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Intermolecular Alkynyl Ligand Transfer in Palladium(II) and Platinum(II) Complexes with −C≡CCOOR and −C≡CPh Ligands. Relative Stability of the Alkynyl Complexes and Conproportionation of Dialkynyl and Diiodo Complexes of These Metals

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An equimolar reaction of *trans*-Pd(C≡CCOOMe)$_2$(PEt$_3$)$_2$ with *trans*-PdI$_2$(PEt$_3$)$_2$ catalyzed by CuI causes conproportionation of the complexes at room temperature, producing *trans*-PdI(C≡COOMe)(PEt$_3$)$_2$ in 88% yield, while the reaction without CuI catalyst gives the monoalkynylpalladium complex in approximately 2% yield after a prolonged period. Similar reactions of *trans*-Pd(C≡CPh)$_2$(PEt$_3$)$_2$ with *trans*-PdI$_2$(PEt$_3$)$_2$ with and without CuI catalyst give the alkynyl ligand transfer reaction product *trans*-PdI(C≡CPh)(PEt$_3$)$_2$ in 95% and 33% yields, respectively. CuI-catalyzed conproportionation of *trans*-Pt(C≡CPh)$_2$(PEt$_3$)$_2$ and *trans*-PtI$_2$(PEt$_3$)$_2$ occurs more slowly than the corresponding reactions of the Pd complexes; *trans*-Pt(C≡CCOOMe)$_2$(PEt$_3$)$_2$ does not react with the diiodoplatinum complex even in the presence of CuI. The alkynyl ligand transfer reaction from *trans*-Pd(C≡CCOOMe)$_2$(PEt$_3$)$_2$ to *trans*-PtI$_2$(PEt$_3$)$_2$ occurs in the presence of CuI catalyst, affording a mixture of several organopalladium and -platinum complexes. The main Pd complex in the reaction mixture is *trans*-PdI(C≡CCOOMe)(PEt$_3$)$_2$, while the Pt-containing product is composed of *trans*-Pt(C≡CCOOMe)$_2$(PEt$_3$)$_2$, *trans*-PtI(C≡CCOOMe)(PEt$_3$)$_2$, and *trans*-PtI$_2$(PEt$_3$)$_2$ in an approximate 1:2:1 molar ratio. Mixing of *trans*-Pd(C≡CCOOMe)$_2$(PEt$_3$)$_2$, *trans*-PdI$_2$(PEt$_3$)$_2$, and *trans*-PtI$_2$(PEt$_3$)$_2$ results in the formation of *trans*-PdI(C≡CCOOMe)(PEt$_3$)$_2$ in a high yield, while the alkynyl ligand transfer from Pd to Pt complexes is almost negligible. *trans*-PtI$_2$(PEt$_3$)$_2$ catalyzes the alkynyl ligand transfer between the dialkynyl- and diiodopalladium(II) complexes and remains unchanged in the reaction mixture.

Introduction

Alkynyl complexes of group 10 metals have been studied extensively and attracted continuous attention from the viewpoints of synthetic organic chemistry and material science. Cross-coupling of aryl and vinyl halides with a terminal alkyne catalyzed by a Pd complex in the presence of CuI and amine to give aryl alkyne and enyne, respectively, was first reported in 1975 and is proposed to involve aryl(alkynyl)- and alkenyl(alkynyl)palladium complexes (Chart 1) as the key intermediates.[1,2] The reaction provides an important method for forming C(sp)−C(sp^2) bonds under mild conditions and was applied to the preparation of various π-conjugated polymers composed of alternating arylene and ethynylene units.[3] These polymers exhibit unique luminescent

Chart 1

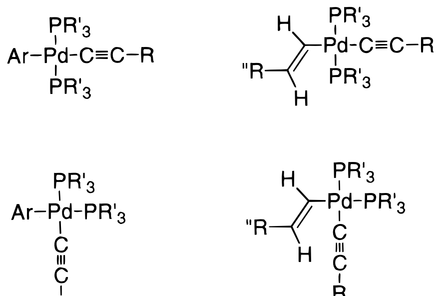

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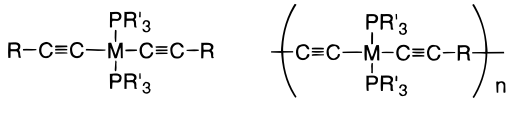
Chart 2



(M = Pd, Pt)

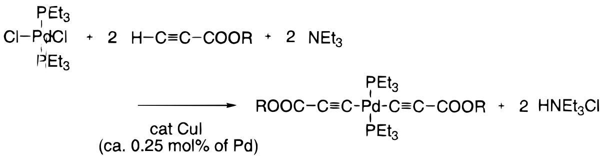
and nonlinear optical properties. The intermolecular transfer of alkynyl ligand between transition metals plays an important role in the above-mentioned cross-coupling reactions. Cu(C≡CR)L (L = amine) generated in situ from a mixture of CuI, terminal alkyne, and amine undergoes alkynyl ligand transfer to PdAr(X)-$(L')_n$ (X = halide, L′ = phosphine), producing PdAr(C≡CR)$(L')_n$, which is responsible for the reductive elimination of the coupling product. Recently, we reported the transfer of phenylethynyl ligands between arylpalladium and arylplatinum complexes with or without CuI catalyst.[4] CuI promotes the reaction by transporting the alkynyl ligand between group 10 metals.

A common method for preparing dialkynyl complexes of Pd and Pt is the reaction of dihalo complexes of these metals with a terminal alkyne in the presence of CuI and amine.[5,6] The reaction was applied to the synthesis of not only dialkynylpalladium and -platinum complexes but also various stable polyyne polymers containing Pd and Pt which have rigid rodlike structures owing to the linear −C≡C−M−C≡C− bond (Chart 2)[7−9] and are regarded as materials with potential optical and liquid crystalline properties.[10] Recently, Louwen et al. suggested that the metal−carbon bonds of di(ethynyl) and di(phenylethynyl) complexes of Pd and Pt are stabilized to a small degree by back-donation of d orbitals of the metal center to π* orbitals of the alkynyl ligand and that an alkynyl ligand with electron-withdrawing groups such as CN and COOR may form a coordination bond with more significant back-donation.[11] This implies that chemical properties alter depending on the substituents of the alkynyl ligands. Palladium alkoxycarbonylethynyl complexes, *trans*-Pd(C≡CCOOR)$_2$(PEt$_3$)$_2$ (R = Me, Et, *t*-Bu), were previously prepared from the reaction of *trans*-PdCl$_2$(PEt$_3$)$_2$ with Cu(C≡CCOOR)(PPh$_3$)$_n$,[12] but their properties have not been investigated in detail.

In this paper we report the structure and properties of palladium and platinum complexes with −C≡CCOOR ligands and compare them with conventional phenylethynyl complexes. The study is mainly focused on the alkynyl ligand transfer among dialkynyl complexes and diiodo complexes of Pd and Pt, which leads to conproportionation of the Pd complexes or ligand transfer from Pd to Pt depending on the kind of alkynyl group and the reaction conditions.

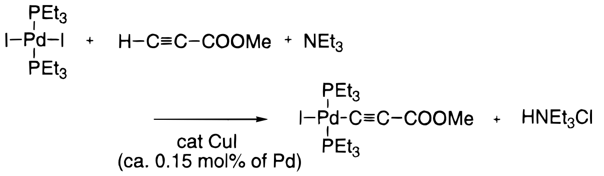
Results

Preparation and Characterization of Pd and Pt Complexes with −C≡CCOOR Ligands. Palladium complexes *trans*-Pd(C≡CCOOR)$_2$(PEt$_3$)$_2$ (**1a**, R = Me; **1b**, R = Et), previously obtained by transmetalation of [Cu(C≡CCOOR)(PPh$_3$)$_m$]$_n$ and PdCl$_2$(PEt$_3$)$_2$, are prepared more conveniently from the 1:2 reaction of *trans*-PdCl$_2$(PEt$_3$)$_2$ with HC≡CCOOR in the presence of CuI catalyst and triethylamine, as shown in eq 1. The NMR (^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H}) spectra of the complexes contain the signals of the alkynyl and PEt$_3$ ligands at expected positions and the relative peak intensities. The trans coordination of **1a** is confirmed from the ^{13}C{^{1}H} NMR spectrum containing a symmetrical triplet at δ 116.2 (J(PC)= 17 Hz) due to the alkynyl carbon attached to Pd. An equimolar reaction of *trans*-PdI$_2$(PEt$_3$)$_2$ with HC≡CCOOMe catalyzed by CuI produces *trans*-PdI(C≡CCOOMe)(PEt$_3$)$_2$ (**2a**) (eq 2). Although **2a** is obtained as a mixture containing much smaller amounts of **1a** and *trans*-PtI$_2$(PEt$_3$)$_2$ and cannot be obtained in pure form due to its instability in NEt$_3$ solution at a high concentration, the ^{31}P{^{1}H} NMR resonance at a different position from the starting complexes (δ 14.6) and the peak area ratio of the ^{1}H NMR signals of alkynyl and



$$\text{Cl-}\overset{\text{PEt}_3}{\underset{\text{PEt}_3}{\text{Pd}}}\text{Cl} + 2\ \text{H-C≡C-COOR} + 2\ \text{NEt}_3 \longrightarrow \text{ROOC-C≡C-}\overset{\text{PEt}_3}{\underset{\text{PEt}_3}{\text{Pd}}}\text{-C≡C-COOR} + 2\ \text{HNEt}_3\text{Cl} \quad (1)$$

1a : R = Me
1b : R = Et



$$\text{I-}\overset{\text{PEt}_3}{\underset{\text{PEt}_3}{\text{Pd}}}\text{-I} + \text{H-C≡C-COOMe} + \text{NEt}_3 \longrightarrow \text{I-}\overset{\text{PEt}_3}{\underset{\text{PEt}_3}{\text{Pd}}}\text{-C≡C-COOMe} + \text{HNEt}_3\text{Cl} \quad (2)$$

2a

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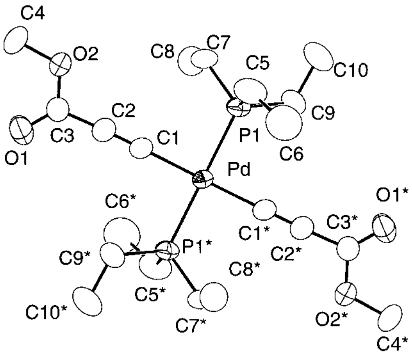


Figure 1. ORTEP drawing of **1a** with 30% ellipsoidal levels. Selected bond distances (Å) and angles (deg): Pd−P1 2.3134(9), Pd−C1 1.999(3), C1−C2 1.193(5), C2−C3 1.445(5), C3−O1 1.190(4), C3−O2 1.326(4), O2−C4 1.445(5), P−Pd−C1 90.1(1) and 89.9(1), Pd−C1−C2 178.9(4), C1−C2−C3 178.3(4).

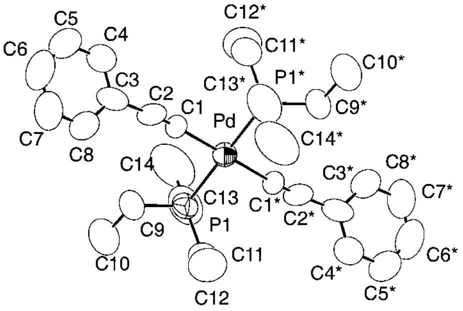


Figure 2. ORTEP drawing of **1c** with 30% ellipsoidal levels. Selected bond distances (Å) and angles (deg): Pd−P1 2.300(2), Pd−C1 2.069(7), C1−C2 1.003(8), C2−C3 1.53(1), P−Pd−C1 92.9(2) and 87.1(2), Pd−C1−C2 176.9(9), C1−C2−C3 175(1).

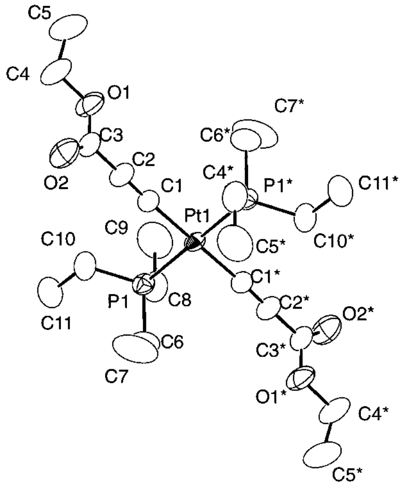


Figure 3. ORTEP drawing of **4b** with 30% ellipsoidal levels. Selected bond distances (Å) and angles (deg): Pt−P1 2.296(1), Pt−C1 1.994(4), C1−C2 1.197(5), C2−C3 1.432(5), P−Pt−C1 93.2(1) and 86.8(1), Pt−C1−C2 176.8(4), C1−C2−C3 178.7(5).

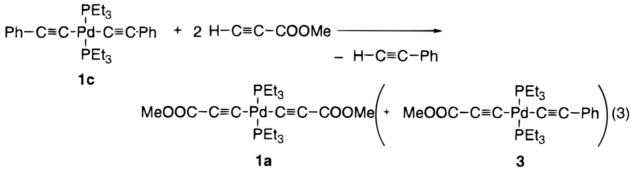
Table 1. $^{13}C\{^1H\}$ NMR Peak Positions of Alkyne and Alkynyl Complexes[a]

	δ	
compound	M−C≡ or H−C≡	≡C−Ph or ≡C−COOR
H−C≡C−COOMe	74.6	74.8
1a[b]	116.2 (41.8)	104.4 (29.6)
4a[b]	111.9 (37.3)	103.2 (28.2)
H−C≡C−Ph	77.8	83.9
1c[b]	111.5 (33.7)	115.8 (31.9)
4c[b]	108.4 (30.6)	110.0 (26.1)

[a] 100 MHz in CD_2Cl_2 at 25 °C. [b] Low magnetic field shift referenced to the corresponding peak of the alkyne (ppm) is shown in parentheses.

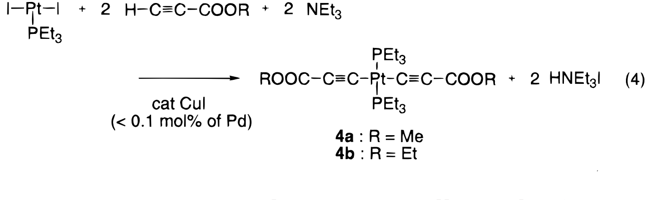
phosphine ligands indicate the proposed structure. Figures 1 and 2 depict the molecular structures of **1a** and *trans*-Pd(C≡CPh)$_2$(PEt$_3$)$_2$ (**1c**), respectively, the latter of which was prepared previously[12] and has an isomorphous crystal lattice to its platinum analogue, *trans*-Pt(C≡CPh)$_2$(PEt$_3$)$_2$ (**4c**).[13] Both molecules have a crystallographic C_2 symmetry around the metal centers and adopt trans structures in a square-planar coordination.

The reaction of **1c** with HC≡CCOOMe in a 1:2 molar ratio for 5 days at room temperature produces phenylacetylene and gives **1a** quantitatively (eq 3). The mixture after reaction for a shorter period exhibits the $^{31}P\{^1H\}$ NMR signal of not only **1a** but also a single resonance at δ 18.4, which can be assigned to *trans*-Pt(C≡CCPh)(C≡CCOOMe)(PEt$_3$)$_2$ (**3**) based on the ^1H NMR signals of the reaction mixture. On the other hand, the reaction of **1a** with HC≡CPh does not cause the alkynyl ligand exchange. These results can be attributed to a higher stability of the Pd−C≡CCOOMe bond of **1a** than the Pd−C≡CPh bond of **1c** or higher acidity of H−C≡CCOOMe than H−C≡CPh.



$$\underset{\mathbf{1c}}{\mathrm{Ph{-}C{\equiv}C{-}\underset{PEt_3}{\overset{PEt_3}{Pd}}{-}C{\equiv}C{\cdot}Ph}} + 2\ \mathrm{H{-}C{\equiv}C{-}COOMe} \xrightarrow[-\ \mathrm{H{-}C{\equiv}C{-}Ph}]{} \underset{\mathbf{1a}}{\mathrm{MeOOC{-}C{\equiv}C{-}\underset{PEt_3}{\overset{PEt_3}{Pd}}{-}C{\equiv}C{-}COOMe}} \left(+ \underset{\mathbf{3}}{\mathrm{MeOOC{-}C{\equiv}C{-}\underset{PEt_3}{\overset{PEt_3}{Pd}}{-}C{\equiv}C{-}Ph}} \right) \quad (3)$$

Platinum complexes with alkoxycarbonylethynyl ligands, *trans*-Pt(C≡CCOOMe)$_2$(PEt$_3$)$_2$ (**4a**) and *trans*-Pt(C≡CCOOEt)$_2$(PEt$_3$)$_2$ (**4b**), are prepared analogously to **1a** and **1b**, as shown in eq 4 and characterized by NMR spectroscopy and X-ray crystallography (Figure 3). The $^{31}P\{^1H\}$ NMR signals contain a single resonance flanked by satellite signals. The J(PtP) values (2277 and 2285 Hz) are consistent with the structures having two PEt$_3$ ligands at mutual trans positions. The $^{13}C\{^1H\}$ NMR signals of the alkynyl carbons also exhibit coupling with ^{195}Pt and ^{31}P nuclei. The J(PtC) values of α- and β-carbons (**4a**, 976 and 275 Hz; **4b**, 989 and 278 Hz) are somewhat larger than those of the phenylethynyl coordinated analogue **4c** (961 and 269 Hz).[14] Table 1 summarizes $^{13}C\{^1H\}$ NMR signal positions of the alkynyl carbons of the complexes. α-Carbon signals of



$$\mathrm{I{-}\underset{PEt_3}{\overset{PEt_3}{Pt}}{-}I} + 2\ \mathrm{H{-}C{\equiv}C{-}COOR} + 2\ \mathrm{NEt_3} \xrightarrow[\substack{\text{cat CuI} \\ (<0.1\text{ mol\% of Pd})}]{} \mathrm{ROOC{-}C{\equiv}C{-}\underset{PEt_3}{\overset{PEt_3}{Pt}}{-}C{\equiv}C{-}COOR} + 2\ \mathrm{HNEt_3I} \quad (4)$$

4a : R = Me
4b : R = Et

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Table 2. Conproportionation of Dialkynyl and Diiodo Complexes of Pd and Pt

run	complex		conditions^a catalyst	conditions^a time	product^b
1	**1a**	$PdI_2(PEt_3)_2$	none	26 h	**2a** (2%)
2	**1a**	$PdI_2(PEt_3)_2$	CuI	<1 h	**2a** (88%)
3	**1c**	$PdI_2(PEt_3)_2$	none	20 h	**2c** (33%)
4	**1c**	$PdI_2(PEt_3)_2$	CuI	3 h	**2c** (95%)
5	**4a**	$PtI_2(PEt_3)_2$	none	22 h	no reaction
6	**4a**	$PtI_2(PEt_3)_2$	CuI	24 h	**5a** (2%)
7	**4c**	$PtI_2(PEt_3)_2$	none	26 h	no reaction
8	**4c**	$PtI_2(PEt_3)_2$	CuI	3 h	**5c** (64%)

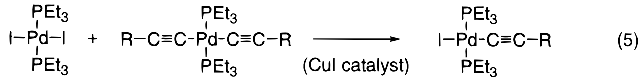
[a] The reaction was carried out in benzene-d_6. [Cu]/[Pd] (or [Pt]) = approximately 0.01. [b] Yield was calculated based on the peak area ratio of $^{31}P\{^1H\}$ NMR signals as follows: Yield= 100[PdI(C≡CR)$(PEt_3)_2$]/([Pd$(C≡CR)_2(PEt_3)_2$] + [PdI(C≡CR)$(PEt_3)_2$] + [$PdI_2(PEt_3)_2$]). No other complexes were found in the ^1H and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture. The relative signal intensity was calibrated by the comparison of the standard mixture of the complexes with that of the ^1H NMR spectra.

1a and **4a** are shifted to lower magnetic field position from the corresponding signals of H−C≡C−COOMe by 41.8 and 37.3 ppm, respectively, whereas the shift of the α-carbon signals of **1c** and **4c** is siginificantly smaller. The difference in the coupling constants and the chemical shifts is related to a difference in the strength of the coordination bond depending on the substituents of the ethynyl groups and may suggest higher stability of M−C bonds in the methoxycarbonylethynyl complexes than that in the phenylethynyl complexes.

Although crystallographic measurement of **1a**, **1c**, and **4a** confirmed the molecular structures with trans coordination, comparison of the bond parameters of the complexes did not provide a clear relationship between the M−C or C≡C bond distances and the substituents of the alkynyl ligand. Pd−C or Pt−C bond distances of **1a** (1.999(3) Å) and **4a** (1.994(4) Å) are significantly shorter than that of **1c** (2.069(7) Å). The Pt−C bond of **4c** (1.98(1) Å) that has an isomorphous crystal lattice to **1c** is the shortest coordination bond of these complexes. C≡C bond distances of **1a**, **4a**, and **4c** (1.193(5)−1.21(1) Å) are longer than that of **1c** (1.003(8) Å), which is exceedingly short for a C≡C triple bond of the coordinated alkynyl group, suggesting invalidity of the position of the alkynyl carbon of **1c** in the crystallographic results. Thus, the bond parameters of the complexes are not suited to discuss stability of the coordination bond. The crystallographic results of *trans*-M$(C≡CX)_2(PR_3)_2$-type complexes (M = Ni, Pd, Pt) presented in the review by Manna et al.[15] do not appear to be conclusive regarding the relationship between the bond parameters and X, whereas *trans*-M(Y)(C≡CX)$(PR_3)_2$-type complexes show a clear dependence of the M−C bond distances on the kind of ligand Y.

Alkynyl Ligand Transfer from Pd$(C≡CR)_2(PEt_3)_2$ (R = COOMe, Ph) to *trans*-$PdI_2(PEt_3)_2$. The bisalkynylpalladium complexes react with *trans*-$PdI_2(PEt_3)_2$ with or without CuI catalyst to afford *trans*-PdI(C≡CR)$(PEt_3)_2$, as summarized in Table 2. Yields of the conproportionation reaction vary significantly depending on the presence of CuI and also on the alkynyl ligand, as described below.

The addition of a catalytic amount of CuI to an equimolar mixture of **1a** and *trans*-$PdI_2(PEt_3)_2$ in benzene-d_6 results in a decrease in the corresponding $^{31}P\{^1H\}$ NMR signals at δ 18.9 and 7.7, and growth of a new peak at δ 14.6 assigned to **2a** (eq 5). The $^{31}P\{^1H\}$ and ^1H NMR spectra after 1 h at 25 °C contain the signals of **1a**, **2a**, and *trans*-$PdI_2(PEt_3)_2$ in a molar ratio of 6:88:6. Further reaction does not cause a variation in the molar ratio of the three complexes, indicating that equilibrium was attained. The ratio of the equilibrated mixture suggests a higher thermodynamic stability of the iodo(alkynyl)palladium complex **2a** than an equimolar mixture of *trans*-$PdI_2(PEt_3)_2$ and **1a**. The reaction without CuI catalyst occurs much more slowly and gives **2a** in approximately 2% yield after 26 h. The bis(phenylethylnyl)palladium complex **1c** also reacts with $PdI_2(PEt_3)_2$ in the presence of CuI catalyst to afford a mixture of three palladium complexes, **1c**, *trans*-PdI(C≡CPh)$(PEt_3)_2$ (**2c**), and *trans*-$PdI_2(PEt_3)_2$. A yield of 95% is attained for **2c**. The phenylethynyl ligand transfer reaction of **1c** to *trans*-$PdI_2(PEt_3)_2$ producing **2c** takes place slowly even in the absence of CuI catalyst and affords the prouct in 33% yield.

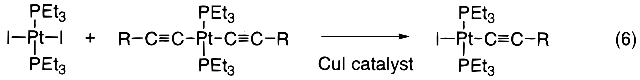


$$I{-}\overset{PEt_3}{\underset{PEt_3}{Pd}}{-}I + R{-}C{\equiv}C{-}\overset{PEt_3}{\underset{PEt_3}{Pd}}{-}C{\equiv}C{-}R \xrightarrow[\text{(CuI catalyst)}]{} I{-}\overset{PEt_3}{\underset{PEt_3}{Pd}}{-}C{\equiv}C{-}R \qquad (5)$$

1a: R = COOMe,
1c: R = Ph

2a: R = COOMe
(2% without CuI; 88% with CuI)
2c: R = Ph
(33% without CuI; 95% with CuI)

The reaction of bis(alkynyl)platinum complexes with *trans*-$PtI_2(PEt_3)_2$ was examined to compare the reaction rate with those of Pd complexes. Complexes **4a** and **4c** do not react with *trans*-$PtI_2(PEt_3)_2$ at room temperature in the absence of CuI catalyst. The addition of CuI catalyst does not enhance conproportionation of **4a** and *trans*-$PtI_2(PEt_3)_2$ and produces the iodo(alkynyl)platinum complex, *trans*-PtI(C≡CCOOMe)$(PEt_3)_2$ (**5a**), in 2% yield after reaction for 24 h. The reaction of **4c** and *trans*-$PtI_2(PEt_3)_2$ proceeds smoothly in the presence of CuI catalyst to afford a mixture of the Pt complexes containing *trans*-PtI(C≡CPh)$(PEt_3)_2$ (**5c**) in 64% yield (eq 6).



$$I{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}I + R{-}C{\equiv}C{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}C{\equiv}C{-}R \xrightarrow[\text{CuI catalyst}]{} I{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}C{\equiv}C{-}R \qquad (6)$$

4a: R = COOMe,
4c: R = Ph

5a: R = COOMe (2%),
5c: R = Ph (64%)

These results suggest several thermodynamic and kinetic features of the alkynyl ligand transfer of Pd and Pt complexes. The CuI-catalyzed reaction of the Pd complexes in eq 5 indicates higher thermodynamic stability of the iodo(alkynyl)palladium(II) complex, *trans*-PdI(C≡CR)$(PEt_3)_2$, than the mixture of bis(alkynyl)- and diiodopalladium(II) complexes. Comparison of the relative reactivity of **1a** and **1c** as well as that of **4a** and **4c** toward the alkynyl ligand transfer with the respective diiodopalladium and -platinum complexes has revealed more facile transfer of the phenylethynyl ligand than the methoxycarbonylethynyl ligand in the reactions of both Pd and Pt complexes. The rates of the alkynyl ligand transfer of **1a** and **1c** with *trans*-$PdI_2(PEt_3)_2$ in the presence of CuI catalyst are too high to be compared.

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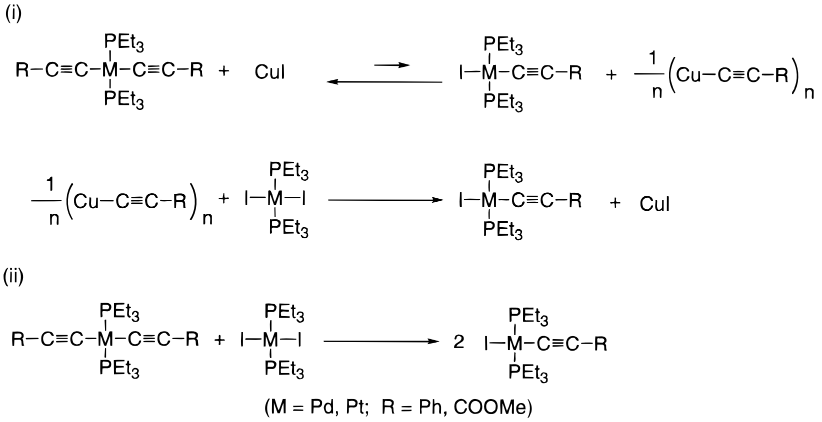
(15) Manna, J.; John, K. D.; Hopkins, M. D. *Adv. Organomet. Chem.* **1995**, *38*, 79, and references therein.

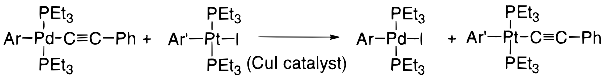
Scheme 1



The reaction of **1c** without the addition of CuI proceeds much faster than that of **1a**, which hardly reacts with *trans*-$PdI_2(PEt_3)_2$. Platinum complex **4c** reacts smoothly with *trans*-$PtI_2(PEt_3)_2$ in the presence of CuI, but the reaction of **4a** with *trans*-$PtI_2(PEt_3)_2$ does not occur under similar conditions.

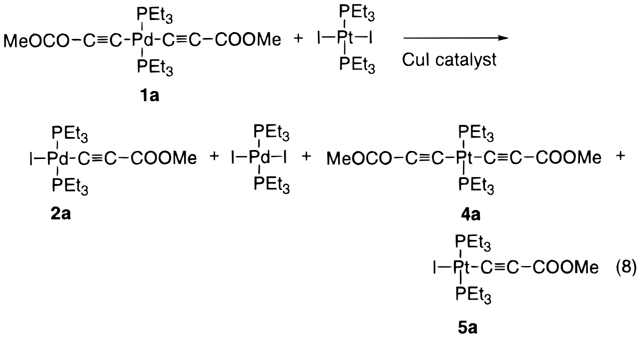
The remarkable effect of CuI catalyst in the enhancement of the reaction is ascribed to its smooth transport of the alkynyl ligand between group 10 metals. Reaction pathways of the alkynyl ligand transfer are shown in Scheme 1. The reaction in the presence of CuI probably involves an alkynylcopper(I) intermediate, as shown in (i) (Scheme 1). The initial alkynyl ligand transfer from the bis(alkynyl)palladium complex to Cu gives an alkynylcopper complex and MI(C≡CR)$(PEt_3)_2$-type complexes (M = Pd, Pt). The resulting alkynylcopper(I) complex easily reacts with diiodo complexes to afford another molecule of the iodo(alkynyl)palladium (or -platinum) complex. A higher stability of the alkynyl complexes of Ni, Pd, and Pt than the alkynylcopper complexes was suggested on the basis of the results of the reaction of alkynylcopper complexes with Pd and Pt complexes with halogeno ligands, producing alkynyl complexes of group 10 metals as well as structures of various multinuclear complexes with alkynyl groups π-bonded to Cu and σ-bonded to Pd and Pt.[16,17] Thus, the second step of (i) in Scheme 1 would proceed rapidly. On the other hand, alkynyl ligand transfer from Pd to Cu was recently reported in the reaction of aryl(phenylethynyl)palladium complexes with CuI in the absence or presence of PPh_3.[4] The alkynyl ligand transfer from Pd to Cu occurs at a high rate, although the equilibrium favors the formation of alkynylpalladium complexes. It was also found that the equilibrium is shifted by the addition of PPh_3 ligand, which alters the stability of the alkynylcopper bond by its ligation to the Cu center having a labile d^{10} configuration. Direct phenylethynyl ligand transfer between Pd complexes (ii) occurs much more slowly than the corresponding reaction involving the alkynylcopper intermediate.

Alkynyl Ligand Transfer of *trans*-Pd(C≡CCOOMe)$_2$(PEt$_3$)$_2$ to *trans*-PtI$_2$(PEt$_3$)$_2$. Previously, we reported the reaction of aryl(phenylethynyl)palladium complex with aryl(iodo)platinum complexes with PEt_3 ligands, resulting in the selective alkynyl group transfer from Pd to Pt, as shown in eq 7.[4] The alkynyl ligand transfer took place at 30−50 °C without catalyst to afford a quantitative amount of aryl(phenylethynyl)platinum complex. The addition of CuI catalyst enhanced the reaction, which is completed within 3 min at room temperature. The reaction appears to suggest facile transfer of the alkynyl ligand of the Pd complex and the thermodynamically much more stable Pt−alkynyl bond than the Pd−alkynyl bond in these aryl-coordinated complexes. Thus, we examined the reaction of dialkynylpalladium complexes with $PtI_2(PEt_3)_2$ with the expectation of smooth ligand transfer from Pd to Pt complexes, but instead obtained results different from those expected based on previous observations.

 (7)

$$\text{Ar}-\text{Pd}(\text{PEt}_3)_2-\text{C}\equiv\text{C}-\text{Ph} + \text{Ar}'-\text{Pt}(\text{PEt}_3)_2-\text{I} \xrightarrow[\text{(CuI catalyst)}]{} \text{Ar}-\text{Pd}(\text{PEt}_3)_2-\text{I} + \text{Ar}'-\text{Pt}(\text{PEt}_3)_2-\text{C}\equiv\text{C}-\text{Ph} \quad (7)$$

Complex **1a** reacts with equimolar *trans*-$PtI_2(PEt_3)_2$ in the presence of CuI at room temperature to give a mixture of Pd and Pt complexes, as shown in eq 8. The addition of CuI is essential for smooth alkynyl ligand transfer from **1a** to other complexes in the reaction mixture. Figure 4 depicts the $^{31}P\{^1H\}$ NMR spectra after the reaction for 10 and 235 min. At the beginning of the reaction, starting complexes **1a** and *trans*-PtI_2-



$$\text{MeOCO}-\text{C}\equiv\text{C}-\text{Pd}(\text{PEt}_3)_2-\text{C}\equiv\text{C}-\text{COOMe} + \text{I}-\text{Pt}(\text{PEt}_3)_2-\text{I} \xrightarrow{\text{CuI catalyst}} \text{I}-\text{Pd}(\text{PEt}_3)_2-\text{C}\equiv\text{C}-\text{COOMe} + \text{I}-\text{Pd}(\text{PEt}_3)_2-\text{I} + \text{MeOCO}-\text{C}\equiv\text{C}-\text{Pt}(\text{PEt}_3)_2-\text{C}\equiv\text{C}-\text{COOMe} + \text{I}-\text{Pt}(\text{PEt}_3)_2-\text{C}\equiv\text{C}-\text{COOMe} \quad (8)$$

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[16] (a) Yamazaki, S.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1993**, 3051. (b) Yamazaki, S.; Deeming, A. J.; Hursthouse, M. B.; Malik, K. M. A. *Inorg. Chim. Acta* **1995**, *235*, 147. (c) Tanaka, S.; Yoshida, T.; Adachi, T.; Yoshida, T.; Onitsuka, K.; Sonogashira, K. *Chem. Lett.* **1994**, 877.

[17] Similar Pt−Ag multinuclear complexes with bridigng alkynyl ligands: (a) Espinet, P.; Forniés, J.; Martinez, F.; Tomás, M.; Lalinde, E.; Teresa Morano, M.; Ruiz, A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1990**, 791. (b) Espinet, P.; Forniés, J.; Martínez, F.; Sotes, M.; Lalinde, E.; Teresa Moreno, M.; Ruiz, A.; Welch, A. J. *J. Organomet. Chem.* **1991**, *403*, 253. (c) Forniés, J.; Lalinde, E. *J. Chem. Soc., Dalton Trans.* **1996**, 2587. (d) Ara, I.; Berenguer, J.; Forniés, J.; Lalinde, E.; Moreno, M. T. *J. Organomet. Chem.* **1996**, *510*, 63.

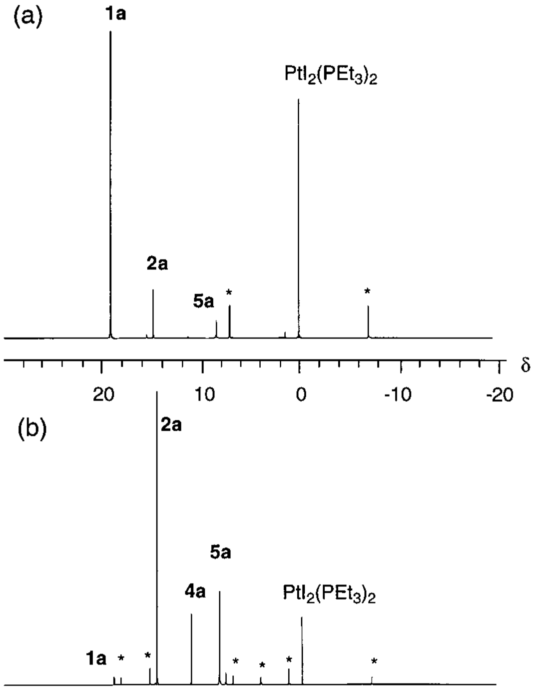


Figure 4. $^{31}P\{^1H\}$ NMR spectra of the reaction mixture of **1a** with $PtI_2(PEt_3)_2$ catalyzed by CuI in benzene-d_6 (a) after 10 min and (b) after 235 min. The peaks with asterisks are due to satellite signals of the PEt_3 ligand of the Pt complexes.

$(PEt_3)_2$ are present in considerable amounts (Figure 4a). After reaction for 4 h, Pd complex **2a** and Pt complexes **4a**, **5a**, and *trans*-$PtI_2(PEt_3)_2$ are present as the major complexes in the reaction mixture (Figure 4b). Figure 5 shows the plots of the time−yield curve of the reaction. Dialkynylpalladium complex **1a** decreases rapidly to about 5% of its original amount during the initial 3 h of the reaction. The amount of **2a** increases at a rate similar to the decrease of **1a**. After 3 h of reaction, the amount of **2a** does not vary further. The amounts of mono- and dialkynylplatinum complexes **4a** and **5a** also increase while keeping their relative approximate 2:1 ratio throughout the reaction. The final ratio of the dialkynyl-, iodo(alkynyl)-, and diiodoplatinum complexes is close to the statistical ratio of 1:2:1. The final ratio of the complexes **1a**, **2a**, *trans*-$PdI_2(PEt_3)_2$, *trans*-$PtI_2(PEt_3)_2$, **4a**, and **5a** is 2:43:5:11:25:14. Remarkably, iodo(alkynyl)palladium(II) complex **2a** exists as the main component among the Pd complexes and does not cause further alkynyl ligand transfer to *trans*-$PtI_2(PEt_3)_2$ or **5a**.

A similar reaction of **1c** with *trans*-$PtI_2(PEt_3)_2$ takes place in the presence of CuI catalyst to afford a mixture of Pd- and Pt-containing products, as shown in eq 9.

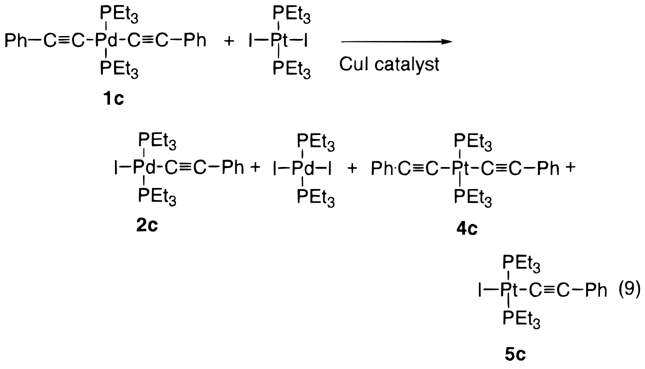


Figure 6 depicts the reaction profile, which is quite different from that of the reaction in eq 8. Consumption of the bis(phenylethynyl)palladium complex is completed within the initial 5 min of the reaction. The resulting iodo(alkynyl)palladium complex **2c** is formed immediately, but is gradually transformed into *trans*-$PdI_2(PEt_3)_2$ through alkynyl ligand transfer with Pt complexes. The reaction mixture after 6 h contains **2c** and *trans*-$PdI_2(PEt_3)_2$ in an approximate 15:85 molar ratio but no **1c**, while the final Pt-containing product is composed of **5c** and **4c** in an approximate 32:68 ratio. Most (>90%) of the phenylethynyl group contained in the initial **1c** is transferred to the Pt complexes by the reaction to afford a mixture of **4c** and **5c** as the Pt-containing species in the reaction mixture. This contrasts with the reaction 8, producing **2a**, which is inert to further alkynyl ligand transfer with iodoplatinum complexes. The consumption of **1c** and the increase in the amounts of palladium complexes **2c** and *trans*-$PdI_2(PEt_3)_2$ in reaction 9 are faster than the reaction of **1a** with *trans*-$PtI_2(PEt_3)_2$.

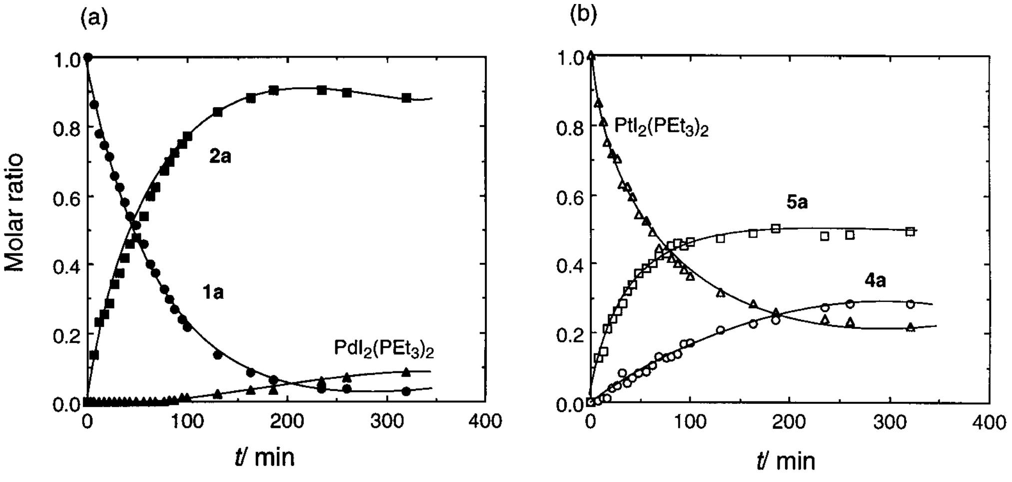


Figure 5. Time−yield curve of the reaction of **1a** with $PtI_2(PEt_3)_2$ catalyzed by CuI. Change in the amounts of (a) Pd complexes and (b) Pt complexes.

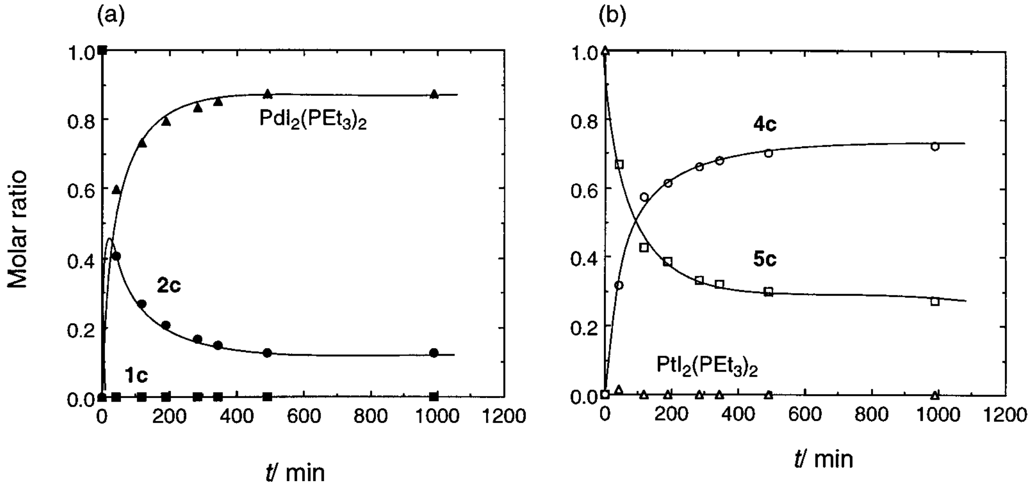
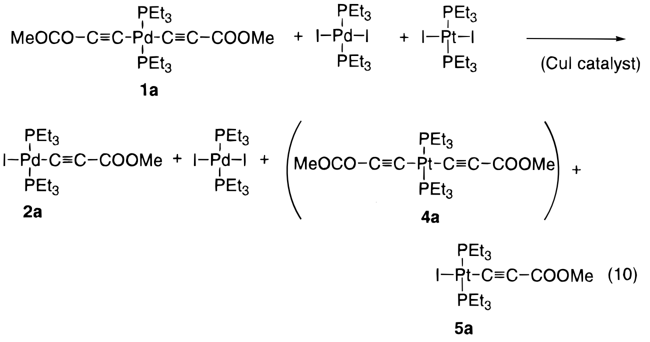


Figure 6. Time−yield curve of the reaction of **1c** with $PtI_2(PEt_3)_2$ catalyzed by CuI. Change in the amounts of (a) Pd complexes and (b) Pt complexes.

Reaction of 1a with a Mixture of *trans*-$PdI_2(PEt_3)_2$ and *trans*-$PtI_2(PEt_3)_2$ To Cause Alkynyl Ligand Transfer. The above reaction 8 suggests either higher thermodynamic stability of **2a** than the other Pd and Pt complexes in the reaction mixture or an inert Pd−C≡CCOOMe bond of the complex to prevent alkynyl ligand transfer to iodoplatinum complexes kinetically. To obtain a more detailed insight into the reactions, the reaction of **1a** with a mixture of *trans*-$PdI_2(PEt_3)_2$ and *trans*-$PtI_2(PEt_3)_2$ was conducted under similar conditions. Unexpected alkynyl ligand transfer reactions took place in the absence of CuI catalyst as described below.

A mixture of **1a**, *trans*-$PdI_2(PEt_3)_2$, and *trans*-$PtI_2(PEt_3)_2$ in a 1:1:1 molar ratio causes a gradual decrease in the amount of **1a** at room temperature accompanied by an increase in the amount of **2a** (eq 10). *trans*-$PtI_2(PEt_3)_2$ also decreases in amount but at a much slower rate. Only 2% of *trans*-$PtI_2(PEt_3)_2$ is transformed to **5a** after reaction for 26 h at room temperature. Yields of the complexes during the reaction are summarized in Table 3. The results clearly indicate that the alkynyl ligand transfer of **1a** to *trans*-$PdI_2(PEt_3)_2$ occurs preferentially in the presence of *trans*-$PtI_2(PEt_3)_2$, which does not react directly with **1a** under these conditions. Since reaction 5 (R = COOMe) does not proceed in the absence of CuI catalyst, the methoxycarbonylethynyl ligand transfer between the Pd complexes is attributed to catalysis by *trans*-$PtI_2(PEt_3)_2$. Actually, the reaction without a decreased amount of *trans*-$PtI_2(PEt_3)_2$ ([**1a**]:[*trans*-$PdI_2(PEt_3)_2$]:[*trans*-$PtI_2(PEt_3)_2$] = 1.0:1.0:0.1 at t = 0) occurs more slowly, as shown in Table 3, suggesting that the alkynyl ligand transfer reaction rate depends on the concentration of *trans*-$PtI_2(PEt_3)_2$.



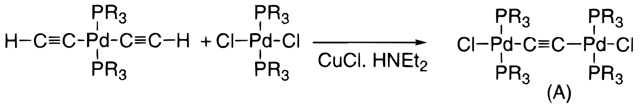
(10)

Table 3. Reaction of 1a and $PdI_2(PEt_3)_2$ in the Presence of $PtI_2(PEt_3)_2$

run	time (h)[a]	molar ratio of the complexes[b] 1a	2a	$PdI_2(PEt_3)_2$	4a	5a	$PtI_2(PEt_3)_2$
1	0	0.500	0.0	0.500	0.0	0.0	0.500
	2.5	0.419	0.098	0.454	0.0	0.0	0.500
	26	0.150	0.642	0.207	0.0	0.010	0.490
	(+ CuI)[c]	0.011	0.905	0.085[d]	0.0	0.189	0.312
2	0	0.500	0.0	0.500	0.0	0.0	0.050
	2	0.496	0.006	0.497	0.0	0.0	0.050
	20	0.464	0.073	0.463	0.0	0.0	0.050

[a] Reaction was carried out at 25 °C in benzene-d_6. [Cu]/[Pd] (or [Pt]) = approximately 0.01. [b] The relative signal intensity was calibrated by the comparison of the standard mixture of the complex with that of the ^1H NMR spectra. [c] The spectrum was obtained soon after addition of CuI catalyst. [d] Disagreement of the ratio of the Pd complexes is due to a somewhat disordered baseline of the spectrum preventing estimation of the precise peak area ratio.

Scheme 2

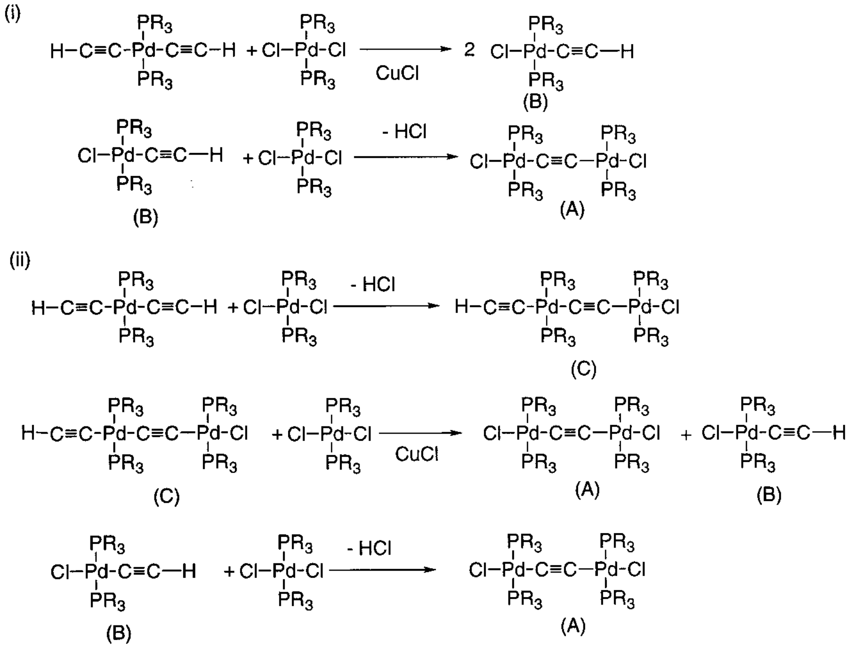


The addition of CuI to the above-mentioned reaction mixture (eq 10) causes a rapid decrease in the amount of the remaining **1a** to an almost negligible amount and the amount of the alkynyl transfer product containing the Pt metal center increases significantly. Thus, CuI facilitates the alkynyl ligand transfer from **1a** to both *trans*-$PdI_2(PEt_3)_2$ and *trans*-$PtI_2(PEt_3)_2$. Even in the presence of CuI catalyst, the alkynyl ligand transfer from **2a** to *trans*-$PtI_2(PEt_3)_2$ is slower than that to *trans*-$PdI_2(PEt_3)_2$. These results indicate that **2a** having I and C≡CCOOMe ligands at mutual trans positions is thermodynamically more stable than the *trans*-PtI(C≡CCOOMe)$(PEt_3)_2$ and the other complexes in the reaction mixture.

Discussion

Alkynyl complexes of transition metals have high thermodynamic stability among organotransition metal

Scheme 3



complexes[18] but often exhibit high chemical reactivity. The reactions of bis(alkynyl)palladium and -platinum complexes described above are influenced by the stability of the coordination bond which varies depending on the metal center and coexisting ligands.

Conproportionation of the dialkynyl and dihalo complexes of group 10 metals is related to the transformation of alkynylpalladium and alkynylplatinum complexes previously reported. Takahashi, Sonogashira, and their co-workers reported the reaction of *trans*-Pd($C{\equiv}CH)_2(PR_3)_2$ and *trans*-$PdCl_2(PR_3)_2$ in the presence of CuI and amines to produce a dinuclear Pd complex with a μ-ethynediyl ligand, $Cl{-}Pd(PR_3)_2{-}C{\equiv}C{-}PdCl(PR_3)_2$ (**A**), as shown in Scheme 2.[19] Complex **A** was regarded as an important intermediate in polymerization of the above two Pd complexes to afford Pd-containing polyyne polymers, $[Pd(PR_3)_2{-}C{\equiv}C{-}]_n$. Two reaction pathways can account for the formation of the dinuclear Pd complex. One of the pathways shown in Scheme 3(i) involves the initial disproportionation of the two starting complexes to afford **B**, which reacts further with *trans*-$PdCl_2(PR_3)_2$ to afford the dinuclear complex **A**. The other pathway (Scheme 3 (ii)) involves the initial condensation of the two starting complexes to produce the dinuclear complex **C**, which undergoes conproportionation-like transfer of the alkynyl and chloro ligands with *trans*-$PdCl_2(PR_3)_2$ to produce **A** and **C**. The resulting complex **C** reacts with *trans*-$PdCl_2(PR_3)_2$ to afford another molecule of **A**. Smooth intermolecular transfer of the alkynyl ligand in the above reaction is due to intermediate alkynylcopper complexes that activate the Pd−Cl bond to cause rapid and reversible alkynyl ligand transfer. Our results in the present study indicate that the reaction proceeds slowly in the absence of these additives and that CuI enhances the reaction significantly. The roles played by $HNEt_2$ used in the above reaction as well as in many other reactions of alkyne and aryl halides to form a C(sp)−C(sp^2) bond under these conditions are its coordination to the Cu center to stabilize alkynylcopper species and/or its facilitation of abstraction of acidic hydrogen of terminal alkyne. The conproportionation of dialkynylpalladium and diiodopalladium complexes appears to be thermodynamically favored in both phenylethynyl and methoxycarbonylethynyl complexes because reaction 5 with CuI catalyst produces **2a** and **2c** as the major products in equilibrium. The conproportionation of *trans*-$Pd(C{\equiv}CR)_2(PEt_3)_2$ with *trans*-$PdI_2(PEt_3)_2$ to produce *trans*-$PdI(C{\equiv}CR)(PEt_3)_2$ is enhanced by the remarkable stability of the Pd complexes with I and C≡CR ligands at the trans coordination sites.

Conversion of **1c** into **1a** in reaction 3 clearly indicates that the Pd−C≡CPh bond is less stable than the Pd−C≡CCOOMe bond. In agreement with these observations, the M−C≡CPh bond exhibits higher reactivity toward the alkynyl ligand transfer reaction than the M−C≡CCOOMe bond; the reactions of *trans*-$M(C{\equiv}CCOOMe)_2(PEt_3)_2$ with *trans*-$M'I_2(PEt_3)_2$ (M, M′ = Pd, Pt) are slower than the corresponding reactions of *trans*-Pd $(C{\equiv}CPh)_2(PEt_3)_2$ in all the combinations of metal centers M and M′. In particular, the *trans*-$PdI(C{\equiv}CCOOMe)(PEt_3)_2$ complex exhibits a strong coordination between the Pd center and the alkynyl ligand and hardly reacts with the *trans*-$PtI_2(PEt_3)_2$ under these conditions. The unique reactivity is probably due to kinetic factors because the addition of CuI enhances the reaction to afford some amount of **5a**. The remarkable thermodynamic stability of **2a** among the Pd and Pt complexes described in the present study can be ascribed to the balance between the electron-releasing iodo ligand and electron-withdrawing methoxycarbonylethynyl ligands at mutual trans positions. On the other

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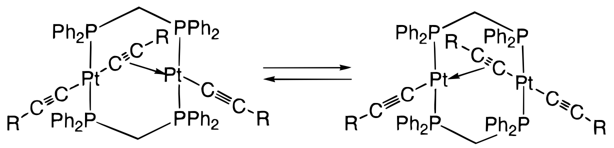
[18] (a) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444. See also: (b) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (c) Bruce, M. I. *J. Organomet. Chem.* **1990**, *400*, 321. (d) Doherty, S.; Corrigan, J. F.; Carty, J. A.; Sappa, E. *Adv. Organomet. Chem.* **1995**, *37*, 39.

[19] (a) Takahashi, S.; Ohyama, Y.; Murata, E.; Sonogashira, K.; Hagihara, N. *J. Polym. Sci.: Polym. Chem. Ed.* **1980**, *18*, 349. (b) Ogawa, H.; Joh, T.; Takahashi, S.; Sonogashira, K. *J. Chem. Soc., Chem. Commun.* **1985**, 1220. (c) Ogawa, H.; Onitsuka, K.; Joh, T.; Takahashi, S. *Organometallics* **1988**, *7*, 2257.

Scheme 4

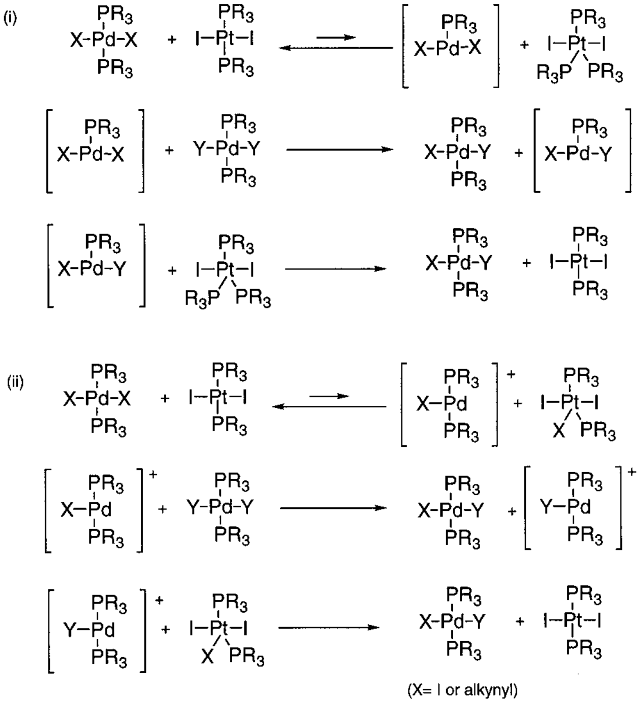


hand, the analogous Pt complex **5a** does not exhibit higher stability than the diiodo and dialkynyl complexes of Pt.

Reactivity of the alkynyl ligand of Pd and Pt complexes toward intermolecular transfer is influenced by coexisting ligands. The ligand transfer of aryl(phenylethynyl)palladium−PEt$_3$ complexes with aryl(iodo)palladium complexes occurs at −30 °C in the absence of CuI. The reaction with aryl(iodo)platinum complexes takes place above 30 °C without the addition of CuI and below room temperature with CuI catalyst. The reaction of bis(phenylethynyl)palladium complexes with *trans*-PdI$_2$(PEt$_3$)$_2$ occurs slowly in the absence of CuI catalyst, and that with *trans*-PtI$_2$(PEt$_3$)$_2$ requires a long time even in the presence of CuI. The electron-releasing aryl group activates the metal−alkynyl bond to weaken the coordination more significantly than the alkynyl ligands in the bis(alkynyl)palladium and platinum complexes. Another activation of the Pt−alkynyl bond was recently reported using diplatinate(II) intermediates. The platinate stabilized by electron-withdrawing aryl ligands such as C$_6$F$_5$ reacts with several transition metal complexes with the alkynyl ligand to cause switching of the alkynyl ligand between σ,π- and π,σ-modes.[20]

Rapid and reversible switching of the coordination of the alkynyl ligand between σ,π- and π,σ-modes was observed in many dinuclear transition metal complexes. A recent report on switching in an A-frame-type dinuclear Pt complex indicated the facile activation of the Pt−alkynyl σ-bond in the bimetallic framework (Scheme 4).[21] *trans*-PtI$_2$(PEt$_3$)$_2$ catalyzes the alkynyl ligand transfer between **1a** and *trans*-PdI$_2$(PEt$_3$)$_2$, producing **2a**, although the performance of the catalyst is lower than that of CuI. Scheme 5 depicts two possible pathways to account for the enhancement of alkynyl ligand transfer by the Pt complex. One involves abstraction of a PEt$_3$ ligand of the Pd complex promoted by *trans*-PtI$_2$(PEt$_3$)$_2$ to form unstable tricoordinated Pd species and PtI$_2$(PEt$_3$)$_3$. The resulting dialkynylpalladium(II) or diiodopalladium(II) complex with a tricoordinated structure would easily react with the four-coordinated Pd(II) complex to result in the intermolecular ligand transfer via an associative intermediate. Formation of tricoordinated complexes was proposed as an intermediate of various reactions of Pd(II) and Pt(II) complexes.[22] Another possible pathway involving abstraction of an iodo ligand of *trans*-PdI$_2$(PEt$_3$)$_2$ by *trans*-PtI$_2$(PEt$_3$)$_2$ leading to a cationic intermediate also accounts for the catalysis by the Pt complex.[23]

Scheme 5



Recently, transmetalation of the aryl complexes of late transition metals or the intermolecular aryl ligands of group 10 metal complexes has been reported using various aryl ligands and supporting neutral ligands. In general, the aryl−metal bond is thermodynamically less stable than the corresponding alkynyl−metal bond,[18] and several aryl−nickel and −palladium complexes have been reported to undergo intermolecular transfer of the aryl ligand.[24] The alkynyl transfer reactions in the previous and present studies appear to be kinetically facilitated because the bimetallic intermediate containing an unsymmetrically bridging alkynyl ligand undergoes rapid $\sigma-\pi$ structural change.

Conclusion

The Pd(II) and Pt(II) complexes with simple square-planar coordination exhibit a variety of ligand transfer reactions depending on the metal center, the substituent of the alkynyl ligand, and the catalyst added. Elucidation of the detailed mechanism and optimization of the reaction conditions are important because the alkynyl

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[20] (a) Berenguer, J. R.; Forniés, J.; Lalinde, E.; Martinez, F. *J. Chem. Soc., Chem. Commun.* **1995**, 1227. (b) Berenguer, J. R.; Forniés, J.; Lalinde, E.; Martínez, F. *Organometallics* **1996**, *15*, 4537. (c) Berenguer, J. R.; Forniés, J.; Lalinde, E.; Martínez, F.; Sánchez, L.; Serrano, B. *Organometallics* **1998**, *17*, 1640.

[21] Yam, V. W.-W.; Yeung, P. K.-Y.; Chan, L.-P.; Kwok, W.-M.; Phillips, D. L.; Yu, K.-L.; Wong, R. W.-K.; Yan, H.; Meng, Q.-J. *Organometallics* **1998**, *17*, 2590.

[22] (a) Ozawa, F.; Ito, T.; Yamamoto, A. *J. Am. Chem. Soc.*, **1980**, *102*, 6457. (b) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857. (c) Alibrandi, G.; Scolaro, L. M.; Romeo, R. *Inorg. Chem.* **1991**, *30*, 4007. (d) Minniti, D. *Inorg. Chem.* **1994**, *33*, 2631.

[23] The addition of PEt$_3$ ceased the alkynyl ligand transfer reaction in eq 10, while NaBF$_4$ enhanced the reaction extremely, giving the products within a few minutes. The results agree with both of the proposed pathways. The NMR measurement of an equimolar mixture of *trans*-PdI$_2$(PEt$_3$)$_3$ and *trans*-PtI$_2$(PEt$_3$)$_3$ exhibited broadened ^{31}P{^{1}H} NMR signals. The Pd and Pt complexes undergo ligand transfer, although the structure of the product is not clear.

[24] Intermolecular aryl ligand transfer of group 10 metal complexes: (a) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643. (b) Ozawa, F.; Kurihara, K.; Fujimori, M.; Hidaka, T.; Toyoshima, T.; Yamamoto, A. *Organometallics* **1989**, *8*, 180. (c) Ozawa, F.; Hidaka, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1987**, *330*, 253. (d) Yamamoto, T.; Wakabayashi, S.; Osakada, K. *J. Organomet. Chem.* **1992**, *428*, 223. (e) Osakada, K.; Sato, R.; Yamamoto, T. *Organometallics* **1994**, *13*, 4645. (f) Casado, A. L.; Casares, J. A.; Espinet, P. *Organometallics* **1997**, *16*, 5730. (g) Casado, A. L.; Espinet, P. *Organometallics* **1998**, *17*, 3677. (h) Casado, A. L.; Espinet, P. *J. Am. Chem. Soc.* **1998**, *120*, 8978.

ligand transfer reaction is involved in various synthetic organic reactions such as metal-catalyzed cross-coupling of alkynes and haloarenes and homocoupling of alkynes. Extension of study to many other transition metal complexes would serve to clarify the thermodynamics of the alkynyl complexes of transition metals and to determine new aspects of their chemical properties.

Experimental Section

General, Measurement, and Materials. Manipulations of the metal complexes were carried out under nitrogen or argon using standard Schlenk techniques. NMR spectra (^{1}H, ^{13}C, and ^{31}P) were recorded on a JEOL EX-400 spectrometer. ^{31}P{^{1}H} NMR peak positions were referenced to external 85% H_3PO_4. Elemental analyses were carried out by Yanaco type MT-5 CHN autocorder.

Preparation of *trans*-Pd(C≡CCOOMe)$_2$(PEt$_3$)$_2$ (1a) and *trans*-Pd(C≡CCOOEt)$_2$(PEt$_3$)$_2$ (1b). To $PdCl_2(PEt_3)_2$ (434 mg, 1.1 mmol) dispersed in NEt_3 (20 mL) were added HC≡CCOOMe (178 mg, 2.1 mmol) and CuI (10 mg, 5.3 μmol) together at room temperature. The initial yellow solution became colorless and was accompanied by the formation of a colorless solid on stirring at room temperature. The solid was separated by filtration. The solvent was evaporated to dryness, and the resulting solid was extracted with hexane several times. Recrystallization of the extract from Et_2O yielded *trans*-Pd(C≡CCOOMe)$_2$(PEt$_3$)$_2$ (**1a**) as colorless crystals (489 mg, 92%). ^{1}H NMR (benzene-d_6): δ 0.94 (m, 18H, P(CH$_2$C*H*$_3$)$_3$), 1.74 (m, 12H, P(C*H*$_2$CH$_3$)$_3$), 3.43 (s, 6H, OCH$_3$). ^{31}P{^{1}H} NMR (benzene-d_6): δ 18.9 (s). ^{13}C{^{1}H} NMR (benzene-d_6): δ 154.5 (CO), 116.2 (t, Pd−C, J(PC) = 17 Hz), 104.4 (PdC≡*C*), 51.1 (OCH$_3$), 17.1 (apparent triplet due to virtual coupling, P(*C*H$_2$CH$_3$)$_3$, 14 Hz), 8.5 (s, P(CH$_2$*C*H$_3$)$_3$). Anal. Calcd for $C_{20}H_{36}O_4P_2Pd$: C, 47.20; H, 7.13. Found: C, 46.96; H, 6.85.

trans-Pd(C≡CCOOEt)$_2$(PEt$_3$)$_2$ (**1b**) was prepared analogously. ^{1}H NMR (benzene-d_6): δ 0.96 (m, 24H, P(CH$_2$C*H*$_3$)$_3$ and OCH$_2$C*H*$_3$), 1.75 (m, 12H, P(C*H*$_2$CH$_3$)$_3$), 4.04 (dd, 4H, OCH$_2$, J = 7 Hz). ^{31}P{^{1}H} NMR (benzene-d_6): δ 18.6 (s). ^{13}C{^{1}H} NMR (benzene-d_6): δ 154.2 (CO), 115.8 (t, Pd−C, J(PC) = 17 Hz), 104.8 (PdC≡*C*), 60.3 (OCH$_2$), 17.2 (apparent triplet due to virtual coupling, P(*C*H$_2$CH$_3$)$_3$, 15 Hz), 14.3 (OCH$_2$CH$_3$), 8.5 (s, P(CH$_2$*C*H$_3$)$_3$). Anal. Calcd for $C_{22}H_{40}O_4P_2Pd$: C, 49.21; H, 7.51. Found: C, 49.46; H, 7.62.

Equiomolar Reaction of *trans*-PdI$_2$(PEt$_3$)$_2$ with HC≡CCOOMe. To $PdI_2(PEt_3)_2$ (220 mg, 0.37 mmol) dispersed in a mixture of NEt_3 (3 mL) and THF (12 mL) were added HC≡CCOOMe (31 mg, 0.37 mmol) and CuI (1 mg, 0.53 μmol) together at room temperature. A colorless solid was formed from the yellow solution on stirring at room temperature. The solid was separated out by filtration. The product obtained after evaporation of most of the solvents exhibits NMR signals due to **1a** and **2a** in an approximate 1:5 molar ratio. Removal of the NEt_3 in high vacuum caused the deposition of Pd metal and prevented the isolation of **2a** from the reaction mixture. ^{1}H NMR data of **2a** (benzene-d_6): δ 0.93 (m, 18H, P(CH$_2$C*H*$_3$)$_3$), 1.91 (m, 12H, P(C*H*$_2$CH$_3$)$_3$), 3.42 (s, 3H, OCH$_3$). ^{31}P{^{1}H} NMR (benzene-d_6): δ 14.6 (s).

Reaction of 1c with HC≡CCOOMe. To an NMR sample tube was charged a benzene-d_6 (0.5 mL) solution of **1c** (11 mg, 0.020 mmol) under nitrogen. After capping the tube by a rubber septum, HC≡CCOOMe (3.3 mg, 0.039 mmol) was added to the solution by a syringe through the septum. The ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded periodically. After the reaction for 5.5 h, the ^{31}P{^{1}H} NMR spectrum showed the signals due to **3** (δ 18.4) and **1c** in an approximate 8:1 peak area ratio. After the reaction for 5 days, the ^{31}P{^{1}H} NMR spectrum contained the signals of **1a**, **3**, and **1c** in approximate 7:3:0.3 ratio. The ^{1}H NMR signals of **3** observed in the mixture after the reaction for 5 days show a reasonable peak area ratio with that obtained from the ^{31}P{^{1}H} NMR spectrum. The signals of **3** were as follows. ^{1}H NMR (benzene-d_6): δ 1.02 (m, 18H, P(CH$_2$C*H*$_3$)$_3$), 1.80 (m, 12H, P(C*H*$_2$CH$_3$)$_3$), 3.48 (s, 3H, OCH$_3$), 7.06 (t, 1H, *para*), 7.52 (d, 2H, *ortho*); meta hydrogens were overlapped with those of other products.

Preparation of *trans*-Pt(C≡CCOOMe)$_2$(PEt$_3$)$_2$ (4a) and *trans*-Pt(C≡CCOOEt)$_2$(PEt$_3$)$_2$ (4b). To $PtI_2(PEt_3)_2$ (462 mg, 0.56 mmol) dispersed in NEt_3 (15 mL) were added HC≡CCOOEt (130 mg, 1.3 mmol) and CuI (approximately 0.1 mg) together at room temperature. The mixture was stirred for 2 h at room temperature, resulting in precipitation of a colorless solid. The solid was removed by filtration. The solvent was evaporated to dryness, and the resulting solid was extracted with hexane several times. Recrystallization of the extract from Et_2O yielded *trans*-Pt(C≡CCOOMe)$_2$(PEt$_3$)$_2$ (**4a**) as colorless crystals (243 mg, 60%). ^{1}H NMR (benzene-d_6) δ 0.91 (m, 18H, P(CH$_2$C*H*$_3$)$_3$), 1.86 (m, 12H, P(C*H*$_2$CH$_3$)$_3$), 3.44 (m, 4H, OCH$_3$). ^{31}P{^{1}H} NMR (benzene-d_6): δ 11.2 (s, J(PPt) = 2277 Hz). ^{13}C{^{1}H} NMR (benzene-d_6): δ 155.1 (CO), 111.9 (t, Pt−C, J(PtC) = 976 Hz, J(PC) = 15 Hz), 103.2 (PtC≡*C*, J(PtC) = 275 Hz), 51.1 (OCH$_3$), 16.5 (apparent triplet due to virtual coupling, P(*C*H$_2$CH$_3$)$_3$, J(PtC) = 37 Hz, 17 Hz), 8.3 (s, P(CH$_2$*C*H$_3$)$_3$). Anal. Calcd for $C_{20}H_{36}O_4P_2Pt$: C, 40.20; H, 6.10. Found: C, 39.96; H, 5.88.

Complex **4b** was obtained analogously (322 mg, 91%). ^{1}H NMR (benzene-d_6): δ 0.92 (m, 18H, P(CH$_2$C*H*$_3$)$_3$), 1.00 (m, 6H, OCH$_2$C*H*$_3$), 1.87 (m, 12H, P(C*H*$_2$CH$_3$)$_3$), 4.07 (m, 4H, OC*H*$_2$-CH$_3$). ^{31}P{^{1}H} NMR (benzene-d_6): δ 11.2 (s J(PtP) = 2285 Hz). ^{13}C{^{1}H} NMR (benzene-d_6): δ 154.8 (CO), 111.5 (t, Pt−C, J(PtC) = 989 Hz, J(PC) = 13 Hz), 103.7 (PtC≡C, J(PtC) = 278 Hz), 60.2 (OCH$_2$), 16.5 (apparent triplet due to virtual coupling, P(*C*H$_2$CH$_3$)$_3$, J(PtC) = 37 Hz, 17 Hz), 14.4 (OCH$_2$*C*H$_3$), 8.3 (s, P(CH$_2$*C*H$_3$)$_3$). Anal. Calcd for $C_{22}H_{40}O_4P_2Pt$: C, 42.23; H, 6.44. Found: C, 41.91; H, 6.22.

Reactions of the Complexes. Complexes **1a** and **1c** used in the reactions with diiodo complexes of Pd and Pt were purified by repeated recrystallization and their purities confirmed. Time−yield curves of the Pd complexes before and after final recrystallization did not show any difference, indicating that CuI is not contaminated in the Pd complexes.

Reaction of 1a and of 1c with *trans*- PdI$_2$(PEt$_3$)$_2$. Complexes **1a** (19.3 mg, 0.038 mmol), *trans*-PdI$_2$(PEt$_3$)$_2$ (22.6 mg, 0.038 mmol), and CuI (0.1 mg, 0.53 μmol) were charged to an NMR sample tube. After addition of benzene-d_6 (0.5 mL) to the mixture, the tube was capped with a rubber septum under argon. The Pd complexes were soon dissolved, while a part of CuI remained undissolved. The ^{31}P{^{1}H} NMR spectra were recorded at 25 °C periodically, and the ^{1}H NMR spectra were checked occasionally.

Reactions of 1a and of 1c with *trans*-PtI$_2$(PEt$_3$)$_2$. Complexes **1a** (33.0 mg, 0.065 mmol), *trans*-PtI$_2$(PEt$_3$)$_2$ (42.7 mg, 0.062 mmol), and CuI (0.1 mg, 0.53 μmol) were charged to an NMR sample tube. After addition of benzene-d_6 (0.5 mL) to the mixture, the tube was capped with a rubber septum under argon. The ^{31}P{^{1}H} NMR spectra were recorded at 25 °C periodically, and the ^{1}H NMR spectra were checked occasionally.

Reactions of 1a with PdI$_2$(PEt$_3$)$_2$ in the Presence of *trans*-PtI$_2$(PEt$_3$)$_2$. Complexes **1a** (9.2 mg, 0.018 mmol), *trans*-PdI$_2$(PEt$_3$)$_2$ (10.9 mg, 0.018 mmol), and *trans*-PtI$_2$(PEt$_3$)$_2$ (12.4 mg, 0.018 mmol) were charged to an NMR sample tube. After addition of benzene-d_6 (0.5 mL) to the mixture, the tube was capped with a rubber septum under argon. The complexes were dissolved immediately. The ^{31}P{^{1}H} NMR spectra were recorded at 25 °C periodically, and the ^{1}H NMR spectra were checked occasionally.

Crystal Structure Determination. Crystals of **1a**, **1c**, and **4b** suitable for crystallography were obtained by recrystallization from hexane. Crystals were mounted in glass capillary tubes under argon. The unit cell parameters were obtained by least-squares refinement of 2θ values of 20 reflections with

Table 4. Data and Details of Structure Refinement

	1a	**1c**	**4b**
formula	$C_{20}H_{36}O_4P_2Pd$	$C_{28}H_{40}P_2Pd$	$C_{22}H_{40}O_4P_2Pt$
molecular wt	508.84	544.98	625.59
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	9.085(2)	9.179(2)	9.323(1)
b (Å)	10.665(2)	10.963(2)	11.125(2)
c (Å)	7.028(2)	14.844(3)	7.498(2)
α (deg)	98.52(2)		104.36(1)
β (deg)	102.77(2)	105.14(2)	98.08(2)
γ (deg)	106.72(2)		111.75(1)
V (Å^3)	619.5	1442	676.0
Z	1	2	1
μ (mm^{-1})	0.898	0.767	5.380
F(000)	264	568	312
D_{calcd} (g cm^{-3})	1.364	1.255	1.537
cryst size (mm)	0.4 × 0.5 × 0.5	0.4× 0.5 × 0.6	0.2× 0.3 × 0.3
2θ range (deg)	5.0−55.0	5.0−45.0	5.0−55.0
no. of unique reflns	2838	1760	2546
no. of reflns used	2357	1099	2387
no. of variables	124	142	214
R (R_w)[a]	0.034 (0.036)	0.043 (0.032)	0.020 (0.023)
GOF	0.89	2.44	1.29
weighting scheme	$[\sigma(F_o)^2]^{-1}$	$[\sigma(F_o)^2]^{-1}$	$[\sigma(F_o)^2]^{-1}$

20° ≤ 2θ ≤ 22°. Intensities were collected on a Rigaku AFC-5R automated four-cycle diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) and the $\omega-2\theta$ method. An empirical absorption correction (ψ scan method) of the collected data was applied. Table 4 summarizes crystal data and details of data refinement.

Calculations were carried out by using the program package teXsan on a VAX-II computer. Atomic scattering factors were taken from the literature.[25] A full-matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms were located by assuming ideal positions and were included in the structure calculation without further refinement of the parameters.

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Supporting Information Available: Crystallographic data of complexes **1a**, **1c**, and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.