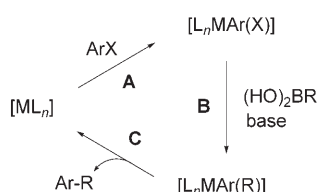


Oxidatively Induced Methyl Transfer from Boron to Platinum in Dimethyldi(2-pyridyl)boratoplatinum Complexes**

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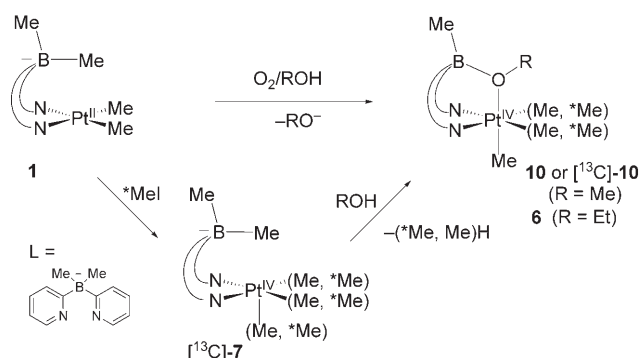
The transition-metal-catalyzed coupling of electrophilic aryl (ArX) and alkyl derivatives (RX) with boronic acids has recently become one of the most versatile approaches for the formation of C–C bonds.^[1] Although the mechanisms of C–X bond cleavage with electron-rich metal complexes (Scheme 1,



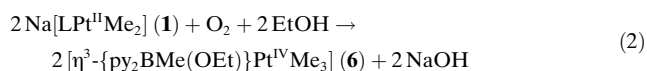
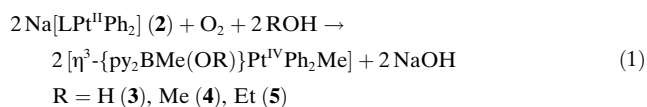
Scheme 1. Mechanism for the transition-metal-catalyzed coupling of boronic acids.

step A)^[2,3] and C–C reductive elimination from transient bis(hydrocarbyl) species (Scheme 1, step C) have been studied in detail for some metals,^[3] less attention has been paid to boron-to-metal hydrocarbyl ligand transfer (Scheme 1, step B).^[4] This transfer has been suggested to occur as an electrophilic aromatic substitution in the case of aryl boron reagents (M = Pt), and a similar mechanism has been postulated for their alkyl analogues.^[5] No information on the transfer of a hydrocarbyl group from boron to a metal atom in a high oxidation state (such as M^{IV}) is available.

Herein we report the results of experimental and computational studies of facile methyl group transfer from an anionic boron center to a coordinatively unsaturated cationic Pt^{IV} atom in transient zwitterionic platinum(IV) borates. This reaction is driven by coordination of a protic solvent and involves the likely formation of a transient Pt^{IV} species from Na[Lt^{II}R₂] (Scheme 2; R = Me (**1**), Ph (**2**); L = dimethyldi(2-pyridyl)borate, py₂BMe₂)^[6] upon oxidation of the metal by O₂ [Eqs. (1) and (2)] or MeI.



Scheme 2. Boron-to-platinum transfer of a methyl group induced by oxidation of the [Lpt^{II}Me₂][−] ion by O₂ or MeI.



A sluggish reaction that leads to a complex mixture of unidentified products occurs when solutions of complex **2** in dry benzene or thf are exposed to air, whereas a clean reaction takes place when water or alcohols (MeOH or EtOH) are present in the reaction mixture. Thus, oxidation of **2** in water occurs rapidly at ambient temperature (3–5 min) to give the hydroxyboratoplatinum(IV) complex **3**, which was isolated from the strongly alkaline reaction mixture in an analytically pure form [90% yield; Eq. (1)]. According to ¹H and ¹³C NMR spectroscopic and single-crystal X-ray diffraction studies (Figure 1), the overall result of this reaction is the substitution of one of the methyl groups of the BMe₂ moiety

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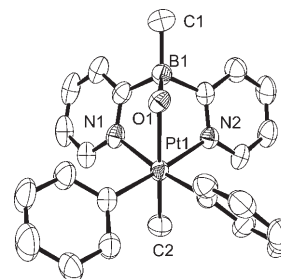


Figure 1. ORTEP drawing of complex **3** showing 50% probability ellipsoids.

of the original ligand **L** by OH and migration of this methyl group to the Pt^{IV} atom. Oxidation of **2** gives the methoxy- (**4**) or ethoxyborato (**5**) analogues of **3** in yields of more than 90% when methanol or ethanol, respectively, are used as solvent.

The dimethylplatinum(II) complex **1** exhibits a similar reactivity. Thus, it reacts with oxygen in ethanol to form the (ethoxyborato)trimethylplatinum(IV) complex **6**, which was isolated after five minutes in an analytically pure form [85% yield; Eq. (2)] and characterized by NMR spectroscopy as well as X-ray diffraction (Figure 2). The use of more acidic solvents such as methanol or water led to lower yields, presumably because of competitive protonolysis of **1**.^[6]

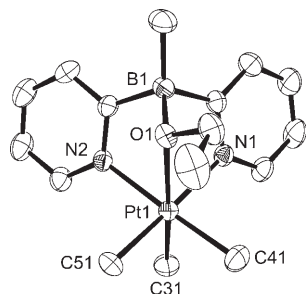
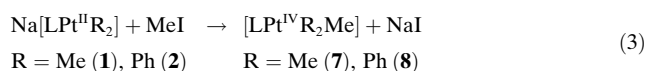


Figure 2. ORTEP drawing of complex **6** showing 50% probability ellipsoids.

The above experiments suggest that the oxygen atom of the dipyridylborato ligands in complexes **3–6** originates from the solvents and not from O₂, therefore it is possible that a similar boron-to-platinum methyl transfer would occur in the presence of a different oxidant, such as MeI. The reaction of **1** with MeI in aprotic thf is virtually instantaneous and leads to the formation of NaI and the air-stable complex **7** [Eq. (3); quantitative by ¹H NMR spectroscopy], which was isolated in 75% yield.



The ¹H NMR spectrum of **7** in [D₈]THF solution confirmed its mirror-symmetric structure. Thus, the boron-bound methyl groups exhibit two broadened multiplets, both of which integrate for three protons, at δ = 0.22 (J_{B,H} = 4.4 Hz) and δ = −0.91 ppm. Remarkably, the higher field resonance has two platinum-195 satellites with a J_{Pt,H} coupling constant of 58.1 Hz. These results suggest the presence of a five-coordinate Pt^{IV} center stabilized by a C–H agostic interaction with one of the boron-bound methyl groups. This hypothesis was confirmed by ¹³C NMR spectroscopy. Specifically, the multiplet of the “free” B–Me group at δ = 9.0 ppm appears as a quartet with a J_{B,C} coupling constant of 45.0 Hz, whereas the signal for the carbon atom of the agostic methyl group at δ = 27.1 ppm appears as a quartet with a smaller J_{B,C} coupling constant of 39.6 Hz and ¹⁹⁵Pt satellites (J_{Pt,C} = 60.3 Hz).

The structure of **7** was confirmed by single-crystal X-ray diffraction (Figure 3). A few five-coordinate Pt^{IV} complexes

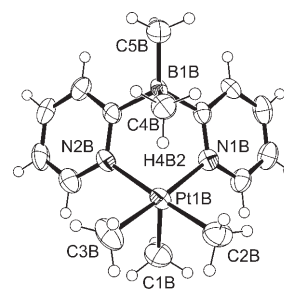


Figure 3. ORTEP drawing of complex **7** showing 50% probability ellipsoids. Selected bond lengths [Å]: Pt1B–H4B2 2.02(3), B1B–C5B 1.593(8), B1B–C4B 1.676(8), Pt1B–C4B 2.761, Pt1B–B1B 3.08.

are known^[7] but, to the best of our knowledge, complexes containing an agostic CH···Pt^{IV} interaction have never been reported. The Pt–H distance (2.02 Å) and the Pt–C4B separation (2.76 Å) are shorter than those found in a related three-coordinate cationic Pt^{II} complex that contains a CH agostic interaction.^[8]

Interestingly, the average B–C bond length calculated for the two crystallographically independent molecules of **7** present in the unit cell for the *endo* methyl group, which is involved in bonding to the Pt^{IV} center (1.66(1) Å), is longer than the B–C bond length of the *exo* methyl group (1.61(1) Å). This observation suggests that the B–C bond that is broken during the migration to the Pt^{IV} center might also be involved in a weak interaction with the metal center. The reduced B–C coupling constant observed for **7** is in agreement with this suggestion.

Complex **2** also reacts cleanly with methyl iodide to produce two isomeric CH-agostic five-coordinate {Ph₂Pt^{IV}} complexes, namely *sym*-**8** and *unsym*-**8** [Figure 4, Eq. (3)]; this reaction is quantitative (NMR spectroscopy). The product exists in acetone, thf, or benzene solution as a rapidly interconverting mixture of these two isomers, which exhibit

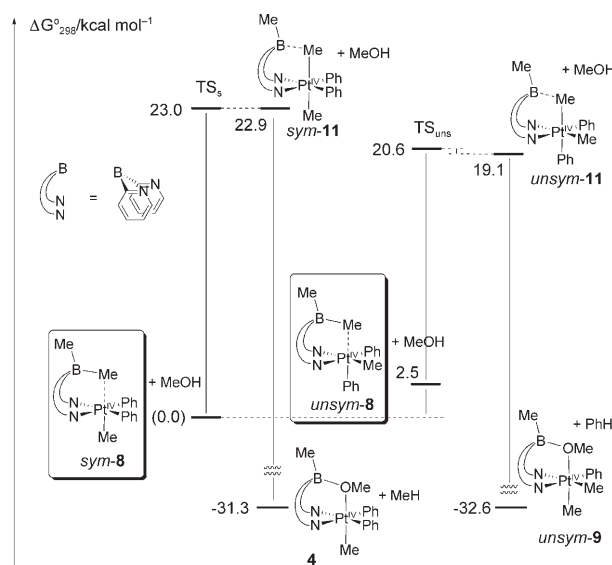
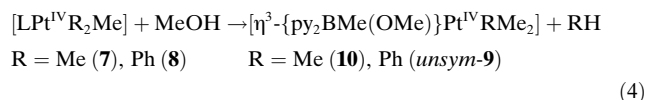


Figure 4. DFT-calculated Gibbs reaction energies for the transformation of **8** into *sym*- and *unsym*-**11**.

sharp PtMe resonances, and could be isolated in an analytically pure form in 73 % yield. The position of the equilibrium depends on the solvent, although in all cases the major isomer was *sym*-**8** (3:1 ratio in acetone).

Thus, no boron-to-platinum(IV) methyl-group transfer is observed upon oxidative addition of methyl iodide to either **1** or **2** in THF solution. However, this transfer is complete after 10 minutes when a sample of **8** is dissolved in [D₃]methanol, and produces the methoxyborato complex *unsym*-**9** and benzene, quantitatively, according to NMR spectroscopy [Eq. (4)].



According to ¹H and ¹³C NMR spectroscopic and X-ray diffraction studies, the single product is *unsym*-**9** that contains one {Pt^{IV}Ph} group (Figure 5). This means that isomeric

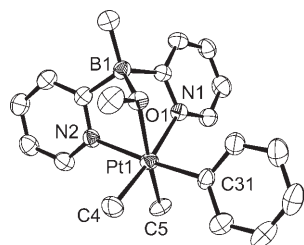
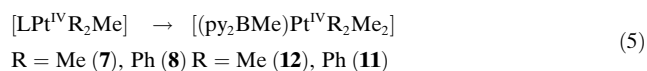


Figure 5. ORTEP drawing of complex **9** showing 50% probability ellipsoids.

complexes **8** react selectively by protonolysis of a Pt–Ph rather than a Pt–Me bond. Accordingly, a slow boron-to-platinum(IV) methyl-group transfer accompanied by protonolysis of the Pt–Me bond leads in the case of the methyl analogue **7** [Eq. (4)] to complex **10** quantitatively after one day.

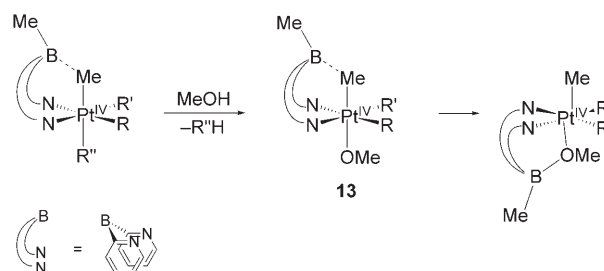
The stereochemical course of the boron-to-platinum(IV) migration of the methyl group was revealed by experiments involving the ¹³C-labeled complex [¹³C]-**7**, which was prepared using ¹³CH₃I [Eq. (3)]. According to ¹H NMR spectroscopy, the label is distributed statistically between the equatorial and axial positions (33 % ¹³C for each of the Pt^{IV}Me groups) 10 minutes after preparation of [¹³C]-**7**, which suggests that a fast exchange of the methyl group occurs in the five-coordinate Pt^{IV} complex **7**.^[7b] Notably, the reaction of [¹³C]-**7** in CD₃OH leads to the formation of a 2:1 mixture of CH₄ and ¹³CH₄ along with complex **10**, which exhibits a signal for the equatorial CH₃ groups with ¹³C satellites corresponding to 33 % ¹³C enrichment and a signal for the axial CH₃ group with ¹³C satellites corresponding to the natural ¹³C abundance. A similar behavior was observed for [¹³C]-**8**. Thus, the methyl group transferred from the boron to Pt^{IV} is not involved in the methanolysis. This fact is consistent with the results of our density functional calculations on the presumed six-coordinate intermediates **11** and **12** [Figure 4, Eq. (5)], where the methyl group transferred participates in a stabilizing three-

center two-electron interaction with the electron-poor boron atom and is therefore “protected” against attack by another electrophile (H⁺). While protonolysis of the axial Pt^{IV}–C bond *trans* to the methyl may be facilitated by the strong *trans* influence of the latter, the axial Pt^{IV}–Ph bond in *unsym*-**11** might be more reactive towards a proton than Pt^{IV}–Me in *sym*-**11** or **12** as a result of the ability of the {Pt^{IV}Ph} fragment to react through an aromatic electrophilic substitution mechanism.^[9]



The calculated Gibbs reaction energy for the transformation of *sym*-**8** to *sym*- and *unsym*-**11** (Figure 4) is positive (19.1–23.0 kcal mol^{−1}), with the lowest energy transition state (TS_{uns}), which connects *unsym*-**8** and *unsym*-**11**, being responsible for formation of the observed product (*unsym*-**9**). The calculated reaction path shows that formation of the Pt^{IV}–C bond and cleavage of the B–C bond are practically synchronous. Thus, the methyl-group transfer may be viewed as an electrophilic substitution at the methyl-group carbon atom, with the Pt^{IV} atom acting as an electrophile and the three-coordinate boron center playing the role of a leaving group.

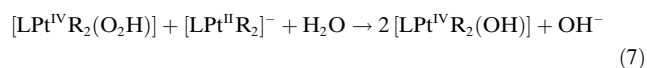
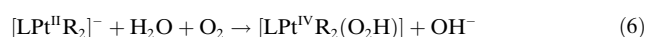
The energy barrier for the methyl transfer might be lowered by coordination of water or an alcohol to the boron atom (Scheme 3; R, R', R'' = Me or Ph). Protonolysis of the



Scheme 3. Photolysis of the Pt–C bond *trans* to the methyl group transferred and formation of the B–O–Pt bridge.

Pt–C bond *trans* to the methyl transferred,^[10] followed by “inversion” of the metallacycle in the transient species **13**, might lead to the observed reaction products (RH and methoxyborates **9** and **10**). According to our calculations, the reaction shown in Equation (4) is favored by about 30 kcal mol^{−1} overall.^[11]

We can postulate a similar mechanism for aerobic reactions [Eqs. (1) and (2)] based on the available observations. In this case, the axial R'' group in Scheme 3 is O₂H or OH formed according to one of the mechanisms suggested for the oxidation of alkylplatinum(II) complexes by O₂ [Eqs. (6) and (7)].^[12,13]



In summary, we have reported a clean intramolecular boron-to-platinum(IV) methyl-group transfer that occurs as an electrophilic substitution at the carbon atom of the methyl group. This reaction involves a five-coordinate Pt^{IV} intermediate that is produced by oxidation of a Pt^{II} precursor and is driven by coordination of a suitable protic nucleophile at the B and Pt^{IV} atoms. Attempts to utilize this reaction in catalytic C–C coupling are currently underway.

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