Formation of *cine*-Substitution Products in the *Suzuki–Miyaura* Cross-Coupling Reaction Catalyzed by Dinuclear Palladium Complexes

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The *Suzuki–Miyaura* coupling reaction catalyzed by dinuclear palladium complexes gave *cine*-substitution products along with ordinary *ipso*-substitution products. In the reaction in (D_6)benzene, the *ipso* position of the *cine*-substitution product was highly deuterated. The H/D exchange also occurred in various positions of benzene rings.

Introduction. – Most organic reactions catalyzed by transition metal complexes take place on a single metal center. If there are more than two metal centers in one molecule, cooperation of the metal centers variegates their catalytic ability [1]. Improvement of the efficiency and selectivity, promotion of reactions that are difficult using a mononuclear complex, and formation of unexpected products can be possible. We previously designed a new chelate-bridging ligand, *N*,*N′*-bis[2-(diphenylphosphino)phenyl]formamidinato (dpfam), for the synthesis of dinuclear Pd complexes, in which two Pd centers are tied in close proximity with or without a metal–metal bond [2]. The dinuclear Pd complexes served as effective catalysts for several valuable transformations of organic compounds [3][4]. For example, dinuclear complex **1a** catalyzed addition reactions of various compounds to alkynes *via* C–H activation [3]. In the course of our study for the applicability of **1**, we found that *cine*-substitution products were formed along with ordinary *ipso*-substitution products when the *Suzuki–Miyaura* coupling reaction was conducted in the presence of **1**.

Although various types of nucleophilic *cine*-substitution reactions have been reported, *cine*-substitution in transition metal-catalyzed cross-coupling reaction seems to be rather rare [5]. There are several reports on *cine*-substitution on alkenylstannanes in *Stille* coupling [6]. A similar reaction takes place on alkenylsilanes in *Hiyama* coupling [7]. In *Negishi* and *Heck* couplings, *cine*-substitution on alkenyl halides and *pseudo*-halides (phosphates and tosylates) are observed [8][9]. Some Rh-catalyzed reactions, in which *cine*-substitution occurs on alkenyl acetates or sulfones, were also reported [10]. While there are several examples for various alkenyl compounds, *cine*-substitution on aryl compounds in cross-couplings is rare [11][2]). Herein, we report *cine*-substitution on aryl bromides in *Suzuki–Miyaura* coupling reaction catalyzed by dinuclear Pd complexes **1**.

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[2]) For examples of formal *cine*-substitution reactions, see [12].

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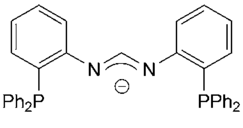
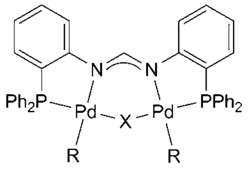


dpfam

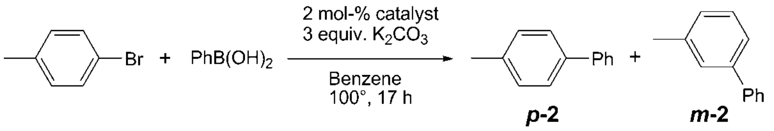


$[Pd_2R_2(\mu\text{-}X)(\mu\text{-dpfam})]$ (**1**)

	R	X
1a	*p*-Me–C_6H_4	OH
1b	*p*-Me–C_6H_4	I
1c	*p*-Me–C_6H_4	Br
1d	*p*-Me–C_6H_4	Cl
1e	*p*-Cl–C_6H_4	I
1f	Me	Cl
1g	(*E*)-PhCH=$CHCH_2$	Cl
1h	Cl	Cl

Results and Discussion. – Initially, we investigated the applicability of **1** as a catalyst for the cross-coupling reaction of *p*-bromotoluene and $PhB(OH)_2$ (*Table 1*). While the dinuclear Pd complexes **1** catalyzed the reaction to give expected ***p*-2** as a major product, unexpectedly, the reaction also afforded *cine*-substitution product ***m*-2**. The ratio ***m*-2**/***p*-2** was affected by ligands of **1**. In the reaction with hydroxo-bridged complex **1a**, the total yield of **2** was high, and the ratio of ***m*-2** was low (*Entry 1*). In contrast, the ratio of ***m*-2** was higher, and the total yield was moderate in the reaction with halogeno-bridged complexes **1b**–**1d** (*Entries 2–4*). The formation of ***m*-2** was restrained in the reaction with methyl, cinnamyl, and chloro complexes **1f**–**1h**

Table 1. Suzuki–Miyaura *Coupling of* p-*Bromotoluene and* $PhB(OH)_2$ *in the Presence of Dinuclear Pd Complexes* **1**[a])



Entry	Catalyst	***p*-2**/***m*-2**[b])	Yield [%][b])
1	**1a**	95:5	80
2	**1b**	77:23	39
3	**1c**	70:30	44
4	**1d**	75:25	58
5	**1e**	69:31	23
6	**1f**	99:1	70
7	**1g**	98:2	28
8	**1h**	100:0	73
9	[Pd(Me)(dpfam)]	–	0

[a]) A mixture of *p*-bromotoluene (0.5 mmol) and $PhB(OH)_2$ (0.5 mmol) in benzene (2.0 ml) was stirred at 100° for 17 h in the presence of a Pd complex (0.01 mmol) and K_2CO_3 (1.5 mmol). [b]) Determined by GC.

(*Entries 6–8*). No *ortho*-isomer of **2** was observed in all reactions. In the case that the yield of **2** was low or moderate, reasonable amounts of *p*-bromotoluene remained unreacted; dehalogenation was not a main side reaction. No products were obtained in the reactions without a catalyst or with a mononuclear complex [2], which has the same chelate-bridging ligand, dpfam (*Entry 9*). Therefore, two Pd centers in **1** seem to be essential for the formation of *cine*-substitution product ***m*-2**.

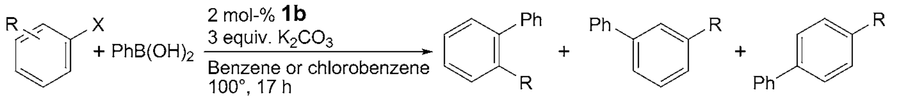
In *Table 2*, the results of the reaction of various monosubstituted bromobenzenes with $PhB(OH)_2$ in the presence of **1b** for 17 h (*Table 2*) are shown. All reactions were not complete at that point, and bromoarenes were still present to a greater or lesser extent. In all reactions of *para*-substituted bromobenzenes except for 1-bromo-4-nitrobenzene, *cine*-substitution was observed (*Entries 1–8*). The ratio of the *cine*-substitution products (*meta*-isomer) was not correlated with the electronic property of substituents, and was in the range of 25% in most reactions. No *tele*-substitution product (*ortho*-isomer) was detected in all reactions. The reactions of *meta*-substituted bromobenzenes afforded results similar to those of *para*-substituted bromobenzenes (*Entries 9–15*). The electronic properties of substituents did not affect the ratio of the *cine*-substitution products (*para*-isomer), which was *ca.* 20% except for the reaction of 1-bromo-3-nitrobenzene (*Entry 15*). Another possible *cine*-substitution product, *ortho*-isomer, was not formed probably due to steric hindrance. In the reactions of *ortho*-substituted bromobenzenes, the ratio of *cine*-substitution products (*meta*-isomer) varied depending upon the substituents. The reactions of *o*-bromotoluene, *o*-bromo-1,1′-biphenyl, and methyl *o*-phenylbenzoate afforded *cine*-substitution products (*meta*-isomers) in selectivities similar to those of *para*- and *meta*-substituted bromobenzenes (*Entries 17–19*). A MeO group raised the selectivity for the *cine*-substitution product ***m*-3** to 48% (*Entry 16*). In contrast, an Ac group inhibited *cine*-substitution probably due to chelation (*Entry 20*).

Aryl iodides, which are more reactive than aryl bromides in most cross-coupling reactions, were unreactive in the *Suzuki–Miyaura* coupling catalyzed by **1b**. In the reaction of *p*-iodoanisole or *p*-iodoacetophenone, only trace amounts of **4** or **7** were formed, and the aryl iodides were recovered. Chloroanisole, anisyl triflate, and anisyl tosylate were also unreactive. The coupling reaction catalyzed by **1b** proceeded only with aryl bromides.

Reaction media were found to exert considerable influence upon the product ratio and the yield. The *cine*-substitution took place exclusively in aromatic solvents (*Table 3*). The reaction of *p*-bromotoluene in 1,4-dioxane or 1,2-dichloroethane afforded only the expected product ***p*-2** (*Entries 1* and *2*). The cross-coupling reaction with **1b** did not proceed in THF, DMF, octane, or cyclohexane. Remarkable differences among aromatic solvents were observed. Methylbenzenes such as toluene, xylene, and mesitylene increased the yield of **2** and decreased the ratio of ***m*-2** (*Entries 4–6*). Other aromatic solvents such as anisole, chlorobenzene, and ethyl benzoate provieded moderate selectivities for ***m*-2** with moderate yields (*Entries 7–10*).

The results collected in *Table 3* indicated that the reactions that gave **2** in higher yield exhibited lower selectivity for ***m*-2**. To elucidate a correlation between the yield and the product ratio, the time course of them in the reaction of *p*-bromotoluene in PhCl was studied (*Fig. 1*). The ratio of ***m*-2** gradually decreased with the progress of the reaction, presumably due to *ipso*-substitution by mononuclear Pd complexes that

Table 2. Suzuki–Miyaura *Coupling of Various Aryl Bromides* (X = Br) *Catalyzed by* **1b**[a])



***o*-3** R = Me_2N ***m*-3** R = Me_2N ***p*-3** R = Me_2N
***o*-4** R = MeO ***m*-4** R = MeO ***p*-4** R = MeO
***o*-5** R = Cl ***m*-5** R = Cl ***p*-5** R = Cl
***o*-6** R = MeOOC ***m*-6** R = MeOOC ***p*-6** R = MeOOC
***o*-7** R = Ac ***m*-7** Ac ***p*-7** R = Ac
***o*-8** R = CF_3 ***m*-8** R = CF_3 ***p*-8** R = CF_3
***o*-9** R = NO_2 ***m*-9** R = NO_2 ***p*-9** R = NO_2

Entry	R	Isomer ratio of **3–9**[b])			Yield [%][c])
		para	*meta*	*ortho*	
1	*p*-Me_2N	76	24	0	40
2	*p*-MeO	75	25	0	76
3	*p*-Me	77	23	0	39[d])
4	*p*-Cl	77	23	0	40
5	*p*-MeOOC	65	35	0	47
6	*p*-Ac	84	16	0	89
7	*p*-CF_3	77	23	0	66
8	*p*-NO_2	> 99	< 1	0	37
9	*m*-MeO	25	75	0	61
10	*m*-Me	18	82	0	29
11	*m*-Cl	22	78	0	34
12	*m*-MeOOC	17	83	0	58
13	*m*-Ac	18	82	0	55
14	*m*-CF_3	13	87	0	74
15	*m*-NO_2	3	97	0	27
16	*o*-MeO	0	48	52	32
17	*o*-Me	0[e])	28	72	45
18	*o*-Ph	0	30	70	5
19	*o*-MeOOC	0	31	69	68
20	*o*-Ac	0	8	92	82

[a]) A mixture of an aryl bromide (0.5 mmol) and $PhB(OH)_2$ (0.5 mmol) in benzene (2.0 ml) was stirred at 100° for 17 h in the presence of **1b** (0.01 mmol) and K_2CO_3 (1.5 mmol). [b]) Determined by GC before isolation. [c]) Total yields of isomers. [d]) Determined by GC. [e]) Trace amounts of ***p*-2**, which was derived from **1b**, were observed.

dissociate from dpfam by decomposition of dinuclear complex **1b**. Considering the curve of the selectivity, the same amounts of ***m*-2** and ***p*-2** might be formed at the beginning of the reaction. It is also noteworthy that the reaction catalyzed by **1b** began to afford coupling products **2** after several hours. The induction period was also observed in the reaction catalyzed by the bromo-bridged complex **1c**. A complex with aryl and halogen ligands $[PdAr(X)L_n]$ is one of the intermediates in the ordinary *Suzuki–Miyaura* coupling reaction. Although **1b** and **1c** contain the similar Ar–Pd–X moiety, they do not seem to be intermediates in the catalytic cycle of the present coupling reaction. In fact, only small amounts of **2** were furnished by treatment of **1b**

Table 3. *Solvent Effect on* cine-*Substitution in the Reaction of* p-*Bromotoluene*[a])

Entry	Solvent	***p*-2/*m*-2**[b])	Yield (%)[c])
1	1,4-Dioxane	$>99:<1$	14
2	1,2-Dichloroethane	$>99:<1$	60
3	Benzene	77:23	39
4	Toluene	96:4	64
5	Xylene	98:2	87
6	Mesitylene	99:1	72
7	Anisole	85:15	61
8	Fluorobenzene	84:16	29
9	Chlorobenzene	78:22	53
10	Ethyl benzoate	82:18	62

[a]) A mixture of *p*-bromotoluene (0.5 mmol) and $PhB(OH)_2$ (0.5 mmol) in solvent (2.0 ml) was stirred at 100° for 17 h in the presence of **1b** (0.01 mmol) and K_2CO_3 (1.5 mmol). [b]) Determined by GC. [c]) Determined by GC.

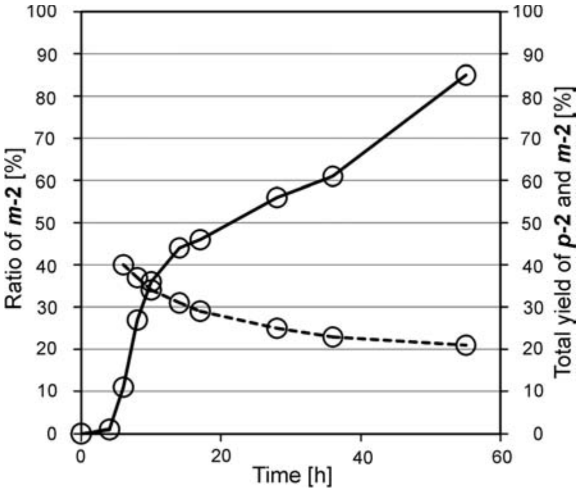


Fig. 1. *Time dependence of product yield* (solid line) *and ratio of* ***m*-2** (dashed line) *in the reaction of* p-*bromotoluene catalyzed by* **1b**

with $PhB(OH)_2$ in the presence or absence of K_2CO_3 at 100° for 6 h. However, **1b** was activated by the treatment with $PhB(OH)_2$; no induction period was observed in the coupling reaction catalyzed by the activated complex.

Results of the pretreatment study are shown in *Fig. 2*. While the induction period was also observed in the reaction of *o*-bromoanisole without the pretreatment (*Fig. 2*; ○), the period disappeared by treating **1b** with $PhB(OH)_2$ prior to addition of *o*-bromoanisole (*Scheme 1* and *Fig. 2*, ●). Hydroxo-bridged complex **1a** was also transformed by the pretreatment with $PhB(OH)_2$ (*Fig. 3*). In the reaction catalyzed by **1a** without pretreatment, the ratio of *cine*-substitution product ***m*-4** was lower than in the reaction catalyzed by **1b** (◇ in *Fig. 3* and ○ in *Fig. 2*). In contrast, the reaction with

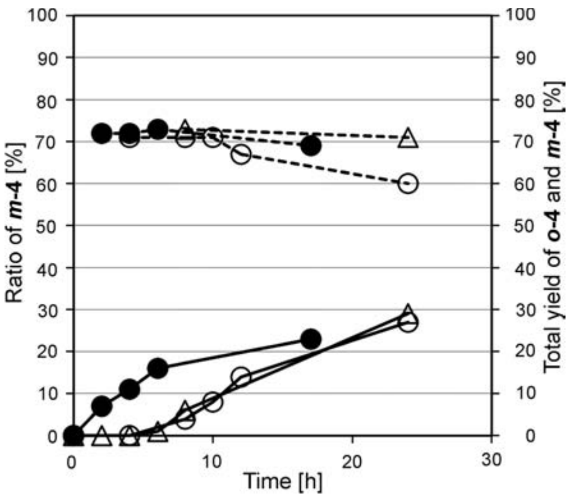
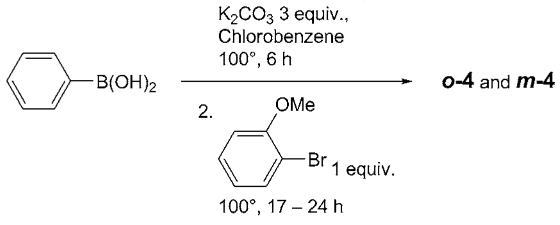


Fig. 2. *Time dependence of product yield* (solid line) *and ratio of* ***m*-4** (dashed line) *in the reaction of* o-*bromoanisole catalyzed by* **1b** *without pretreatment* (○) *and with pretreatment* (●), *and by* **1c** *without pretreatment* (△)

the pretreatment afforded ***m*-4** with moderate selectivity, which was similar to that in the **1b**-catalyzed reaction (◆ in *Fig. 3* and ● in *Fig. 2*). The time dependence of the yield was also similar to that in the reaction catalyzed by **1b** with pretreatment. These results indicated that the same intermediate was formed by the pretreatment of **1a** and **1b** with $PhB(OH)_2$. Since no *cine*-substitution product was obtained in the reaction using mononuclear complexes bearing or not bearing dpfam such as [Pd(dpfam)(Me)] or $[Pd(PPh_3)_4]$, respectively, the common intermediate probably have a dinuclear structure supported by dpfam. Isolation of the intermediate has not been achieved due to difficulty in separation from the excess $PhB(OH)_2$.

Scheme 1. *Reaction with Pretreatment of* **1** *with* $PhB(OH)_2$ *and* K_2CO_3



To determine a source of a H-atom in *ipso*-position of the *cine*-substitution products, the reaction of *o*-bromoanisole with $PhB(OH)_2$ as conducted in (D_6)benzene. As shown in *Scheme 2*, the *ipso*-position of ***m*-4** was highly deuterated. It is obvious that the *ipso*-H-atom was derived from aromatic solvents and not from 1,2-shift of the *cine*-H-atom. Unexpectedly, H/D exchange reactions occurred in various positions of

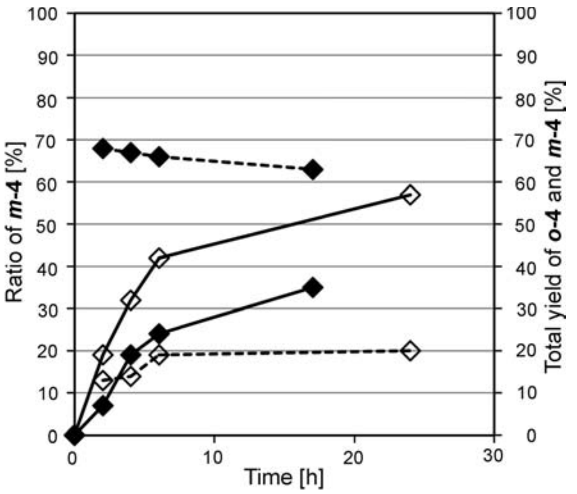
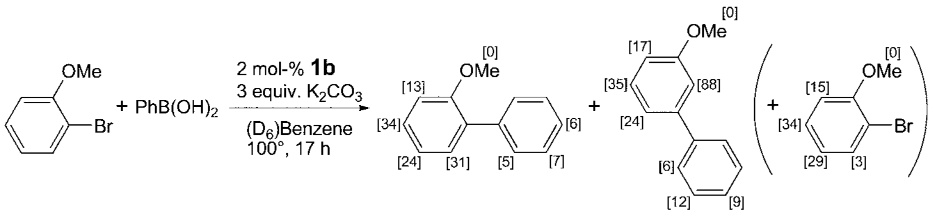


Fig. 3. *Time dependence of product yield* (solid line) *and ratio of* ***m*-4** (dashed line) *in the reaction of* o*-bromoanisole catalyzed by* **1a** *without pretreatment* (◇) *and with pretreatment* (◆)

benzene rings in ***m*-4**, ***o*-4**, and recovered *o*-bromoanisole. Deuteration of unreacted $PhB(OH)_2$ was not verified, because it could not be isolated from the mixture and analyzed by GC/MS. All MeO-substituted benzene rings were similarly deuterated, except for the *cine*- and *ipso*-positions. The D ratio in *cine*-position of ***o*-4** was higher than that of recovered *o*-bromoanisole. The H/D exchange did not occur in the reaction catalyzed by $[Pd(PPh_3)_4]$, and the reaction without **1b** or K_2CO_3 or $PhB(OH)_2$.

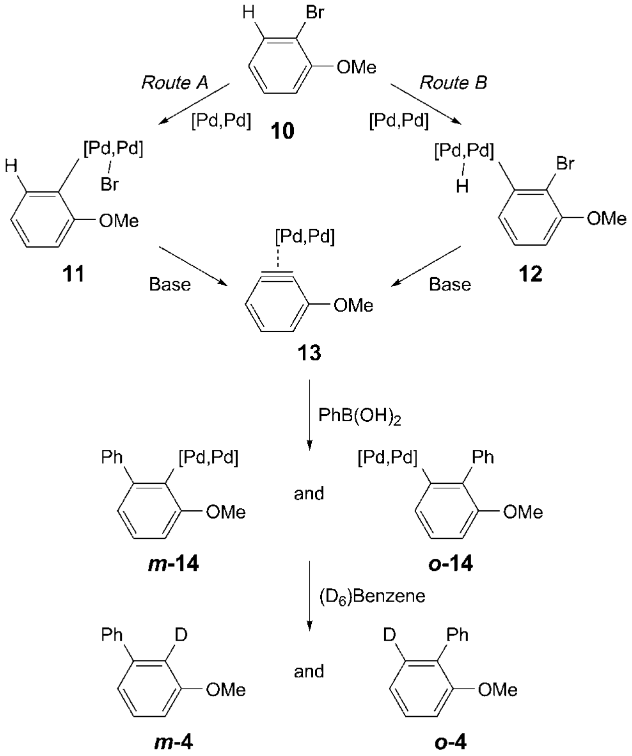
Scheme 2. *Reaction of* o*-Bromoanisole in (D₆)Benzene*



***o*-4** ***m*-4**

The above results indicate that the mechanism of the reaction with **1b** is rather different from that of the reaction with ordinary Pd catalysts, although details are still unclear. Since the *ipso*-position of ***m*-4** and the *cine*-position of ***o*-4** were highly deuterated, the reaction probably proceeded *via* a μ_2-aryne or μ-*o*-arylene complex [13]. Since part of ***o*-4** was formed *via* the normal mechanism catalyzed by mononuclear Pd complexes, the *cine*-position of ***o*-4** could be less deuterated than the *ipso*-position of ***m*-4**. One of possible routes for formation of the dinuclear aryne complex **13** is hydride elimination of arylpalladium complex **11** formed by oxidative addition of *o*-bromoanisole (**10**) to Pd (*Scheme 3*, *Route A*) [13]. However, it does not seem likely, because **1b** or **1c**, which have the Ar–Pd–X moiety, are not intermediates in the present reaction. Considering that the H/D exchange occurred at various positions of aromatic rings, another possible route is elimination of Br from arylpalladium complex **12** formed by C–H palladation (*Route B*) [3a][3]). This mechanism is similar to that of the established aryne formation from aryl halides and strong bases, and consistent with higher reactivity of aryl bromides than aryl iodides [15]. The aryne complex **13** would react with $PhB(OH)_2$ to give phenylaryl complex **14** [16], and then the complex **14** would be deuterated *via* the H/D exchange with (D_6)benzene [17].

Scheme 3. *Proposed Mechanism*



Conclusions. – We found that the *Suzuki–Miyaura* coupling reaction catalyzed by dinuclear Pd complexes **1** gave *cine*-substitution products, along with expected products. Dinuclear structure could be essential for the formation of *cine*-substitution products, because a mononuclear Pd complex bearing dpfam, which is formed by cleavage of **1**, is not effective. Although the precise mechanism for the *cine*-substitution has remained unclear, it is different from that for the ordinary *Suzuki–Miyaura* coupling. The results of the reaction in (D_6)benzene indicated a mechanism *via* aryne

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[3]) Aryne complexes are generated by *ortho*-C–H bond activation, followed by decarboxylation of benzoic acids [14].

or arylene complexes. Time-course experiments showed that the ratio of *cine*-substitution products gradually decreased, probably due to the *ipso*-substitution by mononuclear phosphine-free Pd complexes generated by decomposition of **1**. Further improvement of the stability of the dinuclear structure is necessary for elucidation of the precise reaction mechanism, which will lead to new developments in catalytic transformation of organic compounds.

Experimental Part

General. Aryl halides and $PhB(OH)_2$ were purchased from *Aldrich* and *TCI* and used without further purification. The complexes **1a**–**1c** were prepared according to literature methods [2][3]. Spectroscopic recordings were carried out with the following instruments: *JEOL FT/IR-350* (FT-IR), *Bruker DPX-400* and *DRX-500* (^{1}H- and ^{13}C-NMR), and *Shimadzu GCMS-QP5050A* (MS).

General Procedure for the Reaction of Aryl Bromides with $PhB(OH)_2$ Catalyzed by **1**. To a mixture of **1** (0.010 mmol), $PhB(OH)_2$ (0.50 mmol), and K_2CO_3 (1.5 mmol) were added benzene (2.0 ml) and then an aryl bromide (0.50 mmol) in a pressure vial. After heating at 100° for 17 h, the mixture was cooled to r.t. and filtered through a short plug of SiO_2 with Et_2O as eluent. The ratio of regioisomers was determined by a GC analysis of the filtrate. After evaporation of volatiles, a mixture of 1,1′-biphenyls **2**–**9** was separated from the residue by column chromatography (CC; SiO_2 hexane/AcOEt). Compounds **2** [18], **3** [19], **4** [20], **5** [21], **6** [22], **7** [23–25], **8** [22][26], and **9** [27] were identified by comparison of their spectroscopic data with those in the literature.

Evaluation of Time Courses of the Yield and Ratio of **p-2** *and* **m-2**. To a mixture of **1b** (0.015 mmol), $PhB(OH)_2$ (0.75 mmol), and K_2CO_3 (2.3 mmol) were added PhCl (3.0 ml), *p*-bromotoluene (0.75 mmol), and then dodecane (0.5 mmol) as an internal standard, in a pressure vial. While the mixture was heated at 100°, a small portion (*ca.* 10 μl) of the mixture was syringed periodically, diluted by Et_2O, and analyzed by GC.

Reactions after Pretreatment of **1** *with $PhB(OH)_2$ and K_2CO_3.* To a mixture of **1** (0.015 mmol), $PhB(OH)_2$ (0.75 mmol), and K_2CO_3 (2.3 mmol) were added PhCl (3.0 ml) in a pressure vial. After stirring the mixture for 6 h at 100°, *o*-bromoanisole (**10**; 0.75 mmol) and dodecane were added to the mixture. While the mixture was heated at 100°, a small portion (*ca.* 10 μl) of the mixture was syringed periodically, diluted by Et_2O, and analyzed by GC.

Reaction of **10** *in (D_6)Benzene.* To a mixture of **1b** (0.010 mmol), $PhB(OH)_2$ (0.50 mmol), and K_2CO_3 (1.5 mmol) were added (D_6)benzene (2.0 ml) and then **10** (0.50 mmol) in a pressure vial. After heating at 100° for 17 h, the mixture was cooled to r.t. and filtered through a short plug of SiO_2 with Et_2O as eluent. Recovered **10**, ***o*-4**, and ***m*-4** were separated by prep. GC (*Uniport 80/100 silicone SE-30* 15%, 6 $\phi \times 3$ m). Their deuteraion degrees were determined by their ^{1}H-NMR spectra.

REFERENCES

[1] H. Steinhagen, G. Helmchen, *Angew. Chem., Int. Ed.* **1996**, *35*, 2339; E. K. van den Beuken, B. L. Feringa, *Tetrahedron* **1998**, *54*, 12985; G. J. Rowlands, *Tetrahedron* **2001**, *57*, 1865; 'Multimetallic Catalysis in Organic Synthesis', Eds. M. Shibasaki, Y. Yamamoto, Wiley-VCH, Weinheim, 2004.

[2] N. Tsukada, O. Tamura, Y. Inoue, *Organometallics* **2002**, *21*, 2521.

[3] a) N. Tsukada, T. Mitsuboshi, H. Setoguchi, Y. Inoue, *J. Am. Chem. Soc.* **2003**, *125*, 12102; b) N. Tsukada, K. Murata, Y. Inoue, *Tetrahedron Lett.* **2005**, *46*, 7515; c) N. Tsukada, H. Setoguchi, T. Mitsuboshi, Y. Inoue, *Chem. Lett.* **2006**, *35*, 1164; d) N. Tsukada, S. Ninomiya, Y. Aoyama, Y. Inoue, *Org. Lett.* **2007**, *9*, 2919.

[4] N. Tsukada, Y. Ohba, Y. Inoue, *J. Organomet. Chem.* **2003**, *687*, 436; N. Tsukada, M. Wada, N. Takahashi, Y. Inoue, *J. Organomet. Chem.* **2009**, *694*, 1333; N. Tsukada, A. Takahashi, Y. Inoue, *Tetrahedron Lett.* **2011**, *52*, 248.

[5] J. Suwiński, K. Świerczek, *Tetrahedron* **2001**, *57*, 1639.

[6] K. Kikukawa, H. Umekawa, T. Matsuda, *J. Organomet. Chem.* **1986**, *311*, C44; G. Stork, R. C. A. Isaacs, *J. Am. Chem. Soc.* **1990**, *112*, 7399; V. Farina, M. A. Hossain, *Tetrahedron Lett.* **1996**, *37*, 6997; A. Flohr, *Tetrahedron Lett.* **1998**, *39*, 5177; X. Han, B. M. Stoltz, E. J. Corey, *J. Am. Chem. Soc.* **1999**, *121*, 7600; E. Fillion, N. J. Taylor, *J. Am. Chem. Soc.* **2003**, *125*, 12700; K.-S. Masters, B. L. Flynn, *Adv. Synth. Catal.* **2009**, *351*, 530; Y. Peng, W.-D. Z. Li, *Eur. J. Org. Chem.* **2010**, 6703.

[7] K. Ikenaga, S. Matsumoto, K. Kikukawa, T. Matsuda, *Chem. Lett.* **1990**, *19*, 185; Y. Hatanaka, K.-i. Goda, T. Hiyama, *J. Organomet. Chem.* **1994**, *465*, 97; J. C. Anderson, S. Anguille, R. Bailey, *Chem. Commun.* **2002**, 2018.

[8] D. S. Ennis, T. L. Gilchrist, *Tetrahedron Lett.* **1989**, *30*, 3735; A. L. Hansen, J.-P. Ebran, T. M. Gøgsig, T. Skrydstrup, *J. Org. Chem.* **2007**, *72*, 6464; A. T. Lindhardt, T. M. Gøgsig, T. Skrydstrup, *J. Org. Chem.* **2009**, *74*, 135.

[9] A. L. Hansen, J.-P. Ebran, M. Ahlqust, P.-O. Norrby, T. Skrydstrup, *Angew. Chem., Int. Ed.* **2006**, *45*, 3349; J.-P. Ebran, A. L. Hansen, T. M. Gøgsig, T. Skrydstrup, *J. Am. Chem. Soc.* **2007**, *129*, 6931.

[10] K. Yoshida, T. Hayashi, *J. Am. Chem. Soc.* **2003**, *125*, 2872; J.-Y. Yu, R. Shimizu, R. Kuwano, *Angew. Chem., Int. Ed.* **2010**, *49*, 6396.

[11] D. A. Watson, M. Su, G. Teverovskiy, Y. Zhang, J. García-Fortanet, T. Kinzel, S. L. Buchwald, *Science* **2009**, *325*, 1661.

[12] A. Maehara, H. Tsurugi, T. Satoh, M. Miura, *Org. Lett.* **2008**, *10*, 1159; S. Mochida, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2010**, *12*, 5776; J. Cornella, M. Righi, I. Larrosa, *Angew. Chem., Int. Ed.* **2011**, *50*, 9429; M. Catellani, *Synlett* **2003**, 298.

[13] M. A. Bennett, H. P. Schwemlein, *Angew. Chem., Int. Ed.* **1989**, *28*, 1296.

[14] A. A. Cant, L. Roberts, M. F. Greaney, *Chem. Commun.* **2010**, *46*, 8671.

[15] J. D. Roberts, D. A. Semenow, J. Howard E. Simmons, L. A. Carlsmith, *J. Am. Chem. Soc.* **1956**, *78*, 601.

[16] C. H. Oh, H. H. Jung, K. S. Kim, N. Kim, *Angew. Chem., Int. Ed.* **2003**, *42*, 805.

[17] J. Atzrodt, V. Derdau, T. Fey, J. Zimmermann, *Angew. Chem., Int. Ed.* **2007**, *46*, 7744.

[18] M. E. Mowery, P. Deshong, *J. Org. Chem.* **1999**, *64*, 3266.

[19] C. Nájera, J. Gil-Moltó, S. Karlström, L. R. Favello, *Org. Lett.* **2003**, *5* 1451.

[20] M. Lukeman, P, Wan, *J. Am. Chem. Soc.* **2002**, *124*, 9458.

[21] H.-J. Lehmler, L. W. Robertson, *Chemosphere* **2001**, *45*, 137.

[22] S.-K. Kang, J.-S. Kim, S.-K. Yoon, K.-H. Lim, S. S. Yoon, *Tetrahedron Lett.* **1998**, *39*, 3011.

[23] D. L. Clive, S. Kang, *J. Org. Chem.* **2001**, *66*, 6083.

[24] L. Zhu, J. Duquette, M. Zhang, *J. Org. Chem.* **2003**, *68*, 3729.

[25] S. Schneider, W. Bannwarth, *Helv. Chim. Acta* **2001**, *84*, 735.

[26] J. Hassan, C. Hathroubi, C. Gozzi, M. Lemaire, *Tetrahedron* **2001**, *37*, 7845.

[27] A. Zapf, M. Beller, *Chem. – Eur. J.* **2000**, *6*, 1830.

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