Electronic Supplementary Information (ESI)

ScorpoPhos: A novel phosphine-nitrogen ligand containing a tris(pyrazolyl)borate ligand core

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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. ^{1}H, ^{11}B, ^{13}C{H} and ^{31}P{H} NMR spectra were recorded on Bruker Av-400, DRX-400 or Av-500 spectrometers. VT ^{31}P NMR spectra were recorded by Peter Haycock on a Bruker DRX-400 spectrometer at the Department of Chemistry, Imperial College, London. 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. 2-(Diphenylphosphino)acetophenone[1] and $RuCl_2(DMSO)_4$[2] were synthesised as reported previously.

1. Synthesis of 1-(2'-diphenylphosphino)3-dimethylamino-2-butene-1-one.

2-(Diphenyphosphino)acetophenone (9.80 g, 32.2 mmol) and N,N-dimethylacetamide dimethylacetal (9.4 ml, 64.4 mmol) in toluene (25 ml) were refluxed for 48 h. After cooling to room temperature, toluene and remaining N,N-dimethylacetamide dimethylacetal were removed *in vacuo* to leave a red solid which was triturated with pentane (50 ml), filtered, washed with pentane (40 ml) and dried *in vacuo* to give a red powder. Yield = 11.10 g (92%).

Anal. (%); Calc. (found) for $C_{24}H_{24}NOP$: C, 77.2 (77.2); H, 6.48 (6.50); N, 3.75 (3.70).

MS(ESI +ve), *m/z* = 374 $[M+H]^+$.

^{1}H NMR (+25°C, $CDCl_3$, 400 MHz), δ = 7.59 [ddd ($^{3}J_{HH}$ = 7.4 Hz, $^{4}J_{HH}$ = 4.0 Hz, $^{5}J_{HH}$ = 1.0 Hz), 1H, 6-Ph], 7.37 [ddd ($^{3}J_{HH}$ = 7.6 Hz, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{HH}$ = 1.0 Hz), 1H, 5-Ph], 7.30-7.34 [m, 10H,

o,m,p-Ph], 7.25 [ddd ($^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.3 Hz), 1H, 4-Ph], 7.00 [dd ($^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 3.8 Hz), 1H, 3-Ph], 5.18 [s, 1H, COCH], 2.79 [s, 6H, $N(CH_3)_2$], 2.57 [s, 3H, =C-CH_3].

$^{13}C\{H\}$ NMR (+25°C, $CDCl_3$, 101 MHz), δ = 191.1 [s, CO], 163.0 [s, =*C*(NMe_2)Me], 151.3 [d ($^2J_{CP}$ = 27.7 Hz), 1-Ph], 138.9 [d ($^1J_{CP}$ = 12.1 Hz), *i*-Ph], 134.5 [s, 3-Ph], 134.2 [d ($^1J_{CP}$ = 17.2 Hz), 2-Ph], 133.8 [d ($^2J_{CP}$ = 19.9 Hz), *o*-Ph], 128.6 [d ($^4J_{CP}$ = 3.1 Hz), 5-Ph], 128.3 [d ($^3J_{CP}$ = 6.9 Hz), *m*-Ph], 128.2 [s, *p*-Ph], 128.0 [s, 4-Ph], 127.3 [d ($^3J_{CP}$ = 5.5 Hz), 6-Ph], 96.9 [s, (OC)H*C*=], 39.7 [s, $N(CH_3)_2$], 16.5 [s, =C-*C*H_3].

$^{31}P\{H\}$ NMR (+25°C, $CDCl_3$, 162 MHz), δ = -11.8.

IR (KBr disc), ν/cm^{-1} = 1533 (CO).

2. Synthesis of 3-[2-(diphenylphosphino)phenyl], 5-methyl pyrazole, $Hpz^{phos,Me}$

Hydrazine hydrate (2.3 ml, 6 eq.) was added dropwise to a solution of 1-(2'-diphenylphosphino)3-dimethylamino-2-butene-1-one (7.79 g, 20.9 mmol) in hot degassed ethanol (45 ml). The solution was heated at reflux for 2 hrs, allowed to cool and the ethanol removed *in vacuo*. DCM (100 ml) was added to the resultant solid and the solution dried over $MgSO_4$. Filtration followed by removal of the solvent gave a yellow powder. Purification by flash column chromatography on silica gel (7:1 DCM:ethyl acetate) gave a white powder. Yield = 6.30 g (88 %).

MS(ESI +ve), *m/z* = 343 $[M+H]^+$.

^1H NMR (+25°C, $CDCl_3$, 400 MHz), δ = 10.31 [s(br), 1H, NH], 7.59 [dd ($^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 4.0 Hz,), 1H, 6-Ph], 7.40 [ddd ($^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.1 Hz), 1H, 5-Ph], 7.25-7.38 [m, 11H, *o,m,p*-Ph + 4-Ph], 7.03 [dd ($^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 4.0 Hz), 1H, 3-Ph], 6.09 [s, 1H, 4-pz], 2.24 [s, 3H, CH_3].

$^{13}C\{H\}$ NMR (+25°C, $CDCl_3$, 101 MHz), δ = 137.3 [d ($^1J_{CP}$ = 10.7 Hz), *i*-Ph], 135.8 [d ($^1J_{CP}$ = 16.9 Hz), 2-Ph], 134.4 [s, 3-Ph], 133.9 [d ($^2J_{CP}$ = 20.1 Hz), *o*-Ph], 129.8 [d ($^3J_{CP}$ = 5.0 Hz), 6-Ph], 128.9 [s, 5-Ph], 128.7 [s, *p*-Ph], 128.6 [d ($^3J_{CP}$ = 6.6 Hz), *m*-Ph], 128.2 [s, 4-Ph], 106.0 [s, 4-pz], 12.3 [s, CH_3].

$^{31}P\{H\}$ NMR (+25°C, $CDCl_3$, 162 MHz), δ = -11.7.

IR (KBr disc), ν /cm^{-1} = 3051 (NH).

3. Synthesis of potassium tris{3-[2-(diphenylphosphino)phenyl], 5-methyl pyrazolyl}borate, K[ScorpoPhos]

A mixture of $Hpz^{phos,Me}$ (4.000 g, 11.7 mmol) and potassium borohydride (0.158 g, 2.92 mmol) was heated gently to 160°C causing the solid to melt. The temperature was then increased to 200°C causing the melt to bubble as H_2 was produced. After 30 mins of stirring the temperature was further increased to 220°C. After 5 hrs at this temperature, heating was stopped and the mixture allowed to cool to room temperature, to produce a yellow solid. This was isolated by dissolution in DCM followed by removal of the solvent by rotary evaporation to give an off-white powder. Recrystallisation from DCM/hexane gave a white powder which was analytically pure. Yield = 2.00 g (64 %).

Anal. (%); Calc. (found) for $C_{66}H_{55}BKN_6P_3$: C, 73.7 (73.8); H, 5.16 (5.22); N, 7.82 (7.90).

MS(ESI -ve), *m/z* = 1035 $[ScorpoPhos]^-$.

^1H NMR (+25°C, $CDCl_3$, 400 MHz), δ = 7.72 [dd ($^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 3.9 Hz), 3H, 6-Ph], 7.33 [ddd ($^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.0 Hz), 3H, 5-Ph], 7.10-7.20 [m, 9H, 4-Ph + *p*-Ph], 7.04 [dd ($^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 7.2 Hz), 12H, *m*-Ph], 6.94 [dd ($^3J_{HP}$ = 7.1 Hz), $^3J_{HH}$ = 7.1 Hz), 12H, *o*-Ph], 6.89 [dd ($^3J_{HP}$ = 7.1 Hz, $^3J_{HH}$ = 3.6 Hz), 3H, 3-Ph], 6.15 [s, 3H, 4-pz], 4.67 [s(br), 1H, BH], 2.13 [s, 9H, CH_3].

$^1H\{^{11}B\}$ NMR (+25°C, $CDCl_3$, 400 MHz), As above, except broad BH peak at 4.67 ppm becomes significantly sharper.

$^{13}C\{H\}$ NMR (+25°C, $CDCl_3$, 126 MHz), δ = 150.9 [s, 3-pz], 145.4 [s, 5-pz], 141.0 [d ($^2J_{CP}$ = 25.2 Hz), 1-Ph], 138.9 [d ($^1J_{CP}$ = 13.4 Hz), *i*-Ph], 134.5 [d ($^1J_{CP}$ = 18.8 Hz), 2-Ph], 134.2 [d ($^2J_{CP}$ = 24.3 Hz), 3-Ph], 133.8 [d ($^2J_{CP}$ = 20.3 Hz), *o*-Ph], 129.7 [m, 6-Ph], 128.4 [s, 5-Ph], 128.0 [d ($^3J_{CP}$ = 6.8 Hz), *m*-Ph], 127.9 [s, *p*-Ph], 126.4 [s, 4-Ph], 105.7 [s, 4-pz], 30.9 [s, CH_3].

$^{31}P\{H\}$ NMR (+25°C, $CDCl_3$, 162 MHz), δ = -11.7.

$^{11}B\{H\}$ NMR (+25°C, $CDCl_3$, 128 MHz), δ = -5.1.

IR (KBr disc), ν /cm^{-1} = 2363 (BH).

4. Synthesis of Tl[ScorpoPhos] (1)

A solution of thallium nitrate (0.059 g, 0.22 mmol) in water (2 ml) was added to a solution of K[ScorpoPhos] (0.200 g, 0.19 mmol) in THF (5 ml) and stirred for 30 minutes to produce a faintly cloudy solution. The solution was extracted into DCM (20 ml), washed with water (10 ml) and the organic layer separated, dried over $MgSO_4$, filtered and concentrated to dryness *in vacuo* to give a glassy colourless solid on the walls of the flask. Dissolution in DCM (2 ml) and hexane (10 ml) followed by slow evaporation of the solvent gave a white powder. Recrystallisation from acetone/hexane gave an analytically pure sample. Yield = 0.162 g (70 %). Single crystals suitable for X-ray analysis were grown by slow evaporation of an acetone solution.

Anal. (%): Calc. (found) for $C_{66}H_{55}BN_6P_3Tl$: C, 63.9 (64.0); H, 4.47 (3.56); N, 6.78 (6.85).

MS(ESI -ve), *m*/*z* = 1035 $[ScorpoPhos]^-$.

^1H NMR (+25°C, $CDCl_3$, 400 MHz), δ = 7.54 [m, 3H, 6-Ph], 7.23 [t ($^3J_{HH}$ = 7.3 Hz), 6H, *p*-Ph], 7.10-7.20 [m, 18H, 4-Ph + 5-Ph + *m*-Ph), 6.97 [dd ($^3J_{HP}$ = 6.8 Hz, $^3J_{HH}$ = 6.8 Hz), 12H, *o*-Ph], 6.82 [m, 3H, 3-Ph], 5.62 [s, 3H, 4-pz], 4.68 [s(br), 1H, BH], 2.26 [s, 9H, CH_3].

$^{31}P(H)$ NMR (+25°C, $CDCl_3$, 162 MHz), δ = -3.1 [d ($^1J_{PTh}$ = 1253 Hz)].

$^{11}B\{H\}$ NMR (+25°C, $CDCl_3$, 128 MHz), δ = -5.1.

IR (KBr disc), ν /cm^{-1} = 2512 (BH).

5. Synthesis of Cu[ScorpoPhos] (2)

THF (10 ml) was added to a mixture of K[ScorpoPhos] (0.100 g, 0.09 mmol) and CuCl (0.009 g, 0.09 mmol) immediately forming a yellow solution. ^{31}P NMR spectroscopy of the reaction solution indicated formation of a new species at -9.0 ppm. The solution was filtered and concentrated to dryness *in vacuo* to give a pale yellow solid of analytical purity. Yield = 0.083 g (81 %). Recrystallisation from warm acetone yielded colourless single crystals suitable for X-ray analysis.

Anal. (%): Calc. (found) for $C_{66}H_{55}BCuN_6P_3$: C, 72.1 (72.0); H, 5.04 (5.10); N, 7.64 (7.58).

MS(ESI +ve), *m*/*z* = 1099 [Cu(ScorpoPhos)]$^{+}$.

^{1}H NMR (+25°C, $CDCl_3$, 400 MHz), δ = 7.94 [d ($^{3}J_{HH}$ = 7.6 Hz), 3H, 6-Ph], 7.18 [m, 9H, 5-Ph + *p*-Ph], 7.11 [ddd ($^{3}J_{HH}$ = 7.5 Hz, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{HH}$ = 1.0 Hz), 3H, 4-Ph], 7.06 [dd ($^{3}J_{HH}$ = 7.5 Hz, $^{3}J_{HH}$ = 7.5 Hz), 12H, *m*-Ph], 6.95 [m, 15H, 3-Ph + *o*-Ph], 5.98 [s, 3H, 4-pz], 4.79 [s(br), 1H, BH], 2.31 [s, 9H, CH_3].

^{31}P(H) NMR (+25°C, CD_2Cl_2, 162 MHz), δ = -7.4 [s].

^{31}P(H) NMR (-90°C, CD_2Cl_2, 162 MHz), δ = -14.64 [s(br), 2P, PPh_2], 0.0 [s, 1P, PPh_2–Cu]

^{11}B NMR (+25°C, CD_2Cl_2, 128 MHz), δ = -5.4 [s(br)].

IR (KBr disc), ν /cm^{-1} = 2509 (BH).

NL0711 (1), NL0712 (2)

Supporting Information — X-Ray Crystallography

The structure of **1** (which crystallised in the chiral space group *P*3) was found to contain five crystallographically independent complexes, referred to as **1-A**, **1-B**, **1-C**, **1-D** and **1-E** for the complexes where the atom labels end in "A", "B", "C", "D" and "E" respectively. Two of these have C_1 symmetry [**1-A** and **1-B**] and three have C_3 symmetry [**1-C**, **1-D** and **1-E**], making a total of three complexes in the asymmetric unit. These are shown in Fig. 1 in the main manuscript, and Figs. S2, S4, S6 and S8 in the supporting information respectively. (The two complexes that do not have *crystallographic* C_3 symmetry, **1-A** and **1-B**, do possess *molecular* C_3 symmetry.) Given the twist of each arm of the ligand, the complexes are chiral, and the five independent complexes in the asymmetric unit are not all of the same chirality. Complexes **1-B**, **1-C**, **1-D** and **1-E** all have the same chirality, which is different to that of **1-A**, so in total the asymmetric unit contains two complexes of one chirality, and one complex of the other. Additionally, the crystal studied was a partial racemic twin, meaning that in *ca.* 84% of the unit cells in the crystal studied the chiralities are as shown in the figures, whilst in the other 16% all of the chiralities are reversed.

All five B-H protons in **1** were placed in idealised positions and allowed to ride on their parent atoms at a B–H distance of 1.00 Å, with their thermal parameter tied to the equivalent isotropic thermal parameter of the parent boron centre [U(H) = 1.2U_{eq}(B)]. The sole B–H proton in **2** was found from a ΔF map and refined freely subject to a B–H distance constraint of 1.08 Å.

Amongst the five independent complexes present in the structure of **1**, molecule **1-C** stands out with shorter Tl–N and Tl···B separations, longer Tl–P distances, and larger N–Tl–N angles (Table S1). Assuming no other deformations, all these differences are consistent with the thallium centre in **1-C** being occupying a position closer to the N(1),N(3),N(5) plane than in the other four molecules [*ca.* 1.91 Å for **1-C** *cf.* between 1.96 and 1.99 Å for the others], though the reason for this deformation is unclear.

Table S1. Comparative selected bond lengths (Å) and angles (°) for the five crystallographically independent complexes present in the crystals of **1**.

	1-A	**1-B**	**1-C** [a]	**1-D** [a]	**1-E** [a]
Tl–N(1)	2.642(3)	2.635(3)	2.581(3)	2.632(3)	2.654(3)
Tl–N(3)	2.678(3)	2.622(3)			
Tl–N(5)	2.637(3)	2.643(3)			
Tl–P(1)	3.2273(9)	3.2893(9)	3.4374(10)	3.3169(10)	3.2580(9)
Tl–P(2)	3.2122(9)	3.3476(9)			
Tl–P(3)	3.2488(9)	3.2640(9)			
Tl···B	3.812(4)	3.800(5)	3.729(9)	3.798(9)	3.831(7)
Tl···[N_3] [b]	1.987	1.971	1.905	1.955	1.977
N(1)–Tl–N(3)	68.88(9)	70.84(9)	71.54(11)	70.85(12)	70.60(11)
N(1)–Tl–N(5)	70.04(9)	70.15(9)			

N(3)–Tl–N(5)	71.00(10)	69.31(9)			

[a] The molecule has C_3 symmetry meaning that the Tl–N(3) and Tl–N(5) bonds are symmetry equivalents of the Tl–N(1) bond, the Tl–P(2) and Tl–P(3) bonds are equivalent to the Tl–P(1) bond, and the N(1)–Tl–N(5) and N(3)–Tl–N(5) angles are equivalent to the N(1)–Tl–N(3) angle. [b] This is the deviation of the thallium centre from the plane of the three coordinated nitrogen atoms.

Table S2. Selected bond lengths (Å) and angles (°) for **2**.

Cu–N(1)	2.0987(16)		Cu–N(3)	2.0872(16)
Cu–N(5)	2.0733(16)		Cu–P(1)	2.1745(6)
Cu···P(2)	3.7767(7)		Cu···P(3)	5.7297(7)
Cu···B	3.025(2)		Cu···[N_3] [a]	1.187
N(3)–Cu–N(5)	89.88(6)		N(1)–Cu–N(5)	96.04(6)
N(1)–Cu–N(3)	86.11(6)		N(1)–Cu–P(1)	90.37(5)
N(3)–Cu–P(1)	139.14(5)		N(5)–Cu–P(1)	130.95(5)

[a] This is the deviation of the copper centre from the plane of the three coordinated nitrogen atoms.

Fig. S1 The molecular structure of **1**-**A**, one of the five crystallographically independent complexes present in the crystals of **1** (30% probability ellipsoids).

Fig. S2 The molecular structure of **1**-**B**, one of the five crystallographically independent complexes present in the crystals of **1**.

Fig. S3 The molecular structure of **1**-**B**, one of the five crystallographically independent complexes present in the crystals of **1** (30% probability ellipsoids).

Fig. S4 The molecular structure of **1**-**C**, one of the five crystallographically independent complexes present in the crystals of **1**.

Fig. S5 The molecular structure of **1**-**C**, one of the five crystallographically independent complexes present in the crystals of **1** (30% probability ellipsoids).

Fig. S6 The molecular structure of **1**-**D**, one of the five crystallographically independent complexes present in the crystals of **1**.

Fig. S7 The molecular structure of **1**-**D**, one of the five crystallographically independent complexes present in the crystals of **1** (30% probability ellipsoids).

Fig. S8 The molecular structure of **1**-**E**, one of the five crystallographically independent complexes present in the crystals of **1**.

Fig. S9 The molecular structure of **1**-**E**, one of the five crystallographically independent complexes present in the crystals of **1** (30% probability ellipsoids).

Fig. S10 The molecular structure of **2** (30% probability ellipsoids).

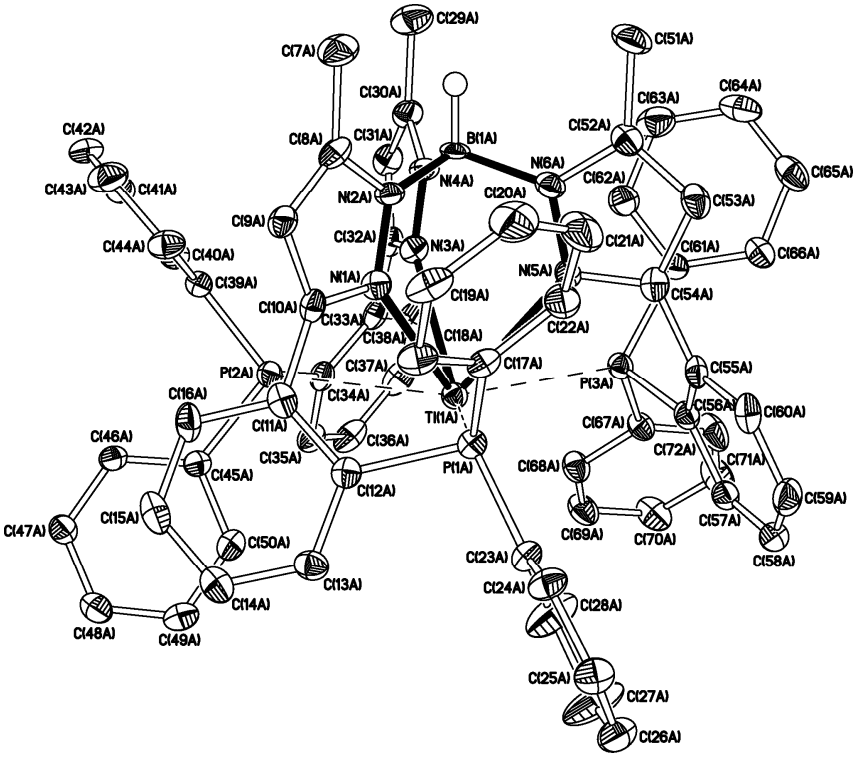
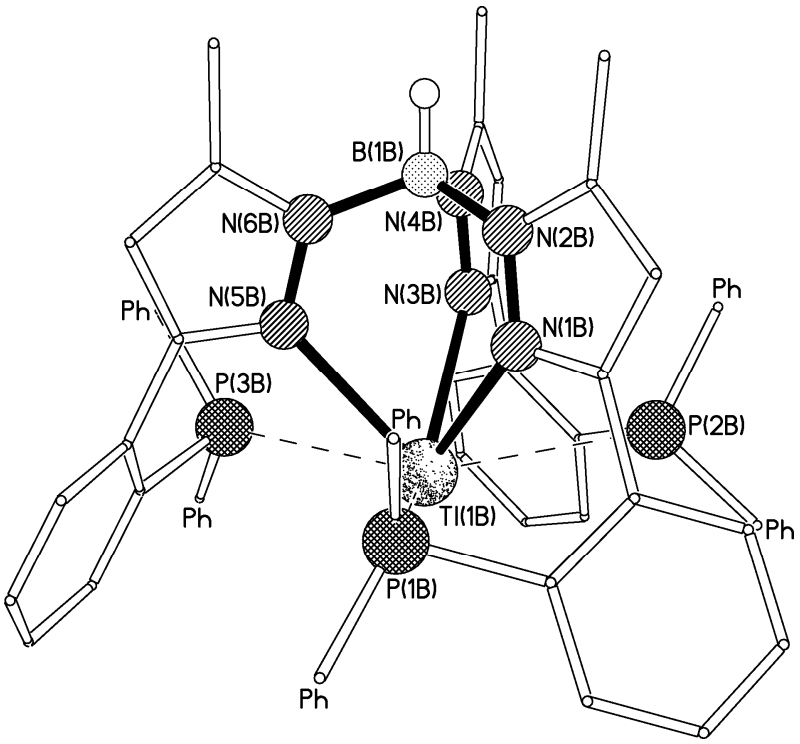


Fig. S1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Ph

Fig. S2

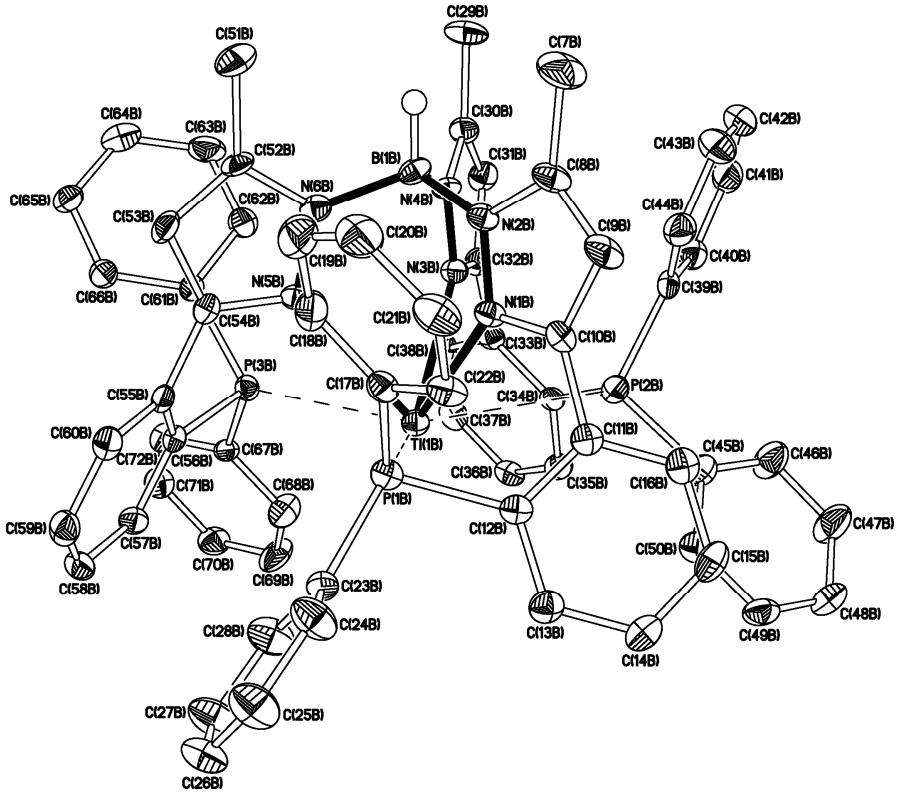
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Fig. S3

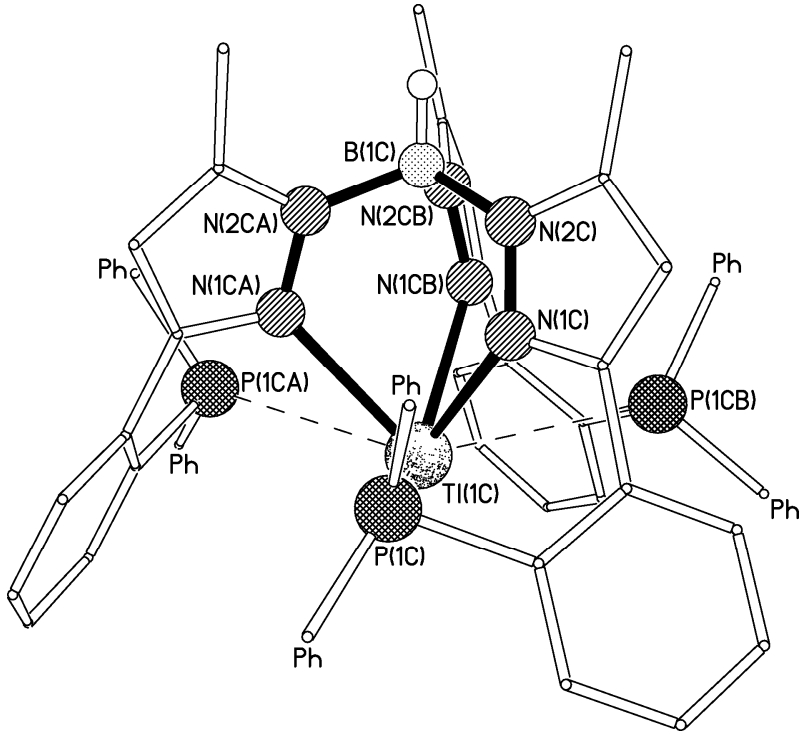
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Fig. S4

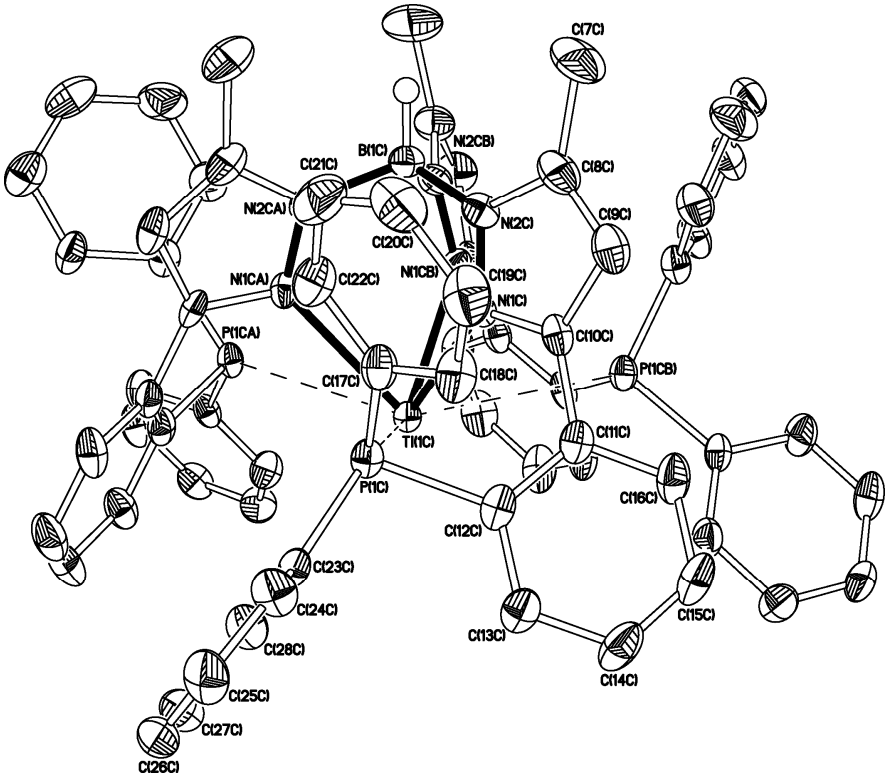
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Fig. S5

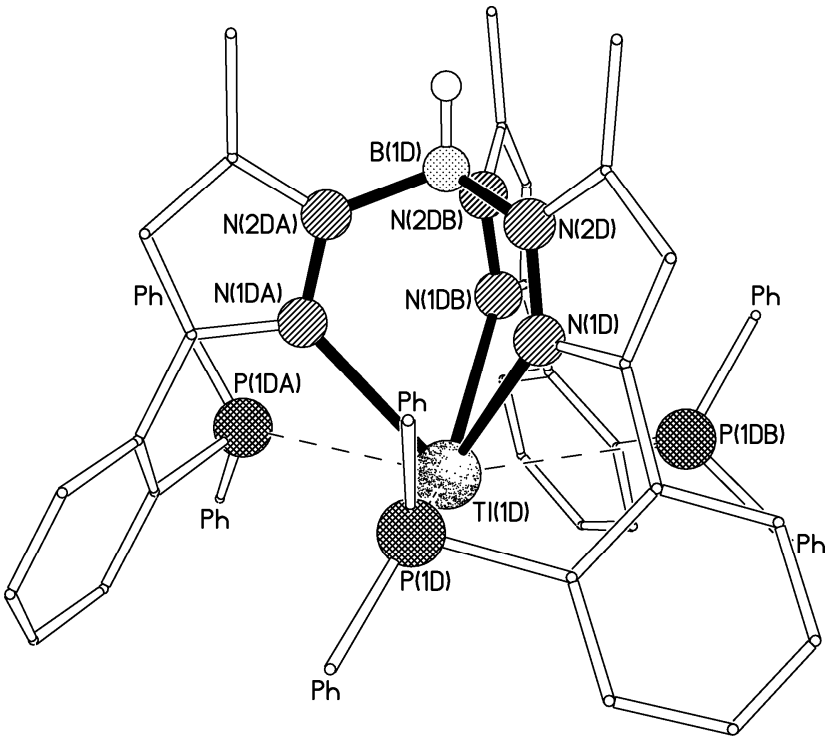
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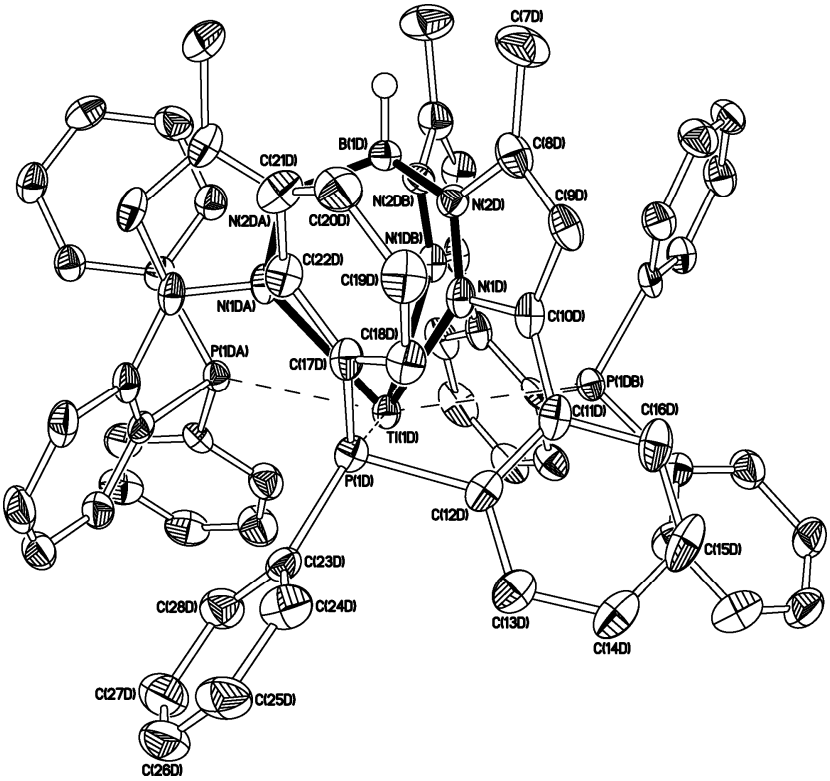
Fig. S6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C(26D)

Fig. S7

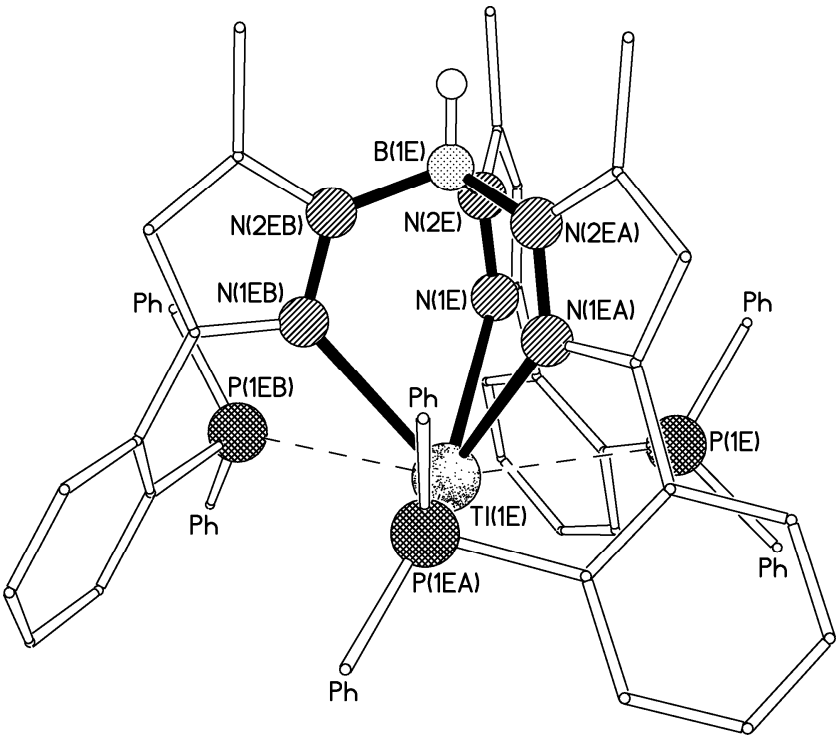
B(1E)
N(2EB)
N(2E)
N(2EA)
N(1EB)
N(1E)
N(1EA)
Ph
Ph
P(1EB)
Ph
P(1E)
Ph
Tl(1E)
Ph
P(1EA)
Ph

Fig. S8

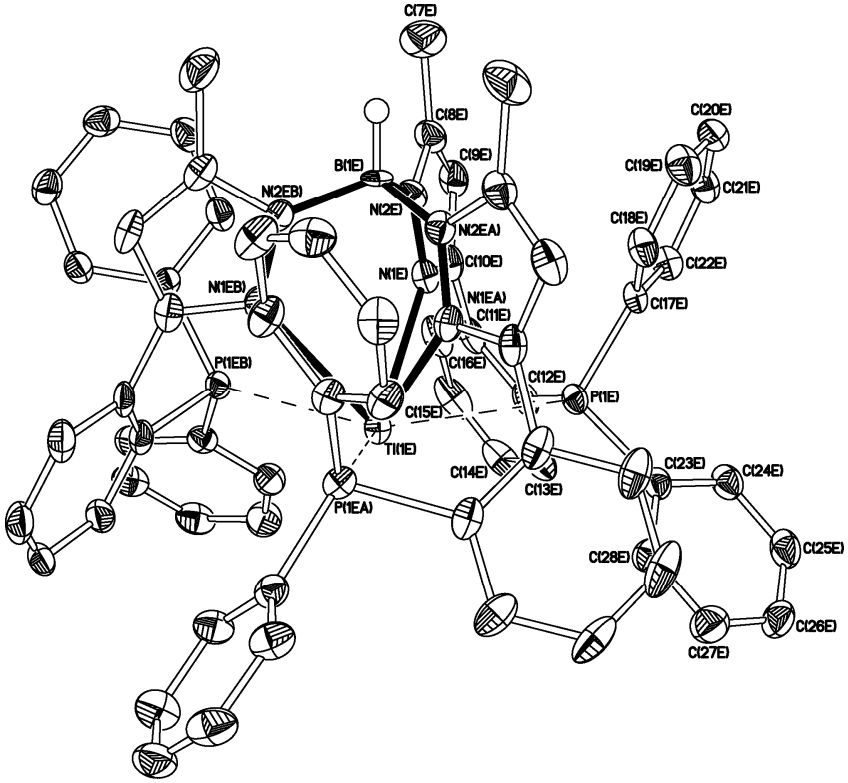
C(7E)
C(8E)
C(20E)
B(1E)
C(9E)
C(19E)
C(21E)
N(2EB)
N(2E)
N(2EA)
C(18E)
C(10E)
C(22E)
N(1E)
N(1EB)
N(1EA)
C(17E)
C(11E)
C(16E)
C(12E)
P(1EB)
P(1E)
C(15E)
Tl(1E)
C(23E)
C(24E)
C(14E)
C(13E)
P(1EA)
C(25E)
C(28E)
C(26E)
C(27E)

Fig. S9

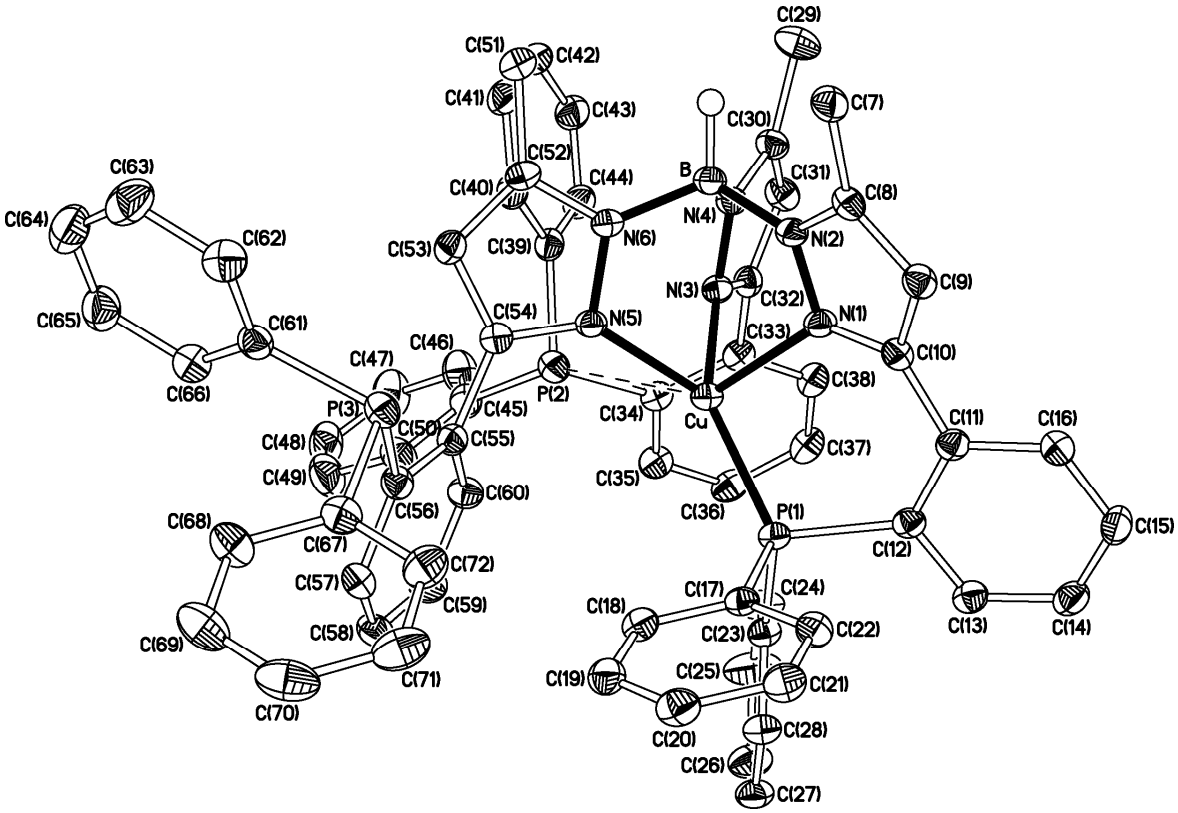

Fig. S10

References

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2. I. P. Evans, A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, 204.