Bull. Chem. Soc. Jpn., **77**, 139–145 (2004)

Intermolecular Phenyl Ligand Transfer of Pt(II) and Pd(II) Complexes with Bidentate Ligand

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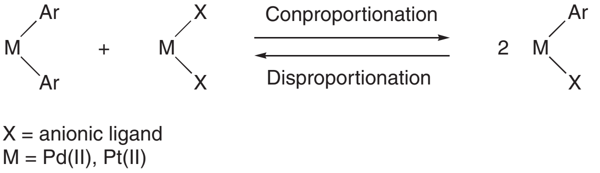
$[PtPh_2(dppe)]$ (dppe = 1,2-bis(diphenylphosphino)ethane) reacts with equimolar $[PtCl_2(cod)]$ (cod = 1,5-cyclooctadiene) to give a mixture of $[PtPh_2(cod)]$ (38%), $[PtCl(Ph)(cod)]$ (53%) and $[PtCl_2(dppe)]$ (72%) via exchange of the phenyl and chloro ligands among the Pt complexes. The reaction is strongly inhibited by addition of Cl^-. The intermolecular phenyl ligand transfer from Pd to Pt is observed in the reaction of $[PdCl(Ph)(bpy)]$ (bpy = 2,2′-bipyridine) with $[PtX_2(cod)]$ (X = Cl, I), which produces $[PtX(Ph)(cod)]$. The reaction of $[PdCl(Ph)(bpy)]$ with $[PdCl_2(cod)]$, giving $[Pd_2(\mu\text{-}Cl)_2\{(4,5\text{-}\eta\text{-}\kappa C^1)\text{-}(C_8H_{12}Ph)\}_2]$, occurs much faster than a similar reaction of $[PdCl(Ph)(bpy)]$ with $[PtCl_2(cod)]$. $[PtPh_2(L_2)]$ (L_2 = cod, dppe) reacts with $[PdCl_2(cod)]$ in CH_2Cl_2 at room temperature to afford $[Pd_2(\mu\text{-}Cl)_2\{(4,5\text{-}\eta\text{-}\kappa C^1)\text{-}(C_8H_{12}Ph)\}_2]$ via intermolecular phenyl ligand transfer from Pt to Pd and subsequent insertion of a C=C bond of cod into the Pd–Ph bond. Cationic Pd complexes $[Pd(acetone)_2(cod)]^{2+}(BF_4^-)_2$ and $[Pd(\eta^3\text{-}C_3H_5)(acetone)_2]^+(BF_4^-)$ react with $[PtPh_2(cod)]$ to form biphenyl. All these results indicate that chloro complexes of Pd and Pt with cod ligand undergo the ligand exchange with the phenyl complexes of these metals.

Intermolecular aryl ligand transfer of Pd(II) and Pt(II) complexes was found in the 1970's, although the reports on this subject are still rare. Scheme 1 depicts conproportionation of the diaryl and dihalogeno complexes of the metals and disproportionation of the monoaryl halogeno complex. These aryl ligand transfer reactions would take place reversibly when the stability values of the starting and resulting complexes are close to each other. Conproportionation of $[PtAr_2(cod)]$ and $[PtCl_2(cod)]$ was reported by Eaborn to give $[PtAr(Cl)(cod)]$.[1] Addition of dppe to the reaction mixture formed three complexes: $[PtAr_2(dppe)]$, $[PtAr(Cl)(dppe)]$, and $[PtCl_2(dppe)]$. An equimolar mixture of $[Pt(C_4H_3S)_2(cod)]$ (C_4H_3S = 2-thienyl) and $[PtCl_2(cod)]$ was converted quantitatively to $[PtCl(C_4H_3S)(dppe)]$, while the reaction of $[Pt(C_6H_4Cl\text{-}3)_2(cod)]$ with $[PtCl_2(cod)]$, followed by addition of dppe, produced a mixture of the diaryl, chloroaryl and dichloro platinum complexes in a statistical ratio (1:2:1). $[Pt(\kappa C\text{-}C_5H_5)_2(CO)(PMe_2Ph)]$ and $[PtCl_2(CO)(PMe_2Ph)]$ underwent conproportionation at room temperature to give $[Pt(\kappa C\text{-}C_5H_5)(Cl)(CO)(PMe_2Ph)]$.[2]

Thermally induced disproportionation of $[PtPh(O_2CCF_3)(dmpe)]$ (dmpe = 1,2-bis(dimethylphosphino)ethane) formed an equimolar mixture of $[PtPh_2(dmpe)]$ and $[Pt(O_2CCF_3)_2(dmpe)]$.[3] Recently we observed disproportionation of $[Pt(Ph)(CH_2COMe)(cod)]$ to give a mixture of $[PtPh_2(cod)]$ and $[Pt(CH_2COMe)_2(cod)]$.[4] The two produced complexes undergo the conproportionation to regenerate the monophenyl platinum complex. The halogeno(aryl)nickel and -palladium complexes with bpy ligand liberated biaryl upon treatment with a polar solvent such as DMF and with $AgBF_4$.[5] The reaction was proposed to involve initial formation of cationic monoaryl complexes of these metals, intermolecular aryl ligand transfer to give intermediate diaryl complexes, and reductive elimination of the product from the diaryl complexes. The organic ligand transfer and subsequent reductive elimination of biaryl were utilized in synthesis of macrocyclic compounds.[6]

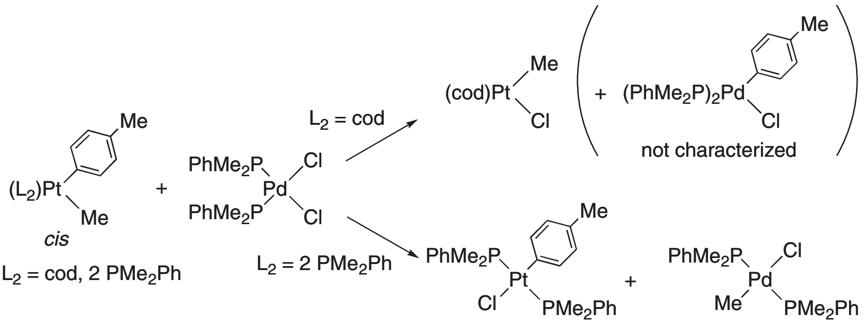


Scheme 1.

The aryl ligand transfer also takes place between the complexes with different metal centers or different auxiliary ligands. Puddephatt found that $[PtAr_2(cod)]$ reacted with $[PtI_2(PMe_2Ph)_2]$ to give a mixture of $[PtAr(I)(cod)]$ and $[PtAr(I)(PMe_2Ph)_2]$ and that the reaction of $[PtAr(Me)(cod)]$ with $[PtI_2(PMe_2Ph)_2]$ afforded $[PtMe(I)(PMe_2Ph)_2]$ via the selective methyl ligand transfer between the two Pt complexes.[7] The reactions of [*cis*-$PdCl_2(PMe_2Ph)_2$] with $[PtMe(C_6H_4Me\text{-}4)(cod)]$ and with $[PtMe(C_6H_4Me\text{-}4)(PMe_2Ph)_2]$ produced different products. The Pt–cod complex underwent aryl ligand transfer from Pt to Pd, while the Pt–PMe_2Ph complex reacted with [*cis*-$PdCl_2(PMe_2Ph)_2$] to exchange the Cl and Me ligands, as shown in Scheme 2.

In this paper, we report phenyl ligand transfer among the Pd(II) and Pt(II) complexes with bidentate ligands such as cod, bpy, and dppe. The chelating ligands fix cis structure of the square-planar complexes, which make the pathway of the intermolecular ligand transfer simpler than those of the complexes with monodentate auxiliary ligands. The reactions of Pd and Pt complexes with aryl and halogeno ligands in this study demonstrate smooth aryl ligand transfer between these group 10 metals.

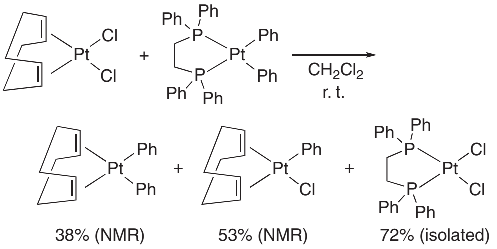
Published on the web January 13, 2004; DOI 10.1246/bcsj.77.139



Scheme 2.

Results and Discussion

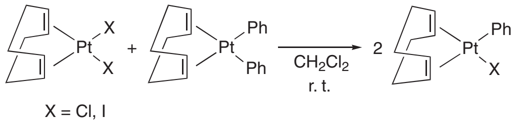
Phenyl Ligand Transfer between Pt Complexes. An equimolar reaction of [$PtPh_2$(dppe)] with [$PtCl_2$(cod)] causes the phenyl ligand transfer to give a mixture of the platinum complexes as shown in Eq. 1.



(1)

The ^1H and $^{31}P\{^1H\}$ NMR spectrum of the products contain the signals of [$PtPh_2$(cod)] (38% by NMR based on [$PtCl_2$(cod)]), [PtCl(Ph)(cod)] (53%), unreacted [$PtCl_2$(cod)] (12%), and Pt–dppe complexes. The $^{31}P\{^1H\}$ NMR spectrum shows the presence of [$PtCl_2$(dppe)] and [$PtPh_2$(dppe)] in approximately 3:1 molar ratio, but does not exhibit the peaks due to [PtCl(Ph)(dppe)]. [$PtCl_2$(dppe)] was isolated in 72% (based on [$PtPh_2$(dppe)]) from column chromatography (SiO_2) of the products. [PtCl(Ph)(dppe)], which should be formed initially in the reaction of [$PtPh_2$(dppe)] with [$PtCl_2$(cod)], is not contained in the products. The complex probably undergoes the disproportionation to give a mixture of [$PtCl_2$(dppe)] and [$PtPh_2$(dppe)] or reacts further with [$PtCl_2$(cod)] to form [PtCl(Ph)(cod)] and [$PtCl_2$(dppe)] during the reaction. The reactions of [$PtPh_2$(cod)] and of [$PtPh_2$(dppe)] with [$PtCl_2$(dppe)] were conducted but did not cause the ligand exchange.

An equimolar mixture of [$PtPh_2$(cod)] and [$PtCl_2$(cod)] in CH_2Cl_2 is converted into [PtCl(Ph)(cod)] (72% by NMR based on [$PtPh_2$(cod)] + [$PtCl_2$(cod)], 3 h; 93%, 24 h) at room temperature (Eq. 2).



(2)

The reactions of [$PtPh_2$(cod)] with [PtX_2(cod)] (X = Cl, I) in 2:1 molar ratio form [PtX(Ph)(cod)] quantitatively. Eaborn previously reported that the reaction of [$Pt(C_6H_4Cl\text{-}3)_2$(cod)] with [$PtCl_2$(cod)] and subsequent addition of dppe gave a mixture of [$Pt(C_6H_4Cl\text{-}3)_2$(dppe)], [$PtCl(C_6H_4Cl\text{-}3)$(dppe)] and [$PtCl_2$(dppe)].[1] By comparison of their results with ours, the formation of three Pt–dppe complexes in their reports is ascribed to initial conproportionation of the two complexes, giving a mixture of three Pt–cod complexes followed by replacement of cod ligand with dppe.

The reaction of [$PtPh_2$(cod)] with the Pt–cod complexes was conducted with additives in order to obtain further insights into the mechanism. Table 1 summarizes the results. Addition of Et_4NCl or KCl inhibits the phenyl ligand transfer from [$PtPh_2$(cod)] to [$PtCl_2$(cod)] (runs 3, 4), indicating that the reaction is initiated by dissociation of the Cl ligand. Addition of

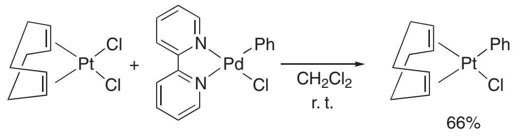
Table 1. Results of Reactions of [$PtPh_2$(cod)] with Pt–cod Complexes[a)]

Run	Complex	Additive	Time	PtCl(Ph)(cod)[b)]
1	[$PtCl_2$(cod)]	none	3 h	72%
2		none	24 h	93%
3		Et_4NCl (0.5 mmol)	3 h	0%
4		KCl (0.5 mmol)[c)]	3 h	0%
5		COD (0.1 mmol)	3 h	57%
6		COD (0.5 mmol)	3 h	51%
7		COD (1 mmol)	3 h	57%
8	[PtI_2(cod)]	none	3 h	36%
9		none	24 h	75%
10	[$Pt(acetone)_2(cod)]^{2+}(BF_4^-)_2$[d)]	none	3 h	94%

a) Conditions: [$PtPh_2$(cod)] (0.10 mmol) and Pt–cod complex (0.10 mmol), solvent: CH_2Cl_2 (runs 1–9) and acetone (run 10), room temperature. b) Yields were based on sum of the starting platinum complexes (0.20 mmol). c) 18-crown-6 ether (0.5 mmol) and water (0.1 cm^3) were added. d) $[Pt(acetone)_2(cod)]^{2+}(BF_4^-)_2$ was generated in situ from $AgBF_4$ and [$PtCl_2$(cod)] in acetone. KCl was added after the reaction.

cod ligand lowers yield of [PtCl(Ph)(cod)] in the reaction (runs 5, 6), although decrease of the yield by cod addition is much smaller than that would be expected from the mechanism of the reaction triggered by cod dissociation. The reaction of [PtI$_2$(cod)] and [PtPh$_2$(cod)] forms [Pt(I)Ph(cod)] in a lower yield than of [Pt(Cl)Ph(cod)] formed from [PtCl$_2$(cod)] and [PtPh$_2$(cod)]. The result is attributed to the dissociation of Cl ligand to form the cationic intermediate being more facile than dissociation of I ligand. Cationic Pt complex with cod, [Pt(acetone)$_2$(cod)]$^{2+}$(BF$_4$$^-$)$_2$, reacts with [PtPh$_2$(cod)] easily, and the reaction for 3 h followed by addition of KCl produces [PtCl(Ph)(cod)] in 94%.

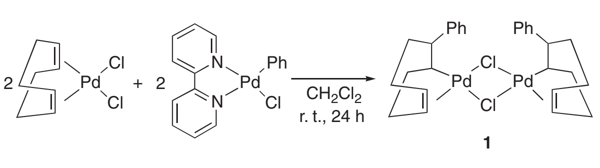
Phenyl Ligand Transfer of Monophenyl Palladium Complexes with Pt and Pd Complexes. Diphenylpalladium complexes with chelating ligands such as cod and dppe decompose easily via intramolecular reductive elimination of biphenyl, and are not suited for the study of the phenyl ligand transfer reactions. Chloro(phenyl)palladium complexes, which do not cause the reductive elimination, are employed in the following study. The reaction of [PdCl(Ph)(bpy)] with [PtCl$_2$(cod)] in CH$_2$Cl$_2$ causes transfer of the phenyl ligand from Pd to Pt to afford [PtCl(Ph)(cod)] (66% after 5 days) (Eq. 3).



(3)

The starting [PtCl$_2$(cod)] remains in the reaction mixture (33%). Pd complexes formed by the reaction are not characterized by the NMR spectroscopy due to their low solubility. The reaction of [PdI(Ph)(bpy)] with [PtCl$_2$(cod)] in a 10:1 molar ratio leads to formation of [PtI(Ph)(cod)] in 96% yield. The reaction of [PdI(Ph)(bpy)] with [PtI$_2$(cod)] (5:1) requires heating at 50 °C and produces [PtI(Ph)(cod)] in 69% after 3 days.

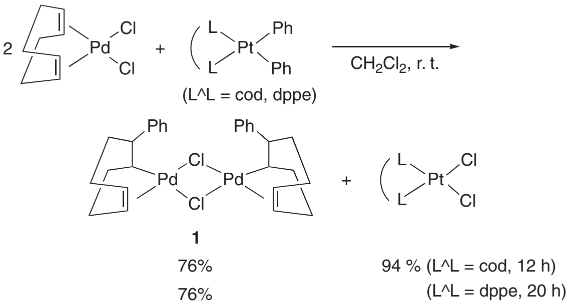
An equimolar reaction of [PdCl(Ph)(bpy)] with [PdCl$_2$(cod)] at room temperature for 24 h forms the dipalladium complex, [Pd$_2$(μ-Cl)$_2${(4,5-η-κC^1)-(C$_8$H$_{12}$Ph)}$_2$] (**1**) in 78% yield (Eq. 4).



(4)

Complex **1** was already prepared from the reaction of [PdCl$_2$(cod)] with Ph$_4$Sn or PhMgBr.[8] The above reaction involves formation of an intermediate [PdCl(Ph)(cod)] via phenyl ligand transfer between the two palladium complexes and insertion of a C=C double bond of the cod ligand into the Pd–Ph bond. Reaction of [PdCl(Ph)(bpy)] with [PdCl$_2$(cod)] in a 2:1 molar ratio gives **1** in 96% yield after 24 h.

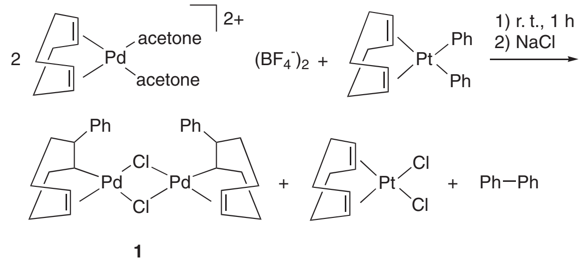
Phenyl Ligand Transfer from Diphenylplatinum Complexes to Pd Complexes. The reaction of [PtPh$_2$(cod)] with [PdCl$_2$(cod)] in a 1:2 molar ratio produces **1** (76% NMR yield) and [PtCl$_2$(cod)] (94%) as shown in Eq. 5.



(5)

1 was isolated in 66% yield from a preparative scale reaction of [PtPh$_2$(cod)] with [PdCl$_2$(cod)] (Pt:Pd = 1:2). A similar reaction of [PtPh$_2$(dppe)] with [PdCl$_2$(cod)] forms **1** (76%) and [PtCl$_2$(dppe)]. The reaction mixture also contains remaining [PdCl$_2$(cod)] (11%). An equimolar reaction of [PtCl(Ph)(cod)] with [PdCl$_2$(cod)] in a dilute CH$_2$Cl$_2$ solution ([Pt] = [Pd] = 0.020 M) converts the complexes into a mixture of **1** and [PtCl$_2$(cod)] quantitatively. Complex **1** is formed via formation of intermediate [PdCl(Ph)(cod)] and insertion of a C=C bond of cod into the Pd–Ph bond. Reaction of [PtPh$_2$(bpy)] with [PdCl$_2$(cod)] forms **1** in 6% yield after 20 h via the phenyl ligand transfer. No phenyl ligand transfer is observed in the reactions of [PtPh$_2$(cod)] with [PdCl$_2$(dppe)] and [PdCl$_2$(bpy)] and of [PtPh$_2$(dppe)] with [PdCl$_2$(dppe)].

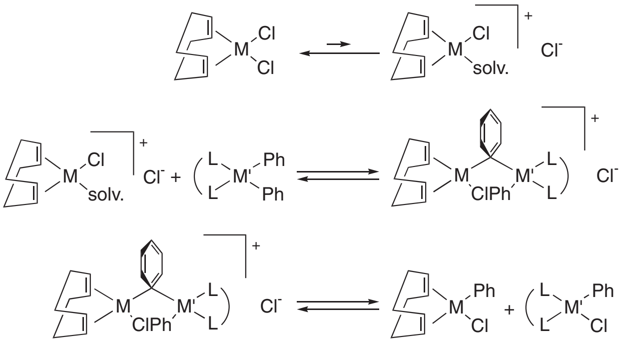
As mentioned before, [PtPh$_2$(cod)] reacts with cationic Pt complex, [Pt(acetone)$_2$(cod)]$^{2+}$(BF$_4$$^-$)$_2$, to cause the phenyl ligand transfer between Pt. An analogous reaction with cationic Pd complexes was examined in order to compare the reactivity of Pt and Pd complexes. [PtPh$_2$(cod)] reacts with [Pd(acetone)$_2$(cod)]$^{2+}$(BF$_4$$^-$)$_2$, prepared in situ from AgBF$_4$ and [PdCl$_2$(cod)] in acetone, and produces biphenyl, **1**, and [PtCl$_2$(cod)] after treatment of the reaction mixture with NaCl as shown in Eq. 6.



(6)

The ^{1}H NMR spectrum of the reaction mixture indicates the absence of [PtPh$_2$(cod)] and [PtCl(Ph)(cod)]. The phenyl ligand transfer from Pt to Pd is rapid and is completed in 1 h. The reaction involves an intermediate cationic phenyl palladium complex [Pd(Ph)(acetone)(cod)]$^+$(BF$_4$$^-$) formed via phenyl ligand transfer from [PtPh$_2$(cod)] to [Pd(acetone)$_2$(cod)]$^{2+}$(BF$_4$$^-$)$_2$. This cationic intermediate undergoes disproportionation to give [PdPh$_2$(cod)] that undergoes facile reductive elimination of biphenyl similarly to the reaction of AgBF$_4$ with [PdI(Ph)(bpy)].[5b] Insertion of a C=C bond of the intermediate and coordination of Cl ligand leads to complex **1**, similarly to the reaction of [PtPh$_2$(cod)] with [PtCl$_2$(cod)].

Cationic π-allylpalladium complex [Pd(η^3-C$_3$H$_5$)(acetone)$_2$]$^+$(BF$_4$$^-$), generated by addition of AgBF$_4$ to an acetone solution of [PdCl(η^3-C$_3$H$_5$)]$_2$, reacts with [PtPh$_2$(cod)] to



Scheme 3.

give biphenyl (95% based on the initial amount of [$PtPh_2$(cod)]) after 46 h. No allylbenzene was formed, suggesting that the reaction does not involve an allyl(phenyl)palladium intermediate that may be expected as a product of the phenyl ligand transfer from [$PtPh_2$(cod)] to [Pd(η^3-C_3H_5)(acetone)$_2$]$^+$(BF_4^-). The reaction of [$PtPh_2$(cod)] with [PdCl(η^3-C_3H_5)]$_2$ occurs slowly to give a mixture of biphenyl (26%) and [PtCl(Ph)(cod)] (40%) even after 12 days.

Reaction Mechanism of Phenyl Ligand Transfer of the Neutral Complexes. Scheme 3 depicts the plausible mechanism of the aryl ligand transfer of the neutral diphenyl and dichloro complexes with cod ligand. Dissociation of Cl ligand from the dichloro complex gives an intermediate cationic complex, [MCl(solvent)(cod)]$^+$(Cl^-). The formed cationic complex and the diphenyl complex produce a dinuclear intermediate with a bridging phenyl ligand. Our previous studies on the chemical properties of halogeno(aryl)nickel and -palladium complexes with bpy ligand revealed that the cationic complexes of these metals caused the smooth intermolecular aryl ligand transfer.[5,6] Transition metal complexes containing aryl ligand bridging to the two metal centers were isolated and characterized.[10]

Table 2 summarizes the results of the exchange of the phenyl and chloro ligands of the neutral Pd and Pt complexes. Transmetalation of the phenyl ligand proceeds only when the chloro complexes have a cod ligand. Cod bonded to dichloro complexes of Pd and Pt seems to play dual roles to enhance the phenyl ligand transfer. The relatively large trans effect of cod promotes dissociation of Cl ligand to give a cationic intermediate [MCl(solvent)(cod)]$^+$(Cl^-). The electron-accepting character of the cod ligand increases the reactivity of the metal center of the cationic intermediate toward formation of the dinuclear intermediate. Table 3 summarizes the $^{13}C\{^1H\}$ NMR data of *cis*-dimethylplatinum complexes.[11–14] Positive chemical shift of CH_3 carbons of [$PtMe_2$(cod)] and [$PtMe_2$(nbd)] (nbd = 2,5-norbornadiene) suggests low electron density of the carbon and less basic nature of the olefin ligand than the diamine whose Pt complexes exhibit the CH_3 carbon signals at negative regions. Thus the cod ligand serves as a π-accepting ligand to make the metal center more electrophilic than dppe or bpy and to enhance ligand exchange.

Summary

This study revealed that exchange of the phenyl and chloro ligands takes place among the Pd and Pt complexes by choosing the cod as the ligand of the chloro complexes. The reaction between the Pt complexes proceeds via cationic intermediate formed by dissociation of Cl ligand. The phenyl ligand transfer from Ph–Pt complexes to [$PdCl_2$(cod)] is followed by the insertion of a C=C bond of cod into Pd–Ph.

Table 2. Results of the Phenyl Ligand Transfer[a)]

	Phenyl complexes			
	[$PtPh_2$(cod)]	[$PtPh_2$(dppe)]	[$PtPh_2$(bpy)]	[PdCl(Ph)(bpy)]
[$PtCl_2$(cod)]	yes	yes	—[b)]	yes
[$PtCl_2$(dppe)]	no	no	—[b)]	—[b)]
[$PdCl_2$(cod)]	yes	yes	yes	yes
[$PdCl_2$(dppe)]	no	no	—[b)]	—[b)]
[$PtCl_2$(bpy)]	no	—[b)]	—[b)]	—[b)]

a) Reaction conditions: [chloro complex]:[phenyl complex] = 1:1–1:5, r.t.–50 °C, 3 h–5 d, See Experimental Section for details. yes: products of the phenyl ligand transfer are observed in the NMR (^1H and $^{31}P\{^1H\}$) spectra. no: products were not observed in the NMR spectra. b) Not applied.

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

Ligand[a)]	cod	nbd	dppe	2-py	RN=CH–CH=NR	tmeda
Chemical shift of CH_3 ligand (ppm)	4.7	4.56	1.0	−8.18	−11.6 (R = *c*-C_5H_{11}) −14.2 (R = C_6H_4Me-4) −15.2 (R = $C_6H_3Me_2$-2,6)	−23.67
$^1J(^{195}Pt–^{13}C)$ (Hz)	773 ± 2	814.5	610	688.5	799.0 (R = *c*-C_5H_{11}) 793.5 (R = C_6H_4Me-4) 785.5 (R = $C_6H_3Me_2$-2,6)	826.2
Reference	11	12	13	12	14	12

a) nbd = 2,5-norbornadiene, py = pyridine, tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

Experimental

General. Manipulations of the complexes were carried out under nitrogen or argon using standard Schlenk techniques. Solvents were purified in the usual manners and stored under argon. NMR spectra (^1H and $^{31}P\{^1H\}$) were recorded on a Varian MERCURY300 spectrometer. $^{31}P\{^1H\}$ NMR peak positions were referenced to external 85% H_3PO_4. [$PtCl_2$(cod)], [PtI_2(cod)], [$PtPh_2$(cod)], [PtCl(Ph)(cod)], [$PtCl_2$(dppe)], [$PtPh_2$(bpy)], [$PdCl_2$(cod)], [$PdCl_2$(bpy)], [$PdCl(\eta^3$-$C_3H_5)]_2$, and [PdI(Ph)(bpy)] were prepared according to the literature methods.[15] [$PtPh_2$(dppe)] and [$PdCl_2$(dppe)] were prepared by the reactions of dppe with [$PtPh_2$(cod)] and with [$PdCl_2$(cod)], respectively. The other chemicals were commercially available.

Preparation of [PdCl(Ph)(bpy)]. [PdCl(Ph)(bpy)] was known,[16] but was prepared by a new procedure in this study. A MeCN (5.0 cm^3) suspension of [PdI(Ph)(bpy)] (294 mg, 0.63 mmol) was mixed with $AgBF_4$ (180 mg, 0.93 mmol) in MeCN (2.0 cm^3). The mixture was stirred for 30 min at room temperature. After addition of NaCl (120 mg, 2.1 mmol) to a reaction mixture, the resulting solid was removed by filtration. Extraction of the product by CH_2Cl_2 from the solid and evaporation of the solvent gave [PdCl(Ph)(bpy)] as a white solid, which was washed with H_2O, Et_2O and dried in vacuo (201 mg, 0.54 mmol, 85%).

Reaction of [$PtPh_2$(dppe)] with [$PtCl_2$(cod)]. A solution of [$PtPh_2$(dppe)] (74.8 mg, 0.10 mmol) and [$PtCl_2$(cod)] (37.4 mg, 0.10 mmol) in CH_2Cl_2 (5.0 cm^3) was stirred for 78 h at room temperature. Evaporation of the solvent gave a mixture of the Pt complexes as a white solid. The ^1H NMR spectra using 1,1,1,2-tetracholoroethane as an internal standard showed the presence of [$PtPh_2$(cod)] (38%), [PtCl(Ph)(cod)] (53%), [$PtCl_2$(cod)] (12%). $^{31}P\{^1H\}$ NMR spectrum of the products revealed the existence of [$PtCl_2$(dppe)] and [$PtPh_2$(dppe)] ([$PtCl_2$(dppe)]:[$PtPh_2$(dppe)] = ca. 3:1). [$PtCl_2$(dppe)] (72%) was isolated by SiO_2 column chromatography (eluent, $CHCl_3$).

Reaction of [$PtPh_2$(cod)] with [PtX_2(cod)] (X = Cl, I). A CH_2Cl_2 (2.0 cm^3) solution of a mixture of [$PtPh_2$(cod)] (0.10 mmol) and [$PtCl_2$(cod)] (0.10 mmol) was stirred for 3 h at room temperature. Evaporation of the solvent gave the products as a white solid. The ^1H NMR spectrum in $CDCl_3$ using 1,1,1,2-tetracholoroethane as an internal standard showed the presence of [PtCl(Ph)(cod)] (72%), [$PtCl_2$(cod)] (14%), and [$PtPh_2$(cod)] (11%). The reaction for 24 h gave [PtCl(Ph)(cod)] (93%) and [$PtCl_2$(cod)] (7%). The reaction of [$PtPh_2$(cod)] (0.20 mmol) and [$PtCl_2$(cod)] (0.10 mmol) for 24 h gave [PtCl(Ph)(cod)] (99%) and [$PtPh_2$(cod)] (42%).

A similar reaction of [$PtPh_2$(cod)] (0.10 mmol) and [PtI_2(cod)] (0.10 mmol) for 24 h gave [PtI(Ph)(cod)] (75%), [$PtPh_2$(cod)] (21%), and [PtI_2(cod)] (25%), while the reaction for 3 h gave [PtI(Ph)(cod)] (36%), [$PtPh_2$(cod)] (54%), and [PtI_2(cod)] (64%) under the same conditions. The reaction of [$PtPh_2$(cod)] (0.20 mmol) with [PtI_2(cod)] (0.10 mmol) for 24 h gave [PtI(Ph)(cod)] ($>$99%) and [$PtPh_2$(cod)] (44%).

Reaction of [$PtPh_2$(cod)] with [$PtCl_2$(cod)] in the Presence of Et_4NCl or KCl. A CH_2Cl_2 (2.0 cm^3) solution of a mixture of [$PtPh_2$(cod)] (0.10 mmol), [$PtCl_2$(cod)] (0.10 mmol), and Et_4NCl (188 mg, 0.53 mmol) was stirred for 3 h at room temperature. Evaporation of the solvent and ^1H NMR measurement of the residue in $CDCl_3$ showed complete recovery of the starting complexes. The reaction in the presence of KCl (37 mg, 0.50 mmol) was carried out by adding 18-crown-6 ether (130 mg, 0.49 mmol) and H_2O (0.1 cm^3) to the reaction mixture. Complexes other than the starting complexes were not observed in the reaction mixture after 3 h.

Reaction of [$PtPh_2$(cod)] and [$PtCl_2$(cod)] in the Presence of Added cod. CH_2Cl_2 (2.0 cm^3) solutions of mixture of [$PtPh_2$(cod)] (0.10 mmol), [$PtCl_2$(cod)] (0.10 mmol), and cod (0.1, 0.5, 1 mmol) were stirred for 3 h at room temperature. Evaporation of the solvent gave the products as a white solid. Table 1 summarized the results.

Reaction of [$PtPh_2$(cod)] with [$Pt(acetone)_2(cod)]^{2+}(BF_4^-)_2$. To an acetone (0.5 cm^3) solution of [$PtCl_2$(cod)] (37.4 mg, 0.10 mmol) was added an acetone (1.5 cm^3) solution of $AgBF_4$ (40.4 mg, 0.21 mmol). After the mixture was stirred for ca. 15 min at room temperature, the resulting AgCl was remove by filtration. After addition of [$PtPh_2$(cod)] (45.7 mg, 0.10 mmol) to the solution, the reaction mixture was stirred for 3 h at room temperature. Excess KCl was added to the solution to convert the cationic or coordinatively unsaturated Pt complexes into the less reactive chloroplatinum complexes. NH_4Cl aq. was added to the solution and the products were extracted with $CHCl_3$. The organic phase was washed with water, dried over $MgSO_4$, filtered, and the solvent was evaporated to give the white solid. The ^1H NMR spectrum in $CDCl_3$, using 1,1,1,2-tetracholoroethane as an internal standard, showed the presence of [PtCl(Ph)(cod)] (94%), [$PtCl_2$(cod)] (4%), and [$PtPh_2$(cod)] (1%).

Reaction of [PtX_2(cod)] with [PdPh(X′)(bpy)] (X, X′ = Cl, I). A CH_2Cl_2 solution (5 cm^3) of [$PtCl_2$(cod)] (37.4 mg, 0.10 mmol) and [PdCl(Ph)(bpy)] (37.5 mg, 0.10 mmol) was stirred for 5 days at room temperature. The ^1H NMR peak area relative to those of 1,1,1,2-tetracholoroethane used as an internal standard, showed the presence of [PtCl(Ph)(cod)] (66%) and [$PtCl_2$(cod)] (33%). Reaction of [$PtCl_2$(cod)] (37.4 mg, 0.10 mmol) with [PdI(Ph)(bpy)] (467 mg, 1.0 mmol) in $CHCl_3$ gave [PtI(Ph)(cod)] (96%).

The products of the reaction of [PtI_2(cod)] (55.7 mg, 0.10 mmol) with [PdI(Ph)(bpy)] (233 mg, 0.50 mmol) in $CHCl_3$ at 50 °C for 3 days were composed of [PtI(Ph)(cod)] (69%) and [PtI_2(cod)] (11%).

Reaction of [PdCl(Ph)(bpy)] with [$PdCl_2$(cod)]. A CH_2Cl_2 (5.0 cm^3) solution of [$PdCl_2$(cod)] (28.6 mg, 0.10 mmol) and [PdCl(Ph)(bpy)] (37.5 mg, 0.10 mmol) was stirred for 24 h at room temperature. After removal of an insoluble solid by filtration, the solvent was evaporated to dryness. The ^1H NMR spectrum of the products, containing 1,1,1,2-tetracholoroethane as an internal standard, showed formation of **1** (0.039 mmol, 78%), [$PdCl_2$(cod)] (0.022 mmol, 22%), and [PdCl(Ph)(bpy)] (0.019 mmol, 19%). The reaction of [$PdCl_2$(cod)] (14.3 mg, 0.050 mmol) and [PdCl(Ph)(bpy)] (37.5 mg, 0.10 mmol) in CH_2Cl_2 (2.5 cm^3) gave **1** (0.024 mmol, 96%).

Reaction of [$PtPh_2$(cod)] with [$PdCl_2$(cod)]. A solution of [$PtPh_2$(cod)] (45.7 mg, 0.10 mmol) and [$PdCl_2$(cod)] (57.1 mg, 0.20 mmol) in CH_2Cl_2 (1.0 cm^3) was stirred for 12 h at room temperature. After removal of a small amount of black solid by filtration, the solvent was evaporated to give a brown solid. The ^1H NMR spectrum in $CDCl_3$, using 1,1,1,2-tetracholoroethane as an internal standard, showed the presence of **1** (76%), [$PtCl_2$(cod)] (94%), and [$PdCl_2$(cod)] (9%).

Isolation of 1 from the Reaction on a Large Scale. A solution of [$PtPh_2$(cod)] (914 mg, 2.0 mmol) and [$PdCl_2$(cod)] (1.14 g, 4.0 mmol) in CH_2Cl_2 (20 cm^3) was stirred for 14 h at room temperature. After removal of a small amount of black solid by filtration, the solvent was evaporated to ca. 5 cm^3 to give a gray solid, which was collected by filtration. Washing the products with $CHCl_3$ (10 cm^3, 2 times) and Et_2O (10 cm^3, 2 times) and drying in vacuo gave **1** as an off-white solid (860 mg, 1.3 mmol, 66%).

Reaction of [PtPh$_2$(dppe)] with [PdCl$_2$(cod)]. A solution of [PtPh$_2$(dppe)] (74.8 mg, 0.10 mmol) and [PdCl$_2$(cod)] (57.1 mg, 0.20 mmol) in CH_2Cl_2 (5.0 cm^3) was stirred for 20 h at room temperature. After removal of a small amount of black solid, the solvent was evaporated to give a brown solid. The ^{1}H NMR spectrum in $CDCl_3$, using 1,1,1,2-tetracholoroethane as an internal standard, revealed formation of **1** (76%) and [PdCl$_2$(cod)] (11%). The ^{31}P{^{1}H} NMR spectrum showed the presence of [PtCl$_2$(dppe)] and the absence of [PtPh$_2$(dppe)] and [PtCl(Ph)(dppe)]. Overlap of the ^{1}H NMR peak of [PtCl$_2$(dppe)] with other products prevented determination of its yield.

Reaction of [PtCl(Ph)(cod)] with [PdCl$_2$(cod)]. A solution of [PtCl(Ph)(cod)] (41.6 mg, 0.10 mmol) and [PdCl$_2$(cod)] (28.6 mg, 0.10 mmol) in CH_2Cl_2 (5.0 cm^3) was stirred for 14 h at room temperature. Evaporation of the solvent gave a gray powder, which was analyzed by ^{1}H NMR spectrum in $CDCl_3$ using 1,1,1,2-tetracholoroethane as an internal standard. Both the products, **1** and [PtCl$_2$(cod)], were formed quantitatively.

Reaction of [PtPh$_2$(bpy)] with [PdCl$_2$(cod)]. A solution of [PtPh$_2$(bpy)] (50.5 mg, 0.10 mmol) and [PdCl$_2$(cod)] (57.1 mg, 0.20 mmol) in CH_2Cl_2 (5.0 cm^3) was stirred for 20 h at room temperature. Although the palladium complex was dissolved, a part of [PtPh$_2$(bpy)] remained undissolved. After the evaporation, the products were analyzed by ^{1}H NMR spectrum in $CDCl_3$ using 1,1,1,2-tetracholoroethane as an internal standard. Complex **1** was formed in 6% yield.

Reactions of [PtPh$_2$(cod)] with [PdCl$_2$(dppe)] and with [PdCl$_2$(bpy)] and Reaction of [PtPh$_2$(dppe)] with [PdCl$_2$(dppe)]. A solution of diphenylplatinum complex (0.10 mmol) and dichloropalladium complex (0.20 mmol) in CH_2Cl_2 (6.0 cm^3) was stirred for 20 h at room temperature. Platinum complex was dissolved, while a part of the palladium remained undissolved. The ^{1}H NMR and ^{31}P{^{1}H} NMR spectrum in $CDCl_3$ revealed recovery of the starting complexes.

Reaction of [PtPh$_2$(cod)] with [Pd(acetone)$_2$(cod)]$^{2+}$(BF$_4^-$)$_2$. To an acetone (1.0 cm^3) solution of [PdCl$_2$(cod)] (57.1 mg, 0.20 mmol) was added an acetone (1.0 cm^3) solution of $AgBF_4$ (92.0 mg, 0.47 mmol). After stirring the mixture for ca. 1 min at room temperature, the resulting AgCl was removed by filtration. [PtPh$_2$(cod)] (45.8 mg, 0.10 mmol) was added to the solution. The reaction mixture was stirred for 1 h at room temperature. Excess NaCl (ca. 1.0 mmol) was added to the solution to convert the cationic or coordinatively unsaturated Pd complexes into the less reactive chloropalladium complexes. The resulting insoluble solid was removed by filtration, followed by evaporation of the solvent. The filtrate was analyzed by ^{1}H NMR using 1,1,1,2-tetracholoroethane as an internal standard. Biphenyl (0.023 mmol) and **1** (0.032 mmol) were formed in the reaction mixture. Formation of [PtCl$_2$(cod)] was observed, but the significant overlapping with other peaks prevented the estimation of the yield.

Reaction of PtPh$_2$(cod) with [Pd(η^3-C$_3$H$_5$)(acetone)$_2$]$^+$(BF$_4^-$). An acetone/CH_2Cl_2 (1:1 vol/vol, 10 cm^3) solution of [PtPh$_2$(cod)] (46.0 mg, 0.10 mmol) and [PdCl(η^3-C$_3$H$_5$)]$_2$ (36.3 mg, 0.10 mmol) was mixed with an acetone (3.0 cm^3) solution of $AgBF_4$ (84.0 mg, 0.43 mmol). After stirring the mixture for 46 h at room temperature, excess NaI (ca. 0.9 mmol) was added to the solution to convert the cationic or coordinatively unsaturated organopalladium complexes to the less reactive iodopalladium complexes. After removal of an insoluble solid by filtration, the solvent was evaporated to dryness. The products contained in the filtrate were analyzed by ^{1}H NMR using 1,1,1,2-tetracholoroethane as an internal standard. Biphenyl (0.095 mmol, 95%) was formed in the reaction mixture.

Reaction of [PtPh$_2$(cod)] with [PdCl(η^3-C$_3$H$_5$)]$_2$. A solution of [PtPh$_2$(cod)] (46.0 mg, 0.10 mmol) and [PdCl(η^3-C$_3$H$_5$)]$_2$ (36.6 mg, 0.10 mmol) in acetone/CH_2Cl_2 (1:1 v/v, 10 cm^3) was stirred for 2 days at room temperature. Evaporation of the solvent gave a gray solid, which was analyzed by ^{1}H NMR in $CDCl_3$ using 1,1,1,2-tetracholoroethane as an internal standard. The products contained biphenyl (0.023 mmol, 5%), [PtPh$_2$(cod)] (0.084 mmol, 84%), [PtCl(Ph)(cod)] (0.012 mmol, 12%), and [PdCl(η^3-C$_3$H$_5$)]$_2$ (0.094 mmol, 94%). The products of the reaction for 12 days contained biphenyl (0.013 mmol, 26%), [PtPh$_2$(cod)] (0.049 mmol, 49%), [PtCl(Ph)(cod)] (0.040 mmol, 40%), and [PdCl(η^3-C$_3$H$_5$)]$_2$ (0.082 mmol, 82%).

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology.

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