Supplementary Information

Hydroboration *via* Metal-Bound *σ*(B-H) Bonds in Ru-(*σ*-Borate) Complexes: A Pathway to *η*^{4}-*HBCC*-*σ*,*π*-Borataallyl Complexes

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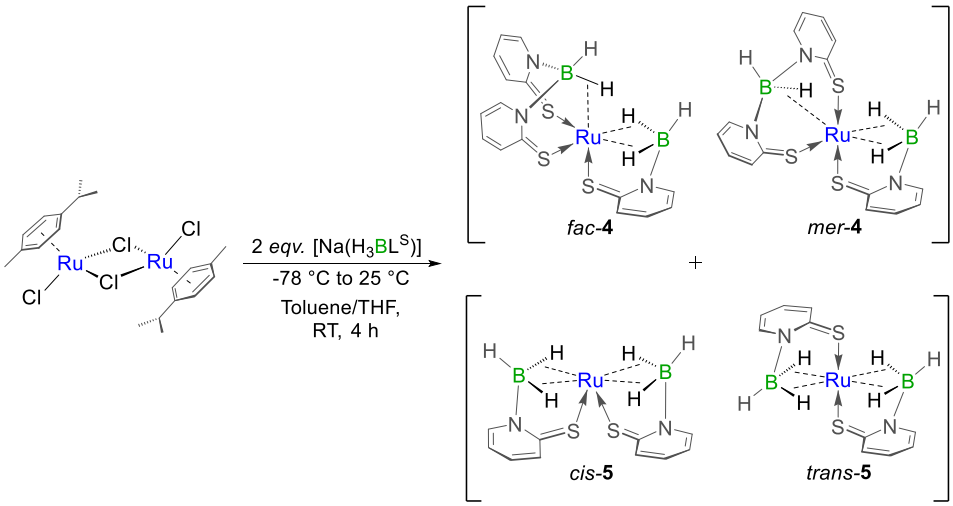
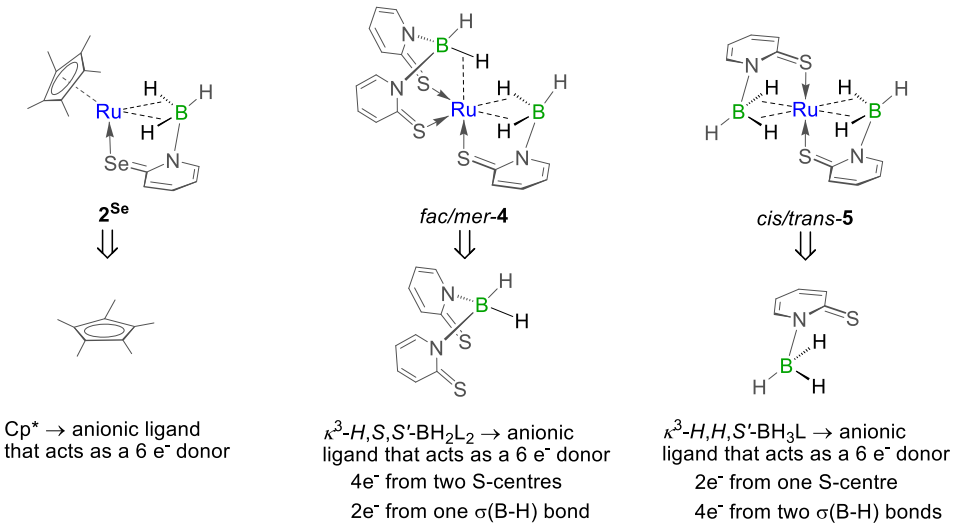
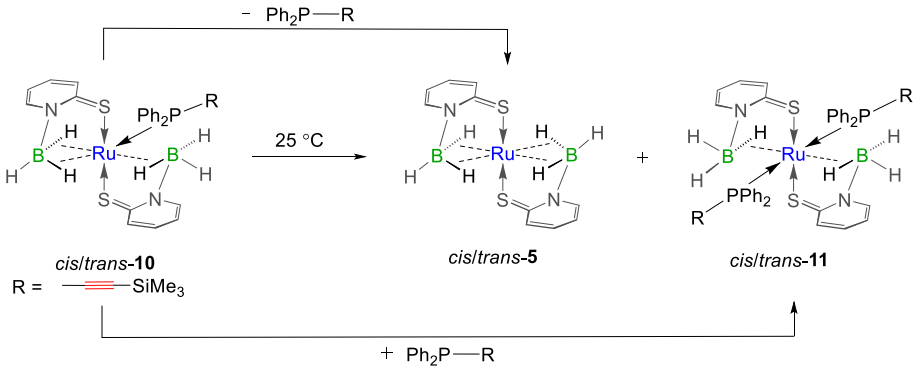
I Supplementary Data



Scheme S1. Syntheses of Ru-(σ-borate) complexes **4** and **5**, explicitly depicting their different isomeric forms.



Scheme S2. Electronic resemblance among the ancillary ligands in complexes **2^{Se}**, **4**, and **5**.



Scheme S3. Transformation of complex**10** into complex **5** and **11**.

II Experimental Details

General procedures and instrumentation: All the syntheses were carried out under argon atmosphere with standard Schlenk and glove box techniques. Solvents were distilled prior to use under an Ar atmosphere. 2-mercaptopyridine, 2-bromopyridine, Se powder, $LiBH_4$, $NaBH_4$, Cp*H, *p*-cymene, $RuCl_3$, methyl propiolate, diphenylacetylene, trimethylsilyl acetylene, n-butyllithium, chlorodiphenylphosphine, potassium carbonate were obtained commercially and used as received (Sigma Aldrich). Compounds such as $Na[(H_3B)L^S]$[1], $[Cp^*RuCl_2]_2$[2], $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$[3], Alkynylphosphine, as well as $PPh_2C_2SiMe_3$[4] were synthesized according to the literature methods. Thin-layer chromatography was carried out on 250-μm aluminium supported silica gel TLC plates. The NMR spectra were recorded on a 500 MHz Bruker FT-NMR spectrometer. Signals for residual protons in the deuterated solvents were used as a reference in ^{1}H NMR ($CDCl_3$, δ = 7.26 ppm, C_6D_6, δ = 7.16) while a sealed tube containing $[Bu_4N][(B_3H_8)]$ in benzene-d_6 (δ_B, ppm, -30.07) was used as an external reference for ^{11}B NMR spectra. Mass Spectra were recorded on Agilent Technologies: 6545-Q-TOF LC/MS mass spectrometer in ESI ionization mode. Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer.

II.1 Synthesis and Characterization

Syntheses of 2^S, 2^{Se}: In a flame-dried Schlenk tube, $LiBH_4$ (0.163 mL, 0.326 mmol) was added dropwise to L^SH (0.036 g, 0.326 mmol) and $L^{Se}H$ (0.051 g, 0.326 mmol), respectively in 10 mL of THF at -78 ºC and further stirred at 25 ºC for 30 min. Further, $[Cp^*RuCl_2]_2$ (0.100 g, 0.163 mmol) dissolved in 10 mL of toluene was added to the solution and allowed to react for 4h at 25 ºC. The colour of the reaction mixture changed from brown to red. The solvent was evaporated in vacuum; residue was extracted into hexane/CH_2Cl_2 (80:20 v/v) and passed through Celite. After the removal of solvent from filtrate, the residue was subjected to chromatographic work-up using silica-gel TLC plates. Elution with hexane/CH_2Cl_2 (50:50 v/v) yielded red **2^S** (0.061 g, 52%), **2^{Se}** (0.052 g, 39%).

2^{Se}: MS (ESI$^+$): *m/z* calculated for $[M+H]^+$: 410.0140, found: 409.9596; ^{1}H NMR (500 MHz, $CDCl_3$, 22 °C): δ = 8.63-6.80 (m, 4H, $H_{Ar(L^{Se})}$), 4.63 (br, 1H, BH_t), 1.99 (s, 15H, Cp*), -8.08 (br, 2H, Ru-*H*-B) ppm; ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, 22 °C): δ = 13.5 (br, 1B) ppm; IR (dicholoromethane, cm^{-1}): $\tilde{\nu}$ = 2354, 2303 (B-H), 1261 (C=Se).

Syntheses of 3a, 3b: In a flame-dried Schlenk tube, a red solution of **2^{Se}** (0.100 g, 0.078 mmol) and one equivalent of methyl propiolate in toluene (10 mL) was stirred for 4h at 25 °C. The colour of the reaction mixture changed from red to orange. The solvent was evaporated in vacuum; residue was extracted into hexane/CH_2Cl_2 (40:60 v/v) and passed through Celite. After the removal of solvent from filtrate, the residue was subjected to chromatographic work-up using silica-gel TLC plates. Elution with hexane/CH_2Cl_2 (40:60 v/v) yielded orange **3a** (0.030 g, 25 %) and orange **3b** (0.033 g, 27 %).

3a: MS (ESI$^+$): *m/z* calculated for $[M]^+$: 492.0362, found: 492.0536;^{1}H NMR (500 MHz, $CDCl_3$, 22 °C): δ = 8.10-6.74 (m, 4H, $H_{Ar(L^{Se})}$), 3.50, 2.17 (s, 2H, H_2C), 3.63 (s, 3H, -OCH_3), 3.23 (br, BH_t), 1.70 (s, 15H, Cp*), -11.75 (br, 1H, Ru-*H*-B) ppm; ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, 22 °C): δ = -4.6 (br, 1B) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 22 °C): δ = 176.7 (s, C=S), 169.4 (s, *C*OOCH$_3$), 147.5 (s, C=N), 136.3, 132.1, 116.6 (s, $Ar_{(L^{Se})}$), 92.9 (s, C_5Me_5), 53.0 (s, B*C*COOCH$_3$), 51.0 (s, CH_2), 29.8 (s, -OCH$_3$), 9.7 (s, C_5Me_5) ppm; IR (dicholoromethane, cm^{-1}): $\tilde{\nu}$ = 2863 (C-H), 2431 (B-H), 1474 (C=C), 1270 (C=Se).

3b: MS (ESI$^+$): *m/z* calculated for $[M]^+$: 492.0293, found: 492.0484;^{1}H NMR (500 MHz, $CDCl_3$, 22 °C): δ = 8.09 - 6.74 (m, 4H, $H_{Ar(L^{Se})}$), 4.00 (br, BH_t), 3.66 (s, 3H, -OCH_3), 3.65 (d, 1H, *H*C), 2.86 (d, 1H, *H*C), 1.75 (s, 15H, Cp*), -11.47 (br, 1H, Ru-*H*-B) ppm; ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, 22 °C): δ = -7.1 (br, 1B) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 22 °C): δ = 176.7 (s, C=S), 169.4 (s, *C*OOCH$_3$), 147.5 (s, C=N), 134.7, 134.0, 116.6 (s, $Ar_{(L^{Se})}$), 92.9 (s, C_5Me_5), 53.0 (s, B*C*H), 51.0 (s, H*C*COOCH$_3$), 29.8 (s, -O*C*H$_3$), 9.7 (s, C_5Me_5) ppm; IR (dicholoromethane, cm^{-1}): $\tilde{\nu}$ = 2888 (C-H), 2465 (B-H), 1454 (C=C), 1243 (C=Se).

Syntheses of *fac/mer*-**6a**-**b**: In a flame-dried Schlenk tube, a brown solution of **4** (0.100 g, 0.218 mmol) and one equivalent of methyl propiolate in toluene (10 mL) was thermalized for 8h at 80°C. The colour of the reaction mixture changed from brown to orange. The solvent was evaporated in vacuum; residue was extracted into hexane/CH_2Cl_2 (30:70 v/v) and passed through Celite. After the removal of solvent from filtrate, the residue was subjected to chromatographic work-up using silica-gel TLC plates. Elution with hexane/CH_2Cl_2 (10:90 v/v) yielded orange *fac/mer*-**6a**-**b** (0.032 g, 27 %).

fac/mer-**6a**-**b**: MS (ESI$^+$): *m/z* calculated for $[M]^+$: 541.9957, found 541.9990; ^{1}H NMR (500 MHz, $CDCl_3$, 22 °C): δ = 8.01-6.49 (m, $H_{Ar(L^S)}$), 5.08 (d, *J* = 13 Hz, BC*H*$_{mer\text{-}6b}$), 4.55 (d, *J* = 13.3 Hz, BC*H*$_{fac\text{-}6b}$), 4.00-3.64 (m, *H*CCOOCH$_3$ *fac*/mer-**6b**), 4.00-3.64 (B*H*$_t$ *fac*/mer-**6a**,**b**), 3.79, 3.32 (s, -OC*H*$_3$ *fac*/mer-**6a**,**b**), 3.20 (s, C*H*$_2$ *mer*-**6a**), 2.35(s, C*H*$_2$ *fac*-**6a**), -7.98 (br, Ru-*H*-B*fac*-**6a**,**b**), -9.19 (br, Ru-*H*-B*mer*-**6a**,**b**), -9.86 (br, Ru-*H*-B*fac*-**6a**,**b**), -15.40 (br, Ru-*H*-B*mer*-**6a**,**b**); ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, 22 °C): δ = 8.2 (br, B*fac*-**6a**,**b**), 6.7 (br, B*mer*-**6a**,**b**), -7.6 (br, B*fac/mer*-**6a**,**b**); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 22 °C): δ = 183.9, 182.7, 178.3 (s, C=S), 172.7 (s, *C*OOCH$_3$), 145.8-144.0 (s, C=N), 134.6-114.9 (s, Ar, L^S), 75.3 (s, B*C*COCH$_3$ *mer*-**6a**), 70.9 (s, B*C*COCH$_3$ *fac*-**6a**), 51.5 (s, B*C*H *fac*/mer-**6b**), 51.3, 51.0(s, CH$_2$ *fac*/mer-**6a**,**b**), 39.6 (s, CCO*C*H$_3$ *fac*/mer-**6a**,**b**), 29.8 (s, -O*C*H$_3$) ppm; IR (dicholoromethane, cm^{-1}): $\tilde{\nu}$ = 2852 (C-H), 2437 (B-H), 1522 (C=C), 1022 (C=S).

Synthesis of 7: In a flame-dried Schlenk tube, a brown solution of **4** (0.100 g, 0.218 mmol) and one equivalent of diphenylacetylene in toluene (10 mL) was thermalized for 48h at 80°C. The colour of the reaction mixture changed from brown to pink. The solvent was evaporated in vacuum; residue was extracted into hexane/CH_2Cl_2 (30:70 v/v) and passed through Celite. After the removal of solvent from filtrate, the residue was subjected to chromatographic work-up using silica-gel TLC plates. Elution with hexane/CH_2Cl_2 (10:90 v/v) yielded pink **7** (0.019 g, 10 %).

7: MS (ESI$^+$): *m/z* calculated for $[M+H]^+$: 864.8560, found 864.9036; ^{1}H NMR (500 MHz, $CDCl_3$, 22 °C): δ = 7.96 - 6.23 (m, H_{Ar}), ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 22 °C): δ = 177.9 – 114.2 (s, ar) ppm; IR (dicholoromethane, cm^{-1}): $\tilde{\nu}$ = 1064 (C=S).

Syntheses of *fac*/*mer*-**8**: In a flame-dried Schlenk tube, a brown solution of **4** (0.100 g, 0.218 mmol) and one equivalent of diphosphinoethynltrimethylsilane toluene (10 mL) was thermalized for 8h at 80°C. The colour of the reaction mixture changed from brown to red. The solvent was evaporated in vacuum; residue was extracted into hexane/CH_2Cl_2 (30:70 v/v) and passed through Celite. After the removal of solvent from filtrate, the residue was subjected to chromatographic work-up using silica-gel TLC plates. Elution with hexane/CH_2Cl_2 (20:80 v/v) yielded pink *fac /mer* -**8** (0.035 g, 22%)**.**

fac /mer -**8**: *m/z* calculated for $[M-H]^+$: 740.0744, found: 740.1042; ^{1}H NMR (500 MHz, $CDCl_3$, 22 °C): δ = 7.94 -6.35 (m, H_{Ar}), 4.26, 4.06 (br, B*H*$_t$), 0.32(s, Si*Me*$_3$ *fac/mer*-**8**), -5.72 (br, Ru-*H*-B) ppm; ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, 22 °C): δ = 8.1 (br, B*fac/mer*-**8**), -19.1 (br, B *fac/mer*-**8**) ppm; ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 22 °C): δ = 38.5 (s, 1P *fac*-**8**), 30.5 (s, 1P *mer*-**8**) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 22 °C): δ = 184.0, 183.6, 180.1 (s, C=S), 145.1, 145.0, 144.5 (s, C=N), 132.5 - 114.3 (s, Ar), 99.1, 98.6 (s, C≡C), 0.3 (s, Si*Me*$_3$) ppm; IR (dicholoromethane, cm^{-1}): $\tilde{\nu}$ = 2423 (B-H), 2297 (C≡C), 1061 (C=S).

Syntheses of *cis*/*trans*-**9**: In a flame-dried Schlenk tube, an orange solution of *cis*/*trans*-**5** (0.100 g, 0.286 mmol) and one equivalent of diphenyl acetylene in toluene (10 mL) of toluene was allowed to react at 25 °C for 4h. The colour of the reaction mixture changed from orange to yellow. The solvent was evaporated in vacuum; residue was extracted into hexane/CH_2Cl_2 (50:50 v/v) and passed through Celite. After the removal of solvent from filtrate, the residue was subjected to chromatographic work-up using silica-gel TLC plates. Elution with hexane/CH_2Cl_2 (60:40 v/v) yielded yellow *cis*/*trans*-**9** (0.017 g, 30 %).

cis/*trans*-**9**: MS (ESI$^+$): *m/z* calculated for $[M-H]^+$: 526.0555, found: 526.0878; ^{1}H NMR (500 MHz, $CDCl_3$, 22 °C): δ = 7.53-6.60 (m, H_{Ar}), 5.04, 4.42, 3.65 (s, C*H*Ph *cis/trans*-**9**), 4.68, 3.35 (br, B*H*$_t$), -7.84 (br, 2H, Ru-*H*-B *cis/mer+trans* -**9**), -8.13 (br, 1H, Ru-*H*-B *cis/mer*-**9**), -8.72 (br, 2H, Ru-*H*-B *cis/fac+trans* -**9**), -9.44(1H, br, Ru-*H*-B *trans* -**9**) , -10.40(1H, br, Ru-*H*-B *cis/fac*-**9**), -12.92(1H, br, Ru-*H*-B *cis/mer*-**9**), -13.52(1H, br, Ru-*H*-B *cis/fac*-**9**), ppm; ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 22 °C): δ = 30.3 (br, 1B *cis+trans* -**9**), -4.9 (br, 1B *cis+trans* -**9**) ppm;

$^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 22 °C): δ = 181.1, 176.2 (s, C=S), 146.3, 146.0, 145.9, 145.3 (s, C=N), 140.1-114.3 (s, Ar), 83.7, 79.3 (s, B*C*CPh), 59.7 (s, H*C*Ph); IR (dicholoromethane, cm^{-1}): $\tilde{\nu}$ = 2852 (C-H), 2491, 2443 (B-H), 1613 (C=C), 1024 (C=S).

Syntheses of *cis/trans*-**10** and *cis/trans*-**11**: In a flame-dried Schlenk tube, an orange solution of *cis*/*trans*-**8** (0.100 g, 0.286 mmol) and one equivalent of diphosphinoethynltrimethylsilane toluene (10 mL) was stirred for 4h at 25°C. The colour of the reaction mixture changed from yellow to brown. The solvent was evaporated in vacuum; residue was extracted into hexane/CH_2Cl_2 (70:30 v/v) and passed through Celite. After the removal of solvent from filtrate, the residue was subjected to chromatographic work-up using silica-gel TLC plates. Elution with hexane/CH_2Cl_2 (50:50 v/v) yielded red *cis /trans* **-10** (0.038 g, 22%) and pink *cis/trans*-**11** (0.060 g, 25 %).

cis/trans-**10**: MS (ESI^+): *m/z* calculated for $[M-H]^+$: 631.0757, found: 631.0781 ^1H NMR (500 MHz, $CDCl_3$, 22 °C): δ = 8.21-6.59 (m, 18H, H_{Ar}), 5.35, 5.26, 5.12 (br, BH_t), 0.32(s, Si$Me_{3\ cis\text{-}10}$), 0.25(s, Si$Me_{3\ trans\text{-}10}$), -5.47 (br, 1H, Ru-*H*-$B_{trans\text{-}10}$), -6.79 (br, 1H, Ru-*H*-$B_{cis\text{-}10}$), -12.72 (br, 2H, Ru-*H*-$B_{trans\text{-}10}$), -13.96 (br, 2H, Ru-*H*-$B_{cis\text{-}10}$) ppm; $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, 22 °C): δ = -2.0 (br, $2B_{trans\text{-}10}$), 0.1(br, $2B_{cis\text{-}10}$) ppm; $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 22 °C): δ = 43.1 (s, $1P_{cis\text{-}10}$), 40.1 (s, $1P_{trans\text{-}10}$) ppm.

cis/trans-**11**: ^1H NMR (500 MHz, $CDCl_3$, 22 °C): δ = 8.10-6.42 (m, 56H, Ar $_{cis/trans\text{-}11}$), 5.99 (br, BH_t), 0.17 (s, 36H, Si$Me_{3\ cis/trans\text{-}11}$), -15.22, (br, 2H, Ru-*H*-$B_{trans\text{-}11}$), -16.24 (br, 2H, Ru-*H*-$B_{cis\text{-}11}$) ppm; $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, 22 °C): δ = 39.6 (br, $4B_{cis/trans\text{-}11}$), $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 22 °C): δ = 32.2 (s, $4P_{cis/trans\text{-}11}$) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 22 °C): δ = 181.3, 179.2 (s, C=S, mp), 151.2, 145.1 (s, C=N), 136.6, - 113.9 (s, Ar), 102.5, 102.0 (s, C≡C), 0.2 (s, SiMe_3) ppm; IR (dicholoromethane, cm^{-1}): $\tilde{\nu}$ = 2465 (B-H), 2227 (C≡C), 1065 (C=S).

II.2 Spectroscopic Details

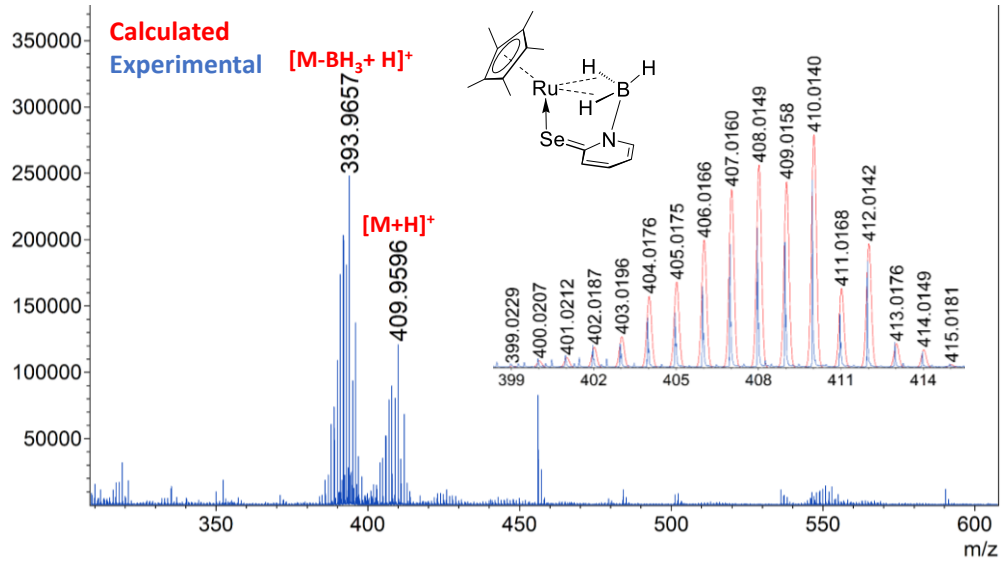


Figure S1. Calculated (red) and experimental (blue) mass spectral isotopic distribution for **2^{Se}** in CH_2Cl_2.

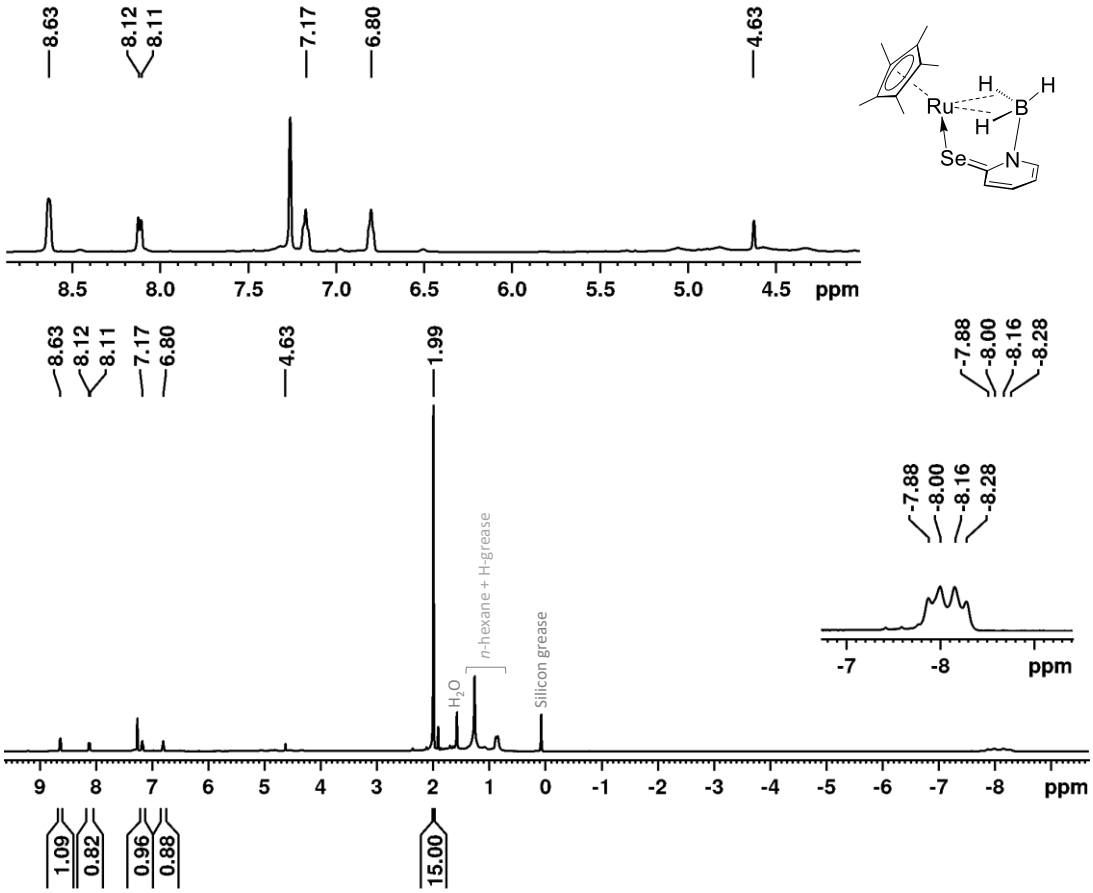


Figure S2. ^{1}H NMR spectrum of **2^{Se}** in $CDCl_3$.

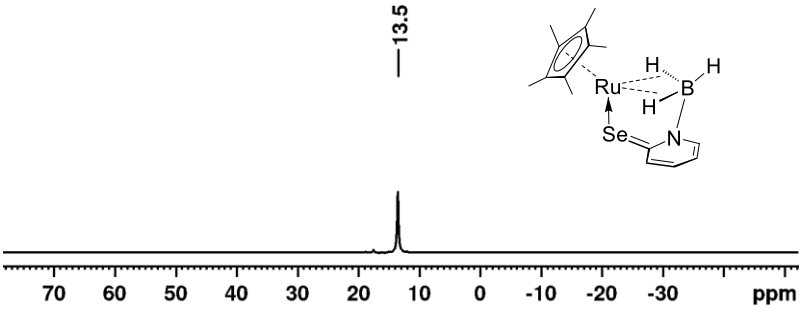


Figure S3. $^{11}B\{^{1}H\}$ NMR spectrum of **2^{Se}** in $CDCl_3$.

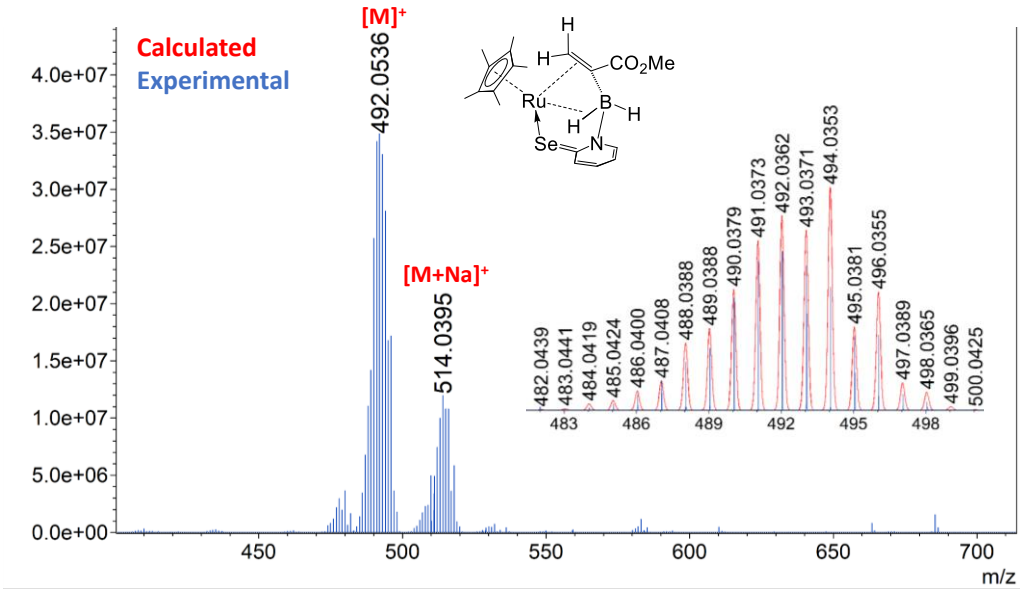


Figure S4. Calculated (red) and experimental (blue) mass spectral isotopic distribution for **3a** in CH_2Cl_2.

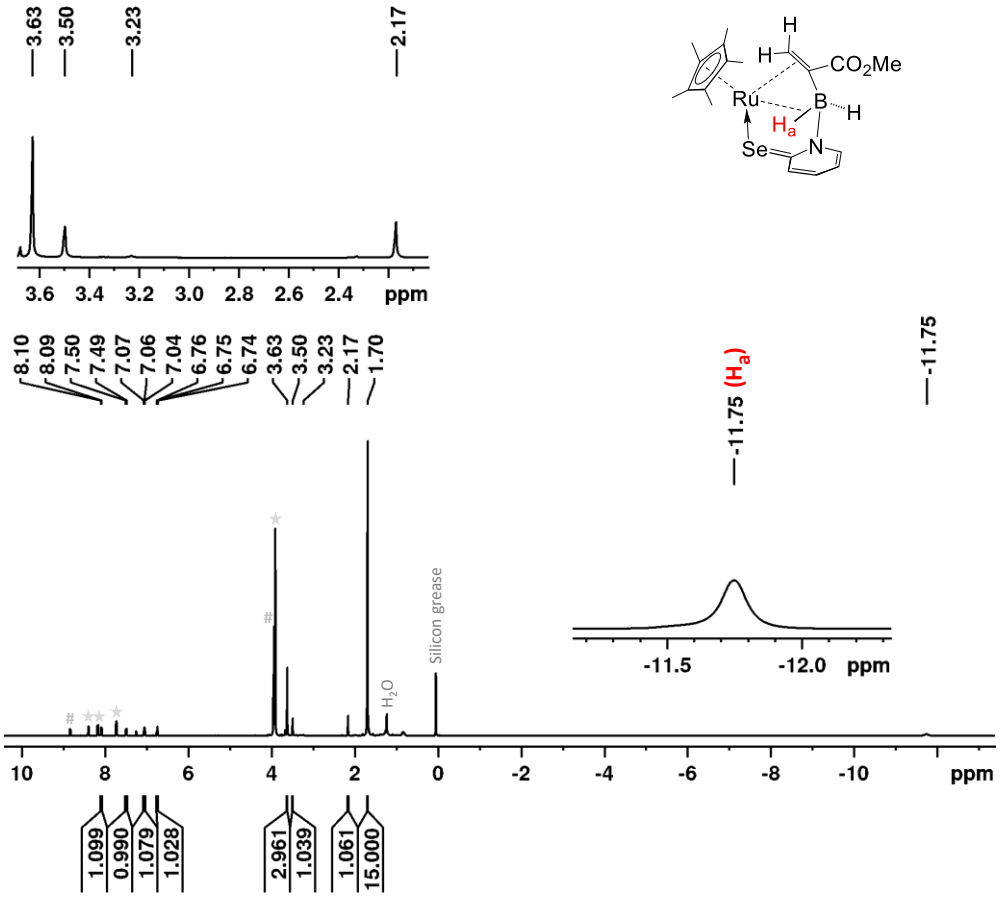


Figure S5. ^{1}H NMR spectrum of **3a** in $CDCl_3$. (* = inseparable impurity of trimethyl-1,2,4-benzenetricarboxylate and # = inseparable impurity of trimethyl-1,3,5-benzenetricarboxylate)

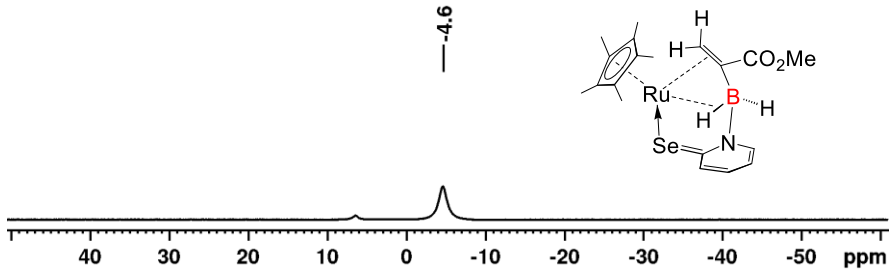


Figure S6. $^{11}B\{^{1}H\}$ NMR spectrum of **3a** in $CDCl_3$.

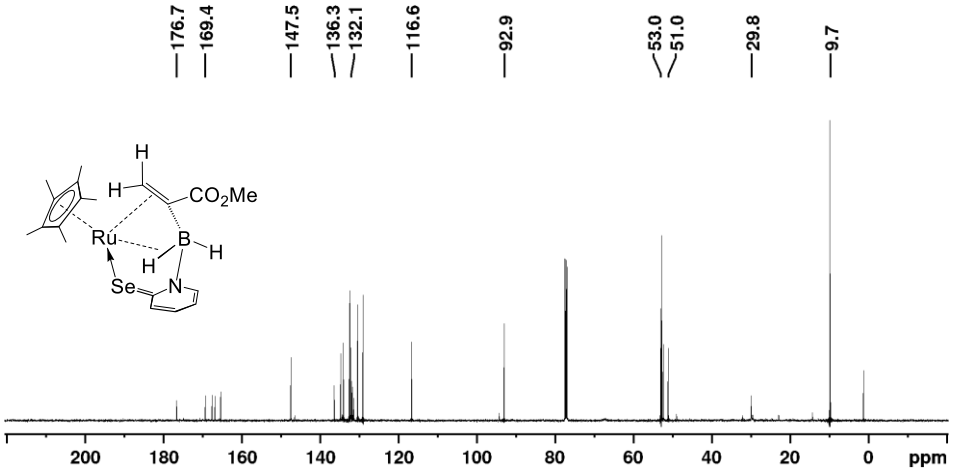


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **3a** in $CDCl_3$.

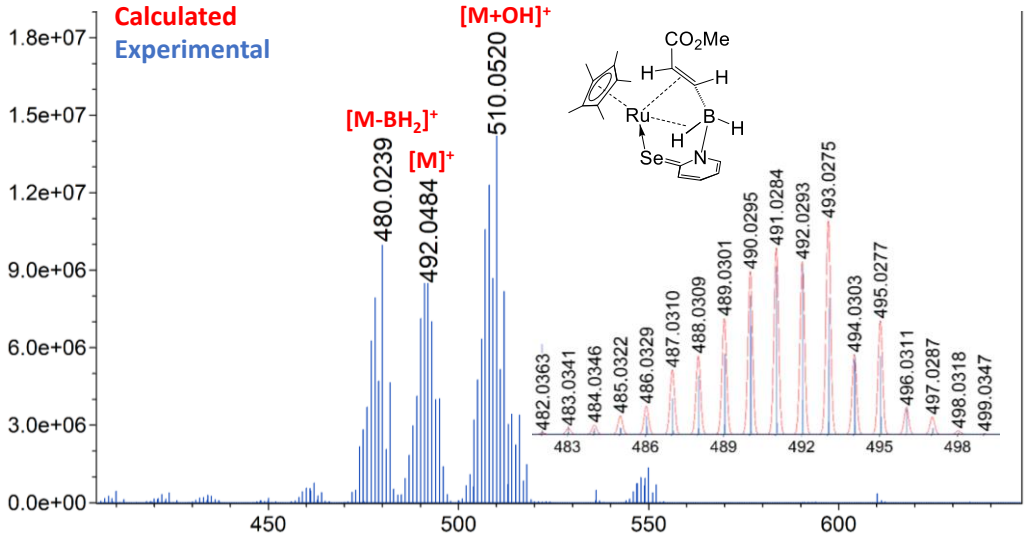


Figure S8. Calculated (red) and experimental (blue) mass spectral isotopic distribution for **3b** in CH_2Cl_2.

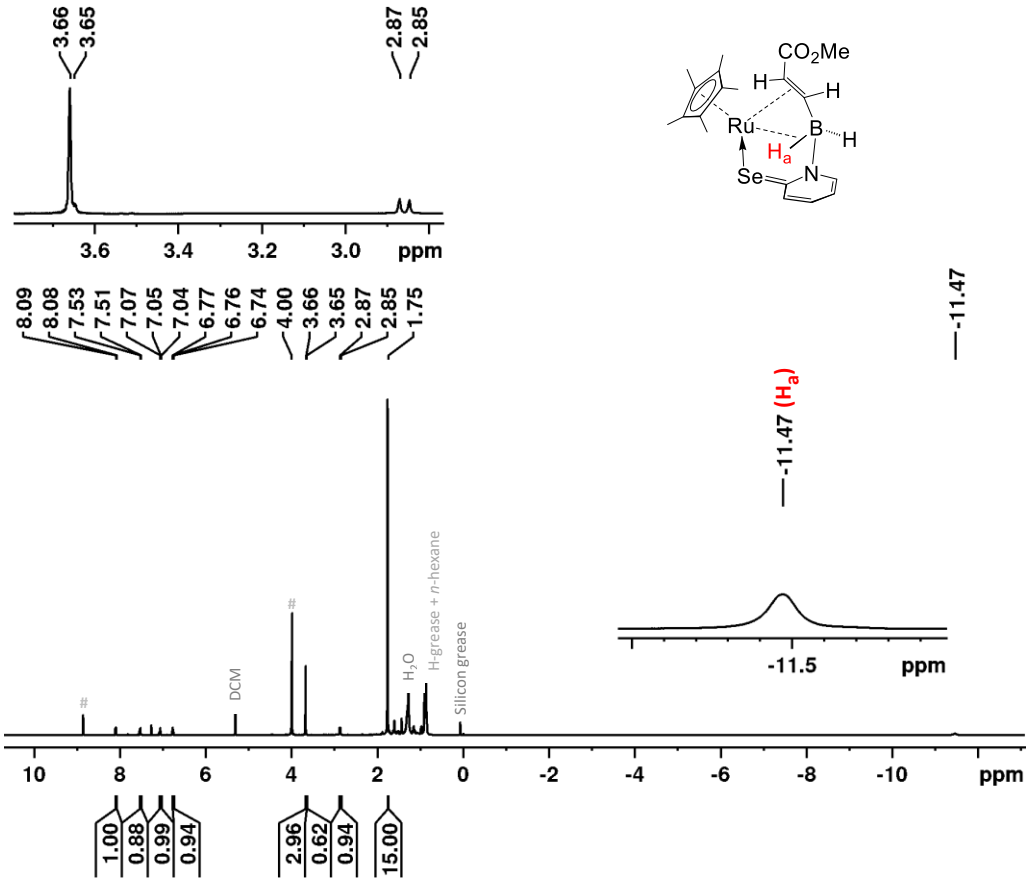


Figure S9. ^{1}H NMR spectrum of **3b** in $CDCl_3$. (# = inseparable impurity of trimethyl-1,3,5-benzenetricarboxylate)

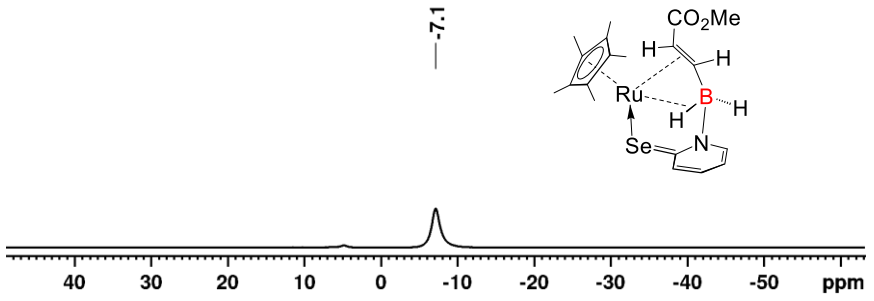


Figure S10. $^{11}B\{^{1}H\}$ NMR spectrum of **3b** in $CDCl_3$.

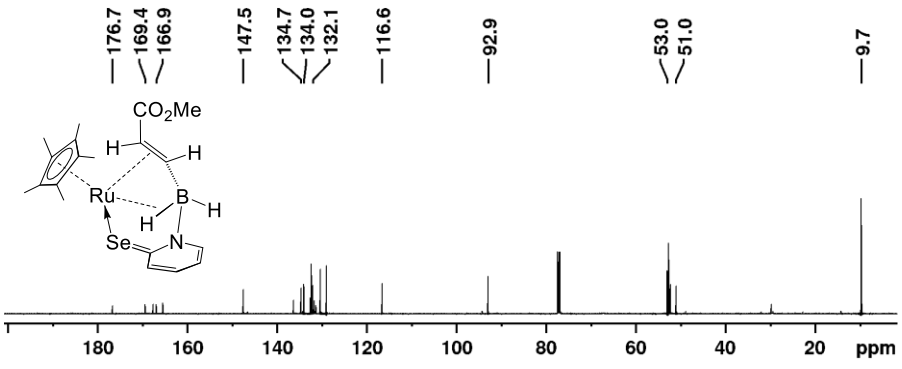


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **3b** in $CDCl_3$.

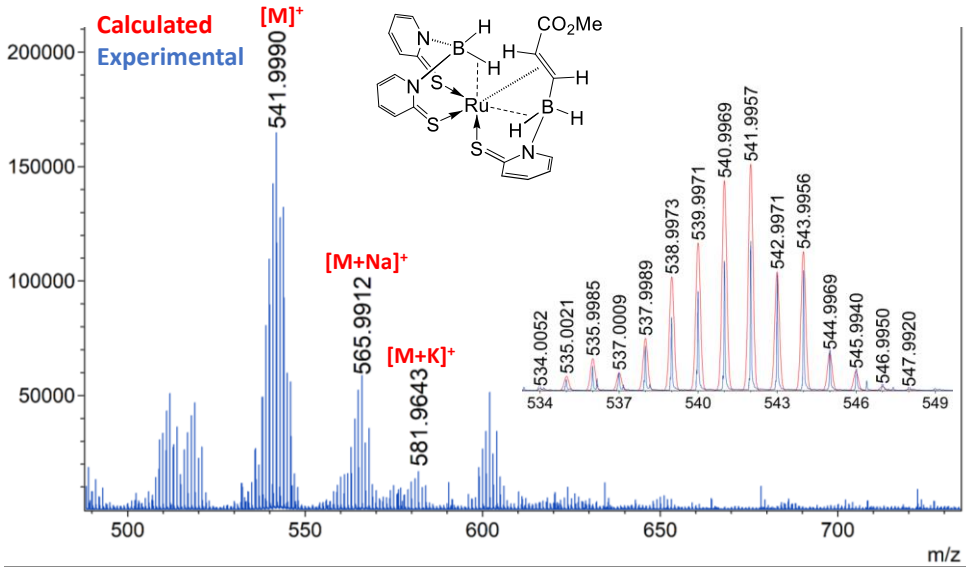


Figure S12. Calculated (red) and experimental (blue) mass spectral isotopic distribution for **6** in CH_2Cl_2.

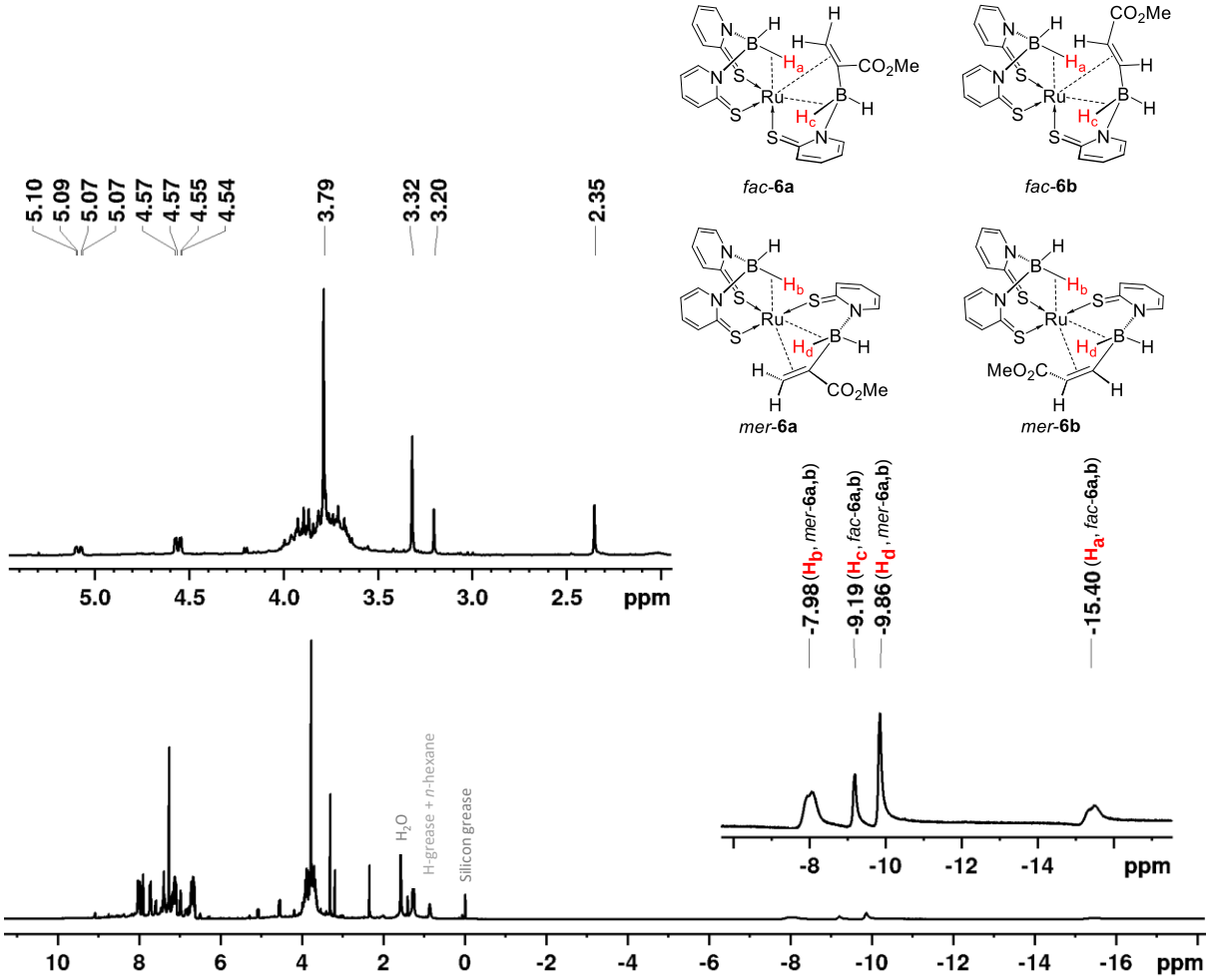


Figure S13. ^{1}H NMR spectrum of **6** in $CDCl_3$.

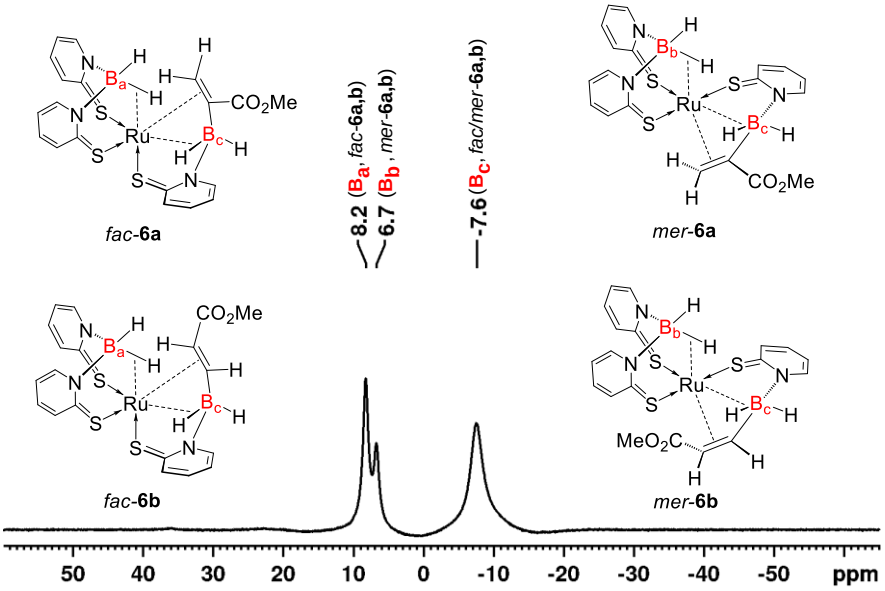


Figure S14. $^{11}B\{^1H\}$ NMR spectrum of **6** in $CDCl_3$.

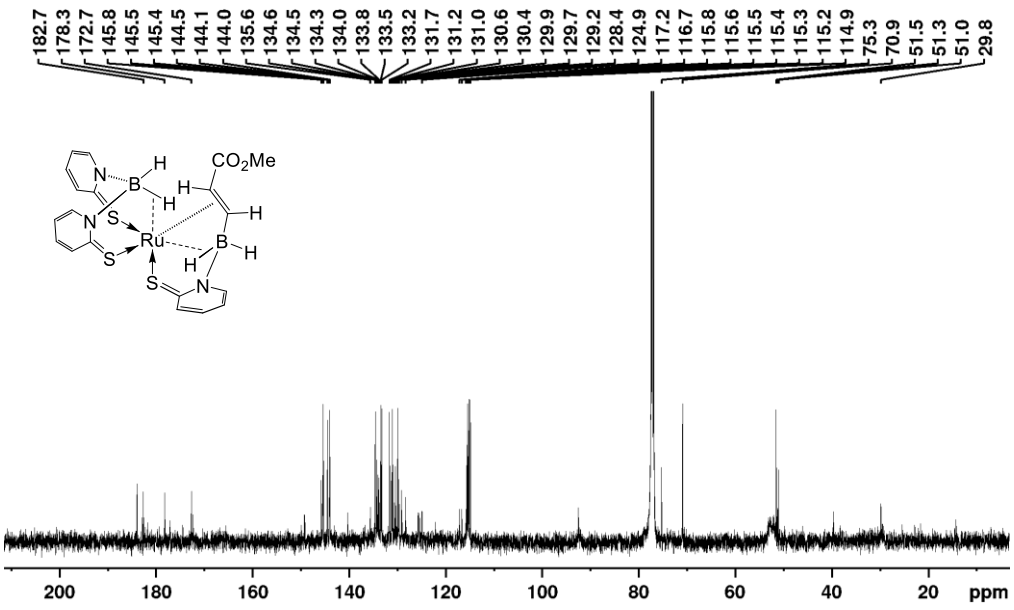


Figure S15. $^{13}C\{^1H\}$ NMR spectrum of **6** in $CDCl_3$.

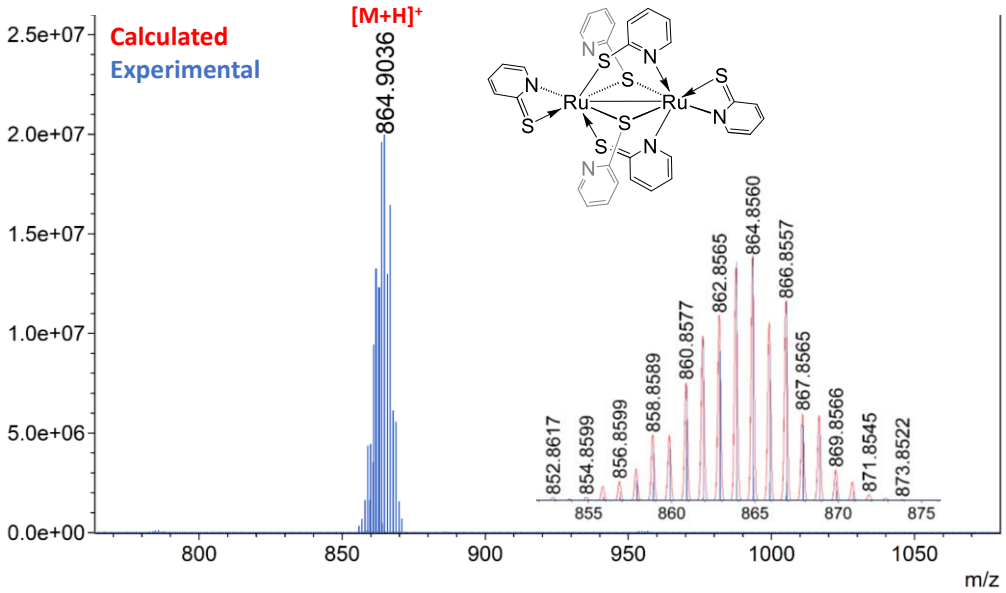


Figure S16. Calculated (red) and experimental (blue) mass spectral isotopic distribution for **7** in CH_2Cl_2.

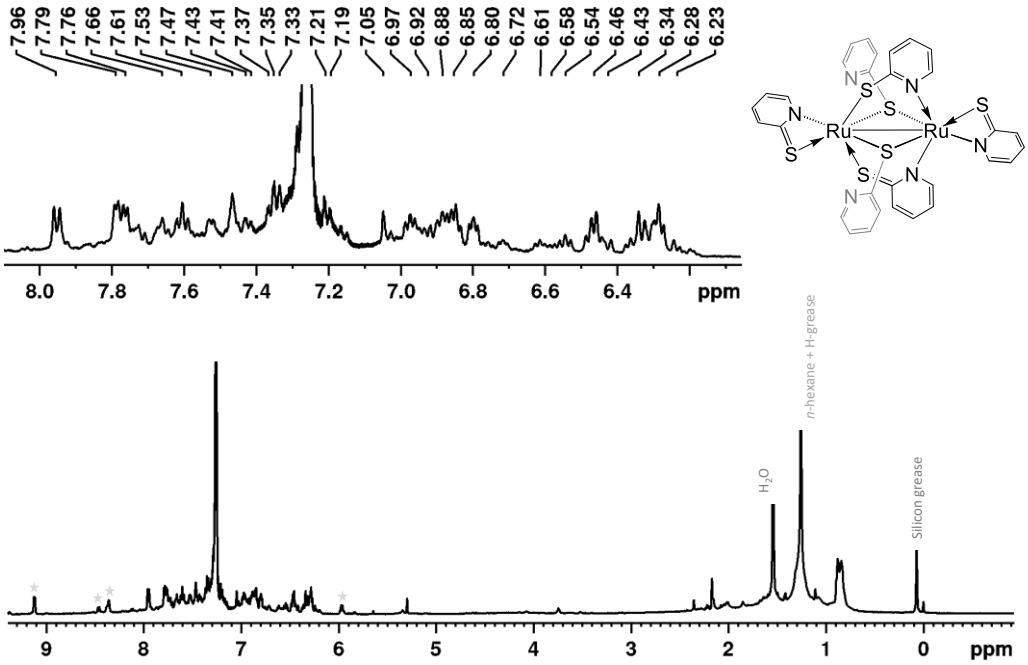


Figure S17. ^1H NMR spectrum of **7** in $CDCl_3$. (* = inseparable impurity)

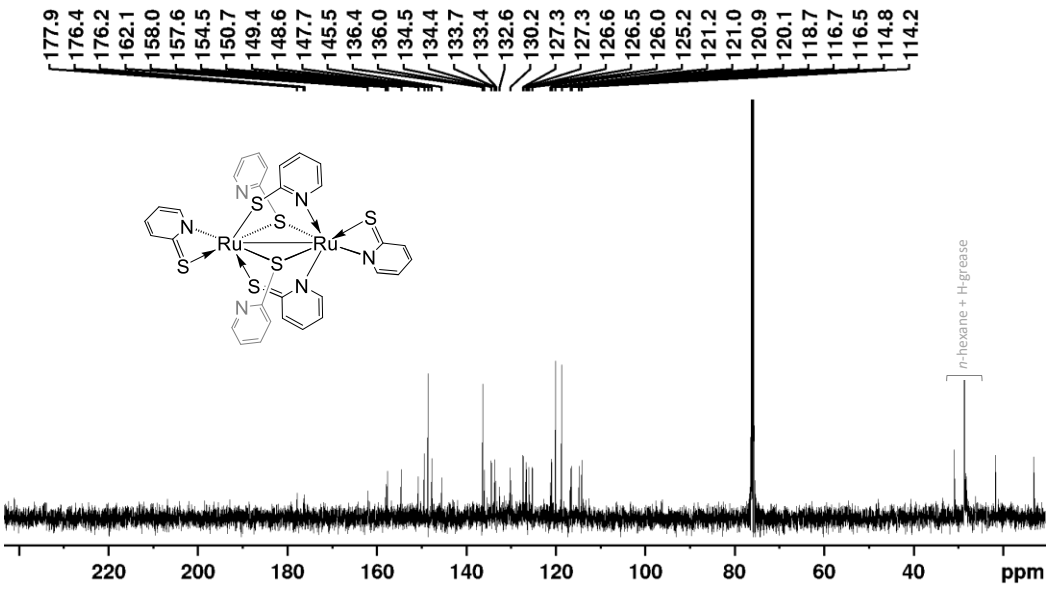


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in $CDCl_3$.

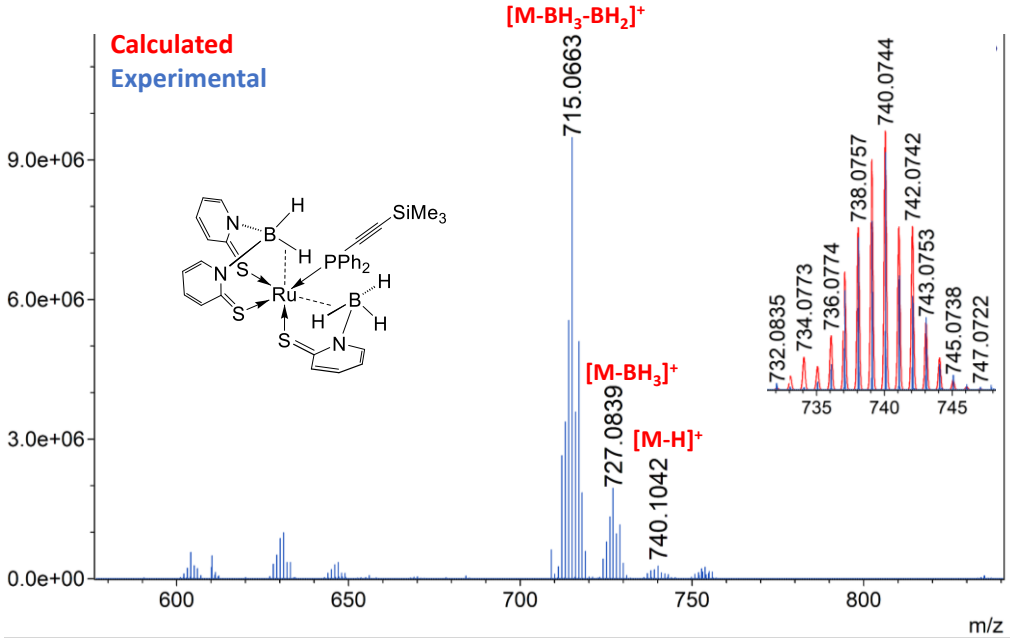


Figure S19. Calculated (red) and experimental (blue) mass spectral isotopic distribution for **8** in CH_2Cl_2.

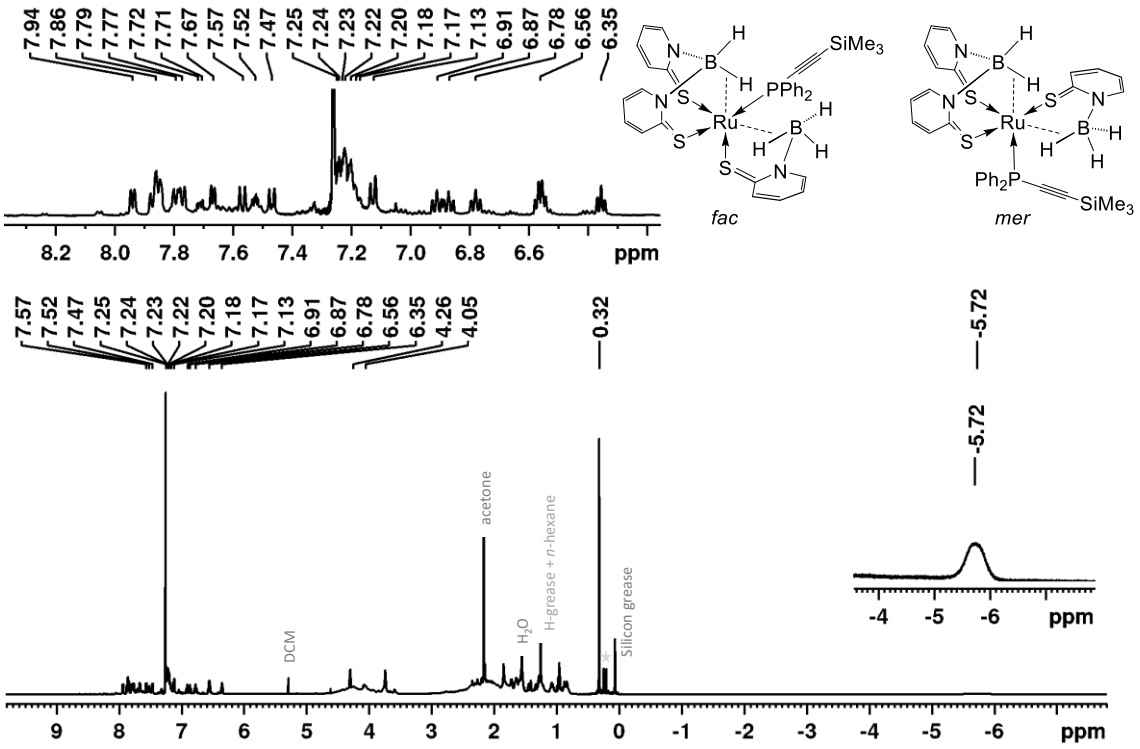


Figure S20. ^{1}H NMR spectrum of **8** in $CDCl_3$. (* = inseparable impurity of diphosphinoethynltrimethylsilane)

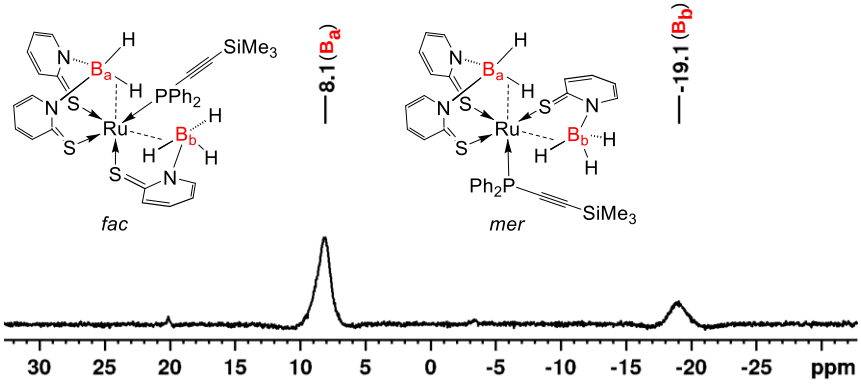


Figure S21. $^{11}B\{^{1}H\}$ NMR spectrum of **8** in $CDCl_3$.

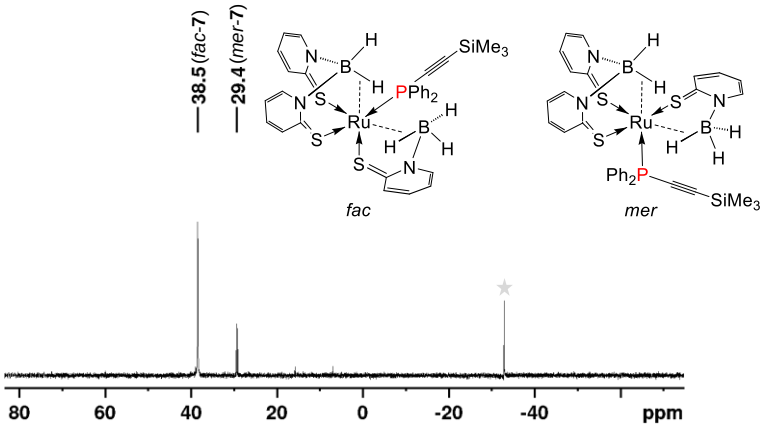


Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum of **8** in $CDCl_3$. (* = inseparable impurity of diphosphinoethynltrimethylsilane)

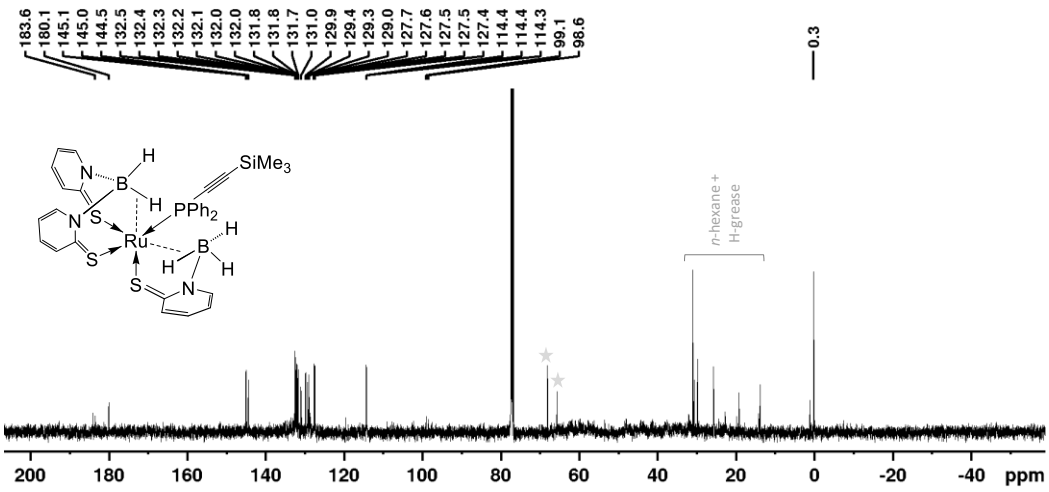


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of **8** in $CDCl_3$. (* = inseparable impurity of diphosphinoethynltrimethylsilane)

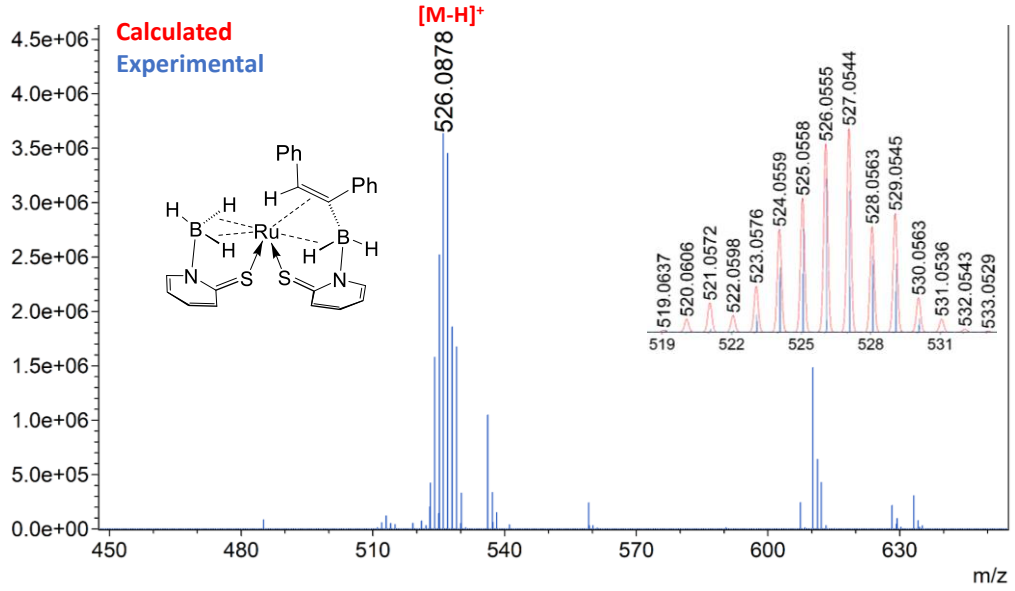


Figure S24. Calculated (red) and experimental (blue) mass spectral isotopic distribution for **9** in CH_2Cl_2.

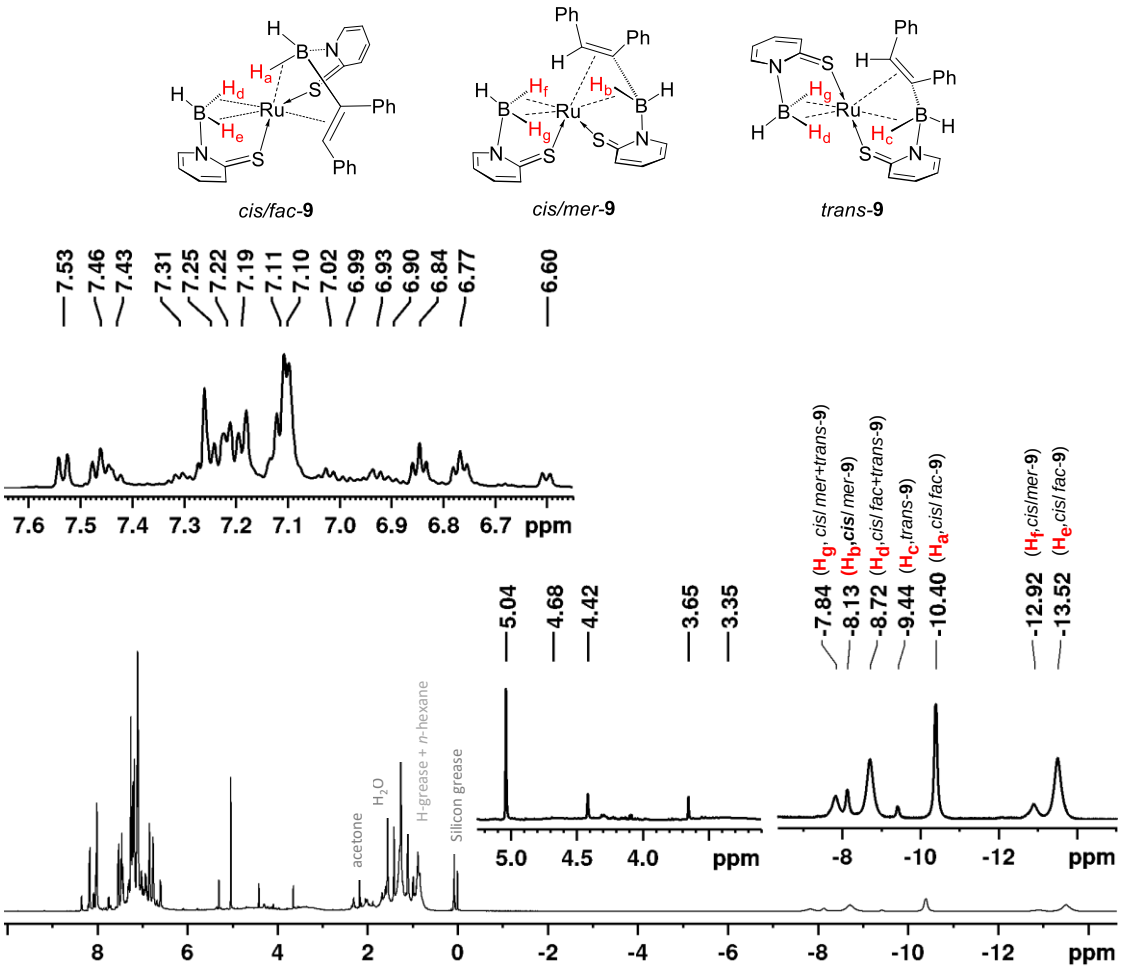


Figure S25. ^{1}H NMR spectrum of **9** in C_6D_6.

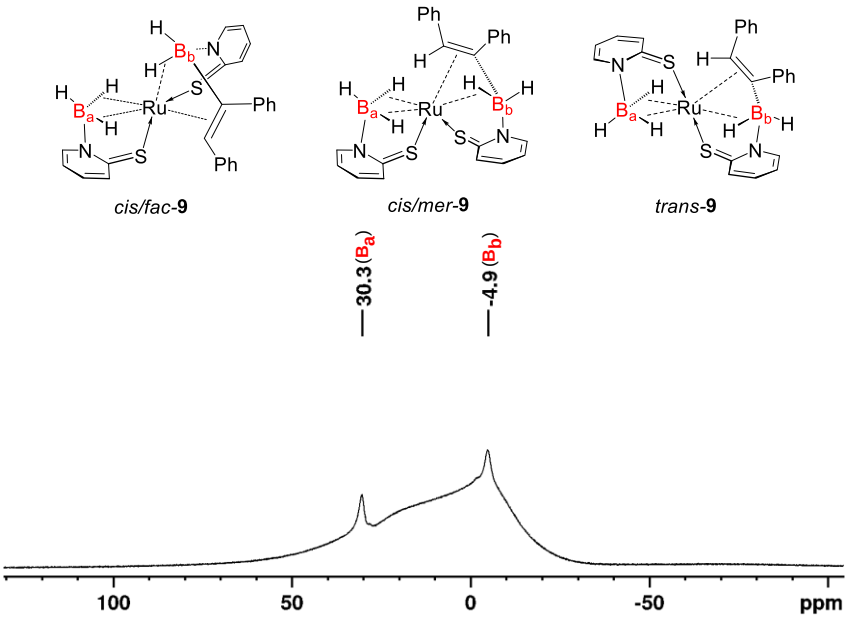


Figure S26. $^{11}B\{^{1}H\}$ NMR spectrum of **9** in C_6D_6.

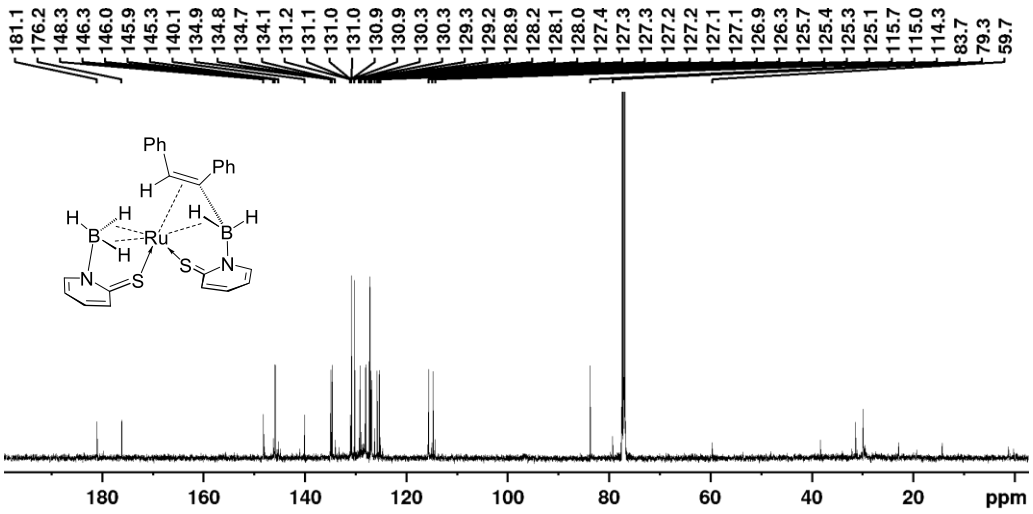


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of **9** in C_6D_6.

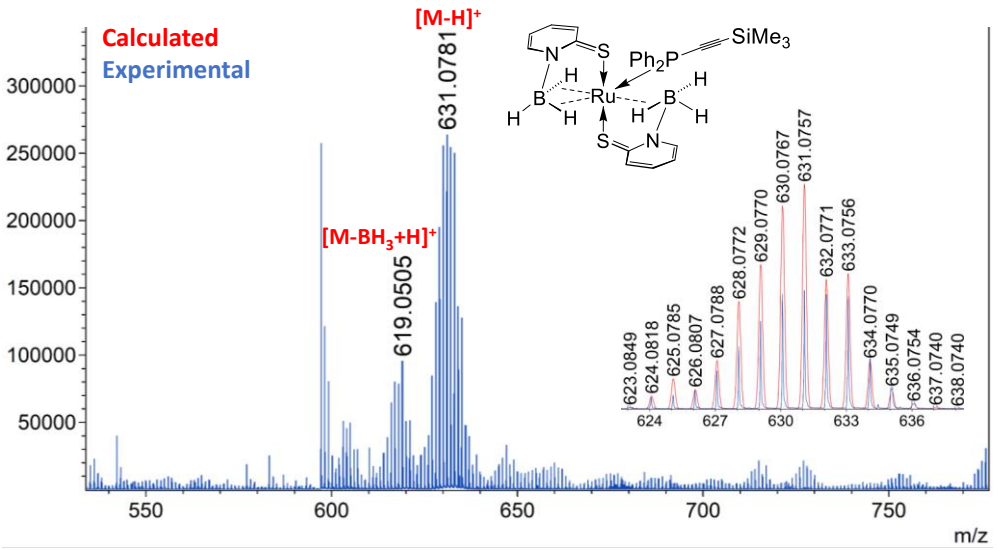


Figure S28. Calculated (red) and experimental (blue) mass spectral isotopic distribution for **10** in CH_2Cl_2.

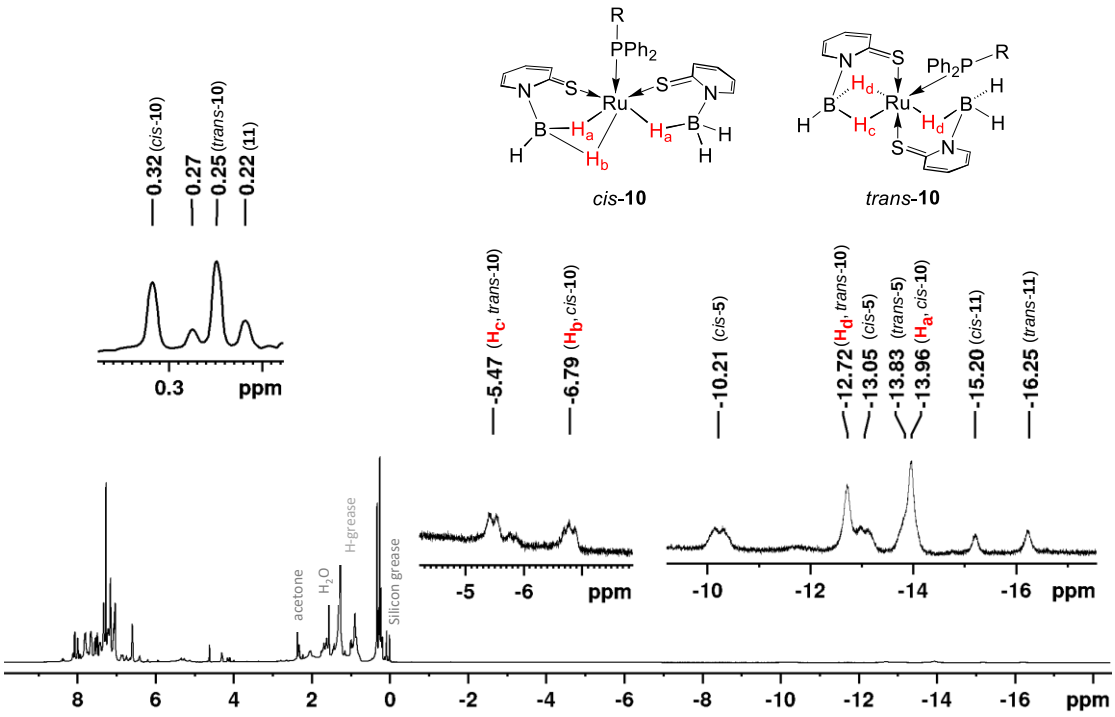


Figure S29. ^{1}H NMR spectrum of **10** (impure) in C_6D_6.

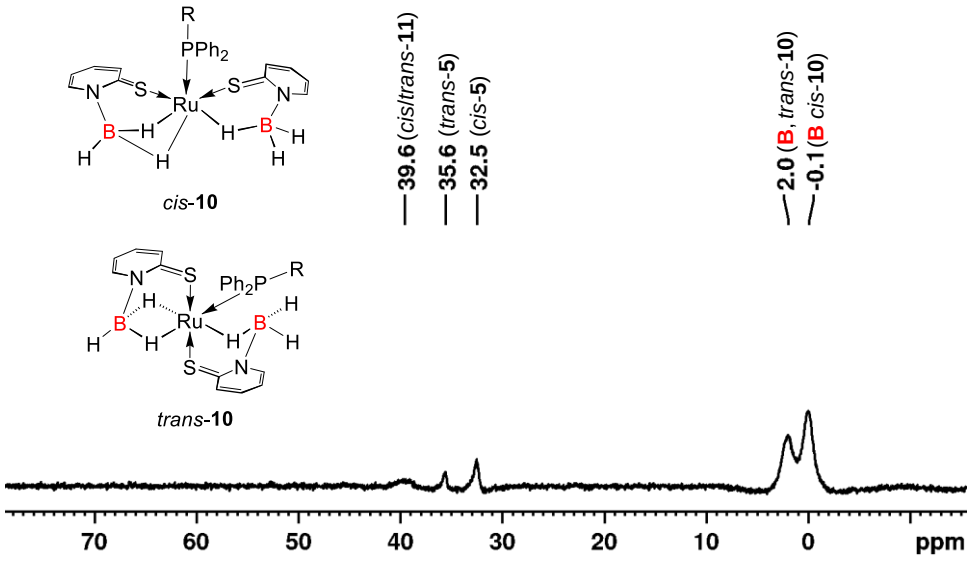


Figure S30. ^{11}B{^{1}H} NMR spectrum of **10** (impure) in C_6D_6.

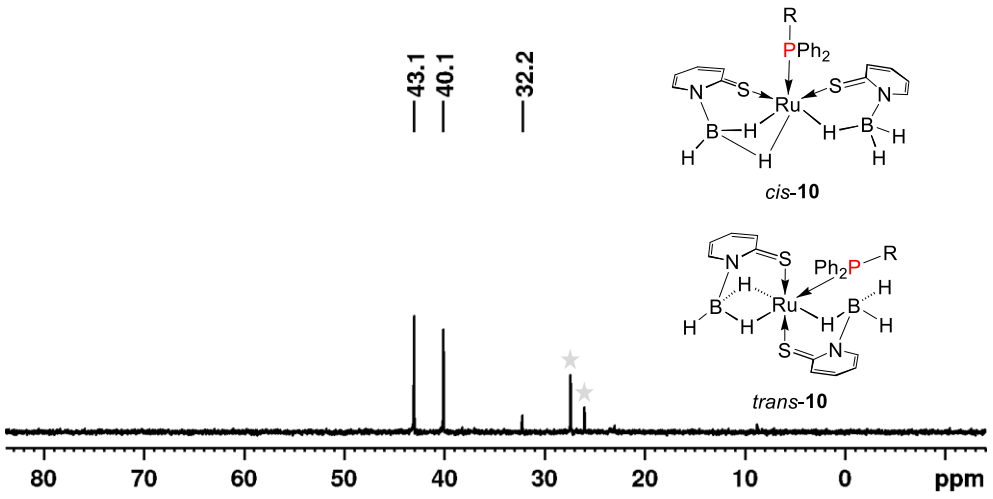


Figure S31. $^{31}P\{^{1}H\}$ NMR spectrum of **10** (impure) in $CDCl_3$. (* = inseparable impurity)

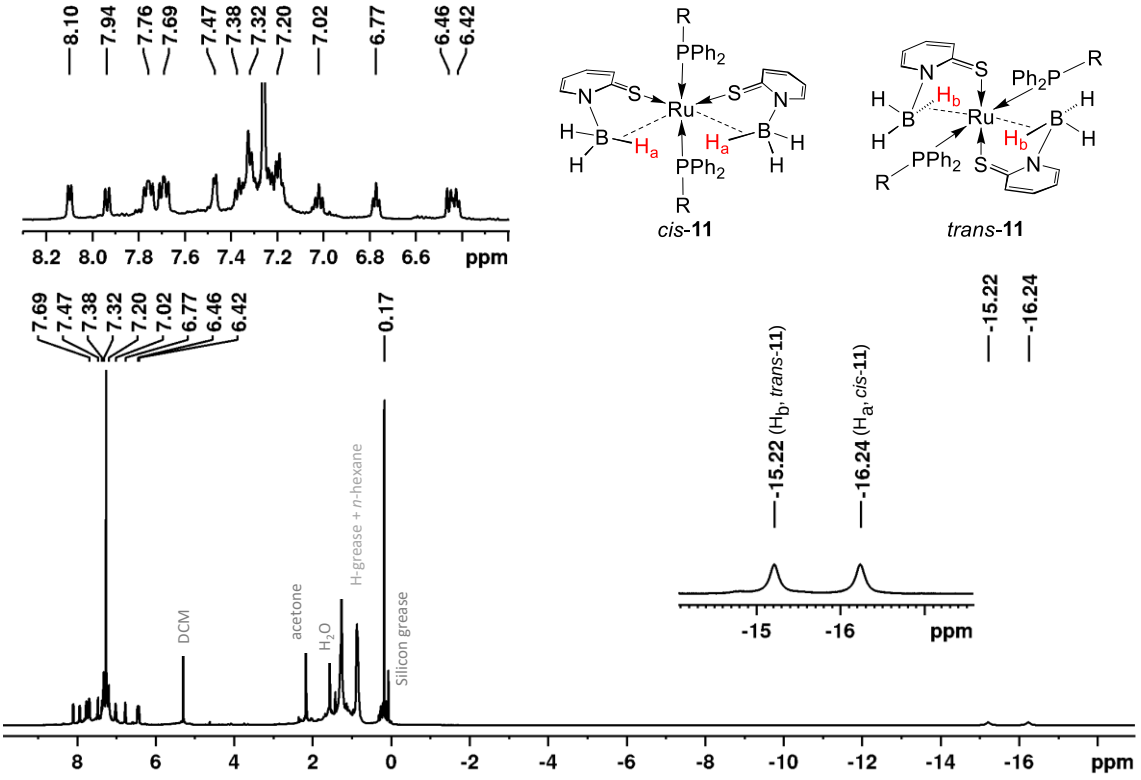


Figure S32. ^{1}H NMR spectrum of **11** in $CDCl_3$.

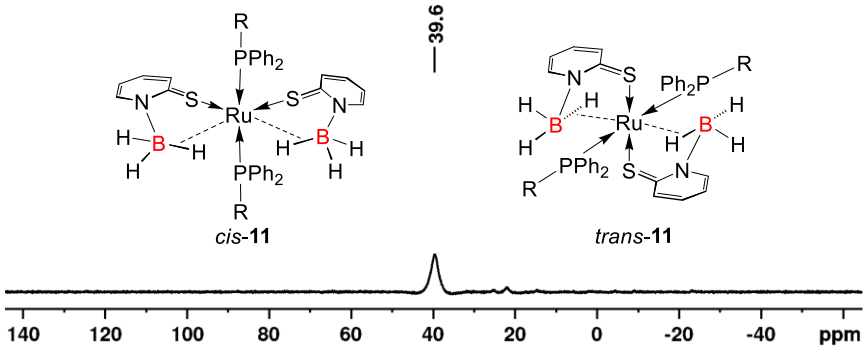


Figure S33. $^{11}B\{^{1}H\}$ NMR spectrum of **11** in $CDCl_3$.

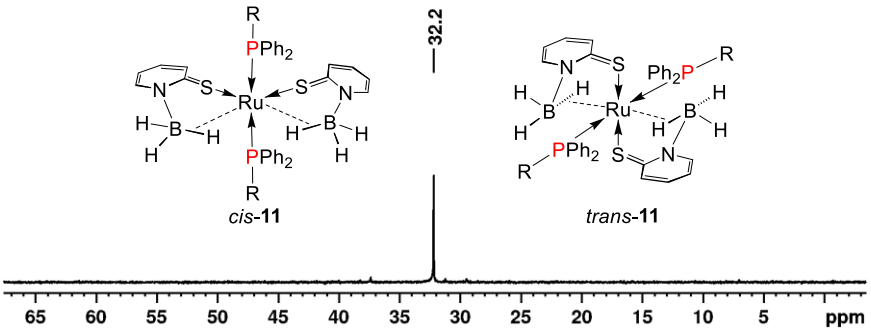


Figure S34. $^{31}P\{^{1}H\}$ NMR spectrum of **11** in $CDCl_3$.

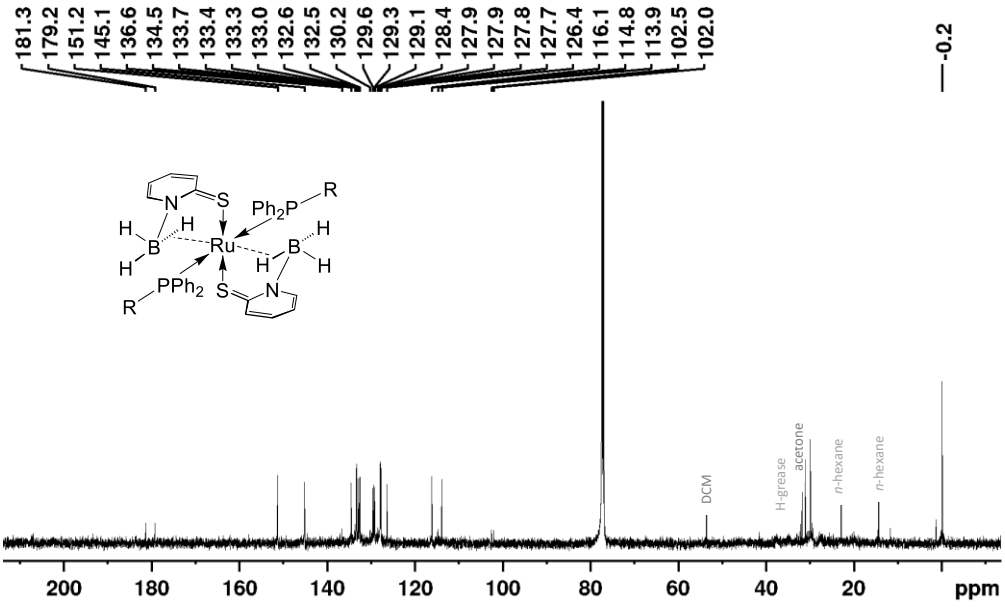


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of **11** in $CDCl_3$.

II.3 X-ray Analysis Details

Suitable X-ray diffraction quality crystals of **3b,** *mer*-**6b**, **7**, *cis*-**9**, *cis*-**10** were grown by slow diffusion of a hexane-CH_2Cl_2 solution at -5 °C. Crystal data of **3b, 7**, *cis*-**9** and *cis*-**10** were collected and integrated using a Bruker V8 Venture diffractometer with Mo-Kα (λ = 0.71073Å) radiation at 287(2) K. Crystal data of *mer*-**6b** was collected and integrated using a Bruker APEX-II CCD diffractometer with graphite monochromated Mo-Kα (λ = 0.71073Å) radiation at 296(2) K. Crystal structures of **3b** were solved with SHELXT-2018 and SHELXS-97[5] and refined with the Jana2020[6] program package. Crystal structures of *mer*-**6b**, **7**, *cis*-**9**, *cis*-**10** were solved using SHELXT-2018 and SHELXS-97[5] and refined using SHELXL−2018, SHELXL-2014 and SHELXL-2019.[7] Using Olex2 all the molecular structures were drawn.[8] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. CCDC: 2456264 (**3b**), 2456659 (*mer*-**6b**), 2456267 (**7**), 2456269 (*cis*-**9**) and 2456270 (*cis*-**10**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for **3b***:* $C_{19}H_{26}BNO_2RuSe$; M_r= 490.9; monoclinic, space group *P 21/n*, a = 8.3439(14) Å, b = 15.119(3) Å, c = 16.364(3) Å, α = 90°, β = 101.227(6)°, γ = 90°; V = 2024.8(6) Å^3; Z = 4; ρ_{calcd} = 1.610 g/cm^3; μ = 2.583 mm^{-1}; F(000) = 982; R_1 = 0.0561; wR_2 = 0.1505; 4820 independent reflections [$2\vartheta \leq 56.678°$] and 454 parameters.

Crystal data for mer-**6b***:* $C_{19}H_{21}B_2N_3O_2RuS_3$; M_r = 542.26; orthorhombic, space group *P 21 21 21* a = 10.847(2) Å, b = 13.888(4) Å, c = 15.322(4) Å, α = 90°, β = 90°, γ = 90°, V = 2308.2(9) Å^3, Z = 4, ρ_{calcd} = 1.560 g/cm^3, μ = 0.971 mm^{-1}, F(000) = 1096, R_1 = 0.0449, wR_2 = 0.0939, 2817 independent reflections [$2\vartheta \leq 43.94°$] and 296 parameters.

Crystal data for **7***:* $C_{30}H_{24}N_6Ru_2S_6$; M_r = 863.05; monoclinic, space group $P2_1/c$ a = 7.7479(11) Å, b = 34.145(6) Å, c = 12.028(3) Å, α = 90°, β = 105.050(4)°, γ = 90°, V = 3072.9(10) Å^3, Z = 4, ρ_{calcd} = 1.866 g/cm^3, μ = 1.425 mm^{-1}, F(000) = 1720, R_1 = 0.0829, wR_2 = 0.1996, 6180 independent reflections [$2\vartheta \leq 52.732°$] and 398 parameters.

Crystal data for cis-**9***:* $C_{24}H_{24}B_2N_2RuS_2$; M_r = 526.25; monoclinic; space group, $P2_1/c$; a = 7.0318(2) Å, b = 26.1017(7) Å, c = 14.5720(3) Å, α =90°, β = 90.176(1)°, γ = 90°; V = 2674.56(12) Å^3; Z = 4, ρ_{calcd} = 1.307 g/cm^3; μ = 0.755 mm^{-1}; F(000) = 1068; R_1 = 0.0304; wR_2 = 0.0727; 4037 independent reflections [$2\vartheta \leq 56.586°$] and 304 parameters.

Crystal data for cis-**10***:* $C_{27}H_{33}B_2N_2PRuS_2Si$; M_r = 631.42; monoclinic, space group *C 2/c*; a = 18.368(4) Å, b = 10.002(2) Å, c = 33.554(8) Å, α = 90°, β = 104.274(6)°, γ = 90°, V = 5974(2) Å^3, Z = 8, ρ_{calcd} = 1.404 g/cm^3, μ = 0.778 mm^{-1}, F(000) = 2592.0, R_1 = 0.1153, wR_2 = 0.2710, 5726 independent reflections [$2\vartheta \leq 51.58°$] and 364 parameters.

III Computational Details

All molecules were fully optimized with the Gaussian 16 program[9] using the gradient-corrected Becke–Lee–Yang–Parr (B3LYP) functional[10] in conjunction with the 6-31g(d)-LANL2DZ basis set from the EMSL Basis Set Exchange Library[11]. The model compounds were fully optimized starting from X-ray coordinates in the gaseous state (no solvent effect). Frequency calculations were carried out for the verification of the nature of the stationary state and to confirm the absence of any imaginary frequency which eventually confirmed the minima on the potential energy hypersurface for all structures. Furthermore, the gauge including atomic orbital (GIAO)[12] method was employed to compute the ^{11}B and ^{1}H chemical shifts. Wiberg bond indices (WBI)[13] was generated from natural bond orbital analysis (NBO)[14]. All the optimized geometries and orbital pictures were drawn by Chemcraft[15] visualization programs. Laplacian electronic distribution plots and Two-dimensional electron density and were generated using the Multiwfn package.[16]

Table.S1. Selected geometrical parameters and Wiberg bond indices (WBI) of **2^{S}**, **2^{Se}**, **3a-b**, *mer*-**6a-b** and *cis*-**9**.

2^{S}				**2^{Se}**			
	Expt.	Cal.	WBI		Expt.	Cal.	WBI
Ru1-B1	-	2.240	0.386	Ru1-B1	-	2.248	0.381
Ru1-S1	-	2.377	0.775	Ru1-S1	-	2.532	0.801
B1-N1	-	1.374	0.723	B1-N1	-	1.552	0.712
C1-S1	-	1.716	1.303	C1-S1	-	1.889	1.206
3a				**3b**			
	Expt.	Cal.	WBI		Expt.	Cal.	WBI
Ru1-B1	-	2.237	0.257	Ru1-B1	2.416	2.374	0.254
Ru1-Se1	-	2.576	0.746	Ru1-Se1	2.476(12)	2.575	0.751
B1-C12	-	1.571	0.916	B1-C12	1.588(14)	1.556	0.969
C12-C13	-	1.410	1.352	C12-C13	1.492(11)	1.400	1.384
B1-N1	-	1.594	0.650	B1-N1	1.501(16)	1.592	0.656
C1-Se1	-	1.897	1.183	C1-Se1	1.984	1.901	1.183
mer-**6a**				*mer*-**6b**			
	Expt.	Cal.	WBI		Expt.	Cal.	WBI
Ru1-B1	-	2.384	0.268	Ru1-B1	2.385(18)	2.400	0.266
Ru1-B2	-	2.681	0.208	Ru1-B2	2.589(15)	2.646	0.220
B1-C6	-	1.576	0.903	B1-C6	1.63(3)	1.559	0.954
C6-C7	-	1.396	1.405	C6-C7	1.402(19)	1.393	1.402
B1-N1	-	1.558	0.663	B1-N1	1.550(18)	1.581	0.670
cis-**9**							
	Expt.	Cal.	WBI				
Ru1-B1	2.331(3)	2.354	0.287				
Ru1-B2	2.148(3)	2.179	0.466				
B1-C11	1.579(4)	1.587	0.875				
C11-C12	1.395(4)	1.398	1.413				
B1-N1	1.564(3)	1.581	0.664				

Table S2. Comparison between experimental and calculated NMR chemical shifts of the isomers of **6**.

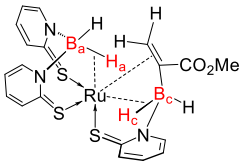
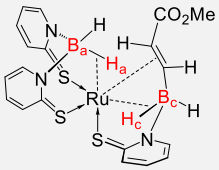
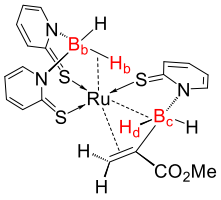
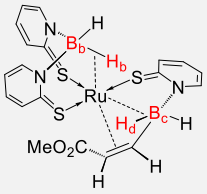
Complexes	^{11}B NMR (ppm)		^{1}H NMR (ppm)	
	Expt	Calc	Expt	Calc
 *fac*-**6a**	8.2 (B_a) -7.6 (B_c)	5.1 (B_a) -15.7 (B_c)	-9.19 (H_c) -15.40 (H_a)	-10.64 (H_c) -13.05 (H_a)
 *fac*-**6b**	8.2 (B_a) -7.6 (B_c)	4.8 (B_a) -16.4(B_c)	-9.19 (H_c) -15.40 (H_a)	-8.5 (H_c) -13.99 (H_a)
 *mer*-**6a**	6.7 (B_b) -7.6 (B_c)	5.0 (B_b) -11.9 (B_c)	-7.98 (H_b) -9.86 (H_d)	-6.34 (H_d) -7.31 (H_b)
 *mer*-**6b**	6.7 (B_b) -7.6 (B_c)	4.9 (B_b) -13.3 (B_c)	-7.98 (H_b) -9.86 (H_d)	-5.93 (H_d) -8.11 (H_b)

Table S3. Calculated natural charges (q), natural valence population (Pop) and HOMO – LUMO gaps of **2^{S}**, **2^{Se}**, **3a-b**, *mer*-**6a-b** and *cis*-**9**.

Complex	**q_{Ru}**	**q_{B}**	**$q_{(C=C)}$**	**Pop(Ru_{val})**	**Pop(B_{val})**	**Pop(C_{val})**	**ΔE_{H-L} (eV)**
2^{S}	-0.432	0.018	-	8.423	2.961	-	3.289
2^{Se}	-0.474	0.010	-	8.464	2.969	-	3.109
3a	-0.473	0.240	-0.372 (C12) -0.327 (C13)	8.459	2.737	4.344 (C12) 4.307 (C13)	3.201
3b	-0.456	0.204	-0.369 (C12) -0.325 (C13)	8.443	2.774	4.350 (C12) 4.3299 (C13)	3.189
mer-**6a**	-0.834	0.248 (B1) 0.441 (B2)	-0.323 (C6) -0.290 (C7)	8.820	2.729 (B1) 2.539 (B2)	4.292 (C6) 4.271 (C7)	3.029
mer-**6b**	-0.838	0.219 (B1) 0.442 (B2)	-0.322 (C6) -0.290 (C7)	8.826	2.759 (B1) 2.537 (B2)	4.303 (C6) 4.262 (C7)	3.098
cis-**9**	-0.773	0.258 (B1) 0.123 (B2)	-0.218 (C11) -0.160 (C12)	8.765	2.719 (B1) 2.854 (B2)	4.189 (C11) 4.133 (C12)	3.260

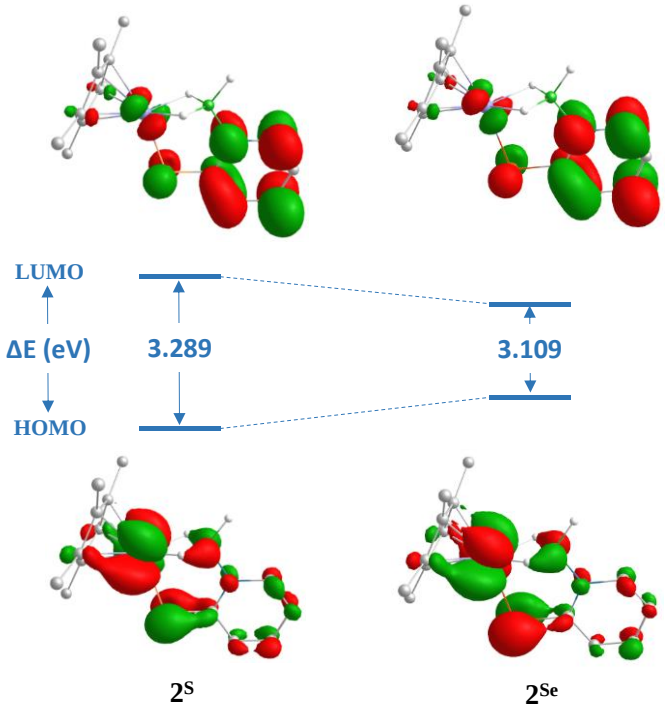


Figure S36. Comparison of HOMO-LUMO gap between **2**^{S} and **2**^{Se}. (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$)

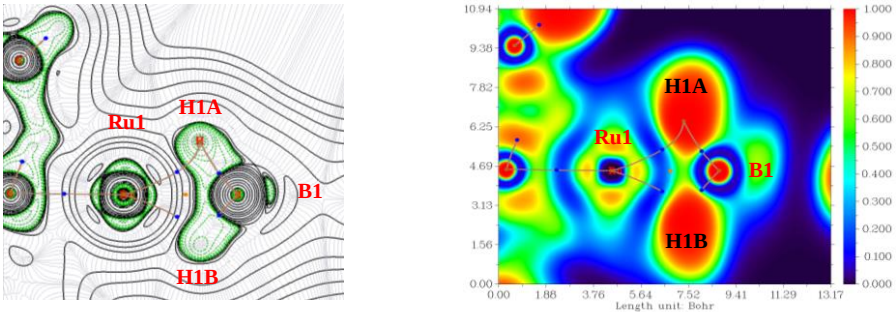


Figure S37. (a) Contour-line diagram of the Laplacian of electron density in the Ru1-H1A-B1-H1B plane of **2**^{S}. The solid brown lines are bond paths, while blue spheres indicate the bond critical points and orange sphere indicates ring critical points. Area of charge concentration [$\nabla^2\rho(r)<0$] are indicated by solid lines and area of charge depletion [$\nabla^2\rho(r)>0$] are shown by dashed lines; (b) ELF plot in Ru1-H1A-B1-H1B plane of **2**^{S}.

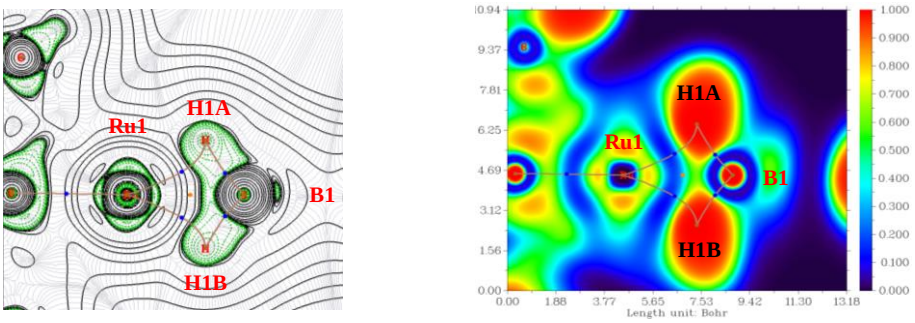


Figure S38. (a) Contour-line diagram of the Laplacian of electron density in the Ru1-H1A-B1-H1B plane of **2**^{Se}; (b) ELF plot in Ru1-H1A-B1-H1B plane of **2**^{Se}.

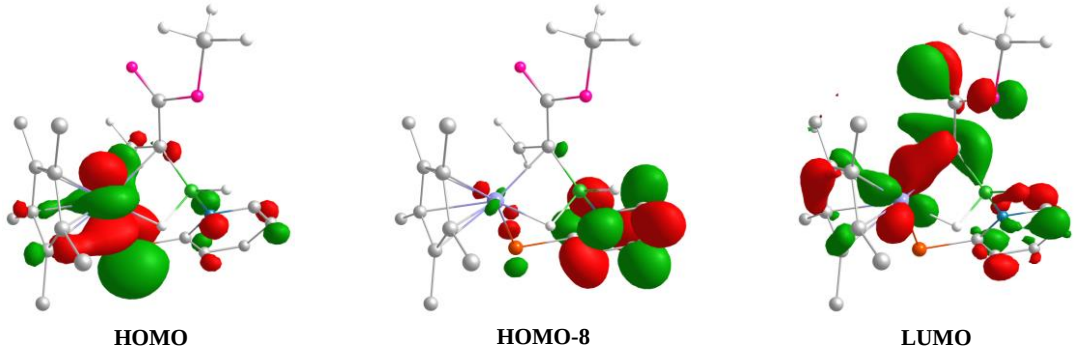


Figure S39. Selected molecular orbitals of **3a**. (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$)

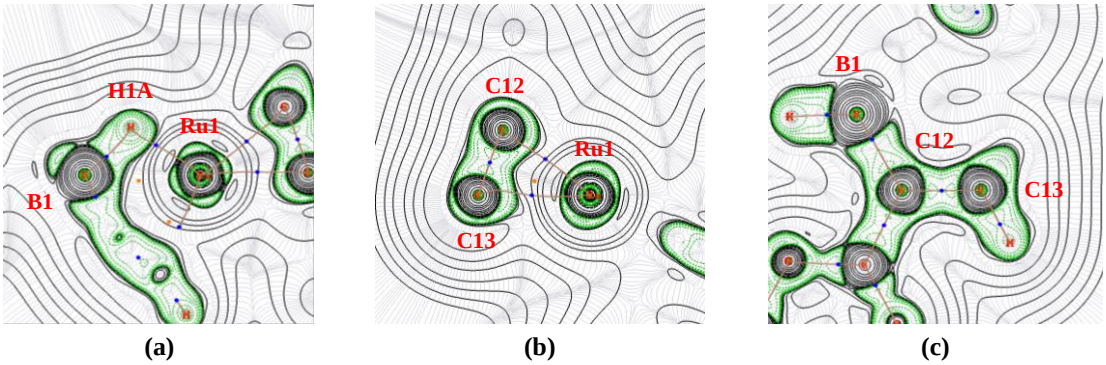


Figure S40. Contour-line diagram of the Laplacian of electron density in the Ru1-H1A-B1 (a), Ru1-C12-C13 (b) and B1-C12-C13 (c) planes of **3a**.

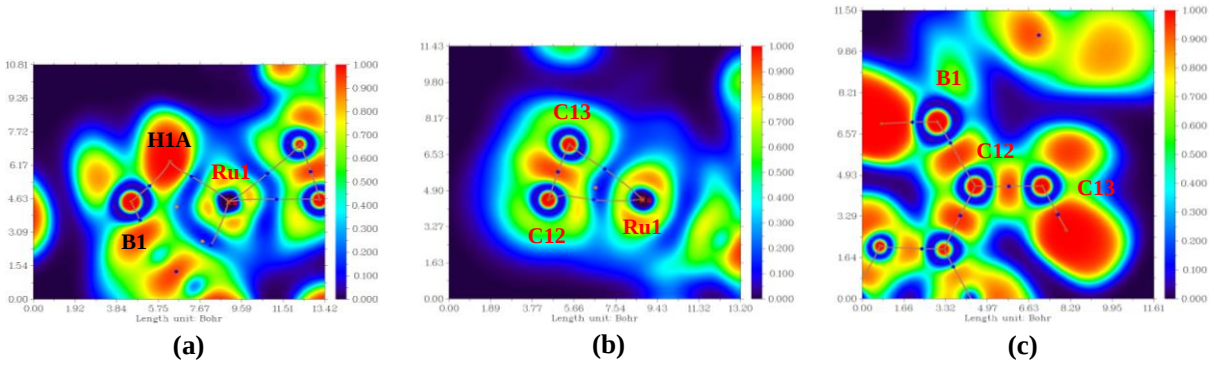


Figure S41. ELF plot in Ru1-H1A-B1 (a), Ru1-C12-C13 (b) and B1-C12-C13 (c) planes of **3a**.

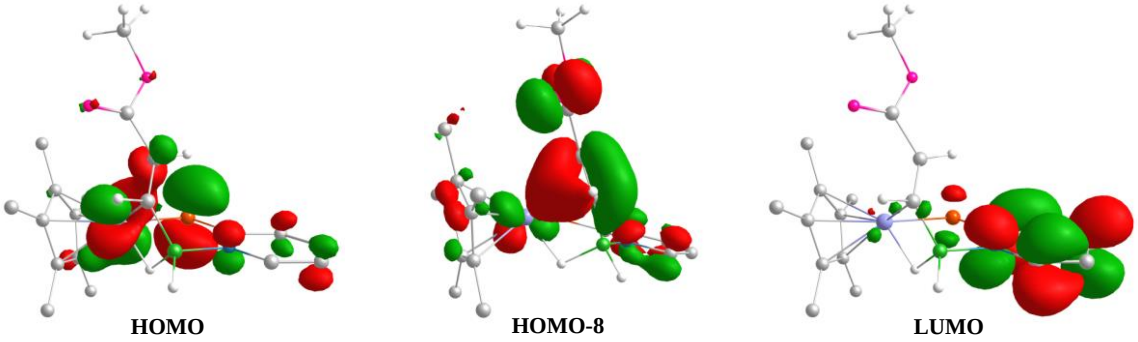


Figure S42. Selected molecular orbitals of **3b**. (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$)

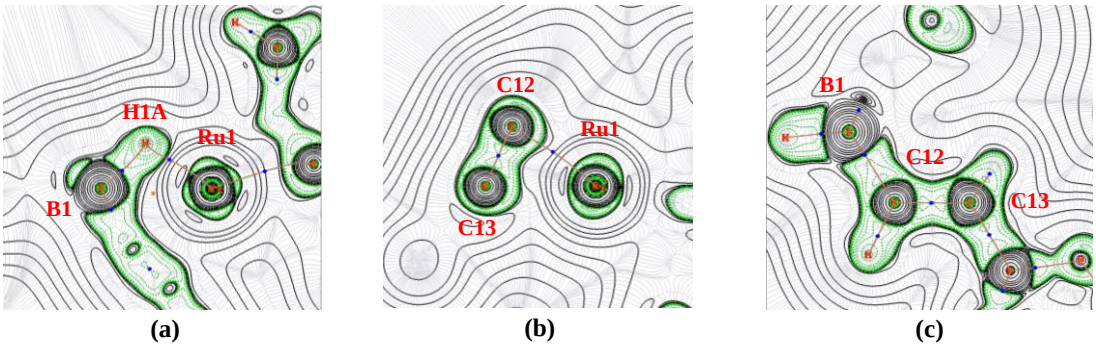


Figure S43. Contour-line diagram of the Laplacian of electron density in the Ru1-H1A-B1 (a), Ru1-C12-C13 (b) and B1-C12-C13 (c) planes of **3b**.

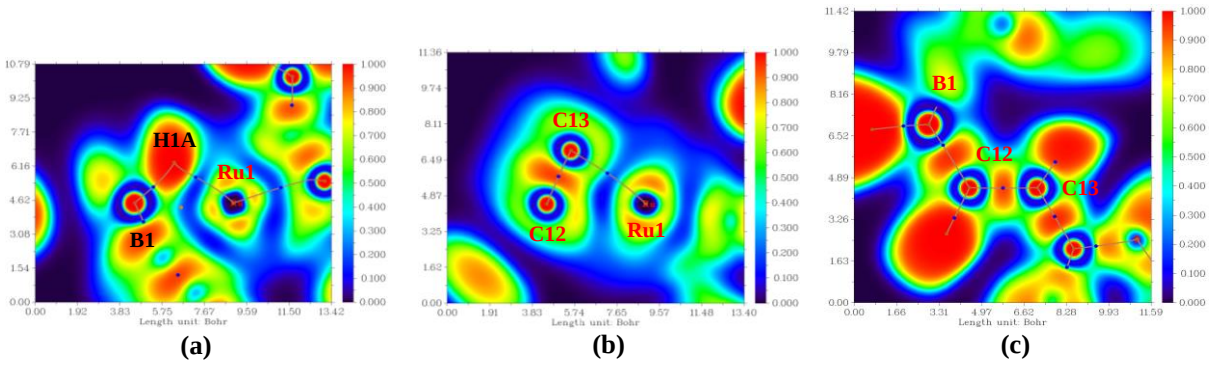


Figure S44. ELF plot in Ru1-H1A-B1 (a), Ru1-C12-C13 (b) and B1-C12-C13 (c) planes of **3b**.

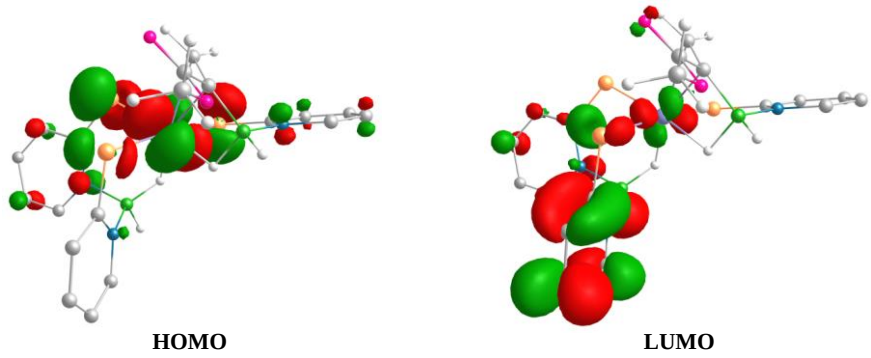


Figure S45. Selected molecular orbitals of *mer*-**6a**. (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$)

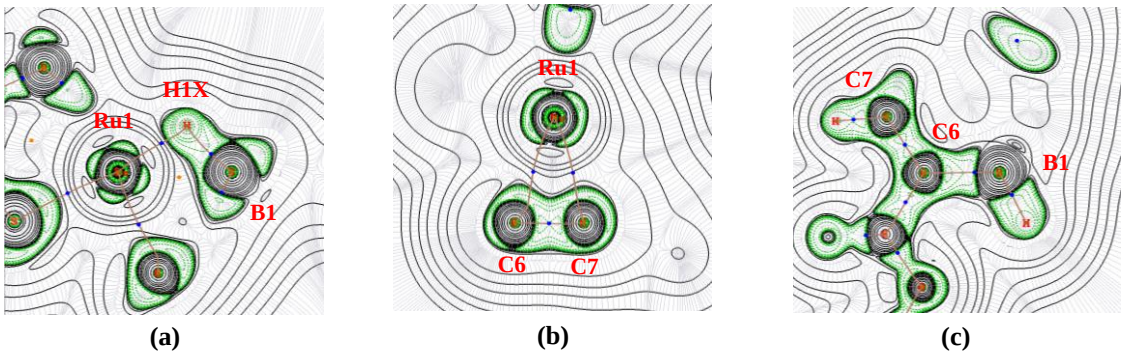


Figure S46. Contour-line diagram of the Laplacian of electron density in the Ru1-H1X-B1 (a), Ru1-C6-C7 (b) and B1-C6-C7 (c) planes of *mer*-**6a**.

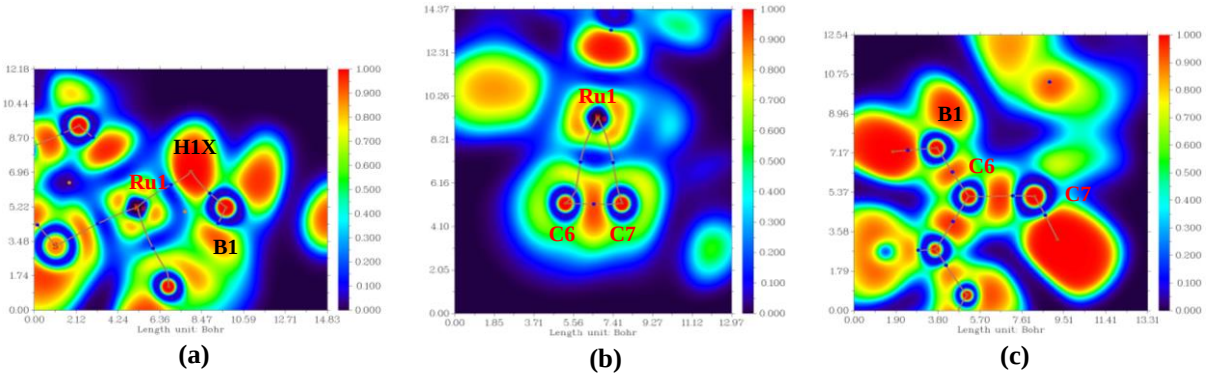


Figure S47. ELF plot in Ru1-H1X-B1 (a), Ru1-C6-C7 (b) and B1-C6-C7 (c) planes of *mer*-**6a**.

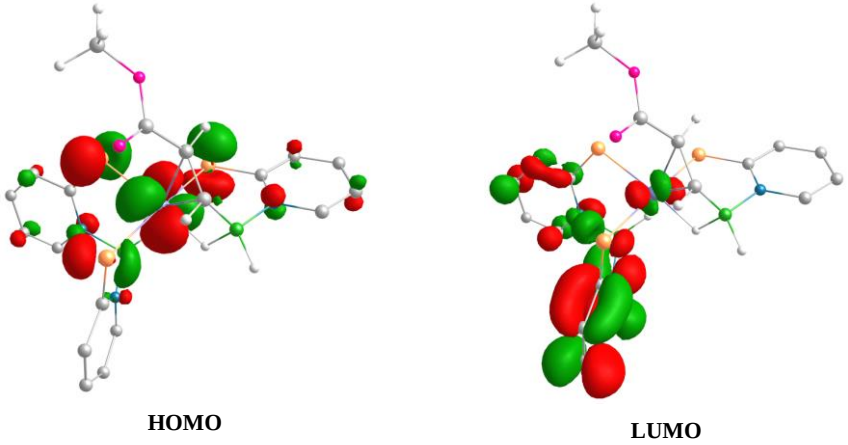


Figure S48. Selected molecular orbitals of *mer*-**6b**. (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$)

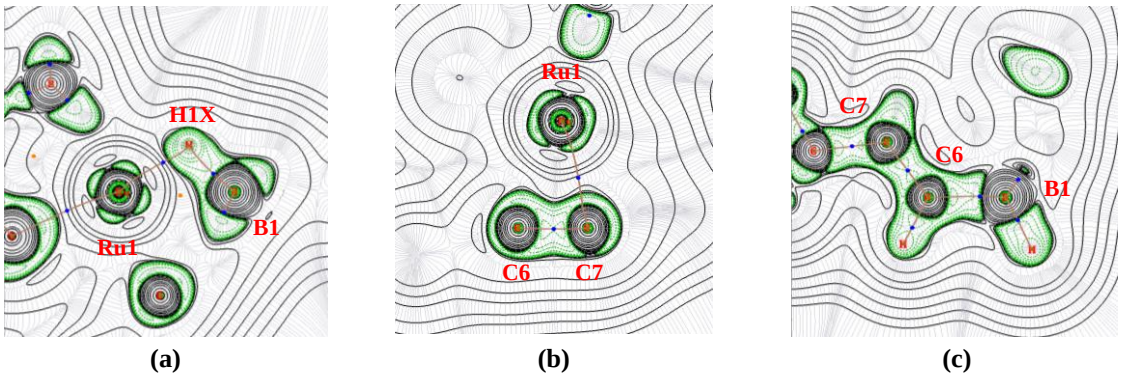


Figure S49. Contour-line diagram of the Laplacian of electron density in the Ru1-H1X-B1 (a), Ru1-C6-C7 (b) and B1-C6-C7 (c) planes of *mer*-**6b**.

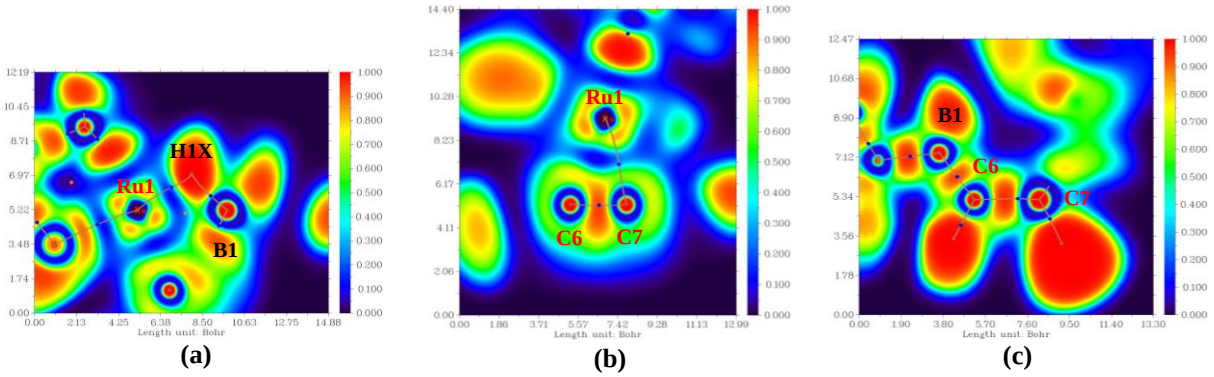


Figure S50. ELF plot in Ru1-H1X-B1 (a), Ru1-C6-C7 (b) and B1-C6-C7 (c) planes of *mer*-**6b**.

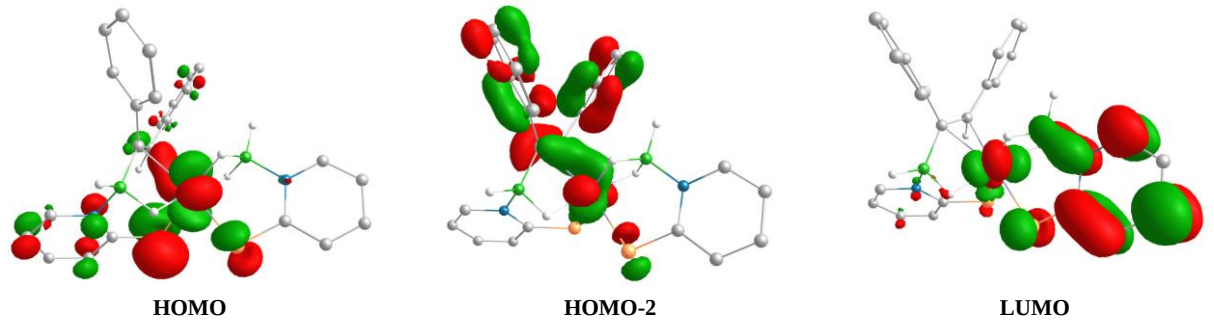


Figure S51. Selected molecular orbitals of *cis*-**9**. (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$)

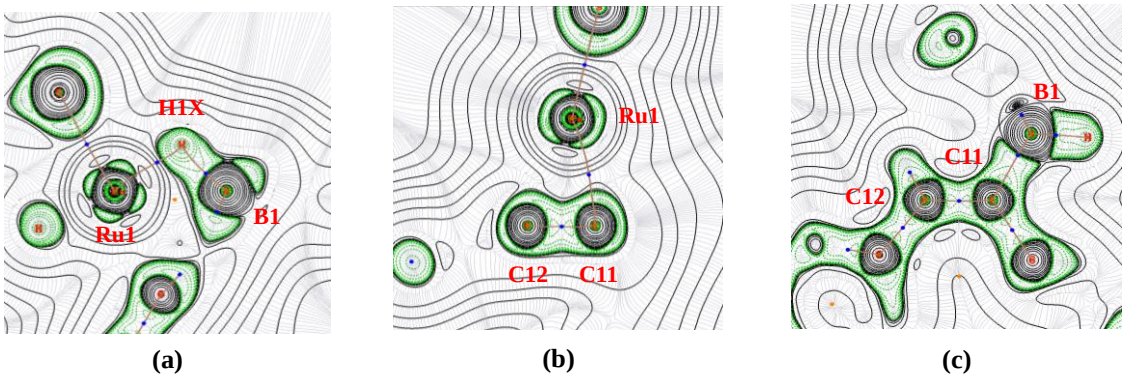
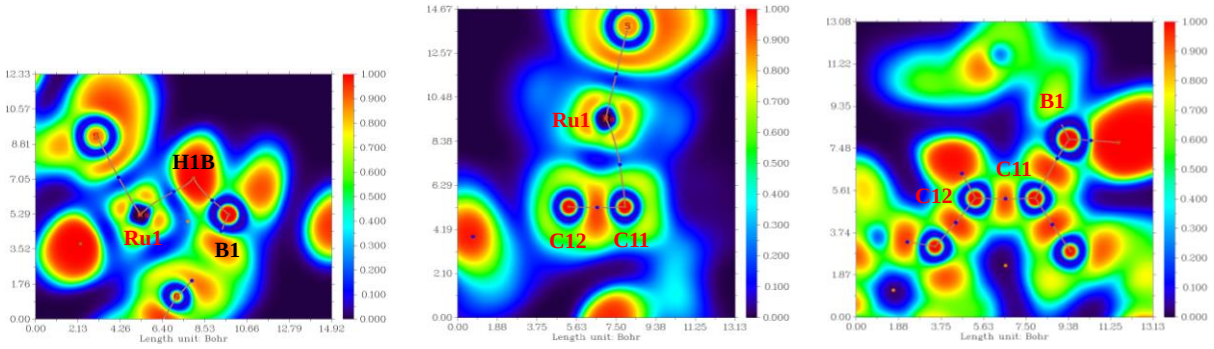


Figure S52. Contour-line diagram of the Laplacian of electron density in the Ru1-H1B-B1 (a), Ru1-C11-C12 (b) and B1-C11-C12 (c) planes of *cis*-**9**.



(a) **(b)** **(c)**

Figure S53. ELF plot in Ru1-H1B-B1 (a), Ru1-C11-C12 (b) and B1-C11-C12 (c) planes of *cis*-**9**.

IV Cartesian Coordinates Of All Optimized Structures

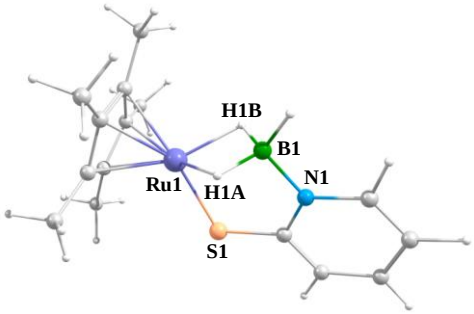


Figure S54. Optimized geometry of **2^{S}**.
Total Energy = --1156.83192933 a. u.

C	2.159938000	1.255055000	-0.032172000
C	2.205722000	0.445134000	1.151344000
C	2.354255000	-0.939738000	0.737131000
C	2.358335000	-0.977149000	-0.686321000
C	2.211344000	0.384788000	-1.171101000
C	2.114572000	2.753234000	-0.071308000
H	1.601014000	3.116750000	-0.962923000
H	3.129338000	3.168381000	-0.078975000
H	1.595807000	3.162703000	0.797120000
C	2.276415000	0.943137000	2.563547000
H	3.318731000	1.093823000	2.872035000
H	1.825304000	0.234426000	3.260423000
H	1.754841000	1.894352000	2.679872000
C	2.568909000	-2.101129000	1.660366000
H	2.015417000	-1.978588000	2.593229000
H	3.630822000	-2.201482000	1.916243000
H	2.246723000	-3.039878000	1.207072000
C	2.580945000	-2.184417000	-1.546720000
H	2.255298000	-3.098745000	-1.048149000
H	3.644778000	-2.297671000	-1.788965000
H	2.034621000	-2.111038000	-2.488954000
C	2.284694000	0.808857000	-2.607088000
H	3.327765000	0.943341000	-2.920356000
H	1.763427000	1.752709000	-2.773677000
H	1.835387000	0.064629000	-3.267098000
C	-2.759348000	0.579008000	-0.000711000
C	-4.030451000	1.207221000	-0.001708000
H	-4.057963000	2.289048000	-0.002937000
C	-5.182045000	0.462033000	-0.001211000
H	-6.149501000	0.950879000	-0.002036000
C	-5.094421000	-0.948174000	0.000389000
H	-5.978237000	-1.571760000	0.000851000
C	-3.854946000	-1.525404000	0.001360000
H	-3.711357000	-2.596956000	0.002573000
B	-1.334302000	-1.516077000	0.001527000
S	-1.305138000	1.491414000	-0.001563000
Ru	0.429551000	-0.134422000	0.000397000
H	-1.483605000	-2.704105000	0.002908000
H	-0.664775000	-1.168399000	-1.046324000
H	-0.664448000	-1.166324000	1.048712000
N	-2.699838000	-0.794603000	0.000811000

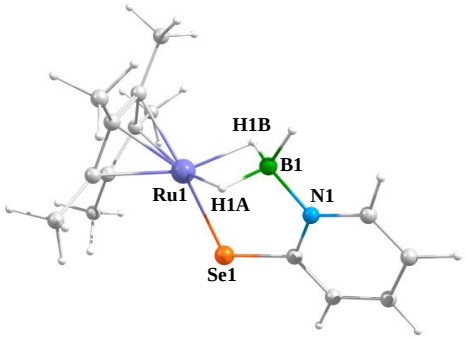


Figure S55. Optimized geometry of **2^{Se}.**
Total Energy = --767.835712322 a. u.

C	2.235504000	1.263123000	-0.032148000
C	2.248663000	0.452065000	1.151629000
C	2.337794000	-0.937946000	0.737895000
C	2.340489000	-0.975430000	-0.687268000
C	2.251796000	0.391663000	-1.171431000
C	2.264641000	2.761905000	-0.071349000
H	1.771199000	3.151210000	-0.963490000
H	3.299450000	3.124588000	-0.079011000
H	1.768366000	3.197508000	0.797568000
C	2.338948000	0.947106000	2.563653000
H	3.386462000	1.054089000	2.872944000
H	1.857808000	0.258133000	3.260233000
H	1.857338000	1.919217000	2.679363000
C	2.504103000	-2.107671000	1.660425000

H	1.959604000	-1.960639000	2.595052000
H	3.561415000	-2.254995000	1.912760000
H	2.138942000	-3.031096000	1.208202000
C	2.512814000	-2.191198000	-1.547064000
H	2.144888000	-3.090174000	-1.049936000
H	3.571534000	-2.351468000	-1.785295000
H	1.973773000	-2.093399000	-2.491280000
C	2.341212000	0.813339000	-2.607098000
H	3.388653000	0.906211000	-2.921025000
H	1.857707000	1.777255000	-2.772621000
H	1.861824000	0.088189000	-3.267179000
C	-2.881361000	0.601149000	-0.001185000
C	-4.182423000	1.150215000	-0.002511000
H	-4.278861000	2.228050000	-0.004344000
C	-5.290004000	0.336612000	-0.001586000
H	-6.285307000	0.765797000	-0.002677000
C	-5.113634000	-1.062272000	0.000791000
H	-5.955617000	-1.741444000	0.001607000
C	-3.839174000	-1.561136000	0.002056000
H	-3.630495000	-2.621606000	0.003858000
B	-1.328354000	-1.426462000	0.002101000
Se	-1.353255000	1.712880000	-0.002670000
Ru	0.456430000	-0.058944000	0.000369000
H	-1.442706000	-2.618704000	0.004060000
H	-0.682907000	-1.056620000	-1.046923000
H	-0.682498000	-1.053623000	1.050055000
N	-2.731182000	-0.760618000	0.001085000

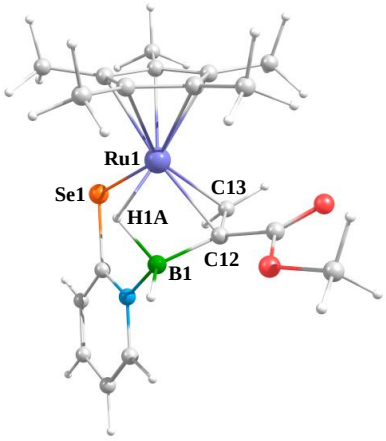


Figure S56. Optimized geometry of **3a**.
Total Energy = -1073.21004164 a. u.

Ru	-0.469707000	-0.350257000	0.009466000
C	3.516111000	1.858111000	0.609686000
H	3.121406000	2.813953000	0.925548000
C	4.860620000	1.638471000	0.450343000
H	5.563492000	2.439531000	0.634771000
C	5.281660000	0.356874000	0.053542000
H	6.335717000	0.138868000	-0.075744000
C	4.340097000	-0.619683000	-0.170872000
H	4.630094000	-1.614879000	-0.481013000
C	0.275872000	0.841057000	-1.759873000
H	1.211741000	0.394548000	-2.063775000
C	0.190694000	1.652912000	-0.609678000
C	-1.085749000	-3.281442000	1.578373000
H	-0.601615000	-3.011307000	2.518120000
H	-0.349054000	-3.817996000	0.978564000
H	-1.898836000	-3.980499000	1.809297000
C	-2.139230000	-0.894532000	1.477512000
C	-1.615244000	-2.074430000	0.863061000
C	-2.538218000	-0.736267000	-0.805332000
C	-2.701515000	-0.060852000	0.457817000
C	-2.180019000	-0.612044000	2.949856000
H	-3.125833000	-0.964520000	3.378650000
H	-1.369211000	-1.114631000	3.478688000
C	-3.519656000	1.173253000	0.688126000
H	-4.566739000	0.902546000	0.872627000
H	-3.168635000	1.734797000	1.555977000
C	-1.869056000	-1.977671000	-0.564976000
C	-3.107077000	-0.267704000	-2.110992000
H	-4.175930000	-0.507644000	-2.164570000
H	-2.617629000	-0.752007000	-2.957128000
H	-2.997353000	0.811281000	-2.232247000
C	-1.640638000	-3.069472000	-1.568295000
H	-2.504475000	-3.744362000	-1.607832000
H	-0.765427000	-3.672256000	-1.319550000
H	-1.486397000	-2.667318000	-2.570506000
N	2.577015000	0.897559000	0.389153000
C	2.962800000	-0.347967000	-0.008271000
H	-2.100898000	0.456439000	3.156254000
H	-3.498253000	1.836595000	-0.176757000
B	1.069070000	1.341636000	0.655292000
H	1.065430000	2.125074000	1.556362000
H	0.514306000	0.268811000	1.296020000
Se	1.688570000	-1.715109000	-0.335357000
C	-0.855131000	2.716172000	-0.633018000
O	-0.825641000	3.509115000	0.467813000
C	-1.733474000	4.619789000	0.466864000
H	-1.547927000	5.146928000	1.401215000
H	-1.540318000	5.273877000	-0.385384000
H	-2.769626000	4.280831000	0.421550000
O	-1.637438000	2.923878000	-1.541398000
H	-0.439243000	1.005890000	-2.558626000

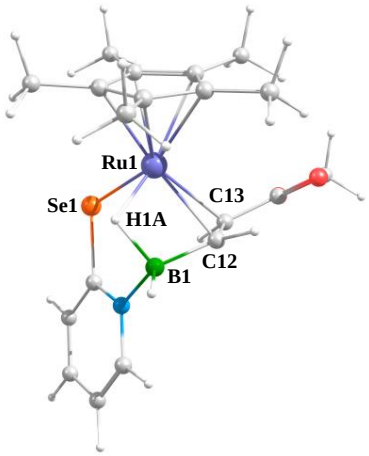


Figure S57. Optimized geometry of **3b**.
Total Energy = -1073.21651032 a. u.

Ru	-0.473539000	-0.449234000	0.194874000
C	3.781553000	0.305888000	1.770776000
H	3.543535000	0.456178000	2.814816000
C	5.062071000	0.411180000	1.291347000
H	5.871367000	0.658885000	1.964716000
C	5.278382000	0.183291000	-0.079336000
H	6.276300000	0.248710000	-0.497787000
C	4.208021000	-0.123138000	-0.886089000
H	4.339954000	-0.300170000	-1.945292000
O	-1.751315000	3.102228000	1.013578000
O	-0.592779000	3.644012000	-0.843141000
C	0.183036000	1.811677000	0.379972000
H	0.988311000	1.885432000	-0.336432000
C	-0.824857000	2.878192000	0.257266000
C	-1.489237000	4.744935000	-1.045887000
H	-1.139308000	5.243686000	-1.947854000
H	-1.459303000	5.428529000	-0.195468000
H	-2.513879000	4.393360000	-1.179976000
C	0.311742000	1.080067000	1.567636000
H	-0.386978000	1.323902000	2.364092000
C	-1.056078000	-3.645681000	-0.595485000
H	-0.453501000	-4.067846000	0.210418000
H	-0.421536000	-3.596184000	-1.481993000
H	-1.871517000	-4.349027000	-0.804909000
C	-1.954264000	-1.845954000	1.097223000
C	-1.594379000	-2.294315000	-0.228975000
C	-2.669246000	-0.236894000	-0.417261000
C	-2.596093000	-0.572737000	0.985435000
C	-1.783420000	-2.633932000	2.361946000
H	-2.675558000	-3.241662000	2.554308000
H	-0.929077000	-3.309498000	2.302466000
C	-3.236241000	0.205112000	2.095925000
H	-4.314094000	0.004496000	2.130072000
H	-2.822046000	-0.071701000	3.067016000
C	-2.058744000	-1.290097000	-1.160646000
C	-3.409706000	0.933167000	-0.988613000
H	-4.465046000	0.671084000	-1.134680000
H	-3.007410000	1.232441000	-1.957995000
H	-3.372266000	1.794767000	-0.321625000
C	-2.026518000	-1.406421000	-2.655710000
H	-2.929201000	-1.913698000	-3.017246000
H	-1.166947000	-1.985260000	-2.997686000
H	-1.981379000	-0.427791000	-3.135896000
N	2.715986000	0.002644000	0.979531000
C	2.900644000	-0.209927000	-0.356011000
H	-1.632180000	-1.983716000	3.224840000
H	-3.093169000	1.278697000	1.965851000
B	1.311175000	-0.103201000	1.723097000
H	1.490892000	-0.530963000	2.830308000
H	0.751069000	-1.203754000	1.148573000
Se	1.448049000	-0.620927000	-1.511584000

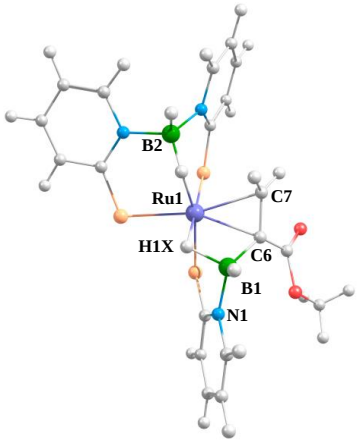


Figure S58. Optimized geometry of *fac*-**6a**.
Total Energy = -2390.07071836 a. u.

C	3.290590000	-1.023143000	-0.455620000
C	4.447623000	-1.565066000	-1.065580000
H	4.435104000	-1.710683000	-2.137697000
C	5.542100000	-1.908526000	-0.309224000
H	6.419449000	-2.332334000	-0.784898000
C	5.511445000	-1.716580000	1.084614000
H	6.348714000	-1.979974000	1.716263000
C	4.377582000	-1.178079000	1.637746000
H	4.281852000	-0.992871000	2.698559000
C	-2.478489000	1.663339000	-0.682427000
C	-3.234685000	2.710346000	-1.279070000
H	-2.975597000	2.997579000	-2.289510000
C	-4.212643000	3.365103000	-0.578937000
H	-4.759687000	4.179863000	-1.039499000
C	-4.479701000	2.990801000	0.757250000
H	-5.214296000	3.507316000	1.359647000
C	-3.781344000	1.940329000	1.283977000
H	-3.947427000	1.590784000	2.293347000
C	-4.352164000	-1.436222000	0.768263000
H	-4.775747000	-0.638359000	1.361789000
C	-5.124763000	-2.464140000	0.311082000
H	-6.182713000	-2.486077000	0.533520000
C	-4.495539000	-3.483775000	-0.437963000
H	-5.069522000	-4.320923000	-0.818383000
C	-3.152452000	-3.402453000	-0.680159000
H	-2.637813000	-4.161985000	-1.253340000
C	-2.372830000	-2.308055000	-0.201879000
B	2.078163000	-0.143226000	1.616371000
B	-2.306879000	-0.093118000	1.217936000
N	3.292319000	-0.833015000	0.898107000
N	-2.825864000	1.251315000	0.586490000
N	-3.008439000	-1.332383000	0.527169000
S	1.916123000	-0.626736000	-1.420432000
S	-1.145648000	0.995454000	-1.508600000
S	-0.700254000	-2.300504000	-0.558253000
Ru	0.145496000	-0.159361000	0.196269000
H	2.184492000	-0.259912000	2.807284000
H	1.056635000	-1.007175000	1.418258000
H	-1.082055000	-0.282490000	1.410471000
H	-2.644705000	-0.084298000	2.371845000
C	1.640985000	1.270523000	1.041248000
C	0.396818000	1.751913000	1.436270000
H	-0.033136000	1.447816000	2.382733000
C	2.391229000	2.172312000	0.109261000
O	3.718476000	1.890412000	0.101067000
C	4.525012000	2.730950000	-0.739446000
H	5.544361000	2.367186000	-0.624136000
H	4.203330000	2.650821000	-1.778928000
H	4.451907000	3.772925000	-0.423548000
H	0.016477000	2.666452000	0.994986000
O	1.926508000	3.099541000	-0.512113000

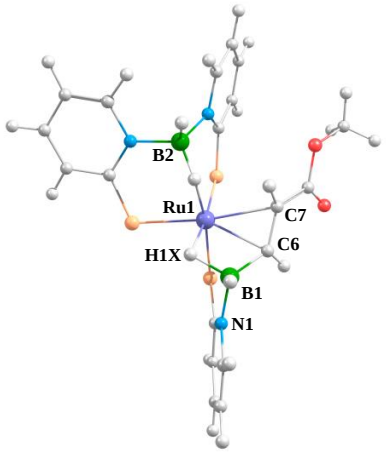


Figure S59. Optimized geometry of *fac*-**6b**.
Total Energy = -2390.07794777a. u.

C	3.824470000	-0.221553000	-0.560062000
C	5.084919000	-0.429538000	-1.174642000
H	5.117529000	-0.489164000	-2.254499000
C	6.221005000	-0.570546000	-0.416022000
H	7.177263000	-0.740850000	-0.897608000
C	6.133729000	-0.501666000	0.987901000
H	7.003126000	-0.616722000	1.620549000
C	4.902927000	-0.273857000	1.547689000
H	4.757663000	-0.191883000	2.616106000
C	-2.484547000	0.811836000	-0.898713000
C	-3.530294000	1.479644000	-1.595654000
H	-3.348876000	1.744813000	-2.628945000
C	-4.700874000	1.812467000	-0.968096000
H	-5.478958000	2.339196000	-1.508989000
C	-4.870843000	1.489674000	0.396279000
H	-5.758640000	1.772190000	0.945237000
C	-3.873475000	0.795309000	1.022245000
H	-3.944718000	0.509085000	2.061904000
C	-3.299826000	-2.593712000	1.099621000
H	-3.894663000	-1.922760000	1.702357000
C	-3.741549000	-3.847978000	0.793708000
H	-4.706148000	-4.182957000	1.149462000
C	-2.898080000	-4.678225000	0.021625000
H	-3.207104000	-5.682670000	-0.243955000
C	-1.682915000	-4.201182000	-0.383285000
H	-1.008752000	-4.808545000	-0.972396000
C	-1.250264000	-2.882494000	-0.052879000
B	2.427177000	0.260790000	1.531299000
B	-1.803131000	-0.609322000	1.174748000
N	3.773412000	-0.125170000	0.805932000
N	-2.718136000	0.411240000	0.397735000
N	-2.093225000	-2.090373000	0.689162000
S	2.405158000	-0.113936000	-1.535712000
S	-0.977962000	0.583970000	-1.669100000
S	0.296679000	-2.397622000	-0.597761000
Ru	0.564231000	-0.108495000	0.064683000
H	2.544007000	0.147503000	2.720658000
H	1.606912000	-0.772905000	1.296333000
H	-0.591332000	-0.350734000	1.332215000
H	-2.127175000	-0.550064000	2.329844000
C	1.815783000	1.566916000	0.913879000
C	0.533376000	2.015592000	1.157327000
H	-0.023832000	1.731302000	2.041148000
C	0.013403000	3.203356000	0.435458000
O	0.586538000	3.833303000	-0.421769000
O	-1.227117000	3.535780000	0.886254000
C	-1.813329000	4.697340000	0.278915000
H	-2.786941000	4.815082000	0.750947000
H	-1.193221000	5.577606000	0.457458000
H	-1.922703000	4.554081000	-0.797152000
H	2.346746000	2.125379000	0.146758000

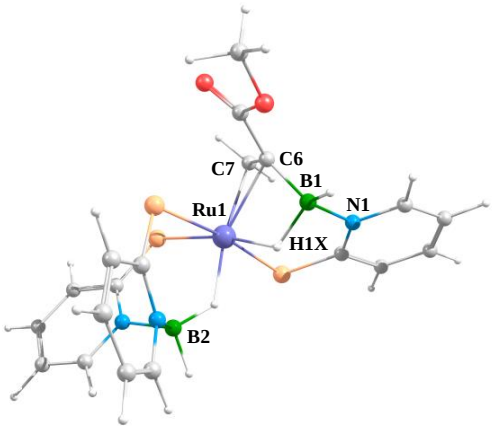


Figure S60. Optimized geometry of *mer*-**6a**.
Total Energy = - 2390.07249812 a. u.

B	-2.349221000	0.766523000	-0.429039000
B	1.793757000	-0.794453000	-1.241668000
C	-3.168680000	-1.675272000	-0.836911000
C	-4.203451000	-2.556840000	-1.245961000
H	-3.994648000	-3.618378000	-1.232470000
C	-5.425657000	-2.074009000	-1.641290000
H	-6.206969000	-2.758823000	-1.951228000
C	-5.653787000	-0.684399000	-1.641730000
H	-6.601206000	-0.260277000	-1.944888000
C	-4.629836000	0.137418000	-1.248906000
H	-4.727118000	1.214191000	-1.234832000
C	-2.013937000	0.897863000	1.105897000
C	-1.901831000	-0.198496000	1.964030000
C	2.520923000	-1.771574000	1.104714000
C	3.563271000	-2.364213000	1.877013000
H	3.319402000	-2.658133000	2.889114000
C	4.819314000	-2.543751000	1.368442000
H	5.597007000	-2.990527000	1.977162000
C	5.089037000	-2.140634000	0.041527000
H	6.063601000	-2.267415000	-0.409512000
C	4.070793000	-1.587755000	-0.679062000
H	4.215788000	-1.278839000	-1.704639000
C	2.816700000	0.862881000	-2.835072000
H	2.822985000	-0.002072000	-3.483500000
C	3.391211000	2.049792000	-3.199814000
H	3.860404000	2.147951000	-4.169076000
C	3.353738000	3.116891000	-2.277022000
H	3.815881000	4.067161000	-2.519491000
C	2.703418000	2.953069000	-1.081350000
H	2.624739000	3.761748000	-0.367088000
C	2.059851000	1.727817000	-0.757607000
N	-3.413907000	-0.329603000	-0.851633000
N	2.809524000	-1.386654000	-0.183095000
N	2.195920000	0.674713000	-1.632160000
Ru	-0.361066000	-0.336984000	0.287667000
S	-1.648517000	-2.314801000	-0.338487000
S	1.131423000	1.599455000	0.672257000
S	0.984482000	-1.604124000	1.836846000
H	0.580748000	-0.980067000	-1.023854000
H	-1.185388000	0.434777000	-1.040718000
H	1.886825000	-1.459043000	-2.237596000
H	-2.583254000	1.768286000	-1.033070000
H	-2.471891000	-1.104104000	1.819928000
C	-1.661702000	2.223626000	1.736342000
O	-1.260731000	2.371626000	2.869197000
O	-1.918510000	3.266799000	0.919408000
C	-1.623096000	4.563292000	1.460648000
H	-2.222574000	4.753396000	2.352751000
H	-0.566006000	4.635134000	1.720628000
H	-1.874581000	5.271083000	0.672818000
H	-1.512212000	-0.028403000	2.961963000

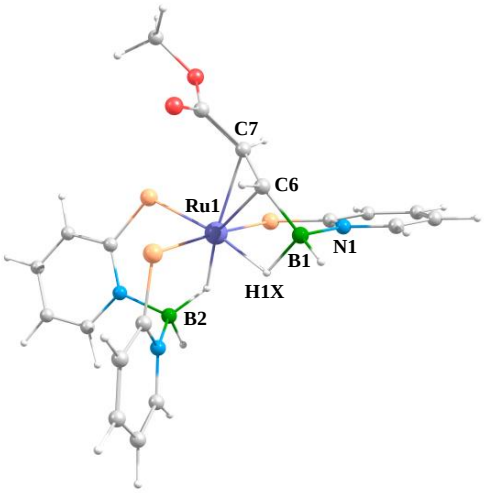


Figure S61. Optimized geometry of *mer*-**6b**.
Total Energy = -2390.08129050 a. u.

B	2.126361000	-1.326936000	1.016999000
B	-1.775169000	-1.115687000	-1.042838000
C	3.272940000	-0.985799000	-1.292674000
C	4.394252000	-1.202830000	-2.136483000
H	4.361239000	-0.783210000	-3.133182000
C	5.478945000	-1.920270000	-1.699085000
H	6.327208000	-2.078562000	-2.355464000
C	5.478680000	-2.449689000	-0.393916000
H	6.311298000	-3.021775000	-0.008174000
C	4.379322000	-2.225034000	0.392457000
H	4.304814000	-2.606542000	1.401399000
C	1.878966000	0.082129000	1.637017000
C	2.007733000	1.310695000	0.992554000
C	1.556521000	2.549746000	1.679785000
C	1.517690000	4.908829000	1.521685000
H	1.953405000	5.055567000	2.511577000
H	0.430540000	4.957503000	1.599745000
H	1.885337000	5.661057000	0.826550000
C	-2.248949000	1.466859000	-1.328694000
C	-3.173346000	2.472744000	-1.735440000
H	-2.831440000	3.498533000	-1.703421000
C	-4.441939000	2.158732000	-2.137733000
H	-5.130459000	2.941073000	-2.435782000
C	-4.842117000	0.804502000	-2.159099000
H	-5.831780000	0.503953000	-2.474516000
C	-3.932221000	-0.138330000	-1.776937000
H	-4.178009000	-1.190762000	-1.791279000
C	-3.057074000	-3.032450000	-0.035019000
H	-3.012936000	-3.393068000	-1.053193000
C	-3.772950000	-3.678552000	0.935007000
H	-4.307776000	-4.587676000	0.696857000
C	-3.791286000	-3.119419000	2.231480000
H	-4.363818000	-3.590231000	3.022633000
C	-3.056911000	-1.991859000	2.491122000
H	-3.018954000	-1.558511000	3.481747000
C	-2.269814000	-1.379206000	1.477741000
N	3.298890000	-1.510526000	-0.028264000
N	-2.662177000	0.157643000	-1.359081000
N	-2.347367000	-1.887816000	0.200939000
O	0.955187000	2.612814000	2.727742000
O	1.924624000	3.646021000	0.972625000
Ru	0.387699000	-0.013461000	0.010923000
S	1.927924000	-0.083719000	-1.880560000
S	-1.237671000	-0.073517000	1.861385000
S	-0.680304000	1.964559000	-0.859304000
H	-0.531940000	-0.964213000	-1.099605000
H	0.977240000	-1.621731000	0.364418000
H	-1.870586000	-1.855848000	-1.984573000
H	2.137734000	-2.250985000	1.781592000
H	2.683579000	1.474696000	0.164974000
H	1.396863000	0.128393000	2.611252000

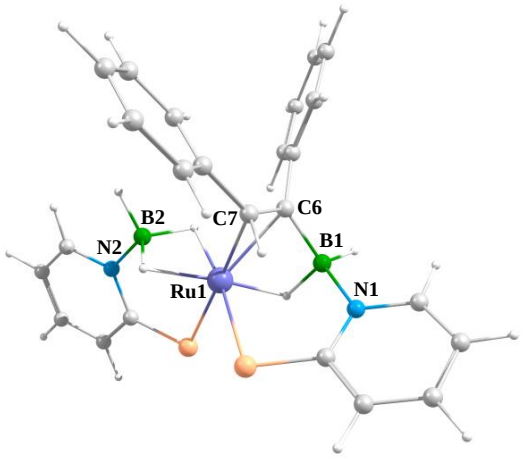


Figure S62. Optimized geometry of *cis*-**9**.
Total Energy = -1978.94046252 a. u.

C	2.104841000	-2.693233000	0.495417000
C	3.038328000	-3.618107000	1.028993000
H	2.744191000	-4.188901000	1.899890000
C	4.273413000	-3.778873000	0.451554000
H	4.979427000	-4.489123000	0.866792000
C	4.613867000	-3.017354000	-0.683522000
H	5.575166000	-3.114484000	-1.169079000
C	3.682929000	-2.140848000	-1.176676000
H	3.866625000	-1.532818000	-2.051989000
C	-3.689400000	-1.215226000	-0.273744000
C	-5.001207000	-1.724200000	-0.453997000
H	-5.107147000	-2.762442000	-0.739480000
C	-6.094013000	-0.916661000	-0.268016000
H	-7.093111000	-1.313407000	-0.407458000
C	-5.911379000	0.432396000	0.107571000
H	-6.750186000	1.096527000	0.264783000
C	-4.635000000	0.893953000	0.273146000
H	-4.413139000	1.912386000	0.560099000
C	1.335695000	0.504879000	-0.614830000
C	1.333745000	0.615363000	0.779499000
C	1.123365000	1.805648000	1.632776000
C	1.643269000	1.761191000	2.938515000
H	2.164378000	0.867546000	3.266681000
C	1.504293000	2.833148000	3.815068000
H	1.920999000	2.769486000	4.814343000
C	0.827103000	3.981316000	3.409455000
H	0.713935000	4.819912000	4.087467000
C	0.290387000	4.037873000	2.122792000
H	-0.245698000	4.923493000	1.798888000
C	0.433669000	2.967553000	1.246174000
H	0.003116000	3.035325000	0.257612000
C	1.304395000	1.684276000	-1.536595000
C	2.298583000	2.665883000	-1.396717000
H	2.999159000	2.595705000	-0.572473000
C	2.397622000	3.725338000	-2.294864000
H	3.173670000	4.471153000	-2.160098000
C	1.505324000	3.828760000	-3.360740000
H	1.578705000	4.654439000	-4.059696000
C	0.522758000	2.853276000	-3.522079000
H	-0.172962000	2.915447000	-4.352071000
C	0.429511000	1.790340000	-2.626307000
H	-0.332677000	1.035296000	-2.773549000
B	1.493282000	-0.921064000	-1.295499000
B	-2.124472000	0.684224000	0.289927000
N	2.457408000	-1.970022000	-0.608973000
N	-3.539280000	0.099671000	0.086882000
Ru	-0.488242000	-0.717198000	-0.040353000
S	0.556583000	-2.496894000	1.227029000
S	-2.308459000	-2.209567000	-0.487198000
H	1.721794000	-0.909515000	-2.471042000
H	0.282018000	-1.520303000	-1.354186000
H	-2.184171000	1.828646000	0.617049000
H	-1.458095000	0.568550000	-0.833588000
H	-1.504821000	0.006219000	1.236129000
H	1.787945000	-0.192575000	1.338471000

IV References

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