Unexpected pincer-type coordination (κ^3 -SBS) within a zerovalent platinum metallaboratrane complex[†]

Gareth R. Owen,*[‡] P. Hugh Gould, Alex Hamilton and Nikolaos Tsoureas

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The first structurally characterised zerovalent platinum complex to contain a tridentate pincer-type coordination mode (κ^3 -SBS) is presented, raising further questions concerning the geometries and *trans* influence of Z-type ligands.

The coordination chemistry of Z-type ligand systems (σ -acceptors) is currently of considerable interest.¹ In particular, the existence of transition metal-borane compounds has been widely debated ever since Shriver reported the first such compound in 1963.² This compound however, along with some further examples,³ was later disproved.⁴ It was not until 1999 when Hill provided conclusive proof and structural characterisation of the first 'metallaboratrane' complex (1, Fig. 1)⁵ establishing an important synthetic route to transition metal-borane complexes. This report sparked considerable development in the field and a number of subsequent synthetic routes have since been realised.^{1c-e} A wide range of metallaboratrane compounds have been prepared based upon sulfur,⁶ phosphorus,⁷ nitrogen⁸ donors in addition to other supporting units.⁹



Fig. 1 Metallaboratrane complex $[Ru\{\kappa^4\text{-}SSBS\text{-}B(mt)_3(CO)(PPh_3)]$ (N–S = mt) (1).

We became interested in the borane functional group for its potential application as a 'hydride store' within transition metal mediated transformations. Indeed, some evidence has been provided for reversible hydride migration between transition metal and boron centres within metallaboratrane complexes.^{10,11} In relation to this, a number of investigations exploring the propensity for hydride migration by varying the substituents at boron have been carried out.^{8b} Additionally, we set out to explore the nature of the metal-boron interaction in more detail and for this purpose have recently reported a new family of flexible scorpionate ligands based on 2-mercaptopyridine.¹² In an attempt to reduce the symmetry of the resulting complexes and to provide systematic information regarding the metal-borane interaction, we also set out to develop a range of new hybrid ligands based on 2-mercaptopyridine (mp) and 1-methyl-imidazoyl-2-thione (mt) units.¹³

A range of complexes containing the hybrid ligand, sodium hydro(2-pyridylthione)bis(methimizole)borate, ^{mp}Bm have been prepared. During the course of our investigations, we synthesised a zerovalent platinum complex expecting to obtain a trigonal bipyramidal complex similar to that previously reported by Crossely and Hill.¹⁴ Herein, we wish to report an unexpected pincer-type coordination of the resulting mixed sulfur/borane ligand, providing a square planar geometry at the zerovalent platinum centre. The implication of *trans* influence of the borane functionality is also discussed.

The synthesis and structural characterisation of the divalent octahedral complex [PtH(PPh₃){ κ^4 -SSBS-B(mt)₃}]Cl (2) has been previously reported.^{14,15} In the presence of DBU (1,8-diaza[5.4.0]bicycloundec-7-ene), complex 2 underwent reductive elimination, resulting in loss of HCl, to form the new complex [Pt(PPh₃){B(mt)₃}] (3) (Scheme 1). In the absence of structural characterisation, the coordination mode of the multidentate ligand was assigned as κ^4 -SSBS on the basis on the ¹H and ¹³C{¹H} NMR spectra which indicated only one chemical environment for the 'mt' rings.



Scheme 1 Synthesis of divalent and zerovalent platinum complexes 3 and 4.

The hybrid ligand, Na[^{mp}Bm] (4)¹³ (Fig. 2) was utilised to prepare the analogous divalent and zerovalent platinum complexes [PtH(PPh₃){B(mt)₂(mp)}]Cl (5) and [Pt(PPh₃){B(mt)₂(mp)}] (6) respectively.



Fig. 2 Hybrid scorpionate, Na[^{mp}Bm] (4).

Complex 5 was characterised by spectroscopic and analytical methods (see ESI[†]) and was found to be analogous to complex 2. The signal corresponding to the phosphorus ligand was

The School of Chemistry, University of Bristol, Bristol, UK BS8 1TS. E-mail: gareth.owen@bristol.ac.uk; Fax: 0117 925 1295; Tel: 0117 928 7652 † Electronic supplementary information (ESI) available: Full experimental details for the preparation of **5** and **6**. CCDC reference number 738770 for **6**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b917733g ‡ Royal Society Dorothy Hodgkin Research Fellow.

particularly broad. The ${}^{31}P{}^{1}H$ NMR spectrum of 5 revealed a single broad signal at 4.0 ppm (CD_2Cl_2 , h.h.w. = 285 Hz) with platinum satellites (${}^{1}J_{PPt} = 1025 \text{ Hz}$). The ${}^{1}H$ NMR spectrum of 5 was consistent with the spectroscopic assignment and structural characterisation for complex 2. The spectrum revealed a single peak, with an integration for one proton, at -13.9 ppm with platinum satellites (${}^{1}J_{PtH} = 1002$ Hz) corresponding to the platinumhydride. This was also confirmed by infrared spectroscopy by the presence of a band at 2182 cm⁻¹. The spectrum further revealed four doublets in the lowfield region of the spectrum at δ 9.21, δ 7.92, δ 7.16 and δ 6.87, each integrating to one proton and corresponding to the CH=CH protons on the mt rings. This observation indicates that the mt rings are in different chemical environments. Two signals (each integrating for three protons) were observed at 3.46 ppm and 3.47 ppm corresponding to the two independent NCH₃ groups. The two distinct chemical shifts of mt ring protons show that they are *cis* to each other in the complex and therefore one mt ring is *trans* to the hydride and the other ring is trans to the mp ring. All other data agree with the spectroscopic and structural assignment of complex 2 and accordingly complex 5 has been assigned as $[PtH(PPh_3)]\kappa^4$ -SSBS- $B(mt)_2(mp)$]Cl (Fig. 3).



Fig. 3 Highlighting the positions of the mt and mp rings within 5 (N–S = mt).

Complex 6, $[Pt(PPh_3){B(mt)_2(mp)}]$, was obtained as a bright orange solid in good yield. The formation of 6 was also confirmed by the spectroscopic and analytical data. The peak corresponding to the phosphine ligand was found at 28.7 ppm (CD₂Cl₂, ${}^{1}J_{PtP} =$ 1410 Hz) [*c.f.* 26.5 (CDCl₃, ${}^{1}J_{PtP} = 1370$ Hz) for 3]. The spectroscopic data were fully consistent with those reported for complex 3. The ¹H NMR spectrum revealed only one chemical environment for the two mt rings (two doublet signal, each integrating for two protons, at 6.72 ppm and 8.50 ppm). Four signals integrating for one proton each, corresponding to the mp ring protons were also observed in the lowfield region of the spectrum. The equivalence of the mt ring protons was therefore consistent with the trigonal bipyramidal geometry that had been assigned to 3. In order to confirm this assignment a crystallographic study was carried out on 6. Single crystals were obtained by layering a dichloromethane solution of 6 with hexane. Unexpectedly, a crystallographic study revealed an unexpected pincer-type coordination mode (κ^3 -SBS) of the borane based ligand where one of the ligand arms (mt) remains uncoordinated (Fig. 4).§ This was surprising since the spectroscopic data suggested chemically equivalent environments for the two mt rings.

The zerovalent platinum centre adopts a distorted square planar geometry with *cis*-inter ligand angles in the range 81.04(6)– $98.434(11)^{\circ}$. The S(1)-Pt(1)-S(2) angle is $163.15(2)^{\circ}$ and the B(1)-Pt(1)-P(1) angle is $172.32(6)^{\circ}$. The boron atom is approximately tetrahedral with angles in the range 106.54(15)– $112.52(16)^{\circ}$. One each of the mt and mp rings are coordinated to the metal



Fig. 4 Crystal structure of complex $6,\dagger$ hydrogens atoms [with the exception of H(11)] have been omitted for clarity (thermal ellipsoids drawn at the 50% level).

centre while the second mt ring is not coordinated and points directly away from the metal centre. The conformation of this ring places one of the *CH* units of the mt ring towards an axial site on the platinum centre, the Pt(1)-H(11) distance of 2.728 Å suggesting a weak interaction with the metal centre. A previous study had shown a difference in the metal-sulfur distances and boron-nitrogen bond distances between the mt and mp heterocycles within complexes containing **mpBm**.¹³ Accordingly, the boron-nitrogen distances, for the coordinated rings, are B(1)-N(1) 1.559(3) Å (mt) and B(1)-N(5) 1.579(3) Å (mp). In this case however, the corresponding platinum-sulfur distances are coincidentally the same [2.2998(5) Å].

The Pt(1)-B(1) bond distance in 6 is 2.129(2) Å and the Pt(1)-P(1) distance is 2.3797(5) Å. The former distance is typical of metallaboratrane complexes.1d The Pt(1)-P(1) distance is also typical of a zerovalent platinum-phosphine bond suggesting a only a moderate trans influence for the borane functional group [c.f. the Pt-P distance in the divalent complex 2, 2.4626(9) Å].¹⁵ The trans influence of σ -acceptor ligand has invoked some discussion since the labilisation of the ligand *trans* to it appears to be related to the stabilisation of atypical geometries rather than direct orbital competition.¹⁶ For example, ligands in the site trans to boron within octahedral complexes have particularly large metal-ligand distances. There are also a number of complexes which either have no ligand (i.e. square based pyramidal complexes) or exhibit reversible coordination at this coordination site.^{8a} On the other hand, trigonal bipyramidal complexes show only moderate trans influences.

There are very few structurally characterised examples of d^{10} metallaboratrane complexes and only one based on platinum (Fig. 5). Bourissou and Ozerov reported the tetracoordinate platinum complex (7) which contains the ligand B(C₆H₄PⁱPr₂)₃



Fig. 5 Square planar, trigonal based pyramidal and trigonal bipyramidal d¹⁰ complexes **7–9**.

which binds to the metal centre with a (κ^4 -PPBP) coordination mode.7f,g In this case the trigonal based pyramidal geometry at the metal centre is enforced by the ligand and there is no ligand *trans* to the boron atom. There are also two related structures involving monovalent gold centres. The first of these, [Au{ κ^3 -PBP- $PhB(C_6H_4P'Pr_2)_2$ Cl] (8), shows a pincer-type coordination mode similar to that observed for 6. A chloride ion is coordinated in the fourth coordination site.^{16a} The second gold structure, $[Au{\kappa^4}-$ *PPBP*-B(C₆H₄PⁱPr₂)₃Cl] (9) shows that, in the presence of an additional donor, a trigonal bipyramidal structure is obtained.^{7g} While complexes 7 and 8 are constrained to the geometries of the respective ligands, it appears possible that complex 9 could interconvert between square planar (κ^3 -PBP) and trigonal bipyramidal (κ^4 -*PPBP*) forms. Finally, Parkin has reported the only zerovalent complexes metallaboratrane complexes based on sulfur donors, $[Pd{\kappa^4-SSBS-B(mt^{Bu})_3}(PMe_3)]$ (10) and $[Pd{\mu-\kappa^1 S, \kappa^3$ -SBS-B(mt^{Bu})₃]₂ (11).⁶ⁿ The geometries at the palladium centre are trigonal bipyramidal for 10 while complex 11 contains a nonidealised geometry involving a bridging coordination mode of the sulfur atoms.

We were therefore intrigued by the coordination mode found in complex 6. The square planar structure indicated by the solid state structure did not correspond with the spectroscopic evidence therefore implying a fluxional process where the coordinated and uncoordinated mt rings rapidly exchange places. In consideration to the complexes 7-11, we postulated two possible mechanisms by which this rapid exchange could occur. Firstly, this could involve simple association and re-association of the uncoordinated ligand 'arm' and rearrangement between trigonal bipyramidal (κ^4 -SSBS/PPh₃) and square planar (κ^3 -SBS/PPh₃) geometries. A second possibility would involve dissociation of the triphenylphosphine ligand to form a 'T-shaped' intermediate (κ^3 -SBS). This would be followed by association of the third sulfur arm (κ^4 -SSBS) forming a structure similar to 7. A 'T-shaped' coordination motif has previously been observed by Braunschweig within a platinum(II) boryl complex.¹⁷ In order to explore this further, we performed low temperature NMR experiments on complex 6. The temperature of a CD_2Cl_2 solution containing 6 was reduced and the NMR spectra were recorded. No significant changes were observed in the ¹H NMR spectrum down to -80 °C, the spectrum still indicating one chemical environment for the mt rings. The signal in the ¹¹B $\{^{1}H\}$ NMR spectrum did broaden significantly at this temperature, however remained centred at the same chemical shift indicating no change in geometry at the boron centre. In order to assess whether the phosphorus ligand was rapidly dissociating and re-coordinating to the platinum centre, tricyclohexylphosphine was added to a solution of 6. Although the more basic phosphine did replace the triphenylphosphine ligand, the reaction was particularly slow and did not go to completion suggesting that this was not the mechanism involved in the rapid exchange of the mt rings in 6. We are currently investigating the mechanism involved in the exchange of the mt rings in 6.

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Notes and references

 $\$ Crystal data for 6: C₃₁H₂₉BN₃PPtS₃, M_w = 804.64, monoclinic, space group P2₁/c, a = 15.9926(2) b = 10.12870(10), c = 20.0351(2) Å, β = 106.5320(10)°, Z = 4, number of reflections measured = 93339, unique = 9540 (R_{int} = 0.0343), The final wR(F₂) was 0.0246 for all data, T = 100 K. Selected bond lengths (Å) and angles (°) for 6: Pt(1)-B(1) 2.129(2), Pt(1)-S(1) 2.2998(5), Pt(1)-S(2) 2.2998(5), Pt(1)-Pt(1) 2.3797(5), B(1)-N(1) 1.559(3), B(1)-N(3) 1.572(3), B(1)-N(5) 1.579(3), B(1)-Pt(1)-S(1) 81.04(6), B(1)-Pt(1)-S(2) 86.50(6), S(1)-Pt(1)-S(2) 163.15(2), B(1)-Pt(1)-Pt(1) 172.32(6), N(1)-B(1)-N(3) 106.54(15), N(1)-B(1)-N(5) 112.52(16), N(3)-B(1)-N(5) 109.01(15).

- (a) R. B. King, Adv. Chem. Ser., 1967, 62, 203; (b) M. L. H. Green, J. Organomet. Chem., 1995, 500, 127; (c) I. Kuzu, I. Krummenacher, F. Armbruster and F. Breher, Dalton Trans., 2008, 5836; (d) F.-G. Fontaine, J. Boudreau and M.-H. Thibault, Eur. J. Inorg. Chem., 2008, 5439; (e) H. Braunschweig, C. Kollann and D. Rais, Angew. Chem., Int. Ed., 2006, 45, 5254.
- 2 D. F. Shriver, J. Am. Chem. Soc., 1963, 85, 3509.
- 3 (a) G. W. Parshall, J. Am. Chem. Soc., 1964, 86, 361; (b) M. P. Johnson and D. F. Shriver, J. Am. Chem. Soc., 1966, 88, 301.
- 4 (a) H. Braunschweig and T. Wagner, *Chem. Ber.*, 1994, **127**, 1613; (b) H. Braunschweig and T. Wagner, *Z. Naturforsch. B.*, 1996, **51**, 1618; (c) H. Braunschweig and C. Kollann, *Z. Naturforsch. B*, 1999, **54**, 839.
- 5 A. F. Hill, G. R. Owen, A. J. P. White and D. J. Williams, *Angew. Chem.*, *Int. Ed.*, 1999, 38, 2759.
- 6 (a) J. S. Figueroa, J. G. Melnick and G. Parkin, Inorg. Chem., 2006, 45, 7056; (b) M. R. St.-J. Foreman, A. F. Hill, G. R. Owen, A. J. P. White and D. J. Williams, Organometallics, 2003, 22, 4446; (c) I. R. Crossley, M. R. St.-J. Foreman, A. F. Hill, G. R. Owen, A. J. P. White, D. J. Williams and A. C. Willis, Organometallics, 2008, 27, 381; (d) M. R. St.-J. Foreman, A. F. Hill, A. J. P. White and D. J. Williams, Organometallics, 2004, 23, 913; (e) D. J. Mihalcik, J. L. White, J. M. Tanski, L. N. Zakharov, G. P. A. Yap, C. D. Incarvito, A. L. Rheingold and D. Rabinovich, Dalton Trans., 2004, 1626; (f) R. J. Blagg, J. P. H. Charmant, N. G. Connelly, M. F. Haddow and A. G. Orpen, Chem. Commun., 2006, 2350; (g) I. R. Crossley, M. R. St.-J. Foreman, A. F. Hill, A. J. P. White and D. J. Williams, Chem. Commun., 2005, 221; (h) V. K. Landry, J. G. Melnick, D. Buccella, K. Pang, J. C. Ulichny and G. Parkin, Inorg. Chem., 2006, 45, 2588; (i) I. R. Crossley, A. F. Hill, E. R. Humphrey and A. C. Willis, Organometallics, 2005, 24, 4083; (j) I. R. Crossley, A. F. Hill and A. C. Willis, Organometallics, 2006, 25, 289; (k) I. R. Crossley, A. F. Hill and A. C. Willis, Organometallics, 2005, 24, 1062; (1) S. Senda, Y. Ohki, T. Hirayama, D. Toda, J.-L. Chen, T. Matsumoto, H. Kawaguchi and K. Tatsumi, Inorg. Chem., 2006, 45, 9914; (m) K. Pang, J. M. Tanski and G. Parkin, Chem. Commun., 2008, 1008; (n) K. Pang, S. M. Quan and G. Parkin, Chem. Commun., 2006, 5015
- 7 (a) J. Grobe, K. Lütke-Brochtrup, B. Krebs, M. Läge, H.-H. Niemeyer and E.-U. Würthwein, Z. Naturforsch., Teil B., 2006, 61, 882; (b) S. Bontemps, M. Sircoglou, G. Bouhadir, H. Puschmann, J. A. K. Howard, P. W. Dyer, K. Miqueu and D. Bourissou, Chem.–Eur. J., 2008, 14, 731; (c) S. Bontemps, H. Gornitzka, G. Bouhadir, K. Miqueu and D. Bourissou, Angew. Chem., Int. Ed., 2006, 45, 1611; (d) M. Sircoglou, G. Bouhadir, N. Saffon, K. Miqueu and D. Bourissou, Organometallics, 2008, 27, 1675; (e) S. Bontemps, G. Bouhadir, K. Miqueu and D. Bourissou, J. Am. Chem. Soc., 2006, 128, 12056; (f) S. Bontemps, G. Bouhadir, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov and D. Bourissou, Angew. Chem., Int. Ed., 2008, 47, 1481; (g) M. Sircoglou, S. Bontemps, G. Bouhadir, N. Saffon, K. Miqueu, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov and D. Bourissou, J. Am. Chem. Soc., 2008, 130, 16729.
- 8 (a) N. Tsoureas, M. F. Haddow, A. Hamilton and G. R. Owen, *Chem. Commun.*, 2009, 2538; (b) N. Tsoureas, T. Bevis, C. P. Butts, A. Hamilton and G. R. Owen, *Organometallics*, 2009, 28, 5222.

- 9 (a) S. A. Westcott, T. B. Marder, R. T. Baker, R. L. Harlow, J. C. Calabrese, K. C. Lam and Z. Lin, *Polyhedron*, 2004, 23, 2665; (b) D. Curtis, M. J. G. Lesley, N. C. Norman, A. G. Orpen and J. Starbuck, *J. Chem. Soc., Dalton Trans.*, 1999, 1687; (c) H. Braunschweig, K. Radacki, D. Rais and G. R. Whittell, *Angew. Chem., Int. Ed.*, 2005, 44, 1192; (d) T. P. Fehlner, *Angew. Chem., Int. Ed.*, 2005, 44, 2056.
- 10 I. R. Crossley and A. F. Hill, Dalton Trans., 2008, 201.
- 11 G. C. Rudolf, A. Hamilton, A. G. Orpen and G. R. Owen, *Chem. Commun.*, 2009, 553.
- 12 G. Dyson, A. Hamilton, B. Mitchell and G. R. Owen, *Dalton Trans.*, 2009, 6120.
- 13 G. R. Owen, P. H. Gould, J. P. H. Charmant, A. Hamilton and S. Saithong, *Dalton Trans.*, 2010, DOI: 10.1039/B911651F.
- 14 I. R. Crossely and A. F. Hill, Organometallics, 2004, 23, 5656.
- 15 I. R. Crossely, A. F. Hill and A. C. Willis, *Organometallics*, 2008, 27, 312.
- 16 (a) M. Sircoglou, S. Bontemps, M. Mercy, N. Saffon, M. Takahashi, G. Bouhadir, L. Maron and D. Bourissou, *Angew. Chem., Int. Ed.*, 2007, 46, 8583; (b) A. F. Hill, *Organometallics*, 2006, 25, 4741; (c) G. Parkin, *Organometallics*, 2006, 25, 4744.
- 17 H. Braunschweig, K. Radacki, D. Rais and D. Scheschkewitz, Angew. Chem., Int. Ed., 2005, 44, 5651.