

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^{II}R₂] (Scheme 2; R = Me, 1; Ph, 4) and in $LPt^{IV}R_2Me$ 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 PtIV 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 compounds⁵ occurring along with the desired crosscoupling 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 solvents⁴ 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 $Pt^{-13}C$ labeled complex [Me₂B(py)₂]Pt^{IV}Me₂*Me, **2-Pt**-¹³C, was prepared from 1 and 1 equiv of *MeI (*Me = 13 CH₃). 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 5⁴). The labeled complex 2-Pt-¹³C is stable in benzene- d_6 or THF d_8 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- d_6 , a stronger nonhydroxylic Lewis base compared to THF, as the solvent. Slow formation of **2-B**-¹³**C** 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 pseudofirst order rate constant of $(5.1 \pm 0.2) \times 10^{-5} \text{ min}^{-1}$ (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^{IV}Me(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

Scheme 1



Scheme 2





Scheme 3



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^{IV}Ph₂Me, 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^{IV}PhMe₂7, 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 boronbound 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^{IV}Me₃, 8 (vide infra) was observed in this system.



Figure 1. Transformation of 2-Pt-¹³C to 2-B-¹³C in DMSO- d_6 solution at 60 °C: (a) plot of the ¹³C-enrichment of a boron-bound methyl group vs time; (b) high-field region of ¹H NMR spectrum of a mixture of 25% 2-Pt-¹³C and 75% 2-B-¹³C with ¹⁹⁵Pt and ¹³C 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 methyl⁹ 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 ¹H and ¹³C 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 ¹H 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}Me₂] with O_2 in *i*-PrOH solution leading to isopropoxo-bridged Pt^{IV}Me₂Ph complex **9** (Figure 2c) (eq 1).

$$\begin{split} \text{Na}[\text{Ph}_2\text{B}(\text{py})_2]\text{PtMe}_2 + 0.5\text{O}_2 + 2i\text{-}\text{PrOH} \rightarrow \\ \text{PhB}(\text{py})_2(\mu\text{-}\text{O}\text{-}i\text{-}\text{Pr})\text{PtMe}_2\text{Ph} + \text{NaO}\text{-}i\text{-}\text{Pr} + \text{H}_2\text{O} \quad (1) \end{split}$$

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.

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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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