Generation of Group VI piano-stool and triple-decker complexes from [(IMes)$_2$PtH(Cl-boratabenzene)] species

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Generation of Group VI piano-stool and triple-decker complexes from 
\([(\text{IMes})_2\text{PtH(Cl-boratabenzene)}]\) species

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Species \([(\text{IMes})_2\text{Pt(H)}(1-\text{Cl-2-SiMe}_3-\text{BC}_2\text{H}_3)]\) (I) was used as source of the Cl-boratabenzene anion for coordination to group VI transition metals, resulting in the formation of piano stool complexes \([(\eta^5-1-\text{Cl-2-SiMe}_3-\text{BC}_2\text{H}_3)\text{M(CO)}_3]\) (M = Cr (2), Mo (4), W (5)) and a homometallic triple-decker complex \([(\text{CO})_3\text{Cr(\eta^5-1-\text{Cl-2-SiMe}_3-\text{BC}_2\text{H}_3)\text{Cr(CO)}_3}]\) (3). All species were spectroscopically characterized and the first X-ray structure of a Cl-boratabenzene species is reported.

Introduction

Since the discovery of the first boratabenzene complex by Herberich in 1970,\textsuperscript{1} the coordination of the bora- and boratabenzene moieties, the neutral and anionic versions of the heterocyclic aromatic ring (Figure 1, I and II), has been carried out with most transition metals.\textsuperscript{2} The boratabenzene moiety serves as an isoelectronic analogue of the ubiquitous cyclopentadienyl ligand and boratabenzene complexes have been shown to act as efficient catalysts for alkene polymerization\textsuperscript{3} and cyclotrimerization,\textsuperscript{4} E-H bond activation,\textsuperscript{5} and as a chirality source.\textsuperscript{6} Also of interest, is the role of the boratabenzene ring in the synthesis of novel generations of optoelectronic materials.\textsuperscript{7}

\[
\text{Borabenzene} \quad \text{Boratabenzene}
\]

\[
\begin{array}{c}
\text{L} = \text{Neutral Lewis base} \\
\text{X} = \text{Anionic Lewis base}
\end{array}
\]

\[
\begin{array}{c}
\text{I} \\
\text{II}
\end{array}
\]

Figure 1. Neutral borabenzene (I) and anionic boratabenzene (II).

Similarly to the coordination of the cyclopentadienyl ligand, the coordination of the boratabenzene is possible by the interaction of the \(\pi\)-system of the aromatic ring with the transition metal. As such, most complexes observed are bound in a \(\eta^3\)-fashion, although ring slippage to a \(\eta^5\)-coordination is sometime observed when \(\pi\)-donating ligands\textsuperscript{8} or bulky substituents\textsuperscript{9} are present on the boron. In the latter case, the boron tends to be farther from the metal center compared to the carbon atoms of the ring. It has been observed in some instances that the ring system can interact in an allylic-like coordination, notably in a recent example reported by our research group of a platinum(II) diterbutylphosphido-boratabenzene (Pt(DTBB)\textsubscript{2}) species having a P-B-C interaction with platinum (Figure 2, III).\textsuperscript{9} To our knowledge, only two examples of an interaction between a borabenzene ligand and a transition metal do not involve the \(\eta^5\)-system of the heterocyclic ring. First, it has been reported by Fu that the Ph\textsubscript{2}P-BC\textsubscript{2}H\textsubscript{3} moiety binds transition metals by the lone pair of the phosphorous moiety (Figure 2, IV);\textsuperscript{10} however, we demonstrated that such coordination mode is only favored when the complex requires only a 2-electron donation to be electronically saturated.\textsuperscript{9} The only other example is species \([(\text{IMes})_2\text{Pt(H)}(1-\text{Cl-2-SiMe}_3-\text{BC}_2\text{H}_3)]\) (I) (Figure 2, I) where the coordination of the \(\pi\)-ring is prevented by the sterical bulk of the N-heterocyclic ligands and leads to a Pt-Cl-B interaction.\textsuperscript{11}

\[
\begin{array}{c}
\text{III} \\
\text{IV} \\
\text{I}
\end{array}
\]

Figure 2. Boratabenzene complexes Pt(DTBB)\textsubscript{2} (III),\textsuperscript{9} Rh(PMe\textsubscript{3})\textsubscript{2}(DPB) (IV),\textsuperscript{10} \([(\text{IMes})_2\text{Pt(H)}(1-\text{Cl-2-SiMe}_3-\text{BC}_2\text{H}_3)]\) (I).\textsuperscript{11}

Although more than 200 bora- and boratabenzene species have been reported, only a handful of halide derivatives of boratabenzene has ever been characterized. In addition of species I, a fluoride analogue was reported in the context of an unusual rearrangement of an iridabenzene where the addition of an excess of boron trifluoride results in the formation of \([(\eta^5)^1\text{-fluoro-3}-\text{5-}]}
dimethyl-1-borabenzene)Jr(PEt$_3$)$_3$]$_{12}^{12}$ However, it is quite surprising that no additional haloborabenzene species has ever been reported since they represent highly desirable targets. Indeed, the B-Cl bond could undergo several transformations of interest, including transmetalation, oxidative addition, or reduction to generate interesting novel species, notably to obtain M-B interactions for the generation of Z-type ligands. 13 We reported that 1 could release the anionic 1-Cl-2-SiMe$_3$-BC$_2$H$_4$ fragment in the presence of Lewis bases (L) to generate the species ([M(Se$_3$)Pt(H)(L)][$\sigma$-Cl-2-SiMe$_3$-BC$_2$H$_4$] (L = PMe$_3$, pyridine, acetonitrile). 14 In the presence of more than one equivalent of the Lewis base, the generation of neutral borabenzene adduct 1-LB-2-SiMe$_3$-BC$_2$H$_4$ was possible if the new boron-LB interaction was strong and thermodynamically favored, such as with pyridine and PMe$_3$. 14,15 Herein, we would like to report that species 1 can also be used as a Cl-borabenzene anion source for coordination to group VI transition metals to generate piano stool complexes [[(η$^6$-1-Cl-2-SiMe$_3$-BC$_2$H$_4$)M(CO)$_3$] (M = Cr (2), Mo (4), W (5)) and homobimetallic triple-decker complex [(CO)$_3$Cr{(η$^6$-1-Cl-2-SiMe$_3$-BC$_2$H$_4$)Cr(CO)$_3$}] (3). All species were spectroscopically characterized and the first X-ray structure of a Cl-borabenzene species is reported.

Results and Discussion

In a typical reaction, a freshly prepared solution of 1 in benzene-d$_6$ was added into a vial containing 0.009 mmol of Li$_3$M(CO)$_3$ (M = Cr, Mo, W; L = CO, CH$_3$CN). The solution was then transferred into a J-YOUNG NMR tube for spectroscopic characterization. For the reaction using the acetonitrile complex (CH$_3$CN)Cr(CO)$_3$, the colourless solution of 1 changed to yellow and progressively to orange as the chromium precursor dissolved, generating species [[(η$^6$-1-Cl-2-SiMe$_3$-BC$_2$H$_4$)Cr(CO)$_3$] (2) and [(CO)$_3$Cr{(η$^6$-1-Cl-2-SiMe$_3$-BC$_2$H$_4$)Cr(CO)$_3$}] (3). When the reaction was carried out in presence of (CH$_3$CN)Mo(CO)$_3$ and (CH$_3$CN)W(CO)$_3$, the reaction mixture changed from yellow to a brownish solution to give [(η$^6$-1-Cl-2-SiMe$_3$-BC$_2$H$_4$)Mo(CO)$_3$] (4) and [(η$^6$-1-Cl-2-SiMe$_3$-BC$_2$H$_4$)Cr(CO)$_3$] (5), respectively (Schemes 1 and 2).

For all samples, $^1$H NMR spectroscopy shows aromatic resonances for the borabenzene moiety of species 1 ($\delta$ = 8.00, 7.41, 6.98, and 5.80) completely disappearing after few minutes, while new resonances appeared at higher field indicative of an η$^6$ coordination of the borabenzene moiety on a metal centre. Indeed, the aromatic protons were observed at $\delta$ = 6.08, 5.85, 5.02, and 4.50 for 2, at $\delta$ = 6.26, 6.12, 5.24, 4.94 for 4, and at $\delta$ = 5.94, 5.81, 5.13 and 4.82 ppm for 5. These chemical shifts are representative of borabenzene piano-stool complexes such as Na[[(η$^6$-C$_5$H$_5$-B-Me(Pr)$_2$]Cr(CO)$_3$]], Li[[[(η$^6$-3,5-Me$_2$C$_5$H$_3$-B-Ni-Pr$_2$]Mo(CO)$_3$]]$_2$DEME, and the tungsten-borabenzene complexes [[η$^6$-C$_5$H$_5$B-Py]W(CO)$_3$]]. It was observed that cationic species [[(IMes)Pt(H)(CH$_3$CN)]$^+$] was generated, which is clearly recognizable by the presence of an hydride at $\delta$ = -19.1 ($^{1}$J$_{P-H}$ = 1518 Hz). However, another hydride resonance was also observed at $\delta$ = -5.1 ($^{1}$J$_{P-H}$ = 1198 Hz), which was a third in intensity compared to the acetonitrile platinum species, suggesting that another counter-ion to the borabenzene complex is present in solution. Conducting the experiment with M(CO)$_3$ rather than the acetonitrile precursor gave more information on the nature of the latter species. Indeed, it was also observed that the formation of the same borabenzene species occurred, but only the hydride at -5.07 ppm was observed, suggesting that the counter-ion consists of [[(IMes)Pt(H)(CO)]$^+$]. However, heating of the solution at 40°C for several hours is needed for the reaction to go to completion using the hexacarbonyl reagents, which also induces further degradation of 1 to [(IMes)$_3$Pt(H)(Cl) (6) and intractable borabenzene species. The reaction with (CH$_3$CN)Cr(CO)$_3$ leads rapidly to the generation of a second borabenzene species which is associated to the formation of the homobimetallic triple-decker complex 3 (Scheme 1). A complete new set of borabenzene aromatic protons was observed at $\delta$ = 5.55, 5.22, 3.67 and 3.00. $^{1}$C($^1$H) NMR spectroscopy of the reaction mixture of 2 and 3 shows CO resonances at 240.2 and 233.1 ppm, in accordance with other borabenzene piano stool complexes reported in the literature such as the previously mentioned Li[[[(η$^6$-3,5-Me$_2$C$_5$H$_3$-B-Ni-Pr$_2$]Mo(CO)$_3$]]$_2$DEME that shows a resonance at 232.9 corresponding to CO ligand, or the neutral borabenzene complex [(η$^6$-C$_5$H$_5$B-THF)Cr(CO)$_3$] with a resonance at 238.0 ppm.

According to $^{13}$C($^1$H) NMR spectroscopy, the carbon resonances of the borabenzene moiety were observed at $\delta$ = 115.9, 112.9, 109.4 and 84.9 for complex 4, and at $\delta$ = 120.7, 108.7, 105.3 and 82.6 for complex 5. In both cases, the C-1 was not observed. Unfortunately, the borabenzene resonances could not be located for 2 and 3. Although the reason for such surprising behaviour is not well understood, it can be speculated that under the time needed for the $^{13}$C NMR acquisition, which consists of several hours, 2 transforms to 3, which then crystallizes out of solution, therefore making impossible the acquisition of good NMR data. Since the scale-up synthesis of the complexes is limited by the difficulty associated with the preparation of 1, which spontaneously degrades according to a first-order mechanism, 20 it is quite difficult to carry out the experiment in more concentrated solutions to get better NMR data. The complex 3 displays a single boron resonance by $^{11}$B NMR spectroscopy at 28.5 ppm which resembles the chemical shift of the borabenzene complex [[η$^6$-C$_5$H$_5$B-THF]Cr(CO)$_3$] at 28.5 ppm, in contrast with the borabenzene complex Na[[η$^6$-C$_5$H$_5$B-Me(Pr)$_2$]Cr(CO)$_3$] at 24.6 ppm, suggesting for the chloride to be a less donating group than the methyl and close to THF. Complexes 4 and 5 exhibit resonances at 22.1 and 25.4, respectively, which are in the expected range for similar borata- and borabenzene complexes such as: Li[[[(η$^6$-3,5-Me$_2$C$_5$H$_3$-B-Ni-Pr$_2$]Mo(CO)$_3$]]$_2$DEME at 24.3 ppm; [[η$^6$-C$_5$H$_5$B-Py]Mo(CO)$_3$]] at 23.5 ppm and [[η$^6$-C$_5$H$_5$B-Py]W(CO)$_3$] at 22.9 ppm. 16-18

![Scheme 1. Synthesis of the piano stool complexes.](image1)

![Scheme 2. Synthesis of Cr derivatives.](image2)
ESI-MS was used to further characterize the new species formed. In the experiments with the acetonitrile precursors, it was possible to observe the presence of a main ion at m/z of 804.3, which corresponds to the 1:4-electron ([IMes]2PtH(4)4) fragment. As we previously reported, the Pt-acetonitrile interaction is relatively weak and dissociates readily during the MS experiments. However, it was also possible to observe the ion for the ([IMes]2PtH(4)4) fragment at m/z = 832.3, confirming the presence of the carbonyl species. Looking at the negative ions, it was possible to observe both [η5-1-Cl-2-SiMe2-BC(5)H5]- and [CO]Cr(η5-1-Cl-2-SiMe2-BC(5)H5)- ions at m/z = 454.9. The Mo and W species were observed at m/z = 364.9 [η5-1-Cl-2-SiMe2-BC(5)H5]Mo(CO)5] and m/z = 450.9 [η5-1-Cl-2-SiMe2-BC(5)H5]W(CO)5], respectively.

FT-IR spectra of complex 3 shows the asymmetric and symmetric stretching frequencies (νCO) at 2159.1, 2029.3 and 1976.8 cm⁻¹, similar to those observed for arenic tricarbonylchromium complexes, despite the anionic character of the boratabenzene ligand. Compared to other anionic piano stool complexes with cyclopentadienyl ligands, such as [Cr(CO)5]Na with bands at 1897, 1793, and 1743,22 the signals of 3 are observed at a higher frequency, which would suggest that the Cr(CO)3 fragments display a distorted trigonal planar geometry. Complex 3 shows a B-CI distance of 1.807(3) Å, which is shorter than the B-CI distance of precursor 1 (1.930 Å according to DFT calculations),11 which is expected since in the latter case the chloride is bridging with the platinum centre. The B-Cr (1) and B-Cr (2) distances, of 2.325(3) and 2.334(3) Å respectively, are on the range of other related complexes such as [η5-1-Cl-2-SiMe2-BC(5)H5]Cr(CO)5] with a B-Cr distance of 2.333(8) Å and [η5-1-Cl-2-SiMe2-BC(5)H5]PyCr(CO)5] bearing a nitrogen-donor ligand on boron with a B-Cr distance of 2.311(5) Å.18,19 The average Cr-C distance for the Cr(CO)3 fragments in complex 3 is of 1.838 Å for Cr(1) and 1.825 Å for Cr(2). The average C-O distance for this complex is 1.159 Å, which is very similar to the distances observed on complexes such as [η5-1-Cl-2-SiMe2-BC(5)H5]Cr(CO)5] that shows an average Cr-C of 1.833 and average O-C distances of 1.155 Å, and complex [η5-1-Cl-2-SiMe2-BC(5)H5]Cr(CO)5] with average distances of 1.825 and 1.159 Å for Cr-C and O-C, respectively. These data once again indicate that the anionic chromium has the same electronic influence than neutral oxygen containing Lewis bases such as THF and oxazoline.19 Whereas the negative charge on boratabenzene ligand in complex 3 increases its donor capability, shorter Cr-C and longer O-C distances are expected; however, we must consider that the electronic density is shared between two Cr(CO)3 fragments.

Conclusions

We have reported that platinum species ([IMes]2PtH(4)1-Cl-2-SiMe2-BC(5)H5)] (1) can serve as a Cl-boratabenzene anion source for generating piano-stool complexes [η5-1-Cl-2-SiMe2-BC(5)H5]M(CO)5] (M = Cr, Mo, W). In the case of the chromium species, it rearranges rapidly to generate the triple-decker boratabenzene species, which was characterized crystallographically. The possibility to coordinate the chloroboratabenzene fragment on transition metals is of interest since the latter fragment is seldom observed in the boratabenzene coordination chemistry. Indeed, as confirmed by the experimental results, the chloride acts as a weak donor for the boratabenzene moiety and looks similar to that of THF adducts. Such chloroboratabenzene species could be of interest in generating new and unusual species by reduction or transmetalation reactions at the boron centre. However, the limitation in this procedure is the difficulty in scaling up the synthesis of 1 to obtain considerable amount of metallic piano-stool samples. We are currently underway to isolate the Cl-boratabenzene moiety using alternative strategies that does not involve 1 to probe the reactivity of the Cl-B interaction in chloroboratabenzene metallic species.

Experimental Section

General considerations

Hexacarbonyl metal complexes of W and Mo were purchased from Strem Chemicals and Cr(CO)5 was purchased from Alfa Aesar and were used as received without further purification. All precursors were prepared under N2 atmosphere with regular Schlenk techniques. All solvents were pre-treated and distilled under N2 atmosphere, over sodium-benzophenone before use. Deuterated solvents are pre-treated with Na/K and vacuum transferred. NMR spectra were recorded in a Varian Inova NMR AS400 spectrometer at 400.00 MHz (1H), 100.58 MHz (13C), 128.33 MHz (15N). HRMS spectra were recorded in an Agilent Technologies 6210 LC Time of Flight Mass Spectrometer. The reaction mixture in benzene solution was directly injected to the nebulizer using ESI-MS ionization in positive and negative modes. FT-IR were taken on a Nicolet Bomem Magna-850, crystals were suspended in Nujol previously degassed by bubbling N2, the sample was prepared inside of an inert atmosphere glove box. All boratabenzene reactions were carried out inside of the glove box, using a J-
Young NMR tube. Compound 111 and (CH3CN)2M(CO)5 were synthesized according to literature procedures.

**General Procedure**
A solution containing 0.004 mmol of [(IMes)Pt(H)(Cl-2-SiMe2-BC2H3)] (1) in 0.8 mL of benzene-d8 was added into a vial containing 0.009 mmol of L,M(CO)5 (M = Cr, Mo, W; L = CO, NCCCH). The solution was then placed in a J-Young NMR tube with reactions with M(CO)5, were heated at 40 °C for 6 h while reactions with (CH3CN)2M(CO)5 were carried out at room temperature.

**Spectroscopic Characterization**
In all experiments, there was a mixture of the cationic platinum species ([IMes]Pt(η3-NCCCH)4]+ and [IMes]Pt(η2-H)(CO)4]+. Each cation has its own spectroscopic properties, but the shift does not change from one experiment to the other (within 0.01 ppm), with the exception of bound acetonylitrile in [(IMes)Pt(η3-NCCCH)4]+, which can go under exchange with free acetonylitrile in solution, therefore showing up at various chemical shifts. To ease the characterization, the spectroscopic data of the cationic species is separated from the data of the anionic boratabenzene complexes.

\[
\text{[(IMes)Pt(η3-NCCCH)]}^+ \\
\text{[(IMes)Pt(η2-H)(CO)]}^+ \\
\text{[(η4-1-Cl-2-SiMe2-BC2H3)](Cr(CO)3)}^+ \\
\text{[(η4-1-Cl-2-SiMe2-BC2H3)](Cr(CO)3)}^- \\
\text{[(η4-1-Cl-2-SiMe2-BC2H3)](Cr(CO)3)}^3 \\
\text{[(η4-1-Cl-2-SiMe2-BC2H3)](Mo(CO)3)}^+ \\
\text{[(η4-1-Cl-2-SiMe2-BC2H3)](Mo(CO)3)}^- \\
\text{[(η4-1-Cl-2-SiMe2-BC2H3)](Mo(CO)3)}^3
\]

**Supporting Information**
(see footnote on the first page of this article): Electronic Supplementary Information (ESI) available: [Multinuclear NMR characterization of complexes 2-5 and crystallographic data for 3].

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Group VI piano stool and a triple-decker complexes of Cl-boratabenzene ligand were prepared. All species were spectroscopically characterized and the first X-ray structure of the Cl-boratabenzene triple-decker complex is reported.

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