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Lewis Acid Adducts

[(IMes)$_2$Pt(H)(ClBC$_5$H$_4$SiMe$_3$)]: a Borabenzene–Platinum Adduct with an Unusual Pt-Cl-B Interaction**

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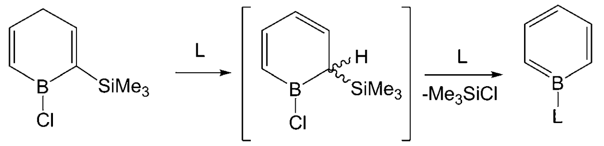
Since the first report of a metallaboratrane by Hill et al. in 1999,[1] there has been a quest for transition metal complexes containing a dative interaction with Group 13 Lewis acids. In a recent report, Braunschweig and co-workers demonstrated that [(PCy$_3$)$_2$Pt^0] (Cy = cyclohexyl) interacts with alanes to form Lewis adducts [(PCy$_3$)$_2$Pt(AlX$_3$)],[2] which are rare examples of well-characterized alane (M→AlR$_3$) complexes.[3,4] However, the analogous reaction with haloboranes does not yield Lewis adducts, but instead forms platinum boryl complexes,[5] a class of anionic boron-containing species of which numerous examples have been reported to date.[6] The only compounds having an M→B dative interaction with boron are supported by ambiphilic ligands.[7–9] The boron atom of bis- or tris(methimazolyl)boranes coordinates selectively to the transition metal in metallaboratranes.[10] In contrast, in addition to interacting with a transition metal, the Lewis acid moiety of phosphinoboranes prepared by Bourissou[11] can interact with an anionic ligand within the coordination sphere, depending on the nature of the transition metal and the ambiphilic ligand. Such an interaction is seldom observed with Lewis acids, and is supported by ambiphilic ligands,[12] with the exception of BF$_4$ adducts and halocarboranes, in which the Lewis acidity of the boron atom can no longer be considered.[13]

Whereas borabenzene adducts are the subject of continuing interest, and in particular for their electronic properties,[14] the coordination modes of these heterocyclic molecules with transition metals are quite limited. A common feature of borabenzenes[15] and boratabenzenes,[16] the analogue with anionic nucleophiles, is their η^6 coordination by the aromatic ring in an analogous fashion to arene and cyclopentadienyl ligands.[17] The exception is a phosphidoboratabenzene, which binds transition metals by the phosphine moiety.[18] Using the efficient and general strategy of forming borabenzene organic adducts from boracyclohexadiene by the elimination of Me$_3$SiCl, which was developed by Fu et al. (Scheme 1),[19] we examined the possibility of using a nucleophilic transition metal complex to stabilize the Lewis acidic boron orbital on borabenzene. By applying this strategy, the isolation of an η^1-borabenzene transition metal adduct, and consequently of an unchelated borane having a dative interaction with a transition metal, could be possible. During these investigations, we observed that the B–Cl oxidative addition of the boracyclohexadiene with platinum(0) species does not occur, in contrast to previously observaions with haloboranes. Instead, formation of a μ-η^1-Cl-borabenzene adduct, which is an unusual bonding mode for an unchelated Lewis acid, was observed.



Scheme 1. Formation of borabenzene adducts from 1-chloro-2-(trimethylsilyl)boracyclohexadiene. L = Lewis base.

As seen in Braunschweig adducts (see above), [(PCy$_3$)$_2$Pt^0] appeared to be a promising and potent nucleophile for borabenzene formation; however, initial experiments with 1-chloro-2-trimethylsilyl-4-isopropylborabenzene (**1a**) were problematic owing to phosphine dissociation. Indeed, free phosphine was shown to interact with boracyclohexadiene precursors to form PCy$_3$–borabenzene adducts.[20] This result prompted us to use N-heterocyclic carbene ligands instead of phosphines because they are known to bind tightly to transition metals whilst offering good steric protection.[21]

The addition of one equiv of boracyclohexadiene **1a** to one equiv of a yellow solution of [(IMes)$_2$Pt^0] (Scheme 2; IMes = 1,3-di(2,4,6-trimethylphenyl)imidazolin-2-ylidene) in [D$_6$]benzene gave a colorless reaction mixture. After 5 min, it was possible to observe one major compound, **2a**, in solution

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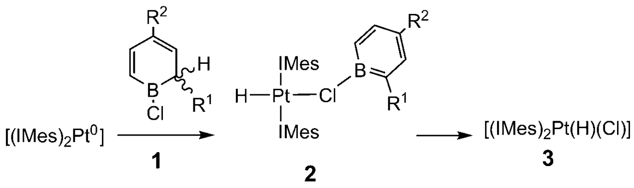

Scheme 2. Formation of borabenzene adducts **2a–c** (**1a:** R^1 = TMS, R^2 = *i*Pr; **1b:** R^1 = TMS, R^2 = H; **1c:** R^1 = H, R^2 = H), and **3** upon formal elimination of the borabenzene moiety.

by ^{1}H NMR spectroscopy. Along with resonances corresponding to the IMes carbene in the NMR spectrum, the presence of a hydride signal at $\delta = -22.41$ ppm was observed with an unprecedented $^1J_{\text{Pt-H}}$ coupling constant of 1910 Hz.[22] Signals were observed that are characteristic for a 2-trimethylsilyl-4-isopropylborabenzene adduct (see the Experimental Section), and the integration of the resonances corresponds to two IMes ligands for one hydride and one borabenzene moiety. A 2D ROESY NMR experiment was also carried out on **2a**. ROE correlations were observed between the borabenzene group and the {(IMes)$_2$Pt(H)(Cl)} fragment. The methyl groups in the *ortho* position of the mesityl group have ROE correlations with both the resonances of TMS group and the hydrogen at $\delta = 5.75$ ppm. Also, the methyl groups in the isopropyl moiety correlate with the aromatic proton in the *meta* position of the mesityl ring. Such correlations imply that the substituents in *ortho* and *meta* positions are in close proximity of the metal center.

Compound **2a** is unstable in solution and decomposes readily. Higher concentration, slight excess of **1a**, or removal of the solvent under reduced pressure increases the decomposition rate dramatically. Under dilute conditions (ca. 10^{-6} M), compound **2a** was the major component in solution for up to three days. However, a single inorganic degradation product, **3**, was always present, and its concentration was shown to be inversely proportional to **2a** in solution. All attempts to crystallize compound **2a** failed, and only **3** was isolated. Compound **3** has very similar ^{1}H NMR spectroscopic features to **2a**, with the IMes resonances and the hydride ($\delta = -17.96$ ppm, $^1J_{\text{Pt-H}} = 1550$ Hz) shifted slightly downfield, although it contains no borabenzene moiety. Suitable crystals for X-ray crystallography were obtained from a saturated solution of **3** in benzene, which allowed its identification as [(IMes)$_2$Pt(H)(Cl)].[23]

The similarity of the spectroscopic features of **2a** and **3** suggest that the former complex should also be a hydridochloroplatinum(II) species, but with a borabenzene bound to it. It is also evident that the aromatization of the borabenzene does not involve the elimination of TMSCl, but instead occurs via C–H bond activation by the Pt^0 precursor, forming the stable hydride complex. To account for the observed data, three different structures were proposed for the adduct; none of these structures has ever been reported with borabenzene. The first proposed structure involves an interaction between the hydride and the borabenzene, but can be ruled out, as no broadening caused by the quadrupolar boron atom is observed for the hydride. Our second hypothetic structure has a Pt→B interaction, which is similar to the phosphinoborane complex interaction reported by Bourrisou.[11c] The final hypothesis involves an interaction between the chloride and the borabenzene, which is quite unusual for a boron-containing species other than BF_4 and halocarboranes. To gain more structural information, the synthesis of two other analogues, using precursors **1b** and **1c**, was undertaken.

The addition of boracyclohexadienes **1b** and **1c** (Scheme 2) to [(IMes)$_2$Pt^0] in [D$_6$]benzene gave similar reactivity to **1a**, affording **2b** and **2c**. The feasibility of the reaction with **2c** confirms that the elimination of TMSCl is not a requirement for the borabenzene adduct formation. It can also be observed by ^{1}H NMR that the borabenzene in **2c** is symmetric on an NMR timescale, as H^2/H^6 and H^3/H^5 are equivalent. However, ^{1}H NMR signals arising from the hydride and the IMes-bound are, within the margin of error, equivalent for all three complexes. Also essentially equivalent are the ^{195}Pt resonances for all borabenzene complexes (**2a** = −4364 ppm, **2b** = **2c** = −4367 ppm), which are upfield from **3** ($\delta = -4285$ ppm). Although the acquisition of an ^{11}B NMR spectrum proved difficult to obtain, especially for **2c**, which decomposed during the acquisition, it was possible to observe that both **2a** and **2b** have similar chemical shifts ($\delta = 36.2$ and 38.8 ppm, respectively), which are in the expected range for borabenzene adducts.[19]

The similarity of the spectroscopic features of the {(IMes)$_2$Pt(H)(Cl)} core in **2a–c** tends to favor the hypothesis of a bridging chloride adduct. Indeed, if a Pt–B interaction were present, a more significant shift in the ^{195}Pt and ^{1}H resonance should arise depending on the nature of the borabenzene. DFT calculations were carried out to credit or discredit the presence of a Pt–B or a Pt–Cl–B interaction. Modeling of **2b** show no minimum energy state that would account for any Pt–B interaction; however the Pt–Cl–B model did show an energy minimum (Figure 1).

In the complex **2b**, a marked interaction between the chlorine and boron atoms is obtained (B–Cl distance of 1.93 Å). An NBO analysis indicates that a covalent bond is formed between these two atoms, and thus that a chloroboratabenzene ligand is obtained. At the same time, the Pt–Cl bond is elongated (2.47 Å in [(IMes)$_2$Pt(H)(Cl)] and 2.56 Å in

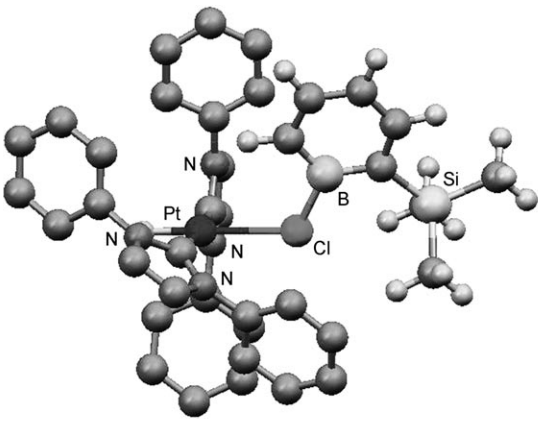

Figure 1. Optimized structure of the chloroboratabenzene complex **2b**. Hydrogen atoms and methyl groups of the 2,4,6-trimethylphenyl groups are omitted for clarity.

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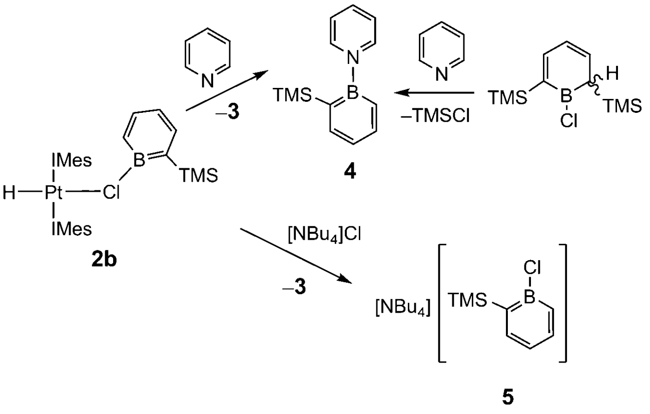
2b), and the Pt–H bond is slightly shortened (1.53 Å in **2b** and 1.56 Å in [$(IMes)_2Pt(H)(Cl)$]), which could account for the large coupling constant between these two elements observed in the borabenzene complexes. At the NBO level, in **2b**, a remaining interaction between chlorine and platinum is found at the second-order donor–acceptor level (circa 20 kcal mol^{-1}). For comparison, a NBO analysis of [$(IMes)_2Pt(H)(Cl)$] already reveals a mainly ionic bond between platinum and chlorine (second-order interaction of more than 90 kcal mol^{-1}). NMR calculations of the ^{11}B nuclear shift were carried out for the complex **2b** and also for the "free" chloroboratabenzene. In complex **2b**, a ^{11}B nuclear shift of 35 ppm is obtained, whereas a value of 51 ppm is found for the "free" chloroboratabenzene. These values are in excellent agreement with the experimental data, and clearly indicate that the chloroboratabenzene is coordinated to the platinum center.

It was not possible to determine the nature of the organic fragment resulting from the dissociation of the borabenzene fragment from complex **2**.[24] However, the addition of 2 equiv or 10 equiv of pyridine to **2b** leads to the formation of the borabenzene adduct **4** in which the trimethylsilyl group is still present (Scheme 3). Formation of the same compound was observed in the addition of pyridine to 1-chloro-2,6-bis(trimethylsilyl)boracyclohexa-2,4-diene by the elimination of TMSCl. The connectivity of **4** was confirmed using X-ray crystallography. It can be speculated that the boron is the subject of a nucleophilic attack, leading to the displacement of **3** by pyridine to form **4**. If such a mechanism occurs, it should be possible to use a chloride anion as a nucleophile to synthesize a chloroboratabenzene salt. Indeed, five minutes after the addition of [NBu_4]Cl to **2b** in [D_6]benzene, it was possible to observe both the clean formation of **3** as the major inorganic compound (ca. 90%) and a new borabenzene fragment (**5**) in the ^1H NMR spectrum. Although it was not possible to isolate the new borabenzene product, a significant upfield shift of the α and β methylene signals of the butyl chains of the tetrabutylammonium cation, which integrates for a 1:1 ratio with the borabenzene fragment, was observed. The absence of such a shift when the only two other species present in solution, **3** and [NBu_4]Cl, are mixed together, suggests formation of a tetrabutylammonium salt of 1-chloro(2-trimethylsilyl)boratabenzene (**5**).



Scheme 3. Nucleophilic displacement of 2-(trimethylsilyl)borabenzene from **2b**.

Compounds **2a–c** are, to our knowledge, the first examples of unsupported M-X-BR_3 complexes in which the Lewis acidity of a borane is still available. The stability of the platinum–NHC bond relative to usual Pt–L dative bonds seems to be a requirement to prevent the weak {$(IMes)_2Pt(H)(Cl)$}–borabenzene adducts from dissociating to form Lewis base/borabenzene adducts. Although it might be economically more viable to use the Fu strategy to generate borabenzene adducts, the synthetic pathway we present will favor the presence of additional functional groups on the borabenzene by not requiring a TMS group, and makes hypothetically possible the interaction with less donating donor ligands to form new and unusual borabenzene adducts, which we are currently examining.

Experimental Section

[$(IMes)_2Pt^0$],[25] **1a,**[14a] **1b**,[19] and **1c**[26] were synthesized according to literature procedures. **2a–c**, **3**: In a typical experiment, a dilute solution of **1** (0.004 mmol) in C_6D_6 is added dropwise to a yellow solution of [$(IMes)_2Pt^0$] (0.0035 g, 0.00425 mmol) in C_6D_6. NMR spectra indicate the formation of species **2**, which decomposes to give **3** over time. This decomposition is greatly accelerated if **1** is present even in slight excess.

2a: ^1H NMR (400 MHz, [D_6]benzene): $\delta = 7.78$ (d, $^4J_{H\text{-}H} = 2.1$ Hz, 1 H, H^3), 7.25 (dd, $^3J_{H\text{-}H} = 10.3$ Hz, $^4J_{H\text{-}H} = 2.1$ Hz, 1 H, H^5), 6.76 (s, 8 H, H^{meta}Mes), 5.94 (s, 4 H, H^{imid}), 5.75 (d, $^3J_{H\text{-}H} = 10.3$ Hz, 1 H, H^6), 3.25 (sept, $^3J_{H\text{-}H} = 6.9$ Hz, 1 H, $CH(CH_3)_2$), 2.32 (s, 12 H, Me^{para}Mes), 1.85 (s, 24 H, Me^{ortho}Mes), 1.64 (d, $^3J_{H\text{-}H} = 6.9$ Hz, 6 H, $CH(CH_3)_2$), 0.59 (s, 9 H, TMS), −22.42 ppm (s, $^1J_{Pt\text{-}H} = 1910$ Hz, 1 H, Pt-H). $^{13}C\{^1H\}$ NMR (75.4 MHz, [D_6]benzene): $\delta = 137.8$ (C^{para}Mes), 137.3 (C^3), 136.5 (C^{ipso}Mes), 135.7 (C^{ortho}Mes), 133.6 (C^5), 129.3 (C^{meta}Mes), 123.7 (C^6), 121.7 (C^{imid}), 26.6 ($CH(CH_3)_2$), 21.3 (Me^{para}Mes), 18.6 (Me^{ortho}Mes), 2.1 ppm (TMS). C_2, C_4, and the carbenic carbon were not observed. ^{195}Pt NMR (85.99 MHz, [D_6]benzene): $\delta = -4364$ ppm (d, $^1J_{Pt\text{-}H} = 1918$ Hz). ^{11}B NMR (128.34 MHz, [D_6]benzene): $\delta = 36.2$ ppm.

2b: ^1H NMR (400 MHz, [D_6]benzene): $\delta = 8.00$ (dd, $J = 7.2$, 1.3 Hz, 1 H, H^3), 7.41 (ddd, $J = 10.3$, 6.7, 1.4 Hz, 1 H, H^5), 6.98 (td, $J = 6.8$, 0.7 Hz, 1 H, H^4), 6.75 (s, 8 H, H^{meta}Mes), 5.95 (s, 4 H, H^{imid}), 5.80 (dt, $J = 10.1$, 0.7 Hz, 1 H, H^6), 2.30 (s, 12 H, Me^{para}Mes), 1.86 (s, 24 H, Me^{ortho}Mes), 0.58 (s, 9 H, TMS), −22.42 ppm (s, $^1J_{Pt-H} = 1915$ Hz, 1 H, Pt-H). $^{13}C\{^1H\}$ NMR (75.4 MHz, [D_6]benzene): $\delta = 139.3$ (C^3), 137.8 (C^{para}Mes) 136.4 (C^{ipso}Mes), 135.6 (C^{ortho}Mes), 135.3 (C^5), 129.3 (C^{meta}Mes), 123.4 (C^6), 121.6 (C^{imid}), 112.5 (C^4), 21.3 (Me^{para}Mes), 18.5 (Me^{ortho}Mes), 2.0 ppm (TMS). C^2 and the carbenic carbon were not observed. ^{195}Pt NMR (85.99 MHz, [D_6]benzene): δ −4367 (d, $^1J_{Pt-H} = 1960$ Hz). ^{11}B NMR (128.34 MHz, [D_6]benzene): $\delta = 38.8$ ppm.

2c: ^1H NMR (400 MHz, [D_6]benzene): $\delta = 7.76$ (dd, $J = 10.5$, 7.1 Hz, 2 H, H^3/H^5), 7.00 (tt, $J = 7.0$, 1.1 Hz, 1 H, H^4), 6.77 (s, 8 H, H^{meta}Mes), 6.31 (dd, $J = 10.5$, 1.1 Hz, 2 H, H^2/H^6), 5.93 (s, 4 H, H^{imid}), 2.30 (s, 12 H, Me^{para}Mes), 1.88 (s, 24 H, Me^{ortho}Mes), −22.44 ppm (s, $^1J_{Pt\text{-}H} = 1905$ Hz, 1 H, Pt-H). $^{13}C\{^1H\}$ (HSQC) NMR (75.4 MHz, [D_6]benzene): $\delta = 133.6$ (C^3 and C^5), 128.8 (C^{meta}Mes), 121.5 (C^{imid}), 120.4 (C^2 and C^6), 111.9 (C^4), 21.1 (Me^{para}Mes), 18.2 ppm (Me^{ortho}Mes). C^{ipso}Mes, C^{ortho}Mes, C^{para}Mes, and the carbenic carbon were not observed. ^{195}Pt NMR (85.99 MHz, [D_6]benzene): $\delta = -4367$ ppm (d, $^1J_{Pt\text{-}H} = 1910$ Hz).

3: ^1H NMR (400 MHz, [D_6]benzene): $\delta = 6.80$ (s, 8 H, H^{meta}Mes), 6.08 (s, 4 H, imidazol), 2.33 (s, 12 H, Me^{para}Mes), 2.07 (s, 24 H, Me^{ortho}Mes), −17.97 ppm (s, $^1J_{Pt\text{-}H} = 1542$ Hz, Pt-H).$^{13}C\{^1H\}$ NMR

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(75.4 MHz, $[D_6]$benzene): $\delta = 180.1$ (carbene), 137.3 (C^{ipso}Mes), 136.9 (C^{para}Mes), 136.1 (C^{ortho}Mes), 129.0 (C^{meta}Mes), 120.8 (C^{imid}), 21.4 (Me^{para}Mes), 18.9 ppm (Me^{ortho}Mes). ^{195}Pt NMR (85.99 MHz, $[D_6]$benzene): $\delta = -4285$ ppm (d, $^1J_{\text{Pt-H}} = 1523$ Hz).

Complete characterization and spectroscopic data of all new compounds can be found in the Supporting Information.

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