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Notes

Transmetalation of Phenylplatinum(II) Complex. Isolation and Characterization of a Dinuclear Intermediate in Intermolecular Phenyl Ligand Transfer

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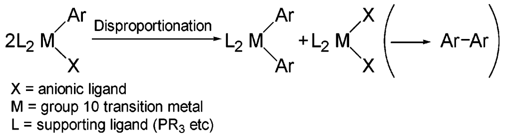
Summary: PtI(Ph)(cod) reacts with TBA^+OH^- (TBA = tetra-n-butylammonium) to form $PtPh_2$(cod) via intermolecular phenyl ligand transfer. An intermediate dinuclear Pt complex with the bridging OH ligand, $[\{Pt(Ph)(cod)\}_2(\mu\text{-}OH)]^+$, was isolated and fully characterized.

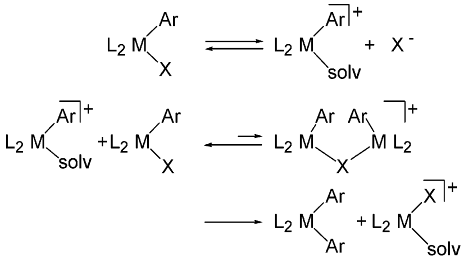
Introduction

Many homo- and cross-coupling reactions of aryl halides catalyzed by group 10 transition metal complexes involve intermolecular transfer of the aryl ligand in their catalytic cycles.[1] Studies of the mechanism of the cross-coupling reactions catalyzed by Pd complexes revealed that the transfer of the aryl ligand between the Pd complexes served to regulate concentration of the *cis*-(alkyl)arylpalladium intermediate and to cause selective reductive elimination of the cross-coupling product.[2] The intermolecular aryl ligand transfer involves intermediate three-coordinated Pd complexes having a T-shaped structure[3] and dinuclear Pd complexes with the bridging ligands. Scheme 1 shows the aryl ligand transfer of the monoaryl complexes of group 10 transition metals to yield diaryl complexes. These disproportionation-type transmetalation reactions were proposed as the key step in coupling reactions. $Ni(cod)_2$ promotes the dehalogenative coupling of Ar−Br in polar solvents,[4] which provides a general synthetic tool for π-conjugated polymers.[5] The kinetic results of the reaction, using 2,2′-bipyridine as the supporting ligand, indicate that the rate-determining step resides in the disproportionation of the intermediate NiBr(Ar)(bpy) to yield $NiAr_2$(bpy) and $NiBr_2$(bpy).[6] Monoaryl complexes of Pd and Pt undergo analogous intermolecular aryl ligand transfer to produce diaryl complexes of these metals[7,8] or biaryls.[9,10] A plausible mechanism of the reaction is shown in Scheme 2, which is the formation of the cationic aryl complex and its reaction with the neutral aryl complex to form the intermediate dinuclear complex with bridging anionic ligand. The dinuclear intermediates of the reactions have not been isolated nor fully characterized because they are readily turned into mononuclear Pt complexes under the reaction conditions used. In this paper, we report disproportionation of PtI(Ph)(cod) to afford $PtPh_2$(cod) induced by the

Scheme 1



Scheme 2



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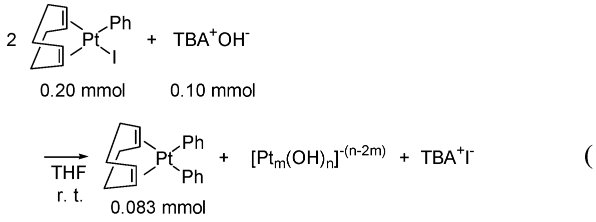
addition of OH^-, which takes place via an isolable dinuclear intermediate.

Results and Discussion

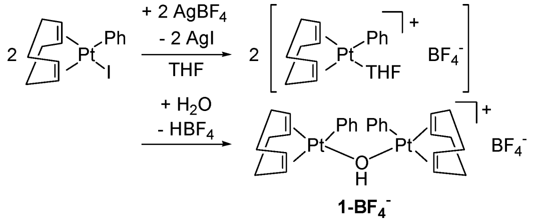
PtI(Ph)(cod) reacts with TBA^+OH^- (TBA = tetra-*n*-butylammonium) in a 2:1 molar ratio at room temperature to afford $PtPh_2$(cod) in 42% yield (eq 1). The simultaneous formation of TBA^+I^- was confirmed by X-ray powder diffraction. Anionic Pt oligomers, $[Pt_m(OH)_n]^{-(n-2m)}$, were also formed on the basis of the ESI/MS and GPC analyses of the products (see Supporting Information). The reaction of $AgBF_4$ with PtI(Ph)(cod)



(1)

in THF followed by the addition of H_2O affords the dinuclear complex $[\{PtPh(cod)\}_2(\mu\text{-}OH)](BF_4)$ (**1-BF₄⁻**), as shown in Scheme 3.

Scheme 3



Single crystals of **1-BF₄⁻** contain two crystallographically independent molecules whose structures are quite similar to each other. Figure 1 shows the molecular structure of the complex having two Pt centers bridged by an OH ligand. Selected bond distances and angles are summarized in Table 1. The Pt−O bond distances (2.030(6)−2.108(6) Å) are similar to those of $[Pt(\mu\text{-}OH)(dppb)]_2(BF_4)_2$ (dppb = 1,2-bis(diphenylphosphino)butane) (2.079(4), 2.081(5) Å)[11] and shorter than the Pt−O bond of the mononuclear complex Pt(Me)(OH)(cod) (2.194(5) Å).[12] The distances between the two Pt centers (3.5477(8), 3.5175(7) Å) are longer than that of the Pt−Pt bond. The Pt−C(phenyl) bond distance is similar to that of the reported phenylplatinum(II) complexes with a cod ligand.[13,14] The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra exhibit signals of the =CH group of the cod ligand at reasonable positions (δ_H 5.54 and 3.72 (J(PtH) = 55 Hz); δ_C 115.9 and 82.3 (J(PtC) = 231 Hz)) at room temperature. The signals flanked by ^{195}Pt satellite signals are assigned to the CH group trans to the OH ligand, which shows a smaller trans influence than the phenyl ligand.[15] The ^1H NMR spectrum at −55 °C exhibits a signal due to the OH ligand (δ_H 4.17). Its position is close to $[Pt(\mu\text{-}OH)(PMe_2Ph)]_2(BF_4)_2$ (δ_H 4.02).[11] The IR spectrum in $CHCl_3$ shows the ν(OH) band at 3428 cm^{-1}, which is in the range of the peaks of the reported Pt complexes with a bridging OH ligand (3200−3570 cm^{-1}).[11,16] Mononuclear hydroxoplatinum complexes show the ν(OH) peak at higher wavenumbers (approximately 3600−3700 cm^{-1}).[12,17] These results indicate that **1-BF₄⁻** retains its dinuclear structure in the solution.

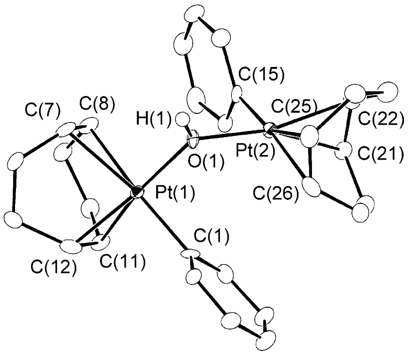


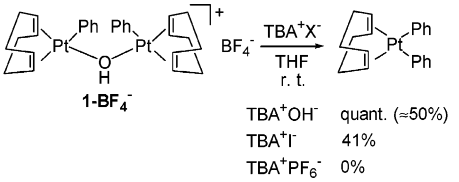
Figure 1. ORTEP drawing of complex **1-BF₄⁻** with 50% ellipsoidal plotting. The cationic part of one of the two crystallographically independent molecules is presented. The Pt(1)−Pt(2) distance is 3.5477(8) Å.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 1-BF₄⁻

atom	atom	
Pt(1)	O(1)	2.096(7)
Pt(1)	C(1)	2.008(9)
Pt(1)	C(7)	2.300(8)
Pt(1)	C(8)	2.332(9)
Pt(1)	C(11)	2.142(8)
Pt(1)	C(12)	2.10(1)
Pt(2)	O(1)	2.030(6)
Pt(2)	C(15)	2.041(9)
Pt(2)	C(21)	2.163(8)
Pt(2)	C(22)	2.17(1)
Pt(2)	C(25)	2.24(1)
Pt(2)	C(26)	2.27(1)

atom	atom	atom	
Pt(1)	O(1)	Pt(2)	118.6(3)

The addition of TBA^+OH^- or TBA^+I^- to **1-BF₄⁻** solution in THF affords $PtPh_2$(cod) in high yields (eq 2). The reaction of $TBA^+PF_6^-$ with **1-BF₄⁻** does not form $PtPh_2$(cod). These results indicate that the anions I^- and OH^- that could coordinate to the metal center induce the *intramolecular* phenyl ligand transfer of **1-BF₄⁻** to yield $PtPh_2$(cod), while PF_6^- does not cause the phenyl ligand transfer.



(2)

Scheme 4 shows a plausible pathway of reaction 1 from the results of Scheme 3 and reaction 2. Pt(OH)(Ph)(cod) is formed by the reaction of OH^- with PtI(Ph)(cod)[18] and reacts with PtI(Ph)(cod) in the reaction mixture to form the dinuclear intermediate **1-I⁻**. The

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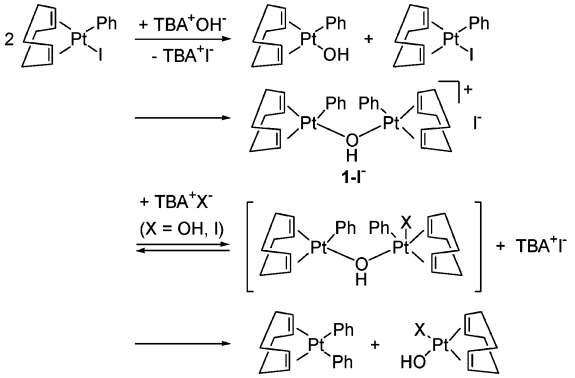
Scheme 4



I^- or OH^- contained in the reaction mixture converts **1-I**$^-$ into $PtPh_2$(cod) and Pt(X)(OH)(cod) (X = OH, I) via an intramolecular phenyl ligand transfer from one Pt to the other. The coordination of the anion to one of the square-planar Pt centers forms a dinuclear intermediate having both a square-planar metal center and a labile pentacoordinated metal center.[19,20] The phenyl ligand transfer from the latter Pt center to the former affords $PtPh_2$(cod). The associative ligand exchange reactions of square-planar complexes are induced by the coordination of a new ligand to the metal center,[21] which is similar to the latter two steps in Scheme 4. The condensation of Pt(OH)(X)(cod) (X = OH, I) accompanied by the elimination of the cod ligand forms $[Pt_m(OH)_n]^{-(n-2m)}$. The isolation of **1-I**$^-$ from the reaction mixture was not feasible probably because I^- causes the intramolecular phenyl ligand transfer of the dinuclear complex.

In conclusion, in this study, we established the pathway of the intermolecular phenyl ligand transfer of the mononuclear Pt complexes. It involves an intermediate dinuclear phenylplatinum complex with a bridging OH ligand. The OH ligand stabilizes the dinuclear structure, which enables isolation of the intermediate complex of this reaction.

Experimental Section

General Procedures. 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. PtI(Ph)(cod) and $PtPh_2$(cod) were prepared according to the literature method.[22] The other chemicals were commercially available. NMR spectra (^{1}H and $^{13}C\{^1H\}$) were recorded on a Varian Mercury 300 or a JEOL GX-500 spectrometer. The chemical shifts were referenced to C_6D_5H (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 a Shimadzu FT/IR-8100 spectrometer. ESI/MS spectra were recorded on a ThermoQuest Finnigan LCQ Duo. Elemental analyses were carried out with a Yanaco MT-5 CHN autorecorder.

Reaction of PtI(Ph)(cod) with TBA^+OH^-. To a THF (2.0 mL) suspension of PtI(Ph)(cod) (102 mg, 0.20 mmol) was added TBA^+OH^- (0.10 mmol) in methanol (70 mg). The initial suspension turned to a colorless homogeneous solution immediately. The mixture was stirred for 1 h at room temperature. The solution was partitioned by addition of saturated NH_4Cl(aq) (ca. 4 mL) and $CHCl_3$ (ca. 2 mL) to the solution. The organic extract was washed with H_2O and dried over $MgSO_4$. Evaporation of solvent gave a mixture of $PtPh_2$(cod) (0.083 mmol, 42%) and PtI(Ph)(cod) (0.024 mmol, 12%). These products were characterized on the basis of the ^{1}H NMR spectrum using 1,1,2,2-tetracholoroethane as an internal standard. Concentration of the water layer gave TBA^+I^-, which was characterized by wide-angle X-ray powder diffraction. ESI/MS and GPC analyses were carried out for the mixture of PtI(Ph)(cod) (102 mg, 0.20 mmol) and TBA^+OH^- (0.30 mmol) after stirring for 1 h in THF. ESI/MS revealed the generation of anionic oligomer $[Pt_m(OH)_n]^{-(n-2m)}$ (m/z = 539−1320). Peaks due to TBA^+ and I^- were also observed. GPC analyses showed the absence of products with higher molecular weights.

Preparation of $[\{Pt(Ph)(cod)\}_2(\mu\text{-}OH)](BF_4)$ (1-BF$_4^-$). THF solvent was bubbled with argon before use. A THF (50 mL) solution of PtI(Ph)(cod) (3.47 g, 6.84 mmol) was mixed with $AgBF_4$ (1.41 g, 7.24 mmol). After stirring the mixture for 10 min at room temperature, the formed AgI was removed by filtration. H_2O (1.0 mL) was added to the filtrate. Stirring the solution for 30 min caused the precipitation of a small amount of a black solid, which was removed by filtration. The filtrate was evaporated to dryness, and the residue was extracted with CH_2Cl_2 (1 mL). Addition of Et_2O to the CH_2Cl_2 solution caused separation of a white solid, which was collected by filtration, washed with Et_2O, and dried in vacuo to give $[\{Pt(Ph)(cod)\}_2(\mu\text{-}OH)](BF_4)$ (**1-BF$_4^-$**) (1.74 g, 2.01 mmol, 59%). ^{1}H NMR (300 MHz, C_6D_6, rt): δ 1.21−1.33 (8H, CH_2), 1.65−1.67 (8H, CH_2), 3.72 (m, 4H, CH, J(PtH) = 55 Hz), 5.54 (br, 4H, CH), 6.97 (m, 2H, C_6H_5-para), 7.10 (m, 4H, C_6H_5-meta), 7.42 (m, 4H, C_6H_5-ortho, J(PtH) = ca. 25 Hz). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.86−2.28 (16H, CH_2), 4.23 (m, 4H, CH), J(PtH) = ca. 65 Hz), 5.18 (br, 4H, CH), 7.03 (m, 2H, C_6H_5-para), 7.17 (m, 4H, C_6H_5-meta), 7.38 (m, 4H, C_6H_5-ortho, J(PtH) = ca. 30 Hz). ^{1}H NMR (300 MHz, $CDCl_3$, −55 °C): δ 1.96−2.05 (12H, CH_2), 2.28−2.35 (4H, CH_2), 4.17 (s, 1H, OH), 4.28 (br, 4H, CH)), 5.01 (br, 4H, CH), 7.06 (t, 2H, C_6H_5-para, J(HH) = 7.0 Hz), 7.22 (t, 4H, C_6H_5-meta, J(HH) = 7.0 Hz), 7.46 (d, 4H, C_6H_5-ortho, J(HH) = 7.0 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, rt): δ 26.9 (CH_2), 31.2 (CH_2), 82.3 (CH, J(PtC) = 231 Hz), 115.9 (br, CH), 125.1 (C_6H_5-para), 128.4 (br, C_6H_5-meta), 134.9 (C_6H_5-ortho), 144.6 (C_6H_5-ipso). The =CH signals at lower field positions do not show satellites due to PtH or PtC coupling either at room temperature or at −55 °C. IR ($CHCl_3$): ν(OH) 3428 cm^{-1}. The spectrum of **1-BF$_4^-$** in a KBr disk does not exhibit ν(OH) peaks. Similar results were reported for Pt(Me)(OH)(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane).[17b] Anal. Calcd for $C_{28}H_{35}BF_4OPt_2$: C, 38.90; H, 4.08. Found: C, 38.92; H, 3.97.

Reaction of $[\{Pt(Ph)(cod)\}_2(\mu\text{-}OH)](BF_4)$ (1-BF$_4^-$) with TBA^+X^- (X = OH, I, PF$_6$). To a suspension of **1-BF$_4^-$** (43 mg, 0.050 mmol) in THF (1.0 mL) was added TBA^+OH^- (0.050 mmol) in methanol (70 mg). The initial suspension soon turned to a colorless solution, which was stirred for 3 h at room

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Table 2. Crystallographic Results of Hydroxo Platinum(II) Complex 1-BF_4^-

formula	$C_{28}H_{35}BF_4OPt_2$
fw	864.55
size of crystal/mm	0.15 × 0.15 × 0.10
cryst syst	monoclinic
space group	$P2_1$ (no.4)
a/Å	10.5185(11)
b/Å	12.548(1)
c/Å	20.266(2)
β/deg	102.507(2)
V/Å^3	2611.4(5)
Z	4
D_c/g cm^{-3}	2.199
no. of reflns measd	37 804
no. of unique reflns	6031
no. of observations ($I > 3.0\sigma(I)$)	5882
no. of variables	719
good of fitness	1.012
R, R_w	0.029, 0.041

temperature. The solution was partitioned by addition of saturated NH_4Cl(aq) (ca. 1 mL) and Et_2O (ca. 2 mL) to the solution. The organic extract was washed with H_2O and dried over $MgSO_4$. Evaporation of the THF/Et_2O solution under reduced pressure gave $PtPh_2$(cod) as a white solid. The product was characterized by ^{1}H NMR spectrum.

A similar reaction of **1-BF_4^-** (40 mg, 0.046 mmol) with TBA^+I^- (37 mg, 0.10 mmol) produced $PtPh_2$(cod) (0.041 mmol, 89%). Reaction of **1-BF_4^-** (43 mg, 0.050 mmol) with $TBA^+PF_6^-$ (39 mg, 0.10 mmol) recovered the starting complexes after 3 h at room temperature.

Crystal Structure Determination. Crystals of **1-BF_4^-** suitable for X-ray diffraction study was obtained by recrystallization from CH_2Cl_2/Et_2O at −25 °C and mounted in a glass capillary tube. 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 $\chi = 45.0°$ and $\phi = 0.0°$. The detector swing angle was −20.30°. The exposure rate was 40.0 [sec/deg]. A second sweep was performed using ω scans from −110.0 to 70.0° in 0.5° steps, at $\chi = 45.0°$ and $\phi = 90.0°$. The crystal-to-detector distance was 44.99 mm. Readout was performed in the 0.070 mm pixel mode. Calculations were carried out by using the program package CrystalStructure 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. Crystallographic data and details of refinement of **1-BF_4^-** are summarized in Table 2.

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Supporting Information Available: ESI/MS and GPC analysis of $[Pt_m(OH)_n]^{-(n-2m)}$, X-ray powder diffraction analysis of TBA^+I^- obtained from the reaction mixture, and crystallographic data of **1-BF_4^-**. This material is available free of charge via the Internet at http://pubs.acs.org.

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