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Mechanism of C–C coupling reactions of aromatic halides, promoted by $Ni(COD)_2$ in the presence of 2,2′-bipyridine and PPh_3, to give biaryls *

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Abstract

Reactions of aryl halides, such as phenyl bromide, *p*-methylphenyl bromide, *p*-acetylphenyl bromide, *p*-methoxyphenyl bromide, phenyl chloride, and phenyl iodide, with $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) in the presence of 2,2′-bipyridine (BPY) or PPh_3 as the auxiliary ligand give the corresponding biaryl as the coupling product at 50–70 °C in DMF. Reaction of phenyl bromide with $Ni(COD)_2$–BPY in benzene at room temperature gives NiBr(Ph)(BPY) (**1**). Heating a DMF solution of a mixture of **1** and phenyl bromide at 60 °C gives biphenyl, while **1** dissolved in DMF liberates biphenyl at room temperature. Reaction of a large excess amount of phenyl bromide with the $Ni(COD)_2$-BPY system obeys second-order kinetics to the nickel complex. Concentration of phenyl bromide in the range 0.2–7.2 mol dm^{-3} influences the reaction rate to little extent. Temperature dependence of the rate constants gives the kinetic parameters of $\Delta G^{\ddagger}_{333} = 90$ kJ mol^{-1}, $\Delta H^{\ddagger}_{333} = 60$ kJ mol^{-1} and $\Delta S^{\ddagger}_{333} = -90$ J mol^{-1} K^{-1}, respectively. The reactivity of phenyl halide increases in the order, PhCl < PhBr < PhI. Substitution of the para hydrogen of phenyl bromide with an electron-withdrawing group causes lowering of the rate constant, whereas introduction of an electron-donating group like OCH_3 enhances the reaction. The Hammett plot of the reaction shows linear correlation between the σ value of the substituent and the logarithm of the second-order rate constants giving the ρ value of -2.4. Based on the results, the mechanism of the coupling reaction of PhBr is proposed to involve disproportionation of the intermediate NiBr(Ph)(BPY) as the rate determining step to give $NiPh_2(BPY)$ which is responsible for the reductive elimination of biphenyl under the reaction conditions.

Introduction

Transition metal promoted coupling of organic halide leading to C–C bond formation plays an important role in synthetic organic reactions as well as in polymer synthesis. Zerovalent nickel complexes such as $Ni(CO)_4$, $Ni(PPh_3)_n$, and $Ni(COD)_2$ are effective for dehalogenative dimerization of various organic halides such as aryl halide, vinyl halide, allylic halide, and benzyl halide [1–3]. The nickel

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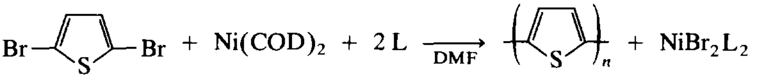
* Dedicated to Professor Akio Yamamoto on his retirement from Tokyo Institute of Technology and in honor of his contribution to organometallic chemistry.

complex promoted intramolecular coupling of allylic halide was applied to synthesis of large-ring cyclic dienes and vitamin K [4,5]. Homocoupling of aryl halide or benzyl halide was achieved using a catalytic amount of Ni^{II} complexes in the presence of zinc powder [6–8].

In the course of our study on the electrical conducting polymers with π-conjugated structures we have developed polycondensation of Br–Y–MgBr (Y = 1,4-phenylene, 2,5-thienylene, 3-methyl-2,5-thienylene, etc.) using nickel complex catalyzed cross-coupling of organomagnesium compounds with organic halides [9]. More recently, we have observed $Ni(COD)_2$ promoted dehalogenative condensation of dihaloaromatic compounds to give the π-conjugated polymers [10,11]. This preparation method gives poly(2,5-thienylene) which shows higher electrical conductivity and crystallinity than that prepared by the above cross-coupling procedure. In addition, the latter preparation method enabled polycondensation of 2,5-dibromopyridine to give poly(2,5-pyridinediyl), which had not been obtained by the other polycondensation methods.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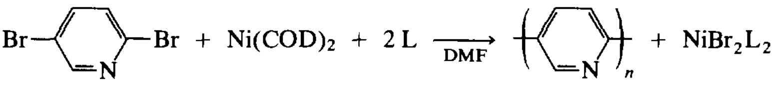
(2)

$(L = PPh_3, \frac{1}{2}BPY)$

A polar solvent such as DMF is suitable for reactions 1 and 2 as well as for the coupling reaction of aryl halide promoted by $Ni(COD)_2$ [2].

These coupling reactions of aryl halides promoted by zero valent nickel complexes seem to involve oxidative addition of the substrate to the Ni^0 complex and reductive elimination of the product from a diorganonickel intermediate as crucial steps. However, the detailed mechanism for the clean coupling of the aromatic halides has not been studied in detail. Although there have been many fundamental studies on the C–C coupling from the organonickel complexes from experimental [12–18] and theoretical [19,20] aspects, only few reports have been published on the details of the reductive elimination to cause C–C bond formation in polar solvents such as DMF and DMSO [21].

In order to elucidate the reaction mechanism we examined the kinetic measurement of the coupling reaction of aromatic halides using $Ni(COD)_2$–2,2′-bipyridine system in DMF. Here we report the kinetic features of the reaction as well as the chemical properties of the possible intermediate NiBr(Ph)(BPY), and discuss the pathways of the coupling reaction.

Results

Coupling of aryl halide promoted by $Ni(COD)_2$ in the presence of BPY or PPh_3

Reaction of $Ni(COD)_2$ with excess phenyl bromide in the presence of 2,2′-bipyridine at 50–70 °C in DMF proceeds smoothly to give biphenyl in above 80% yield. The color of the reaction mixture changes from yellow to purple immediately showing the formation of Ni(BPY)(COD) [22], and then into red in a quite a short

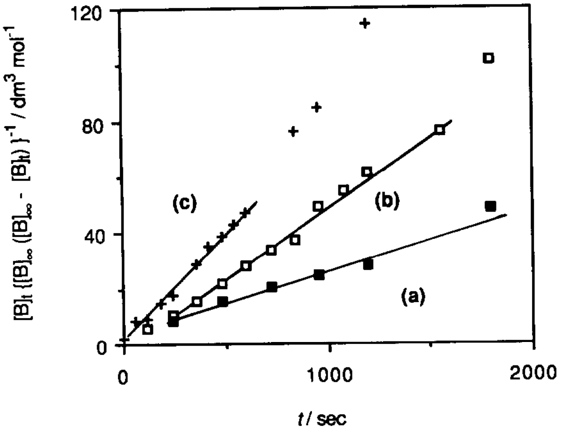

Fig. 1. Second-order plots of the coupling reaction of phenyl bromide promoted by $Ni(COD)_2$ in the presence of 2,2'-bipyridine (reaction 3). [B] denotes the concentration of biphenyl produced. Reactions were carried out in DMF at (a) 50 ° C, (b) 60 ° C, and (c) 70 ° C. $[Ni(COD)_2]_0 = 0.043\text{–}0.051$ mol dm^{-3}; $[BPY]_0 = 0.047 - 0.051$ mol dm^{-3}; $[PhBr]_0 = 5.0\text{–}5.8$ mol dm^{-3}.

period. The reaction mixture undergoes further color change to green showing formation of $NiBr_2(BPY)$.

$$Ni(COD)_2 + 2\,PhBr + BPY \longrightarrow Ph{-}Ph + NiBr_2(BPY) \qquad (3)$$

The coupling reaction of phenyl bromide promoted by $Ni(COD)_2\text{–}PPh_3$ mixture also gives biphenyl under similar conditions. Semmelhack and his co-workers have reported similar dimerization of aryl halide using $Ni(COD)_2$ without addition of the auxiliary ligand [2]. The reaction without the ligand is completed within 10 min at 60 ° C in DMF, and it seems to proceed faster than reaction 3.

Formation of biphenyl in the reaction of the $Ni(COD)_2\text{–}BPY$ (1 : 1) system with phenyl bromide (100–120 equiv of $Ni(COD)_2$) at 50–70 ° C was followed by means of a gas chromatograph. The reaction obeys second-order kinetics to the nickel complex [23*]. Figure 1 shows typical second-order plots which show linear correlation up to 70% conversion. Table 1 summarizes the kinetic results of the coupling of phenyl bromide and those of similar aryl halides under various conditions. The rate constants of the reaction at 60 ° C using phenyl bromide at the concentrations of 4.9–7.2 mol dm^{-3} are observed in the range 0.043–0.053 dm^3 mol^{-1} s^{-1} (runs 2, 6–9 in Table 1) and do not depend on the substrate concentration. The reaction of $Ni(COD)_2\text{–}BPY$ mixture with 2 equiv of phenyl bromide (0.24 mol dm^{-3}, run 5) at 60 ° C also roughly obeys second-order kinetics, and gives the rate constant of 0.060 dm^3 mol^{-1} s^{-1}. Figure 2 shows dependence of the rate constants on the concentration of phenyl bromide both at 60 ° C and at 70 ° C. The concentration of phenyl bromide does not influence the rate constants essentially. All these results indicate that the rate-determining step of the coupling reaction involves a bimolecular reaction process between the nickel complex rather than reaction of the nickel complex with phenyl bromide.

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* Reference numbers with asterisk indicate notes in the list of references.

Table 1

Kinetic results of the coupling reaction of aryl halides promoted by $Ni(COD)_2$ [a]

Run	ArX	$[ArX]_0$ ($mol\ dm^{-3}$)	$[Ni(COD)_2]_0$ ($mol\ dm^{-3}$)	$[Ligand]_0$ [b] ($mol\ dm^{-3}$)	Temp. (K)	k ($dm^3\ mol^{-1}\ s^{-1}$)
1	PhBr	5.0	0.043	0.047	323	0.024
2	PhBr	5.6	0.051	0.051	333	0.053
3	PhBr	5.8	0.051	0.053	338	0.081
4	PhBr	5.6	0.047	0.048	343	0.092
5	PhBr	0.24	0.12	0.12	333	0.060
6	PhBr	4.9	0.065	0.072	333	0.045
7	PhBr	6.7	0.039	0.040	333	0.047
8	PhBr	7.2	0.038	0.040	333	0.043
9	PhBr	7.2	0.025	0.027	333	0.048
10	PhBr	0.19	0.11	0.11	343	0.094
11	p-$MeCOC_6H_4Br$	4.5	0.046	0.049	333	0.0059
12	p-MeC_6H_4Br	5.0	0.051	0.051	333	1.1
13	p-$MeOC_6H_4Br$	2.1	0.048	0.048	333	6.0
14	PhCl	6.0	0.057	0.057	333	0.0081
15	PhI	5.0	0.046	0.046	333	> 1.5 [c]
16	PhBr	5.2	0.061	0.123	333	0.0013
17 [d]	PhBr	5.7	0.051	0.055	333	0.038
18	PhBr	0.28	0.13	0.27 [e]	333	0.16

[a] The reaction was carried out in DMF under argon or nitrogen atmosphere. The final product yields are in the range 75–100%. [b] 2,2′-Bipyridine is used as the auxiliary ligand except for run 18. [c] Precise rate constant is not determined owing to the rapid reaction. [d] 1,5-Cyclooctadiene (0.10 mol dm^{-3}) is added to the reaction mixture. [e] PPh_3 is used as the ligand.

The Eyring plot of the reaction is shown in Fig. 3. Temperature dependence of the reaction of phenyl bromide gives the kinetic parameters of $\Delta G^{\ddagger}_{333} = 90$ kJ mol^{-1}, $\Delta H^{\ddagger}_{333} = 60$ kJ mol^{-1} and $\Delta S^{\ddagger}_{333} = -90$ J mol^{-1} K^{-1}, respectively. Substitution of the *para* hydrogen of phenyl bromide with an electron-withdrawing group

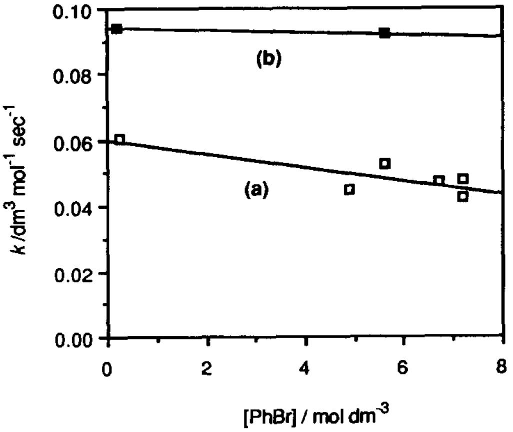


Fig. 2. Dependence of the initial concentration of phenyl bromide on the second-order rate constants of reaction 3 at (a) 60 ° C and (b) 70 ° C. Detailed reaction conditions and the rate constants are shown in Table 1 (Runs 2, 4–10).

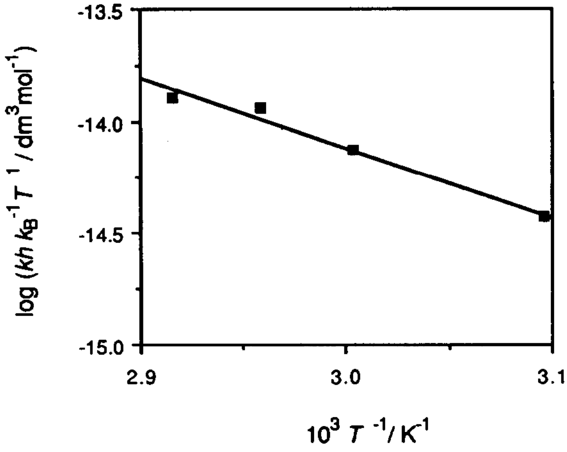


Fig. 3. Eyring plot of reaction 3. Detailed reaction conditions and the rate constants are shown in Table 1 (runs 1–4).

causes lowering of the rate constant (run 11 in Table 1), whereas introduction of electron-donating groups like CH_3 and OCH_3 enhances the reaction (runs 12, 13 in Table 1). Figure 4 shows the Hammett plot of the reaction. The log *k* values change linearly depending on the σ value of the substituents. The ρ value of the reaction is determined as -2.4 from the slope of the plot. The coupling reaction of phenyl chloride with $Ni(COD)_2$–BPY proceeds much more slowly than the reaction of phenyl bromide (run 14 in Table 1), while the reaction of phenyl iodide (run 15 in Table 1) is much faster than these reactions.

The coupling reaction of phenyl bromide promoted by $Ni(COD)_2$ in the presence of PPh_3 also obeys second-order kinetics similarly to the reaction using 2,2′-bipyridine as the ligand. The rate constant of the reaction using 2 equiv of

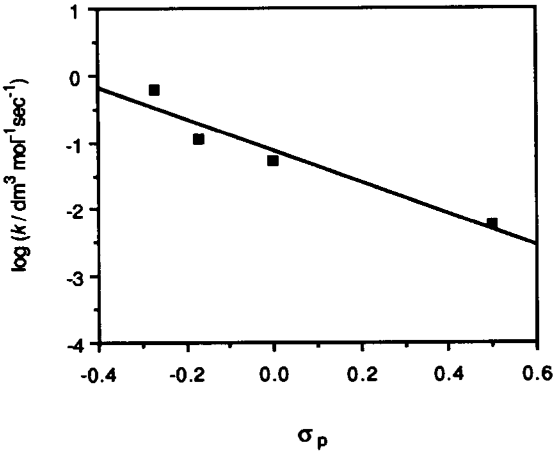
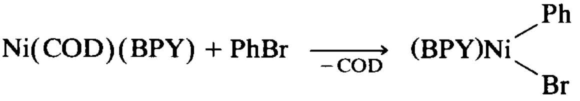


Fig. 4. Hammett plot of the coupling reaction of p-XC_6H_4Br ($X = CH_3CO$, H, CH_3, and CH_3O) to give p-XC_6H_4–C_6H_4–p-X promoted by $Ni(COD)_2$ in the presence of 2,2′-bipyridine. Detailed reaction conditions and the rate constants are shown in Table 1 (runs 2, 11–13).

PPh_3 to $Ni(COD)_2$ is considerably larger than the reaction with BPY ligand (run 18 in Table 1).

Preparation and properties of NiBr(Ph)(BPY) (1)

Reaction of a 1:1 mixture of $Ni(COD)_2$ and 2,2′-bipyridine with excess amount of phenyl bromide proceeds smoothly at room temperature to give a red solid which shows the IR spectrum identical with that of NiBr(Ph)(BPY) (**1**).

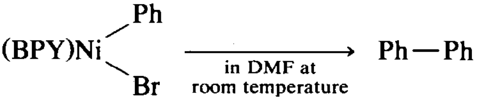


$$\mathrm{Ni(COD)(BPY)} + \mathrm{PhBr} \xrightarrow[-\mathrm{COD}]{} \mathrm{(BPY)Ni}\begin{smallmatrix}\diagup \mathrm{Ph} \\ \diagdown \mathrm{Br}\end{smallmatrix} \qquad (4)$$

(**1**)

Complex **1** has been prepared separately by reaction of $NiEt_2(BPY)$ with an excess amount of phenyl bromide [24].

A DMF solution of **1** gives biphenyl (80% yield) after stirring for 10 min at room temperature accompanied by deposition of a small amount of nickel metal.

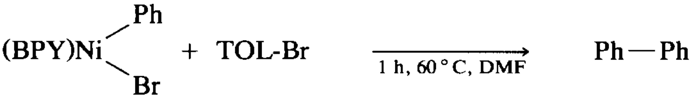


$$\mathrm{(BPY)Ni}\begin{smallmatrix}\diagup \mathrm{Ph} \\ \diagdown \mathrm{Br}\end{smallmatrix} \xrightarrow[\text{room temperature}]{\text{in DMF at}} \mathrm{Ph{-}Ph} \qquad (5)$$

(**1**)

A DMF solution of **1** containing equimolar phenyl bromide is stable at room temperature, and does not cause the formation of biphenyl. Complex **1** is stable with and without phenyl bromide in toluene solutions at room tempeature. Heating the toluene solution under much more severe conditions (12 h at 70 °C) affords biphenyl in 36% yield. These results seem to indicate that decomposition of **1** giving biphenyl is retarded by addition of phenyl bromide and that the polar solvent DMF promotes the reaction significantly.

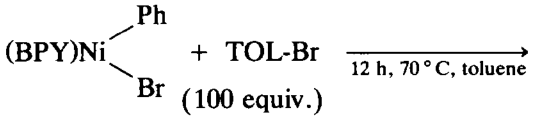
On the other hand, reaction of complex **1** with excess *p*-methylphenyl bromide (100 equiv of **1**) at 60 °C in DMF gives biphenyl in 61% yield. The absence of 4-methylbiphenyl or 4,4′-dimethylbiphenyl in the reaction mixture is confirmed by GC analysis [25*]. Probably the bimolecular reaction of **1** to give biphenyl is considered to occur prior to reaction of **1** with *p*-methylphenyl bromide that would afford 4-methylbiphenyl.



$$\mathrm{(BPY)Ni}\begin{smallmatrix}\diagup \mathrm{Ph} \\ \diagdown \mathrm{Br}\end{smallmatrix} + \mathrm{TOL\text{-}Br} \xrightarrow[1\ \mathrm{h},\ 60\,^{\circ}\mathrm{C},\ \mathrm{DMF}]{} \mathrm{Ph{-}Ph} \qquad (6)$$

(**1**) $(\mathrm{TOL} = p\text{-}CH_3C_6H_4)$

On the other hand, reaction of **1** with *p*-methylphenyl bromide in toluene shows somewhat different features from reaction 6. More severe conditions (at 70 °C for 12 h) than that of 6 are required for the completion of the reaction because formation of biaryl is much slower in toluene than the reaction in DMF.



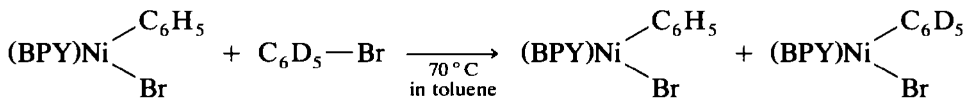
(1)

$$\text{Ph—Ph} + \text{Ph—TOL} + \text{TOL—TOL} \quad (7)$$

8% 8% 21%

(TOL = p-$CH_3C_6H_4$)

GC analysis of the reaction mixture shows formation of a mixture of biphenyl, 4-methylbiphenyl, and 4,4′-dimethylbiphenyl. The amount of the two latter products derived from *p*-methylphenyl bromide is larger than that of biphenyl. In order to reveal the pathway of formation of these products, reaction of **1** with deuterated phenyl bromide was examined in toluene.



(1) (1-d_5)

(8)

Formation of a considerable amount of the aryl-exchanged product, (BPY)NiBr(C_6D_5) (**1**-d_5), is observed in the reaction mixture (cf. Fig. 5 and Experimental) after the reaction for 30 min at 70 °C although formation of biphenyl is negligible

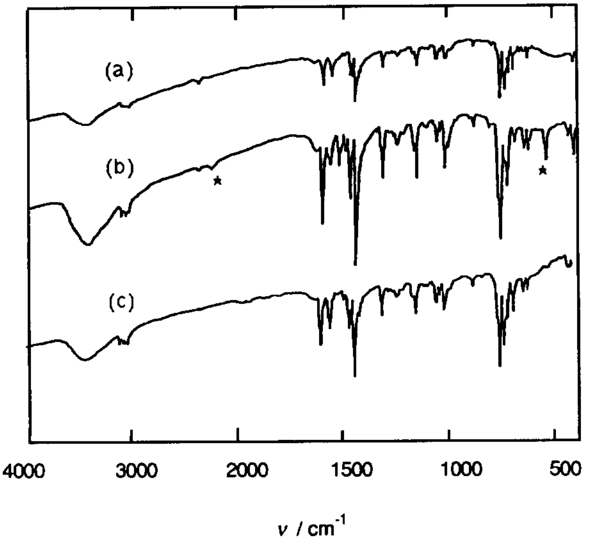


Fig. 5. IR spectra of (a) complex 1, (b) the reaction product of 1 with deuterated phenyl bromide, and (c) the reaction product of 1 with non-deuterated phenyl bromide. The peaks with mark are owing to the deuterated phenyl ligand.

at that time. The reaction 8 suggests formation of intermediate $NiBr(C_6H_4\text{-}p\text{-}Me)(BPY)$ (**2**) in the reaction mixture of **7**. Formation of 4-methylbiphenyl and 4,4′-dimethylbiphenyl can be attributed to the reaction of **1** with **2** and that between **2**, respectively. Direct reaction of **1** with *p*-methylphenyl bromide and of **2** with *p*-methylphenyl bromide also accounts for formation of these hydrocarbon products, respectively. Our present data are not sufficient to exclude one of the above two reaction pathways for formation of 4-methylbiphenyl and 4,4′-dimethylbiphenyl. Kochi and his co-worker discussed details of a similar reaction of $NiBr(Ph)(PPh_3)_2$ with *o*-methoxyphenyl bromide in cyclohexane to give $NiBr(C_6H_4\text{-}o\text{-}OMe)(PPh_3)_2$ accompanied by liberation of phenyl bromide [26]. This reaction was considered to involve Ni^I and Ni^{III} species as the intermediates.

Although the exchange of the aryl group between the aryl nickel complex and aryl bromide does not occur at 60 °C in DMF, the aryl group exchange is observed in toluene at higher temperature. Clean coupling of aryl group ligating to the nickel center in DMF is probably owing to facile disproportionation of monoaryl nickel complexes NiX(Ar)(BPY) in the solvent.

Reactions of a mixture of aryl halides with $Ni(COD)_2$–BPY

Reaction of the $Ni(COD)_2$–BPY system with a mixture of phenyl bromide and *p*-methylphenyl bromide (61 and 52 equiv of $Ni(COD)_2$, respectively) gives a mixture of biphenyl, 4-methylbiphenyl, and 4,4′-dimethylbiphenyl in yields of 33%, 29%, and 3%, respectively.

$$Ni(COD)_2 + BPY + \underset{61\text{ equiv}}{Ph{-}Br} + \underset{52\text{ equiv}}{TOL{-}Br} \xrightarrow[60\,^{\circ}C,\ DMF]{} \underset{33\%}{Ph{-}Ph} + \underset{29\%}{Ph{-}TOL} + \underset{3\%}{TOL{-}TOL} \quad (9)$$

$$(TOL = p\text{-}CH_3C_6H_4)$$

The amount of phenyl moiety incorporated from phenyl bromide into the product is larger than that of the *p*-methylphenyl moiety derived from *p*-methylphenyl bromide. This fact is in contrast with the observation that the rate constant for the coupling reaction of phenyl bromide promoted by the $Ni(COD)_2$–BPY system is smaller than that of *p*-methylphenyl bromide. The reaction mixture probably contains two intermediate aryl nickel complexes **1** and **2** formed from oxidative addition of phenyl bromide and *p*-methylphenyl bromide to Ni(BPY)(COD), respectively. Formation of 4-methylbiphenyl and 4,4′-dimethylbiphenyl is responsible for the reaction of **1** with **2** and for that between two molecules of **2**, respectively. The relative amounts of the coupling products in reaction 9 seems to be principally determined by the ease of the oxidative addition of the aryl bromides.

Discussion

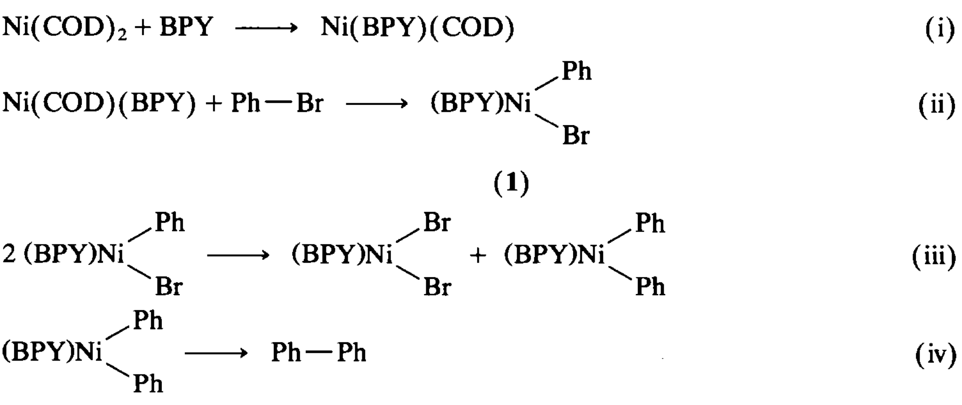
Since the reaction of $Ni(COD)_2$–BPY system with phenyl bromide at room temperature gives NiBr(Ph)(BPY) **1**, formation of biphenyl observed in the reaction at higher temperature in DMF proceeds through formation and subsequent degradation of **1**.

Formation of **1** involves oxidative addition of phenyl bromide to Ni(BPY)(COD) which is generated in the reaction mixture. Since oxidative addition of carboxylic ester to Ni(BPY)(COD) leading C–O bond cleavage is more facile than that to $Ni(COD)_2$ [27], Ni(BPY)(COD) is considered as the most reactive species toward oxidative addition of phenyl bromide among zero valent nickel complexes in the reaction mixture. Addition of 2 equiv of 2,2′-bipyridine to the reaction mixture causes significant lowering of the reaction rate. This result is probably owing to much slower oxidative addition of phenyl bromide to $Ni(BPY)_2$, which is the major Ni(0) complex in the reaction mixture, than that to Ni(BPY)(COD).

Several pathways are possible for formation of biphenyl from complex **1** in the presence of excess phenyl bromide. Previously we have proposed tetravalent nickel intermediate in the reaction of dimethylnickel complexes with propyl bromide to give a mixture of propane and methane [28]. The corresponding Pd^{IV} complexes with three alkyl or aryl ligands have been isolated using 2,2′-bipyridine as the auxiliary ligand [29,30]. Similar Pd^{IV} complexes with phosphine ligands were postulated as the intermediate in the reaction of dimethylpalladium complex with methyl iodide to give ethane as the coupling product [31]. The oxidative addition of the organic halide to the dialkyl nickel complex seems to be facilitated by electron donating two alkyl ligands which makes the electron density of the nickel center considerably higher than the other Ni^{II} complexes [12a]. There have been no reports on formation of tetravalent nickel complexes with two alkyl and two halogen ligands from the reaction of monoalkyl nickel complex with organic halide. On the other hand, Kochi and his co-workers have reported the coupling reaction of aryl nickel complex with organic halide to cause C–C bond formation through the intermediate radical complex [14]. However, the above two reaction pathways proposed for the reactions of organonickel complexes with organic halide do not agree with the kinetic results of reaction 3 whose rate is independent of the concentration of phenyl bromide and is second-order to the nickel complex.

The conceivable pathway for reaction 3 is shown in Scheme 1.

The reaction involves the oxidative addition (ii) of phenyl bromide to Ni(BPY)(COD) to give **1** and its subsequent disproportionation (iii) to give $NiBr_2(BPY)$ and $NiPh_2(BPY)$, the latter of which undergoes facile reductive elimination of biphenyl (iv). The disproportionation of monoalkyl nickel complex



$$Ni(COD)_2 + BPY \longrightarrow Ni(BPY)(COD) \qquad \text{(i)}$$

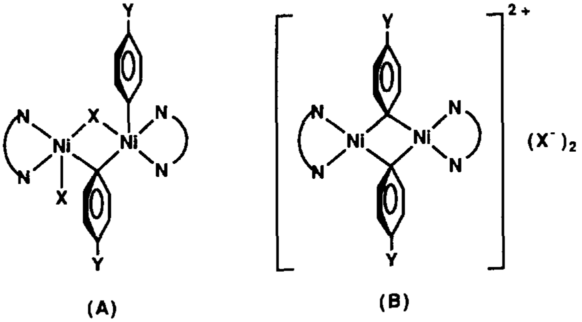
$$Ni(COD)(BPY) + Ph{-}Br \longrightarrow (BPY)Ni\begin{smallmatrix} Ph \\ Br \end{smallmatrix} \qquad \text{(ii)}$$

(1)

$$2\,(BPY)Ni\begin{smallmatrix} Ph \\ Br \end{smallmatrix} \longrightarrow (BPY)Ni\begin{smallmatrix} Br \\ Br \end{smallmatrix} + (BPY)Ni\begin{smallmatrix} Ph \\ Ph \end{smallmatrix} \qquad \text{(iii)}$$

$$(BPY)Ni\begin{smallmatrix} Ph \\ Ph \end{smallmatrix} \longrightarrow Ph{-}Ph \qquad \text{(iv)}$$

Scheme 1.



Scheme 2.

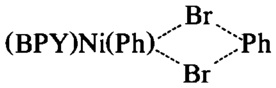
such as NiCl(Et)(bpy) was reported to proceed quite rapidly even at room temperature [32]. Complex NiMe(ACAC)(PPh$_3$) (ACAC = 2,4-pentanedionato) reacted with pyridine to give Ni(ACAC)$_2$(PY)$_2$ (PY = pyridine) accompanied by evolution of ethane [33]. The reaction was considered to involve disproportionation of the complex to give dimethyl nickel complex which underwent reductive elimination of ethane under the reaction conditions. The reaction also obeys second-order kinetics to the nickel complex. Thermal reaction of NiCl(Ar)(PPh$_3$)$_2$ gave NiCl(PPh$_3$)$_2$ accompanied by formation of biphenyl [34]. The reaction can be interpreted to involve disproportionation of the complex followed by reductive elimination of biaryl to give NiCl$_2$(PPh$_3$)$_2$ and Ni(PPh$_3$)$_n$ which reacted further to give NiCl(PPh$_3$)$_2$.

A possible mechanism for the disproportionation of **1** involves dinuclear nickel complex with bridging phenyl and bromo ligands such as **A** in Scheme 2. A nickel complex with two bridging methyl ligands has been prepared and characterized unambiguously by means of X-ray crystallography [35]. Although bridging phenyl nickel complexes have not been reported, the corresponding dinuclear palladium complex with a bridging phenyl ligand has been proposed as the key intermediate of the ligand exchange reaction [36]. A heterodinuclear complex containing rhodium and titanium atoms which are bound through a bridging phenyl ligand has been isolated [37].

Phenyl halides show difference in the reactivity of coupling reaction promoted by the Ni(COD)$_2$–BPY in the order, PhCl < PhBr < PhI. Significant difference in the reaction rate of coupling of various para substituted aryl bromide is also noted in the order, $CH_3CO < H < CH_3 < OCH_3$. These results can be explained as follows on the basis of the mechanism for disproportionation involving **A** as the intermediate. The nickel halogen bond strength decreases in the order, NiCl > NiBr > NiI, while the nickel carbon bond strength of para-substituted phenyl nickel complex decreases in the order of the substituents, $CH_3CO > H > CH_3 > CH_3O$. Since the disproportionation of (BPY)NiX(Ar) proceeds through metathesis-like activation of both the nickel carbon and the nickel-halogen bonds through intermediate **A**, the reaction rate increases in the order, PhCl < PhBr < PhI, and p-$CH_3COC_6H_4Br$ < C_6H_5Br < p-$CH_3C_6H_4Br$ < p-$CH_3OC_6H_4Br$. Alternative intermediate **B** in Scheme 2 also accounts for the enhancement of the reaction by polar solvent such as DMF and difference of the reactivity for the coupling among

PhCl, PhBr, and PhI. Our present data are not sufficient to determine the structure of the intermediate of (iii) in Scheme 1 between **A** and **B** unambiguously.

However, the observation that formation of biphenyl from isolated NiBr(Ph)(BPY) proceeds much more smoothly in polar solvent like DMF than in non-polar solvent like toluene (see above) suggests participation of a certain ionic species. The suppression effect of PhBr against the formation of biphenyl from isolated NiBr(Ph)(BPY) at room temperature may be accounted for by formation of a less reactive adduct like



$$(BPY)Ni(Ph)\begin{matrix} \cdot^{Br}\cdot \\ \cdot_{Br}\cdot \end{matrix}Ph$$

in which ionic dissociation of Br^- is retarded. At higher temperature (e.g. 60 ° C), PhBr will be dissociated from the adduct to promote the C–C coupling according to Scheme 1.

Reductive elimination of biaryl from the diaryl nickel complex $NiAr_2(BPY)$ seems to be quite fast although properties of *cis*-diaryl nickel compounds were not studied in detail owing to the thermal instability. Previously we observed more rapid reductive elimination of *cis*-NiMeAr(DMPE) (DMPE = 1,2-bis[dimethylphosphino]ethane) than *cis*-$NiMe_2$(DMPE) [15]. Attempts to isolate the corresponding *cis*-$NiAr_2$(DMPE) was not successful owing to the extremely rapid reductive elimination of biaryl. This facile reductive elimination of the aryl ligand has been well discussed from the theoretical aspects [38].

In summary, the coupling reaction proceeds through several steps as shown in Scheme 1. The rate-determining step is considered for the process (iii) based on the kinetic results of the whole reaction. Processes (i), (ii), and (iv) have been recognized as quite rapid reactions in the previous studies on various organonickel complexes. A large negative $\Delta S^{\ddagger}$ value of the coupling reaction also agrees with the reaction mechanism.

The results of competing coupling between phenyl bromide and *p*-methylphenyl bromide by the $Ni(COD)_2$–BPY system (eq. 9) can be explained on the basis of the mechanism in Scheme 1. Oxidative addition of phenyl bromide to the Ni(0) complex is faster than that of *p*-methylphenyl bromide owing to the lower electron density on the carbon bonded to halogen. Accordingly, the reaction mixture contains a larger amount of monoaryl nickel intermediate **1** than the corresponding **2**. Since the aryl ligand in the complexes does not undergo exchange with that of coexisting aryl bromide in DMF, biphenyl is obtained from reaction between two molecules of **1** in higher yield than 4-methylbiphenyl and 4,4′-dimethylbiphenyl which are formed by the reaction of **2** with **1** and the bimolecular reaction of **2**, respectively. Thus the phenyl moiety is incorporated into the reaction product to a larger extent than the *p*-methylphenyl moiety despite the smaller rate constant of phenyl bromide for the coupling reaction than *p*-methylphenyl bromide.

The rate constant of biphenyl formation in the reaction of **1** with phenyl bromide (run 2 in Table 1) is smaller than that of the reaction of $Ni(COD)_2$–BPY mixture with phenyl bromide. The rate constant of the reaction of **1** with phenyl bromide is improved to a considerable extent by addition of 1,5-cyclooctadiene although it is smaller than that of reaction 3 under similar conditions (Table 2). Final yields of biphenyl in reaction 5 with and without addition of 1,5-

Table 2

Kinetic results of the reaction of NiBr(Ph)(BPY) with phenyl bromide [a]

Run	$[PhBr]_0$ (mol dm^{-3})	$[NiBr(Ph)(BPY)]_0$ (mol dm^{-3})	Yield (%) [b]	k (dm^3 mol^{-1} s^{-1})
1	5.0	0.043	27	0.024
2 [c]	5.6	0.051	35	0.036

[a] The reaction was carried out at 60 °C in DMF for 20 h (run 1) and 24 h (run 2), respectively. [b] Final yields of biphenyl based on **1** by GC are shown. [c] 1,5-Cyclooctadiene (0.10 mol dm^{-3}) is added to the reaction mixture.

cyclooctadiene are not high (< 40%) while the yield of reaction 3 attains above 80%. Despite the disagreement of reaction rate and yield among reactions 3 and 5 the other kinetic features as well as reactivities of these nickel complexes seem to indicate strongly the intermediacy of **1** in the Ni^0 complex promoted coupling of phenyl halide. A small amount of nickel(0)–COD complexes in the reaction mixture of 3 may make oxidative addition of phenyl bromide to Ni^0 species generated by the disproportionation of **1** followed by reductive elimination of biphenyl more facile although our data are not sufficient to reveal these details of the reactions.

Conclusion

$Ni(COD)_2$ promotes dehalogenative dimerization of aryl halide to give biaryl in the presence of a proper amount of 2,2'-bipyridine or PPh_3 as the ligand in DMF. This reaction proceeds through initial oxidative addition of the substrate to Ni(BPY)(COD) generated in the reaction mixture to give NiX(Ar)(BPY) which undergoes disproportionation reaction and subsequent formation of biaryl. The disproportionation process of relatively stable NiX(Ar)(BPY) to give $NiAr_2(BPY)$, which is ready to undergo quite facile reductive elimination of the product, is the rate-determining step of the reaction. Choice of the polar solvent which makes the disproportionation process much easier than non-polar solvents is essential for the clean formation of the coupling product.

Experimental

All the manipulations of the complexes were carried out under a nitrogen or argon atmosphere. Gas chromatographic analysis was performed on a Shimadzu GC-3BT gas chromatograph using a 2 m column packed with Silicone OV-1. IR spectra were measured on a JASCO IR810 spectrophotometer. $Ni(COD)_2$ [39], NiBr(Ph)(BPY) [24] and $NiEt_2(BPY)$ [40] were prepared according to the literature method, respectively. C_6D_5Br was purchased from CEA (Commisariat à l'Energie Atomique).

Kinetic measurement of the coupling reaction of aryl halides promoted by $Ni(COD)_2$–BPY system

A typical reaction was carried out as follows. To a Schlenk flask containing $Ni(COD)_2$ (160 mg, 0.58 mmol), 2,2'-bipyridine (90 mg, 0.58 mmol) and 4-methylbiphenyl (for the GC standard) was added a mixture of DMF (5 ml) and phenyl bromide (9.1 g, 58 mmol) at room temperature. After immersing the flask in a thermostatted oil bath, the amount of the biphenyl formed was determined periodically by GC analysis of the reaction mixture. The initially yellow reaction mixture is turned to purple instantly and then into red in a quite short period. On proceeding with the reaction, the mixture underwent further color change to green.

Kinetics of the reactions of the Ni^0 complex with phenyl chloride, phenyl iodide, *p*-acetylphenyl bromide, *p*-methyphenyl bromide, and *p*-methoxyphenyl bromide were measured similarly under the conditions shown in Table 1. GC standard compounds were chosen from 2,3-dimethylnaphthalene, triphenyl methane, and phenanthrene depending on the measurement conditions.

Reaction of $Ni(COD)_2$–BPY wityh phenyl bromide at room temperature

To a Schlenk flask containing $Ni(COD)_2$ (410 mg, 1.5 mmol), 2,2′-bipyridine (250 mg, 1.6 mmol) and phenyl bromide (1 ml) was added benzene (20 ml) at room temperature. Stirring the reaction mixture at room temperature caused color change of the mixture from purple to brown. After the reaction for 2 h the solvent was removed. The resulting red-brown solid was washed with hexane several times and dried *in vacuo*. The IR spectrum of the product agreed with that of **1** prepared separately.

Kinetic measurement of reaction of 1 with phenyl bromide

To a Schlenk flask containing $Ni(COD)_2$ (210 mg, 0.57 mmol), phenyl bromide (9.9 g, 63 mmol) and 2,3-dimethylnaphthalene (for the GC standard) was added DMF (5 ml) at room temperature. After immersing the flask in a thermostatted oil bath the amount of the biphenyl formed was determined periodically by GC analysis of the reaction mixture.

Reaction with added 1,5-cyclooctadiene was carried out similarly.

Thermal decomposition of 1

To a Schlenk flask containing **1** (200 mg, 0.54 mmol) and 4-methylbiphenyl (for GC standard) was added DMF (5 ml) at room temperature. Gradual deposition of black nickel was observed. GC analysis of the reaction mixture after stirring for 10 min at the temperature showed formation of biphenyl (0.22 mmol, 80% yield). The amount of biphenyl formed did not change after further stirring for 30 min at room temperature.

The reaction in toluene was carried out for 12 h at 70 ° C. GC analysis of the reaction mixture indicated formation of biphenyl in 36% yield.

Reaction of 1 with p-*methylphenyl bromide in DMF*

To a Schlenk flask containing **1** (220 mg, 0.59 mmol), *p*-methylphenyl bromide (9.8 g, 57 mmol), 1,5-cyclooctadiene (0.13 g, 1.2 mmol) and 2,3-dimethylnaphthalene (for the GC standard) was added DMF (5 ml) at room temperature. After stirring the reaction mixture for 1 h at 60 ° C GC analysis of the reaction mixture showed formation of biphenyl (0.18 mmol, 61% yield). Formation of 4-methylbiphenyl and 4,4′-dimethylbiphenyl was not observed in the reaction mixture at all. Further reaction at 60 ° C did not cause an increase in the amount of the products.

Reaction of a mixture of phenyl bromide and p*-methylphenyl bromide with the* $Ni(COD)_2$*–BPY system in DMF*

To a Schlenk flask containing $Ni(COD)_2$ (130 mg, 0.47 mmol), 2,2′-bipyridine (76 mg, 0.50 mmol) and 2,3-dimethylnaphthalene (for the GC standard) was added DMF (5 ml) and a mixture of phenyl bromide (4.5 g, 29 mmol) and *p*-methylphenyl bromide (4.2 g, 24 mmol) at room temperature. The reaction mixture was stirred in a thermostatted oil bath at 60 ° C. GC analysis after 4 min reaction shows formation of biphenyl (0.038 mmol, 8% of $Ni(COD)_2$) and 4-methylbiphenyl (0.047 mmol, 10% of $Ni(COD)_2$). After 20 min the yields of the products were raised to 24 and 17%, respectively. After 24 h, the reaction mixture contained biphenyl, 4-methylbiphenyl, and 4,4′-dimethylbiphenyl in 33%, 29%, and 3% yields, respectively.

Reaction of 1 with p*-methylphenyl bromide in toluene*

To a Schlenk flask containing **1** (37 mg, 0.089 mmol) and *p*-methylphenyl bromide (170 mg, 0.92 mmol) was added toluene (15 ml) at room temperature. On stirring the reaction mixture at 70 ° C for 12 h the initially yellow reaction mixture was turned into dark brown. GC analysis after quenching the reaction mixture by aq. HCl showed the formation of biphenyl (0.007 mmol, 8% of **1**), 4-methylbiphenyl (0.007 mmol, 8% of **1**), and 4,4′-dimethylbiphenyl (0.019 mmol, 21% of **1**).

Reaction of 1 with C_6D_5Br *in toluene*

To a Schlenk flask containing a toluene (15 ml) solution of **1** (77 mg, 0.21 mmol) was added C_6D_5Br (620 mg, 3.8 mmol) at room temperature. After stirring the reaction mixture for 30 min at 70 ° C the solvent was removed by evaporation. The residual red solid was washed with hexane repeatedly. The IR spectrum of the product showed peaks at ca. 2200 cm^{-1} and 550 cm^{-1}, which were assigned to ν(C–D) and δ(C–D) vibrations, respectively. The product in the reaction of **1** with non-deuterated phenyl bromide under the same conditions gave the IR spectrum which agrees well with that of **1**, indicating the presence of an only negligible amount of biphenyl product in the reaction mixture.

The above exchange of the phenyl ligand with deuterated phenyl bromide did not occur at room temperature.

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References

1 P.W. Jolly and G. Wilke, The Organic Chemistry of Nickel, Vol. II. Organic Synthesis, Academic Press, New York, 1975.

2 (a) M.F. Semmelhack, P.M. Helquist and L.D. Jones, J. Am. Chem. Soc., 93 (1971) 5908; (b) M.F. Semmelhack, P.M. Helquist and J.D. Gorzynski, ibid., 94 (1972) 9234; (c) M.F. Semmelhack and L.S. Ryono, ibid., 97 (1975) 3873; (d) M.F. Semmelhack, P. Helquist, L.D. Jones, L. Keller, L. Mendelson, L.S. Ryono, J.G. Smith and R.D. Stauffer, ibid., 103 (1981) 6460.

3 A.S. Kende, L.S. Liebeskind and D.M. Braitsch, Tetrahedron Lett., (1975) 3375.

4 R. Baker, Chem. Rev., 73 (1973) 487.

5 K. Sato, S. Inoue and K. Saito, J. Chem. Soc., Perkin Trans., 1, (1973) 2289.

6 M. Zembayashi, K. Tamao, J. Yoshida and M. Kumada, Tetrahedron Lett., (1977) 4089.

7 (a) K. Takagi, N. Hayama and S. Inokawa, Bull. Chem. Soc. Jpn., 53 (1980) 3691; (b) K. Takagi, H. Mimura and S. Inokawa, Bull. Chem. Soc. Jpn., 57 (1984) 3517.

8 M. Iyoda, M. Sakaitani, H. Otsuka and M. Oda, Chem. Lett., (1985) 127.

9 (a) T. Yamamoto, Y. Hayashi and A. Yamamoto, Bull. Chem. Soc. Jpn., 51 (1978) 2091; (b) T. Yamamoto, K. Sanechika and A. Yamamoto, ibid., 56 (1983) 1497.

10 T. Yamamoto, T. Ito and K. Kubota, Chem. Lett., (1988) 153.

11 (a) T. Yamamoto, A. Morita, T. Maruyama, Z.-H. Zhou, T. Kanbara and K. Sanechika, Polym. J., 22 (1990) 187; (b) T. Yamamoto, A. Morita, T. Kanbara and S. Sasaki, Synth. Met., 39 (1990) 269.

12 (a) T. Yamamoto, A. Yamamoto and S. Ikeda, J. Am. Chem. Soc., 93 (1971) 3350, 3360; (b) T. Yamamoto and A. Yamamoto, J. Organomet. Chem., 57 (1973) 1271; (c) T. Kohara, T. Yamamoto and A. Yamamoto, J. Organomet. Chem., 192 (1980) 265.

13 B. Åkermark and A. Ljungqvist, J. Organomet. Chem., 149 (1978) 97.

14 (a) D.G. Morrel and J.K. Kochi, J. Am. Chem. Soc., 97 (1975) 7262; (b) G. Smith and J.K. Kochi, J. Organomet. Chem., 198 (1980) 199.

15 S. Komiya, Y. Abe, A. Yamamoto and T. Yamamoto, Organometallics, 2 (1983) 1466.

16 R.J. McKinney and D.C. Roe, J. Am. Chem. Soc., 107 (1985) 261.

17 H. Kurosawa, J. Organomet. Chem., 334 (1987) 243 and refs. cited therein.

18 (a) R.H. Grubbs, A. Miyashita, M. Liu and P. Burk, J. Am. Chem. Soc., 100 (1978) 2418; (b) R.H. Grubbs and A. Miyashita, ibid., 100 (1978) 7416.

19 B. Åkermark, H. Johansen, B. Roos and U. Wahlgen, J. Am. Chem. Soc., 101 (1979) 5876.

20 K. Tatsumi, A. Nakamura, S. Komiya, A. Yamamoto and T. Yamamoto, J. Am. Chem. Soc., 106 (1984) 8181.

21 Reductive elimination of dimethylpalladium complexes having phosphine ligands was studied in DMSO. See: A. Gillie and J.K. Stille, J. Am. Chem. Soc., 102 (1980) 4933.

22 (a) H. Mori, K. Ikeda, I. Nagaoka, S. Hirayanagi, M. Ikeyama and A. Kihi, Jap. Pat., 70-28574, (1970); Chem. Abstr., 74 (1971) 3729; (b) P. Binger, M.J. Doyle, J. McMeeking, C. Krüger and Y.-H. Tsay, J. Organomet. Chem., 135 (1977) 405.

23 As discussed later, the rate-determining step of the reaciton involves bimolecular disproportionation of NiBr(Ph)(BPY) generated rapidly in the reaction mixture. The kinetic formula of the reaction can be expressed with the second-order reaction on NiBr(Ph)(BPY) rather than on $Ni(COD)_2$ or the other corresponding zero valent nickel species.

24 (a) M. Uchino, A. Yamamoto and S. Ikeda, J. Organomet. Chem., 24 (1970) C63; (b) M. Uchino, K. Asagi, A. Yamamoto and S. Ikeda, ibid., 84 (1975) 93.

25 Reaction of 1 with *p*-methylphenyl bromide at 70 ° C in the presence of 1,5-cyclooctadiene or that without addition of 1,5-cyclooctadiene at 60 ° C sometimes causes formation of 4-methylbiphenyl to some extent even in DMF solution. However, the reaction mixture at the initial stage of the reaction contains biphenyl (30–40% of the total amount of biaryl products) as the exclusive coupling product.

26 T.T. Tsou and J.K. Kochi, J. Am. Chem. Soc., 101 (1979) 7547.

27 T. Yamamoto, J. Ishizu, T. Kohara, S. Komiya and A. Yamamoto, J. Am. Chem. Soc., 102 (1980) 3758.

28 T. Yamamoto, T. Kohara, K. Osakada and A. Yamamoto, Bull. Chem. Soc. Jpn., 56 (1983) 2147.

29 P.K. Beyers, A.J. Canty, B.W. Skelton and A.H. White, J. Chem. Soc., Chem. Commun., (1986) 1722.

30 W. de Graaf, J. Boersma, W.J.J. Smeets, A.L. Spek and G. van Koten, Organometallics, 8 (1989) 2907.

31 (a) A. Gillie and J.K. Stille, J. Am. Chem. Soc., 102 (1980) 4933; (b) A. Moravskiy and J.K. Stille, ibid., 103 (1981) 4182.

32 T. Yamamoto, T. Kohara and A. Yamamoto, Bull. Chem. Soc. Jpn., 54 (1981) 2010.

33 T. Yamamoto, T. Saruyama, Y. Nakamura and A. Yamamoto. Bull. Chem. Soc. Jpn., 49 (1976) 589.

34 S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto and K. Ataka, J. Am. Chem. Soc., 95 (9173) 3180.

35 C. Krüger, J.C. Sekutowski, H. Berke and R. Hoffmann, Z. Naturforsch., Teil B, 33 (1978) 1110.

36 F. Ozawa, T. Hidaka, T. Yamamoto and A. Yamamoto, J. Organomet. Chem., 330 (1987) 253.

37 J.W. Park, L.M. Henling, W.P. Schaefer and R.H. Grubbs, Organometallics, 10 (1991) 171.

38 J.J. Low and W.A. Goddard III, J. Am. Chem. Soc., 106 (1984) 6928, 8321.

39 R.A. Schunn, Inorg. Synth., 15 (1974) 5.

40 T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuji and S. Ikeda, J. Am. Chem. Soc., 88 (1966) 5198.