Preparation and Properties of *trans*-Pd(Ar)(C≡CPh)(PEt_3)$_2$. Intermolecular Alkynyl Ligand Transfer between Copper(I) and Palladium(II) Complexes Relevant to Palladium Complex Catalyzed Cross-Coupling of Terminal Alkyne with Haloarene in the Presence of CuI Cocatalyst

Kohtaro Osakada,* Reiko Sakata, and Takakazu Yamamoto*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

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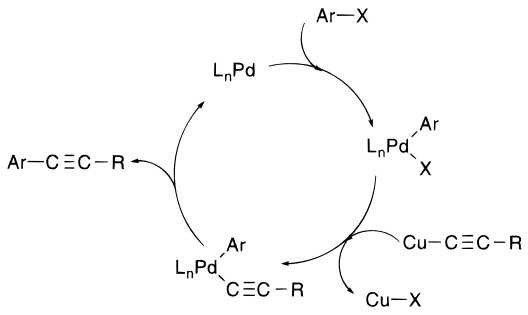
trans-Pd(C_6H_4Me-*p*)(I)(PEt_3)$_2$ (**2a**) reacts with [Cu(C≡CPh)(PPh_3)]$_4$ (Pd:Cu = 1:1) at room temperature to give the cross-coupling product PhC≡CC_6H_4Me-*p* (**3a**) in 74% yield. Reactions of **2a** with [Cu(C≡CPh)(PPh_3)]$_4$ at −30 °C as well as of *trans*-Pd(C_6H_4X-*p*)(I)(PEt_3)$_2$ (**2a**, X = Me; **2b**, X = OMe; **2c**, X = F) with the alkynylcopper complex and additional PPh_3 (2 mol/mol of Cu) at room temperature give mixtures of PhC≡CC_6H_4X-*p* (**3a**, X = Me; **3b**, X = OMe; **3c**, X = F) and *trans*-Pd(C_6H_4X-*p*)(C≡CPh)(PEt_3)$_2$ (**4a**, X = Me; **4b**, X = OMe; **4c**, X = F). Complexes **4a**,**b** have been isolated from the latter reaction mixtures and fully characterized. Pd−C(alkynyl) and Pd−C(aryl) bond distances in **4a** are 2.016(8) and 2.062(7) Å, respectively. Addition of CuI to a solution of **4a** at room temperature causes complete conversion of **4a** into **2a** and **3a** in 1 h. The relative molar ratio between **2a** and **4a** after reaction for 2 h varies, depending on the amount of added PPh_3. Reactions of *trans*-Pt(C_6H_4X-*p*)(I)(PEt_3)$_2$ (**5b**, X = OMe; **5c**, X = F) with [Cu(C≡CPh)(PPh_3)]$_4$ at room temperature afford *trans*-Pt(C_6H_4X-*p*)(C≡CPh)(PEt_3)$_2$ (**6b**, X = OMe; **6c**, X = F), respectively. Heating an equimolar mixture of **4a** and **5b** at 35−50 °C leads to inter-metal exchange of the alkynyl and iodo ligands, giving **2a** and **6b** quantitatively. The reaction follows the kinetics that is first order in concentration of **4a** and in that of **5b**. The kinetic parameters are obtained as $\Delta H^{\ddagger}$ = 110 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −58 J mol^{-1} deg^{-1}, and $\Delta G^{\ddagger}$ = 127 kJ mol^{-1} at 298 K. The alkynyl ligand migration from Pd(II) to Pt(II) is enhanced by addition of a catalytic amount of CuI.

Introduction

Palladium complex catalyzed cross-coupling of a terminal alkyne with bromoarene or with bromoalkene gives arylacetylene or enynes selectively under mild conditions and has been applied to the synthesis of various organic molecules as well as π-conjugated polymers.[1−3] Scheme 1 depicts a possible mechanism of the reaction. According to the pathway, Cu(C≡CR), generated in situ from a mixture of CuI, terminal alkyne, and amine, undergoes alkynyl ligand transfer to Pd(Ar)(X)(L)$_n$ (X = halide), giving Pd(Ar)(C≡CR)(L)$_n$, which is responsible for reductive elimination of the coupling product.[2a]

Scheme 1. Possible Mechanism of the Cross-Coupling of 1-Alkyne and Aryl Halide



Although the Pd complex bearing both aryl and alkynyl ligands is believed to play an important role in

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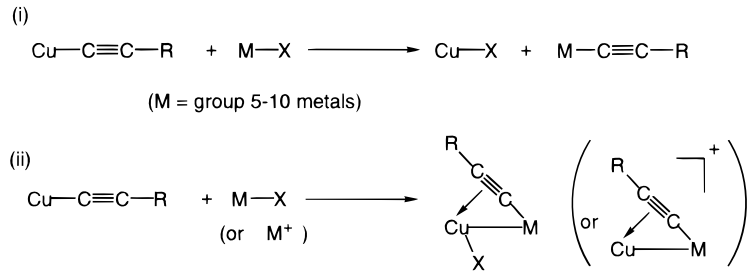
Scheme 2



the above catalytic reaction, there have been only a few reports on Pd(Ar)(C≡CR)(L)$_n$ type complexes with a highly electron withdrawing Ar group (C_6F_5).[4]

On the other hand, alkynylcopper compounds, [Cu(C≡CR)]$_n$, isolated or generated *in situ* from the reaction of CuI, base, and alkyne, have been reported to react readily with group 5−10 transition-metal complexes to give σ-alkynyl complexes of these metals (Scheme 2(i))[5−8] or bimetallic complexes containing an alkynyl ligand that is π-bonded to the Cu(I) center and σ-bonded to other transition metals such as Re, Fe, Ru, Ir, and Pt (Scheme 2(ii)).[9−14] The intermolecular transfer of the alkynyl ligand from Cu(I) to Pd(II) and to Pt(II) in the former reactions is utilized for synthesis of alkynyl complexes (e.g., Pd(C≡CR)$_2$L$_n$) of group 10 metals. Similar alkynyl ligand transfer from an alkynylcopper(I) complex to arylpalladium halide complexes would give Pd(Ar)(C≡CR)L$_n$ type complexes, whose chemical properties are of interest with regard to the mechanism of the above cross-coupling reaction.

In this paper, we report the preparation of *trans*-PdAr(C≡CPh)(PEt_3)$_2$ complexes *via* such alkynyl ligand transfer from an alkynylcopper(I) complex to PdAr(I)L$_n$ type complexes. The isolated *trans*-PdAr(C≡CPh)(PEt_3)$_2$ complexes show interesting reactivity. For example, they react with CuI to cause a reverse type of alkynyl ligand transfer from Pd(II) to Cu(I) as well as liberation of ArC≡CPh as the coupling product. Similar alkynyl ligand transfer also takes place from Pd(II) to Pt(II), and such chemical reactivity of the *trans*-PdAr(C≡CPh)(PEt_3)$_2$ type complexes will be presented in this paper. Part of this work has been reported in a preliminary form.[15]

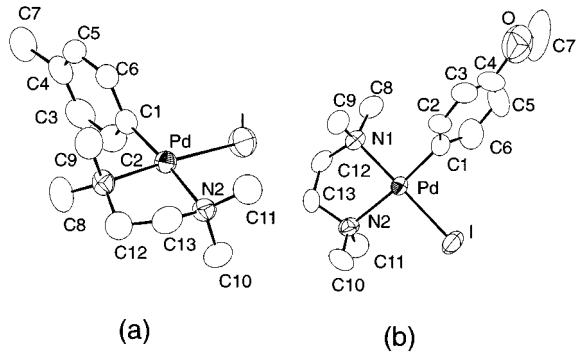


Figure 1. ORTEP drawings of (a) Pd(C_6H_4Me-*p*)(I)(tmeda) (**1a**) at the 50% ellipsoid level and (b) Pd(C_6H_4OMe-*p*)(I)(tmeda) (**1b**) at the 30% ellipsoid level.

Results

Preparation and Characterization of *trans*-Pd(C_6H_4X-*p*)(I)(PR_3)$_2$ (X = Me, OMe, F; R = Et, Me, Ph). Organopalladium complexes with a tmeda (*N*,*N*,*N*′*N*′-tetramethylethylenediamine) ligand serve as convenient precursors of the complexes with phosphine ligands because their labile Pd−N bonds undergo facile substitution by the more π-acidic P ligands.[16] Pd(C_6H_4X-*p*)(I)(tmeda) (**1a**, X = Me; **1b**, X = OMe; **1c**, X = F) have been prepared according to a procedure already reported and characterized by NMR spectra as well as X-ray crystallography. Figure 1 shows the molecular structures of **1a** and **1b** to have a slightly distorted square planar coordination around the Pd center. Selected bond distances and angles are summarized in Table 1. The difference between the two Pd−N bond distances in each molecule (Pd−N1 = 2.143(5) Å and Pd−N2 = 2.203(5) Å in **1a** and Pd−N1 = 2.130(7) Å and Pd−N2

(4) Preparation and characterization of *trans*- and *cis*-Pd(C_6F_5)(C≡CR)(PR_3)$_2$ have been reported. Even the cis complexes do not undergo coupling of the alkynyl and aryl ligands, probably due to the very stable Pd−C_6F_5 bond. See: Espinet, P.; Forniés, J.; Martínez, F.; Sotes, M.; Lalinde, E.; Moreno, M. T.; Ruiz, A.; Welch, A. J. *J. Organomet. Chem.* **1991**, *403*, 253.

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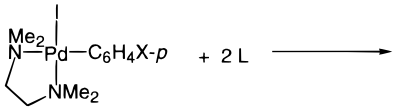
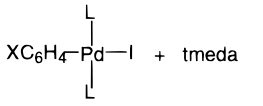
Table 1. Selected Bond Distances (Å) and Angles (deg) of 1a,b, 4a, and 6c

	1a	1b	4a	6c
Pd−I	2.584(3)	2.596(5)		
Pd−C1	1.988(6)	1.956(9)	2.016(8)	1.99(1) (Pt−C1)
C1−C2			1.196(9)	1.21(1) (C1−C2)
Pd−C9			2.062(7)	2.02(1) (Pt−C9)
Pd−N1	2.143(5)	2.130(7)		
Pd−N2	2.203(5)	2.195(7)		
Pd−P1			2.300(2)	2.313(3) (Pt−P1)
Pd−P2			2.292(2)	2.282(3) (Pt−P2)
I−Pd−C1	89.1(2)	89.8(2)		
I−Pd−N1	176.8(1)	177.2(2)		
I−Pd−N2	95.1(1)	95.3(2)		
C1−Pd−N1	92.2(2)	91.6(3)		
C1−Pd−N2	175.4(2)	174.8(3)		
N1−Pd−N2	83.4(2)	83.3(3)		
C1−Pd−P1			87.4(2)	86.2(3) (C1−Pt−P1)
C1−Pd−P2			92.3(2)	91.5(3) (C1−Pt−P2)
C9−Pd−P1			91.2(2)	91.2(3) (C9−Pt−P1)
C9−Pd−P2			89.1(2)	90.5(3) (C9−Pt−P2)
C1−Pd−C9			176.7(3)	172.7(7) (C1−Pt−C9)
P1−Pd−P2			176.81(8)	174.8(1) (P1−Pt−P2)
Pd−C1−C2			174.6(7)	175(1) (Pt−C1−C2)
C1−C2−C3			179.0(7)	176(1) (C1−C2−C3)

= 2.195(7) Å in **1b**) is ascribed to a larger trans influence of the aryl than of the iodo ligand. Complexes **1a**−**c** readily react with 2 equiv of PEt_3 to give the corresponding aryliodopalladium complexes *trans*-Pd(C_6H_4X-*p*)(I)(PEt_3)$_2$ (**2a**, X = Me; **2b**, X = OMe; **2c**, X = F), as shown in eq 1. Similar reactions of **1a** with PMe_3 and



1a: X = Me;
1b: X = OMe;
1c: X = F



(1)

2a: X = Me, L = PEt_3;
2b: X = OMe, L = PEt_3;
2c: X = F, L = PEt_3;
2d: X = Me, L = PMe_3;
2e: X = Me, L = PPh_3.

with PPh_3 give *trans*-Pd(C_6H_4Me-*p*)(I)(PR_3)$_2$ (**2d**, R = Me; **2e**, R = Ph). The NMR spectra of the complexes are consistent with the trans structure.

Reaction of 2a−c with [Cu(C≡CPh)(PPh_3)]$_4$ To Cause Alkynyl Ligand Transfer. Table 2 summarizes the results of the reactions of **2a**−**c** with the alkynylcopper(I) complex causing alkynyl ligand transfer from Cu to Pd and/or coupling of the alkynyl and aryl groups depending on the conditions. Complex **2a** reacts with [Cu(C≡CPh)(PPh_3)]$_4$ (Pd:Cu = 1:1) at room temperature to give the coupling product PhC≡CC_6H_4-Me-*p* (**3a**; 74%). The NMR spectrum of the reaction mixture showed the presence of starting complex **2a** (26%) also. Although Cu-containing products in this reaction have not been fully characterized, [Cu(C≡CPh)-(PPh_3)]$_4$ seems to be converted to the corresponding iodocopper complexes during the reaction. A 1:2 reaction of the complexes causes complete conversion of **2a** to **3a**. Reaction of **2a** with [Cu(C≡CPh)(PPh_3)]$_4$ (Pd:Cu = 1:1) at −30 °C does not give the coupling product **3a** but gives a mixture of *trans*-Pd(C_6H_4Me-*p*)(C≡CPh)(PEt_3)$_2$ (**4a**) (65%) and **2a** (35%).

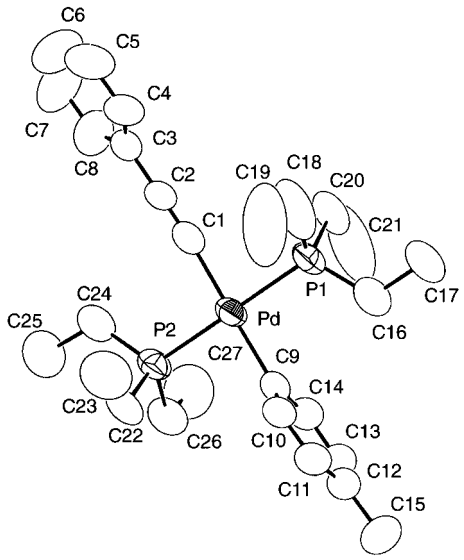
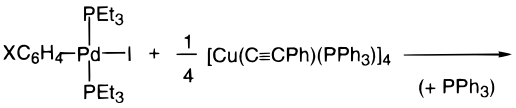
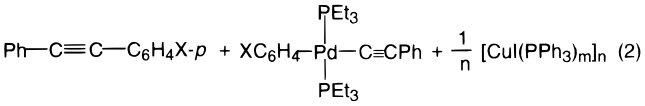


Figure 2. ORTEP drawing of *trans*-Pd(C_6H_4Me-*p*)(C≡C-Ph)(PEt_3)$_2$ (**4a**) at the 30% ellipsoid level.



2a: X = Me
2b: X = OMe
2c: X = F



3a: X = Me
3b: X = OMe
3c: X = F

4a: X = Me
4b: X = OMe
4c: X = F

Addition of PPh_3 ligand to the reaction mixture of **2a** and [Cu(C≡CPh)(PPh_3)]$_4$ at room temperature makes isolation of the inorganic products possible, as shown below. The hexane-insoluble fraction of the product is a mixture of PPh_3-coordinated Cu complexes from which CuI(PPh_3)$_3$ is isolated in 51% yield. The hexane extract from the reaction mixture contains **2a** (21%), **3a** (36%), and **4a** (42%), as revealed by the ^{1}H NMR spectrum. Aryl(alkynyl)palladium complex **4a** is isolated as colorless crystals by repeated recrystallization of the hexane-soluble fraction of the product from acetone. The low isolated yield (3%) is mainly due to the solubility of the complex being similar to that of **2a**. Figure 2 shows the molecular structure of **4a**, as determined by X-ray crystallography. The molecule has a trans configuration around the Pd center. The fact that the Pd−C(alkynyl) bond (2.016(8) Å) is shorter than the Pd−C(aryl) bond (2.062(7) Å), despite a larger trans influence for aryl over alkynyl ligands,[17] is due to the partial contribution of a vinylidene structure (Pd$^-$=C=C$^+$−Ph) in the coordination of the phenylethynyl group to the Pd center.[18] The ^{13}C{^{1}H} NMR spectrum shows signals due to α- and *β*-alkynyl carbons at *δ* 119.8 and 111.3 as a triplet

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Table 2. Reaction of 2a−c with [Cu(C≡CPh)(PPh$_3$)]$_4$

	reacn conditions[a]				products (yield %)[b,c]		
					Pd complex		
run no.	Pd complex	additive[d]	temp/°C	time/min			PhC≡CC$_6$H$_4$X-*p*
1	**2a**		room temp	60	**2a** (26)		**3a** (74)
2[e]	**2a**		room temp	60			**3a** (100)
3	**2a**		−30 °C	20	**2a** (35)	**4a** (65)	
4	**2a**	PPh$_3$	room temp	210	**2a** (21)	**4a** (42)	**3a** (36)
5	**2b**	PPh$_3$	room temp	60	**2b** (41)	**4b** (42)	**3b** (17)
6	**2c**	PPh$_3$	room temp	60	**2c** (23)	**4c** (64)	**3c** (13)[f]
7	**2d**		room temp	240	**2d** (46)		**3a** (54)
8	**2e**		−30 °C	60			**3a** (>95)
9	**1a**		room temp	20			**3a** (78)

[a] Reactions were performed in toluene, except for runs 3 and 8, which were carried out in CH_2Cl_2. [b] Yields by NMR. [c] CuI(PPh$_3$)$_3$ was isolated in 45% (run 4) and 49% (run 5) yields. [d] [PPh$_3$]/[Pd] = 2.0. [e] Pd/Cu ratio is 1:2. [f] Formation of **2c**, **3c**, and **4c** was confirmed by the ^{1}H NMR spectrum of the reaction mixture, but separation of the products was not plausible.

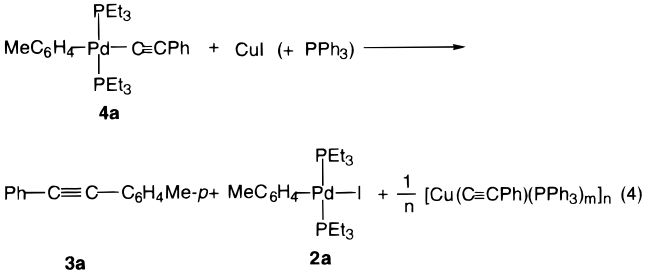
(J(CP) = 20 Hz) and a singlet, respectively. A similar reaction of **2b** with [Cu(C≡CPh)(PPh$_3$)]$_4$ in the presence of PPh$_3$ gives a mixture of **2b**, PhC≡CC$_6$H$_4$OMe-*p* (**3b**), and *trans*-Pd(C$_6$H$_4$OMe-*p*)(C≡CPh)(PEt$_3$)$_2$ (**4b**), in a ratio of 41:17:42. Complex **4b** is isolated from the reaction mixture by fractional recrystallization and has been characterized by NMR spectroscopy.[19] The reaction mixture of **2c** and [Cu(C≡CPh)(PPh$_3$)]$_4$ in the presence of PPh$_3$ also contains **2c**, **3c**, and *trans*-Pd(C$_6$H$_4$F-*p*)(C≡CPh)(PEt$_3$)$_2$ (**4c**) in a ratio of 23:13:64, although isolation of **4c** from the mixture has not been successful. Complexes **4a** and **4b**, once isolated, are stable and do not undergo reductive elimination of **3a** and **3b** in the solution at room temperature.

NMR measurement of the reaction mixture of **2a** and [Cu(C≡CPh)(PPh$_3$)]$_4$ at low temperature has provided detailed information on the initial product of reaction 2. The ^{1}H and ^{31}P{^{1}H} NMR spectra of a toluene-d_8 solution of **2a** and [Cu(C≡CPh)(PPh$_3$)]$_4$ (Pd:Cu = 1:1) soon after dissolution of the complexes in CD_2Cl_2 at −30 °C show the presence of **2a** and **4a** in a 36:64 ratio. Raising the temperature of the solution to −10 °C for 3 min results in a change of the relative ratio of the complexes to 49:51, although liberation of **3a** is negligible at this stage. Partial conversion of **4a** to **2a** due to the temperature change can be attributed to a shift of equilibrium between the complexes under these conditions:

$$\mathbf{2a} + {}^1/_4[\mathrm{Cu(C{\equiv}CPh)(PPh_3)}]_4 \rightleftarrows \mathbf{4a} + (1/n)[\mathrm{Cu(I)(PPh_3)}]_n \quad (3)$$

Further raising of the reaction temperature to 25 °C causes conversion of **4a** into **2a** and the coupling product **3a**.

Alkynyl Ligand Transfer from 4a to CuI. As shown above, the alkynyl ligand migration from [Cu(C≡CPh)(PPh$_3$)]$_4$ to *trans*-Pd(C$_6$H$_4$X-*p*)(I)(PEt$_3$)$_2$ appears to be reversible. More direct evidence for reversibility of the alkynyl ligand transfer is obtained from an NMR study on the reaction of **4a** with CuI. Reactions of **4a** with CuI at 25 °C in the presence and absence of added PPh$_3$ give a mixture of **2a** and **3a**, as shown in eq 4. A similar reaction with addition of PEt$_3$ (3 mol/mol of CuI) does not cause alkynyl ligand transfer from Pd(II) to Cu(I) at all, presumably due to blocking of the reaction site. Figure 3 summarizes the profiles of the reactions



with and without PPh$_3$ addition. The reaction without PPh$_3$ (Figure 3a) causes consumption of **4a** in 1 h accompanied by formation of **2a** and **3a**. Addition of PPh$_3$ to the reaction mixture changed the profile, depending on the molar ratio of the Pd complex and PPh$_3$, as shown in parts b−d of Figure 3. Reactions of 1, 3, and 5 equiv of added PPh$_3$ with **4a** result in formation of **2a**, **3a**, and **4a** in the ratios of 36:35:29, 29:22:49, and 28:14:59, respectively, after 2 h. In each reaction, the decrease in the amount of **4a** and the increase of **2a** almost cease after 2 h, although concomitant formation of coupling product **3a** results in a slow decrease of both complexes throughout the measurement. Complexes **2a** and **4a** seem to be in equilibrium under these conditions during the reaction. The molar ratio between **4a** and **2a** after the reaction for 2 h increases with an increase in the PPh$_3$/Pd ratio.

Preparation of *trans*-Pt(C$_6$H$_4$OMe-*p*)(I)(PEt$_3$)$_2$ and Its Reactions with [Cu(C≡CPh)(PPh$_3$)]$_4$ and with 4a. Aryliodoplatinum(II) complexes *trans*-Pt(C$_6$H$_4$X-*p*)(I)(PEt$_3$)$_2$ (**5b**, X = OMe; **5c**, X = F) are prepared by oxidative addition of IC$_6$H$_4$OMe-*p* and of IC$_6$H$_4$F-*p*, respectively, to Pt(PEt$_3$)$_4$. The ^{1}H and ^{31}P NMR spectra agree well with the trans structure of the complexes. Reactions of **5b,c** with [Cu(C≡CPh)(PPh$_3$)]$_4$ (Pt:Cu = 1:1) convert the Pt complex into *trans*-Pt(C$_6$H$_4$X-*p*)(C≡CPh)(PEt$_3$)$_2$ (**6b**, X = OMe; **6c**, X = F) immediately. Coupling products **3b,c** are not formed in the reaction mixtures at all, due to the high stability of **6b,c**. Complex **6b** does not react with CuI at room temperature. The ^{13}C{^{1}H} NMR spectrum of **6b** shows signals due to the α- and β-alkynyl carbons at δ 114.3 and 109.9, respectively. The ^1J(CPt) value observed for the former signal (890 Hz) is larger than that observed in the *ipso* carbon signal of the aryl ligand (673 Hz). Appearance of the alkynyl carbon signals as well as some aryl carbon signals as triplets due to P−C coupling indicates the trans structure of **6b** unambiguously. The trans structure of **6c** has been confirmed by X-ray crystallography, as shown in Figure 4. The fact that

(19) Preliminary results of the X-ray crystallography of **4b** show the trans structure of the complex.

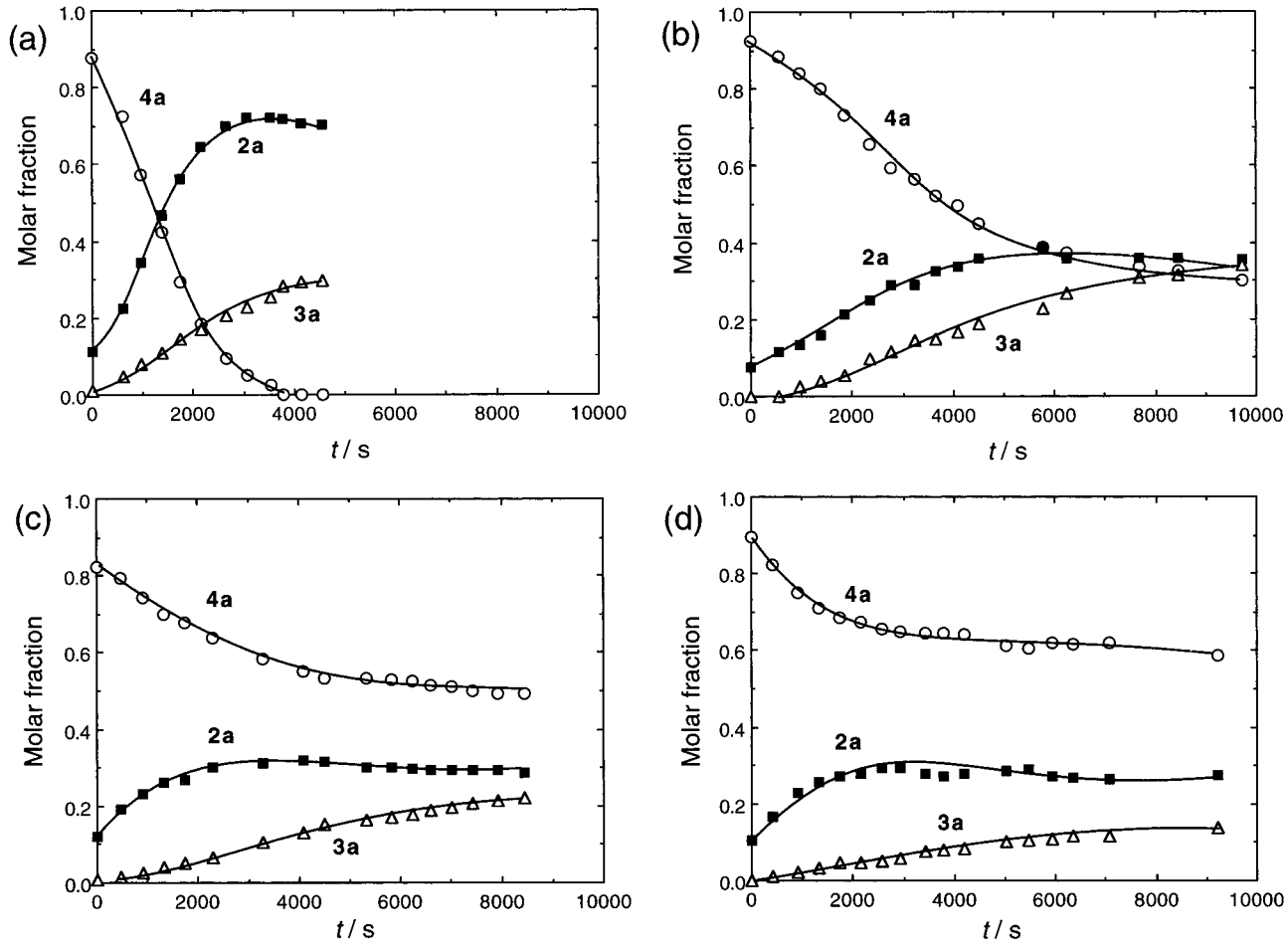
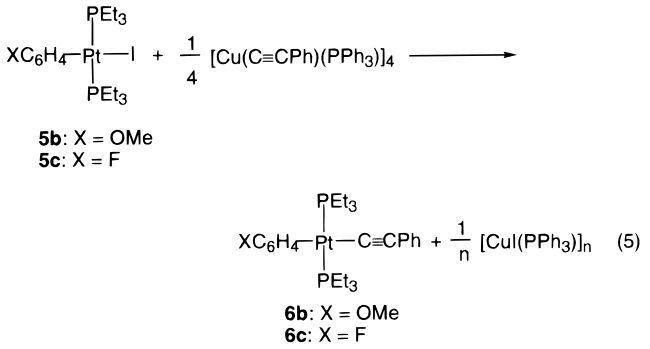
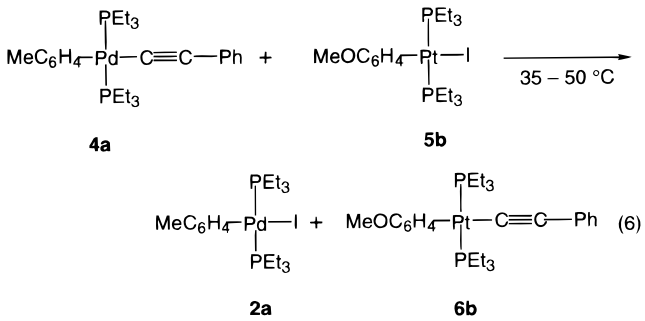


Figure 3. Reaction profiles of **4a** with CuI: (a) without addition of PPh_3; (b) with addition of PPh_3 (1 mol/mol of **4a**); (c) with addition of PPh_3 (3 mol/mol of **4a**); (d) with addition of PPh_3 (5 mol/mol of **4a**). The molar fractions of the compounds are determined from ^1H NMR peaks ($C_6H_4CH_3$ region); the temperature was 25 °C.





the Pt−C(alkynyl) bond (1.99(1) Å) is shorter than the Pt−C(aryl) bond (2.02(1) Å) of **6c** and the above difference between the two ^1J(CPt) values of **6b** suggest a partial contribution of the vinylidene structure to the Pt−alkynyl bond of the complexes.

Heating a toluene solution of an equimolar mixture of **4a** and **5b** at 50 °C causes intermolecular alkynyl ligand transfer from the former complex to the latter, giving a mixture of **2a** and **6b**. The reaction proceeds irreversibly and is almost completed within 9 h. Figure 5 shows the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture containing the complexes **2a**, **4a**, **5b**, and **6b**. The $^{31}P\{^1H\}$ and ^1H NMR spectra taken during the reaction do not show any peaks due to compounds other than the above four complexes, indicating that the aryl groups behave as spectator ligands and do not undergo migration between the metal centers. Figure 6 shows time−yield curves of the complexes shown in eq 6 for a 1:1 reaction of **4a** and **5b**. Sufficient linearity of the plots of $[\mathbf{4a}]_0/[\mathbf{4a}]_t$ suggests that the reaction obeys first-order kinetics with respect to both [**4a**] and [**5b**]. The presence of a large excess amount of **5b** gives a pseudo-first-order kinetic condition, and the first-order plots of [**4a**] show good linearity, as shown in Figure 7. The temperature dependence of the rate constants of the reactions under pseudo-first-order conditions gives the kinetic parameters $\Delta H^{\ddagger} = 110$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -58$ J mol^{-1} deg^{-1}, and $\Delta G^{\ddagger} = 127$ kJ mol^{-1} at 298 K.

Addition of CuI (2.09 μM, [Cu]/[Pd] = 0.10) to the reaction mixture causes consumption of more than 90% of the starting materials within 5 min at 50 °C, while the reaction without the additive requires ca. 3 h to obtain conversion of 50% of the starting materials at the same temperature. Enhancement of the reaction

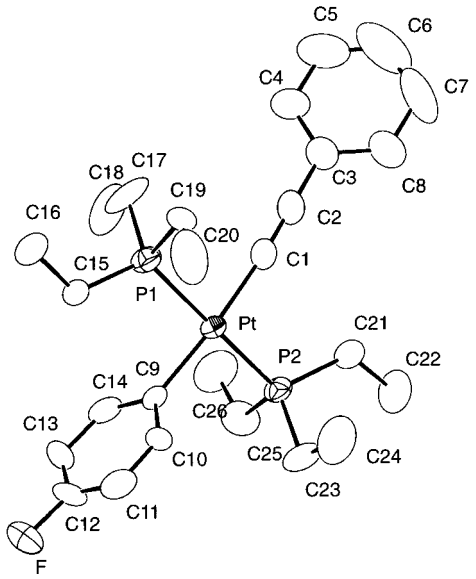


Figure 4. ORTEP drawing of *trans*-Pt(C_6H_4F-*p*)(C≡C-Ph)(PEt_3)$_2$ (**5c**) at the 30% ellipsoid level.

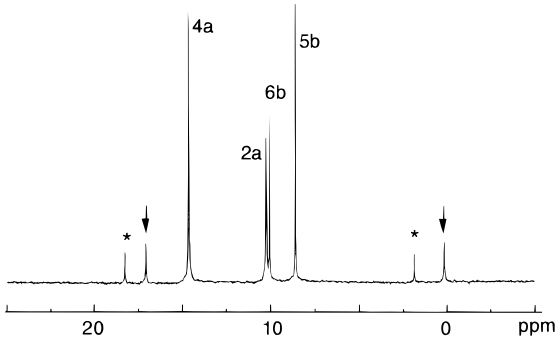
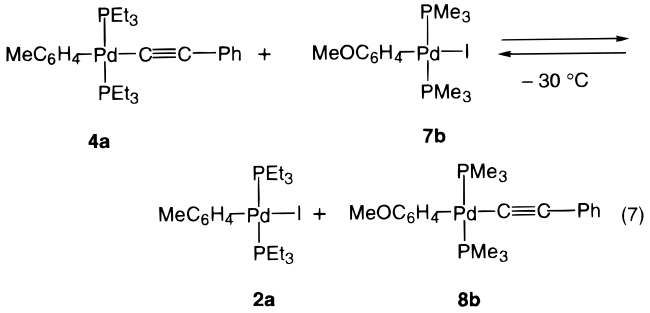


Figure 5. $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture of **4a** and **5b** at 50 °C. The peaks with arrows and with asterisks are due to the satellite peaks of **5b** and **6b**, respectively.

by CuI suggests a pathway for alkynyl ligand transfer from Pd and Pt assisted by the Cu compound.

Equimolar reaction of **4a** and *trans*-Pd(C_6H_4OMe-*p*)I(PMe_3)$_2$ (**7b**) at −30 °C even in the absence of CuI results in alkynyl ligand exchange between the complexes to give a mixture of **2a**, *trans*-Pd(C_6H_4OMe-*p*)(C≡CPh)(PMe_3)$_2$ (**8b**), and the above two complexes.[20]



The results indicate that the alkynyl ligand transfer between the Pd centers proceeds much more readily than the alkynyl ligand transfer from Pd to Pt complexes.

(20) The NMR spectra of the reaction mixture after 1 h at −30 °C showed conversion of ca. 10% of **4a** and **7b** into **2a** and **8b**, while raising the temperature caused formation of many Pd complexes, probably due to accompanying exchange of the phosphine ligands among the complexes.

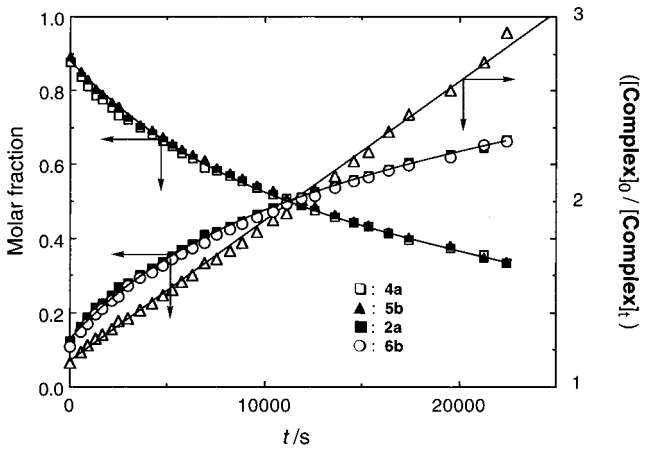


Figure 6. Time−yield curves and second-order plots of an equimolar reaction of **4a** and **5b** to give **2a** and **6b**. $[\mathbf{4a}]_0 = [\mathbf{5b}]_0 = 0.055$ M.

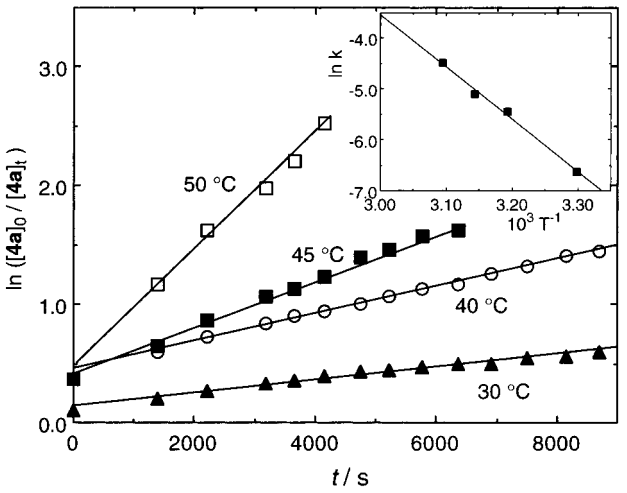
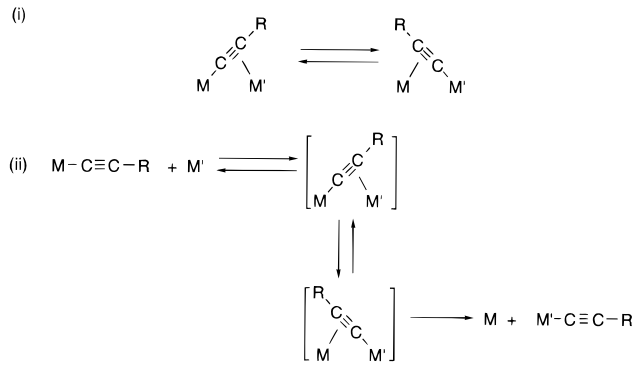


Figure 7. Pseudo-first-order plots of reaction 6 at 30−50 °C. An Arrhenius plots of the kinetic data is shown in the inset.

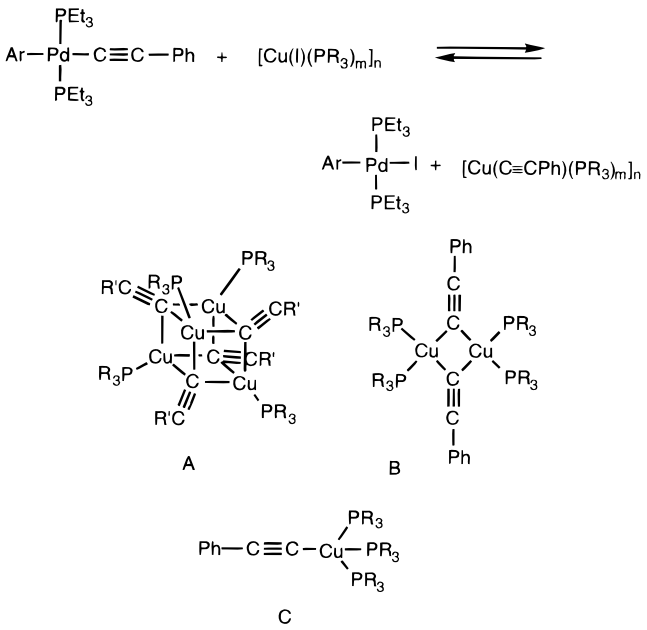
Scheme 3



Discussion

Many dinuclear transition-metal complexes with bridging alkynyl ligands bonded to the metal centers in a $\sigma-\pi$ manner undergo rapid switching of μ-η^1:η^2 to μ-η^2:η^1 coordination, as shown in Scheme 3(i). The reaction proceeds through concerted cleavage and formation of the σ- and π-bonds between the alkynyl carbons and two metal centers,[21] except for diiron complexes with bridging ethynyl ligands, which undergo similar changes of the coordination mode induced by a 1,2-shift of the ethynyl hydrogen.[22] The intermolecular transfer of the

Scheme 4



alkynyl ligand among Cu, Pd, and Pt in the present study as well as in the previous studies seems to proceed through formation of bimetallic intermediates and their rapid structural change, as depicted in Scheme 3(ii).

The present study on the reactions of $Pd(Ar)(I)(PEt_3)_2$ with $[Cu(C{\equiv}CPh)]_n$ and of $Pd(Ar)(C{\equiv}CPh)(PEt_3)_2$ with CuI has disclosed reversible alkynyl ligand transfer between the Cu and Pd complexes. On the other hand, the reactions of $[Cu(C{\equiv}CPh)]_n$ and of $Pd(Ar)(C{\equiv}CPh)(PEt_3)_2$ with $Pt(Ar)(I)(PEt_3)_2$ give $PtAr(C{\equiv}CPh)(PEt_3)_2$ quantitatively without any sign of reverse alkynyl ligand transfer from alkynylplatinum complexes already produced to the iodo complexes of Cu or Pd. The highly stable Pt−C(alkynyl) bond compared with the corresponding Cu−C(alkynyl) and Pd−C(alkynyl) bonds is attributed to significant back-donation of the alkynyl group to the Pt center.

Reactions of **4a** with CuI give various reaction profiles, depending on the presence of tertiary phosphine added to the reaction mixture. The reaction with added PEt_3 (3 mol/mol of **4a**) does not cause alkynyl ligand transfer from Pd to Cu at all, while the reaction without phosphine addition leads to complete conversion of **4a** into a mixture of **3a** and **2a**. Addition of PPh_3 causes partial conversion of **4a**, suggesting an equilibrium between **4a** and **2a** under these conditions. The total reaction and the structures of related copper complexes are shown in Scheme 4. Alkynylcopper and iodocopper species in the reaction are composed of mixtures of complexes with several structures, such as those shown in Scheme 4. These complexes, formulated as $[Cu(I)(PR_3)_m]_n$ and $[Cu(C{\equiv}CPh)(PR_3)_m]_n$, could have versatile multinuclear structures with bridging coordination of iodo and alkynyl ligands.[23] The complexes A (R = Ph, $SiMe_3$) have been obtained and characterized by X-ray crystallography.[8,23e] B and C show the most reasonable structures for the formulas, $[Cu(C{\equiv}CPh)(PR_3)_2]_n$ and $[Cu(C{\equiv}CPh)(PR_3)_3]_n$, respectively. Each of the complexes is obtained by using a PPh_3 ligand in the present study (see Experimental Section). These complexes in solution are considered to be in rapid equilibrium involving dissociation and ligation of the phosphine ligands due to the labile d^{10} metal center. The presence of added PEt_3 or excess amounts of PPh_3 in the reaction mixture tends to destabilize alkynylcopper species (or stabilize iodocopper species) and shift the equilibrium in Scheme 4. The obtained results here can be rationalized by assuming that ligation of phosphine ligands destabilizes σ-donation in the alkynyl−copper bonding[24] and cleaves the bridging coordination of the alkynyl ligand to form less stable mononuclear alkynylcopper species such as $[Cu(C{\equiv}CR)(PR'_3)_3]$.

The alkynyl ligand transfer between Cu and Pd complexes is accompanied by coupling of the aryl and phenylethynyl groups to give ArC≡CPh. Formation of the coupling product in the reaction of **2e**, having PPh_3 ligands, with $[Cu(C{\equiv}CPh)(PPh_3)]_4$ at −30 °C is accounted for by assuming initial alkynyl ligand transfer to give *cis*- or *trans*-$Pd(C_6H_4Me\text{-}p)(C{\equiv}CPh)(PPh_3)_2$. The cis complex would liberate arylphenylacetylene by direct reductive elimination, while the trans isomer would undergo reductive elimination through dissociation of the PPh_3 ligand, which is less basic and more bulky than PEt_3, or trans−cis isomerization involving dissociation of PPh_3 followed by reductive elimination. Reactions of **2a**−**c** with $[Cu(C{\equiv}CPh)(PPh_3)]_4$ and of **4a** with CuI also give the coupling product ArC≡CPh. The aryl(alkynyl)palladium complexes with a trans structure **4a,b** do not undergo spontaneous reductive elimination of the two organic ligands at room temperature due to their rigid trans coordination with compact and highly basic PEt_3 ligands, preventing isomerization of the trans to the cis structure that is suited for reductive elimination of the product. Coexistence of CuI in solution with **2a** causes coupling of the aryl and alkynyl ligands at room temperature.

There seem to be two plausible mechanisms for the coupling of the aryl and phenylethynyl groups in the presence of CuI. One involves CuI-induced removal of a PEt_3 ligand of the Pd complex to cause dissociative

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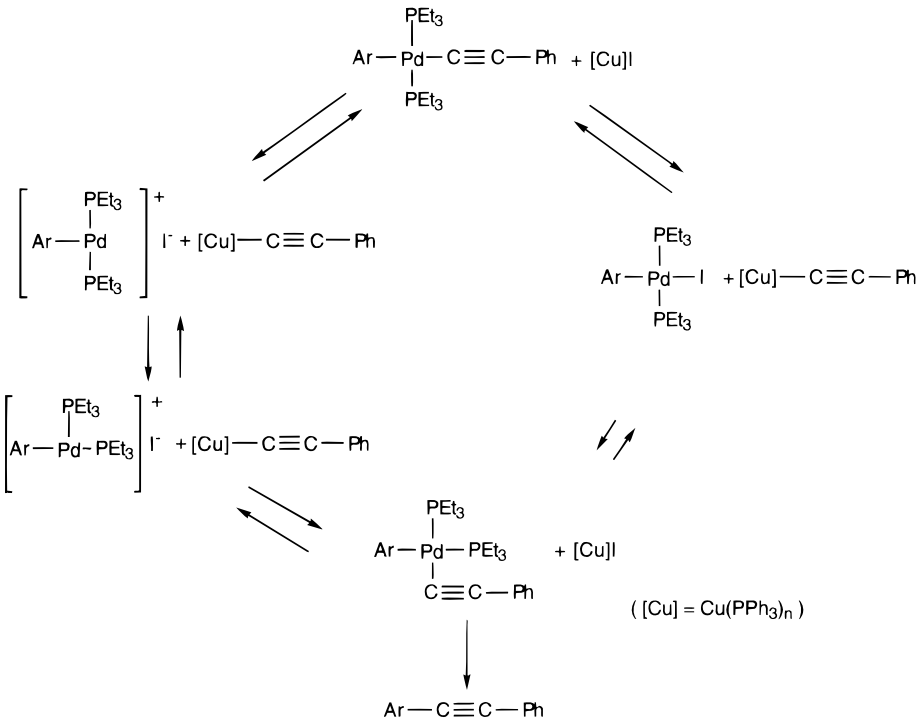
Scheme 5



reductive elimination of the aryl and alkynyl ligands from Pd(Ar)(C≡CPh)(PEt_3) through trans to cis isomerization in the three-coordinate species.[25] Another possible mechanism is shown in Scheme 5. According to the mechanism, alkynyl ligand transfer between Pd and Cu gives a mixture of *trans*- and *cis*-PdAr(C≡CPh)(PEt_3)$_2$. The cis complex formed seems to undergo rapid reductive elimination of the product, since the cis isomer is almost negligible in the NMR spectra of the reaction mixture. Our experimental results are not sufficient to compare the probability of cationic or neutral intermediates in the reaction and also in the catalytic cross-coupling of alkyne and haloarene. The pathway of trans−cis isomerization of the aryl(alkynyl)palladium complex given in Scheme 5 resembles CuI- or HgI_2-induced *cis*- to *trans*-Pt(C≡CPh)$_2$(PPh_2Me)$_2$ isomerization involving reversible alkynyl transfer between the metal centers.[7,26] Similar structural changes of square-planar diorganopalladium complexes in the presence of organomagnesium compounds also proceed through reversible alkyl ligand transfer between Pd and Mg centers.[27]

In general, the aryl-metal bond is thermodynamically less stable than the corresponding alkynyl−metal bond[28] and several aryl−nickel and −palladium complexes have been reported to undergo intermolecular transfer of the aryl ligands.[29] The alkynyl transfer reactions in the present study always occur prior to aryl ligand migration that would give diarylpalladium complexes or cause reductive elimination of biaryls.[30] The alkynyl ligand transfer seems to be kinetically favored, because the bimetallic intermediate with an unsymmetrically bridging alkynyl ligand undergoes rapid $\sigma-\pi$ structural change, as shown in Scheme 3(i).

Alkynyl group transfer from PdAr(C≡CPh)(PEt_3)$_2$ to PtAr(I)(PEt_3)$_2$ occurs with gentle heating. The kinetic results indicate that the reaction proceeds through a bimetallic transition state probably containing a μ-η^1:η^1-alkynyl ligand bonded both to Pd and to Pt centers.[31] Enhancement of the reaction by addition of CuI is rationalized by assuming two independent reaction pathways in the presence of CuI. Scheme 6 depicts pathway i, involving direct ligand exchange through a transition state with bridging alkynyl ligands, and pathway ii, in which the alkynyl ligand transfer from Pd to Pt is assisted by more rapid alkynyl ligand transfer between Cu and Pd. The latter pathway contributes significantly in the presence of a catalytic amount of CuI because of the large effect of addition of a catalytic amount of CuI. Amounts of the coupling products (ArC≡CPh) are almost negligible in this reaction mixture. This suggests that transfer of the alkynyl ligand of the once formed alkynylcopper to the arylpalladium iodo complex in pathway ii to generate *cis*-PdAr(C≡CPh)L_2 is slower than the alkynyl ligand transfer reaction from the alkynylcopper species to Pt, giving a Pt alkynyl product.

(25) Pd(0) species, once formed through reductive elimination of the coupling product, may also abstract PEt_3 coordinated to the Pd complex to enhance the formation of the three-coordinate species.

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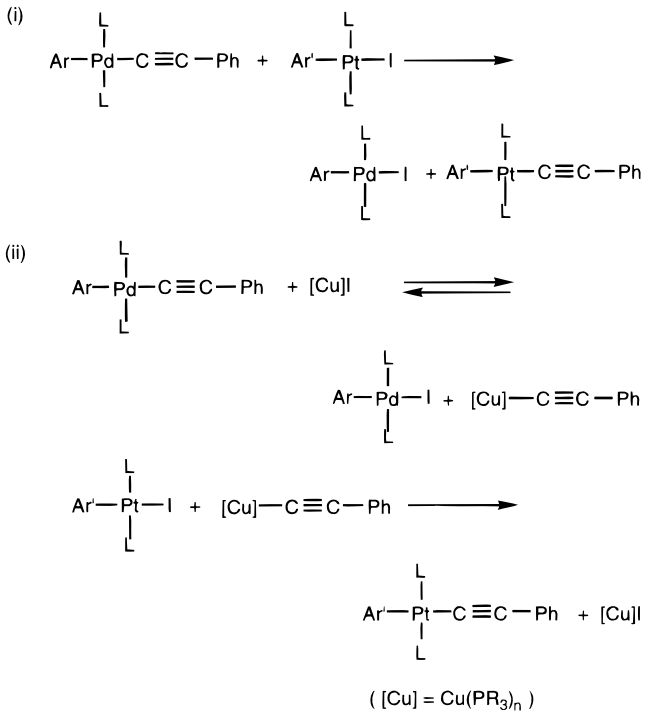
Scheme 6



Conclusion

Intermolecular transfer of an alkynyl ligand bonded to Cu(I) to arylpalladium halo complexes occurs under mild conditions to give the corresponding arylpalladium alkynyl complexes, which are isolated and characterized by use of the PEt_3 ligand. The alkynyl ligand transfer sometimes proceeds reversibly to give an equilibrated mixture of the Cu− and Pd−alkynyl complexes, although the reaction is accompanied by irreversible coupling of the aryl and alkynyl groups of the complexes. Alkynyl ligand transfer from arylpalldium to arylplatinum complexes requires more severe conditions but is facilitated by addition of CuI, which seems to transport the alkynyl group from Pd to Pt complexes. The present study has disclosed alkynyl ligand transfer among Cu(I), Pd(II), and Pt(II) complexes and the role of intermolecular organic ligand transfer in selective cross-coupling reactions catalyzed by Pd(II) complexes in the presence of CuI. CuI in the catalytic process serves to make cross-coupling efficient by promoting selective and reversible transfer of the alkynyl ligand between the metal centers.

Experimental Section

General Considerations, Measurement, and Materials. Manipulations of the metal complexes were carried out under nitrogen or argon using standard Schlenk techniques. $Pd_2(dba)_3$[32] and $Pt(PEt_3)_4$[33] were prepared according to the literature. IR and NMR spectra (^1H, ^{13}C, and ^{31}P) were recorded on a JASCO 810 spectrophotometer and on a JEOL EX-400 spectrometer, respectively. $^{31}P\{^1H\}$ NMR peak positions were referenced to external 85% H_3PO_4. Elemental analyses were carried out with a Yanagimoto Type MT-2 CHN autocorder.

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Complex **1a**, prepared according to the already reported procedure, showed NMR peaks identical with the literature data.[16] Similar reactions of 4-iodoanisole and of 4-fluoroiodobenzene with $Pd_2(dba)_3$ in the presence of tmeda gave **1b** (79%) and **1c** (79%), respectively. Data for **1b**: ^1H NMR (C_6D_6) δ 1.49 (t, 2H, CH_2, J = 4 Hz), 1.60 (t, 2H, CH_2, J = 4 Hz), 1.68 (s, 6H, NCH_3), 2.26 (s, 6H, NCH_3), 3.43 (s, 3H, OCH_3), 6.80 (d, 2H, $C_6H_2H_2$, J = 9 Hz), 7.36 (d, 2H, $C_6H_2H_2$, J = 9 Hz). Anal. Calcd for $C_{13}H_{23}ION_2Pd$: C, 34.19; H, 5.08; N, 6.13. Found: C, 34.09; H, 5.11; N, 6.18. Data for **1c**: ^1H NMR (C_6D_6) δ 1.41 (t, 2H, CH_2, J = 5 Hz), 1.51 (t, 2H, CH_2, J = 5 Hz), 1.54 (s, 6H, NCH_3), 2.21 (s, 6H, NCH_3), 6.85 (d, 2H, $C_6H_2H_2$, J = 9 Hz), 7.29 (dd, 2H, $C_6H_2H_2$, J(HH) = 9 Hz, J(HF) = 6 Hz). Anal. Calcd for $C_{12}H_{20}FIN_2Pd$: C, 32.41; H, 4.53; N, 6.30. Found: C, 32.35; H, 4.61; N, 6.39.

$[Cu(C{\equiv}CPh)(PPh_3)]_4$[8,23e] was prepared by the reaction of $[Cu(C{\equiv}CPh)]_n$ with PPh_3 as shown below. A mixture of $[Cu(C{\equiv}CPh)]_n$ (2.56 g, 16 mmol) and PPh_3 (12.1 g, 46 mmol) was dissolved in THF (40 mL) containing $HNEt_2$ (5.5 mL) with gentle heating. The initial yellow dispersion gradually turned into a greenish brown solution. After the mixture was stirred for an additional 18 h at room temperature, the solvent was evaporated to dryness. The product was extracted with toluene (50 mL) at room temperature. A slightly green solid obtained from washing the toluene-insoluble fraction with Et_2O gave $[Cu(C{\equiv}CPh)(PPh_3)]_4$ (3.00 g, 45%). IR (KBr) ν(C≡C): 2018 cm^{-1} (lit.[23e] 2014 cm^{-1}). Anal. Calcd for $C_{104}H_{80}P_4Cu_4$: C, 73.14; H, 4.72. Found: C, 73.05; H, 4.91. The toluene-soluble fraction was washed with Et_2O to give $[Cu(C{\equiv}CPh)(PPh_3)_2]_2$ (2.23 g, 21%) as a colorless solid. Anal. Calcd for $C_{88}H_{70}P_4Cu_2$: C, 75.83; H, 5.30. Found: C, 76.12; H, 5.43. IR(KBr) ν(C≡C): 2040 cm^{-1}.

A similar reaction of $[Cu(C{\equiv}CPh)]_n$ (0.30 g, 1.8 mmol) and PPh_3 (2.33 g, 8.9 mmol) gave a mixture of $[Cu(C{\equiv}CPh)(PPh_3)]_4$ and $Cu(C{\equiv}CPh)(PPh_3)_3$, the latter of which was isolated from the toluene-soluble fraction (5 mL) of the product. IR (KBr) ν(C≡C): 2042 cm^{-1}. Anal. Calcd for $C_{62}H_{50}P_3Cu$: C, 78.25; H, 5.30. Found: C, 78.26; H, 5.56.

Preparation of 2a−c. To **1a** (1.80 g, 4.1 mmol) dispersed in Et_2O (65 mL) was added PEt_3 (1.13 g, 9.6 mmol) dropwise at 0 °C. After the cooling bath was removed, the reaction mixture was stirred at room temperature for 20 min to cause separation of a yellow solid from the yellow-orange solution. The resulting solid was collected by filtration and recrystallized from Et_2O to give **2a** as pale yellow crystals (1.90 g, 83%). ^1H NMR (C_6D_6): δ 0.89 (m, 18H, P(CH$_2$CH_3)$_3$), 1.56 (m, 12H, P(CH_2CH$_3$)$_3$), 2.18 (s, 3H, CH_3), 6.90 (d, 2H, $C_6H_2H_2$, J = 7 Hz), 7.21 (d, 2H, $C_6H_2H_2$, J = 7 Hz). $^{31}P\{^1H\}$ NMR: 25 °C in C_6D_6, δ 10.3 (s); (−30 °C in CD_2Cl_2, δ 11.0 (s). Anal. Calcd for $C_{19}H_{37}IP_2Pd$: C, 40.70; H, 6.65. Found: C, 40.48; H, 6.75.

Similar reactions of **1b** and of **1c** gave *trans*-Pd(C_6H_4X-*p*)(I)(PEt_3)$_2$ (**2b**, X = OMe, 11%; **2c**, X = F, 87%). Data for **2b**: ^1H NMR (C_6D_6) δ 0.89 (m, 18H, P(CH$_2$CH_3)$_3$), 1.59 (m, 12H, P(CH_2CH$_3$)$_3$), 3.40 (s, 3H, CH_3), 6.79 (d, 2H, $C_6H_2H_2$, J = 9 Hz), 7.14 (d, 2H, $C_6H_2H_2$, J = 9 Hz); $^{31}P\{^1H\}$ NMR (25 °C in C_6D_6) δ 10.7 (s). Anal. Calcd for $C_{19}H_{37}IOP_2Pd$: C, 39.57; H, 6.47. Found: C, 39.16; H, 6.52. Data for **2c**: ^1H NMR (C_6D_6) δ 0.83 (m, 18H, P(CH$_2$CH_3)$_3$), 1.52 (m, 12H, P(CH_2CH$_3$)$_3$), 6.82 (t, 2H, $C_6H_2H_2$, J(HH) = 9 Hz, J(HF) = 9 Hz), 7.14 (dd, 2H, $C_6H_2H_2$, J(HH) = 9 Hz, J(HF) = 6 Hz); $^{31}P\{^1H\}$ NMR (25 °C in C_6D_6) δ 10.6 (s). Anal. Calcd for $C_{18}H_{34}FIP_2Pd$: C, 38.28; H, 5.58. Found: C, 38.19; H, 5.96.

Reaction of 2a−c with $[Cu(C{\equiv}CPh)(PPh_3)]_4$. 1. Reaction at Room Temperature. Addition of a toluene (2 mL) solution of **2a** (123 mg, 0.22 mmol) to $[Cu(C{\equiv}CPh)(PPh_3)]_4$ (102 mg, 0.24 mmol of Cu) at room temperature caused an immediate color change of the solution from yellow to black. After further stirring for 5 h at room temperature, the solvent was evaporated to dryness. ^1H NMR spectrum measurement of the product using diphenylmethane as an internal standard showed the presence of **2a** (26% yield) and **3a** (74% yield) in the product.

2. Reaction at −30 °C. To [Cu(C≡CPh)(PPh_3)]$_4$ (88 mg, 0.21 mmol of Cu) was added a CH_2Cl_2 (1 mL) solution of **2a** (110 mg, 0.20 mmol) cooled to −30 °C. Stirring of the reaction mixture was continued at −30 °C with occasional warming of the flask at room temperature over a short period. Soon after complete dissolution of the starting materials the solvent was evaporated to dryness. The Pd-containing products were extracted with hexane (5 mL) to remove Cu complexes by filtration. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the hexane extract showed the presence of **2a** (35%) and **4a** (65%) and the absence of **3a**.

3. Reaction at Room Temperature with PPh_3 Addition. To a toluene (3 mL) solution of [Cu(C≡CPh)(PPh_3)]$_4$ (408 mg, 0.96 mmol of Cu) and PPh_3 (502 mg, 1.9 mmol) was added a toluene (4 mL) solution of **2a** (521 mg, 0.93 mmol) at room temperature. Stirring the mixture caused dissolution of the initial pale green suspension to give a yellow-orange solution. After reaction for 4 h the solvent was evaporated to dryness. At this stage the ^{1}H NMR measurement of the reaction mixture showed the presence of **2a** (21%), **3a** (36%), and **4a** (42%). Extraction of the product with hexane (5 mL) followed by repeated recrystallization from acetone gave **4a** as colorless crystals (13.4 mg, 3%). IR (KBr) ν(C≡C): 2092 cm^{-1}. ^{1}H NMR (C_6D_6): δ 0.98 (m, 18H, P(CH_2CH_3)$_3$), 1.57 (m, 12H, P(CH_2-CH_3)$_3$), 2.29 (s, 3H, CH_3), 7.00 (t, 1H, C_6H_4H, J = 7 Hz), 7.08 (d, 2H, $C_6H_2H_2$, J = 7 Hz), 7.16 (t, 2H, $C_6H_3H_2$, J = 7 Hz), 7.46 (d, 2H, $C_6H_2H_2$, J = 7 Hz), 7.62 (d, 2H, $C_6H_3H_2$, J = 7 Hz). ^{31}P{^{1}H} NMR: 25 °C, C_6D_6, δ 14.5 (s); −30 °C, CD_2Cl_2, δ 14.8 (s). ^{13}C{^{1}H} NMR (25 °C in CD_2Cl_2): δ 8.4 (P(CH_2CH_3)$_3$), 16.2 (apparent triplet due to virtual coupling, P(CH_2CH_3)$_3$), 21.0 (CH_3), 111.3 (C≡C), 119.8 (t, Pd*C*≡C, J(CP) = 20 Hz), 124.8, 127.9, 128.2, 129.7, 130.7, 131.0, 138.2, 157.2. Anal. Calcd for $C_{27}H_{42}P_2Pd$: C, 60.62; H, 7.91. Found: C, 60.23; H, 8.12. The hexane-insoluble solid in the product was washed with Et_2O to give CuI(PPh_3)$_3$ as a pale green solid (459 mg, 51%). Anal. Calcd for $C_{54}H_{45}IP_3Cu$: C, 66.36; H, 4.64. Found: C, 66.37; H, 4.69.

A similar reaction of **2b** with [Cu(C≡CPh)(PPh_3)]$_4$ in the presence of PPh_3 gave **4b**, which was isolated by recrystallization of the hexane-soluble fraction of the product (5%). IR (KBr) ν(C≡C): 2092 cm^{-1}. ^{1}H NMR (C_6D_6): δ 0.98 (m, 18H, P(CH_2CH_3)$_3$), 1.56 (m, 12H, P(CH_2CH_3)$_3$), 3.48 (s, 3H, OCH_3), 6.95 (t, 1H, C_6H_4H, J = 7 Hz), 7.01 (d, 2H, $C_6H_2H_2$, J = 7 Hz), 7.18 (t, 2H, $C_6H_3H_2$, J = 7 Hz), 7.39 (d, 2H, $C_6H_2H_2$, J = 7 Hz), 7.63 (d, 2H, $C_6H_3H_2$, J = 7 Hz). ^{31}P{^{1}H} NMR (25 °C, C_6D_6): δ 14.8 (s). ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2): δ 8.4 (P(CH_2CH_3)$_3$), 16.2 (apparent triplet due to virtual coupling, P(CH_2CH_3)$_3$), 54.3 (OCH_3), 111.2 (C≡*C*), 113.3 (*ortho* carbon of 4-methoxyphenyl ligand), 119.7 (t, Pd*C*≡C), 124.9 (*C*H, *para* carbon of the C≡CC_6H_5 group), 128.3, 129.7 (*C*C≡C), 131.0, 138.3, 150.0 (t, J(CP) = 7 Hz), 156.1 (*C*OMe). Anal. Calcd for $C_{27}H_{42}OP_2Pd$: C, 58.86; H, 7.68. Found: C, 58.95; H, 7.98.

Reaction of **2c** with [Cu(C≡CPh)(PPh_3)]$_4$ in the presence of PPh_3 gave **4c**, which was characterized by ^{1}H NMR in a mixture with **2c** and **3c**. Isolation of the complex was not feasible due to the low crystallinity. ^{1}H NMR of **4c** (C_6D_6): δ 0.93 (m, 18H, P(CH_2CH_3)$_3$), 1.49 (m, 12H, P(CH_2CH_3)$_3$), 6.97 (t, 1H, C_6H_4H, J = 7 Hz), 7.38 (d, 2H, $C_6H_2H_2$, J = 7 Hz), 7.59 (d, 2H, $C_6H_3H_2$, J = 7 Hz). Other peaks were overlapped with those of **2c** and **3c**. ^{31}P{^{1}H} NMR (25 °C, C_6D_6): δ 14.7 (s).

Preparation of 2d and Its Reaction with [Cu(C≡CPh)(PPh_3)]$_4$. To a THF (40 mL) solution of **1a** (993 mg, 2.3 mmol) was added PMe_3 (350 mg, 4.6 mmol) in one portion at 0 °C. Stirring the reaction mixture at room temperature resulted in formation of a red solution, which was evaporated to dryness. The product was recrystallized from Et_2O to give **2d** as yellow crystals (160 mg, 15%). ^{1}H NMR (400 MHz at 25 °C in C_6D_6): δ 0.98 (apparent triplet due to virtual coupling, 18H, CH_3), 2.17 (s, 3H, CH_3), 6.89 (d, 2H, $C_6H_2H_2$, J = 8 Hz), 7.05 (d, 2H, $C_6H_2H_2$, J = 8 Hz). ^{31}P{^{1}H} NMR (160 MHz, 25 °C, C_6D_6): δ −21.3 (s). Anal. Calcd for $C_{13}H_{25}IP_2Pd$: C, 32.76; H, 5.29. Found: C, 32.67; H, 5.19.

A mixture of **2d** (50 mg, 0.10 mmol) and [Cu(C≡CPh)(PPh_3)]$_4$ (43 mg, 0.10 mmol of Cu) was dissolved in toluene (2 mL) at room temperature to cause an immediate color change of the solution to black. After the reaction mixture was stirred for 4 h at room temperature, the solvent was evaporated to dryness. The ^{1}H NMR spectrum of the resulting black solid showed the presence of **2d** (46%) and **3a** (54%).

Preparation of 2e and Its Reaction with [Cu(C≡CPh)(PPh_3)]$_4$. A mixture of **1a** (152 mg, 0.34 mmol) and PPh_3 (182 mg, 0.69 mmol) was dispersed in Et_2O (10 mL) at room temperature. Stirring the pale pink mixture for 2 h caused a color change of the solid to pale yellow. The solid product was collected by filtration and dried in vacuo to give **2e** as a pale yellow solid (253 mg, 87%). ^{1}H NMR (C_6D_6): δ 1.93 (s, 3H, CH_3), 6.15 (d, 2H, $C_6H_2H_2$, J = 7 Hz), 6.69 (d, 2H, $C_6H_2H_2$, J = 7 Hz), 6.98 (br, 18H, P($C_6H_3H_2$)$_3$), 7.73 (br, 12H, P($C_6H_3H_2$)$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 22.5 (s). Anal. Calcd for $C_{43}H_{37}IP_2Pd$: C, 60.83; H, 4.39. Found: C, 60.92; H, 4.57.

A mixture of **2e** (135 mg, 0.16 mmol) and [Cu(C≡CPh)-(PPh_3)]$_4$ (70 mg, 0.16 mmol of Cu) was dissolved in CH_2Cl_2 (3 mL) at −30 °C. Stirring the pale green reaction mixture at −30 °C caused deposition of a black solid. After 1 h the ^{1}H NMR spectrum of the reaction mixture showed formation of phenyl(4-methylphenyl)acetylene (95%).

Reaction of 1a with [Cu(C≡CPh)(PPh_3)]$_4$. A mixture of **1a** (113 mg, 0.25 mmol) and [Cu(C≡CPh)(PPh_3)]$_4$ (103 mg, 0.24 mmol) was dissolved in THF (2 mL) with stirring at room temperature. The initial orange solution soon turned into a yellow solution, from which a black solid began to precipitate. After the mixture was stirred for 20 min at room temperature, the ^{1}H NMR analysis of the product showed formation of **3a** (78%).

Reaction of 4a with CuI. A typical experiment was carried out as follows. An NMR tube containing **4a** (5.70 mg, 1.07×10^{-2} mmol), CuI (2.20 mg, 1.16×10^{-2} mmol), PPh_3 (3.32 mg, 1.26×10^{-2} mmol), and anisole (2 μL, internal standard) was connected to a vacuum line. Benzene-d_6 (ca. 0.5 mL) was introduced by trap-to-trap distillation. After the sample tube was sealed, changes in the peaks in the region of the tolyl methyl hydrogens were monitored by comparison with the peak of the internal standard.

Preparation of 5b,c. A mixture of Pt(PEt_3)$_4$ (1.32 g, 2.0 mmol) and 4-iodoanisole (1.21 g, 5.2 mmol) was dissolved in toluene (17 mL) with heating under reflux for 1 h. The initial yellow solution turned colorless, accompanied by deposition of a small amount of colorless solid. Evaporating the solvent to dryness followed by washing the product with hexane gave **5b** as a colorless solid (1.0 g, 75%). ^{1}H NMR (in C_6D_6): δ 0.87 (m, 18H, P(CH_2CH_3)$_3$), 1.71 (m, 12H, PCH_2), 3.43 (s, 3H, OCH_3), 6.77 (d, 2H, $C_6H_2H_2$, J = 8 Hz), 7.32 (d, 2H, $C_6H_2H_2$, J(HH) = 8 Hz, J(HPt) = 65 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 8.9 (s, J(PPt) = 2727 Hz)). Anal. Calcd for $C_{19}H_{37}IOP_2Pt$: C, 34.29; H, 5.60. Found: C, 33.99; H, 6.09.

A similar reaction of Pt(PEt_3)$_4$ with 4-fluoroiodobenzene gave **5c** (77%). ^{1}H NMR (400 MHz, C_6D_6): δ 0.82 (m, 18H, P(CH_2CH_3)$_3$), 1.67 (m, 12H, P(CH_2CH_3)$_3$), 6.80 (dd, 2H, $C_6H_2H_2$, J(HH) = 7 Hz, J (HF)= 9 Hz), 7.23 (d, 2H, $C_6H_2H_2$, J(HH) = 7 Hz, J(HPt) = 68 Hz). ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ 8.4 (s, J(PPt) = 2696 Hz)). Anal. Calcd for $C_{18}H_{34}FIP_2Pt$: C, 33.09; H, 5.25. Found: C, 33.18; H, 5.10.

Reactions of 5b,c with [Cu(C≡CPh)(PPh_3)]$_4$. Preparation of 6b,c. A toluene (2 mL) dispersion of **5b** (170 mg, 0.26 mmol), [Cu(C≡CPh)(PPh_3)]$_4$ (109 mg, 0.26 mmol of Cu), and PPh_3 (134 mg, 0.51 mmol) was stirred at room temperature. The pale green solid gradually dissolved to give slightly brown solution from which a colorless solid separated. After 1 h of stirring the solvent was evaporated to dryness. The product was extracted with hexane (12 mL) at room temperature and then recrystallized from acetone to give **6b** as colorless crystals (31 mg, 20%). IR (KBr) ν(C≡C): 2098 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 0.96 (m, 18H, CH_3), 1.66 (m, 12H, PCH_2), 3.50 (s, 3H, OCH_3), 6.96 (d, 2H, $C_6H_2H_2$, J = 7 Hz), 7.02 (t, 1H,

Table 3. Crystallographic Data and Details of Refinement for 1a,b, 4a, and 6c

	1a	1b	4a	6c
chem formula	$C_{13}H_{23}IN_2Pd$	$C_{13}H_{23}IN_2OPd$	$C_{27}H_{42}P_2Pd$	$C_{26}H_{39}FP_2Pt$
fw	440.64	456.64	534.98	627.63
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)	$P2_1/a$ (No. 14)	$P2_1$ (No. 4)
a, Å	13.176(8)	13.311(10)	13.902(10)	9.087(4)
b, Å	9.530(9)	9.524(8)	12.187(4)	11.907(4)
c, Å	25.922(10)	26.42(2)	17.988(9)	13.378(6)
β, deg	95.29(4)	94.60(7)	111.22(6)	107.64(3)
V, Å^3	3240	3337	2841	1379
Z	8	8	4	2
μ, cm^{-1}	30.02	29.22	7.66	52.71
F(000)	1712	1776	1120	624
D_{calcd}, g cm^{-3}	1.806	1.818	250	1.512
cryst size, mm × mm × mm	0.2 × 0.2 × 0.2	0.4 × 0.6 × 0.6	0.2 × 0.4 × 0.4	0.2 × 0.4 × 0.4
2θ range, deg	3.0−50.0	3.0−55.0	3.0−52.8	3.0−55.0
hkl ranges	$0 \le h \le 15$	$0 \le h \le 17$	$0 \le h \le 16$	$0 \le h \le 11$
	$-30 \le k \le 30$	$0 \le k \le 12$	$0 \le k \le 14$	$0 \le k \le 15$
	$0 \le l \le 11$	$-34 \le l \le 34$	$-21 \le l \le 19$	$-16 \le l \le 16$
no. of unique rflns	3049	4090	5274	3336
no. of rflns used ($I \ge 3\sigma(I)$)	2300	2992	3844	2564
no. of variables	154	163	271	270
$R(F_o)$[a]	0.032	0.055	0.066	0.036
$R_w(F_o)$[a]	0.033	0.052	0.069	0.029

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w|F_o - F_c|^2/\sum w|F_o|^2]^{1/2}$; weighting scheme $w = [\{\sigma(F_o)\}^2]^{-1}$.

C_6H_4H, J = 7 Hz), 7.17 (t, 2H, $C_6H_3H_2$, J = 7 Hz), 7.48 (d, 2H, $C_6H_2H_2$, J = 7 Hz), 7.61 (d, 2H, $C_6H_2H_2$, J = 7 Hz). $^{31}P\{^1H\}$ NMR (160 MHz in C_6D_6): δ 10.2 (s, J(PPt) = 2641 Hz). $^{13}C\{^1H\}$ NMR (100 MHz in CD_2Cl_2): δ 8.1 (s, $P(CH_2CH_3)_3$, J(CPt) = 26 Hz), 16.2 (apparent triplet, $P(CH_2CH_3)_3$, J(CPt) = 35 Hz), 55.1 (OCH_3), 109.9 (≡*C*C, J(CPt) = 22 Hz), 113.7 (*C*HCPt, J(CPt) = 50 Hz), 114.3 (Pt*C*≡, t, J(PC) = 15 Hz, J(CPt) = 890 Hz), 124.8 (para carbon of the C≡CC_6H_5 ligand), 128.2, 130.0 (≡C*C*, J(CPt) = 22 Hz), 131.0, 139.1, 145.0 (Pt*C*(*ipso*), t, J(PC) = 10 Hz, J(CPt) = 673 Hz), 155.5 (O*C*). Anal. Calcd for $C_{27}H_{42}OP_2Pt$: C, 50.72; H, 7.57. Found: C, 50.18; H, 6.50.

A similar reaction of **5c** with $[Cu(C{\equiv}CPh)(PPh_3)]_4$ gave **6c** (90%). IR (KBr) ν(C≡C): 2094 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 0.91 (m, 18H, $P(CH_2CH_3)_3$), 1.60 (m, 12H, $P(CH_2CH_3)_3$), 6.99 (d, 2H, $C_6H_2H_2$, J = 8 Hz), 7.03 (t, 1H, C_6H_4H, J = 7 Hz), 7.17 (t, 2H, $C_6H_3H_2$, J = 7 Hz), 7.41 (d, 2H, $C_6H_2H_2$, J(HH) = 7 Hz, J(HPt) = 39 Hz), 7.61 (d, 2H, $C_6H_2H_2$, J = 8 Hz). $^{31}P\{^1H\}$ NMR (160 MHz, C_6D_6): δ 9.8 (s, J(PPt) = 2621 Hz). Anal. Calcd for $C_{26}H_{39}FP_2Pt$: C, 49.78; H, 6.22. Found: C, 49.87; H, 6.43.

Kinetic Measurements. A typical experimental procedure is as follows. Complexes **4a** (1.85 mg, 3.46 × 10^{-5} mmol) and **5b** (22.6 mg, 3.40 × 10^{-4} mmol) as well as diphenylmethane (internal standard) were dissolved in C_6D_6 (0.586 mL). The resulting solution was transferred through a silicon rubber tube into an NMR sample tube fitted with a glass stopcock. After the solution was degassed, the sample tube was sealed with a flame. The peak areas of the ^1H NMR peaks due to Me hydrogens of C_6H_4Me-*p* and of C_6H_4OMe-*p* groups of the complexes compared with the peak of the internal standard were monitored in an NMR apparatus whose probe was maintained at 50 °C. The second-order rate constants were obtained as follows: 1.33 × 10^{-3} L mol^{-1} s^{-1} (303 K), 4.31 × 10^{-3} L mol^{-1} s^{-1} (313 K), 6.08 × 10^{-3} L mol^{-1} s^{-1} (318 K), and 1.13 × 10^{-2} L mol^{-1} s^{-1} (323 K).

Reaction of 4a and 7b. Complexes **7b** and **8b** were prepared similarly to the PEt_3-coordinated complexes. **7b**: ^1H NMR (400 MHz, −30 °C, CD_2Cl_2) δ 1.19 (apparent triplet due to virtual coupling, 18H, CH_3), 3.683 (s, 3H, OCH_3), 6.67 and 7.05 (d, 4H, C_6H_4, J = 8 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, 25 °C, C_6D_6) −21.0 ppm (s). **8b**: ^1H NMR (400 MHz, −30 °C, CD_2Cl_2) δ 1.19 (apparent triplet due to virtual coupling, 18H, CH_3), 3.68 (s, 3H, OCH_3), 6.63 and 7.13 (d, 4H, C_6H_4, J = 8 Hz), 7.18 (t, 1H, C_6H_4H, J = 7 Hz), 7.34 (d, 2H, $C_6H_3H_2$, J = 7 Hz), 7.54 (t, 2H, $C_6H_3H_2$, J = 7 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, −30 °C, CD_2Cl_2) −17.3 ppm (s). Complexes **4a** (5.20 mg, 0.98 × 10^{-2} mmol) and **7b** (4.80 mg, 0.97 × 10^{-2} mmol) were dissolved in CD_2Cl_2 (ca. 0.6 mL) at −60 °C. The solution was transferred into an NMR tube through a Teflon tube at that temperature. Measurement of the ^1H and $^{31}P\{^1H\}$ NMR spectra at −30 °C has revealed partial formation of **3a** and **8b**.

Crystal Structure Determination. Crystals of **1a** and **1b** suitable for crystallography were obtained by recrystallization from THF, while **4a** and **6c** were recrystallized from acetone. Crystals were mounted in glass capillary tubes under argon. The unit cell parameters were obtained by least-squares refinement of 2θ values of 25 reflections with 25° ≤ 2θ ≤ 35°. 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. Empirical absorption correction (ψ-scan method) of the collected data was applied. Table 3 summarizes crystal data and details of the 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.[34] 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: Tables giving crystallographic data for **1a**, **2b**, **4a**, and **6c** (20 pages). Ordering information is given on any current masthead page.

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(34) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, U.K., 1974; Vol. IV.