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Transmetallation of alkynyl and aryl complexes of Group 10 transition metals

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Contents

Abstract

This article reviews recent studies on intermolecular transfer of alkynyl and aryl ligands of Ni, Pd, and Pt complexes. The reactions of aryl and alkynyl groups bonded to the Group 10 metal complexes are of significant importance relevant to the mechanism of synthetic organic reactions catalyzed by complexes of these metals. The reaction of alkynylcopper–PPh_3 complexes with dichloropalladium complexes leads to formation of mono- and dialkynylpalladium complexes via transmetallation. Aryl(iodo)palladium complexes react with the alkynylcopper complexes to result in rapid and reversible transfer of the alkynyl ligand between Cu(I) and Pd(II) compounds. Aryl(phenylethynyl)palladium complexes with PEt_3 ligands react with aryl(iodo)–palladium and platinum complexes to afford aryl(phenylethynyl)platinum complex. An associative pathway for the reaction is proposed based on the kinetic results. The intermolecular transfer of the alkynyl ligand from Pd(II) to Pt(II) complexes is significantly enhanced by addition of CuI. Aryl ligand transfer of

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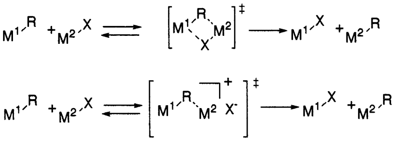
NiBr(Ar)(bpy) (bpy = 2,2′-bipyridine) takes place smoothly in DMF to afford an equimolar mixture of dibromo- and diaryl-nickel complexes the latter of which are responsible for reductive elimination of biaryl. A detailed kinetic study of the reaction disclosed the pathway involving a dinuclear Ni intermediate. The introduction of CO_2 into a DMF solution of NiBr(Ph)(bpy) results in formation of biphenyl and benzoic acid. The disproportionation and CO_2 insertion into the Ni–aryl bond of NiBr(Ar)(bpy) involves the common cationic intermediate $[Ni(Ar)(bpy)(DMF)]^+Br^-$ formed in polar DMF. Also referred to are recent, related studies on transmetallation of alkynyl and aryl complexes of Group 10 metals.

Keywords: Transmetallation; Group 10 elements; Alkynyl complex; Aryl complex; Coupling reaction

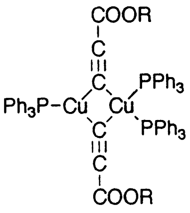
1. Introduction

Alkyl, aryl, and alkynyl complexes of transition metals undergo various unique reactions such as reductive elimination, β-hydrogen elimination, and insertion of small molecules into the metal–carbon σ-bond [1–3]. These reactions play important roles in many synthetic organic reactions catalyzed by transition metal complexes such as homo- and cross-coupling reactions, polymerization, hydrogenation, and carbonylation of the organic substrates. Transmetallation, also common in the synthetic organic reactions, has attracted a lot less attention than other fundamental reactions of the organotransition metal complexes. Scheme 1 depicts typical transmetallation reactions including intermolecular exchange of the organo and halogeno (or pseudo halogeno) ligands. The reaction proceeds smoothly in a concerted manner to afford new metal–carbon bond under mild conditions. Since the metal–carbon σ-bond does not dissociate spontaneously during the reaction, the intermolecular ligand transfer occurs via a bimetallic intermediate.

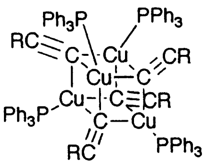
Here, we describe results of our recent study as well as studies by other research groups on the reactions of organometallic complexes of Group 10 metals with halogeno complexes leading to intermolecular exchange of these ligands. Relevance of the transmetallation of organometallic complexes to the mechanism of catalytic cross- and homo-coupling will also be conferred. Chart 1 summarizes structures of the metal complexes described in the present article.



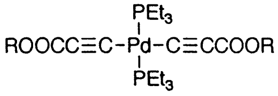
Scheme 1.



1: R = Me
2: R = Et,
3: R = ^{t}Bu

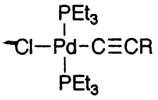


4: R = $SiMe_3$
5: R = Ph,
6: R = C_6H_4Me-*p*



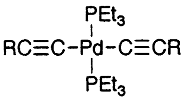
$\mathrm{ROOCC{\equiv}C{-}\overset{PEt_3}{\underset{PEt_3}{Pd}}{-}C{\equiv}CCOOR}$

7: R = Me
8: R = Et,
9: R = ^{t}Bu



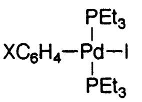
$\mathrm{Cl{-}\overset{PEt_3}{\underset{PEt_3}{Pd}}{-}C{\equiv}CR}$

10 : R = $SiMe_3$
11a: R = Ph,
12a: R = C_6H_4Me-*p*



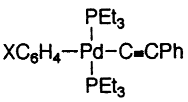
$\mathrm{RC{\equiv}C{-}\overset{PEt_3}{\underset{PEt_3}{Pd}}{-}C{\equiv}CR}$

11b: R = Ph,
12b: R = C_6H_4Me-*p*



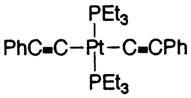
$\mathrm{XC_6H_4{-}\overset{PEt_3}{\underset{PEt_3}{Pd}}{-}I}$

13: X = Me
14: X = F
15: X = OMe



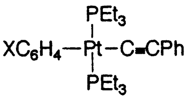
$\mathrm{XC_6H_4{-}\overset{PEt_3}{\underset{PEt_3}{Pd}}{-}C{\equiv}CPh}$

16: X = Me
17: X = F
18: X = OMe



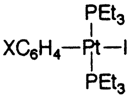
$\mathrm{PhC{\equiv}C{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}C{\equiv}CPh}$

19



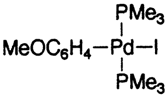
$\mathrm{XC_6H_4{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}C{\equiv}CPh}$

20: X = F
23: X = OMe



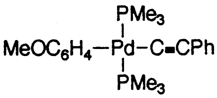
$\mathrm{XC_6H_4{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}I}$

21: X = F
22: X = OMe



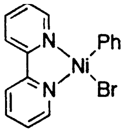
$\mathrm{MeOC_6H_4{-}\overset{PMe_3}{\underset{PMe_3}{Pd}}{-}I}$

24



$\mathrm{MeOC_6H_4{-}\overset{PMe_3}{\underset{PMe_3}{Pd}}{-}C{\equiv}CPh}$

25



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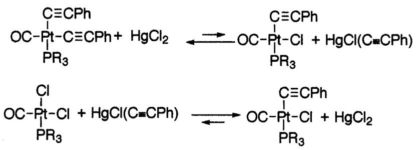
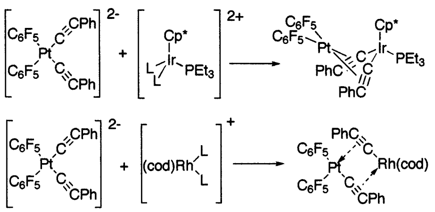
(Chart 1)



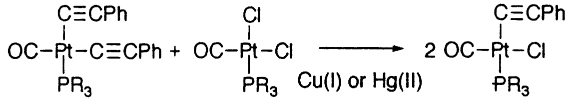
Scheme 2.



Scheme 3.

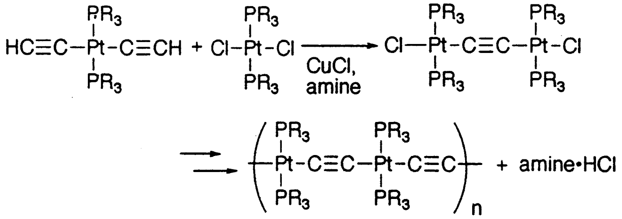
2. Alkynyl ligand transfer of Cu(I) to Pd(II) and to Pt(II) complexes

The intermolecular transfer of the alkynyl ligand of Pt complexes occurs with aid of catalytic amounts of CuCl, CuI, or $HgCl_2$. The reaction of a bis(phenylethynyl)platinum complex with a dichloroplatinum complex in the presence of $HgCl_2$ was reported to give chloro(phenylethynyl)platinum complex selectively as shown in Eq. (1) [4–6].



$$\mathrm{OC{-}\overset{C\equiv CPh}{\underset{PR_3}{Pt}}{-}C\equiv CPh} + \mathrm{OC{-}\overset{Cl}{\underset{PR_3}{Pt}}{-}Cl} \xrightarrow[\text{Cu(I) or Hg(II)}]{} 2\,\mathrm{OC{-}\overset{C\equiv CPh}{\underset{PR_3}{Pt}}{-}Cl} \qquad (1)$$

The reaction involves intermediate HgCl(C≡CPh) which is formed via transmetallation from Pt to Hg and transfers the alkynyl ligand to the dichloroplatinum complex (Scheme 2). The direct ligand exchange between the two platinum complexes is less plausible because CuCl, CuI or $HgCl_2$ addition is essential for the smooth ligand transfer. Vreize and van Koten et al. reported organoplatinum complexes with $HgCl_2$ or CuCl containing a direct Pt–M (M = Cu, Hg) bond [7,8], which suggests intermediacy of the heterobimetallic complexes in the transmetallation. Conproportionation of diethynylplatinum and dichloroplatinum complexes in the presence of CuCl and amine was noted in polycondensation of these complexes to give the Pt containing polyyne polymers (Eq. (2)) [9,10].



$$\mathrm{HC\equiv C{-}\overset{PR_3}{\underset{PR_3}{Pt}}{-}C\equiv CH} + \mathrm{Cl{-}\overset{PR_3}{\underset{PR_3}{Pt}}{-}Cl} \xrightarrow[\text{CuCl, amine}]{} \mathrm{Cl{-}\overset{PR_3}{\underset{PR_3}{Pt}}{-}C\equiv C{-}\overset{PR_3}{\underset{PR_3}{Pt}}{-}Cl}$$

$$\longrightarrow \left(\mathrm{{-}\overset{PR_3}{\underset{PR_3}{Pt}}{-}C\equiv C{-}\overset{PR_3}{\underset{PR_3}{Pt}}{-}C\equiv C{-}}\right)_n + \text{amine•HCl} \qquad (2)$$

The platinate complexes with phenylethynyl ligands react with Rh and Ir complexes to cause activation of the platinum-alkynyl σ-bond and afford new Pt–Rh (or Ir) heterobimetallic complexes with η^1,η^2-bonded alkynyl ligands as shown in Scheme 3 [11,12]. The Pt-alkynyl σ-bonds of the anionic complexes seem to be more labile than those of neutral Pt(II) alkynyl complexes which do not cause direct ligand transfer to Group 8–10 transition metal complexes.

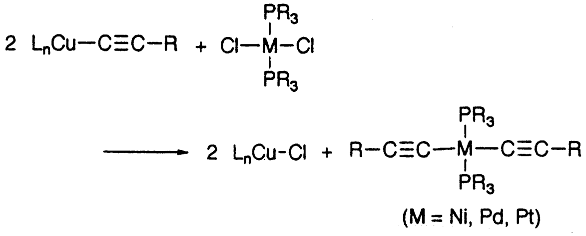
Palladium complexes catalyzed cross-coupling of terminal alkyne with bromoarene or with bromoalkene provides an excellent route to aryl acetylene and enyne, which has been applied to the synthesis of various organic molecules as well as π-conjugated polymers (Eqs. (3) and (4)) [13–31].

$$\text{Ar—Br} + \text{H—C}\equiv\text{C—R} \xrightarrow[\text{CuI, amine}]{\text{Pd complex}} \text{Ar—C}\equiv\text{C—R} + \text{amine}\cdot\text{HBr} \tag{3}$$

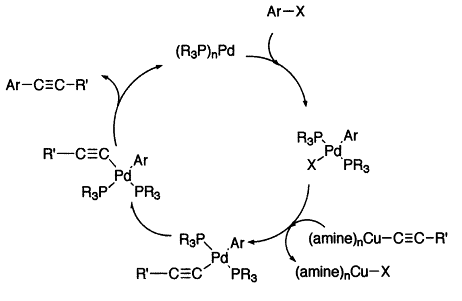
$$\text{Br—Ar—Br} + \text{H—C}\equiv\text{C—R—C}\equiv\text{C—H} \xrightarrow[\text{CuI, amine}]{\text{Pd complex}} \left(\text{Ar—C}\equiv\text{C—R—C}\equiv\text{C}\right)_n \tag{4}$$

The CuI and amine co-catalyst in the reaction mixture is essential to promote the catalytic cross-coupling efficiently and selectively. Scheme 4 depicts a proposed pathway for the reaction, which involves formation of Pd(Ar)(X)(L)$_n$ (X = halide) and its further reaction with (amine)$_n$Cu(C≡CR) to cause alkynyl ligand transfer affording Pd(Ar)(C≡CR)(PR$_3$)$_n$. A detailed mechanism of oxidative addition of bromoarene to Pd(0)–PR$_3$ complexes giving Pd(Ar)(X)(L)$_n$ and related reactions was elucidated by Amatore et al. [32–34]. The aryl(alkynyl)palladium complexes are of importance as the key intermediate of the above cross-coupling reaction, whereas the reports on isolation of this type of complexes are quite scarce. Preparation of Pd(Ar)(C≡CR)(PR$_3$)$_2$ type complexes was achieved by adopting a highly electron withdrawing perfluorophenyl ligand [35], but the Pd–perfluorophenyl bond exhibits an extremely low reactivity toward coupling or transmetallation even when the organic ligands occupy mutually *cis* positions. Mechanistic details of the transmetallation of the alkynyl ligand from alkynylcopper intermediates to aryl(halogeno)palladium complexes and the chemical properties of the aryl(alkynyl)palladium complexes remained unelucidated.

A number of alkynyl complexes of Ni, Pd, and Pt with phosphine ligands were prepared from the reaction of terminal alkyne with dihalogeno complexes of these metals in the presence of a catalytic amount of CuI and base (Eq. (5)).



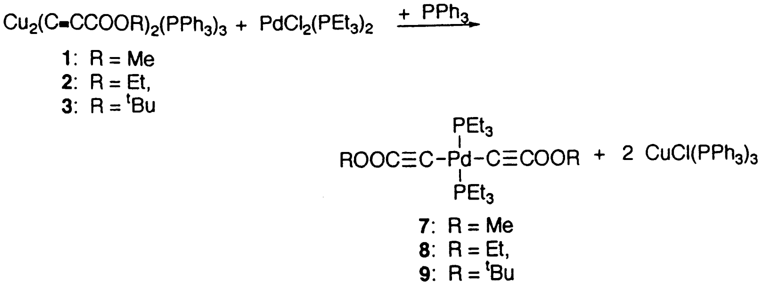
$$2\ \text{L}_n\text{Cu—C}\equiv\text{C—R} + \text{Cl—}\underset{\text{PR}_3}{\overset{\text{PR}_3}{\text{M}}}\text{—Cl} \longrightarrow 2\ \text{L}_n\text{Cu-Cl} + \text{R—C}\equiv\text{C—}\underset{\text{PR}_3}{\overset{\text{PR}_3}{\text{M}}}\text{—C}\equiv\text{C—R} \quad (\text{M} = \text{Ni, Pd, Pt}) \tag{5}$$



Scheme 4.

The reaction probably involves an intermediate alkynylcopper(I) complex which undergoes transmetallation of the alkynyl ligand to Ni, Pd, and Pt. Actually, the ligand transfer from Cu to the late transition metals occurs in the reaction of phosphine free alkynylcopper with late transition metal chloro complexes. Phenylethynylcopper, $[Cu(C{\equiv}CPh)]_n$, reacts with $PtCl_2(PEt_3)_2$ in the presence of tmeda (*N*,*N*,*N′*,*N′*-tetramethylethylenediamine) to give $Pt(C{\equiv}CPh)_2(PEt_3)_2$ [9]. Reactions of $[Cu(C{\equiv}CR)]_n$, prepared in situ from terminal alkyne, CuI, and amines, with dichloro complexes of Ni(II), Pd(II), and Pt(II) also give alkynyl complexes of these metals [10,36,37]. However, the reaction of alkynyl copper complexes having auxiliary tertiary phosphine ligands with dihalogeno palladium(II) complexes had no precedents. Similar alkynyl ligand transfer from an alkynylcopper(I) complex to arylpalladium halide complex would provide the $Pd(Ar)(C{\equiv}CR)(L)_n$ type product.

Before preparation of the aryl(alkynyl)palladium complexes, we examined the reaction of alkynylcopper–PPh_3 complexes, **1**–**6**, with $PdCl_2(PEt_3)_2$ with expectation of smooth transmetallation from Cu(I) to Pd(II) and formation of the bis(alkynyl)palladium complexes. The equimolar reactions of $Cu_2(\mu\text{-}C{\equiv}CCOOR)_2(PPh_3)_3$ (**1**: R = Me, **2**: R = Et, **3**: R = Bu-*t*) with $PdCl_2(PEt_3)_2$ in the presence of PPh_3 gives the corresponding dialkynyl palladium complexes *trans*-$Pd(C{\equiv}CCOOR)_2(PEt_3)_2$ (**7**: R = Me, **8**: R = Et, **9**: R = Bu-*t*) accompanied by formation of $CuCl(PPh_3)_3$ (Eq. (6)) [38].



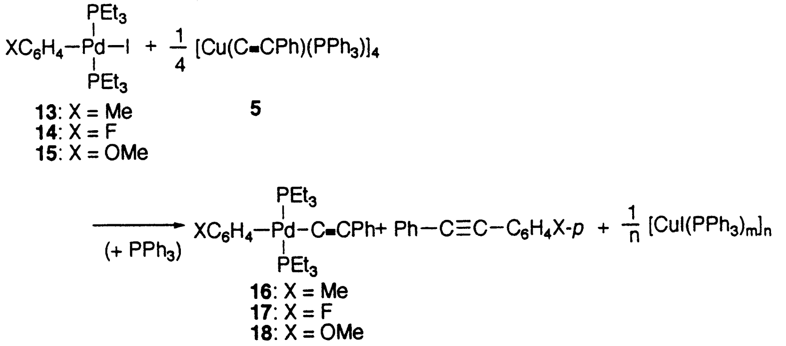
$$Cu_2(C{\equiv}CCOOR)_2(PPh_3)_3 + PdCl_2(PEt_3)_2 \xrightarrow{+\ PPh_3} ROOC{\equiv}C\text{-}\underset{\substack{|\\PEt_3}}{\overset{\substack{PEt_3\\|}}{Pd}}\text{-}C{\equiv}COOR + 2\ CuCl(PPh_3)_3 \qquad (6)$$

The absence of other products in the reaction mixture indicates that exchange of the phosphine ligands between Cu(I) and Pd(II) did not occur under the conditions.

$[Cu(C{\equiv}CSiMe_3)(PPh_3)]_4$ (**4**) reacts with $PdCl_2(PEt_3)_2$ in the presence of PPh_3 to give $CuCl(PPh_3)_3$ and *trans*-$PdCl(C{\equiv}CSiMe_3)(PEt_3)_2$ (**10**). The reaction of $[Cu(C{\equiv}CPh)(PPh_3)]_4$ (**5**) with $PdCl_2(PEt_3)_2$ in the presence of PPh_3 gives a mixture of *trans*-$PdCl(C{\equiv}CPh)(PEt_3)_2$ (**11a**) (56%), *trans*-$Pd(C{\equiv}CPh)_2(PEt_3)_2$ (**11b**) (39%), and $CuCl(PPh_3)_3$. Complexes **11a** and **11b** were isolated from the mixture by fractional crystallization. The reaction of $[Cu(C{\equiv}CC_6H_4Me\text{-}p)(PPh_3)]_4$ (**6**) with $PdCl_2(PEt_3)_2$ also gives a mixture of *trans*-$PdCl(C{\equiv}CC_6H_4Me\text{-}p)(PEt_3)_2$ (**12a**) and *trans*-$Pd(C{\equiv}CC_6H_4Me\text{-}p)_2(PEt_3)_2$ (**12b**) in a 24:76 molar ratio.

Thus, the alkynyl ligand transfer from the alkynylcopper(I)–PPh_3 complex to the dichloro palladium complex gave the expected alkynylpalladium complexes at room temperature (r.t.). The transmetallation is then applied to the synthesis of $Pd(Ar)(C{\equiv}CR)(PR_3)_2$ type complexes [39]. *Trans*-$Pd(C_6H_4X\text{-}p)(I)(PEt_3)_2$ (**13**: X = Me, **14**: X = F, **15**: X = OMe) obtained from the ligand exchange of $Pd(C_6H_4X$-

p)(I)(tmeda) with PEt_3 [40–43] were allowed to react with the phenylethynyl copper complex **5** as summarized in Table 1. The reaction brought about not only alkynyl ligand transfer from Cu to Pd but also coupling of the alkynyl and aryl groups (Eq. (7)).



(7)

Complex **13** reacts with **5** (Pd:Cu = 1:1) at r.t. to give $PhC{\equiv}CC_6H_4Me$-p (74%) together with unreacted **13** (26%). A 1:2 reaction of the complexes causes complete conversion of **13** to the diarylalkyne. The reaction of **13** with **5** (Pd:Cu = 1:1) at − 30°C does not give the coupling product $PhC{\equiv}CC_6H_4Me$-p but gives a mixture of **13** (35%) and *trans*-$Pd(C_6H_4Me$-$p)(C{\equiv}CPh)(PEt_3)_2$ (**16**) (65%). Addition of PPh_3 to the reaction of **13** with **5** at r.t. makes isolation of the resulting Pd complex possible. The hexane extract from the reaction mixture contains **13** (21%), $PhC{\equiv}CC_6H_4Me$-p (36%), and **16** (42%).

The reaction mixture of **14** with **5** in the presence of PPh_3 also contains **14**, $PhC{\equiv}CC_6H_4F$-p, and *trans*-$Pd(C_6H_4F$-$p)(C{\equiv}CPh)(PEt_3)_2$ (**17**) in a ratio of 23:13:64.

Table 1
Reaction of **13**–**15** with **5**

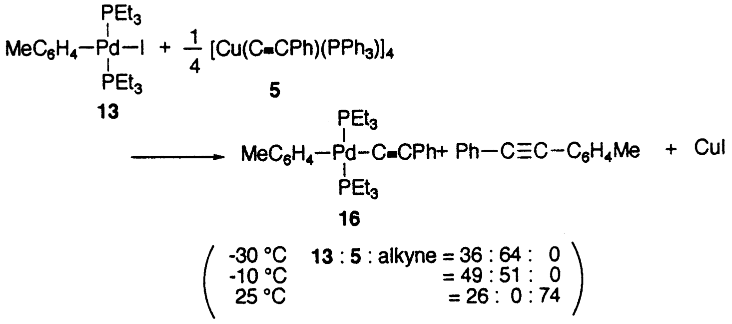
Complex	Conditions			Products (yield %)[a]		
	Additive[b]	Temperature (°C)	Time (min)	Pd complexes		$PhC{\equiv}CC_6H_4X$-p
13[c]	–	r.t.	60			$PhC{\equiv}CC_6H_4Me$-p (100)
13	–	r.t.	60	**13**(26)		$PhC{\equiv}CC_6H_4Me$-p (74)
13	–	−30	20	**13**(35)	**16**(65)	
13	PPh_3	r.t.	210	**13**(21)	**16**(42)	$PhC{\equiv}CC_6H_4Me$-p (36)
14	PPh_3	r.t.	60	**14**(23)	**17**(64)	$PhC{\equiv}CC_6H_4F$-p (13)
15	PPh_3	r.t.	60	**15**(41)	**18**(42)	$PhC{\equiv}CC_6H_4OMe$-p (17)

[a] $CuI(PPh_3)_3$ was isolated in 45–49% yields.
[b] $[PPh_3]/[Pd] = 2.0$.
[c] $[Pd]/[Cu] = 0.5$.

A similar reaction of **15** with **5** in the presence of PPh_3 gives a mixture of **15**, $PhC{\equiv}CC_6H_4OMe$-*p*, and *trans*-$Pd(C_6H_4OMe$-*p*$)(C{\equiv}CPh)(PEt_3)_2$ (**18**), in a ratio of 41:17:42. Complexes **16** and **18** once isolated are stable and do not undergo reductive elimination of $PhC{\equiv}CC_6H_4Me$-*p* and $PhC{\equiv}CC_6H_4OMe$-*p* in the solution at r.t., whereas the above reaction mixtures contain substantial amounts of the coupling products.

The molecular structures of the obtained aryl(alkynyl)palladium complexes with *trans* coordination were determined by X-ray crystallography. Table 2 compares selected bond distances of **16** with those of bis(phenylethynyl)palladium complex **11b**. Structural parameters of related Pt complexes *trans*-$Pt(C{\equiv}CPh)_2(PEt_3)_2$ (**19**) and *trans*-$Pt(C_6H_4F$-*p*$)(C{\equiv}CPh)$-$(PEt_3)_2$ (**20**) are also shown. 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 of aryl than alkynyl ligand of **16** [44]. The bis(alkynyl) and aryl(alkynyl)platinum complexes do not exhibit such a significant difference in the bond parameters [45]. The recent theoretical and spectroscopic studies on the bis(phenylethynyl)palladium complexes have revealed negligible back donation from the Pd(II) center [46], which is different from the other Group 8–10 transition metal alkynyl complexes [47–49].

The NMR spectra of a mixture of **13** and **5** at low temperature has provided detailed information on the initial product of the reaction in Eq. (8).



$$\mathrm{MeC_6H_4{-}\underset{PEt_3}{\overset{PEt_3}{Pd}}{-}I} + \frac{1}{4}\,[\mathrm{Cu(C{\equiv}CPh)(PPh_3)}]_4 \longrightarrow \mathrm{MeC_6H_4{-}\underset{PEt_3}{\overset{PEt_3}{Pd}}{-}C{\equiv}CPh} + \mathrm{Ph{-}C{\equiv}C{-}C_6H_4Me} + \mathrm{CuI} \quad (8)$$

13 **5** **16**

-30 °C **13** : **5** : alkyne = 36 : 64 : 0
-10 °C = 49 : 51 : 0
25 °C = 26 : 0 : 74

The ^1H- and $^{31}P\{^1H\}$-NMR spectra of a solution soon after dissolution of **13** and **5** (Pd:Cu = 1:1) at −30°C reveals the presence of **13** and **16** in a 36:64 ratio. Warming the solution to −10°C for 3 min results in a change in the relative ratio

Table 2
Selected bond distances of alkynylpalladium and platinum complexes

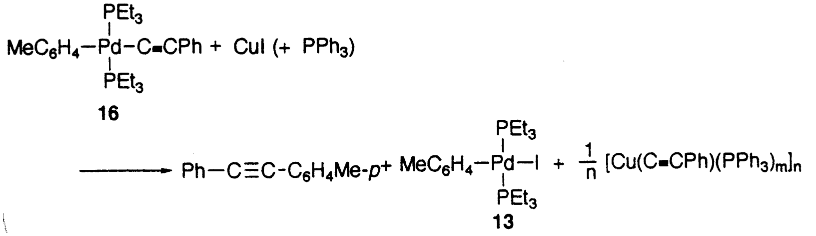
Complex[a]	M–C(alkynyl)	C≡C	M–C(aryl)	Ref.
$Pd(C{\equiv}CPh)_2(PEt_3)_2$ (**11b**)	2.069(7)	1.020(8)		[b]
$Pd(C_6H_4Me$-*p*$)(C{\equiv}CPh)(PEt_3)_2$ (**16**)	2.016(8)	1.196(9)	2.062(7)	[34]
$Pt(C{\equiv}CPh)_2(PEt_3)_2$ (**19**)	1.98(1)	1.21(1)		[40]
$Pt(C_6H_4F$-*p*$)(C{\equiv}CPh)(PEt_3)_2$ (**20**)	1.99(1)	1.21(1)	2.02(1)	[34]

[a] Complexes have *trans* structure.

[b] K. Osakada, M. Hamada, T. Yamamoto, unpublished results.

of the complexes to 49:51. Partial conversion of once formed **16** to regenerate **13** by raising the temperature suggests the presence of equilibrium between the palladium complexes in the presence of copper compounds. Keeping the reaction temperature at 25°C causes conversion of **16** into both **13** and the coupling product, $PhC{\equiv}CC_6H_4Me$-*p*.

The alkynyl ligand migration from **5** to *trans*-$Pd(C_6H_4X$-*p*$)(I)(PEt_3)_2$ appears to be reversible as described above. Results of the reaction of **16** with CuI provided more direct evidence for reversibility of the akynyl ligand transfer. The reactions at 25°C in the presence and absence of added PPh_3 gave a mixture of **13** and $PhC{\equiv}CC_6H_4Me$-*p* (Eq. (9)).



(9)

$$\underset{\mathbf{16}}{MeC_6H_4-\overset{PEt_3}{\underset{PEt_3}{Pd}}-C{\equiv}CPh} + CuI\ (+\ PPh_3) \longrightarrow Ph-C{\equiv}C-C_6H_4Me\text{-}p + \underset{\mathbf{13}}{MeC_6H_4-\overset{PEt_3}{\underset{PEt_3}{Pd}}-I} + \frac{1}{n}[Cu(C{\equiv}CPh)(PPh_3)_m]_n \qquad (9)$$

Fig. 1 summarizes the profiles of the reactions with and without PPh_3 addition. The reaction without PPh_3 (Fig. 1(a)) causes consumption of **16** and formation of **13** and $PhC{\equiv}CC_6H_4Me$-*p* in 1 h, while the reaction with added PPh_3 (three times molar of **16**) shows a different profile. Addition of PPh_3 with one, three, and five times molar of **16** to the reaction mixture results in the formation of **13**, $PhC{\equiv}CC_6H_4Me$-*p*, and **16** after 2 h in the ratios of 36:35:29, 29:22:49, and 28:14:59, respectively. In each reaction, a decrease in the amount of **16** and increase in **13** almost cease after 2 h although formation of $PhC{\equiv}CC_6H_4Me$-*p* causes slow decrease of both complexes. The results indicate that complexes **13** and **16** are in equilibrium under the conditions. The molar ratio of **16** to **13** after the reaction for 2 h increases with an increase in the PPh_3/Pd ratio. The reaction without phosphine addition leads to complete conversion of **16** into a mixture of $PhC{\equiv}CC_6H_4Me$-*p* and **13**.

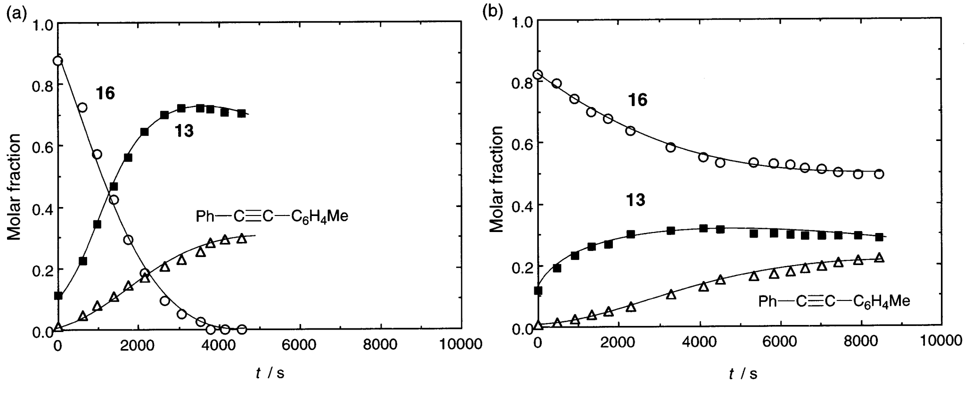
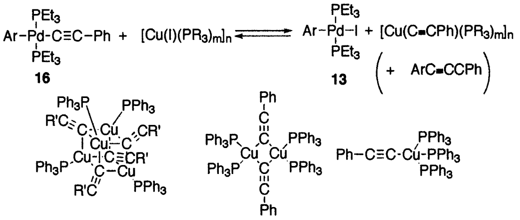


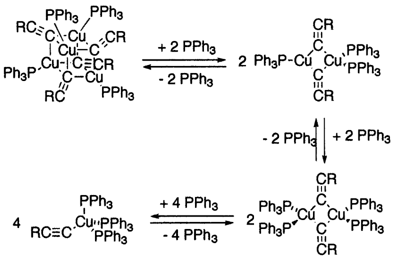
Fig. 1. Reaction profiles of **16** with CuI (a) without addition of PPh_3 and (b) with addition of PPh_3 (3 mol/**16**).



Scheme 5.

Scheme 5 summarizes the total reaction and structures of related copper complexes. Alkynylcopper and iodocopper compounds in the reaction mixture contain complexes with several structures since the complexes formulated as $[Cu(I)(PPh_3)_m]_n$ and $[Cu(C{\equiv}CPh)(PPh_3)_m]_n$ could have versatile multinuclear structures with bridging coordination of iodo and alkynyl ligands formulated as $[Cu_x(C{\equiv}CPh)_y(I)_{x-y}$-$(PPh_3)_z]$. These complexes in solution are in rapid equilibrium involving dissociation and ligation of the phosphine ligands owing to the labile d^{10} metal center. The presence of excess added PPh_3 tends to destabilize alkynylcopper species (or stabilize iodocopper species) and shifts the equilibrium to more significant formation of the Cu–I bond via transmetallation of the alkynyl ligand from Cu(I) to Pd(II). These mono-, di-, and tetranuclear alkynylcopper(I) complexes with PPh_3 ligands were prepared and characterized well. The NMR study of the complexes showed rapid and reversible structural change of the complexes. For example, the NMR spectra of unsymmetrical dinuclear complex **1** exhibit the presence of mono- and tetranuclear alkynylcopper complexes as minor species together with the main complex **1** in the solution at low temperature (ca. − 70°C), and show their mutual transformation on the NMR time scale at r.t. (Scheme 6) [38].

The alkynyl ligand transfer between Cu and Pd complexes in reaction (7) is accompanied by coupling of the aryl and phenylethynyl groups to give ArC≡CPh. The reactions of **13**–**15** with **5** and of **16** with CuI also give the coupling product, ArC≡CPh. *Trans*-aryl(alkynyl)palladium complexes **16** and **18** do not undergo spontaneous reductive elimination of ArC≡CPh at r.t. due to their rigid *trans* coordination. The compact and highly basic PEt_3 ligands prevent the complexes



Scheme 6.

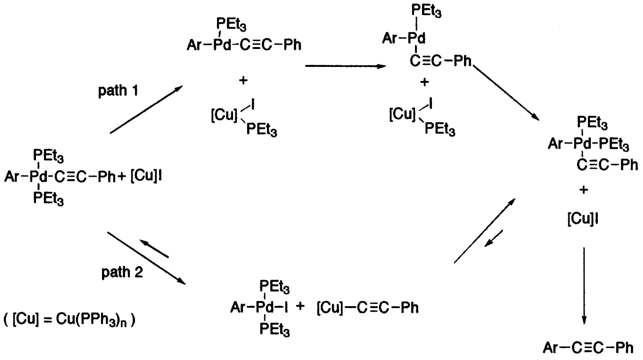
from isomerization of the *trans* to *cis* structure that is suited to reductive elimination of the product. Addition of CuI causes coupling of the aryl and alkynyl ligands of **13** at r.t.

Scheme 7 depicts two plausible mechanisms for the coupling of the aryl and phenylethynyl groups in the presence of CuI. One involves CuI induced transfer of a PEt_3 ligand of the Pd complex followed by *trans–cis* isomerization of the resulting three-coordinated labile and unstable intermediate, $Pd(Ar)(C{\equiv}CPh)(PEt_3)$, and reductive elimination of the product from *cis*-$Pd(Ar)(C{\equiv}CPh)(PEt_3)_n$ ($n = 1$ or 2) (path 1). The other involves repetition of reversible transmetallation of the alkynyl ligand between Cu(I) and Pd(II) to form a mixture of *trans*- and *cis*-$PdAr(C{\equiv}CPh)(PEt_3)_2$ (path 2). According to these mechanisms, the *cis* complex seems to undergo rapid reductive elimination of the product, since the *cis* isomer is almost negligible in the NMR spectra of the reaction mixture. The above pathway of *trans–cis* isomerization of the aryl(alkynyl)palladium complex resembles isomerization of CuI or $HgCl_2$ promoted *cis*- to *trans*-$Pt(C{\equiv}CPh)_2(PR_3)_2$ involving reversible alkynyl transfer between the metal centers [4–6]. Part of the reductive elimination may be due to *cis* and *trans* isomerization promoted by Pd(0) species generated in a small amount during the reaction.

Aryl(iodo)platinum(II) complexes, *trans*-$Pt(C_6H_4X\text{-}p)(I)(PEt_3)_2$ (**21**: X = F, **22**: X = OMe), react with **5** (Pt:Cu = 1:1) to immediately convert the Pt complexes into *trans*-$Pt(C_6H_4X\text{-}p)(C{\equiv}CPh)(PEt_3)_2$ (**20**: X = F, **23**: X = OMe). Organic products caused by the reductive elimination are not formed in the reaction mixtures at all due to high stability of the Pt–C bonds of **20** and **23**. The alkynyl ligand transfer from Cu(I) to Pt(II) complexes occurs irreversibly, and complex **23** does not react with CuI at r.t.

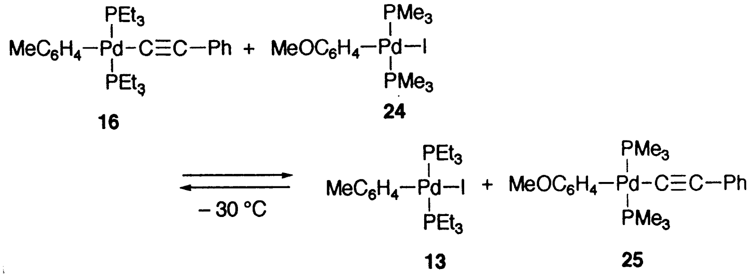
3. Alkynyl ligand transfer of Pd(II) and Pt(II) complexes

Most alkynyl ligand transfer between Pd and Pt complexes requires the addition of CuI, $HgCl_2$, and AgCl as already reported. The equimolar reaction of **16** and



Scheme 7.

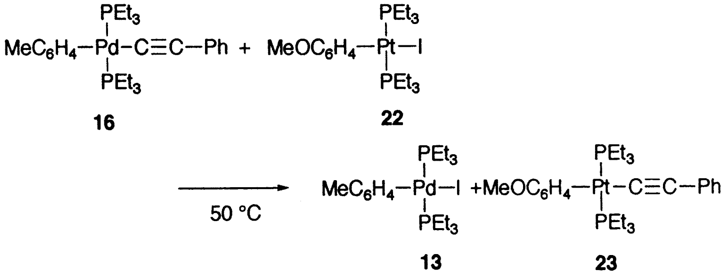
trans-Pd(C_6H_4OMe-*p*)I(PMe_3)$_2$ (**24**) at −30°C in the absence of CuI or other additives causes the alkynyl ligand exchange between the complexes to give a mixture of **13** and *trans*-Pd(C_6H_4OMe-*p*)(C≡CPh)(PMe_3)$_2$ (**25**), and the two starting complexes (Eq. (10)) [50].



(10)

The results indicate that the alkynyl ligand transfer between the Pd centers proceeds directly at the low temperature.

Heating of a toluene solution of an equimolar mixture of **16** and **22** at 50°C causes intermolecular alkynyl ligand transfer from the former complex to the latter giving a mixture of **13** and **23** (Eq. (11)).



(11)

The irreversible ligand transfer from the Pd to Pt complex is almost completed within 9 h. The $^{31}P\{^1H\}$- and ^1H-NMR spectra do not show any signals 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 during the reaction. The time–yield curves of the equimolar reaction of the complexes are shown in Fig. 2(a). Sufficient linearity of the plots of [**16**]$_0$/[**16**]$_t$ suggests that the reaction obeys the first-order kinetics of the Pd and Pt complexes. The reaction with a large excess amount of **22** under a pseudo-first-order kinetic condition gives the linear first-order plots of [**16**] as shown in Fig. 2(b). Temperature dependence of the rate constants of the reactions provided 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. The kinetics results involving second-order kinetic formulae and a negative activation entropy indicate that the reaction proceeds via a bimetallic transition state probably containing μ-η^1,η^1-alkynyl ligand bonded to Pd and Pt centers [51].

Addition of CuI ([Cu]/[Pd] = 0.10) to the transmetallation from Pd(II) to Pt(II) causes consumption of almost all the starting materials in 5 min at 50°C, while the reaction without the additive requires ca. 3 h to obtain conversion of 50% of the

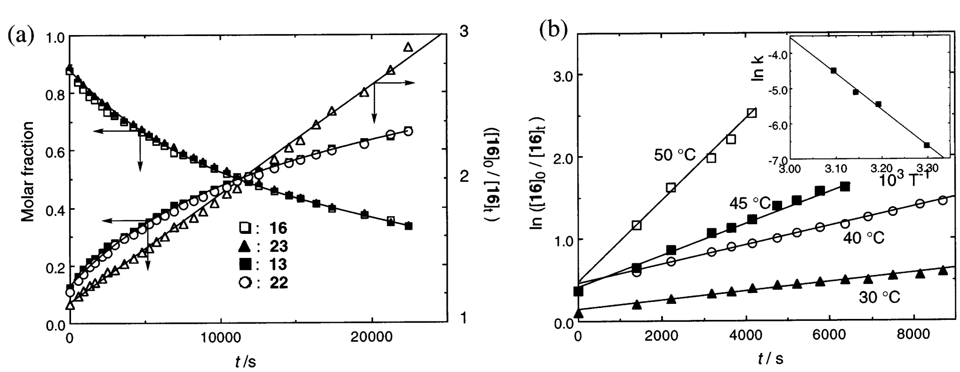
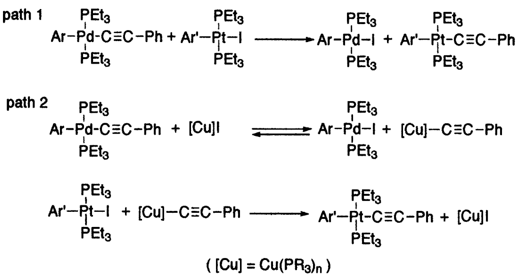


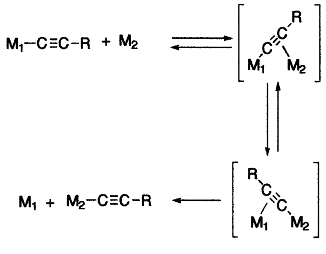
Fig. 2. Kinetic results of alkynyl ligand transfer from Pd(II) to Pt(II) complexes. (a) Time–yield curve and second-order plots of an equimolar reaction of **16** and **22** to give **13** and **23** at 50°C. $[\mathbf{16}]_0 = [\mathbf{22}]_0 =$ 0.055 M. (b) Pseudo-first-order plots of the reaction at 30–50°C in the presence of a large excess of **22**. Arrhenius plots of the kinetic data are shown in the inset.

starting complexes at that temperature. Enhancement of the reaction by addition of CuI is rationalized by assuming two independent reaction pathways in the presence of CuI. Scheme 8 depicts path 1 involving a direct ligand exchange through a transition state with bridging alkynyl ligands and path 2 in which the stepwise alkynyl ligand transfer occurs rapidly from Pd to Cu and from Cu to Pt. The latter pathway proceeds much faster than the former in the presence of the CuI additive.

Dinuclear transition metal complexes with bridging alkynyl ligands bonded to the metal centers undergo rapid switching of μ-η^1,η^2 to μ-η^2,η^1 coordination as shown in Scheme 9. The reaction proceeds through concerted cleavage and formation of the σ- and π-bond between the alkynyl carbons and two metal centers [52], although a diiron complex with bridging ethynyl ligand changes the coordination mode similarly but induced by 1,2-shift of the ethynyl hydrogen [53]. The intermolecular transfer of the alkynyl ligand among Cu, Pd, and Pt in the present study as well as in the previous studies seems to occur via formation of the bimetallic intermediates and their rapid structural change. Rapid and reversible switching of coordination between μ–η^1,η^2– and μ–η^2,η^1–bonding was observed in the NMR study of Fe and Mo multimetallic complexes containing bridging alkynyl ligands



Scheme 8.



Scheme 9.

[54–58]. The irreversible alkynyl ligand transfer reactions from copper to other late transition metals shown above suggest lower thermodynamic stability of Cu(I)–alkynyl σ-bond than σ-bond between alkynyl group and Group 6–10 transition metals. In general, the aryl–transition metal bond is thermodynamically less stable than the corresponding alkynyl–metal bond [59]. The alkynyl transfer in the present system takes place prior to intermolecular aryl ligand migration, probably because of a much higher stability of the alkynl group bridged bimetallic intermediate in the former reaction than the aryl group bridged intermediate in the latter.

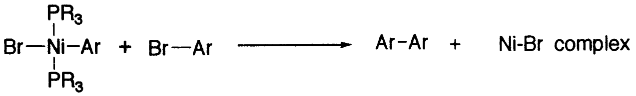
4. Aryl ligand transfer of Ni(II) complexes

Ni(0) complexes promoted dehalogenative condensation of haloarenes [60–64] and dehalogenative polycondensation of dihaloarylene are of high synthetic utility since the latter reactions afford a number of biaryls and π-conjugated polymers [65–68] as shown in Eqs. (12) and (13).

$$2\ \mathrm{Ar{-}Br} + \mathrm{Ni(cod)_2} + \mathrm{bpy} \longrightarrow \mathrm{Ar{-}Ar} + \mathrm{NiBr_2(bpy)} + 2\ \mathrm{cod} \tag{12}$$

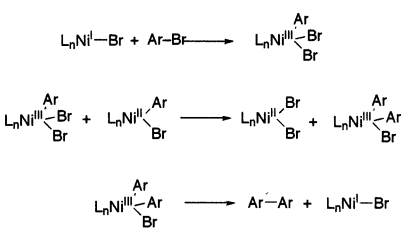
$$\mathrm{Br{-}Ar'{-}Br} + \mathrm{Ni(cod)_2} + \mathrm{bpy} \longrightarrow \left[\mathrm{Ar'} \right]_n + \mathrm{NiBr_2(bpy)} + 2\ \mathrm{cod} \tag{13}$$

Halo(aryl)nickel complexes, Ni(X)(Ar)(L)$_2$ (L = phosphine etc.), were reported to react with haloarene to give the corresponding biaryls (Eq. (14)) [69], which appears to be related to the coupling of haloarene promoted by Ni(0) complexes.



$$\mathrm{Br{-}}\underset{\mathrm{PR_3}}{\overset{\mathrm{PR_3}}{\mathrm{Ni}}}\mathrm{{-}Ar} + \mathrm{Br{-}Ar} \longrightarrow \mathrm{Ar{-}Ar} + \text{Ni-Br complex} \tag{14}$$

Kochi and co-workers proposed the mechanism of the reaction involving labile Ni(I) and Ni(III) intermediates shown in Scheme 10, based on detailed kinetic results of the reaction using PEt$_3$ ligands in THF and spectroscopic observation of the reaction mixture [70]. The characteristics of their reactions are rapid aryl group exchange between the coordinated aryl ligand bonded to the labile metal centers and uncoordinated haloarenes. The mechanism involving the Ni(II) and Ni(III) intermediate is also proposed in the addition of a C–Cl bond of CCl$_4$ to alkenes



Scheme 10.

catalyzed by a Ni complex [71,72]. Results of the study on the reaction of NiBr(Ar)(bpy) in the presence and absence of BrAr in DMF solvent gave quite different features of the reaction as described below [73]. NiBr(Ph)(bpy) (**26**) is prepared from the oxidative addition of bromobenzene to Ni(cod)$_2$ (cod = 1,5-cyclooctadiene) in toluene and is stable in the solid state. On dissolution of **26** in DMF at r.t., immediate evolution of biphenyl was noted even in the absence of additional bromobenzene in the solution. The reaction of **26** with 4-bromotoluene in DMF gave biphenyl only at the initial period of the reaction, indicating that the coupling reaction is not related to the exchange of the phenyl ligand with aryl group of bromoarene triggered by Ni(I) or Ni(III) complexes. Thus, we began to reinvestigate the coupling of bromoarene promoted by Ni(cod)$_2$ in DMF which is a common solvent used in the above coupling reaction.

The reaction of Ni(cod)$_2$ with excess bromobenzene in the presence of bpy actually gives biphenyl in a high yield, although completion of the reaction requires heating at 60–70°C. Green NiBr$_2$(bpy) was isolated as the inorganic product. Formation of the coupling product obeys second-order kinetics to the concentration of NiBr(Ph)(bpy) as depicted in Fig. 3(a). Table 3 summarizes kinetic results of the reaction under several reaction conditions. The relationship of the rate con-

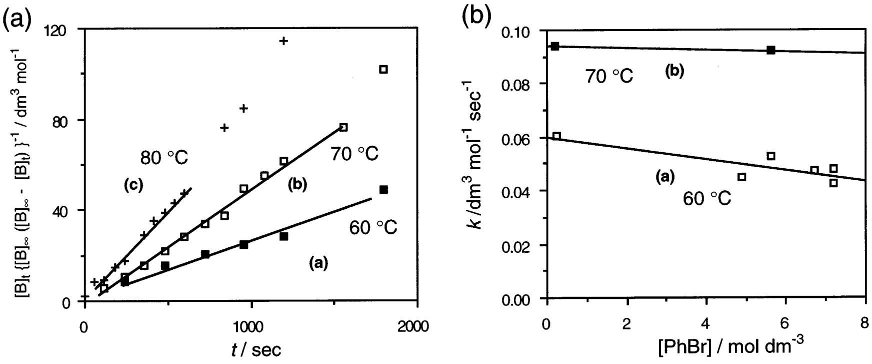


Fig. 3. Kinetic results of the coupling reaction of phenyl bromide promoted by Ni(cod)$_2$ in the presence of 2,2′-bipyridine [reaction (12)]. (a) Second-order plots of the reaction. [B] denotes the concentration of biphenyl produced. Reactions were carried out in DMF at 50, 70, and 80°C. $[\mathrm{Ni(cod)_2}]_0 = 0.043–0.051$ mol dm^{-3}; $[\mathrm{bpy}]_0 = 0.047–0.051$ mol dm^{-3}; $[\mathrm{PhBr}]_0 = 5.0–5.8$ mol dm^{-3}. (b) Dependence of the initial concentration of phenyl bromide on the second-order rate constants of the reaction at 60 and 70°C.

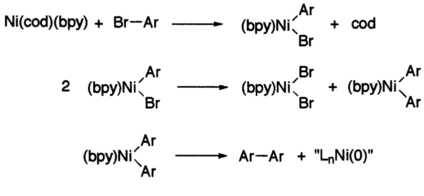
Table 3
Kinetic results of coupling of haloarene with $Ni(cod)_2$-bpy

Ar–X	Ligand	k ($dm^3\ mol^{-1}\ s^{-1}$)
PhBr	bpy	0.053
PhCl	bpy	0.0081
PhI	bpy	>1.5
PhBr	$2PPh_3$	0.16
p-$MeCOC_6H_4Br$	bpy	0.0059
p-MeC_6H_4Br	bpy	1.1
p-$MeOC_6H_4Br$	bpy	6.0

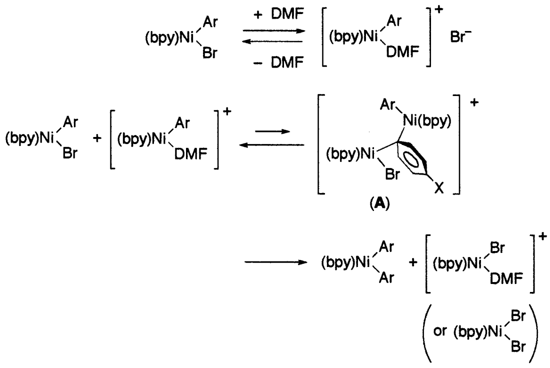
stants to concentration of bromobenzene is plotted in Fig. 3(b). The observed second-order rate constants vary to a minor extent depending on the concentration of bromobenzene in the solution. These results suggest that the rate determining step of the coupling reaction involves a bimolecular reaction process of the monoraylnickel complex rather than the reaction of the complex with bromoarene.

The plausible pathway for reaction (12) is shown in Scheme 11 which involves oxidative addition of bromobenzene to the Ni(0) complex to give **26** and its subsequent disproportionation to give an equimolar mixture of $NiBr_2(bpy)$ and $NiPh_2(bpy)$, the latter of which undergoes facile reductive elimination of biphenyl. Reductive elimination of biaryl from the diarylnickel complex $NiAr_2(bpy)$ seems to occur quite easily. The facile reductive elimination from the *cis*-diorgano transition metal was discussed from theoretical aspects [74]. Diarylplatinum complexes with a *cis* coordination undergo reductive elimination of biaryl much faster than reductive elimination of alkane from *cis*-dialkylplatinum complexes [75].

A possible mechanism for the disproportionation of **26** involves a dinuclear nickel intermediate with bridging phenyl ligands such as (A) in Scheme 12. A nickel complex with two bridging methyl ligands has been prepared and characterized unambiguously by means of X-ray crystallography [76]. The remarkable effect of the DMF solvent on the intermolecular aryl ligand transfer reaction is attributed to its enhancement of the cationic intermediate formation. Ishiguro and Ozutsumi [77], have reported calorimetric studies on the complexation of halogeno and bipyridine ligands to the Ni^{2+} ion and suggested thermodynamically more favorable formation of the cationic Ni(II)–bipyridine complex than the neutral one in DMF. The disproportionation of NiCl(Et)(bpy) was previously reported to occur at



Scheme 11.



Scheme 12.

r.t. in THF to give $NiCl_2(bpy)$ and $NiEt_2(bpy)$ [78]. Complex **26** does not react under similar conditions and releases biphenyl only in DMF probably due to a higher stability of the Ni–Ar bond in comparison with the Ni–Et bond.

Other kinetic results of the reaction of bromobenzene and its substituted derivatives are consistent with the above mechanism as described below. Phenyl halides show different reactivity of the coupling reaction depending on the kind of halogen in the order, $PhCl < PhBr < PhI$. Since Ph–Cl is much less reactive toward the oxidative addition to Ni(0) complex, its coupling reaction involves the initial activation of Cl–C bond as the rate determining step and is slower than the reactions of Ph–Br and Ph–I. A significant difference in the reaction rate of coupling of various *para* substituted bromobenzenes is also noted in the order, $CH_3CO < H < CH_3 < OCH_3$. The results can be explained as follows based on the mechanism for disproportionation which involves a dinuclear intermediate. The nickel–carbon bond strength of a *para*-substituted phenyl nickel complex decreases in the order of the substituents, $CH_3CO > H > CH_3 > OCH_3$. The disproportionation of NiAr(X)(bpy) requires activation of the nickel–carbon bond through intermediate (A). Less stable or more reactive Ni–aryl bonds undergo activation during formation of the dinuclear intermediate with greater ease to provide the order of the coupling reaction rates, $p\text{-}CH_3COC_6H_4Br < C_6H_5Br < p\text{-}CH_3C_6H_4Br < p\text{-}CH_3OC_6H_4Br$.

NiBr(Ph)(bpy) reacts with CO_2 in DMF to give a mixture of biphenyl (9%/Ni) and benzoic acid (54%/Ni), the latter of which is obtained by acidolysis of the reaction mixture (Eq. (15)) [79].

$$\mathrm{Ni(cod)_2 + bpy + Br{-}Ph} \xrightarrow[\mathrm{DMF}]{+\,\mathrm{CO_2}} \xrightarrow{+\,\mathrm{HCl_{aq}}} \mathrm{Ph{-}Ph + Ph{-}COOH} \tag{15}$$

The IR spectra of the inorganic product prior to the acidolysis indicates CO_2 insertion into the Ni–phenyl bond. Table 4 summarizes results of the carboxylation reaction under various conditions. *p*-Bromotoluene and *p*-bromofluorobenzene react similarly with CO_2 to give the corresponding aromatic carboxylic acids in 79 and 54% yield, respectively. The reactions without bpy and PPh_3 ligands give almost negligible amounts of the carboxylation product.

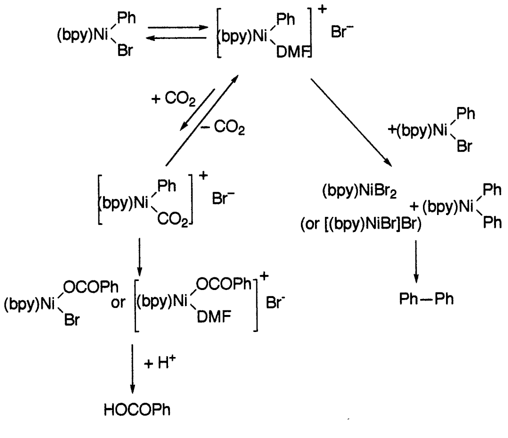
Table 4
Reaction of bromoarene with CO_2 by $Ni(cod)_2$-bpy[b]

ArBr	Conditions				Products (%)[a]	
	$[Ni(cod)_2]$ (M)	$\frac{[ArBr]}{[Ni(cod)_2]}$	Solvent	Ligand	ArCOOH	Ar–Ar
PhBr	0.030	1.0	DMF	bpy	54	9
PhBr	0.120	1.0	DMF	bpy	35	26
PhBr	0.030	1.0	DMF	–	3	9
PhBr	0.120	2.0	DMF	bpy	17	50
PhBr	0.120	2.0	DMF	–	4	81
PhBr	0.180	2.0	THF	bpy	0	81
PhBr	0.180	2.0	Benzene	bpy	0	83
p-MeC_6H_4Br	0.030	1.0	DMF	bpy	79	5
p-$MeOC_6H_4Br$	0.030	1.0	DMF	bpy	54	

[a] Yields based on the amount of $Ni(cod)_2$ used.
[b] $[bpy]/[Ni(cod)_2] = 1.0$, $[PPh_3]/[Ni(cod)_2] = 2.0$.

Concomitant biaryl formation takes place through disproportionation of the initially formed NiBr(Ar)(bpy) to give $NiBr_2(bpy)$ and $NiAr_2(bpy)$ as described above. The reaction using $Ni(cod)_2$ at 0.120 M gave biphenyl in a higher yield (26%) than the reaction using the complex at 0.030 M (9%). The reaction involving the bimetallic disproportionation is significantly enhanced in the solution with the higher concentration of the complex.

The reactions of bromobenzene with CO_2 in THF and in benzene give biphenyl exclusively but require higher temperatures than the reactions in DMF. Carboxylation was not noted even at the elevated temperature, probably due to inhibition of the reaction by the less polar solvents than DMF. The coupling reaction in the solvents seems to occur via Ni(I) and Ni(III) intermediates as proposed by Kochi



Scheme 13.

et al. Thus, the DMF solvent promotes both dehalogenative coupling and carboxylation of bromobenzene promoted by Ni(cod)$_2$-(bpy). The significant acceleration of the carboxylation by DMF suggests the reaction path involving a cationic intermediate such as [Ni(Ph)(bpy)(DMF)]$^+$Br$^-$. Scheme 13 depicts a plausible mechanism for the carboxylation and coupling of bromobenzene in DMF, which involves the cationic intermediate common to both reactions. [Ni(Ph)(bpy)(DMF)]$^+$Br$^-$ undergoes CO_2 insertion into the Ni–C bond or intermolecular aryl ligand transfer to give NiAr$_2$(bpy) depending on the reaction conditions. The intermediate complex has both the labile DMF ligand which could be replaced easily by CO_2 molecule and the metal center with high Lewis acidity to form a stable bond with CO_2 oxygen. Thus, the reaction affords products of both the homocoupling and the carboxylation.

As shown above, cationic arylnickel complexes with bipyridine ligand undergo smooth intermolecular aryl ligand exchange. Recently, some diarylpalladium complexes were reported to cause intermolecular exchange through non-ionic intermediate species [80–82]. Coordinatively unsaturated Pd intermediates formed via dissociation of neutral supporting ligand such as phosphine and thioether are responsible for the transmetallation reactions.

5. Conclusions

Alkynyl and aryl complexes of Group 10 transition metals undergo transmetallation with halogenated complexes of these metals. Direct intermolecular transfer of the alkynyl ligands sometimes occurs although the CuI aided path is kinetically more favorable in the reaction with added CuI. Detailed reports of aryl ligand transfer are still rare, and its elucidation of future interest. Design of the method to generate coordinatively unsaturated species suited for transmetallation seems to be helpful for further progress of study in this field.

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