Mechanism of the Cross-Coupling Reaction of Phenyl Iodide and Methylmagnesium Iodide Catalyzed by *trans*-PdPh(I)(PEt2Ph)2

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The reaction of phenyl iodide with methylmagnesium iodide in the presence of a catalytic amount of *trans*-PdPh(I)(PEt2Ph)2 (1) yields toluene, the cross-coupling product, over 90% selectivity together with biphenyl. ^{31}P NMR examination on the catalytic system has revealed the presence of four kinds of diorganopalladium(II) species in the system: *trans*- and *cis*-PdMePh(PEt2Ph)2 (2 and 3, respectively) and *trans*- and *cis*-PdMe2(PEt2Ph)2 (4 and 5, respectively). Complexes 2–5 have been prepared independently and their thermolysis behavior and reactions with phenyl iodide and methylmagnesium iodide examined. The *trans*-methylphenyl complex (2) is relatively stable toward the reductive elimination to afford toluene in the presence and absence of phenyl iodide, but it readily undergoes intermolecular reactions with methylmagnesium iodide to give *trans*- and *cis*-dimethyl complexes (4 and 5, respectively) and phenylmagnesium iodide. The dimethyl complexes further react with phenylmagnesium iodide generated in the system to produce the *cis*-methylphenylpalladium (3) and methylmagnesium iodide. Complex 3 thus formed is very unstable under the catalytic conditions and smoothly affords toluene, the cross-coupling product. The toluene formation from 3 proceeds via an intramolecular reductive elimination process without predissociation of the phosphine ligand. No acceleration effect of phenyl iodide on the reductive elimination is observed. On the basis of the experimental results a mechanism of the catalytic cross-coupling reaction is proposed.

Introduction

The cross-coupling reaction of organic halides (RX) and organometallic compounds of main elements (R'm) catalyzed by nickel and palladium complexes (L_nM) is widely used in organic synthesis.[1] Scheme I represents the generally accepted mechanism for the catalytic reaction. In this scheme the reaction of monoorganometal halide (B) with R'm gives a diorganometal complex (A), which affords the cross-coupling product (R–R') on reductive elimination with concomitant oxidative addition of RX to regenerate the intermediate monoorganometal species (B). Although Scheme I represents the essential feature of the catalytic cross-coupling reaction, the mechanistic details remain to be established. Thus Scheme I does not specify the configurations of the intermediate species A and B. Detailed mechanisms of interactions of A and B with RX and R'm are not specified either.

Previously, Stille's and our groups examined thermolysis behavior of *trans*- and *cis*-dialkylbis(tertiary phosphine)palladium(II) complexes.[2-4] Interactions of isolated dialkyl- and diarylpalladium(II) complexes with organomagnesium and -lithium compounds[5,6] and with organic

Scheme I

$$m = MgX, Li, R_3Sn; \quad X = halogen$$
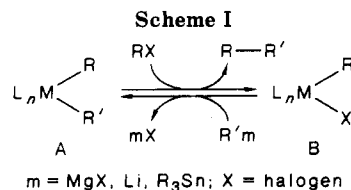
halides[7-9] have been also investigated. These studies revealed: (i) for reductive elimination from diorganopalladium to take place, the two organo groups must be situated at mutually cis positions; (ii) reductive elimination of alkane from *cis*-dialkyl complexes proceeds through a dissociative pathway involving a T-shaped *cis*-[PdR2L]-type intermediate; (iii) trans to cis isomerization of dimethyl complexes is promoted by methylmagnesium compounds; (iv) diorganopalladium complexes form tri- and tetraorganopalladate species in solution containing organolithium compounds; (v) *cis*-dimethylpalladium(II) interacts with methyl iodide to form trimethylpalladium(IV) iodide, which affords ethane on reductive elimination;[3,8] (vi) reactions of *trans*-diarylpalladium(II) complexes with methyl and aryl iodides, on the other hand, do not involve Pd(IV) intermediates but proceed via an intermolecular process between the diaryl complexes and mo-

(1) (a) Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669. (b) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340. (c) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, p 799. (d) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158 and references cited therein.

(2) (a) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868. (b) Ozawa, F.; Ito, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 6457. (c) Ozawa, F.; Kurihara, K.; Yamamoto, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 399.

(3) (a) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933. (b) Loar, M. K.; Stille, J. K. *Ibid.* **1981**, *103*, 4174.

(4) See also: Kurosawa, H.; Emoto, M.; Ohnishi, H.; Miki, K.; Kasai, N.; Tatsumi, K.; Nakamura, a. *J. Am. Chem. Soc.* **1987**, *109*, 6333. Kurosawa, H.; Urabe, A.; Miki, K.; Kasai, N. *Organometallics* **1986**, *5*, 2002. Lau, J.; Sustmann, R. *Tetrahedron Lett.* **1985**, *26*, 4907. Sustmann, R.; Lau, J. *Chem. Ber.* **1986**, *119*, 2531.

(5) Ozawa, F.; Kurihara, K.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1985**, *279*, 233.

(6) (a) Nakazawa, H.; Ozawa, F.; Yamamoto, A. *Organometallics* **1983**, *2*, 241. (b) Negishi, E.; Akiyoshi, K.; Takahashi, T. *J. Chem. Soc., Chem. Commun.* **1987**, 477. (c) Negishi, E.; Takahashi, T.; Akiyoshi, K. *J. Organomet. Chem.* **1987**, *334*, 181.

(7) (a) Ozawa, F.; Fujimori, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1986**, *5*, 2144. (b) Ozawa, F.; Hidaka, T.; Yamamoto, T.; Yamamoto, A. *J. Organometal. Chem.* **1987**, *330*, 253.

(8) (a) Moravskiy, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4182. (b) Milstein, D.; Stille, J. K. *Ibid.* **1979**, *101*, 4981.

(9) (a) Kurosawa, H.; Emoto, M.; Urabe, A. *J. Chem. Soc., Chem. Commun.* **1984**, 968. (b) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *Ibid.* **1986**, 1722. (c) Diversi, P.; Fasce, D.; Santini, R. *J. Organomet. Chem.* **1984**, *269*, 285.

nomethyl- or monoarylpalladium species generated in the systems. These observations have shed light on reactions not explicitly represented in Scheme I, but obviously more studies are required to clarify the mechanistic details.

Among a variety of the previously prepared organo-palladium complexes those having two PEt_2Ph ligands provide an almost complete array of complexes conceivable as intermediates in the catalytic cross-coupling reactions. These PEt_2Ph-coordinated palladium complexes are readily characterized by ^{31}P NMR spectroscopy and allow us to study the behavior of these complexes in the actual catalytic system. Comparison of the chemical properties of these isolated PEt_2Ph-coordinated organopalladium complexes with the ^{31}P NMR spectra of the catalytic system gives us insight into what are actually taking place in the catalytic cross-coupling reaction. The study has revealed involvement of processes that hitherto have not been considered as will be discussed in this paper.

Results

^{31}P NMR Study on the Catalytic Cross-Coupling of Phenyl Iodide and Methylmagnesium Iodide Promoted by *trans*-$PdPh(I)(PEt_2Ph)_2$ (1).

The reaction of phenyl iodide (0.99 M) and methylmagnesium iodide (1.24 M) in Et_2O containing *trans*-$PdPh(I)(PEt_2Ph)_2$ (1; 0.10 M) at 36 °C for 20 h afforded 85%/PhI of toluene and 6% of biphenyl at 97% conversion of phenyl iodide. No ethane formation was observed.
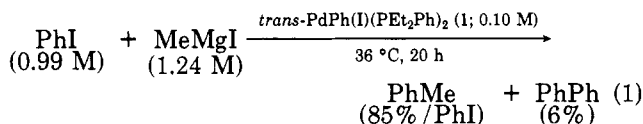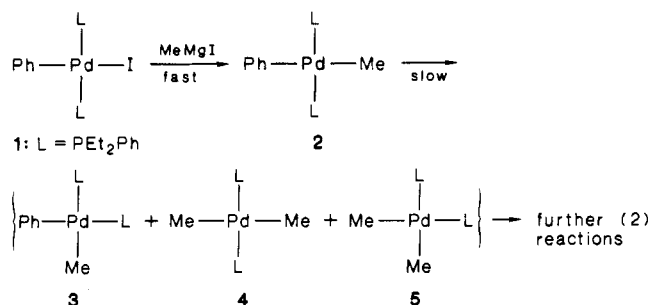
$$\text{PhI} + \text{MeMgI} \xrightarrow[\text{36 °C, 20 h}]{\textit{trans}\text{-PdPh(I)(PEt}_2\text{Ph)}_2 \text{ (1; 0.10 M)}}$$
$$\text{(0.99 M)} \quad \text{(1.24 M)}$$
$$\text{PhMe} + \text{PhPh} \quad (1)$$
$$\text{(85\%/PhI)} \quad \text{(6\%)}$$

Figure 1 shows the change of palladium species in the catalytic system with time as followed by, $^{31}P\{^1H\}$ NMR spectroscopy. In the ^{31}P NMR spectrum *trans*-PdMePh-$(PEt_2Ph)_2$ (2) is generated at the initial stage of the reaction by the rapid interaction of the starting complex 1 with methylmagnesium iodide as the sole observable palladium species in the system (26.1 ppm, s; downfield from an external PPh_3 reference). On standing at 35 °C, the sample solution produced signals arising from *cis*-$PdMePh(PEt_2Ph)_2$ (3; 11.0 and 17.8 ppm (AB, J_{PP} = 23 Hz)), *trans*-$PdMe_2(PEt_2Ph)_2$ (4; 31.8 ppm, (s)), and *cis*-$PdMe_2(PEt_2Ph)_2$ (5; 17.2 ppm (s)), which gradually grew at the expense of the signal due to 2, indicating that the following sequence of reactions is taking place: Prepa-

ration and properties of complexes 2–5 observed in the catalytic system are described below.

Preparation of *trans*- and *cis*-PdMePhL₂. Among the palladium complexes observed in the catalytic system, *trans*- and *cis*-dimethyl complexes (4 and 5, respectively) are already known.[2a] We describe here the preparation of *trans*- and *cis*-$PdMePh(PEt_2Ph)_2$ (2 and 3, respectively).

The trans complex 2 was prepared by the reaction of *trans*-$PdPh(Br)(PEt_2Ph)_2$ with an equimolar amount of
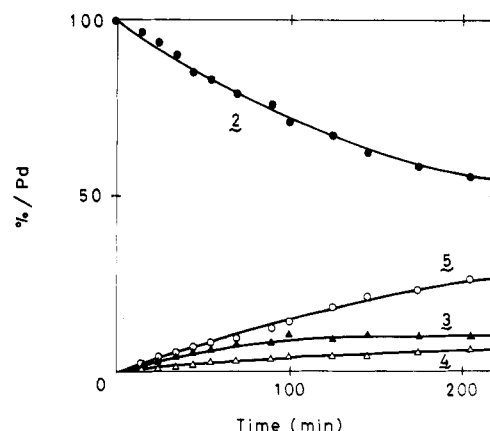
Figure 1. The change of palladium species with time in the catalytic cross-coupling reaction of phenyl iodide (0.99 M) with methylmagnesium iodide (1.24 M) promoted by *trans*-PdPh-$(I)(PEt_2Ph)_2$ (1; 0.10 M) in Et_2O at 35 °C: **2**, *trans*-PdMePh-$(PEt_2Ph)_2$; **3**, *cis*-$PdMePh(PEt_2Ph)_2$; **4**, *trans*-$PdMe_2(PEt_2Ph)_2$; **5**, *cis*-$PdMe_2(PEt_2Ph)_2$.

Table I. List of Isolated PdRArL₂ Complexes

configuratn	R	Ar	L^a
trans	Me	Ph	PEt_2Ph (2)
	Me	*m*-tolyl	PEt_2Ph
	Me	Ph	PEt_3
	Et	Ph	PEt_3
cis	Me	Ph	PEt_2Ph (3)
	Me	*p*-tolyl	PEt_2Ph
	Me	p-ClC_6H_4	PEt_2Ph
	Me	p-FC_6H_4	PEt_2Ph
	Me	p-$CF_3C_6H_4$	PEt_2Ph
	Me	Ph	PMe_2Ph
	Me	Ph	$^1/_2$dmpe
	Me	Ph	$^1/_2$dppe

^{a}Abbreviations: dmpe = $Me_2PCH_2CH_2PMe_2$; dppe = $Ph_2PCH_2CH_2PPh_2$.

MeLi in Et_2O. The reaction gave 2 in a 93% selectivity together with a minor amount of the cis isomer 3, which was removed by recrystallization.
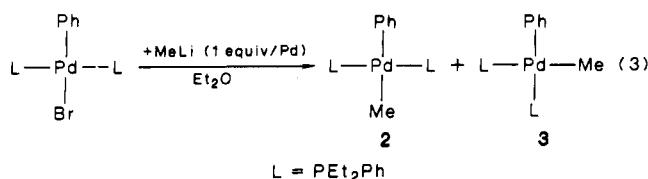
The selective synthesis of *cis*-$PdMePh(PEt_2Ph)_2$ (3) was achieved by a route through the previously reported *cis*-$[PdMe_2Ph(PEt_2Ph)]^-Li^+$ species.[6a] Treatment of
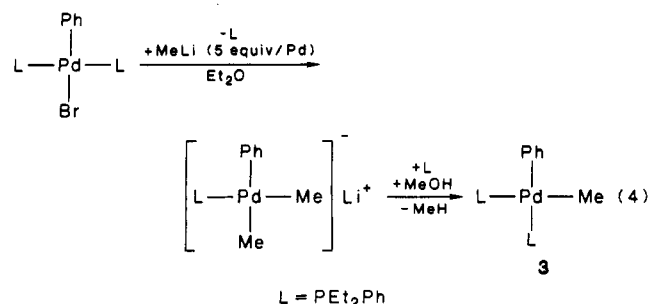
trans-$PdPh(Br)(PEt_2Ph)_2$ with excess (five times) MeLi afforded the *cis*-dimethylphenylpalladate. Methanolysis of the palladate species without isolation selectively protonated the methyl group trans to the phenyl group, and the *cis*-methylphenyl complex (3) was cleanly formed with evolution of methane as confirmed by NMR spectroscopy.
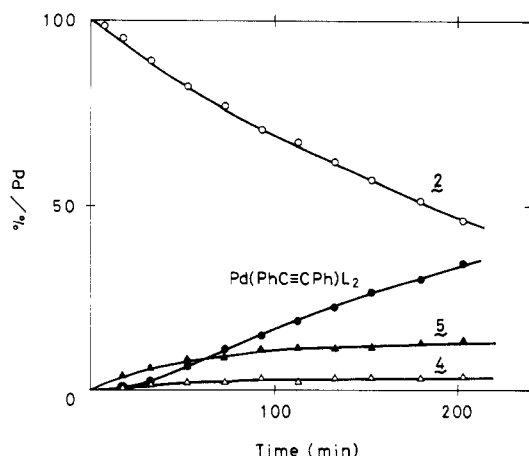
Figure 2. The change of palladium species with time in the reaction of *trans*-PdMePh(PEt$_2$Ph)$_2$ (2; 0.10 M) with methylmagnesium iodide (1.24 M) in Et$_2$O containing PhC≡CPh (0.20 M) at 35 °C: 4, *trans*-PdMe$_2$(PEt$_2$Ph)$_2$; 5, *cis*-PdMe$_2$(PEt$_2$Ph)$_2$.

A variety of *trans*- and *cis*-PdR(Ar)L$_2$ type complexes could be prepared by similar methods (Table I). The *cis*-methylphenyl complexes having chelating diphosphine ligands were synthesized by ligand-exchange reactions. The reaction of 3 with 1,2-bis(dimethylphosphino)ethane (dmpe) in Et$_2$O proceeded smoothly at −30 °C to give *cis*-PdMePh(dmpe). A similar ligand exchange reaction attempted with the trans complex 2 instead of 3, the cis isomer, gave a white insoluble solid product instead of *cis*-PdMePh(dmpe). Identification of the solid could not be achieved because of its insoluble character in most organic solvents. The substance is probably polymeric with a bridging dmpe ligand. *cis*-PdMePh(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane) was prepared by the reaction of dppe with *cis*-PdMePh(PMePh$_2$)$_2$, generated from *trans*-PdPh(Br)(PMePh$_2$)$_2$ and MeLi (see Experimental Section).

Reactions of *trans*-PdMePh(PEt$_2$Ph)$_2$ (2). We next examined the possibility that toluene could be formed by thermolysis of 2 or by the reactions of 2 with phenyl iodide or methylmagnesium iodide.

1. **Thermolysis.** The isolated complex 2 is considerably stable in pure solvents such as Et$_2$O and benzene and no decomposition was observed at 36 °C. Addition of coordinatively unsaturated [Pd^0(PEt$_2$Ph)$_2$] species generated from *trans*-PdEt$_2$(PEt$_2$Ph)$_2$[2b] to the system, on the other hand, resulted in a rapid decomposition of 2 to give a quantitative amount of toluene. The toluene formation was effectively blocked by addition of tolan or PEt$_2$Ph, which trap the [Pd^0(PEt$_2$Ph)$_2$] species as Pd(PhC≡CPh)(PEt$_2$Ph)$_2$ and Pd(PEt$_2$Ph)$_n$ (n = 3 or 4), respectively.

Since in the actual catalytic solution the [Pd^0(PEt$_2$Ph)$_2$] species produced is considered to undergo a rapid oxidative addition of phenyl iodide to give *trans*-PdPh(I)(PEt$_2$Ph)$_2$, it is unlikely that the thermolysis of the relatively stable complex 2 is responsible for the toluene formation in the catalytic system.

2. **With Methylmagnesium Iodide.** Complex 2 readily formed toluene in a solution containing MeMgI. Figure 2 illustrates the change in 2 (0.10 M) with MeMgI (1.24 M) in Et$_2$O at 35 °C with time as followed by ^{31}P{^{1}H} NMR spectroscopy. This reaction was carried out in the presence of PhC≡CPh (0.20 M) in order to avoid the thermolysis of 2 on interaction with coordinatively unsaturated [Pd^0(PEt$_2$Ph)$_2$] produced by reductive elimination. With the progress of the reaction the amounts of *trans*- and *cis*-PdMe$_2$(PEt$_2$Ph)$_2$ (4 and 5, respectively) increased with decreasing 2. On further reaction, the amount of Pd-

(PhC≡CPh)(PEt$_2$Ph)$_2$ gradually increased with the formation of toluene,[10] while the amounts of 4 and 5 remained constant before their eventual disappearance. The presence of small amounts (less than 1%) of *cis*-PdMePh-(PEt$_2$Ph)$_2$ (3) and *trans*-PdPh$_2$(PEt$_2$Ph)$_2$[6a] in the system was also noted. The relative ratio of 4 and 5 (1:4) was in agreement with the equilibrium constant observed in the *trans*–cis isomerization of PdMe$_2$(PEt$_2$Ph)$_2$ catalyzed by methylmagnesium compounds.[5]

The results in Figure 2 suggest the occurrence of the following sequence of reactions. The interaction of 2 with

L = PEt$_2$Ph
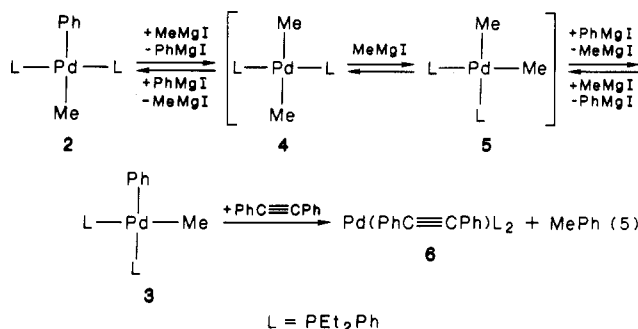
MeMgI gives PhMgI and the dimethylpalladium complexes (4 and 5), which are in a rapid equilibrium with each other in the system. The trans–cis isomerization between 4 and 5 proceeds through an intermolecular process involving methyl exchange between the dimethylpalladium and methylmagnesium halide.[5] As described below, the dimethylpalladium complexes thus produced readily react with PhMgI generated in the system to give *cis*-methylphenyl complex 3, which affords toluene and Pd(PhC≡CPh)(PEt$_2$Ph)$_2$ (6) on reductive elimination.

The occurrence of the exchange reactions of the organic groups between the palladium species and methylmagnesium iodide was supported by a deuterium-labeling experiment. Thus the reaction of *trans*-Pd(CH$_3$)Ph-(PEt$_2$Ph)$_2$ (2, 0.11 M) with CD$_3$MgI (1.20 M) in Et$_2$O containing tolan (0.12 M) at 36 °C for 5 h yielded 48%/2 of toluene composed of PhCH$_3$ and PhCD$_3$ in a 9/91 ratio.

As shown in eq 5, the reaction of 2 with MeMgI generates PhMgI accompanied by formation of 4 and 5. In order to examine the possibility that 2 gives toluene on interaction with PhMgI, the reaction of 2 (0.10 M) with PhMgBr (0.50 M) in Et$_2$O containing tolan (0.20 M) at room temperature was examined by ^{31}P NMR spectroscopy. The reaction gave a minor amount of toluene but predominantly yielded *trans*-PdPh$_2$(PEt$_2$Ph)$_2$ together with MeMgBr, the formation of which was confirmed by ^{1}H NMR.
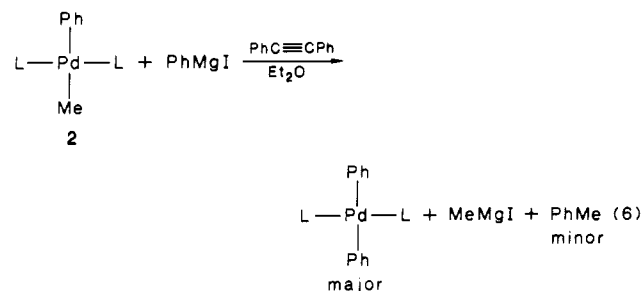
3. **With Phenyl Iodide.** The reaction of *trans*-PdMePh(PEt$_2$Ph)$_2$ (2; 0.10 M) with phenyl iodide (1.0 M)

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(10) The ^{31}P{^{1}H} chemical shift of Pd(PhC≡CPh)(PEt$_2$Ph)$_2$ was observed as a singlet at δ 23.3. It has been confirmed by means of GLC that the amount of toluene is comparable with that of Pd(PhC≡CPh)-(PEt$_2$Ph)$_2$.
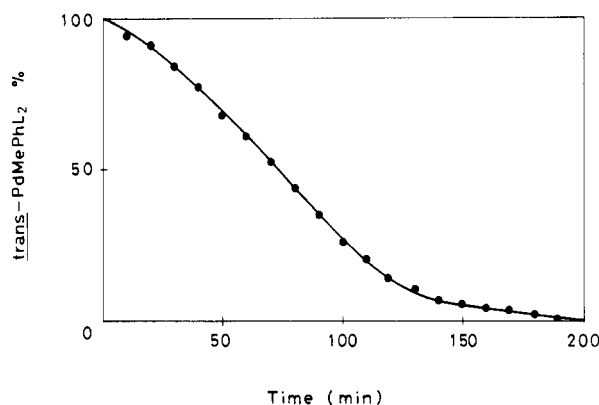
Figure 3. Time–conversion curve of trans-PdMePh(PEt$_2$Ph)$_2$ (2) in the reaction with phenyl iodide in benzene at 45 °C.
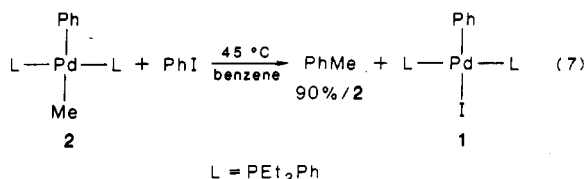
Table II. Reactions of trans-PdMePh(PEt$_2$Ph)$_2$ (2) with m-Tolyl Iodide in the Absence and Presence of trans-PdPh(I)(PEt$_2$Ph)$_2$ (1)^a

run	m-tolyl iodide (M)	1 (M)	product ratio^b m-xylene	toluene
1	1.0	0.00	79	21
2	1.0	0.10	62	38
3	1.0	0.30	57	43
4	0.50	0.30	59	41
5	0.20	0.30	54	46

^{a} Reaction conditions: [2] = 0.10 M, in benzene at 45 °C. ^{b} Values at 100% conversion of 2.

in benzene at 45 °C yielded 90%/2 of toluene together with trans-PdPh(I)(PEt$_2$Ph)$_2$. No formation of biphenyl

$$L\!-\!\underset{\underset{2}{\overset{|}{Me}}}{\overset{\overset{Ph}{|}}{Pd}}\!-\!L \;+\; PhI \xrightarrow[\text{benzene}]{45\ ^\circ C} PhMe \;+\; L\!-\!\underset{\underset{1}{\overset{|}{I}}}{\overset{\overset{Ph}{|}}{Pd}}\!-\!L \quad (7)$$
$$90\%/2$$
$$L = PEt_2Ph$$

was observed. The toluene formation was totally suppressed by the addition of free PEt$_2$Ph (1 equiv/2) to the system.

Reaction 7 accelerated with time as illustrated in Figure 3. A similar acceleration effect has been observed also in the reactions of trans-PdAr$_2$(PEt$_2$Ph)$_2$ (Ar = phenyl and m-tolyl) with RI (R = Me and Ar) affording ArR.[7] In the previous studies we have shown that the reactions of trans-diarylpalladium complexes with organic halides proceed through an intermolecular process between the diarylpalladium and trans-PdR(I)(PEt$_2$Ph)$_2$, which is formed by oxidative addition of RI to [Pd^0(PEt$_2$Ph)$_2$] generated in the reaction. The time–conversion curve in Figure 3 suggests the occurrence of a similar intermolecular process in the reaction of 2 and phenyl iodide.

Treatment of 2 (0.10 M) with m-tolyl iodide (1.0 M) in benzene at 45 °C yielded m-xylene and toluene in a 79/21 ratio (Table II, run 1). Addition of trans-PdPh(I)-(PEt$_2$Ph)$_2$ (1) to the system significantly improved the selectivity for toluene formation (runs 2 and 3), while the ratio of m-xylene to toluene was independent of the concentration of m-tolyl iodide (runs 3–5). The results in Table II again suggest that the toluene formation in reaction 7 proceeds through an intermolecular process between 2 and 1.

The toluene formation in reaction (7) is accounted for by the following mechanism (Scheme II), which is assumed from the analogy with the mechanisms of RAr formation in the reactions of trans-PdAr$_2$(PEt$_2$Ph)$_2$ with RI.[7] In this
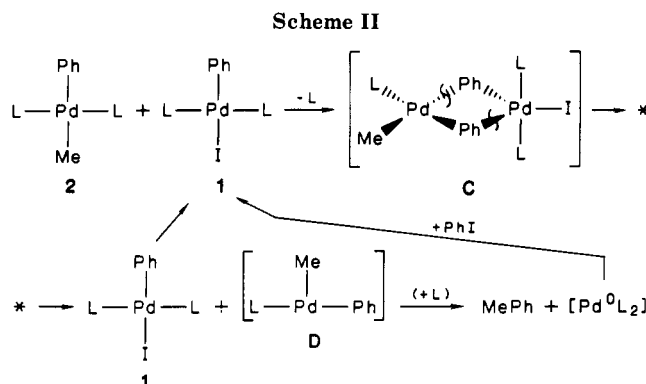
Scheme II

scheme the dissociation of L from 2 gives a three-coordinate complex which forms a bridged intermediate (C) on interaction with the monophenyl complex 1. Cleavage of the two Pd–Ph bonds in C produces 1 and a three-coordinate [PdMePhL] species (D), which has a favorable geometry for the reductive elimination affording toluene and a Pd(0) species. The Pd(0) species thus formed further binds L and reacts with phenyl iodide to reproduce 1.

The validity of the intermolecular process in Scheme II is supported by the following experiments. Table III lists the results of the reaction of 2 and trans-Pd(m-tolyl)I-(PEt$_2$Ph)$_2$ in the absence of aryl iodides.[11] The reaction produced m-xylene and toluene. The selectivity for m-xylene formation increased with an increasing amount of trans-Pd(m-tolyl)I(PEt$_2$Ph)$_2$ added to the system.

The process for formation of m-xylene and toluene in the reactions in Table III can be expressed by eq 8. The

Table III. Reactions of trans-PdMePh(PEt$_2$Ph)$_2$ (2) with trans-Pd(m-tolyl)I(PEt$_2$Ph)$_2$^{a}

run	amount of monotolyl complex (mol/mol of 2)	product ratio^b (m-xylene/toluene) found	calcd
1	1.0	62/38	62/38
2	3.0	82/18	85/15
3	5.0	91/9	91/9

^{a} Reactions were carried out in benzene containing dimethyl maleate (2 equiv/2) at 53 °C. ^{b} Values at 100% conversion of 2.
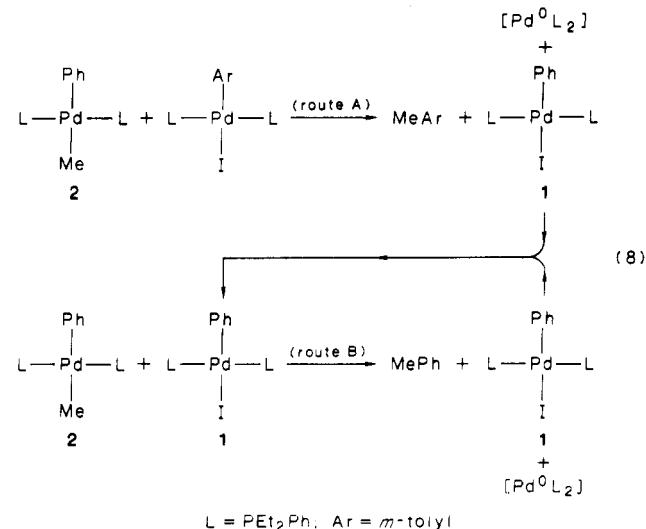
(11) The reactions were carried out in the presence of dimethyl maleate (dmm). In the absence of dmm a coordinatively unsaturated [Pd^0(PEt$_2$Ph)$_2$] species, which is afforded by the reactions of 1 and trans-Pd(m-tolyl)I(PEt$_2$Ph)$_2$, induces rapid decomposition of 1 to give toluene (see text).[7] In the presence of dmm the [Pd^0(PEt$_2$Ph)$_2$] species is effectively trapped as Pd(dmm)(PEt$_2$Ph)$_2$.

<div align="center">

Table IV. Products in Thermolysis of *cis*-PdMeArL₂ Complexes[a]

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	complex			temp	additive	products (%/Pd)[c]					
run	Ar	L[b]	solvent	(°C)[d]	(equiv/Pd)	MeAr	ArAr	ArH	C₂H₆	C₂H₄	CH₄
1	Ph	PEt₂Ph (3)	benzene	rt	tolan (3)	95	0	0	0	0	0
2	Ph	PEt₂Ph (3)	CH₂Cl₂	rt	tolan (2)	91	0	0	0	0	0
3	Ph	PEt₂Ph (3)	benzene	rt	PEt₂Ph (1)	100	0	0	0	0	0
4	p-tolyl	PEt₂Ph	CH₂Cl₂	rt	PEt₂Ph (1)	99	0	0	0	0	0
5	p-ClC₆H₄	PEt₂Ph	CH₂Cl₂	rt	PEt₂Ph (1)	100	0	0	0	0	0
6	p-FC₆H₄	PEt₂Ph	benzene	30	tolan (3)	85	0	0	0	0	0
7	Ph	PMe₂Ph	CH₂Cl₂	rt	tolan (2)	34	7	4	0	0	0
8	Ph	¹/₂dmpe	CH₂Cl₂	rt	tolan (2)	12	15	12	0	5	50
9	Ph	¹/₂dmpe	CH₂Cl₂	rt	dmpe (1)	9	0	2	0	32	38
10	Ph	¹/₂dppe	benzene	15–40	...	58	13	0	0	0	0
11	Ph	¹/₂dppe	benzene	35–40	dppe (2)	79	0	0	0	0	0

[a] [*cis*-PdMeArL₂] = ca. 0.1 M. [b] Abbreviations: dmpe = Me₂PCH₂CH₂PMe₂; dppe = Ph₂PCH₂CH₂PPh₂. [c] The products were analyzed after the reaction mixtures were stirred overnight. [d] rt = room temperature.

reaction of 2 with *trans*-Pd(*m*-tolyl)I(PEt₂Ph)₂ gives *m*-xylene together with monophenylpalladium (1) and a [Pd⁰(PEt₂Ph)₂] species (route A). Complex 1 reacts with 2 to yield toluene, [Pd⁰(PEt₂Ph)₂], and 1, which further reacts with 2 (route B). If the monophenyl- and mono-tolylpalladium complexes have the same reactivity toward 2, the ratio of *m*-xylene and toluene produced can be estimated as listed in Table III.[7a] The calculated values are in good agreement with the experimental values.

Reactions of *trans*- and *cis*-PdMe₂(PEt₂Ph)₂ (4 and 5, Respectively). 1. With Phenylmagnesium Halides. The results in Figure 2 indicate that the toluene formation in the reaction of 2 and MeMgI involves formation of *trans*- and *cis*-dimethylpalladium complexes (4 and 5, respectively) as transient intermediates. As represented in eq 5, the toluene formation from 4 and 5 may involve interactions of the dimethyl complexes with PhMgI generated in the system.

The reactions of 4 and 5 with PhMgX (X = Br and I), indeed, took place under very mild conditions to give toluene in almost quantitative yields.[12] Figure 4 shows a change in the ³¹P{¹H} NMR spectrum of a reaction solution of *trans*-dimethylpalladium (4; 0.10 M) mixed with PhMgBr (0.50 M) in Et₂O containing tolan (0.20 M) with time. The reaction smoothly proceeded even at 0 °C to give toluene together with Pd(PhC≡CPh)(PEt₂Ph)₂. As can be seen from the spectra, the presence of considerable amounts of *trans*- and *cis*-PdMePh(PEt₂Ph)₂ (2 and 3, respectively) and a small amount of *cis*-PdMe₂(PEt₂Ph)₂ (5) in the system was observed throughout the reaction. At the completion of the reaction, the peaks due to the starting complex 4 and the intermediate species (2, 3, and 5) disappeared to be dominated by the signal of Pd-(PhC≡CPh)(PEt₂Ph)₂. The reaction of *cis*-dimethyl-palladium (5) with phenylmagnesium halides showed a similar spectroscopic change.

2. With Phenyl Iodide. Previously Stille reported that treatment of dimethylpalladium(II) having tertiary phosphine ligands with MeI markedly enhanced the ethane formation.[8] The reaction was assumed to involve a tri-methylpalladium(IV) iodide intermediate formed by an oxidative addition of MeI to the dimethylpalladium(II). In contrast to the reaction with MeI, the *trans*- and *cis*-dimethylpalladium complexes (4 and 5, respectively) have shown poor reactivity toward phenyl iodide. For example, the reaction of 4 with an excess amount (20 times) of PhI at 35 °C for 24 h gave only 4%/4 of toluene.

Reactions of *cis*-PdMePh(PEt₂Ph)₂ (3). 1. Thermolysis. The experimental results described above
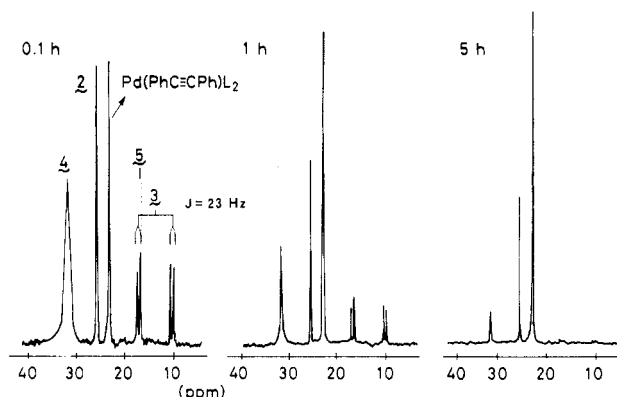

Figure 4. ³¹P{¹H} NMR spectroscopic change in the reaction system of *trans*-PdMe₂(PEt₂Ph)₂ (4; 0.10 M) mixed with PhMgBr (0.50 M) in Et₂O containing PhC≡CPh (0.20 M) at 0 °C: **2**, *trans*-PdMePh(PEt₂Ph)₂; **3**, *cis*-PdMePh(PEt₂Ph)₂; **5**, *cis*-PdMe₂(PEt₂Ph)₂.

strongly suggest that the *cis*-PdMePh(PEt₂Ph)₂ (3) serves as a probable intermediate for the toluene formation. The results of thermolysis of isolated *cis*-PdMeArL₂-type complexes in solution under various reaction conditions are listed in Table IV. The *cis*-methylarylpalladium complexes having two PEt₂Ph ligands selectively gave the corresponding MeAr regardless of the presence or absence of free tertiary phosphine ligands (runs 1–6). The ther-molysis of *cis*-PdMePh(dppe) in the presence of free dppe also yielded toluene selectively (run 11), while the same complex afforded considerable amount of biphenyl together with toluene in solution without free dppe (run 10). The *cis*-methylphenyl complexes having PMe₂Ph or dmpe as ligands gave complicated results indicating the partial involvement of the ligands in thermolysis.

The cis complex 3 afforded the intramolecular reductive elimination product (CH₃Ph) over 94% selectivity even in the presence of excess amounts of CD₃I and *m*-tolyl iodide (Table V). Treatment of *cis*-PdMePh(dppe) with *m*-tolyl iodide in solution containing free dppe also yielded only toluene.

2. Kinetic Study on the Reductive Elimination. The ArMe formation from the *cis*-PdMeAr(PEt₂Ph)₂ complexes in C₆D₆ at 24 °C was followed by ¹H NMR spectroscopy. The reaction proceeded obeying the first-order rate law over 3 half-lives. Addition of free PEt₂Ph did not alter the reaction rate. The rate of ArMe formation was not affected by addition of PhI (Table VI).

These kinetic features in the ArMe formation from *cis*-methylaryl complexes are in sharp contrast with those observed in the reductive elimination of *cis*-dimethylbis-(tertiary phosphine)palladium(II) complexes where the reaction was effectively suppressed by the addition of a

(12) Complexes 4 and 5 reacted with various organomagnesium halides (RMgX) including tolyl-, phenyl-, benzyl-, and styrylmagnesium halides to give corresponding cross-coupling products (RMe) in good yields.

Table V. Thermolysis Products of *cis*-PdMePhL₂ Complexes in the Presence of Organic Iodides (RI)[a]

run	complex (L)	RI (equiv/Pd)	additive (eq/Pd)	products (%/Pd)		
				CH_3Ph	RPh	CH_3R
1	PEt_2Ph (3)	m-MeC₆H₄I (10)	...	94	0	5
2	PEt_2Ph (3)	m-MeC₆H₄I (10)	tolan (1)	99	0	1
3	PEt_2Ph (3)	m-MeC₆H₄I (10)	PEt_2Ph (1)	99	0	0
4	PEt_2Ph (3)	CD_3I (10)	...	97	3	0
5	$^1/_2$dppe	m-MeC₆H₄I (20)	dppe (2)	94	0	0

[a] Reaction temperature: room temperature (runs 1–4), 35–40 °C (rum 5). Solvent: CH_2Cl_2 (runs 1–3), benzene (runs 4 and 5).

Table VI. First-Order Rate Constants for Reductive Elimination of *cis*-PdMeAr(PEt₂Ph)₂ Complexes[a]

| Ar(Pd⟨○⟩Y)					
Y	σ_π^+	σ_i	σ_p	additive (mol/L)	$10^3 k_{obsd}$ (s⁻¹)
F	−0.118	0.363	0.06	...	0.13
				PEt_2Ph (0.1)	0.16
Me	−0.078	−0.045	−0.17	...	0.40
				PEt_2Ph (0.1)	0.40
				PhI (1.0)	0.41
Cl	−0.070	0.348	0.23	...	0.37
				PEt_2Ph (0.1)	0.35
				PhI (1.0)	0.38
H	0	0	0	...	0.51
				PEt_2Ph (0.1)	0.49
CF₃	(0.24)[b]	0.30	0.54	...	3.0
				PEt_2Ph (0.1)	2.4

[a] Reactions were carried out in C_6D_6 containing 0.3 mol/L of tolan at 24 ± 1 °C and followed by ^1H NMR spectroscopy. Tolan was added for trapping [Pd⁰L₂] species generated in the system.[2a,3a] It has been confirmed that the addition of tolan to the system does not affect the rate for ArMe formation. [b] σ_π^- value.

small amount of free tertiary phosphine while the addition of MeI markedly enhanced the rate of reductive elimination.[2a,3a] Furthermore, the reductive elimination of *cis*-PdMeAr(PEt₂Ph)₂ complexes proceeded much more rapidly than *cis*-PdMe₂(PEt₂Ph)₂ (10^4 k_{obsd} = 5.3 s⁻¹ at 45 °C).[2a]

The rate of ArMe formation (k_{obsd}) significantly varied with nature of the para substituent on the phenyl group (Table VI). Among various Hammett parameters,[13] σ_π^+ values reflecting the resonance effect of the substituents showed a relatively good correlation with logarithms of the k_{obsd} values (ρ = 3.2; r = 0.976). On the other hand, no correlation was observed between the log k_{obsd} values and σ_i or σ_P values. The trend indicates that the higher π-electron density on the phenyl group makes the reductive elimination proceed more slowly.

Discussion

The present study revealed that the mechanism of toluene formation in the cross-coupling reaction of phenyl iodide and methylmagnesium iodide catalyzed by a PEt₂Ph-coordinated palladium complex is more complicated than that represented by Scheme I. Not only was participation of the phenylpalladium iodide complex (1) and the *cis*-methylphenylpalladium complex (3) revealed, but also involvement of the *trans*-methylphenyl complex (2) and the *cis*- and *trans*-dimethyl complexes (4 and 5, respectively) was found. On the basis of the $^{31}P\{^1H\}$ NMR studies on the reactions of the isolated complexes 2, 4, and 5 with methyl- and phenylmagnesium halides, the occurrence of the interconversion of these species with each other and with 3 was demonstrated. Scheme III shows the mechanism of the cross-coupling reaction proposed with

Scheme III. Proposed Mechanism for the Catalytic Cross-Coupling Reaction of Phenyl Iodide and Methylmagnesium Iodide Promoted by *trans*-PdPh(I)L₂[a]

[a] L = PEt₂Ph.
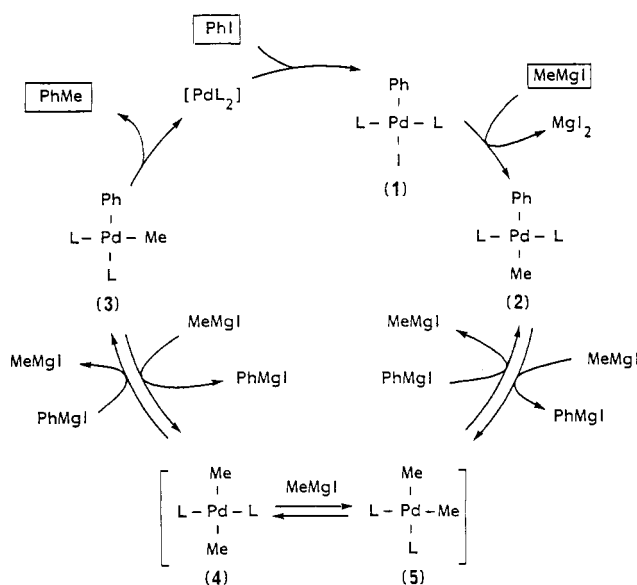
these new findings taken into account. The first step of the catalytic reaction is the methylation of the starting monophenylpalladium iodide (1) with MeMgI. This reaction proceeds readily with the retention of the original trans configuration of 1. Since the *trans*-methylphenylpalladium (2) thus formed has a geometry unsuitable for direct reductive elimination, the complex must be first isomerized to its cis isomer (3). The interconversion of 2 to 3 does not proceed spontaneously but can be achieved by processes involving the participation of the transient dimethylpalladium intermediates (4 and 5). Thus the reaction of 2 with MeMgI gives 4 and 5 with release of PhMgI. Interactions of 4 and 5 with the liberated PhMgI affords the *cis*-methylphenylpalladium complex (3). Complex 3 thus produced (being thermally unstable) undergoes reductive elimination to give toluene and a [Pd⁰L₂] species, which rapidly reacts with PhI to regenerate 1 as the carrier of the catalytic cycle.

In catalytic systems the possibility that a minor amount of a catalytic species having a high activity is responsible for the real catalysis rather than an identifiable catalytic species having less activity is difficult to exclude.[14] In the present system, however, the catalytic reaction rate is rather low and all of the diorganopalladium complexes, except for the *cis*-diphenylpalladium complex that would give biphenyl on reductive elimination, have been characterized and their reactions have been thoroughly examined. Therefore, it is likely that the species observed by $^{31}P\{^1H\}$ NMR spectroscopy in the catalytic system are

(13) Inamoto, N. *Hammett Soku*; Maruzen: Tokyo, 1983.

(14) Halpern, J. *Science (Washington, D.C.)* 1982, *217*, 401.

acting as the real catalytic intermediates. Nevertheless, other possible routes not represented in Scheme III still deserve examination.
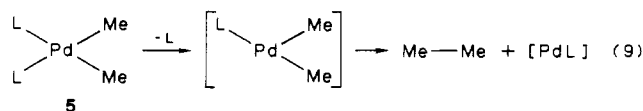
Direct conversion of **2** by interaction with MeMgI into **3** is a route alternative to the indirect processes from **2** to **4** and **5** and then to **3** as shown in Scheme III. However, the results shown in Figure 2 indicate that the dimethylpalladium complex **5** together with **4** are formed *prior to* the formation of the reductive elimination product. Thus the direct route from **2** to **3** appears to be a minor route, if any.

Another possible route to give **3** from **2** is the reaction of **2** with monophenylpalladium iodide (**1**) as represented in Scheme II. However, this process cannot constitute the main route either since **1** is very rapidly converted into **2** in the catalytic system containing an excess amount of MeMgI as can be seen from Figure 1.
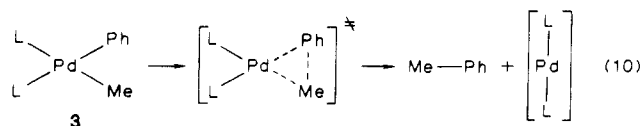
It is sometimes assumed that the reductive elimination of the diorganopalladium(II) complexes in the presence of excess amounts of organic halides proceeds through a triorganopalladium(IV) halide intermediate. However, the direct participation of organic halides to induce the reductive elimination is excluded from the data shown in Table V where the *cis*-methylphenylpalladium complex (**3**) was decomposed in the presence of *m*-tolyl iodide. The reactions cleanly eliminate toluene without forming any other coupling product which would be expected if the reaction proceeds through a triorganopalladium(IV) iodide.

The minor amount of biphenyl formed in the catalytic reaction (eq 1) may arise from the reductive elimination of the *cis*-diphenylpalladium complex. Although the *cis*-diphenylpalladium complex, presumably quite unstable, was not detected in the catalytic system, it may be formed by the interaction of the *trans*-diphenylpalladium complex formed by eq 6 with PhMgI.

The remaining questions are concerned about the selectivity for the cross-coupling reaction and the role of the tertiary phosphine ligands. In the catalytic systems we observe the formation of two types of *cis*-diorganopalladium complexes having a favorable geometry for reductive elimination: *cis*-PdMePhL$_2$ (**3**) and *cis*-PdMe$_2$L$_2$ (**5**). The *cis*-dimethylpalladium complex (**5**) is known to reductively eliminate ethane on thermolysis by a dissociative process involving a three-coordinate [PdMe$_2$L] intermediate[2a,3] and was once considered as a model for a catalyst for the C–C bond formation. However, the kinetic

$$\underset{\textbf{5}}{\underset{L}{\overset{L}{\diagdown}}Pd\underset{Me}{\overset{Me}{\diagup}}} \xrightarrow{-L} \left[\underset{L}{\overset{L}{\diagdown}}Pd\underset{Me}{\overset{Me}{\diagup}}\right] \longrightarrow Me\!-\!Me \;+\; [PdL] \quad (9)$$

results showed that the toluene formation from **3** proceeds much more rapidly than the reductive elimination of ethane from **5**. It was also indicated that the toluene formation takes place from the four-coordinate species without predissociation of L.[15]

$$\underset{\textbf{3}}{\underset{L}{\overset{L}{\diagdown}}Pd\underset{Me}{\overset{Ph}{\diagup}}} \longrightarrow \left[\underset{L}{\overset{L}{\diagdown}}Pd\underset{Me}{\overset{Ph}{\diagup}}\right]^{\ddagger} \longrightarrow Me\!-\!Ph \;+\; \left[\underset{L}{\overset{L}{\underset{|}{Pd}}}\right] \quad (10)$$

The fact that no ethane formation was observed in the present catalytic reaction may be due to the difference in

the rates of reactions 9 and 10.[16]

Finally, the role of the ditertiary phosphines deserves a comment. In the catalytic cross-coupling processes employment of a particular type of bidentate ligand causes an effective formation of the cross-coupling products without causing β-hydrogen elimination when an alkylmagnesium halides with β-hydrogens are used. For example, Hayashi and Kumada reported that 1,1'-bis(diphenylphosphino)ferrocene ligand (dppf) is the most suitable ligand for promoting the cross-coupling.[1d] It was also noted that 1,2-bis(diphenylphosphino)butane (dppb) proved to be a better ligand than 1,2-bis(diphenylphosphino)ethane ligand for the catalysis. One obvious reason for the effectiveness of the ditertiary phosphine ligands is their ability to form a chelate ring with the palladium atom allowing the two organic groups forced to come to the adjacent sites (cis) to be cross-coupled. This may preclude the possibility for the catalyst complex to take a trans configuration, from which the β-hydrogen elimination process is known to occur in the case of *trans*-PdEt$_2$(PR$_3$)$_2$,[2b,17] while the *cis*-PdEt$_2$(PR$_3$)$_2$ gives selectively a reductive elimination product.[2a] The chelate ring size of the ditertiary phosphines may have some effects on the reductive elimination. Being less prone to partially dissociate, a diorganopalladium complex having a chelate ring would show less trend to undergo the dissociative process, although such a dissociative process is not required for the reductive elimination of *cis*-PdMeArL$_2$-type complexes. Another possible factor is the allowance of the chelated phosphines to conform to the structural change in a reductive elimination process like eq 10. When the two L's in eq 10 are linked to form a chelate ring, the reductive elimination process to bring the two L's into the mutually trans position would be hindered. If the ditertiary phosphine forming a less rigid chelate ring is more susceptible to the structural deformation such as shown in eq 10, less energy would be required for the reductive elimination to proceed. Part of the reasons for effectiveness of the dppb ligand or dppf (1,1'-bis(diphenylphosphino)ferrocene) employed by Hayashi and Kumada[1d] may be associated with the above effect of forming a flexible chelate. In fact, the results shown in Table IV suggest that methylphenylpalladium complexes having ditertiary phosphines such as dmpe and dppe capable of forming rigid five-membered rings liberate thermolysis products other than toluene. These byproducts may have been formed by internal metalation processes involving the ditertiary phosphine ligands.

Conclusion

The present study revealed that the mechanism of the cross-coupling reaction of aryl halide and alkylmagnesium halide catalyzed by a monotertiary phosphine coordinated palladium complex is more complicated than previously assumed. The involvement of four intermediate methylphenylpalladium and dimethylpalladium complexes in both cis and trans isomers was established, and intercon-

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(15) Reductive elimination taking place directly from a four-coordinate d^8 diorganometal complex has some precedents: ref 3b. Kohara, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1980**, *192*, 265. Abis, L.; Sen. A. Halpern, J. *J. Am. Chem. Soc.* **1979**, *100*, 2915.

(16) It is a general trend that an organo group bound with an sp^2 carbon to a metal (e.g. aryl and alkenyl groups) is eliminated more readily than an alkyl ligand, which is attached with sp^3 carbon to a metal: ref 3b. Komiya, S.; Ozaki, S.; Shibue, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1555. Komiya, S.; Abe, Y.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1983**, *2*, 1446. Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1306, 1310. Chang, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4298. The recent theoretical study revealed that ease of reductive elimination of diorganometal complexes is lowered in the order diaryl > arylalkyl > dialkyl: Tatsumi, K.; Nakamura, A. preivate communication.

(17) It has been confirmed that *trans*-PdEtPh(PEt$_3$)$_2$ exclusively gives ethylene and benzene on its thermolysis in solution.

version processes among these species promoted by organomagnesium compounds were confirmed. Employment of ditertiary phosphine ligands may be causing the intermediates to have cis configurations and eliminates the complication arising from trans–cis isomerization, although the effect of the ring size of the diphosphine-coordinated palladium chelate on the reductive elimination of arylalkane remains to be clarified.

Experimental Section

All manipulations were carried out under an atmosphere of argon or nitrogen or in vacuo. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on a JEOL FX-100 spectrometer by Dr. Y. Nakamura and Ms. R. Ito of our laboratory. ^{1}H and ^{13}C NMR signals are referred to Me$_4$Si as an internal standard and ^{31}P NMR signals to PPh$_3$ as an external reference. Elemental analyses were carried out by Dr. M. Tanaka and Mr. T. Saito of our laboratory by using a Yanagimoto CHN autocorder type MT-2 and a Yazawa halogen analyzer.

The reactions of diorganopalladium complexes with organic halides were carried out as described previously.[7] Organic compounds formed by the reactions were analyzed by HPLC (Shimadzu LC-4A, RI detector, Zorbax ODS column, MeOH–H$_2$O (4:1)) and GLC (Shimadzu GC-3BT, Silicone DC-550 3-m column). Ratio of PhCH$_3$ and PhCD$_3$ produced in the deuterium-labeling experiments was determined by mass spectrometry using a Hitachi M-80 GC–MS spectrometer. The authentic sample of PhCD$_3$ for the mass analysis was prepared by the cross-coupling reaction of PhI and CD$_3$MgI in the presence of *trans*-PdPh(I)(PEt$_2$Ph)$_2$. *trans*-PdPh(I)(PEt$_2$Ph)$_2$ (1), *trans*-Pd(*m*-tolyl)I(PEt$_2$Ph)$_2$, and *trans*- and *cis*-PdMe$_2$(PEt$_2$Ph)$_2$ (4 and 5, respectively) were prepared as reported previously.[2a,7a]

Preparation of *trans*-PdMePh(PEt$_2$Ph)$_2$ (2). To a heterogeneous white mixture of *trans*-PdPh(Br)(PEt$_2$Ph)$_2$ (0.60 g, 1.1 mmol) and Et$_2$O (5 mL) containing styrene (23 μL) was added an Et$_2$O solution (2.1 mL) of MeLi (1.2 mmol) at −70 °C. On stirring at −10 to 0 °C, the system turned to a pale yellow homogeneous solution. After 2 h dioxane (85 μL, 1.0 mmol) was added to the system at −30 °C to precipitate LiBr generated in the system. The resulting white powder of the dioxane adduct of LiBr was removed by filtration at −40 °C, and the filtrate was concentrated to almost dryness. Addition of hexane (5 mL) to the system at −70 °C gave a white precipitate, which was recrystallized from Et$_2$O containing a small amount of styrene below −10 °C to yield white crystals of 2 (0.22 g, 41%): decomp pt 49–53 °C; ^{1}H NMR (CD$_2$Cl$_2$, −20 °C) δ −0.85 (t, *J* = 5.9 Hz, 3 H, PdC*H$_3$*), 0.90 (quintet, *J* = 7.7 Hz, 12 Hz, PC*H$_2$*CH$_3$), 1.6–1.7 (m, 8 H, PC*H$_2$*CH$_3$); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −20 °C) δ 26.1 (s). Anal. Calcd for C$_{27}$H$_{38}$P$_2$Pd: C, 61.1; H, 7.2. Found: C, 60.8; H, 7.1.

Similarly prepared was *trans*-PdMe(*m*-tolyl)(PEt$_2$Ph)$_2$ (35%, white crystals): decomp pt 44–47 °C; ^{1}H NMR (CD$_2$Cl$_2$, −20 °C) δ −0.85 (t, *J* = 5.9 Hz, 3 H, PdC*H$_3$*), 0.90 (quintet, *J* = 7.8 Hz, 12 H, PC*H$_2$*CH$_3$), 1.5–1.8 (m, 8 H, PC*H$_2$*CH$_3$), 2.13 (s, 3 H, tolyl CH$_3$); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −20 °C) δ 26.3 (s). Anal. Calcd for C$_{28}$H$_{40}$P$_2$Pd: C, 61.7; H, 7.4. Found: C, 61.4; H, 7.5.

Preparation of *trans*-PdMePh(PEt$_3$)$_2$. To a heterogeneous white mixture of *trans*-PdPhCl(PEt$_3$)$_2$ (0.44 g, 0.97 mmol) and Et$_2$O (2 mL) was added an Et$_2$O solution (4.3 mL) of MeLi (1.9 mmol) at −70 °C. The system turned to a colorless homogeneous solution on stirring at −10 to 0 °C. After 2 h Me$_3$SiCl (130 μL, 1.0 mmol) was added at −30 °C, and the system was concentrated to almost dryness. Addition of hexane (15 mL) at −70 °C yielded LiCl as a white precipitate, which was removed by filtration at −40 °C. Concentration of the filtrate at −10 °C gave a white precipitate, which was recrystallized from cold Et$_2$O to yield crystals of *trans*-PdMePh(PEt$_3$)$_2$ (0.16 g, 38%): decomp pt 58 °C; ^{1}H NMR (CD$_2$Cl$_2$, −20 °C) δ −0.64 (t, *J* = 5.7 Hz, 3 H, PdC*H$_3$*), 1.10 (quintet, *J* = 5.6 Hz, 18 H, PC*H$_2$*CH$_3$), 1.3–1.6 (m, 12 H, PC*H$_2$*CH$_3$); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −20 °C) 22.4 (s). Anal. Calcd for C$_{19}$H$_{38}$P$_2$Pd: C, 52.5; H, 8.8. Found: C, 52.4; H, 9.0.

Similarly prepared was *trans*-PdEtPh(PEt$_3$)$_2$ by using EtLi in place of MeLi (54%, white crystals): ^{1}H NMR (CD$_2$Cl$_2$, −10 °C) 0.43 (q, *J* = 8 Hz, 2 H, PdC*H$_2$*CH$_3$), 1.06 (quintet, *J* = 8 Hz, 21 H, PdCH$_2$C*H$_3$* and PC*H$_2$*CH$_3$), 1.50 (m, 12 H, PC*H$_2$*CH$_3$); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, room temperature) δ 19.8 (s).

Preparation of *cis*-PdMePh(PEt$_2$Ph)$_2$ (3). To a heterogeneous white mixture of *trans*-PdPh(Br)(PEt$_2$Ph)$_2$ (0.30 g, 0.50 mmol) and Et$_2$O (5 mL) containing styrene (10 μL) was added an Et$_2$O solution of MeLi (3.3 mL, 2.5 mmol) at −40 °C. The system was stirred at +20 °C for 1 h to give a colorless homogeneous solution. After the system was cooled to −70 °C, an Et$_2$O solution (1.5 mL) of MeOH (3.7 mmol) was added. The resulting colorless solid of LiOMe was removed by filtration at −30 °C, and the filtrate was concentrated to dryness to yield a colorless oily product. The oily product was again dissolved in an Et$_2$O–pentane mixture (1:4, ca. 5 mL) at −20 °C, and the resulting solution was stirred at −40 °C to give a white precipitate. The crude product was recrystallized from cold Et$_2$O–pentane (4:1) containing a small amount of styrene to yield white crystals of 3 (0.13 g, 47%): decomp pt 44–45 °C; ^{1}H NMR (CD$_2$Cl$_2$, −30 °C) δ 0.03 (dd, *J* = 6 and 9 Hz, 3 H, PdC*H$_3$*); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C) δ 3.2 (dd, *J* = 10 and 99 Hz, PdMe), 173.7 (dd, *J* = 16 and 123 Hz, PdPh); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C) 12.1 and 18.1 (AB, *J* = 24 Hz). Anal. Calcd for C$_{27}$H$_{38}$P$_2$Pd: C, 61.1; H, 7.2. Found: C, 61.0; H, 7.3.

A series of *cis*-PdMeAr(PEt$_2$Ph)$_2$ complexes and *cis*-PdMePh(PMe$_2$Ph)$_2$ listed in Table I were prepared by similar methods from *trans*-PdAr(Br)(PEt$_2$Ph)$_2$ complexes and MeLi. *cis*-PdMe(*p*-tolyl)(PEt$_2$Ph)$_2$ (55%, white crystals): decomp pt 43–44 °C; ^{1}H NMR (CD$_2$Cl$_2$, −30 °C) δ 0.01 (dd, *J* = 6 and 9 Hz, 3 H, PdC*H$_3$*), 2.28 (s, 3 H, tolyl-C*H$_3$*); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C) δ 3.4 (dd, *J* = 10 and 99 Hz, PdMe), 168.4 (dd, *J* = 16 and 126 Hz, PdPh); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C) δ 12.2 and 18.1 (AB, *J* = 24 Hz). Anal. Calcd for C$_{28}$H$_{40}$P$_2$Pd: C, 61.7; H, 7.4. Found: C, 61.7; H, 7.6. *cis*-PdMe(*p*-ClC$_6$H$_4$)(PEt$_2$Ph)$_2$ (70%, white crystals): decomp pt 47–55 °C; ^{1}H NMR (CD$_2$Cl$_2$, −30 °C) δ −0.03 (dd, *J* = 6 and 9 Hz, 3 H, PdC*H$_3$*); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C) δ 3.2 (dd, *J* = 10 and 98 Hz, PhMe), 172.0 (dd, *J* = 16 and 123 Hz, PdPh); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C) δ 11.7 and 18.5 (AB, *J* = 24 Hz). Anal. Calcd for C$_{27}$H$_{37}$ClP$_2$Pd: C, 57.4; H, 6.6; Cl, 6.3. Found: C, 57.8; H, 6.8; Cl, 6.8. *cis*-PdMe(*p*-FC$_6$H$_4$)(PEt$_2$Ph)$_2$ (47%, pale red crystals): decomp pt 43–49 °C; ^{1}H NMR (CD$_2$Cl$_2$, −30 °C) δ −0.01 (dd, *J* = 7 and 9 Hz, 3 H, PdC*H$_3$*); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C) δ 3.4 (dd, *J* = 9 and 99 Hz, PdMe), 166.4 (dd, *J* = 13 and 126, PdPh); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C) 12.1 and 18.5 (AB, *J* = 24 Hz). Anal. Calcd for C$_{27}$H$_{37}$FP$_2$Pd: C, 59.1; H, 6.8. Found: C, 58.9; H, 6.9. *cis*-PdMe(*p*-CF$_3$C$_6$H$_4$)(PEt$_2$Ph)$_2$ (48%, colorless oil): ^{1}H NMR (CD$_2$Cl$_2$, −30 °C) δ −0.04 (dd, *J* = 6 and 9 Hz, 3 H, PdC*H$_3$*); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C) δ 3.3 (dd, *J* = 9 and 97 Hz, PdMe), 182.6 (dd, *J* = 15 and 124, PdPh); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C) 11.4 and 18.6 (AB, *J* = 25 Hz). *cis*-PdMePh(PMe$_2$Ph)$_2$ (84%, white crystals): ^{1}H NMR (CD$_2$Cl$_2$, −30 °C) δ 0.15 (dd, *J* = 6 and 9 Hz, 3 H, PdC*H$_3$*); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C) δ 5.1 (dd, *J* = 9 and 101 Hz, PdMe) 170.0 (dd, *J* = 15 and 126, PdPh); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C) −2.7 and −5.9 (AB, *J* = 25 Hz). Anal. Calcd for C$_{23}$H$_{30}$P$_2$Pd: C, 58.2; H, 6.4. Found: C, 58.1; H, 6.6.

Preparation of *cis*-PdMePh(dmpe) (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$). To a Schlenk tube containing *cis*-PdMePh(PEt$_2$Ph)$_2$ (3; 0.23 g, 0.43 mmol) were added Et$_2$O (6 mL) and dmpe (80 μL, 0.48 mmol at −30 °C). After being stirred at the same temperature for 1 h, the solution was concentrated to almost dryness. Addition of hexane (20 mL) to the system yielded a white precipitate, which was filtered, washed with hexane (10 mL × 2), and dried in vacuo. The crude product was recrystallized from cold CH$_2$Cl$_2$–Et$_2$O to give white crystals of *cis*-PdMePh-(dmpe) (52%): ^{1}H NMR (CD$_2$Cl$_2$, −60 °C) δ −0.03 (dd, *J* = 7 and 8 Hz, 3 H, PdC*H$_3$*); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C) δ −2.5 (dd, *J* = 9 and 106 Hz, PdMe), 170.2 (dd, *J* = 13 and 136 Hz, PdPh); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C) δ 27.1 and 30.8 (AB, *J* = 12 Hz). Anal. Calcd for C$_{13}$H$_{24}$P$_2$Pd: C, 44.8; H, 6.9. Found: C, 44.2; H, 7.0.

Preparation of *cis*-PdMePh(dppe) (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$). *cis*-PdMePh(dppe) was prepared by the ligand-exchange reaction of *cis*-PdMePh(PMePh$_2$)$_2$ with dppe. A similar ligand-exchange reaction with *cis*-PdMePh(PEt$_2$Ph)$_2$ in place of *cis*-PdMePh(PMePh$_2$)$_2$ did not proceed.

To a white heterogeneous mixture of *trans*-PdPh(Br)(PEt$_2$Ph)$_2$ (3.7 g, 5.6 mmol) and Et$_2$O (60 mL) containing styrene (1 mL) was added an Et$_2$O solution of MeLi (62 mL, 28 mmol) at −50 °C. The system was stirred for 1 h at +20 °C to give a homo-

geneous colorless solution. After the system was cooled to –78 °C, an Et$_2$O solution (16 mL) of MeOH (42 mmol) was added. The resulting colorless solid of LiOMe was removed by filtration at –40 °C, and the filtrate was concentrated to dryness to give a colorless oily product. Addition of ca. 5 mL of pentane to the system at –78 °C yielded a pale red precipitate of cis-PdMePh-(PMePh$_2$)$_2$, which was filtered, washed with pentane (30 mL × 2), and dried in vacuo below –30 °C (78%). Formation of the complex was, however, confirmed by NMR spectroscopy: ^{1}H NMR (CD$_2$Cl$_2$, –50 °C) δ 0.19 (dd, J = 3 and 9 Hz, 3 H, PdCH$_3$); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, –50 °C) δ 10.5 and 15.5 (AB, J = 23 Hz).

To a Schlenk tube containing cis-PdMePh(PMePh$_2$)$_2$ (0.63 g, 1.0 mmol) and dppe (0.84 g, 2.1 mmol) were added Et$_2$O (16 mL), CH$_2$Cl$_2$ (7 mL), and styrene (100 μL) at –40 °C. The system was stirred at 0 °C for 2 h. The solution was concentrated to almost dryness, and 20 mL of hexane was added to –70 °C. The resulting white precipitate was filtered, washed with Et$_2$O (2 mL), and dried in vacuo. The crude product was dissolved in Et$_2$O (5 mL) and CH$_2$Cl$_2$ (12 mL) containing styrene (60 μL) at 10 °C, and the solution was allowed to stand at –20 °C for 2 days to yield white crystals of cis-PdMePh(dppe) (0.22 g, 35%): ^{1}H NMR (CD$_2$Cl$_2$, –30 °C) δ 0.36 (dd, J = 2 and 7 Hz, 3 H, PdCH$_3$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, –30 °C) δ 2.1 (dd, J = 8 and 98 Hz, PdMe), 169.7 (dd, J = 12 and 115 Hz, PdPh); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, –30 °C) δ 41.5 and 49.1 (AB, J = 12 Hz). Anal. Calcd for C$_{33}$H$_{32}$P$_2$Pd: C, 66.4; H, 5.4. Found: C, 66.9; H, 5.9.

Catalytic Cross-Coupling Reaction. To a Schlenk tube containing trans-PdPh(I)(PEt$_2$Ph)$_2$ (0.065 g, 0.10 mmol) and PhI (110 μL, 0.99 mmol) was added an Et$_2$O solution of MeMgI (1 mL, 1.24 mmol) at –20 °C. The system was sealed and stirred at 36 °C. After 20 h, 5 mL of an aqueous HCl solution (1 N) was added at –10 °C to quench the reaction. GLC analysis of the Et$_2$O layer revealed the formation of toluene (85%/PhI) and biphenyl (6%) at 97% conversion of PhI.

Reactions of Diorganopalladium Complexes with Organomagnesium Halides. A typical procedure to record the spectroscopic change as shown in Figure 2 is as follows. To a Schlenk tube containing trans-PdMePh(PEt$_2$Ph)$_2$ (2; 0.054 g, 0.10 mmol) and tolan (0.036 g, 0.20 mmol) was added an Et$_2$O solution of MeMgI (1.0 mL, 1.24 mmol) by means of a measuring pipette.

The sample solution was transferred into an NMR sample tube below –10 °C. The sealed tube was placed in an NMR probe controlled to 35 ± 1 °C. The change in amounts of the palladium species with time was followed by measuring the relative area of the signals.

Kinetic Study on the Reductive Elimination of cis-PdMePh(PEt$_2$Ph)$_2$ (3). Complex 3 (~0.10 mmol) and Ph$_2$CH$_2$ (0.10 mmol) and the appropriate amounts of tolan, PEt$_2$Ph, and/or an organic iodide were placed in a Schlenk tube, and 1.0 mL of C$_6$D$_6$ was added by means of a measuring pipette. The sample solution was transferred into an NMR sample tube below +5 °C. The sealed tube was placed in a thermostated NMR probe (±1 °C). The amount of toluene produced on thermolysis with time was determined by measuring the ratio of the area of Ph$_2$CH$_2$ and PhCH$_3$ signals.

Registry No. 1, 113530-53-3; 2, 113566-59-9; 3, 113530-48-6; 4, 77831-30-2; 5, 77881-04-0; trans-PdMe(m-tolyl)(PEt$_2$Ph)$_2$, 117339-69-2; trans-PdMePh(PEt$_3$)$_2$, 116244-36-1; trans-PdEtPh(PEt$_3$)$_2$, 117308-37-9; cis-PdMe(p-tolyl)(PEt$_2$Ph)$_2$, 113530-49-7; cis-PdMe(p-ClC$_6$H$_4$)(PEt$_2$Ph)$_2$, 113530-50-0; cis-PdMe(p-FC$_6$H$_4$)(PEt$_2$Ph)$_2$, 113530-51-1; cis-PdMe(p-CF$_3$C$_6$H$_4$)(PEt$_2$Ph)$_2$, 113530-52-2; cis-PdMePh(PMe$_2$Ph)$_2$, 117308-38-0; cis-PdMePh(dmpe), 117308-39-1; cis-PdMePh(dppe), 117308-40-4; trans-PdPh(Br)(PEt$_2$Ph)$_2$, 115680-90-5; trans-Pd-(m-tolyl)(Br)(PEt$_2$Ph)$_2$, 117308-41-5; trans-PdPhCl(PEt$_3$)$_2$, 15697-59-3; trans-PdMe(p-tolyl)(PEt$_2$Ph)$_2$, 117308-42-6; trans-PdMe(p-ClC$_6$H$_4$)(PEt$_2$Ph)$_2$, 117339-85-2; trans-PdMe(p-FC$_6$H$_4$)(PEt$_2$Ph)$_2$, 117308-43-7; trans-PdMe(p-CF$_3$C$_6$H$_4$)-(PEt$_2$Ph)$_2$, 117308-44-8; trans-PdPh(Br)(PMe$_2$Ph), 117308-45-9; cis-PdMePh(PMePh$_2$)$_2$, 117308-46-0; PhI, 591-50-4; MeMgI, 917-64-6; trans-Pd(m-tolyl)I(PEt$_2$Ph)$_2$, 104114-87-6; m-MeC$_6$H$_4$I, 625-95-6; CD$_3$I, 865-50-9; toluene, 108-88-3; biphenyl, 92-52-4; m-tolyl iodide, 625-95-6; m-xylene, 108-38-3; p-xylene, 106-42-3; p-chlorotoluene, 106-43-4; p-fluorotoluene, 352-32-9.

Isometallocenes. 2.[1]
(Aminoarene)(tetramethylcyclobutadiene)cobalt(I) Hexafluorophosphates

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A range of both ring and nitrogen-substituted aromatic amines have been shown to give the title complexes in good yield when treated with tricarbonyl(tetramethylcyclobutadiene)cobalt(I) hexafluorophosphate and trimethylamine N-oxide. Various bases deprotonate the complexes with NH groups, but the resultant neutral complexes proved too unstable for full characterization. Iodomethane converts these neutral intermediates to the (N,N-dialkylamino)arene complexes.

Introduction

In part 1[1] we reported the formation of a range of (arene)(tetramethylcyclobutadiene)cobalt(I) salts by reaction of dicarbonyliodo(tetramethylcyclobutadiene)cobalt, C$_4$Me$_4$Co(CO)$_2$I, with arenes in the presence of aluminum

chloride. Although this route is applicable to a wide range of arenes, the yields are only moderate. Moreover, the iodo complex is obtained from the tricarbonyl salt 1, making it desirable to seek a direct route from the latter. This was indeed found in its reaction with arene plus trimethylamine N-oxide. Two examples of its use were described:[1] anisole giving comparable yields by both methods (the yield of 20% reported[1] using Me$_3$NO has subsequently been improved to 38%), whereas the benzene complex was

(1) Cook, M. R.; Härter, P.; Pauson, P. L.; Šraga, J. *J. Chem. Soc., Dalton Trans* 1987, 2757.