Synthesis of Aryl-Platinum Dinuclear Complexes via *ortho* C−H Bond Activation of Phenol and Transmetalation of Arylboronic Acid

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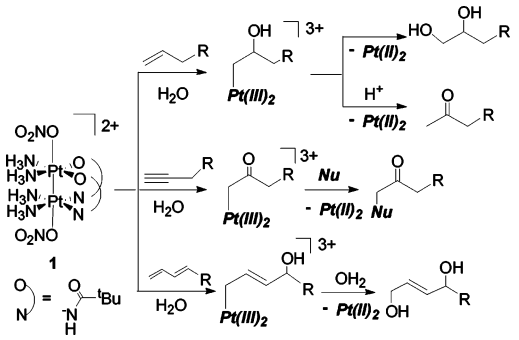
The reaction of the pivalamidate-bridged platinum(III) dinuclear complex $[Pt_2(NH_3)_4(^tBuCONH)_2(OH_2)_2]^{4+}$ with phenol in water gave 2-hydroxyphenyl platinum dinuclear complex $[Pt_2(NH_3)_4(^tBuCONH)_2(C_6H_4(OH))]^{3+}$ via *ortho* C−H bond activation in the axial position. The identical compound and the analogous phenyl complex $[Pt_2(NH_3)_4(^tBuCONH)_2(C_6H_5)]^{3+}$ could alternatively be synthesized from the reactions of $[Pt_2(NH_3)_4(^tBuCONH)_2(OH_2)_2]^{4+}$ with the corresponding arylboronic acids via transmetalation. The reactivities of the novel aryl-Pt_2 compounds toward nucleophiles and the effect of UV light irradiation were investigated. The ESR spectra showed that the axial aryl−Pt bond is homolytically cleaved by UV light irradiation to give the aryl radical and the Pt(III)−Pt(II) paramagnetic complex.

Introduction

Cisplatin (*cis*-$Pt(NH_3)_2Cl_2$)-derived amidate-bridged platinum(III) dinuclear complexes expressed in the general formula $[Pt^{III}_2(NH_3)_4(\mu\text{-amidate})_2LL']^{n+}$ (L,L′ = axial ligands)[1] have, along with other Pt(III) dinuclear compounds bearing other bridging ligands,[2] built up a new class of high-valent platinum chemistry. In addition to the basic interest in the reactivity of the $Pt(III)_2$ complexes in contrast to those of Pt(II) and Pt(IV) complexes, the Pt(III) dinuclear compounds are expected to be potential catalysts for oxidation of unsaturated organic substrates. We previously reported the reaction of the pivalamidate-bridged Pt(III) dinuclear complex HH-$[Pt^{III}_2(NH_3)_4(^tBuCONH)_2(NO_3)_2](NO_3)_2\cdot 2H_2O$ (**1**) (HH is head to head) with various unsaturated compounds such as alkenes,[3a−c,e] alkynes,[3f] and dienes[3d,e] (Scheme 1). Some of the reactions catalytically gave the oxidized

Scheme 1



compounds with the reversible two-electron redox process between **1** and the corresponding Pt^{II} complex $[Pt^{II}_2(NH_3)_4(^tBuCONH)_2](NO_3)_2$ (**2**). Precise kinetic studies were undertaken to elucidate the role of the metal−metal bond in the reaction, and the result showed that the electron delocalization through the metal−metal bond plays an important role to stabilize the reaction intermediates and to promote the reaction smoothly.[4] The reactions described above correspond to double nucleophilic addition on olefins and are totally new and specific only to Pt(III) compounds.

In an analogous study, α-C−H bond cleavage of ketones was found (Scheme 2).[5] In the reaction, the competitive mechanisms of radical cleavage (methylene

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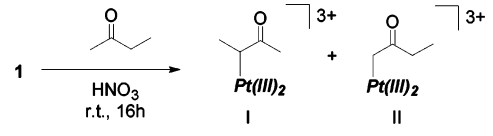
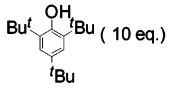
Scheme 2

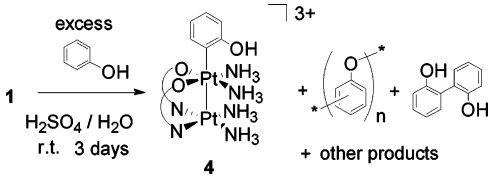


Entry	Condition	Molar ratio (I/II)	Total yield (I + II)%
1	Hg lamp-light	2.5	56
2	room-light	1.5	65
3	dark	1.1	68
4	 (10 eq.)	0.1	72

C−H) and electrophilic displacement (methyl C−H) proceed in parallel. It was suggested that the axial site of complex **1** has the properties of both a strong Lewis acid and a radical agent. These reactivities indicate that the electron distribution along the Pt(III)−Pt(III) bond has both Pt(III)−Pt(III) (d^7−d^7) and Pt(IV)−Pt(II) (d^6−d^8) natures; that is, these two or sometimes three oxidation states, if the reverse Pt(II)−Pt(IV) is counted,[4] exist as resonant forms.

As an extension of the organometallic chemisty of **1**, the reaction with aromatic compounds is examined in the present study. The C−H bond activation using oxidative addition of halo- or pseudohalobenzene to low-valent transition metals has made a great contribution to C−C bond formation in organic synthesis.[6] On the other hand, C−H bond activation of aromatic compounds by transition metal complexes under mild conditions is still the research target in halide-free processes and has been extensively studied by many researchers.[7−10] However, practically useful catalytic systems have been reported only for the substrates bearing chelation assistance by a carbonyl group on the aromatic substrate.[7,8] Since the first report on the attractive but impractical oxidation of alkanes and arenes by Shilov (catalytic to $Pt^{II}Cl_4^{2-}$ but stoichiometric amount of $Pt^{IV}Cl_6^{2-}$ was used as the oxidant),[9] the research has been focused on the use of electrophilic late transition metal complexes, especially on Pt(II) complexes.[9,10] In these systems, the proposed catalytic cycle basically consists of the following three steps: (i) electrophilic activation of R−H with Pt(II) to give the alkyl-Pt(II) complex, (ii) oxidation to the corresponding alkyl-Pt(IV) complex with suitable oxidant, and (iii) nucleophilic attack on the alkyl-Pt(IV) complex to release R−Y and regeneration of the Pt(II) complex (Y = Cl or OH). Although each individual step is known to proceed in several platinum complexes, a single complex capable of completing the catalytic cycle has not yet been found.[10] There seems to be a dilemma in this catalytic reaction; that is, the catalyst should be electron deficient to activate the R−H (step i) but should also be electron rich to be readily oxidized (step ii). Electron deficiency due to the high oxidation state and the reversible redox behavior of complex **1** noted above are expected to be an advantage for the catalyst in such chemistry.

Scheme 3



Here, we report the regioselective C−H bond activation of phenol to give a novel aryl-platinum dinuclear complex having a phenolic *ortho* carbon atom bound to one of the axial positions of the $Pt(III)_2$ complex. Furthermore, the alternative synthetic approach to the aryl-platinum dinuclear complexes by using transmetalation of the corresponding aryl boronic acids is also reported. Studies on the reactivity of these complexes revealed that a facile cleavage of the aryl−Pt bond occurs specifically by UV light irradiation. Radical cleavage of the aryl−Pt_2 bonds to give the aryl radicals and the paramagnetic Pt(III)−Pt(II) complex is supported by ESR spectroscopy.

Results and Discussion

Synthesis of the 2-Hydroxyphenyl-Pt(III) Complex. The reaction of complex **1**, which was prepared in situ by the oxidation of the Pt-blue complex HH-$[Pt_4(NH_3)_8(^t\mathrm{BuCONH})_4](NO_3)_5$ (**3**)[3b] with $Na_2S_2O_8$ in 0.1 M H_2SO_4 solution, with excess phenol at room temperature for 3 days gave the *ortho* C−H-activated $Pt(III)_2$ complex $[Pt_2(NH_3)_4(^t\mathrm{BuCONH})_2(C_6H_4(OH))](NO_3)(SO_4)\cdot C_6H_5OH\cdot 2H_2O$ (**4**). In this reaction, poly(phenylene oxide), 2,2′-biphenol, and other unidentified products were also precipitated (Scheme 3).[12] Without H_2SO_4 in the solution, formation of these oxidized and polymerized products preferentially proceeded. Therefore, H_2SO_4 was added for the synthesis of **4**.

There seems to be four possible mechanisms for the formation of **4** (Scheme 4). The first is an electrophilic substitution of H^+ on the aromatic ring with **1** through the π-complex or the η^1-arene complex[13] (route a, **I**, or **I′**), which is transformed into a Wheland-type complex (**II**). The η^1-arene complex is one of the well-established intermediates for the C−H activation of arenes. Some precedents such as $Ru(PPh_3)_3Cl_2$[13c] and $[Rh(PPh_3)_3]^+$[13d] have been structurally characterized, in which an *ortho* H atom of phosphine coordinates to the metal. Shul'pin reported that the Wheland-type complex is an interme-

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(12) The ESI-MS and ^{1}H NMR spectra, after separation with GPC, were placed in the Supporting Information. Althouth the yields of these compounds could not be determined because of the incomplete separation and characterization, the weight of the obtained precipitate was only 2 mg against the 19 mg of phenol added.

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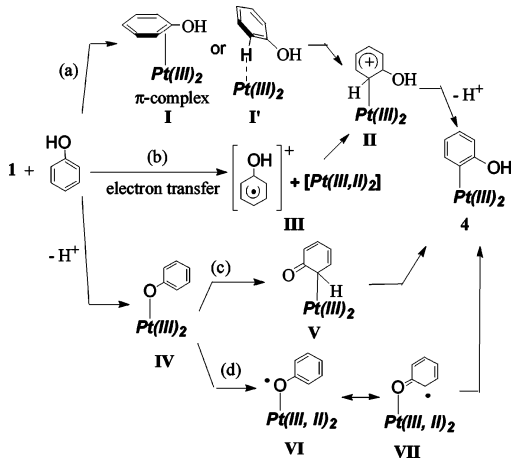
Scheme 4. Possible Formation Mechanisms



diate for the reactions of arenes with H_2PtCl_6.[9b,14] The second possibility is a radical mechanism of electron transfer from phenol to **1** to give a radical ion pair (**III**) (route b). A radical mechanism was also proposed in the photoinduced reaction of H_2PtCl_6 with arenes, in which a radical ion pair $[ArH]^+ \cdot [Pt^{III}Cl_5]^{2-}$ was observed in the ESR spectrum at 77 K.[14] The initially formed radical pair was thought to be transformed to the Wheland complex. The last two (routes c and d) are the rearrangements of the Pt atom in the phenoxide intermediate (**IV**).

In the reported reactions of monosubstituted aromatic compounds bearing OH, OMe, Me, F, COMe, CO_2H, Cl, or NO_2 with H_2PtCl_4, the *para* and *meta* C−H bond activated compounds were obtained as a mixture and no *ortho* C−H bond activated product was obtained, presumably because of the steric hindrance of the substituent.[14] In contrast, *ortho* platination favorably occurred at room temperature in our present reaction, and at elevated temperatures (313−343 K) *para* platination was observed in small amount in the ^{1}H NMR spectrum.

To investigate the formation mechanism of complex **4**, the reaction of complex **1** with phenol was monitored with ^{1}H NMR spectroscopy (Figure 1). After phenol addition, the peaks of the ^{t}Bu groups became broadened, and at the same time the peak at 1.2 ppm of compound **4** appeared and increased. Formation of **4** was also observed as the increase of the peaks of the hydroxyphenyl group of **4**. No peak was observed for the intermediate. However the new peaks were broadened and suggest that some exchange reaction occurs on the NMR time scale. Even at 5 °C, any peak shape change was not observed. On the other hand, existence of an intermediate was evidenced by the UV−vis spectral change of the reaction solution (Figure 2). The absorption of **1** at 350 nm gradually decreases, and the isosbestic points at 334 and 386 nm in the early reaction stage gradually move to 337 and 392 nm, respectively (the inset of Figure 2), suggesting that the reaction proceeds via at least two steps.

In the phenol reaction, complex **2** was not observed. Thus, the oxidation state of the Pt complex seems to be maintained. The addition of 100 equiv of the radical-

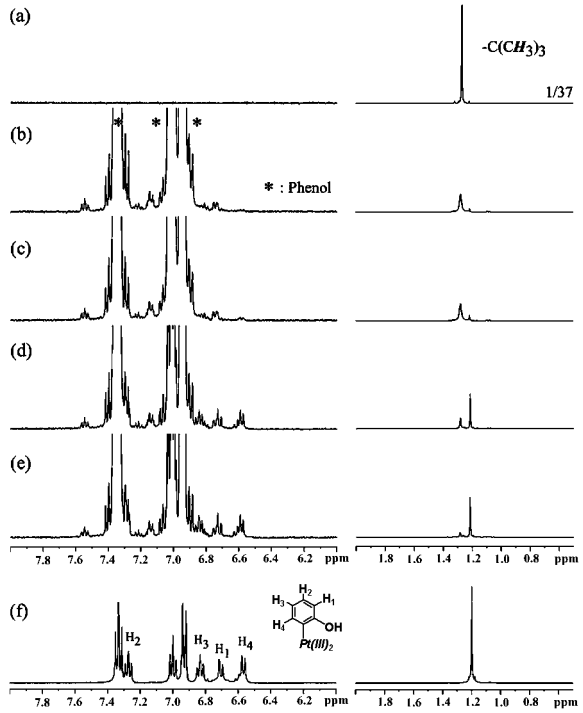


Figure 1. ^{1}H NMR spectral change of the reaction of **1** with phenol in D_2O (a−e): (a) only complex **1**, (b) reaction solution after 13 min, (c) after 34 min, (d) after 576 min, (e) after 4292 min; (f) only complex **4** in D_2O.

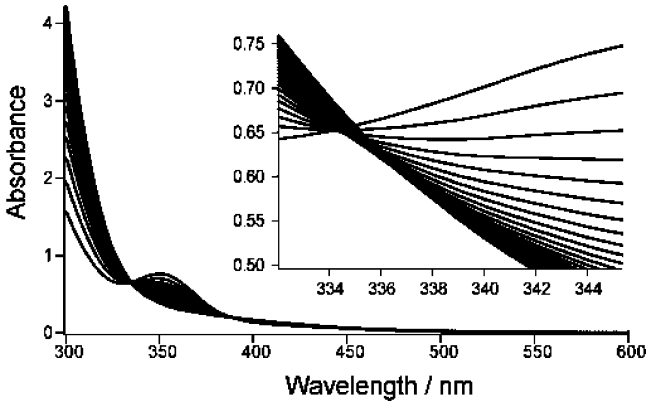


Figure 2. UV/vis spectral change of the reaction of complex **1** with phenol, recorded every 20 min at 40 °C. [Complex **1**] = 0.47 mM, [phenol] = 100 mM, and $[H^+]$ = 2.0 M. The inset shows the magnified figure in the region 326−346 nm.

trapping agent 2,4,6-tri-*tert*-butylphenol did not affect the formation of complex **4**, which reduces the possibility of the radical route b. However, we could not determine which of the routes in Scheme 4 is correct.

Although we cannot account for the reason from these experimental data why the *ortho* C−H bond was selectively activated, it seems that the hydrogen bonding between the oxygen atom of the phenol and a proton of the equatorial NH_3 ligand acts as an anchor to selectively activate the *ortho* C−H bond of phenol. As is shown in the next paragraph, the crystal structure analysis indicates that the steric hindrance is not so critical in the present reaction with phenol compared to Shul'pin's reaction,[14] and such a hydrogen bonding between the phenolic oxygen and the NH_3 ligand exists in the crystal structure as discussed later.

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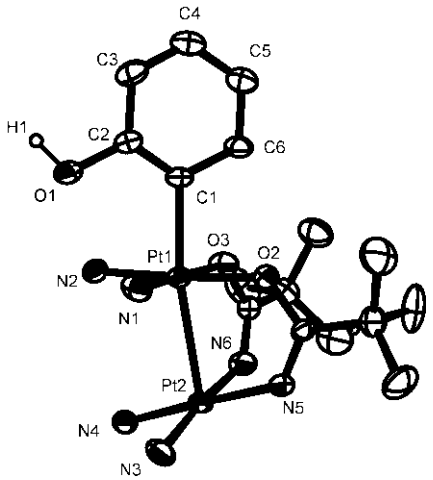

Figure 3. Crystal structure of the complex cation of **4**.

Nonsubstituted benzene or methoxybenzene did not react with **1** even with heating. The fact that methoxybenzene did not react with **1** suggests that the route a in Scheme 4 is most probable. Iodobenzene reacted with heating to give *p*-benzoquinone, but the complex decomposed. Chlorobenzene and bromobenzene did not react at all. The reaction with acetophenone was reported previously, in which the sp^3 C−H bond is activated rather than the aryl C−H bond to give the corresponding ketomethylene-Pt dinuclear complex.[5b]

Characterization of Complex 4. The structure of complex **4** was confirmed by the ^{1}H, ^{13}C, and ^{195}Pt NMR spectra and X-ray diffraction analysis. The ORTEP drawing and the selected structural parameters of the cation of complex **4** are given in Figure 3 and Table 1 with the corresponding data for other related compounds. As is shown in Figure 3, the 2-hydroxyphenyl group is bound to the N_2O_2-coordinated platinum atom. The Pt−Pt distance (2.6836(17) Å) is slightly shorter than those of the previously reported alkyl-Pt−Pt complexes (Table 1).[16] This suggests that the *trans* influence of the 2-hydroxyphenyl group is weaker than the alkyl groups having an sp^3-hybridized carbon. The Pt−C(1) bond length (2.073(10) Å) in the axial position is comparable to those of the previously reported Pt−C_{axial} single bonds in the alkyl-Pt_2 complexes.

The six carbon and one oxygen atom in the axial ligand exist in the same plane. The OH proton of the axial ligand (H(1)) was directly observed. It was also observed in the ^{1}H NMR spectrum in DMSO-d_6 at 10.6 ppm (Experimental Section). The hydroxyl group of the axial ligand exists between the two NH_3 ligands and possibly makes H_2N−H···OH hydrogen bondings (the N(1)−O(1) and N(2)−O(1) separations are 2.85 and 2.83 Å, respectively).

The ^{195}Pt{^{1}H} NMR spectra of complex **4** in D_2O (Figure 4) showed two largely separated peaks at −48 and −2130 ppm. The former peak had a satellite of ^{195}Pt (natural abundance = 33.8%, I = 1/2), and each peak is further split by two magnetically equivalent ^{14}N nuclei (I = 1) into five lines. The latter peak has a broad pattern owing to two sets of two magnetically equivalent nitrogen atoms. However, the peak clearly showed the satellite of ^{195}Pt. From these patterns and our previous data, the assignment was determined as shown in Figure 4.

Reaction of 1 with Substituted Phenols. To investigate the generality of the phenol reaction, we examined the reactions with other substituted phenols. The reaction of **1** with 4-methylphenol did not give the *ortho* C−H activation product. The ^{1}H NMR spectrum of the reaction solution did not show formation of an aryl complex. In this reaction, a dark green oil[17] and the reduced Pt complex **2** were obtained. The formation of 4,4′-dimethyl-2,2′-biphenol and 4-hydroxybenzoic acid in addition to the oligomers was confirmed by ^{1}H NMR spectroscopy (Scheme 5). Different from the phenol reaction, electron transfer between the substrate and the Pt(III) complex is preferred to the formation of the aryl-Pt_2 complex, and the substrate is oxidized. The phenoxyl radical stabilized by the methyl group at C4 would cause such substrate oxidation. In the phenol reaction, formation of **4** would be much faster than such electron transfer, and since **4** is stable in solution, **2** was not observed.

The reaction of **1** with 2,6-dimethylphenol having no *ortho* C−H bond did not afford the aryl-Pt_2 complex, either. In this reaction, the oxidatively coupled 2,2′,6,6′-tetramethyl-4,4′-biphenol, its further oxidized product 2,2′,6,6′-tetramethyl-4,4′-biphenoquinone (DPQ), and poly(2,6-dimethyl-phenyleneoxide) (PPO) were obtained from the $CDCl_3$ phase (Scheme 6).[18] The former two products were obtained catalytically relative to **1**.

Oxidative polymerization of 2,6-dimethylphenol to PPO catalyzed by a Cu^{2+} complex has widely been studied.[19] In the presence of amine in addition to the Cu salt, PPO is produced, whereas DPQ is produced in the absence of amine (Scheme 7). The mechanistic study suggested that, in both reactions, one-electron redox seems to take place in the Cu^{2+}-phenoxide or Cu^{2+}-phenol complex producing Cu^+.[19] Only a few Pt-phenoxide complexes have so far been isolated.[20] Phenoxide complex was not observed or isolated in the present reaction, although redox reaction in the intermediate state seems possible also in the present reaction (Scheme 4, route d).

Alternative Synthetic Method of the Aryl-Pt(III) Dinuclear Complexes via Reaction of 1 with Arylboronic Acids. All of the organoplatinum(III) dinuclear complexes previously reported by us have an sp^3-hybridized carbon atom bound to $Pt(III)_2$, and the α-carbon has electrophilic character, reacting easily with various nucleophiles to release the nucleophile-substituted prod-

(15) In the low-field region, no peak was observed except for those of the excess phenol.

(16) The metal−metal distances of the previously reported alkyl-Pt(III)-Pt(III) complexes are in the range 2.68 to 2.74 Å.

(17) The GPC chart of the products is placed in the Supporting Information.

(18) The products were identified by comparison of the ^{1}H NMR spectra with the authentic sample (2,2′,6,6′-tetramethyl-4,4′-biphenol), and the data (the ^{1}H NMR data of 2,2′,6,6′-tetramethyl-4,4′-biphenoquinone and poly(2,6-dimethylphenyleneoxide) were reported in ref 19c.

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Table 1. Selected Bond Distances (Å) of the Complexes 4, 4′, 5, and the Previously Reported Complexes

	complex **4**	complex **4′**	complex **5**	acetonyl[a]	2-hydroxycyclohexyl[b]
Pt1−Pt2	2.6836(17)	2.6861(4)	2.7542(11)	2.6892(6)	2.734(2)
Pt1−C1	2.073(10)	2.064(6)	2.052(14)	2.095(9)	2.11(3)
C1−C2	1.337(16)	1.390(9)	1.48(2)		
C2−C3	1.399(17)	1.397(9)	1.38(2)		
C3−C4	1.332(18)	1.376(10)	1.30(2)		
C4−C5	1.394(19)	1.388(11)	1.46(3)		
C5−C6	1.375(16)	1.386(9)	1.37(3)		
C6−C1	1.412(16)	1.379(9)	1.27(2)		
C2−O1	1.382(15)	1.370(8)			

[a] Reference 3b. [b] Reference 3c.

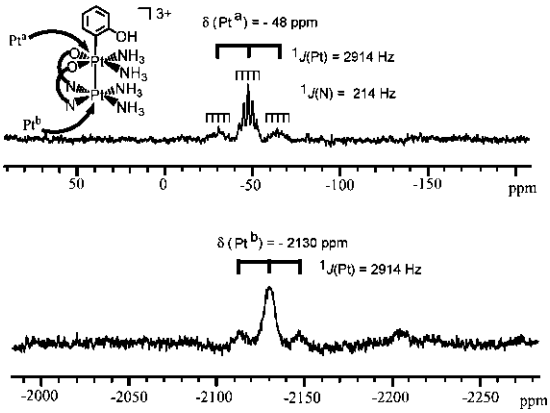
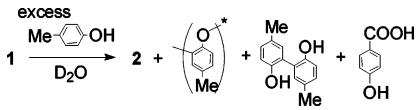
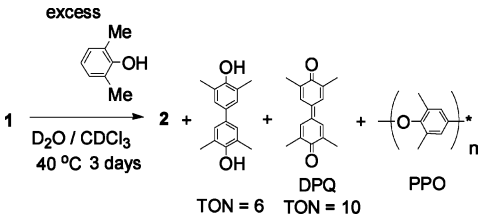


Figure 4. $^{195}Pt\{^1H\}$ NMR spectra of complex **4** in D_2O. The N_2O_2C(aryl)-coordinated platinum (top) and N_4-coordinated platinum (bottom).

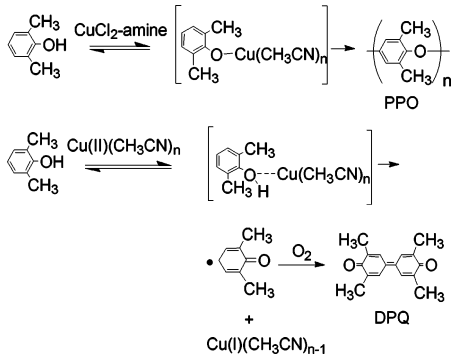
Scheme 5



Scheme 6

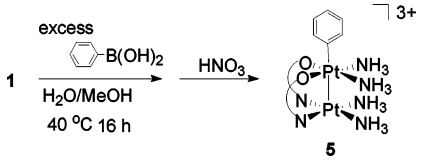


Scheme 7

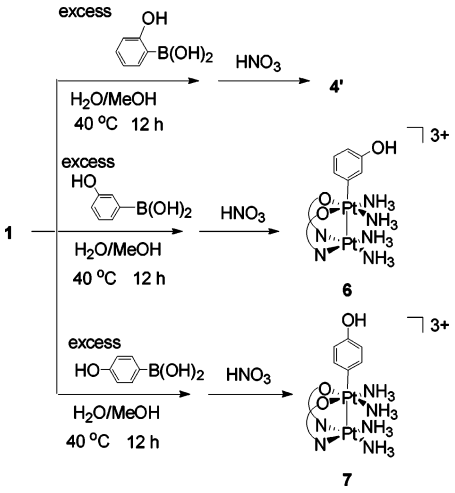


ucts and complex **2** as shown in Scheme 1. To our knowledge, only one example having an sp^2-hybridized carbon atom in the axial position of $Pt(III)_2$ was reported, in which the C5−H bond of methyluracil was activated to afford $[Pt_2(\mu\text{-meu})_2(\text{meu})]^{3+}$ (meu is methyluracilyl).[21] However, its reactivity has not been reported.

Scheme 8



Scheme 9



As a more versatile and widely applicable route to various aryl derivatives, the reaction of **1** with arylboronic acids was developed to give various aryl-Pt_2 complexes in moderate yields. The phenyl-Pt_2 complex $[Pt_2(NH_3)_4(^t\text{BuCONH})_2(C_6H_5)](NO_3)_3\cdot 2H_2O$ (**5**), 2-hydroxyphenyl-Pt_2 complex $[Pt_2(NH_3)_4(^t\text{BuCONH})_2(C_6H_4(OH))](NO_3)_3\cdot H_2O$ (**4′**), 3-hydroxy-phenyl-Pt_2 complex $[Pt_2(NH_3)_4(^t\text{BuCONH})_2(C_6H_4(OH))](NO_3)_3\cdot H_2O$ (**6**), and 4-hydroxy-phenyl-Pt_2 complex $[Pt_2(NH_3)_4(^t\text{BuCONH})_2(C_6H_4(OH))](NO_3)_3\cdot H_2O$ (**7**) were prepared in the reactions of **1** with the corresponding boronic acids in 53%, 66%, 82%, and 46% yields, respectively (Schemes 8 and 9).

Complexes **5** and **4′** were obtained as single crystals suitable for X-ray diffraction. The ORTEP drawing, the structural parameters, and the crystal data of complex **5** are given in Figure 5 and Tables 1 and 2.[22]

The structural feature of complex **4′** resembles that of complex **4**, whereas the Pt(1)−Pt(2) bond distance of complex **5** is slightly longer than those of complexes **4** and **4′**. It is notable that the orientation of the phenyl ring in complex **5** is different from that of **4**. The phenyl

(21) Schöllhorn, H.; Thewalt, U.; Lippert, B. *J. Chem. Soc., Chem. Commun.* **1986**, 258.

(22) The ORTEP drawing of complex **4′** is placed in the Supporting Information.

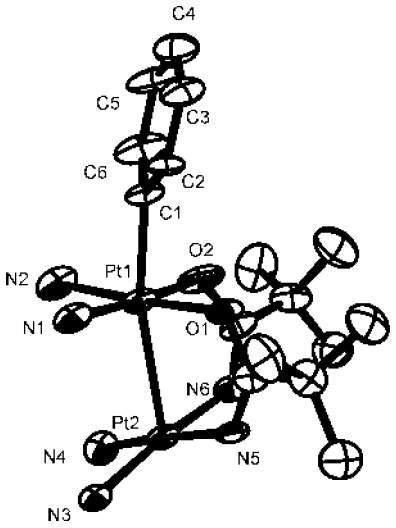


Figure 5. Crystal structure of the complex cation of **5**.

plane in complex **5** is rotated 90° compared to that of complex **4**, as seen in Figures 3 and 5. The ring orientations in **4** and **4′** come from the hydrogen bondings of HO(phenol)···HNH_2 as described earlier.

The above reactions are the first synthesis of organoplatinum(III) complexes by transmetalation. Since aryl boronic acids are useful reagents for the Suzuki–Miyaura coupling[23] and many variations are commercially available, the present transmetalation provides a general route to synthesize aryl-Pt_2 complexes.

Reactions of the Aryl-Pt Dinuclear Complexes with Nucleophiles. The alkyl-Pt dinuclear complexes such as ketonyl-Pt_2 complexes easily undergo nucleophilic attack of OH^-, halide (Cl^- or Br^-), and amines to give the α-nucleophile-substituted ketones.[3f,5] This reactivity is considered to be due to the approximate charge distribution of the complexes as R(ketonyl)-Pt(IV)-Pt(II). Namely, this alkyl group is electrophilic, similar to that of alkyl-Pt(IV) complexes.[24] The ^{195}Pt NMR chemical shifts of complexes **4**, **4′**, and **5** show the same trend of the electron localization. On the basis of this localization, reactions of the aryl-Pt_2 complexes with nucleophiles were examined.

An excess of halide ions (NaCl or NaBr in D_2O) did not react with **5** even at high temperature (70 °C). The reaction with more basic nucleophiles such as MeONa in CD_3OD for 48 h did not afford any nucleophile-substituted product. The ^1H NMR spectrum showed broad unidentified signals. After further prolonged reaction at room temperature for 2 days, the solution gave anisole in a low yield (10%). The reaction of **5** with $HNEt_2$ in $CDCl_3$ did not give *N,N*-diethylaniline at all. These results show that the nucleophilic attack on the α-aryl carbon is not straightforward, unlike the alkyl carbon on Pt(III), and follows the general fact that an S_N2 reaction is usually not possible on an sp^2-hybridized carbon atom. In view of the fact that the reaction of the phenyl-Pt(IV) complex with Cl^- gives chlorobenzene and biphenyl,[25] the electrophilicity of the aryl carbon on Pt(III) seems to be less than that on Pt(IV). The reactions of **4′** were examined with the same nucleophiles, but the results were the same.

Photoreactions of Complexes 5 and 4′ and ESR Spectroscopic Examination. The high stability of the aryl–Pt_2 bond of complex **5** toward nucleophiles and protic acid would be attributable to the covalent bond nature of the Pt–C bond. To activate the aryl–Pt_2 bond, **5** was irradiated with a low-pressure Hg lamp in D_2O for 2 min. The color of the solution changed from yellow to green, and the ^1H NMR spectrum in CD_3OD/D_2O (3:2 in v/v) showed the formation of phenol and benzene in 28% and 11% yields, respectively (Scheme 10). To identify the reaction more closely, ESR measurements of the reaction solution were carried out. As shown in Figure 6a, the frozen solution of complex **5** gives no signal before light irradiation. The spectrum (Figure 6b) of the frozen solution at 77 K after irradiation clearly shows that the aryl–Pt_2 bond is homolytically cleaved to give an organic radical ($g = 2.0032$) and two species of Pt^{III}–Pt^{II} mixed-valent complexes with 85:15 abundances ($g_{Pt\perp a} = 2.3879$, $g_{Pt\parallel a} = 1.9810$ (85%), $g_{Pt\perp b} = 2.2829$, $g_{Pt\parallel b} = 1.9316$ (15%), $a_{\perp 1} = 12.65$ mT, $a_{\perp 2} = 25.65$ mT). The solution color changed to green and the ESR parameters were very similar to those of platinum-blue Pt(II,III) mixed-valent complexes,[1] suggesting the possible photoreaction of **5** as in Scheme 10. The spectrum in Figure 6c was measured after irradiation to the frozen sample of Figure 6b for an additional 30 min. The hyperfine splitting of $a_{org\perp}$ (13.11 mT) appeared. Such a splitting was not observed for the solution of part c after thawing and freezing again without irradiation. In this case, the signal of $g = 2.0032$ without the hyperfine splitting was observed. From the comparison with the reported spectra of the phenyl radical ($g = 2.003$, $a(H^{ortho}) = 1.71$, $a(H^{meta}) = 0.65$ mT)[26b] and phenoxyl radical ($g = 2.005$, $a(H^{ortho}) = 0.67$, $a(H^{meta}) = 0.19$, $a(H^{para}) = 1.02$ mT),[26d] the identity of the present organic radical in Figure 6c is not clear.

It is not clear why the two different Pt species exist; one plausible explanation is that there are two electronic isomers; one has the unpaired electron at one Pt atom, and the other on the other Pt atom. These electronic isomers may be possible since the two Pt atoms are in different coordination environments (N_2O_2–Pt vs N_4–Pt). It was shown previously that the d_{z^2} electrons of the Pt–Pt bond are easily redistributed along the bond during the reactions of the Pt(III) dinuclear complex with olefins.[4]

The Pt–C bond of complex **4′** was also activated by light irradiation. The ESR spectra of the irradiated solution show the analogous photocleavage of the Pt–C bond (Figure 7). The color change of the reaction and the ESR and ^1H NMR spectra showed that **4′** is more stable than **5**, and longer irradiation is necessary.

Since aryl radicals are short-lived species,[26] their use in organic reactions is limited.[27] The present reaction

(23) Miyaura, N.; Suzuki, A. *Chem. Rev*. **1995**, *95*, 2457.

(24) The alkyl-Pt(IV) is electrophilic and easily undergoes nucleophilic attack; see: (a) Jain, V. K.; Rao, G. S. *Adv. Orgamonet. Chem.* **1986**, *27*, 113. (b) Williams, B. S.; Goldberg, K. I. *J. Am. Chem. Soc*. **2001**, *123*, 2576.

(25) (a) Shul'pin, G. B.; Shilov, A. E.; Kitaigorodskii, A. N. *J. Organomet. Chem*. **1980**, *201*, 319. (b) Sanders, J. R.; Webster, D. E.; Wells, P. B. *J. Chem. Soc., Dalton Trans.* **1975**, 1191.

(26) (a) Kasai, P. H.; Hedaya, E.; Whipple, E. B. *J. Am. Chem. Soc*. **1969**, *91*, *16*, 4364. (b) Nagai, S.; Ohnishi, S.; Nitta, I. *J. Phys. Chem.* **1969**, *73*, 2438. (c) Bennett, J. E.; Mile, B. *J. Phys. Chem*. **1971**, *75*, 22, 3432. (d) Neta, P.; Fessenden, R. W. *J. Phys. Chem.* **1974**, *78*, 523.

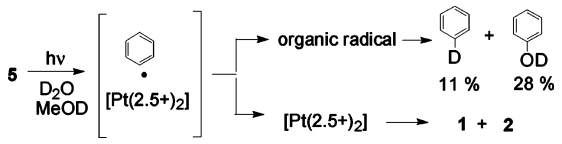
(27) Semmelhack, M. F.; Bargar, T. *J. Am. Chem. Soc*. **1980**, *102*, 7765.

Table 2. Crystallographic Data for Complexes 4, 4′, and 5

	4	4′	5
formula	$C_{22}H_{47}N_7O_{13}Pt_2S$	$C_{16}H_{41}N_9O_{14}Pt_2$	$C_{16}H_{39}N_9O_{12}Pt_2$
fw	1039.87	973.70	939.69
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	18.550(16)	9.6633(13)	9.782(4)
b (Å)	11.817(10)	10.1921(14)	10.042(5)
c (Å)	17.874(16)	31.498(4)	14.711(7)
α (deg)			89.424(8)
β (deg)	114.291(15)	96.791(3)	88.328(9)
γ (deg)			83.705(8)
V (Å^3)	3571(5)	3080.4(7)	1435.6(11)
T (K)	120(2)	120(2)	120(2)
Z	4	4	2
ρ_{calcd} (g cm^{-3})	1.927	2.095	2.169
cryst dimens (mm)	0.47 × 0.17 × 0.14	0.25 × 0.19 × 0.06	0.50 × 0.20 × 0.02
abs coeff (mm^{-1})	7.949	9.147	9.804
absorp corr	empirical	empirical	empirical
θ range (deg)	2.10 to 27.75	1.30 to 27.52	1.38 to 27.50
no. of reflns collected	20 645	18 370	8164
no. of indep reflns	7972 [R(int) = 0.1120]	6659 [R(int) = 0.0535]	5789 [R(int) = 0.0563]
R^a	0.0615	0.0327	0.0962
$R_w{}^b$	0.1462	0.0839	0.2337
GOF^c	0.966	1.081	1.05

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$. ^{c} GOF $= [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(n-p)]^{1/2}$.

Scheme 10



provides a useful method to generate aryl radicals under mild conditions.

Conclusions

The reaction of **1** with phenol selectively activates the *o*-C−H bond to give the aryl-Pt(III) complex **4**, in contrast with $H_2Pt(IV)Cl_6$, which activates only the *p*- and *m*-C−H bonds of phenol.[14] The hydrogen bond between the phenolic oxygen and the NH_3 ligands would be responsible for such regioselectivity. The reactions of **1** with 4-methylphenol or 2,6-dimethylphenol did not give the aryl-Pt(III) complexes, and instead, oxidative homocoupling and oligomerization took place accompanied by the reduction of **1** to **2**. As a more general synthetic route to aryl-Pt(III) complexes, transmetalation using arylboronic acid was developed. The aryl Pt−C bonds are unreactive compared to the previously reported electrophilic Pt−C(alkyl) bonds and do not react with either nucleophiles or electrophile (H^+) under identical conditions. The aryl Pt(III)−C bond is however homolytically cleaved on UV irradiation to give an aryl radical.

Experimental Section

Carbon, hydrogen, and nitrogen analyses were carried out on a Perkin-Elmer PE 2400II elemental analyzer. The NMR spectra were recorded on a Bruker Avance-400 spectrometer, operating at 400 MHz for ^{1}H, 100 MHz for ^{13}C, and 86.0 MHz for ^{195}Pt. Chemical shifts are reported in δ (ppm) units referenced to Me_4Si at 0 ppm in $CDCl_3$ or to Me_4NClO_4 at 3.19 ppm in D_2O for ^{1}H. The ^{1}H and ^{13}C NMR spectra in DMSO-d_6 were referenced to the solvent peaks (the quintet at 2.49 ppm for ^{1}H and the septet at 39.5 ppm for ^{13}C). In the ^{195}Pt spectra, Na_2PtCl_6 (0 ppm) and K_2PtCl_4 (−1624 ppm) in D_2O were employed as the external references. The ESR spectra were measured on a JEOL JES-TE200 spectrometer. The UV−vis spectra were measured on a Shimadzu UV-2550 spectrophotometer. The ESI-MS spectra were measured on a Thermo Quest LCQ spectrometer. The GPC analyses were carried out on a Japan Analytical Industry LC-918 with a polystyrene column. Commercially available phenol and its derivatives, aryl boronic acids, and other reagents were used without further purification. Complex **3**[3b] was synthesized as reported in the literature. The light irradiation was carried out with a

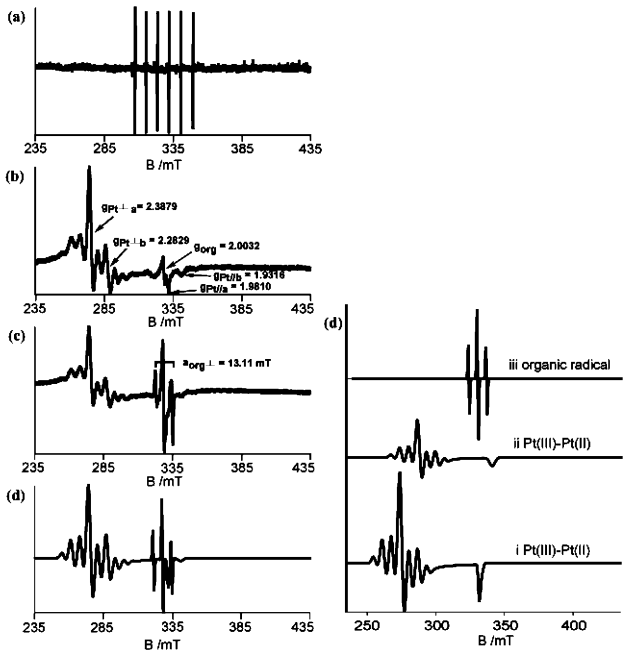


Figure 6. ESR spectra of the photoirradiated frozen solution (77 K in D_2O) of complex **5**. (a) Before irradiation. The six lines are due to the Mn^{2+} marker. (b) After irradiation for 5 min at room temperature (and then frozen). (c) After irradiation for 30 min to the frozen solution of b. (d) Simulation spectrum (total of the three components in e). (e) Simulation spectra of the two Pt(III)-Pt(II) complexes (i, 85%+ ii, 15%) and the organic radical (iii). Conditions: frequency: (a) 9.1806 G, (b) 9.1811 G, (c) 9.1830 G; modulation: 0.25 mT; power: 5 mW.

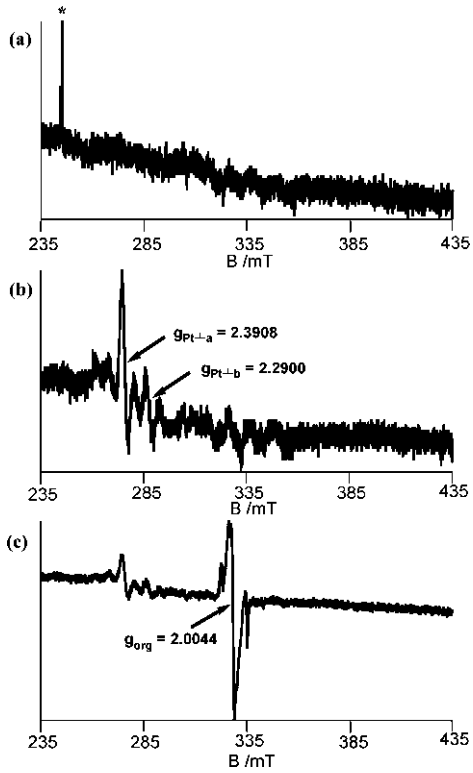


Figure 7. ESR spectra of the photoirradiated frozen solution (77 K in D_2O) of complex **4′**. (a) Before irradiation. The peak with * is due to the liquid N_2 bubble. (b) After irradiation for 50 min at room temperature (and then frozen). (c) Spectrum after irradiation of the frozen solution of b for 90 min. Conditions: frequency: (a) 9.1795 G, (b) 9.1821 G, (c) 9.1821 G; modulation: 0.25 mT; power: 5 mW.

Shimadzu SP-200 mercury lamp without a monochromator. The sample solution in a quartz reactor (UV cell) or an ESR quartz tube was placed 30 cm away from the light source. All procedures were carried out under air.

Preparation of Complex 4. Complex **1** (0.02 mmol) was generated in the reaction of complex **3** (16.3 mg, 0.01 mmol) with $Na_2S_2O_8$ (4.8 mg, 0.02 mmol) in aqueous solution (1 mL) at room temperature for 5 min. After the dark blue solution completely changed to yellow, 10 equiv of phenol (19 mg) was added. The reaction mixture was stirred at room temperature for 3 days. The resulting brown precipitate (2 mg), which was identified to be the mixture of oligomers, was removed by centrifugation. The supernatant was left standing at room temperature to evaporate H_2O slowly under air. High solubility of complex **4** and precipitation of the oligomers on concentration disturbed isolation of the pure compound in high yield. To facilitate the precipitatation of **4**, an excess (10 equiv) of Na_2SO_4, $NaClO_4$, $NaNO_3$, or $NaPF_6$ was added to the reaction solution. But the yields were not so improved. The yield of the ClO_4 salt was less than 34% (contains impurities probably of hydration water, phenol, and $NaClO_4$). The yields of other salts could not be determined because of the contamination of impurities (checked by ^1H NMR and elemental analyses). The reaction in 0.1 M H_2SO_4 suppressed the formation of the oligomers to some extent. A few crystals suitable for X-ray structure analysis were grown by standing the solution for a month at 5 °C.

^1H NMR (400 MHz, DMSO-d_6): δ 1.10 (s, 18H), 4.64 (br, 6H, N*H*$_3$), 5.80 (br, 6H, N*H*$_3$), 6.49 (d, J = 8.00 Hz, 1H, *H6*), 6.56 (d, J = 8.00 Hz, 1H, *H3*), 6.69 (dd, J = 8.00 Hz, 8.00 Hz, 1H, *H5*), 7.15 (dd, J = 8.00 Hz, 8.00 Hz, 1H, *H4*), 7.50 (br, 2H, N*H*(amidate)), 10.57 (s, 1H, Pt-PhO*H*). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 27.5 (s, C(*C*H$_3$)$_3$), 108.3 (s, Pt-*C*), 116.0 (s, *C3*), 118.7 (s, *C5*) 129.1 (s, *C4*), 131.4 (s, *C6*) 154.6 (s, *C2*), 190.2 (s, HN*C*O). $^{195}Pt\{^1H\}$ NMR (86 MHz, D_2O): δ −48 ppm (N_2O_2-C coordinated, J_{Pt-Pt} = 2914 Hz, J_{N-Pt} = 214 Hz), −2130 ppm (N_4 coordinated, J_{Pt-Pt} = 2914 Hz).

Preparation of Complex 4′. To a 2 mL aqueous solution of complex **1** (0.04 mmol), prepared as described above, were added MeOH (1 mL) and 2-hydroxyphenylboronic acid (27.6 mg, 0.20 mmol). The solution was stirred at room temperature for 24 h. During the reaction, a pale yellow (almost colorless) powder precipitated. The precipitate was collected by centrifugation, washed with acetone, and dried in vacuo to yield 24.6 mg (66%) of the sulfate salt $[Pt_2(NH_3)_4(^t$BuCONH CONH$)_2$-$(C_6H_4(OH))]_2(SO_4)_3\cdot 4H_2O$ (**4″**). An additional 1.4 mg (4%) of the precipitate was obtained by gradual evaporation of the solvent. The nitrate salt (complex **4′**), which is used for X-ray diffraction, was prepared by recrystallization of 26 mg (0.027 mmol) of complex **4″** in 2.1 mL of 1.0 M HNO_3.

The results of the elemental analyses are as follows.

Complex **4′**: Calcd for $[Pt_2(NH_3)_4(^t$BuCONH$)_2(C_6H_4(OH))]$-$(NO_3)_3\cdot H_2O$: C, 20.11; H, 4.11; N, 13.19. Found: C, 20.30; H, 4.09; N, 12.84.

Complex **4″**: Calcd for $[Pt_2(NH_3)_4(^t$BuCONH$)_2(C_6H_4(OH))]_2$-$(SO_4)_3\cdot 4H_2O$: C, 20.62; H, 4.44; N, 9.02. Found: C, 20.67; H, 4.76; N, 8.78.

The ^1H, ^{13}C, and ^{195}Pt NMR spectra of complexes **4′** and **4″** are identical to those of complex **4**.

Reactions of 1 with Phenol Derivatives. To an aqueous (D_2O 2 mL) solution of complex **1** (0.02 mmol) was added 20 equiv of 4-methylphenol. The color of the solution immediately changed from yellow to green, and a dark green oil was formed. In the ^1H NMR spectrum of the reaction solution after 3 days, complex **2** and 4-hydroxybenzoic acid (12% based on **1**) were observed. Other products were extracted with $CHCl_3$ and separated by GPC chromatography. The elution was analyzed by ESI-MS and ^1H NMR spectroscopy to identify 4,4′-dimethyl-2,2′-biphenol and oligomers. The reaction of **1** with 2,6-dimethylphenol was also carried out in $D_2O/CDCl_3$ (2 mL/2 mL) at 40 °C for 3 days. 2,2′,6,6′-Tetramethyl-4,4′-biphenol (30% based on substrate), 2,2′,6,6′-tetramethyl-4,4′-biphenoquinone (50% based on substrate), and poly(2,6-dimethylphenyleneoxide) were obtained from the $CDCl_3$ phase.

Preparation of Complex 5. To a 2 mL aqueous solution of complex **1** (0.04 mmol), prepared as described earlier, was added 10 equiv of phenylboronic Acid (0.4 mmol, 48.8 mg) and the solution were heated to 40 °C for 14 h. The resulting pale yellow solution was filtered to remove the impurities. The filtrate was cooled to room temperature, and 0.2 mL of concentrated HNO_3 was added to precipitate complex **5**. After standing the solution for one night at 5 °C, the pale yellow precipitate was collected by filtration, washed with acetone, and dried in vacuo. Yield: 65%.

^1H NMR (400 MHz, DMSO-d_6): δ 1.08 (s, 18H), 4.64 (br, 6H, N*H*$_3$), 5.85 (br, 6H, N*H*$_3$) 6.80 (d, J = 8.00 Hz, 2H, *H2*), 7.15 (dd, J = 8.00 Hz, 8.00 Hz, *H3*), 7.29 (t, J = 8.00 Hz, 1H, *H4*). $^{195}Pt\{^1H\}$ NMR (86 MHz, DMSO-d_6): δ −35 ppm (N_2O_2-C coordinated, J_{Pt-Pt} = 2992 Hz), −2198 ppm (N_4 coordinated, J_{Pt-Pt} = 2992 Hz). $^{13}C\{^1H\}$ NMR (86 MHz, DMSO-d_6): δ 27.5 (s, C(*C*H$_3$)$_3$), 39.6 (s, *C*(CH$_3$)$_3$), 124.5 (s, Pt-*C*), 127.8 (s, *C3*), 128.1 (s, *C4*), 129.2 (s, *C2*), 190.0 (s, HN*C*O). Anal. Calcd for $[Pt_2(NH_3)_4((CH_3)_3CCONH)_2(C_6H_5)](NO_3)_3\cdot H_2O$: C, 20.45; H, 4.18; N, 13.42. Found: C, 20.61; H, 4.13; N, 13.32.

Preparation of Complexes 6 and 7. Complexes **6** and **7** were synthesized similarly to **4′**, by using 3-hydroxyphenylboronic acid and 4-hydroxyphenylboronic acid, respectively. The yields, elemental analyses, and ^1H NMR data are as follows.

Complex **6**: Yield: 82%. Anal. Calcd for $[Pt_2(NH_3)_4$-$(^t$BuCONH$)_2(C_6H_4(OH))](NO_3)_3\cdot H_2O$: C, 20.11; H, 4.11; N, 13.19. Found: C, 20.55; H, 4.15; N, 12.95. ^1H NMR (400 MHz, D_2O): δ 1.19 (s, 18H), 6.25 (s with broad platinum satellite, 1H, *H2*), 6.37 (d with a broad ^{195}Pt satellite, J = 8.40 Hz, 1H,

H6), 6.94 (d, $J = 8.00$ Hz, 1H, *H4*), 7.04 (dd, $J = 8.00$ and 8.40 Hz, 1H, *H5*).

Complex **7**: Yield: 46%. Anal. Calcd for $[Pt_2(NH_3)_4(^tBuCONH)_2(C_6H_4(OH))](NO_3)_3 \cdot H_2O$: C, 20.11; H, 4.11; N, 13.19. Found: C, 20.20; H, 4.26; N, 12.81. ^{1}H NMR (400 MHz, D_2O): δ 1.18 (s, 18H), 6.70 (d with a broad ^{195}Pt satellite, $J = 9.20$ Hz, 2H, *H2*), 6.79 (d, $J = 9.20$ Hz, 2H, *H3*).

Crystal Structure Determination of 4, 4′, and 5. Crystals of **4**, **4′**, and **5** suitable for X-ray diffraction analysis were coated with epoxy resin. Diffraction data were collected on a Bruker SMART 1000 CCD diffractometer by using Mo Kα radiation. All the intensity data were processed by the SAINT plus program package. The structure solution was performed with the SHELXTL software package. All non-hydrogen atoms were refined anisotropically. Details of the crystallographic analysis are summarized in the Supporting Information.

Simulation of the ESR Spectrum. The ESR spectrum of the photoreaction solution of **5** was simulated by summing the spectra for the four possible patterns of the Pt isotope combinations: ^{z}Pt−^{z}Pt (43.8%), ^{195}Pt−^{z}Pt (22.4%), ^{z}Pt−^{195}Pt (22.4%), and ^{195}Pt−^{195}Pt (11.4%), where ^{z}Pt is the Pt isotopomers which have no nuclear spins. The hyperfine interaction of the organic radical was considered only for one Pt nucleus.

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Supporting Information Available: ESI-MS, ^{1}H NMR spectra, GPC charts of the oligomers produced, and CIF files of complexes **4**, **4′**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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