Electronic Supplementary Information for Dalton Transactions

Supplementary Data for '*Unexpected Pincer-type Coordination (κ^3-SBS) within a Zerovalent Platinum Metallaboratrane Complex*'

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General Methods:

All manipulations were performed in a Braun glovebox with an O_2 and H_2O atmosphere of below 5 ppm or by using standard Schlenk techniques. Solvents were dried by passing through alumina columns under a stream of N_2 and stored under N_2 over 4 Å molecular sieves in Young's ampoules. NMR solvents were degassed by three freeze-thaw cycles and were stored under N_2 over 4 Å molecular sieves in Young's ampoules. ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$, $^{11}B\{^{1}H\}$, ^{11}B-NMR, VT-$^{1}H/^{11}B\{^{1}H\}$ and $^{11}B\{^{1}H\}$-NMR were acquired on a JEOL ECP300 spectrometer operating at 300 MHz (^{1}H), at ambient temperature unless otherwise stated. Spectra were referenced to internal standards, to the residual protio solvent (^{1}H) or the signals of the solvent (^{13}C). $^{11}B\{^{1}H\}$ and ^{11}B were referenced externally relative to $BF_3.OEt_2$ and $^{31}P\{^{1}H\}$ to H_3PO_4 85% in D_2O. Mass spectra were recorded on a VG Analytic Quattro on ESI^+ mode. Elemental analyses were performed at the micro-analytical laboratory of the School of Chemistry at the University of Bristol. Infra red spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer (solid state-neat).

[PtH(PPh$_3$){κ^4-*SSBS*-B(mt)$_2$(mp)}]Cl (5)

A Schlenk flask was charged with [Pt(PPh$_3$)$_2$Cl$_2$] (0.2 g, 0.253 mmol) and the solid dissolved in DCM (10 mL). Na[HB(mp)(mt)$_2$] (0.094 g, 0.0253 mmol) was added in one portion to the stirring solution resulting in a rapid colour change to yellow solution. After 1 hour, the solution was filtered through celite to remove NaCl. The volume of the reaction mixture was reduced under vacuum and hexane (20 mL) was added to precipitate a yellow solid. The solid was isolated by filtration and dried under vacuum. Yield = 0.150 g, 0.178 mmol, 71 %).

NMR (CD_2Cl_2) δ: ^{1}H δ -13.98 (d, 1H, $^{2}J_{HP}$ = 4.7 Hz, $^{1}J_{PtH}$ = 1002 Hz, Pt*H*), 3.46 (s, 3H, NC*H*$_3$), 3.47 (s, 3H, NC*H*$_3$), 6.96 (dd, 1H, d, $^{3}J_{HH}$ = 2.2 Hz, 1.5 Hz, ^{mt}CH), 7.24 (m, 1H, ^{mt}CH), 7.30 (m, 1H, ^{mp}CH), 7.37 (m, 1H, ^{mp}CH), 7.42 – 7.50 (m, 15H, PC_6H_5 + 1H, ^{mp}CH), 7.91 (d, 1H, $^{3}J_{HH}$ = 2.2 Hz, ^{mt}CH), 9.20 (d, 1H, $^{3}J_{HH}$ = 2.5 Hz, ^{mt}CH),

9.57 (d, 1H, $^{3}J_{HH}$ = 6.2 Hz, ^{mp}CH). $^{13}C\{^{1}H\}$ δ: 34.5 (mt, *C*H_3), 34.9 (mt, *C*H_3), 119.4 (mt), 120.5 (mp), 121.9 (mt), 125.5 (mt), 126.3 (mt), 127.4 (mp, $^{3}J_{PtC}$ = 51.7 Hz), 129.3 (d, *m*-PC_6H_5, $^{3}J_{PC}$ = 9.7 Hz), 131.4 (s, *p*-PC_6H_5), 131.7 (d, *i*-PC_6H_5, $^{1}J_{PC}$ = 36.9 Hz), 134.3 (d, *o*-PC_6H_5, $^{2}J_{PC}$ = 12.1 Hz), 139.5 (mp), 144.8 (mp), 162.7 (d, 15.3 Hz, C=S^{mt}), 163.8 (d, 20.6 Hz, C=S^{mt}), 173.2 (d, 14.1 Hz, C=S^{mp}). $^{11}B\{^{1}H\}$ NMR 6.5 (br, h.h.w. = 260 Hz, d, $^{2}J_{PB}$ = 105 Hz, $^{1}J_{PtB}$ = 460 Hz). $^{31}P\{^{1}H\}$ 4.0 (m, br, h.h.w. = 285 Hz, $^{1}J_{PtB}$ = 115 Hz, $^{1}J_{PtP}$ = 1025 Hz). IR: 2182 cm^{-1} (Pt-H). MS-ESI^{+} 829 [M – Cl + Na], 579 [M - PPh_3]$^{+}$. Anal. Found: C, 42.61; H, 3.72; N, 8.15. Calculated for $C_{31}H_{30}BClN_5PPtS_3.0.5CH_2Cl_2$: C, 42.82; H, 3.54; N, 7.93

[Pt(PPh$_3$){B(mt)$_2$(mp)}] (6)

A Schlenk was charged with **5** (0.100 g, 0.119 mmol) and MeOH (10 mL) providing a yellow solution. DBU (215 μl, 0.119 mmol,) was added to stirring solution yielding an orange precipitate. After 2 hours, the mixture was filtered yielding a bright orange solid. The solid was dried under vacuum. Yield = 0.060 g, 0.075 mmol, 63 %). Orange crystals were obtained by layering a DCM solution of **6** with hexane.

NMR (CD_2Cl_2) ^{1}H δ 3.44 (6H, s, NC*H*$_3$), 6.68 (1 H, ddd, $^{3}J_{HH}$ = 7.1 Hz, $^{3}J_{HH}$ = 6.1 Hz, $^{4}J_{HH}$ = 1.2 Hz, 5-^{mp}C*H*), 6.71 (2H, dd, $^{3}J_{HH}$ = 2.2 Hz, $^{4}J_{HH}$ = 0.7 Hz, NCHC*H*NCH$_3$), 7.16 (1H, ddd, $^{3}J_{HH}$ = 8.3 Hz, $^{4}J_{HH}$ = 1.2 Hz, $^{5}J_{HH}$ = 0.7 Hz 3-^{mp}CH), 7.27 (1H, ddd, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 7.1 Hz, $^{4}J_{HH}$ = 1.5 Hz 4-^{mp}CH), 7.40 [9H, m, *m/p*-P(C$_6$*H*$_5$)$_3$], 7.51 [6H, m, *o*-P(C$_6$*H*$_5$)$_3$], 8.33 (2H, d, $^{3}J_{HH}$ = 2.2 Hz, NC*H*CHNCH$_3$), 8.73 (br, 1H, ddd, $^{3}J_{HH}$ = 6.1 Hz, $^{4}J_{HH}$ and $^{5}J_{HH}$ coupling constants unresolved, 6-^{mp}C*H*). $^{13}C\{^{1}H\}$ δ 34.5 (^{mt}CH$_3$), 113.8 (^{mp}CH), 119.8 (^{mt}CH), 124.9 (^{mt}CH), 128.24 (d, *m*-PC_6H_5, $^{3}J_{PC}$ = 8.6 Hz), 130.3 (*p*-PC_6H_5), 132.5 (^{mp}CH), 134.4 (d, *o*-PC_6H_5, $^{2}J_{PC}$ = 13.4 Hz), 134.8 (d, *i*-PC_6H_5, $^{1}J_{PC}$ = 31.9 Hz), 139.0 (^{mp}CH), 146.1 (^{mp}CH), the signals for the *C*=S groups were not observed. $^{11}B\{^{1}H\}$ NMR (96.2 MHz) 11.4 (br, h.h.w. = 444 Hz, $^{2}J_{PB}$ = unresolved, $^{1}J_{PtB}$ = 570 Hz). $^{31}P\{^{1}H\}$ NMR (121.7 MHz) 28.7 (br, h.h.w. = 273 Hz, $^{1}J_{PPt}$ = 1410 Hz). IR: no Pt-H stretch present. Anal. Found: C, 45.87; H, 4.01; N, 8.93. Calculated for $C_{31}H_{29}BN_5PPtS_3$: C, 46.27; H, 3.63; N, 8.70.

X-ray Crystallography:

Data for **6** were collected on a Bruker Kappa Apex II CCD detector diffractometer with a fine-focus sealed tube Mo/Ka radiation source and a Cryostream Oxford Cryosystems low temperature device, operating in ω scanning mode with ψ and ω

scans to fill the Ewald sphere. The programs used for control and integration were APEX II, SAINT v7.34A and XPREP v2005/4.[S1] The crystal was mounted on a glass fibre with silicon grease, from Parafin oil.

All solutions and refinements were performed using the Bruker Shelxtl software and all software packages within. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogens were added using a riding model.

Data collection parameters and refinement information are presented in Table S1 in this supplementary data manuscript. Anisotropic parameters, bond lengths and (torsion) angles for **6** is available from the cif file.

References

S1. Bruker-AXS, 2007; Bruker-AXS, 2005

S2. R. Hooft, COLLECT; Nonius BV, 1997-2000; Z. Otwinowski, W. Minor, SCALEPACK, DENZO, *Methods Enzymol*. 1997, **276**, 307.

Complex	**6**
Chemical Formula	$C_{31}H_{29}BN_5PPtS_3$
Formula weight	804.64
Crystal system	Monoclinic
Space group (no)	$P2_1/c$
a / *Å*	15.9926(2)
b / *Å*	10.12870(10)
c / *Å*	20.0351(2)
β / °	106.5320(10)
Z	4
T/K	100(2)
μ / mm^{-1}	4.794
No. of data collected	93339
No. of unique data	9540
Goodness of fit on F^2	1.070
$R_{int.}$	0.0343
Final $R(\|F\|)$ for $F_0 > 2\sigma(F_0)$	0.0205
Final $R(F^2)$ for all data	0.0246

Table S1: Data collection and refinement information for **6**.