Chemical Properties of Mononuclear and Dinuclear Phenylplatinum(II) Hydroxo Complexes with Cod Ligands. Transmetalation of Arylboronic Acids, Coupling of the Phenyl Ligands, and Carbonylation

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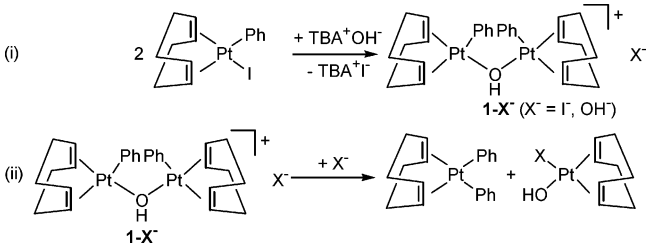
The reaction of bpy with [{Pt(Ph)(cod)}$_2$(μ-OH)](BF$_4$) (**1-BF$_4$**; cod = 1,5-cyclooctadiene) in acetone splits a Pt−O bond to yield a mixture of Pt(CH$_2$COMe)(Ph)(cod) (**2**) and [Pt(Ph)(bpy)(cod)](BF$_4$) (**3-BF$_4$**), whereas a similar reaction in toluene produces **3-BF$_4$** and Pt(OH)(Ph)(cod) (**4**). The complex **4** was obtained in solution and was not isolated as analytically pure crystals because of its gradual disproportionation, giving PtPh$_2$(cod) (**5**). The dinuclear complex **1-BF$_4$** reacts with ArB(OH)$_2$ (Ar = Ph, C$_6$H$_2$F$_3$-2,4,6) to form **5** and Pt(C$_6$H$_2$F$_3$-2,4,6)(Ph)(cod) (**6**), respectively, via aryl group transfer from boron to platinum. The accompanying formation of B(OH)$_3$ has been confirmed by ^{11}B{^{1}H} NMR spectroscopy. The reaction of BF$_3$·Et$_2$O with **1-BF$_4$** followed by the addition of NH$_4$Cl(aq) produces biphenyl and PtCl$_2$(cod), which takes place possibly via a dinuclear intermediate. The cationic dinuclear complex **1-BF$_4$** reacts with CO (1 atm) to form benzophenone. Since the reactions of AgBF$_4$ with Pt(COPh)(I)(cod) (**7**) and CO with [Pt(Ph)(THF)(cod)](BF$_4$) also yield benzophenone, the above carbonylation of **1-BF$_4$** is considered to involve mononuclear intermediates.

Introduction

Organoplatinum(II) hydroxo complexes have long been known, ever since the pioneering report by Bennett et al.[1] The hydroxo ligand of a mononuclear Pt(II) complex was reported to exhibit a nucleophilic character[2] in a way similar to that for the more common corresponding alkoxoplatinum(II) complexes.[3,4] The unique properties of a hydroxo ligand in organoplatinum chemistry is a tendency to coordinate to two metal centers as a bridging ligand easily.[5,6] These dinuclear Pt complexes are stabilized by the highly basic OH ligand and flexible Pt−OH−Pt bonding. Recently, we have reported that the reaction of TBA$^+$OH$^-$ (TBA$^+$ = tetra-*n*-butylammonium) with PtI(Ph)(cod) (cod = 1,5-cyclooctadiene) formed a diphenylplatinum complex via intermolecular phenyl ligand transfer, as shown in Scheme 1.[7] The reaction involves the intermediate dinuclear platinum complex [{Pt(Ph)(cod)}$_2$(μ-OH)](X$^-$) (**1-X$^-$**; X$^-$ = I$^-$, OH$^-$), and the corresponding complex with another counteranion [{Pt(Ph)(cod)}$_2$(μ-OH)](BF$_4$) (**1-BF$_4$**) was obtained by an independent preparation route. The complex **1-X$^-$** further reacts with TBA$^+$X$^-$ (X$^-$ = OH$^-$, I$^-$) to result in a smooth transfer of a phenyl ligand between Pt centers, affording a mononuclear diphenylplatinum complex. In this paper, we report the chemical properties of the dinuclear complex **1-BF$_4$** with a bridging hydroxo ligand and of a related mononuclear complex with a nonbridging hydroxo ligand.

Scheme 1



Results and Discussion

Reaction of Arylboronic Acid with Hydroxoplatinum Complexes. The complex **1-BF$_4$** reacts with an equimolar amount of bpy in acetone to produce a mixture of PtPh(CH$_2$-

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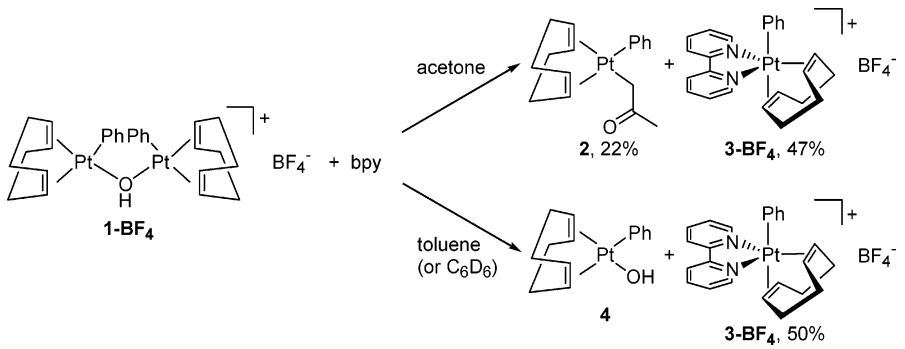
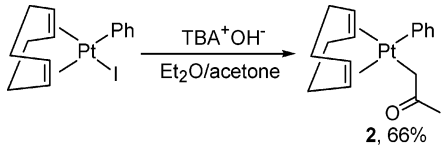
Scheme 2



COMe)(cod) (**2**)[8] and [PtPh(bpy)(cod)](BF_4) (**3-BF$_4$**), as shown in Scheme 2. Since the dissolution of **1-BF$_4$** in acetone does not form **2**, the reaction is induced by the coordination of bpy to a Pt center of **1-BF$_4$**. The complex **2** was also obtained by the reaction of acetone with PtI(Ph)(cod) in the presence of Ag_2O.[8] The reaction of TBA^+OH^- with PtI(Ph)(cod) in Et_2O/acetone (100/1) produces **2** in 66% yield, as shown in eq 1.



(1)

This reaction as well as the upper reaction of Scheme 2 may proceed via a mononuclear or dinuclear intermediate with a OH ligand, which undergoes protonation by acetone, giving a product with an acetonyl ligand. The complex **3-BF$_4$** has been isolated and characterized by ^{1}H NMR and ESIMS spectroscopy as well as by elemental analysis. The ^{1}H NMR spectrum of **3-BF$_4$** shows two =CH hydrogen signals at δ 3.54 and 5.75 ($J(^{195}Pt^1H)$ = 75, 25 Hz) and four signals at δ 8.03, 8.31, 8.58, and 9.80, assigned to aromatic hydrogens of the bpy ligand. A complex with another counteranion, **3-PF$_6$**, was prepared separately by treatment of PtI(Ph)(cod) with $AgPF_6$ and then with bpy and characterized by X-ray crystallography (Figure 1). The complex has trigonal-bipyramidal coordination around a platinum(II) center which has a Ph ligand and a C=C bond of a cod ligand at the apical position. The Pt1−C11 and Pt1−C12 bond distances (2.35(1) and 2.34(1) Å) are elongated significantly from the Pt1−C7 and Pt1−C8 bond distances (2.09(1) and 2.07(1) Å), close to the values for another trigonal

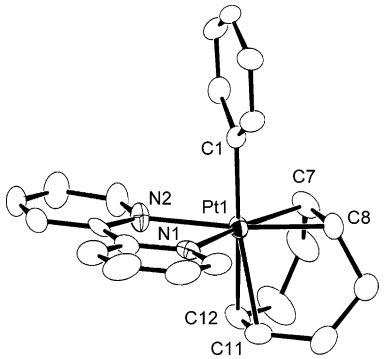
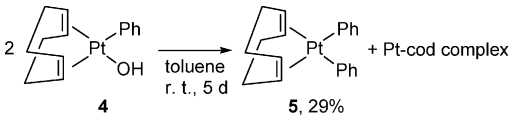


Figure 1. ORTEP diagram of [Pt(Ph)(bpy)(cod)](PF_6) (**3-PF$_6$**) with ellipsoids drawn at the 30% probability level. The PF_6 anion and hydrogen atoms are omitted for clarity. Selected bond distances (Å): Pt1−N1 = 2.238(8), Pt1−N2 = 2.211(8), Pt1−C1 = 2.038(9), Pt1−C7 = 2.09(1), Pt1−C8 = 2.07(1), Pt1−C11 = 2.35(1), Pt1−C12 = 2.34(1).

pentacoordinate methylplatinum(II) complex with a cod ligand and a diimine ligand.[9] The Pt1−C1 bond distance is close to those of reported phenylplatinum(II) complexes with a cod ligand.[8,9]

A similar reaction in toluene yields a mixture of **3-BF$_4$** and Pt(OH)(Ph)(cod) (**4**). **4** is obtained in toluene (or C_6D_6) solution after the removal of **3-BF$_4$** from the reaction mixture by filtration. The isolation of **4** as analytically pure crystals was not feasible due to gradual disproportionation to give $PtPh_2$(cod) (**5**) in the solution (vide infra), although Pt(OH)(Me)(cod) has been isolated.[10] The structure of **4** was confirmed by the IR and NMR data of the solution, as described below. The IR spectrum of **4** shows ν(OH) bands at 3677 and 3600 cm^{-1}. The peak positions are within the range of those of the OH ligand of the reported mononuclear organoplatinum hydroxo complexes (3509−3690 cm^{-1}).[1,3,10−12] The bridging OH ligand of dinuclear platinum complexes including **1-BF$_4$** shows the ν(OH) peak at lower wavenumber (3250−3600 cm^{-1}).[6,7] The ^{1}H NMR spectrum of **4** exhibits two =CH hydrogen signals of the cod ligand (δ 5.69, J(PtH) = 36 Hz and δ 3.76, J(PtH) = 60 Hz). The former signal flanked with a smaller ^{195}Pt−^{1}H coupling constant is assigned to the CH=CH group trans to the Ph ligand, which shows a larger trans influence than the OH ligand.[12] The OH hydrogen signal is observed at δ 3.39 in C_6D_6, while the ^{1}H NMR spectrum of **1-BF$_4$** in $CDCl_3$ shows the signals for the bridging OH ligand only at a low temperature (δ 4.17, −55 °C).[7] Leaving a toluene solution of **4** for 5 days at room temperature results in the formation of $PtPh_2$(cod) (**5**; 29%) via intermolecular phenyl ligand transfer, as shown in eq 2. The solutions of PtPhI(L_2) and of [PtPh(acetone)(L_2)](BF_4)



(2)

(L_2 = bpy, cod) do not generate the diphenylplatinum complex via disproportionation.[8,13]

The complex **1-BF$_4$** reacts with $ArB(OH)_2$ (Ar = Ph, $C_6H_2F_3$-2,4,6) in the presence of H_2O ([Pt]:[H_2O] = 1:11) in toluene to

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(9) Bianca, F. D.; Bandoli, G.; Dolmella, A.; Antonaroli, S.; Crociani, B. *Dalton Trans.* **2002**, 212.
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Scheme 3

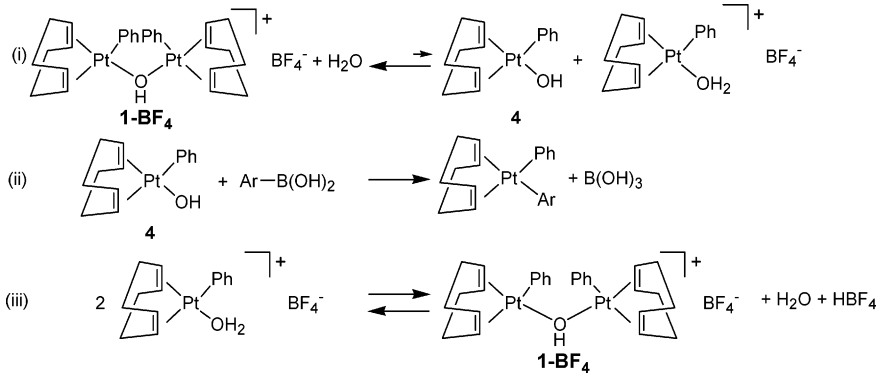
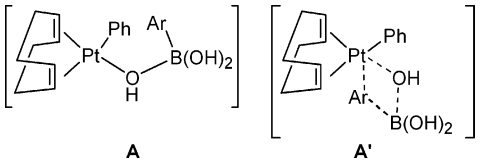
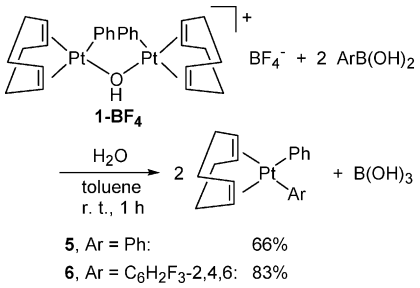


Chart 1

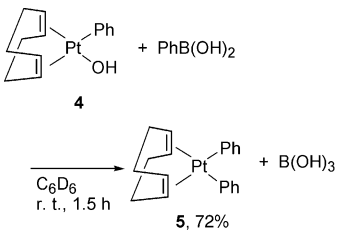


afford the respective diarylplatinum complexes Pt(Ar)(Ph)(cod) (**5**, Ar = Ph (66%); **6**, Ar = $C_6H_2F_3$-2,4,6 (83%)) as shown in eq 3. The accompanying formation of $B(OH)_3$ is confirmed by



(3)

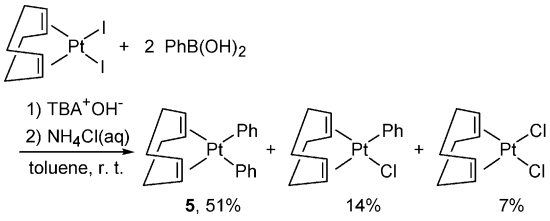
$^{11}B\{^1H\}$ NMR spectroscopy. The complex **6** is characterized by the ^1H NMR spectrum, which exhibits hydrogen signals of the Ph ligand (δ 6.80, 6.98, 7.26) and the $C_6H_2F_3$-2,4,6 ligand (δ 6.38). The complex **6** was also prepared from the reaction of 2,4,6-$C_6H_2F_3Li$ with PtI(Ph)(cod). The reactions without the addition of H_2O produce **5** and **6** in yields lower than those from eq 3 (38% and 36%, respectively). The reaction of $PhB(OH)_2$ with the mononuclear complex **4** prepared in situ forms the diphenyl complex **5** via the transmetalation of the Ph group from B to Pt, as shown in eq 4.



(4)

Scheme 3 shows a plausible mechanism to account for reaction 3. In the presence of water, **1-BF$_4$** is in equilibrium with **4** and a cationic phenylplatinum complex with an aqua ligand, $[PtPh(OH_2)(cod)](BF_4)$, in solution (Scheme 3(i)). The formed complex **4** reacts with $ArB(OH)_2$ to produce the diarylplatinum complex and $B(OH)_3$ similarly to reaction 4 (Scheme 3(ii)). The reaction may proceed via the intermediate **A** (Chart 1), which is formed by the coordination of the OH ligand to the boron atom of arylboronic acid, giving a four-coordinate boron center. The intramolecular activation of the B−C bond of **A** would form a new Pt−Ar bond, accompanied by the elimination of $B(OH)_3$. An alternative concerted mechanism, involving the intermediate **A′** with a four-membered ring, forms Pt−C and B−O bonds of the products simultaneously. The coupling of $[PtPh(OH_2)(cod)](BF_4)$ accompanied by deprotonation may regenerate **1-BF$_4$** (Scheme 3(iii)). Reaction of H_2O with $[PtPh(THF)(cod)](BF_4)$ was reported to produce **1-BF$_4$**.[7]

The reaction without the addition of H_2O yields the diaryl complexes in lower yields. Scheme 4 gives a summary of a pathway of the reaction of $ArB(OH)_2$ with **1-BF$_4$** in the absence of H_2O. $ArB(OH)_2$ reacts with **1-BF$_4$** to generate **4**, and it is likely that the structure of the other complex is the cationic phenylplatinum complex with arylboronic acid as the ligand (Scheme 4(i)). The complex **4** is responsible for transmetalation (Scheme 4(ii)), similarly to Scheme 3. ^1H NMR spectra of the reaction mixture showed the presence of an intermediate complex, although it was not characterized unambiguously (see the Experimental Section). The reaction of $PhB(OH)_2$ with PtI_2-(cod) in the presence of TBA^+OH^- forms $PtPh_2(cod)$ (**5**) via the transmetalation of two phenyl groups from boron to platinum, as shown in eq 5. The addition of TBA^+OH^- is



(5)

indispensable for the formation of **5**. A cationic complex without a OH ligand, $[Pt(cod)(THF)_2](BF_4)_2$, does not react with $PhB(OH)_2$. These results indicate that the hydroxo ligand that bonded to Pt formed by the reaction of TBA^+OH^- with $PtI_2(cod)$ induces the transmetalation of $PhB(OH)_2$.[14]

Pd- and Rh-complex-catalyzed synthetic organic reactions using arylboronic acids such as Suzuki−Miyaura coupling[15] and 1,4-addition of arylboronic acid to α, β-unsaturated carbonyl

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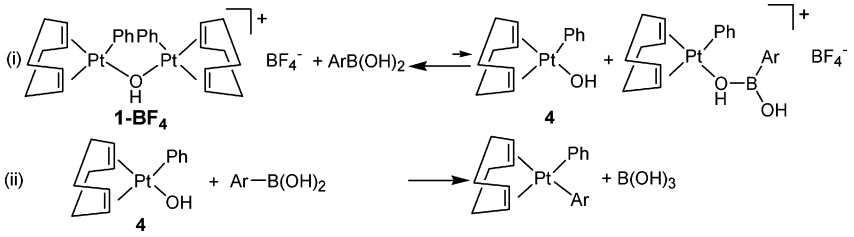
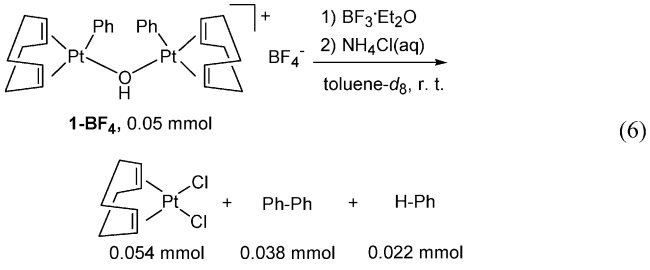
Scheme 4



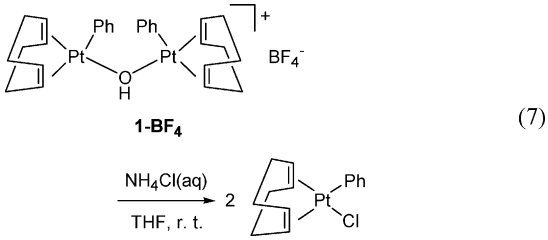
compounds[16] involve the transmetalation of arylboronic acids with Pd.[17] Recent reports on stoichiometric reactions of arylboronic acid with organopalladium revealed details of the transmetalation reactions. Miyaura reported the reaction of (4-$MeOC_6H_4$)$B(OH)_2$ with $[PdPh(\mu\text{-}OH)(PPh_3)]_2$, affording 4-methoxybiphenyl through diarylpalladium intermediate complexes;[18] moreover, the cationic OH-free complex $[Pd(dppe)(MeCN)_2](BF_4)_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) also reacts with $PhB(OH)_2$ in the presence of PPh_3 and H_2O to form $[Pd(Ph)(dppe)(PPh_3)](BF_4)$ via transmetalation.[19] An aryl(iodo)palladium complex with phosphine ligands reacts with arylboronic acid in the presence of Ag_2O and H_2O to produce a diarylpalladium complex.[20] The additives were considered to generate hydroxopalladium species, which are responsible for the transmetalation of arylboronic acids. Reports on the reactions of arylboronic acids with platinum complexes suggested that the transmetalation of such boronic acids requires the addition of TBA^+F^- or Ag_2O.[21,22] Reaction 4 in this study indicates that the hydroxoplatinum complex reacts with arylboronic acids directly to induce the transfer of the aryl group of the arylboronic acids, even in the absence of such additives. Our recent study has revealed that the Pt(II) complex with a chelating dehydro(arylboronic anhydride) ligand undergoes B−C bond activation in the absence of a nucleophile.[23]

Reaction of BF_3·Et_2O with Hydroxoplatinum Complex. The reaction of BF_3·Et_2O with **1-BF_4** in toluene-d_8 at room temperature for 12 h, followed by treatment with NH_4Cl(aq), produces a mixture of $PtCl_2$(cod) (54%), Ph−Ph (76%), and benzene (22%), as shown in eq 6. An ^1H NMR measurement



(6)

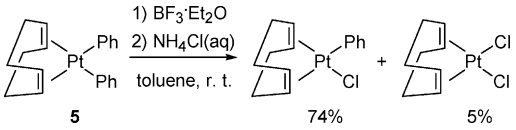
of the reaction mixture before the addition of NH_4Cl(aq) indicates that biphenyl and benzene are released from the complex by the addition of NH_4Cl. The reaction of NH_4Cl with **1-BF_4** produces PtCl(Ph)(cod) via the substitution of the OH ligand with the Cl ligand, as shown in eq 7. Sharp reported



(7)

substitution of the bridging OH ligand without migration of other ligands; addition of BF_3·Et_2O to $[Pt(\mu\text{-}OH)(L_2)]_2(BF_4)_2$ (L_2 = $(C_6H_4Me\text{-}4)N{=}C(Me)C(Me){=}N(C_6H_4Me\text{-}4)$) yields $[Pt(\mu\text{-}Cl)(L_2)]_2(BF_4)_2$, whose Cl ligand is derived from the solvent.[6e]

The reductive elimination of biaryl from mononuclear diarylplatinum complexes takes place at high temperatures,[24] while $PtPh_2$(cod) (**5**) is stable and does not induce the coupling of phenyl groups at room temperature and 50 °C in solution. The addition of electron-withdrawing ligands was reported to induce reductive elimination from dialkyl transition-metal complexes.[25] Thus, we conducted the reaction of Lewis acidic BF_3 with complex **5** to obtain further insight into the role of BF_3 in the reactions. The reaction of $PtPh_2$(cod) (**5**) with BF_3·Et_2O and NH_4Cl(aq) forms a mixture of PtCl(Ph)(cod) (74%) and $PtCl_2$(cod) (5%), as shown in eq 8. Significant formation of biphenyl



(8)

was not observed, indicating that reaction 6 does not involve the coupling of phenyl ligands from mononuclear diphenylplatinum complexes such as **5**.

Recently, Kubas and Peters have studied the chemical properties of cationic phenylplatinum complexes with chelating diphosphines independently and reported that the cationic methylplatinum(II) complexes in arene are converted into dinuclear platinum(II) complexes whose metal centers are connected with a formally dianionic, bis-π-allylic ligand.[26,27]

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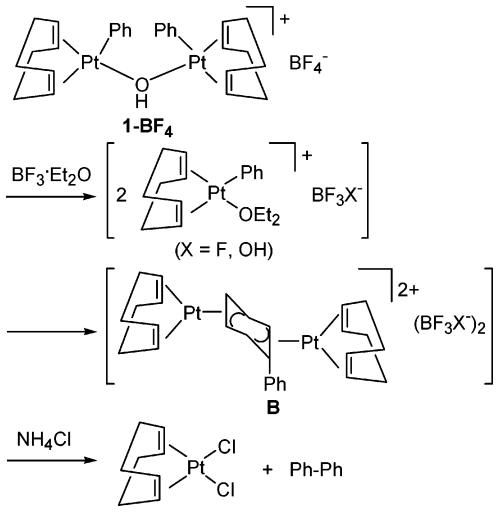
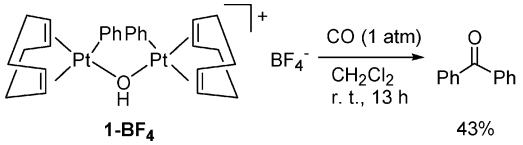
Scheme 5



The bridging biaryl ligands are liberated upon treatment of the dinuclear complex with I_2 or HCl.[26] The formation of the dinuclear Pt complexes may take place via a bimolecular coupling or initial disproportionation of a monophenyl platinum complex, which was discussed by Kubas and Peters. Scheme 5 shows a plausible mechanism proposed to explain reaction 6 on the basis of these previous results. The reaction of $BF_3{\cdot}Et_2O$ with **1-BF$_4$** eliminates the bridging OH ligand to form the cationic mononuclear platinum(II) complex $[PtPh(OEt_2)(cod)]^+$-$(BF_3X)^-$ (X = F, OH). Because the initially formed mononuclear complex has a labile OEt_2 ligand, it undergoes facile coupling of two complex molecules accompanied by C−C bond formation to form the complex **B** with a bridging biphenyl ligand. **B** reacts with NH_4Cl to release biphenyl and $PtCl_2(cod)$. NMR measurement of the reaction mixture did not provide evidence for structures of the proposed intermediate **B**, possibly due to its low solubility.

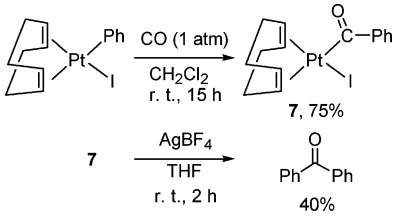
Reaction of CO with Hydroxoplatinum Complexes. The palladium-complex-catalyzed carbonylation of aryl halides under a CO atmosphere provides a means of synthesizing ketone and esters.[28] The complex **1-BF$_4$** forms benzophenone under a CO atmosphere (1 atm), as shown in eq 9. The carbonylation of



(9)

mononuclear diorganopalladium and platinum complexes as well as a dinuclear complex with a bridging aryl ligand with a long tether was reported to produce the corresponding ketones.[29,30] Scheme 6 shows a summary of the reactions of related mononuclear phenylplatinum complexes leading to carbonylation. The reaction of PtI(Ph)(cod) with CO (1 atm) causes the insertion of CO into the Pt−C bond to form PtI(COPh)(cod) (**7**), which has been characterized by NMR and IR spectroscopy as well as by comparison of the NMR and IR data with those

Scheme 6



of PtCl(COPh)(cod).[31] Figure 2 depicts the molecular structure of **7** obtained by X-ray crystallography. The bond distances of

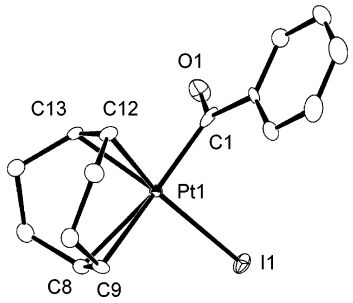
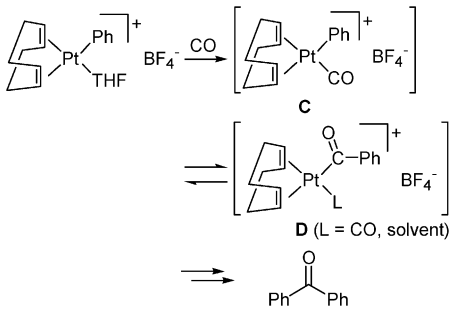


Figure 2. ORTEP diagram of complex **7** with ellipsoids drawn at the 50% probability level. Selected bond distances (Å): Pt1−I1 = 2.6149(3), Pt1−C1 = 2.032(4), Pt1−C8 = 2.329(4), Pt1−C9 = 2.348(4), Pt1−C12 = 2.156(4), Pt1−C13 = 2.181(4), C1−O1 = 1.203(5).

Pt1−C8 and Pt1−C9 (2.329(4), 2.348(4) Å) were significantly longer than those of Pt1−C12 and Pt1−C13 (2.156(4), 2.181(4) Å) due to the trans influence of the aroyl ligand being greater than that of the iodo ligand. The reaction of $AgBF_4$ with **7** in THF affords benzophenone in 40% yield. The cationic phenylplatinum complex $[PtPh(THF)(cod)](BF_4)$, formed in situ by the reaction of $AgBF_4$ and PtI(Ph)(cod), also reacts with CO (1 atm) to give benzophenone in 40% yield.

Scheme 7 shows a pathway of carbonylation; $[PtPh(THF)(cod)](BF_4)$ undergoes the migratory insertion of CO into the

Scheme 7



Pt−Ph bond to form an intermediate cationic complex with a benzoyl ligand, **D**. **D** is in a rapid equilibrium with $[PtPh(CO)(cod)](BF_4)$ (**C**) via a reversible deinsertion and insertion of CO (Scheme 8(i)). Intermolecular phenyl ligand transfer from **C** to **D** in the reaction mixture forms benzophenone, as shown in Scheme 8(ii).

Reaction 9, which forms benzophenone from the dinuclear complex **1-BF$_4$**, is explained as follows. **1-BF$_4$** reacts with CO to form a mixture of PtPh(OH)(cod) (**4**) and $[PtPh(CO)(cod)](BF_4)$. The latter undergoes migratory insertion of CO into the

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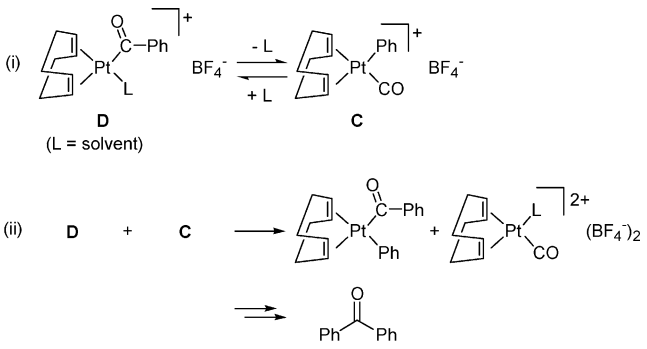
Scheme 8



Pt−Ph bond to form [Pt(COPh)(CO)(cod)](BF$_4$). The intermolecular transmetalation of a phenyl ligand between **4** (or [PtPh(CO)(cod)](BF$_4$)) with [Pt(COPh)(CO)(cod)](BF$_4$) forms the product via intermediate PtPh(COPh)(cod). The mononuclear complexes in Schemes 6 and 7 form benzophenone in yields similar to that of the reaction of CO with **1-BF$_4$** and are considered to be the intermediates of carbonylation of the dinuclear complexes.

In conclusion, we have demonstrated the reactions of the hydroxoplatinum complex [{Pt(Ph)(cod)}$_2$(μ-OH)](BF$_4$) (**1-BF$_4$**) as well as the mononuclear phenylplatinum hydroxo complex. Transmetalation of arylboronic acids yields symmetrical or unsymmetrical diarylplatinum complexes under mild conditions. Coupling of the phenyl ligands of **1-BF$_4$** caused by addition of BF$_3$·Et$_2$O is considered to involve a dinuclear intermediate, while carbonylation of **1-BF$_4$**, giving PhCOPh, takes place via insertion of CO into a Pt−C bond and successive intermolecular transmetalation of the phenyl ligand.

Experimental Section

General Considerations. Manipulations of the complexes were carried out under nitrogen or argon using standard Schlenk techniques. Dried solvents were purchased from Kanto Chemical Co., Inc. TBA$^+$OH$^-$ (37% in methanol) was purchased from Tokyo Kasei Kogyo Co., Ltd. **1-BF$_4$**, PtX$_2$(cod) (X = Cl, I, Ph), and PtI(Ph)(cod) were prepared by literature methods.[7,32] Pt(C$_6$H$_2$F$_3$-2,4,6)(Ph)(cod) (**6**) was prepared according to the procedures reported for similar complexes.[24b] Other chemicals were commercially available. NMR spectra (^{1}H, ^{11}B{^{1}H}, ^{13}C{^{1}H}, ^{19}F{^{1}H}) were recorded on Varian MERCURY300 and JEOL EX-400 spectrometers. The chemical shifts were referenced with C$_6$D$_5$H (δ 7.15) or CHCl$_3$ (δ 7.24) for ^{1}H and CDCl$_3$ (δ 77.0) for ^{13}C. IR absorption spectra were recorded on Shimadzu FT/IR-8100 spectrometers. Electrospray ionization mass spectrometry (ESIMS) was recorded on a ThermoQuest Finnigan LCQ Duo. Elemental analyses were carried out with a Yanaco MT-5 CHN autorecorder.

Reaction of bpy with 1-BF$_4$ in Acetone. To an acetone (2.0 mL) suspension of **1-BF$_4$** (65 mg, 0.075 mmol) was added bpy (12 mg, 0.077 mmol). The mixture was stirred for 20 min at room temperature. Addition of hexane (20 mL) to the reaction mixture caused separation of a yellow solid, which was collected by filtration to give **3-BF$_4$** (44 mg, 0.071 mmol, 95%). Evaporation of the filtrate formed a pale yellow solid of Pt(CH$_2$COMe)(Ph)(cod) (**2**; 0.033 mmol, 44%), which was characterized by comparison of the ^{1}H NMR spectrum with authentic samples. Data for **3-BF$_4$** are as follows. ^{1}H NMR (300 MHz, acetone-d_6, room temperature): δ 2.32−2.82 (6H, CH$_2$), 2.95−3.05 (2H, CH$_2$), 3.54 (m, 2H, CH cod (basal), J(PtH) = 75 Hz), 5.75 (m, 2H, CH cod (apical, trans to C), J(PtH) = 25 Hz), 6.71−6.76 (3H, *meta* Ph, *para* Ph), 7.14 (m, 2H, *ortho* Ph, J(HH) = 41 Hz), 8.03 (ddd, 2H, H4 bpy, J(HH) = 8, 5, 1 Hz), 8.31 (ddd, 2H, H5 bpy, J(HH) = 8, 8, 2 Hz), 8.58 (ddd, 2H, H6 bpy, J(HH) = 8, 1, 1 Hz), 9.80 (ddd, 2H, H3 bpy, J(HH) = 5, 2, 1 Hz, J(HH) = ca. 15 Hz). ESIMS (CH$_3$CN): m/z 536 [M − BF$_4$]$^+$. Anal. Calcd for C$_{24}$H$_{25}$F$_4$N$_2$BPt + H$_2$O: C, 44.94; H, 4.24; N, 4.37. Found: C, 44.89; H, 4.38; N, 4.36.

Preparation of [PtPh(bpy)(cod)](PF$_6$) (3-PF$_6$). To a THF solution of PtI(Ph)(cod) (254 mg, 0.50 mmol) was added AgPF$_6$ (135 mg, 0.53 mmol) to induce separation of AgI. After 10 min of stirring at room temperature, bpy (79 mg, 0.51 mmol) was added to the reaction mixture and the mixture was stirred for a further 10 min. After removal of insoluble AgI, the solvent was evaporated to dryness and the solid residue was extracted with CH$_2$Cl$_2$. The extract was concentrated to ca. 3 mL, and subsequent addition of Et$_2$O (100 mL) to the product caused separation of a off-white solid, which was washed with Et$_2$O and dried in vacuo to give **3-PF$_6$** (250 mg, 0.37 mmol, 74%). ^{1}H NMR (300 MHz, acetone-d_6, room temperature): δ 2.33−2.53 (4H, CH$_2$), 2.68−2.72 (2H, CH$_2$ cod), 2.96−3.01 (2H, CH$_2$), 3.54 (m, 2H, CH cod (basal), J(PtC) = 76 Hz), 5.75 (m, 2H, CH cod (apical), J(PtH) = 26 Hz), 6.71−6.75 (3H, *meta* Ph, *para* Ph), 7.14 (m, 2H, *ortho* Ph, J(PtH) = 39 Hz), 8.03 (ddd, 2H, H4 bpy, J(HH) = 7, 5, 1 Hz), 8.32 (dd, 2H, H5 bpy, J(HH) = 8, 8 Hz), 8.57 (d, 2H, H6 bpy, J(HH) = 8 Hz), 9.80 (d, 2H, H3 bpy, J(HH) = 5 Hz, J(PtH) = ca. 14 Hz). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6, room temperature): δ 27.9 (CH$_2$, J(PtC) = 26 Hz), 35.0 (CH$_2$, J(PtC) = 35 Hz), 60.7 (CH cod (apical), J(PtC) = 529 Hz), 121.2 (CH cod (basal), J(PtC) = 30 Hz), 124.4 (C4 bpy), 124.9 (*para* Ph), 128.9 (*meta* Ph, J(PtC) = 46 Hz), 129.0 (C5 bpy), 134.4 (*ortho* Ph), 136.9 (*ipso* Ph), 141.1 (C6 bpy), 152.5 (C3 bpy, J(PtC) = 31 Hz), 153.0 (C2 bpy). Anal. Calcd for C$_{24}$H$_{25}$F$_6$N$_2$PPt: C, 42.30; H, 3.70; N, 4.11. Found: C, 41.93; H, 3.75; N, 4.07.

Reaction of bpy with 1-BF$_4$ in C$_6$D$_6$. To a C$_6$D$_6$ (2.0 mL) suspension of **1-BF$_4$** (65 mg, 0.075 mmol) was added bpy (11 mg, 0.070 mmol). The mixture was stirred for 20 min at room temperature. The solid that was not soluble in C$_6$D$_6$ was removed by filtration. The filtrate contained Pt(OH)(Ph)(cod) (**4**), which was characterized by ^{1}H NMR and IR spectroscopy of the solution. ^{1}H NMR (300 MHz, C$_6$D$_6$, room temperature): δ 1.44−1.59 (4H, CH$_2$), 1.74−1.93 (4H, CH$_2$), 3.39 (br, 1H, OH), 3.76 (m, 2H, CH cod (trans to OH), J(PtH) = 60 Hz), 5.69 (m, 2H, CH cod (trans to Ph), J(PtH) = 36 Hz), 7.04 (m, 1H, *para* Ph), 7.12−7.18* (2H, *meta* Ph), 7.45 (m, 2H, *ortho* Ph, J(PtH) = 54 Hz). The peak with an asterisk is overlapped significantly with the signal of C$_6$D$_5$H. ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$, room temperature): δ 27.3 (CH$_2$), 31.8 (CH$_2$), 79.5 (br, CH cod, trans to OH), J(PtC) = 200 Hz), 115.0 (br, CH cod (trans to Ph), J(PtC) = 60 Hz), 125.2 (br, *para* Ph), 128.8 (*meta* Ph), 134.9 (*ortho* Ph), 147.2 (br, *ipso* Ph). The ^{13}C{^{1}H} NMR spectrum of **4** was obtained as a mixture with PtPh$_2$(cod) (**5**), formed by disproportionation of **4** (eq 4). IR (C$_6$D$_6$): ν(OH); 3600, 3677 cm^{-1}.

Reaction of PtI(Ph)(cod) with TBA$^+$OH$^-$ in Et$_2$O/Acetone. To a Et$_2$O/acetone (100 mL/1 mL) solution of PtI(Ph)(cod) (152 mg, 0.30 mmol) was added TBA$^+$OH$^-$ (0.40 mmol) in methanol. The mixture was stirred for 1 h at room temperature. The resulted solid was removed by filtration. Evaporation of solvent gave a crude product that was dissolved in Et$_2$O (10 mL). This solution was washed with H$_2$O (10 mL, 5 times), dried over MgSO$_4$, and filtered. Evaporation of the solvent under reduced pressure gave **2** as a white solid (87 mg, 0.20 mmol, 66%).

Reaction of 4 in Toluene. A solution of Pt(OH)(Ph)(cod) (**4**) was prepared from the reaction of bpy (12 mg, 0.077 mmol) with **1-BF$_4$** (65 mg, 0.075 mmol) for 20 min at room temperature. [PtPh(bpy)(cod)](BF$_4$) (**3-BF$_4$**; 46 mg, 0.074 mmol, 99%) was separated as a colorless solid from the solution and removed by filtration. The filtrate that contained **4** as an exclusive Pt complex was stirred for 5 days at room temperature. Evaporation of the solvent gave a solid containing PtPh$_2$(cod) (**5**; 0.011 mmol, 29%). The yield was

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determined by integration of the ^{1}H NMR signal using trichloroethylene as an internal standard.

Reaction of ArB(OH)$_2$ (Ar = Ph, C$_6$H$_2$F$_3$-2,4,6) with 1-BF$_4$. To a toluene (2.0 mL) suspension of **1-BF$_4$** (43 mg, 0.05 mmol) was added H_2O (20 μL, 0.11 mmol) and ($C_6H_2F_3$-2,4,6)ArB(OH)$_2$ (18 mg, 0.10 mmol). The mixture was stirred for 1 h at room temperature. Evaporation of the solvent gave a mixture containing Pt($C_6H_2F_3$-2,4,6)(Ph)(cod) (**6**; 0.083 mmol, 83%), which was extracted by $CDCl_3$ and characterized on the basis of ^{1}H NMR spectroscopy using diphenylethane as an internal standard. The solid that was not dissolved in $CDCl_3$ contained $B(OH)_3$, which was identified by its ^{11}B{^{1}H} NMR spectrum in acetone-d_6 (BF_3·Et_2O, internal standard). A similar reaction of PhB(OH)$_2$ (13 mg, 0.10 mmol) with **1-BF$_4$** (43 mg, 0.05 mmol) yielded **5** (0.066 mmol, 66%).

The reactions in the absence of water yielded Pt($C_6H_2F_3$-2,4,6)(Ph)(cod) (**6**) (36%) and $PtPh_2$(cod) (38%) (**5**), respectively.

NMR measurement of the reaction mixture of PhB(OH)$_2$ (6.1 mg, 0.05 mmol) with **1-BF$_4$** (22 mg, 0.025 mmol) was conducted in toluene-d_8 (1.0 mL). The ^{11}B{^{1}H} NMR spectrum after 1 h at room temperature showed signals at δ 28 (broad) and -0.8. The signals are assigned to PhB(OH)$_2$ and BF_4, respectively. ^{1}H NMR spectrum of the mixture showed signals due to **1-BF$_4$** and $PtPh_2$(cod) (δ 4.80) and minor peaks at δ 6.21, 3.71, and 3.43, which are assigned to two signals of CH cod hydrogen and one BOH hydrogen of an intermediate complex.

Preparation of Pt(C$_6$H$_2$F$_3$-2,4,6)(Ph)(cod) (6). To an Et_2O (2.0 mL) solution of ($C_6H_2F_3$-2,4,6)Br (420 mg, 2.0 mmol) was added ^{n}BuLi (1.56 M hexane solution, 1.3 mL, 2.0 mmol) at -40 °C. After the mixture was stirred for 1 h at -40 °C, PtI(Ph)(cod) (660 mg, 1.3 mmol) was added at that temperature. The reaction mixture was stirred for a further 1 h and then gradually warmed to 0 °C. After quenching of the reaction by saturated NH_4Cl(aq) (30 mL), products were extracted with Et_2O (20 mL). The combined organic extracts were washed with water (50 mL) and dried over $MgSO_4$. Removal of the solvent and washing the remaining solid with cold hexane (10 mL, 2 times) yielded Pt($C_6H_2F_3$-2,4,6)(Ph)(cod) (**6**; 386 mg, 0.75 mmol, 58%). ^{1}H NMR (300 MHz, $CDCl_3$, room temperature): δ 2.42$-$2.58 (8H, CH_2), 5.03 (m, 2H, CH cod, J(PtH) = 47 Hz), 5.27 (m, 2H, CH cod, J(PtH) = 38 Hz), 6.38 (m, 2H, $C_6H_2F_3$), 6.80 (m, 1H, *para* Ph), 6.98 (m, 2H, *meta* Ph), 7.26 (m, 2H, *ortho* Ph, J(PtH) = 64 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, room temperature): δ 29.6 (CH_2), 30.3 (CH_2, J(PtC) = 10 Hz), 99.2 (ddd, *meta* $C_6H_2F_3$, J(FC) = 33.4, 24.2, 4.0 Hz), 102.7 (CH, J(PtC) = 85 Hz), 105.8 (CH, J(PtC) = 39 Hz), 123.2 (*para* Ph, J(PtC) = 11 Hz), 127.9 (*meta* Ph, J(PtC) = 68 Hz), 134.7 (*ortho* Ph, J(PtC) = 35 Hz), 149.2 (*ipso* Ph), 159.0 (m, $C_6H_2F_3$), 162.2 (m, $C_6H_2F_3$), 165.3 (dd, $C_6H_2F_3$, J(FC) = 25.4, 15.0 Hz). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, room temperature): δ -118.5 (m, 1F), -92.3 (m, 2F, J(PtF) = 367 Hz). Anal. Calcd for $C_{20}H_{19}F_3Pt$: C, 46.97; H, 3.74; F, 11.14. Found: C, 46.66; H, 3.51; F, 10.81.

Reaction of PhB(OH)$_2$ with 4. To a C_6D_6 (1.0 mL) suspension of **1-BF$_4$** (86 mg, 0.1 mmol) was added bpy (15 mg, 0.1 mmol). The mixture was stirred for 20 min at room temperature. The **3-BF$_4$** that formed was separated from the solution and removed by filtration. The combined filtrate and washings of **3-BF$_4$** with C_6D_6 contained **4** as an almost exclusive Pt complex. PhB(OH)$_2$ (6.1 mg, 0.05 mmol) and 1,2-diphenylethane (7.4 mg, 0.042 mmol) (internal standard for NMR) were added to the solution. The ^{1}H NMR spectra were recorded at room temperature occasionally. The solution after 1.5 h contained $PtPh_2$(cod) (**5**; 0.036 mmol, 72%) and Pt(Ph)(OH)(cod) (**4**; 0.012 mmol, 24%). The solid which separated from C_6D_6 was characterized by its ^{11}B{^{1}H} NMR spectrum in acetone-d_6.

Reaction of PhB(OH)$_2$ and TBA$^+$OH$^-$ with PtI$_2$(cod). To a toluene (2.0 mL) suspension of PtI_2(cod) (56 mg, 0.10 mmol) and PhB(OH)$_2$ (24 mg, 0.20 mmol) was added TBA^+OH^- (0.20 mmol) in methanol (140 mg). The mixture was stirred for 4 h at room temperature. The solution was partitioned by addition of saturated NH_4Cl(aq) and toluene (2 mL) to the solution. The organic extract was washed with H_2O (4 mL) and dried over $MgSO_4$. Evaporation of solvent gave a mixture of $PtPh_2$(cod) (**5**; 0.051 mmol, 51%), PtCl(Ph)(cod) (0.014 mmol, 14%), and $PtCl_2$(cod) (0.007 mmol, 7%). These products were characterized on the basis of ^{1}H NMR spectroscopy. The yields were determined by integration of the ^{1}H NMR signal using diphenylethane as an internal standard. A similar reaction in the absence of TBA^+OH^- recovered unreacted PtI_2(cod).

Reaction of PhB(OH)$_2$ with [Pt(cod)(THF)$_2$](BF$_4$)$_2$. To a THF (1.0 mL) suspension of PtI_2(cod) (56 mg, 0.10 mmol) was added a THF (1.0 mL) solution of $AgBF_4$ (40 mg, 0.21 mmol). After the mixture was stirred for 1 h at room temperature, the resulting AgI was removed by filtration. After addition of PhB(OH)$_2$ (24 mg, 0.20 mmol) to the filtrate, the reaction mixture was stirred for 12 h at room temperature. Saturated NH_4Cl(aq) (2 mL) was added to the solution to convert the cationic or coordinatively unsaturated Pt complexes into the corresponding chloroplatinum complexes, and the products were extracted. The extract was washed with water (10 mL) and dried over $MgSO_4$. The absence of $PtPh_2$(cod) (**5**) and PtPh(Cl)(cod) in the reaction mixture was confirmed by ^{1}H NMR spectroscopy.

Reaction of 1-BF$_4$ and BF$_3$·Et$_2$O. To a toluene-d_8 (1.0 mL) suspension of **1-BF$_4$** (43 mg, 0.05 mmol) was added BF_3·Et_2O (15 μL, 0.12 mmol). Stirring the mixture for 12 h at room temperature caused separation of a yellow solid from the solution. The solution contained small amounts of biphenyl (<0.003 mmol, <6%) and benzene (<0.006 mmol, <6%), which were characterized by a ^{1}H NMR spectrum. The yields were determined by integration of the ^{1}H NMR signal using trichloroethylene as an internal standard. Saturated NH_4Cl(aq) (1 mL) was added to the mixture, which was stirred for a further 10 min at room temperature. ^{1}H NMR spectrum indicated formation of biphenyl (0.038 mmol, 76%), benzene (0.022 mmol, 22%), $PtCl_2$(cod) (0.054 mmol, 54%), and cod (0.006 mmol, 12%).

Reaction of BF$_3$·Et$_2$O with 5. To a toluene (1.0 mL) solution of **5** (46 mg, 0.1 mmol) was added BF_3·Et_2O (13 μL, 0.10 mmol). After the mixture was stirred for 6 h at room temperature, saturated NH_4Cl(aq) (2 mL) was added to the mixture. The products were extracted with THF (2 mL, 3 times), and the combined organic phase was washed with water (5 mL, 2 times), dried over $MgSO_4$, and filtered. Evaporation of the solvent gave solids containing PtCl(Ph)(cod) (0.074 mmol, 74%), $PtCl_2$(cod) (0.005 mmol, 5%), and biphenyl (0.003 mmol, 3%), which were characterized by a ^{1}H NMR spectrum in $CDCl_3$. The yields were determined by integration of the ^{1}H NMR signal using trichloroethylene as an internal standard.

Reaction of NH$_4$Cl with 1-BF$_4$. To a THF (2.0 mL) suspension of **1-BF$_4$** (87 mg, 0.10 mmol) was added 1.0 M NH_4Cl(aq) (1.0 mmol, 1 mL). The mixture was stirred for 5 h at room temperature. The product was extracted with Et_2O, and the organic extract was washed with water and dried over $MgSO_4$. Evaporation of the solution gave a solid containing PtCl(Ph)(cod) (0.16 mmol, 80%), which was characterized by a ^{1}H NMR spectrum. The yield was determined by integration of the ^{1}H NMR signal using diphenylmethane as internal standard.

Carbonylation of 1-BF$_4$. To a CH_2Cl_2 (2.0 mL) solution of **1-BF$_4$** (89 mg, 0.10 mmol) in a Schlenk flask was introduced CO at 1 atm. The solution was stirred for 13 h at room temperature. Addition of Et_2O to the solution caused separation of a solid, which was removed by filtration. Evaporation of the solution gave a solid containing PhCOPh (0.043 mmol, 43%), which was characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. The yield was determined by integration of the ^{1}H NMR signal using 1,1,2,2-tetrachloroethane as an internal standard.

Carbonylation of PtI(Ph)(cod). To a CH_2Cl_2 (15 mL) solution of PtI(Ph)(cod) (766 mg, 1.5 mmol) in a Schlenk flask was introduced CO at 1 atm. The solution was stirred for 15 h at room temperature. Evaporation of the solution gave a yellow solid. Recrystallization from CH_2Cl_2/Et_2O (5 mL/50 mL) gave PtI(COPh)(cod) (**7**; 607 mg, 1.1 mmol, 73%). ^{1}H NMR (300 MHz, $CDCl_3$, room temperature): δ 2.09−2.57 (8H, CH_2), 4.68 (m, 2H, CH cod (trans to I), J(PtH) = 77 Hz), 5.87 (m, 2H, CH cod (trans to C), J(PtH) = 22 Hz), 7.40 (m, 2H, *meta* Ph), 7.44 (m, 1H, *para* Ph), 8.00 (m, 2H, *ortho* Ph). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, room temperature): δ 28.1 (CH_2, J(PtC) = 24 Hz), 31.6 (CH_2, J(PtC) = 25 Hz), 91.4 (CH cod, J(PtC) = 195 Hz), 117.8 (CH cod), 128.1, 130.3, 132.1, 145.7, 208.7 (C═O). IR (KBr): ν(C═O); 1640 cm^{-1}. Anal. Calcd for $C_{15}H_{17}OIPt$: C, 33.66; H, 3.20. Found: C, 33.39; H, 3.16.

PtI(COPh)(cod) (**7**) was stable in the solid state. No decarbonylation was observed, even after the solid was kept under reduced pressure (3×10^{-4} atm) at room temperature for 6 h.

Reaction of $AgBF_4$ with PtI(COPh)(cod) (7). To a THF (2.0 mL) solution of **7** (54 mg, 0.10 mmol) was added $AgBF_4$ (20 mg, 0.10 mmol). The mixture was stirred for 1 h at room temperature followed by addition of saturated NH_4Cl(aq) (4 mL). The product was extracted with Et_2O, and the combined organic extract was dried over $MgSO_4$. The solvent was removed by evaporation to give a mixture containing PhCOPh (0.020 mmol, 40%), which was characterized on the basis of ^{1}H NMR spectroscopy. The yields were determined by integration of the ^{1}H NMR signal using trichloroethylene as an internal standard. A similar reaction in acetone gave PhCOPh (0.019 mmol, 38%) also.

Carbonylation of [PtPh(THF)(cod)](BF$_4$). To a THF (2.0 mL) solution of PtI(Ph)(cod) (101 mg, 0.2 mmol) was added $AgBF_4$ (38 mg, 0.2 mmol) in THF (2.0 mL). The mixture was stirred for 10 min at room temperature followed by removal of the formed AgI by filtration. CO (1 atm) was introduced to the solution, which was stirred for another 2 h at room temperature. Saturated NH_4Cl(aq) (5 mL) was added to the solution. The organic extract was washed with water (5 mL) and dried over $MgSO_4$. The solvent was removed by evaporation to give a mixture containing PhCOPh (0.039 mmol, 39%) and free cod (trace), which were characterized on the basis of ^{1}H NMR spectroscopy. The yield was determined by integration of the ^{1}H NMR signal using trichloroethylene as an internal standard.

Crystal Structure Determination. Crystals of **3-PF$_6$** and **7** suitable for X-ray diffraction study were obtained by recrystallization from acetone/Et_2O and CH_2Cl_2/Et_2O, respectively, and mounted in a glass capillary tube. The data were collected to a maximum 2θ value of 55°. 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°. Calculations were carried out by using a program package CrystalStructure for Windows.[33] The structure was solved by direct methods and expanded using Fourier techniques. Crystal data and detailed results of refinement are summarized in Table 1.

Table 1. Crystal Data and Details of Structure Refinement of 3-PF$_6$ and 7

	3-PF$_6$	**7**
formula	$C_{24}H_{25}F_6N_2PPt$	$C_{15}H_{17}IOPt$
mol wt	681.53	535.29
cryst syst	orthorhombic	monoclinic
space group	*Pbca* (No. 61)	$P2_1/n$ (No. 14)
a/Å	17.465(7)	8.887(1)
b/Å	15.145(7)	12.414(1)
c/Å	17.870(8)	13.254(2)
β/deg	-	92.967(1)
V/Å^3	4727(4)	1460.3(3)
Z	8	4
F(000)	2640.00	984.00
D_{calcd}/ g cm^{-3}	1.915	2.435
cryst size/mm	0.40 × 0.20 × 0.10	0.40 × 0.40 × 0.20
no. of unique rflns	5384	3269
no. of used rflns ($I \geq 1.0\sigma(I)$)	4983	3229
no. of variables	332	180
R ($I \geq 1.0\ \sigma(I)$)	0.042	0.027
R_w ($I \geq 1.0\ \sigma(I)$)	0.076	0.041
goodness of fit	1.06	1.02

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Supporting Information Available: Crystallographic data of **3-PF$_6$** and **7** as CIF files, and figures giving the ^{11}B{^{1}H} NMR spectrum obtained after reaction 3 and IR, ^{1}H NMR, and ^{13}C{^{1}H} NMR spectra of Pt(OH)(Ph)(cod) (**4**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) Crystal Structure: Crystal Analysis Package; Rigaku and Rigaku/MSC, 2000−2006.