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Reversible carbon–boron bond formation at platinum centers through σ -BH complexes†

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A reversible carbon–boron bond formation has been observed in the reaction of the coordinatively unsaturated, cyclometalated, Pt(II) complex [Pt(I^tBuⁱPr')(I^tBuⁱPr)](BAR^F), **1**, with tricoordinated boranes HBR₂. X-ray diffraction studies provided structural snapshots of the sequence of reactions involved in the process. At low temperature, we observed the initial formation of the unprecedented σ -BH complexes [Pt(HBR₂)(I^tBuⁱPr')(I^tBuⁱPr)](BAR^F), one of which has been isolated. From –15 to +10 °C, the σ -BH species undergo a carbon–boron coupling process leading to the platinum hydride derivative [Pt(H)(I^tBuⁱPr–BR₂)(I^tBuⁱPr)](BAR^F), **4**. Surprisingly, these compounds are thermally unstable undergoing carbon–boron bond cleavage at room temperature that results in the 14-electron Pt(II) boryl species [Pt(BR₂)(I^tBuⁱPr)₂](BAR^F), **2**. This unusual reaction process has been corroborated by computational methods, which indicate that the carbon–boron coupling products **4** are formed under kinetic control whereas the platinum boryl species **2**, arising from competitive C–H bond coupling, are thermodynamically more stable. These findings provide valuable information about the factors governing productive carbon–boron coupling reactions at transition metal centers.

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1. Introduction

The formation of C–B bonds, mediated by transition metal complexes, has become an important tool for the synthesis of organoboron compounds,¹ an important family of organic molecules in synthetic organic chemistry and in materials science.² From the mechanistic point of view, there have been several reports that point to the participation of σ -BH (σ -borane) complexes as key intermediates in the formation of the carbon–boron bonds in metal-alkyl or -aryl compounds. For example, Hartwig *et al.* have shown, by means of DFT calculations, that σ -BH complexes of rhodium and tungsten are transient species in the borylation of alkanes, where the driving force is the formation of the C–B bonds (Scheme 1).³

Although most of this type of C–H borylation processes have been carried out using rhodium and iridium systems,⁴ there

have been a few reports on the utilization of platinum complexes for the formation of C–B bonds, either in stoichiometric reactions or in catalytic processes.⁵ Turculet and Stradiotto reported the dehydrogenative coupling of B–H/C–H bonds at a Pt(II) center,^{5a} whereas Chatani, Tobisu *et al.* suggested the participation of σ -BH complexes in the platinum-catalyzed borylation of arenes.^{5b,c} However, the interaction of tricoordinated hydroboranes with platinum centers leading to σ -BH complexes has proven elusive.⁶ In addition, examples of transition metal σ -borane alkyl complexes [M(R)(HBR₂)] are extremely rare, and those that have been isolated did not show further reactivity involving the formation of carbon–boron bonds.⁷ Isolation of this type of compounds might offer an invaluable opportunity for determining the factors that can lead



Scheme 1 σ -BH complexes proposed as intermediates in the borylation of C–H bonds of alkanes reported by Hartwig *et al.*³

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to competitive carbon–boron or carbon–hydrogen coupling products.

In this article, we report the spectroscopic observation and isolation of platinum σ -BH complexes that undergo either a carbon–boron coupling process or formation of platinum–boryl complexes as a function of temperature. The whole sequence of events underlying these processes has been followed by NMR and X-ray diffraction studies and investigated by DFT calculations.

2. Results and discussion

2.1 Synthesis of Pt(II) boryl complexes

In previous studies we have reported that some low-coordinate cationic platinum(II) complexes can interact with tetra-coordinated boranes, $L \cdot BH_3$ (L = pyridine, amine), leading to stable adducts or to catalytic boron–nitrogen coupling products (amine–borane dehydrocoupling).⁸ In this context we have examined the reactivity of these platinum systems with tri-coordinated boranes derived from dioxa- and diaza-boroles. We have chosen cationic platinum(II) complex $[Pt(I^tBu^iPr)(I^tBu^iPr)][BAR^F]$, **1**, as starting material (where I^tBu^iPr is 1-*tert*-butyl-3-isopropylimidazol-2-ylidene, and I^tBu^iPr its cyclometalated form through the *tert*-butyl substituent), since this system has been successfully used for the isolation of related σ -SiH derivatives.⁹ When complex **1** was treated with either pinacol- (HBpin, **a**) or catechol–borane (HBcat, **b**), or 1,3,2-benzodiazaborolane (HBdab, **c**) in CH_2Cl_2 at 25 °C, boryl complexes **2a–c** were formed quantitatively according to NMR spectroscopy (Scheme 2). The reaction proceeds smoothly but reaction times vary considerably from dioxaboroles to the diazaborole, from 10 min to 15 h. The 1H NMR spectra of these species reveal a highly symmetric environment of the NHC ligands, indicating their chemical equivalence.

The $^{11}B\{^1H\}$ NMR spectra exhibit two sets of signals, one for the Pt–B fragment and the other for the BAR^F anion. The former resonate at δ 12.7, 14.7 and 8.8 for **2a–c**, respectively, showing coupling to ^{195}Pt in the range 1390–1700 Hz (see ESI†). Crystals of **2c** suitable for X-ray diffraction studies were grown by slow diffusion of CH_2Cl_2 solutions into pentane. Fig. 1 shows an ORTEP-type view of the cation. The platinum atom is



Scheme 2 Reaction of complex **1** with hydroboranes.

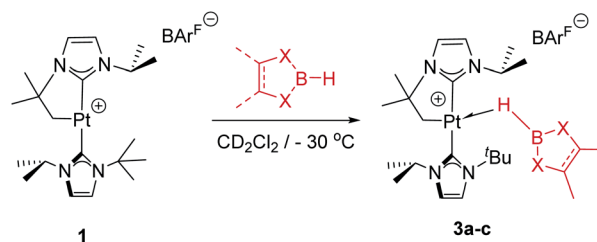


Fig. 1 ORTEP representation of the cation of complex **2c**. Hydrogen atoms (except those of the NH moieties) have been omitted for clarity. Selected bond distances (Å) and angles (°): Pt1–B1, 1.988(6); Pt1–C1, 2.015(5); Pt1–C11, 2.016(5); B1–N6, 1.424(7); B1–N5, 1.433(7); C1–Pt1–C11, 173.5(2); B1–Pt1–C1, 92.9(2); B1–Pt1–C11, 93.6(2).

surrounded by only three ligands, with a formal vacant site *trans* to the boryl moiety. Very weak, at best, agostic interactions are present in the molecule (the closest C to Pt is 3.1 Å away).¹⁰ The Pt–B distance of 1.988(6) Å is similar to that reported by Braunschweig in related systems of the type *trans*- $[(Cy_3P)_2Pt\{B(X)X'\}]$.¹¹

2.2 Low-temperature reactivity studies: characterization and isolation of σ -BH Pt(II) complexes

In order to look for intermediates in the reaction process, and in particular to detect σ -BH complexes, low temperature NMR experiments have been carried out. The reaction of **1** with a slight excess of pinacolborane in an NMR tube in CD_2Cl_2 at -30 °C led to a clean reaction with formation of a new species that, according to multinuclear NMR, is the σ -BH complex **3a** (Scheme 3). The 1H NMR is characterized by a broad signal in the hydride region at -3.93 ppm, showing coupling to ^{195}Pt ($J_{H,Pt} = 357$ Hz). This signal becomes narrower upon ^{11}B decoupling (see Fig. S11 in the ESI†) and it has been assigned to the bridging Pt–H–B proton. The $^{11}B\{^1H\}$ spectrum shows, besides the signal for the BAR^F anion and some excess of HBpin, a very broad signal at 21.8 ppm.¹² A similar behavior has been observed in the reaction of **1** with HBcat leading to **3b** (1H NMR: -3.28 ppm, $J_{H,Pt} = 327$ Hz; $^{11}B\{^1H\}$ NMR: 21.3 ppm) and with HBdab producing **3c** (1H NMR: -2.32 ppm, $J_{H,Pt} = 339$ Hz; ^{11}B



Scheme 3 Formation of σ -BH complexes **3a–c** at low T.



{¹H} NMR: 18.6 ppm). All these sigma complexes are stable at temperatures ranging from -15 to $+10$ °C, with complex **3c** being the most stable. In line with these findings, DFT calculations estimate favorable ΔG of formation at -30 °C of -2.3 , -0.6 and -3.1 kcal mol⁻¹ for **3a**, **3b** and **3c**, respectively (see Fig. S33 in the ESI†).

The increased thermal stability of complex **3c** has allowed us to obtain crystals suitable for X-ray diffraction analysis by slow diffusion of CH₂Cl₂ solution into pentane at -25 °C (Fig. 2). The platinum center is found in a nearly planar environment, with two NHCs and one $-\text{CH}_2-$ unit occupying three coordination sites and the B–H moiety the fourth. The angle defined by atoms C13–Pt1–H1 and Pt1–H1–B1 are $168.5(1)^\circ$ and $105(2)^\circ$, respectively, very close to those observed in the related σ -SiH derivative [Pt(HSiEt₃)(^tBu¹Pr′)(^tBu¹Pr)] [BAR^F] ($173.1(1)^\circ$ and $103(2)^\circ$).⁹ The Pt1–H1 and H1–B1 bond distances are 1.69(4) Å and 1.19(3) Å, respectively. The latter is slightly elongated with respect to the B–H bond of boranes¹³ and comparable to related σ -BH primary aminoborane complexes.¹⁴ The Pt1⋯B1 distance of 2.31 Å is considerably larger than the sum of covalent radii (2.2 Å), suggesting that, if any, the interaction between these two atoms is weak.¹⁵ In fact, topological analysis of the electron density and its laplacian (see ESI†) revealed the presence of bond critical points (BCPs) between Pt and H, and H and B, yet no BCP between Pt and B was observed.¹⁶ This fact suggests that the coordination mode is better described as η^1 -BH instead of the common η^2 -BH mode reported for other transition metals.^{6,13,17} Bonding interactions were further analyzed in terms of localized orbitals.¹⁸ The centroid of the localized orbital corresponding to the B–H bond (X_{BH} , Fig. 3) is close to the H center, in agreement with a marked hydride character of this H atom, and is displaced from the B–H axis towards Pt, indicative of a perturbed sigma bond. At the same time, one Pt centroid (X_{Pt}) is slightly moved away (0.431 Å) from the nucleus, compared to the other Pt centroids (0.345–0.398 Å), and pointing to B. We have previously characterized similar interactions in cationic Pt(II) σ -silane complexes, which adopt a rare η^1 -SiH coordination mode.⁹



Fig. 2 Molecular structure of the cationic component as determined by X-ray diffraction of complex **3c** (ellipsoids at 30% probability). Selected bond distances (Å) and angles (°): Pt1–H1, 1.69(4); H1–B1, 1.19(3); Pt1–C13, 2.054(2); Pt1–H1–B1, 105(2); C13–Pt1–H1, 168.5(1).

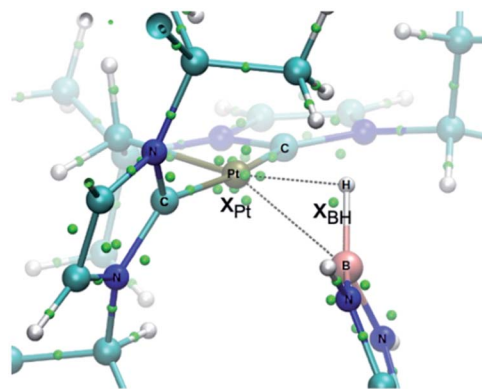
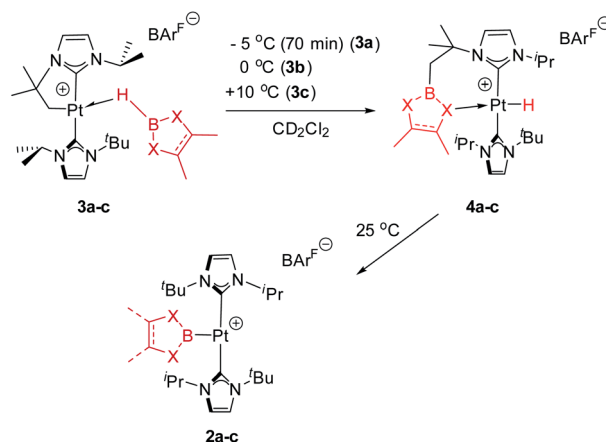


Fig. 3 Localized orbital analysis of **3c**. The molecular structure is overlaid with the centroids of the localized orbitals (small green dots). Dotted lines highlight the Pt–B and Pt–H distances.

As in the previously characterized η^1 -SiH platinum complexes,⁹ the coordination of the σ -bonded ligand is very flexible. We computed the energetic cost of deforming the Pt–H–B angle in **3c** (see Table S4 and Fig. S40†). Starting from the energy minimum at 101.6° , closing the angle to 78° or opening it to 154° requires less than 6 kcal mol⁻¹. More acute angles (68°) lead to borane dissociation instead of B–H bond cleavage, which contrasts with what was observed between **1** and hydrosilanes, for which closing the Pt–H–Si angle led ultimately to the Si–H oxidative addition.⁹ Importantly, QTAIM analysis did not reveal any BCP between Pt and B in structures with acute Pt–H–B angles (Fig. S38 and S39†).

2.3 Thermal evolution of σ -BH Pt(II) complexes: reversible C–B coupling en route to boryl complexes

As mentioned before complexes **3a–c** are only marginally thermally stable, and upon warming at temperatures above -15 °C (**3a**), 0 °C (**3b**) or $+10$ °C (**3c**) undergo a rearrangement that involves the cleavage of the B–H bond and the formation of a new C–B bond leading to complexes **4a–c** (Scheme 4). The reaction is particularly clean in the case of complex **3a**, for



Scheme 4 Rearrangement of complexes **3a–c**.



Fig. 7 C–H (top) and C–B (bottom) bond forming events from the analysis of the movements of the centroids of the localized orbitals, represented by small purple dots. Isosurfaces of the localized orbitals involved in the bond-breaking/bond-forming processes are also shown. For each process the deduced arrow-pushing scheme is also shown.

moiety is being formed. Conversely, in the formation of the C–B bond the centroid of the C–Pt bond moves from the C–Pt axis to the B–C axis, while the centroid of the B–H bond moves from the B–H axis to the H–Pt axis (again, a sigma-CAM rearrangement). Formally, a borinium²⁷ is being transferred to the methylene fragment and a metal-hydride is being formed. Therefore, the possibility to generate both boryl and borinium species from a platinum σ -BH complex is the underlying reason that allows both C–B and C–H bond coupling processes to take place in this system.

3. Conclusion

The low-electron count Pt(II) complex $[\text{Pt}(\text{I}^t\text{Bu}^i\text{Pr})(\text{I}^t\text{Bu}^i\text{Pr})][\text{BAR}^F]$, **1**, reacts with tri-coordinated boranes in a set of reactions that start with formation of σ -BH complexes, **3**, in which the interaction of the B–H fragment with the cationic platinum center adopts a rare η^1 -BH coordination mode. These species evolve, as a function of temperature, by either formation of hydride complexes $[\text{Pt}(\text{H})(\text{I}^t\text{Bu}^i\text{Pr}-\text{BR}_2)(\text{I}^t\text{Bu}^i\text{Pr})][\text{BAR}^F]$, **4**, or platinum boryl derivatives $[\text{Pt}(\text{BR}_2)(\text{I}^t\text{Bu}^i\text{Pr})_2][\text{BAR}^F]$, **2**. We were able to detect species **3**, **4** and **2** by means of low temperature



NMR spectroscopy and, in some cases, by X-ray diffraction, providing snapshots of this unusual reactivity. DFT-based analyses support σ -complex assisted metathesis mechanisms (σ -CAM),²⁶ preceded by *trans* to *cis* isomerization of the NHC ligands. These calculations indicate that carbon-boron coupling products are energetically more accessible and that the competitive process leading to C–H bond coupling is more energy demanding. However, as the temperature increases, the thermodynamic stability of the final products determines the formation of the C–H bond coupling products. Steric effects between the substituents at the boryl fragment and the spectator NHC ligand in complexes **3a-cis** and **3a-cis'** might be behind the different energetic barriers. These results contribute to the mechanistic understanding of the factors that can lead to productive borylation and advance the design of new effective catalytic systems for such reactions.

Conflicts of interest

There are no conflicts to declare.

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- Different functionals and basis sets have been employed in these calculations, and no BCP between B and Pt has been observed in any case (see ESI† for more details).



