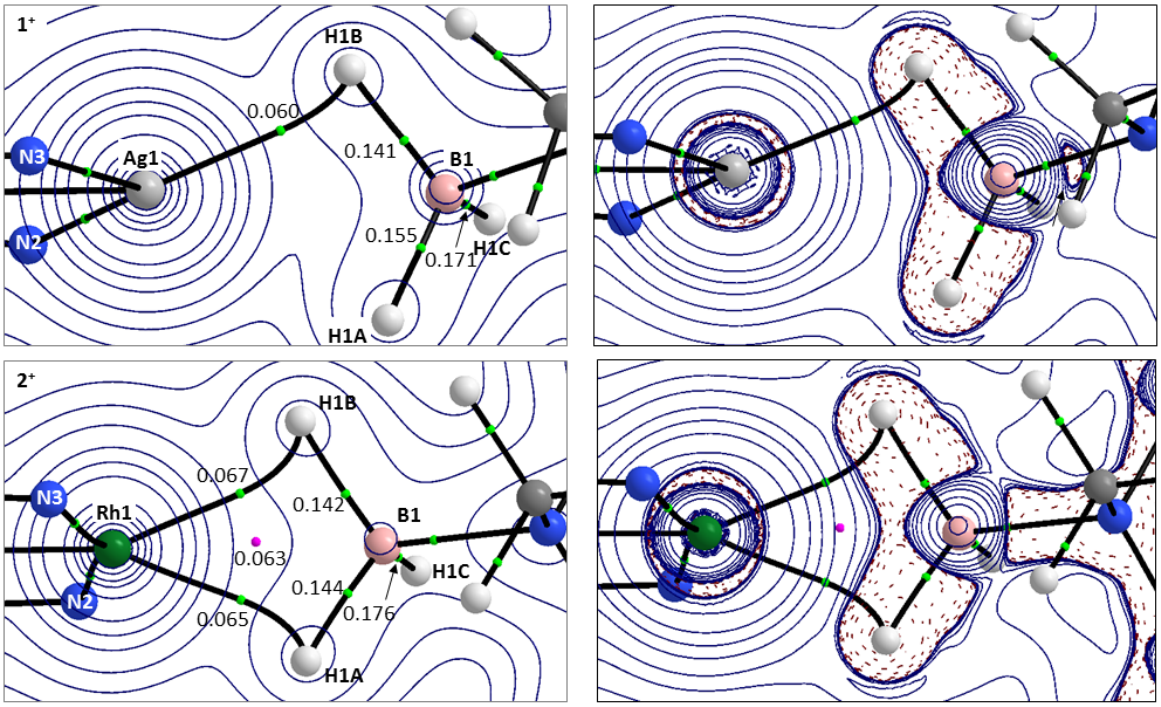
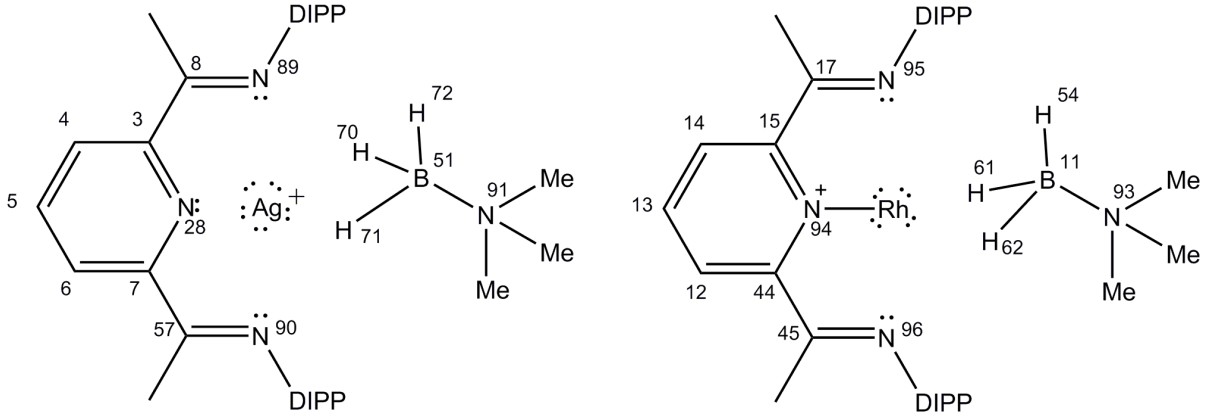


Figure S11. Details from the QTAIM molecular graphs and Laplacian contours plots for $\mathbf{1}^+$ (top) and $\mathbf{2}^+$ (bottom), focussing on the M···$H_3B{\cdot}NMe_3$ regions. Contours are plotted in the M-H1B-H1A plane with selected atoms, bond paths and critical points lying above or below this plane being cloaked for clarity. Values of ρ(r), the electron densities at selected BCPs (green circles) and RCPs (pink circles) are shown $eÅ^{-3}$. Areas of charge accumulation ware shown as dashed red lines and charge depletion as solid blue lines

2.3. NBO Calculations

For both $\mathbf{1}^+$ and $\mathbf{2}^+$ the CHOOSE option was employed to define the Lewis structures shown below that allowed for direct comparison between the two species, based upon the numbering scheme indicated (key centres only). Both Lewis structures described > 97.9% of the total electron density.



With the $CHOOSE card as follows:

$\mathbf{1}^+$:

```
$CHOOSE
  LONE 28 1 50 5 89 1 90 1 END
  BOND S 1 37 S 2 13 D 3 4 S 3 8 S 3 28 S 4 5 S 4 14 D 5 6 S 5 15 S 6 7 S 6 16
       D 7 28 S 7 57 S 8 9 D 8 89 S 9 25 S 9 26 S 9 27 S 10 11 S 10 37 D 10 52
       S 11 12 S 11 13 S 11 17 S 12 18 S 12 19 S 12 20 S 13 21 S 13 22 S 23 29
       S 24 58 S 29 30 S 29 31 S 29 92 S 30 32 S 30 33 S 30 34 S 31 35 S 31 36
       S 31 97 D 37 38 S 38 39 S 38 42 S 39 43 D 39 53 S 40 45 S 40 46 S 40 88
       S 40 91 S 41 47 S 41 48 S 41 49 S 41 91 S 44 65 S 51 70 S 51 71 S 51 72
       S 51 91 S 52 53 S 52 89 S 53 54 S 54 55 S 54 56 S 54 66 S 55 67 S 55 68
       S 55 69 S 56 75 S 56 76 S 56 77 S 57 58 D 57 90 S 58 78 S 58 79 S 59 61
       S 59 90 D 59 92 D 60 61 S 60 73 S 60 94 S 61 62 S 62 63 S 62 64 S 62 74
       S 63 80 S 63 81 S 63 82 S 64 83 S 64 84 S 64 85 S 65 86 S 65 87 S 65 91
       S 92 93 D 93 94 S 93 95 S 94 96 END
 $END
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$\mathbf{2}^+$:

```
$CHOOSE
  LONE 95 1 96 1 97 4 END
  BOND S 1 2 S 1 3 S 1 4 S 1 25 S 5 8 S 5 9 S 5 36 S 5 69 S 6 32 S 7 33
       S 10 37 S 11 54 S 11 61 S 11 62 S 11 93 D 12 13 S 12 44 S 12 46 S 13 14
       S 13 47 D 14 15 S 14 48 S 15 17 S 15 94 S 16 45 S 16 87 S 16 88 S 16 89
       S 17 18 D 17 95 S 18 90 S 18 91 S 18 92 S 19 20 D 19 24 S 19 96 D 20 21
       S 20 25 S 21 22 S 21 49 D 22 23 S 22 50 S 23 24 S 23 51 S 24 27 S 25 26
       S 25 52 S 26 58 S 26 59 S 26 60 S 27 28 S 27 29 S 27 53 S 28 63 S 28 64
       S 28 65 S 29 66 S 29 67 S 29 68 D 30 31 S 30 35 S 30 95 S 31 32 S 31 36
       D 32 33 S 33 34 D 34 35 S 34 55 S 35 38 S 36 37 S 36 56 S 37 70 S 37 71
       S 38 39 S 38 40 S 38 57 S 39 72 S 39 73 S 39 74 S 40 75 S 40 76 S 40 77
       S 41 78 S 41 79 S 41 80 S 41 93 S 42 81 S 42 82 S 42 83 S 42 93 S 43 84
       S 43 85 S 43 86 S 43 93 S 44 45 D 44 94 D 45 96 S 94 97 END
 $END
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NBO Orbital Plots

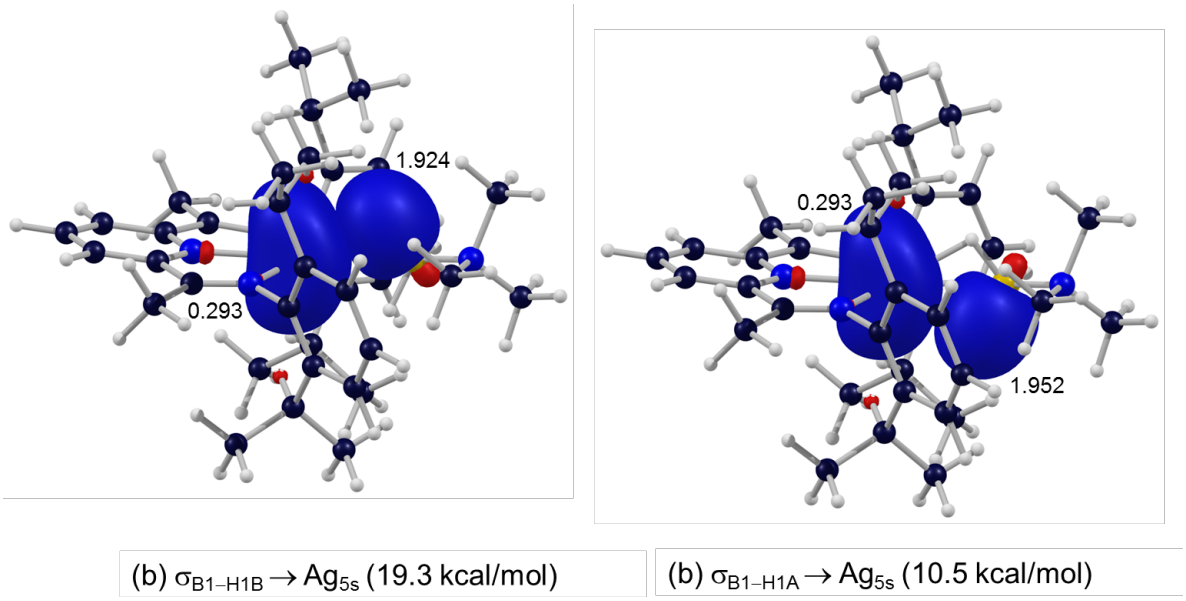
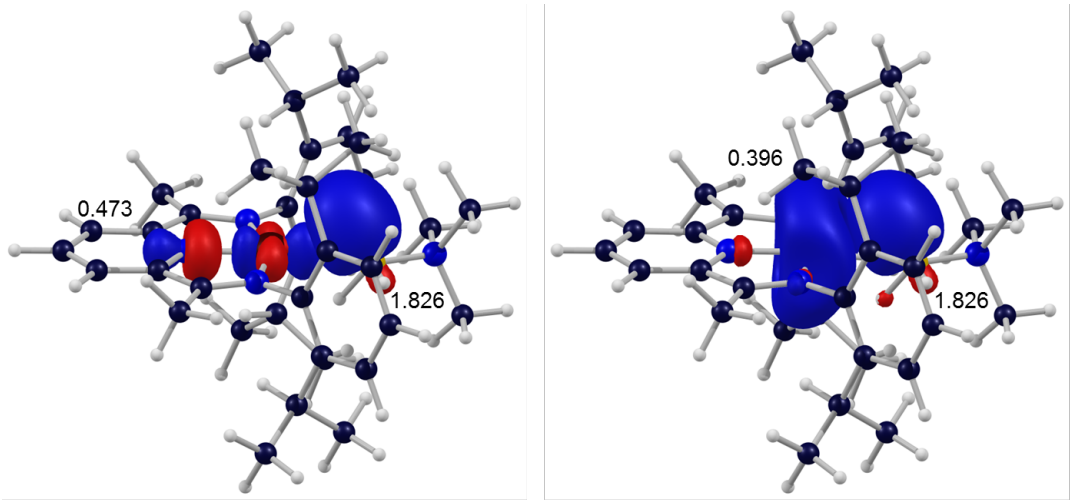
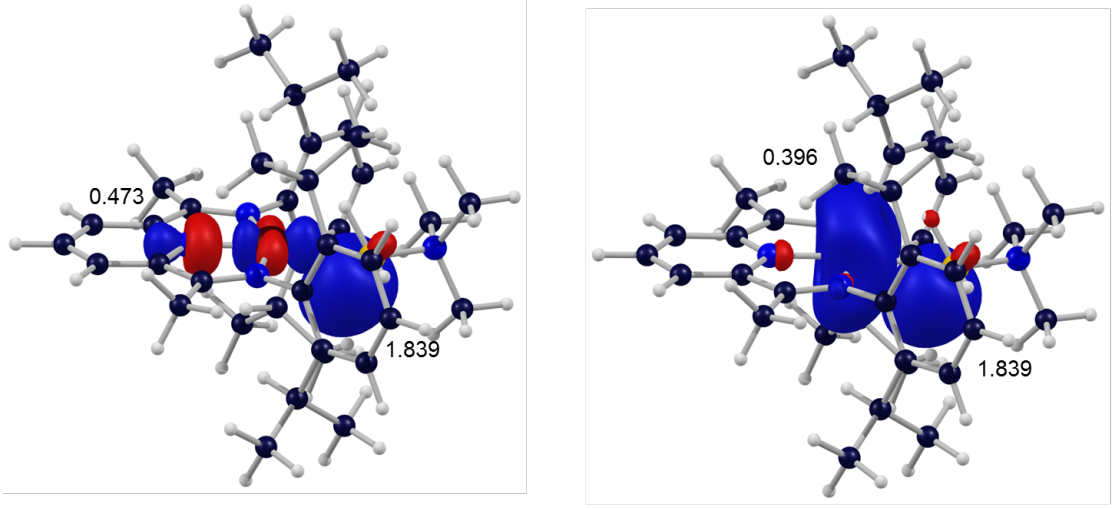


Figure S12. NBO donor-acceptor pairs for $\mathbf{1}^{+}$ with NBO occupancies as indicated.



(a) $\sigma_{B1-H1A} \rightarrow \sigma^*_{Rh-N}$ (25.2 kcal/mol) (b) $\sigma_{B1-H1A} \rightarrow Rh_{5s}$ (9.0 kcal/mol)



(c) $\sigma_{B1-H1B} \rightarrow \sigma^*_{Rh-N}$ (28.5 kcal/mol) (d) $\sigma_{B1-H1B} \rightarrow Rh_{5s}$ (8.7 kcal/mol)

Figure S13. NBO donor-acceptor pairs for $\mathbf{1}^+$ with NBO occupancies as indicated.

2.4. Non-Covalent Interaction Plots

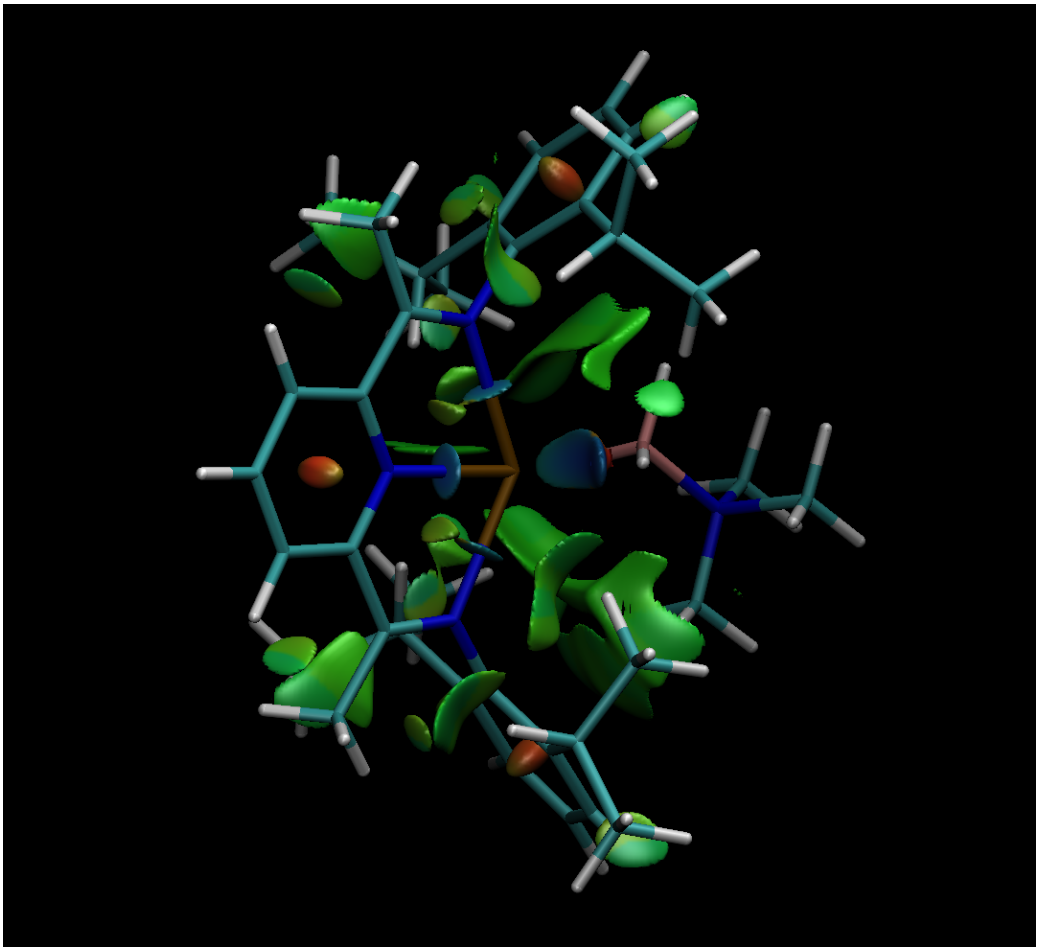


Figure S14. Full NCI plot for $\mathbf{1}^{+}$; isosurfaces generated for s = 0.3 au and -0.07 < ρ < 0.07 au.

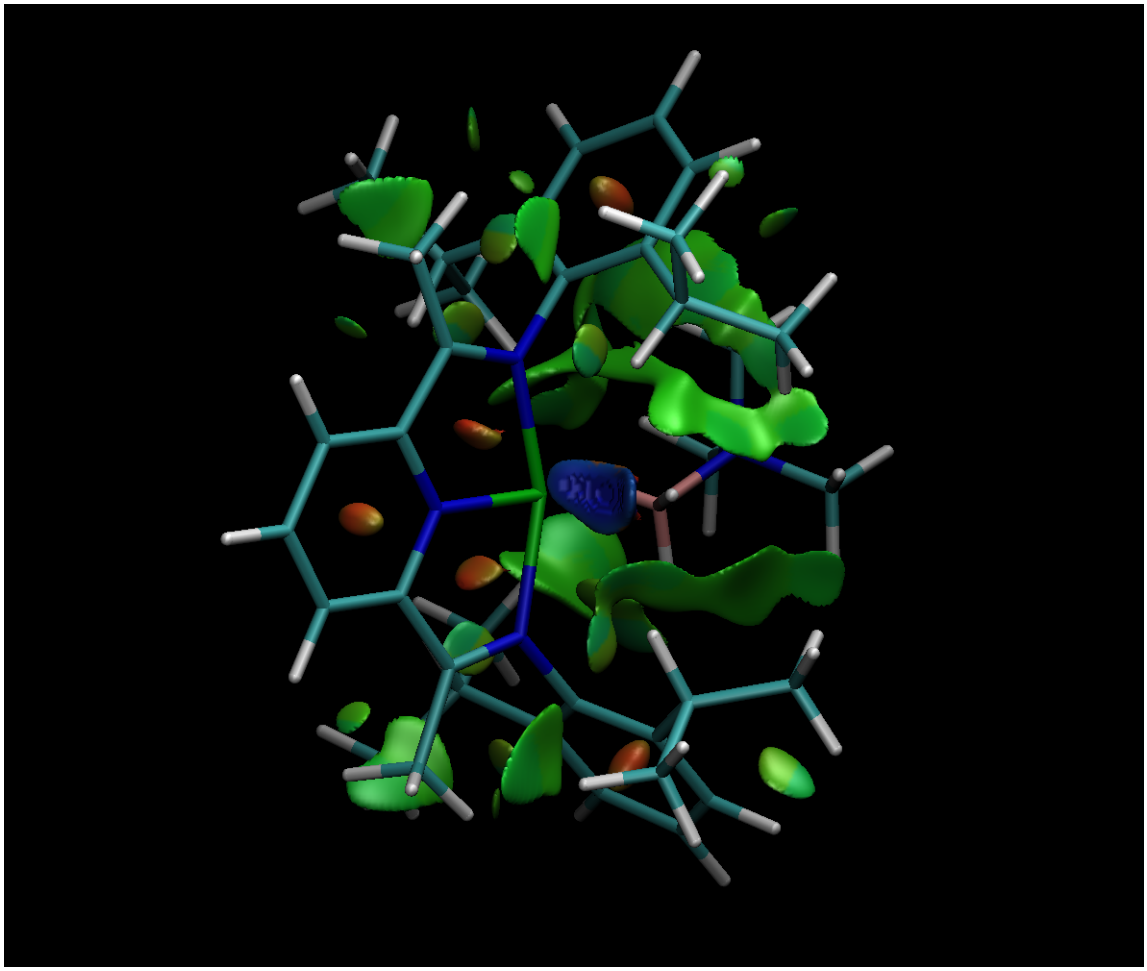


Figure S15. Full NCI plot for $\mathbf{2}^{+}$; isosurfaces generated for s = 0.3 au and -0.07 < ρ < 0.07 au.

2.5. Computed Cartesian Coordinates (Å) and Energies (a.u.) for all species.

1^+ (fully optimised)

SCF = -1795.75233617
H(0 K)= -1794.932053
H(298 K)= -1794.881053
G(298 K)= -1795.019705
Lowest Frequencies = 9.733cm-1, 14.322cm-1

H	5.11597	-2.01169	2.17008
H	3.91140	-1.76668	3.98990
C	1.00888	3.01984	0.13869
C	0.99078	4.42621	0.24806
C	-0.24337	5.08492	0.29750
C	-1.42141	4.33204	0.24646
C	-1.33569	2.92633	0.13969
C	2.30162	2.25390	0.10337
C	3.59117	3.03913	0.02417
C	3.73986	-0.57489	1.31978
C	3.01061	-0.27898	2.63089
C	3.65286	0.92581	3.36190
C	2.92423	-1.48910	3.58193
H	1.92077	4.99644	0.29290
H	-0.28616	6.17493	0.37984
H	-2.39257	4.82902	0.28757
H	1.97542	0.01245	2.36134
H	4.69374	0.69582	3.64804
H	3.09221	1.16819	4.28106
H	3.67342	1.82799	2.72843
H	2.50281	-2.37890	3.08337
H	2.27874	-1.24621	4.44253
H	-1.97244	-0.21114	2.28899
H	-4.02321	3.45739	0.91947
H	4.45808	2.36490	0.04493
H	3.67515	3.73965	0.87328
H	3.63363	3.64080	-0.90062
N	-0.13659	2.30535	0.06698
C	-2.96269	-0.59787	2.60377
C	-3.64907	0.51423	3.43391
C	-2.71965	-1.84623	3.47448
H	-3.77982	1.44065	2.84960
H	-3.05373	0.75831	4.33098
H	-4.64935	0.18809	3.76784
H	-3.65377	-2.22744	3.92208
H	-2.04277	-1.59857	4.30989
C	4.80898	-1.48604	1.26078
C	5.48897	-1.73342	0.05911
C	5.10608	-1.06002	-1.10641
C	1.91983	-3.33490	-0.32632
C	-0.01981	-4.72133	0.21090
H	6.31917	-2.44631	0.03421
H	5.63864	-1.26036	-2.04229
H	1.06963	-5.05898	-2.20649
H	2.53762	-4.24311	-0.42170
H	1.94780	-2.97221	0.71005
H	0.60208	-5.62660	0.11304
H	-1.06008	-4.94437	-0.06336
H	0.01028	-4.35497	1.24660
Ag	-0.01848	-0.02596	-0.06018
B	-0.46813	-2.34490	-0.56554
C	3.38002	0.11731	0.12506
C	4.05556	-0.11881	-1.10800
C	3.65862	0.55961	-2.42287
C	4.85920	1.24584	-3.11338
C	2.97794	-0.44382	-3.38396
C	-2.57085	2.06837	0.11185
C	-3.91336	2.76393	0.06738
C	-3.49268	-0.13717	0.13922
C	-5.21317	-1.37291	-1.03910
C	-4.21452	-0.37916	-1.06606
C	-3.90034	0.32818	-2.38738
C	-5.15023	0.98365	-3.01741
C	-3.23492	-0.64882	-3.38613
C	0.46042	-4.14455	-2.11441
H	2.91371	1.34304	-2.20026
H	5.36228	1.96330	-2.44393
H	4.52318	1.79174	-4.01124
H	5.61494	0.51172	-3.44060
H	-0.40654	-1.97281	0.62345
H	-0.05113	-1.51097	-1.41152
H	-1.59358	-2.68172	-0.84935
H	-5.77651	-1.58121	-1.95494
H	-3.16920	1.13152	-2.18895
H	3.66163	-1.27078	-3.64397
H	2.68241	0.05590	-4.32256
H	2.06861	-0.87601	-2.93048
H	-4.02705	3.35789	-0.85642
H	-4.72794	2.02838	0.11189
H	-5.89957	0.22833	-3.30939
H	-4.87340	1.53927	-3.92969
H	-5.64204	1.68621	-2.32396
H	-2.32220	-1.09549	-2.95821
H	-2.96495	-0.12448	-4.31943
H	-3.92187	-1.47196	-3.64890
H	0.85557	-3.36279	-2.77816
H	-0.58322	-4.35677	-2.38497
H	2.30907	-2.54897	-0.98844
N	2.22943	0.96023	0.17918
N	-2.40464	0.78385	0.17731
N	0.49956	-3.64228	-0.69825
C	-3.74560	-0.88952	1.32418
C	-4.76833	-1.85211	1.29326
C	-5.50124	-2.09597	0.12345
H	-4.99449	-2.42302	2.19890
H	-6.29332	-2.85142	0.11842
H	-2.26423	-2.66356	2.89067

1^+ (partially optimised)

SCF = -1795.73341663

H	4.66306	-1.88806	2.43450
H	3.20594	-1.60623	4.01374
C	0.96199	3.08105	-0.01837
C	0.93940	4.47307	-0.10436
C	-0.28815	5.10673	-0.15340
C	-1.44944	4.35359	-0.11198
C	-1.34343	2.96517	-0.04954
C	2.23941	2.30414	0.07297
C	3.51877	3.06715	0.25978
C	3.44459	-0.46318	1.37146
C	2.56351	-0.09706	2.55724
C	3.17466	1.06901	3.33397
C	2.29325	-1.26735	3.49324
H	1.86583	5.05106	-0.13531
H	-0.34317	6.19796	-0.21991
H	-2.42571	4.84212	-0.14239
H	1.58695	0.23743	2.15177
H	4.15708	0.78603	3.75151
H	2.52655	1.36508	4.17771
H	3.33232	1.95954	2.70532
H	1.86558	-2.13338	2.95937
H	1.57478	-0.97174	4.27660
H	-1.79164	0.06141	2.16873
H	-4.01592	3.46307	0.72916
H	4.36511	2.38632	0.42630
H	3.44660	3.76329	1.11294
H	3.74299	3.67926	-0.63304
N	-0.15864	2.35550	-0.00148
C	-2.73224	-0.37390	2.56303

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C  -3.43120  0.69890  3.38707
C  -2.34966 -1.56733  3.43595
H  -3.66955  1.59547  2.78869
H  -2.80586  1.02077  4.23889
H  -4.38403  0.32023  3.79767
H  -3.22348 -2.00286  3.95110
H  -1.64319 -1.25396  4.22426
C   4.47879 -1.38793  1.47846
C   5.28415 -1.67417  0.39060
C   5.07444 -1.05089 -0.82340
C   2.09106 -3.27816 -0.52266
C   0.41960 -4.82397  0.27176
H   6.09998 -2.39785  0.49416
H   5.72910 -1.28987 -1.66681
H   1.07495 -5.01082 -2.22150
H   2.73398 -4.11710 -0.83907
H   2.37752 -2.97131  0.49411
H   1.08263 -5.66441  0.00180
H  -0.62883 -5.13396  0.15680
H   0.58504 -4.57483  1.33289
Ag -0.05015 -0.01379 -0.09631
B  -0.30901 -2.45565 -0.19665
C   3.26493  0.16934  0.13394
C   4.05858 -0.11376 -0.99118
C   3.79424  0.56676 -2.32897
C   4.98066  0.52383 -3.28879
C   2.55822 -0.00973 -3.01855
C  -2.54839  2.06718 -0.02520
C  -3.89949  2.71525 -0.07445
C  -3.39089 -0.14556  0.12150
C  -5.08283 -1.52127 -0.86764
C  -4.11578 -0.52371 -1.01985
C  -3.80517  0.02753 -2.40440
C  -5.05198  0.36877 -3.21560
C  -2.93399 -0.96497 -3.16351
C   0.42894 -4.14413 -2.01430
H   3.58494  1.63460 -2.12365
H   5.90407  0.91627 -2.83025
H   4.76541  1.13131 -4.18366
H   5.18762 -0.50182 -3.64190
H   0.02842 -2.00745  0.90801
H  -0.18635 -1.64867 -1.15996
H  -1.44236 -2.87789 -0.17989
H  -5.66746 -1.83731 -1.73754
H  -3.22113  0.95864 -2.28764
H   2.72845 -1.06608 -3.29669
H   2.33357  0.54185 -3.94821
H   1.66003  0.03375 -2.37710
H  -4.04285  3.24527 -1.03335
H  -4.69769  1.96698  0.02656
H  -5.64058 -0.53031 -3.46677
H  -4.77054  0.84198 -4.17205
H  -5.72146  1.06248 -2.67880
H  -2.00669 -1.19807 -2.61392
H  -2.65629 -0.56953 -4.15728
H  -3.47344 -1.91590 -3.32155
H   0.66484 -3.30971 -2.68737
H  -0.63135 -4.41457 -2.11112
H   2.24370 -2.42242 -1.19316
N   2.13965  1.03626  0.00265
N  -2.33158  0.81390  0.03144
N   0.68015 -3.67629 -0.54487
C  -3.57344 -0.77311  1.36507
C  -4.55870 -1.76034  1.45436
C  -5.30585 -2.11934  0.35918
H  -4.73492 -2.25408  2.41535
H  -6.07685 -2.89195  0.45348
H  -1.87207 -2.36504  2.84352
```

2^+ (fully optimised)

SCF = -1759.39187615
H(0 K)= -1758.568902
H(298 K)= -1758.519576
G(298 K)= -1758.652046
Lowest Frequencies = 2.756cm-1, 24.742 cm-1

C	-4.16327	0.80526	-3.34427
H	-4.53626	1.64664	-2.73716
H	-3.74758	1.21675	-4.27976
H	-5.03208	0.17942	-3.61204
C	4.20784	0.62640	-3.34986
H	5.12509	-2.01818	-2.15647
H	6.04494	-2.85435	-0.00025
H	5.08528	0.00613	-3.60232
H	3.79256	1.01825	-4.29422
H	3.44201	-2.05687	-3.73692
B	0.41568	-1.90994	0.00396
C	-1.07479	4.42368	-0.00162
C	0.15438	5.09940	-0.00162
C	1.34828	4.36021	-0.00136
C	1.29796	2.95653	-0.00104
C	-3.64217	2.74883	-0.00221
C	2.42497	2.03881	-0.00086
C	3.82939	2.57910	-0.00144
C	-3.09367	-0.07920	-0.00127
C	-3.61953	-0.52105	-1.24682
C	-4.69285	-1.43419	-1.21441
C	-5.22744	-1.89090	-0.00225
C	-4.69714	-1.43041	1.21036
C	-3.62422	-0.51682	1.24377
C	-3.08907	-0.01586	-2.59213
C	-2.57150	-1.16765	-3.48244
C	-3.09883	-0.00757	2.58956
C	-4.17834	0.80869	3.33933
C	-2.57691	-1.15614	3.48156
C	3.17673	-0.22370	-0.00024
C	3.67581	-0.69550	-1.24399
C	4.71339	-1.64725	-1.21174
C	5.23311	-2.11992	-0.00024
C	4.71566	-1.64480	1.21126
C	3.67819	-0.69292	1.24355
C	3.14191	-0.19744	-2.58928
C	2.62963	-1.35958	-3.46881
C	3.14675	-0.19240	2.58891
C	4.21471	0.63095	3.34715
C	2.63415	-1.35285	3.47052
C	-1.84335	-3.28143	0.00583
C	0.10127	-4.10754	-1.21275
C	0.10086	-4.10342	1.22781
C	-1.09527	3.01823	-0.00132
C	-2.25976	2.15529	-0.00148
H	-2.01662	4.97822	-0.00182
H	0.18300	6.19189	-0.00183
H	2.31672	4.86646	-0.00136
H	-5.12486	-1.78218	-2.15891
H	-6.06731	-2.59298	-0.00264
H	-5.13241	-1.77555	2.15441
H	-2.23021	0.64794	-2.39059
H	-2.24305	0.66045	2.38906
H	1.58744	-2.18101	0.00417
H	5.12909	-2.01385	2.15597
H	2.27901	0.46234	-2.38901
H	2.28443	0.46823	2.38902
H	-3.36744	-1.89609	-3.71500
H	-2.19448	-0.77102	-4.44037
H	-1.74049	-1.70741	-2.99620
H	0.07810	-1.24717	-1.03326
H	0.07830	-1.24414	1.03918
H	-5.04399	0.17859	3.60736
H	-3.76582	1.22384	4.27459
H	-4.55537	1.64706	2.73056
H	-1.74162	-1.69125	2.99750
H	-2.20450	-0.75716	4.44033
H	-3.36946	-1.88888	3.71218
H	4.56872	1.48197	-2.75501
H	1.84532	-1.93399	-2.94891
H	2.20531	-0.96882	-4.40958
H	4.57616	1.48518	2.75074
H	3.80104	1.02466	4.29144
H	5.09155	0.00979	3.59952
H	3.44603	-2.05088	3.73822
H	2.21168	-0.96046	4.41145
H	1.84836	-1.92679	2.95237
H	-2.18442	-2.74046	0.89725
H	-2.18420	-2.74392	-0.88777
H	-2.25608	-4.30371	0.00775
H	-0.33258	-5.12107	-1.19599
H	-0.23836	-3.57196	-2.11053
H	1.19844	-4.16342	-1.21469
H	1.19805	-4.15909	1.23043
H	-0.23931	-3.56497	2.12365
H	-0.33276	-5.11710	1.21417
H	-3.78692	3.38872	0.88646
H	-3.78451	3.39211	-0.88879
H	-4.42049	1.97523	-0.00467
H	4.57507	1.77444	-0.00258
H	3.99531	3.21541	-0.88891
H	3.99663	3.21399	0.88681
N	-0.34663	-3.34544	0.00617
N	0.08411	2.29892	-0.00098
N	2.10146	0.74646	-0.00034
N	-1.98479	0.84780	-0.00097
Rh	0.03490	0.37088	0.00020

2^+ (partially optimised)

SCF = -1759.37466969

C	-4.02948	0.46574	-3.37685
H	-4.41886	1.35805	-2.85888
H	-3.60516	0.79381	-4.34156
H	-4.89196	-0.18584	-3.60125
C	3.68921	0.65467	-3.29006
H	4.85397	-2.21327	-2.15580
H	5.89285	-2.89926	-0.03382
H	4.68285	0.25076	-3.55408
H	3.20120	0.97325	-4.22813
H	3.50927	-2.03618	-3.85794
B	0.41219	-1.87548	0.16467
C	-1.04771	4.39226	-0.23445
C	0.17680	5.06028	-0.21574
C	1.35037	4.33514	-0.14871
C	1.30416	2.95176	-0.10117
C	-3.59939	2.71098	-0.16231
C	2.41815	2.02060	-0.05457
C	3.82487	2.54150	-0.00386
C	-3.05017	-0.07059	0.00891
C	-3.55088	-0.63023	-1.17437
C	-4.61693	-1.52110	-1.07658
C	-5.16395	-1.84002	0.15163
C	-4.65053	-1.27693	1.29890
C	-3.58213	-0.38755	1.26203
C	-2.97486	-0.26860	-2.53987
C	-2.44602	-1.47952	-3.28489
C	-3.03557	0.20622	2.55480
C	-4.12329	0.96225	3.31829
C	-2.42001	-0.84881	3.43921
C	3.12390	-0.22798	-0.03541
C	3.51040	-0.79878	-1.25434
C	4.51594	-1.76042	-1.21770
C	5.09591	-2.14794	-0.03455
C	4.65844	-1.60412	1.16349
C	3.66599	-0.63897	1.18782
C	2.85061	-0.38663	-2.56433
C	2.57872	-1.57735	-3.48124
C	3.17812	-0.06974	2.51153
C	4.27580	0.66904	3.25533
C	2.58110	-1.14342	3.40380
C	-1.76645	-3.26211	0.14728
C	0.21019	-4.10262	-0.98423
C	0.02746	-3.90856	1.59359
C	-1.06649	3.00388	-0.16665

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C  -2.22099  2.13232 -0.13863
H  -1.98695  4.94872 -0.28624
H   0.20416  6.15221 -0.25923
H   2.31815  4.84349 -0.13094
H  -5.03302 -1.96231 -1.98891
H  -6.01069 -2.53193  0.21201
H  -5.09469 -1.53271  2.26757
H  -2.12467  0.41768 -2.38090
H  -2.23959  0.92453  2.29248
H   1.59099 -2.10676  0.22247
H   5.10947 -1.93584  2.10529
H   1.87390  0.06818 -2.31361
H   2.36985  0.65082  2.29316
H  -3.22298 -2.24936 -3.43754
H  -2.07639 -1.18993 -4.28389
H  -1.60004 -1.94799 -2.75256
H   0.09919 -1.29158 -0.92737
H   0.03519 -1.14618  1.13579
H  -4.92196  0.28471  3.66708
H  -3.70071  1.45315  4.21180
H  -4.60173  1.74078  2.70048
H  -1.56436 -1.34457  2.94767
H  -2.04132 -0.40464  4.37632
H  -3.15039 -1.62850  3.72091
H   3.85712  1.55840 -2.68070
H   2.00114 -2.36464 -2.96857
H   2.00325 -1.25433 -4.36579
H   4.73181  1.47069  2.65013
H   3.88330  1.12867  4.17910
H   5.09218 -0.01244  3.55418
H   3.33123 -1.90368  3.68611
H   2.19818 -0.70132  4.34021
H   1.74547 -1.66344  2.90781
H  -2.16166 -2.64411  0.96354
H  -2.07311 -2.81904 -0.80762
H  -2.17529 -4.28324  0.22473
H  -0.22629 -5.11417 -0.95922
H  -0.11643 -3.56516 -1.88335
H   1.30705 -4.15520 -0.95619
H   1.11647 -3.94451  1.73698
H  -0.42715 -3.25773  2.35069
H  -0.39886 -4.92304  1.65272
H  -3.77350  3.33537  0.73284
H  -3.72739  3.37095 -1.03861
H  -4.37519  1.93622 -0.19606
H   4.56455  1.73604 -0.09065
H   4.00008  3.27104 -0.81343
H   3.99905  3.07275  0.94935
N  -0.27537 -3.30669  0.22657
N   0.10174  2.29988 -0.11467
N   2.07883  0.76157 -0.04399
N  -1.94723  0.85179 -0.06405
Rh  0.05008  0.39281 -0.02924
```

3. References

S1. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518-1520.

2. H. Nishida, N. Takada, M. Yoshimura, T. Sonoda and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2600-2604.

3. E. L. Dias, M. Brookhart and P. S. White, *Organometallics*, 2000, **19**, 4995-5004.

4. Y. Zhang, A. M. Santos, E. Herdtweck, J. Mink and F. E. Kühn, *New J. Chem.*, 2005, **29**, 366-370.

5. A. T. Lubben, J. S. McIndoe and A. S. Weller, *Organometallics*, 2008, **27**, 3303-3306.

6. G. J. P. Britovsek, M. Bruce, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. Mastroianni, S. J. McTavish, C. Redshaw, G. A. Solan, S. Strömberg, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 1999, **121**, 8728-8740.

7. J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105-107.

8. *Agilent (2014). CrysAlis PRO. Agilent Technologies Ltd, Yarnton, Oxfordshire, England.*

9. G. Sheldrick, *Acta Crystallographica Section A*, 2015, **71**, 3-8.

10. G. Sheldrick, *Acta Crystallographica Section A*, 2008, **64**, 112-122.

11. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.

12. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Wallingford CT, 2013

13. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100.

14. J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822-8824.

15. D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta.*, 1990, **77**, 123-141.

16. W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257-2261.

17. P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta.*, 1973, **28**, 213-222.

18. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.

19. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.
20. S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200-1211.
21. A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639-5648.
22. J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999-3094.
23. R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, **1990**.
24. AIMAll (Version 13.02.26, Professional), T. A. Keith and T. K. Gristmill, Software, Overland Park KS, USA (aim.tkgristmill.com), 2015
25. NBO 6.0., E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI., 2013
26. J. Contreras-García, E. R. Johnson, S. Keinan, R. Chaudret, J.-P. Piquemal, D. N. Beratan and W. Yang, *J. Chem. Theor Comput.*, 2011, **7**, 625-632.
27. E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen and W. Yang, *J. Am. Chem. Soc.*, 2010, **132**, 6498-6506.
28. Chemcraft version 1.7 see http://www.chemcraftprog.com,
29. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466-470.