Supplementary Information

for

Photochemical Synthesis of Transition Metal-Capped Uranium(VI) Nitride Complexes

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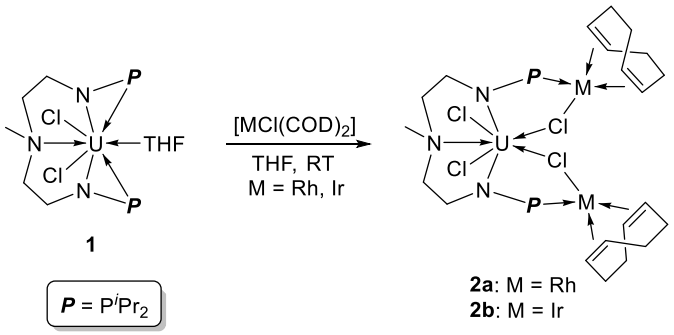
1. Experimental Procedure

General Procedure: All manipulations were performed under an atmosphere of argon or nitrogen using standard Schlenk techniques or in a glovebox. Commercially available chemicals were used as received without further purification. The solvents were obtained by passing through a Solve Purer G5 (MIKROUNA) solvent purification system and further dried over 4 Å molecular sieves. THF-d_8 was dried over Na/K and stored under an Ar or N_2 atmosphere prior to use. Nuclear magnetic resonance spectroscopy was performed using a Bruker AVIII-400 (^{1}H 400 MHz; ^{13}C{^{1}H} 101 MHz; ^{31}P{^{1}H} 162 MHz) spectrometer at room temperature (RT). The ^{1}H and ^{13}C{^{1}H} NMR chemical shifts (δ) are relative to tetramethylsilane, and ^{31}P{^{1}H} NMR chemical shifts are relative to 85% H_3PO_4. Absolute values of the coupling constants are provided in Hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), multiplet (m), and broad (br). Magnetic susceptibility measurements on crystalline samples were performed using a Quantum Design SQUID VSM magnetometer from 300 to 1.8 K under an external magnetic field of 1000 Oe. The sample was added to a pre-weighed SQUID capsule in a glovebox. The capsule was then sealed, weighed, and transferred to the SQUID cavity for the magnetic measurement. All magnetic data were corrected for the diamagnetic contributions of the sample holder and of the core diamagnetism of the samples using Pascal's constant.[1] Elemental analyses (C, H, N) were performed on a Vario EL III elemental analyzer at the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. Complex **1** was prepared according to previously reported procedure.[2]

Synthesis of [{U{N(CH$_3$)(CH$_2$CH$_2$NP^{i}Pr$_2$)$_2$}(Cl)$_2$[(μ-Cl)Rh(COD)]$_2$}] (2a) and [{U{N(CH$_3$)(CH$_2$CH$_2$NP^{i}Pr$_2$)$_2$}(Cl)$_2$[(μ-Cl)Ir(COD)]$_2$}] (2b)



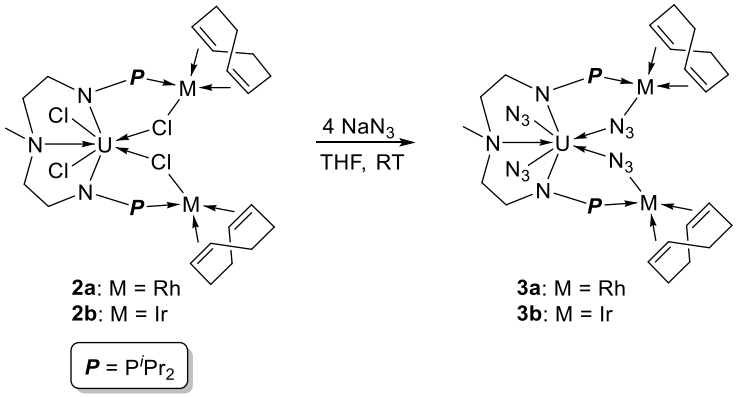
A solution of complex **1** (72 mg, 0.1 mmol, 1 equiv.) in THF was added dropwise to a THF solution of [RhCl(COD)]$_2$ (49 mg, 0.1 mmol, 1 equiv.) under an atmosphere of nitrogen. The mixture was stirred overnight at RT, and then the solvents were removed under reduced pressure and the residues were extracted with toluene. The filtrate was concentrated to 1 mL and placed at -30 ^{o}C for 24 h. Green crystals of **2a** (93 mg, 81%) suitable for X-ray diffraction were obtained. Orange crystals of **2b** (98 mg, 74%) were obtained following the same procedure in which complex **1** (72 mg, 0.1 mmol, 1 equiv.) was treated with 1 equiv. [IrCl(COD)]$_2$ (67 mg, 0.1 mmol, 1 equiv.).

2a: ^{1}H NMR (THF-d$_8$, 400 MHz, ppm) δ 25.93 (s, 2H), 20.98 (s, 6H), 17.66 (s, 2H), 16.78 (s, 2H), 14.16 (s, 2H), 13.35 (s, 2H), 11.06 (s, 2H), 10.35 (s, 12H), 8.71 (s, 6H), 5.15 (s, 6H), 2.80 (s, 12H), -1.19 (s, 2H), -3.12 (s, 2H), -4.04 (s, 2H), -39.61 (s, 1H), -42.76 (s, 1H), -46.13 (s, 1H). ^{31}P{^{1}H} NMR (THF-d$_8$, 162 MHz, ppm) δ 78.94 (d, $^1J_{P\text{-}Rh}$ = 392 Hz), -87.20 (br). Anal. Calcd. for $C_{33}H_{63}Cl_4Rh_2N_3P_2U$·toluene: C, 38.69; H, 5.76; N, 3.38. Found: C, 38.12; H, 5.88; N, 3.36.

2b: ^{1}H NMR (THF-d$_8$, 400 MHz, ppm) δ 22.79 (s, 2H), 19.36 (s, 6H), 16.40 (s, 3H), 15.35 (s, 3H), 11.84 (s, 6H), 9.55 (s, 2H), 8.85 (s, 7H), 8.29 (s, 3H), 7.50 (s, 6H), 5.87 (s, 2H), 4.82 (s, 1H), 3.65

(s, 1H), 3.24 (s, 1H), -0.47 (s, 4H), -1.73 (s, 4H), -3.29 (s, 4H), -10.87 (s, 1H), -31.83 (s, 1H), -39.26 (s, 2H), -40.94 (s, 2H), -49.69 (s, 2H). $^{31}P\{^{1}H\}$ NMR (THF-d_8, 162 MHz, ppm) δ 63.59, -150.90. Anal. Calcd. for $C_{33}H_{63}Cl_4Ir_2N_3P_2U$·toluene: C, 33.83; H, 5.04; N, 2.96. Found: C, 33.67; H, 5.20; N, 2.92.

Synthesis of [{U{N(CH$_3$)(CH$_2$CH$_2$NP^{i}Pr$_2$)$_2$}(N$_3$)$_2$[(μ-N$_3$)Rh(COD)]$_2$}] (3a) and [{U{N(CH$_3$)(CH$_2$CH$_2$NP^{i}Pr$_2$)$_2$}(N$_3$)$_2$[(μ-N$_3$)Ir(COD)]$_2$}] (3b)



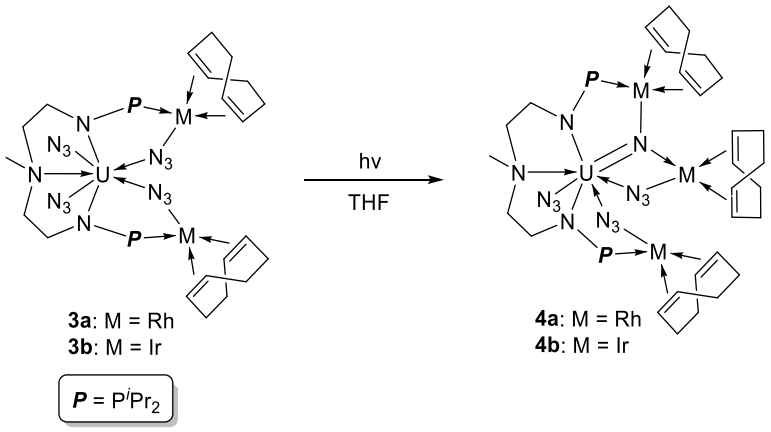
A solution of complex **2a** (57 mg, 0.05 mmol, 1 equiv.) in THF was added to a mixture of NaN_3 (13 mg, 0.2 mmol, 4 equiv.) in THF under an atmosphere of nitrogen. The mixture was stirred overnight at RT and then the mixture was filtered. The filtrate was concentrated to 1 mL and placed at -30 ºC for 24 h, producing brown crystals of **3a** suitable for X-ray diffraction (41 mg, 70%). Red crystals of **3b** (44 mg, 65%) were obtained following the same procedure by treatment of **2b** (66 mg, 0.05 mmol, 1 equiv.) with 4 equiv. NaN_3 (13 mg, 0.2 mmol, 4 equiv.).

3a: ^{1}H NMR (THF-d_8, 400 MHz, ppm) δ 67.46 (s, 1H), 59.45 (s, 1H), 19.80 (s, 6H), 7.00 (s, 12H), -3.17 (s, 12H), -8.97 (s, 6H), -10.60 (s, 6H), -12.85 (s, 6H), -15.62 (s, 1H), -22.34 (s, 2H), -25.67 (s, 1H), -31.81 (s, 2H), -42.28 (s, 2H), -44.68 (s, 3H), -49.98 (s, 1H), -50.01 (s, 1H). $^{31}P\{^{1}H\}$ NMR

(THF-d_8, 162 MHz, ppm) δ 76.79 (d, $^1J_{P\text{-}Rh}$ = 392 Hz), 77.58 (d, $^1J_{P\text{-}Rh}$ = 396 Hz). Anal. Calcd. for $C_{33}H_{63}N_{15}P_2Rh_2U{\cdot}THF$: C, 35.61; H, 5.74; N, 16.84. Found: C, 35.80; H, 5.73; N, 16.44.

3b: ^{1}H NMR (THF-d_8, 400 MHz, ppm) δ 70.12 (s, 1H), 61.77 (s, 1H), 21.97 (s, 6H), 5.05 (s, 12H), -2.46 (s, 12H), -9.88 (s, 6H), -11.40 (s, 6H), -13.63 (s, 6H), -15.90 (s, 2H), -23.74 (s, 2H), 33.15 (s, 1H), -33.19 (s, 1H), -42.70 (s, 2H), -46.20 (s, 3H), -52.59 (s, 1H), -52.63 (s, 1H). $^{31}P\{^1H\}$ NMR (THF-d_8, 162 MHz, ppm) δ 64.60, 64.41. Anal. Calcd. for $C_{33}H_{63}Ir_2N_{15}P_2U{\cdot}THF$: C, 31.15; H, 5.02; N, 14.73. Found: C, 31.17; H, 4.98; N, 13.99.

Synthesis of [{U{N(CH$_3$)(CH$_2$CH$_2$NP^{i}Pr$_2$)$_2$}(N$_3$)[(*μ*-N$_3$)Rh(COD)]$_2$[(*μ*-N)Rh(COD)]}] (4a) and [{U{N(CH$_3$)(CH$_2$CH$_2$NP^{i}Pr$_2$)$_2$}(N$_3$)[(*μ*-N$_3$)Ir(COD)]$_2$[(*μ*-N)Ir(COD)]}] (4b)



A solution of complex **3a** (59 mg, 0.05 mmol, 1 equiv.) in THF (5 mL) was transferred into a Schlenk tube under an atmosphere of nitrogen and then irradiated with a 40 W UV lamp for 2 days. The solvents were removed under reduced pressure and the residues were extracted with toluene. The filtrate was concentrated to 0.5 mL and placed at RT for 48 h, giving brown crystals of **4a** suitable for X-ray diffraction (36 mg, 54%). Brown crystals of **4b** were obtained following the same

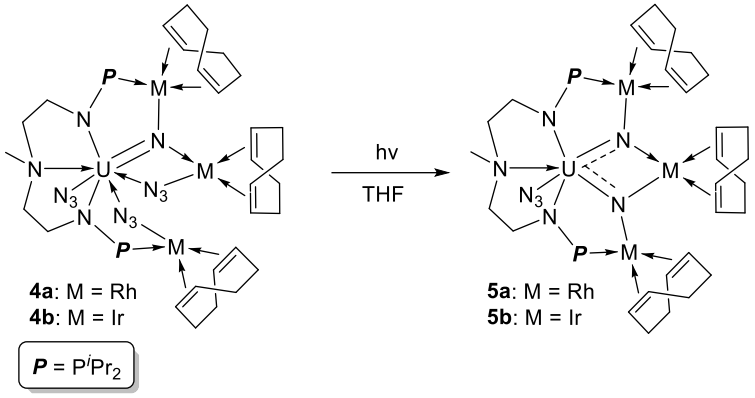
procedure by exposing a THF solution of complex **3b** (68 mg, 0.05 mmol, 1 equiv.) to UV light for 1 days (42 mg, 52%).

4a: ^{1}H NMR (THF-d_8, 400 MHz, ppm) δ 23.37 (s, 1H), 15.28 (s, 2H), 12.58 (s, 1H), 9.79 (s, 1H), 9.49 (s, 1H), 9.08 (s, 3H), 8.33 (s, 3H), 8.18 (s, 1H), 6.89 (s, 1H), 6.69 (s, 1H), 6.23 (s, 2H), 5.80 (s, 2H), 5.62 (s, 2H), 5.53 (s, 1H), 5.26 (s, 2H), 5.04 (s, 2H), 4.88 (s, 3H), 4.82 (s, 1H), 4.47 (s, 1H), 4.40 (s, 6H), 3.77 (s, 6H), 3.68 (s, 1H), 2.95 (s, 2H), 1.28 (s, 6H), 0.99 (s, 2H), 0.66 (s, 2H), 0.46 (s, 3H), 0.02 (s, 2H), -0.39 (s, 2H), -0.77 (s, 2H), -2.89 (s, 1H), -4.05 (s, 1H), -5.45 (s, 1H), -6.08 (s, 1H), -8.05 (s, 4H), -10.79 (s, 1H), -12.46 (s, 1H). ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz, ppm) δ 94.65 (br), 76.79 (d, $^{1}J_{P\text{-}Rh}$ = 392 Hz). Anal. Calcd. for $C_{41}H_{75}N_{13}P_2Rh_3U$: C, 36.24; H, 5.56; N, 13.40. Found: C, 36.59; H, 5.63; N, 13.35.

4b: ^{1}H NMR (THF-d_8, 400 MHz, ppm) δ 24.73 (s, 1H), 16.26 (s, 1H), 15.08 (s, 1H), 12.34 (s, 1H), 11.32 (s, 1H), 10.70 (s, 1H), 10.42 (s, 1H), 9.53 (s, 3H), 8.26 (s, 1H), 7.58 (s, 1H), 6.66 (s, 2H), 6.47 (s, 3H), 6.17 (s, 2H), 5.96 (s, 2H), 5.33 (s, 4H), 5.15 (s, 2H), 5.09 (s, 3H), 4.85 (s, 2H), 4.73 (s, 6H), 4.55 (s, 6H), 4.46 (s, 1H), 4.35 (s, 2H), 4.19 (s, 2H), 1.56 (s, 3H), 0.96 (s, 6H), 0.90 (s, 2H), -0.40 (s, 2H), -0.40 (s, 2H), -0.48 (s, 2H), -3.20 (s, 1H), -5.36 (s, 1H), -6.87 (s, 1H), -9.53 (s, 4H), -10.95 (s, 1H), -12.17 (s, 2H), -12.48 (s, 1H). ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz, ppm) δ 73.08, 68.63. Anal. Calcd. for $C_{41}H_{75}N_{13}P_2Ir_3U{\cdot}1.5$toluene: C, 35.05; H, 4.97; N, 10.32. Found: C, 35.14; H, 4.99; N, 10.44.

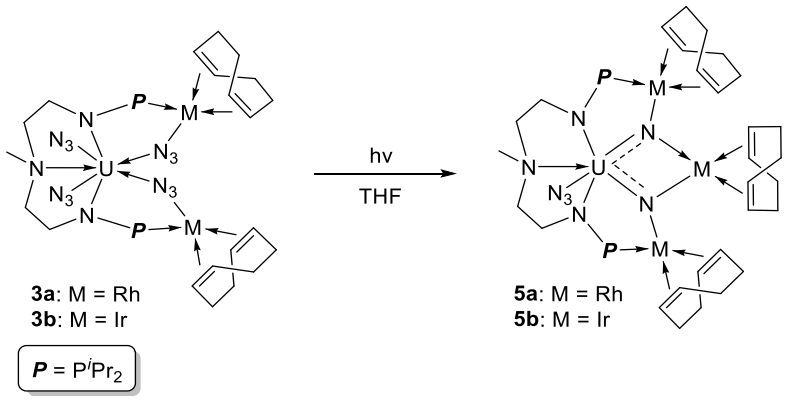
Synthesis of [{U{N(CH$_3$)(CH$_2$CH$_2$NP^{i}Pr$_2$)$_2$}(N$_3$){[(μ-N)Rh(COD)]$_2$[Rh(COD)]}}] (5a) and [{U{N(CH$_3$)(CH$_2$CH$_2$NP^{i}Pr$_2$)$_2$}(N$_3$){[(μ-N)Ir(COD)]$_2$[Ir(COD)]}}] (5b)

Method A:



A solution of complex **4a** (34 mg, 0.025 mmol, 1 equiv.) in THF (5 mL) was transferred into a Schlenk tube under an atmosphere of nitrogen and then irradiated with a 40 W UV lamp for 2 days. The mixture was filtered and the filtrate was concentrated to 0.5 mL and placed at RT for 48 h, brown crystals of **5a** suitable for X-ray diffraction were obtained (21 mg, 65%). Brown crystals of **4b** were obtained following the same procedure by exposing a THF solution of complex **5b** (41 mg, 0.025 mmol, 1 equiv.) to UV light for 1 days (23 mg, 58%).

Method B:



A solution of complex **3a** (59 mg, 0.05 mmol, 1 equiv.) in THF (5 mL) was transferred into a Schlenk tube under an atmosphere of nitrogen and then irradiated with a 40 W UV lamp for 4 days. The mixture was filtered and the filtrate was concentrated to 0.5 mL and placed at RT for 48 h, brown crystals of **5a** suitable for X-ray diffraction were obtained (24 mg, 38%). Brown crystals of **5b** were obtained using the same procedure by exposing a THF solution of complex **3b** (68 mg, 0.05 mmol, 1 equiv.) to UV light for 2 days (25 mg, 32%).

5a: ^{1}H NMR (THF-d_8, 400 MHz, ppm) δ 6.36 (s, 2H), 5.88 (s, 2H), 4.91-4.95 (m, 5H), 3.34-3.42 (m, 6H), 2.84-2.96 (m, 6H), 2.35-2.42 (m, 12H), 2.15-2.20 (m, 6H), 1.54-1.57 (m, 12H), 1.10-1.19 (m, 24H). ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz, ppm) δ 41.48 (d, $^{1}J_{P\text{-}Rh}$ = 372 Hz). Anal. Calcd. for $C_{41}H_{75}N_8P_2Rh_3U$: C, 38.21; H, 5.87; N, 8.69. Found: C, 38.24; H, 5.97; N, 8.50.

5b: ^{1}H NMR (THF-d_8, 400 MHz, ppm) δ 6.36 (s, 2H), 5.88 (s, 2H), 4.56-4.57 (m, 5H), 3.36-3.43 (m, 6H), 2.88-2.94 (m, 6H), 2.40-2.48 (m, 12H), 2.18-2.22 (m, 6H), 1.51-1.58 (m, 12H), 1.23-1.27 (m, 24H). ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz, ppm) δ 29.30. Anal. Calcd. for $C_{41}H_{75}N_8P_2Ir_3U$: C, 31.63; H, 4.86; N, 7.20. Found: C, 32.63; H, 4.89; N, 7.36.

Protonation of complexes 4 and 5 with acid

An excess of pyridine hydrochloride (10.7 mg, 0.093 mmol, 25 equiv.) was added to a brown solution of **4a** (5.0 mg, 0.0037 mmol, 1 equiv.) in THF (1 ml). The mixture was stirred at RT overnight, affording a pale-yellow solution and a white precipitate. The supernatant was removed and the solid was washed three times with 1.0 mL of THF. The solid was dried under vacuum. The amount of ammonia was evaluated by quantitative ^{1}H NMR with dibromomethane as an internal

standard. The NH_4Cl was formed in 73% yield (Fig. S9).

An excess of pyridine hydrochloride (9.0 mg, 0.078 mmol, 25 equiv.) was added to a brown solution of **4b** (5.0 mg, 0.0031 mmol, 1 equiv.) in THF (1 ml). The mixture was stirred at RT overnight, affording a pale-yellow solution with a white precipitate. The supernatant was removed and the solid was washed three times with 1.0 mL of THF. The solid was dried under vacuum. The amount of ammonia was evaluated by quantitative ^1H NMR with dibromomethane as an internal standard. The NH_4Cl was formed in 82% yield (Fig. S10).

An excess of pyridine hydrochloride (22.5 mg, 0.13 mmol, 50 equiv.) was added to a brown solution of **5a** (5.0 mg, 0.0039 mmol, 1 equiv.) in THF (1 ml). The mixture was stirred at RT overnight, affording a pale-yellow solution with a white precipitate. The supernatant was removed and the solid was washed three times with 1.0 mL of THF. The solid was dried under vacuum. The amount of ammonia was measured by quantitative ^1H NMR with dibromomethane as an internal standard. The NH_4Cl was formed in 75% yield (Fig. S11).

An excess of pyridine hydrochloride (18.6 mg, 0.13 mmol, 50 equiv.) was added to a brown solution of **5b** (5.0 mg, 0.0032 mmol, 1 equiv.) in THF (1 ml). The mixture was stirred at RT overnight, affording a pale-yellow solution with a white precipitate. The supernatant was removed and the solid was washed three times with 1.0 mL of THF. The solid was dried under vacuum. The amount of ammonia was measured by quantitative ^1H NMR with dibromomethane as an internal standard. The NH_4Cl was formed in 68% yield (Fig. S12).

Reaction of complexes 4 and 5 with H_2 and PyHCl

In an NMR tube, a brown solution of **4a** (5.0 mg, 0.0037 mmol, 1 equiv.) in 0.5 ml of THF-d_8 was frozen and degassed three times then exposed to 1 atm of H_2 at RT. The NMR tube was closed and

left at RT for 24 h, then all the volatiles were vacuum transferred into a Schlenk flask containing a PyHCl (10.7 mg, 0.093 mmol, 25 equiv.) solution in DMSO-d_6. No NH_4Cl was detected. An excess of pyridine hydrochloride (10.7 mg, 0.093 mmol, 25 equiv.) in THF was added to the residue remaining in the NMR tube. The mixture was stirred at RT overnight, affording a pale-yellow solution with a white precipitate. The supernatant was removed and the solid was washed three times with 1.0 mL of THF. The solid was dried under vacuum. The amount of ammonia (58%) was measured by quantitative ^{1}H NMR spectrum with dibromomethane as an internal standard (Fig. S13).

In an NMR tube, a brown solution of **4b** (5.0 mg, 0.0031 mmol, 1 equiv.) in 0.5 ml of THF-d_8 was frozen and degassed three times and exposed to 1 atm of H_2 at RT. The NMR tube was closed and left at RT for 24 h, then all the volatiles were vacuum transferred into a Schlenk flask containing a PyHCl (9.0 mg, 0.078 mmol, 25 equiv.) solution in DMSO-d_6. No NH_4Cl was detected. An excess of pyridine hydrochloride (9.0 mg, 0.078 mmol, 25 equiv.) in THF was added to the residue left in the NMR tube. The mixture was stirred at RT overnight, affording a pale-yellow solution with a white precipitate. The supernatant was removed and the solid was washed three times with 1.0 mL of THF. The solid was dried under vacuum. The amount of ammonia (67%) was measured by quantitative ^{1}H NMR spectrum with dibromomethane as an internal standard (Fig. S14).

In an NMR tube, a brown solution of **5a** (5.0 mg, 0.0039 mmol, 1 equiv.) in 0.5 ml of THF-d_8 was frozen and degassed three times and exposed to 1 atm of H_2 at RT. The NMR tube was closed and left at RT for 24 h, then all the volatiles were vacuum transferred into a Schlenk flask containing a PyHCl (22.5 mg, 0.13 mmol, 50 equiv.) solution in DMSO-d_6. No NH_4Cl was detected. An excess of pyridine hydrochloride (22.5 mg, 0.13 mmol, 50 equiv.) in THF was added to the residue left in

the NMR tube. The mixture was stirred at RT overnight, affording a pale-yellow solution with a white precipitate. The supernatant was removed and the solid was washed three times with 1.0 mL of THF. The solid was dried under vacuum. The amount of ammonia (54%) was measured by quantitative ^{1}H NMR spectrum with dibromomethane as an internal standard (Fig. S15).

In an NMR tube, a brown solution of **5b** (5.0 mg, 0.0032 mmol, 1 equiv.) in 0.5 ml of THF-d_8 was frozen and degassed three times and exposed to 1 atm of H_2 at RT. The NMR tube was closed and left at RT for 24 h, then all the volatiles were vacuum transferred into a Schlenk flask containing a PyHCl (18.6 mg, 0.13 mmol, 50 equiv.) solution in DMSO-d_6. No NH_4Cl was detected. An excess of pyridine hydrochloride (18.6 mg, 0.13 mmol, 50 equiv.) in THF was added to the residue left in the NMR tube. The mixture was stirred at RT overnight, affording a pale-yellow solution with a white precipitate. The supernatant was removed and the solid was washed three times with 1.0 mL of THF. The solid was dried under vacuum. The amount of ammonia (41%) was measured by quantitative ^{1}H NMR spectrum with dibromomethane as an internal standard (Fig. S16).

2. Supporting Figures

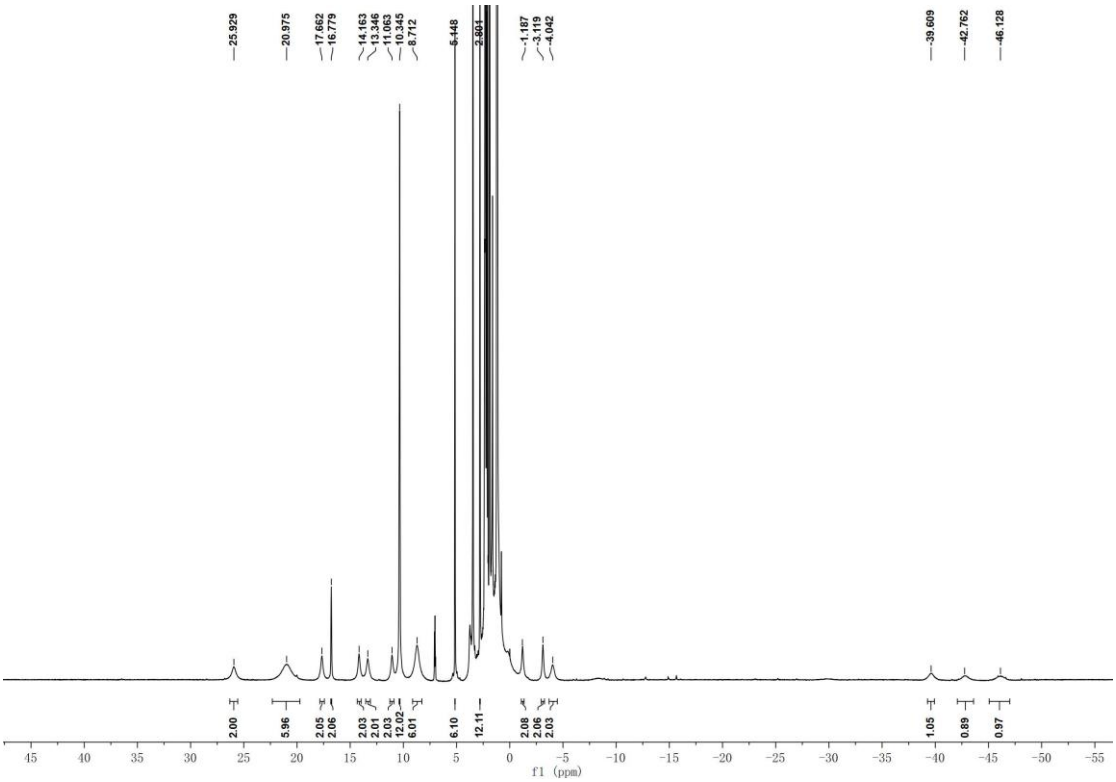


Fig. S1. The ^{1}H NMR (THF-d_8, 400 MHz) spectrum of complex **2a**.

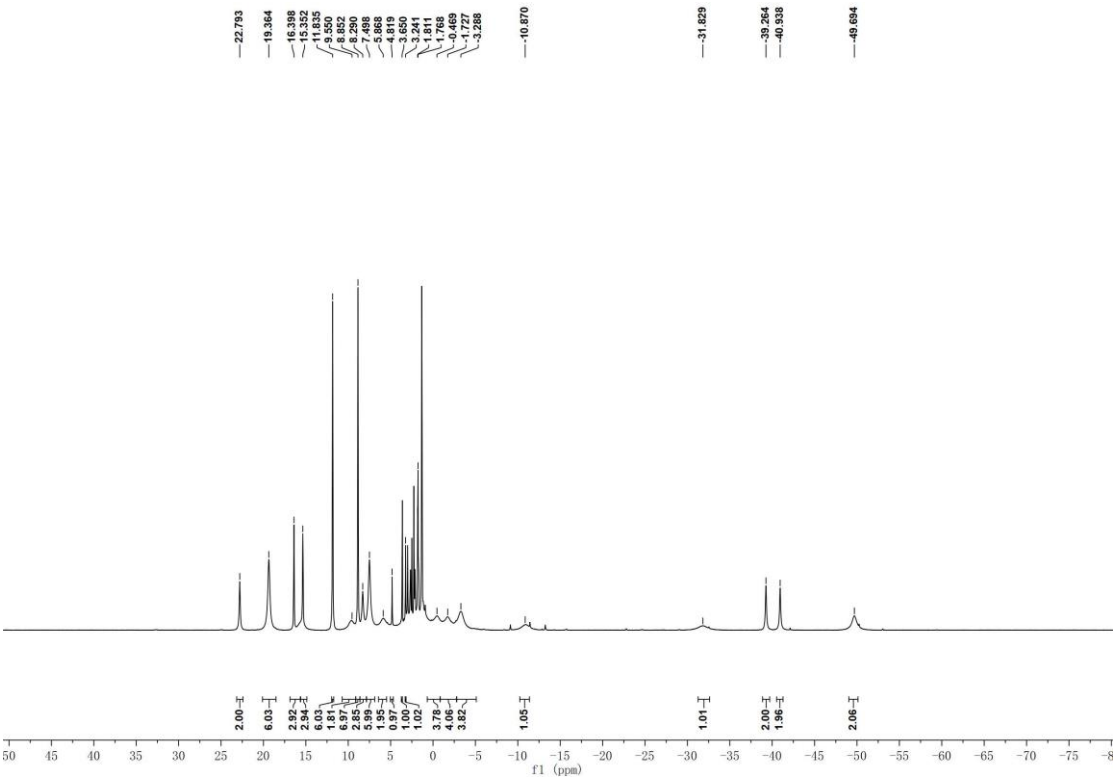


Fig. S2. The ^{1}H NMR (THF-d_8, 400 MHz) spectrum of complex **2b**.

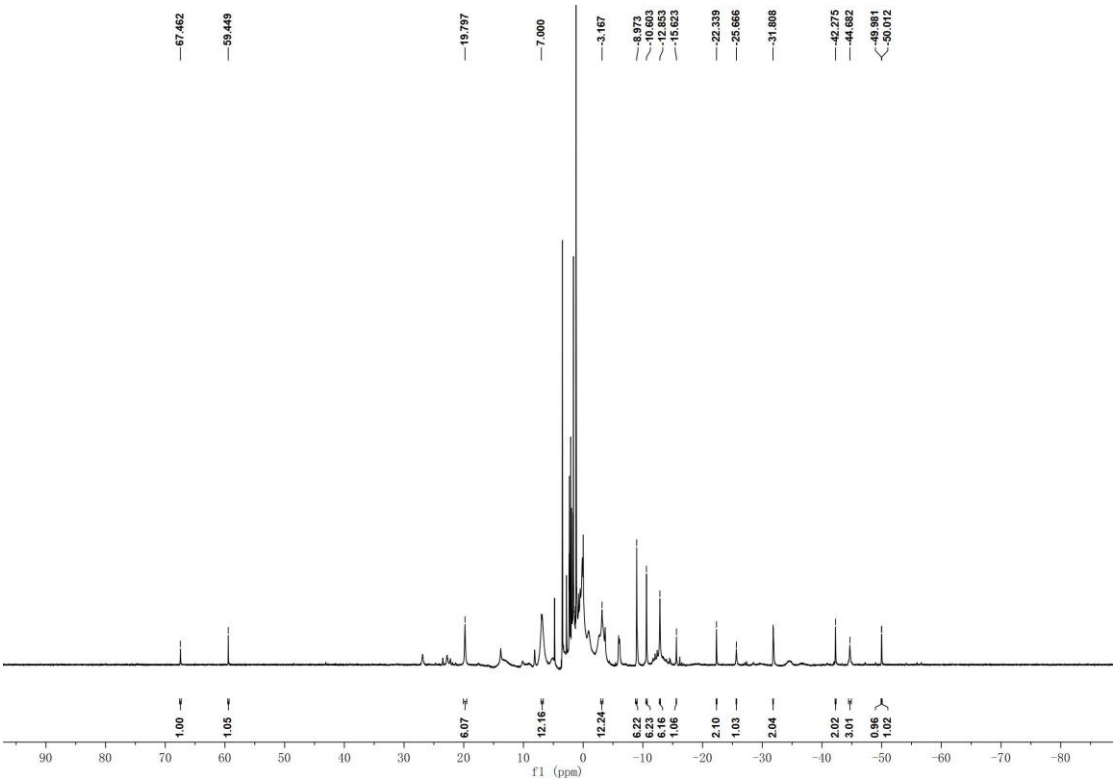


Fig. S3. The ^{1}H NMR (THF-d_8, 400 MHz) spectrum of complex **3a**.

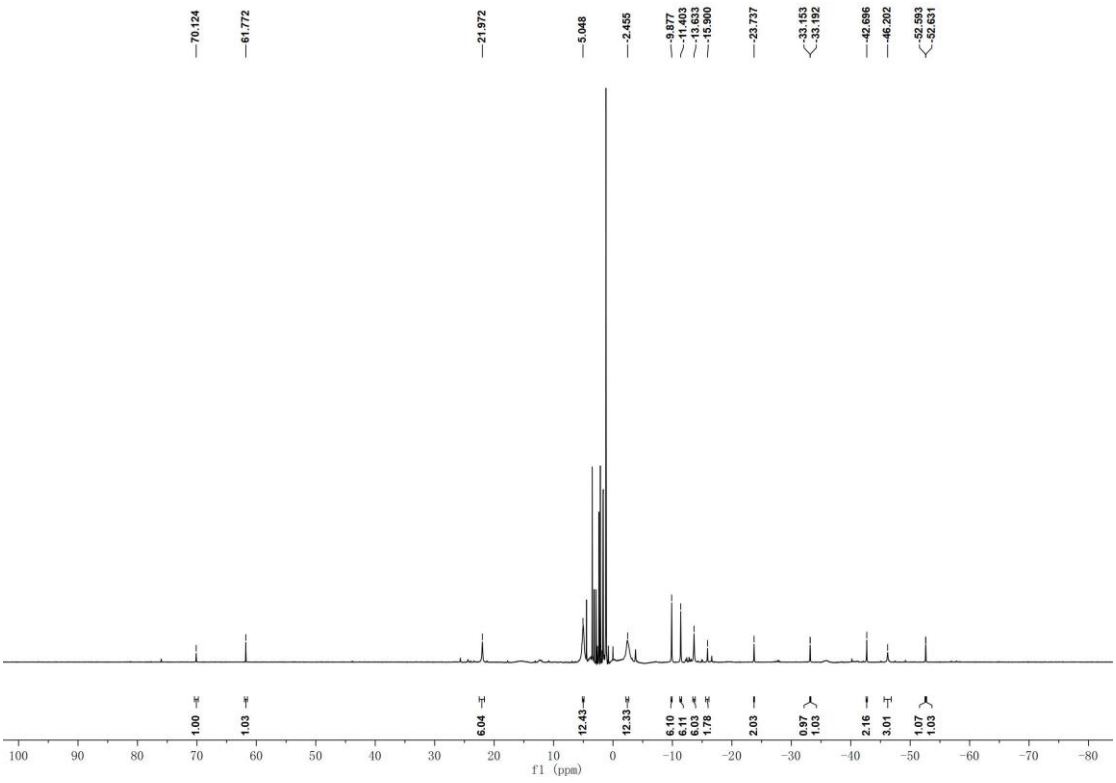


Fig. S4. The ^{1}H NMR (THF-d_8, 400 MHz) spectrum of complex **3b**.

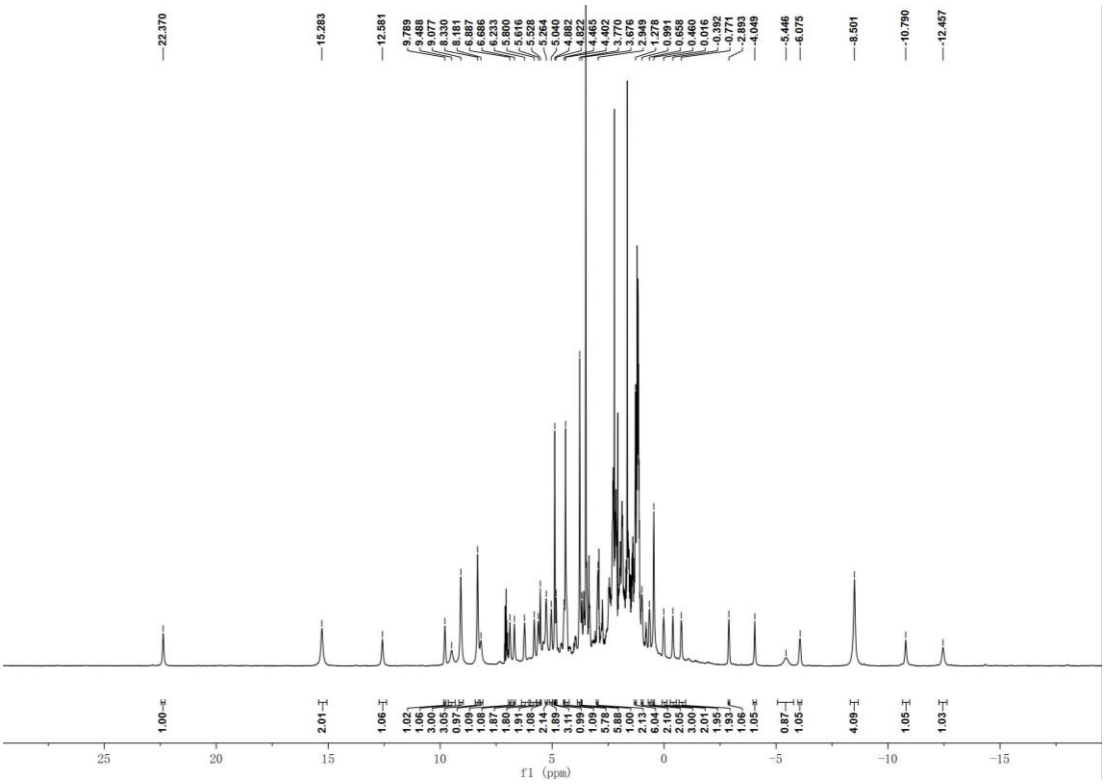


Fig. S5. The ^{1}H NMR (THF-d_8, 400 MHz) spectrum of complex **4a**.

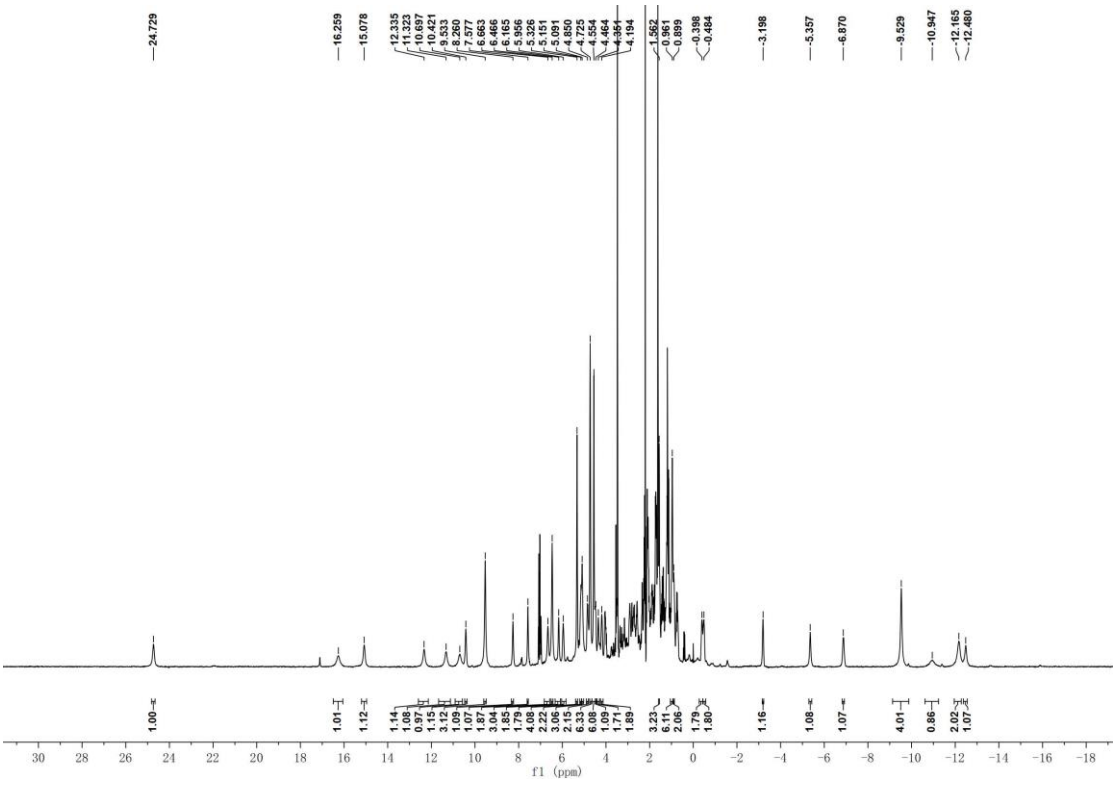


Fig. S6. The ^{1}H NMR (THF-d_8, 400 MHz) spectrum of complex **4b**.

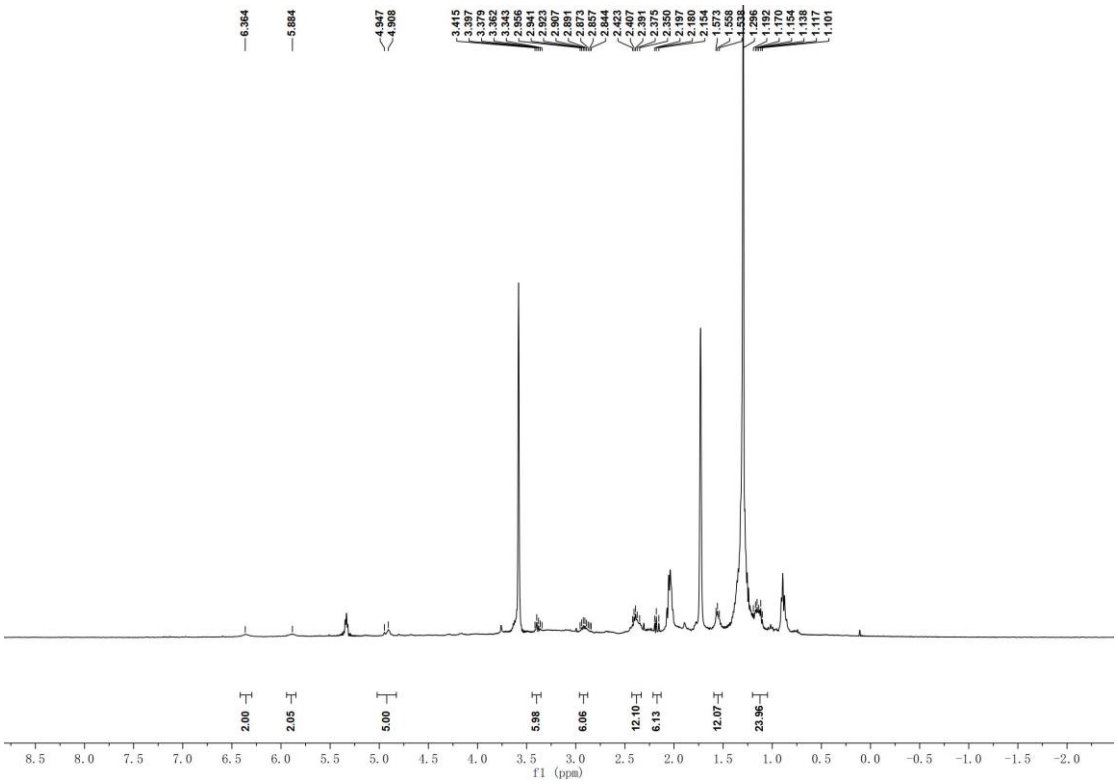


Fig. S7. The ^{1}H NMR (THF-d_8, 400 MHz) spectrum of complex **5a**.

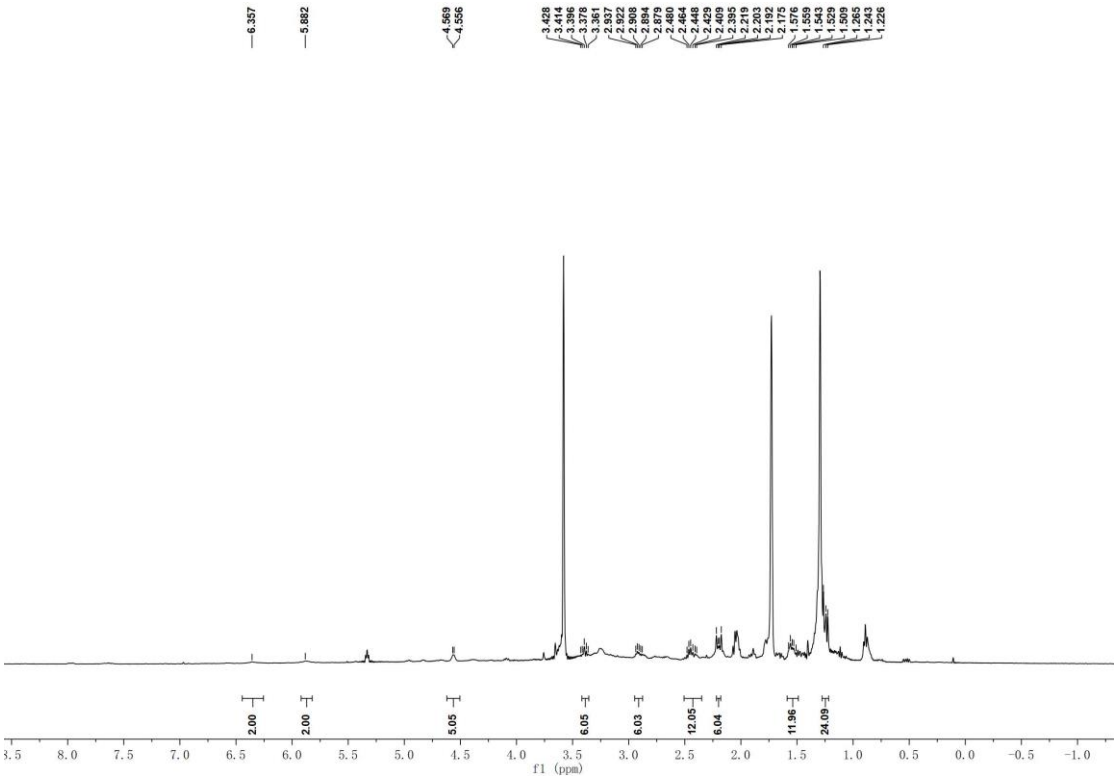


Fig. S8. The ^{1}H NMR (THF-d_8, 400 MHz) spectrum of complex **5b**.

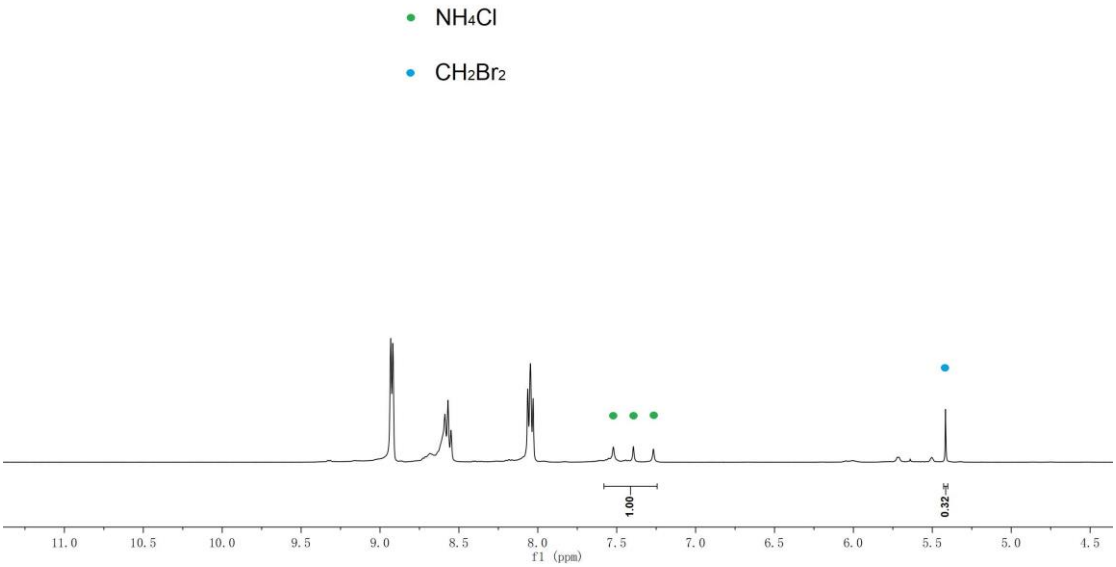


Fig. S9. The ^{1}H NMR (DMSO-d_6, 400 MHz) spectrum for the reaction of complex **4a** with PyHCl (73% yield of ammonia).

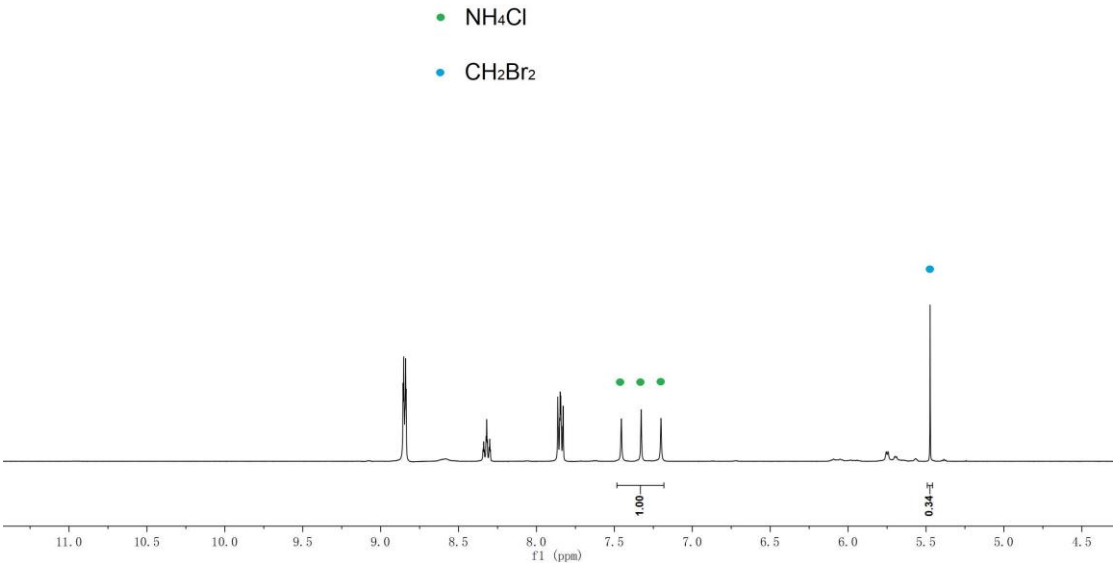


Fig. S10. The ^{1}H NMR (DMSO-d_6, 400 MHz) spectrum for the reaction of complex **4b** with PyHCl (82% yield of ammonia).

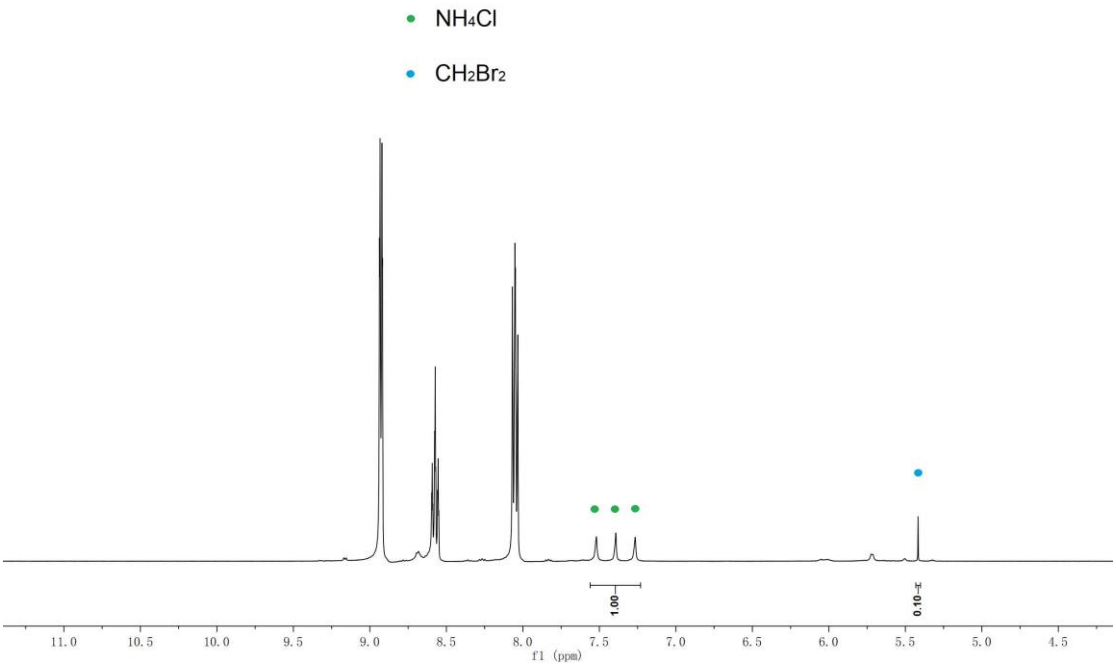


Fig. S11. The ^{1}H NMR (DMSO-d_6, 400 MHz) spectrum for the reaction of complex **5a** with PyHCl (75% yield of ammonia).

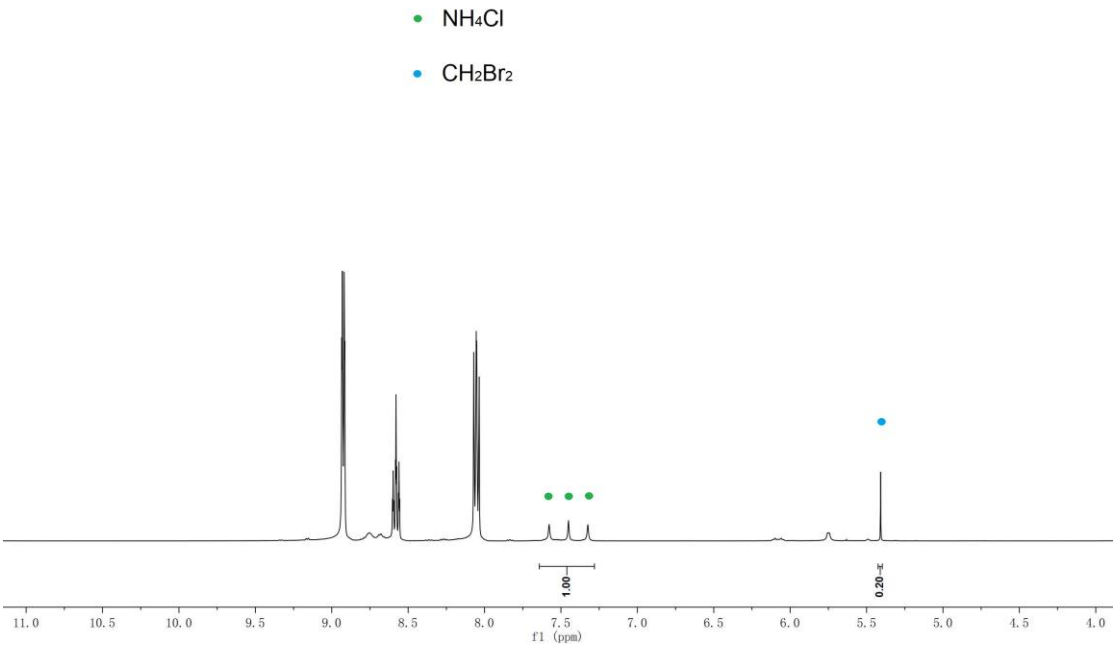


Fig. S12. The ^{1}H NMR (DMSO-d_6, 400 MHz) spectrum for the reaction of complex **5a** with PyHCl (68% yield of ammonia).

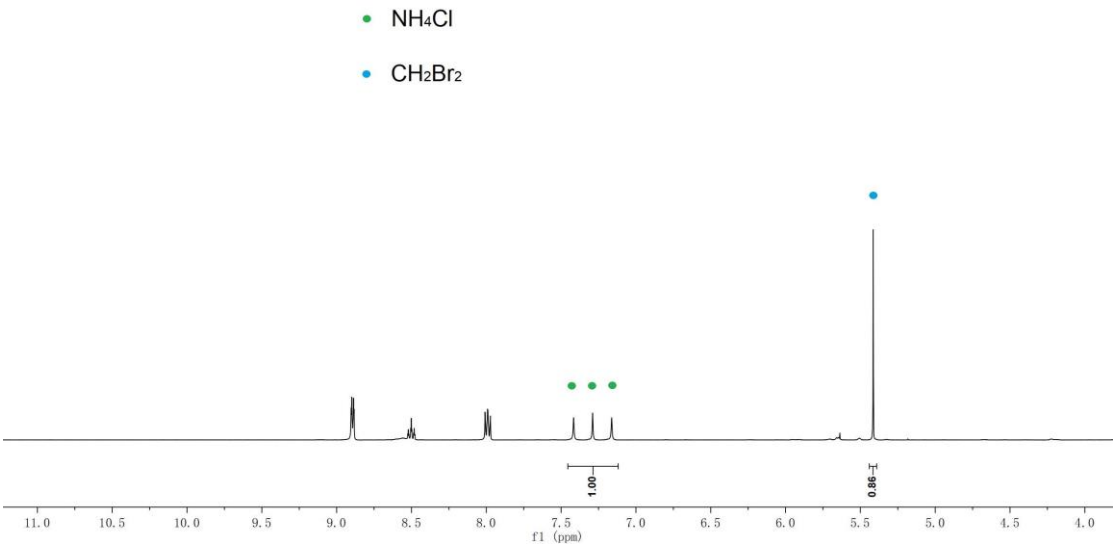


Fig. S13. The ^{1}H NMR (DMSO-d_6, 400 MHz) spectrum for the reaction of complex **4a** with H_2 after evaporation of the addition of excess PyHCl to the residue (58% yield of ammonia).

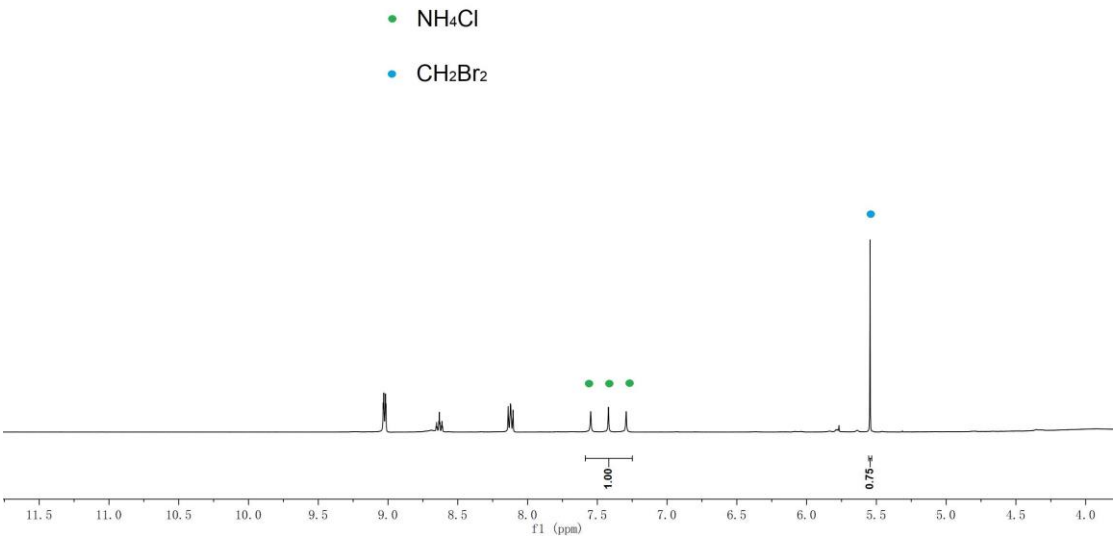


Fig. S14. The ^{1}H NMR (DMSO-d_6, 400 MHz) spectrum for the reaction of complex **4b** with H_2 after evaporation of the addition of excess PyHCl to the residue (67% yield of ammonia).

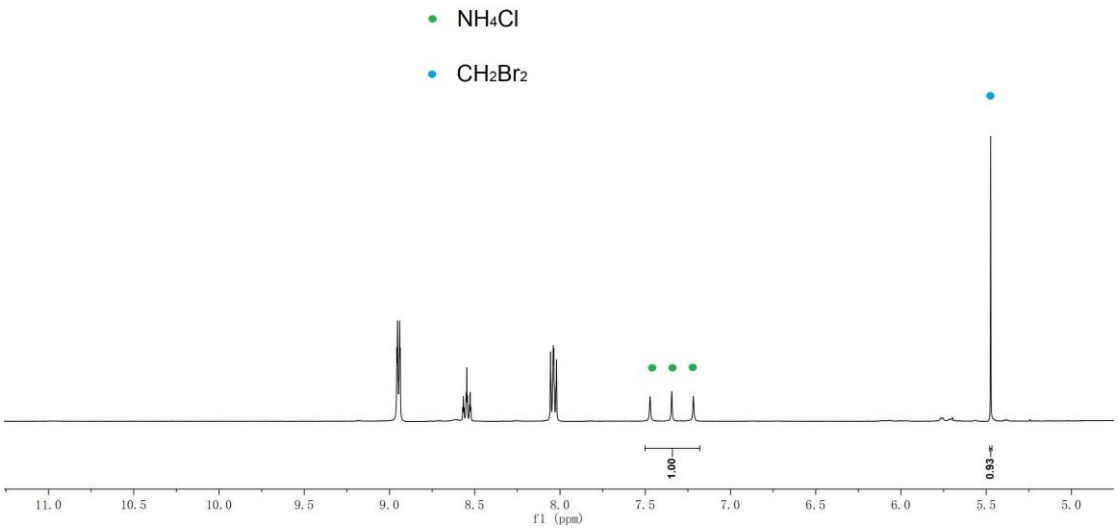


Fig. S15. The ^{1}H NMR (DMSO-d_6, 400 MHz) spectrum for the reaction of complex **5a** with H_2 after evaporation of the addition of excess PyHCl to the residue (54% yield of ammonia).

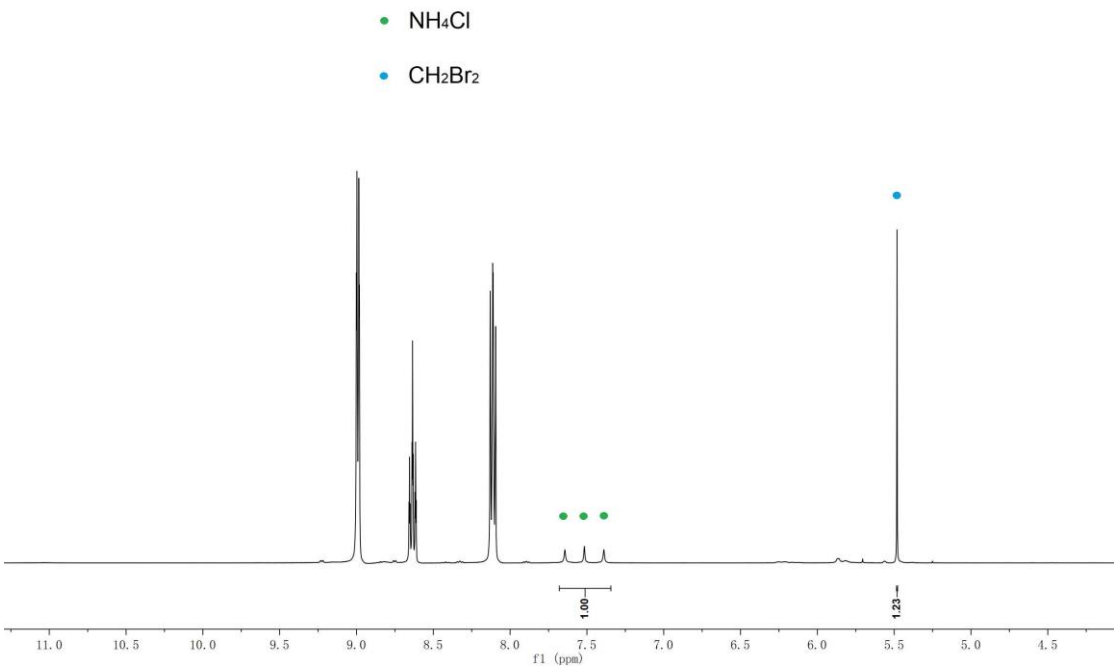


Fig. S16. The ^{1}H NMR (DMSO-d_6, 400 MHz) spectrum for the reaction of complex **5b** with H_2 after evaporation of the addition of excess PyHCl to the residue (41% yield of ammonia).

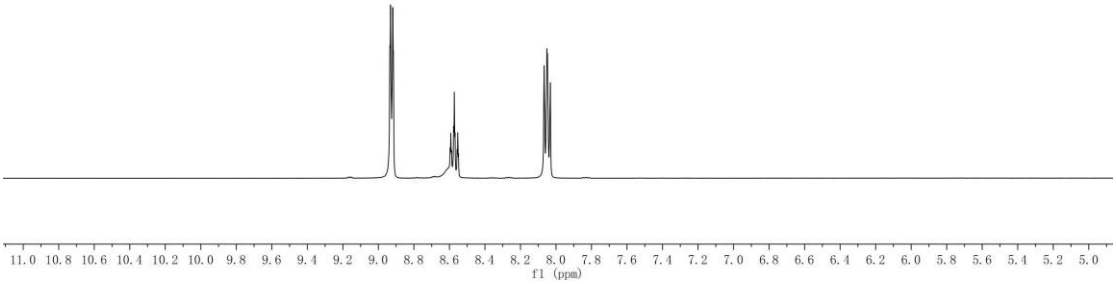


Fig. S17. The ^{1}H NMR (DMSO-d_6, 400 MHz) spectrum for the reaction of complex **3a** with excess PyHCl. No NH^{4+} was formed in the reaction.

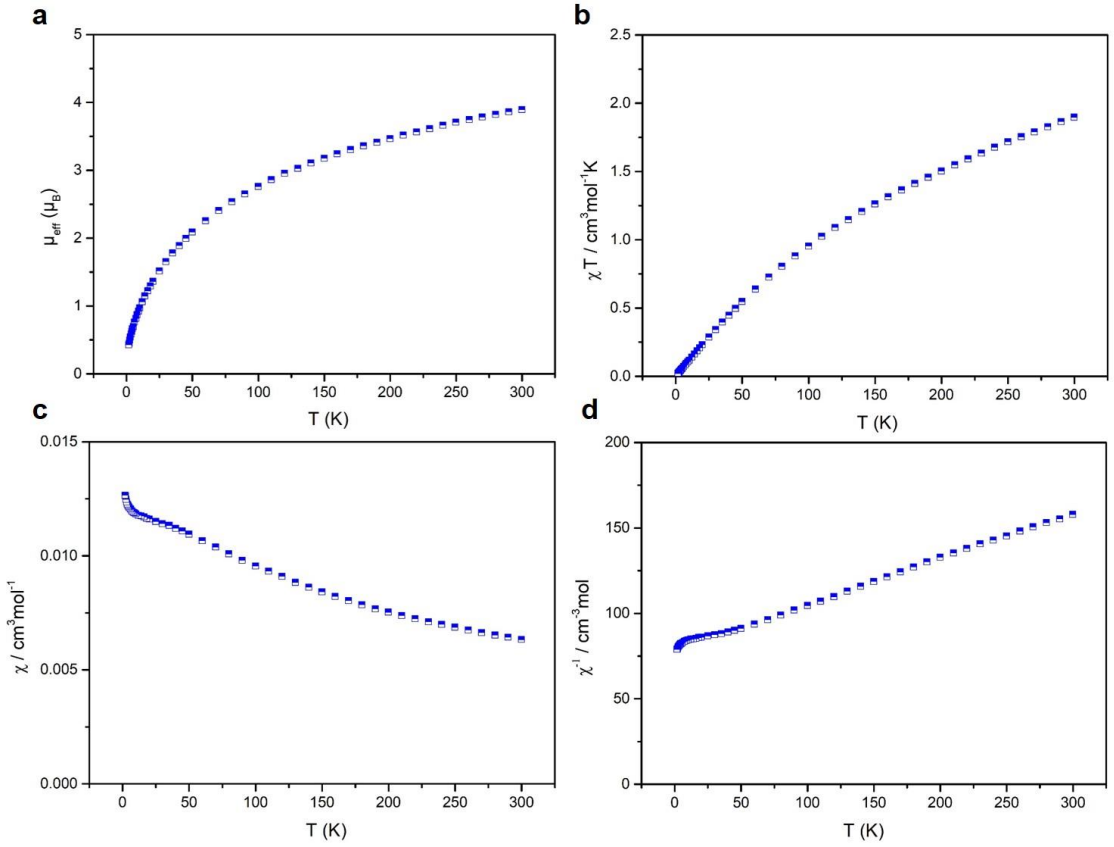


Fig. S18. Variable-temperature data of **3a**. (a) μ_{eff} vs T, (b)) χT vs T, (c) χ vs T, and (d) 1/χ vs T.

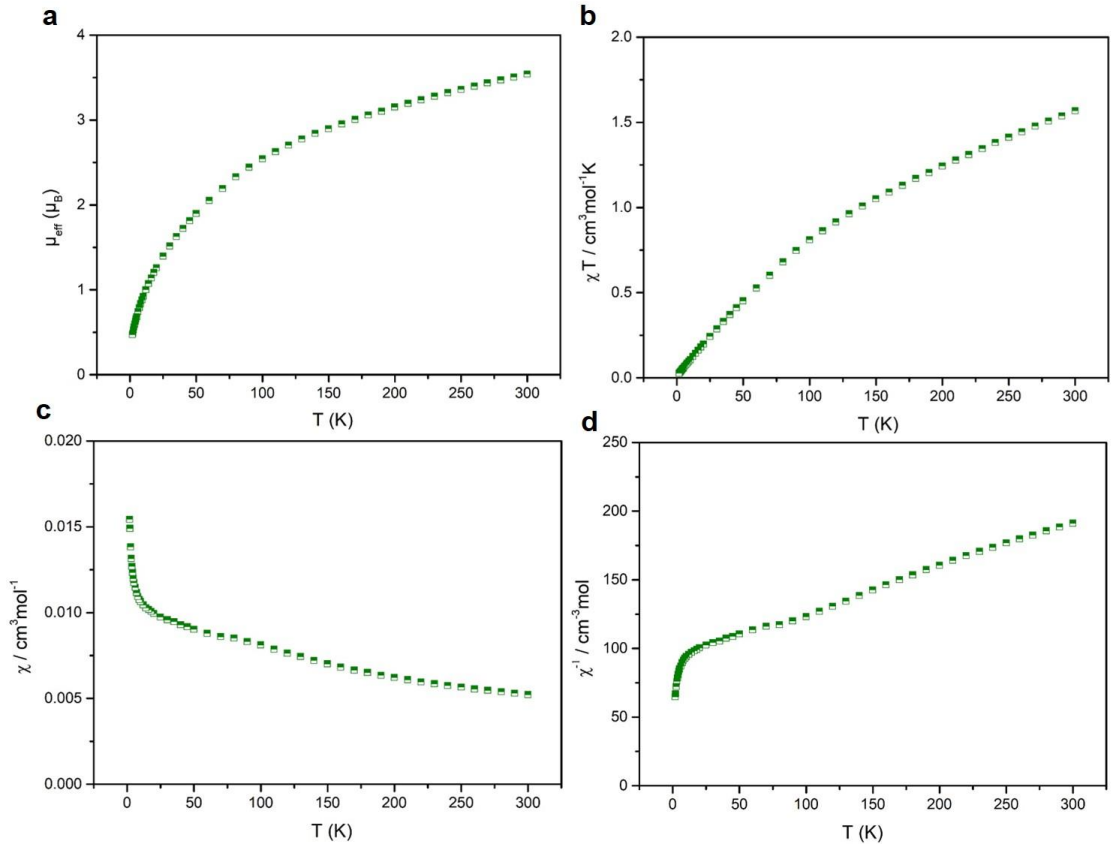


Fig. S19. Variable-temperature data of **3b**. (a) μ_{eff} vs T, (b)) χT vs T, (c) χ vs T, and (d) 1/χ vs T.

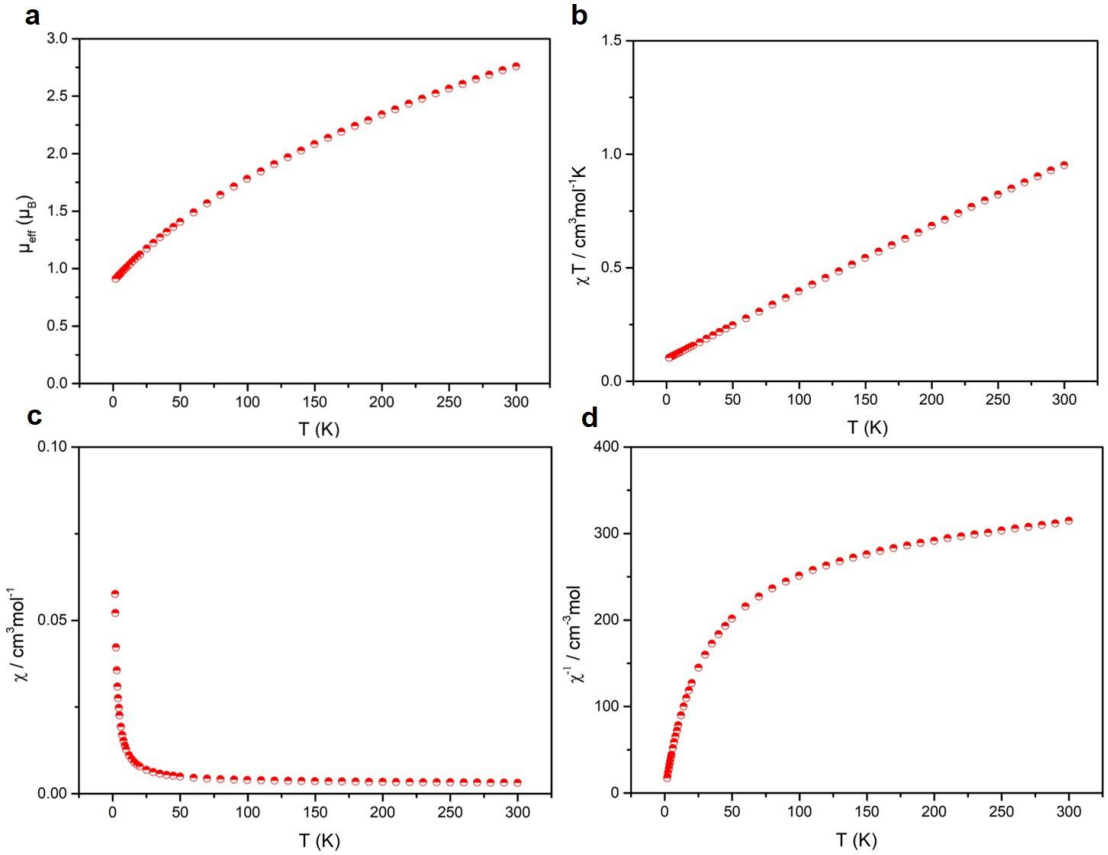


Fig. S20. Variable-temperature data of **4a**. (a) μ_{eff} vs T, (b)) χT vs T, (c) χ vs T, and (d) 1/χ vs T.

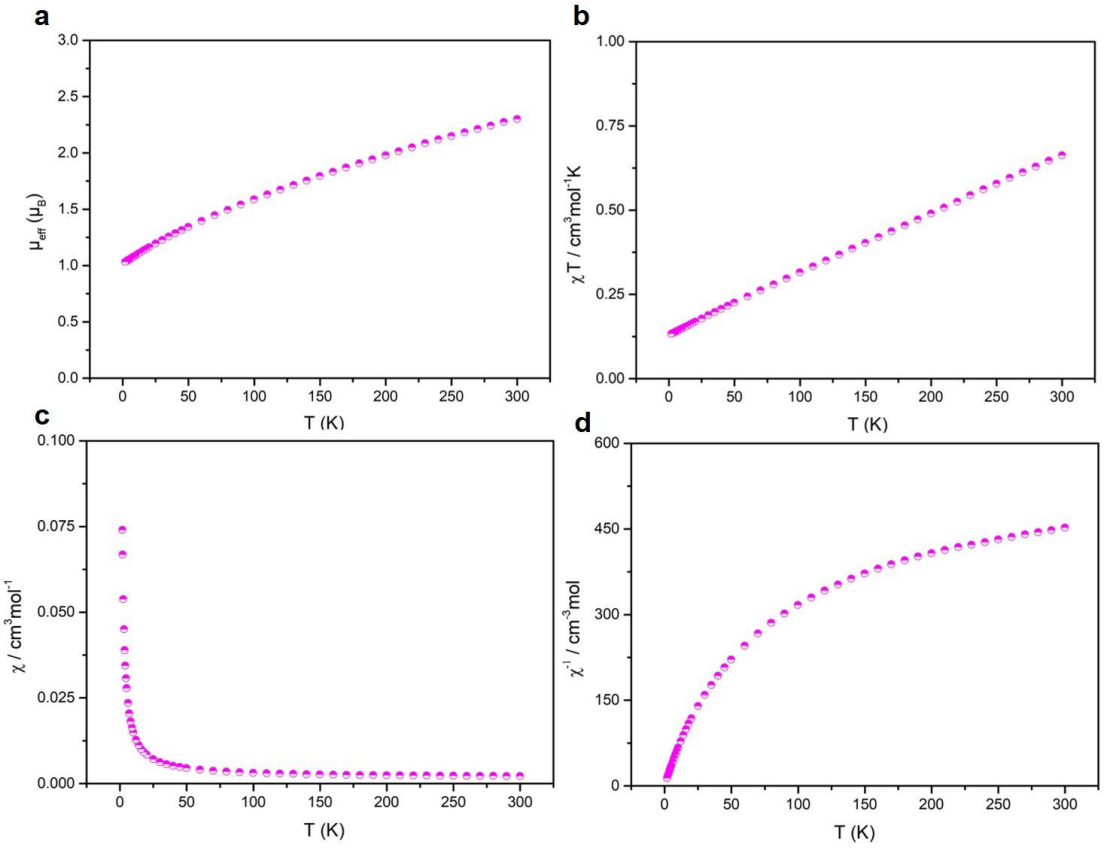


Fig. S21. Variable-temperature data of **4b**. (a) μ_{eff} vs T, (b)) χT vs T, (c) χ vs T, and (d) 1/χ vs T.

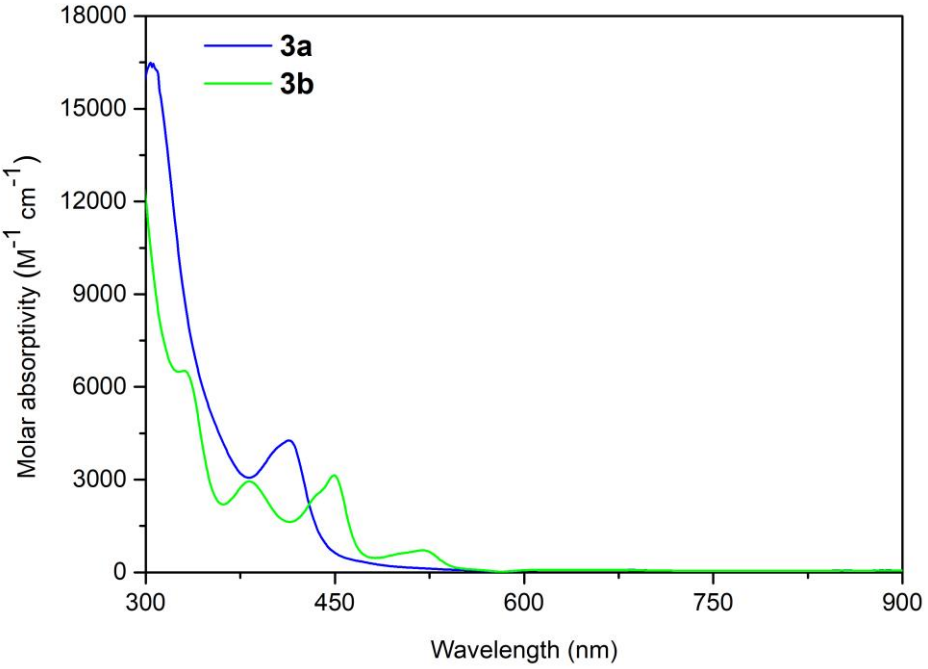


Fig. S22. UV−visible absorption spectra of complexes **3a** and **3b** measured in THF at RT.

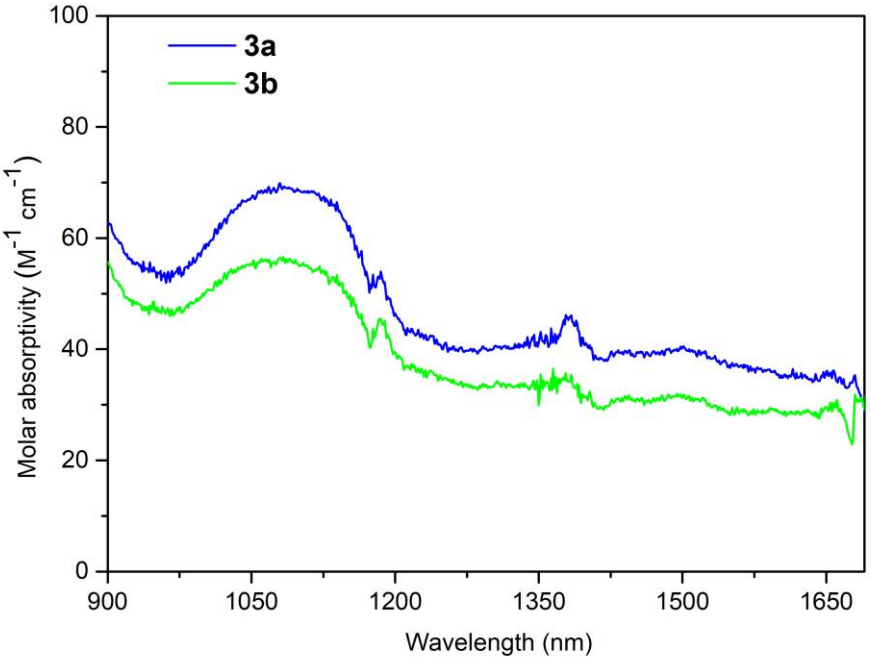


Fig. S23. Near-infrared absorption spectra of complexes **3a** and **3b** measured in THF at RT.

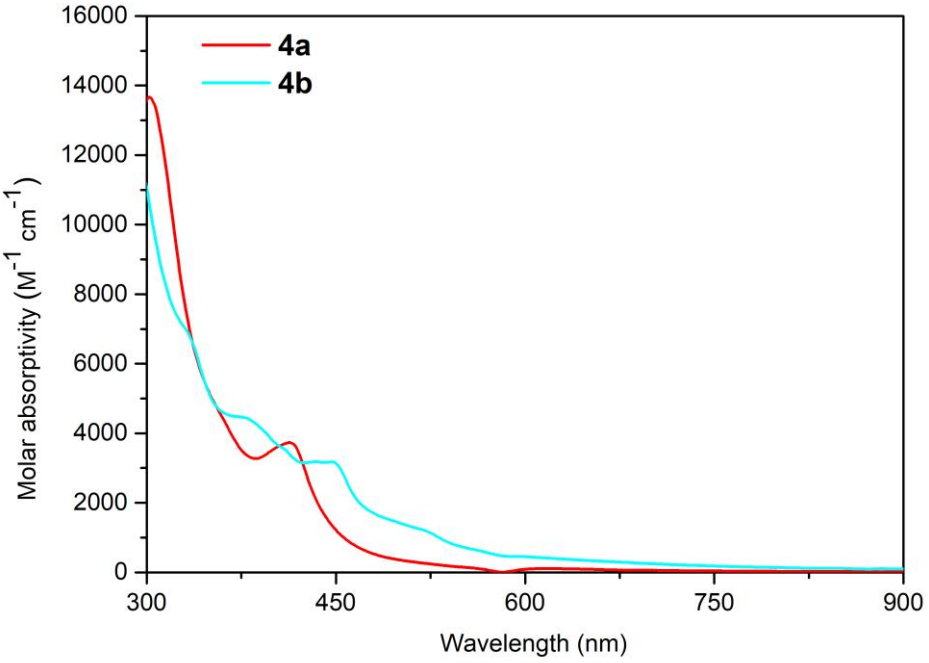


Fig. S24. UV−visible absorption spectra of complexes **4a** and **4b** measured in THF at RT.

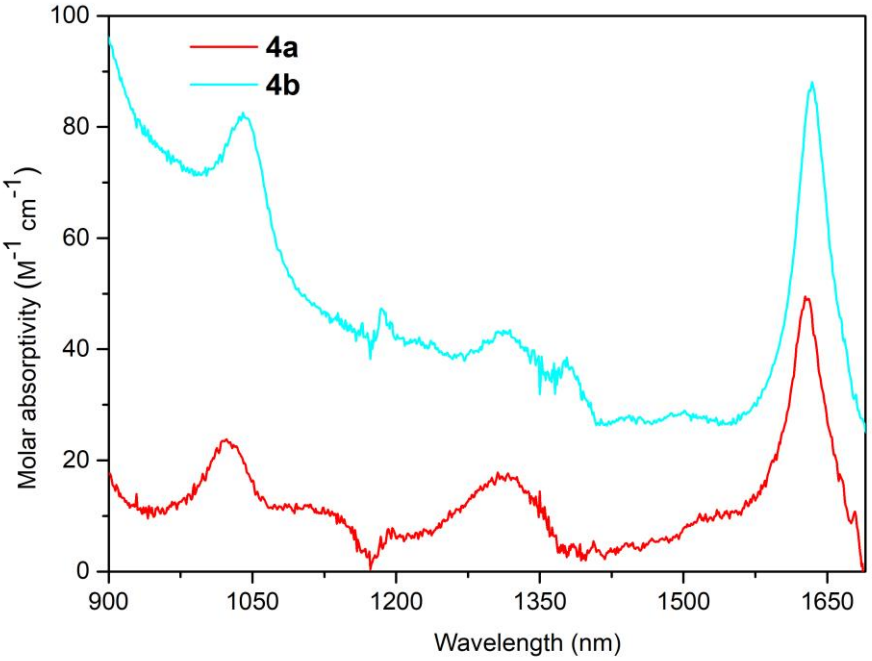


Fig. S25. Near-infrared absorption spectra of complexes **4a** and **4b** measured in THF at RT.

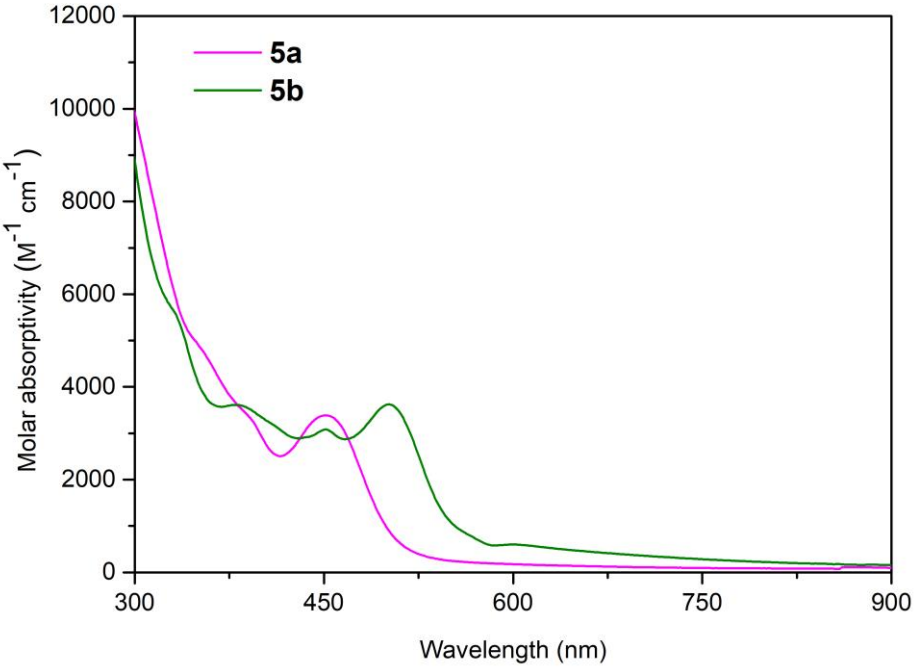


Fig. S26. UV−visible absorption spectra of complexes **5a** and **5b** measured in THF at RT.

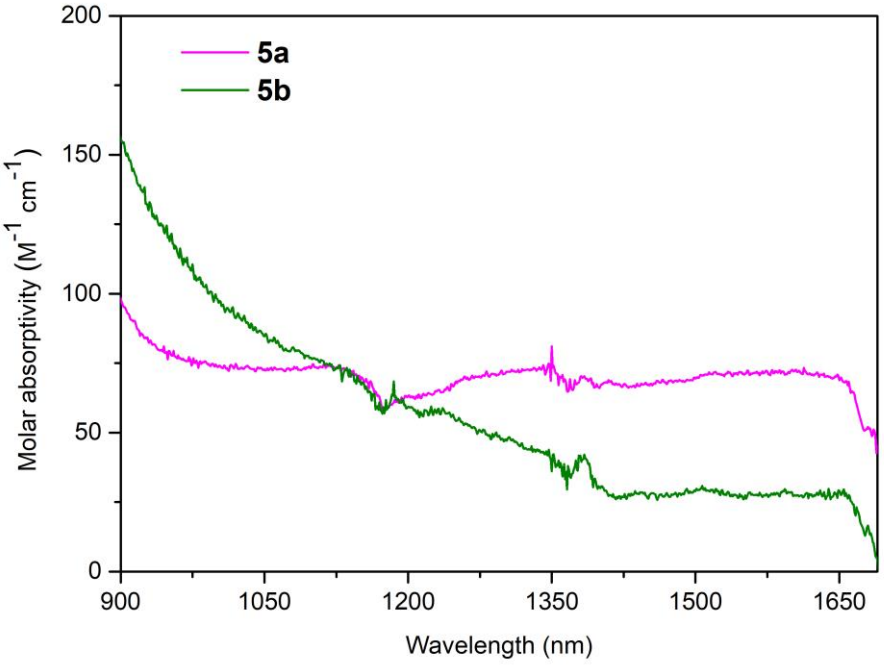


Fig. S27. Near-infrared absorption spectra of complexes **5a** and **5b** measured in THF at RT.

3. X-ray crystallographic analysis

The crystallographic data were collected using a Bruker APEX-II CCD area detector with a radiation source of Ga(Kα) (1.34139 Å) or Mo(Kα) (0.71073 Å). Multi-scan or empirical absorption corrections (SADABS) were applied. The structures were solved using Patterson methods, expanded using difference Fourier syntheses, and refined using full-matrix least squares fitting on F^2 using the Bruker SHELXTL-2014 program package.[3,4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms. In complexes **3a** and **3b**, the restraint (SIMU) was employed to refine the disordered N atoms. In complexes **4a** and **4b,** pseudo-isotropic (ISOR) and SIMU restraints were applied for the refinement of the disordered atoms. In complexes **5a** and **5b**, the restraint (SIMU) was used to refine the carbon atoms of cyclooctadiene groups. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data-request/cif). Details regarding the data collection and refinement for these complexes are given in Table S1.

Table S1. Crystal data and structural refinements for **2**-**5**.

	2		**3**	
	2a·toluene	**2b**·toluene	**3a**	**3b**
empirical formula	$C_{40}H_{71}Cl_4N_3P_2Rh_2U$	$C_{40}H_{71}Cl_4Ir_2N_3P_2U$	$C_{33}H_{63}N_{15}P_2Rh_2U$	$C_{33}H_{63}Ir_2N_{15}P_2U$
formula weight	1241.58	1420.16	1175.77	1354.35
temperature, K	193(2)	193(2)	173(2)	193(2)
wavelength, Å	0.71073	0.71073	0.71073	0.71073
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	P21/n	P21/n	P21/n	P21/n
a, Å	13.6450(3)	13.6338(10)	17.2026(6)	17.2027(6)
b, Å	23.4982(6)	23.4552(18)	14.8535(5)	14.9033(5)
c, Å	14.2779(4)	14.2487(10)	17.5846(5)	17.5252(5)
α, °	90	90	90	90
β, °	93.5780(10)	93.489(3)	107.3340(10)	107.3940(10)
γ, °	90	90	90	90

V, Å^3	4569.0(2)	4548.1(6)	4289.1(2)	4287.6(2)
Z	4	4	4	4
d_{calcd}, g cm^{-3}	1.805	2.074	1.821	2.098
μ, mm^{-1}	4.585	9.727	4.645	10.079
F(000)	2448.0	2704.0	2312.0	2568.0
crystal size, mm	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1	0.13 × 0.12 × 0.1	0.13 × 0.12 × 0.1
θ_{max},°	27.502	27.402	25.343	25.349
reflns collected	42158	41852	52012	32209
indep reflns	10479 [R_{int} = 0.0388, R_{sigma} = 0.0333]	10427 [R_{int} = 0.0550, R_{sigma} = 0.0508]	7834 [R_{int} = 0.0548, R_{sigma} = 0.0330]	7846 [R_{int} = 0.0813, R_{sigma} = 0.0675]
data/restraints/params	10479/0/479	10427/0/479	7834/96/487	7846/48/487
goodness-of-fit on F^2	1.044	1.037	1.039	1.043
final R ($I > 2\sigma(I)$)	R_1 = 0.0228, wR_2 = 0.0509	R_1 = 0.0315, wR_2 = 0.0537	R_1 = 0.0310, wR_2 = 0.0769	R_1 = 0.0404, wR_2 = 0.0947
R indices (all data)	R_1 = 0.0272, wR_2 = 0.0523	R_1 = 0.0473, wR_2 = 0.0583	R_1 = 0.0360, wR_2 = 0.0794	R_1 = 0.0513, wR_2 = 0.1014
Residual electron density (e. Å^{-3}) max/min	1.40/-0.90	1.25/-1.44	1.18/-1.09	1.99/-1.64
CCDC	2104709	2104710	2104711	2104712
	4		**5**	
	4a·1.5 toluene	**4b**·1.5 toluene	**5a**	**5b**
empirical formula	$C_{51.5}H_{87}N_{13}P_2Rh_3U$	$C_{51.5}H_{87}N_{13}P_2Ir_3U$	$C_{41}H_{75}N_8P_2Rh_3U$	$C_{41}H_{75}Ir_3N_8P_2U$
formula weight	1497.04	1764.91	1288.79	1556.66

temperature, K	193(2)	193(2)	193(2)	193(2)
wavelength, Å	0.71073	0.71073	1.34139	1.34139
crystal system	Triclinic	Triclinic	Orthorhombic	Orthorhombic
space group	P-1	P-1	Pnma	Pnma
a, Å	10.4530(4)	10.4461(3)	20.762(9)	20.757(7)
b, Å	15.7083(6)	15.7690(5)	19.974(9)	20.007(6)
c, Å	18.5359(8)	18.4599(7)	10.945(5)	10.946(4)
α, °	84.196(2)	84.4400(10)	90	90
β, °	74.207(2)	73.9370(10)	90	90
γ, °	78.8360(10)	78.7250(10)	90	90
V, Å^3	2869.5(2)	2862.73(16)	4539(4)	4546(3)
Z	2	2	4	4
d_{calcd}, g cm^{-3}	1.733	2.047	1.886	2.275
μ, mm^{-1}	3.763	9.873	13.980	19.108
F(000)	1488.0	1680.0	2536.0	2920.0
crystal size, mm	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1
θ_{max},°	27.508	27.520	54.185	53.878
reflns collected	26679	26915	41885	47269
indep reflns	12981 [R_{int} = 0.0382, R_{sigma} = 0.0542]	13033 [R_{int} = 0.0306, R_{sigma} = 0.0454]	4309 [R_{int} = 0.0867, R_{sigma} = 0.0389]	4265 [R_{int} = 0.0966, R_{sigma} = 0.0429]
data/restraints/params	12981/168/667	13033/168/666	4309/48/263	4265/48/263
goodness-of-fit on F^2	1.140	1.051	1.071	1.041
final *R* (*I* > 2σ(*I*))	R_1 = 0.0408, wR_2 = 0.1046	R_1 = 0.0270, wR_2 = 0.0601	R_1 = 0.0323, wR_2 = 0.0788	R_1 = 0.0336, wR_2 = 0.0839
R indices (all data)	R_1 = 0.0449, wR_2 = 0.1070	R_1 = 0.0329, wR_2 = 0.0625	R_1 = 0.0365, wR_2 = 0.0810	R_1 = 0.0385, wR_2 = 0.0865

Residual electron density (e. Å^{-3}) max/min	2.77/-0.97	1.37/-1.89	1.52/-1.46	1.56/-1.42
CCDC	2104713	2104714	2104715	2104716

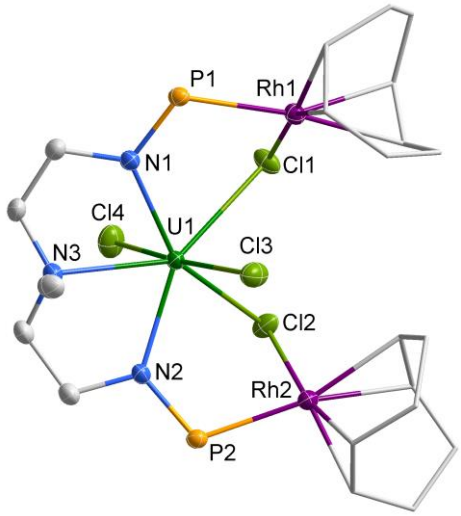


Fig. S28. X-ray molecular structure of complex **2a** drawn with 50% probability. Hydrogen atoms, solvents and isopropyl moieties in P^{i}Pr$_2$ are omitted for clarity.

Table S2. Selected bond distances (Å) and angles (˚) for **2a**.

U1-N1	2.349(2)	U1-N2	2.338(2)
U1-N3	2.567(2)	U1-Cl1	2.8325(7)
U1-Cl2	2.8150(8)	U1-Cl3	2.6452(8)
U1-Cl4	2.6483(8)	Rh1-P1	2.3301(8)
Rh1-Cl1	2.3779(8)	Rh2-P2	2.3293(8)
Rh2-Cl2	2.3652(8)		
Cl2-U1-Cl1	71.75(2)	N1-U1-Cl1	79.31(6)
Cl3-U1-Cl1	89.45(2)	N1-U1-Cl2	150.58(6)

Cl3-U1-Cl2	95.28(2)	N1-U1-Cl3	89.50(6)
Cl3-U1-Cl4	172.59(3)	N1-U1-Cl4	92.73(6)
Cl4-U1-Cl1	84.03(2)	N1-U1-N3	66.13(8)
Cl4-U1-Cl2	79.36(3)	N2-U1-Cl1	150.18(6)
N2-U1-Cl3	89.78(6)	N3-U1-Cl1	141.56(6)
N2-U1-Cl4	94.13(6)	N3-U1-Cl2	138.65(6)
N2-U1-N1	130.49(8)	N3-U1-Cl3	105.90(6)
N2-U1-N3	66.60(8)	N3-U1-Cl4	81.45(6)
Rh1-Cl1-U1	95.39(2)	P1-Rh1-Cl1	88.76(3)
Rh2-Cl2-U1	93.37(2)		

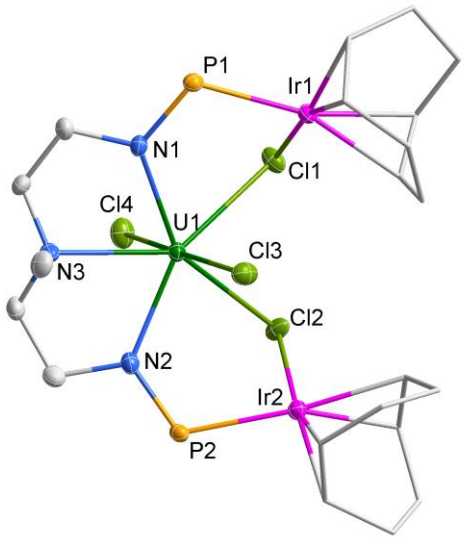


Fig. S29. X-ray molecular structure of complex **2b** drawn with 50% probability. Hydrogen atoms, solvents and isopropyl moieties in P^{i}Pr$_2$ are omitted for clarity.

Table S3. Selected bond distances (Å) and angles (˚) for **2b**.

U1-N1	2.330(4)	U1-N2	2.345(4)
U1-N3	2.556(4)	U1-Cl1	2.8492(14)
U1-Cl3	2.6358(13)	U1-Cl2	2.8612(14)

U1-Cl4	2.6439(14)	Ir2-Cl2	2.3634(13)
Ir1-Cl1	2.3557(14)	Ir2-P2	2.3319(14)
Ir1-P1	2.3335(14)		
Cl1-U1-Cl2	70.29(4)	N3-U1-Cl1	138.47(11)
Cl3-U1-Cl1	97.66(4)	N3-U1-Cl2	141.99(11)
Cl3-U1-Cl2	90.88(4)	N3-U1-Cl3	104.81(11)
Cl3-U1-Cl4	173.47(5)	N3-U1-Cl4	81.52(11)
Cl4-U1-Cl1	78.15(4)	N2-U1-Cl1	149.03(11)
Cl4-U1-Cl2	83.00(4)	N2-U1-Cl2	79.48(11)
N1-U1-Cl1	78.63(11)	N2-U1-Cl3	89.22(11)
N1-U1-Cl2	148.78(11)	N2-U1-Cl4	91.91(11)
N1-U1-Cl3	90.25(11)	N2-U1-N3	66.62(15)
N1-U1-Cl4	93.79(11)	Ir1-Cl1-U1	92.95(4)
N1-U1-N3	66.97(15)	Ir2-Cl2-U1	94.66(4)
N1-U1-N2	131.74(15)		

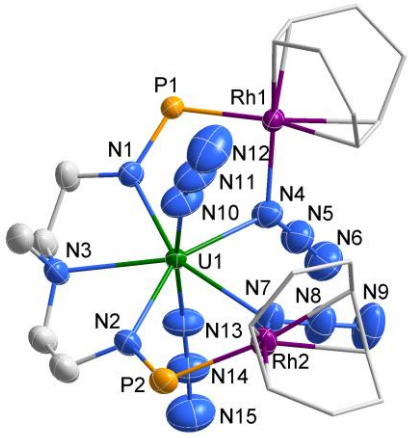


Fig. S30. X-ray molecular structure of complex **3a** drawn with 50% probability. Hydrogen atoms and isopropyl moieties in P^iPr_2 are omitted for clarity.

Table S4. Selected bond distances (Å) and angles (˚) for **3a**.

U1-N1	2.355(4)	U1-N2	2.360(4)
U1-N3	2.588(4)	U1-N4	2.453(5)
U1-N7	2.515(5)	U1-N10	2.307(5)
U1-N13	2.304(5)	N4-N5	1.197(7)
N5-N6	1.159(7)	N7-N8	1.228(7)
N8-N9	1.144(7)	N10-N11	1.140(7)
N11-N12	1.147(8)	N13-N14	1.179(7)
N14-N15	1.138(8)	Rh2-P2	2.3304(15)
Rh1-P1	2.3142(13)	Rh2-N7	2.103(5)
Rh1-N4	2.091(5)		
N10-U1-Rh1	70.39(17)	N10-U1-N7	87.0(2)
N10-U1-N4	98.8(2)	N10-U1-N2	90.7(2)
N10-U1-N3	106.2(2)	N10-U1-N1	92.64(19)
N7-U1-Rh1	91.59(13)	N7-U1-N3	140.80(16)
N4-U1-Rh1	33.59(11)	N4-U1-N7	75.20(16)
N4-U1-N3	135.70(16)	N13-U1-Rh1	107.90(14)
N13-U1-N10	172.0(2)	N13-U1-N7	85.2(2)
N13-U1-N4	77.39(18)	N13-U1-N2	89.46(18)
N13-U1-N3	81.17(19)	N13-U1-N1	93.39(18)
N2-U1-Rh1	158.61(11)	N2-U1-N7	77.15(16)
N2-U1-N4	150.19(16)	N2-U1-N3	66.20(15)
N3-U1-Rh1	127.56(10)	N1-U1-Rh1	62.43(10)
N1-U1-N7	152.25(16)	N1-U1-N4	77.45(16)
N1-U1-N2	130.59(16)	N1-U1-N3	65.58(14)
N7-Rh2-P2	85.19(16)	P1-Rh1-U1	67.66(3)

N4-Rh1-U1	40.45(13)	N4-Rh1-P1	86.62(14)
N2-P2-Rh2	113.64(16)	N1-P1-Rh1	110.42(16)
N11-N10-U1	168.6(6)	N10-N11-N12	178.7(10)
Rh2-N7-U1	113.8(2)	N8-N7-U1	125.2(4)
N8-N7-Rh2	118.1(5)	N9-N8-N7	178.9(7)
Rh1-N4-U1	105.97(19)	N5-N4-U1	128.7(4)
N5-N4-Rh1	124.4(4)	N6-N5-N4	175.8(7)
N14-N13-U1	160.5(5)	N15-N14-N13	177.2(9)
P2-N2-U1	122.6(2)	P1-N1-U1	119.3(2)

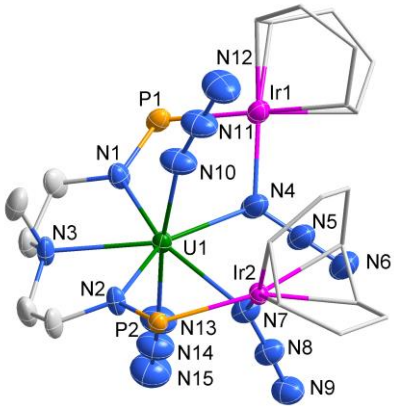


Fig. S31. X-ray molecular structure of complex **3b** drawn with 50% probability. Hydrogen atoms and isopropyl moieties in P^iPr_2 are omitted for clarity.

Table S5. Selected bond distances (Å) and angles (°) for **3b**.

U1-N1	2.369(7)	U1-N2	2.340(6)
U1-N3	2.569(6)	U1-N4	2.533(8)
U1-N7	2.475(7)	U1-N10	2.295(8)
U1-N13	2.311(8)	N4-N5	1.244(11)
N5-N6	1.137(11)	N7-N8	1.229(10)

N8-N9	1.117(10)	N10-N11	1.148(11)
N11-N12	1.157(12)	N13-N14	1.168(11)
N14-N15	1.126(12)	Ir1-N4	2.086(8)
Ir1-P1	2.336(2)	Ir2-N7	2.072(7)
Ir2-P2	2.321(2)		
N1-U1-Ir2	159.09(17)	N1-U1-N3	66.4(2)
N1-U1-N4	77.4(2)	N1-U1-N7	149.4(2)
N2-U1-Ir2	62.85(16)	N2-U1-N1	130.9(2)
N2-U1-N3	65.4(2)	N2-U1-N4	151.7(2)
N2-U1-N7	77.6(2)	N3-U1-Ir2	127.86(15)
N4-U1-Ir2	90.4(2)	N4-U1-N3	141.7(3)
N7-U1-Ir2	33.32(17)	N7-U1-N3	135.8(2)
N7-U1-N4	74.6(2)	N10-U1-Ir2	71.9(3)
N10-U1-N1	90.2(3)	N10-U1-N2	93.2(3)
N10-U1-N3	105.2(3)	N10-U1-N4	86.6(3)
N10-U1-N7	100.1(3)	N10-U1-N13	171.7(3)
N13-U1-Ir2	107.2(2)	N13-U1-N1	89.0(3)
N13-U1-N2	93.6(3)	N13-U1-N3	82.0(3)
N13-U1-N4	85.2(3)	N13-U1-N7	76.7(3)
N4-Ir1-P1	85.7(2)	P2-Ir2-U1	67.50(5)
N7-Ir2-U1	41.0(2)	N7-Ir2-P2	86.7(2)
N1-P1-Ir1	114.3(3)	N2-P2-Ir2	110.3(2)
P1-N1-U1	122.2(4)	P2-N2-U1	119.2(3)
Ir1-N4-U1	113.8(3)	N5-N4-U1	124.6(6)
N5-N4-Ir1	119.4(6)	N6-N5-N4	178.2(12)
Ir2-N7-U1	105.7(3)	N8-N7-U1	128.3(6)
N8-N7-Ir2	125.1(6)	N9-N8-N7	176.1(11)
N11-N10-U1	165.6(9)	N10-N11-N12	178.7(13)

N14-N13-U1	161.4(8)	N15-N14-N13	178.2(14)

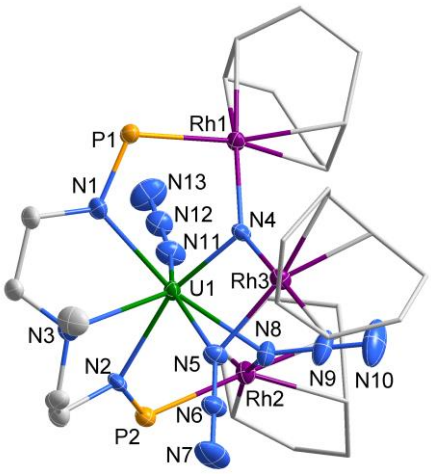


Fig. S32. X-ray molecular structure of complex **4a** drawn with 50% probability. Hydrogen atoms, solvents and isopropyl moieties in P^{i}Pr$_2$ are omitted for clarity.

Table S6. Selected bond distances (Å) and angles (˚) for **4a**.

U1-N1	2.334(5)	U1-N2	2.328(5)
U1-N3	2.740(5)	U1-N4	1.963(5)
U1-N5	2.431(5)	U1-N8	2.507(5)
U1-N11	2.373(5)	N5-N6	1.201(7)
N6-N7	1.147(8)	N8-N9	1.226(8)
N9-N10	1.133(9)	N11-N12	1.170(8)
N12-N13	1.150(8)	Rh1-N4	2.087(5)
Rh2-N8	2.095(5)	Rh3-N4	2.081(5)
Rh3-N5	2.099(6)	Rh1-P1	2.2976(16)
Rh2-P2	2.3515(17)		
Rh3-U1-Rh1	73.860(12)	N1-U1-N8	164.41(18)
N4-U1-Rh1	36.12(14)	N1-U1-N5	115.36(18)

N4-U1-Rh3	38.14(14)	N1-U1-N11	90.0(2)
N4-U1-N8	84.48(19)	N1-U1-N3	64.18(17)
N4-U1-N5	78.52(19)	N11-U1-Rh1	68.70(15)
N4-U1-N2	162.40(19)	N11-U1-Rh3	132.41(15)
N4-U1-N1	86.7(2)	N11-U1-N8	78.62(19)
N4-U1-N11	98.3(2)	N11-U1-N5	154.0(2)
N4-U1-N3	121.92(19)	N11-U1-N3	128.37(19)
N8-U1-Rh1	98.26(13)	N3-U1-Rh1	127.68(11)
N8-U1-Rh3	78.81(12)	N3-U1-Rh3	97.64(12)
N8-U1-N3	131.38(17)	N4-Rh1-U1	33.67(14)
N5-U1-Rh1	114.26(13)	N4-Rh3-U1	35.62(14)
N5-U1-Rh3	40.44(13)	N4-Rh3-N5	84.2(2)
N5-U1-N8	75.37(17)	N5-Rh3-U1	48.69(14)
N5-U1-N3	71.96(17)	U1-N4-Rh1	110.2(2)
N2-U1-Rh1	153.47(13)	U1-N4-Rh3	106.2(2)
N2-U1-Rh3	130.31(13)	Rh3-N4-Rh1	142.0(3)
N2-U1-N8	79.22(18)	Rh2-N8-U1	108.8(2)
N2-U1-N5	90.86(18)	N9-N8-U1	122.4(4)
N2-U1-N1	110.67(19)	N9-N8-Rh2	121.3(4)
N2-U1-N11	85.0(2)	Rh3-N5-U1	90.87(19)
N2-U1-N3	66.44(17)	N6-N5-U1	146.6(5)
N1-U1-Rh1	67.39(13)	N6-N5-Rh3	122.5(5)
N1-U1-Rh3	101.84(14)	N10-N9-N8	177.8(9)
N7-N6-N5	179.1(9)	N13-N12-N11	179.6(9)
N12-N11-U1	163.4(5)		

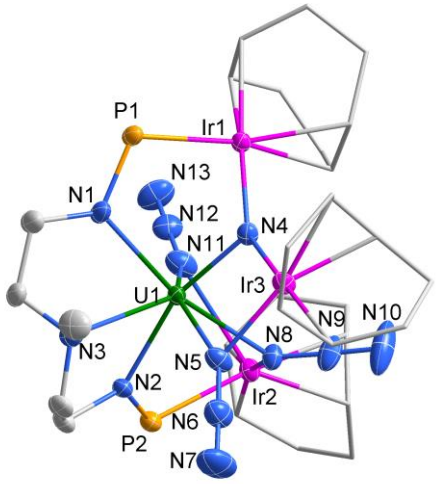


Fig. S33. X-ray molecular structure of complex **4b** drawn with 50% probability. Hydrogen atoms, solvents and isopropyl moieties in P^iPr_2 are omitted for clarity.

Table S7. Selected bond distances (Å) and angles (˚) for **4b**.

U1-N1	2.326(4)	Ir2-P2	2.3595(11)
U1-N2	2.313(4)	Ir3-N4	2.055(4)
U1-N3	2.726(3)	Ir3-N5	2.089(4)
U1-N4	2.011(4)	N5-N6	1.231(6)
U1-N5	2.384(4)	N6-N7	1.142(7)
U1-N8	2.498(4)	N8-N9	1.223(5)
U1-N11	2.386(4)	N9-N10	1.142(6)
Ir1-P1	2.3012(11)	N11-N12	1.205(6)
Ir1-N4	2.064(4)	N12-N13	1.142(6)
Ir2-N8	2.094(4)		
N1-U1-Ir1	67.08(9)	N5-U1-Ir1	114.44(10)
N1-U1-Ir3	102.34(10)	N5-U1-Ir3	40.88(10)
N1-U1-N8	162.91(13)	N5-U1-N8	76.07(14)
N1-U1-N11	93.70(16)	N5-U1-N11	149.57(16)

N1-U1-N5	116.26(14)	N5-U1-N3	71.96(13)
N1-U1-N3	64.61(13)	N8-U1-Ir1	97.49(9)
N2-U1-Ir1	153.72(9)	N8-U1-Ir3	79.03(9)
N2-U1-Ir3	130.18(9)	N8-U1-N3	132.38(13)
N2-U1-N8	79.40(13)	N11-U1-Ir1	70.92(11)
N2-U1-N11	83.29(14)	N11-U1-Ir3	131.11(10)
N2-U1-N5	90.34(14)	N11-U1-N8	73.51(15)
N2-U1-N3	66.63(12)	N11-U1-N3	130.47(13)
N2-U1-N1	110.92(13)	N7-N6-N5	178.2(6)
N3-U1-Ir1	127.56(9)	N10-N9-N8	177.8(6)
N3-U1-Ir3	97.84(9)	N13-N12-N11	176.8(6)
N4-U1-Ir1	35.31(11)	N4-Ir1-U1	34.28(10)
N4-U1-Ir3	38.77(10)	N4-Ir3-U1	37.80(10)
N4-U1-N1	86.75(15)	N4-Ir3-N5	86.04(15)
N4-U1-N2	162.22(15)	N5-Ir3-U1	48.32(11)
N4-U1-N3	122.61(13)	U1-N4-Ir1	110.41(16)
N4-U1-N5	79.58(14)	U1-N4-Ir3	103.42(17)
N4-U1-N8	83.95(14)	Ir3-N4-Ir1	144.1(2)
N4-U1-N11	97.97(14)	Ir2-N8-U1	106.32(15)
Ir3-U1-Ir1	73.603(6)	N9-N8-U1	124.3(3)
N9-N8-Ir2	122.0(3)	N12-N11-U1	152.3(4)
Ir3-N5-U1	90.80(15)	N6-N5-U1	147.0(3)
N6-N5-Ir3	122.0(3)		

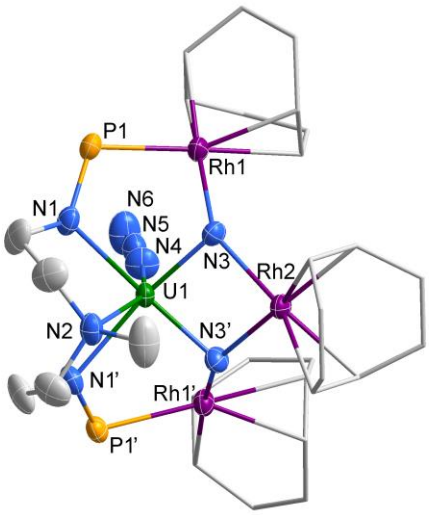


Fig. S34. X-ray molecular structure of complex **5a** drawn with 50% probability. Hydrogen atoms and isopropyl moieties in P^{i}Pr$_2$ are omitted for clarity.

Table S8. Selected bond distances (Å) and angles (˚) for **5a**.

U1-N1	2.298(5)	U1-N1’	2.298(5)
U1-N2	2.703(6)	U1-N3’	1.975(5)
U1-N3	1.975(5)	U1-N4	2.334(7)
Rh1-N3	2.082(4)	Rh1-P1	2.3257(16)
U1-P1	3.2239(18)	U1-P1’	3.2238(18)
Rh2-N3	2.067(4)	Rh2-N3’	2.067(4)
N4-N5	1.172(10)	N5-N6	1.181(10)
Rh1’-U1-Rh1	114.11(3)	Rh2-U1-Rh1’	79.492(15)
Rh2-U1-Rh1	79.492(15)	N1-U1-Rh1’	155.14(12)
N1’-U1-Rh1	155.14(12)	N1’-U1-Rh1’	71.05(12)
N1-U1-Rh1	71.06(12)	N1’-U1-Rh2	124.95(12)
N1-U1-Rh2	124.95(12)	N1-U1-N1’	94.5(2)
N1’-U1-N2	67.15(14)	N1-U1-N2	67.15(14)
N1-U1-N4	96.53(17)	N1’-U1-N4	96.53(17)

N2-U1-Rh1’	121.30(3)	N2-U1-Rh1	121.30(3)
N2-U1-Rh2	92.39(14)	N3’-U1-Rh1	111.19(13)
N3-U1-Rh1	39.18(12)	N3-U1-Rh1’	111.19(13)
N3’-U1-Rh1’	39.18(12)	N3-U1-Rh2	43.87(13)
N3’-U1-Rh2	43.87(13)	N3’-U1-N1	164.52(17)
N3’-U1-N1’	88.26(18)	N3-U1-N1’	164.52(17)
N3-U1-N1	88.26(18)	N3’-U1-N2	100.20(16)
N3-U1-N2	100.20(16)	N3’-U1-N3	85.2(3)
N3-U1-N4	98.30(19)	N3’-U1-N4	98.30(19)
N4-U1-Rh1	66.34(8)	N4-U1-Rh1’	66.34(8)
N4-U1-Rh2	112.85(19)	N4-U1-N2	154.8(2)
N3-Rh1-U1	36.82(12)	N3’-Rh2-U1	41.46(13)
N3-Rh2-U1	41.46(13)	N3’-Rh2-N3	80.6(3)
U1-N3-Rh1	104.00(19)	U1-N3-Rh2	94.68(19)
Rh2-N3-Rh1	144.3(2)	N5-N4-U1	173.4(7)
N4-N5-N6	178.5(9)		

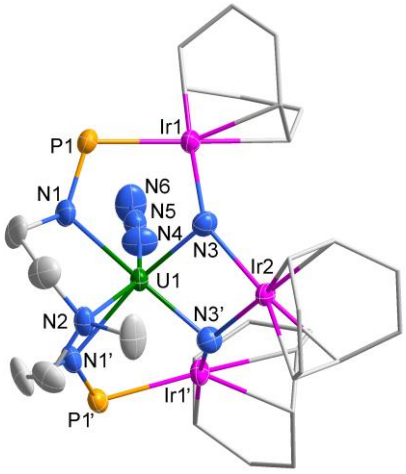


Fig. S35. X-ray molecular structure of complex **5b** drawn with 50% probability. Hydrogen atoms and isopropyl moieties in P^iPr_2 are omitted for clarity.

Table S9. Selected bond distances (Å) and angles (˚) for **5b**.

U1-N1	2.292(6)	U1-N1’	2.292(6)
U1-N2	2.720(7)	U1-N3’	2.005(6)
U1-N3	2.005(6)	U1-N4	2.329(8)
Ir1-P1	2.3278(18)	Ir1-N3	2.059(6)
Ir2-N3	2.047(6)	Ir2-N3’	2.047(6)
N4-N5	1.173(11)	N5-N6	1.170(12)
U1-P1	3.2156(19)	U1-P1’	3.2156(19)
Ir1'-U1-Ir1	113.66(3)	Ir2-U1-Ir1	79.160(13)
Ir2-U1-Ir1’	79.161(13)	N1-U1-Ir1’	155.94(16)
N1-U1-Ir1	71.36(14)	N1’-U1-Ir1’	71.36(14)
N1’-U1-Ir1	155.94(16)	N1-U1-Ir2	124.49(16)
N1’-U1-Ir2	124.49(15)	N1-U1-N1’	94.8(3)
N1-U1-N2	66.96(17)	N1’-U1-N2	66.96(17)
N1-U1-N4	96.6(2)	N1’-U1-N4	96.6(2)
N2-U1-Ir1	121.36(4)	N2-U1-Ir1’	121.36(4)
N2-U1-Ir2	92.15(17)	N3’-U1-Ir1	109.97(17)
N3-U1-Ir1’	109.97(17)	N3-U1-Ir1	39.01(16)
N3’-U1-Ir1’	39.01(16)	N3-U1-Ir2	43.36(17)
N3’-U1-Ir2	43.35(17)	N3-U1-N1	88.7(2)
N3-U1-N1’	164.2(2)	N3’-U1-N1	164.2(2)
N3’-U1-N1’	88.7(2)	N3’-U1-N2	100.6(2)
N3-U1-N2	100.6(2)	N3’-U1-N3	83.9(3)
N3-U1-N4	98.3(2)	N3’-U1-N4	98.3(2)
N4-U1-Ir1	66.62(11)	N4-U1-Ir1’	66.62(11)
N4-U1-Ir2	113.4(3)	N4-U1-N2	154.4(3)
N3-Ir2-U1	42.24(17)	N3-Ir1-U1	37.79(17)

N3'-Ir2-U1	42.24(17)	N3'-Ir2-N3	81.7(3)
U1-N3-Ir1	103.2(3)	U1-N3-Ir2	94.4(3)
Ir2-N3-Ir1	146.0(3)	N5-N4-U1	174.5(9)
N6-N5-N4	179.2(11)		

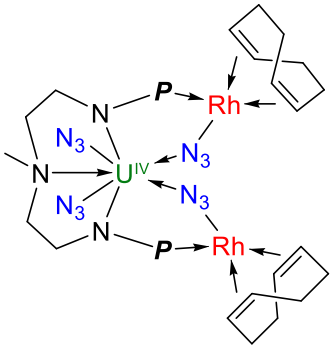
4. Theoretical Calculations

All calculations were performed using Gaussian09 suite of programs[5] using the Becke's 3-parameter hybrid functional[6] combined with the non-local correlation functional provided by Perdew/Wang.[7] The U, Ir, Rh, Cl and P atoms were represented with a small-core Stuttgart-Dresden relativistic effective core potential associated with their adapted basis set.[8-10] Additionally, the P and Cl basis set were augmented by a d-polarization function (α_P= 0.340 and α_C = 0.632)[11] to represent the valence orbitals. All the other atoms C, N and H were described with a 6-31G (d,p), double –ζ quality basis set.[12,13] The enthalpy energy was computed at T = 298 K in the gas phase.

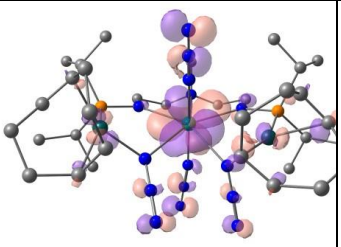
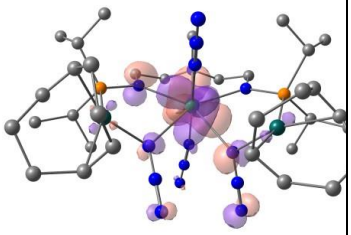
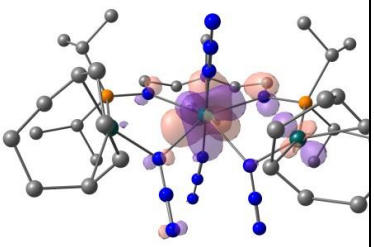
Table S10. Calculated NBO compositions of the U-N natural orbitals in the complexes **4** and **5**.

	WBI_{U-N}	N%	U%	U 6d:5f	N%	U%	U 6d:5f
		σ-component			π-component		
U1-N4							
4a	1.96	68.06	31.94	19.61:78.23	72.48	27.52	38.87:59.04
4b	1.83	72.25	27.75	32.70:59.24	74.55	25.45	33.05:57.37
U1-N3							
5a	1.91	71.28	28.72	28.69:68.04	72.40	27.60	38.54:58.34
5b	1.80	71.78	28.22	37.69:58.81	74.49	25.51	39.33:49.55
U1-N3'							
5a	1.92	86.57	13.43	44.50:33.28	72.35	27.65	38.80:58.46
5b	1.80	71.87	28.13	36.89:59.30	74.74	25.26	40.64:48.11

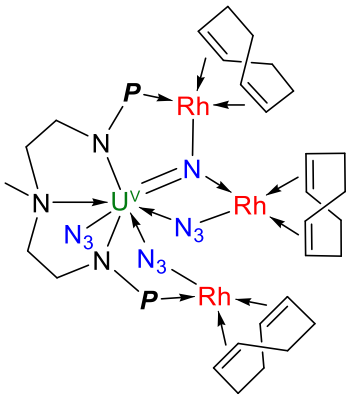
Complex Rh 3a:

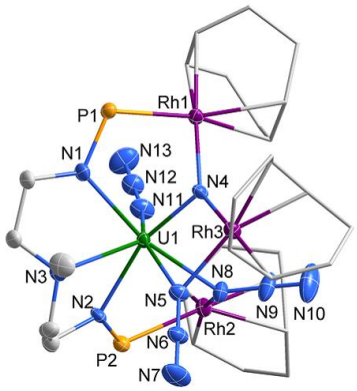


Spin density on U(IV) = 2.155959

LUMO	SOMO	SOMO-1
		
-1.488202404 eV	-4.90353032 eV	-4.929925572 eV

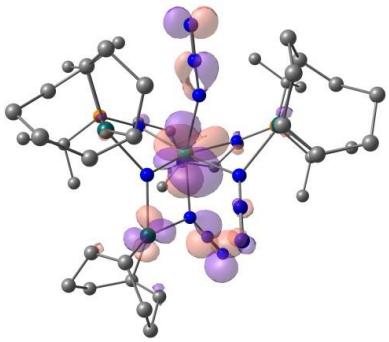
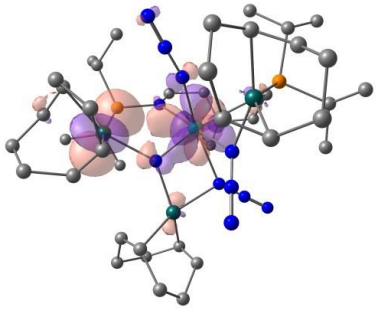
Complex Rh 4a:





Spin density on U(V) = 1.235121

Distances	EXP	computational	Wiberg Bond Index
U1-N4	1.963(5)	1.93200	1.9569
U1-N5	2.431(5)	2.42466	0.5673
U1-N8	2.507(5)	2.52730	0.7667
U1-N11	2.373(5)	2.33398	0.7126
Rh1-N4	2.087(5)	2.12066	0.4538
Rh3-N4	2.081(5)	2.12596	0.4497
Rh3-N5	2.099(6)	2.11456	0.3955
Rh2-N8	2.095(5)	2.12485	0.4187

LUMO	SOMO
	
-1.476501416 eV	-4.954416012 eV

1. BD (1) U 1 - N 4
(31.94%) 0.5652* U 1 s(0.98%)p 1.18(1.15%)d20.09(19.61%)f80.16(78.23%)
(68.06%) 0.8250* N 1 s(34.73%)p 1.87(65.11%)d 0.00(0.16%)

2. BD (2) U 1 - N 4
(27.52%) 0.5246* U 1 s(0.77%)p 1.69(1.30%)d50.52(38.87%)f76.74(59.04%)

(72.48%) 0.8514* N 1 s(7.40%)p12.50(92.46%)d 0.02(0.15%)

3. BD (1) U 1 - N 5

(21.55%) 0.4643* U 1 s(0.02%)p99.99(2.79%)d99.99(45.55%)f99.99(51.62%)

(78.45%) 0.8857* N 2 s(0.13%)p99.99(99.83%)d 0.33(0.04%)

4. BD (1) U 1 - N 8

(10.93%) 0.3306* U 1 s(11.09%)p 1.92(21.35%)d 3.57(39.57%)f 2.52(27.99%)

(89.07%) 0.9438* N 4 s(57.71%)p 0.73(42.24%)d 0.00(0.05%)

5. BD (1)Rh 3 - N 5

(25.98%) 0.5097*Rh 2 s(4.95%)p 0.46(2.28%)d18.74(92.77%)

(74.02%) 0.8603* N 2 s(7.29%)p12.71(92.65%)d 0.01(0.06%)

6. BD (1)Rh 2 - P 2

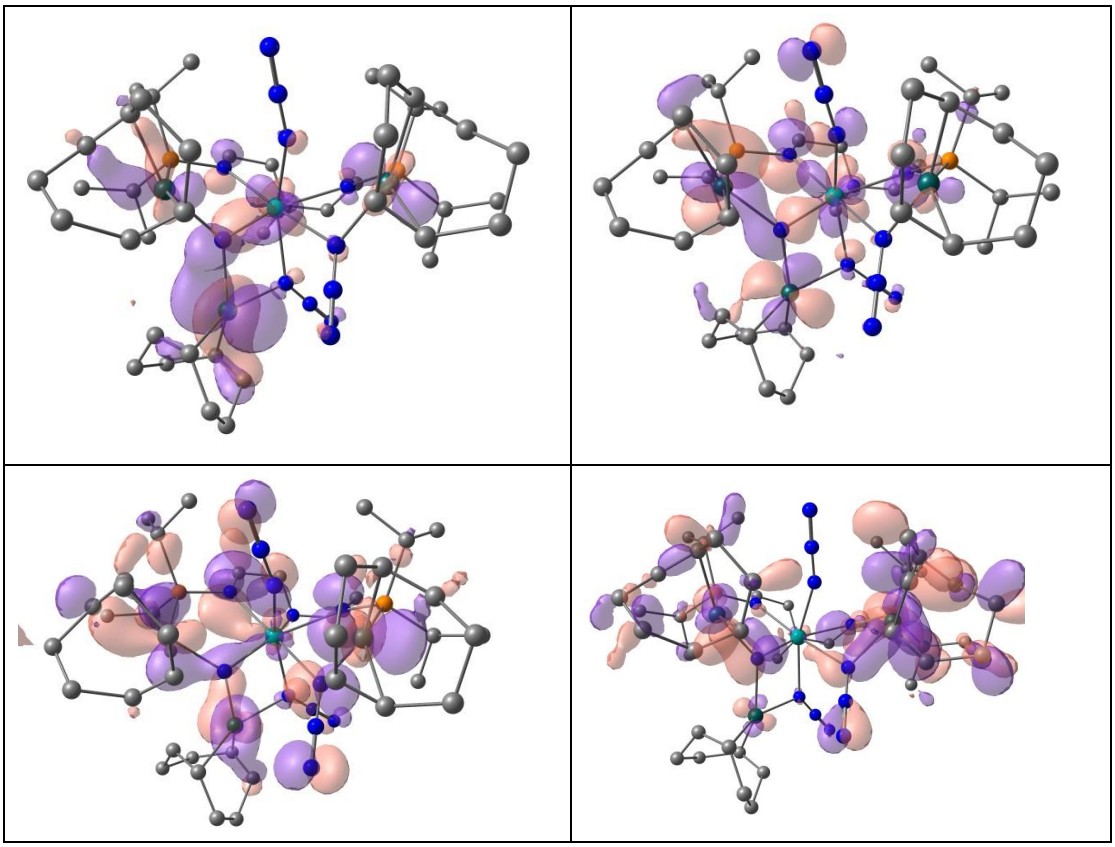
(36.04%) 0.6003*Rh 3 s(12.26%)p 1.19(14.58%)d 5.97(73.17%)

(63.96%) 0.7998* P 2 s(35.24%)p 1.83(64.66%)d 0.00(0.10%)

7. BD (1)Rh 1 - P 1

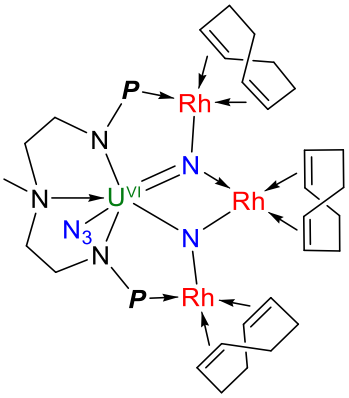
(39.94%) 0.6320*Rh 1 s(10.68%)p 0.89(9.48%)d 7.47(79.84%)

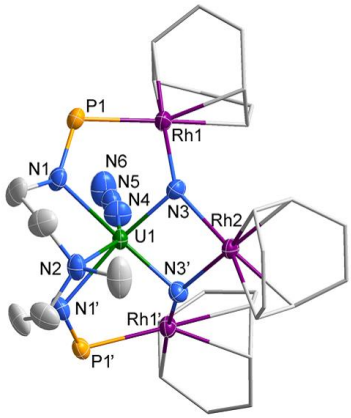
(60.06%) 0.7750* P 1 s(34.93%)p 1.86(64.94%)d 0.00(0.12%)



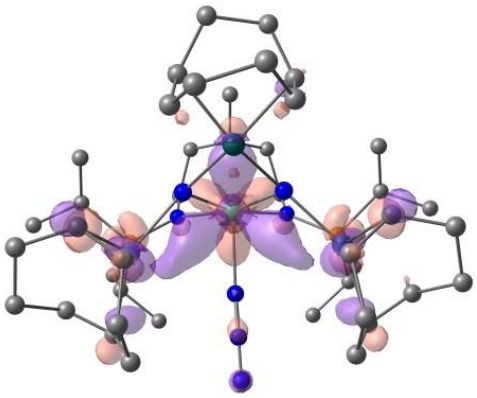
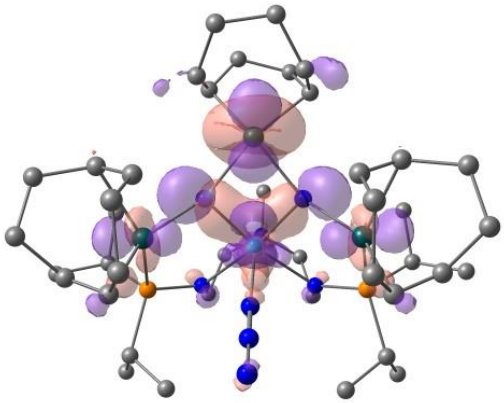
Bonding U-N-Rh Molecular orbitals of complex **4a**.

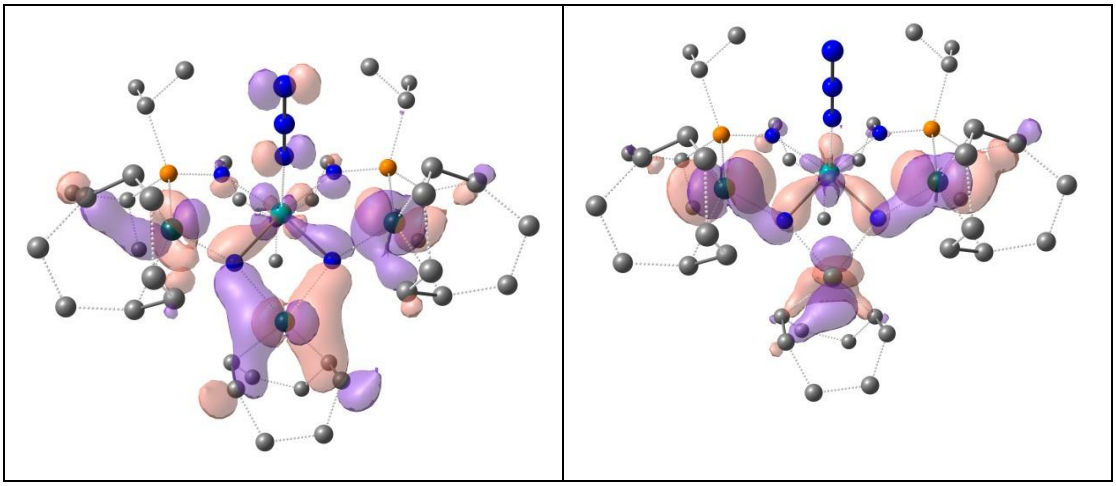
Complex Rh 5a:





Distances	EXP	computational	Wiberg Bond Index
U1-N3	1.975(5)	1.94775	1.9128
U1-N3’	1.975(5)	1.95004	1.9208
U1-N4	2.334(7)	2.30051	0.7622
Rh1-N3	2.082(4)	2.08718	0.5116
Rh2-N3	2.067(4)	2.09437	0.4873
Rh2-N3’	2.067(4)	2.09940	0.4898
Rh1’-N3’	2.082(4)	2.10116	0.5076

LUMO	HOMO
	
-1.34425304 eV	-4.429504248 eV



Bonding U-N-Rh Molecular orbitals of complex **5a**.

1. BD (1) U 1 - N 3
(28.72%) 0.5359* U 1 s(1.23%)p 1.62(2.00%)d23.28(28.69%)f55.21(68.04%)
(71.28%) 0.8443* N 1 s(36.52%)p 1.73(63.36%)d 0.00(0.11%)
2. BD (2) U 1 - N 3
(27.60%) 0.5253* U 1 s(0.30%)p 9.24(2.80%)d99.99(38.54%)f99.99(58.34%)
(72.40%) 0.8509* N 1 s(1.75%)p56.24(98.16%)d 0.06(0.10%)
3. BD (1) U 1 - N 4
(14.91%) 0.3862* U 1 s(5.25%)p 1.86(9.75%)d 5.47(28.70%)f10.72(56.25%)
(85.09%) 0.9224* N 2 s(27.81%)p 2.59(72.13%)d 0.00(0.05%)
4. BD (1) U 1 - N 3'
(13.43%) 0.3665* U 1 s(6.69%)p 2.32(15.52%)d 6.65(44.50%)f 4.97(33.28%)
(86.57%) 0.9304* N 3 s(33.89%)p 1.95(66.07%)d 0.00(0.04%)
6. BD (2) U 1 - N 3'
(27.65%) 0.5259* U 1 s(0.18%)p14.50(2.55%)d99.99(38.80%)f99.99(58.46%)
(72.35%) 0.8506* N 7 s(0.98%)p99.99(98.92%)d 0.10(0.10%)
9. BD (1)Rh 1 - P 1
(37.75%) 0.6144*Rh 1 s(10.52%)p 1.28(13.44%)d 7.23(76.04%)

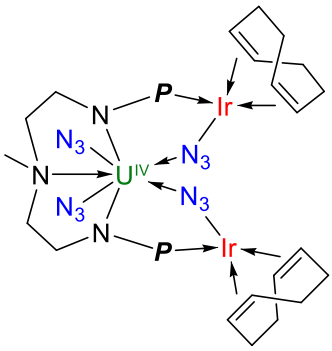
(62.25%) 0.7890* P 1 s(36.77%)p 1.72(63.14%)d 0.00(0.10%)

10.BD (1)Rh 1' - P 1'

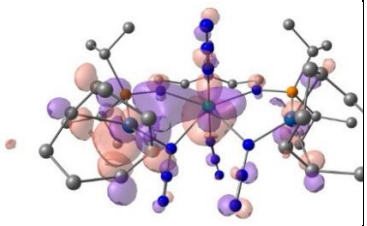
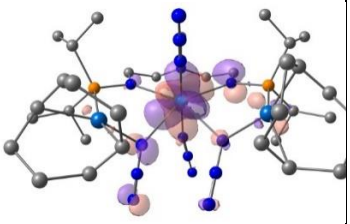
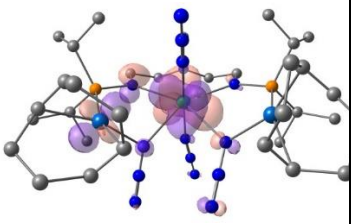
(38.02%) 0.6166*Rh 3 s(10.76%)p 1.18(12.71%)d 7.11(76.53%)

(61.98%) 0.7873* P 2 s(36.62%)p 1.73(63.28%)d 0.00(0.10%)

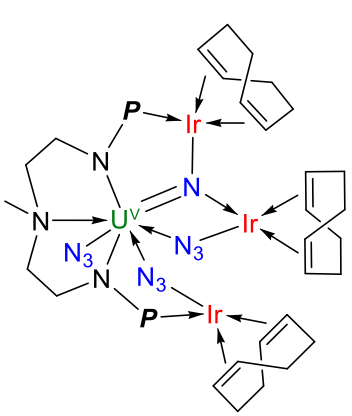
Complex Ir 3b:

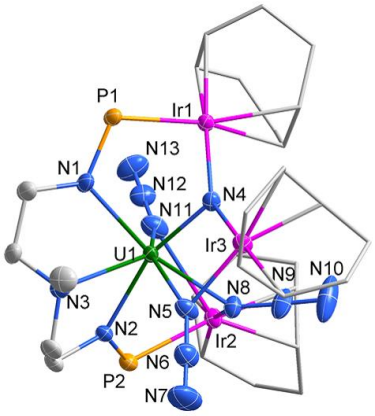


Spin density on U(IV) = 2.157306

LUMO	SOMO	SOMO-1
		
-1.603851704 eV	-4.988430512 eV	-5.010199792 eV

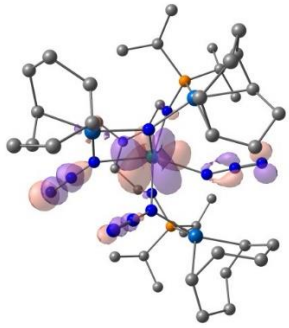
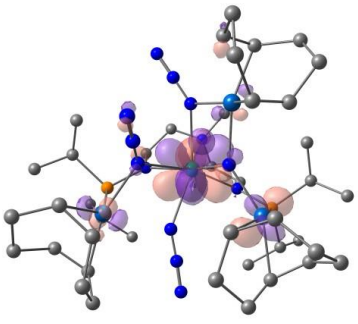
Complex Ir 4b:





Spin density on U(V) = 1.241344

Distances	EXP	computational	Wiberg Bond Index
U1-N4	2.011(4)	1.95753	1.8346
U1-N5	2.384(4)	2.41684	0.5639
U1-N8	2.498(4)	2.50375	0.4828
U1-N11	2.386(4)	2.37141	0.6438
Ir1-N4	2.064(4)	2.10941	0.4878
Ir3-N4	2.055(4)	2.11079	0.4970
Ir3-N5	2.089(4)	2.11702	0.4310
Ir2-N8	2.094(4)	2.13794	0.4662

LUMO	SOMO
	
-1.717324076 eV	-5.183265568 eV

4. BD (1) U 1 - N 5

(10.97%) 0.3312* U 1 s(13.90%)p 1.32(18.35%)d 2.45(34.02%)f 2.43(33.72%)

(89.03%) 0.9436* N 2 s(39.80%)p 1.51(60.17%)d 0.00(0.03%)

5. BD (1) U 1 - N 4

(12.76%) 0.3572* U 1 s(12.17%)p 1.51(18.31%)d 3.13(38.13%)f 2.58(31.37%)

(87.24%) 0.9340* N 4 s(70.19%)p 0.42(29.80%)d 0.00(0.00%)

8. BD (1) U 1 - N 8

(11.03%) 0.3321* U 1 s(14.85%)p 1.40(20.72%)d 2.19(32.56%)f 2.15(31.85%)

(88.97%) 0.9432* N 3 s(40.51%)p 1.47(59.46%)d 0.00(0.03%)

9. BD (1) U 1 - N 4

(27.75%) 0.5268* U 1 s(7.50%)p 0.06(0.49%)d 4.36(32.70%)f 7.90(59.24%)

(72.25%) 0.8500* N 1 s(32.86%)p 2.04(67.01%)d 0.00(0.13%)

10.BD (2) U 1 - N 4

(25.45%) 0.5045* U 1 s(0.72%)p12.33(8.83%)d46.13(33.05%)f80.08(57.37%)

(74.55%) 0.8634* N 1 s(3.80%)p25.27(96.07%)d 0.03(0.13%)

11.BD (1)Ir 3 - N 5

(23.49%) 0.4846*Ir 2 s(15.03%)p 1.08(16.22%)d 4.57(68.75%)

(76.51%) 0.8747* N 2 s(33.25%)p 2.01(66.71%)d 0.00(0.03%)

12.BD (1)Ir 3 - C 1

(68.83%) 0.8297*Ir 2 s(1.46%)p 0.82(1.20%)d66.60(97.34%)

(31.17%) 0.5583* C 1 s(10.82%)p 8.24(89.13%)d 0.00(0.05%)

13.BD (1)Ir 3 - C 2

(71.86%) 0.8477*Ir 2 s(0.09%)p47.31(4.39%)d99.99(95.52%)

(28.14%) 0.5304* C 2 s(10.79%)p 8.26(89.15%)d 0.01(0.06%)

14.BD (1)Ir 2 - P 2

(35.38%) 0.5948*Ir 3 s(30.96%)p 0.71(21.95%)d 1.52(47.09%)

(64.62%) 0.8038* P 2 s(35.82%)p 1.79(64.02%)d 0.00(0.16%)

15.BD (1)Ir 2 - N 8

(23.90%) 0.4889*Ir 3 s(22.59%)p 0.78(17.58%)d 2.65(59.84%)

(76.10%) 0.8724* N 3 s(34.12%)p 1.93(65.84%)d 0.00(0.04%)

16.BD (1)Ir 2 - C 3

(72.07%) 0.8489*Ir 3 s(2.23%)p 1.04(2.33%)d42.77(95.44%)

(27.93%) 0.5285* C 3 s(11.53%)p 7.67(88.41%)d 0.01(0.06%)

17.BD (1)Ir 2 - C 4

(65.47%) 0.8092*Ir 3 s(12.24%)p 0.28(3.48%)d 6.88(84.28%)

(34.53%) 0.5876* C 4 s(11.78%)p 7.48(88.14%)d 0.01(0.07%)

18.BD (1)Ir 1 - P 1

(34.29%) 0.5856*Ir 1 s(42.58%)p 0.35(14.80%)d 1.00(42.62%)

(65.71%) 0.8106* P 1 s(34.39%)p 1.90(65.43%)d 0.01(0.18%)

19.BD (1)Ir 1 - N 4

(24.63%) 0.4962*Ir 1 s(31.49%)p 0.37(11.65%)d 1.81(56.86%)

(75.37%) 0.8682* N 1 s(41.80%)p 1.39(58.17%)d 0.00(0.03%)

20.BD (1)Ir 1 - C 5

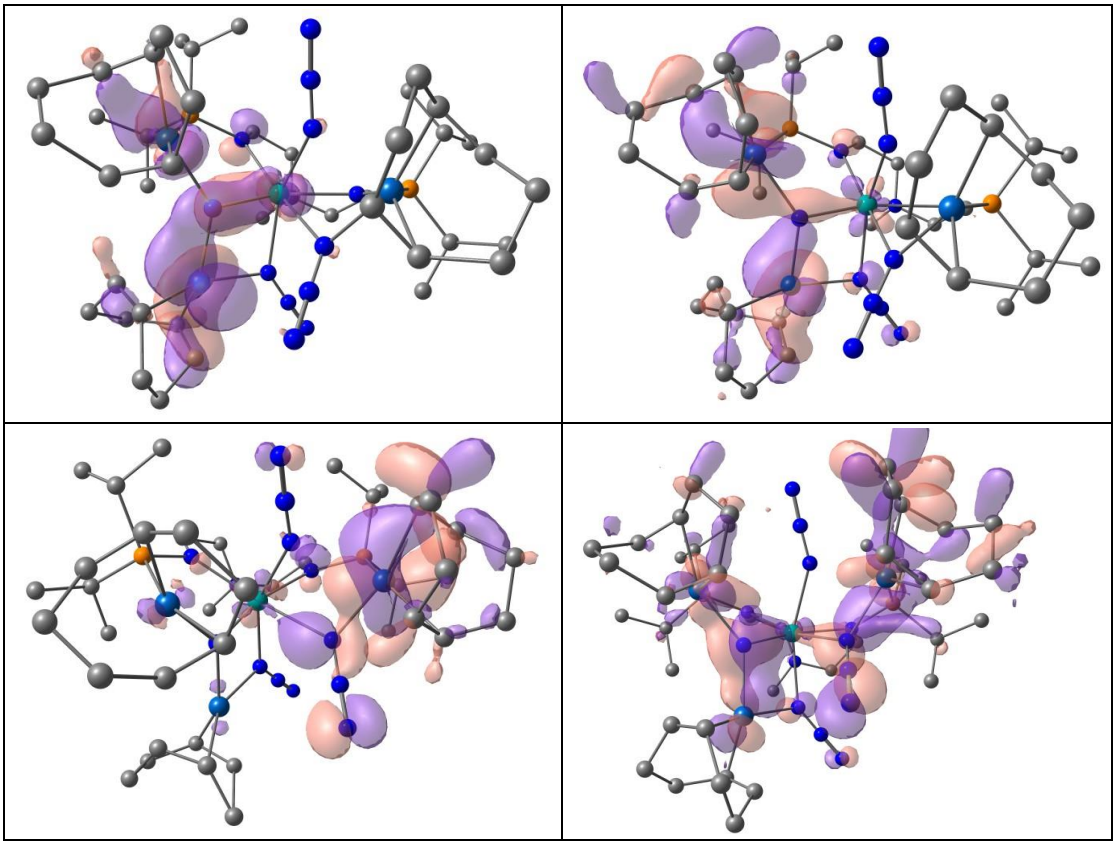
(70.57%) 0.8400*Ir 1 s(0.26%)p 6.16(1.60%)d99.99(98.14%)

(29.43%) 0.5425* C 5 s(11.28%)p 7.86(88.67%)d 0.00(0.05%)

21.BD (1)Ir 1 - C 6

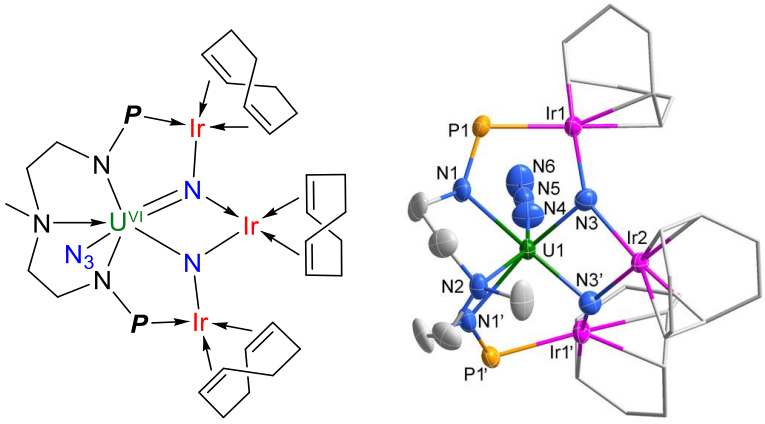
(78.07%) 0.8836*Ir 1 s(1.45%)p 0.18(0.26%)d67.62(98.29%)

(21.93%) 0.4683* C 6 s(8.08%)p11.37(91.87%)d 0.01(0.05%)

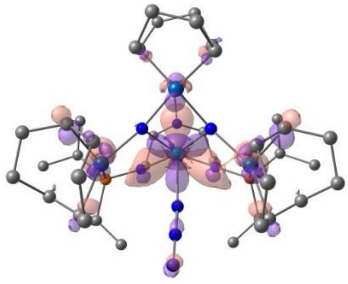
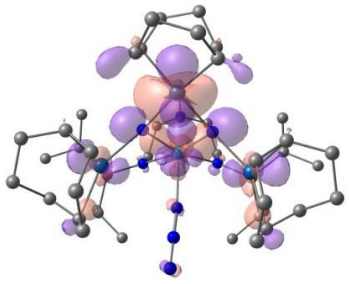


Bonding U-N-Ir Molecular orbitals of complex **4b**.

Complex Ir 5b:



Distances	EXP	computational	Wiberg Bond Index
U1-N3	2.005(6)	1.97696	1.8000
U1-N3’	2.005(6)	1.97514	1.8006
U1-N4	2.329(8)	2.28623	0.7938
Ir1-N3	2.059(6)	2.08279	0.5596
Ir2-N3	2.047(6)	2.08505	0.5289
Ir2-N3’	2.047(6)	2.08578	0.5255
Ir1’-N3’	2.059(6)	2.07683	0.5595

LUMO	HOMO
	
-1.631879652 eV	-4.444198512 eV

4. BD (1) U 1 - N 3

(28.22%) 0.5312* U 1 s(3.12%)p 0.10(0.32%)d12.09(37.69%)f18.86(58.81%)

(71.78%) 0.8472* N 1 s(30.79%)p 2.24(69.11%)d 0.00(0.10%)

5. BD (2) U 1 - N 3

(25.51%) 0.5051* U 1 s(0.17%)p65.49(10.91%)d99.99(39.33%)f99.99(49.55%)

(74.49%) 0.8631* N 1 s(0.20%)p99.99(99.71%)d 0.44(0.09%)

6. BD (1) U 1 - N 4

(14.59%) 0.3819* U 1 s(6.74%)p 2.74(18.47%)d 6.82(45.96%)f 4.27(28.80%)

(85.41%) 0.9242* N 3 s(70.49%)p 0.42(29.51%)d 0.00(0.00%)

9. BD (1) U 1 - N 3'

(28.13%) 0.5304* U 1 s(3.26%)p 0.15(0.49%)d11.30(36.89%)f18.16(59.30%)

(71.87%) 0.8478* N 2 s(31.76%)p 2.15(68.14%)d 0.00(0.10%)

10.BD (2) U 1 - N 3'

(25.26%) 0.5026* U 1 s(0.10%)p99.99(11.12%)d99.99(40.64%)f99.99(48.11%)

(74.74%) 0.8645* N 2 s(0.22%)p99.99(99.69%)d 0.39(0.09%)

11.BD (1)Ir 1 - P 1

(38.29%) 0.6188*Ir 1 s(33.12%)p 0.44(14.48%)d 1.58(52.40%)

(61.71%) 0.7855* P 1 s(36.52%)p 1.73(63.27%)d 0.01(0.21%)

12.BD (1)Ir 1 - N 3

(28.18%) 0.5308*Ir 1 s(25.03%)p 0.44(11.12%)d 2.55(63.85%)

(71.82%) 0.8475* N 1 s(35.46%)p 1.82(64.50%)d 0.00(0.04%)

13.BD (1)Ir 1 - C 1

(67.40%) 0.8210*Ir 1 s(17.42%)p 0.18(3.15%)d 4.56(79.43%)

(32.60%) 0.5709* C 1 s(9.89%)p 9.10(90.03%)d 0.01(0.08%)

14.BD (1)Ir 1 - C 2

(70.79%) 0.8414*Ir 1 s(1.45%)p 0.65(0.95%)d67.12(97.60%)

(29.21%) 0.5405* C 2 s(10.99%)p 8.09(88.94%)d 0.01(0.07%)

15.BD (1)Ir 2 - N 3

(26.01%) 0.5100*Ir 2 s(31.53%)p 0.43(13.52%)d 1.74(54.96%)

(73.99%) 0.8602* N 1 s(33.49%)p 1.98(66.47%)d 0.00(0.05%)

16.BD (1)Ir 2 - N 3'

(24.80%) 0.4979*Ir 2 s(34.21%)p 0.46(15.68%)d 1.46(50.11%)

(75.20%) 0.8672* N 2 s(32.78%)p 2.05(67.17%)d 0.00(0.05%)

17.BD (1)Ir 2 - C 3

(71.60%) 0.8462*Ir 2 s(0.37%)p 4.25(1.57%)d99.99(98.06%)

(28.40%) 0.5329* C 3 s(10.83%)p 8.23(89.12%)d 0.00(0.05%)

18.BD (1)Ir 2 - C 45

(70.48%) 0.8395*Ir 2 s(3.81%)p 0.30(1.16%)d24.95(95.03%)

(29.52%) 0.5433* C 4 s(10.68%)p 8.36(89.26%)d 0.01(0.06%)

19.BD (1)Ir 1' - P 2

(38.26%) 0.6186*Ir 3 s(33.92%)p 0.40(13.73%)d 1.54(52.34%)

(61.74%) 0.7857* P 6 s(36.30%)p 1.75(63.49%)d 0.01(0.21%)

20.BD (1)Ir 1' - N 4

(28.11%) 0.5302*Ir 3 s(25.82%)p 0.41(10.63%)d 2.46(63.55%)

(71.89%) 0.8479* N 2 s(35.18%)p 1.84(64.78%)d 0.00(0.04%)

21.BD (1)Ir 1' - C 48

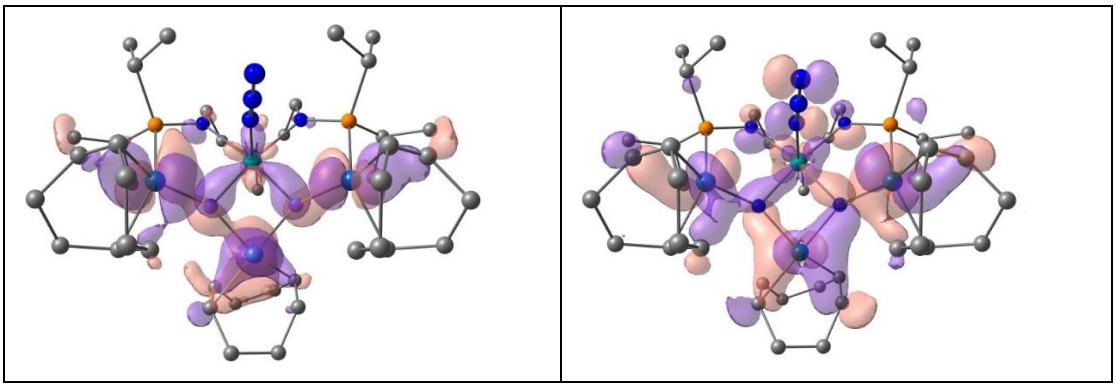
(68.53%) 0.8278*Ir 3 s(16.88%)p 0.16(2.75%)d 4.76(80.37%)

(31.47%) 0.5610* C 5 s(9.63%)p 9.38(90.30%)d 0.01(0.08%)

22.BD (1)Ir 1' - C 52

(70.56%) 0.8400*Ir 3 s(1.59%)p 0.61(0.96%)d61.44(97.45%)

(29.44%) 0.5426* C 6 s(11.00%)p 8.09(88.93%)d 0.01(0.07%)



Bonding U-N-Ir Molecular orbitals of complex **5b**.

Cartesian coordinates of all optimized structures

116
Complex 3a
U 10.314443 9.864864 9.703125
Rh 11.408005 12.004927 6.587664
Rh 6.607920 10.557996 9.821893
P 13.171387 11.219235 7.981856
P 7.482385 9.732243 11.877464
N 9.270109 14.384659 9.971273
N 11.033857 5.506463 8.387655
N 7.255592 7.297455 7.865813
N 8.964175 9.140371 5.676588
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N 7.618388 8.260297 8.370502
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N 10.633315 7.667519 9.235939
N 11.880234 9.269187 11.734198
N 9.868280 12.108344 9.950479
N 8.025171 9.277773 8.907252
N 9.154297 9.388627 11.737001
N 12.632185 10.298662 9.322645
N 10.413552 10.236694 7.193432
C 6.229225 13.085212 8.178450
C 11.395725 12.603828 3.611676
C 3.912146 10.975557 8.320628
C 9.617023 14.337004 5.539555
C 12.294641 13.718929 4.167706
C 10.616449 14.908131 6.561193
C 15.814996 12.180029 8.866482
C 11.162070 8.248325 12.507972
C 5.429295 13.391798 9.456879
C 13.567250 8.767277 6.644175
C 3.615368 10.837888 9.824661
C 14.840461 10.733358 5.710448
C 13.692452 9.711694 10.140147
C 13.103087 8.721615 11.133532
C 9.644044 12.822146 5.503340
C 13.748874 13.272226 9.830186
C 12.165193 10.456920 12.546764
C 14.298251 10.067786 6.975333
C 7.021564 6.977058 11.449892
C 8.202353 12.039627 13.319532

C 5.144650 8.225738 12.575504
C 11.869268 14.074389 6.700136
C 12.615848 13.515322 5.642240
C 7.179391 10.237293 14.762668
C 4.783728 11.217364 10.708119
C 14.357715 12.576892 8.608945
C 10.422889 12.063431 4.633272
C 5.622776 12.333776 10.532939
C 5.357421 10.657686 7.990024
C 9.781085 8.754589 12.893464
C 6.368580 11.607893 7.903616
C 7.203299 10.881975 13.373086
C 6.659838 8.106173 12.413736
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H 3.667159 11.983226 7.970498
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H 9.812205 14.733678 4.537952
H 13.229257 13.744784 3.597086
H 11.831073 14.700593 4.023900
H 10.879757 15.946300 6.304275
H 10.138791 14.951852 7.545704
H 16.307968 11.779949 7.976775
H 16.382784 13.065254 9.179347
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H 5.752889 14.360261 9.850915
H 4.362126 13.496761 9.233185
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H 14.256071 8.062401 6.163833
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H 3.364988 9.793126 10.041962
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H 14.441777 9.163780 9.548151
H 14.256278 10.479401 10.693932
H 13.846901 8.462812 11.907108
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H 12.683588 13.484217 9.704811
H 11.232551 10.880401 12.921075
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H 10.109119 11.036226 4.449561
H 6.170497 12.676784 11.408398
H 5.535384 9.694061 7.514495
H 9.871375 9.445217 13.747842
H 9.217117 7.888080 13.271201
H 7.267814 11.315298 7.364795
H 6.201748 11.292681 13.184581
H 7.092637 7.879357 13.396282

116
Complex 3b
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Ir 11.422442 2.856502 6.565016
Ir 6.622561 4.322550 9.803675
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P 7.510772 5.152499 11.856812
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N 10.889877 8.281968 8.704668

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N 8.033960 5.594819 8.869145
C 11.419535 2.237816 3.581156
C 9.618330 0.533145 5.497065
C 10.612015 -0.064999 6.508400
C 6.235091 1.779840 8.151337
C 12.315894 1.126694 4.149323
C 3.921405 3.884561 8.315391
C 15.800697 2.622268 8.892096
C 11.853091 0.783174 6.684188
C 11.186271 6.658290 12.451352
C 13.717031 5.161962 10.105571
C 13.638034 6.051380 6.598444
C 5.454267 1.469470 9.439585
C 13.701899 1.572621 9.831010
C 14.904813 4.059549 5.711715
C 13.129415 6.164939 11.086405
C 3.619699 3.989883 9.821381
C 7.014629 7.896244 11.408153
C 12.185957 4.448750 12.518598
C 10.469267 2.806769 4.610410
C 9.806528 6.156048 12.845894
C 12.624633 1.346455 5.627037
C 9.668886 2.050524 5.485296
C 8.244009 2.845309 13.284373
C 14.339682 2.252500 8.616023
C 4.810288 3.649918 10.694395
C 14.349387 4.747583 6.958735
C 7.230427 4.644785 14.739548
C 5.368441 4.219472 7.994533
C 5.162587 6.634860 12.561837
C 6.389169 3.260930 7.901241
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C 6.674767 6.771793 12.385626
C 5.668359 2.532311 10.510734

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H 12.382418 0.566376 7.612222
H 11.758786 6.966117 13.343324
H 11.080051 7.525273 11.792657
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H 8.084350 7.943059 11.187418
H 12.665214 3.679554 11.912691
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H 9.242552 7.026650 13.214072
H 9.899881 5.476128 13.708529

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H 8.799532 2.551173 5.908463
H 9.252930 3.185353 13.536244
H 7.968274 2.063868 14.002121
H 8.293389 2.396567 12.289452
H 14.339253 1.530211 7.789842
H 4.704174 4.027290 11.711326
H 15.186939 4.979261 7.629409
H 6.474524 5.428045 14.839278
H 7.002851 3.879159 15.491542
H 8.198865 5.078127 15.005488
H 5.526592 5.163853 7.474205
H 4.881679 5.843157 13.263917
H 4.746389 7.574016 12.945668
H 4.678397 6.426825 11.602921
H 7.265561 3.541382 7.318815
H 6.241984 3.593378 13.164321
H 7.114714 7.011289 13.362006
H 6.189806 2.168664 11.394731

135
Complex 4a
U 10.309548 11.051849 4.365285
Rh 8.815400 8.385327 3.278965
Rh 8.356138 12.704884 7.189172
Rh 8.500183 11.976158 1.632423
P 10.803771 12.049190 1.146851
P 10.691142 12.342988 7.620095
N 6.743356 9.288649 6.154408
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N 7.587573 10.067517 6.124795
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N 9.459751 14.422614 4.296844
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N 11.500214 11.486499 6.352288
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C 6.075570 7.133289 3.382241
C 6.815761 14.568942 1.663602
C 6.978316 5.917725 3.638502

C 12.745945 13.584954 -0.445967
C 12.955820 13.705992 8.921021
C 7.877417 6.798924 0.828149
C 13.717152 11.255256 3.812607
C 10.224620 11.874962 10.396477
C 11.696891 14.713546 1.548995
C 6.937087 14.061428 9.590669
C 6.754656 12.567980 -0.795905
C 13.365094 8.874978 3.687022
C 9.129443 6.088193 1.376775
C 10.895045 11.258232 9.168703
C 8.249258 14.806285 7.489458
C 10.365625 9.849163 8.909911
C 8.036550 13.969205 0.980008
C 7.062675 15.395530 6.760519
C 6.203333 12.736801 9.334783
C 13.357445 9.948043 5.822080
C 11.097359 9.362249 0.300333
C 12.083837 14.647133 6.747425
C 12.887728 11.130953 6.648563
C 6.307407 13.709431 2.836891
C 10.548957 11.021343 -1.502024
C 5.684894 12.136376 0.217991
C 6.380988 12.234314 7.919966
C 11.722536 13.897312 8.031673
C 5.833817 14.468556 6.755900
C 11.493532 13.685243 0.433990
C 8.002980 13.103341 -0.132614
C 11.299578 10.791628 -0.189576
C 8.202522 14.182625 8.752316
C 8.418179 6.347874 3.862036
C 9.386209 6.399646 2.837158
C 6.804973 8.255248 2.676435
C 7.623520 8.124743 1.532770
C 6.302561 11.538284 1.465696
C 13.136558 11.596378 2.451925
C 6.226032 13.001829 6.756893
C 6.543620 12.232562 2.640918
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H 5.731003 7.529224 4.342156
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H 6.926242 5.206648 2.806481

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H 13.562316 12.116641 4.468307
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H 10.596622 12.878094 10.629587
H 12.484115 14.405894 2.243293
H 11.993065 15.676428 1.115499
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H 6.281292 14.915110 9.388209
H 6.342167 13.305281 -1.502912
H 7.043867 11.699367 -1.400475
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H 5.132552 12.828685 9.574233
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H 12.864049 9.038789 6.178091
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H 6.698969 11.650678 3.547157

135
Complex 4b
U 12.915507 11.426601 13.216533
Ir 11.404991 8.801898 12.112508
Ir 11.032365 13.169949 15.913298
Ir 11.093205 12.392032 10.484007
P 13.401174 12.502184 10.007978
P 13.351149 12.722796 16.441239
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N 12.158126 13.636144 13.626264

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C 15.939755 10.240161 14.606288
C 15.925551 9.248690 12.432996
C 12.896928 12.356142 19.216265
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H 16.205873 13.701477 9.004110
H 15.431540 9.327836 14.930922
H 17.024517 10.071552 14.739937
H 15.641100 9.371128 11.388200
H 17.003768 9.019604 12.477439
H 15.371945 8.398785 12.835017
H 11.819976 12.468155 19.062796
H 13.049721 11.745751 20.114328
H 13.315472 13.347266 19.419406
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