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COMMUNICATION

Reactivity of a Cl-boratabenzene Pt(II) complex with Lewis bases: generation of the kinetically favoured Cl-boratabenzene anion†

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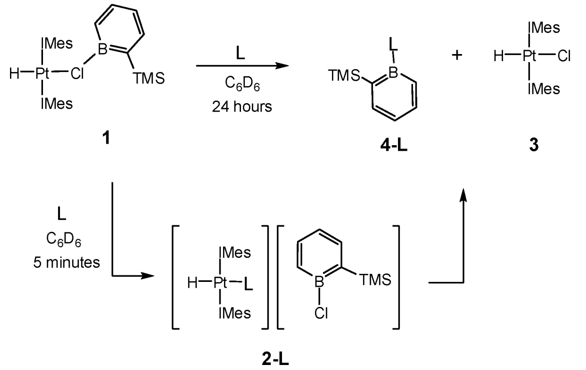
Complex [(IMes)$_2$Pt(H)(ClBC$_5$H$_4$SiMe$_3$)] (IMes = 1,3-di(2,4,6-trimethylphenyl)imidazolin-2-ylidene) reacts with Lewis bases (L = pyridine, trimethylphosphine, acetonitrile, *tert*-butylisocyanide) to generate the kinetically favoured ion pairs [(IMes)$_2$Pt(H)(L)][ClBC$_5$H$_4$SiMe$_3$]. Over time, the formation of the thermodynamically favoured borabenzene-L adducts is observed with L = pyridine and trimethylphosphine.

Derivatives and metal complexes of borabenzene, and its anionic analogue boratabenzene, have a large range of applications,[1] notably as sources of chirality,[2] as catalysts for cyclotrimerization,[3] alkene polymerization[4] and C–H bond activation,[5] and for their optoelectronic properties.[6] A large variety of derivatives of borabenzene and boratabenzene have been synthesized,[7] but in order to form a thermally stable adduct,[8,9] a strong nucleophile needs to be present on boron, thus limiting the range of possible substituents. A class of boratabenzene species that would be of particular interest for further functionalization are haloboratabenzenes (X = Cl$^-$, Br$^-$, or I$^-$). Indeed, unlike most boratabenzene species reported with alkyl, amido, or phosphido substituents, the B–X bonds can undergo a large range of reactivities including transmetallation, oxydative cleavage, or reduction, which could lead to species unobtainable by other synthetic pathways. Although the most common precursors for borabenzene synthesis are chloroboracyclohexadienes, only one serendipitous report of a fluoroboratabenzene species exists,[10] resulting from an unusual rearrangement of an iridium metallabenzene.[11]

As part of our program aimed at the exploration of novel bonding modes for the borabenzene moiety – notably to generate novel Z-type interactions with transition metals[12] – we recently reported the synthesis of species [(IMes)$_2$Pt(H)(ClBC$_5$H$_4$SiMe$_3$)] (**1**),[13] one of the rare borabenzene metal complexes where the π system of the heterocycle is not involved in binding the transition metal.[14] We wish to report that species **1** reacts unexpectedly with Lewis bases (L = pyridine (**Py**), trimethylphosphine (**PMe$_3$**), acetonitrile (**MeCN**), and *tert*-butylisocyanide (**2-BuNC**)) to generate the ionic pair [(IMes)$_2$Pt(H)(L)]$^+$[ClBC$_5$H$_4$SiMe$_3$]$^-$. Coordination isomers [(IMes)$_2$Pt(H)(Cl)] and 1-L-2-SiMe$_3$-borabenzene were calculated to be thermodynamically favoured compared to the ion pair, and were observed in the presence of pyridine and PMe$_3$. It is the first report of the synthesis of borabenzene adducts from a boratabenzene precursor, and gives valuable insight on the stability of the chloroboratabenzene anion.

In our investigation on the Lewis acidity of the boron centre of **1**, we observed that the borabenzene fragment could be transferred to pyridine to generate a pyridine-borabenzene adduct (**4-Py**) 24 h after the addition of 2 equivalents of pyridine in benzene-*d*$_6$.[13] However, close monitoring of the reaction mixture allowed the observation of a transient species, **2-Py** (Scheme 1). Using ^{1}H NMR spectroscopy, we observed that the hydride of **2-Py** was upfield (δ –20.10) and that the $^1J_{\text{Pt–H}}$ was significantly lower (1348 Hz) than for **1** (δ –22.42, $^1J_{\text{Pt–H}}$ = 1915 Hz). In addition to the signals for the N-heterocyclic ligands, a new set of resonances was observed at δ = 8.05, 7.81, 7.03, and 6.85 with the H–H coupling constants expected for borabenzene species. Monitoring this reaction mixture over a 24 h period did show that the resonances associated with **2-Py** disappeared at a similar rate to the formation of [(IMes)$_2$Pt(H)(Cl)] (**3**).



Scheme 1 Generation of **2-L** and **4-L** from **1**.

Analogues of **2-Py** were observed in the presence of acetonitrile (**2-MeCN**), trimethylphosphine (**2-PMe$_3$**), and *tert*-butylisocyanide (**2-BuNC**). Although the resonances for the Pt–H shifted significantly for the three other complexes (δ –19.13, $^1J_{\text{Pt–H}}$ = 1551 Hz (**2- MeCN**); δ –5.65, $^1J_{\text{Pt–H}}$ = 1060 Hz (**2-PMe$_3$**); δ –7.79, $^1J_{\text{Pt–H}}$ = 1101 Hz (**2-BuNC**)), the ^{1}H and ^{13}C resonances

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† Electronic supplementary information (ESI) available: Synthetic procedures, NMR, MS, and DFT data for all products. See DOI: 10.1039/c1dt11756d

Table 1 Reaction coordinates minimized using DFT

L	$\Delta E_{1\to 2L}$ (kcal mol^{-1})	$\Delta E_{2L+3\to 4L}$ (kcal mol^{-1})	$\Delta E_{2L+3\to 4L}{}^{C6D6}$ (kcal mol^{-1})	dist$_{Pt-H}$ (Å)
CN*t*Bu	−22.7	−6.6	−0.3	1.60
PMe_3	−5.6	−8.4	−3.2	1.59
Py	−50.5	−9.6	−4.8	1.56
MeCN	−12.2	−1.1	+3.7	1.56
PCy_3	26.0	−32.7	−21.8	N.A.

associated to the borabenzene moiety were very similar from one compound to the next, although some small variations were observed.[15] The coordination of the phosphine in **2-PMe$_3$** was confirmed using $^{31}P\{^1H\}$ and ^1H NMR spectroscopy, where the $^1J_{Pt-P}$ and $^2J_{H-P}$ of 1060 and 187 Hz, respectively, are characteristic of phosphine coordination *trans* to a hydride. The $^{11}B\{^1H\}$ NMR chemical shifts for all **2-L** were, within experimental error, at 38 ppm. It should be noted that species **2-PCy$_3$** was not observed when tricyclohexylphosphine was added to **1**.

We propose that **2-L** consists of the ion pair $[(IMes)_2Pt(H)(L)][ClBC_5H_4SiMe_3]$. To support this hypothesis, the generation of $[(IMes)_2Pt(H)(L)]BF_4$ was carried out by the addition of $AgBF_4$ to a solution of $[(IMes)_2Pt(H)(Cl)]$ in benzene-d_6 in the presence of excess L (see ESI†). With all L, the products displayed the same resonances associated to the cationic centre of species **2-L**, although solubility issues did not allow for clean isolation of the ionic species. ESI-MS or HRMS studies in benzene also gave probing evidences of the existence of **2-L** (see ESI†). The ionic species $[(IMes)_2Pt(H)(L)]^+$ for **2-PMe$_3$** (m/z = 881.2), **2-Py** (m/z = 884.1), and **2-BuNC** (m/z = 887.1) were observed, although in all samples the principal ion corresponded to $[(IMes)_2Pt(H)]^+$ (m/z = 804.6). The chloroboratabenzene anion was also observed in the HRMS anionic mode at m/z = 183.0694.

It was possible to model these complexes using DFT (see ESI for computational details†). The structure of **2-Py** is presented in Fig. 1 and those of the other complexes are available in the ESI.† The formation of the ion pair **2-L** from **1** was shown to be exothermic for all species, with the exception of **2-PCy$_3$** where the reaction is disfavoured by 26.0 kcal mol^{-1} (Table 1). All species have the platinum atom in a square planar environment, with the L ligand *trans* to the hydride. The biggest distortion from ideal geometry, in all cases, is being caused by steric repulsion between L and the IMes ligands. The 1-Cl-2-SiMe$_3$-boratabenzene anion is identical in all **2-L** complexes and does not have any significant interaction with the cation.

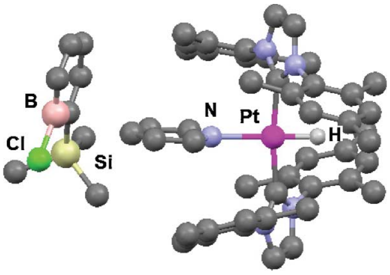


Fig. 1 B3PW91/SDDALL(Pt,Cl,Si)/6-31g(d,p (N,C,H,B)) optimized structure **2-Py**. Hydrogen atoms are omitted for clarity.

With time, species **2-L** generally degrades to generate **3**. However, in the case of the pyridine analogue, the generation of the adduct **4-Py** was observed.[13] Species **4-PMe$_3$** was also observed from **2-PMe$_3$**, based on a comparison with independently synthesized 1-PMe$_3$-2-SiMe$_3$-borabenzene, albeit in very low yield because of several side reactions. The transformation of **2-L** to **3** and **4-L** was also investigated using DFT (Table 1). In the gas phase, the neutral adducts were favoured thermodynamically over the ion pair, whereas the formation of **4-MeCN** was calculated to be endothermic in benzene. As can be expected from the experimental results, **4-Py** gives the most stable neutral system with reaction coordinates at −4.8 kcal mol^{-1} in benzene followed by **4-PMe$_3$** (−3.2 kcal mol^{-1}). Although the formation of 1-PCy$_3$-2-SiMe$_3$-borabenzene is favoured, its absence in solution seems to indicate that the formation of **2-L** is a prerequisite for its generation.

To obtain more information on the mechanism of the transformation of **1** to **4-Py**, solutions with various equivalents of pyridine were monitored using ^1H NMR spectroscopy. When one equivalent of pyridine was added to the solution, the complete generation of **2-Py** was observed within 30 min. Monitoring of the solution over a period of one week did not reveal the presence of a significant concentration of **4-Py**. However, when 5 equivalents of pyridine were added to **1**, it was possible to observe the gradual conversion of **2-Py** to **4-Py** over a period of a few hours. These results suggest that an excess of pyridine is required to generate 1-pyridine-2-SiMe$_3$-borabenzene. More interestingly, thirty minutes after the addition of half an equivalent of pyridine, all of it was consumed and both **2-Py** and **1** were observed in solution. Whereas the resonances for the $[(IMes)_2Pt(H)(py)]^+$ were sharp, the $[ClBC_5H_4SiMe_3]^-$ resonances for **1** and **2-Py** were significantly broadened (see Fig. S16†). Variable temperature NMR spectroscopy did show that the peaks associated to both chloroboratabenzene species become sharper on cooling and coalesce into a single set of resonances upon warming. Such a phenomenon points towards a fluxional process where the chloroboratabenzene anion of **2-L** can undergo ligand exchange with the chloroboratabenzene of **1**, as seen in Fig. 2. Modelling of the bandwidth of the TMS resonances with WINDNMR-Pro[16] allowed the determination of the exchange rates and activation parameters ($\Delta H^{\ddagger}$ = 12.8 ± 0.3 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −8 ± 1 cal mol^{-1} K^{-1}).

The first step of this transformation, the formation of **2-L**, is expected to occur by a mechanism similar to the $[ClBC_5H_4SiMe_3]^-$ exchange between **1** and **2-L**, where in this situation the chloroboratabenzene anion acts as the Lewis base. The negative value for the entropy of the transition state of −8 ± 1 cal mol^{-1} K^{-1} suggests an associative pathway, but the relatively small values cannot discredit a dissociative pathway. Despite our efforts, no

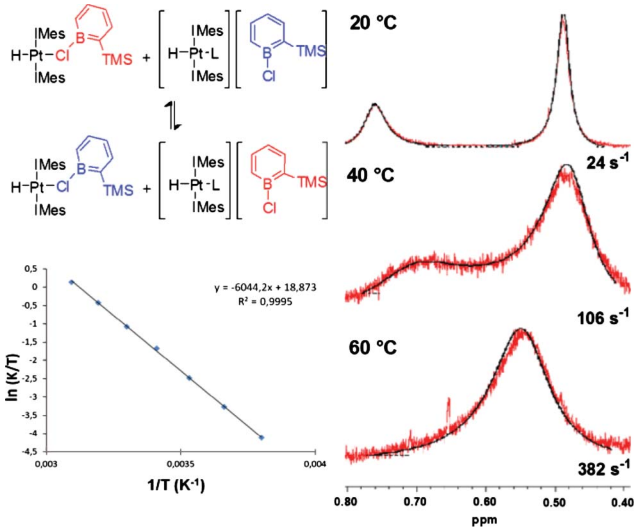
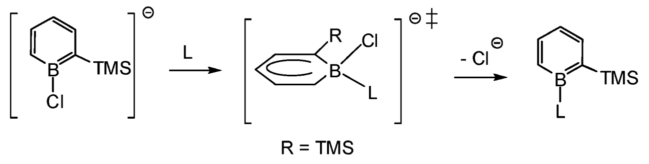


Fig. 2 Experimental (red) and simulated (black) ^{1}H NMR spectra of the -SiMe$_3$ region of **1** and **2-Py** at various temperatures with the associated rate constant. Eyring plot for the exchange of the 1-Cl-2-TMS-boratabenzene moieties in **1** and **2-Py**.

transition state associated with a concerted pathway could be optimized. However, the energy associated with the cleavage of the platinum chlorobotabenzene moiety (62.6 kcal mol^{-1}) is overcome by the large electrostatic interaction (ion pairing in the range of 48.5 to 62.5 kcal mol^{-1}) in **2-L**. Although the chloroboratabenzene moiety is formally a nucleophilic substrate because of the anionic charge, the boron atom in borabenzene is known to remain electrophilic.[17] If an excess of L ligand is available, it can undergo an associative substitution *via* the same intermediate speculated by Fu for the formation of *R*-boratabenzene adducts from 1-PMe$_3$-borabenzene in the presence of organic nucleophiles.[18] The $\Delta E^{\ddagger}$ for the transition state observed in Scheme 2 was calculated to be 27 kcal mol^{-1} for L = **Py**. The chloride liberated by this substitution could then coordinate to the platinum centre, forming the strong Pt–Cl bond of **3**, calculated to be of 94.7 kcal mol^{-1}.



Scheme 2 Associative mechanism for the dissociation of Cl$^-$ from **2-L** to generate **4-L**.

Conclusions

In this report, the generation of the ionic pair **2-L** from an unusual platinum chloroboratabenzene species in the presence of L = pyridine, PMe$_3$, MeCN and CN*t*Bu is reported. With PMe$_3$ and pyridine, an associative substitution at boron can occur since these Lewis bases are known to strongly stabilize borabenzene adducts. It exposes the difficulties associated with the generation of this interesting boratabenzene moiety using traditional nucleophilic substitution reactions on neutral borabenzenes. Indeed, the evidence shows that it is a thermodynamically unstable species compared to the most common adducts. The rich and unusual chemistry of **1** with other substrates, and the coordination chemistry of the chloroboratabenzene anion are currently underway.

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