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Arylplatinum Complexes with Arylboronate Ligands. Their Preparation, Structure, and Relevance to Transmetalation

Ivayla Pantcheva, Yasushi Nishihara,[†] and Kohtaro Osakada*

Chemical Resources Laboratory, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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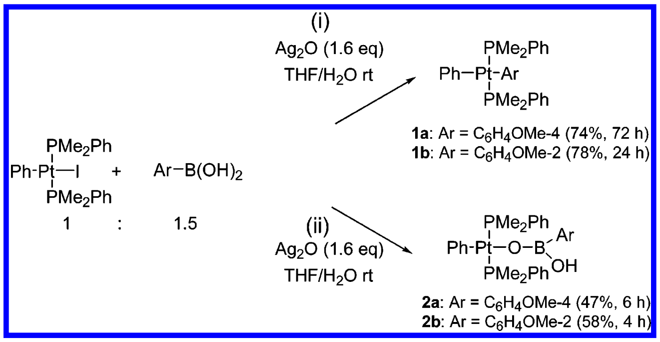
Summary: The reactions of arylboronic acids with trans-PtPh(I)(PMe_2Ph)$_2$ afford new arylboronato platinum complexes, trans-PtPh(OB(OH)Ar)(PMe_2Ph)$_2$, and diarylplatinum complexes, trans-PtPh(Ar)(PMe_2Ph)$_2$.

Transmetalation of arylboronic acid with the complexes of late transition metals, Pd,[1] Rh,[2] and Pt,[3] is involved as a crucial step in synthetic organic reactions such as the cross-coupling and 1,4-addition reactions catalyzed by these metals. There have been only a few reports on the stoichiometric transmetalation of arylboronic acids with organotransition-metal complexes, although transmetalation of organomagnesium and organoaluminum compounds provides a common route to the alkyl and aryl complexes of transition metals. Arylpalladium halogeno complexes undergo transmetalation by arylboronic acids to produce diarylpalladium complexes in the presence of a base such as OH^- or Ag_2O. This reaction has been studied in relation to the mechanism of the cross-coupling reaction catalyzed by the Pd complexes. The added base is proposed to have a dual role in the transmetalation: activation of the B−C bond of the arylboronic acid and of the Pd−halogen bond of the complex.[4,5] A dicationic palladium complex with labile MeCN ligands, $[Pd(dppe)(NCMe)_2]^{2+}$, reacts with arylboronic acid without addition of base to yield a complex with a Pd−Ph bond.[6] $PtCl_2(P(OAr)_3)_2$ also catalyzes the cross-coupling reaction of arylboronic acids with aryl halides, which probably involves a transmetalation reaction.[3] Studies on the stoichiometric reaction of arylboronic acids with Pt complexes would reveal detailed mechanisms of transmetalation using Pt complexes. In this paper, we report the reaction of arylboronic acids with a phenylplatinum iodo complex in the presence of base and isolation of a new type of platinum(II) complex having an arylboronato (O−B(OH)−Ar) ligand.[7]

Scheme 1



The reactions of $ArB(OH)_2$ (Ar = C_6H_4OMe-4, C_6H_4OMe-2) with *trans*-PtPh(I)(PMe_2Ph)$_2$ in the presence of Ag_2O and H_2O produce the diarylplatinum complexes, *trans*-PtPh(Ar)(PMe_2Ph)$_2$ (**1a**, Ar = C_6H_4OMe-4; **1b**, Ar = C_6H_4OMe-2), at room temperature (24−72 h), as shown in Scheme 1. Reaction i includes intermolecular transfer of the aryl group from B to Pt.

The reaction mixtures after 4−6 h contain new Pt complexes with an arylboronate ligand, *trans*-PtPh(OB(OH)Ar)(PMe_2Ph)$_2$ (**2a**, Ar = C_6H_4OMe-4; **2b**, Ar = C_6H_4OMe-2). Figure 1 shows the molecular structures of **1a** and **2a** determined by X-ray crystallography.[8] Both complexes have typical square-planar geometry around the Pt(II) center. The Pt−C bond distance of **2a** (2.000(9) Å) is shorter than those of **1a** (2.095(6) and 2.096(6) Å), which is ascribed to the trans influence of the aryl ligand being greater than that of the arylboronate ligand. The geometry of **2a** with the arylboronato and phenyl ligands at mutually trans positions renders the Pt−O bond (2.094(6) Å) longer than those of the previously reported alkoxoplatinum complexes.[9] The B−O1 bond length (1.32(1) Å) is slightly shorter than B−O2 (1.39(1) Å), and both distances fall into the distance of triangular BO_3 groups of the organoboron compounds.[10] Complexes **2a** and **2b**, once isolated, are stable in solution; the ^1H and $^{31}P\{^1H\}$ NMR spectra do

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[†] Present address: Department of Chemistry, Okayama University, 3-1-1 Tsushimanaka, Okayama 700-8530, Japan.

(1) For reviews on the Suzuki−Miyaura reaction see: (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Miyaura, N. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI: London, 1998; Vol. 6, pp 187−243. (c) Stanforth, S. P. *Tetrahedron* **1998**, *54*, 263−303. (d) Tamao, K.; Miyaura, N. In *Topics in Current Chemistry*; Springer-Verlag: Berlin, 2002; Vol. 219, p 11.

(2) (a) Hayashi, T.; Takahashi, M.; Takaya, Y.; Ogasawara, M. *J. Am. Chem. Soc.* **2002**, *124*, 5052. (b) Hayashi, T.; Senda, T.; Ogasawara, M. *J. Am. Chem. Soc.* **2000**, *122*, 10716.

(3) Bedford, R. B.; Hazelwood, S. L.; Albisson, D. A. *Organometallics* **2002**, *21*, 2599.

(4) Aliprantis, A. O.; Canary, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 6985.

(5) (a) Nishihara, Y.; Onodera, H.; Osakada, K. *Chem. Commun.* **2004**, 192. (b) Osakada, K.; Onodera, H.; Nishihara, Y. *Organometallics* **2005**, *24*, 190.

(6) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Organometallics* **2004**, *23*, 4317.

(7) There have been no reports on transition-metal complexes having an arylboronato ligand (M−O−B(OH)−Ar). A limited number of complexes with similar coordination bonds have been reported. See: Bartlett, R. A.; Ellison, J. J.; Power, P. P.; Shoner, S. C. *Inorg. Chem.* **1991**, *30*, 2888 (M−O−B−Ar_2, M = Fe, Mn). Miyamoto, T.; Ichida, H. *Chem. Lett.* **1991**, 435 (Pt−O−B(OH)−O−). Vidovic, D.; Moore, J. A.; Jones, J. N.; Cowley, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 4566 (Al−O−B(N−)$_2$).

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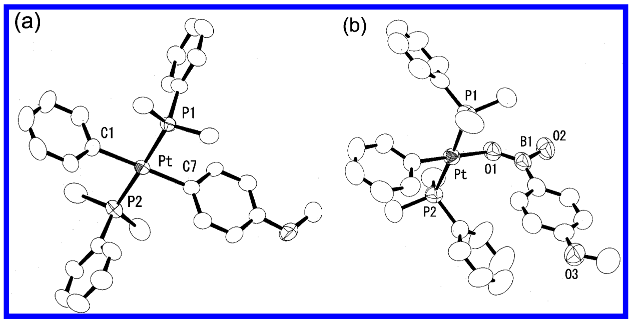

Figure 1. ORTEP drawings of (a) **1a** and (b) **2a** with 50% thermal ellipsoid plotting. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg) of **1a**: Pt−C1 = 2.095(6), Pt−C7 = 2.096(6), Pt−P1 = 2.283(2), Pt−P2 = 2.283(3); P1−Pt−P2 = 177.84(7), P1−Pt−C1 = 90.1(2), P1−Pt−C7 = 90.7(2), P2−Pt−C1 = 88.1(2), P2−Pt−C7 = 91.2(2), C1−Pt−C7 = 179.0(2). Selected distances (Å) and angles (deg) of **2a**: Pt−C1 = 2.000(9), Pt−O1 = 2.094(6), Pt−P1 = 2.283(3), Pt−P2 = 2.277(3); P1−Pt−C1 = 91.6(3), P1−Pt−P2 = 172.8(1), P1−Pt−O1 = 87.0(2), P2−Pt−O1 = 91.5(2), P2−Pt−C1 = 89.8(3), C1−Pt−O1 = 178.4(3).

not change for 24 h at room temperature. The ^{1}H NMR spectra contain an apparent triplet due to virtual coupling at 1.18−1.30 ppm. The ^{31}P{^{1}H} and ^{11}B NMR spectra of **2a** and **2b** in C_6D_6 exhibit signals with reasonable positions and coupling constants (δ_P −3.36 for **2a** (J(PtP) = 2890 Hz) and −2.36 for **2b** (J(PtP) = 3002 Hz); δ_B 29.64 for **2a** and 28.27 for **2b**). Figure 2 depicts the change in amounts of the complexes during reaction i using (4-methoxyphenyl)boronic acid. The starting complex *trans*-PtPh(I)(PMe$_2$Ph)$_2$ is consumed and converted into a mixture of **2a** and uncharacterized Pt complexes.[11,12] Further reaction leads to the formation of **1a** almost quantitatively.

Ag$_2$O may play dual roles in the reactions of Scheme 1: abstraction of the iodo ligand from the starting complex and activation of the arylboronate ligand. Since OH$^-$ could coordinate to the B center of the arylboronate bonded to Pt and activate the B−C bond, the reaction of OH$^-$ with **2a** was conducted. Stirring a THF solution of **2a**, 4-methoxyphenylboronic acid, and TBAOH$^-$ (TBA = NBu$_4^+$) in a 1:1.5:1.6 molar ratio produces a mixture of the phenylplatinum hydroxo complex PtPh(OH)(PMe$_2$Ph)$_2$ and **2a** in a 60:40 molar ratio. Since the reaction mixture of Ag$_2$O with PtPh(I)(PMe$_2$Ph)$_2$ also forms PtPh(OH)(PMe$_2$Ph)$_2$ in part, this complex may be involved in the upper reactions of Scheme 1. PtPh(OH)(PMe$_2$Ph)$_2$, prepared as shown above, has a trans structure initially but undergoes isomerization to produce a mixture of cis and trans isomers during the reaction.[13] Addition of a large excess amount of (4-methoxyphenyl)boronic acid to the reaction mixture regenerates **2a** via reversible exchange of the OH and arylboronato ligands in the presence of a base. The reaction of **2a**, (4-methoxyphenyl)boronic acid, and TBAOH$^-$ in a 1:1.5:10 molar ratio forms mixtures of PtPh(OH)(PMe$_2$Ph)$_2$ and **1a** in a 58:62 molar ratio after 3 h and in a 25:75 molar ratio after 36 h. Scheme 2 summarizes the results of the reactions.

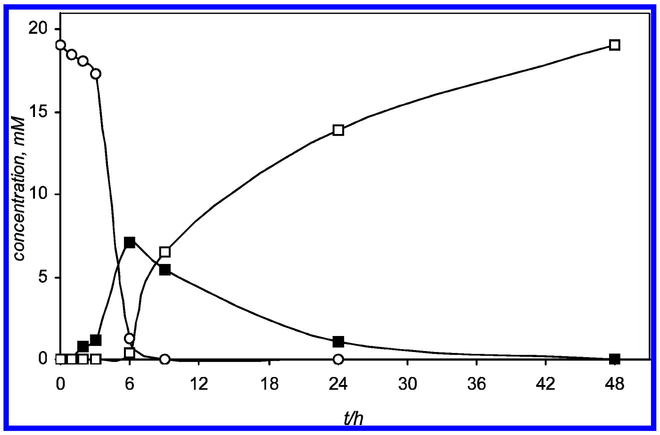

Figure 2. Time profile of the reaction of (4-methoxyphenyl)boronic acid with PhPt(I)(PMe$_2$Ph)$_2$ in the presence of Ag$_2$O: (○) PtPh(I)(PMe$_2$Ph)$_2$; (□) **1a**; (■) **2a**. PtPh(I)(PMe$_2$Ph)$_2$ (0.16 mmol), Ag$_2$O (0.26 mmol), and (4-methoxyphenyl)boronic acid (0.24 mmol) are reacted in THF/H$_2$O (8 mL/0.4 mL) in the presence of Ph$_2$CH$_2$ (internal standard, 0.24 mmol). Part of the solution (ca. 0.7 mL) is transferred to a Schlenk flask periodically. After removal of the solvent of each sample by evaporation, the product is characterized by ^{1}H NMR.

A mixture of **2a** and (4-methoxyphenyl)boronic acid in the presence of Ag$_2$O and H$_2$O also produces **1a**. Formation of diarylplatinum complexes requires a base such as Ag$_2$O or OH$^-$, because leaving a mixture of **2a** and (4-methoxyphenyl)boronic acid in THF does not produce the diarylplatinum complex at all. Addition of (2-methoxyphenyl)boronic acid to a THF solution of **2a** results in partial conversion of the complex into **2b** via exchange of the arylboronate ligand, even in the absence of Ag$_2$O. This ligand exchange makes it difficult to determine by crossover experiments whether the formation of **1a** from **2a** in Scheme 2 is an intramolecular reaction.

In summary, we succeeded in the isolation of platinum complexes that contain a unique arylboronate

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(8) Crystal data and details of the structure refinement of **1a**: $C_{29}H_{34}OP_2Pt$, M_r = 655.62, 0.32 × 0.28 × 0.05 mm, monoclinic, a = 7.585(3) Å, b = 39.428(4) Å, c = 9.540(3) Å, β = 110.67(2)°, V = 2669(1) Å^3, space group $P2_1/a$ (No. 14), Z = 4, D_{calcd} = 1.631 g cm^{-3}, F(000) = 1296.00, μ(MoKα) = 5.38 mm^{-1}, Mo Kα radiation (λ = 0.710 70 Å), 6687 total reflections measured, 6241 unique reflections (R_{int} = 0.033), 4249 observations (I > 3.00σ(I)), 298 variables, R(I > 3.00σ(I)) = 0.035, R_w(I > 3.00σ(I)) = 0.035. Crystal data and details of the structure refinement of **2a**: $C_{29}H_{35}BO_3P_2Pt$, M_r = 699.44, 0.30 × 0.22 × 0.04 mm, monoclinic, a = 13.683(9) Å, b = 9.430(3) Å, c = 23.089(5) Å, β = 92.10(3)°, V = 2977(2) Å^3, $P2_1/n$ (No. 14), Z = 4, D_{calcd} = 1.560 g cm^{-3}, F(000) = 1384.00, μ(Mo Kα) = 4.83 mm^{-1}, Mo Kα radiation (λ = 0.710 70 Å), 7567 total reflections measured, 7271 unique reflections (R_{int} = 0.041), 4080 observations (I > 3.00σ(I)), 325 variables, R(I > 3.00σ(I)) = 0.054, R_w(I > 3.00σ(I)) = 0.046.

(9) (a) Strukul, G.; Michelin, R. A.; Orbell, J.; Randaccio, L. *Inorg. Chem.* **1983**, *22*, 3706. (b) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163 and references therein. (c) Osakada, K.; Kim, Y.-J.; Yamamoto, A. *J. Organomet. Chem.* **1990**, *382*, 303.

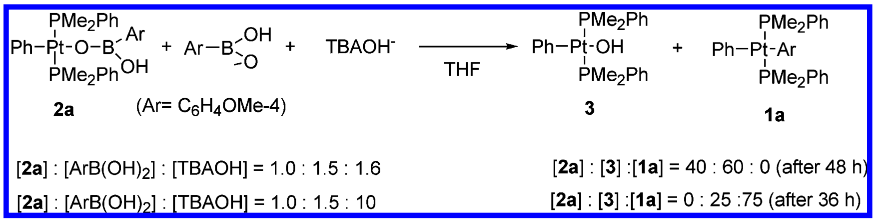
(10) Behm, H. *Acta Crystallogr., Sect. C* **1988**, *44*, 1348.

(11) Gillespie, R. J.; Bytheway, I.; Robinson, E. A. *Inorg. Chem.* **1998**, *37*, 2811.

(12) Yield of **2a** determined by ^{1}H NMR of the reaction mixture after 6 h is lower than the yield of the isolated complex from the reaction under the same conditions. It may be due to conversion of a part of the uncharacterized Pt complexes formed at this stage into **2a** during isolation process.

(13) Bennett et al. reported that the reaction of KOH with [PtPh(acetone)(PMe$_2$Ph)$_2$]$^+$ produced PtPh(OH)(PMe$_2$Ph)$_2$ as a mixture of the cis and trans isomers (Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, 119). Our attempts to prepare PtPh(OH)(PMe$_2$Ph)$_2$ via the reaction of NBu$_4^+$OH$^-$ with the cationic complex also formed a cis and trans mixture of the complex. The NMR spectra of the reaction mixture in Scheme 2 contain signals whose positions and coupling constants are identical with the data of Bennett. The initial product of our reactions is *trans*-PtPh(OH)(PMe$_2$Ph)$_2$, although it could not be isolated due to facile change of it into the cis isomer.

Scheme 2



ligand (O−B(OH)−Ar) from the reaction of arylboronic acid with a phenylplatinum iodo complex. These new complexes can be regarded as possible intermediates of the stoichiometric transmetalation of arylboronic acid with Pt complexes on the basis of the results of the reactions in Schemes 1 and 2, although a part of the detailed reaction mechanism remains obscured.

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Supporting Information Available: Text giving experimental details and characterization data for the new compounds prepared in this paper and text and tables giving details of the X-ray crystal structure determinations of **1a** and **2a**; X-ray data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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