Electronic Supporting Information

Consecutive N$_2$ Loss from a Uranium Diphosphazide Complex

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Experimental Details

All air and moisture sensitive manipulations were carried out under an inert atmosphere of argon either on a double manifold vacuum line or in an MBraun glove box. Solvents used for these manipulations were purified by an MBraun solvent purification system, stored in PTFE-sealed glass vessels and stored over sodium benzophenone ketyl (THF) or "titanocene" (pentane, heptane, benzene, toluene). Deuterated solvents were dried over sodium benzophenone ketyl (benzene–d_6, THF–d_8) of CaH$_2$ (chloroform–d_1). Solvents were degassed by three freeze–pump–thaw cycles, distilled and stored over 4 Å molecular sieves in PTFE-sealed glass vessels under argon. All NMR spectra were recorded at ambient temperature with a Bruker Avance II (300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C, 121.49 MHz for ^{31}P) NMR spectrometer at ambient temperature. Chemical shifts are reported in parts per million (ppm) relative to the external standards SiMe$_4$ (^{1}H, ^{13}C), and 85% H$_3$PO$_4$ (^{31}P). Internal references were from residual ^{1}H and ^{13}C signals in C$_6$D$_5$H (δ 7.16, 128.1), CHCl$_3$ (δ 7.26, 77.16) and THF (δ 1.72 and 3.58, 67.21 and 25.31), respectively (s = singlet, d = doublet, t = triplet, q = quartet, sp = septet, m = multiplet, br = broad, ov = overlapping signals). NMR assignments were aided by the use of ^{13}C{^{1}H}-DEPT-90, ^{13}C{^{1}H}-DEPT-135, ^{1}H–^{13}C{^{1}H}-HSQC, ^{13}C{^{1}H} APT and ^{1}H–^{1}H-COSY experiments. IR measurements were carried out on a Bruker Tensor 37 FT Infrared spectrometer (vs = very sharp, s = sharp, w = wide, vw = very wide, ov = overlapping). Elemental analyses (EA) were performed using an Elementar Vario Microcube instrument. The compound 2-azidoaniline was prepared according to Driver *et al.*[1] UCl$_4$(dme)$_2$ was prepared by a modified literature procedure.[2] 18-crown-6 was purchased from Strem Chemicals, Inc. and recrystallized from acetonitrile before use. All other materials were purchased from commercial sources (*e.g.* Sigma Aldrich, Alfa Aesar, Cambridge Isotopes Laboratories, etc.) and used as received.

Note 1: All uranium compounds in this paper are paramagnetic. For paramagnetic compounds, $w_{1/2}$ denotes width at half height in hertz.

Note 2: Organic azides are both toxic and explosive. Care should be taken while handling azides, particularly if they are solvent free and/or at elevated temperatures.

**Note 3:** Phosphines are toxic and care should be taken while handling.

Note 4: ^{238}U is a weak α-emitter with a half life of 4.47 x 10^9 years.
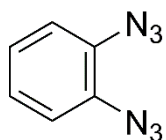
1,2-diazidobenzene: A solution comprised of 35 mL of 1M HCl and 30 mL of distilled H_2O was added to 2-azidoaniline[2] (0.510 g, 3.80 mmol) in a 250 mL round-bottomed flask equipped with a Teflon® coated stir bar. The solution was stirred at ambient temperature until the solid was dissolved, after which the mixture was cooled to –5 °C using an ice/salt water bath. Solid $NaNO_2$ (0.500 g, 7.247 mmol) was added to the flask and the reaction mixture was stirred at –5° C for 1 hour. The solution was treated with a 5 mL aqueous solution of NaN_3 (470 mg, 7.23 mmol) and stirred for 2 hours, after which a light orange solid was isolated by cold filtration. The resulting product was a red oil at ambient temperature. Yield: 0.523 g (85.9%). Single crystals suitable for X-ray diffraction were obtained from a solution of petroleum ether at –35 °C. ^1H NMR (chloroform–d_1, 300.13 MHz): δ 7.07 (ov m, 4H, Ph CH). $^{13}C\{^1H\}$ NMR (chloroform–d_1, 75.47 MHz): δ 131.22 (s, CN$_3$), 126.02 (s, Ph CH), 120.30 (s, Ph CH). IR (neat): ν_{max} (cm^{-1}) 2089 (vw), 1589 (s), 1488 (s), 1448 (s), 1297 (w), 1273 (w), 1154 (s), 1145(s), 1085 (s), 744 (s), 697 (s), 647 (s), 527 (s).
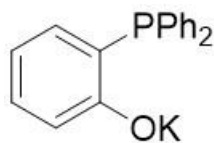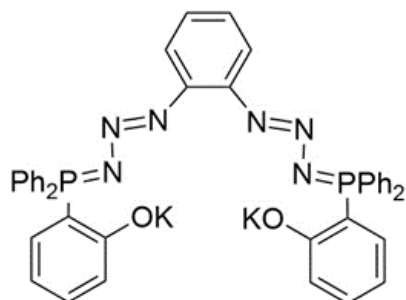
(2–OK–C$_6$H$_4$)PPh$_2$: In an inert atmosphere glove box, 2-(diphenylphosphino)phenol (0.1185 g, 0.426 mmol) and KH (0.0188 g, 0.468 mmol) were combined in a 20 mL scintillation vial equipped with a Teflon® coated stir bar. The solids were dissolved in 8 mL of THF and gas evolution was observed from the cloudy solution. The reaction mixture was stirred for 15 minutes at ambient temperature until gas evolution ceased and the solution became clear and colourless. The reaction was stirred for another 18 hours and the solvent was removed *in vacuo* to produce a white solid (0.1297 g, 96.2% yield) ^1H NMR (THF–d_8, 300.13 MHz): δ 7.25-7.16 (m, 10H, Ar CH), 6.87 (td, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.9 Hz, Ar CH), 6.41 (ddd, 1H, $^3J_{HP}$ = 6.3 Hz, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.9 Hz, Ar CH), 6.03 (m, 2H, Ar CH) . $^{13}C\{^1H\}$ NMR (THF–d_8, 75.47 MHz): δ 174.63 (d, $^1J_{CP}$ = 19.2 Hz), 140.63 (d, $^1J_{CP}$ = 10.3 Hz), 134.77 (d, $^2J_{CP}$ = 18.8 Hz), 134.39 (s), 131.69 (s), 129.11 (d, $^3J_{CP}$ = 6.7 Hz), 128.80 (s), 123.39 (d, $^2J_{CP}$ = 7.7 Hz), 118.32 (s), 111.33 (s). $^{31}P\{^1H\}$ (THF–d_8, 121.49 MHz) δ –19.14 (s). Anal. Calcd. (%) for C$_{18}$H$_{14}$KOP: C: 68.33; H: 4.46. Found C: 68.09; H: 4.61.
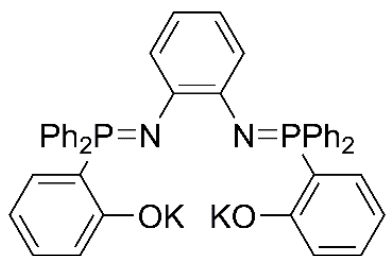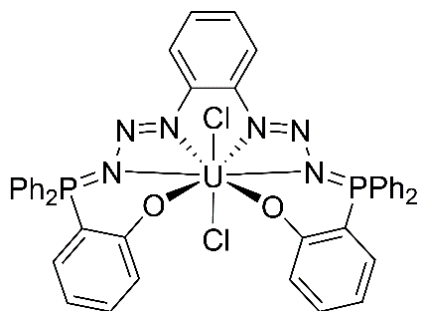
K$_2$L: In an inert atmosphere glove box, 1,2-diazidobenzene (0.0544 g, 0.339 mmol) was dissolved in 1 mL of THF in a 20 mL scintillation vial. The 1,2-diazidobenzene solution was added to a stirring THF (8 mL) solution of (2–OK–C$_6$H$_4$)PPh$_2$ (0.2145 g, 0.678 mmol). The reaction mixture was stirred at 50 °C for 8 hours to ensure full conversion to K$_2$L resulting in a clear, orange solution. The THF was removed *in vacuo* to give a bright yellow solid (0.2500 g, 99.8% yield). ^1H NMR (THF–d_8, 300.13 MHz): δ 7.86–7.78 (ov m, 8H, Ar CH), 7.42–7.33 (ov m, 14H, Ar CH), 7.00–6.85 (m, 4H, Ar CH), 6.58 (br s, 2H, Ar CH), 6.15–6.07 (m, 4H, Ar CH). $^{13}C\{^1H\}$ NMR (THF–d_8, 75.47 MHz): δ 176.19 (d, $^1J_{CP}$ = 4.8 Hz), 147.6 (d, $^1J_{CP}$ = 23.0 Hz), 136.66 (s), 136.08 (d, $^2J_{CP}$ = 9.0 Hz), 135.24 (s), 134.43 (s), 132.43 (d, $^2J_{CP}$ = 9.4 Hz), 130.94 (s), 128.78 (d, $^3J_{CP}$ = 11.6 Hz), 121.16 (s), 119.34 (s), 119.19(s), 116.54 (s),

109.77 (s), 109.61 (s). ^{31}P{^{1}H} (THF–d_8, 121.49 MHz) δ 11.42 (s). Anal. Calcd. (%) for C$_{42}$H$_{32}$K$_2$N$_2$O$_2$P$_2$: C: 68.46; H: 4.38; N: 3.80. Found C: 67.83; H: 5.12; N: 3.90.

K$_2$L″: In an inert atmosphere glove box, 1,2-diazidobenzene (0.0579 g, 0.362 mmol) was dissolved in 2 mL of toluene and added to a stirring toluene (8 mL) solution of (2–OK–C$_6$H$_4$)PPh$_2$ (0.2288 g, 0.723 mmol). A bright yellow precipitate formed immediately upon addition of the diazide. The reaction mixture was stirred at ambient temperature for 15 minutes. The solution was decanted from the precipitate and the remaining solvent removed *in vacuo* to afford a bright yellow solid. The resulting product was washed with pentane (3 × 1 mL) (0.2138 g, 75% yield). ^{1}H NMR (THF–d_8, 300.13 MHz): δ 7.77-7.71 (ov m, 6H, Ar C*H*), 7.60–7.54 (m, 2H, Ar C*H*), 7.36–7.34 (m, 4H, Ar C*H*), 7.24-7.07 (ov m, 10H, Ar C*H*), 7.02–6.94 (m, 2H, Ar C*H*), 6.87–6.84 (m, 2H, Ar C*H*), 6.60–6.49 (m, 2H, Ar C*H*), 6.20–6.15 (m, 2H, Ar C*H*), 5.94–5.92 (m, 2H, Ar C*H*). ^{31}P{^{1}H} (THF–d_8, 121.49 MHz) δ 28.34 (br s). ^{13}C data is unavailable due to decomposition in solution and low solubility in common organic solvents. Anal. Calcd. (%) for C$_{42}$H$_{32}$K$_2$N$_6$O$_2$P$_2$: C: 63.62; H: 4.07; N: 10.60. Found C: 62.73; H: 4.41; N: 10.73.

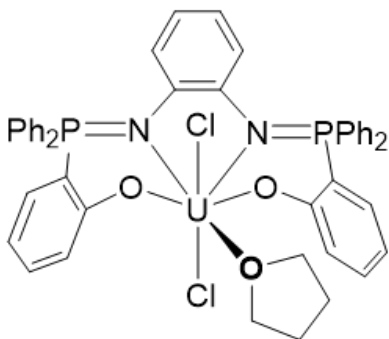**Complex 1:** In an inert atmosphere glove box, solid K$_2$L″ (0.0443g, 0.0559 mmol) and UCl$_4$ (0.0212g, 0.0558 mmol) were added to a 20 mL scintillation vial containing 3 mL THF. The mixture was agitated for 30 seconds until the all K$_2$L″ had been consumed and a dark orange solution prevailed. Toluene (3 mL) was added to the solution to precipitate KCl and the THF/toluene solution was filtered quickly through Celite®. The solvent was removed *in vacuo* to afford an orange-brown solid (0.0377g 66.0% yield). Suitable crystals for X-ray diffraction were obtained in benzene–d_6 by leaving the solution at ambient temperature for 6 hours. Due to decomposition of 1 to 2 in solution, NMR spectra of compound **1** contain an impurity of **2**. ^{1}H NMR (THF–d_8, 300.13 MHz): δ 24.55 (w$_{1/2}$ = 16.2 Hz), 19.88 (w$_{1/2}$ = 11.6 Hz), 16.89 (w$_{1/2}$ = 27.0 Hz), 14.07 (w$_{1/2}$ = 16.1 Hz), 12.81 (w$_{1/2}$ = 11.4 Hz), 12.52 (w$_{1/2}$ = 15.7 Hz), 12.02 (w$_{1/2}$ = 24.1 Hz), 7.55 (w$_{1/2}$ = 10.8 Hz), 7.31 (w$_{1/2}$ = 16.8 Hz). ^{31}P{^{1}H} NMR (THF-d_8, 121.49 MHz): δ 49.61 (s, 2P, *P*N$_3$). Anal. Calcd. (%) for C$_{42}$H$_{32}$N$_6$O$_2$P$_2$U: C: 49.28; H: 3.15; N: 8.21. Found C: 49.17; H: 3.39; N: 8.22.
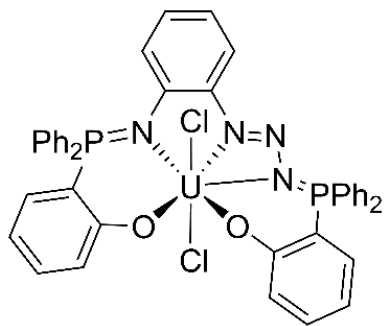
Complex 2: Synthesis 1- In an inert atmosphere glove box, solid K$_2$L″ (0.010 g, 0.0130 mmol) and UCl$_4$(dme)$_2$ (0.0073 g, 0.0130 mmol) were added to a J. Young NMR tube containing 0.5 mL of THF-d_8. The mixture was agitated for 2 minutes during which all of K$_2$L″ had been consumed and a dark orange solution prevailed. The solution was heated for 12 hours at 45 °C to ensure full conversion of **1** to **2**. Crystals suitable for X-ray diffraction were obtained at ambient temperature from benzene after 24 hours. An isolated yield could not be determined due to persistent impurities (complex **4**).
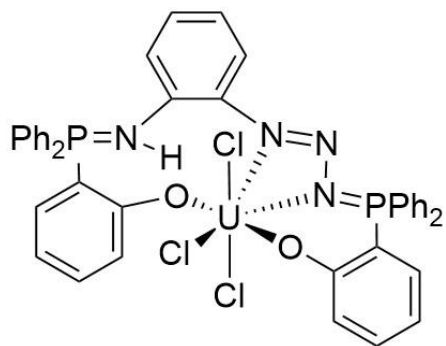
Synthesis 2- In an inert atmosphere glove box, solid Complex **1** (0.0377g, 0.0369 mmol) was added to a 20 mL scintillation vial containing 3 mL THF and a Teflon® coated stir bar. The dark orange solution was stirred at 80°C for 2 hours to ensure full conversion of **1** to **2**. The solvent was removed *in vacuo* to afford a brown solid and the product was washed with heptane (3 x 1 mL) (0.0299 g, 81.5% crude yield). An isolated yield could not be obtained due to impurities of **4**. ^{1}H NMR (THF–d_8, 300.13 MHz): δ 29.29 (w$_{1/2}$ = 29 Hz), 26.62 (w$_{1/2}$ = 29 Hz), 23.45 (w$_{1/2}$ = 26 Hz), 23.19 (w$_{1/2}$ = 20 Hz), 21.08 (w$_{1/2}$ = 25 Hz), 18.75 (w$_{1/2}$ = 17 Hz), 17.21 (w$_{1/2}$ = 13 Hz), 14.53 (w$_{1/2}$ = 19 Hz), 11.26 (w$_{1/2}$ = 18 Hz), 11.07 (w$_{1/2}$ = 16 Hz), 9.81 (w$_{1/2}$ = 18 Hz), 9.46 (w$_{1/2}$ = 17 Hz), –3.06 (w$_{1/2}$ = 14 Hz). ^{31}P{^{1}H} NMR (THF-d_8, 121.49 MHz): 104.07 (s, 1P), 71.15 (s, 1P). Anal. Calcd. (%) for C$_{42}$H$_{32}$Cl$_2$N$_4$O$_2$P$_2$U: C: 50.67; H: 3.24; N: 5.63. Found C: 50.21; H: 3.41; N: 5.71. While this compound could not be separated from small impurities of complex **4**, the obtained elemental analysis data is within acceptable standards, likely due to the similarity of the chemical composition of complexes **4** and **2**.

Complex 3: In an inert atmosphere glove box, solid K$_2$L (0.0200 g, 0.0271 mmol) was added to a 20 mL scintillation vial containing UCl$_4$(dme)$_2$ (0.0152 g, 0.0272 mmol) and a Teflon® coated stir bar. To this mixture, 6 mL of THF was added and the cloudy green solution was stirred for 4 hours. The solution was then filtered through Celite® and the solvent was removed *in vacuo* to afford a pale green solid (0.0164 g yield, 62.4%). Crystals suitable for X-ray diffraction were obtained from a saturated solution of THF at ambient temperature after 12 hours.

^{1}H NMR (THF–d_8, 300.13 MHz): δ 32.27 (w$_{1/2}$ = 121 Hz), 25.86 (w$_{1/2}$ = 146 Hz), 20.64 (w$_{1/2}$ = 93 Hz), 17.99 (w$_{1/2}$ = 113 Hz), 13.48 (w$_{1/2}$ = 1123 Hz), 10.34 (w$_{1/2}$ = 255 Hz), 9.59 (w$_{1/2}$ = 239 Hz), 8.02 (w$_{1/2}$ = 78 Hz), 7.82 (w$_{1/2}$ = 31 Hz), 5.37 (w$_{1/2}$ = 67 Hz), 5.20 (w$_{1/2}$ = 57 Hz), –1.41 (w$_{1/2}$ = 165 Hz), –5.84 (w$_{1/2}$ = 69 Hz) ^{31}P{^{1}H} NMR (THF–d_8, 121.49 MHz): δ –56.40 (br s, 2P, *P*=N). Anal. Calcd. (%) C$_{84}$H$_{64}$Cl$_4$N$_4$O$_4$P$_4$U$_2$: C: 53.14; H: 3.88; N: 2.69. Found C: 53.53; H: 3.98; N: 3.19.

Complex 4: In an inert atmosphere glove box, solid K_2L'' (0.0114 g, 0.0144 mmol) was added to a vial containing UCl_4 (0.0053 g, 0.0140 mmol). To this mixture, 6 mL of THF was added and the dark orange solution was agitated until the K_2L'' had been completely consumed, about 2 minutes. The THF solution was heated at 50 °C for 10 minutes. The solvent was removed *in vacuo* and the compound was extracted with 2 mL benzene and filtered through Celite®. Crystals suitable for X-ray diffraction were obtained from benzene at ambient temperature after 24 hours (Yield 0.0019 g, 12% yield). ^1H NMR (THF–d_8, 300.13 MHz): δ 61.57 ($w_{1/2}$ = 26 Hz), 50.28 ($w_{1/2}$ = 98 Hz), 38.75 ($w_{1/2}$ = 48 Hz), 34.15 ($w_{1/2}$ = 30 Hz), 33.62 ($w_{1/2}$ = 18 Hz), 28.65 ($w_{1/2}$ = 29 Hz), 26.67 ($w_{1/2}$ = 16 Hz), 25.71 ($w_{1/2}$ = 21 Hz), 25.14 ($w_{1/2}$ = 21 Hz), 15.35 ($w_{1/2}$ = 15 Hz), 8.60 ($w_{1/2}$ = 19 Hz), 7.68 ($w_{1/2}$ = 18 Hz), 6.37 ($w_{1/2}$ = 16 Hz), 6.17 ($w_{1/2}$ = 26 Hz), 5.41 ($w_{1/2}$ = 17 Hz), –1.72 ($w_{1/2}$ = 16 Hz), –21.33 ($w_{1/2}$ = 13 Hz). $^{31}P\{^1H\}$ NMR (THF-d_8, 121.49 MHz): 88.93 (d, $^3J_{PH}$ = 13.4 Hz, 1P, doublet is due to incomplete ^1H decoupling), –38.16 (s, 1P). This product is a minor impurity and has eluded preparation on a large scale. As a consequence, only small quantities of non-analytically pure material were available for combustion analysis, and repeated attempts failed to provide acceptable data.
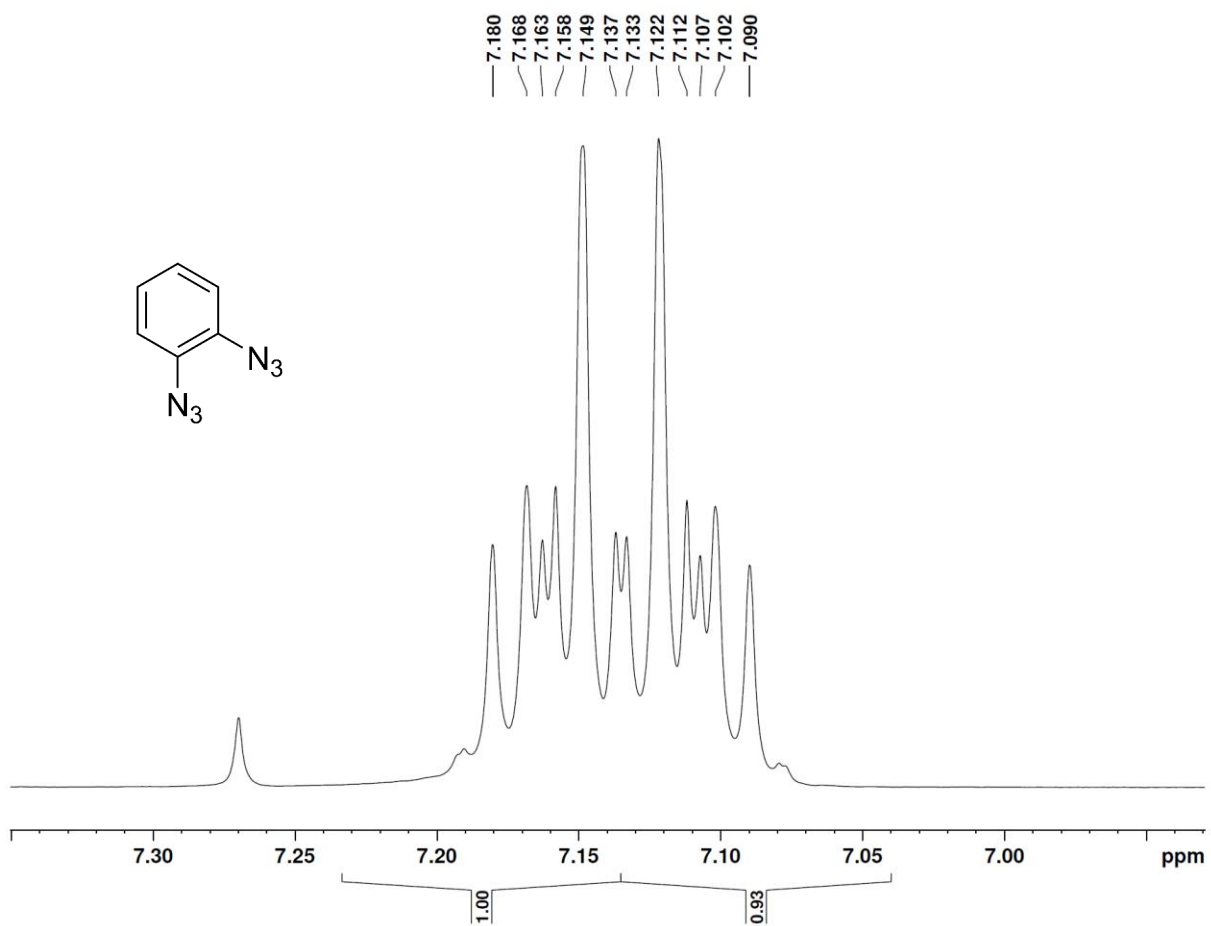
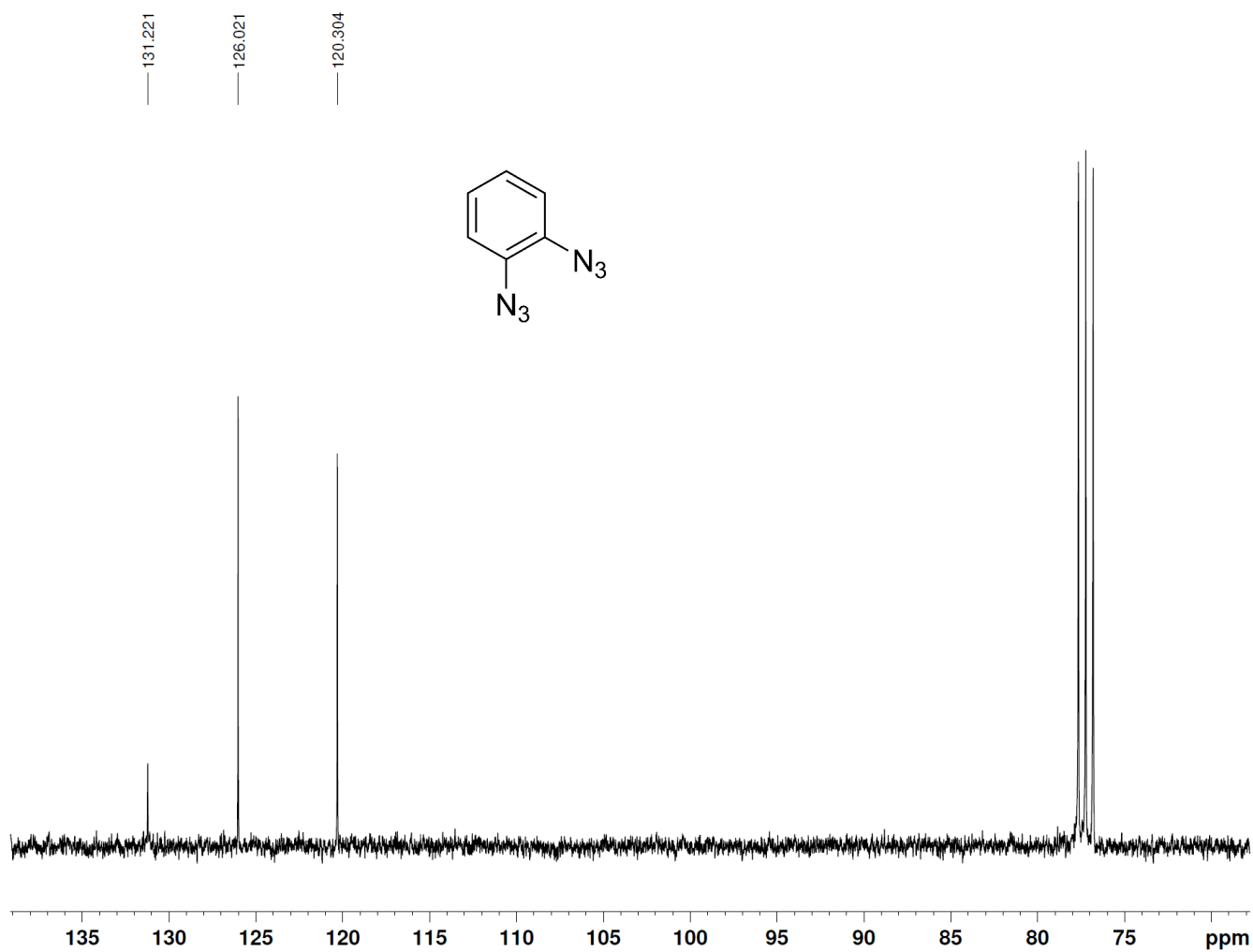**Figure S1.** ^{1}H NMR spectrum of 1,2-diazidobenzene in CDCl$_3$.

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of 1,2-diazidobenzene in CDCl$_3$.
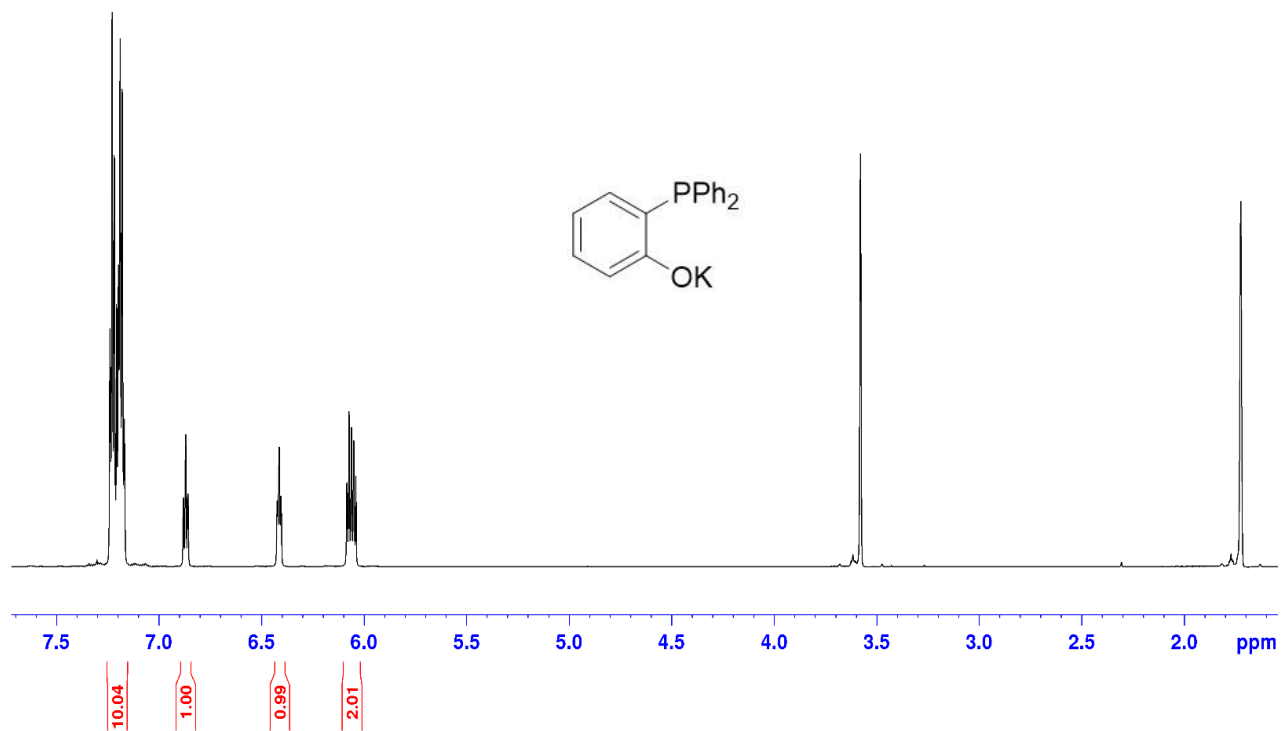
Figure S3. ^{1}H NMR spectrum of (2–OK–C_6H_4)PPh_2 in THF-d_8
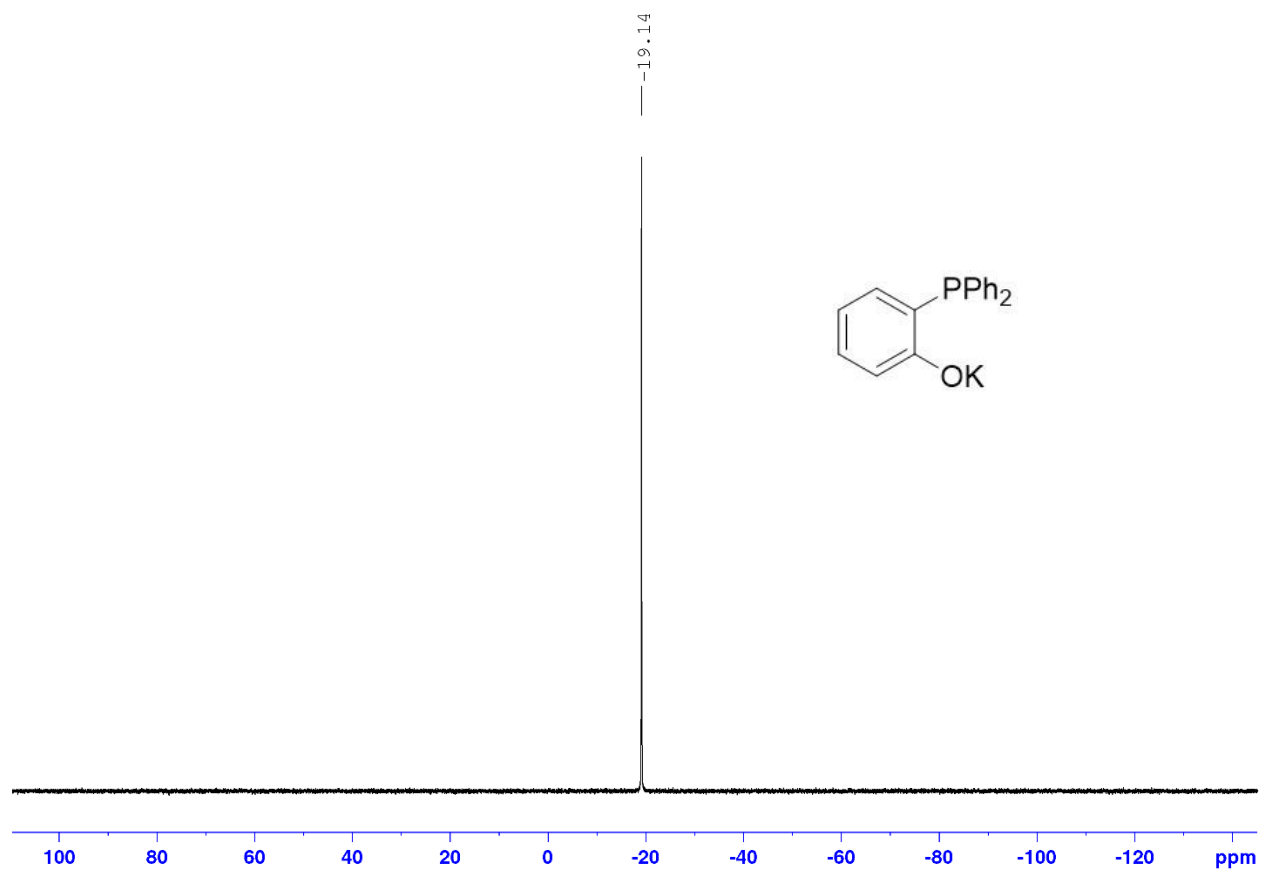
Figure S4. ^{31}P NMR spectrum of (2–OK–C$_6$H$_4$)PPh$_2$ in THF-d_8
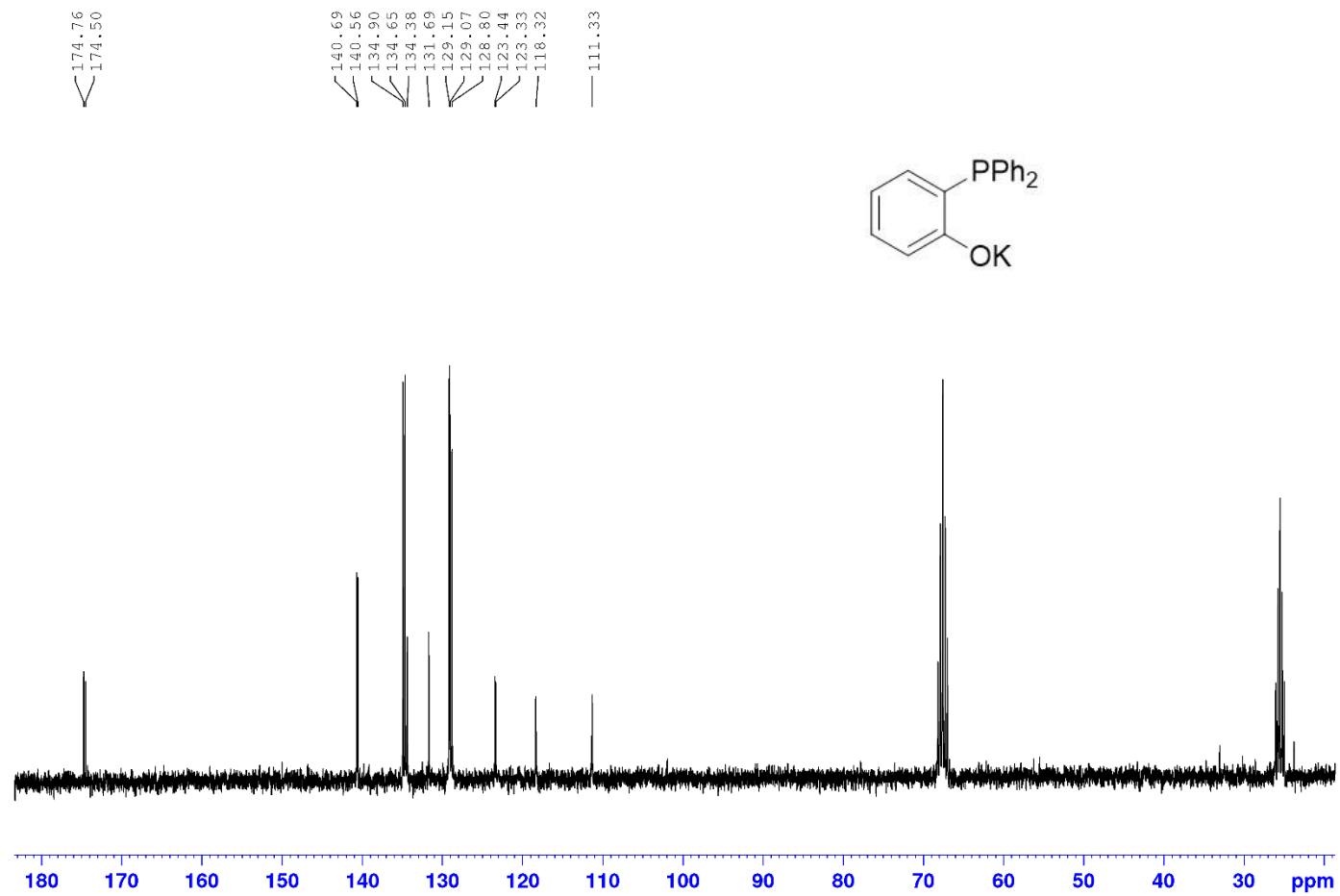
Figure S5. $^{13}C\{^1H\}$ NMR spectrum of (2–OK–C_6H_4)PPh_2 in THF-d_8
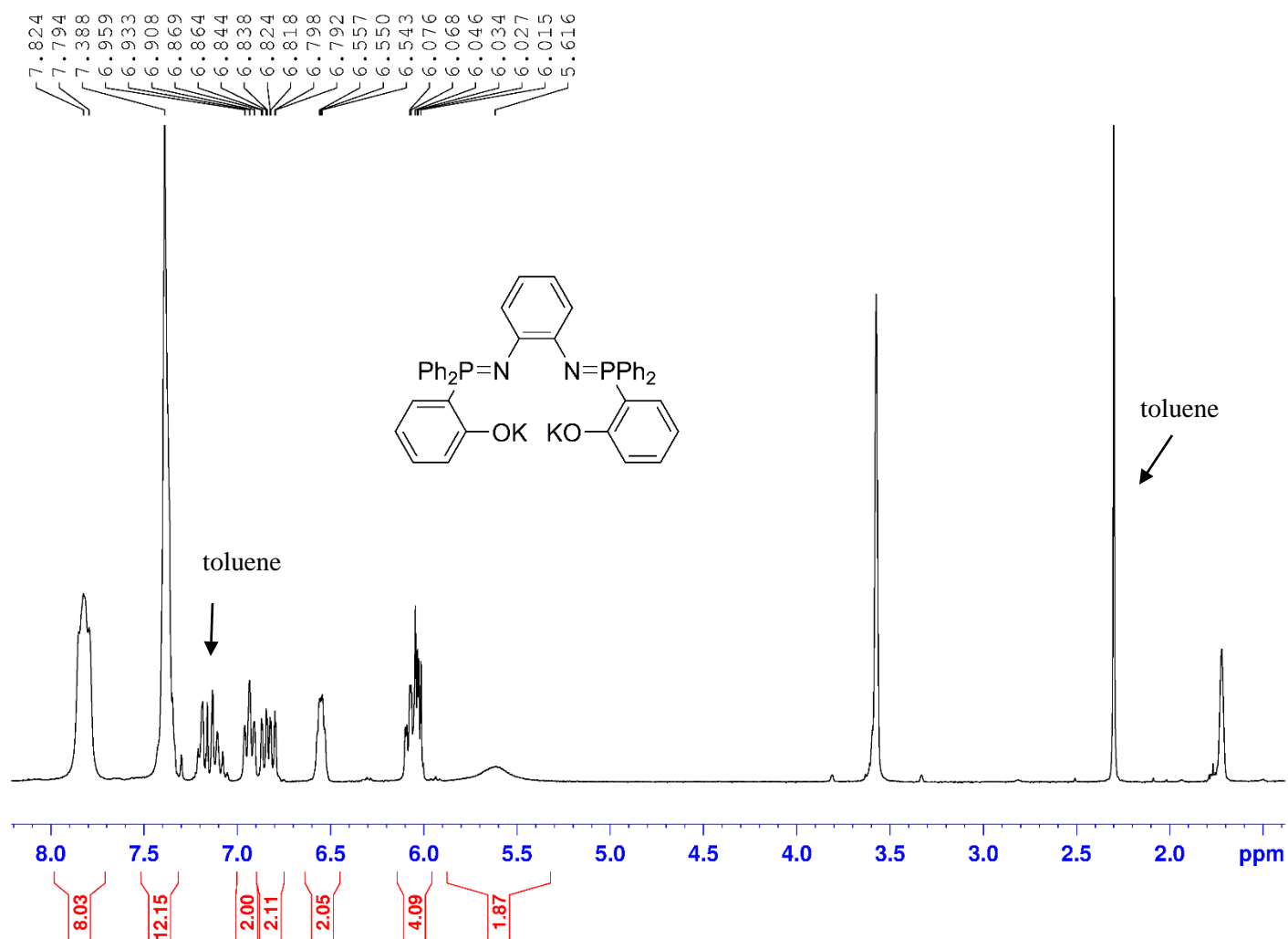
Figure S6. ^{1}H NMR spectrum of **K₂L** in THF–d_8.
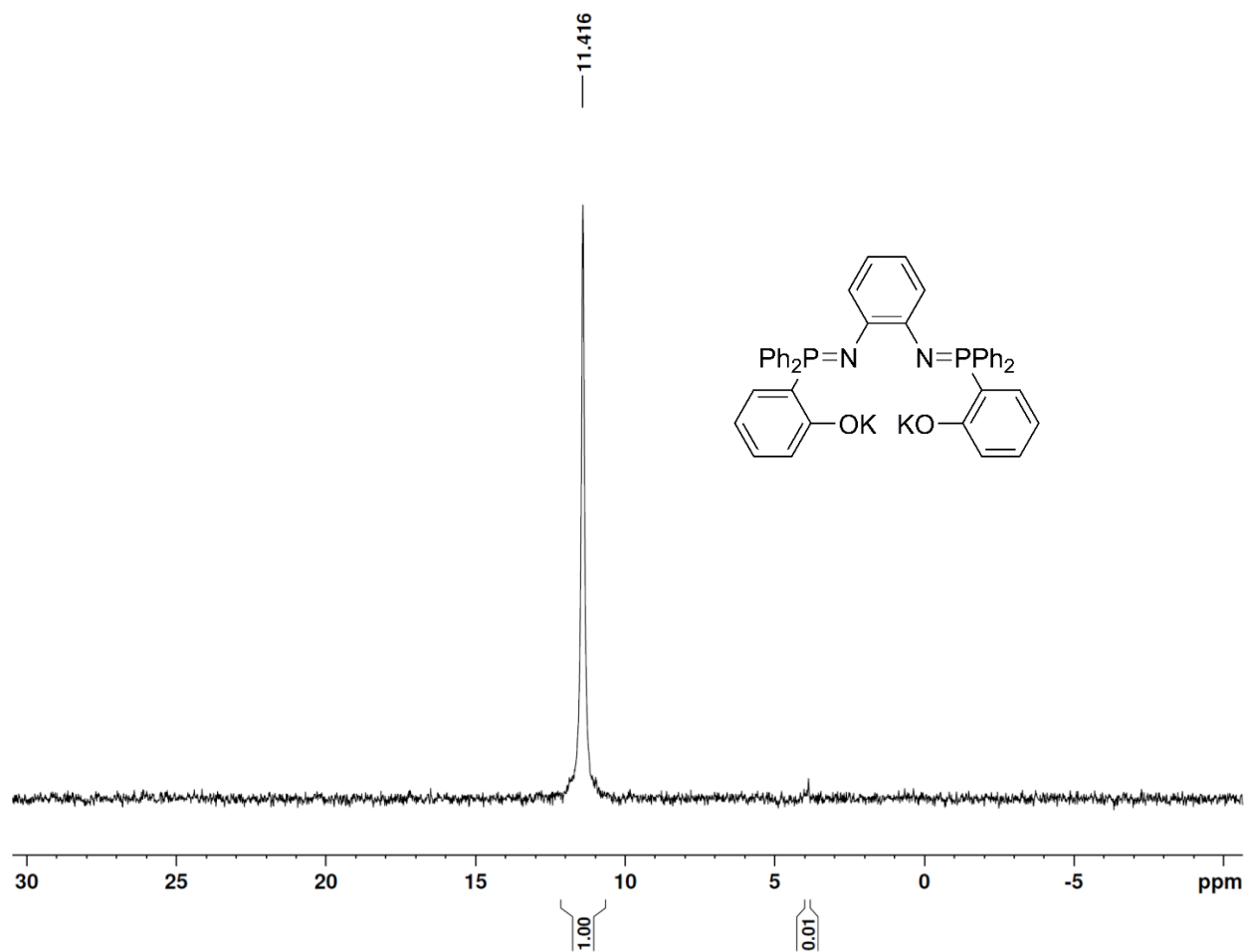
Figure S7. ^{31}P NMR spectrum of **K₂L** in THF–d_8.
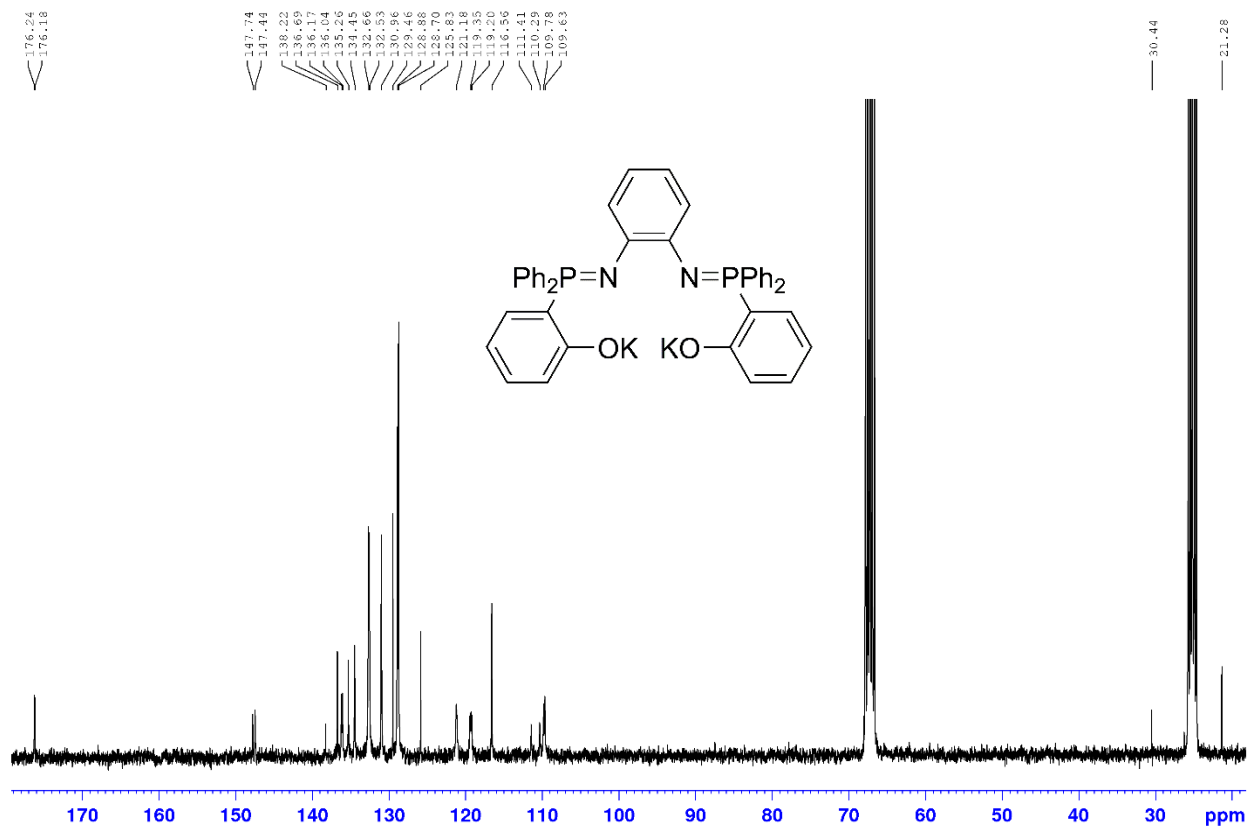
Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **K₂L** in THF–d_8.
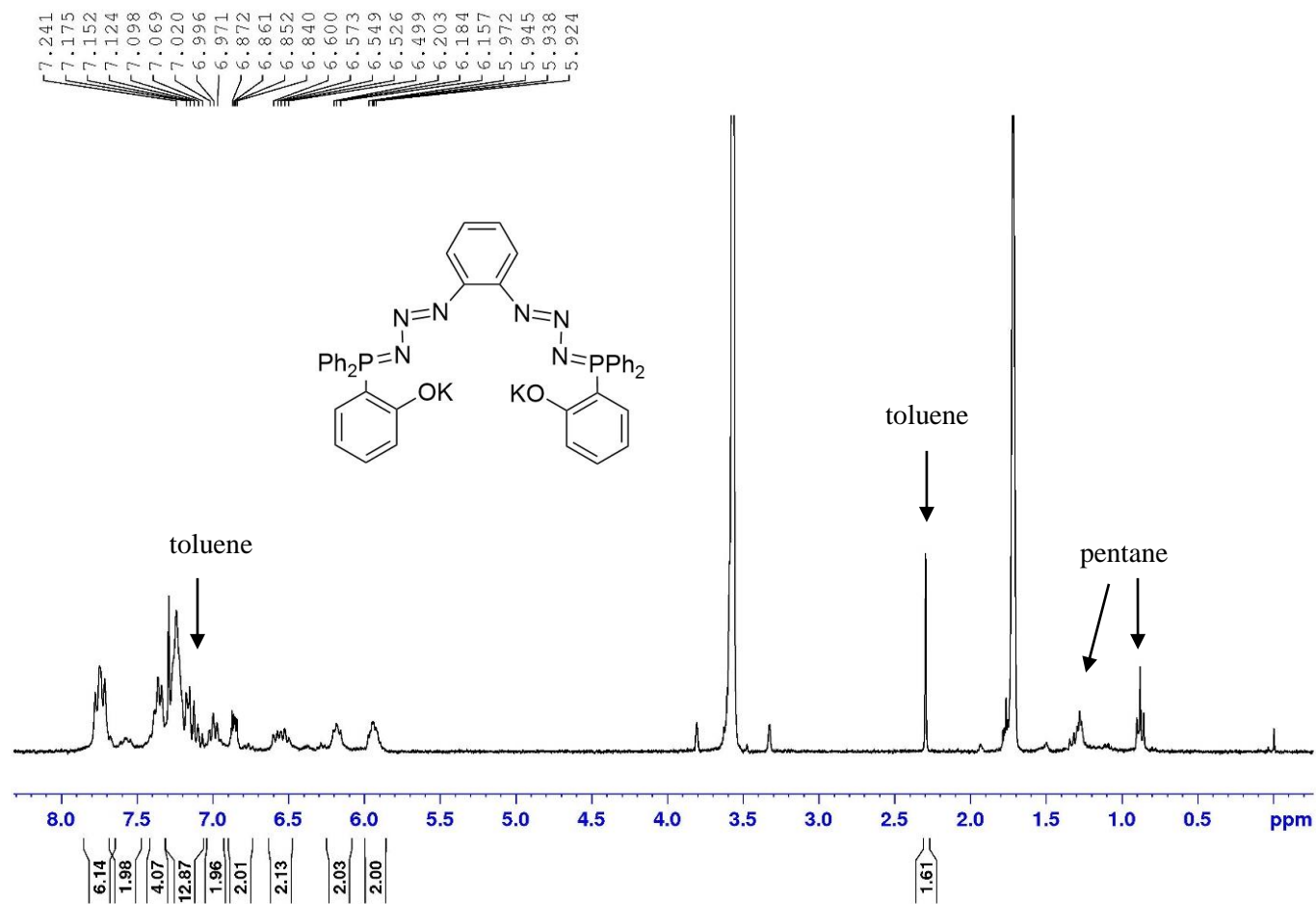
Figure S9. ^{1}H NMR spectrum of **K₂L''** in THF–d_8.
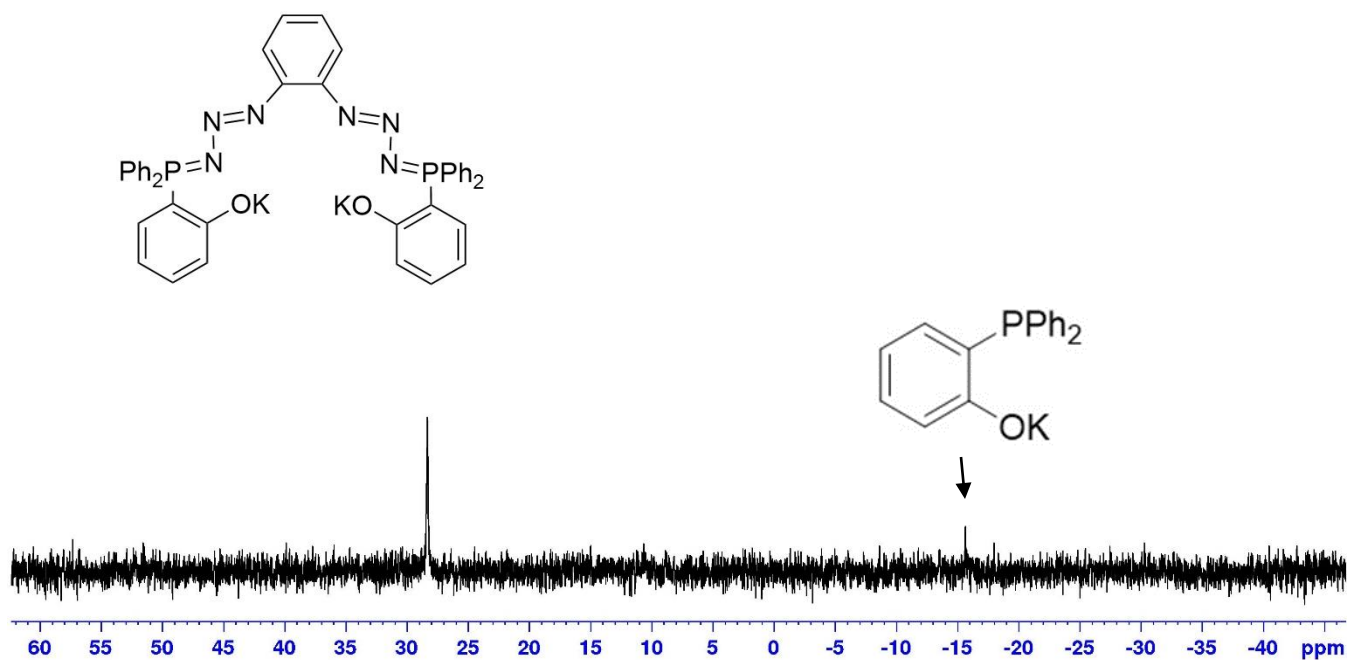
Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of **K₂L''** with small impurity of (2–OK–C₆H₄)PPh₂ in THF–d_8.
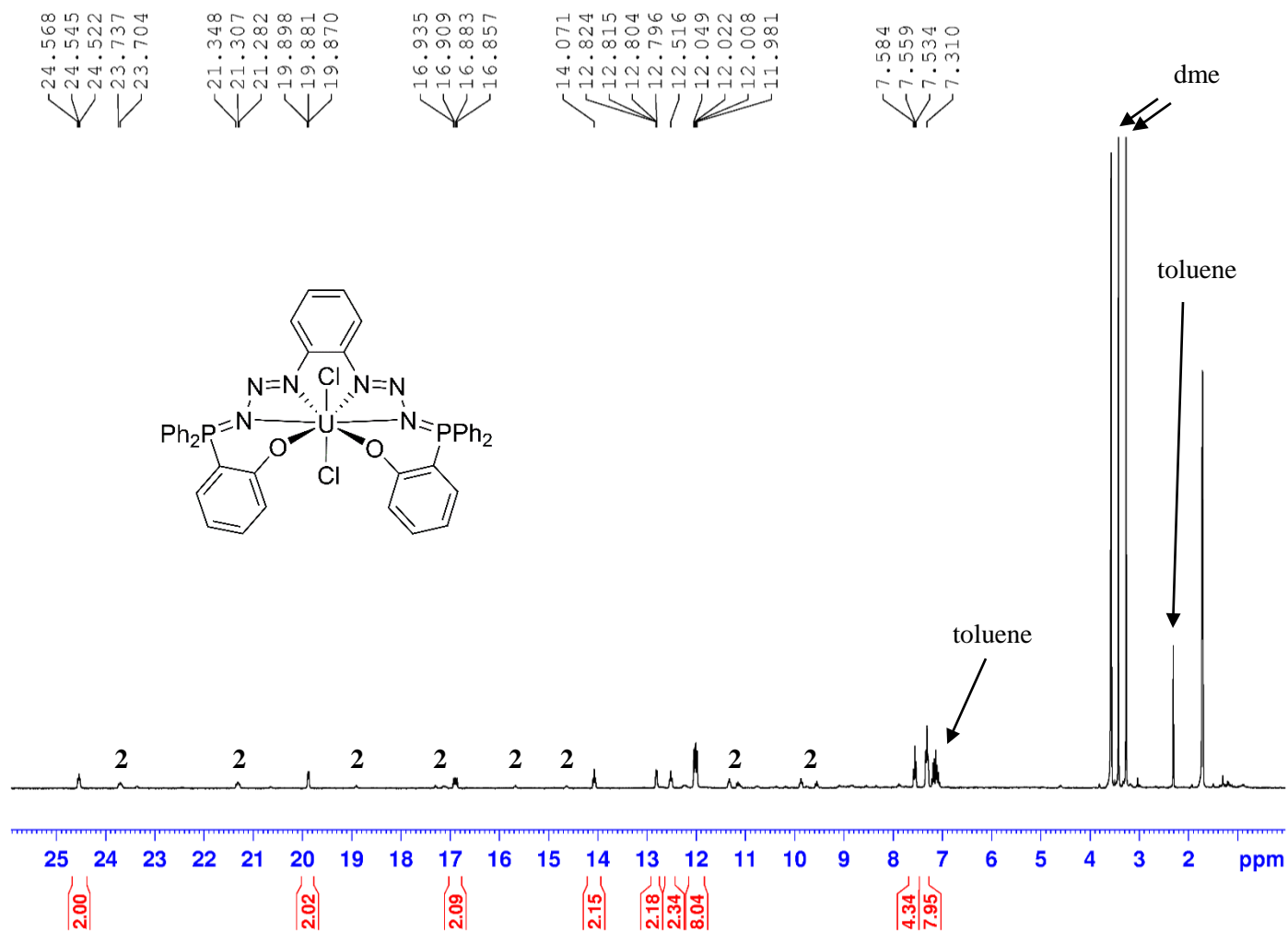
Figure S11. ^{1}H NMR spectrum of complex **1** in THF–d_8 with toluene and complex **2** impurity.
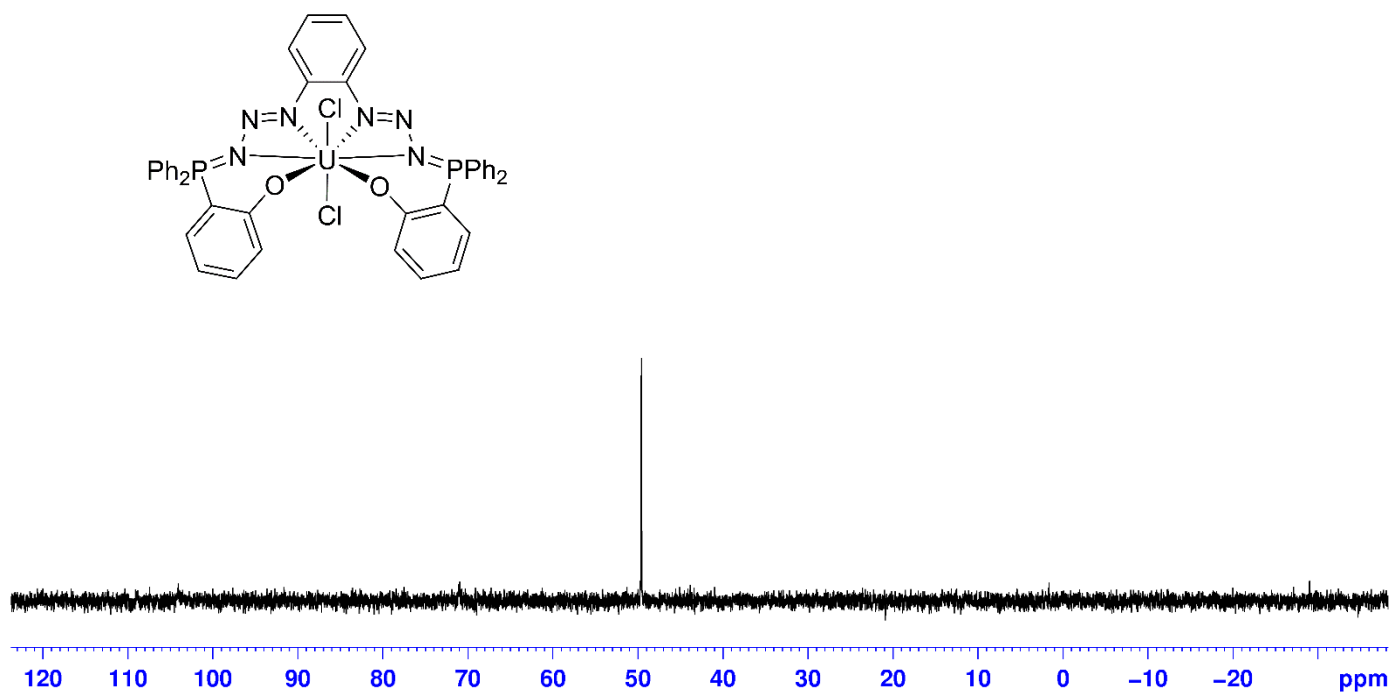
Figure S12. ^{31}P{^{1}H} NMR spectrum of complex **1** in THF–d_8.
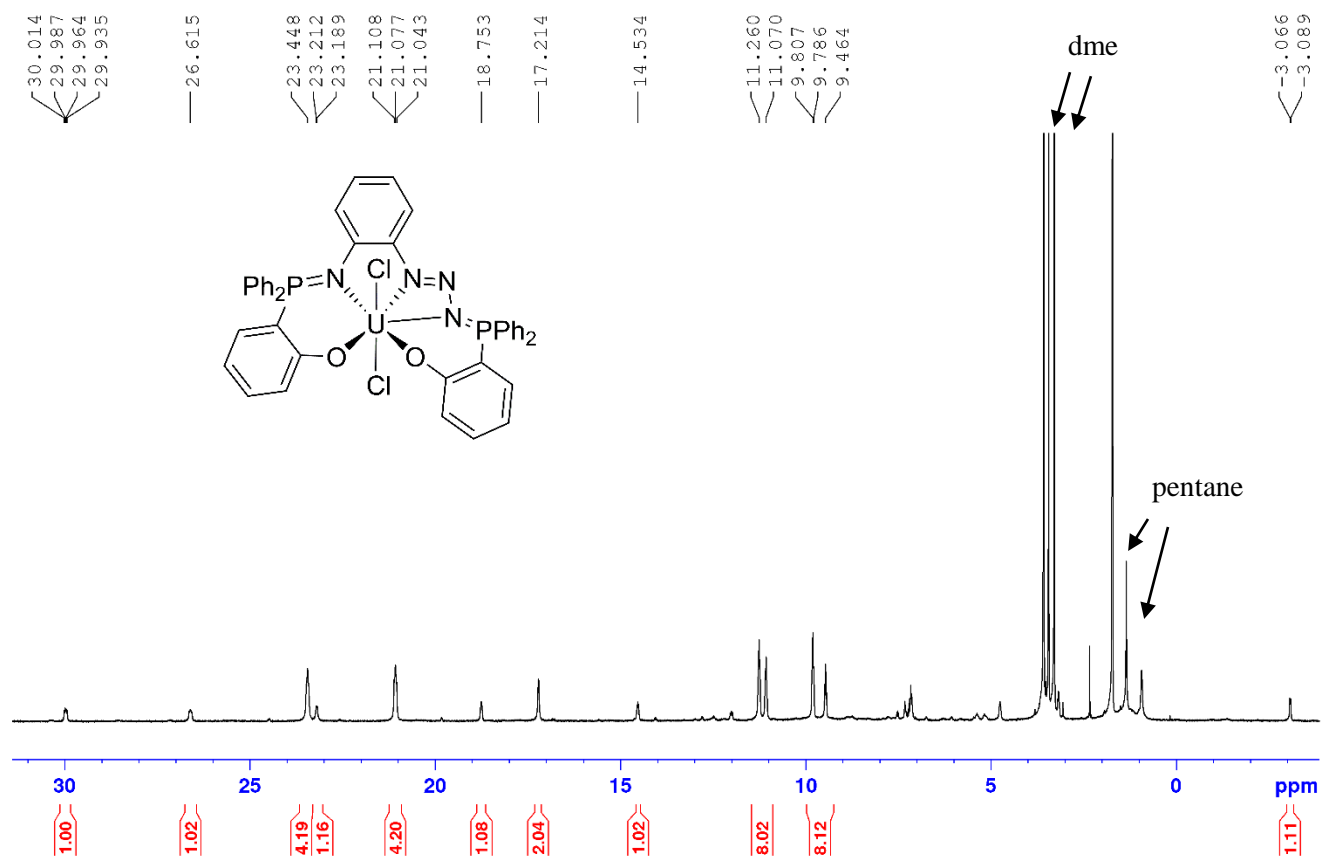
Figure S13. ^{1}H NMR spectrum of complex **2** in THF–d_8.
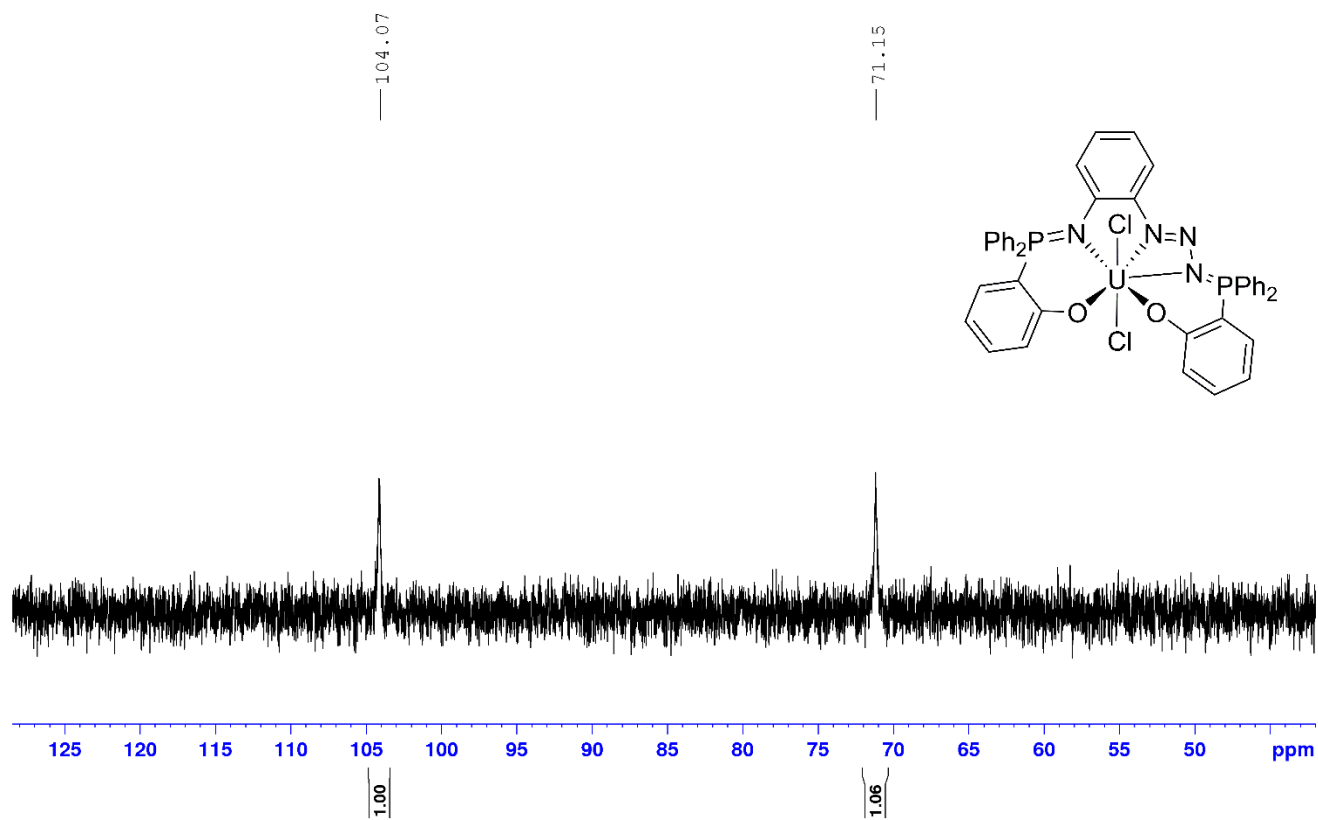
Figure S14. $^{31}P\{^{1}H\}$ NMR spectrum of complex **2** in THF–d_8.
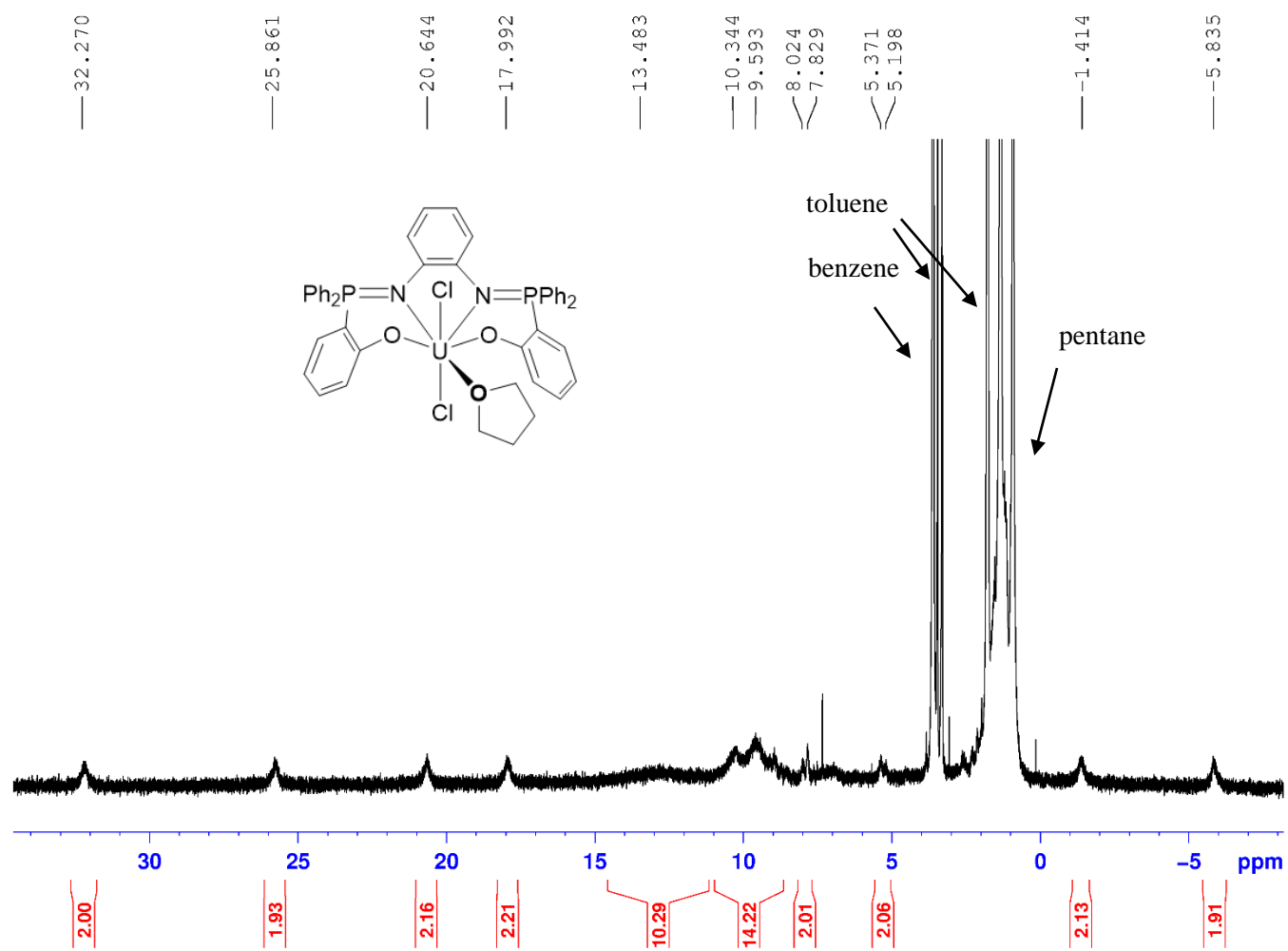
Figure S15. ^{1}H NMR spectrum of complex **3** in THF–d_8.
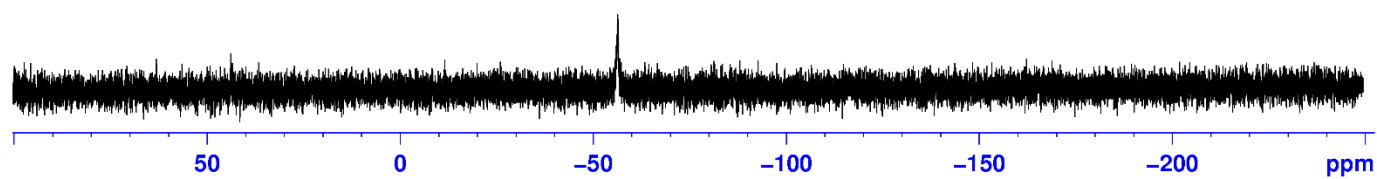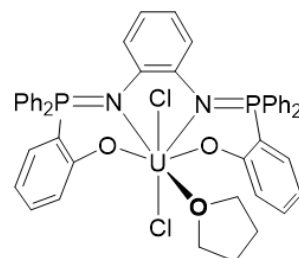
Figure S16. $^{31}P\{^1H\}$ NMR spectrum of complex **3** in THF–d_8.
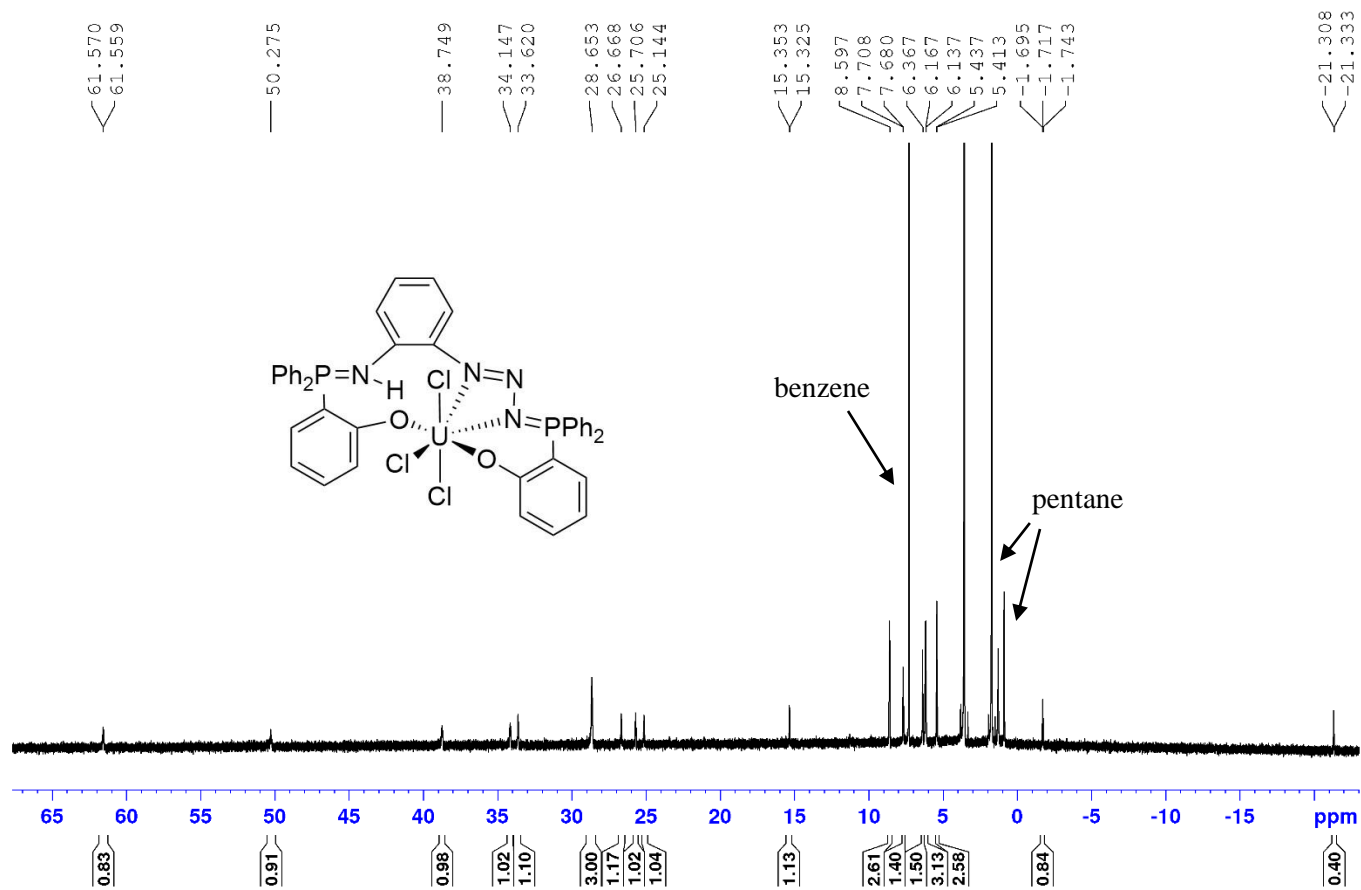
Figure S17. ^{1}H NMR spectrum of complex **4** in THF–d_8.
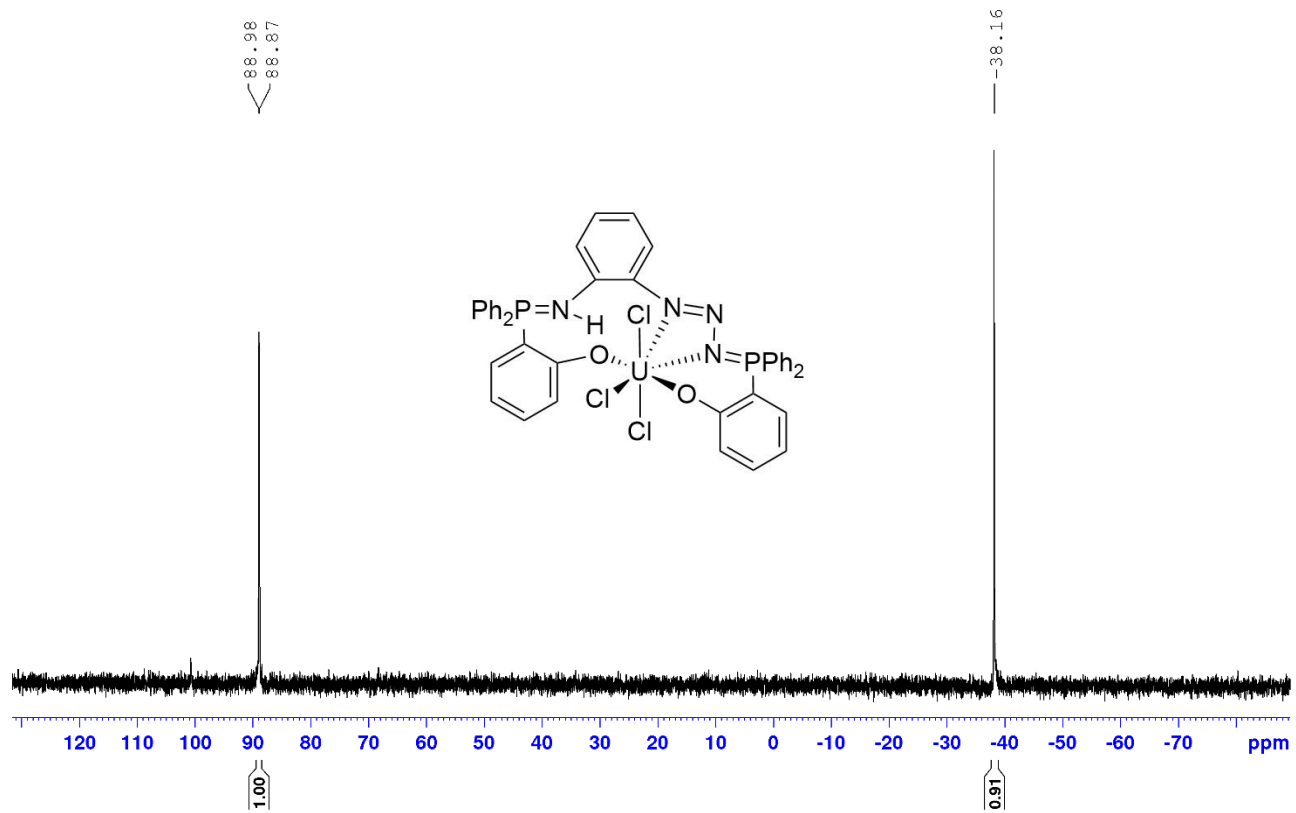
Figure S18. $^{31}P\{^1H\}$ NMR spectrum of complex **4** in THF–d_8.

Crystallographic details

Unfortunately, single crystals of **3** grown in THF and [KL][K(18-crown-6)] in toluene succumb to rapid decomposition upon removal from the mother liquor, resulting in the crystals becoming covered with amorphic material. However, inner portions of the crystals remain intact, allowing for modest diffraction of X-ray radiation, despite interference from the polycrystalline material. The data is not ideal, however, and therefore discussions of the metrical parameters are not included in the body of the manuscript. The data set does, however, allow for qualitative discussions associated with the connectivity of atoms, and thus, the geometry of complex **3** and [KL][K(18-crown-6)]. The structure of **3** is depicted in Fig. S19. The structure of [KL][K(18-crown-6)] is depicted in Fig. S20.
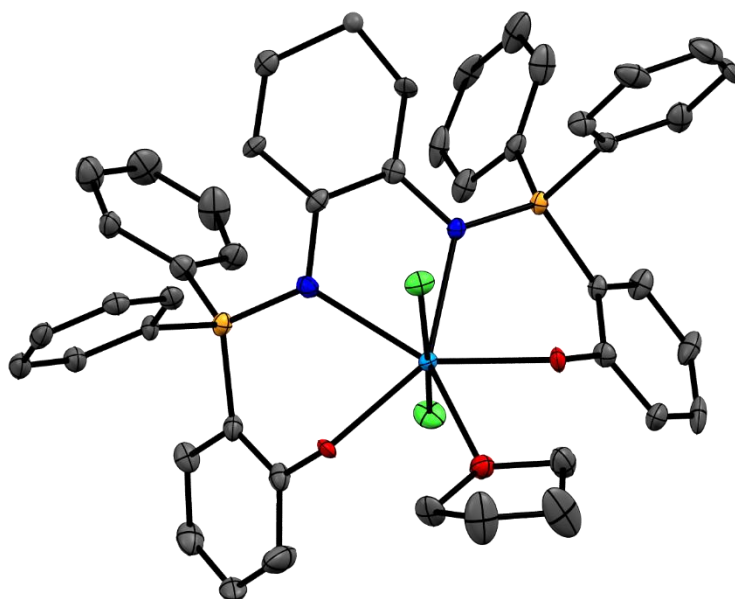
Figure S19. Connectivity structure of **3.**
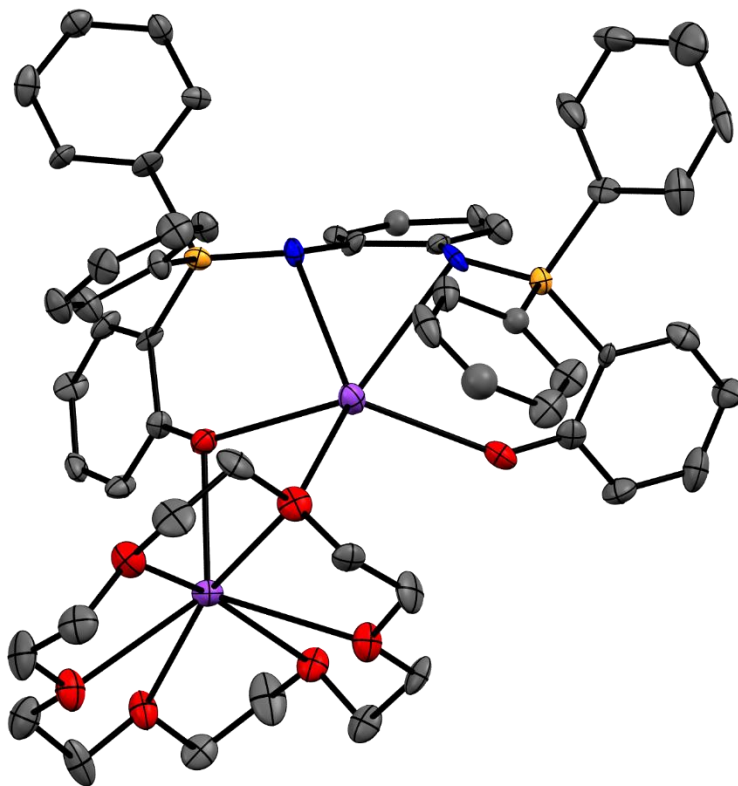
Figure S20. Connectivity structure of the product of K$_2$L″ with one equivalent of 18-crown-6 grown from toluene, [KL][K(18-crown-6)]).

Single crystals of 2-azidoaniline were grown from petroleum ether by evaporation. Single crystals of 1,2-diazidobenzene were grown in a –35° C freezer from petroleum ether and were kept cold while mounting using a steel trough with a cold nitrogen stream. Compounds **1**, **2**, and **4** were grown from benzene and were coated in a dry Paratone® oil under an inert argon atmosphere. Crystals were mounted using MiTeGen Microloops™. Crystal data was collected on a Rigaku SuperNova, Dual, Cu at zero, Pilatus 200K diffractometer. Samples were cooled to 100 K using an Oxford Cryostream device. Data reduction was accomplished by the CrysAlis^{Pro} (version 1.171.38.43) software package. Absorption corrections were applied by multi-scan techniques and empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Structures were solved in the Olex2[5] environment using intrinsic phasing and refined by full-matrix least squares method on F^2 using the SHELX software suite.[6-7] All non-hydrogen (except N–H) atoms were refined anisotropically, C–H hydrogens were calculated and refined isotropically as a riding model. N–H hydrogens were located by the Fourier difference maps and refined isotropically. Summary of the crystallographic data can be found below in **Table S1.**
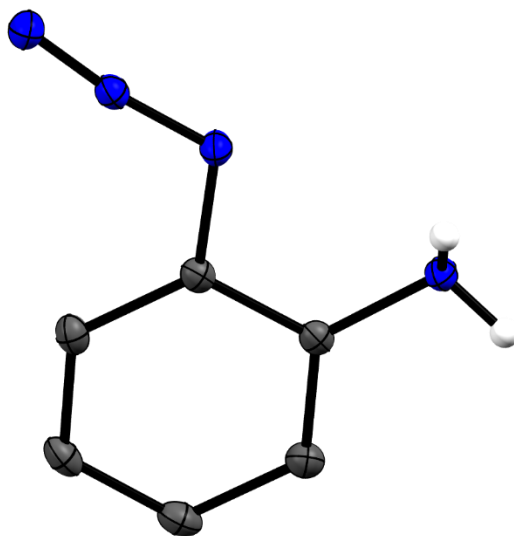
Figure S21. X-ray crystal structure of 2-azidoaniline with thermal ellipsoids drawn at 30% probability
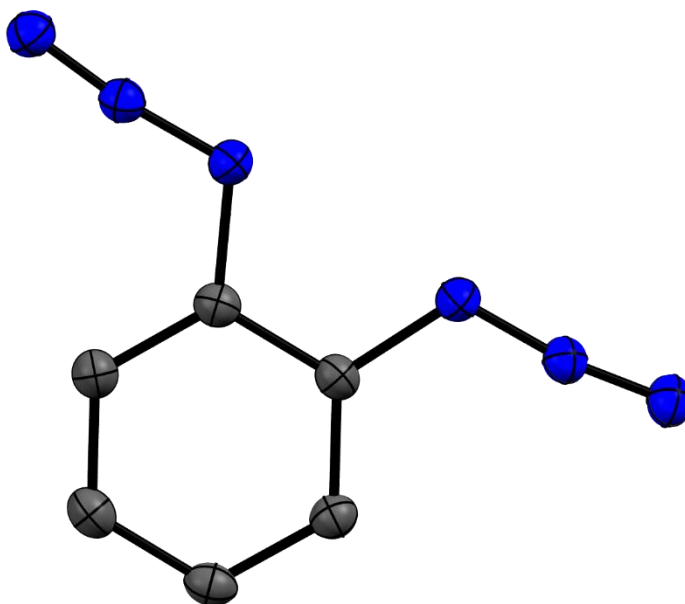
Figure S22. X-ray crystal structure of 1,2-diazidoenzene with thermal ellipsoids drawn at 30% probability
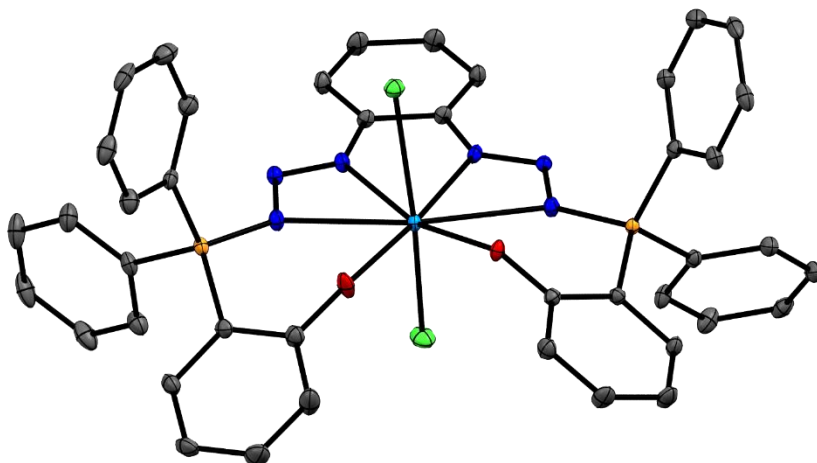
Figure S23. X-ray crystal structure of **1** with thermal ellipsoids drawn at 30% probability.

Figure S24. X-ray crystal structure of **2** with thermal ellipsoids drawn at 30% probability.

Figure S25. X-ray crystal structure of **4** with thermal ellipsoids drawn at 30% probability.

Table S1. Crystallographic data and structure refinement for 2-azidoaniline, 1,2-diazidobenzene and complexes **1, 2, 3** and **4**.

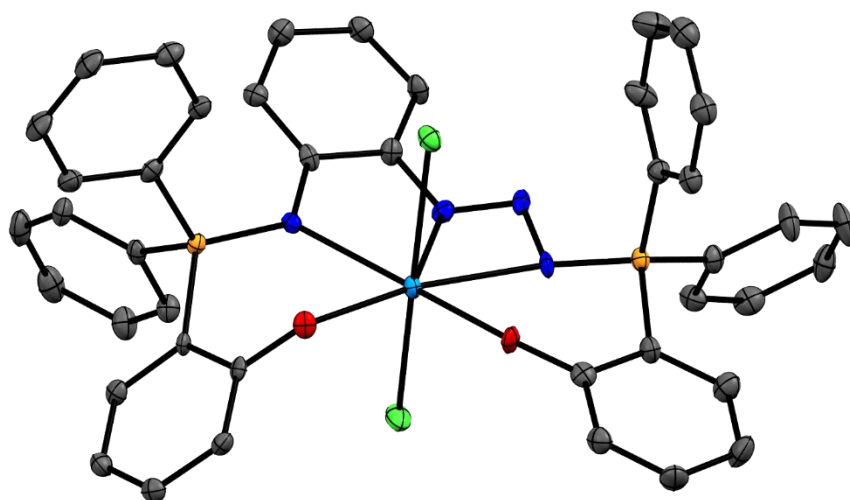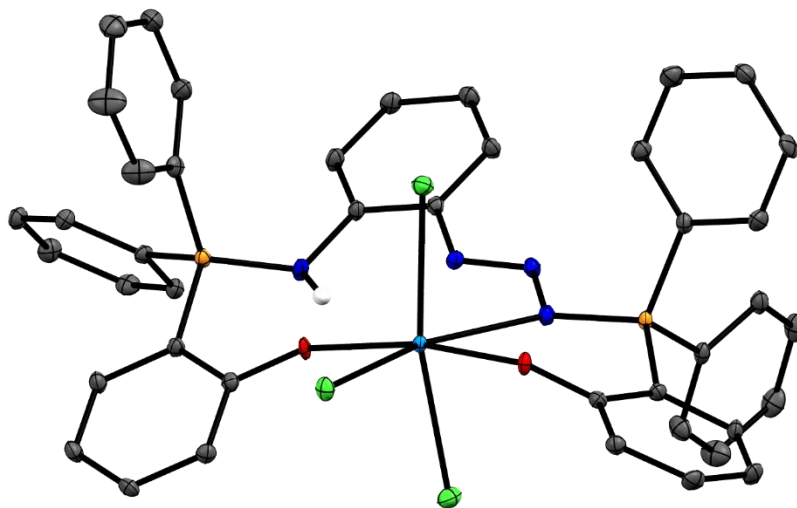|	2-azidoaniline	1,2-diazidobenzene	1 ·(C_6H_6)	2	3	4 · 2(C_6H_6)	[KL][K(18-crown-6)]
CCDC #	1533033	1533034	1533036	1942135	N/A	1533037	N/A
Empirical formula	$C_6H_6N_4$	$C_6H_4N_6$	$C_{48}H_{38}Cl_2N_6O_2P_2U$	$C_{42}H_{32}Cl_2N_4O_2P_2U$	$C_{46}H_{40}Cl_2N_2O_3P_2U$	$C_{54}H_{45}Cl_3N_4O_2P_2U$	$C_{58}H_{58}K_2N_2O_9P_2$
Formula weight/g mol^{-1}	134.15	160.15	1101.71	995.58	1039.67	1188.26	1069.22
Temperature/K	100	100	100	100	112.1(7)	100	217(100)
Crystal system	orthorhombic	monoclinic	triclinic	orthorhombic	triclinic	monoclinic	orthorhombic
Space group	Pccn	$P2_1/c$	P-1	$Pca2_1$	P-1	$P2_1/c$	Pbca
a/Å	20.3467(3)	6.7390(4)	10.72961(8)	20.8270(3)	10.5372(2)	13.79440(10)	21.006(5)
b/Å	13.1849(3)	20.3245(11)	11.58355(6)	11.8420(2)	10.7422(2)	17.44271(12)	19.068(6)
c/Å	4.90129(8)	5.2307(3)	19.45445(11)	15.7786(3)	21.1847(5)	20.42070(16)	27.591(6)
α/°	90	90	103.8451(5)	90	101.388(2)	90	90
β/°	90	95.700(5)	95.7658(6)	90	94.545(2)	94.9425(7)	90
γ/°	90	90	102.8388(6)	90	115.774(2)	90	90
Volume/Å^3	1314.87(4)	712.88(7)	2258.65(2)	3891.53(11)	2079.53(8)	4895.19(6)	11051(5)
Z	8	4	2	4	2	4	8
ρ_{calc}g/cm^3	1.355	1.492	1.620	1.699	1.660	1.611	1.285
μ/mm^{-1}	0.752	0.887	12.240	14.116	13.239	11.821	2.526
F(000)	560.0	328.0	1080.0	1936.0	1020.0	2340.0	4496.0
Crystal size/mm^3	0.2 x 0.2 x 0.2	0.2 x 0.2 x 0.15	0.5 x 0.1 x 0.1	0.1 x 0.05 x 0.01	0.3 x 0.2 x 0.05	0.3 x 0.3 x 0.3	0.2 x 0.25 x 0.1
Radiation (Å)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.99 to 154.892	13.204 to 160.6	8.13 to 160.384	7.466 to 133.99	8.668 to 160.642	6.674 to 159.382	7.666 to 104.37
Index ranges	-25 ≤ h ≤ 25 -15 ≤ k ≤ 16 -6 ≤ l ≤ 6	-6 ≤ h ≤ 8 -25 ≤ k ≤ 25 -6 ≤ l ≤ 6	-13 ≤ h ≤ 13 -13 ≤ k ≤ 14 -24 ≤ l ≤ 24	-24 ≤ h ≤ 24, -13 ≤ k ≤ 14, -17 ≤ l ≤ 18	-10 ≤ h ≤ 13, -12 ≤ k ≤ 13, -27 ≤ l ≤ 26	-17 ≤ h ≤ 17 -13 ≤ k ≤ 22 -24 ≤ l ≤ 26	-19 ≤ h ≤ 9, -7 ≤ k ≤ 19, -14 ≤ l ≤ 25
Reflections collected	6939	7702	87431	20838	46261	55054	7967
Independent reflections	1371 R_{int} = 0.0200 R_{sigma} = 0.0116	1543 R_{int} = 0.0679 R_{sigma} = 0.0336	9778 R_{int} = 0.0408 R_{sigma} = 0.0188	6585 R_{int} = 0.0596, R_{sigma} = 0.0573	9068 R_{int} = 0.0645, R_{sigma} = 0.0435	10594 R_{int} = 0.0315 R_{sigma} = 0.0217	4674 R_{int} = 0.1127, R_{sigma} = 0.1866
Data/restraints/parameters	1371/0/100	1543/0/109	9778/0/551	6585/19/478	9068/0/500	10594/0/596	4674/0/642
Goodness-of-fit on F^2 (S)^a	1.079	1.044	1.122	1.001	1.158	1.119	0.979
Final R indexes [I>=2σ (I)]^b	R_1 = 0.0321 wR_2 = 0.0865	R_1 = 0.0552 wR_2 = 0.1445	R_1 = 0.0234 wR_2 = 0.0574	R1 = 0.0336, wR2 = 0.0802	R_1 = 0.1064, wR_2 = 0.2949	R_1 = 0.0290 wR_2 = 0.0804	R_1 = 0.0902, wR_2 = 0.2112
Final R indexes [all data]^b	R_1 = 0.0333 wR_2 = 0.0875	R_1 = 0.0644 wR_2 = 0.1537	R_1 = 0.0242 wR_2 = 0.0577	R1 = 0.0373, wR2 = 0.0817	R_1 = 0.1076, wR_2 = 0.2952	R_1 = 0.0300 wR_2 = 0.0812	R_1 = 0.1735, wR_2 = 0.2613
Largest diff. peak/hole / e Å^{-3}	0.22/-0.17	0.27/-0.26	1.24/-1.54	1.76/-1.63	11.78/-8.77	1.30/-1.24	0.79/-0.36

Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by Rigaku.

^{a} $S = [w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0540P)^2 + 22.8160P]^{-1}$ where $P = [Max(F_o^2, 0) + 2F_c^2]/3$).

^{b} $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2-azidoanline. U$_{eq}$ is defined as 1/3 of of the trace of the orthogonalised U$_{IJ}$ tensor.

Atom	x	y	z	U(eq)
N1	7030.7(4)	3542.1(6)	2775.2(18)	20.2(2)
N3	5653.7(4)	3514.0(6)	8507.7(19)	21.3(2)
N2	6085.2(4)	3513.0(7)	6711.1(18)	22.2(2)
N4	5278.4(5)	3410.0(7)	10191.6(19)	27.3(3)
C1	6668.2(5)	4428.0(7)	3252(2)	19.0(2)
C2	6186.0(5)	4451.9(8)	5299(2)	19.5(2)
C4	5977.9(5)	6220.4(8)	4449(2)	26.2(3)
C3	5841.6(5)	5336.9(8)	5876(2)	23.1(3)
C6	6799.4(5)	5326.0(8)	1848(2)	23.2(3)
C5	6460.7(5)	6213.9(8)	2445(2)	27.3(3)

Table S3. Anisotropic Displacement Parameters (Å^2×10^3) for 2-azidoanline. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U$_{11}$	U$_{22}$	U$_{33}$	U$_{23}$	U$_{13}$	U$_{12}$
N1	22.2(4)	17.7(4)	20.6(4)	-0.6(3)	2.3(3)	0.4(3)
N3	22.3(4)	18.6(4)	22.9(5)	-1.4(3)	-1.1(4)	2.4(3)
N2	24.4(5)	19.1(5)	23.1(5)	-0.5(3)	5.2(4)	1.9(3)
N4	27.6(5)	27.1(5)	27.3(5)	1.1(4)	6.0(4)	3.7(4)
C1	19.5(5)	17.9(5)	19.7(5)	-2.3(4)	-4.1(4)	0.2(4)
C2	20.8(5)	17.4(5)	20.3(5)	-1.4(4)	-3.5(4)	-0.6(4)
C4	27.5(5)	17.9(5)	33.3(6)	-3.4(4)	-5.9(5)	5.1(4)
C3	22.1(5)	21.9(5)	25.2(5)	-4.6(4)	-1.3(4)	2.1(4)
C6	23.9(5)	22.9(5)	22.8(5)	1.3(4)	-1.4(4)	-0.2(4)
C5	31.0(6)	19.9(6)	31.1(6)	3.9(4)	-5.4(5)	0.7(4)

Table S4. Bond Lengths for 2-azidoanline.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.4010(13)	C1	C6	1.3952(15)
N3	N2	1.2436(12)	C2	C3	1.3902(14)
N3	N4	1.1327(13)	C4	C3	1.3868(16)
N2	C2	1.4331(13)	C4	C5	1.3891(17)
C1	C2	1.4036(15)	C6	C5	1.3896(15)

Table S5. Bond Angles for 2-azidoanline.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N4	N3	N2	172.66(10)	C3	C2	N2	123.69(9)
N3	N2	C2	116.24(8)	C3	C2	C1	121.11(10)
N1	C1	C2	120.39(9)	C3	C4	C5	119.53(10)
C6	C1	N1	121.63(9)	C4	C3	C2	120.10(10)
C6	C1	C2	117.85(9)	C5	C6	C1	121.08(10)
C1	C2	N2	115.20(9)	C4	C5	C6	120.32(10)

Table S6. Torsion Angles for 2-azidoanline.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C1	C2	N2	-2.44(13)	C1	C6	C5	C4	-0.57(16)
N1	C1	C2	C3	177.23(9)	C2	C1	C6	C5	-0.40(15)
N1	C1	C6	C5	-176.44(10)	C3	C4	C5	C6	0.81(16)
N3	N2	C2	C1	-179.05(9)	C6	C1	C2	N2	-178.53(9)
N3	N2	C2	C3	1.29(15)	C6	C1	C2	C3	1.14(15)
N2	C2	C3	C4	178.73(9)	C5	C4	C3	C2	-0.07(16)
C1	C2	C3	C4	-0.92(16)					

Table S7. Hydrogen Atom Coordinates ($\text{Å} \times 10^4$) and Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for 2-azidoanline.

Atom	x	y	z	U(eq)
H1A	6775	3024	2869	24
H1B	7205	3571	1177	24
H4	5748	6813	4830	31
H3	5519	5337	7221	28
H6	7119	5330	490	28
H5	6558	6807	1498	33

Table S8. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for 1,2-diazidobenzene. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
C1	6532(2)	5882.1(7)	5109(3)	32.3(4)
C2	6677(2)	6328.2(8)	3100(3)	32.4(4)
C3	5149(3)	6778.2(8)	2465(3)	35.0(4)
C4	3467(3)	6777.0(8)	3805(3)	37.9(4)
C5	3318(3)	6329.8(9)	5786(3)	39.0(4)
C6	4845(2)	5886.9(8)	6438(3)	36.0(4)
N1	8187(2)	5450.9(7)	5665(3)	37.3(4)
N2	8016(2)	5055.2(7)	7454(3)	35.2(4)

N3	8033(2)	4676.4(7)	9033(3)	39.9(4)
N4	8438(2)	6285.5(7)	1816(3)	38.4(4)
N5	8657(2)	6703.3(7)	133(3)	35.4(4)
N6	9063(3)	7045.1(8)	-1440(3)	42.2(4)

Table S9. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 1,2-diazidobenzene. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a*^2U_{11}+2hka*b*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	32.5(8)	29.8(8)	34.5(8)	-3.6(6)	1.9(6)	-0.5(6)
C2	31.5(8)	32.9(8)	32.9(8)	-3.7(6)	3.6(6)	-1.0(6)
C3	37.8(8)	30.2(8)	36.5(9)	-0.8(6)	1.6(6)	-0.6(6)
C4	34.3(8)	34.0(8)	44.7(10)	-6.3(7)	0.3(7)	3.2(6)
C5	34.7(8)	41.1(9)	41.9(10)	-7.0(7)	7.4(7)	-2.0(7)
C6	36.5(9)	36.4(9)	35.3(9)	-2.0(6)	4.2(6)	-2.5(7)
N1	35.9(8)	36.8(7)	39.5(8)	6.2(6)	5.4(6)	2.1(5)
N2	34.0(7)	34.5(7)	36.9(8)	-0.8(6)	2.7(5)	-0.4(5)
N3	41.1(8)	37.6(8)	40.7(8)	3.3(6)	2.4(6)	-0.2(6)
N4	39.3(8)	36.3(7)	40.7(8)	6.2(6)	9.3(6)	4.2(6)
N5	37.3(7)	34.3(7)	35.0(7)	-1.8(6)	5.3(5)	-0.9(5)
N6	48.2(9)	38.6(8)	41.0(8)	1.8(6)	9.9(6)	-2.8(6)

Table S10. Bond Lengths for 1,2-diazidobenzene.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.398(2)	C4	C5	1.389(3)
C1	C6	1.390(2)	C5	C6	1.384(2)
C1	N1	1.426(2)	N1	N2	1.2476(19)
C2	C3	1.393(2)	N2	N3	1.129(2)
C2	N4	1.423(2)	N4	N5	1.2425(19)
C3	C4	1.390(2)	N5	N6	1.131(2)

Table S11. Bond Angles for 1,2-diazidobenzene.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	N1	116.10(14)	C5	C4	C3	120.00(15)
C6	C1	C2	119.56(15)	C6	C5	C4	120.15(16)
C6	C1	N1	124.34(15)	C5	C6	C1	120.39(16)
C1	C2	N4	116.04(14)	N2	N1	C1	114.85(13)
C3	C2	C1	119.97(15)	N3	N2	N1	173.55(16)
C3	C2	N4	123.99(15)	N5	N4	C2	117.14(14)
C4	C3	C2	119.94(16)	N6	N5	N4	171.74(17)

Table S12. Torsion Angles for 1,2-diazidobenzene.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	-0.9(2)	C6	C1	C2	C3	0.7(2)
C1	C2	N4	N5	-175.65(14)	C6	C1	C2	N4	-179.22(14)
C2	C1	C6	C5	0.0(2)	C6	C1	N1	N2	1.2(2)
C2	C1	N1	N2	-179.58(13)	N1	C1	C2	C3	-178.48(14)
C2	C3	C4	C5	0.4(2)	N1	C1	C2	N4	1.6(2)
C3	C2	N4	N5	4.4(2)	N1	C1	C6	C5	179.13(15)
C3	C4	C5	C6	0.3(2)	N4	C2	C3	C4	179.03(15)
C4	C5	C6	C1	-0.5(3)					

Table S13. Hydrogen Atom Coordinates ($\mathring{A}\times10^4$) and Isotropic Displacement Parameters ($\mathring{A}^2\times10^3$) for 1,2-diazidobenzene.

Atom	x	y	z	U(eq)
H3	5256	7086	1118	42
H4	2420	7082	3366	45
H5	2166	6328	6694	47
H6	4741	5584	7803	43

Table S14. Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($\mathring{A}^2\times10^3$) for Complex **1**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
C1	4834(3)	4173(3)	886.6(15)	17.0(5)
C2	4084(3)	3710(3)	205.8(16)	23.5(6)
C3	3064(3)	4211(3)	44.0(17)	27.0(7)
C4	2794(3)	5152(3)	555.8(18)	27.6(7)
C5	3523(3)	5615(3)	1235.7(17)	23.0(6)
C6	4548(3)	5118(3)	1403.1(15)	16.6(5)
C7	8613(3)	6095(3)	4102.8(15)	16.6(5)
C8	8219(3)	7201(3)	4274.8(15)	16.4(5)
C9	8984(3)	8227(3)	4813.9(17)	22.8(6)
C10	10126(3)	8166(3)	5182.9(19)	29.2(7)
C11	10503(3)	7068(3)	5020.9(19)	30.1(7)
C12	9771(3)	6055(3)	4488.5(17)	24.0(6)
C13	9794(3)	2622(3)	1533.0(17)	20.1(6)
C14	9888(3)	3336(3)	2242.3(18)	24.8(6)
C15	11133(4)	3799(4)	2660(2)	38.3(9)
C16	12210(3)	3540(4)	2396(2)	37.9(9)
C17	12114(3)	2821(3)	1702(2)	30.2(7)
C18	10912(3)	2372(3)	1271.0(18)	24.8(6)
C19	8412(3)	1708(3)	59.6(16)	22.1(6)

C20	9137(3)	2679(3)	-161.4(19)	29.0(7)
C21	9219(4)	2542(4)	-879(2)	37.6(9)
C22	8583(4)	1450(4)	-1381(2)	41.4(10)
C23	7853(5)	487(4)	-1172.8(19)	40.1(9)
C24	7769(4)	608(3)	-446.1(18)	30.8(7)
C25	7529(3)	544(3)	1159.9(15)	19.8(6)
C26	8309(4)	-217(3)	1299.5(18)	27.4(7)
C27	7759(4)	-1316(3)	1445.4(18)	33.8(8)
C28	6450(4)	-1655(3)	1449.8(17)	32.6(8)
C29	5662(4)	-909(3)	1308.0(19)	34.9(8)
C30	6198(3)	197(3)	1162.3(18)	27.4(7)
C31	5497(3)	6802(3)	4412.2(16)	17.9(5)
C32	4201(3)	6317(3)	4094.3(17)	24.3(6)
C33	3295(3)	5915(3)	4499(2)	31.6(8)
C34	3659(4)	6003(3)	5215(2)	31.0(8)
C35	4936(4)	6498(3)	5536.6(18)	28.0(7)
C36	5863(3)	6895(3)	5138.5(17)	22.6(6)
C37	6714(3)	8823(3)	3858.0(15)	17.1(5)
C38	7133(3)	9200(3)	3275.1(16)	24.2(6)
C39	7139(4)	10377(3)	3225.6(17)	28.3(7)
C40	6738(3)	11172(3)	3760.9(18)	25.0(7)
C41	6352(3)	10809(3)	4348.5(18)	24.5(6)
C42	6324(3)	9628(3)	4400.0(17)	22.7(6)
Cl1	5316.3(7)	2678.0(6)	2523.5(4)	22.05(14)
Cl2	8721.2(8)	6180.1(7)	1986.2(5)	31.52(17)
N1	7409(2)	2979(2)	1223.2(13)	19.6(5)
N2	6375(2)	3016(2)	774.4(13)	17.9(5)
N3	5917(2)	3825(2)	1152.0(13)	18.2(5)
N4	6411(2)	6341(2)	3073.4(13)	18.1(5)
N5	5412(2)	6319(2)	2580.3(13)	16.2(5)
N6	5402(2)	5423(2)	2051.2(13)	17.5(5)
O1	8868(2)	3579(2)	2517.3(12)	27.0(5)
O2	7922(2)	5098.7(18)	3603.0(10)	17.5(4)
P1	8247.2(7)	1978.6(6)	987.3(4)	16.63(14)
P2	6682.4(6)	7273.9(6)	3877.1(4)	14.03(13)
U1	7257.0(2)	4456.5(2)	2424.9(2)	13.38(3)

Table S15. Anisotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for Complex **1**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	18.5(13)	17.2(13)	15.1(13)	4.1(11)	0.1(10)	5.8(11)
C2	27.2(15)	25.5(15)	15.9(14)	0.2(12)	1.4(12)	9.3(12)
C3	26.3(16)	32.7(17)	17.9(15)	1.6(13)	-7.3(12)	9.6(13)

C4	25.6(16)	29.3(17)	27.3(17)	4.0(13)	-4.5(13)	13.8(13)
C5	25.7(15)	21.8(15)	21.1(15)	0.8(12)	1.9(12)	11.6(12)
C6	17.2(13)	17.2(13)	15.1(13)	4.4(11)	-1.0(10)	5.2(10)
C7	18.1(13)	16.4(13)	14.7(13)	4.1(10)	3.3(10)	2.7(10)
C8	16.0(13)	17.8(13)	15.3(13)	3.0(11)	2.4(10)	5.5(10)
C9	22.4(14)	17.5(14)	23.5(15)	-3.3(12)	-1.3(12)	7.1(12)
C10	22.3(15)	23.9(16)	31.9(18)	-3.7(13)	-8.7(13)	4.5(12)
C11	21.4(15)	27.7(17)	36.1(19)	1.8(14)	-9.5(13)	9.5(13)
C12	22.4(15)	23.4(15)	27.0(16)	4.7(12)	1.7(12)	10.7(12)
C13	18.7(14)	16.3(13)	26.6(15)	5.9(12)	4.3(12)	6.8(11)
C14	24.5(15)	24.3(16)	25.8(16)	3.8(13)	2.6(12)	10.8(12)
C15	29.6(18)	42(2)	35(2)	-7.7(16)	-6.2(15)	18.5(16)
C16	21.9(16)	34.6(19)	51(2)	1.7(17)	-3.8(15)	8.6(14)
C17	18.5(15)	27.9(17)	48(2)	12.3(15)	10.5(14)	10.3(13)
C18	24.4(15)	24.3(16)	29.8(17)	7.4(13)	10.8(13)	11.3(12)
C19	28.9(15)	25.2(15)	18.6(14)	6.9(12)	9.3(12)	16.0(13)
C20	35.5(18)	27.0(17)	31.5(18)	11.3(14)	14.9(14)	14.7(14)
C21	48(2)	45(2)	37(2)	23.0(17)	26.3(17)	24.5(18)
C22	66(3)	53(2)	23.4(17)	16.3(17)	22.9(18)	37(2)
C23	69(3)	36(2)	20.5(17)	3.1(15)	9.8(17)	27.9(19)
C24	49(2)	24.8(16)	21.6(16)	4.6(13)	10.0(15)	15.1(15)
C25	27.7(15)	14.9(13)	14.8(13)	0.3(10)	5.4(11)	4.6(11)
C26	36.6(18)	23.7(16)	24.8(16)	7.4(13)	6.3(14)	11.8(14)
C27	56(2)	21.7(16)	23.9(17)	6.0(13)	2.9(16)	12.5(16)
C28	58(2)	14.9(15)	17.2(15)	2.3(12)	2.4(15)	-3.2(14)
C29	36.3(19)	31.1(18)	28.7(18)	6.5(14)	4.0(15)	-6.8(15)
C30	30.2(17)	22.5(16)	26.9(16)	4.2(13)	4.4(13)	4.6(13)
C31	20.8(14)	14.4(13)	19.0(14)	2.7(11)	4.1(11)	7.2(11)
C32	22.4(15)	24.9(16)	22.7(15)	0.4(12)	5.5(12)	5.8(12)
C33	24.7(16)	26.6(17)	37.3(19)	-0.4(14)	11.0(14)	0.8(13)
C34	39.8(19)	17.7(15)	41(2)	8.7(14)	27.6(16)	9.2(13)
C35	43.4(19)	25.8(16)	25.3(16)	10.9(13)	16.0(14)	21.1(15)
C36	27.0(15)	23.7(15)	20.6(15)	5.9(12)	6.9(12)	12.6(12)
C37	16.6(13)	15.3(13)	18.3(14)	1.9(11)	0.3(10)	5.8(10)
C38	35.7(17)	19.3(15)	15.5(14)	1.7(11)	3.9(12)	6.3(13)
C39	41.9(19)	21.9(16)	18.4(15)	6.5(12)	0.8(13)	3.4(14)
C40	24.0(15)	15.9(14)	30.9(17)	4.0(12)	-6.7(13)	4.1(12)
C41	23.3(15)	17.5(14)	33.7(17)	3.6(12)	7.0(13)	9.7(12)
C42	21.7(14)	19.9(14)	26.0(16)	4.1(12)	5.6(12)	5.7(12)
Cl1	21.8(3)	22.2(3)	21.3(3)	6.6(3)	3.5(3)	3.3(3)
Cl2	31.1(4)	28.9(4)	40.1(4)	17.2(3)	14.3(3)	6.7(3)
N1	21.9(12)	21.7(12)	16.5(12)	2.1(10)	2.1(9)	11.8(10)
N2	20.2(12)	18.5(12)	15.1(11)	3.0(9)	3.5(9)	6.8(9)
N3	20.1(12)	18.4(12)	17.6(12)	3.2(9)	4.9(9)	8.7(10)

N4	19.3(11)	21.4(12)	12.8(11)	1.7(9)	-0.1(9)	7.7(10)
N5	15.8(11)	15.8(11)	15.9(11)	2.0(9)	1.9(9)	4.9(9)
N6	21.8(12)	14.5(11)	13.8(11)	-0.1(9)	2.6(9)	4.3(9)
O1	24.0(11)	38.8(13)	21.7(11)	2.3(9)	0.9(9)	22.5(10)
O2	24.4(10)	15.6(9)	11.2(9)	0.8(7)	-1.1(8)	6.9(8)
P1	19.7(3)	15.8(3)	16.0(3)	2.9(3)	5.8(3)	7.9(3)
P2	15.3(3)	13.7(3)	12.5(3)	1.0(2)	1.7(2)	5.5(2)
U1	15.88(5)	12.94(5)	11.81(5)	1.93(3)	2.69(3)	5.97(3)

Table S16. Bond Lengths for Complex **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.394(4)	C25	P1	1.794(3)
C1	C6	1.410(4)	C26	C27	1.386(5)
C1	N3	1.402(4)	C27	C28	1.373(6)
C2	C3	1.391(4)	C28	C29	1.389(6)
C3	C4	1.393(5)	C29	C30	1.390(5)
C4	C5	1.384(4)	C31	C32	1.394(4)
C5	C6	1.395(4)	C31	C36	1.400(4)
C6	N6	1.402(4)	C31	P2	1.797(3)
C7	C8	1.413(4)	C32	C33	1.382(5)
C7	C12	1.401(4)	C33	C34	1.383(5)
C7	O2	1.329(3)	C34	C35	1.380(5)
C8	C9	1.409(4)	C35	C36	1.386(5)
C8	P2	1.778(3)	C37	C38	1.389(4)
C9	C10	1.381(4)	C37	C42	1.396(4)
C10	C11	1.394(5)	C37	P2	1.796(3)
C11	C12	1.383(5)	C38	C39	1.388(5)
C13	C14	1.409(4)	C39	C40	1.387(5)
C13	C18	1.411(4)	C40	C41	1.380(5)
C13	P1	1.776(3)	C41	C42	1.389(4)
C14	C15	1.410(5)	Cl1	U1	2.6419(7)
C14	O1	1.322(4)	Cl2	U1	2.6218(8)
C15	C16	1.374(5)	N1	N2	1.357(3)
C16	C17	1.388(5)	N1	P1	1.629(2)
C17	C18	1.383(5)	N1	U1	2.590(2)
C19	C20	1.402(5)	N2	N3	1.268(3)
C19	C24	1.393(5)	N3	U1	2.586(2)
C19	P1	1.790(3)	N4	N5	1.357(3)
C20	C21	1.382(5)	N4	P2	1.630(2)
C21	C22	1.381(6)	N4	U1	2.641(2)
C22	C23	1.383(6)	N5	N6	1.272(3)
C23	C24	1.401(5)	N6	U1	2.613(2)
C25	C26	1.396(4)	O1	U1	2.204(2)

C25	C30	1.396(5)	O2	U1	2.2213(19)		

Table S17. Bond Angles for Complex **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C6	120.5(3)	C41	C40	C39	120.5(3)
C2	C1	N3	127.9(3)	C40	C41	C42	120.3(3)
N3	C1	C6	111.6(2)	C41	C42	C37	119.3(3)
C3	C2	C1	118.7(3)	N2	N1	P1	121.38(19)
C2	C3	C4	120.5(3)	N2	N1	U1	102.88(16)
C5	C4	C3	121.5(3)	P1	N1	U1	134.75(13)
C4	C5	C6	118.5(3)	N3	N2	N1	103.7(2)
C5	C6	C1	120.4(3)	C1	N3	U1	131.03(18)
C5	C6	N6	128.7(3)	N2	N3	C1	122.7(2)
N6	C6	C1	110.9(2)	N2	N3	U1	106.11(18)
C12	C7	C8	117.9(3)	N5	N4	P2	120.62(19)
O2	C7	C8	122.7(3)	N5	N4	U1	102.56(16)
O2	C7	C12	119.4(3)	P2	N4	U1	136.20(13)
C7	C8	P2	120.6(2)	N6	N5	N4	104.1(2)
C9	C8	C7	120.3(3)	C6	N6	U1	130.41(18)
C9	C8	P2	118.8(2)	N5	N6	C6	122.7(2)
C10	C9	C8	120.6(3)	N5	N6	U1	106.81(17)
C9	C10	C11	119.0(3)	C14	O1	U1	145.2(2)
C12	C11	C10	121.2(3)	C7	O2	U1	140.11(18)
C11	C12	C7	120.9(3)	C13	P1	C19	109.99(15)
C14	C13	C18	120.2(3)	C13	P1	C25	108.89(14)
C14	C13	P1	119.5(2)	C19	P1	C25	109.04(14)
C18	C13	P1	120.3(2)	N1	P1	C13	105.57(13)
C13	C14	C15	117.3(3)	N1	P1	C19	112.05(14)
O1	C14	C13	122.5(3)	N1	P1	C25	111.22(14)
O1	C14	C15	120.2(3)	C8	P2	C31	108.63(13)
C16	C15	C14	121.6(3)	C8	P2	C37	110.34(13)
C15	C16	C17	121.1(3)	C37	P2	C31	108.26(13)
C18	C17	C16	118.9(3)	N4	P2	C8	105.15(13)
C17	C18	C13	120.9(3)	N4	P2	C31	112.33(13)
C20	C19	P1	117.9(2)	N4	P2	C37	112.07(13)
C24	C19	C20	119.9(3)	Cl2	U1	Cl1	163.07(3)
C24	C19	P1	122.1(3)	Cl2	U1	N4	81.17(6)
C21	C20	C19	120.0(3)	N1	U1	Cl1	86.20(6)
C22	C21	C20	120.1(4)	N1	U1	Cl2	85.69(6)
C21	C22	C23	120.7(3)	N1	U1	N4	147.29(8)
C22	C23	C24	119.9(4)	N1	U1	N6	102.50(7)
C19	C24	C23	119.4(3)	N3	U1	Cl1	78.59(6)
C26	C25	C30	120.2(3)	N3	U1	Cl2	85.01(6)

C26	C25	P1	119.7(2)	N3	U1	N1	47.02(8)
C30	C25	P1	120.1(2)	N3	U1	N4	101.78(7)
C27	C26	C25	119.8(3)	N3	U1	N6	55.64(7)
C28	C27	C26	120.1(3)	N4	U1	Cl1	97.98(6)
C27	C28	C29	120.8(3)	N6	U1	Cl1	83.50(6)
C28	C29	C30	120.0(3)	N6	U1	Cl2	83.80(6)
C29	C30	C25	119.3(3)	N6	U1	N4	46.50(7)
C32	C31	C36	119.8(3)	O1	U1	Cl1	99.98(7)
C32	C31	P2	119.4(2)	O1	U1	Cl2	90.53(7)
C36	C31	P2	120.8(2)	O1	U1	N1	67.28(8)
C33	C32	C31	119.5(3)	O1	U1	N3	114.31(8)
C32	C33	C34	120.6(3)	O1	U1	N4	142.12(8)
C35	C34	C33	120.3(3)	O1	U1	N6	168.75(8)
C34	C35	C36	120.0(3)	O1	U1	O2	79.67(8)
C35	C36	C31	119.8(3)	O2	U1	Cl1	93.38(6)
C38	C37	C42	120.4(3)	O2	U1	Cl2	101.59(6)
C38	C37	P2	117.6(2)	O2	U1	N1	146.29(7)
C42	C37	P2	122.0(2)	O2	U1	N3	164.73(8)
C39	C38	C37	119.7(3)	O2	U1	N4	66.18(7)
C40	C39	C38	119.8(3)	O2	U1	N6	110.94(7)

Table S18. Torsion Angles for Complex **1**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	-0.5(5)	C30	C25	P1	C13	143.2(3)
C1	C6	N6	N5	173.9(3)	C30	C25	P1	C19	-96.8(3)
C1	C6	N6	U1	-3.4(4)	C30	C25	P1	N1	27.3(3)
C2	C1	C6	C5	-1.0(4)	C31	C32	C33	C34	0.7(5)
C2	C1	C6	N6	178.6(3)	C32	C31	C36	C35	0.3(4)
C2	C1	N3	N2	1.4(5)	C32	C31	P2	C8	-154.8(2)
C2	C1	N3	U1	-173.6(2)	C32	C31	P2	C37	85.4(3)
C2	C3	C4	C5	0.0(6)	C32	C31	P2	N4	-38.9(3)
C3	C4	C5	C6	0.0(5)	C32	C33	C34	C35	0.3(5)
C4	C5	C6	C1	0.5(5)	C33	C34	C35	C36	-0.9(5)
C4	C5	C6	N6	-179.1(3)	C34	C35	C36	C31	0.6(5)
C5	C6	N6	N5	-6.4(5)	C36	C31	C32	C33	-1.0(5)
C5	C6	N6	U1	176.3(2)	C36	C31	P2	C8	24.0(3)
C6	C1	C2	C3	1.0(5)	C36	C31	P2	C37	-95.9(3)
C6	C1	N3	N2	-177.9(3)	C36	C31	P2	N4	139.9(2)
C6	C1	N3	U1	7.2(4)	C37	C38	C39	C40	0.5(5)
C7	C8	C9	C10	-0.2(5)	C38	C37	C42	C41	0.3(5)
C7	C8	P2	C31	87.1(3)	C38	C37	P2	C8	86.6(3)
C7	C8	P2	C37	-154.3(2)	C38	C37	P2	C31	-154.6(2)
C7	C8	P2	N4	-33.3(3)	C38	C37	P2	N4	-30.2(3)

C8	C7	C12	C11	0.0(5)	C38	C39	C40	C41	1.0(5)
C8	C7	O2	U1	65.5(4)	C39	C40	C41	C42	-1.9(5)
C8	C9	C10	C11	-0.8(5)	C40	C41	C42	C37	1.2(5)
C9	C8	P2	C31	-86.9(3)	C42	C37	C38	C39	-1.2(5)
C9	C8	P2	C37	31.6(3)	C42	C37	P2	C8	-94.0(3)
C9	C8	P2	N4	152.6(2)	C42	C37	P2	C31	24.7(3)
C9	C10	C11	C12	1.5(6)	C42	C37	P2	N4	149.2(2)
C10	C11	C12	C7	-1.1(6)	N1	N2	N3	C1	178.9(3)
C12	C7	C8	C9	0.6(4)	N1	N2	N3	U1	-5.1(2)
C12	C7	C8	P2	-173.3(2)	N2	N1	P1	C13	157.0(2)
C12	C7	O2	U1	-115.7(3)	N2	N1	P1	C19	37.3(3)
C13	C14	C15	C16	-1.8(6)	N2	N1	P1	C25	-85.1(3)
C13	C14	O1	U1	-61.2(5)	N3	C1	C2	C3	-178.2(3)
C14	C13	C18	C17	-0.2(5)	N3	C1	C6	C5	178.3(3)
C14	C13	P1	C19	155.5(2)	N3	C1	C6	N6	-2.0(3)
C14	C13	P1	C25	-85.1(3)	N4	N5	N6	C6	-176.5(2)
C14	C13	P1	N1	34.4(3)	N4	N5	N6	U1	1.3(2)
C14	C15	C16	C17	0.8(7)	N5	N4	P2	C8	-169.6(2)
C15	C14	O1	U1	118.5(4)	N5	N4	P2	C31	72.5(2)
C15	C16	C17	C18	0.5(6)	N5	N4	P2	C37	-49.7(3)
C16	C17	C18	C13	-0.8(5)	O1	C14	C15	C16	178.5(4)
C18	C13	C14	C15	1.4(5)	O2	C7	C8	C9	179.5(3)
C18	C13	C14	O1	-178.8(3)	O2	C7	C8	P2	5.5(4)
C18	C13	P1	C19	-27.6(3)	O2	C7	C12	C11	-178.9(3)
C18	C13	P1	C25	91.8(3)	P1	C13	C14	C15	178.4(3)
C18	C13	P1	N1	-148.7(2)	P1	C13	C14	O1	-1.9(4)
C19	C20	C21	C22	0.3(5)	P1	C13	C18	C17	-177.1(3)
C20	C19	C24	C23	-0.2(5)	P1	C19	C20	C21	-175.6(3)
C20	C19	P1	C13	-50.8(3)	P1	C19	C24	C23	174.9(3)
C20	C19	P1	C25	-170.2(2)	P1	C25	C26	C27	178.9(3)
C20	C19	P1	N1	66.3(3)	P1	C25	C30	C29	-179.0(3)
C20	C21	C22	C23	0.3(6)	P1	N1	N2	N3	175.2(2)
C21	C22	C23	C24	-0.9(6)	P2	C8	C9	C10	173.8(3)
C22	C23	C24	C19	0.8(6)	P2	C31	C32	C33	177.8(3)
C24	C19	C20	C21	-0.3(5)	P2	C31	C36	C35	-178.5(2)
C24	C19	P1	C13	134.0(3)	P2	C37	C38	C39	178.1(3)
C24	C19	P1	C25	14.6(3)	P2	C37	C42	C41	-179.0(2)
C24	C19	P1	N1	-108.9(3)	P2	N4	N5	N6	-173.7(2)
C25	C26	C27	C28	0.3(5)	U1	N1	N2	N3	5.0(2)
C26	C25	C30	C29	0.3(5)	U1	N1	P1	C13	-36.6(2)
C26	C25	P1	C13	-36.1(3)	U1	N1	P1	C19	-156.30(18)
C26	C25	P1	C19	83.9(3)	U1	N1	P1	C25	81.4(2)
C26	C25	P1	N1	-152.0(2)	U1	N4	N5	N6	-1.3(2)
C26	C27	C28	C29	0.1(5)	U1	N4	P2	C8	21.2(2)

C27	C28	C29	C30	-0.3(5)	U1	N4	P2	C31	-96.8(2)
C28	C29	C30	C25	0.1(5)	U1	N4	P2	C37	141.09(18)
C30	C25	C26	C27	-0.4(5)					

Table S19. Hydrogen Atom Coordinates ($Å×10^4$) and Isotropic Displacement Parameters ($Å^2×10^3$) for Complex **1**.

Atom	x	y	z	U(eq)
H2	4262	3077	-134	28
H3	2559	3916	-409	32
H4	2109	5476	438	33
H5	3335	6243	1573	28
H9	8718	8952	4922	27
H10	10636	8848	5534	35
H11	11260	7016	5276	36
H12	10051	5337	4385	29
H15	11228	4292	3126	46
H16	13016	3852	2688	45
H17	12847	2645	1529	36
H18	10840	1898	803	30
H20	9562	3415	175	35
H21	9703	3185	-1026	45
H22	8645	1362	-1863	50
H23	7419	-241	-1515	48
H24	7288	-41	-303	37
H26	9195	12	1295	33
H27	8276	-1823	1541	41
H28	6087	-2393	1549	39
H29	4776	-1150	1311	42
H30	5675	701	1067	33
H32	3949	6264	3614	29
H33	2431	5583	4287	38
H34	3041	5726	5482	37
H35	5175	6566	6020	34
H36	6725	7222	5353	27
H38	7407	8666	2920	29
H39	7410	10632	2835	34
H40	6729	11956	3723	30
H41	6109	11356	4712	29
H42	6049	9376	4791	27

Table S20. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for Complex **2**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
U1	4396.5(2)	2269.4(2)	4681.1(3)	18.69(10)
Cl00	4021.8(15)	3169(3)	3258.7(18)	39.9(7)
Cl1	4590.7(12)	1632(2)	6263.5(16)	27.4(5)
P1	2929.1(10)	532(2)	4532.9(15)	18.7(6)
P2	5270.3(12)	4859(2)	5467.3(17)	20.9(5)
O1	5422(3)	2638(6)	4470(4)	24.8(18)
O2	4351(3)	577(6)	4120(5)	21.9(15)
N1	3246(4)	1646(7)	4954(5)	18.5(17)
N2	4602(4)	4257(7)	5155(6)	23.9(18)
N3	4075(4)	4360(7)	5664(5)	22.6(18)
N4	3686(4)	3616(7)	5380(5)	22.7(17)
C1	2899(5)	2223(8)	5591(7)	22(2)
C01B	2828(5)	3994(10)	6447(7)	28(2)
C2	2375(5)	1823(10)	6060(6)	24(2)
C3	2090(5)	2461(10)	6688(8)	29(2)
C4	2301(5)	3544(9)	6880(7)	28(2)
C5	3124(5)	3316(9)	5817(7)	24(2)
C6	2986(4)	-675(9)	5228(7)	24(2)
C7	2774(5)	-1762(10)	4960(7)	30(2)
C8	2865(6)	-2690(10)	5489(9)	36(3)
C9	3178(6)	-2559(10)	6255(9)	36(3)
C10	3389(5)	-1493(10)	6517(8)	33(3)
C11	3290(5)	-566(10)	6001(7)	24(2)
C12	2111(4)	785(9)	4218(7)	22(2)
C13	2025(5)	1728(9)	3674(7)	26(2)
C14	1424(5)	1956(11)	3350(8)	35(3)
C15	908(5)	1287(12)	3547(9)	42(3)
C16	987(5)	371(12)	4092(9)	43(3)
C17	1583(5)	113(10)	4425(7)	28(2)
C18	3310(4)	131(9)	3557(6)	16.9(18)
C19	3993(4)	144(8)	3499(7)	20(2)
C20	4275(5)	-264(9)	2760(7)	23(2)
C21	3904(5)	-712(9)	2111(7)	25(2)
C22	3249(5)	-722(9)	2181(7)	27(2)
C23	2961(5)	-312(9)	2893(7)	23(2)
C24	5573(5)	4325(10)	6456(7)	27(2)
C25	5171(5)	4314(12)	7147(8)	38(3)
C26	5387(7)	3878(15)	7908(9)	51(4)
C27	6021(6)	3488(11)	7988(9)	40(3)
C28	6409(6)	3541(11)	7306(8)	35(3)

C29	6196(5)	3954(9)	6526(7)	28(2)
C30	5160(5)	6340(10)	5567(7)	27(2)
C31	4696(6)	6876(10)	5057(7)	31(2)
C32	4614(6)	8022(11)	5101(8)	35(3)
C33	4978(6)	8632(10)	5666(9)	38(3)
C34	5421(7)	8117(12)	6170(11)	50(4)
C35	5512(6)	6982(11)	6125(10)	42(3)
C36	5847(4)	4512(8)	4658(10)	26.5(18)
C37	6317(5)	5305(10)	4476(7)	35(3)
C38	6823(6)	5042(11)	3926(9)	43(3)
C39	6822(6)	3956(11)	3550(8)	38(3)
C40	6361(5)	3187(10)	3740(7)	30(2)
C41	5848(5)	3421(9)	4300(7)	25(2)

Table S21. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Complex **2**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U1	18.13(14)	15.78(17)	22.15(15)	-2.4(2)	-1.85(19)	-0.18(10)
Cl00	54.9(16)	34.6(16)	30.2(14)	6.6(12)	-15.5(12)	-12.0(14)
Cl1	31.9(11)	22.4(13)	28.0(12)	-2.7(10)	-5.7(9)	3.2(10)
P1	18.1(9)	15.4(12)	22.5(17)	-0.5(9)	1.4(8)	-1.7(8)
P2	22.7(11)	14.8(12)	25.1(12)	-1.4(10)	-2.0(9)	-1.1(10)
O1	13(3)	27(4)	35(5)	-4(3)	3(2)	-7(3)
O2	14(3)	18(4)	33(4)	-2(3)	-2(3)	8(3)
N1	24(4)	14(4)	18(4)	-1(3)	-1(3)	2(3)
N2	25(4)	17(5)	30(5)	-5(4)	-7(3)	-9(3)
N3	22(4)	16(4)	29(5)	4(4)	-6(3)	-4(3)
N4	25(4)	17(4)	26(4)	2(3)	3(3)	2(3)
C1	18(4)	19(6)	28(5)	-4(4)	-8(4)	4(4)
C01B	26(5)	20(6)	37(6)	-12(5)	-1(4)	3(4)
C2	28(5)	22(6)	24(5)	1(4)	-1(4)	4(4)
C3	26(5)	26(6)	36(6)	3(5)	2(4)	3(4)
C4	29(5)	24(6)	31(6)	-5(5)	1(4)	6(4)
C5	19(5)	20(6)	33(6)	-2(4)	-1(4)	2(4)
C6	16(4)	26(6)	31(6)	4(4)	5(4)	0(4)
C7	33(5)	29(6)	27(6)	1(4)	6(4)	-3(5)
C8	43(7)	16(6)	48(8)	7(5)	9(5)	-1(5)
C9	43(7)	19(6)	47(7)	9(5)	10(6)	1(5)
C10	32(6)	32(7)	34(6)	8(5)	3(4)	4(5)
C11	27(5)	18(6)	26(5)	1(4)	6(4)	2(4)
C12	21(4)	18(5)	28(5)	-8(4)	2(4)	0(4)
C13	23(5)	20(6)	34(6)	1(5)	-4(4)	3(4)
C14	28(5)	29(6)	47(7)	-1(5)	-9(5)	3(5)

C15	23(5)	47(8)	56(8)	-16(6)	-7(5)	6(5)
C16	24(5)	44(8)	62(9)	-14(7)	3(5)	-12(5)
C17	23(4)	21(6)	39(6)	-2(4)	2(4)	-5(4)
C18	12(4)	15(5)	24(5)	-2(4)	-1(3)	-4(4)
C19	23(5)	8(5)	30(5)	1(4)	-1(4)	-2(4)
C20	22(4)	18(6)	29(5)	1(4)	7(4)	-1(4)
C21	31(5)	17(5)	27(6)	-2(4)	3(4)	5(4)
C22	31(5)	26(6)	24(5)	-2(4)	-5(4)	-1(5)
C23	24(5)	14(5)	31(6)	-1(4)	3(4)	3(4)
C24	30(5)	23(6)	28(6)	-1(4)	-2(4)	-2(4)
C25	30(5)	54(8)	30(6)	-7(5)	-6(4)	12(5)
C26	49(7)	73(11)	31(7)	-1(6)	1(5)	13(7)
C27	49(7)	31(7)	40(7)	-2(5)	-9(5)	8(5)
C28	33(6)	31(7)	42(7)	-3(5)	-9(5)	4(5)
C29	28(5)	22(6)	33(6)	-2(4)	-4(4)	3(4)
C30	18(5)	28(6)	35(6)	-3(5)	-3(4)	-1(4)
C31	41(6)	21(6)	29(5)	-1(5)	-1(4)	7(5)
C32	34(6)	32(7)	40(6)	7(5)	1(5)	9(5)
C33	31(6)	17(6)	68(9)	-5(6)	5(5)	0(5)
C34	51(7)	26(7)	72(10)	-21(7)	-21(7)	-2(6)
C35	46(7)	21(6)	59(9)	-6(6)	-21(6)	-5(5)
C36	28(4)	22(5)	30(5)	-4(6)	-2(6)	-2(3)
C37	39(5)	25(6)	43(8)	0(5)	7(5)	2(5)
C38	42(6)	29(7)	57(9)	1(6)	17(6)	-10(6)
C39	36(6)	42(8)	34(6)	-8(5)	13(5)	-3(5)
C40	40(6)	19(6)	32(6)	-3(5)	1(5)	2(5)
C41	26(5)	22(6)	27(5)	3(4)	-6(4)	7(4)

Table S22. Bond Lengths for Complex **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
U1	Cl00	2.604(3)	C9	C10	1.398(18)
U1	Cl1	2.640(3)	C10	C11	1.382(16)
U1	O1	2.205(6)	C12	C13	1.420(16)
U1	O2	2.193(7)	C12	C17	1.396(14)
U1	N1	2.545(8)	C13	C14	1.379(15)
U1	N2	2.506(8)	C14	C15	1.370(19)
U1	N3	2.997(9)	C15	C16	1.39(2)
U1	N4	2.439(8)	C16	C17	1.381(17)
P1	N1	1.617(8)	C18	C19	1.425(12)
P1	C6	1.806(11)	C18	C23	1.379(15)
P1	C12	1.800(10)	C19	C20	1.393(15)
P1	C18	1.796(10)	C20	C21	1.387(15)
P2	N2	1.640(8)	C21	C22	1.369(15)

P2	C24	1.798(11)	C22	C23	1.364(15)
P2	C30	1.776(12)	C24	C25	1.374(17)
P2	C36	1.800(13)	C24	C29	1.375(15)
O1	C41	1.312(13)	C25	C26	1.383(19)
O2	C19	1.333(12)	C26	C27	1.403(19)
N1	C1	1.414(13)	C27	C28	1.348(19)
N2	N3	1.365(13)	C28	C29	1.396(17)
N3	N4	1.277(12)	C30	C31	1.409(16)
N4	C5	1.405(13)	C30	C35	1.375(17)
C1	C2	1.400(15)	C31	C32	1.369(17)
C1	C5	1.421(15)	C32	C33	1.375(19)
C01B	C4	1.398(16)	C33	C34	1.36(2)
C01B	C5	1.419(15)	C34	C35	1.360(19)
C2	C3	1.381(16)	C36	C37	1.386(15)
C3	C4	1.390(17)	C36	C41	1.410(15)
C6	C7	1.426(16)	C37	C38	1.400(17)
C6	C11	1.380(16)	C38	C39	1.416(18)
C7	C8	1.392(17)	C39	C40	1.358(17)
C8	C9	1.38(2)	C40	C41	1.412(16)

Table S23. Bond Angles for Complex **2**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl00	U1	Cl1	168.02(9)	C3	C2	C1	121.9(11)
Cl00	U1	N3	92.36(17)	C2	C3	C4	121.7(11)
Cl1	U1	N3	77.36(17)	C3	C4	C01B	119.6(10)
O1	U1	Cl00	94.5(2)	N4	C5	C1	112.5(9)
O1	U1	Cl1	92.92(19)	N4	C5	C01B	124.2(10)
O1	U1	N1	174.4(3)	C01B	C5	C1	123.2(10)
O1	U1	N2	72.2(3)	C7	C6	P1	120.9(8)
O1	U1	N3	97.5(2)	C11	C6	P1	119.6(9)
O1	U1	N4	121.7(3)	C11	C6	C7	119.3(10)
O2	U1	Cl00	90.7(2)	C8	C7	C6	119.5(11)
O2	U1	Cl1	97.3(2)	C9	C8	C7	120.0(12)
O2	U1	O1	99.3(2)	C8	C9	C10	120.5(12)
O2	U1	N1	76.2(2)	C11	C10	C9	119.7(12)
O2	U1	N2	170.4(3)	C6	C11	C10	121.0(11)
O2	U1	N3	162.6(2)	C13	C12	P1	114.6(7)
O2	U1	N4	138.9(2)	C17	C12	P1	125.9(9)
N1	U1	Cl00	88.98(18)	C17	C12	C13	119.4(9)
N1	U1	Cl1	84.34(17)	C14	C13	C12	119.5(10)
N1	U1	N3	86.7(2)	C15	C14	C13	121.0(12)
N2	U1	Cl00	85.7(2)	C14	C15	C16	119.8(11)
N2	U1	Cl1	87.7(2)	C17	C16	C15	120.8(11)

N2	U1	N1	112.5(3)	C16	C17	C12	119.5(11)
N2	U1	N3	26.9(3)	C19	C18	P1	119.5(7)
N4	U1	Cl00	86.6(2)	C23	C18	P1	121.3(7)
N4	U1	Cl1	81.5(2)	C23	C18	C19	118.8(9)
N4	U1	N1	62.7(3)	O2	C19	C18	121.0(9)
N4	U1	N2	49.8(3)	O2	C19	C20	120.9(8)
N4	U1	N3	24.5(3)	C20	C19	C18	118.1(9)
N1	P1	C6	111.7(4)	C21	C20	C19	121.1(9)
N1	P1	C12	111.3(4)	C22	C21	C20	119.9(10)
N1	P1	C18	112.8(4)	C23	C22	C21	120.2(10)
C12	P1	C6	111.2(5)	C22	C23	C18	122.0(9)
C18	P1	C6	106.4(5)	C25	C24	P2	118.6(8)
C18	P1	C12	103.1(4)	C25	C24	C29	120.6(11)
N2	P2	C24	113.9(5)	C29	C24	P2	120.9(9)
N2	P2	C30	110.2(5)	C24	C25	C26	119.6(11)
N2	P2	C36	104.7(5)	C25	C26	C27	120.5(13)
C24	P2	C36	107.5(5)	C28	C27	C26	118.5(12)
C30	P2	C24	108.4(5)	C27	C28	C29	121.9(11)
C30	P2	C36	112.0(5)	C24	C29	C28	118.9(11)
C41	O1	U1	145.8(6)	C31	C30	P2	118.9(9)
C19	O2	U1	132.3(6)	C35	C30	P2	122.2(9)
P1	N1	U1	123.4(4)	C35	C30	C31	118.9(11)
C1	N1	U1	117.4(6)	C32	C31	C30	120.1(11)
C1	N1	P1	118.6(7)	C31	C32	C33	119.1(11)
P2	N2	U1	130.0(5)	C34	C33	C32	121.1(11)
N3	N2	U1	97.0(5)	C35	C34	C33	120.4(12)
N3	N2	P2	117.8(7)	C34	C35	C30	120.4(12)
N2	N3	U1	56.1(5)	C37	C36	P2	117.6(8)
N4	N3	U1	52.4(5)	C37	C36	C41	122.4(11)
N4	N3	N2	103.9(8)	C41	C36	P2	119.7(8)
N3	N4	U1	103.0(6)	C36	C37	C38	120.6(11)
N3	N4	C5	122.0(9)	C37	C38	C39	117.5(11)
C5	N4	U1	124.2(7)	C40	C39	C38	121.1(11)
N1	C1	C5	116.8(9)	C39	C40	C41	122.8(11)
C2	C1	N1	127.5(9)	O1	C41	C36	124.3(10)
C2	C1	C5	115.6(10)	O1	C41	C40	120.1(10)
C4	C01B	C5	117.9(10)	C36	C41	C40	115.6(10)

Table S24. Hydrogen Atom Coordinates ($\text{Å} \times 10^4$) and Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for Complex **2**.

Atom	x	y	z	U(eq)
H01B	2980.03	4714.91	6568.15	34
H2	2214.99	1106.3	5944.74	29

H3	1747.56	2158.52	6990.09	35
H4	2093.87	3967.3	7294.64	34
H7	2575.53	-1851.18	4436	36
H8	2715.15	-3397.53	5326.26	43
H9	3249.46	-3184.1	6599.18	44
H10	3594.58	-1408.69	7036.49	40
H11	3429.52	141.32	6177.75	28
H13	2371.93	2187.76	3536.2	31
H14	1367.59	2573.49	2993.83	42
H15	506.9	1443.1	3316.77	50
H16	634.33	-72.35	4233.88	52
H17	1632.02	-503.97	4784.06	33
H20	4718.81	-235.27	2699.57	28
H21	4100.67	-1005.78	1629.55	30
H22	3000.36	-1009.52	1741.87	32
H23	2515.54	-331.36	2932.13	28
H25	4755.72	4597.63	7102.43	46
H26	5111.27	3842.7	8370.51	61
H27	6169.29	3200.34	8499.94	48
H28	6831.7	3294.52	7356.08	42
H29	6470.97	3977.06	6062.15	33
H31	4444.54	6450.56	4688.43	37
H32	4316.9	8382.1	4754.56	43
H33	4919.88	9409.03	5704.99	46
H34	5663.46	8545.35	6547.33	60
H35	5814.99	6637.43	6472.76	50
H37	6295.73	6017.72	4721.6	43
H38	7146.73	5560.6	3812.38	51
H39	7143.95	3766.93	3166.88	45
H40	6382.67	2476.19	3491.37	36

Table S25. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for Complex **4**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
C1	6715(2)	4628.2(18)	4813.3(16)	14.6(6)
C2	6082(3)	4254(2)	5207.3(18)	19.4(7)
C3	5793(3)	4598(2)	5767.3(17)	20.5(7)
C4	6143(3)	5325(2)	5943.2(17)	19.7(7)
C5	6769(3)	5702.4(19)	5555.4(19)	21.1(7)
C6	7046(3)	5362.7(18)	4981.4(16)	16.1(6)
C7	7535(3)	1868.7(19)	4220.3(16)	16.7(6)
C8	6998(3)	1472(2)	4660.4(18)	21.1(7)
C9	7480(3)	1158(2)	5226.9(18)	25.6(8)

C10	8476(3)	1236(2)	5348(2)	29.7(9)
C11	9013(3)	1634(3)	4905(2)	32.8(9)
C12	8535(3)	1952(2)	4344.6(19)	25.3(8)
C13	7426(2)	2073(2)	2785.1(16)	16.3(7)
C14	7404(2)	2557(2)	2236.1(16)	15.4(6)
C15	7606(3)	2255(2)	1629.3(17)	18.0(7)
C16	7809(3)	1479(2)	1570.9(18)	22.0(7)
C17	7843(3)	993(2)	2110.6(19)	22.3(7)
C18	7660(3)	1287.9(19)	2719.8(18)	19.7(7)
C19	5673(3)	2181.2(19)	3460.1(16)	16.3(6)
C20	5332(3)	1483(2)	3193(2)	25.0(8)
C21	4343(3)	1325(2)	3119(2)	28.2(8)
C22	3685(3)	1866(2)	3307(2)	24.7(8)
C23	4013(3)	2557(2)	3565.5(19)	25.9(8)
C24	5007(3)	2721(2)	3646.2(18)	20.3(7)
C25	8574(2)	6059.9(19)	3254.7(16)	15.2(6)
C26	8506(3)	6663.6(19)	3706.3(16)	16.1(6)
C27	9097(3)	7316(2)	3668.8(18)	19.7(7)
C28	9752(3)	7372(2)	3197.3(18)	20.8(7)
C29	9839(2)	6764(2)	2763.9(17)	18.1(7)
C30	9261(3)	6116(2)	2792.9(16)	17.0(6)
C31	8100(2)	7244.7(19)	5007.6(16)	15.2(6)
C32	8685(3)	6952(2)	5546.1(18)	19.7(7)
C33	8994(3)	7438(2)	6056.1(18)	22.2(7)
C34	8766(3)	8213(2)	6027.1(18)	22.7(7)
C35	8207(3)	8508(2)	5489.0(18)	20.4(7)
C36	7865(2)	8023.8(19)	4978.1(16)	16.3(6)
C37	6524(3)	7015(2)	4036.7(18)	19.5(7)
C38	5798(3)	7129(2)	4470(2)	24.4(8)
C39	4951(3)	7501(2)	4259(2)	28.0(8)
C40	4814(3)	7784(3)	3621(2)	31.9(9)
C41	5520(3)	7668(3)	3191(2)	40.3(11)
C42	6373(3)	7279(3)	3396(2)	32.3(9)
Cl1	5551.8(6)	4587.5(5)	2786.7(4)	22.83(17)
Cl2	7683.0(6)	5028.4(4)	1687.9(4)	18.97(15)
Cl3	9260.6(6)	3820.9(5)	2943.4(4)	24.81(17)
N1	7179(2)	3305.5(16)	3617.0(14)	15.9(5)
N2	6929(2)	3574.8(16)	4204.0(14)	15.4(5)
N3	7036(2)	4298.9(15)	4228.4(14)	14.1(6)
N4	7695(3)	5735.4(17)	4580.6(17)	20.3(6)
O1	7174.1(18)	3296.1(12)	2282.1(11)	15.2(4)
O2	7998.6(18)	5436.2(13)	3268.8(11)	15.4(4)
P1	6957.4(6)	2380.4(4)	3529.1(4)	13.59(15)
P2	7684.6(6)	6630.9(5)	4334.4(4)	14.78(16)

U1	7453.2(2)	4344.0(2)	2825.2(2)	11.67(5)
C51	9112(4)	9424(3)	3314(3)	41.1(11)
C52	8709(4)	9692(3)	3878(3)	44.3(12)
C53	7718(4)	9659(2)	3921(3)	43.1(12)
C54	7112(4)	9364(3)	3414(3)	41.4(12)
C55	7511(4)	9093(3)	2857(2)	42.8(12)
C56	8503(4)	9121(3)	2811(3)	40.8(11)
C61	4530(3)	607(2)	5271(2)	26.0(8)
C62	4310(3)	417(3)	4620(2)	31.4(9)
C63	4784(3)	-191(3)	4349(2)	33.2(9)
C71	9539(3)	4414(3)	5303(3)	35.6(10)
C72	9960(3)	5009(3)	5677(2)	31.3(9)
C73	10425(3)	5594(3)	5378(2)	32.1(9)

Table S26. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Complex **4**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	16.6(15)	13.3(15)	14.0(15)	2.4(12)	1.2(12)	0.9(12)
C2	23.3(18)	17.0(15)	19.1(17)	-0.3(13)	8.0(14)	-3.4(13)
C3	23.5(17)	20.8(17)	18.2(16)	2.3(14)	7.5(13)	-1.4(14)
C4	27.2(18)	18.9(17)	13.9(15)	-1.8(13)	6.9(13)	1.0(14)
C5	30(2)	13.9(16)	20.7(18)	-3.4(12)	8.5(15)	-0.5(13)
C6	21.4(16)	11.6(15)	16.0(15)	1.2(12)	5.6(13)	0.1(12)
C7	25.0(17)	11.0(14)	14.5(15)	-0.2(12)	4.6(13)	0.6(12)
C8	28.3(18)	14.6(15)	21.2(17)	2.1(13)	7.2(14)	-0.4(13)
C9	39(2)	20.9(17)	17.2(17)	5.0(14)	5.4(15)	-0.4(15)
C10	41(2)	28(2)	20.0(18)	6.2(15)	-1.8(16)	6.4(17)
C11	28(2)	43(2)	26(2)	5.7(18)	-0.3(16)	1.6(18)
C12	27.1(19)	26.8(19)	22.0(18)	6.9(15)	2.1(15)	-3.9(15)
C13	18.1(17)	13.3(16)	18.4(17)	-2.2(12)	6.1(13)	-0.2(11)
C14	15.3(15)	15.7(16)	15.3(15)	1.3(12)	3.2(12)	-0.6(12)
C15	19.9(16)	18.0(16)	16.6(16)	-0.7(13)	3.6(13)	-0.7(13)
C16	22.9(17)	22.5(18)	21.6(17)	-9.0(14)	7.2(14)	0.7(14)
C17	27.9(18)	14.9(16)	25.2(18)	-5.4(14)	9.1(14)	2.4(14)
C18	25.1(17)	10.7(15)	23.7(17)	1.6(13)	5.6(14)	0.0(13)
C19	21.1(16)	12.3(14)	15.9(15)	-0.6(12)	3.0(12)	-1.9(12)
C20	24.4(19)	17.5(17)	34(2)	-6.2(15)	7.8(15)	0.3(14)
C21	25.8(19)	18.6(17)	41(2)	-12.2(16)	10.1(17)	-12.9(15)
C22	21.6(18)	24.8(18)	28.7(19)	-1.6(15)	8.1(15)	-6.5(14)
C23	26.8(19)	26.0(19)	25.9(19)	-8.0(15)	8.1(15)	1.3(15)
C24	23.5(17)	17.4(16)	20.4(17)	-3.8(13)	3.6(13)	-0.3(13)
C25	16.9(15)	14.9(15)	13.9(15)	3.2(12)	1.5(12)	1.1(12)
C26	20.1(16)	12.8(15)	16.0(15)	-0.5(12)	5.2(12)	-0.5(12)

C27	22.9(17)	14.4(15)	22.3(17)	-0.6(13)	5.0(14)	-4.0(13)
C28	21.0(17)	17.9(16)	23.8(17)	-0.4(14)	4.1(14)	-7.4(13)
C29	15.6(15)	20.9(16)	18.5(16)	2.6(13)	4.6(12)	-3.7(13)
C30	20.4(16)	17.2(15)	13.9(15)	-1.5(12)	3.6(12)	0.4(13)
C31	18.0(15)	13.7(15)	14.1(15)	-1.8(12)	3.9(12)	0.9(12)
C32	19.7(16)	15.9(15)	23.9(18)	3.5(13)	4.7(13)	2.0(13)
C33	18.3(16)	27.7(19)	20.0(17)	3.6(14)	-2.3(13)	1.6(14)
C34	25.9(18)	24.4(18)	17.6(17)	-7.1(14)	0.2(14)	-0.7(14)
C35	25.5(18)	15.0(15)	21.1(17)	-4.8(13)	4.5(14)	-0.6(13)
C36	19.0(16)	15.5(15)	14.2(15)	0.0(12)	0.5(12)	1.8(12)
C37	20.4(16)	15.4(15)	22.6(17)	-7.8(13)	1.0(13)	-3.7(13)
C38	26.5(19)	21.7(17)	26.1(19)	3.9(15)	8.8(15)	1.1(14)
C39	23.6(19)	23.0(18)	38(2)	1.9(16)	9.3(16)	-1.3(15)
C40	21.4(19)	35(2)	38(2)	-4.0(18)	-3.7(16)	-1.4(16)
C41	31(2)	66(3)	22(2)	2(2)	-5.9(17)	8(2)
C42	29(2)	50(3)	17.2(18)	-6.2(17)	-1.3(15)	3.4(18)
Cl1	19.0(4)	24.0(4)	26.3(4)	6.6(3)	6.5(3)	2.8(3)
Cl2	27.0(4)	17.2(3)	13.0(3)	2.3(3)	3.5(3)	-1.4(3)
Cl3	20.4(4)	25.6(4)	28.3(4)	-2.4(3)	0.9(3)	4.9(3)
N1	20.4(14)	11.7(12)	15.9(13)	-2.2(10)	3.4(11)	-0.8(10)
N2	18.4(13)	13.8(13)	13.9(13)	-1.5(10)	1.5(10)	-2.9(10)
N3	19.3(14)	12.9(13)	10.7(13)	-0.7(9)	4.0(11)	0.6(10)
N4	31.3(17)	10.8(13)	21.1(16)	-4.9(11)	15.7(13)	-1.5(11)
O1	23.6(12)	8.7(10)	13.1(11)	-1.0(8)	0.1(9)	-1.8(9)
O2	23.3(12)	7.6(10)	15.8(11)	-4.5(9)	5.0(9)	-6.0(9)
P1	19.2(4)	8.6(3)	13.3(4)	0.5(3)	3.4(3)	-1.3(3)
P2	18.8(4)	10.8(3)	15.2(4)	-1.8(3)	4.2(3)	-1.4(3)
U1	15.45(7)	8.70(7)	11.06(7)	0.29(3)	2.26(4)	-0.27(3)
C51	45(3)	34(2)	45(3)	11(2)	10(2)	10.2(19)
C52	67(3)	24(2)	41(3)	7.3(19)	-1(2)	8(2)
C53	72(4)	21(2)	40(3)	9.0(18)	26(2)	10(2)
C54	53(3)	32(3)	41(3)	8.6(18)	18(2)	4.5(19)
C55	52(3)	36(3)	42(3)	9(2)	12(2)	5(2)
C56	52(3)	33(2)	39(3)	8(2)	15(2)	12(2)
C61	25(2)	18.9(18)	35(2)	-1.3(14)	6.6(17)	-1.1(13)
C62	27(2)	36(2)	31(2)	8.8(18)	1.3(16)	8.5(17)
C63	31(2)	43(2)	24.7(19)	-6.9(18)	-0.4(16)	2.1(18)
C71	30(2)	37(2)	41(3)	13.1(19)	13.1(19)	14.0(17)
C72	28(2)	47(2)	19.2(17)	5.7(17)	2.4(15)	16.7(18)
C73	25(2)	38(2)	33(2)	-1.2(17)	1.3(17)	11.8(16)

Table S27. Bond Lengths for Complex **4**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.398(5)	C31	C36	1.397(5)
C1	C6	1.393(5)	C31	P2	1.797(3)
C1	N3	1.430(4)	C32	C33	1.382(5)
C2	C3	1.380(5)	C33	C34	1.387(5)
C3	C4	1.392(5)	C34	C35	1.386(5)
C4	C5	1.388(5)	C35	C36	1.392(5)
C5	C6	1.396(5)	C37	C38	1.406(5)
C6	N4	1.422(4)	C37	C42	1.385(6)
C7	C8	1.396(5)	C37	P2	1.793(4)
C7	C12	1.389(5)	C38	C39	1.374(6)
C7	P1	1.797(4)	C39	C40	1.391(6)
C8	C9	1.396(5)	C40	C41	1.382(6)
C9	C10	1.382(6)	C41	C42	1.391(6)
C10	C11	1.401(6)	Cl1	U1	2.6516(8)
C11	C12	1.386(6)	Cl2	U1	2.6545(8)
C13	C14	1.402(5)	Cl3	U1	2.6463(8)
C13	C18	1.416(5)	N1	N2	1.359(4)
C13	P1	1.784(3)	N1	P1	1.649(3)
C14	C15	1.397(5)	N1	U1	2.479(3)
C14	O1	1.332(4)	N2	N3	1.272(4)
C15	C16	1.389(5)	N3	U1	2.972(3)
C16	C17	1.387(5)	N4	P2	1.641(3)
C17	C18	1.389(5)	O1	U1	2.155(2)
C19	C20	1.400(5)	O2	U1	2.213(2)
C19	C24	1.391(5)	C51	C52	1.403(8)
C19	P1	1.799(4)	C51	C56	1.374(8)
C20	C21	1.387(5)	C52	C53	1.377(8)
C21	C22	1.386(6)	C53	C54	1.374(8)
C22	C23	1.377(5)	C54	C55	1.389(7)
C23	C24	1.395(5)	C55	C56	1.380(7)
C25	C26	1.408(5)	C61	C62	1.377(6)
C25	C30	1.396(5)	C61	C63[1]	1.378(6)
C25	O2	1.349(4)	C62	C63	1.387(6)
C26	C27	1.406(5)	C63	C61[1]	1.378(6)
C26	P2	1.784(3)	C71	C72	1.385(7)
C27	C28	1.380(5)	C71	C73[2]	1.396(7)
C28	C29	1.393(5)	C72	C73	1.376(7)
C29	C30	1.387(5)	C73	C71[2]	1.396(7)
C31	C32	1.403(5)			

[1]1-X,-Y,1-Z; [2]2-X,1-Y,1-Z

Table S28. Bond Angles for Complex **4**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	N3	123.2(3)	C41	C40	C39	119.8(4)
C6	C1	C2	119.7(3)	C40	C41	C42	120.3(4)
C6	C1	N3	117.2(3)	C37	C42	C41	120.0(4)
C3	C2	C1	120.9(3)	N2	N1	P1	112.0(2)
C2	C3	C4	119.4(3)	N2	N1	U1	112.78(19)
C5	C4	C3	120.3(3)	P1	N1	U1	132.95(15)
C4	C5	C6	120.4(3)	N3	N2	N1	109.9(3)
C1	C6	C5	119.3(3)	C1	N3	U1	153.4(2)
C1	C6	N4	119.2(3)	N2	N3	C1	112.8(3)
C5	C6	N4	121.4(3)	N2	N3	U1	91.15(19)
C8	C7	P1	121.8(3)	C6	N4	P2	128.5(3)
C12	C7	C8	120.5(3)	C14	O1	U1	145.4(2)
C12	C7	P1	117.3(3)	C25	O2	U1	150.0(2)
C7	C8	C9	119.2(4)	C7	P1	C19	109.44(16)
C10	C9	C8	120.3(4)	C13	P1	C7	110.53(16)
C9	C10	C11	120.4(4)	C13	P1	C19	107.56(16)
C12	C11	C10	119.4(4)	N1	P1	C7	109.55(15)
C11	C12	C7	120.2(4)	N1	P1	C13	108.02(16)
C14	C13	C18	119.8(3)	N1	P1	C19	111.70(15)
C14	C13	P1	121.0(3)	C26	P2	C31	110.51(16)
C18	C13	P1	118.3(3)	C26	P2	C37	110.37(17)
C15	C14	C13	119.3(3)	C37	P2	C31	104.68(15)
O1	C14	C13	121.0(3)	N4	P2	C26	105.16(16)
O1	C14	C15	119.7(3)	N4	P2	C31	109.81(17)
C16	C15	C14	120.1(3)	N4	P2	C37	116.35(17)
C17	C16	C15	121.3(3)	Cl1	U1	Cl2	95.42(3)
C16	C17	C18	119.3(3)	Cl1	U1	N3	76.09(6)
C17	C18	C13	120.2(3)	Cl2	U1	N3	154.57(5)
C20	C19	P1	119.6(3)	Cl3	U1	Cl1	168.44(3)
C24	C19	C20	119.2(3)	Cl3	U1	Cl2	93.00(3)
C24	C19	P1	121.2(3)	Cl3	U1	N3	99.33(6)
C21	C20	C19	120.6(3)	N1	U1	Cl1	86.01(7)
C22	C21	C20	119.7(3)	N1	U1	Cl2	159.36(7)
C23	C22	C21	120.0(4)	N1	U1	Cl3	83.33(7)
C22	C23	C24	120.8(4)	N1	U1	N3	45.47(8)
C19	C24	C23	119.6(3)	O1	U1	Cl1	89.32(7)
C30	C25	C26	118.5(3)	O1	U1	Cl2	87.75(6)
O2	C25	C26	121.1(3)	O1	U1	Cl3	83.09(7)
O2	C25	C30	120.4(3)	O1	U1	N1	71.66(9)
C25	C26	P2	122.0(3)	O1	U1	N3	115.65(8)
C27	C26	C25	119.8(3)	O1	U1	O2	168.50(9)

C27	C26	P2	118.2(3)	O2	U1	Cl1	100.07(7)
C28	C27	C26	120.9(3)	O2	U1	Cl2	84.78(6)
C27	C28	C29	119.2(3)	O2	U1	Cl3	88.57(7)
C30	C29	C28	120.8(3)	O2	U1	N1	115.32(9)
C29	C30	C25	120.8(3)	O2	U1	N3	73.46(8)
C32	C31	P2	120.5(3)	C56	C51	C52	118.8(5)
C36	C31	C32	120.2(3)	C53	C52	C51	120.3(5)
C36	C31	P2	119.3(3)	C54	C53	C52	120.7(5)
C33	C32	C31	119.1(3)	C53	C54	C55	119.1(5)
C32	C33	C34	120.8(3)	C56	C55	C54	120.5(5)
C35	C34	C33	120.3(3)	C51	C56	C55	120.6(5)
C34	C35	C36	119.9(3)	C62	C61	C63^1	120.1(4)
C35	C36	C31	119.7(3)	C61	C62	C63	119.8(4)
C38	C37	P2	120.2(3)	C61^1	C63	C62	120.1(4)
C42	C37	C38	119.4(4)	C72	C71	C73^2	120.5(4)
C42	C37	P2	120.1(3)	C73	C72	C71	120.0(4)
C39	C38	C37	120.1(4)	C72	C73	C71^2	119.5(4)
C38	C39	C40	120.3(4)				

^{1}1-X,-Y,1-Z; ^{2}2-X,1-Y,1-Z

Table S29. Torsion Angles for Complex **4**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	-0.5(6)	C28	C29	C30	C25	0.3(5)
C1	C6	N4	P2	137.3(3)	C30	C25	C26	C27	2.3(5)
C2	C1	C6	C5	2.4(5)	C30	C25	C26	P2	-177.6(3)
C2	C1	C6	N4	179.5(3)	C30	C25	O2	U1	-8.2(6)
C2	C1	N3	N2	-19.0(5)	C31	C32	C33	C34	-2.6(5)
C2	C1	N3	U1	134.0(4)	C32	C31	C36	C35	-0.6(5)
C2	C3	C4	C5	0.6(6)	C32	C31	P2	C26	-92.8(3)
C3	C4	C5	C6	0.8(6)	C32	C31	P2	C37	148.3(3)
C4	C5	C6	C1	-2.3(6)	C32	C31	P2	N4	22.7(3)
C4	C5	C6	N4	-179.3(4)	C32	C33	C34	C35	1.2(6)
C5	C6	N4	P2	-45.7(5)	C33	C34	C35	C36	0.6(6)
C6	C1	C2	C3	-1.1(5)	C34	C35	C36	C31	-0.9(5)
C6	C1	N3	N2	162.1(3)	C36	C31	C32	C33	2.3(5)
C6	C1	N3	U1	-44.9(6)	C36	C31	P2	C26	84.8(3)
C6	N4	P2	C26	-167.1(3)	C36	C31	P2	C37	-34.0(3)
C6	N4	P2	C31	73.9(4)	C36	C31	P2	N4	-159.6(3)
C6	N4	P2	C37	-44.7(4)	C37	C38	C39	C40	-1.5(6)
C7	C8	C9	C10	-0.3(6)	C38	C37	C42	C41	1.4(6)
C8	C7	C12	C11	0.7(6)	C38	C37	P2	C26	-172.6(3)
C8	C7	P1	C13	-125.8(3)	C38	C37	P2	C31	-53.7(3)

C8	C7	P1	C19	-7.5(3)	C38	C37	P2	N4	67.7(3)
C8	C7	P1	N1	115.3(3)	C38	C39	C40	C41	2.0(7)
C8	C9	C10	C11	0.3(6)	C39	C40	C41	C42	-0.9(7)
C9	C10	C11	C12	0.2(7)	C40	C41	C42	C37	-0.9(8)
C10	C11	C12	C7	-0.6(7)	C42	C37	C38	C39	-0.3(6)
C12	C7	C8	C9	-0.2(5)	C42	C37	P2	C26	0.3(4)
C12	C7	P1	C13	61.2(3)	C42	C37	P2	C31	119.3(3)
C12	C7	P1	C19	179.5(3)	C42	C37	P2	N4	-119.3(3)
C12	C7	P1	N1	-57.7(3)	N1	N2	N3	C1	175.5(3)
C13	C14	C15	C16	1.2(5)	N1	N2	N3	U1	7.2(3)
C13	C14	O1	U1	49.6(5)	N2	N1	P1	C7	-53.7(3)
C14	C13	C18	C17	-1.7(5)	N2	N1	P1	C13	-174.1(2)
C14	C13	P1	C7	-154.4(3)	N2	N1	P1	C19	67.8(3)
C14	C13	P1	C19	86.1(3)	N3	C1	C2	C3	-179.9(3)
C14	C13	P1	N1	-34.6(3)	N3	C1	C6	C5	-178.7(3)
C14	C15	C16	C17	-1.9(6)	N3	C1	C6	N4	-1.6(5)
C15	C14	O1	U1	-131.8(3)	O1	C14	C15	C16	-177.4(3)
C15	C16	C17	C18	0.7(6)	O2	C25	C26	C27	-178.3(3)
C16	C17	C18	C13	1.1(6)	O2	C25	C26	P2	1.7(5)
C18	C13	C14	C15	0.6(5)	O2	C25	C30	C29	178.4(3)
C18	C13	C14	O1	179.2(3)	P1	C7	C8	C9	-172.9(3)
C18	C13	P1	C7	36.7(3)	P1	C7	C12	C11	173.7(3)
C18	C13	P1	C19	-82.8(3)	P1	C13	C14	C15	-168.2(3)
C18	C13	P1	N1	156.5(3)	P1	C13	C14	O1	10.4(5)
C19	C20	C21	C22	0.6(6)	P1	C13	C18	C17	167.4(3)
C20	C19	C24	C23	0.2(5)	P1	C19	C20	C21	-178.4(3)
C20	C19	P1	C7	-77.4(3)	P1	C19	C24	C23	177.9(3)
C20	C19	P1	C13	42.7(3)	P1	N1	N2	N3	-174.6(2)
C20	C19	P1	N1	161.1(3)	P2	C26	C27	C28	179.4(3)
C20	C21	C22	C23	0.0(6)	P2	C31	C32	C33	180.0(3)
C21	C22	C23	C24	-0.4(6)	P2	C31	C36	C35	-178.2(3)
C22	C23	C24	C19	0.3(6)	P2	C37	C38	C39	172.7(3)
C24	C19	C20	C21	-0.7(6)	P2	C37	C42	C41	-171.6(4)
C24	C19	P1	C7	104.9(3)	U1	N1	N2	N3	-9.4(3)
C24	C19	P1	C13	-134.9(3)	U1	N1	P1	C7	145.0(2)
C24	C19	P1	N1	-16.6(3)	U1	N1	P1	C13	24.5(3)
C25	C26	C27	C28	-0.5(5)	U1	N1	P1	C19	-93.6(2)
C25	C26	P2	C31	156.0(3)	C51	C52	C53	C54	0.1(7)
C25	C26	P2	C37	-88.7(3)	C52	C51	C56	C55	1.1(7)
C25	C26	P2	N4	37.6(3)	C52	C53	C54	C55	0.3(7)
C26	C25	C30	C29	-2.2(5)	C53	C54	C55	C56	-0.1(7)
C26	C25	O2	U1	172.4(3)	C54	C55	C56	C51	-0.7(8)
C26	C27	C28	C29	-1.4(6)	C56	C51	C52	C53	-0.9(7)
C27	C26	P2	C31	-23.9(3)	C61	C62	C63	C61[1]	0.4(7)

C27	C26	P2	C37	91.4(3)	C63[1]	C61	C62	C63	-0.4(7)
C27	C26	P2	N4	-142.4(3)	C71	C72	C73	C71[2]	0.5(7)
C27	C28	C29	C30	1.5(6)	C73[2]	C71	C72	C73	-0.5(7)

[1]1-X,-Y,1-Z; [2]2-X,1-Y,1-Z

Table S30. Hydrogen Atom Coordinates ($Å\times10^4$) and Isotropic Displacement Parameters ($Å^2\times10^3$) for Complex **4**.

Atom	x	y	z	U(eq)
H2	5854	3767	5090	23
H3	5368	4347	6025	25
H4	5956	5558	6322	24
H5	7006	6185	5679	25
H8	6328	1418	4577	25
H9	7129	894	5524	31
H10	8793	1023	5726	36
H11	9683	1686	4987	39
H12	8886	2222	4051	30
H15	7605	2573	1264	22
H16	7924	1281	1162	26
H17	7987	476	2065	27
H18	7692	969	3086	24
H20	5773	1122	3063	30
H21	4123	858	2945	34
H22	3022	1762	3258	30
H23	3568	2919	3688	31
H24	5222	3188	3823	24
H27	9046	7715	3966	24
H28	10131	7809	3169	25
H29	10290	6792	2452	22
H30	9331	5714	2501	20
H32	8862	6437	5560	24
H33	9359	7244	6423	27
H34	8989	8535	6370	27
H35	8060	9028	5469	24
H36	7482	8218	4619	20
H38	5892	6952	4900	29
H39	4466	7565	4544	34
H40	4248	8049	3484	38
H41	5425	7851	2762	48
H42	6843	7197	3103	39
H51	9779	9451	3280	49
H52	9111	9892	4225	53

H53	7457	9840	4296	52
H54	6444	9345	3443	50
H55	7107	8891	2511	51
H56	8762	8933	2438	49
H61	4216	1016	5453	31
H62	3845	696	4364	38
H63	4639	-318	3909	40
H71	9229	4018	5507	43
H72	9928	5012	6130	38
H73	10712	5992	5628	38
H4A	7830(40)	5460(30)	4320(30)	32(14)

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