Communication
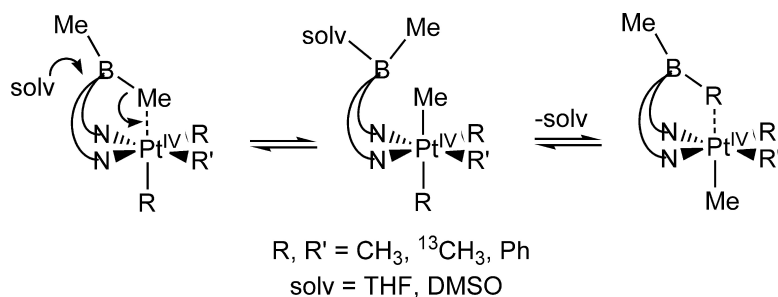
Bidirectional Transfer of Phenyl and Methyl Groups between Pt and Boron in Platinum Dipyridylborato Complexes

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

R, R' = CH$_3$, ^{13}CH$_3$, Ph
solv = THF, DMSO

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Bidirectional Transfer of Phenyl and Methyl Groups between Pt^IV and Boron in Platinum Dipyridylborato Complexes

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Organoboron compounds are widely used in organic synthesis as a source of nucleophilic hydrocarbyl groups for transition metal catalyzed construction of C−C bonds.[1] Despite the widespread use of Suzuki−Miyaura coupling reaction, the mechanism of one of its key steps (b, Scheme 1) involving hydrocarbyl transfer between boron and a transition metal atom catalyst is poorly studied.[2−4] Previously we reported facile boron-to-Pt^IV methyl group transfer observed upon oxidation of Pt^II with O2 in dimethyldipyridylborato complexes Na[LPt^IIR2] (Scheme 2; R = Me, **1**; Ph, **4**) and in LPt^IVR2Me complexes (R = Me, **2**; Ph, **5**) in hydroxylic solvents R′OH, both leading to products of the structural type **3**.[4] The hydrocarbyl migration was suggested to occur as an electrophilic substitution at one of the carbon atoms of the BMe2 fragment with five-coordinate electrophilic Pt^IV assisted by nucleophilic attack of the solvent at the boron atom. In this work we disclose that *methyl* migration between B and Pt^IV can be *reversible* and that phenyl group transfer between B and Pt^IV centers can occur in both directions, from B to Pt^IV and from Pt^IV to B. These observations imply, in particular, that under certain basic conditions there might be an additional pathway leading to products of homocoupling of organoboron compounds[5] occurring along with the desired cross-coupling between a boron reagent and an electrophile.

Considering formation of a strong B−O bond in **3** as the driving force of B-to-Pt^IV hydrocarbyl migration in hydroxylic solvents[4] we hypothesized that in the presence of a poor nonhydroxylic Lewis base hydrocarbyl transfer between B and Pt^IV may become reversible. To probe reversibility of methyl transfer in **2** a Pt−^13C-labeled complex [Me2B(py)2]Pt^IVMe2*Me, **2-Pt-^13C**, was prepared from **1** and 1 equiv of *MeI (*Me = ^13CH3). Five minutes after mixing the reagents, a statistical distribution of the label among the three Pt-bound methyl ligands was reached resulting in their effective 33% ^13C-enrichment (compare to fluxional behavior of **5**[4]). The labeled complex **2-Pt-^13C** is stable in benzene-d6 or THF-d8 in the temperature range of 20°−60 °C for at least 2 weeks and shows no sign of ^13C-label incorporation in the BMe2 moiety.[7] This situation changed when we used DMSO-d6, a stronger nonhydroxylic Lewis base compared to THF, as the solvent. Slow formation of **2-B-^13C** isomers with the ^13C-label evenly distributed between *exo-* (J_{CH} = 115 Hz) and *endo-* (J_{CH} = 109.3 Hz) methyl groups of the BMe2 fragment was seen at 60 °C with the observed pseudo-first order rate constant of (5.1 ± 0.2) ×10^−5 min^−1 (Scheme 3). The ^13C-enrichment for each of the boron-bound methyl groups was 15% versus the expected statistical value of 20% after 19 days (Figure 1).

To account for these observations we suggest the following mechanism (Scheme 3). The first step involves B-to-Pt^IV migration leading to a tetrahydrocarbyl Pt^IV species **6** that is facilitated by concurrent nucleophilic attack of solvent at the boron atom. Dissociation of one of the pyridine nitrogens from Pt^IVMe(R)2R′ in **6** with subsequent scrambling of hydrocarbyl groups in the resulting five coordinate metal intermediate, re- coordination of the pyridyl group leading to transient **6′** and, ultimately, ^13CH3 group
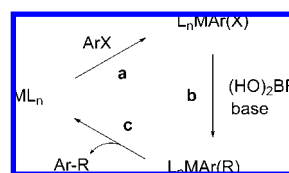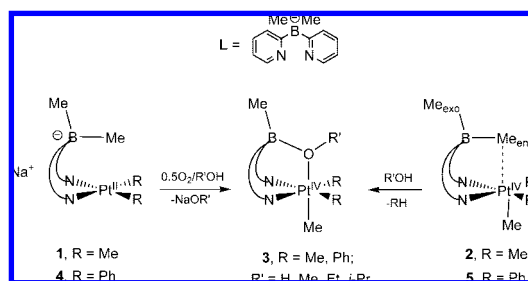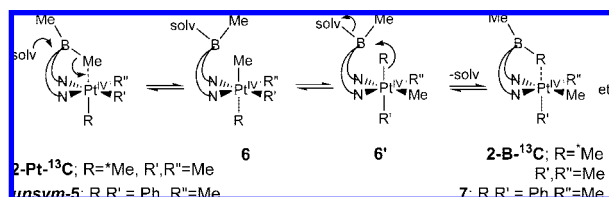
transfer from Pt^IV to B leads to an *endo*-B−^13C-labeled species, **2-B-^13C**. Finally, the interconversion of the *endo-* to the *exo*-B-^13C labeled **2-B-^13C** might imply platinum chelate ring inversion combined with a Berry pseudorotation at the 5-coordinate Pt^IV center.[8]

Similar experiments were performed with the diphenyl analogue of **2**, LPt^IVPh2Me, **5**. No reaction was seen in benzene solutions of **5** at 60 °C after 3 days. By contrast, isomerization of **5** to C_s-symmetrical phenylborato complex [MeBPh(py)2]Pt^IVPhMe2 **7**, involving Pt^IV-to-B phenyl migration, was complete at 60 °C after 24 h in THF solution. As in the case of trimethyl Pt^IV complex **2**, the use of more Lewis basic solvent DMSO allowed for faster transformation; isomerization of **5** to **7** was possible at 22 °C. These observations also suggest that **7** is more thermodynamically stable than **5**. According to our DFT estimates, the standard Gibbs energy of isomerization of **5** to **7** is −3.1 kcal/mol. The effect of the boron-bound Ph group on the position of the hydrocarbyl transfer equilibrium shown in Scheme 3 may be due to a better ability of the B−Ph fragment to donate to the Pt^IV center compared to the B−Me group in **5**. No second Pt^IV-to-B phenyl migration that would lead to diphenyldipyridylborato complex L′Pt^IVMe3, **8** (vide infra) was observed in this system.

Scheme 1

Scheme 2

Scheme 3
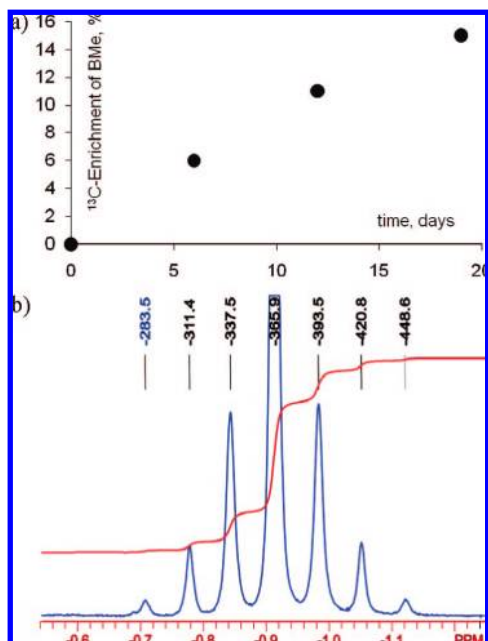
Figure 1. Transformation of **2-Pt**-^{13}**C** to **2-B**-^{13}**C** in DMSO-d_6 solution at 60 °C: (a) plot of the ^{13}C-enrichment of a boron-bound methyl group vs time; (b) high-field region of ^{1}H NMR spectrum of a mixture of 25% **2-Pt**-^{13}**C** and 75% **2-B**-^{13}**C** with ^{195}Pt and ^{13}C satellites after 19 days. The horizontal axis labels are in ppm; the peak labels are in Hertz.
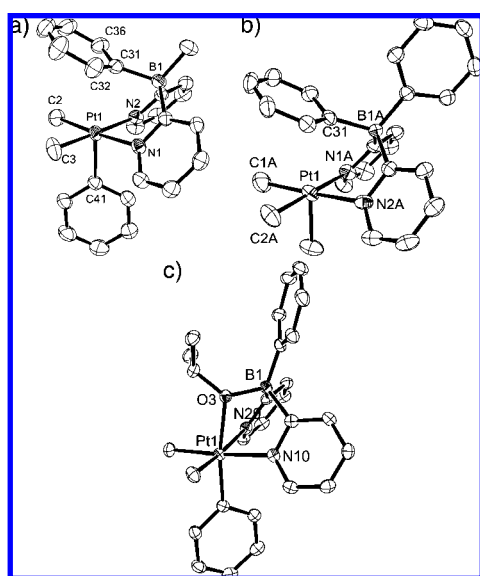
Figure 2. ORTEP drawings (50% probability ellipsoids) of complexes **7** (a), **8** (b), and **9** (c). Hydrogen atoms are omitted for clarity.
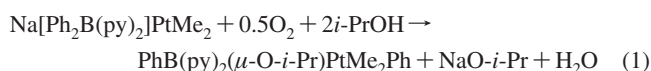
Complex **7** could be isolated from the solution in THF in pure form in 89% yield and fully characterized including single crystal X-ray diffraction analysis (Figure 2a). The compound features a phenyl group attached to B with the B1−C31 distance of 1.654(4) Å. The B-bound phenyl *ipso*-carbon atom is involved in a weak interaction with the Pt^{IV} with Pt1−C31 separation of 2.646(3) Å.

Interestingly, compared to the methyl group exchange between B and Pt^{IV} in **2**, a similar methyl for phenyl group exchange in **5** is more facile under same conditions. This behavior might stem from weaker trans-influence of R = phenyl versus methyl[9] affecting the relative kinetic accessibility of intermediate **6** and/or involvement of the pyridyl dissociation mechanism in the subsequent

isomerization of **6** and **6**′. The presence of a bulky Ph group in the equatorial plane of **6** would diminish the energy required for dissociation of an adjacent pyridyl.

To probe the option of B-to-Pt^{IV} Ph group transfer we attempted transformation of **8** to its isomer **7**. Complex **8**[8] was characterized by ^{1}H and ^{13}C NMR spectroscopy and by X-ray diffraction (Figure 2b). Similar to **7**, one of the boron-bound phenyl groups in **8** is involved in stabilization of the Pt^{IV} center with a B1A−C31A distance of 1.643(7) Å and Pt1A−C31A distance of 2.624(4) Å. According to our DFT calculations, the Gibbs energy of isomerization of **8** to **7** is −0.4 kcal/mol. No changes were seen in ^{1}H NMR spectra of **8** in both THF-d_8 and DMSO-d_6 after 5 days at 60 °C. We presume that the stability of phenylborato Pt^{IV} species **8** as well as **7** might be of kinetic origin, and solvent nucleophilicity is not sufficient to decrease the reaction barrier noticeably.

The viability of B-to-Pt^{IV} phenyl group transfer in Pt−dipyridylborate systems was demonstrated in a reaction of Na[L′Pt^{II}Me$_2$] with O$_2$ in *i*-PrOH solution leading to isopropoxo-bridged Pt^{IV}Me$_2$Ph complex **9** (Figure 2c) (eq 1).

$$Na[Ph_2B(py)_2]PtMe_2 + 0.5O_2 + 2i\text{-PrOH} \rightarrow$$
$$PhB(py)_2(\mu\text{-O-}i\text{-Pr})PtMe_2Ph + NaO\text{-}i\text{-Pr} + H_2O \quad (1)$$

Strongly nucleophilic *i*-PrO− present in the reaction mixture might contribute substantially in diminishing the activation barrier of the overall B-to-Pt^{IV} phenyl group transfer.

In summary, we showed that phenyl group migration between Pt^{IV} and B centers can occur in both directions and is accelerated by Lewis bases. The prevailing product is determined by a stronger donor group bridging Lewis acidic B and Pt^{IV} centers. In the case of dimethylborato trimethyl Pt^{IV} complex **2** and the use of aprotic weakly nucleophilic DMSO, methyl migration between Pt^{IV} and B centers is reversible.

Supporting Information Available: Experimental details, CIF files for **7**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) The BMe$_2$ fragment in **2-Pt**-^{13}**C** produces two signals in the ^{1}H NMR spectrum in THF-d_8 at +0.14 ppm (BMe$_{exo}$) and−0.91 ppm (agostic methyl group, BMe$_{endo}$, J_{PtH} = 58.1 Hz).
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