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Synthesis and Reactivity of a Platinum(II) Complex with a Chelating Dehydro(arylboronic anhydride) Ligand. Transmetalation of Arylboronic Acid

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The reaction of $ArB(OH)_2$ (Ar = C_6H_4OMe-4, Ph, C_6H_4COMe-4) with PtI_2(dppe) in THF in the presence of Ag_2O and H_2O at room temperature produced a Pt complex with a chelating dehydro(arylboronic anhydride) ligand, $\overline{\mathrm{Pt(OBArOBArO)}}$(dppe) (**1a**, Ar = C_6H_4OMe-4; **1b**, Ar = Ph; **1c**, Ar = C_6H_4COMe-4). The complexes were characterized by NMR spectroscopy and X-ray crystallography. Reactions of protonic acids, such as HCl, CF_3COOH, and CH_3COOH, with **1a** yielded complexes with chloro and carboxylate ligands, PtX_2(dppe) (**2**, X = Cl; **3**, X = $OCOCF_3$; **4**, X = OCOMe). The complexes **1a**−**c** react with arylboronic acids bearing the same aryl group as the ligands of the complexes to form diarylplatinum complexes, $PtAr_2$(dppe) (**5a**, Ar = C_6H_4OMe-4; **5b**, Ar = Ph; **5c**, Ar = C_6H_4COMe-4), respectively. Reactions of 4-$MeCOC_6H_4B(OH)_2$ with **1b** and of $PhB(OH)_2$ with **1c** in 2:1 molar ratios form mixtures of three diarylplatinum complexes in a statistical ratio.

Introduction

Arylboronic acids have been employed as a convenient source of aryl groups in synthetic organic reactions catalyzed by Pd, Rh, Ni, and Pt complexes.[1] These reactions, including cross-coupling with organic halides (Suzuki−Miyaura coupling)[2] and the 1,4-addition of an aryl group to α,β-unsaturated carbonyl compounds,[3] are believed to involve the activation of the B−C bond promoted by transition metals as a crucial step. Despite the wide use of the above catalytic reactions, there have been a few reports on the stoichiometric reactions of arylboronic acids with transition-metal complexes, yielding aryltransition-metal complexes via the activation of the B−C bond. The transmetalation of aryllithium, arylmagnesium, and arylaluminum reagents provides a general method of preparing aryltransition-metal complexes.[4] Arylpalladium[5−7] and arylrhenium[8] complexes have been obtained from the transmetalation of arylboronic acid with complexes of these metals. Recently, our group as well as that of Clarke et al. have reported the transmetalation of arylboronic acids with Pt complexes.[9,10] The reaction of arylboronic acids with *trans*-$PtPh(I)(PMe_2Ph)_2$ in the presence of Ag_2O/H_2O afforded a platinum complex containing an arylboronate ligand, *trans*-$Pt(OB(OH)C_6H_4OMe\text{-}4)(Ph)(PMe_2Ph)_2$.[9] This complex further reacts with a mixture of 4-$MeOC_6H_4B(OH)_2$ and Ag_2O in the presence of H_2O to yield *trans*-$Pt(C_6H_4OMe\text{-}4)(Ph)(PMe_2Ph)_2$ via the activation of the B−C bond of the arylboronate ligand of the complex or that of the added arylboronic acid, and the transfer of the aryl group from arylboronic acid to PtPh(Br)(dppe) occurs in the presence of NBu_4F to form $PtPh_2$(dppe).[10]

In this paper, we report the preparation of platinum(II) complexes with a chelating dehydro(arylboronic anhydride) ligand and their reaction with arylboronic acids, affording diarylplatinum complexes via the transfer of aryl groups from boron to platinum.

Results and Discussion

PtI_2(dppe) reacts with a 2-fold molar amount of $ArB(OH)_2$ (Ar = C_6H_4OMe-4, Ph, C_6H_4COMe-4) in THF to produce $\overline{\mathrm{Pt(OBArOBArO)}}$(dppe) (**1a**, Ar = C_6H_4OMe-4; **1b**, Ar = Ph; **1c**, Ar = C_6H_4COMe-4) with a six-membered ring composed of one Pt, three O, and two B atoms. The reaction proceeds

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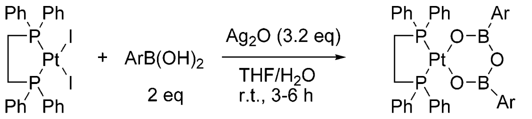
smoothly in the presence of Ag_2O and H_2O and is completed in 3−6 h at room temperature (eq 1).



(1)

1a: Ar = C_6H_4OMe-4, 86%
1b: Ar = C_6H_5, 69%
1c: Ar = C_6H_4COMe-4, 82%

There are two possible pathways for the formation of **1a**−**c**; one involves stepwise replacement of two iodo ligands with arylboronate groups and the ensuing intramolecular dehydration of the OH groups of the two arylboronate ligands, and the other is initial formation of arylboronic anhydride, which undergoes a metathesis reaction with the diiodoplatinum complex. The dehydration of two B(OH) groups giving a product with B−O−B bonds occurs easily in both the absence and the presence of transition metals. Arylboronic acids are equilibrated with the corresponding arylboroxine via reversible cleavage and the formation of B−O bonds. The cyclization of arylboronic acid accompanied by dehydration occurs in the presence of the Rh complex to form bicyclic boron-containing anions.[11] A Pt complex with a similar six-membered cyclic structure, $Pt(O_3B_2(OH)_2)(C_6H_{14}N_2)$ ($C_6H_{14}N_2$ = *trans*-1,2-cyclohexanediamine), has been prepared by the reaction of $K_2B_4O_7$ with $Pt(OH)_2(C_6H_{14}N_2)$ in the presence of $B(OH)_3$.[12]

Figure 1 shows the molecular structures of **1b**,**c** determined by X-ray crystallography. The complexes have a square-planar geometry around the Pt(II) center, which is coordinated by chelating dppe and dehydro(arylboronic anhydride) ligands. The six-membered ring formed by the coordination of the dehydro(arylboronic anhydride) to Pt is essentially planar. The Pt−O bonds of one and one-half crystallographically independent molecules of **1b** (2.033(3), 2.042(2), and 2.043(2) Å) and of two molecules of **1c** (2.026(6), 2.031(6), 2.051(6), and 2.054(6) Å) are similar to those reported for $Pt(O_3B_2(OH)_2)(C_6H_{14}N_2)$[12] (ca. 2.0 Å) or slightly longer. The average Pt−O bond distance of the complexes is shorter than the Pt−O bond of *trans*-$Pt(OB(OH)C_6H_4OMe\text{-}4)(Ph)(PMe_2Ph)_2$ (2.094(6) Å), owing to the large trans influence of the phenyl ligand situated at the trans position of the complex.[9] The distances between the coordinating oxygen and boron atoms (1.30−1.34 Å) are shorter than the B−OB bonds (1.37−1.41 Å); the standard covalent bond length is 1.36 Å. The B−O bond distances reported for compounds containing a boroxine ring ranged from 1.35 to 1.48 Å.[13] The B−O−B and O−B−O angles of **1b**,**c** are larger than 124°, whereas the O−Pt−O angle is fixed close to 90° (91.4(1), 90.0(1), 91.4(2), and 90.0(2)°).

The $^{31}P\{^1H\}$ NMR spectra of **1a**−**c** contain a single signal at 25−26 ppm flanked by ^{195}Pt satellites (*J*(PtP) = 3536−3567 Hz). The peak positions are close to those reported for mononuclear Pt(II) complexes with dppe and O ligands, $Pt(OSiEt_3)_2$(dppe) (25.9 ppm, *J*(PtP) = 3591 Hz)[14] and Pt(*S*-VANOL)(dppe) (24.7 ppm, *J*(PtP) = 3633 Hz).[15] Broad $^{11}B\{^1H\}$ NMR signals of **1b**,**c** are observed at 24−25 ppm, and their positions are normal because of the presence of tricoordinate boron nuclei in the ligands of transition-metal complexes.[13,16]

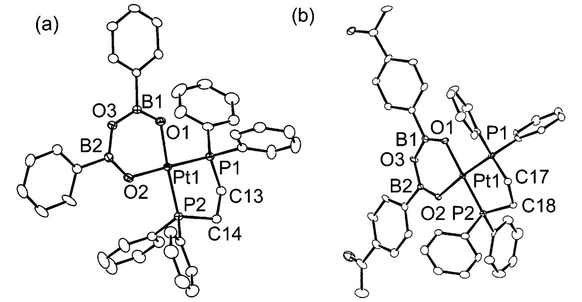
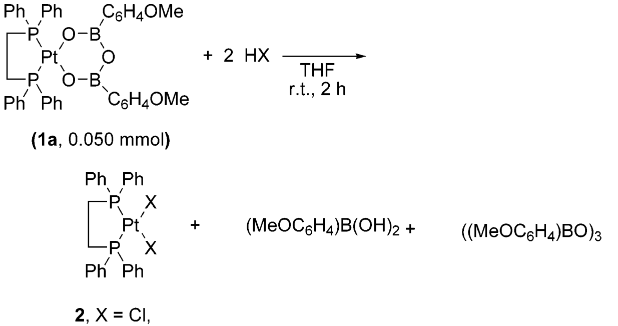


Figure 1. ORTEP drawings of (a) **1b** and (b) **1c** with ellipsoids at the 30% probability level. One of the crystallographically independent half-molecules of **1b** and one of the two independent molecules of **1c** are shown. Selected bond distances (Å) and angles (deg) of **1b** (two independent molecules): Pt1−O1 = 2.043(2), Pt1−O2 = 2.033(3), Pt1−P1 = 2.214(1), Pt1−P2 = 2.2133(8), B1−O1 = 1.322(4), B2−O2 = 1.324(4), B1−O3 = 1.398(6), B2−O3 = 1.393(4), Pt2−O4 = 2.042(2), Pt2−P3 = 2.259(7), B3−O4 = 1.320(4), B3−O5 = 1.391(5); O1−Pt1−O2 = 91.4(1), Pt1−O1−B1 = 124.6(2), Pt1−O2−B2 = 125.4(2), O1−B1−O3 = 126.0(3), O2−B2−O3 = 125.5(4), B1−O3−B2 = 126.7(2), O4−Pt2−O4′ = 90.0(1), Pt2−O4−B3 = 124.4(2), B3−O5−B3′ = 125.4(3), O4−B3−O5 = 124.8(4). Selected bond distances (Å) and angles (deg) of **1c** (two independent molecules): Pt1−O1 = 2.026(6), Pt1−O2 = 2.031(6), Pt1−P1 = 2.209(2), Pt1−P2 = 2.213(2), B1−O1 = 1.34(1), B2−O2 = 1.33(1), B1−O3 = 1.37(1), B2−O3 = 1.40(1); O1−Pt1−O2 = 91.4(2), Pt1−O1−B1 = 124.2(6), Pt1−O2−B2 = 125.3(6), O1−B1−O3 = 126.8(9), O2−B2−O3 = 125.4(8), B1−O3−B2 = 126.5(7); Pt2−O6 = 2.051(6), Pt2−O7 = 2.054(6), Pt2−P3 = 2.210(2), Pt2−P4 = 2.231(2), B3−O6 = 1.33(1), B4−O7 = 1.30(1), B3−O8 = 1.38(1), B4−O8 = 1.41(1); O6−Pt2−O7 = 90.0(2), Pt2−O6−B3 = 122.6(6), Pt2−O7−B4 = 124.2(6), O6−B3−O8 = 128.0(9), O7−B4−O8 = 126.9(8), B3−O8−B4 = 124.0(7).

1a reacts with 2-fold molar amounts of HCl and of CF_3COOH to form complexes with chloro and trifluoroacetate ligands, **2** and **3**, as shown in eq 2. The NMR spectra of the reaction mixtures showed the formation of 4-$MeOC_6H_4B(OH)_2$ and the boroxine formed by the dehydrative cyclotrimerization of such a compound. The products were characterized by NMR



(2)

2, X = Cl, 0.049 mmol, 97% — 0.035 mmol — 0.020 mmol
3, X = CF_3COO, 0.045 mmol, 91% — 0.027 mmol — 0.020 mmol
4, X = CH_3COO,

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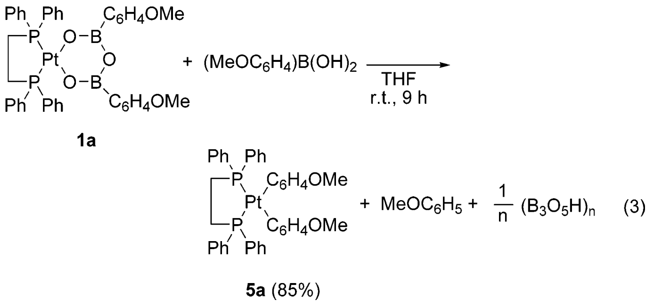
spectroscopy and elemental analyses, and **3** was characterized by X-ray diffraction analysis. The ^1H and $^{31}P\{^1H\}$ NMR data of the complexes are characteristic of platinum(II) complexes with Cl and O ligands at the trans positions of phosphorus nuclei.[17] The reaction of CH_3COOH with **1a** in an NMR tube indicates the formation of $Pt(OCOMe)_2(dppe)$ (**4**).

The reaction of $4\text{-}MeOC_6H_4B(OH)_2$ with **1a** in a 2:1 molar ratio in THF at room temperature produced a diarylplatinum(II) complex, $Pt(C_6H_4OMe\text{-}4)_2(dppe)$ (**5a**), in 85% yield, as shown in eq 3.



Pt–C and Pt–P bond distances determined by X-ray crystallography are in the normal range when compared with the parameters of diarylplatinum complexes reported previously.[18] The reaction proceeds smoothly at room temperature without any other additives, whereas the reaction of $4\text{-}MeOC_6H_4B(OH)_2$ with *trans*-$Pt(OB(OH)(C_6H_4OMe))(Ph)(PMe_2Ph)_2$ to give *trans*-$Pt(C_6H_4OMe)(Ph)(PMe_2Ph)_2$ requires the addition of Ag_2O and H_2O.[9]

^1H and ^{13}C NMR spectra of the reaction mixture in THF indicate the formation of anisole. An aqueous extract of the products shows ^{11}B NMR and IR peaks assigned to boric acid. The above reaction is considered to form an anhydride of boric acid formulated as $(B_3O_5H)_n$, which is converted into boric acid upon hydrolysis. Figure 2 shows changes in the amounts of $4\text{-}MeOC_6H_4B(OH)_2$ and **5a**, as monitored by ^1H NMR spectroscopy in THF-d_8, during the reaction. The amount of **1a** was not determined precisely, because **1a** did not dissolve completely in the solvent. The signal of the OMe hydrogen of $4\text{-}MeOC_6H_4B(OH)_2$ (3.76 ppm in THF-d_8) decreases in its intensity in peak area during the reaction for 9 h. The signal of **5a** (3.75 ppm) increases in intensity in peak area for a period of 9 h and attains a 99% yield after that. The peak area change of these ^1H NMR signals corresponds to that of the $^{31}P\{^1H\}$ NMR peaks for the same sample. A ^1H NMR signal at 3.66 ppm and a pair of $^{31}P\{^1H\}$ NMR signals at 44.8 and 29.0 ppm are also observed in the spectra during the reaction. These signals are assigned to an intermediate Pt complex for the formation of **5a**, because they keep increasing in peak area for the initial 4 h and then decrease until 9 h after start of the reaction. The Pt–P coupling constant of the former $^{31}P\{^1H\}$ NMR signal is 1716 Hz, indicating that the signal can be assigned to the phosphorus nucleus at the trans position of the aryl ligand. A much larger $J(PtP)$ value of the latter signal (4200 Hz) suggests that the phosphorus atom is bonded at the trans position of an oxygen-coordinating ligand. There are several possible structures of the ligand, because the dehydro(arylboronic anhydride) ligand could undergo B–O bond cleavage in the presence of arylboronic acid (vide infra). The amounts of intermediates are plotted in Figure 2 by assuming that the ^1H NMR signal at 3.66 ppm is caused by one OMe group contained in the complex.

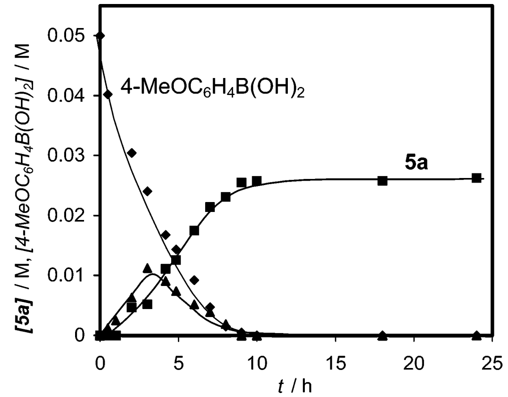


Figure 2. Plots of concentrations of $4\text{-}MeOC_6H_4B(OH)_2$ and **5a** during the reaction of $4\text{-}MeOC_6H_4B(OH)_2$ with **1a** in a 2:1 molar ratio. The amounts of $4\text{-}MeOC_6H_4B(OH)_2$ and **5a** at each time were determined by comparing the relative ^1H NMR peak areas of OMe hydrogen signals using diphenylmethane as an internal standard. Plots denoted by black triangles correspond to the intermediate complex with a 4-methoxyphenyl ligand and an O-coordinating ligand (see text).

The reactions of $PhB(OH)_2$ with **1b** and of $4\text{-}MeCOC_6H_4B(OH)_2$ with **1c** in NMR scale (THF-benzene-d_8) also form the corresponding diarylplatinum complexes **5b**,**c**, respectively. Figure 3 shows a change in the $^{31}P\{^1H\}$ NMR spectra during the former reaction: a decrease in signal peak area at 25.1 ppm ($J(PtP) = 3541$ Hz) due to **1b** and an increase in the signal peak area of the **5b** produced (41.3 ppm, $J(PtP) = 1690$ Hz). Two signals at 45.2 ppm ($J(PtP) = 1700$ Hz) and 30.0 ppm ($J(PtP) = 4195$ Hz) are also observed during the reaction and are assigned to the unsymmetrical intermediate complexes with a phenyl ligand and an O-coordinating ligand, respectively.

Reactions of $4\text{-}MeCOC_6H_4B(OH)_2$ with **1b** and of $PhB(OH)_2$ with **1c** in a 2:1 molar ratio were conducted to monitor both the transmetalation and scrambling of aryl groups by $^{31}P\{^1H\}$ NMR spectroscopy. Figure 4 shows the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture after aryl group transfer from B to Pt. The three possible diarylplatinum complexes **5b**,**c** and $Pt(C_6H_4COMe)(Ph)(dppe)$ are formed in an almost 1:1:2 ratio, indicating that the random scrambling of aryl groups occurs during transmetalation. $Pt(C_6H_4COMe)(Ph)(dppe)$ was characterized by comparing its NMR data with those of the complex prepared independently of the reaction of $4\text{-}MeCOC_6H_4B(OH)_2$ with $PtI(Ph)(dppe)$ in the presence of Ag_2O.

Scheme 1 depicts possible pathways for the reaction of arylboronic acid with the dehydro(arylboronic anhydride) ligand bound to Pt, leading to the formation of a new aryl–platinum bond. Reaction i involves the addition of an O–H bond of arylboronic acid to a Pt–O bond of the complex to produce intermediate **A**. The subsequent intramolecular metathesis-type bond exchange between the Pt–O bond of the arylboronate ligand and the B–C bond of the other O ligand forms an aryl–platinum bond. The aryl ligand introduced to the product is derived from the dehydrido(arylboronic anhydride) ligand of the starting complex. Reaction ii proceeds via a direct metathesis of the added arylboronic acid with the Pt–O bond of the complex to form a new bond between the Pt center and the aryl group in the arylboronic acid.

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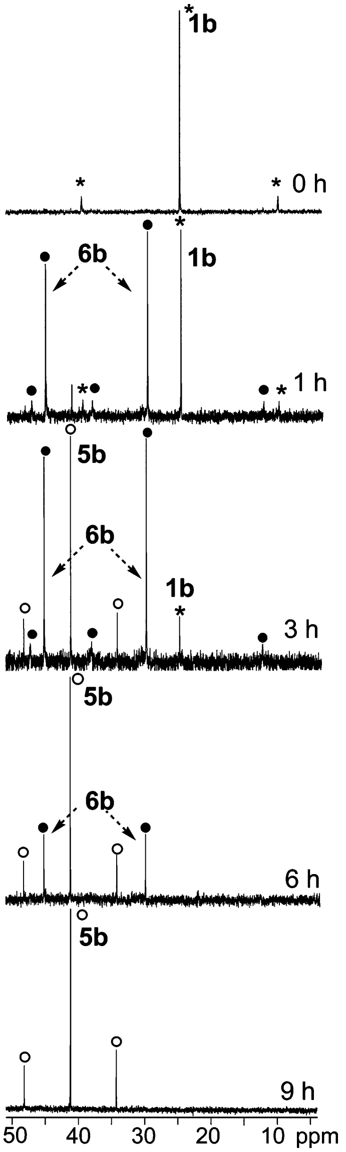


Figure 3. Change in $^{31}P\{^1H\}$ NMR spectra during reaction of $PhB(OH)_2$ with **1b** in THF−benzene-d_6. Peaks denoted by black dots are due to intermediate complexes with phenyl and O-coordinating ligands (see text).

The above reactions involve the activation of the Pt−O bond and the formation of the Pt−C bond involving the four-membered intermediate shown in Scheme 2. The addition of an O−H bond to the Pt−O bond causes the exchange of the arylboronate ligand (reaction i), whereas that of the B−C bond produces arylplatinum complexes and compounds containing a B−O−B bond (reaction ii).

Scheme 3 depicts a pathway for the formation of the aryl−platinum bond, which involves the initial cleavage of a B−O bond of the complex by arylboronic acid. The addition of an O−H bond of the arylboronic acid to a bond between boron and oxygen atoms at the β- and γ-positions of a platinacycle forms intermediate **B** (reaction i). The Ar−B group of the intermediate **B** is derived from arylboronic acid and undergoes an intramolecular metathesis reaction with the Pt−O bond, giving an arylplatinum complex. Reaction pathway ii involves the activation of the bond between the coordinating oxygen atom and adjacent boron atom by arylboronic acid to form an intermediate complex with an OH ligand, **C**.

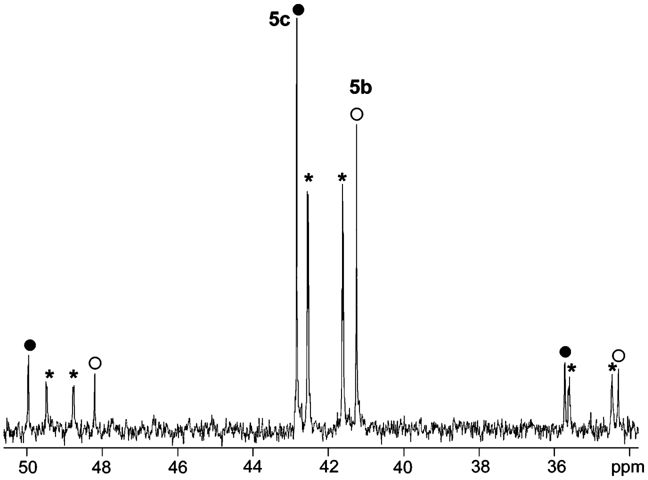
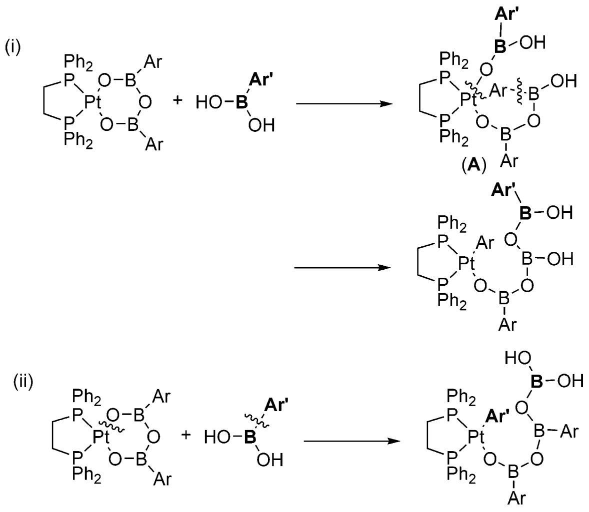
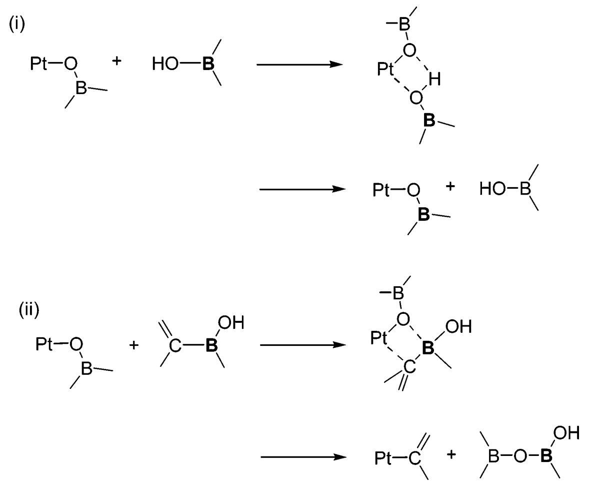


Figure 4. $^{31}P\{^1H\}$ NMR spectrum of reaction mixture of 4-$MeCOC_6H_4B(OH)_2$ with **1b** after transmetalation in THF−benzene-d_6. Peaks denoted by asterisks correspond to that of Pt(C_6H_4COMe-4)(Ph)(dppe).

Scheme 1

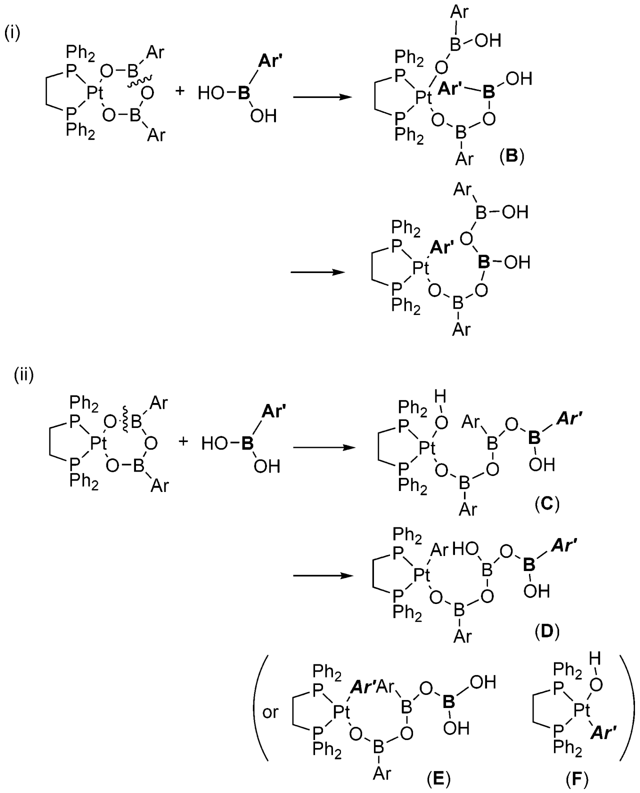


Scheme 2



The aryl group in the ligand undergoes a metathesis reaction with the Pt−O bond of the OH ligand to produce complexes containing the aryl ligand **D** or **E**. The reaction with the Pt−O bond of the boronate ligand of **B** yields the arylplatinum hydroxide complex **F**, accompanied by the elimination of cyclic boron-containing compounds. The complexes obtained by the reactions in Schemes 1 and 3 can be transformed into diaryl-

Scheme 3

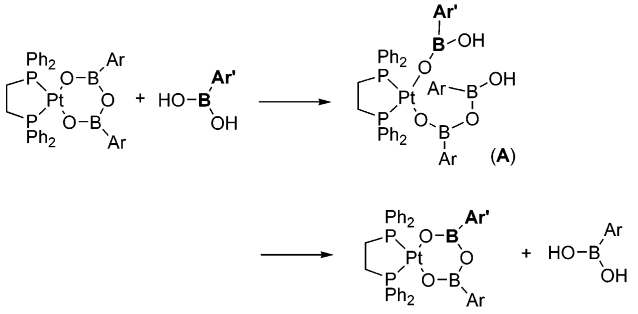


platinum complexes by further intramolecular or intermolecular metathesis-type reactions between the B−C and Pt−O bonds.

The experimental results obtained at present are not sufficient to compare the plausibility of the reactions shown in Schemes 1 and 3 as pathways for the formation of the aryl−platinum bond. These reactions, occurring in a parallel manner, account for the scrambling of the aryl group in the reactions of 4-$MeCOC_6H_4B(OH)_2$ with **1b** and of $PhB(OH)_2$ with **1c**. The preferential formation of the monoaryl complex **F** by reaction ii in Scheme 3, followed by the reaction of arylboronic acid with the OH ligand of **F**, is also consistent with the formation of diaryl complexes accompanied by the scrambling of the aryl groups between the complex and arylboronic acid. The hydroxide ligand of complex **C** (and **F**) shows a more pronounced nucleophilic nature than the arylboronate ligand in the complexes of the above reactions and undergoes a metathesis reaction with electrophilic boron-containing ligands more easily.[19,20] On the other hand, reaction ii in Scheme 3, involving a metathesis reaction of the B−O bond close to the Pt center, suffers from a more severe steric congestion between the substituents of the complex and arylboronic acid than reaction i in Scheme 1 and reaction i in Scheme 3.

The results can be explained well by assuming that the random scrambling of aryl groups occurs prior to transmetalation. Scheme 4 depicts a possible reaction pathway that leads to the exchange of aryl groups.

Scheme 4



Intermediate **A** formed in reaction i of Scheme 1 causes a metathesis reaction of O−H and B−O bonds to regenerate a cyclic complex with a dehydro(arylboronic anhydride) ligand having a different aryl ligand from the starting complex.

Most stoichiometric transmetalations of arylboronic acids with transition-metal complexes are assisted by the addition of a nucleophile such as OH^- or Ag_2O as well as fluoride. These additives may play two possible roles during the reaction: one involves the formation of arylborate by the coordination of an anion to the boron center of arylboronic acid, and the other involves addition of the nucleophile, which promotes the activation of the bond between a transition metal and a halogeno ligand as well and produces a cationic complex with an electrophilicity higher than that of the neutral complex. Transmetalation without base addition has also been reported. The reaction of arylboronic acid with a dicationic palladium complex forms a monocationic phenylpalladium complex, accompanied by the elimination of HBF_4 without base addition.[5] The alkoxide ligand bonded to Re shows a high reactivity toward arylboronic acid to cause transmetalation under mild conditions.[8] The Pt complexes in this study also exhibit a high reactivity toward arylboronic acid to induce the aryl group transfer from boron to platinum.

In conclusion, we succeeded in preparing and characterizing six-membered cyclic platinum(II) complexes containing three O, two B, and one Pt atom. The Pt−O bond of the complexes reacted with arylboronic acid to afford diarylplatinum(II) complexes. The aryl group transfer from boron to platinum proceeds via the intermolecular metathesis of Pt−O and B−C bonds or the intramolecular metathesis of the acyclic intermediate formed by the arylboronic acid induced cleavage of a B−O bond of the complex.

Experimental Section

General Procedures and Materials. All experiments were carried out under N_2 or Ar using the standard Schlenk technique. The NMR spectra (^1H, $^{11}B\{^1H\}$, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, $^{31}P\{^1H\}$) were recorded on JNM-La-500, JEOL EX-400, and Varian 300 spectrometers. Residual peaks of solvent were used as the reference for ^1H NMR and $^{13}C\{^1H\}$ NMR (acetone-d_6, δ 29.8). External references were used for $^{11}B\{^1H\}$ NMR ($BF_3 \cdot OEt_2$), $^{31}P\{^1H\}$ NMR (85% H_3PO_4), and $^{19}F\{^1H\}$ ($CFCl_3$). IR spectra were taken on a Shimadzu FTIR8100A (KBr, 4000−400 cm^{-1}) spectrophotometer. Elemental analyses were carried out with a Yanaco MT-5 CHN Autocorder and a LECO VTF-900 Oxygen Analyzer. Arylboronic acids and dppe were commercially available (Tokyo Chemical Industry Co., Ltd. or Aldrich Chemical Co. Inc.) and used as received. PtI_2(dppe) was prepared as described in the literature.[21]

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Synthesis of $\overline{\mathrm{Pt(OBArOBArO)}}$(dppe) (1a, Ar = C_6H_4OMe-4; 1b, Ar = C_6H_5; 1c, Ar = C_6H_4COMe-4). To a THF/H_2O (50 mL/1 mL) solution of PtI_2(dppe) (847 mg, 1.0 mmol) were added Ag_2O (753 mg, 3.2 mmol) and 4-MeO-$C_6H_4B(OH)_2$ (304 mg, 2.0 mmol) at room temperature. The reaction mixture was stirred for 3 h. After filtration of the black solid, composed of AgI and unreacted Ag_2O, the resulting solution was added dropwise to hexane (500 mL) to yield **1a** as a white solid, which was filtered off and dried under vacuum. Yield: 751 mg, 86%. Anal. Calcd for $C_{40}H_{38}B_2O_5P_2Pt$: C, 54.76; H, 4.37; O, 9.12. Found: C, 54.35; H, 4.52; O, 8.95. ^1H NMR (300 MHz, $CDCl_3$): δ 8.08−8.03 (m, 8H, PC_6H_5-*o*), 7.94 (d, 4H, ^3J(H−H) = 8.1 Hz, BC_6H_4OMe-4-*o*), 7.43−7.41 (m, 12H, PC_6H_5-*m, p*), 6.84 (d, 4H, ^3J(H−H) = 8.7 Hz, BC_6H_4-OMe-4-*m*), 3.81 (s, 6H, O*Me*), 2.44−2.39 (m, 4H, PC*H*$_2$). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 25.2 (s with satellites, *J*(PtP) = 3537 Hz).

Complexes **1b**,**c** were prepared similarly as colorless crystals from the corresponding arylboronic acids in 69% and 82% yields, respectively.

Data for **1b** are as follows. Anal. Calcd for $C_{38}H_{34}B_2O_3P_2Pt$: C, 55.84; H, 4.19; O, 5.87. Found: C, 55.85; H, 4.20; O, 5.82. ^1H NMR (300 MHz, C_6D_6): δ 8.57 (d, 4H, ^3J(HH) = 7.5 Hz, BC_6H_5-*o*), 7.94 (m, 8H, PC_6H_5-*o*), 7.79−7.34 (m, 6H, BC_6H_5-*m, p*), 6.90 (br s, 12H, PC_6H_5-*m,p*), 1.72−1.67 (m, 4H, PC*H*$_2$). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 25.2 (s, *J*(PtP) = 3536 Hz). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ 24.94 (br).

Data for **1c** are as follows. Anal. Calcd for $C_{42}H_{38}B_2O_5P_2Pt$: C, 55.96; H, 4.25; O, 8.87. Found: C, 55.43; H, 4.15; O, 8.78. ^1H NMR (300 MHz, $CDCl_3$): δ 8.06−7.98 (m, 12H, BC_6H_4COMe-*o*, PC_6H_5-*o*), 7.87 (d, 4H, ^3J(H−H) = 7.5 Hz, BC_6H_4COMe-*m*), 7.48−7.42 (12H, PC_6H_5-*m,p*), 2.60 (s, 6H, CO*Me*), 2.46−2.41 (m, 4H, PC*H*$_2$). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 26.4 (s, *J*(PtP) = 3567 Hz). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ 24.5 (br).

Reaction of HCl with 1a. To a THF (2 mL) solution of **1a** (43.9 mg, 0.05 mmol) was added HCl (3.7% in H_2O, 83 μL, 0.1 mmol). The reaction mixture was stirred at room temperature for 2 h. Addition of hexane gave $PtCl_2$(dppe) (**2**) as a white solid, which was filtered off and dried under vacuum (32.3 mg, 97%). Anal. Calcd for $C_{26}H_{24}B_2Cl_2P_2Pt$: C, 47.00; H, 3.64; Cl, 10.67. Found: C, 47.30; H, 3.69; O, 10.09. ^1H NMR (300 MHz, acetone-d_6): δ 7.99−7.92 (m, 8H, PC_6H_5-*o*), 7.59−7.53 (m, 12H, PC_6H_5-*m,p*), 2.65−2.59 (m, 4H, PC*H*$_2$). $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6): δ 43.2 (s, *J*(PtP) = 3595 Hz). Evaporation of the solvent from hexane solution gave a solid (13.5 mg) containing a mixture of 4-$MeOC_6H_4B(OH)_2$ and $(4\text{-}MeOC_6H_4)_3B_3O_3$ in a 2:3 ratio. Their ^1H NMR data were compared with those obtained from commercially available products.

Reaction of CF_3COOH with 1a. To a THF solution containing **1a** (43.9 mg, 0.05 mmol) was added CF_3COOH (neat, 11.4 μL, 0.1 mmol). The reaction mixture was stirred at room temperature for 2 h. The resulting solution was added to hexane to give $Pt(OCOCF_3)_2$(dppe) (**3**) as a white precipitate in 91% yield (37.3 mg). The hexane fraction contained a mixture of arylboronic acid and its anhydride in a 1:2 ratio (13.1 mg). Crystals of **3** suitable for X-ray analyses were grown by slow diffusion of hexane into a THF solution. Anal. Calcd for $C_{30}H_{24}F_6O_4P_2Pt$: C, 43.97; H, 2.95; F, 13.91. Found: C, 44.16; H, 2.71; F, 13.84. ^1H NMR (300 MHz, acetone-d_6): δ 7.97−7.95 (m, 8H, PC_6H_5-*o*), 7.63−7.54 (m, 12H, PC_6H_5-*m,p*), 2.69−2.64 (m, 4H, PC*H*$_2$). $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6): δ 34.8 (s, *J*(PtP) = 3841 Hz). $^{19}F\{^1H\}$ NMR (282.5 MHz, C_6D_6): δ −74.4 (s).

Reaction of CH_3COOH with 1a. The reaction of **1a** with a stoichiometric amount of CH_3COOH was followed by $^{31}P\{^1H\}$ NMR spectroscopy using THF/C_6D_6 as solvent. The product of the reaction was identified as $Pt(OCOCH_3)_2$(dppe) (**4**).

Reaction of 4-$MeOC_6H_4B(OH)_2$ with 1a. To a THF solution (2 mL) containing **1a** (88 mg, 0.10 mmol) was added4-$MeOC_6H_4B(OH)_2$ (30 mg, 0.2 mmol), and the reaction mixture was stirred at room temperature for 16 h. The solvent was evaporated to dryness under reduced pressure. The residue that formed was washed with water. Evaporation of water of the washing at 80 °C under vacuum gave boric acid (12.8 mg, 52%). Data for H_3BO_3 are as follows. ^1H NMR (300 MHz, acetone-d_6): δ 5.82 (s, OH, boroxine), 2.90 (s, OH, boric acid), 2.87 (s, OH, water), ^{11}B NMR (160.4 MHz, acetone-d_6): δ 19.9 (s). Addition of hexane to the solid product after washing with water caused separation of a white solid which was washed with hexane to give **5a** as a white solid (69.1 mg, 85%). Evaporation of the hexane extract gave anisole (11 mg, 51%). NMR data for C_6H_5OMe are as follows. ^1H NMR (300 MHz, $CDCl_3$): δ 7.25 (2H, t, C_6H_5-*o*), 6.9 (m, 3H, C_6H_5-*m,p*), 3.75 (s, 3H, OMe), ^{13}C NMR (75 MHz, $CDCl_3$): 159.7, 129.5, 120.7, 114.0, 55.1. NMR data for **5a** are as follows. ^1H NMR (300 MHz, $CDCl_3$): δ 7.51−7.31 (m, 20H), 7.02 (t, 4H, ^3J(HH) = 7.3 Hz, ^4J(PH) = 14.7 Hz, PtC_6H_4-*o*), 6.41 (d, 4H, ^3J(H−H) = 7.2 Hz, PtC_6H_4-*m*), 3.61 (s, 6H, O*Me*), 2.28−2.23 (m, 4H, PC*H*$_2$). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 41.9 (s, *J*(PtP) = 1711 Hz). ^1H NMR (300 MHz, C_6D_6): δ 7.56−7.47 (m, 12H), 7.04−6.98 (m, 12H), 6.74 (d, 4H, ^3J(HH) = 9.4 Hz, PtC_6H_4-*m*), 3.31 (s, 6H, O*Me*), 1.91−1.85 (m, PC*H*$_2$); $^{31}P\{^1H\}$ NMR (121.5 Hz, C_6D_6): δ 42.2 (s, *J*(PtP) = 1691 Hz).

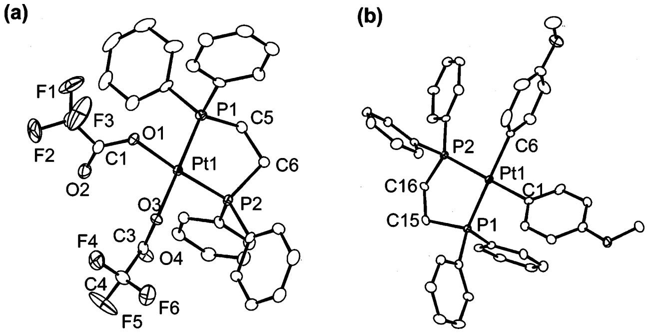

Figure 5. (a) ORTEP drawing of **3** with ellipsoids at the 30% probability level. One of the two crystallographically independent molecules is shown. Selected bond distances (Å) and angles (deg): Pt1−O1 = 2.078(4), Pt1−O3 = 2.096(4), Pt1−P1 = 2.221(2), Pt1−P2 = 2.207(2); O1−Pt1−O3 = 85.8(2), P1−Pt1−P2 = 86.60(6), O1−Pt1−P1 = 96.7(1), O3−Pt1−P1 = 175.6(1), O3−Pt1−P2 = 173.7(1), O3−Pt1−P2 = 90.5(1). (b) ORTEP drawing of **5a** with ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Pt1−C1 = 2.093(6), Pt1−C8 = 2.080(6), Pt1−P1 = 2.286(1), Pt1−P2 = 2.289(1); C1−Pt1−C8 = 87.9(2), P1−Pt1−P2 = 86.34(5), C1−Pt1−P1 = 94.9(2), C1−Pt1−P2 = 176.4(2), C8−Pt1−P1 = 171.9(2), C8−Pt1−P2 = 91.3(2).

The reaction on an NMR scale was carried out by the following procedure. To **1a** (22 mg, 0.025 mmol) in THF-d_8 (1 mL) were added 4-$MeOC_6H_4B(OH)_2$ (7.5 mg, 0.050 mmol) and Ph_2CH_2 as an internal standard (12.5 μL, 0.075 mmol). The changes in the reaction mixture were followed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

Reactions of Arylboronic Acids with 1a−c on an NMR Scale. In general experiments, NMR tubes were loaded with complexes **1a**−**c** (0.050 mmol) and the corresponding boronic acids in 1:2 molar ratios in a THF/C_6D_6 mixed solvent system. The changes in the crude reaction mixtures were detected by $^{31}P\{^1H\}$ NMR spectroscopy. In most cases the complexes formed were not isolated but characterized spectroscopically.

Preparation of $Pt(C_6H_4COMe\text{-}4)(Ph)$(dppe). To a THF/$H_2O$ solution (5/0.5 mL) containing Pt(I)(Ph)(dppe) (159.5 mg, 0.20 mmol) were added 4-$COMeC_6H_4B(OH)_2$ (49.19 mg, 0.30 mmol) and Ag_2O (74.16 mg, 0.32 mmol) in this order. The reaction mixture was stirred at room temperature for 48 h. After filtration of the residue, composed of AgI and unreacted Ag_2O, the resulting

Table 1. Crystal Structure Data and Refinement Details for Complexes 1b,c, 3, and 5a

	1b	**1c**	**3**·THF	**5a**
formula	$C_{38}H_{34}B_2O_3P_2Pt$	$C_{42}H_{38}B_2O_5P_2Pt$	$C_{32}H_{28}O_{4.5}F_6P_2Pt$	$C_{40}H_{38}O_2P_2Pt$
M_r	817.34	901.42	855.60	807.78
cryst syst	monoclinic	orthorhombic	monoclinic	triclinic
space group	$C2/c$ (No. 15)	$Pca2_1$ (No. 29)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a/Å	30.007(4)	16.026(2)	14.916(2)	10.382(2)
b/Å	15.3558(11)	21.295(2)	18.975(2)	11.367(2)
c/Å	26.908(6)	22.041(2)	22.898(3)	14.227(3)
α/deg	90	90	90	92.374(2)
β/deg	123.706(6)	90	93.4410(2)	93.196(3)
γ/deg	90	90	90	98.853(4)
V/Å^3	10 314(3)	7522(1)	6469(1)	1654.2(5)
Z	12	8	8	2
μ(Mo Kα)/ mm^{-1}	0.4194	0.3846	0.4492	0.4356
F(000)	4848	3584	3344	804
D_c/g cm^{-3}	1.579	1.592	1.757	1.622
cryst size/mm	0.30 × 0.20 × 0.05	0.25 × 0.25 × 0.10	0.30 × 0.30 × 0.30	0.32 × 0.08 × 0.04
2θ range/deg	5.0−55.0	5.0−55.0	5.0−55.0	5.0−55.0
no. of unique rflns	11 148	8823	14 530	7107
no. of rflns used ($>2\sigma(I)$)	10 126	8823	10 643	6571
no. of variables	674	1013	876	444
R	0.0287	0.0480	0.0400	0.0419
R_w	0.0373	0.0892	0.0457	0.0650
GOF	1.001	0.837	0.915	0.999

solution was mixed with hexane (70 mL) to cause separation of Pt(C_6H_4COMe-4)(Ph)(dppe) as a white residue, which was filtered off and dried under vacuum. Yield: 135.6 mg, 86%. ^{1}H NMR (300 MHz, C_6D_6): δ 7.82−7.60 (m, 4H, PtC_6H_4COMe-4-*o*,*m*), 7.46−7.34 (m, 8H, PC_6H_5-*o*), 7.07−6.87 (m, 17H), 2.08 (s, 3H, CO*M*e), 1.87−1.80 (m, 4H, PCH_2). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 42.8 (J(PtP) = 1668 Hz), trans to Ph, 41.9 (J(PtP) = 1718 Hz), trans to C_6H_4COMe-4.

Crystal Structure Determination. Crystals suitable for X-ray diffraction study were obtained by recrystallization from THF/hexane solutions and mounted in glass capillary tubes on a Rigaku AFC-7R automated CCDC diffractometer equipped with Mo Kα radiation (λ = 0.7107 Å). The data were collected to a maximum 2θ value of 55.0°. A total of 720 oscillation images were collected. A sweep of data was done using ω scans from −110.0 to 70.0° in 0.5° steps, at χ = 45.0° and ϕ = 0.0°. The detector swing angle was −20.42°. A second sweep was performed using ω scans from −110.0 to 70.0° in 0.5° steps, at χ = 45.0° and ϕ = 90.0°. The crystal-to-detector distance was 44.84 mm. Readout was performed in the 0.070 mm pixel mode. Calculations were carried out by using the program package Crystal Structure for Windows. The structure was solved by direct methods and expanded using Fourier techniques. A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters.

The absolute configuration of the crystal of **1c** could not be determined from crystallographic results, due to insufficient quality of the diffraction data. The two independent molecules in the crystal show orientations of the phenyl planes different from each other. Figure 5 depicts crystallographic structures of **3** and **5b**. Crystal structure data and refinement details are given in Table 1.

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Supporting Information Available: Crystallographic data and complete tables of non-hydrogen and selected hydrogen parameters, bond lengths and angles, calculated hydrogen atom parameters, and anisotropic thermal parameters (CIF files) of **1b**,**c**, **3**, and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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