Electronic Supplementary Information (ESI)

A novel tetrakis(pyrazolyl)borate ligand bearing triphenylphosphine oxide substituents

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Experimental

All reagents, unless stated otherwise were purchased from commercial suppliers without further purification. Elemental analyses were performed by Stephen Boyer at the London Metropolitan University. ^1H, ^{11}B, $^{13}C\{H\}$ and $^{31}P\{H\}$ NMR spectra were recorded on Bruker Av-400, DRX-400 or Av-500 spectrometers. Pseudo-triplets which occur as a result of identical *J*-value coupling to two chemically inequivalent protons are assigned as *dd* (doublet of doublets) and are recognised by the inclusion of only one *J*-value. Chemical shifts are reported in ppm using the residual proton impurities in the solvents. Mass spectra were recorded on a Micromass Autospec Q spectrometer by Mr J. Barton and Mr G. Tucker of the Department of Chemistry, Imperial College, London. Infrared absorption spectra were collected as KBr discs using a Perkin Elmer RX FT-IR spectrometer. 3-[2-(diphenylphosphinyl)phenyl]pyrazole, $pz^{phos(O)}$, was synthesised as reported previously.[1]

1. Synthesis of potassium tetrakis{3-[2-(diphenylphosphinyl)phenyl]pyrazolyl}borate, $K[T_kp^{phos(O)}]$

Under an atmosphere of nitrogen, a finely ground mixture of $pz^{phos(O)}$ (3.000 g, 8.7 mmol) and potassium borohydride (0.094 g, 1.74 mmol) was stirred and gradually heated using a heating mantle. At approximately 160°C a pale brown melt had formed which appeared to bubble gently. At 260°C the temperature remained constant and the mixture was stirred for two hours and the melt did not change greatly in appearance and no precipitation was observed. Addition of ethanol (50 ml) gave a brown solution which was filtered and concentrated to dryness to give a pale brown powder. ^1H NMR spectroscopy showed the product to be contaminated by some unreacted $pz^{phos(O)}$. Recrystallisation of the crude solid from hot THF gave pure $K[T_kp^{phos(O)}]$ as a white solid. Yield = 1.405 g (56 %). ^1H NMR (+25°C, $CDCl_3$, 400 MHz), δ = 7.68 [dd ($^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 4.0 Hz), 4H, 6-Ph], 7.62 [dd ($^3J_{HP}$ = 11.9 Hz, $^3J_{HH}$ = 7.2 Hz), 16H, *o*-Ph], 7.55 [dd ($^3J_{HH}$ = 7.6 Hz), 4H, 5-Ph], 7.43 [t ($^3J_{HH}$ = 6.9 Hz), 8H, *p*-Ph], 7.33 [ddd ($^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 2.6 Hz), 16H, *m*-Ph], 7.27 [m, 4H, 4-Ph], 7.19 [dd ($^3J_{HP}$ = 14.1 Hz, $^3J_{HH}$ = 7.3 Hz), 4H, 3-Ph], 6.49 [d ($^3J_{HH}$ = 2.2 Hz), 4H, 5-pz], 6.03 [d ($^3J_{HH}$ = 2.2 Hz), 4H, 4-pz]. ^{11}B NMR (+25°C, $CDCl_3$, 128 MHz), δ = 0.7 [s]. $^{31}P\{H\}$ NMR (+25°C,

$CDCl_3$, 162 MHz), δ = 30.9 [s]. $^{13}C\{H\}$ NMR (+25°C, $CDCl_3$, 126 MHz), δ = 152.1 [s, 3-pz], 141.1 [s, 1-Ph], 135.7 [s, 5-pz], 133.9 [d ($^2J_{CP}$ = 12.7 Hz), 3-Ph], 133.1 [d ($^3J_{CP}$ = 9.9 Hz), 6-Ph], 133.1 [d ($^1J_{CP}$ = 133.1 Hz), *i*-Ph], 131.8 [m, *o*-Ph + 4-Ph], 131.4 [s, *p*-Ph], 130.1 [d ($^1J_{CP}$ = 103.0 Hz), 2-Ph], 128.2 [d ($^3J_{CP}$ = 12.1 Hz), *m*-Ph], 126.6 [d ($^3J_{CP}$ = 12.8 Hz), 4-Ph], 107.1 [s, 4-pz]. IR (KBr disc), ν/cm^{-1} = 3055m, 1636w, 1590w, 1482s, 1438s, 1426m, 1259w, 1137w, 1192s, 1116s, 1071m. MS(ESI -ve), *m*/*z* = 1383 $[T_kp^{phos(O)}]^-$.

2. Synthesis of Tl[$T_kp^{phos(O)}$]

A solution of thallium nitrate (0.034 g, 0.13 mmol) in a mixture of THF (2 ml) and water (2 ml) was added to a solution K[$T_kp^{phos(O)}$] (0.150 g, 0.11 mmol) in a mixture of THF (20 ml) and DCM (20 ml) and stirred for one hour. The solution was extracted into DCM (80 ml), dried over magnesium sulphate, filtered and concentrated to dryness *in vacuo* to give Tl[$T_kp^{phos(O)}$] as a white solid. Yield = 0.120 g (70 %). Single crystals suitable for X-ray analysis were grown by slow diffusion of pentane vapour into a solution of the product in chloroform. Anal. (%): Calc. (found) for $C_{84}H_{64}BN_8O_4P_4Tl$: C, 63.5 (63.4); H, 4.06 (3.97); N, 7.05 (6.96). ^1H NMR (+25°C, $CDCl_3$, 400 MHz), δ = 8.00 [dd ($^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 4.1 Hz), 4H, 6-Ph], 7.65 [dd ($^3J_{HP}$ = 11.7 Hz, $^3J_{HH}$ = 7.4 Hz), 16H, *o*-Ph], 7.57 [m, 12H, *p*-Ph + 5-Ph], 7.40 [ddd ($^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 2.8 Hz), 16H, *m*-Ph], 7.20-7.30 [m, 6H, 4-Ph + 3-Ph], 6.49 [d ($^3J_{HH}$ = 2.2 Hz), 4H, 5-pz], 6.03 [d ($^3J_{HH}$ = 2.2 Hz), 4H, 4-pz]. ^{11}B NMR (+25°C, $CDCl_3$, 128 MHz), δ = 0.3 [s]. $^{31}P\{H\}$ NMR (+25°C, $CDCl_3$, 162 MHz), δ = 30.3 [s]. IR (KBr disc), ν/cm^{-1} = 3055m, 1636w, 1591w, 1482m, 1438m, 1385w, 1340w, 1260w, 1186s, 1116s, 1071m. MS(ESI -ve), *m*/*z* = 1383 $[T_kp^{phos(O)}]^-$.

3. Synthesis of [Eu$T_kp^{phos(O)}$\{NO_3\}][NO_3]

A solution of K[$T_kp^{phos(O)}$] (0.075 g, 0.05 mmol) in methanol (5 ml) was added to a solution of europium(III) nitrate pentahydrate in methanol (2 ml) and stirred for two hours. Despite no precipitation, the 31P NMR of the reaction solution indicated formation of a new species. The solution was concentrated to dryness *in vacuo*, extracted into DCM (80 ml) leaving some insoluble white solid, filtered through celite and concentrated to dryness *in vacuo* to give a white solid. Yield = 75 mg (90 %). Single crystals suitable for X-ray analysis were grown by slow diffusion of ether vapour into a solution of the product in methanol. Anal. (%): Calc. (found) for $C_{84}H_{64}BEuN_{10}O_{10}P_4$: C, 60.8 (60.7); H, 3.89 (3.99); N, 8.44 (8.35). ^1H NMR (+25°C, $CDCl_3$, 400 MHz) (all peaks paramagnetically broadened), δ = 8.91 [s], 8.24 [m], 7.89 [m], 7.70 [t], 7.41 [m], 7.28 [m], 7.03 [s], 3.64 [s], 2.43 [s], 2.19 [s], 1.78 [s]. ^{11}B NMR (+25°C, $CDCl_3$, 128 MHz), δ = -12.9 [s]. $^{31}P\{H\}$ NMR (+25°C, $CDCl_3$, 162 MHz), δ = 37.1 [s], -11.3 [s(br)]. IR (KBr disc), ν/cm^{-1} = 2964m, 1636w, 1485m, 1437m, 1384m, 1356w, 1262s, 1177m, 1147s, 1091s, 1025s. MS(ESI +ve), *m*/*z* = 1581 [$EuT_kp^{phos(O)}\{NO_2\}]^+$.

X-Ray Crystallography

Crystal data for **$Tl[T_kp^{phos(O)}]$**: $[C_{84}H_{64}BN_8O_4P_4Tl]\cdot 3.5CHCl_3\cdot 0.5C_5H_{12}$, M = 2042.35, triclinic, $P\bar{1}$ (no. 2), a = 14.6110(3), b = 19.0394(3), c = 19.8132(4) Å, α = 62.012(2), β = 73.056(2), γ = 85.878(2)°, V = 4642.07(15) Å^3, Z = 2, D_c = 1.461 g cm^{-3}, μ(Mo-Kα) = 2.164 mm^{-1}, T = 173 K, colourless blocks, Oxford Diffraction Xcalibur 3 diffractometer; 21105 independent measured reflections, F^2 refinement, R_1 = 0.043, wR_2 = 0.085, 14291 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 58°], 1165 parameters. CCDC 653717.

Crystal data for **$[EuT_kp^{phos(O)}\{NO_3\}][NO_3]$**: $[C_{84}H_{64}BN_9O_7P_4Eu](NO_3)\cdot 4MeOH$, M = 1788.27, monoclinic, $P2_1/c$ (no. 14), a = 25.0529(2), b = 13.1352(1), c = 26.4601(2) Å, β = 106.560(1)°, V = 8346.19(11) Å^3, Z = 4, D_c = 1.423 g cm^{-3}, μ(Cu-Kα) = 6.686 mm^{-1}, T = 173 K, colourless blocks, Oxford Diffraction Xcalibur PX Ultra diffractometer; 16144 independent measured reflections, F^2 refinement, R_1 = 0.034, wR_2 = 0.092, 14231 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 143°], 1093 parameters. CCDC 653718.

The structure of **$Tl[T_kp^{phos(O)}]$** revealed disorder in the C(75) phenyl ring; two orientations were identified of *ca.* 67 and 33% occupancy, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically. The included chloroform solvent was found to be distributed across four distinct sites. At two of these sites the solvent molecule was both full occupancy and ordered. The third site was also full occupancy, but the molecule was found to be disordered across three orientations of *ca.* 40, 34 and 26% occupancy; the chlorine atoms of all three orientations were the only atoms refined anisotropically. The fourth site is adjacent to a centre of symmetry and so has a maximum occupancy of 50%; the molecule in this site is ordered and was refined anisotropically. The included pentane solvent was found to be adjacent to an independent centre of symmetry and disordered; two orientations were identified of *ca.* 27 and 23% occupancy, and both were refined isotropically.

The non-coordinated nitrate anion in the structure of **$Eu[T_kp^{phos(O)}\{NO_3\}][NO_3]$** was found to be disordered; three orientations were identified of *ca.* 51, 25 and 24% occupancy, and they were all refined isotropically. The included methanol solvent molecules were found to be located at four full occupancy sites. Two of these are ordered, but at the other two the molecules were found to be disordered. At one of these sites two orientations were identified of *ca.* 60 and 40% occupancy, with the non-hydrogen atoms of the major occupancy orientation being refined anisotropically. At the other disordered site three orientations were identified of *ca.* 42, 39 and 19% occupancy, and they were all refined isotropically.

Table S1. Selected bond lengths (Å) and angles (°) for **Tl[T$_{k}$p$^{phos(O)}$]**.

Tl–O(1)	2.541(2)	Tl–N(1)	2.536(3)
Tl–N(3)	2.587(3)	B–N(2)	1.547(4)
B–N(4)	1.561(5)	B–N(6)	1.513(5)
B–N(8)	1.524(5)		
O(1)–Tl–	74.78(8)	O(1)–Tl–	83.30(9)
N(1)–Tl–	75.72(9)	N(2)–B–N(4)	113.2(3)
N(2)–B–N(6)	109.1(3)	N(2)–B–N(8)	107.3(3)
N(4)–B–N(6)	107.7(3)	N(4)–B–N(8)	108.5(3)
N(6)–B–N(8)	111.1(3)		

Table S2. Selected bond lengths (Å) and angles (°) for **Eu[T$_{k}$p$^{phos(O)}$\{NO$_3$\}][NO$_3$]**.

Eu–O(1)	2.303(2)	Eu–O(2)	2.299(2)
Eu–O(3)	2.2710(19)	Eu–N(1)	2.608(2)
Eu–N(3)	2.529(2)	Eu–N(5)	2.546(2)
Eu–O(101)	2.442(2)	Eu–O(102)	2.664(3)
B–N(2)	1.549(4)	B–N(4)	1.548(4)
B–N(6)	1.565(4)	B–N(8)	1.525(4)
O(1)–Eu–O(2)	126.32(7)	O(1)–Eu–O(3)	116.45(7)
O(1)–Eu–N(1)	72.79(8)	O(1)–Eu–N(3)	79.81(7)
O(1)–Eu–N(5)	139.99(7)	O(1)–Eu–O(101)	81.21(9)
O(1)–Eu–O(102)	68.75(8)	O(2)–Eu–O(3)	113.58(7)
O(2)–Eu–N(1)	139.12(7)	O(2)–Eu–N(3)	73.34(7)
O(2)–Eu–N(5)	73.40(7)	O(2)–Eu–O(101)	97.15(9)
O(2)–Eu–O(102)	70.50(7)	O(3)–Eu–N(1)	75.96(7)
O(3)–Eu–N(3)	141.16(8)	O(3)–Eu–N(5)	72.55(7)
O(3)–Eu–O(101)	71.80(8)	O(3)–Eu–O(102)	119.96(8)
N(1)–Eu–N(3)	76.19(7)	N(1)–Eu–N(5)	72.26(7)
N(1)–Eu–O(101)	122.91(9)	N(1)–Eu–O(102)	141.48(8)
N(3)–Eu–N(5)	73.51(7)	N(3)–Eu–O(101)	146.99(8)
N(3)–Eu–O(102)	98.64(8)	N(5)–Eu–O(101)	135.14(8)
N(5)–Eu–O(102)	143.77(7)	O(101)–Eu–	49.05(8)
N(2)–B–N(4)	108.0(3)	N(2)–B–N(6)	109.5(2)
N(2)–B–N(8)	112.7(2)	N(4)–B–N(6)	112.1(2)
N(4)–B–N(8)	108.3(2)	N(6)–B–N(8)	106.3(3)

Fig. S1 The molecular structure of **Tl[T$_{\kappa}$p$^{\mathrm{phos(O)}}$]** (30% probability ellipsoids).

Fig. S2 The molecular structure of **Eu[T$_{\kappa}$p$^{\mathrm{phos(O)}}$\{NO$_3$\}][NO$_3$]** (30% probability ellipsoids).

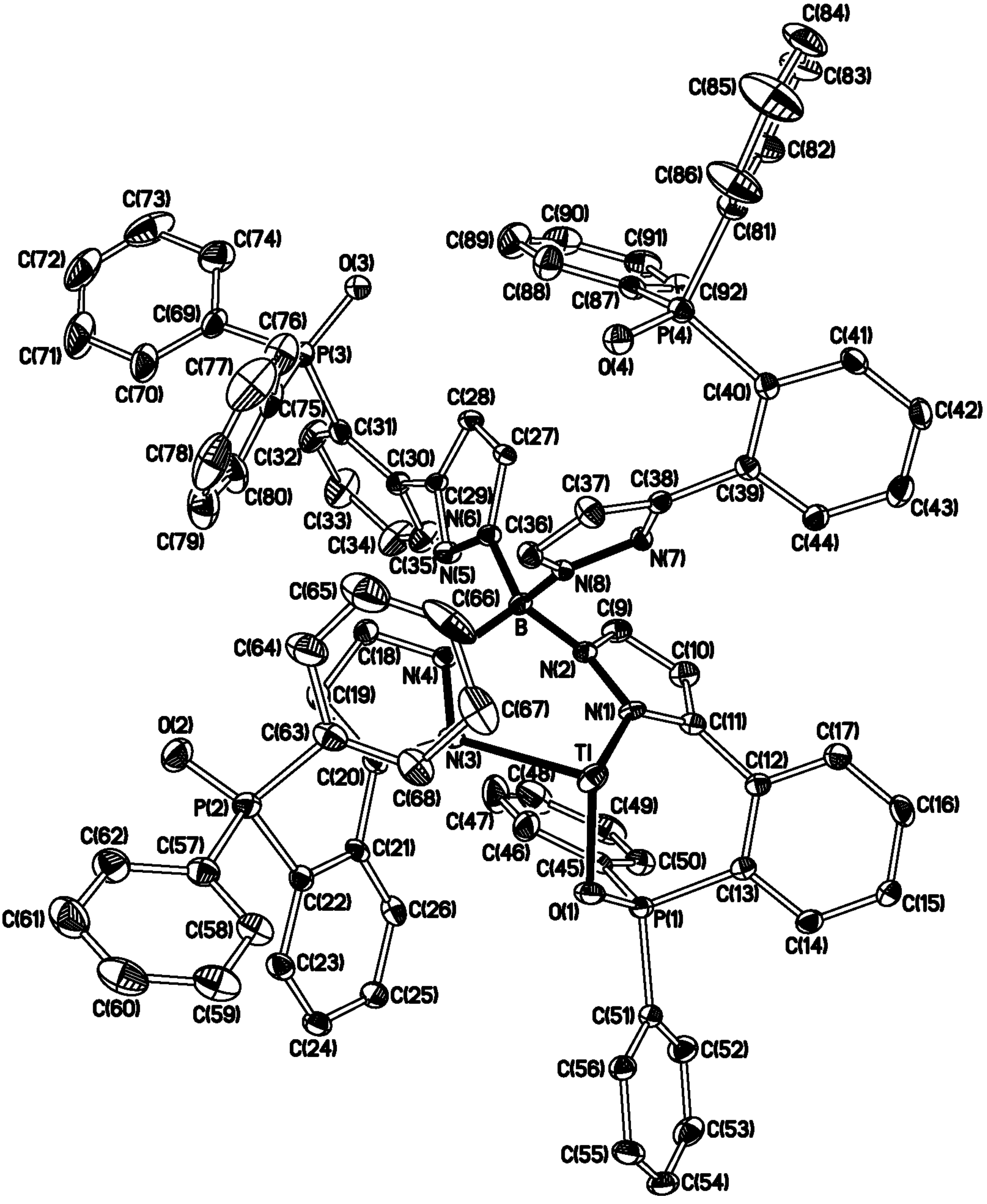
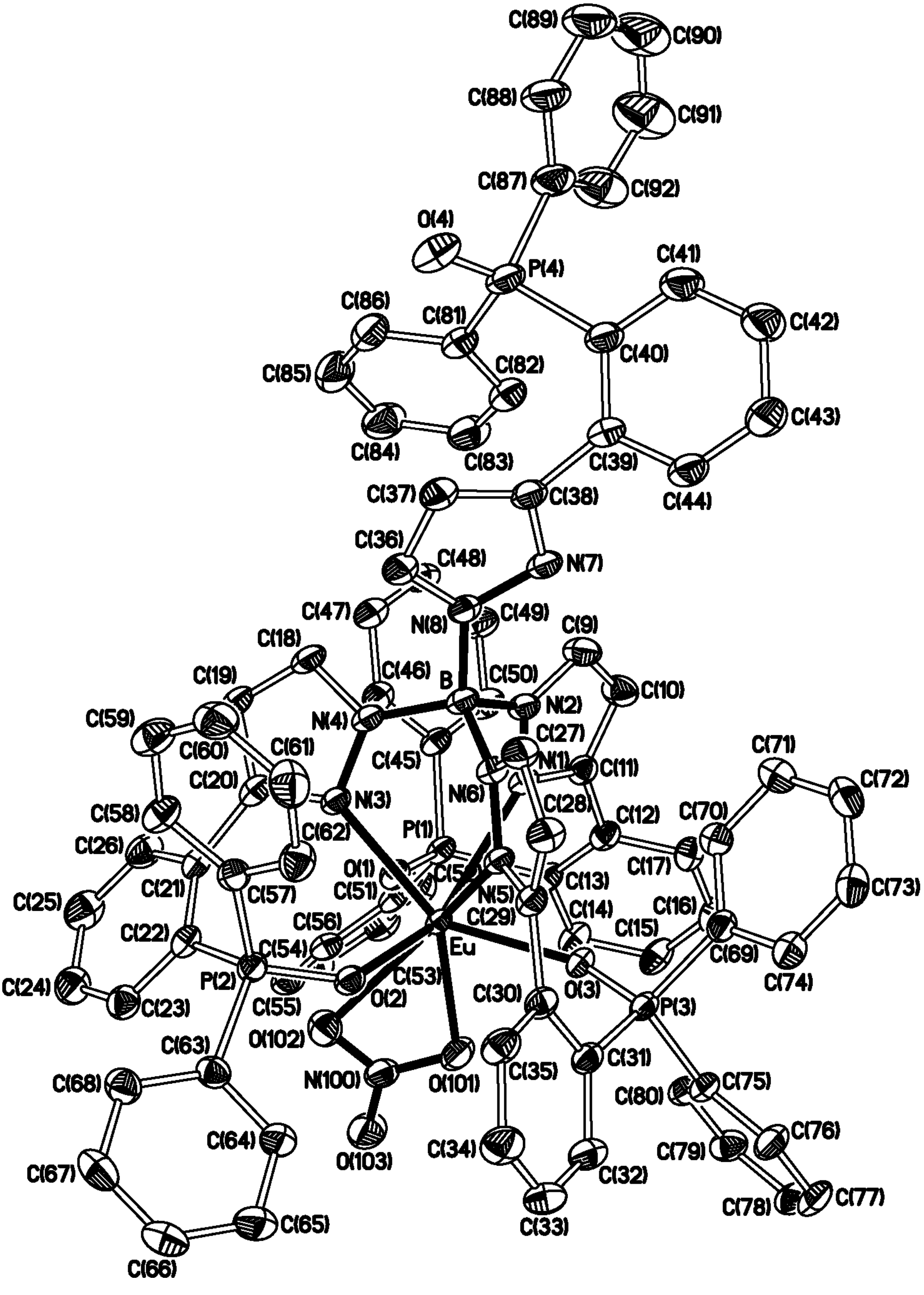


Fig. S1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O(103)
C(67)
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C(78)
C(77)
C(65)
C(33)
C(66)

Fig. S2

References

1. S. Kealey, N. J. Long, P. W. Miller, A. J. P. White, P. B. Hitchcock and A. Gee, *Dalton Trans.*, 2007, 2823.