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VIP

Neutral and Anionic Transition-Metal-Base-Stabilized Metalloborylene Complexes

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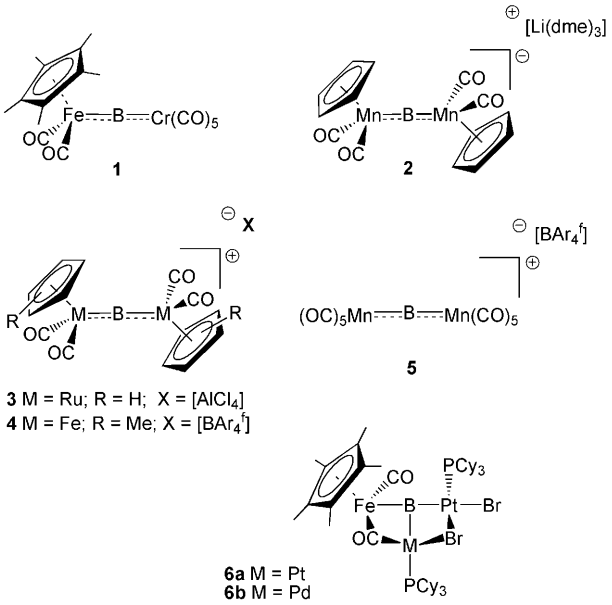
The realization of molecular boron species in which all valences are saturated by electron-precise bonds to d-block metals marks a significant recent development in borylene complex chemistry.[1] This group of species, which display "naked" boron $^-$ that is, a boride $^-$ as ligand, comprises neutral (e.g. **1**),[2;3] cationic (**3**–**5**),[4;5]and even anionic metalloborylenes (**2**)[6] with sp-hybridized two-coordinate boron centers as well as trimetalloboranes (**6**) that are derived from trigonal-planar, sp^2-hybridized boron[7] (Scheme 1).

With the aim of increasing the number of metal–boron bonds by subsequent oxidative addition of B–Br bonds,[8] we reported the reaction of $[M(PCy_3)_2]$ (M = Pt, Pd) with the heterodinuclear boryl complex $[(\eta^5\text{-}C_5Me_5)(OC)_2Fe(\mu\text{-}BBr)Pt(PCy_3)Br]$.[9] Indeed, the trinuclear complexes $[(\eta^5\text{-}C_5Me_5)(OC)Fe(\mu\text{-}CO)M(PCy_3)(\mu\text{-}Br)Pt(PCy_3)Br(\mu_3\text{-}B)]$ (**3a**, **b**; M = Pt, Pd), were isolated after oxidative addition of the B–Br bond to Pt and Pd, respectively.[10]

However, the coordination geometry at the boron atom was unexpected, as the Fe-B-Pt moiety adopts an almost linear arrangement, whereas the $[M(PCy_3)_2]$ (M = Pt, Pd) fragments are coordinated orthogonally through the boron center to this unit. Density functional theory (DFT), as well as electron localization function (ELF) calculations revealed that this coordination mode is best described in terms of a metalloborylene complex fragment $[(\eta^5\text{-}C_5H_5)(CO)_2Fe{=}B{=}PtB_2(PCy_3)]$, stabilized by a transition-metal base moiety $[M(PCy_3)]$. Thus, these unprecedented trinuclear species complete the hitherto known coordination modes for boride ligands.



Scheme 1. Selected metalloborylene complexes bearing a linear M=B=M moiety

At this point we became interested, whether these highly unusual T-shaped boride complexes were accessible by a rational and direct synthetic approach, that is, the reaction of a metalloborylene complex with a suitable metal–base species. For this purpose, we chose the stable species **1** and **2** in combination with electron-rich Pt^0/Pd^0 complex fragments, as the latter have already demonstrated their propensity to bind efficiently via dative bonds to metal-coordinated boron-centered ligands.[9,11–14]

Upon reaction of $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}(\mu_2\text{-}B)\{Cr(CO)_5\}]$ (**1**) with one equivalent of $[Pt(P\mathit{i}Pr_3)_3]$ in toluene at room temperature the solution immediately turned dark red and a single new compound formed as shown by $^{11}B\{^1H\}$ NMR spectroscopy (Scheme 2). The solvent was removed and the

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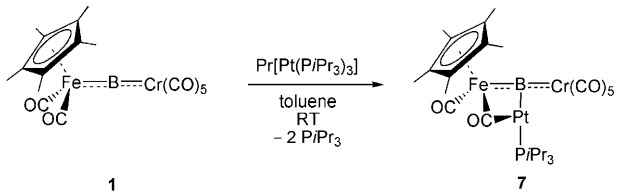

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Scheme 2. Synthesis of compound **7**.

crude solid was dissolved in hexane. Concentration and cooling provided dark red crystals of the complex [{(η^5-C_5Me_5)(CO)Fe(μ-CO)}Pt(P*i*Pr$_3$)Cr(CO)$_5$(μ^3-B)] (**7**).

The $^{11}B\{^1H\}$ NMR spectrum shows a broad signal at $\delta =$ 228 ppm, which is shifted downfield with respect to that of the precursor **1** ($\delta = 204.6$ ppm). The $^{31}P\{^1H\}$ NMR spectrum displays a sharp resonance at $\delta = 59.7$ ppm (^1J(Pt, P) = 4731 Hz). The large value of the Pt–P coupling constant is comparable to that reported for **6a** (^1J(Pt, P) = 4703 Hz). The most significant resonance of **7** in the IR spectrum can be found at 1787 cm^{-1} and indicates the bridging CO between the Pt and the Fe atom.

The molecular structure of **7** (Figure 1) reveals that the B–Cr distance (2.032(4) Å) is somewhat elongated compared to that of the starting metalloborylene complex (**1**:

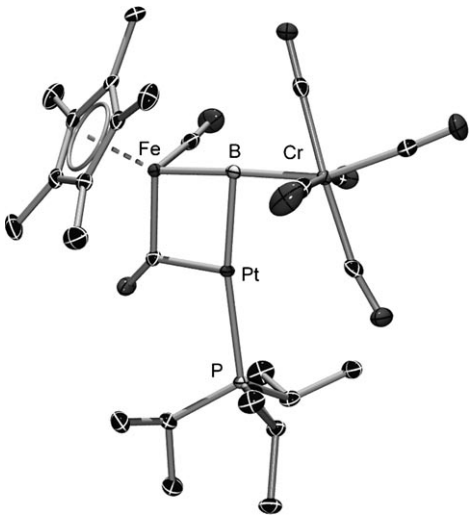
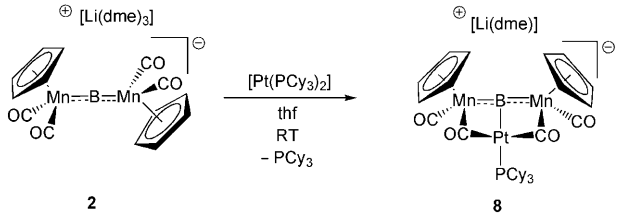


Figure 1. Molecular structure of **7**. Selected bond lengths [Å] and angles [°]: B–Fe 1.870(3), B–Cr 2.976(1), B–Pt 2.052(3); Fe-B-Cr 174.68(16), Fe-B-<Pt83.79(11), Pt-B-Cr 93.52(11). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability.

1.975(3) Å). In contrast, the Fe–B distance (1.870(3) Å) is only slightly greater than that in **1** (1.867(9) Å), presumably due to the presence of a bridging carbonyl ligand between iron and platinum. Notably, all three metal–boron distances are comparable to those found in iron borylene[15,16] and chromium borylene[17,18] species, thus indicating a non-negligible amount of multiple-bond character. The Pt–B bond length of 2.052(3) Å is rather long and exceeds those commonly found in Pt–boryl complexes,[19,20] thus being comparable to a value of 2.158(4) Å found for the dative interaction between platinum and boron in the aforementioned trinuclear species **6a**.

To investigate the generality of this direct synthetic approach and to test for potential limitations, we treated the anionic metalloborylene [Li(dme)$_3$][{(η^5-C_5H_5)Mn(CO)$_2$}$_2$-(μ_2-B)] (**2**) with one equivalent of [Pt(PCy$_3$)$_2$] under similar conditions (Scheme 3).



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Scheme 3. Synthesis of compound **8**.

Multinuclear NMR spectroscopy suggested again the formation of a single boron-containing species [Li(dme)$_3$][{(η^5-C_5H_5)(CO)Mn(μ-CO)}$_2$Pt(PCy$_3$)(μ_3-B)] (**8**), as indicated by a broad signal in the $^{11}B\{^1H\}$ NMR spectrum at δ = 214.6 ppm, which is considerably downfield shifted with respect to that of the precursor **2** ($\delta = 195.3$ ppm). Likewise, the $^{31}P\{^1H\}$ NMR spectrum shows a sharp resonance at δ = 54.1 ppm (^1J(Pt, P) = 4480 Hz) similar to that of **7** and thus attributed to the [Pt(PCy$_3$)] fragment. Additionally, a second resonance at $\delta = 9.81$ ppm is observed in the reaction mixture that indicates the presence of liberated PCy$_3$. Similar to **7**, a blue-shifted signal in the IR spectrum at 1609 cm^{-1} can be detected indicative of bridging CO groups.

After the mixture had been stirred for 24 h at ambient temperature, filtered, and the solution had been concentrated in vacuo, orange crystals of **8** suitable for X-ray diffraction were isolated in 59% yield (Figure 2). The isolated crystals contain two molecules of **8**, in which the anions [{(η^5-C_5H_5)(CO)Mn(μ-CO)}$_2$Pt(PCy$_3$)(μ_3-B)] [**8**]$^-$ are connected by two Li(dme) units, each one coordinating to a bridging and a terminal CO group. In agreement with this observation, signals for one equivalent of dme were found in the ^{1}H and the ^{13}C NMR spectra of **8**.

The anion [**8**]$^-$ adopts approximately C_s symmetry in the crystal and shows an overall geometry very similar to that of **7**. In particular, the boron center resides less than 0.1 Å above the Mn1-Mn2-Pt plane and is almost linearly coordinated by the two manganese atoms (Mn1-B-Mn2 168.32(11)°). The Mn–B distances of 1.905(2) Å and 1.903(2) Å, respectively, are somewhat longer than in terminal manganese–borylene complexes (1.809(9) Å)[21] but significantly shorter than in manganese–boryl species (2.060(5) Å),[22] thus indicating a certain amount of multiple-bond character in the Mn–B interaction.

The T-shaped coordination of the boron atom is completed by the [Pt(PCy$_3$)] fragment, which displays relevant bond angles of 83.16(7)° (Mn1-B-Pt) and 85.70(7)° (Mn2-B-Pt),

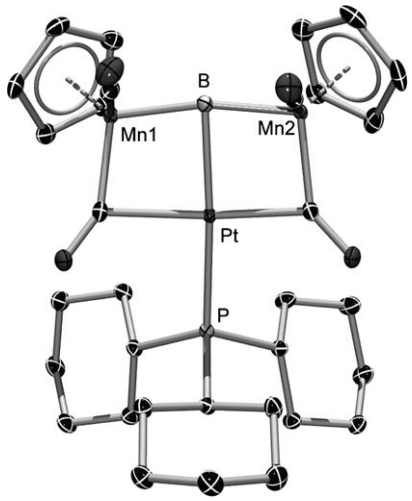

Figure 2. Molecular structure of $[\mathbf{8}]^-$. Selected bond lengths [Å] and angles [°]: Mn1–B 1.905(2), Mn2–B 1.903(2), B–Pt 2.110(2); Mn1-B-Mn2 168.32(11), Mn1-B-Pt 83.16(7), Mn2-B-Pt 85.80(7). The [Li(dme)] cation and hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability.

respectively. The Pt–B distance was found to be 2.110(2) Å and thus, somewhat longer than in **7**, which is presumably due to the presence of two bridging CO groups that increase the coordination number of the platinum center.

The common structural features of **7** and **8**, that is, a linear M-B-M moiety with significant multiple-bond character and a $[Pt(PR_3)]$ fragment coordinated orthogonally to this unit through the boron atom thus constituting the highly unusual T-shaped coordination of boron, provides convincing evidence as to the bonding situation. Hence, these novel trimetallic boride species are to be described as transition-metal-base-stabilized metalloborylenes.

In conclusion, we have reported an unprecedented direct synthetic approach for T-shaped trimetalloborides, that is the addition of late transition-metal bases to the boron center of a metalloborylene species. Particularly interesting is the finding that not only neutral, but also anionic metalloborylenes are susceptible to the formation of dative metal–boron bonds, despite a certain nucleophilic character of the boron atom.[6;23] Thus, the scope of these unusual species has been extended by two novel examples, including the first anionic trinuclear metal–boron complex.

Experimental Section

Details of the experimental and crystallographic procedures can be found in the Supporting Information.

Keywords: boron · borylene complexes · coordination chemistry · platinum · transition metals

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