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Transmetalation of arylpalladium and platinum complexes. Mechanism and factors to control the reaction

Yuji Suzaki, Takeyoshi Yagyu, Kohtaro Osakada *

Chemical Resources Laboratory, Mail Box R1-03, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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Abstract

This article reviews recent studies on intra- and intermolecular transfer of the aryl ligand bonded to Pd(II) and Pt(II). Cationic arylpalladium complexes with bpy and THF ligands undergo intermolecular aryl group transfer to produce biaryl via a diarylpalladium intermediate. This reaction is applied to cyclization of cationic dinuclear arylpalladium complexes, affording the crown ether derivative with biphenylene units. Analogous arylplatinum complexes do not form diaryl complexes via transmetalation, while they react with CO and phenylallene to cause replacement of the coordinated solvent and insertion of the small molecules into the Pt–C bond, respectively. Conproportionation of $PtCl_2$(cod) and $PtPh_2$(cod) produces PtCl(Ph)(cod), which is induced by dissociation of a Cl ligand from the former complex. $PtCl_2$(cod) reacts also with diarylplatinum complexes with bpy and dppe. Disproportionation of $PtPh(CH_2COMe)$(cod) and conproportionation of $PtPh_2$(cod) and $Pt(CH_2COMe)_2$(cod) take place at 50 °C, but the rates of apparently reversible reactions differ from each other. Addition of OH^- to a solution of PtI(Ph)(cod) causes intermolecular phenyl ligand transfer to produce $PtPh_2$(cod). The dinuclear intermediate complex with bridging OH ligand is prepared from an independent route and fully characterized. The complex causes transmetalation of aryl group of aryl boronic acid.

Keywords: Platinum; Palladium; Transmetalation; Boronic acid; OH ligand

1. Background

Transmetalation is one of the fundamental reactions of organotransition metal complexes and involves transfer of alkyl or aryl ligand from one metal to the other [1,2]. Detailed reaction mechanisms of transmetalation still remain unclarified in many cases, although it is closely related to a number of synthetic organic reactions catalyzed by transition metal complexes. One of the difficulties of the mechanistic studies of transmetalation lies in intermediacy of dinuclear complexes in the reactions. Other fundamental reactions of organotransition metal complexes such as oxidative addition, reductive elimination, β-hydrogen elimination, and insertion of small molecules into M–C and M–H bonds involve the intermediate or transition state containing one transition metal center, which renders elucidation of the mechanism by kinetic measurement, etc. relatively easy. This article focuses on recent studies of our group on mechanism of transmetalation of aryl ligand between Pt and Pd complexes.

We reported the reaction of NiAr(Br)(bpy) which released Ar–Ar easily in DMF solution [2–4]. The reaction is related to the mechanism of a Ni(0) complex-promoted coupling of aryl bromide and polycondensation of arylenedihalides (Eq. (1)) [5–13].

$$2\ \mathrm{Ar{-}X} \xrightarrow{\text{Ni(0) complex}} \mathrm{Ar{-}Ar} \qquad (1)$$
X = halogen

Detailed kinetic studies on this reaction and the properties of bpy-coordinated arylnickel complexes indicate the mechanism shown in Scheme 1. In DMF, the aryl(bromo)-nickel complex undergoes dissociation of the bromo ligand

* Corresponding author. Fax: +81 45 924 5224.
E-mail address: kosakada@res.titech.ac.jp (K. Osakada).

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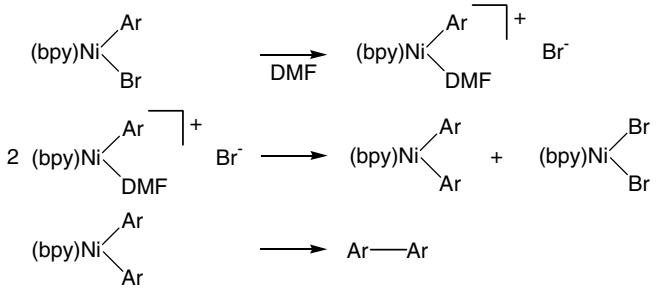
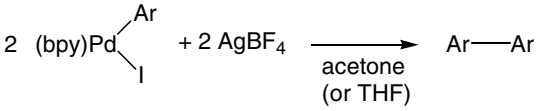


Scheme 1.

to form cationic arylnickel complex with the coordinated solvent. The formed cationic complex undergoes facile disproportionation to yield diarylnickel complex which undergoes smooth reductive elimination of biaryl. Although this mechanism was well supported by the above results, the proposed cationic intermediate, $[NiAr(bpy)(DMF)]^{+}Br^{-}$, was not detected in the reaction mixture due to its rapid transmetalation and successive reductive elimination. Thus, we conducted studies on chemical properties of Pd and Pt analogues of the arylnickel complexes with bpy ligand, which is described in the following section.

2. Cationic arylpalladium and platinum complexes and their relevance to transmetalation

PdAr(I)(bpy) (Ar = Ph, 3,5-$Me_2C_6H_3$) are stable in polar solvents such as DMF and do not undergo spontaneous disproportionation. The reaction of $AgBF_4$ with these complexes in acetone or THF produces biaryl as shown in Eq. (2), while the reaction in MeCN results in isolation of the cationic arylpalladium complex $[PdAr(NCMe)(bpy)]^{+}(BF_4^{-})$ [14]. The reaction forming

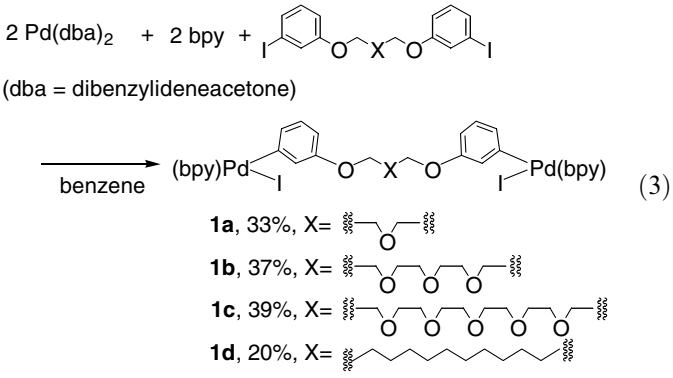


(2)

biaryl is considered to proceed via cationic arylpalladium–bpy complex which is converted into diarylpalladium complex via the dinuclear intermediate complex with a bridging aryl ligand as shown in Scheme 2. MeCN ligand of the cationic square-planar Pd complex is not liberated easily from the metal center, while dissociation of labile THF ligand from the cationic complex leads to the dinuclear species with bridging aryl ligand. The produced $PdAr_2(bpy)$ undergoes rapid reductive elimination of biaryl and is not isolated from the reaction mixture (Scheme 2(ii)).

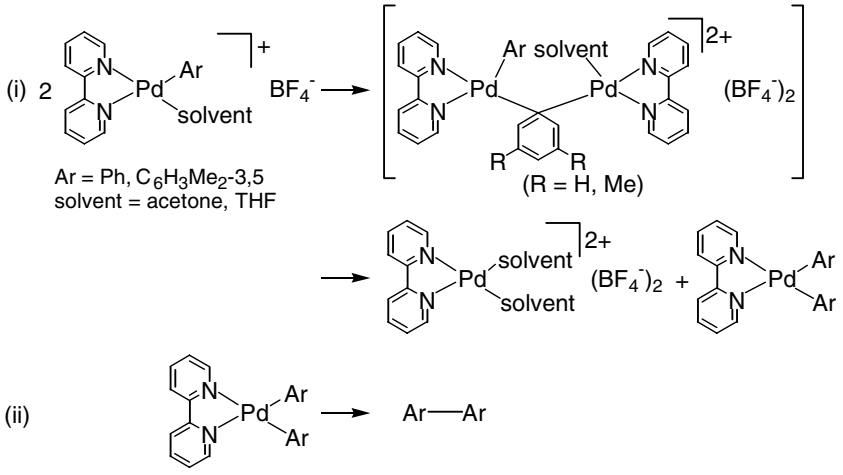
Disproportionation of cationic monoaryl complex, forming biaryl, is applied to dinuclear cationic palladium complex whose metal centers are bridged by long tether with expecting formation of macrocyclic compound via intramolecular transmetalation. Scheme 3 displays outline of this study. Reaction of $AgBF_4$ with dipalladium complexes with bpy, iodo, and bridging bisaryl ligands forms the dicationic dinuclear Pd complex whose intramolecular transmetalation and coupling of the ligand would form macrocycle.

Preparation of dinuclear palladium complex with long $(CH_2CH_2O)_n$ tether is easily accomplished according to the reaction shown in Eq. (3) [15,16]. The NMR spectra

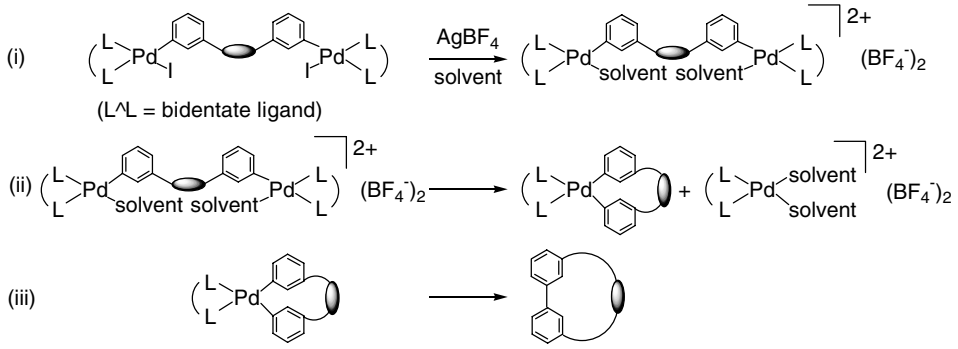


(3)

of the complexes are consistent with symmetrical dinuclear complex having two Pd centers with the same coordination environment. Carbonylation of **1b** converts it into complex

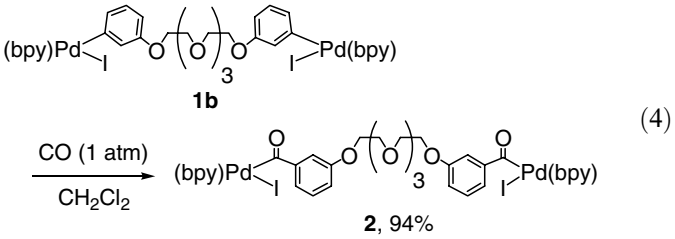


Scheme 2.



Scheme 3.

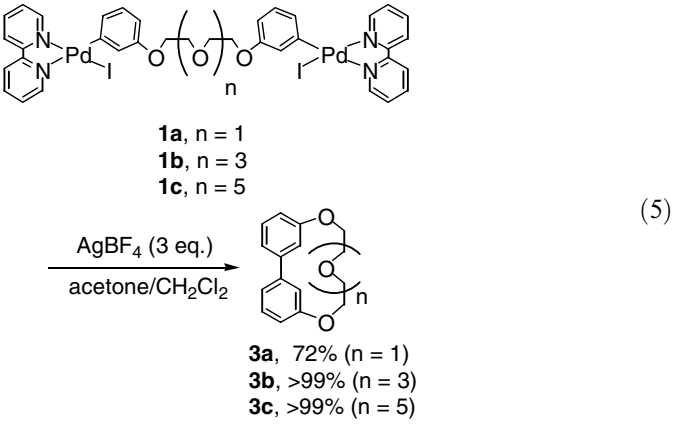
2 with two aroylpalladium centers via insertion of CO molecules into the two Pd–C bonds, as shown in Eq. (4). Complex **2** also has a symmetrical structure with two equivalent Pd centers.



(4)

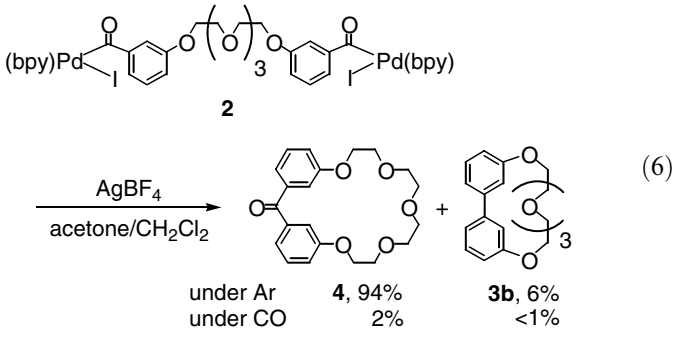
Insertion of CO into the Pd–C bond of arylpalladium complexes with the diimine ligands were reported by several researchers including van Asselt et al. and Vicente et al. [17–19].

Dinuclear palladium complexes, $[(bpy)(I)Pd\{C_6H_4\text{-}(OCH_2CH_2)_{0.5n+0.5}\}]_2O$ ($n = 1$ (**1a**), 3 (**1b**), 5 (**1c**)), $[(bpy)(I)Pd\{C_6H_4O(CH_2)_6\}]_2$ (**1d**), and $[(bpy)(I)Pd\{CO\text{-}C_6H_4(OCH_2CH_2)_2\}]_2O$ (**2**) are employed in the study of the cyclization reactions involving intramolecular transmetalation. Reaction of $AgBF_4$ with **1b** ($[\mathbf{1b}]_0 = 5$ mM, $[\mathbf{1b}]:[AgBF_4] = 1:3$) in acetone/$CH_2Cl_2$ (1:1) forms the crown ether with 3,3′-biphenylene group in the macrocycle as shown in Eq. (5). Cyclization reactions of **1a**, **1b**, and



(5)

1c take place smoothly even when the concentration of the complexes are as high as 100 mM and afford the corresponding crown ethers, **3a** (72%), **3b** (>99%), and **3c** (>99%), respectively. Fig. 1 shows change of the reaction. Rate of formation of the crown-type product is faster in the mixed solvent than that in DMF. The reaction of equimolar $AgBF_4$ with the Pd complex ($[\mathbf{1b}]:[AgBF_4] = 1:2$) in acetone/$CH_2Cl_2$ forms the product **3b** in lower yield (80%). Thus, addition of excess Ag^+ to the Pd complex is helpful for the cyclization of the ligand smoothly. The reaction of $AgBF_4$ with dinuclear aroyl complex **2** yields the crown ether having benzophenone group **4** (94%) and a minor amount of carbonyl-free product **3b** (6%) (Eq. (6)). Presence of CO (1 atm) causes decrease of yields of both the products and forms **4** and **3b** in 2% and <1%, respectively (Eq. (6)).



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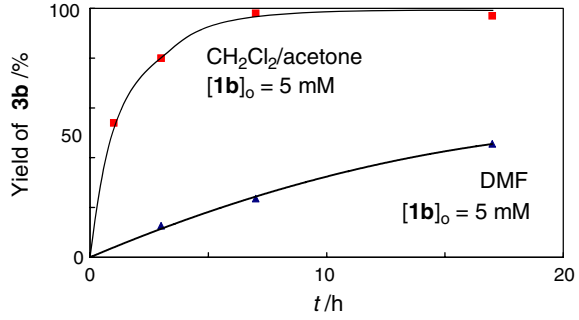
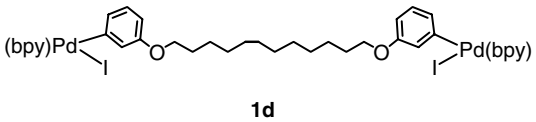


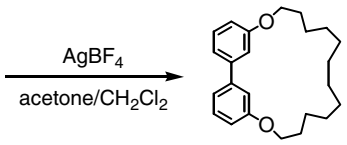
Fig. 1. Profile of the cyclization reaction of **1b** (in CH_2Cl_2/acetone, $[\mathbf{1b}]_0 = 5$ mM).

Scheme 4 illustrates the plausible mechanism to account for the reactions of aryl and aroyl ligands bonded to dinuclear palladium complexes. Complex **2** reacts with $AgBF_4$ to form a dicationic complex, $[\{(bpy)(L)PdCOC_6H_4(OCH_2CH_2)_2\}_2O]^{2+}(BF_4^-)_2$ (**A**) (L = acetone, CO). Decarbonylation of an aroyl ligand of **A** [20] produces $[(bpy)(L)Pd\{C_6H_4(OCH_2CH_2)_4OC_6H_4COPd(L)(bpy)\}]^{2+}(BF_4^-)_2$ (**B**). Aryl ligand contained in **B** undergoes intramolecular transfer from the Pd to the other, giving an intermediate with a cyclometalated aryl–aroyl ligand bonded to Pd, and then reductive elimination of benzophenone-containing crown ether **4** takes place. Coupling of two aroyl ligands of intermediate **A** forming a double carbonylation product does not take place at all. It is probably because dissociation of labile acetone ligand from palladium leads to facile decarbonylation, which occurs prior to intramolecular transfer of the aroyl ligand. The result of the reaction of $AgBF_4$ under CO atmosphere with **2**, giving **4** and **3b** in much lower yields, suggests that the carbonyl ligand bonded to the intermediate strongly prevents not only decarbonylation but also transfer of the aroyl ligand.

The reaction of $AgBF_4$ with dinuclear complex **1d** with polymethylene bridging group in low concentration ($[\mathbf{1d}]_0 = 1.7$ mM) also forms cyclic product **5** via intramolecular transfer of the aryl group followed by intramolecular coupling of the ligand in 78% yield (Eq. (7)). The reaction with higher concentration of the complex ($[\mathbf{1d}]_0 = 34$ mM) forms the cyclic product in low yield (23%) due to concurrent formation of linear polymeric products which are characterized by GPC analysis of the reaction mixture. Averaged molecular weight (M_n) of the latter product is determined to be approximately 5000 based on polystyrene standards.



1d

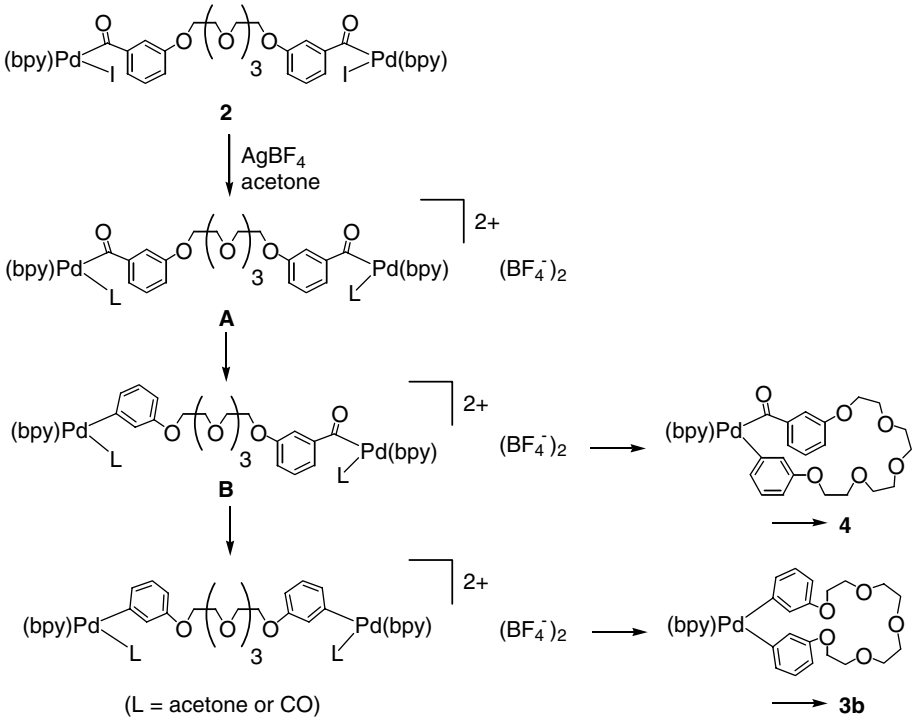


(7)

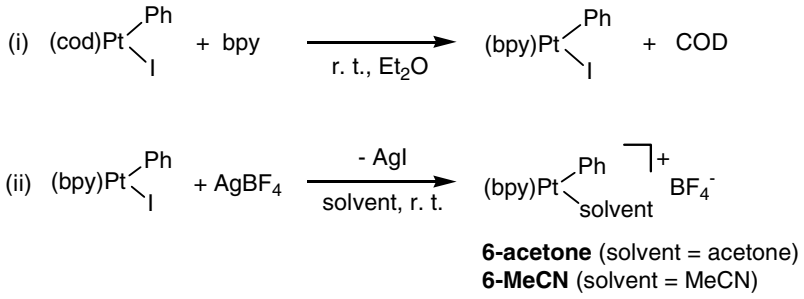
5, 78% ($[\mathbf{1d}]_0 = 1.7$ mM)
23% ($[\mathbf{1d}]_0 = 34$ mM)

Different results of the reaction of **1b** (or **1c**) and **1d** depending on the concentration can be explained as follows. Bridging oligoether chain of **1b** and **1c** coordinates to Ag^+ as a polydentate ligand and functions as a template for the cyclization. Complex **1d**, however, is not expected to cyclize with help of such a template effect. Thus, the dinuclear complex with a similar structure, but with a polymethylene chain between the two aryl ligands, produces undesirable linear polymer products even in the presence of Ag^+.

Pt analogues of the cationic arylpalladium complex, $[PdAr(solvent)(bpy)]^+(BF_4^-)$, is prepared according to Scheme 5 [21]. PtPh(I)(bpy), prepared from ligand substitution of PtPh(I)(cod) with bpy, reacts with $AgBF_4$ in the solvents such as acetone and MeCN to afford the corresponding cationic complexes $[PtPh(solvent)(bpy)]^+(BF_4^-)$ (solvent = acetone (**6-acetone**), MeCN (**6-MeCN**)).



Scheme 4.

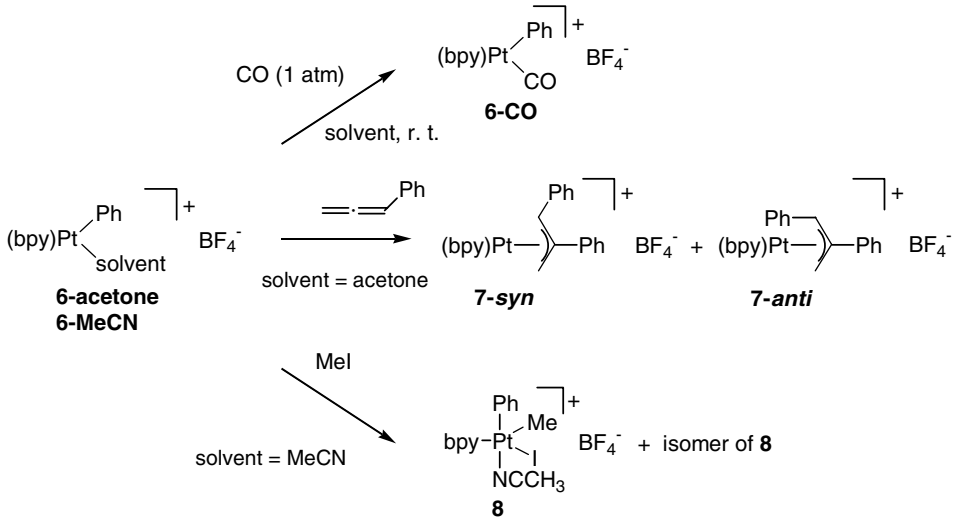


Scheme 5.

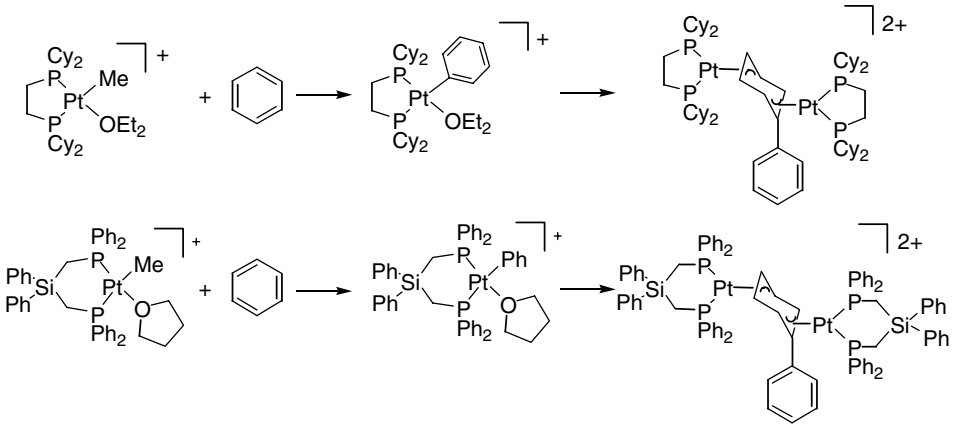
$[PtPh(NCMe)(bpy)]^{+}(BF_4^{-})$ (**6-MeCN**) was isolated as an analytically pure complex, although $[PtPh(acetone)(bpy)]^{+}(BF_4^{-})$ (**6-acetone**) is hygroscopic in the solid state and is characterized by NMR spectroscopy in the solution. The ^1H NMR spectrum of **6-MeCN** in CD_3CN shows exchange of the coordinated solvent with deuterated one but no other change for a month at 50 °C. Complex **6-acetone** in acetone-d_6 solution does not undergo intermolecular transfer of the aryl ligands, although $[PdPh(acetone)(bpy)]^{+}(BF_4^{-})$ releases biaryl spontaneously in solution (Eq. (2)).

Scheme 6 summarizes reactions of the cationic arylplatinum complexes having bpy ligand. $[PtPh(solvent)(bpy)]^{+}(BF_4^{-})$ (**6-acetone**, **6-MeCN**) undergoes carbonylation under 1 atm of CO to afford $[PtPh(bpy)(CO)]^{+}(BF_4^{-})$ (**6-CO**) which is isolated from the reaction mixtures. The reaction of CO with **6-MeCN** requires 7 days for completion at room temperature, while the complex with labile acetone ligand, **6-acetone**, reacts with CO more smoothly to produce the carbonyl complex within 3 h. Complex **6-acetone** reacts with phenylallene to cause insertion of a double bond into the Pt–C bond to yield the π-allylplatinum complex $[Pt\{\eta^3-CH_2C(Ph)CH(Ph)\}(bpy)]^{+}(BF_4^{-})$ (**7-*syn***, **7-*anti***). The product is composed of the isomers with phenyl substituents at the *syn* and *anti* positions of the π-allylic ligand (52:48). Recrystallization of the product yielded single crystals of **7-*syn*** which is characterized by X-ray crystallography. Complex **6-MeCN** undergoes oxidative addition of MeI to afford cationic Pt(IV) complex formulated as $[Pt(I)(Me)(Ph)(NCMe)(bpy)]^{+}(BF_4^{-})$ (**8**). The crystal structure of one of the products contains Me and iodo ligand at trans positions of the bpy ligand. Most of octahedral Pt(IV) complexes formed via oxidative addition of alkyl halides to the Pt(II) complexes with chelating *N*-ligand contain the alkyl and halo ligands at the apical positions via formal trans addition [22]. Thus, complex **8** obtained from this reaction probably has the thermodynamically stable structure formed via thermal isomerization of the initial trans addition product.

Recently, Kubas and Peters independently reported that the reaction of arene with the cationic methylplatinum(II) complexes produced dinuclear platinum(II) complexes whose metal centers were bridged by a formally dianionic, bis-π-allylic ligand, as shown in Scheme 7 [23,24]. The bridging biaryl ligand is liberated upon treatment of the dinuclear complex with I_2 or HCl. Combination of the chelating phosphine ligands and labile Et_2O or THF ligand enabled the C–C bond formation, although it may be under

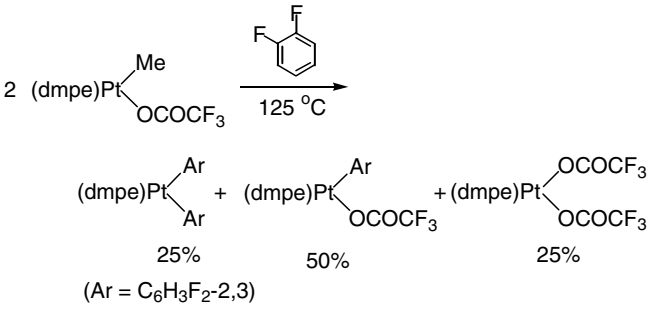


Scheme 6.



Scheme 7.

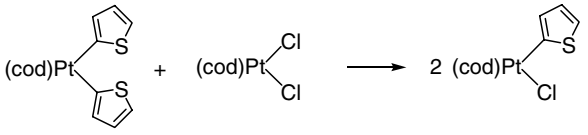
discussion whether the biphenyl formation is ascribed to aryl ligand transfer between the Pt centers or to intermolecular reductive elimination of the two cationic complexes. Cationic arylplatinum complexes with bpy mentioned in this section do not undergo such C–C bond formation. Other examples of intermolecular aryl ligand transfer of the Pt complexes will be raised in the following sections.



(9)

3. Transmetalation of neutral Pd and Pt complexes

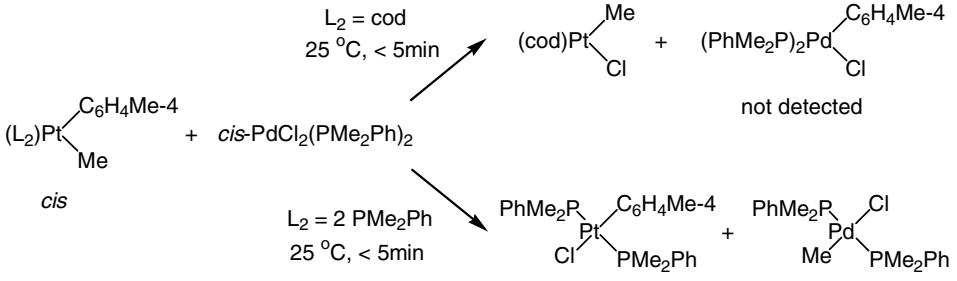
Several neutral arylplatinum complexes were also reported to undergo transfer of the aryl ligands between the Pt centers. Eaborn found that conproportionation reaction of $PtR_2(cod)$ ($R = 2$-thienyl) and $PtCl_2(cod)$ yielded chloro(thienyl)platinum complex via transfer of the thienyl ligand between the Pt centers, as shown in Eq. (8) [25].



(8)

Peters reported the reaction of 1,2-difluorobenzene with $PtMe(OCOCF_3)(dmpe)$ (dmpe = 1,2-bis(dimethylphosphino)ethane), which forms a mixture of $PtAr_2(dmpe)$ (25%, Ar = $C_6H_3F_2$-2,3), $PtAr(OCOCF_3)(dmpe)$ (50%), and $Pt(OCOCF_3)_2(dmpe)$ (25%), as shown in Eq. (9) [26]. This reaction involves the activation of a C–H bond of the arene promoted by the methylplatinum complex and intermolecular transfer of the aryl ligand. Aryl ligand transfer between the Pt and Pd complexes was also reported. *cis*-$PtMe(C_6H_4Me\text{-}4)(L_2)$ (L_2 = cod, $2PMe_2Ph$) reacts with *cis*-$PdCl_2(PMe_2Ph)_2$ to form different products depending on the kind of the auxiliary ligand at the Pt center (Scheme 8) [27]. $PtMe(C_6H_4Me\text{-}4)(cod)$ having cod ligand reacts with Pd complex to form PtCl(Me)(cod) via transfer of the chloro ligand from Pd to Pt. Transfer of the aryl ligand from Pt to Pd should take place at the same time, but the corresponding arylpalladium product was not isolated from the reaction mixture. The reaction of $PtMe(C_6H_4Me\text{-}4)(PMe_2Ph)_2$ causes transfer of the methyl ligand from Pt to Pd and forms a mixture of $PtCl(C_6H_4Me\text{-}4)(PMe_2Ph)_2$ and $PdCl(Me)(PMe_2Ph)_2$.

In this section, the reactions involving transfer of aryl ligands between Pd and Pt complexes are described [28]. The cod ligand plays an important role in the aryl ligand



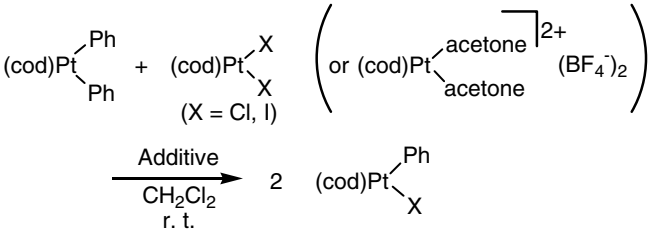
Scheme 8.

Table 1
Conproportionation of $PtPh_2(cod)$ and Pt–cod (Eq. (10))[a]

Run	Pt–cod complex	Additive	Time (h)	PtX(Ph)(cod)[b] (%)
1	X = Cl	None	3	72
2		None	24	93
3		Et_4NCl (0.50 mmol)	3	0
4		KCl (0.50 mmol)[c]	3	0
5		COD (0.10 mmol)	3	57
6		COD (0.50 mmol)	3	51
7		COD (1.0 mmol)	3	57
8	X = I	None	3	36
9		None	24	75
10	$[Pt(acetone)_2(cod)]^{2+}(BF_4^-)_2$[d]	None	3	94

[a] Conditions: $PtPh_2(cod)$ (0.10 mmol), Pt–cod complex (0.10 mmol), solvent: CH_2Cl_2 (runs 1–9), acetone (run 10), room temperature.
[b] Yield of the product are based on the Pt complex used (0.20 mmol).
[c] An aqueous solution (0.1 mL) of [18]crown-6 was added.
[d] $[Pt(acetone)_2(cod)]^{2+}(BF_4^-)_2$ was generated in situ from $AgBF_4$ and $PtCl_2(cod)$. The reaction mixture was terminated by addition of KCl which quenched the cationic complex to give the inactive neutral chloro complex.

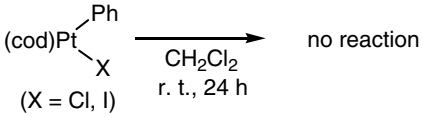
transfer. At first, we conducted the reaction in order to elucidate the mechanism of the reaction of thienylplatinum complex shown in Eq. (8). A mixture of $PtPh_2(cod)$ and $PtX_2(cod)$ (X = Cl, I) undergoes conproportionation, giving PtX(Ph)(cod) via intermolecular exchange of the phenyl and chloro (or iodo) ligands, as shown in Eq. (10). Table 1 summarizes results of the reactions under several conditions. The conproportionation of $PtPh_2(cod)$ with



(10)

$PtCl_2(cod)$ is effectively inhibited by addition of Et_4NCl and KCl (runs 3 and 4), while addition of cod ligand to the reaction mixture affects yield of the product to a limited extent (runs 5–7). These results indicate that dissociation of a halogeno ligand from the Pt–cod complex induces the aryl group transfer between the Pt centers. Lower reactivity of $PtI_2(cod)$ than that of $PtCl_2(cod)$ (runs 8 and 9) may be ascribed to less labile character of the iodo ligand than that of the chloro ligand. Cationic halogeno-free Pt complex $[Pt(acetone)_2(cod)]^{2+}(BF_4^-)_2$ undergoes more facile aryl ligand transfer of the phenyl ligand than $PtX_2(cod)$ (X = Cl, I) (run 10).

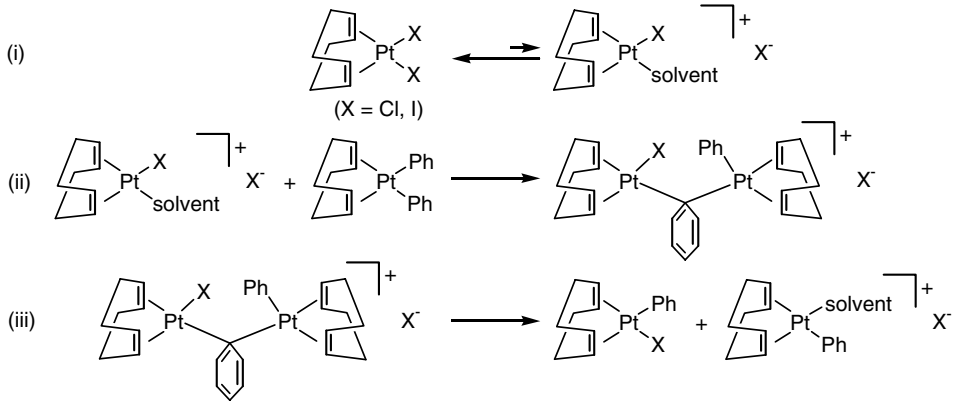
Since isolated halo(phenyl)platinum complexes PtX(Ph)(cod) (X = Cl, I) are stable in solution and do not undergo spontaneous disproportionation reaction that would form a mixture of diphenyl and dihalo complexes, as shown in Eq. (11). Thus, the conproportionation reaction



(11)

in Eq. (10) is irreversible at room temperature probably due to unfavorable dissociation of the halo ligand from the halo(phenyl)platinum complex. Another explanation for these results may involve formally reversible reactions in Eqs. (10) and (11) and much higher thermodynamic stability of PtX(Ph)(cod) than that of the mixture of the diphenyl and dihalo complexes.

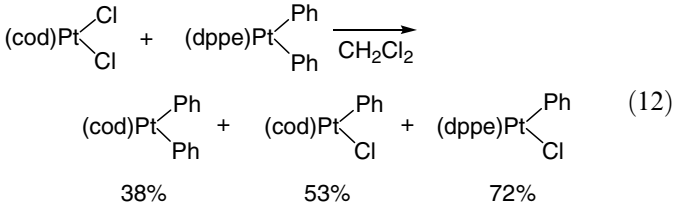
Scheme 9 summarizes plausible mechanism of the above reactions. Partial dissociation of a halogeno ligand from the dihaloplatinum complex generates cationic intermedi-



Scheme 9.

ate $[PtX(solvent)(cod)]^+X^-$ (X = Cl, I) (i). The formed cationic complex reacts with diphenylplatinum complex to produce intermediate dinuclear species that contains bridging phenyl ligand (ii). Activation of a Pt–Ph bond of the bridging phenyl ligand yields neutral and cationic monophenyl complexes (iii), and the latter complex undergoes ligation of the halo ligand to generate neutral halo(phenyl)platinum complex. The dinuclear complexes with a bridging aryl ligand between the two Pt (or Pd) centers were reported [29–33].

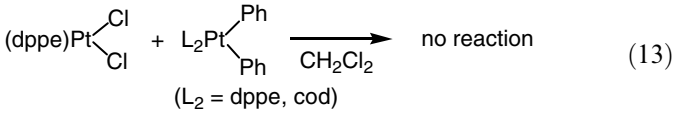
The reaction of $PtPh_2$(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane) with $PtCl_2$(cod) forms a mixture of $PtPh_2$(cod) (38%), PtCl(Ph)(cod) (53%), and PtCl(Ph)(dppe) (72%) smoothly, as shown in Eq. (12).



(12)

Formation of PtCl(Ph)(dppe) indicates occurrence of aryl ligand transfer between the Pt centers during the reaction.

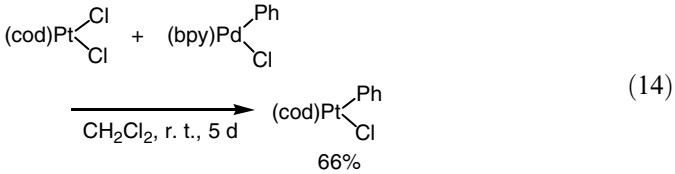
On the other hand, $PtCl_2$(dppe) and $PtPh_2(L_2)$ (L_2 = dppe, cod) do not cause any intermolecular exchange of the phenyl and chloro ligands, as shown in Eq. (13).



(13)

Comparison of the reactions in Eqs. (12) and (13) indicates that the phenyl ligand transfer between the Pt centers highly depends on the kind of chelating ligand; dichloroplatinum complex with cod ligand undergoes aryl ligand transfer from aryl platinum complexes with other chelating ligands.

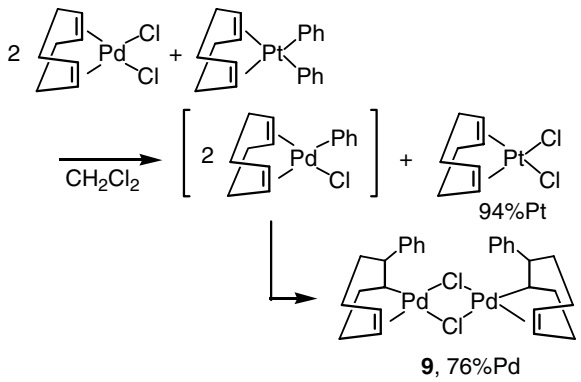
The reaction of $PtCl_2$(cod) with excess PdCl(Ph)(bpy) in CH_2Cl_2 forms PtCl(Ph)(cod), as shown in Eq. (14). The products of the reaction do not contain $PtPh_2$(cod).



(14)

$PdCl_2$(bpy) should also be formed although limited solubility of the complex prevents full characterization of the complex contained in the reaction mixture.

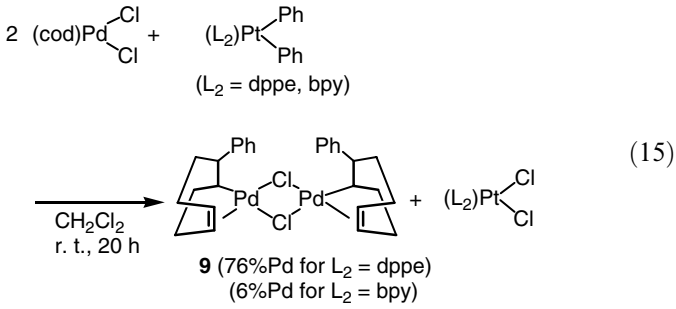
Reaction of $PdCl_2$(cod) and $PtPh_2$(cod) in CH_2Cl_2 produces the dinuclear palladium complex **9** (76%) and $PtCl_2$(cod) (94%), as shown in Scheme 10. Formation of **9** by the reaction is explained by transfer of the phenyl ligand from Pt to Pd, as described below. Transmetalation of the Pd and Pt complexes forms PdCl(Ph)(cod) initially.



Scheme 10.

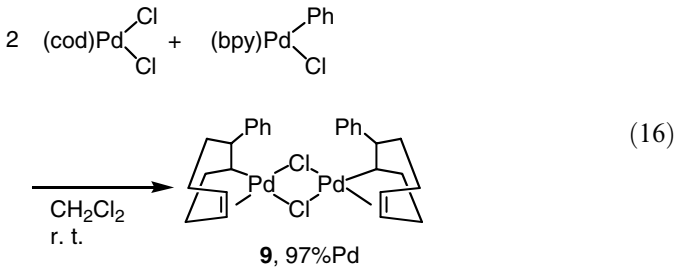
Insertion of a C=C double bond of the cod ligand into the Pd–Ph bond produces the 2-phenyl-5-cyclooctenyl ligand bonded to Pd center. A similar reaction was reported by Albeniz et al. who observed the reaction of C_6F_5Li with $PdCl_2$(cod) to form $[Pd(\mu\text{-}Cl)(\eta^1,\eta^2\text{-}C_8H_{12}C_6F_5)]_2$ via intermediate Pd complex with C_6F_5 ligand [34,35]. The mechanism of this reaction was revealed based on isolation of an intermediate $PdCl(C_6F_5)$(cod) with stable C_6F_5 ligand from the reaction mixture.

The reaction of $PdCl_2$(cod) with $PtPh_2$(dppe) also produces dinuclear complex **9** in 76% yield as shown in Eq. (15). $PtPh_2$(bpy) reacts with $PdCl_2$(cod) to form the same complex but in a low yield (6%) after the reaction for 20 h.



(15)

Low yield of the product is partly due to low solubility of the $PtPh_2$(bpy) in the solvent. PdCl(Ph)(bpy) also functions as the source of phenyl ligand that is transferred to the Pd–cod complex with chloro ligands, as shown in Eq. (16). Solubility of PdCl(Ph)(bpy) is also limited, but the heterogeneous reaction in CH_2Cl_2 forms the dinuclear complex **9** in 97% yield after 20 h at room temperature.



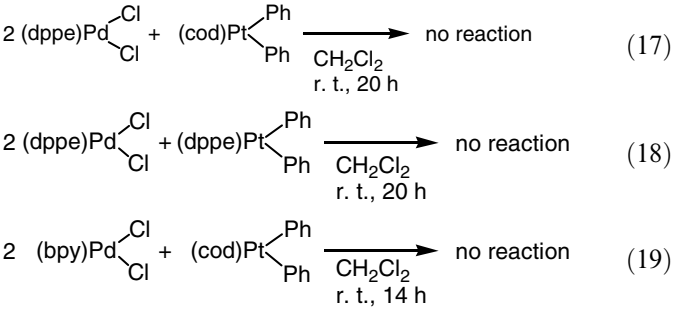
(16)

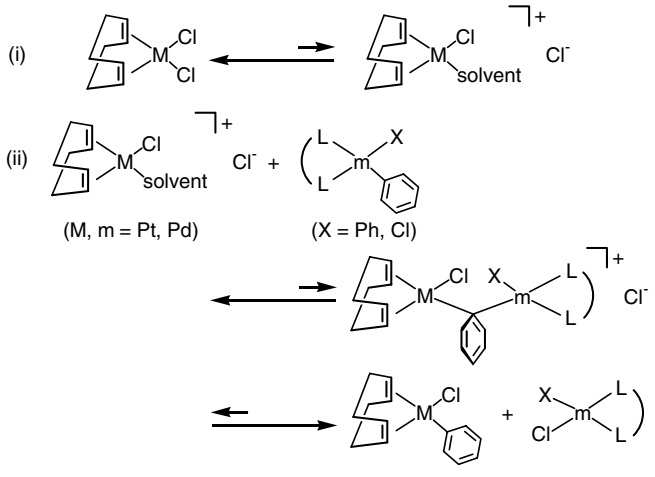
Table 2
Transmetalation between dichloro and diphenyl complexes of Pd and Pt[a]

	Phenyl complexes			
	$PtPh_2$(cod)	$PtPh_2$(dppe)	$PtPh_2$(bpy)	PdCl(Ph)(bpy)
$PdCl_2$(cod)	Y	Y	Y	Y
$PtCl_2$(cod)	Y	Y		Y
$PtCl_2$(dppe)	N	N		
$PdCl_2$(dppe)	N	N		
$PtCl_2$(bpy)	N			

[a] Y: Phenyl complex formed via transmetalation was observed spectroscopically; N: formation of phenyl complex via transmetalation was not confirmed.

Dichloropalladium complexes with other chelating ligands such as $PdCl_2$(dppe) and $PdCl_2$(bpy) do not react with the diphenyl complexes of Pt, as shown in Eqs. (17)–(19).





Scheme 11.

Table 2 summarizes relative reactivities of the phenyl and chloro complexes with various chelating auxiliary ligands. Transmetalation of the diphenyl complexes with dichloro complexes of Pd and Pt takes place smoothly when the dichloro complex contains cod ligand, while the dichloro complexes with dppe and bpy ligand do not undergo transmetalation with diphenyl complexes. Kind of the auxiliary ligands on the diphenyl complexes do not affect the reaction results.

These observations suggest the plausibility of the mechanism shown in Scheme 11, which involves dissociation of the chloro ligand of the dichloro complexes as the initiation step of transmetalation. Cationic chloro complex forms dinuclear complex with bridging phenyl ligand easily, and cleavage of a metal–carbon bond of the bridging ligand results in chloro(phenyl)platinum (or palladium) complex.

Among three chelating ligands, cod, bpy, and dppe, the cod ligand is known to show higher π-acceptor ability than bpy and lower σ-donor ability than the other two ligands. Table 3 compares $^{13}C\{^1H\}$ NMR data of the dimethylplatinum complexes with several chelating ligands [36–39]. Peak positions of the methyl ligand bonded to Pt are influenced significantly by the chelating ligands used. The complexes with cod and dppe ligands having strong π-acceptor character exhibit the methyl carbon signals at the positions lower than the complex with diimine ligand by more than 10 ppm. It indicates low electron density of the methyl group of $PtMe_2$(cod) due to the electronic character of the ligand.

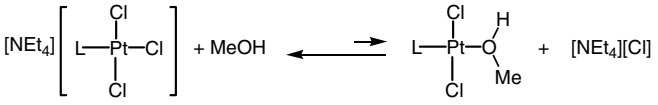
Enhancement of the transmetalation by the cod ligand may be explained as below. A large trans effect of the cod ligand promotes dissociation of the chloro ligand

Table 3
$^{13}C\{^1H\}$ NMR data of *cis*-$PtMe_2$(ligand)

Ligand	cod	nbd[a]	dppe	2 py[b]	ArN = CH–CH = NAr[c]	tmeda[d]
Me peak positions (δ_c)	4.7	4.56	1.0	−8.18	−14.2	−23.67
J(PtC)/Hz	773 ± 2	814.5	610	688.5	793.5	826.2
Reference	[36]	[37]	[38]	[37]	[39]	[37]

[a] nbd = 2,5-norbornadiene.
[b] py = pyridine.
[c] Ar = $C_6H_3Me_2$-2,6.
[d] tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

bonded at the trans position of the cod, which facilitates the transmetalation by the dissociation mechanism. At the same time, facile association of the cationic intermediate with neutral diaryl complex via bridging coordination of the aryl ligand should also be taken into consideration. Electronically deficient Pt center of the cationic complex with cod ligand is favorable for formation of the bridging ligand. The latter factor seems to be more operative because Tobe and Gosling studied the solvolysis of $[NEt_4][PtCl_3(L)]$ in methanol (Eq. (20)) and concluded that



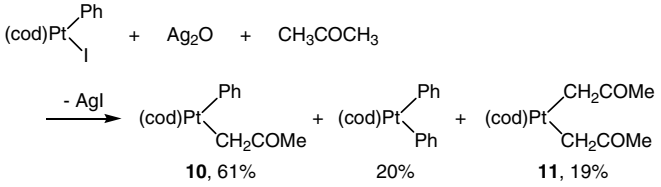
(L = C_2H_4, $OSMe_2$, SMe_2, $AsEt_3$, $P(OMe)_3$, PPh_3, $P(n\text{-}Bu)_3$, PEt_3)

(20)

the Cl ligand at trans position of olefin ligand is not dissociated to a significant degree due to rapid ligation of Cl ligand to neutral Pt center [40]. So the concentration of the cationic complexes $[MCl(solvent)(cod)]^+(Cl^-)$ (M = Pt, Pd) in solution is not higher than those of $[MCl(solvent)(L_2)]^+(Cl^-)$ (L_2 = dppe, bpy) in Scheme 11, and cod ligand of the dichloro complex enhances the transmetalation by facile formation of the dinuclear intermediate with bridging ligand.

4. Transmetalation of acetonylplatinum complexes

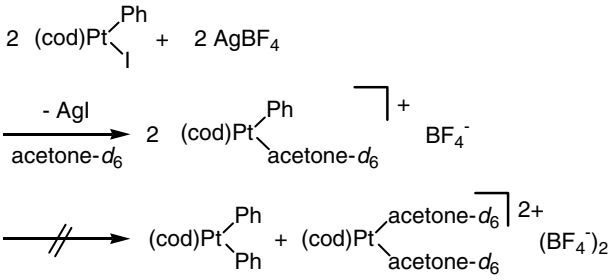
Phenylplatinum complex with acetonyl ligand also undergoes intermolecular transfer of the phenyl ligand. The reaction of Ag_2O with PtI(Ph)(cod) in acetone forms a mixture of $Pt(CH_2COMe)(Ph)(cod)$ (**10**, 61%), $PtPh_2$-(cod) (20%), and $Pt(CH_2COMe)_2(cod)$ (**11**, 19%), as shown in Eq. (21) [41].



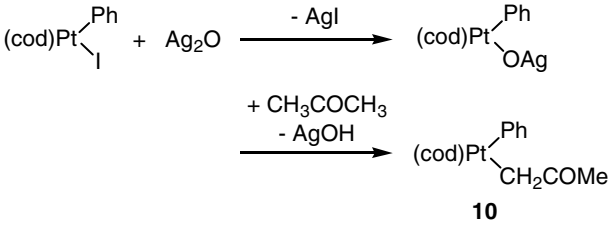
(21)

The produced complexes were characterized by X-ray crystallography and comparison of the NMR data with authentic complexes prepared independently. The yields of the products suggests the initial formation of **10** and its disproportionation to form $PtPh_2(cod)$ and **11**. Cationic phenylplatinum complex with acetone-d_6 ligand, $[PtPh(acetone\text{-}d_6)(cod)]^+(BF_4^-)$, prepared in situ from the reaction of $AgBF_4$ and PtI(Ph)(cod) in acetone-d_6 does not cause disproportionation reaction at 50 °C (Scheme 12). Thus, the cationic arylplatinum complex with coordinated acetone and cod ligands is not the intermediate for formation of the diphenyl complex.

Scheme 13 shows a plausible pathway for formation of **10**. Ag_2O abstracts iodo ligand of PtI(Ph)(cod) to cause



Scheme 12.



Scheme 13.

elimination of AgI. The AgO^- ligand formed by the reaction is highly basic and activates a C–H bond of acetone to form the acetonyl ligand. Thus, Ag_2O exhibits dual roles such as Pt–I bond activation and C–H bond activation of the acetone. The reaction of acetone with a dichloroplatinum complex in the presence of Ag_2O was reported to form $PtCl(CH_2COMe)(PEt_3)_2$ [42]. Wimmer et al. [43] and Mintcheva et al. [44] independently reported activation of O–H

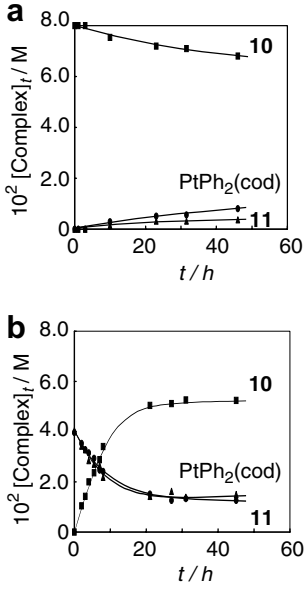
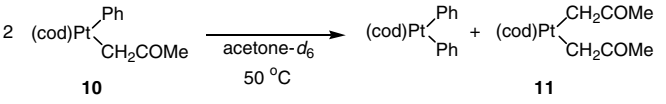


Fig. 2. (a) Profile of disproportionation of **10** into **11** and $PtPh_2(cod)$ in acetone-d_6 at 50 °C. (b) Profile of conproportionation of **11** and $PtPh_2(cod)$ into **10** in acetone-d_6 at 50 °C.

bond of the ligand (aqua ligand or silanolate ligand) by Ag_2O.

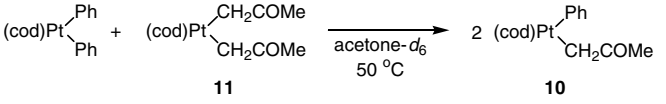
Heating of acetone-d_6 solution of Pt(CH_2COMe)(Ph)-(cod) (**10**) at 50 °C forms a mixture of $PtPh_2$(cod) and Pt(CH_2COMe)$_2$(cod) (**11**), as shown in Eq. (22). Fig. 2(a) shows



(22)

change of **10** in acetone-d_6 ($[\mathbf{10}]_0 = 8.0 \times 10^{-2}$ M) into a mixture of $PtPh_2$(cod) and **11**, the ratio of the complex attains to 75:13:12 after 70 h. The reaction rate does not change by addition of Ag_2O to the reaction mixture. Thus, formation of **10** in the reaction in Scheme 13 is induced by Ag_2O, although the disproportionation of the complex is not related to the added Ag_2O. This reaction accompanies exchange of the acetonyl ligand with the deuterated acetone via protonation of the acetonyl ligand by the solvent.

An equimolar mixture of $PtPh_2$(cod) and **11** in acetone-d_6 ($[PtPh_2(cod)]_0 = [\mathbf{11}]_0 = 4.0 \times 10^{-2}$ M) undergoes conproportionation and gives a mixture of **10**, $PtPh_2$(cod), and **11** in 65:19:16 after the reaction for 46 h (Eq. (23)).



(23)

Fig. 3 shows progress of the reactions in Eqs. (22) and (23) in C_6D_6. Complex **10** ($[\mathbf{10}]_0 = 8.0 \times 10^{-2}$ M) in C_6D_6 is converted into a mixture of **10**, $PtPh_2$(cod), and **11** in **10**:**11** = 90:5 after 70 h. An equimolar mixture of

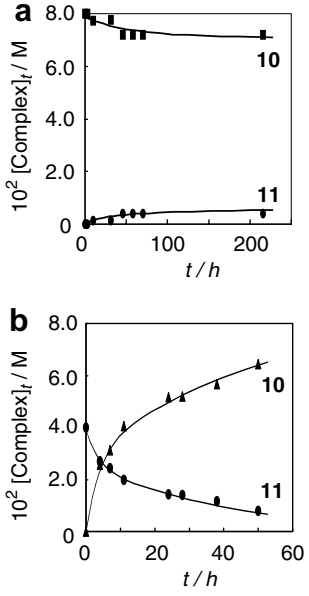
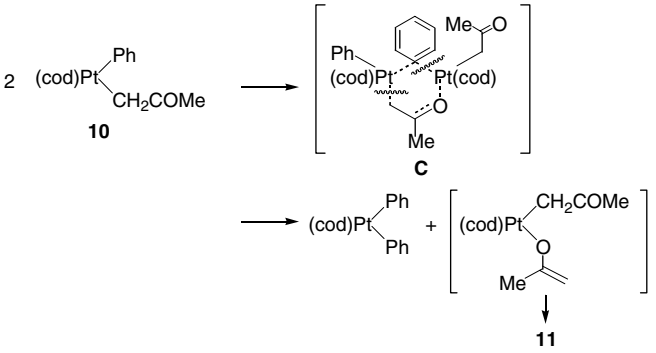


Fig. 3. (a) Profile of disproportionation of **10** into **11** and $PtPh_2$(cod) in benzene-d_6 at 50 °C. (b) Profile of conproportionation of **11** and $PtPh_2$(cod) into **10** in benzene-d_6 at 50 °C.

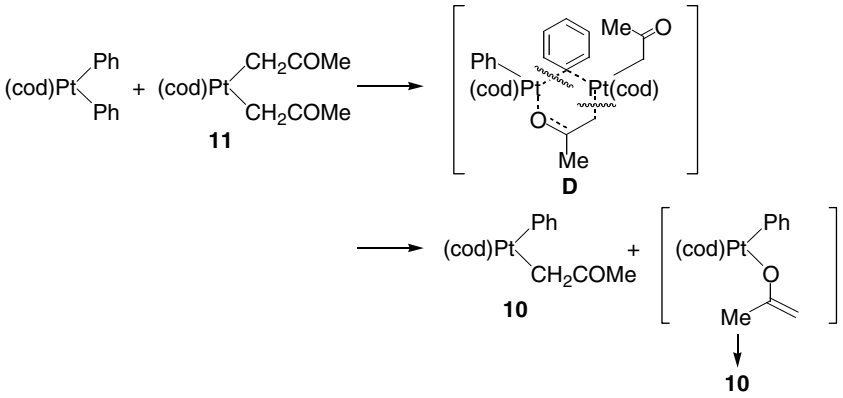
$PtPh_2$(cod) and **11** ($[PtPh_2(cod)]_0$, $[\mathbf{11}]_0 = 4.0 \times 10^{-2}$ M) in C_6D_6 changes the ratio of the complexes as shown in Fig. 3(b). After 50 h, the ratio between **10** and **11** becomes 80:10. The curves in these figures suggest that the disproportionation occurs slower than the conproportionation under similar conditions although the complexes are apparently in equilibrium in the solutions. Schemes 14 and 15 show possible mechanisms of the ligand transfer between two Pt centers to account for the above results. Disproportionation of **10** involves a dinuclear intermediate **C** in which the two Pt centers are bridged by a phenyl and κ^2-C–O-acetonyl ligand (Scheme 14). Cleavage of Pt–C bonds of coordinated acetonyl and phenyl groups at shown positions leads to $PtPh_2$(cod) and an enolate isomer of **11**. The latter product is soon converted to thermodynamically stable **11**. Conproportionation of $PtPh_2$(cod) and **11** also proceeds via dinuclear intermediate with bridging phenyl and κ^2-C–O-acetonyl ligand (Scheme 15). Bridging coordination of the ligand probably takes place via coordination of the carbonyl oxygen to another Pt center, and direction of bridging acetonyl ligand differ between the intermediates of disproportionation **C** and conproportionation **D**. Different structure of the dinuclear intermediates may render the rates of these apparently reversible reactions different. Dinuclear and multinuclear palladium complexes with unsymmetrically bridged acetonyl ligands were reported, as shown in Chart 1; [Pd{$CH_2C(O)Me$}Cl]$_n$ and [Pd$_2${$CH_2C(O)Me$}{μ-κ^2-C,O-$CH_2C(O)Me$}(μ-Cl)Cl(dmso)$_2$] contain unsymmetrically bridged acetonyl ligands [45].

5. Transmetalation of hydroxoplatinum complexes

Organoplatinum(II) hydroxo complexes have long been studied and were reported to exhibit a nucleophilic character [46,47] in a similar way to the more common alkoxoplatinum(II) complexes [48–53]. The hydroxo platinum complexes show a tendency to form dinuclear complex by bridging of the OH ligand [54–60]. These dinuclear Pt complexes are stabilized by highly basic OH ligand and flexible Pt–OH–Pt bonding. Transmetalation involving mononuclear and dinuclear hydroxoplatinum complexes as the intermediates is described in this section [61,62].



Scheme 14.



Scheme 15.

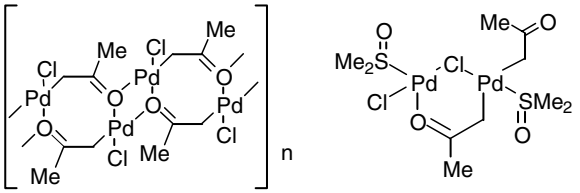
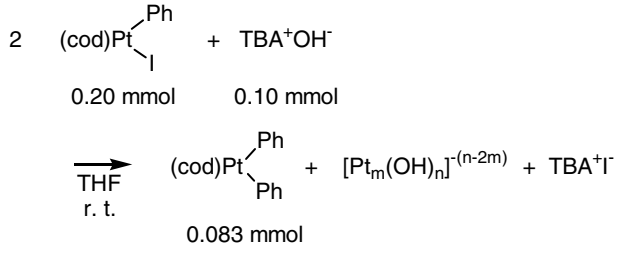


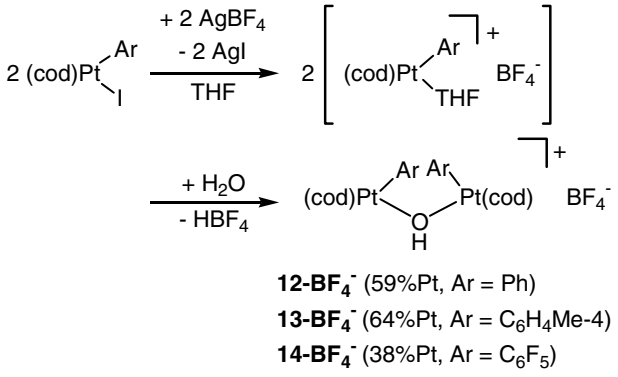
Chart 1.

The reaction of $[^nBu_4N]^+[OH]^-$ (TBA^+OH^-) with PtI(Ph)(cod) in a 2:1 molar ratio forms $PtPh_2(cod)$, as shown in Eq. (24).



(24)

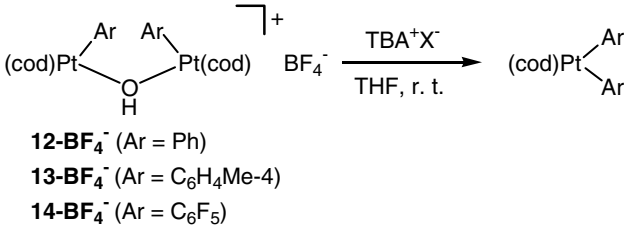
Since PtI(Ph)(cod) does not undergo spontaneous disproportionation to form the diphenyl complex (Eq. (11)), TBA^+OH^- promotes the transmetalation of the phenylplatinum complex. Analyses of the products by wide-angle X-ray diffraction, GPC, and MS measurement indicate formation of $[^nBu_4N]^+[I]^-$ (TBA^+I^-) and anionic Pt-containing oligomer, $[Pt_m(OH)_n]^{-(n-2m)}$.



12-BF_4^- (59%Pt, Ar = Ph)
13-BF_4^- (64%Pt, Ar = C_6H_4Me-4)
14-BF_4^- (38%Pt, Ar = C_6F_5)

Scheme 16.

In order to clarify structure of the intermediates, the following experiments were conducted. Reaction of $AgBF_4$ with PtI(Ar)(cod) (Ar = Ph, C_6H_4Me-4, C_6F_5), followed by addition of a small amount of H_2O to the resultant $[PtAr(THF)(cod)]^+(BF_4^-)$, yields the dinuclear Pt complexes with a bridging hydroxo ligand, $[\{PtAr(cod)\}_2(\mu\text{-}OH)]^+(BF_4^-)$ (Ar = Ph (**12-BF_4^-**), C_6H_4Me-4 (**13-BF_4^-**), C_6F_5 (**14-BF_4^-**)) (Scheme 16). The obtained complexes were fully characterized by X-ray crystallography, NMR spectroscopy, and elemental analyses [63]. Table 4 summarizes spectroscopic data of the complexes. The IR spectra contain the stretching vibration of OH ligand at the characteristic positions as the bridging ligand (3345–3432 cm^{-1}). The ^1H NMR peaks of OH hydrogen appear at 4.1–4.6 ppm at −55 °C in $CDCl_3$, but the signals are not observed at room temperature. The dinuclear complexes with bridging hydroxo ligand, **12-BF_4^-** and **13-BF_4^-** react with TBA^+X^- ($X^- = I^-$, OH^-) in a 2:1 molar ratio to yield $PtAr_2(cod)$, as shown in Eq. (25).



12-BF_4^- (Ar = Ph)
13-BF_4^- (Ar = C_6H_4Me-4)
14-BF_4^- (Ar = C_6F_5)

(25)

The results are summarized in Table 5. The reaction takes place by addition of TBA^+I^- or TBA^+OH^-, giving $PtAr_2(cod)$ (Ar = Ph, C_6H_4Me-4) via transfer of the aryl ligand, while addition of $TBA^+PF_6^-$ to **12-BF_4^-** does not cause the aryl ligand transfer at all (run 3). Complex **14-BF_4^-** having stable Pt–C_6F_5 bond does not undergo transmetalation even in the presence of TBA^+OH^- (run 5). Scheme 17 shows the plausible reaction mechanism based on the above results. TBA^+OH^- reacts with PtI(Ph)(cod) to form Pt(OH)(Ph)(cod) (**15**) and TBA^+I^-. Mononuclear phenyl-

Table 4
IR and ^{1}H NMR data of $[\{PtAr(cod)\}_2(\mu\text{-}OH)]^+(BF_4^-)$ (Ar = Ph(**12-BF$_4^-$**), C_6H_4Me-4(**13-BF$_4^-$**), C_6F_5(**14-BF$_4^-$**))

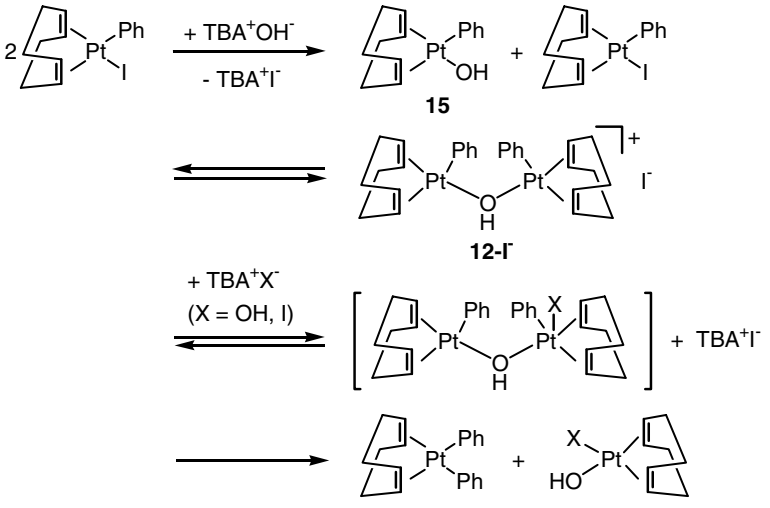
Complex	IR, ν(OH)	δ_H (OH) (solvent, temperature)
12-BF$_4^-$ (Ar = Ph)	3428 cm^{-1} ($CHCl_3$) Not detected (KBr)	4.17 ($CDCl_3$, −55 °C) Not detected ($CDCl_3$ or C_6D_6, r.t.)
13-BF$_4^-$ (Ar = C_6H_4Me-4)	3432 cm^{-1}($CHCl_3$)	4.13 ($CDCl_3$, −55 °C) Not detected ($CDCl_3$ or C_6D_6, r.t.)
14-BF$_4^-$ (Ar = C_6F_5)	3345 cm^{-1} (KBr)	4.61 ($CDCl_3$, −55 °C) Not detected ($CDCl_3$ or acetone-d_6, r.t.)

Table 5
Reaction of tetrabutylammonium salt with the dinuclear Pt complexes

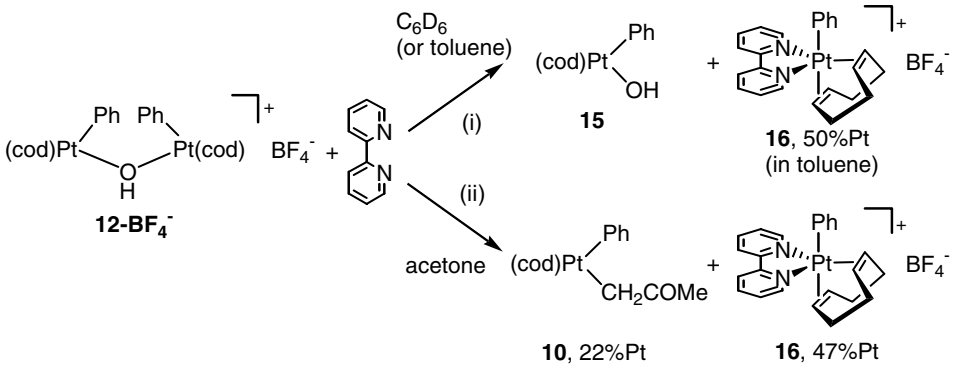
Run	Complex	TBA^+X^-	$PtAr_2$(cod)
1	**12-BF$_4^-$** (Ar = Ph)	TBA^+OH^-	Quant (~50%Pt)
2		TBA^+I^-	41%Pt
3		$TBA^+PF_6^-$	0%
4	**13-BF$_4^-$** (Ar = C_6H_4Me-4)	TBA^+OH^-	48%Pt
5	**14-BF$_4^-$** (Ar = C_6F_5)	TBA^+OH^-	0%

hydroxo complex **15** reacts further with PtI(Ph)(cod) to form the dinuclear complex with a bridging hydroxo ligand, having iodo as the counter anion, $[\{PtPh(cod)\}_2(\mu\text{-}OH)]^+(I^-)$ (**12-I$^-$**). OH^- or I^- in the solution coordinates to a Pt center of the dinuclear complex to form the intermediate having a penta-coordinate Pt center. Phenyl ligand transfer takes place from the penta-coordinated Pt center to square-planar Pt center accompanied by cleavage of a Pt–O bond. The last reaction step involves cleavage of Pt–Ph bond of the penta-coordinative center, which is similar to associative ligand substitution of the square planar transition metal complexes, involving a trigonal-bipyramidal intermediate. The isolated dinuclear complex **12-BF$_4^-$** is stable in the solution and does not cause the phenyl ligand transfer because BF_4^- counter anion is much less basic than OH^- and I^- and does not form an intermediate complex with penta-coordinate Pt center.

The initial mononuclear intermediate Pt(OH)(Ph)(cod) (**15**) is prepared in situ from an independent reaction of bpy with equimolar **12-BF$_4^-$** in benzene-d_6 or in toluene (Scheme 18(i)). Complex Pt(CH_2COMe)(Ph)(cod) (**10**) is obtained from a similar reaction in acetone (Scheme 18(ii)). Isolation of **15** as crystals is not feasible due to its spontaneous disproportionation, but its solution was obtained by removing **16** which is insoluble in the aromatic solvents by filtration. The ^{1}H NMR and IR spectra of the solution indicate the presence of non-bridging OH ligand, showing the OH vibration (3677 and 3600 cm^{-1}) within the normal range of non-bridging OH ligand (3600–3690 cm^{-1}) [43,64–69]. They are at much higher wavenumber than those of **12-BF$_4^-$**, **13-BF$_4^-$**, and **14-BF$_4^-$** (3345–3428 cm^{-1}) with bridging OH ligand. The ^{1}H NMR spectrum of **15** exhibits the signal of OH hydrogen at 3.39 ppm at room temperature.

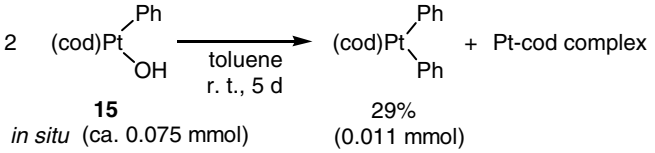


Scheme 17.



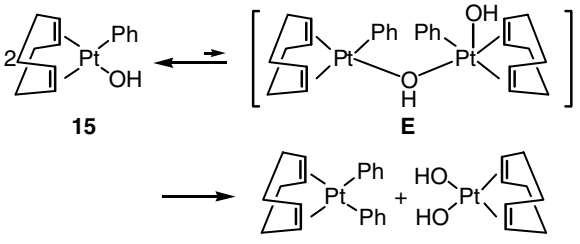
Scheme 18.

The $^{13}C\{^1H\}$ NMR spectrum of complex **15** after prolonged measurement indicate formation of $PtPh_2(cod)$, indicating gradual disproportionation reaction in the solution. Disproportionation of complex **15** shown in Eq. (26) is responsible for formation of the diphenyl complex,



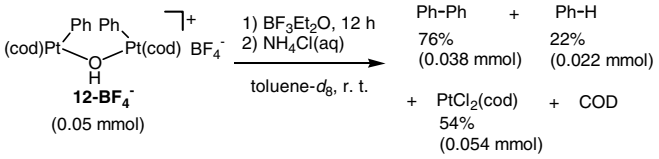
(26)

which is contrasted with the results that both PtPh(X)(cod) (X = Cl, I) and $[PtPh(acetone\text{-}d_6)(cod)]^+(BF_4^-)$ does not undergo the disproportionation reaction (Eq. (11), Scheme 12). Scheme 19 displays the reaction mechanism for the transmetalation reaction of **15**. Dimerization of Pt(OH)(Ph)(cod) (**15**) takes place via bridging coordination of the hydroxo ligand. The neutral dinuclear intermediate **E** having a penta-coordinate and square-planar Pt centers causes phenyl ligand transfer between the Pt centers.



Scheme 19.

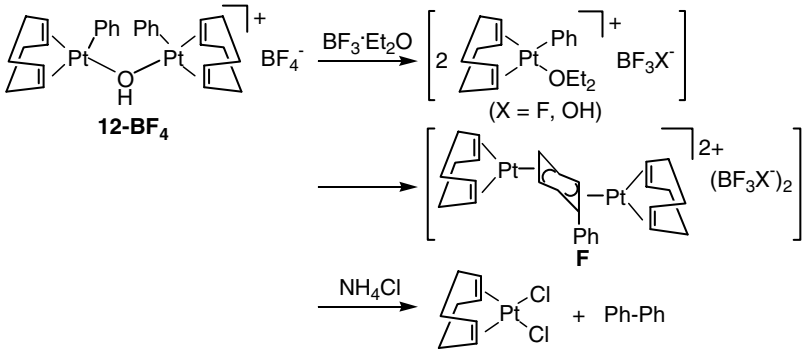
The reaction of $BF_3 \cdot Et_2O$ with **12-BF$_4^-$** in toluene-d_8 at room temperature for 12 h, followed by treatment with NH_4Cl(aq), produces a mixture of $PtCl_2(cod)$ (54%), Ph–Ph (76%), and benzene (22%), as shown in Eq. (27).



(27)

Scheme 20 shows a mechanism for the reaction proposed based on the reports by Kubas and Peters [23,24]. The reaction of $BF_3 \cdot Et_2O$ with **12-BF$_4^-$** forms the cationic mononuclear platinum(II) complex $[PtPh(OEt_2)(cod)]^+(BF_3X^-)$ (X = F, OH) via abstraction of the OH ligand by BF_3. The formed mononuclear complex with a labile OEt_2 ligand undergoes facile formation of dinuclear intermediate **F** accompanied by C–C bond formation between the phenyl ligand of two cationic Pt complex molecules. NH_4Cl promotes liberation of biphenyl and formation of $PtCl_2(cod)$.

Reaction of arylboronic acids with **12-BF$_4^-$** in 1:2 molar ratio leads to transfer of the aryl ligand from boron to platinum, giving mononuclear diarylplatinum complexes, as shown in Eq. (28) and the results are summarized in Table 6.

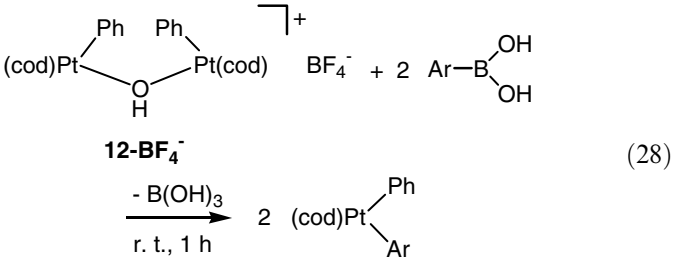


Scheme 20.

Table 6
Reaction of arylboronic acid with **12-BF$_4^-$**[a]

Run	Ar–B(OH)$_2$	Solvent	PtAr(Ph)(cod)[b] (%)
1	($C_6H_2F_3$-2,4,6)B(OH)$_2$	Toluene	36
2		Toluene/H_2O[c]	83
3	PhB(OH)$_2$	Toluene	38
4		Toluene/H_2O[c]	66
5		THF	Mixture
6	(C_6H_4OMe-4)B(OH)$_2$	Toluene	14 (64[d])
7		Toluene/H_2O[c]	2

[a] At room temperature, 1 h.
[b] Yield based on Pt.
[c] toluene/H_2O = 100/1.
[d] Yield of $PtPh_2$(cod).



(28)

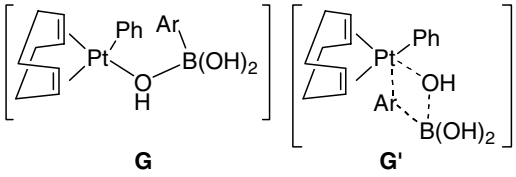
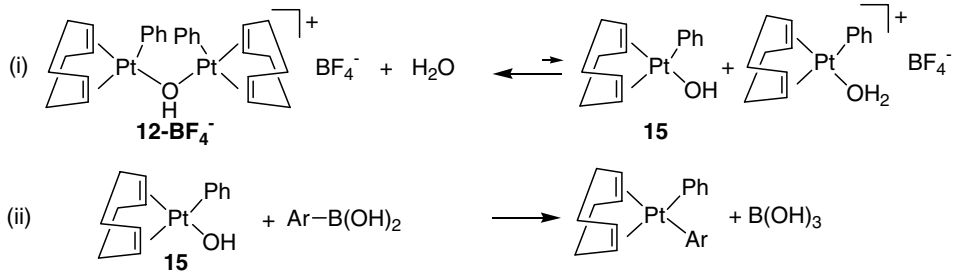


Chart 2.

The reaction of trifluorophenylboronic acid forms unsymmetrical diaryl platinum complex Pt($C_6H_2F_3$-2,4,6)(Ph)(cod) as a major product (36%). A small amount (<1%) of Pt($C_6H_2F_3$-2,4,6)$_2$(cod) is also detected probably due to disproportionation or other scrambling reaction. Addition of water to the reaction mixture increases the yield of Pt($C_6H_2F_3$-2,4,6)(Ph)(cod) (83%) (run 2). The product insoluble in toluene contains B(OH)$_3$ indicating that substitution of aryl group of the arylboronic acid with OH ligand or OH group from water occurs during the reaction. The reaction of phenylboronic acid shows the same tendency (run 3–5). The reaction of 4-methoxyphenylboronic acid produces $PtPh_2$(cod) as a major product, indicating occurrence of intramolecular transfer of the phenyl ligand prior to the transmetalation of the arylboronic acid (runs 6 and 7). Thus, not only transmetalation of arylboronic acid but also intramolecular aryl ligand transfer takes place during the reaction; ratio of the products depends on reactivity of arylboronic acid toward the transmetalation.

Yields of the diaryl complex in the reaction of ($C_6H_2F_3$-2,4,6)B(OH)$_2$ and of PhB(OH)$_2$ without addition of H_2O do not exceed 50% (36% (Ar = $C_6H_2F_3$-2,4,6), 38% (Ar = Ph)). [PtPh(solvent)(cod)]$^+$(BF$_4^-$) is also produced by the reaction, but it does not undergo further reaction in the absence of water. Addition of water converts the mononuclear cationic complex into **12-BF$_4^-$**, similarly to the reaction in Scheme 16.

Scheme 21 summarizes a pathway of the reaction of ArB(OH)$_2$ with **12-BF$_4^-$** in the presence of H_2O. The reaction of H_2O with **12-BF$_4^-$** generates **15** and a cationic phenylplatinum complex with aquo ligand (i). Complex **15** is responsible for transmetalation. Activation of B–C bond in reaction (28) may proceed via intermediate **G** (Chart 2) which is formed by 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 and Pt–O bonds of **G** forms a new Pt–Ar bond, accompanied by the elimination of B(OH)$_3$. An alternative concerted mechanism, involving the intermediate **G′** with a four-membered ring, may also be possible for the simultaneous formation of Pt–C and B–O bonds of the products. The coupling of [PtPh(OH$_2$)(cod)]$^+$(BF$_4^-$) accompanied by deprotonation may regenerate **12-BF$_4^-$** (Scheme 15). Reaction of H_2O with [PtPh(THF)(cod)]$^+$(BF$_4^-$) was reported to produce **12-BF$_4^-$** [61].



Scheme 21.

6. Conclusion

The arylpalladium and platinum complexes undergo intermolecular or intramolecular aryl ligand transfer from one metal to the other. The reaction is regulated by structure, auxiliary ligand, and the ligand that promotes the aryl ligand transfer. Neutral square-planar complexes are able to undergo the transmetalation when cod is selected as a bidentate ligand of dihalogeno complex. Reaction proceeds via initial dissociation of a halogeno ligand to form cationic complex. Actual role of the auxiliary ligand is to control the reactivity of the cationic mononuclear species which undergoes facile formation of dinuclear intermediate having bridging aryl ligand. Cationic complexes undergo more facile aryl ligand transfer probably because of kinetically favored formation of the dinuclear intermediates. The OH ligand enhances the transmetalation between the Pt complex. The role of OH ligand is to form stable dinuclear intermediate that is isolated in this study and to form pentacoordinate metal center that releases aryl ligand in the intramolecular transmetalation. The dinuclear hydroxoplatinum complex is in equilibrium with the mononuclear complex with OH ligand and activates C–B bond of aryl boronic acid in the transmetalation.

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Appendix

Data of unpublished complexes are as follows: Data for **1a**: ^{1}H NMR (300 MHz, $CDCl_3$, r.t.): δ 3.85 (br, 4H, CH_2), 4.07 (br, 4H, CH_2), 6.47 (m, 2H, C_6H_4), 6.85–6.98 (6H, C_6H_4), 7.28 (2H), 7.46 (2H), 7.57 (2H), 7.94–7.96 (4H), 8.04–8.06 (4H), 9.52 (2H). Anal. Calc. for $C_{36}H_{32}I_2N_4O_3Pd_2$: C, 41.76; H, 3.12; N, 5.41; I, 24.52. Found: C, 41.74; H, 3.51; N, 5.13; I, 24.05%. Data fot **13-BF$_4^-$**: ^{1}H NMR (300 MHz, C_6D_6, r.t.): δ 1.16–1.36 (8H, CH_2), 1.62–1.68 (8H, CH_2), 2.21 (s, 6H, CH_3), 3.78 (m, 4H, CH (trans to O), J(PtH) = 72 Hz), 5.49 (br, 4H, CH (trans to C)), 6.96 (d, 4H, *meta*-C_6H_4, J(HH) = 8 Hz), 7.37 (d, 4H, *ortho*-C_6H_4, J(HH) = 8 Hz). ^{1}H NMR (300 MHz,$CDCl_3$, r.t.): δ 1.96–2.11 (8H, CH_2), 2.25–2.38 (8H, CH_2), 2.31 (s, 6H, CH_3), 4.24 (m, 4H, CH (trans to O), J(PtH) = 69 Hz), 5.23 (br, 4H, CH (trans to C)), 7.04 (d, 4H, *meta*-C_6H_4, J(HH) = 8 Hz), 7.28 (d, 4H, *ortho*-C_6H_4, J(HH) = 8 Hz, J(PtH) = ca. 36 Hz). ^{1}H NMR (400 MHz, $CDCl_3$, −55 °C): δ 1.95–2.05 (8H, CH_2), 2.22–2.34 (8H, CH_2), 2.31 (s, 6H, CH_3), 4.13 (s, 1H, OH), 4.28 (m, 4H, CH (trans to O)), 4.95 (brs, 4H, CH (trans to C)), 7.06 (d, 4H, *meta*-C_6H_4, J(HH) = 8 Hz), 7.35 (d, 4H, *ortho*-C_6H_4, J(HH) = 8 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, r.t.): δ 20.7 (CH_3), 27.0 (CH_2), 31.3 (CH_2), 82.1 (CH (trans to O), J(PtC) = 218 Hz), 115.9 (CH (trans to C)), 129.2 (*meta*-C_6H_4), 134.4 (*para*-C_6H_4), 134.7 (*ortho*-C_6H_4), 140.7 (*ipso*-C_6H_4). IR ($CHCl_3$): ν(OH); 3432 cm^{-1}. Anal. Calc. for $C_{30}H_{39}BF_4OPt_2$: C, 40.37; H, 4.40. Found: C, 40.11; H, 4.33%. Data fot **14-BF$_4^-$**: ^{1}H NMR (300 MHz, $CDCl_3$, r.t.): δ 2.26–2.36 (8H, CH_2), 2.45–2.58 (8H, CH_2), 4.78 (m, 4H, CH (trans to O), J(PtH) = 68 Hz), 5.96 (m, 4H, CH (trans to C), J(PtH) = ca. 30 Hz). ^{1}H NMR (400 MHz, $CDCl_3$, −55 °C): δ 2.24–2.57 (16H, CH_2), 4.61 (s, 1H, OH), 4.76 (m, 4H, CH (trans to O)), 5.87 (m, 4H, CH (trans to C)). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, r.t.): δ 28.3 (CH_2), 32.3 (CH_2), 87.5 (CH, J(PtH) = 198 Hz), 117.0 (CH, J(PtC) = 54 Hz), 136.4–148.1 (C_6F_5). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, r.t.): δ −161.2 (m, 2F, *meta*-C_6F_5), −156.5 (m, 1F, *para*-C_6F_5), −151.4 (BF_4), −151.3 (BF_4), −122.8 (m, 2F, *ortho*-C_6F_5, J(PtF) = 251 Hz). IR (KBr disk): ν(OH); 3345 cm^{-1}. Anal. Calc. for $C_{28}H_{25}BF_{14}OPt_2$: C, 32.20; H, 2.41. Found: C, 31.81; H, 2.20%.

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