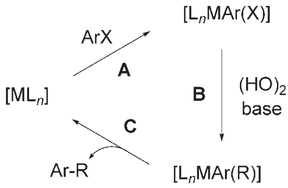
DOI: 10.1002/anie.200701257

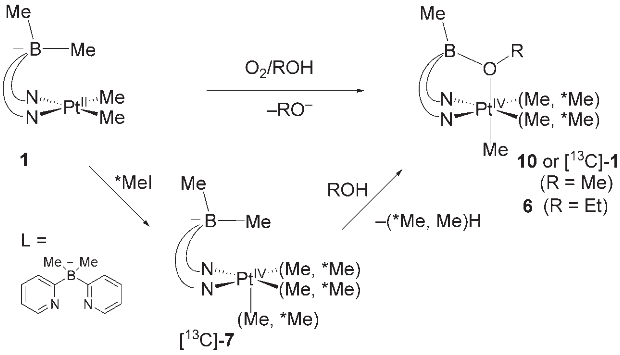
Oxidatively Induced Methyl Transfer from Boron to Platinum in Dimethyldi(2-pyridyl)boratoplatinum Complexes**

*Eugene Khaskin, Peter Y. Zavalij, and Andrei N. Vedernikov**

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, 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.



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



Scheme 2. Boron-to-platinum transfer of a methyl group induced by oxidation of the $[LPt^{II}Me_2]^-$ ion by O_2 or MeI.

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 $Na[LPt^{II}R_2]$ (Scheme 2; R = Me (**1**), Ph (**2**); L = dimethyldi(2-pyridyl)borate, $py_2BMe_2^-$)[6] upon oxidation of the metal by O_2 [Eqs. (1) and (2)] or MeI.

$$2\,Na[LPt^{II}Ph_2]\ (\mathbf{2}) + O_2 + 2\,ROH \rightarrow 2\,[\eta^3\text{-}\{py_2BMe(OR)\}Pt^{IV}Ph_2Me] + 2\,NaOH \qquad (1)$$

$$R = H\ (\mathbf{3}),\ Me\ (\mathbf{4}),\ Et\ (\mathbf{5})$$

$$2\,Na[LPt^{II}Me_2]\ (\mathbf{1}) + O_2 + 2\,EtOH \rightarrow 2\,[\eta^3\text{-}\{py_2BMe(OEt)\}Pt^{IV}Me_3]\ (\mathbf{6}) + 2\,NaOH \qquad (2)$$

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 ^{13}C 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 BMe_2 moiety

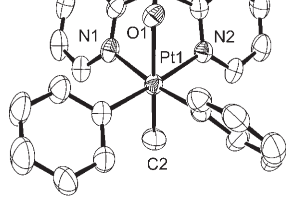


Figure 1. ORTEP drawing of complex **3** showing 50% probability ellipsoids.

---

[*] E. Khaskin, Dr. P. Y. Zavalij, Prof. A. N. Vedernikov
Department of Chemistry and Biochemistry
University of Maryland
College Park, MD 20742 (USA)
Fax: (+1) 301-314-9121
E-mail: avederni@umd.edu

[**] We thank the University of Maryland, the Donors of the American Chemical Society Petroleum Research Fund (PRF#42307-AC3), and the National Science Foundation (CHE-0614798) for financial support.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

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]

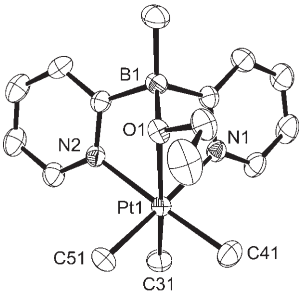


Figure 2. ORTEP drawing of complex **6** showing 50% probability ellipsoids.

The above experiments suggest that the oxygen atom of the dipyridylborato ligands in complexes **3**–**6** originates from the solvents and not from O_2, 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.

$$\begin{array}{ll} Na[LPt^{II}R_2] + MeI \; \rightarrow & [LPt^{IV}R_2Me] + NaI \\ R = Me\,(\mathbf{1}),\ Ph\,(\mathbf{2}) & R = Me\,(\mathbf{7}),\ Ph\,(\mathbf{8}) \end{array} \tag{3}$$

The ^1H NMR spectrum of **7** in [D_8]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 $\delta = 0.22$ ($J_{B,H} = 4.4$ Hz) and $\delta = -0.91$ 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 ^{13}C NMR spectroscopy. Specifically, the multiplet of the "free" B−Me group at $\delta = 9.0$ 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 $\delta = 27.1$ ppm appears as a quartet with a smaller $J_{B,C}$ coupling constant of 39.6 Hz and ^{195}Pt satellites ($J_{Pt,C} = 60.3$ Hz).

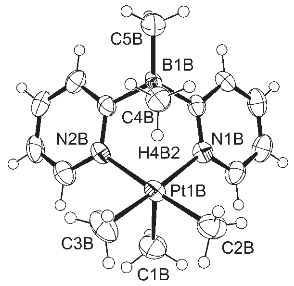


Figure 3. ORTEP drawing of complex **7** showing 50% probability ellipsoids. Selected bond lenghts [Å]: Pt1B−H4B2 2.02(3), B1B−C5B 1.593(8), B1B−C4B 1.676(8), Pt1B−C4B 2.761, Pt1B−B1B 3.08.

The structure of **7** was confirmed by single-crystal X-ray diffraction (Figure 3). A few five-coordinate Pt^{IV} complexes 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 {Ph_2Pt^{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

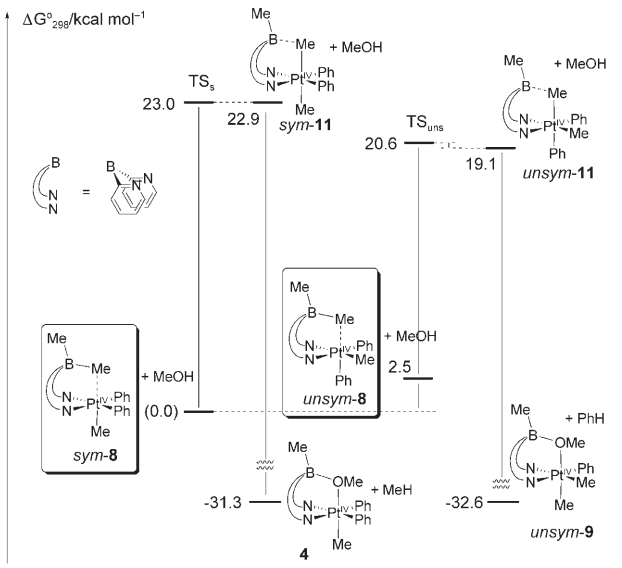


Figure 4. DFT-calculated Gibbs reaction energies for the transformation of **8** into *sym*- and *unsym*-**11**.

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 [D$_3$]methanol, and produces the methoxyborato complex *unsym*-**9** and benzene, quantitatively, according to NMR spectroscopy [Eq. (4)].

$$[\mathrm{LPt^{IV}R_2Me}] + \mathrm{MeOH} \rightarrow [\eta^3\text{-}\{\mathrm{py_2BMe(OMe)}\}\mathrm{Pt^{IV}RMe_2}] + \mathrm{RH}$$
$$\mathrm{R = Me\ (\mathbf{7}),\ Ph\ (\mathbf{8})} \qquad \mathrm{R = Me\ (\mathbf{10}),\ Ph\ (\mathit{unsym}\text{-}\mathbf{9})} \tag{4}$$

According to ^{1}H and ^{13}C 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 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.

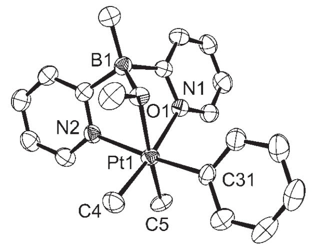


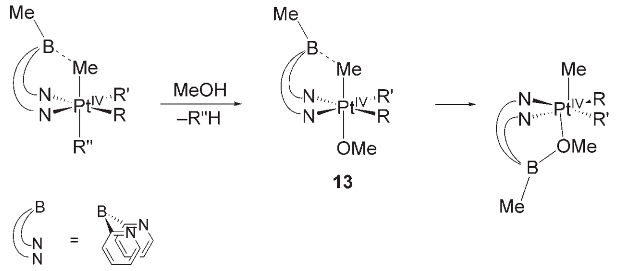
Figure 5. ORTEP drawing of complex **9** showing 50 % probability ellipsoids.

The stereochemical course of the boron-to-platinum(IV) migration of the methyl group was revealed by experiments involving the ^{13}C-labeled complex [^{13}C]-**7**, which was prepared using ^{13}CH$_3$I [Eq. (3)]. According to ^{1}H NMR spectroscopy, the label is distributed statistically between the equatorial and axial positions (33 % ^{13}C for each of the Pt^{IV}Me groups) 10 minutes after preparation of [^{13}C]-**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 [^{13}C]-**7** in CD$_3$OH leads to the formation of a 2:1 mixture of CH$_4$ and ^{13}CH$_4$ along with complex **10**, which exhibits a signal for the equatorial CH$_3$ groups with ^{13}C satellites corresponding to 33 % ^{13}C enrichment and a signal for the axial CH$_3$ group with ^{13}C satellites corresponding to the natural ^{13}C abundance. A similar behavior was observed for [^{13}C]-**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]

$$[\mathrm{LPt^{IV}R_2Me}] \rightarrow [\mathrm{(py_2BMe)Pt^{IV}R_2Me_2}]$$
$$\mathrm{R = Me\ (\mathbf{7}),\ Ph\ (\mathbf{8})\ R = Me\ (\mathbf{12}),\ Ph\ (\mathbf{11})} \tag{5}$$

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$_{\mathrm{uns}}$), 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 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]



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

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 O$_2$H or OH formed according to one of the mechanisms suggested for the oxidation of alkylplatinum(II) complexes by O$_2$ [Eqs. (6) and (7)].[12,13]

$$[\mathrm{LPt^{II}R_2}]^- + \mathrm{H_2O} + \mathrm{O_2} \rightarrow [\mathrm{LPt^{IV}R_2(O_2H)}] + \mathrm{OH^-} \tag{6}$$

$$[\mathrm{LPt^{IV}R_2(O_2H)}] + [\mathrm{LPt^{II}R_2}]^- + \mathrm{H_2O} \rightarrow 2\,[\mathrm{LPt^{IV}R_2(OH)}] + \mathrm{OH^-} \tag{7}$$

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.

Received: March 21, 2007

Keywords: agostic interactions · boron · platinum · reaction mechanisms · transmetalation

---

[1] *Homogeneous Catalysis, Understanding the Art* (Ed.: P. W. N. M. van Leeuwen), Kluwer, Boston, **2004**.

[2] F. Barrios-Landeros, J. F. Hartwig, *J. Am. Chem. Soc.* **2005**, *127*, 6944 – 6945.

[3] R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, 3rd ed., Wiley, Hoboken, NJ, **2005**.

[4] P. Zhao, C. D. Incarvito, J. F. Hartwig, *J. Am. Chem. Soc.* **2007**, *129*, 1876 – 1877, and references therein.

[5] K. Siegmann, P. S. Pregosin, L. M. Venanzi, *Organometallics* **1989**, *8*, 2659 – 2664.

[6] E. Khaskin, P. Y. Zavalij, A. N. Vedernikov, *J. Am. Chem. Soc.* **2006**, *128*, 13054 – 13055.

[7] a) U. Fekl, K. I. Goldberg, *Adv. Inorg. Chem.* **2003**, *54*, 259 – 320, and references therein; b) S. M. Kloek, K. I. Goldberg, *J. Am. Chem. Soc.* **2007**, *129*, 3460 – 3461.

[8] M. J. Ingleson, M. F. Mahon, A. S. Weller, *Chem. Commun.* **2004**, 2398 – 2399.

[9] A. E. Shilov, G. B. Shulpin, *Chem. Rev.* **1997**, *97*, 2879 – 2932.

[10] J. E. Hux, R. J. Puddephatt, *Inorg. Chim. Acta* **1985**, *100*, 1 – 5.

[11] An alternative mechanism suggested by one of the referees differs from that shown in Figure 4 by the order in which protonolysis of the Pt^{IV}–C bond and boron-to-platinum methyl transfer occur. To the best of our knowledge, trimethylplatinum(IV) complexes are not prone to protodemetalation reactions, whereas tetramethylplatinum(IV) species can react with acids (Ref. [10]). The pronounced difference in the basicity of $\{Pt^{IV}R_4\}$ and $\{Pt^{IV}R_3\}$ species argues against the alternative mechanism where protonolysis of a Pt^{IV}–C bond precedes boron-to-platinum methyl transfer.

[12] V. V. Rostovtsev, L. M. Henling, J. A. Labinger, J. E. Bercaw, *Inorg. Chem.* **2002**, *41*, 3608 – 3619.

[13] J. R. Khusnutdinova, P. Y. Zavalij, A. N. Vedernikov, *Organometallics* **2007**, *26*, 2402 – 2413.