Synthesis and Characterization of Platinum and Palladium Complexes Featuring a Rare Secondary Borane Pincer Motif

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Abstract

The synthesis and characterization of a series of platinum and palladium complexes containing a secondary borane Z-class ligand supported by 2-mercaptopyridine heterocycles is reported herein. Addition of two equivalents of $Na[H_2B(mp)_2]$ to $[Pt(\mu\text{-}Cl)(COE^{OMe})]_2$ (where COE^{OMe} = 8-methoxycyclooct-4-en-1-ide) in the presence of two equivalents of a tertiary phosphine $\{PR_3$ = PPh_3, PCy_3, $PCyp_3$, $P(o\text{-}tol)_3$, $PPh_2(o\text{-}tol)$ and $PPh_2(2\text{-}(3\text{-}methyl)indolyl)\}$ leads to the formation of the complexes $[Pt\{\kappa^3\text{-}S,B,S\text{-}HB(mp)_2\}(PR_3)]$ (**1 − 6**). Addition of two equivalents of $Na[H_2B(mp)_2]$ to $[Pd(\mu\text{-}Cl)(COE^{OMe})]_2$ in the presence of two equivalents of a tertiary phosphine $\{PR_3 = PPh_3$, PCy_3, $PCyp_3$, and $PPh_2(o\text{-}tol)\}$ leads to the formation of the complexes $[Pd\{\kappa^3\text{-}S,B,S\text{-}HB(mp)_2\}(PR_3)]$ (**7 − 10**). It was also demonstrated that the synthesis of the palladium complex **7** could be achieved from the palladium precursor, $[PdCl(Me)(COD)]$ (where COD = 1,5-cyclooctadiene) as an alternative synthetic strategy. In the above reactions, either the COE^{OMe}

fragment or the methyl fragment serve to act as a "hydride acceptor" facilitating the ultimate transformation of the borohydride based ligand, $[H_2B(mp)_2]^-$ to the corresponding secondary borane κ^3-*S,B,S* coordinated $HB(mp)_2$ pincer ligand. The complexes $[Pd\{\kappa^3$-*S,B,S*-$HB(mp)_2\}(PR_3)]$ and $[Pt\{\kappa^3$-*S,B,S*-$HB(mp)_2\}(PR_3)]$ are rare examples of metal-borane complexes where one hydrogen substituent remains at the boron center. These compounds have particularly short palladium– and platinum–boron distances, the shortest of the structurally characterized compounds being 2.067(6) Å for $[Pd\{\kappa^3$-*S,B,S*-$HB(mp)_2\}(PPh_2(o$-tol))] and 2.076(10) Å, for $[Pt\{\kappa^3$-*S,B,S*-$HB(mp)_2\}(PCy_3)]$, respectively (the shorter distances of two independent complexes in the unit cells of both structures).

Introduction

The ubiquitous pincer motif, involving meridional coordination of a tridentate ligand (*i.e.* a κ^3–*L,E,L* coordination mode), is notorious for its ability to furnish highly stable transition metal based catalysts (Figure 1).[1] As a result pincer-type complexes have been the focus of intense investigation over many years.[2] There have been a wealth of derivatives featuring a diverse range of donor atoms including phosphorus,[3] nitrogen,[4] sulfur,[5] oxygen,[6] carbon[7] and others[8] in various combinations. Despite the wide range however, those pincers featuring boron based motifs remain rare and are limited to a handful of examples (Figure 2).[3i,9-15] Furthermore, whilst there are many examples of pincer ligands where the central unit of the pincer ligand is a secondary group (i.e. where it contains a E–H group),[3,4,5a,b,6,7a,b,8a] there are only few examples featuring a secondary borane as the central unit.[3i,12-15] We have a particular interest in transition metal complexes containing boron based ligands, specifically those containing borane functionalities where the boron acts as a Z-type ligand.[16,17] Indeed, several research groups are exploring the propensity of this functional group to act as an acceptor group for a hydrogen atom or other functional groups

(Scheme 1).[16a] The potential for groups to be stored at the boron center opens up the possibility for a mechanism of ligand cooperation in which the ligand is intimately involved in the transformations at the metal center as a means to facilitate catalytic transformations.[18] Various iterations of ligand cooperation have been established some of which involve the storage of hydrogen atoms, other functional groups and also the storage of dihydrogen upon the ligand.[19-21] In terms of those transformations at a borane based ligand, Hill was the first to demonstrate that a stored hydride on a borohydride could be delivered to the metal center.[22] Hill later showed that the process of hydride migration between boron and metal centers was reversible.[23,24] We later demonstrated that it was possible to cleave dihydrogen as a means of "recharging" a borane functional group with hydrogen to reform a borohydride unit.[21a] The Peters' group later carried out some seminal work providing a multitude of examples highlighting the cleavage of dihydrogen and other element–hydrogen bonds across a transition metal–borane species.[21b,25]
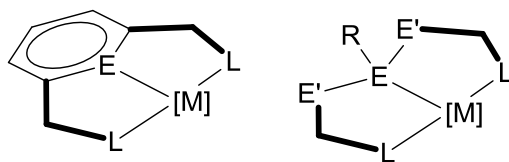

Figure 1 – Highlighting the typical structural features of pincer-type ligands (κ^3- *L,E,L*) containing different donor atoms, **E** and **L**. The structure on the left highlights the ubiquitous pincer structures supported by the substituted phenyl or pyridyl rings while the structure on the right indicates those more diverse pincer ligands ([**M**] represents a metal center and remaining co-ligands, **E'**—**L** represents various three atom tethers positioning the central atom within a five membered ring with the metal center).
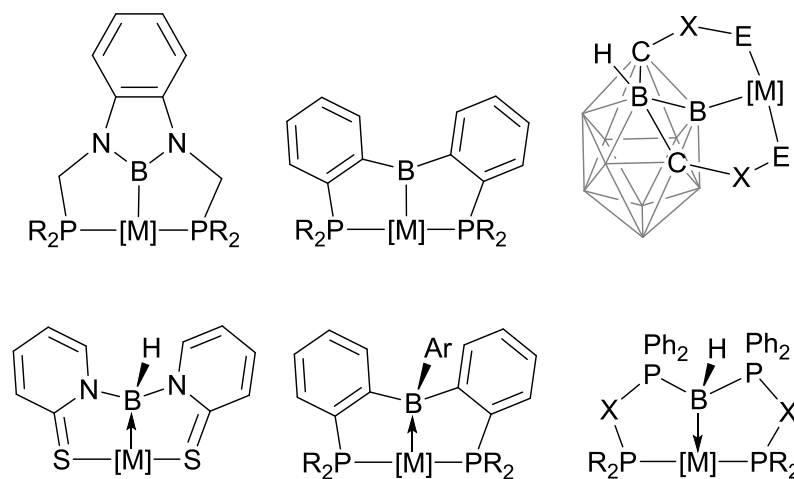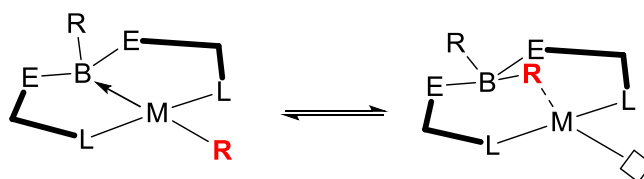
Figure 2 – Highlighting the range of boryl and borane pincer-type ligands (κ^3- *L,B,L*) containing different donor atoms. There are very limited examples of secondary borane pincer complexes.

Scheme 1 – The ability of metal bound borane functional groups to act as acceptors for groups such as hydride, alkyl, aryl and other groups leaving an empty coordination site (the red **R** represents these various groups).

In 2009, we reported the synthesis of a family of borohydride ligands[26a] containing the heterocycle 2-mercaptopyridine (*i.e.* [HB(mp)$_3$]$^-$ and [H$_2$B(mp)$_2$]$^-$, where mp = 2-mercaptopyridyl) and have now reported their coordination to a range of transition metal centers including copper,[26a] platinum,[14,26b] ruthenium,[26c] rhodium[26d,e] and palladium.[14,26c] Malik and Panda have reported a series of Group II main group coordination compounds containing these ligands.[27a] Some further examples of complexes containing these ligands have been provided by Ghosh albeit via a different strategy.[27b,c] We have demonstrated the capacity of this ligand system to deliver hydride to the

metal center in the case of the rhodium, palladium and platinum complexes with an apparent increased propensity compared to other sulfur based heterocycles.[26d] Despite a now expansive range of transition metal complexes containing Z-type ligands, there are surprisingly still very few examples of those featuring secondary borane functional groups. [3i,12-15,26d,28] We therefore wish to report the synthesis and characterization of a number of palladium and platinum pincer complexes containing such functional groups to further expand this range.

Results and Discussion

As indicated above, the flexible scorpionate ligand, hydrobis(2-mercaptopyridyl)borate (abbreviated as [**Bmp**]$^-$ or [H$_2$B(mp)$_2$]$^-$),[26a] has previously been utilized as a pro-ligand for the secondary borane complexes containing the neutral ligand, HB(mp)$_2$.[14,26d] Furthermore, the COE^{OMe} (COE^{OMe} = 8-methoxycyclooct-4-en-1-ide) unit has been used as a means of accepting one of the hydrogen substituents from the borohydride unit.[14] This reactivity was further explored in an attempt to expand the scope of this reactivity with a range of tertiary phosphine ligands {PR$_3$ = PPh$_3$, PCy$_3$, PCyp$_3$, P(o-tol)$_3$, PPh$_2$(o-tol) and PPh$_2$(2-(3-methyl)indolyl)}. Accordingly, two equivalents of a tertiary phosphine were added to a DCM solution of the bimetallic precursor [Pt(μ-Cl)(COE^{OMe})]$_2$[29] followed by two equivalents of Na[**Bmp**], in close succession. In all cases, the colourless reaction mixtures instantly became yellow and progressively changed to an orange to red colour depending on the specific phosphine ligand used. The precursor, Na[**Bmp**] exhibits limited solubility in the chlorinated solvent, however, it was apparent that the suspended material was consumed over the course of 1 – 4 h. Aliquots of the reaction mixtures were taken at several points during the course of the reactions. Their ^{31}P{^{1}H}, ^{11}B and ^{11}B{^{1}H} NMR spectra were then recorded. The ^{31}P{^{1}H} NMR spectra was utilized in order to confirm the coordination of the phosphine ligands to the platinum centers which slowly occurred over time. As a result of its

limited solubility, it was not possible to determine whether there was any unreacted Na[**Bmp**] present within the mixtures by boron NMR (although this was clear from our observations). Nevertheless, the boron spectra provided information regarding the progress of reactivity within the mixtures. The ^{11}B{^{1}H} NMR spectra of all reaction mixtures gave two new signals, one at around 7.9 ppm and the second in the region of 14.5 ppm – 17.9 ppm in various ratios depending on the identity of the phosphine ligand. The former signal represented an "intermediate species" (**Pt$_{int}$**) which appeared to be common in all reaction mixtures observed within the reaction mixtures in the first 10 min. The length of time the intermediate persisted was dependent on the specific phosphine ligand used. The reactions were considered to have gone to completion when the ^{11}B NMR showed only the latter species as indicated above. The timescales required for the reaction to reach completion ranged between 1 – 4 h. At this point the reaction mixtures were filtered and worked up as described in the Experiment Section. The complexes were fully characterised (*vide infra*) as [Pt{κ^3-*S,B,S*-HB(mp)$_2$}(PR$_3$)]; R = PPh$_3$ (**1**), PCy$_3$ (**2**), PCyp$_3$ (**3**), P(*o*-tol)$_3$ (**4**), PPh$_2$(*o*-tol) (**5**) and PPh$_2$(2-(3-methyl)indolyl) (**6**) and where isolated as intense orange to red solids (Scheme 2). The complexes containing the triarylphosphines were orange while those containing the trialkylphosphines were red.
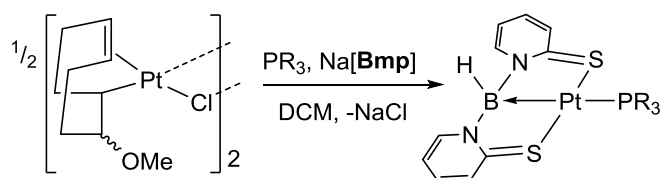
Scheme 2 – Synthesis of [Pt{κ^3-*S,B,S*-BH(mp)$_2$}(PR$_3$)], PR$_3$ = PPh$_3$ (**1**), PCy$_3$ (**2**), PCyp$_3$ (**3**), P(o-tol)$_3$ (**4**), PPh$_2$(o-tol) (**5**) and PPh$_2$(2-(3-methyl)indolyl) (**6**). This reaction proceeds *via* an intermediate species, **Pt$_{int}$**, and the COE^{OMe} unit is lost together with one hydride from the **Bmp** ligand; see text for details.

It was of interest to us to confirm the identity of the intermediate species **Pt_int** within these reactions. We were, of course, able to obtain some evidence for its identity by examining the spectroscopic data of the reaction mixtures. During the course of our investigations, we also found that when PMe$_3$ was used as a potential ligand, **Pt_int** was the only observed species by ^{11}B NMR spectroscopy. Even when this reaction was left for a number of days there was no indication of the analogous final product to that of the other reactions. There was no spectroscopic evidence that the PMe$_3$ ligand had coordinated to the platinum center.[30] It appeared as though the phosphine ligand was not involved in the reaction. On the other hand, when the reaction was carried out in the absence of a phosphine ligand, the reaction mixture decomposed within a matter of minutes. Selected spectroscopic data were obtained from the reaction involving PMe$_3$.[31] The ^{11}B{^{1}H} NMR spectrum revealed a peak at 7.9 ppm with platinum satellites, $^1J_{PtB} = 500$ Hz. This value is in the region observed for other platinum–borane (Z-type) complexes[26b,32] confirming that the borohydride unit of the [H$_2$B(mp)$_2$] ligand has been transformed allowing for a Pt–B interaction.[33] The corresponding proton NMR spectrum confirmed that one of the hydrogen substituents from the borohydride unit of [H$_2$B(mp)$_2$] had been transferred to the platinum center, as evidenced by a platinum–hydride signal at –13.31 ppm ($^1J_{PtH} = 1400$ Hz). The spectrum also confirmed that the newly formed borane ligand, [HB(mp)$_2$], was coordinated to the platinum center where the two mp rings were in different chemical environments. Finally, the spectrum also confirmed that the COE^{OMe} unit was coordinated to the platinum center, in the **Pt_int** species, via one carbon where the double bond was uncoordinated (two signals at 5.60 and 5.86 ppm each integrating to 1 H with no $^1J_{PtH}$ coupling between the metal center and the olefinic protons). All of this evidence suggests that the identity of **Pt_int** as [PtH{κ^3-*S,B,S*-HB(mp)$_2$}{COE^{OMe}}] as shown in Figure 3.[34]
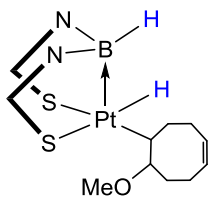
Figure 3 – Postulated structure of **Pt$_{int}$** based on the spectroscopic evidence (N━S represents the mercaptopyridyl supporting units).

A similar methodology was employed to synthesize the corresponding palladium pincer complexes. In a typical reaction, the dimeric precursor [Pd(μ-Cl)(COE^{OMe})]$_2$[35] was dissolved in DCM to which was added, two equivalents of a phosphine ligand followed by two equivalents of Na[**Bmp**]. Upon addition of Na[**Bmp**], the reaction mixture immediately became orange, deepening over time with the final solutions being brown in colour. As with the platinum reactions, each was monitored by $^{31}P\{^1H\}$, ^{11}B and $^{11}B\{^1H\}$ NMR spectroscopy. These reactions went to completion significantly faster than the platinum based counterparts and so no clear intermediate species was detected by NMR spectroscopy. In all cases, the ^{11}B NMR spectra revealed only one signal, corresponding to the expected product, within 20 min. Once the reactions were deemed to have gone to completion, the products [Pd{κ^3-S,B,S-HB(mp)$_2$}(PR$_3$)]; R = PPh$_3$ (**7**), PCy$_3$ (**8**), PCyp$_3$ (**9**) and PPh$_2$(o-tol) (**10**) where isolated *via* a similar workup to that of the platinum complexes.

Within the reactions above, we successfully demonstrated that the COE^{OMe} fragment serves as an efficient a hydride acceptor to furnish the secondary borane pincer complexes **1** to **10**. We were also interested to see whether other fragments could also be employed. Accordingly, we tested the complexes [MCl(Me)(COD)] (where M = Pt or Pd) as alternative metal precursors, expecting that the methyl fragment would provide a means of hydride abstraction from the borohydride ligands. Indeed, this strategy was successful used to synthesis the palladium complex **7** in very high yield

(Scheme 3). Unfortunately, it could not be utilized to synthesize the platinum complexes since the reactions led to complicated reaction mixtures which did not indicate any signs of the formation of the corresponding pincer complexes. Similar complicated reaction mixtures were found by Crossley when allyl units were utilized as hydride acceptors with platinum complexes.[36] It appears that the COE^{OMe} unit is the only reported species which has been successfully utilized as a hydrogen acceptor in the synthesis of secondary borane platinum complexes.
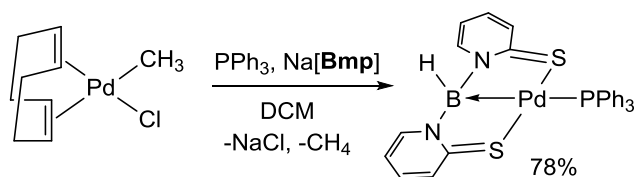
Scheme 3 – Alternative synthesis of $[Pd\{\kappa^3\text{-}S,B,S\text{-}BH(mp)_2\}(PPh_3)]$ (**7**).

Characterization of Complexes 1 – 10.

The ten complexes were all fully characterized by NMR spectroscopy, IR spectroscopy and elemental analysis (see experimental section). Selected spectroscopic data have been provided in Table 1 for comparison. For the platinum complexes **1 – 6**, the coordination of the various phosphorus ligands to the platinum center was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy which showed a broad single resonance for each case at chemical shifts typical for the specific phosphine coordinated to a platinum center. All signals exhibited $^1J_{PtP}$ platinum satellites in the range of 1440 to 1585 Hz. These values and the broadness of the signals are typical of a phosphine ligand *trans* to a (quadrupolar) boron based ligand.[14,26b,32] The ^1H NMR spectra for complexes **1 – 6** confirmed the absence of the original organic fragment contained in the precursors (*i.e.* COE^{OMe} or Me) and confirmed that no transition metal–hydride species had been formed. All spectra confirmed the presence of the two 2-mercaptopyridyl heterocycles within the complex. These protons gave a total integration value of eight compared to the expected number of protons for the corresponding

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phosphine ligand. No other proton environments were apparent in the standard ^{1}H NMR experiments however an additional signal, which integrated for one additional proton, was observed in the corresponding ^{1}H{^{11}B} spectra. This corresponds to a B–H unit and confirms that one of the hydrogen substituents of the former anionic [**Bmp**]$^-$ ligand had been lost to form a neutral [HB(mp)$_2$] ligand. Interestingly, the chemical shift of this B*H* proton was found in a very narrow range for the six complexes (6.52 – 6.68 ppm). Furthermore, these signals also exhibited platinum satellites with J$_{PtH}$ coupling constants ranging between 99 – 118 Hz. These values are lower than have been reported for direct Pt–H–B interactions in which the hydrogen bridges the boron and platinum centers[37] and are more similar to a ^{2}J$_{PtH}$ coupling[38,39] thereby suggesting a Pt–B(H) connectivity with no direct platinum-hydrogen interactions in any of the complexes **1** – **6**. To the best of our knowledge, there is only two other examples of a nitrogen substituted borane species (either primary or secondary) featuring a Pt–B(H) interaction. In the first example the motif is within a macropolyhedral boron-containing cluster making any detail comparison challenging.[39] Very recently, Neshat and co-workers have reported an octahedral platinum complex featuring a secondary borane complex which was structurally characterized and found to have a facial-κ^3-*S,B,S* coordination mode with a very similar ligand in the solid state.[12] The complex also contained a hydride ligand which was found to reversibly migrate to the boron center (to form the corresponding borohydride species) when placed in solvent.

Table 1 – $^{31}P\{^1H\}$, $^{11}B\{^1H\}$ NMR and infrared spectroscopic data for pincer complexes containing the κ^3–S,B,S-HB(mp)$_2$ ligand.

Complex	$^{31}P\{^1H\}$ (ppm)	$^1J_{PtP}$ (Hz)	$^{11}B\{^1H\}$ (ppm)	^{11}B hhw[a] (Hz)	^1H BH (ppm)	IR (B-H••M) power film (cm^{-1})
[Pt{HB(mp)$_2$}(PPh$_3$)][b] (**1**)	30.3	1540	15.2	480	6.68	2318
[Pt{HB(mp)$_2$}(PCy$_3$)] (**2**)	36.5	1570	17.9	520	6.60	2310
[Pt{HB(mp)$_2$}(PCyp$_3$)] (**3**)	37.3	1585	17.9	460	6.52	2304
[Pt{HB(mp)$_2$}{P(o-tol)$_3$}] (**4**)	27.4	1440	14.5	475	6.64	2321
[Pt{HB(mp)$_2$}{PPh$_2$(o-tol)}] (**5**)	25.5	1485	15.6	440	6.68	2323
[Pt{HB(mp)$_2$}(PPh$_2$(^{Me}In)] (**6**)	12.9	1497	16.4	470	6.67	2318
[Pd{HB(mp)$_2$}(PPh$_3$)][b] (**7**)	11.2		12.5	280	5.82	2353
[Pd{HB(mp)$_2$}(PCy$_3$)] (**8**)	21.0		14.6	300	5.67	2344
[Pd{HB(mp)$_2$}(PCyp$_3$)] (**9**)	20.3		14.7	281	5.63	2331
[Pd{HB(mp)$_2$}{PPh$_2$(o-tol)}] (**10**)	5.6		13.6	300	5.81	2347

[a] – hhw is the width of the signal at the half position, [b] – from reference 14

Further detail concerning the nature of the BH interaction with the platinum center was obtained by ^{11}B NMR spectroscopy. The chemical shifts of the boron nuclei, for complexes **1** – **6** were located within the range 14.5 ppm to 17.9 ppm. This significant downfield shift relative to Na[**Bmp**] (–0.9 ppm, MeCN-d$_3$), confirmed the transformation of the borohydride functional group to a metal bound borane functional group.[26a] The two complexes containing the trialkylphosphines, exhibited the most downfield chemical shifts, 17.9 ppm for both PCyp$_3$ and

PCy$_3$. Curiously, this suggests that the more electron donating phosphines provide the most deshielded boron center. Unfortunately in all of the platinum containing complexes, the boron signals were too broad (between 440 – 520 Hz, in the ^{11}B NMR spectrum) to obtain $^1J_{BH}$ and $^1J_{PtB}$ coupling constants. In the case of the $^1J_{PtB}$ coupling, this was clearly evident in the line shape of the signals however accurate measurement of the coupling was not possible (see spectra in the ESI). Confirmation that the B–H units contained no significantly interaction with the platinum centers came from the solid state infrared spectra which all revealed a band in the region 2304 – 2323 cm^{-1} characteristic of a terminal B–H stretching mode with little deviation between the complexes. For the palladium complexes **7 – 10**, the coordination of the various phosphorus ligands to the palladium center was confirmed by ^{31}P{^{1}H} NMR spectroscopy. The ^{1}H NMR spectra for complexes **7 – 10** where similar to that those of complexes **1 – 6** thus confirming the formation of the complexes, [Pd{κ^3-*S,B,S*-BH(mp)$_2$}(PR$_3$)] (PR$_3$ = PPh$_3$ (**7**); PCy$_3$ (**8**); PCyp$_3$ (**9**) and PPh$_2$(o-tol)} (**10**). As with the platinum complexes, the B*H* proton, was located in the corresponding ^{1}H{^{11}B} spectra between 5.63 – 5.82 ppm. In most spectra, this signal was too broad to observe any fine coupling however in the case of [Pd{κ^3-*S,B,S*-BH(mp)$_2$}(PCyp$_3$)] (**9**) the signal appeared as a doublet with a $^3J_{PH}$ coupling constant of 5.9 Hz. The chemical shifts of the boron nuclei, for complexes **7 – 10** were located within the range 12.5 ppm to 14.7 ppm in the ^{11}B NMR spectra. These complexes were less stable in CDCl$_3$ solvent than the corresponding platinum complexes. When they were left to stand in this solvent for prolonged periods of time, they slowly started to form the corresponding tris-substituted complexes, [Pd{κ^4-*S,B,SS*-B(mp)$_3$}(PR$_3$)].[14] The B–H stretching frequencies of in **7 – 10** were found between 2331 and 2353 cm^{-1}, again typical of a terminal B–H unit. Finally, elemental analytical data were consistent with the molecular composition of the products **1 – 10**.

Structural characterization of 1, 2, 3, 7, 8, 9, 10.

Several crystal structures of the newly synthesized complexes were obtained in order to explore the structural features of the borane pincer complexes in more detail. Crystals suitable for X-ray diffraction of **2**, **3**, **8** and **9** were all obtained by allowing saturated diethyl ether solutions of the complexes stand under an inert atmosphere for several days. Single crystals of **10** were obtained from a heated saturated solution of the complex in toluene, which was allowed to slowly cool to room temperature. All the crystals obtained from both platinum and palladium complexes were orange in colour. Tables containing a detailed comparison of all structures have been provided within the electronic supporting information. The crystalline material of all complexes, with the exception of complex **8**, were found to contain two independent complexes within the asymmetric unit. Furthermore, in a number of the structures there was additional disorder over the positions of some of the atoms within the structure. Accordingly, there were up to four sets of bond distances and angles for each complex. Further details concerning the disorder have been provided in the electronic supporting information. All structures confirmed the pincer type coordination mode (i.e. meridional κ^3-S,B,S) of the HB(mp)$_2$ ligand, selected structures are provided in Figures 4 and 5. All seven structures exhibit distorted square-planar geometries around the metal centers with *cis* inter-ligand angles ranging between 74.7(6)° to 105.18(7)° across the complexes. The sum of the four cis-angles about the metal center within each complex ranged from 360.27° to 365.417°. This relatively narrow range reflects the tendency of the palladium and platinum centers to adopt square planar geometries. The S(1)–M–S(2) angles within the platinum complexes varied from 156.8(4)° to 162.9(2)° whilst the same angles in the palladium complexes varied from 155.275(17)° to 161.9(4)°. The boron centers are tetrahedral as expected, with varying degrees of distortion. The sum angles of the three non-hydrogen substitutents lie in the range 326.46° to 342.57° (where

idealised tetrahedral would be 328.5°). The conformation of the binding of the $HB(mp)_2$ ligand is of interest. In most cases, it appears that one of the mercaptopyridyl units is co-planar with the metal–borane vector (as evidenced by the S–M–B–N torsion angles) while the second mp unit is twisted with a S–M–B–N torsion angle in the region of approximately 40°. The pincer motif in these complexes holds the B–H unit away from the metal center. This is consistent with the spectroscopic evidence described in the characterization section above. The boron center appears to be locked into a specific position, in close proximity to the metal centers, by the two mercaptopyridyl supporting units. This is demonstrated by the fact that the Pt(1)–B(1) and Pd(1)–B(1) distances are not unaffected, to any significant degree, by the differing trans influences of the various phosphine ligands. The Pt(1)–B(1) distances for complexes **1 – 3** all lie within the narrow range, 2.076(10) – 2.104(10) Å. For complexes **7 – 10**, this range is slightly smaller, 2.067(6) – 2.094(3) Å.[40] These distances are amongst the shortest platinum–borane and palladium–borane distances found on the Cambridge Structural Database (CSD).[41] This suggests that the $HB(mp)_2$ ligand has a constrained conformation when it is acting as a pincer ligand. Whilst the borane unit is less affected by the ligand trans to it, its corresponding impact on the phosphine ligands appears to be more significant. For example, the Pt(1)-P(1) distances of the structures for complex **2** are 2.349(3) Å and 2.377(3) Å. These values are much longer than the majority of the crystallographically characterised platinum–tricyclohexylphosphine complexes in the CSD, indicating that the trans influence of the borane unit is high.[16,42,43] Furthermore, the Pt(1)-P(1) distances of the structures for complex **3**, 2.3591(5) Å and 2.3863(5) Å, are also particularly long. With only five reported structures of platinum–tricyclopentylphosphine complexes to date, no clear comparisons can be made however these are significantly longer than any of those reported distances for a Pt–$PCyp_3$ bond. Similar observations are found for the palladium complexes. For

example, in the tricyclohexylphosphine complex **8**, where the Pd(1)–P(1) distance is 2.4662(5) Å. Out of the 153 structurally characterised complexes in the CSD, there is only one example of a Pd–PCy₃ distance which is longer than the one found in complex **8**.[44]
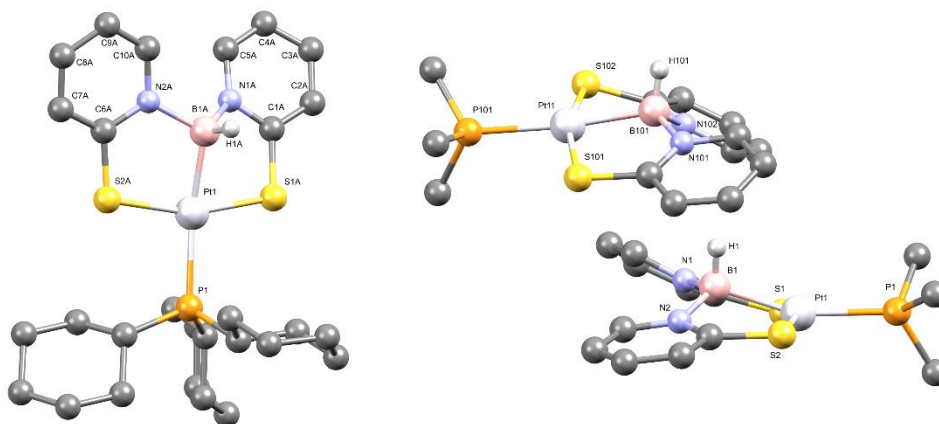

Figure 4 – Crystal structures of platinum complexes **2** and **3**. One of the two independent molecules in the asymmetric unit is shown for [Pt{κ³-*S,B,S*-BH(mp)₂}(PCy₃)] (**2**) (left); both molecules in the asymmetric unit are shown for [Pt{κ³-*S,B,S*-BH(mp)₂}(PCp₃)] (**3**) (right). Hydrogen atoms, with the exception of those on boron, and any component of disorder have been omitted for clarity. For the PCp₃ ligands in **3** only the α-carbons are shown.
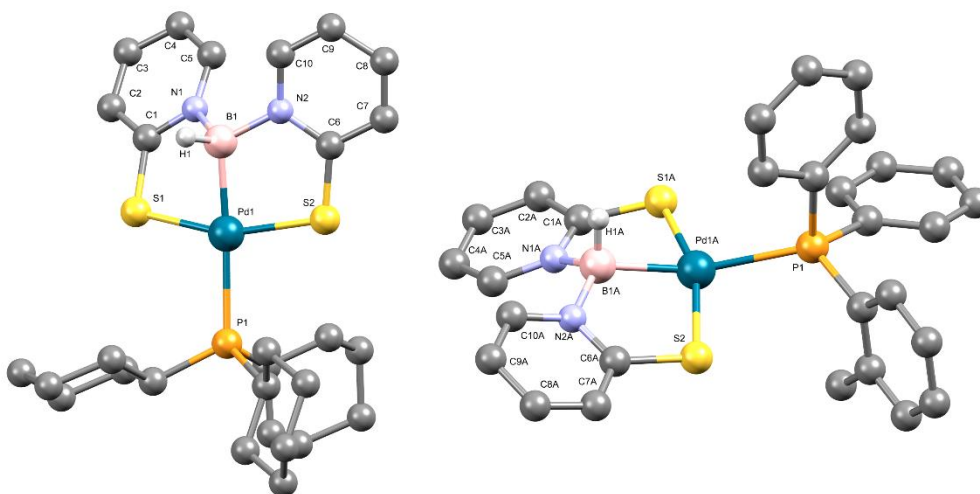
Figure 5 – Crystal structures of palladium complexes **8** and **10** (complex **9** is shown in the supporting information). There was only one independent molecule in the asymmetric unit for [Pd{κ^3-*S,B,S*-BH(mp)$_2$}(PCy$_3$)] (**8**) (shown on the left); one of the two independent molecules in the asymmetric unit is shown for [Pd{κ^3-*S,B,S*-BH(mp)$_2$}(PPh$_2$(*o*-tol)] (**10**) (right). Hydrogen atoms, with the exception of those on boron, and any component of disorder have been omitted for clarity.

Further reactivity

One characteristic of these complexes, that is evident in their NMR spectra, is the lability of the triarylphosphine ligands. In particular, we found that the P(o-tol)$_3$ ligand dissociated from complex **4** when it was placed in solution (as evidenced by ^{31}P NMR spectroscopy). This is perhaps expected given the apparent large trans influence of the borane functional group (*vide supra*)[43] and the large cone angle for P(o-tol)$_3$ (194°).[45] This led us to carry out some test reactions to probe the potential to substitute phosphine ligands. The lability appears to be strongly dependent on the steric properties of the phosphine. The most sterically hindered ligand, P(o-tol)$_3$ in complex **4** was readily displaced by PCy$_3$ within 10 min and also by the less electron rich PPh$_3$ in a similar time frame. For complex **2**, the sterically bulky PCy$_3$ (170°) ligand was found to be partially displaced by the much weaker donating phosphine, PPh$_3$ although this ligand substitution reaction never went to completion.

Some examples demonstrating the activation of element–element bonds across transition metal–borane bonds have been reported.[21,25] The activation of hydrogen–hydrogen across the platinum–borane and palladium–borane bond in complexes **1** to **10** has been investigated. Aside from the lability of the phosphine ligands the complexes, the pincer motif itself appears to be remarkably robust and stable. Toluene-d$_8$ solutions of the complexes were heated to 110 °C in the presence of

hydrogen for several days. Periodic analysis of the solutions by NMR showed no indications of H_2 activation and very little decomposition. The activation of other element–hydrogen (e.g. C–H, Si–H) and element–element bonds is currently under investigation.

Conclusions

In summary, the synthesis and characterization of a range of platinum and palladium pincers complexes bearing a novel secondary borane central unit has successfully been achieved. The application of the COE^{OME} fragment to act as a hydrogen acceptor unit has been expanded further as a generalized procedure. The utilization of the methyl fragment as an alternative methodology has been proven for palladium. Spectroscopic studies have been carried out on the newly formed complexes providing detailed information on the nature of the interaction of the BH unit with the metal centers. Furthermore, crystallographic studies reveal that the pincer motif, involving the HB(mp)$_2$ ligand, has very similar features in all complexes. It appears that the borane unit has a high trans influence resulting in a labilisation of the phosphine trans to it within the complexes. Our initial investigations looking at the activation of E–H bonds across the Pt–B and Pd–B bonds in the complexes have thus far been unsuccessful. This has been attributed to the stable pincer motif which is so characteristic of pincer ligands. We are currently exploring this further and are looking at ways in which the meridional coordination mode can be disturbed as a means of promoting reactivity.

Experimental

General remarks. All manipulations were conducted under inert atmosphere using standard Schlenk line techniques. Solvents were supplied extra dry from Acros Organics and were stored

over 4 Å molecular sieves. CDCl$_3$ NMR solvent was stored in a Young's ampules under N$_2$, over 4 Å molecular sieves and was degassed through three freeze-pump-thaw cycles prior to use. All reagents were used as purchased from commercial sources. The precursors, Na[H$_2$B(mp)$_2$],[26a] [Pt(μ-Cl)(COE^{OMe})]$_2$,[29] [Pd(μ-Cl)(COE^{OMe})]$_2$,[35] [PtCl(Me)(COD)],[46a] [PdCl(Me)(COD)][46b] and PPh$_2$(2-(3-methyl)indolyl)[47] were synthesized according to published methods. All NMR experiments where conducted on a Bruker 400 MHz AscendTM 400 spectrometer. The spectra were referenced internally, to the residual protic solvent (^{1}H) or the signals of the solvent (^{13}C). Proton (^{1}H) and carbon (^{13}C) assignments were supported by HSQC, HMBC and COSY NMR experiments. In the assignment of the proton NMR spectra the symbol τ is used to represent an apparent triplet in cases where a doublet of doublet signal is expected. Infrared spectra where recorded on a Perkin-Elmer Spectrum Two ATR FT-IR spectrometer. Mass spectra were recorded by the EPSRC NMSF at Swansea University. Elemental analysis was performed at London Metropolitan University by their elemental analysis service.

Synthesis of [Pt{κ^3-*S*,*B*,*S*-HB(mp)$_2$}(PCy$_3$)] (2). A Schlenk flask was charged with [PtCl(COE^{OMe})]$_2$ (100 mg, 1.35×10^{-4} mmol) which was subsequently fully dissolved in 30 mL of DCM. PCy$_3$ (75.7 mg, 2.70×10^{-4} mol) was added to the solution followed by Na[**Bmp**] (69.3 mg, 2.70×10^{-4} mol). The reaction mixture was continuously stirred and allowed to react for 2.5 h. The mixture was then filtered and the volume was reduced to <1 mL under reduced pressure. Hexane (20 mL) was added to the stirring solution to precipitate a small amount of deep orange/ red solid. More solid was precipitated out of solution by reducing the volume of the hexane to approximately 1 mL. The solid product was separated from the remaining solution *via* cannula filtration before being washed with pentane (5 mL) and dried under dynamic vacuum. Yield: 91.6 mg, 1.29×10^{-4} mol, 48%. ^{1}H NMR δ (CDCl$_3$): 1.26 (m, 3H, ^{Cy4}CH$_2$), 1.27 (m, 6H, ^{Cy}CH$_2$), 1.52

(m, 6H, $^{Cy}CH_2$), 1.69 (m, 3H, $^{Cy4}CH_2$), 1.80 (m, 6H, $^{Cy}CH_2$), 2.02 (m, 6H, $^{Cy}CH_2$), 2.03 (m, 3H, ^{Cy1}CH), 6.70 (τd, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1 Hz, 2H, ^{mp5}CH), 7.30 (τd, $^3J_{HH}$ = 7.6 Hz, 2H, ^{mp4}CH), 7.52 (d, $^3J_{HH}$ = 8.4 Hz, 2H, ^{mp3}CH), 7.98 (d, $^3J_{HH}$ = 6.1 Hz, 2H, ^{mp6}CH). $^1H\{^{11}B\}$ NMR δ (CDCl$_3$): 6.6 (br. d, $^2J_{PtH}$ = 98.9 Hz, BH). ^{11}B NMR δ (CDCl$_3$): 17.9 (s, h.h.w. = 520 Hz, BH). $^{11}B\{^1H\}$ NMR δ (CDCl$_3$): 17.9 (s, h.h.w. = 440 Hz, BH). $^{31}P\{^1H\}$ NMR δ (CDCl$_3$): 36.5 (br. s, $^1J_{PtP}$ = 1570 Hz, h.h.w. = 150 Hz, PCy$_3$). $^{13}C\{^1H\}$ NMR δ (CDCl$_3$): 26.7 (s, $^{Cy}CH_2$), 27.7 (d, J_{CP} = 10 Hz, $^{Cy}CH_2$), 30.0 (d, J_{CP} = 1.8 Hz, $^{Cy}CH_2$), 34.4 (d, J_{CP} = 127 Hz, ^{Cy}CH), 114.5 (s, ^{mp5}C), 129.9 (s, J_{PtC} = 80.6 Hz, ^{mp3}C), 135.4 (s, J_{PtC} = 23 Hz, ^{mp4}C), 142.4 (d, J_{PtC} = 142 Hz, ^{mp5}C), 178.6 (d, $^3J_{CP}$ = 19.3 Hz, ^{mp2}C). IR (cm^{-1}, ATR powder film) 2922m, 2847m (C-H, PC$_6$H$_{11}$), 2310w (B-H), 1597m, 1541m, 1461m, 1418m, 1162m. ESI + MS: m/z 696.22 [M – B]$^+$, 585 [M – {HB(mp)}]$^+$, 281 [HPCy$_3$]$^+$. Anal. [Found (calc)] for C$_{28}$H$_{42}$BN$_2$PPtS$_2$: C 47.61% (47.52%), H 6.04% (5.98%), N 3.93% (3.96%).

Synthesis of [Pt{κ^3-*S,B,S*-HB(mp)$_2$}(PCyp$_3$)] (3). A Schlenk flask was charged with [PtCl(COE^{OMe})]$_2$ (100 mg, 1.35 × 10^{-4} mol) which was subsequently fully dissolved in 30 mL of DCM. PCyp$_3$ (1.286 mL of 0.21 M in toluene, 2.70 × 10^{-4} mol) was added to the solution followed by Na[**Bmp**] (69.3 mg, 2.70 × 10^{-4} mol). The reaction mixture was continuously stirred and allowed to react for 2.5 h. The mixture was then filtered and the volume was reduced to <1 mL under reduced pressure. Hexane (20 mL) was added to the stirring solution to precipitate a small amount of deep orange/ red solid. More solid was precipitated out of solution by reducing the volume of the hexane to approximately 1 mL. The solid product was separated from the remaining solution via cannula filtration before being washed with pentane (5 mL) and dried under dynamic vacuum. Yield: 85.3 mg, 1.28 × 10^{-4} mol, 47%. ^1H NMR δ (CDCl$_3$): 1.54 (m, 6H, $^{Cyp3}CH_2$), 1.74 (m, 6H, $^{Cyp3}CH_2$), 1.81(m, 6H, $^{Cyp2}CH_2$), 1.92 (bm, 6H, $^{Cyp2}CH_2$), 2.30 (m, 3H, ^{Cyp1}CH), 6.70 (τd,

J_{HH} = 6.5 Hz, 2H, ^{mp5}CH), 7.30 (τd, J_{HH} = 7.5 Hz, 2H, ^{mp4}CH), 7.52 (d, J_{HH} = 8.5 Hz, 2H, ^{mp3}CH), 7.97 (d, J_{HH} = 6.2 Hz, 2H, ^{mp6}CH). ^{1}H{^{11}B} NMR δ (CDCl$_3$): 6.52 (bs, $^2J_{PtH}$ = 118 Hz, h.h.w. = 17.3 Hz, BH). ^{11}B NMR δ (CDCl$_3$): 17.9 (s, h.h.w. = 460 Hz, BH). ^{11}B{^{1}H} NMR δ (CDCl$_3$): 17.9 (s, h.h.w. = 400 Hz, BH). ^{31}P{^{1}H} NMR δ (CDCl$_3$): 37.3 (br. s, $^1J_{PtP}$ = 1585 Hz, h.h.w. = 190 Hz, PCyp$_3$). ^{13}C{^{1}H} NMR δ (CDCl$_3$): 26.3 (d, $^3J_{CP}$ = 8.3 Hz, ^{Cyp3}C), 30.2 (d, $^2J_{CP}$ = 5.2 Hz, ^{Cyp2}C), 37.1 (d, $^1J_{CP}$ = 16.2 Hz, $^2J_{PtC}$ = 8.7 Hz, ^{Cyp1}C), 114.6 (s, ^{mp5}C), 130.0 (s, J_{PtC} = 82 Hz, ^{mp3}C), 135.6 (s, J_{PtC} = 23 Hz, ^{mp4}C), 142.4 (d, J_{PtC} = 30 Hz, ^{mp6}C), 178.8 (d, $^3J_{CP}$ = 19.9 Hz, ^{mp2}C). IR (cm^{-1}, ATR powder film) 2948m, 2864m, 2304w (B-H), 1599, 1542, 1462, 1416. MS (ESI)$^+$: m/z 654.17 [M − B], 543.16 [M − {HB(mp)}]$^+$, 239.19 [HPCyp$_3$]$^+$. Anal. [Found (calc)] for C$_{25}$H$_{36}$BN$_2$PPtS$_2$: C 44.96% (45.12%), H 5.48% (5.45%), N 4.28% (4.21%).

Synthesis of [Pt{κ³-*S,B,S*-HB(mp)₂}(P(o-tol)₃)] (4). A Schlenk flask was charged with [PtCl(COE^{OMe})]$_2$ (100 mg, 1.35 × 10^{-4} mol) which was subsequently fully dissolved in 30 mL of DCM. P(o-tol)$_3$ (82.2 mg, 2.70 × 10^{-4} mol) was added to the solution followed by Na[**Bmp**] (69.3 mg, 2.70 × 10^{-4} mol). The reaction mixture was continuously stirred and allowed to react for approximately 4 h. The mixture was then filtered and the volume reduced to <1 mL under reduced pressure. Hexane (30 mL) was added to the stirring solution to precipitate a small amount of deep orange/ red solid. More solid was precipitated out of solution by reducing the volume of the hexane to approximately 1 mL. The solid product was separated from the remaining solution via cannula filtration before being washed with hexane (5 mL) and dried under vacuum. Yield: 102.6 mg, 1.40 × 10^{-4} mol, 52%. ^{1}H NMR δ (CDCl$_3$)[48]: 2.28 (s, 9H, $^{(o\text{-}tol)}$CH$_3$), 6.70 (τd, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.1 Hz, 2H, ^{mp5}CH), 7.20 (unresolved, 3H, $^{(o\text{-}tol)}$CH), 7.26 (unresolved, 2H, ^{mp4}CH), 7.29 (unresolved, 6H, $^{(o\text{-}tol)}$CH), 7.40 (d, $^3J_{HH}$ = 8.5 Hz, 2H, ^{mp3}CH), 7.77 (t, 3H, $^{(o\text{-}tol)}$CH), 7.92 (d, $^3J_{HH}$ = 6.2 Hz, 2H, ^{mp6}CH). ^{1}H{^{11}B} NMR δ (CDCl$_3$): 6.64 (s, $^2J_{PtH}$ = 114 Hz, BH). ^{11}B NMR δ (CDCl$_3$): 14.5 (s,

h.h.w. = 475 Hz, BH). $^{11}B\{^1H\}$ NMR δ (CDCl$_3$): 14.5 (s, h.h.w. = 435 Hz, BH). $^{31}P\{^1H\}$ NMR δ (CDCl$_3$): 27.4 (br. s, $^1J_{PtP}$ = 1440 Hz, h.h.w. = 170 Hz, P(o-tol)$_3$). $^{13}C\{^1H\}$ NMR δ (CDCl$_3$): 23.4 (d, $^3J_{CP}$ = 7 Hz, $^{(o\text{-}tol)}$CH$_3$), 114.7 (s, ^{mp5}C), 125.6 (d, J_{CP} = 9.4 Hz, $^{(o\text{-}tol)}$C), 129.7 (s, $^{(o\text{-}tol)}$C), 130.1 (s, ^{mp3}C), 131.0 (d, J_{CP} = 28 Hz, $^{(o\text{-}tol)}$C), 131.6 (d, J_{CP} = 6.1 Hz, $^{(o\text{-}tol)}$C), 135.1 (d, J_{CP} = 14.5 Hz, $^{(o\text{-}tol)}$C), 135.5 (s, J_{PtC} = 23.2 Hz, ^{mp4}C), 142.2 (d, J_{PtC} = 31.8 Hz, ^{mp6}C), 143.2 (d, J_{CP} = 9.9 Hz, $^{(o\text{-}tol)}$C), 178.8 (d, $^3J_{CP}$ = 20.5 Hz, ^{mp2}C). IR (cm^{-1}, ATR powder film) 2321w (B-H), 1603, 1541, 1462. MS (ESI)$^+$: m/z 720.12 [M − B]. Anal. [Found (calc)] for C$_{31}$H$_{30}$BN$_2$PPtS$_2$: C 51.15% (50.90%), H 3.96% (4.13%), N 3.94% (3.83%).

Synthesis of [Pt{κ^3-S,B,S-HB(mp)$_2$}(PPh$_2$(o-tol))] (5). A Schlenk flask was charged with [PtCl(COE^{OMe})]$_2$ (100 mg, 1.35×10^{-4} mol) which was subsequently fully dissolved in 30 mL of DCM. Ph$_2$P(o-tol) (74.6 mg, 2.70×10^{-4} mol) was added to the solution followed by Na[**Bmp**] (69.3 mg, 2.70×10^{-4} mol). The reaction mixture was continuously stirred and allowed to react for 3 h. The mixture was then filtered and the volume was reduced to <1 mL under reduced pressure. Hexane (20 mL) was added to the stirring solution to precipitate an orange solid. The solid product was separated from the remaining solution via cannula filtration before being washed with additional hexane (5 mL) and dried under dynamic vacuum. Yield: 93.5 mg, 1.33×10^{-4} mol, 49%. ^1H NMR δ (CDCl$_3$)[48]: 2.54 (s, 3H, $^{(o\text{-}tol)}$CH$_3$), 6.74 (τd, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, ^{mp5}CH), 6.80 (t, 1H, $^{(o\text{-}tol)5}$CH), 7.12 (t, 1H, $^{(o\text{-}tol)4}$CH), 7.27 (unresolved, 1H, $^{(o\text{-}tol)3}$CH), 7.27 (unresolved, 1H, $^{(o\text{-}tol)6}$CH), 7.30 (τd, $^3J_{HH}$ = 7.4 Hz, 2H, ^{mp4}CH), 7.37 (m, 4H, $^{m\text{-}Ph}$CH), 7.38 (m, 2H, $^{p\text{-}Ph}$CH), 7.48 (d, $^3J_{HH}$ = 8.5 Hz, 2H, ^{mp3}CH), 7.68 (m, 4H, $^{o\text{-}Ph}$CH), 7.96 (d, $^3J_{HH}$ = 6.2 Hz, 2H, ^{mp6}CH). $^1H\{^{11}B\}$ NMR δ (CDCl$_3$): 6.68 (s, $^2J_{PtH}$ = 118 Hz, BH). ^{11}B NMR δ (CDCl$_3$): 15.6 (br. s, h.h.w. = 440 Hz, BH). $^{11}B\{^1H\}$ NMR δ (CDCl$_3$): 15.6 (br. s, h.h.w. = 400 Hz, BH). $^{31}P\{^1H\}$ NMR δ (CDCl$_3$): 25.5 (br. s, $^1J_{PtP}$ = 1485 Hz, h.h.w. = 147 Hz, Ph$_2$P(o-tol)). $^{13}C\{^1H\}$ NMR δ (CDCl$_3$):

23.3 (d, $^3J_{CP}$ = 10.8 Hz, $^{(o\text{-}tol)}CH_3$), 115.0 (s, ^{mp5}C), 125.4 (d, $^4J_{CP}$ = 5.9 Hz, $^{(o\text{-}tol)4}C$), 128.5 (d, $^4J_{CP}$ = 9.1 Hz, $^{p\text{-}Ph}C$), 129.5 (s, $^{(o\text{-}tol)6}C$), 129.7 (s, $^{m\text{-}Ph}C$), 130.1 (s, ^{mp3}C), 131.0 (d, $^3J_{CP}$ = 6.6 Hz, $^{(o\text{-}tol)3}C$), 132.9 (d, $^3J_{CP}$ = 5.7 Hz, $^{(o\text{-}tol)5}C$), 133.5 (d, $^1J_{CP}$ = 30.4 Hz, $^{(o\text{-}tol)2}C$), 134.5 (d, $^{i\text{-}Ph}C$), 134.7 (d, $^2J_{CP}$ = 13.7 Hz, $^{o\text{-}Ph}C$), 135.8 (s, J_{PtC} = 22.7 Hz, ^{mp4}C), 142.3 (d, J_{PtC} = 27.6 Hz, ^{mp6}C), 142.4 (d, $^{(o\text{-}tol)1}C$), 178.6 (d, $^3J_{CP}$ = 20.6 Hz, ^{mp2}C). IR (cm^{-1}, ATR powder film) 2323w (B-H). MS (ESI)$^+$: *m/z* 692.09 [M – B], 581.08 [M – {HB(mp)}]$^+$. Anal. [Found (calc)] for C$_{29}$H$_{26}$BN$_2$PPtS$_2$•⅔CH$_2$Cl$_2$: C 46.85% (46.89%), H 3.65% (3.60%), N 4.06% (3.69%).

Synthesis of [Pt{κ^3-*S*,*B*,*S*-HB(mp)$_2$}(PPh$_2$(^{Me}In)) (6). A Schlenk flask was charged with [PtCl(COE^{OMe})]$_2$ (100 mg, 1.35 × 10^{-4} mol) which was subsequently fully dissolved in 30 mL of DCM. Ph$_2$P(^{Me}In) (85.2 mg, 2.70 × 10^{-4} mol) was added to the solution followed by Na[**Bmp**] (69.3 mg, 2.70 × 10^{-4} mol). The reaction mixture was continuously stirred and allowed to react for 3 h. The mixture was then filtered and the volume was reduced to <1 mL under reduced pressure. Hexane (20 mL) was added to the stirring solution to precipitate an orange solid. The solid product was separated from the remaining solution via cannula filtration before being washed with additional hexane (5 mL) and dried under dynamic vacuum. Yield: 130.8 mg, 1.76 × 10^{-4} mol, 65%. ^{1}H NMR δ (CDCl$_3$)[48]: 1.99 (s, 3H, CH$_3$), 6.79 (τd, $^3J_{HH}$ = 6.4 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, ^{mp5}CH), 7.10 (t, 1H, ^{In}CH), 7.20 (t, 1H, ^{In}CH), 7.35 (unresolved, 2H, $^{mp}CH^4$), 7.35 (unresolved, 1H, ^{In}CH), 7.38 (unresolved, 4H, ^{Ph}CH), 7.41 (unresolved, 2H, ^{Ph}CH), 7.58 (unresolved, 1H, ^{In}CH), 7.51 (d, $^3J_{HH}$ = 8.5 Hz, 2H, ^{mp3}CH), 7.60 (m, 4H, $^{o\text{-}Ph}CH$), 7.99 (d, $^3J_{HH}$ = 6.2 Hz, 2H, ^{mp6}CH), 9.11 (s, 1H, ^{In}NH). ^{1}H{^{11}B} NMR δ (CDCl$_3$): 6.67 (s, BH). ^{11}B NMR δ (CDCl$_3$): 16.4 (s, h.h.w. = 470 Hz, BH). ^{11}B{^{1}H} NMR δ (CDCl$_3$): 16.4 (s, h.h.w. = 435 Hz, BH). ^{31}P{^{1}H} NMR δ (CDCl$_3$): 12.9 (br. s, $^1J_{PtP}$ = 1497 Hz, h.h.w. = 175 Hz, PPh$_2$(^{Me}In)). ^{13}C{^{1}H} NMR δ (CDCl$_3$): 10.4 (d, $^3J_{CP}$ = 1.5 Hz, CH$_3$), 115.2 (s, ^{mp5}C), 119.1 (s, ^{In}C), 123.1 (s, ^{In}C), 124.7 (d, $^1J_{CP}$ = 44.9 Hz, ^{In2}C), 120.0 (d, $^2J_{CP}$

= 3.9 Hz, [In3]C), 129.8 (d, $^3J_{CP}$ = 6.1 Hz, [In3a]C), 137.1 (d, $^3J_{CP}$ = 9.1 Hz, [In7a]C), 130.0 (s, [mp3]C), 128.3 (d, J_{PC} = 9.5 Hz, [Ph]C), 129.5 (d, J_{PC} = 1.7 Hz, [Ph]C), 132.9 (d, J_{PC} = 13.8 Hz, [Ph]C), 132.6 (d, $^1J_{CP}$ = 11.0 Hz, [i-Ph]C), 136.0 (s, [mp4]C), 142.3 (s, [mp6]C), 178.1 (d, $^3J_{CP}$ = 20.8 Hz, [mp2]C), IR (cm^{-1}, ATR powder film) 2318w (B-H). MS (ESI)$^+$: *m/z* missing 731.1 [M − B]$^+$, 316.1 [HPPh([Me]In)]$^+$. Anal. [Found (calc)] for C$_{31}$H$_{27}$BN$_3$PPdS$_2$: C 50.04% (50.14%), H 3.62% (3.67%), N 5.58% (5.66%).

Attempts to isolate and characterise [PtH{κ³-S,B,S-HB(mp)₂}(COE^{OMe})] (Pt$_{int}$). A Schlenk flask was charged with [PtCl(COE^{OMe})]₂ (25 mg, 3.38 × 10^{-5} mol) which was subsequently fully dissolved in 7.5 mL of DCM. PMe₃ 1M in THF (67.5μL, 6.75 × 10^{-5} mol) was added to the solution followed by Na[**Bmp**] (17.3 mg, 6.75 × 10^{-5} mol). The reaction mixture was continuously stirred and allowed to react for 2.5 h. The mixture was then filtered and reduced to ¼ its original volume under reduced pressure. Hexane (15 mL) was added to the stirring solution to precipitate a small amount of pale yellow solid. The solid product was separated from the remaining solution via cannula filtration before being washed with pentane (4 mL) and dried under vacuum. The compound started to decompose when it was placed back into solvent. Selected characterisation: ^{1}H NMR δ (CDCl₃): 1.25-2.57 (m, [coe]CH₂), 3.07 (m, [coe]CH), 3.26 (s, [OMe]CH₃), 3.68 (m, [coe]CH), 5.60 (m, [coe]CH), 5.86 (m, [coe]CH), 6.74 (s, 2H, [mp]CH), 7.21 (t, 2H, [mp]CH), 7.48 (m, [mp]CH), 7.55 (m, [mp]CH), 8.02 (s, [mp]CH), 8.26 (s, [mp]CH). ^{1}H NMR δ (CD₂Cl₂): -13.31 (s, $^1J_{PtH}$ = 1400 Hz, PtH). ^{11}B NMR δ (CDCl₃): 7.9 (bs, h.h.w. = 420 Hz, BH). ^{11}B{^{1}H} NMR δ (CDCl₃): 7.9 (bs, $^1J_{PtB}$ = 500 Hz, BH).

Synthesis of [Pd{κ³-S,B,S-HB(mp)₂}(PPh₃)] (7) from Pd(COD)MeCl. A Schlenk flask was charged with [Pd(Me)Cl(COD)] (25 mg, 9.43 × 10^{-5} mol) which was fully dissolved in 5 mL of DCM. PPh₃ (24.7 mg, 9.43 × 10^{-5} mol) was added to the solution followed by Na[**Bmp**] (24.2 mg, 9.43 × 10^{-5} mol). The reaction mixture was continuously stirred and allowed to react for 1 h. The

mixture was then filtered and the volume was reduced to <1 mL under reduced pressure. Hexane (15 mL) was added to the stirring solution to precipitate an orange solid. The solid product was separated from the remaining solution via cannula filtration before being washed with additional hexane (5 mL) and dried under dynamic. Yield: 171.2 mg, 2.78×10^{-4} mol, 78%. The characterisation for this complex was the same as previously reported for this complex starting from [PdCl(COE^{OMe})]$_2$.[25a]

Synthesis of [Pd{κ^3-S,B,S-HB(mp)$_2$}(PCy$_3$)] (8). A Schlenk flask was charged with [PdCl(COE^{OMe})]$_2$ (100 mg, 1.78×10^{-4} mol) which was fully dissolved in 30 mL of DCM. PCy$_3$ (100.1 mg, 3.57×10^{-4} mol) was added to the solution followed by Na[**Bmp**] (91.2 mg, 3.54×10^{-4} mol). The reaction mixture was continuously stirred and allowed to react for 1 h. The mixture was then filtered and the volume was reduced to <1 mL under reduced pressure. Hexane (20 mL) was added to the stirring solution to precipitate a small amount of deep orange/ red solid. More solid was precipitated from the solution by reducing the volume of the hexane to approximately 1 mL. The solid product was separated from the remaining solution via cannula filtration before being washed with pentane (5 mL) and dried under dynamic vacuum. Yield: 103.9 mg, 1.68×10^{-4} mol, 47%. ^{1}H NMR δ (CDCl$_3$): 1.27 (bm, 3H, ^{Cy4}CH$_2$), 1.27 (bm, 6H, ^{Cy3}CH$_2$), 1.49 (bm, 6H, ^{Cy2}CH$_2$), 1.68 (bs, 3H, ^{Cy4}CH$_2$), 1.79 (bd, 6H, ^{Cy3}CH$_2$), 1.86 (m, 3H, ^{Cy1}CH), 1.98 (bd, 6H, ^{Cy2}CH$_2$), 6.71 (τd, $^3J_{HH}$ = 6.6 Hz, 2H, ^{mp5}CH), 7.29 (τd, $^3J_{HH}$ = 7.5 Hz, 2H, ^{mp4}CH), 7.54 (d, $^3J_{HH}$ = 8.5 Hz, 2H, ^{mp3}CH), 7.74 (d, $^3J_{HH}$ = 6.2 Hz, 2H, ^{mp6}CH). ^{1}H{^{11}B} NMR δ (CDCl$_3$): 5.67 (bd, h.h.w. = 16.4 Hz, BH). ^{11}B NMR δ (CDCl$_3$): 14.7 (s, h.h.w. = 300 Hz, BH). ^{11}B{^{1}H} NMR δ (CDCl$_3$): 14.6 (s, h.h.w. = 220 Hz, BH). ^{31}P{^{1}H} NMR δ (CDCl$_3$): 21.0 (br s, h.h.w. = 190 Hz, PCy$_3$). ^{13}C{^{1}H} NMR δ (CDCl$_3$): 26.7 (s, ^{Cy4}C), 27.9 (d, $^3J_{CP}$ = 9.8 Hz, ^{Cy3}C), 30.6 (d, $^2J_{CP}$ = 4.4 Hz, ^{Cy2}C), 33.7 (d, $^1J_{CP}$ = 5.4 Hz, ^{Cy1}C), 114.2 (s, ^{mp5}C), 130.6 (s, ^{mp3}C), 135.6 (s, ^{mp4}C), 141.3 (d, $^4J_{CP}$ = 2.2 Hz,

mp6C), 179.1 (d, mp2C). IR (cm^{-1}, ATR powder film) 2919, 2344 (B-H), 1598 s, 1540 s (pyridine). MS (ESI)$^+$: m/z 607.16 [M – B]. Anal. [Found (calc)] for $C_{28}H_{42}BN_2PPdS_2 \cdot \frac{1}{4}CH_2Cl_2$: C 52.83% (53.00%), H 6.76% (6.69%), N 4.63% (4.38%).

Synthesis of [Pd{κ³-S,B,S-HB(mp)₂}(PCyp₃)] (9). A Schlenk flask was charged with [PdCl(COE^{OMe})]₂ (100 mg, 1.78×10^{-4} mol) which was fully dissolved in 30 mL of DCM. P(c-C₅H₉)₃ (1.7 mL of 0.21 M in toluene, 3.57×10^{-4} mol) was added to the solution followed by Na[**Bmp**] (91.2 mg, 3.54×10^{-4} mol). The reaction mixture was continuously stirred and allowed to react for 1 h. The mixture was then filtered and the volume was reduced to <1 mL under reduced pressure. Hexane (30 mL) was added to the stirring solution to precipitate an orange/ red solid. The solid product was separated from the remaining solution via cannula filtration before being washed with pentane (5 mL) and dried under dynamic vacuum. Yield: 114.5 mg, 1.99×10^{-4} mol, 56 %. ^{1}H NMR δ (CDCl₃): 1.53 (m, 6H, ^{Cyp3}CH₂), 1.74 (m, 6H, ^{Cyp3}CH₂), 1,74 (m, 6H, ^{Cyp3}CH₂), 1.92 (m, 6H, ^{Cyp2}CH₂), 2.09 (m, 3H, ^{Cyp1}CH), 6.71 (τd, $^3J_{HH}$ = 6.6 Hz, 2H, ^{mp5}CH), 7.29 (τd, $^3J_{HH}$ = 7.6 Hz, 2H, ^{mp4}CH), 7.52 (d, $^3J_{HH}$ = 8.5 Hz, 2H, ^{mp3}CH), 7.73 (d, $^3J_{HH}$ = 6.3 Hz, 2H, ^{mp6}CH). ^{1}H{^{11}B} NMR δ (CDCl₃): 5.63 (d, $^3J_{PH}$ = 5.9 Hz, h.h.w. = 14.7 Hz, BH). ^{11}B NMR δ (CDCl₃): 14.7 (s, h.h.w. = 281 Hz, BH). ^{11}B{^{1}H} NMR δ (CDCl₃): 14.7 (s, h.h.w. = 200 Hz, BH). ^{31}P{^{1}H} NMR δ (CDCl₃): 20.3 (br. d, h.h.w. = 200 Hz, PCyp₃). ^{13}C{^{1}H} NMR δ (CDCl₃): 26.3 (d, $^3J_{CP}$ = 8.0 Hz, ^{Cyp3}C), 30.6 (d, $^2J_{CP}$ = 7.4 Hz, ^{Cyp2}C), 36.3 (d, $^1J_{CP}$ = 8.5 Hz, ^{Cyp1}C), 114.2 (s, ^{mp5}C), 130.5 (s, ^{mp3}C), 135.6 (s, ^{mp4}C), 141.3 (d, $^4J_{CP}$ = 2.4 Hz, ^{mp6}C), 179.1 (d, $^3J_{CP}$ = 19.9 Hz, ^{mp2}C). IR (cm^{-1}, ATR powder film) 2331 (B-H). MS (ESI)$^+$: m/z 565.11 [M – B]. Anal. [Found (calc)] for $C_{25}H_{36}BN_2PPdS_2$: C 52.12% (52.05%), H 6.46% (6.29%), N 5.00% (4.86%).

Synthesis of [Pd{κ³-S,B,S-HB(mp)₂}(Ph₂P(o-tol))] (10). A Schlenk flask was charged with [PdCl(COE^{OMe})]₂ (100 mg, 1.78×10^{-4} mol) which was fully dissolved in 30 mL of DCM. PPh₂(o-

tol) (99 mg, 3.57×10^{-4} mol) was added to the solution followed by Na[**Bmp**] (91.2 mg, 3.54×10^{-4} mol). The reaction mixture was continuously stirred and allowed to react for 1 h. The mixture was then filtered and the volume was reduced to <1 mL under reduced pressure. Hexane (20 mL) was added to the stirring solution to precipitate an orange solid. The solid product was separated from the remaining solution via cannula filtration before being washed with additional hexane (5 mL) and dried under dynamic. Yield: 171.2 mg, 2.78×10^{-4} mol, 78%. ^{1}H NMR δ (CDCl$_3$)[48]: 2.56 (s, 3H, CH$_3$), 6.74 (τd, ^{3}J$_{HH}$ = 6.7 Hz, 2H, ^{mp5}CH), 6.76 (t, 1H, $^{(o\text{-}tol)}$CH), 7.10 (t, 1H, $^{(o\text{-}tol)}$CH), 7.26 (unresolved, 1H, $^{(o\text{-}tol)}$CH), 7.30 (τd, ^{3}J$_{HH}$ = 7.4 Hz, 2H, ^{mp4}CH), 7.33 (unresolved, 1H, $^{(o\text{-}tol)}$CH), 7.37 (m, 2H, ^{Ph}CH), 7.37 (m, 4H, ^{Ph}CH), 7.60 (m, 4H, ^{Ph}CH), 7.50 (d, ^{3}J$_{HH}$ = 8.5 Hz, 2H, ^{mp3}CH), 7.74 (d, ^{3}J$_{HH}$ = 6.2 Hz, 2H, ^{mp6}CH). ^{1}H{^{11}B} NMR δ (CDCl$_3$): 5.81 (s, BH). ^{11}B NMR δ (CDCl$_3$): 13.5 (s, h.h.w. = 300 Hz, BH). ^{11}B{^{1}H} NMR δ (CDCl$_3$): 13.6 (s, h.h.w. = 240 Hz, BH). ^{31}P{^{1}H} NMR δ (CDCl$_3$): 5.6 (br. s, h.h.w. = 185 Hz, Ph$_2$P(o-tol)). ^{13}C{^{1}H} NMR δ (CDCl$_3$): 23.2 (d, CH$_3$), 114.4 (s, ^{mp5}C), 125.6 (d, $^{(o\text{-}tol)4}$C), 128.5 (d, J$_{PC}$ = 8.8 Hz, ^{Ph}C), 129.3 (s, ^{Ph}C), 130.5 (s, ^{mp3}C), 130.9 (d, J$_{PC}$ = 6.2 Hz, $^{(o\text{-}tol)3}$C), 132.5 (d, J$_{PC}$ = 4.4 Hz, $^{(o\text{-}tol)5}$C), 134.6 (d, J$_{PC}$ = 15.4 Hz, ^{Ph}C), 135.7 (s, ^{mp4}C), 141.1 (s, ^{mp6}C), 179.1 (d, ^{3}J$_{CP}$ = 16.1 Hz, ^{mp2}C). IR (cm^{-1}, ATR powder film) 2347w (B-H). ESI + MS: *m/z* 603.0 [M – BH]$^+$, 494.0 [M – {HB(mp)}]$^+$. Unfortunately, satisfactory elemental analysis could not be obtained for this compound.

X-ray Crystallography

Single-crystal X-ray diffraction studies of complexes **2, 3, 8, 9** and **10** were carried out at the UK National Crystallography Service at the University of Southampton.[49] Single crystals of complexes **2, 3, 8** and **9** were obtained by allowing a saturated ether solution stand at room temperature. Single crystals of complex **10** were obtained from a concentrated toluene-d$_8$ solution. A single crystal from each sample was mounted on a MITIGEN holder in perfluoroether oil on a

Rigaku FRE+ equipped with HF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector. The crystals were kept at T = 100(2) K during data collection. Data were collected and processed and empirical absorption corrections were carried out using CrysAlisPro[50] The structures were solved by Intrinsic Phasing using the ShelXT structure solution program[51] and refined on $F_o{}^2$ by full-matrix least squares refinement with version 2014/7 of ShelXL[52] as implemented in Olex2,[53] The structures for complexes **2**, **3**, **9** and **10** contained various degrees of disorder. They also contained two independent complexes in the asymmetric unit. In complex **2**, the structure contained disorder of the [HB(mp)$_2$] ligand occupying in a ratio of 51:49 in each complex. In complex **3**, the structure contained disorder of two of the cyclopentene rings of one complex occupying in ratios of 44:55 and 84:16, respectively. In complex **9**, the structure also contained disorder of two of the cyclopentene rings of one complex occupying in ratios of 53:47 and 79:21, respectively. In complex **10**, the structure contained disorder of the [HB(mp)$_2$] ligand in one complex occupying in a ratio of 80:20. Complex **8** only contained one complex within the asymmetric unit with no disorder. All hydrogen atom positions were calculated geometrically and refined using the riding model. Crystal Data for **2**. C$_{28}$H$_{42}$BN$_2$PPtS$_2$, M_r = 707.62, monoclinic, P2$_1$/n (No. 14), a = 17.3342(3) Å, b = 9.8075(2) Å, c = 34.4228(5) Å, β = 94.7630(10)$^\circ$, $\alpha = \gamma$ = 90°, V = 5831.84(18) Å^3, T = 100(2) K, Z = 8, Z' = 2, μ(MoK$_\alpha$) = 5.030, 54250 reflections measured, 13345 unique (R_{int} = 0.0575) which were used in all calculations. The final wR_2 was 0.0795 (all data) and R_1 was 0.0442 (I > 2(I)). Crystal Data for **3**. C$_{25}$H$_{36}$BN$_2$PS$_2$Pt, M_r = 665.55, triclinic, P-1 (No. 2), a = 9.49076(18) Å, b = 16.1437(3) Å, c = 17.6862(4) Å, α = 75.2432(18)$^\circ$, β = 75.3619(18)$^\circ$, γ = 84.6537(16)$^\circ$, V = 2534.17(9) Å^3, T = 100(2) K, Z = 4, Z' = 2, μ(MoK$_\alpha$) = 5.782, 33047 reflections measured, 11545 unique (R_{int} = 0.0187) which were used in all calculations. The final wR_2 was 0.0407 (all data) and R_1 was 0.0177 (I > 2(I)). Crystal Data for **8**.

$C_{28}H_{42}BN_2PS_2Pd$, $M_r = 618.93$, monoclinic, $P2_1/c$ (No. 14), a = 14.9962(4) Å, b = 9.5779(2) Å, c = 20.0916(6) Å, $\beta = 95.606(3)°$, $\alpha = \gamma = 90°$, $V = 2872.00(13)$ Å^3, $T = 100(2)$ K, $Z = 4$, $Z' = 1$, $\mu(MoK_\alpha) = 0.867$, 21729 reflections measured, 6541 unique ($R_{int} = 0.0620$) which were used in all calculations. The final wR_2 was 0.0838 (all data) and R_1 was 0.0319 (I > 2(I)). Crystal Data for **9**. $C_{25}H_{36}BN_2PS_2Pd$, $M_r = 576.86$, triclinic, P-1 (No. 2), a = 9.4416(3) Å, b = 16.2327(4) Å, c = 17.7301(5) Å, $\alpha = 75.064(2)°$, $\beta = 75.481(2)°$, $\gamma = 84.696(2)°$, $V = 2540.60(13)$ Å^3, $T = 100(2)$ K, $Z = 4$, $Z' = 2$, $\mu(MoK_\alpha) = 0.975$, 33439 reflections measured, 11550 unique ($R_{int} = 0.0210$) which were used in all calculations. The final wR_2 was 0.0555 (all data) and R_1 was 0.0233 (I > 2(I)). Crystal Data for **10**. $C_{29}H_{26}BN_2PPdS_2$ $0.2(C_7D_8)$, $M_r = 634.85$, triclinic, P-1 (No. 2), a = 10.0339(4) Å, b = 14.6916(5) Å, c = 19.2246(8) Å, $\alpha = 89.410(3)°$, $\beta = 75.465(3)°$, $\gamma = 86.799(3)°$, $V = 2738.96(19)$ Å^3, $T = 100(2)$ K, $Z = 4$, $Z' = 2$, $\mu(MoK_\alpha) = 0.912$, 32792 reflections measured, 12331 unique ($R_{int} = 0.0292$) which were used in all calculations. The final wR_2 was 0.1105 (all data) and R_1 was 0.0478 (I > 2(I)). A summary of the crystallographic data collection parameters and refinement details for all complexes are presented in the supporting information. Anisotropic parameters, bond lengths and (torsion) angles for these structures are available from the CIF files which have been deposited with the Cambridge Crystallographic Data Centre and given the following deposition numbers, 1842135 (**2**), 1842137 (**3**), 1842138 (**8**), 1842139 (**9**) and 1842136 (**10**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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34 We originally suggested in reference 14, that the identity of **Pt$_{int}$** was [Pt{κ^3-*S,S,H*-H$_2$B(mp)$_2$}{COE^{OMe}}] since we did not observe a platinum–hydride in our preliminary investigations. We now have clear evidence of a Pt–H species. This, in addition to the large $^{1}J_{PtB}$ coupling constant provides clear evidence of the transfer of hydride from borohydride to metal center and that **Pt$_{int}$** is [PtH{κ^3-*S,B,S*-HB(mp)$_2$}{η^2-COE^{OMe}}].

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ASSOCIATED CONTENT

The following files are available free of charge.

Crystallographic parameters, selected distances and angles for all crystal structures in addition to selected spectroscopic data are provided in the Electronic Supporting Information.

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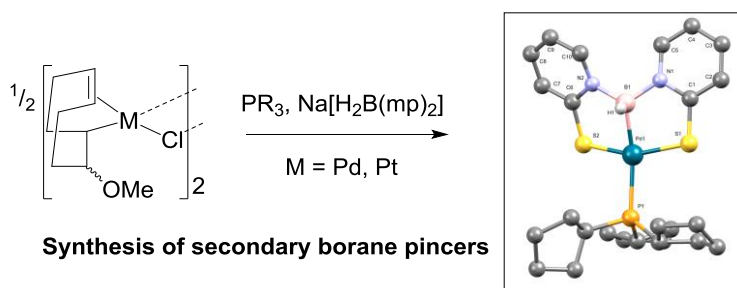
Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. The authors declare no competing financial interest.

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Graphical Abstract

Synthesis of secondary borane pincers

A general method for the synthesis of palladium and platinum pincer complexes containing a κ^3-S,B,S coordinated $HB(mp)_2$ ligand (where mp – 2-mercaptopyridyl) is presented providing a rare set of pincer complexes containing a secondary borane functional group as the central species.