

Stopping Hydrogen Migration in its Tracks: The First Successful Synthesis of Group Ten Scorpionate Complexes Based on Azaindole Scaffolds

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Abstract

The first successful synthesis and characterization of group ten complexes featuring flexible scorpionate ligands based on 7-azaindole heterocycles are reported herein. Addition of two equivalents of either $K[HB(\text{azaindoly})_3]$ or $Li[HB(\text{Me})(\text{azaindoly})_2]$ to $[M(\mu\text{-Cl})(\eta^1, \eta^2\text{-COE}^{\text{OMe}})]_2$ leads to the formation of two equivalents of the complexes $[M\{\kappa^3\text{-}N,N,H\text{-}HB(\text{azaindoly})_3\}(\eta^1, \eta^2\text{-COE}^{\text{OMe}})]$ and $[M\{\kappa^3\text{-}N,N,H\text{-}HB(\text{Me})(\text{azaindoly})_2\}(\eta^1, \eta^2\text{-COE}^{\text{OMe}})]$ (where $M = \text{Pt}, \text{Pd}$; $\text{COE}^{\text{OMe}} = 8\text{-methoxycyclooct-4-en-1-ide}$), respectively. In these reactions, the borohydride group is directed towards the metal center forming square based pyramidal complexes. In contrast to analogous complexes featuring other flexible scorpionate ligands, no hydrogen migration from boron is observed in the complexes studied. The fortuitous linewidths

observed in some of the ^{11}B NMR spectra allow for a closer inspection of the B–H•••metal unit in scorpionate complexes than has previously been possible.

Introduction

Over many years now, we have developed a number of anionic poly(azaindoly)borate and neutral poly(azaindoly)borane ligands derived from the parent ligand $[\mathbf{Tai}]^- [\text{HB}(7\text{-azaindoly})_3]^-$.¹⁻⁴ This ligand was originally synthesized by Wang in 2005¹ and we have subsequently prepared several new derivatives as indicated in Chart 1.^{3,4} A large number of complexes have now been established displaying the coordination modes $\kappa^2\text{-}N,H$, $\kappa^2\text{-}N,(\mu\text{-}H)$, $\kappa^2\text{-}N,N$, $\kappa^3\text{-}N,N,H$, $\kappa^3\text{-}N,N,N$, $\kappa^3\text{-}N,B,N$ and $\kappa^4\text{-}N,N,B,N$.¹⁻⁴ Notwithstanding these examples however, the coordination chemistry of azaindole based scorpionates with group ten metals is currently unknown. Indeed, in their original publication introducing the $[\mathbf{Tai}]^-$ ligand, Wang reported the failure to isolate stable complexes with palladium(II) and platinum(II) precursors [in addition to group 11 silver(I) salts]. They cited reduction and subsequent decomposition of these metal salts as likely cause.¹ At first, this would perhaps be surprising given the large number of group ten complexes known bearing the closely related Trofimenko type pyrazolyl (nitrogen donor) scorpionates⁵ and related systems featuring Pt•••H–B or Pd•••H–B motifs.⁶ Based on our previous observations involving the $[\mathbf{Tai}]^-$ ligand and its derivatives, in addition to the reactivity observed with the more “flexible scorpionates”,^{3a,7a} we felt that it is almost certain that hydride migration from boron to metal center was somehow implicated in these observations (Scheme 1).^{7,8} We use the term “flexible scorpionate ligands” to represent those ligands which contain an additional atom between the donor atom and the borohydride unit when compared to the original Trofimenko-type scorpionates (Chart 2). The consequences of this larger chelation size facilitates direct reactivity between the

metal and boron centers. In the latter compounds, formation of a metal–boron bond is possible and results in the formation of five membered chelates.

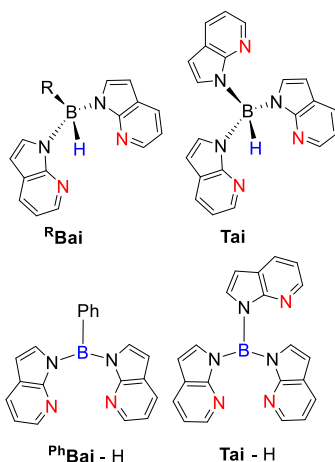
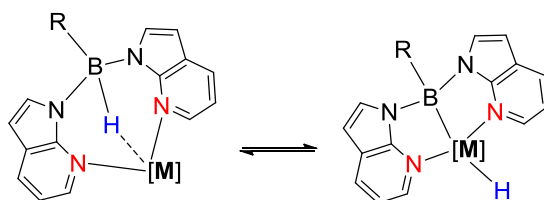


Chart 1 – Anionic and neutral boron based ligands containing azaindolyl units. The colored nitrogen atoms highlight the potential sites which are available for coordination to metal centers

(R = phenyl, mesityl, naphthyl, methyl).



Scheme 1 – Hydrogen migration from azaindole based ligands to the metal center ([M] represents the metal center and remaining co-ligands; R = azaindolyl, phenyl; the geometries at the boron and metal centers are not implied here for reasons of clarity).

There are currently only a handful of examples of a platinum(II) or palladium(II) complex featuring a flexible scorpionate ligand where the hydride remains at the boron center (as borohydride).^{8b,9-11} In all other cases, spontaneous migration of hydride from the boron center to metal center occurs.¹² In the only two platinum examples involving migration,^{8b,9} the location of

the hydride species was found to be reversible between the two centers. In one case, whilst the borohydride unit was found to remain in the solid state, the hydride was found to migrate to the platinum center (resulting in platinum–boron bond formation) in solution. Attempts by others to synthesize platinum complexes containing flexible scorpionate ligands have also led to further unwanted reactivity and intractable mixtures.¹⁰

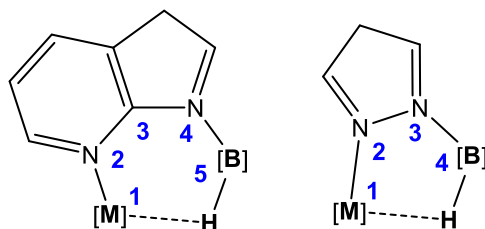


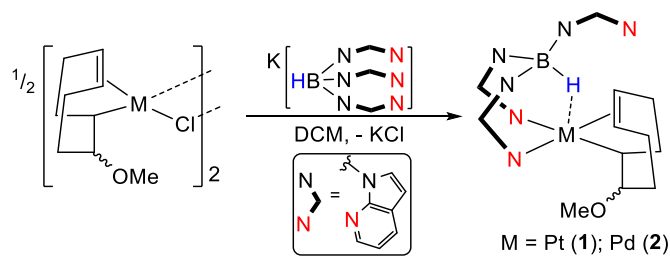
Chart 2 – Comparison of azaindolyl based (flexible) and a pyrazolyl based (rigid, Trofimenko-type) scorpionate ligands. Activation of the B–H bond in the former ligands results in the formation of five-membered chelates. B–H bond activation is less likely for the pyrazolyl based ligands due to limitations of the ring size. For clarity only one heterocycle is shown; scorpionate ligands generally consist of two or more heterocycles.

To date, there are no reported group ten complexes containing any of the poly(azaindolyl)borate ligands. Herein, we wish to report the first successful synthesis of palladium and platinum complexes bearing the poly(azaindolyl)borate ligands. In the complexes we report, the [Tai][−] and [MeBai][−] (Chart 1) ligands are stable against spontaneous hydride migration and are the first examples of group ten complexes containing poly(azaindolyl)borate ligands. Additionally, the serendipitous features of the ¹¹B NMR spectra of these group ten complexes provide a rare opportunity to examine more closely the interaction of the B–H unit with the metal center.

Results and Discussion

In accordance with the established literature, our exploratory experiments by adding one equivalent of K[**Tai**] to archetypical d⁸ metal precursors such as [MCl₂(COD)] (M = Pt or Pd) also resulted in non-isolatable products and/or rapid decomposition.¹³ We suggested in previous publications that the presence of the second halide might be involved in further unwanted reactivity, such as the elimination of HCl.^{12d} In that same report (and a subsequent one) we established the 8-methoxycyclooct-4-en-1-ide (COE^{OMe}) unit as a novel hydrogen atom acceptor *en route* to group ten metal-borane complexes.^{12d,f} Indeed, this moiety is one of several hydrogen atom acceptor groups which have been employed to target metal–borane complexes.^{3b-d,f,h,7a,8a-c,14} A range of platinum and palladium complexes were prepared by addition of one equivalent of Na[**Bmp**] [**Bmp** = H₂B(2-mercaptopyridyl)₂] to one half equivalents of [MCl(η¹,η²-COE^{OMe})₂] (where M = Pt, Pd), in the presence of a tertiary phosphine ligand.^{12d,f} The enhanced propensity for [**Bmp**][−] to “sting” relative to other scorpionate ligands,^{8c} meant that rapid hydrogen migration occurred and the COE^{OMe} unit was eliminated.

Based on this strategy, we attempted to prepare group ten complexes containing the poly(azaindoly)borate ligands utilizing the [PtCl(η¹,η²-COE^{OMe})₂] and [PdCl(η¹,η²-COE^{OMe})₂] as precursors. This methodology was indeed successful. The complexes, [Pt{κ³-*N,N,H*-HB(azaindoly)₃}(η¹,η²-COE^{OMe})] (**1**) and [Pd{κ³-*N,N,H*-HB(azaindoly)₃}(η¹,η²-COE^{OMe})] (**2**) were prepared by addition of two equivalents of K[**Tai**] to solutions of either [PtCl(COE^{OMe})₂] or [PdCl(COE^{OMe})₂] in DCM, as shown in Scheme 2. The reaction components were added together at 0 °C for the first 30 min and subsequently left to stir for a further 30 min at room temperature. Following removal of all volatiles, the desired products were extracted into diethyl ether and isolated as off-white solids.



Scheme 2 – Synthesis of $[M\{\kappa^3\text{-}N,N,H\text{-HB(azaindoly)}_3\}(\eta^1,\eta^2\text{-COE}^{\text{OMe}})]$, $M = \text{Pt}$ (**1**), Pd (**2**).

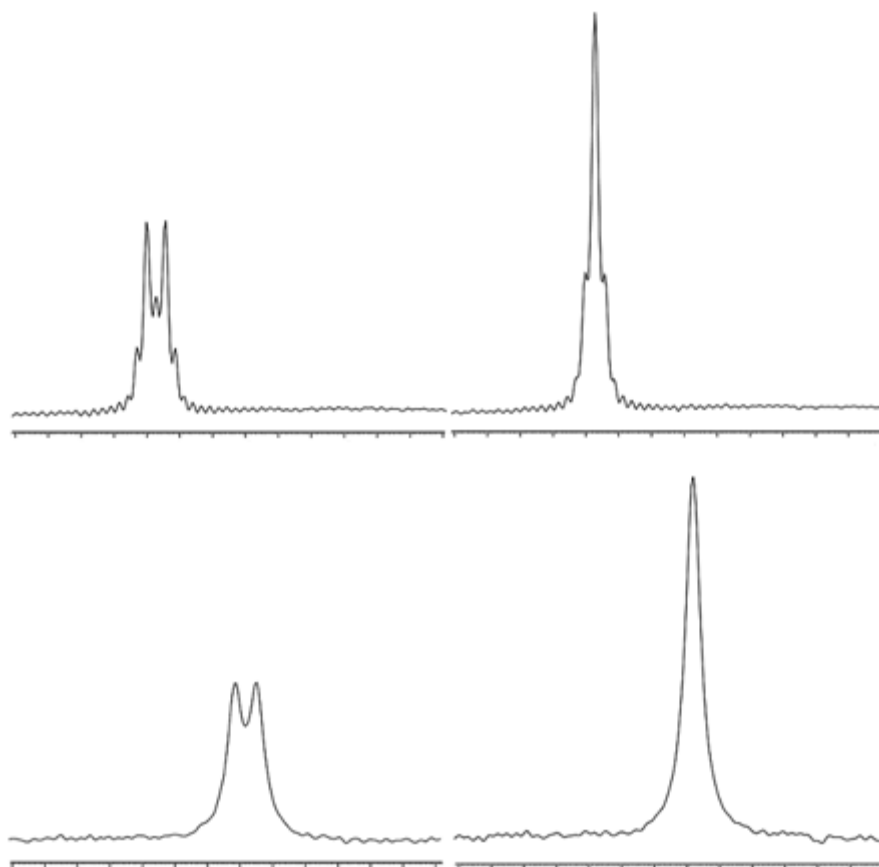


Figure 1 – ^{11}B (left) and $^{11}\text{B}\{^1\text{H}\}$ (right) NMR spectra of complexes **1** (top) and **2** (bottom). Each increment on the scale represents 1 ppm.

The two complexes were stable in the solid state. However, solutions of the compounds tended to darken slowly over time, generating platinum or palladium black. Nevertheless, complexes **1** and **2** were fully characterized via spectroscopic and analytical methods (Table 1). Complexation

of the [T*ai*]⁻ ligand to the metal centers was confirmed by ¹¹B NMR spectroscopy (Figure 1). A downfield chemical shift was observed from -5.3 ppm for the ligand (in CD₃CN) to 1.8 ppm for complex **1** and -3.2 ppm for complex **2** (both in CDCl₃). A similar change in chemical shift is observed when the [T*ai*]⁻ ligand coordinates to group nine complexes.^{3a} These chemical shifts are consistent with a κ³-*N,N,H* coordination mode within the resulting complexes. Confirmation that the hydrogen substituent remained at the boron centers in **1** and **2** was obtained by comparing the ¹¹B and ¹¹B{¹H} NMR spectra; the signals in the former spectra were found to be doublets whilst in the ¹¹B{¹H} spectra they were singlets. The ¹¹B NMR spectra also provided additional information for complex **1** with regards to ²J_{PtB} coupling. It is well-documented that boron NMR typically furnishes broad signals due to the fact that it is a quadrupolar nucleus.¹⁵ Whilst tetra-coordinated boron species tend to be sharper, the signals are commonly not sufficiently resolved in order to observe coupling constants lower than 100 Hz. In many of the reported compounds featuring Pt••H–B units, no J_{PtB} constant has been reported.¹⁶ In most cases the corresponding signals have been described as being broad. A survey of the literature revealed six articles, featuring one or more Pt••H–B units, where J_{PtB} coupling constants were reported. The recorded coupling constants, which may be described as ²J_{PtB} coupling, range between 74 Hz and 270 Hz.¹⁷ As expected, direct Pt–B bonding results in larger coupling constants up to around 600 Hz which are much more clear within the corresponding spectra.^{17b,c,d} As shown in Figure 1, the boron signal in the ¹¹B{¹H} NMR spectra of complex **1** is fortuitously sharp [half height width (hhw) = 35 Hz]. This has allowed for the determination of the ²J_{PtB} constant for this complex, which is 75 Hz as platinum satellites. The lower coupling constant value suggests that there is little direct Pt–B interaction within complex **1**. The ¹J_{BH} coupling constants of 75 Hz for **1** and 82 Hz for **2**, obtained from their boron coupled spectra, indicate a reduction in the B–H bond order with respect to the

free ligand ($^1J_{\text{BH}}$ for $\text{K}[\mathbf{Tai}] = 111$ Hz). This confirms a $\kappa^3\text{-}N,N,H$ coordination mode for the ligand in solution. The infrared spectra of powder samples for both **1** and **2** showed characteristic bands at 2151 cm^{-1} and 2158 cm^{-1} in the region expected for the B–H units interacting with the transition metal centers, confirming the same coordination mode in the solid state samples.⁴

Table 1 – Selected NMR and infrared spectroscopic data for complexes **1** – **4**.

Complex	$^{11}\text{B}\{^1\text{H}\}$ (ppm) ^a	$^1J_{\text{BH}}$ (Hz)	$^2J_{\text{PtB}}$ (Hz)	$^{11}\text{B}\{^1\text{H}\}$ hhw ^d (Hz)	^{11}B hhw ^d (Hz)	$^1\text{H}\{^{11}\text{B}\}$ BH (ppm)	IR (B-H••M) powder film (cm^{-1})
$[\text{Pt}\{\mathbf{Tai}\}(\text{COE}^{\text{OMe}})]$ (1)	1.8 ^a	75	75	35	163	4.80	2151
$[\text{Pd}\{\mathbf{Tai}\}(\text{COE}^{\text{OMe}})]$ (2)	-3.2 ^a	82		80	174	7.21	2158
$[\text{Pt}\{\mathbf{MeBai}\}(\text{COE}^{\text{OMe}})]$ (3)	-0.3 ^b	ur ^c	ur ^c	129	186	3.14	1933
$[\text{Pd}\{\mathbf{MeBai}\}(\text{COE}^{\text{OMe}})]$ (4)	-5.7 ^b	55		102	184	5.48	2187

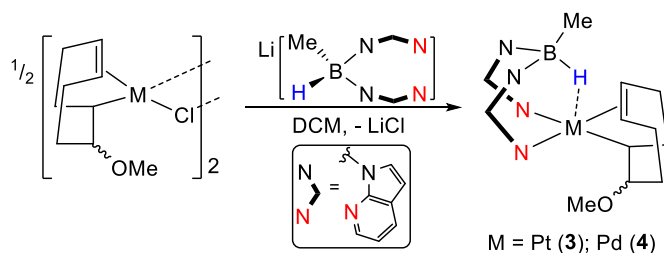
^a – in CDCl_3 ; ^b – in C_6D_6 ; ^c – no coupling was apparent in the ^{11}B NMR signal due to the broad nature of the signal (ur = unresolved); ^d – hhw is the width of the signal at the half position.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of complex **1**, were rather broad and unresolved. This is due to the fluxional coordination of the $[\mathbf{Tai}]^-$ ligand to the platinum center where the “free azaindolyl arm” of the ligand is exchanging places with the coordinated “azaindolyl arms” slowly on the NMR timescale. Similar fluxional behavior was observed for the related complex $[\text{Ir}\{\kappa^3\text{-}N,N,H\text{-HB}(\text{azaindolyl})_3\}(\text{COD})]$.^{3a} Nevertheless, the spectra for **1** were consistent with the formation of $[\text{Pt}\{\kappa^3\text{-}N,N,H\text{-HB}(\text{azaindolyl})_3\}(\eta^1, \eta^2\text{-COE}^{\text{OMe}})]$. In order to confirm this, the corresponding NMR spectra were recorded at $0\text{ }^\circ\text{C}$. This reduction in temperature was sufficient to stop the fluxional

processes involving the $[\mathbf{Tai}]^-$ ligand. At this temperature, both ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were fully consistent with three chemical environments for the azaindolyl units, *i.e.* one coordinated azaindolyl unit *trans* to a σ -bound carbon of the COE^{OMe} ligand, one coordinated azaindolyl unit *trans* to the π -bound double bond of the COE^{OMe} ligand and one uncoordinated azaindolyl unit. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for complex **2** were, on the other hand, much more resolved and indicated that the “azaindolyl arms” were rapidly exchanging on the NMR timescale at room temperature. The ^1H NMR spectrum revealed six signals in the aromatic region of the spectrum, five corresponding to each of the chemical environments on the azaindolyl rings, each signal integrating for three protons, and one additional broad signal corresponding to the BH unit (integrating for one proton). The latter signal was further confirmed as the BH unit in the corresponding $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum. The remaining twelve signals in the standard ^1H NMR experiment corresponded to the proton environments of the COE^{OMe} ligand consistent with a η^1, η^2 coordination mode. This consisted of two coordinated double bond protons (at 5.84 ppm and 4.79 ppm), one σ -bound Pd-CH functional group at 3.22 ppm, one CH group containing the OMe group at 3.70 ppm and the four remaining CH_2 units. The $^{13}\text{C}\{^1\text{H}\}$, COSY, HSQC and HMBC NMR experiments were also fully consistent with the ^1H NMR assignment. Finally, both mass spectrometry and elemental analytical data were consistent with the molecular compositions of the two products, $[\text{Pt}\{\kappa^3\text{-}N,N,H\text{-HB}(\text{azaindolyl})_3\}(\eta^1, \eta^2\text{-COE}^{\text{OMe}})]$ (**1**) and $[\text{Pd}\{\kappa^3\text{-}N,N,H\text{-HB}(\text{azaindolyl})_3\}(\eta^1, \eta^2\text{-COE}^{\text{OMe}})]$ (**2**). As indicated above, these samples were not stable when left for extended periods of time in solution. We were therefore only able to obtain single crystals of complex **1** (*vide infra*). As outlined below, the resulting crystal structure was fully consistent with the above assignments.

The fluxional behavior in **1** and **2** occurs via exchange between the non-coordinated and coordinated “azaindoyl arms” of the [T**ai**][−] ligand. By preparing complexes containing just two azaindoyl groups both arms could coordinate to the metal to make “static” complexes, i.e. non-fluxional. We recently reported the synthesis of Li[HB(Me)(azaindoyl)₂], Li[^{Me}B**ai**]⁴ and therefore employed this ligand in the synthesis of the complexes, [Pt{κ³-*N,N,H*-HB(Me)(azaindoyl)₂}(η¹,η²-COE^{OMe})] (**3**) and [Pd{κ³-*N,N,H*-HB(Me)(azaindoyl)₂}(η¹,η²-COE^{OMe})] (**4**) (Scheme 3). They were both synthesized via a similar methodology as outlined above with the lithium salt of the ligand precursor in high yielding reactions. Once isolated, solutions of the samples appeared to be much more stable than their [T**ai**][−] counterparts. Curiously, the boron signals for complexes **3** and **4** were a little broader than found for complexes **1** and **2** (Table 1). The boron signal for the platinum complex **3** was broader than the palladium complex **4**. This is the opposite trend for complexes **1** and **2**. The ¹¹B{¹H} signal for **3** was the broadest of the four complexes (hwh 129 Hz) which meant that the ²J_{PtB} coupling was not apparent in this signal. Furthermore, the absence of any fluxional processes involving the κ³-*N,N,H* coordinated [Me**Bai**][−] ligand meant that their corresponding ¹H and ¹³C{¹H} NMR spectra were more resolved and revealed the two different chemical environments of the “azaindoyl arms” of the ligand (see supporting information – Figures S9 and S11). For example, the ¹H NMR spectrum of complex **4** exhibited 10 proton environments for the two chemically inequivalent azaindoyl rings. As is the case with the spectra for **1** and **2**, the signals corresponding to the double bond and sigma bound C(H) unit of the COE^{OMe} ligand on complexes **3** and **4** were very broad in both the ¹H and ¹³C{¹H} NMR spectra indicating separate fluxional behavior in the coordination of this ligand to the metal centers. Complexes **3** and **4** were further characterized by infrared spectroscopy. Powder samples gave characteristic bands for the (B-H••M) units at 1933 cm^{−1} and 2187 cm^{−1}, respectively. In

comparison to the other three complexes (Table 1), the band corresponding to the B–H stretch in $[\text{Pt}\{\text{MeBai}\}(\text{COE}^{\text{OMe}})]$ is of particularly low frequency suggesting a stronger interaction of the B–H unit with the platinum center in this complex.⁶ Finally, satisfactory elemental analysis of the four complexes confirmed that they were isolated as analytically pure samples.



Scheme 3 – Synthesis of $[\text{M}\{\kappa^3\text{-}N,N,H\text{-HB}(\text{Me})(\text{azaindolyl})_2\}(\eta^1,\eta^2\text{-COE}^{\text{OMe}})]$, M = Pt (**3**), Pd (**4**).

Structural characterization of **1**, **3** and **4**.

Crystal structures were obtained of three of the four complexes in order to explore the structural features and interaction of the B–H unit with the metal centers in more detail. Crystals suitable for X-ray diffraction of **1**, **3** and **4** were all obtained by allowing saturated diethyl ether or hexane solutions of the complexes stand under an inert atmosphere overnight or over a few days. The crystal structures obtained from the complexes are shown in Figure 2 – 4. Selected bond lengths and distances are highlighted in Table 2 for comparison. Crystallographic parameters for these complexes are provided in Table S1 in the electronic supporting information. All structures confirmed the facial $\kappa^3\text{-}N,N,H$ coordination modes of the $[\text{Tai}]^-$ and $[\text{MeBai}]^-$ ligands to the metal centers and that the COE^{OMe} ligand remains coordinated via a η^1,η^2 -coordination mode. The structures reveal five coordinate square based pyramidal geometries around the metal centers with some distortion from the idealized 90° angles. In all three cases, the positioning of the B–H unit was highly distorted from the idealized axial position due to the constraints of the $\kappa^3\text{-}N,N,H$

coordination mode. Furthermore, there are significant differences in the positioning of the B–H unit with respect to the metal centers in the three complexes. For example, the BH••M distances are 2.2922(3) Å for **1**, 1.9452(4) Å for **3** and 2.06032(10) Å for **4**. The corresponding B•••M distances are 3.118(8) Å, 2.862(10) Å and 2.9492(19) Å, respectively. This indicates that the B–H unit in the ^{Me}**Bai** complexes resides more closely to the metal centers than the same unit in the **Tai** complex. The two azaindolyl moieties coordinate via the nitrogen atom of the pyridine heterocycles. The eight-membered rings formed adopt boat-boat conformations dictated by the planarity of the azaindole heterocycles thus pushing the B–H group towards the metal center. When the centroid of the double bond of COE^{OMe} ligand is considered as a point of coordination of this unit, the *cis* inter-ligand angles of the square plane range between 84.90(5)° and 97.04(19)° across the three complexes. The sum of the four *cis*-angles about the metal center in each complexes **1**, **3** and **4** are 359.7(4)°, 360.6(6)° and 360.35(10)°, respectively. This relatively narrow range reflects the tendency of the palladium and platinum centers to adopt square planar geometries. While these values are extremely close to the idealized 360°, this does not reflect the specific positioning of the double bond with the metal centers which is different in all these cases. In complex **1**, the centroid of the double bond is only 0.002(10) Å away from the plane defined by the other three ligands on the square plane [*i.e.* N(2), N(4) and C(22)]. For complex **3**, the double bond sits a significant distance below the square plane where the corresponding distance is 1.288(12) Å. For complex **4**, one of the carbons of the double bond occupies the space very close to the plane [C(18) is 0.110(3) Å below the plane] and the centroid is a distance of 0.744(2) Å away from the plane. This deviation from the plane seems to be related to the degree of interaction of the B–H unit with the metal center. For example, in complex **1**, where there is little deviation, the Pt–B distance is 3.118(8) Å while in the case of complex **3**, where the double bond sits well

below the plane, the corresponding Pt–B distance is 2.862(10) Å. The boron centers in the three complexes show some degree of deviation from an idealized tetrahedral. The sum angles of the three non-hydrogen substituents are 331.6(10)° for **1**, 336.7(13)° for **3** and 334.1(3)° for **4**.

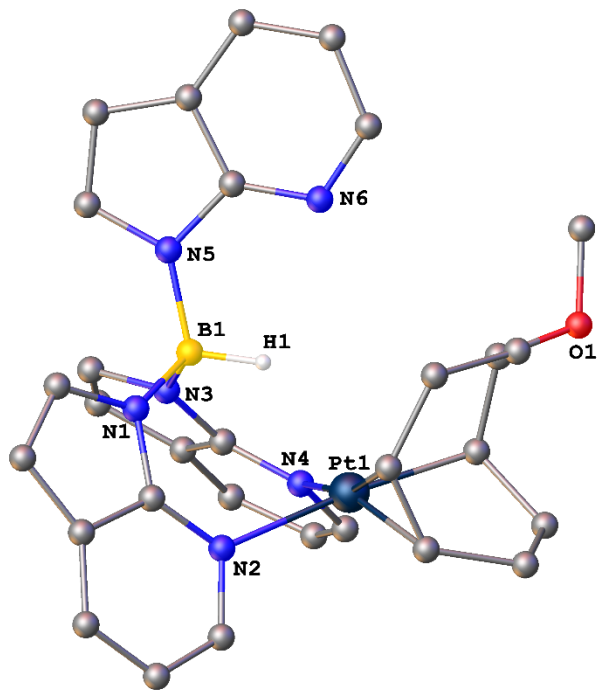


Figure 2 – Crystal structure of $[\text{Pt}\{\kappa^3\text{-}N,N,H\text{-HB(azaindoly)}_3\}(\text{COE}^{\text{OMe}})]$ (**1**). Hydrogen atoms, with the exception of that on boron, have been omitted for clarity.

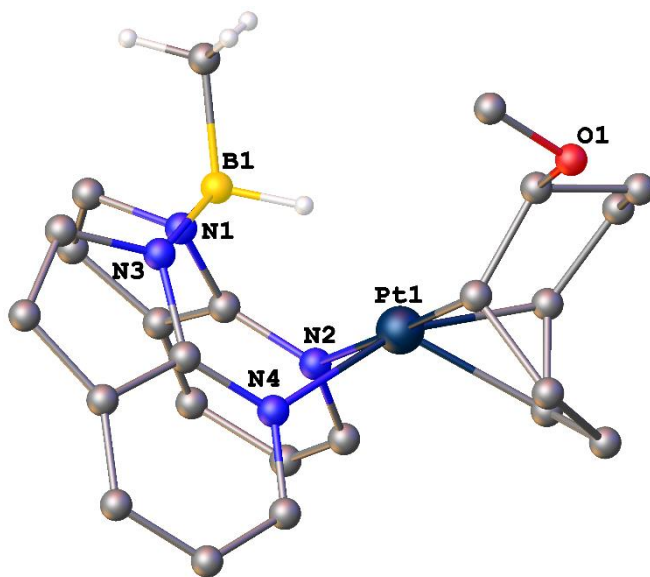


Figure 3 – Crystal structure of $[\text{Pt}\{\kappa^3\text{-}N,N,H\text{-HB(Me)(azaindoly)}\}_2(\text{COE}^{\text{OMe}})]$ (**3**). Hydrogen atoms, with the exception of that on boron and the BMe group, have been omitted for clarity.

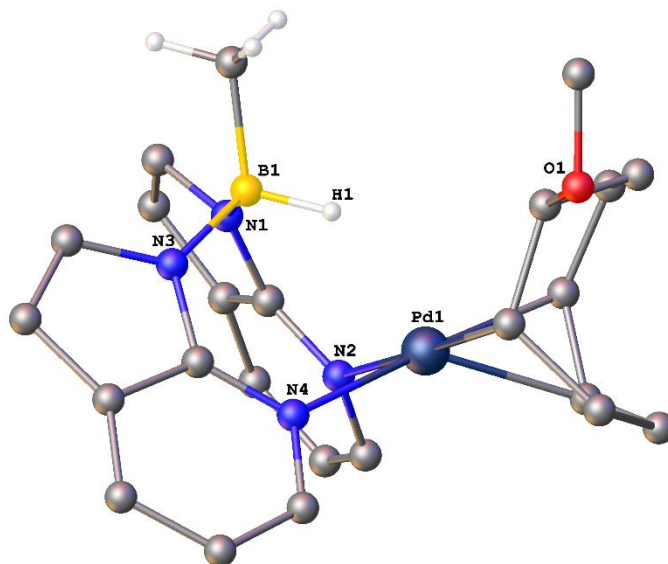


Figure 4 – Crystal structure of $[\text{Pd}\{\kappa^3\text{-}N,N,H\text{-HB(Me)(azaindoly)}\}_2(\text{COE}^{\text{OMe}})]$ (**4**). Hydrogen atoms, with the exception of that on boron and the BMe group, have been omitted for clarity.

Conclusions

In summary, stable group ten complexes containing $[\text{Tai}]^-$ and $[\text{MeBai}]^-$ have been reported providing the first examples of group ten to contain these flexible scorpionate ligands. Their syntheses have been achieved by utilizing complexes containing the 8-methoxycyclooct-4-en-1-ide unit. These azaindoly based ligands do not exhibit the hydride migration reactivity which had previously been observed with the $[\text{Bmp}]^-$ ligand. This contrasting reactivity allows for the isolation and inspection of the first group ten complexes to contain the poly(azaindoly)borate scorpionate ligands. The fortuitous linewidths observed in the ^{11}B NMR spectra of complex **1** allowed a closer examination of the B–H•••metal interactions within these scorpionate complexes.

Table 2 – Selected distances and angles for complexes **1**, **3**, and **4**.

Distances (Å) / Angles (°)	Complex 1	Complex 3	Complex 4
M–N _{trans} to σ bound C	2.182(6)	2.157(7)	2.2124(14)
M–N _{trans} to π bound C=C	2.089(6)	2.184(7)	2.1788(14)
M–C _{coordinated} via σ -bond	2.058(7)	2.068(8)	2.0422(16)
M–C _{coordinated} via π -bond	2.131(7) / 2.110(8)	2.096(9) / 2.081(9)	2.1551(17) / 2.1389(17)
M–(Centroid of C=C)	2.0053(3)	1.9601(4)	2.02985(16)
η^2 -C=C	1.381(11)	1.443(15)	1.399(3)
M---B	3.118(8)	2.862(10)	2.9492(19)
B-H (restrained)	1.100	1.100	1.100
M---HB	2.2922(3)	1.9452(4)	2.06032(10)
B–N _{trans} to σ bound C	1.559(10)	1.545(13)	1.566(2)
B–N _{trans} to π bound C=C	1.561(10)	1.541(13)	1.560(3)
B–N _{free} azaindoyl or B–C _{Me}	1.542(10)	1.606(14)	1.609(3)
N–M–N	93.5(2)	90.9(3)	94.44(5)
C–M–(Centroid of C=C)	85.4(2)	85.1(3)	84.90(5)
C _{coordinated} via σ -bond–M–N	90.6(3)	87.6(3)	87.44(6)
N–M–(Centroid of C=C)	90.17(16)	97.04(19)	93.57(4)
Σ of angles at boron ^a	331.6(10)	336.7(13)	334.1(3)
Σ of cis angles at M ^a	359.7(4)	360.6(6)	360.35(10)

^a – involving non-hydrogen substituents only.

Experimental

General Remarks

All manipulations were carried out using standard Schlenk techniques. Solvents were supplied extra dry from Acros Organics and were stored over 4 Å molecular sieves. The CD₃CN and C₆D₆ NMR solvents were also stored in Young's ampules under N₂, over 4 Å molecular sieves and were

degassed through three freeze-thaw cycles prior to use. All reagents were used as purchased from commercial sources. The ligands, $K[\mathbf{Tai}]$,¹ $Li(NCMe)_2[\mathbf{MeBai}]$ ⁴ and complexes $[PtCl(\eta^1, \eta^2-COE^{OMe})_2]$ ¹⁸ and $[PdCl(\eta^1, \eta^2-COE^{OMe})_2]$ ¹⁹ were synthesised according to standard literature procedures. NMR experiments were conducted on a Bruker 400 MHz Ascend™ 400 spectrometer. All NMR spectra were recorded at approximately 298 K unless otherwise stated. Proton (¹H) and carbon (¹³C) assignments (Figure 5) were supported by HSQC, HMBC and COSY NMR experiments. Infrared spectra were recorded on Perkin-Elmer Spectrum Two 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.

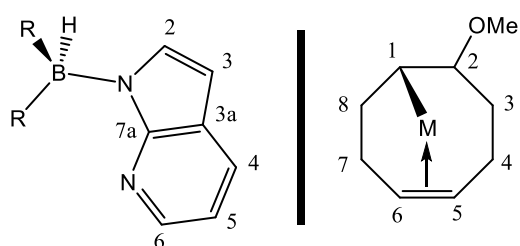


Figure 5 – Numbering scheme used for NMR assignments (R = Me or 7-azaindoly)

Synthesis of $[Pt\{\kappa^3-N,N,H-HB(\text{azaindoly})_3\}(\eta^1, \eta^2-COE^{OMe})]$ (**1**)

A Schlenk flask was charged with $[PtCl(COE^{OMe})_2]$ (0.057 g, 0.077 mmol) and DCM (5 mL) under a nitrogen atmosphere. The solution was cooled to 0 °C (ice bath) and $K[\mathbf{Tai}]$ (0.065 g, 0.162 mmol, 2.1 eq.) dissolved in DCM (5 mL) was added to give a pale yellow solution. After 30 min the reaction mixture was allowed to warm to room temperature and further stirred for 30 min. The mixture was filtered via cannula into a Schlenk flask. All volatiles were removed and the residue extracted with diethyl ether (2 × 6 mL). The ether was removed in vacuum from the combined extracts to give the product as a yellow solid (0.047 g, 0.067 mmol, 44%).

^1H NMR δ (CH_2Cl_2 , 273 K): 8.61 [1H, br dd, $^3J_{\text{HH}} = 5.21$ Hz, $^4J_{\text{HH}} =$ unresolved, aza- $\text{CH}(6)$], 8.16 [1H, dd, $^3J_{\text{HH}} = 4.62$ Hz, $^4J_{\text{HH}} = 1.54$ Hz, aza- $\text{CH}(6')$], 7.96 [2H, overlapping m, aza- $\text{CH}(4)$ and aza- $\text{CH}(4')$], 7.92 [1H, d, $^3J_{\text{HH}} = 3.21$ Hz, aza- $\text{CH}(2)$], 7.89 [1H, br dd, $^3J_{\text{HH}} = 7.74$ Hz, $^4J_{\text{HH}} =$ unresolved, aza- $\text{CH}(4'')$], 7.81 [1H, d, $^3J_{\text{HH}} = 3.32$ Hz, aza- $\text{CH}(2'')$], 7.79 [1H, br d, $^3J_{\text{HH}} = 5.42$ Hz, aza- $\text{CH}(6'')$], 7.65 [1H, d, $^3J_{\text{HH}} = 3.36$ Hz, aza- $\text{CH}(2')$], 7.04 [2H, overlapping m, aza- $\text{CH}(5)$ and aza- $\text{CH}(5')$], 6.89 [1H, dd, $^3J_{\text{HH}} = 7.72$ Hz, $^3J_{\text{HH}} = 5.44$ Hz, aza- $\text{CH}(5'')$], 6.63 [2H, $2 \times$ overlapping d, $^3J_{\text{HH}} = 3.72$ Hz, aza- $\text{CH}(3)$ and aza- $\text{CH}(3'')$], 6.61 [1H, d, $^3J_{\text{HH}} = 3.46$ Hz, aza- $\text{CH}(3')$], 4.33 [1H, t, $^3J_{\text{HH}} = 8.13$ Hz, $J_{\text{PH}} = 112.39$ Hz, =CH, $\text{COE}^{\text{OMe}}(5)$], 3.36 [1H, br m, =CH, $\text{COE}^{\text{OMe}}(6)$], 3.08 [1H, m, $\text{COE}^{\text{OMe}}(2)$], 2.70 [3H, s, OCH_3], 2.46 [1H, m, $\text{COE}^{\text{OMe}}(4)$], 2.33 [1H, br m, $\text{COE}^{\text{OMe}}(1)$], 2.24 – 2.09 [2H, overlapping m, $\text{COE}^{\text{OMe}}(7)$], 2.01 [1H, m, $\text{COE}^{\text{OMe}}(8)$], 1.67 [1H, m, $\text{COE}^{\text{OMe}}(4)$], 1.56 – 1.43 [3H, overlapping m, $2 \times \text{COE}^{\text{OMe}}(3)$ and $\text{COE}^{\text{OMe}}(8)$]. $^1\text{H}\{^{11}\text{B}\}$ partial NMR (δ , CD_2Cl_2): 4.80 [v br s. BH]. $^{13}\text{C}\{^1\text{H}\}$ NMR δ (CD_2Cl_2): 152.64 [aza-C(7a')], 150.94 [aza-C(7a'')], 150.62 [aza-C(7a)], 143.50 [aza-C(6)], 142.14 [aza-C(6')], 139.54 [aza-C(6'')], 133.16 [aza-C(2')], 132.19 [aza-C(2)], 131.87 [aza-C(2'')], 129.83 [aza-C(4) and aza-C(4'')], 127.84 [aza-C(4')], 124.82 [aza-C(3a)], 124.35 [aza-C(3a'')], 123.37 [aza-C(3a')], 115.67 [aza-C(5'')], 115.50 [aza-C(5) and aza-C(5')], 102.32 [aza-C(3)], 101.81 [aza-C(3'')], 101.38 [aza-C(3')], 84.12 [$\text{COE}^{\text{OMe}}(2)$], 74.93 [=CH, $\text{COE}^{\text{OMe}}(5)$], 55.67 [OCH_3], 50.57 [=CH, $\text{COE}^{\text{OMe}}(6)$], 34.60 [$\text{COE}^{\text{OMe}}(8)$], 28.95 [$\text{COE}^{\text{OMe}}(4)$], 28.59 [$\text{COE}^{\text{OMe}}(3)$], 27.64 [$\text{COE}^{\text{OMe}}(7)$], 25.55 [$\text{COE}^{\text{OMe}}(1)$]. ^{11}B -NMR δ (CD_2Cl_2): 1.75 (d, $^1J_{\text{BH}} = 73.4$ Hz, $^2J_{\text{PtB}} = 74.6$ Hz, hhw = 106.6 Hz, BH); $^{11}\text{B}\{^1\text{H}\}$ NMR δ (CD_2Cl_2): 1.75 (s, $^2J_{\text{PtB}} = 74.8$ Hz, hhw = 36.2 Hz, BH). ^{11}B -NMR δ (CDCl_3): 1.83 (d, $^1J_{\text{BH}} = 74.6$ Hz, $^2J_{\text{PtB}} = 74.9$ Hz, hhw = 163.2 Hz, BH); $^{11}\text{B}\{^1\text{H}\}$ NMR δ (CDCl_3): 1.83 (s, $^2J_{\text{PtB}} = 75.1$ Hz, hhw = 34.9 Hz, BH). MS m/z (ESI+): 698.24 [$\text{M}]^+$. IR (powder film): 2151

cm⁻¹ (ν_{BH}). Elem. Anal.: Calcd for C₃₀H₃₁BN₆OPt: C 51.66; H 4.48; N 12.05; Found: C 51.76; H 4.54; N 11.88.

Synthesis of [Pd{ κ^3 -*N,N,H*-HB(azaindoly)₃}(η^1, η^2 -COE^{OMe})] (2)

A Schlenk flask was charged with [PdCl(COE^{OMe})₂] (0.121 g, 0.215 mmol) and DCM (15 mL). The flask was placed in an cooled to 0 °C (ice bath) and K[Tai] (0.183 g, 0.455 mmol, 2.1 eq.) was added to give a pale yellow solution. Additional DCM (3 mL) was added to wash any remaining solid into the solution. After 30 min the reaction mixture was allowed to warm to room temperature and further stirred for 30 min. The mixture was filtered via cannula to remove the KCl salt formed. All volatiles were removed under reduced pressure and the desired product was extracted from the residue with diethyl ether (2 × 8 mL). The ether solvent was then removed under reduced pressure to give the product as a yellow solid (0.196 g, 0.322 mmol, 75%).

¹H NMR (δ , CDCl₃): 8.22 [3H, br s, aza-CH(6)], 8.02 [3H, d, ³J_{HH} = 3.12 Hz, aza-CH(2)], 7.87 [3H, dd, ³J_{HH} = 7.70 Hz, ⁴J_{HH} = unresolved, aza-CH(4)], 6.96 [3H, dd, ³J_{HH} = 7.70 Hz, ³J_{HH} = 5.16 Hz, aza-CH(5)], 6.45 [3H, d, ³J_{HH} = 3.31 Hz, aza-CH(3)], 5.84 [1H, s, =CH, COE^{OMe}(6)], 4.79 [1H, s, =CH, COE^{OMe}(5)], 3.70 [1H, s, CH, COE^{OMe}(2)], 3.22 [1H, s, CH, COE^{OMe}(1)], 2.94 [3H, s, CH₃, OMe], 2.81 [1H, m, CH₂, COE^{OMe}(4)], 2.54 [2H, m, CH₂, COE^{OMe}(4) and COE^{OMe}(7)], 2.44 [1H, m, CH₂, COE^{OMe}(8)], 2.30 [1H, m, CH₂, COE^{OMe}(7)], 1.95 [2H, s, CH₂, COE^{OMe}(3)], 1.68 [1H, m, CH₂, COE^{OMe}(8)]. ¹H{¹¹B} partial NMR (δ , CDCl₃): 7.21 [s, BH]. ¹³C{¹H} NMR (δ , CDCl₃): 151.16 [aza-C(7a)], 141.19 [aza-C(6)], 134.01 [aza-C(2)], 128.80 [aza-C(4)], 124.45 [aza-C(3a)], 114.88 [aza-C(5)], 100.80 [CH=CH, COE^{OMe}(6)], 100.49 [aza-C(3)], 89.30 [=CH, COE^{OMe}(5)], 83.33 [CH, COE^{OMe}(2)], 56.45 [OCH₃], 46.97 [COE^{OMe}(1)], 35.23 [COE^{OMe}(8)], 30.04 [COE^{OMe}(3)], 28.60 [COE^{OMe}(4)], 27.63 [COE^{OMe}(7)]. ¹¹B NMR (δ , CDCl₃): -3.2 (d, ¹J_{BH} = 82 Hz, h.h.w. = 173.9 Hz). ¹¹B{¹H} NMR (δ , CDCl₃): -3.21 (s, h.h.w. = 80.1 Hz). MS *m/z* (ESI+):

608.18 [M]⁺. IR (powder film): 2158 cm⁻¹ (ν_{B-H}). Elem. Anal.: Calcd for C₃₀H₃₁BN₆OPd: C 59.18; H 5.13; N 13.80; Found: C 59.01; H 5.32; N 13.70.

Synthesis of [Pt{ κ^3 -*NNH*-HB(Me)(azaindoly)₂}(η^1, η^2 -COE^{OMe})] (3)

A Schlenk flask was charged with the solid precursor [PtCl(COE^{OMe})₂] (104.6 mg, 0.141 mmol) and the ligand Li(MeCN)₂[^{Me}Bai] (98.2 mg, 0.280 mmol, 2 equiv.). Dry/degassed DCM (8 mL) was added under a nitrogen atmosphere to give a light brown suspension. The mixture was further stirred for 2 h and filtered via cannula into a Schlenk flask. The solvent was removed under reduced pressure and the residue extracted with hexanes (3 × 5 mL). The combined hexanes phase was filtered through a short pad of celite (4 × 2 cm). All volatiles were removed to give the product as an off-white solid which was recrystallized from a concentrated diethyl ether solution (60.4 mg, 0.101 mmol, 71%).

¹H NMR δ (C₆D₆): 8.40 [2H, dd, ³J_{HH} = 5.23 Hz, ⁴J_{HH} = 1.09 Hz, aza-CH(6)], 7.59 [1H, d, ³J_{HH} = 3.34 Hz, aza-CH(2)], 7.54 [1H, ³J_{HH} = 3.34 Hz, aza-CH(2')], 7.40 [2H, overlapping m, aza-CH(4) and aza-CH(6')], 7.33 [1H, dd, ³J_{HH} = 7.72 Hz, ⁴J_{HH} = 1.07 Hz, aza-CH(4')], 6.49 [1H, dd, ³J_{HH} = 7.70 Hz, ³J_{HH} = 5.31 Hz, aza-CH(5)], 6.45 [2H, overlapping d, aza-CH(3) and aza-CH(3')], 6.33 [2H, d, ³J_{HH} = 7.70 Hz, ³J_{HH} = 5.33 Hz, aza-CH(5')], 3.88 [1H, dt, ³J_{HH} = 11.35 Hz, ³J_{HH} = 3.70 Hz, COE^{OMe}(2)], 3.79 [1H, br t, ³J_{HH} = 8.49 Hz, J_{PH} = 109.14 Hz, COE^{OMe}(6)], 3.08 [1H, m, =CH, COE^{OMe}(5)], 2.98 [3H, s, OCH₃], 2.43 [1H, br m, COE^{OMe}(1)], 2.33 [1H, m, COE^{OMe}(7)], 2.16 [1H, br m, COE^{OMe}(4)], 2.10 – 1.99 [2H, overlapping m, COE^{OMe}(4) and COE^{OMe}(8)], 1.99 – 1.76 [3H, overlapping m, 2 × COE^{OMe}(3) and COE^{OMe}(8)], 1.66 [1H, m, COE^{OMe}(7)], 1.22 [3H, CH₃, d, ²J_{BH} = 2.52 Hz]. Partial ¹H{¹¹B} δ (C₆D₆): 3.14 [1H, br s, BH]. ¹³C{¹H} NMR δ (C₆D₆): 152.49 [aza-C(7a')], 151.59 [aza-C(7a)], 142.80 [aza-C(6)], 138.35 [aza-C(6')], 130.98 [aza-C(2)], 130.83 [aza-C(2')] 129.41 [aza-C(4)], 129.28 [aza-C(4')], 125.21 [aza-C(3a)], 124.53 [aza-

C(3a'), 115.00 [aza-C(5')], 114.97 [aza-C(5)], 102.30 [aza-C(3')], 101.74 [aza-C(3)], 84.89 [s, COE^{OMe}(2)], 69.93 [=CH, COE^{OMe}(6)], 55.86 [OCH₃], 47.57 [=CH, COE^{OMe}(5)], 35.05 [COE^{OMe}(8)], 29.63 [COE^{OMe}(3)], 29.21 [COE^{OMe}(7)], 27.74 [COE^{OMe}(4)], 25.81 [COE^{OMe}(1)], 5.40 [br s, BCH₃ observed indirectly from HSQC]. ¹¹B-NMR δ(C₆D₆): -0.28 (br s, hhw = 185.8 Hz, BH); ¹¹B{¹H} NMR δ(C₆D₆): -0.28 (s, hhw = 128.8 Hz). IR (powder film): 1933 cm⁻¹ (ν_{BH}). Elem. Anal.: Calcd for C₂₄H₂₉BN₄OPt: C 48.41; H 4.91; N 9.41; Found: C: 48.53; H 4.96; N 9.26.

Synthesis of [Pd{κ³-N,N,H-HB(Me)(azaindoly)l₂}(η¹,η²-COE^{OMe})] (4)

A Schlenk flask was charged with the solid precursor [PdCl(COE^{OMe})₂] (80.3 mg, 0.143 mmol) and the ligand, Li(MeCN)₂[^{Me}Bai] (100.5 mg, 0.287 mmol, 2 equiv.). Dry/degassed DCM (5 mL) was added under a nitrogen atmosphere to give a yellow solution which became cloudy after 3 minutes. The mixture was further stirred for 90 min and filtered via cannula into a Schlenk flask. All volatiles were removed under reduced pressure to give the product as an off-white solid which was recrystallized from a concentrated diethyl ether solution (50.4 mg, 0.099 mmol, 70%).

¹H NMR δ (C₆D₆): 8.12 [1H, br s, aza-CH(6')], 7.74 [2H, d, ³J_{HH} = 3.30 Hz, aza-CH(2) and aza-CH(2')], 7.64 [1H, br s, aza-CH(6)], 7.45 [1H, br dd, ³J_{HH} = 7.63 Hz, ⁴J_{HH} = unresolved, aza-CH(4)], 7.41 [1H, dd, ³J_{HH} = 7.63 Hz, ⁴J_{HH} = unresolved, aza-CH(4')], 6.54 [1H, dd, ³J_{HH} = 6.08 Hz, ³J_{HH} = unresolved, aza-CH(5')], 6.44 [1H, br dd, ³J_{HH} = 6.12 Hz, ³J_{HH} = unresolved, aza-CH(5)], 6.35 [2H, d, ³J_{HH} = 3.19 Hz, aza-CH(3) and aza-CH(3')], 5.48 [1H, v br s, BH], 5.17 [1H, br s, =CH, COE^{OMe}],²⁰ 4.26 [1H, br s, =CH, COE^{OMe}],²⁰ 3.78 [1H, br s, COE^{OMe}(2)], 3.12 [1H, br m, COE^{OMe}(1)], 2.80 [3H, s, OCH₃], 2.36 [2H, m, COE^{OMe}(7) and COE^{OMe}(8)], 2.15 [1H, m, COE^{OMe}(4)], 2.08 [1H, m, COE^{OMe}(7)], 2.02 – 1.86 [3H, overlapping m, COE^{OMe}(4) and 2 × COE^{OMe}(3)], 1.78 [1H, m, COE^{OMe}(8)], 1.23 [3H, BCH₃, d, ³J_{BH} = 3.88 Hz]. Partial ¹H{¹¹B} δ(C₆D₆): 5.48 [1H, br s, BH]. ¹³C{¹H} NMR δ (C₆D₆): 151.31 [aza-C(7a)], 150.92 [aza-C(7a')],

140.74 [aza-C(6)], 140.08 [aza-C(6')], 132.09 [aza-C(2)], 132.02 [aza-C(2')], 129.12 [aza-C(4)], 129.06 [aza-C(4')], 125.31 [aza-C(3a)], 125.11 [aza-C(3a')], 114.54 [aza-C(5')], 114.38 [aza-C(5)], 100.80 [aza-C(3')], 100.65 [aza-C(3)], 83.83 [br s, $COE^{OMe}(2)$], 56.08 [OCH₃], 47.33 [$COE^{OMe}(1)$], 35.45 [$COE^{OMe}(8)$], 30.86 [$COE^{OMe}(3)$], 28.57 [$COE^{OMe}(7)$], 27.59 [$COE^{OMe}(4)$], 4.53 [br s, BCH₃ observed indirectly from HSQC].²⁰ ¹¹B-NMR $\delta(C_6D_6)$: -5.70 (d, $^1J_{BH} = 55.2$ Hz, hhw = 184.2 Hz, BH); ¹¹B{¹H} NMR $\delta(C_6D_6)$: -5.70 (s, hhw = 102.3 Hz). IR (powder film): 2187 cm⁻¹ (ν_{BH}). Elem. Anal.: Calcd for C₂₄H₂₉BN₄OPd: C 56.88; H 5.77; N 11.06 Found: C: 56.95; H 5.65; N 10.88.

X-ray Crystallography

Single-crystal X-ray diffraction studies of complexes **1**, **3** and **4** were carried out at the UK National Crystallography Service at the University of Southampton.²¹ Single crystals of each of the complexes were obtained by allowing a saturated ether solution stand at room temperature. 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.²² The structures were solved by Intrinsic Phasing using the ShelXT structure solution program²³ and refined on F_o^2 by full-matrix least squares refinement with version 2018/3 of ShelXL²⁴ as implemented in Olex2.²⁵ All hydrogen atom positions were calculated geometrically and refined using the riding model. The structures for complexes **1** and **3** were each refined as a two-component multi-crystal [**1**: Rot(UB1,UB2) = 6.5° around -0.25 0.5 -1 (direct axis); **3**: Rot(UB1,UB2) = 2° around 1 0 0 (direct axis)]. Crystal Data for **1**. C₃₀H₃₁BN₆OPt, $M_r = 697.51$, triclinic, *P*-1 (No. 2), a = 10.3824(3) Å, b = 12.0277(5) Å, c = 12.4516(5) Å, $\alpha = 101.051(3)^\circ$, $\beta =$

106.869(3)°, $\gamma = 111.203(3)^\circ$, $V = 1308.35(10) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 2$, $Z' = 1$, $\mu(\text{MoK}\alpha) = 5.399$, 11785 reflections measured, 11785 unique which were used in all calculations. The final wR_2 was 0.1288 (all data) and R_I was 0.0521 ($I > 2(I)$). Data for **3**. $\text{C}_{24}\text{H}_{29}\text{BN}_4\text{OPt}$, $M_r = 595.41$, monoclinic, $P2_1/c$ (No. 14), $a = 8.7220(4) \text{ \AA}$, $b = 13.9705(6) \text{ \AA}$, $c = 19.3419(8) \text{ \AA}$, $\beta = 101.482(4)^\circ$, $\alpha = \gamma = 90^\circ$, $V = 2309.66(18) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $Z' = 1$, $\mu(\text{MoK}\alpha) = 6.098$, 12941 reflections measured, 12941 unique which were used in all calculations. The final wR_2 was 0.1237 (all data) and R_I was 0.0573 ($I > 2(I)$). Data for **4**. $\text{C}_{24}\text{H}_{29}\text{BN}_4\text{OPd}$, $M_r = 506.72$, monoclinic, $P2_1/c$ (No. 14), $a = 8.0262(2) \text{ \AA}$, $b = 19.0533(6) \text{ \AA}$, $c = 14.7733(5) \text{ \AA}$, $\beta = 101.494(3)^\circ$, $\alpha = \gamma = 90^\circ$, $V = 2213.91(12) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $Z' = 1$, $\mu(\text{MoK}\alpha) = 0.862$, 26066 reflections measured, 5083 unique ($R_{int} = 0.0312$) which were used in all calculations. The final wR_2 was 0.0539 (all data) and R_I was 0.0218 ($I > 2(I)$). 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, 1864609 (**1**), 1864611 (**3**) and 1864610 (**4**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

ASSOCIATED CONTENT

The following files are available free of charge.

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

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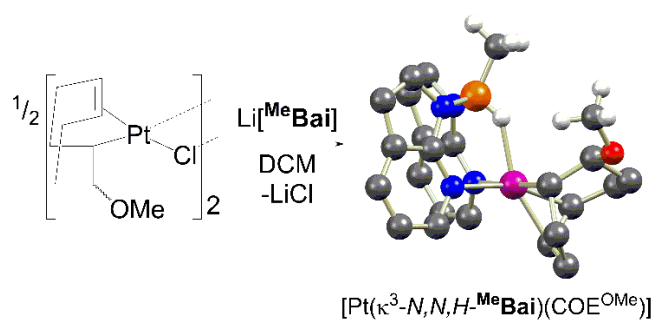
Author Contributions

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



The synthesis of the first group ten complexes containing azaindoly based scorpionates is reported herein. Fortuitous linewidths of the boron NMR signals have allowed a closer inspection of the B–H•••M interactions.