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# Dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II): An Effective Catalyst for Cross-Coupling of Secondary and Primary Alkyl Grignard and Alkylzinc Reagents with Organic Halides[1]

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**Abstract:** Several phosphine–palladium and –nickel complexes were examined for their catalytic activity in the reaction of *sec*-butylmagensium chloride with bromobenzene, (*E*)-$\beta$-bromostyrene, 4-bromoanisole, and 2-bromotoluene. Dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) [$PdCl_2$(dppf)] was found to be by far the most active and selective catalyst to give the corresponding *sec*-butyl derivatives in high yields with no byproducts. The palladium–dppf complex was also found highly effective in catalyzing the reaction of *n*-butylmagnesium chloride and *sec*- and *n*-butylzinc chloride with organic bromides to give the corresponding cross-coupling products in high yields. The structure of $PdCl_2$(dppf) has been determined by an X-ray diffraction study. It is proposed that the high efficiency of $PdCl_2$(dppf) catalyst can be ascribed to its large P–Pd–P angle and small Cl–Pd–Cl angle.

Since Corriu[2] and Kumada[3] reported in 1972 that the cross-coupling of Grignard reagents with aryl and alkenyl halides could be catalyzed by nickel–phosphine complexes, a wide variety of such coupling reactions have been developed and some of them have achieved great success in synthetic organic chemistry (Scheme I).[4] Thus, the cross-coupling reaction has been extended to involvement of aryl and alkenyl ethers,[5] sulfides,[6] selenides,[7] and phosphates.[8] Recent studies by Negishi have demonstrated the synthetic utility of the cross-coupling reaction by showing that organometallics containing zinc,[9] aluminum,[10] and zirconium[11] can enter into cross-coupling by use of a palladium catalyst. Organolithium,[12] -tin,[13] and -borane[14] reagents have also been used for the cross-coupling reaction.

**Scheme I**

$$\text{R-m} + \text{R}'\text{-X} \xrightarrow{\text{ML}_n} \text{R-R}' + \text{mX}$$

$$\text{M} = \text{Ni, Pd}$$

$$\text{m} = \text{Mg, Zn, Al, Zr, B, Sn, Li}$$

$$\text{R}' = \text{aryl, alkenyl}$$

$$\text{X} = \text{Cl, Br, I, OR, SR, SeR, OP(O)(OR)}_2$$

Although organometallic reagents with methyl, aryl, alkenyl, benzyl, or alkynyl groups have been successfully used for cross-coupling, those with alkyl groups containing $\beta$-hydrogen(s) have not always given satisfactory results. The cross-coupling of secondary or tertiary alkyl reagents has been found to be especially difficult because it is accompanied by isomerization of the alkyl group and/or reduction of the halides.[15,16] The side reactions could be depressed to some extent by an appropriate choice of catalyst, but perfect selectivity has not been achieved yet.[17] For example,[15a] in the reaction of isopropylmagnesium chloride with chlorobenzene, even dichloro[1,3-bis(diphenylphosphino)propane]nickel(II), which is the most selective catalyst thus far reported, gave a 4% yield of isomerized product, *n*-propylbenzene, together with the expected product, isopropylbenzene. Use of dichlorobis(triphenylphosphine)nickel(II) as a catalyst resulted in the formation of a less than 10% yield of isopropylbenzene and considerable amounts of *n*-propylbenzene and benzene. The isomerization and reduction must occur by $\beta$-hydride elimination of an alkylmetal species generated in the catalytic cycle to give a hydrido–olefin complex[4,15,18] (vide infra), and selective cross-coupling free from side reactions would be realized by the de-

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† Kyoto University.

‡ Osaka City University.

[1] Part of this paper appeared previously: Hayashi, T.; Konishi, M.; Kumada, M. *Tetrahedron Lett.* **1979**, *21*, 1871.

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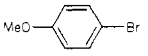
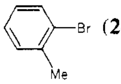
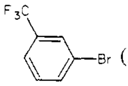
Table I. Cross-Coupling of *sec*-Butylmagnesium Chloride (**1a**) with Organic Bromides (**2**) in Diethyl Ether[a]

| | | reaction conditions | | yield, %[b] | | |
|---|---|---|---|---|---|---|
| catalyst | bromide (**2**) | temp | time, h | *sec*-BuR (**3**) | *n*-BuR (**4**) | other |
| $PdCl_2(dppf)$ | PhBr (**2a**) | rt | 1 | 95 (80)[c] | 0 | 0[d] |
| $Pd(PPh_3)_4$ | | rt | 24 | 4 | 6 | 31[d] |
| $PdCl_2(PPh_3)_2$ | | rt | 24 | 5 | 6 | 9[d] |
| $PdCl_2(dppe)$ | | rt | 48 | 0 | 0 | 96[d] |
| $PdCl_2(dppe)$ | | reflux | 8 | 4 | 1 | 30[d] |
| $PdCl_2(dppp)$ | | rt | 24 | 43 | 19 | 23[d] |
| $PdCl_2(dppb)$ | | rt | 8 | 51 | 25 | 1[d] |
| $NiCl_2(PPh_3)_2$ | | rt | 23 | 3 | 5 | 4[d] |
| $NiCl_2(dppp)$ | | rt | 23 | 29 | 3 | 5[d] |
| $PdCl_2(dppf)$ | (*E*)-PhCH=CHBr (**2b**)[e] | 0 °C | 2 | 97 (78)[c] | 0 | 0[f] |
| $PdCl_2(dppf)$[g] | | rt | 20 | 93 | 0 | 0[f] |
| $Pd(PPh_3)_4$ | | 0 °C | 3 | 33 | 36 | 4[f] |
| $PdCl_2(dppe)$ | | 0 °C | 5 | 3 | 3 | 38[f] |
| $PdCl_2(dppp)$ | | 0 °C | 5.5 | 76 | 5 | 6[f] |
| $PdCl_2(dppb)$ | | 0 °C | 3.5 | 53 | 25 | 8[f] |
| $NiCl_2(PPh_3)_2$ | | rt | 24 | 56 | 3 | 3[f] |
| $NiCl_2(dppp)$ | | 0 °C | 5 | 88 | 1 | 1[f] |
| $PdCl_2(dppf)$ |  (**2c**) | rt | 19 | 75 (71)[c] | 1 | 10[h] |
| $PdCl_2(PPh_3)_2$ | | rt | 18 | 3 | 2 | 22[h] |
| $PdCl_2(dppp)$ | | rt | 18 | 4 | 1 | 13[h] |
| $PdCl_2(dppb)$ | | rt | 20 | 9 | 37 | 17[h] |
| $NiCl_2(PPh_3)_2$ | | rt | 18 | 3 | 8 | 54[h] |
| $NiCl_2(dppp)$ | | rt | 18 | 43 | 7 | 7[h] |
| $PdCl_2(dppf)$ |  (**2d**) | rt | 19 | 58 (55)[c] | 0 | 0[i] |
| $PdCl_2(PPh_3)_2$ | | rt | 20 | 0 | 2 | 30[i] |
| $PdCl_2(dppp)$ | | rt | 20 | 3 | 1 | 66[i] |
| $NiCl_2(PPh_3)_2$ | | rt | 20 | 3 | 5 | 19[i] |
| $NiCl_2(dppp)$ | | rt | 20 | 41 | 4 | 22[i] |
| $PdCl_2(dppf)$ | $CH_2$=CMeBr (**2e**) | 0 °C | 8 | 80 | 0 | - |
| $PdCl_2(dppf)$ |  (**2f**) | rt | 20 | (72)[c] | 0 | - |

[a] **1**/**2** ≅ 1.5–3; catalyst/**2** = $10^{-2}$, unless otherwise noted. [b] Determined by GLC using an internal standard. [c] Isolated yield. [d] Recovered bromobenzene (**2a**) (%). When the yields of **3a** and **4a** were low compared to the amount of consumed **2a**, the corresponding amount of benzene **5a** was detected by GLC. [e] The coupling products, *sec*-butyl- and *n*-butylstyrene have *E* configuration (>99%). [f] Yield (%) of styrene (**5b**). [g] Catalyst/**2b** = $10^{-4}$. [h] Yield (%) of anisole (**5c**). [i] Recovered 2-bromotoluene (**2d**) (%).

Table II. Cross-Coupling of *n*-Butylmagnesium Chloride (**1b**) with Organic Bromides (**2**) in Diethyl Ether[a]

| | | reaction conditions | | yield, %[b] | |
|---|---|---|---|---|---|
| catalyst | bromide (**2**) | temp | time, h | *n*-BuR (**4**) | other |
| $PdCl_2(dppf)$ | PhBr (**2a**) | rt | 24 | 92 | 2[c] |
| $PdCl_2(dppe)$ | | reflux | 7 | 3 | 28[c] |
| $PdCl_2(dppp)$ | | reflux | 8 | 12 | 45[c] |
| $PdCl_2(dppb)$ | | rt | 24 | 54 | 31[c] |
| $NiCl_2(PPh_3)_2$ | | rt | 24 | 14 | 0[c] |
| $NiCl_2(dppp)$[d] | | rt | 24 | 42 | 47[c] |
| $PdCl_2(dppf)$ | (*E*)-PhCH=CHBr (**2b**) | rt | 20 | 90 | |

[a] *n*-BuMgCl/**2** = 1.5; catalyst/**2** = $10^{-2}$. [b] Determined by GLC using an internal standard. [c] Recovered bromobenzene (%). [d] This nickel complex catalyzed the reaction of *n*-BuMgBr with PhCl at diethyl ether reflux temperature to give *n*-BuPh (**4a**) quantitatively (ref 18).

velopment of a catalyst that can make the reductive elimination of the coupling product much faster than β-elimination.

Here we report that dichloro[1,1′-bis(diphenylphosphino)-ferrocene]palladium(II) is an effective catalyst for the reaction of secondary and primary alkyl Grignard and alkylzinc reagents with organic halides to give the corresponding coupling products selectively in exceedingly high yields.

## Results

**Cross-Coupling.** In the first set of experiments, the reaction of *sec*-butylmagnesium chloride (**1a**) with organic halides, bromobenzene (**2a**), (*E*)-β-bromostyrene (**2b**), 4-bromoanisole (**2c**), and 2-bromotoluene (**2d**) was carried out in the presence of a variety of phosphine–palladium and –nickel complexes (eq 1). Reaction conditions and the results obtained are summarized in Table I. Dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II), [$PdCl_2(dppf)$], was found to catalyze the reaction with bromobenzene (**2a**) to give *sec*-butylbenzene (**3a**) selectively in essentially quantitative yield with no byproducts. All other phosphine–palladium or –nickel complexes used were much less active and less selective. Thus, palladium complexes with triphenylphosphine ligand, $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$, both of which are considered to generate catalytically active species "$Pd(PPh_3)_2$" and have been used conventionally for many of the palladium-catalyzed coupling reactions,[4,9–11] gave only a 4–5% yield of *sec*-butylbenzene (**3a**), along with a 6% yield of *n*-butylbenzene (**4a**) and a considerable amount of benzene (**5a**). Of

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(17) The selectivity is dependent on the structure of secondary alkyl reagents as well as the catalyst. For example, the reaction of 1-phenylethyl Grignard reagents usually proceeds with high selectivity while that of isopropyl or *sec*-butyl Grignard reagents does not. See, for example: Hayashi, T.; Konishi, M.; Fukushima, M.; Mise, T.; Kagotani, M.; Tajika, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 180 and references therein.

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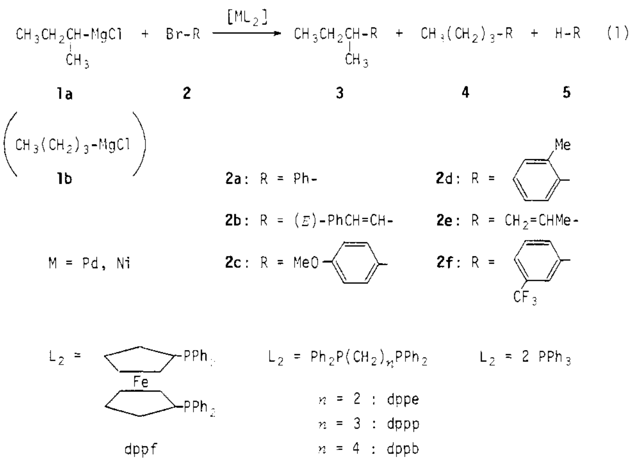


$$\underset{\mathbf{1a}}{\mathrm{CH_3CH_2\underset{CH_3}{\underset{|}{C}}H\text{-}MgCl}} + \underset{\mathbf{2}}{\mathrm{Br\text{-}R}} \xrightarrow{[\mathrm{ML_2}]} \underset{\mathbf{3}}{\mathrm{CH_3CH_2\underset{CH_3}{\underset{|}{C}}H\text{-}R}} + \underset{\mathbf{4}}{\mathrm{CH_3(CH_2)_3\text{-}R}} + \underset{\mathbf{5}}{\mathrm{H\text{-}R}} \quad (1)$$

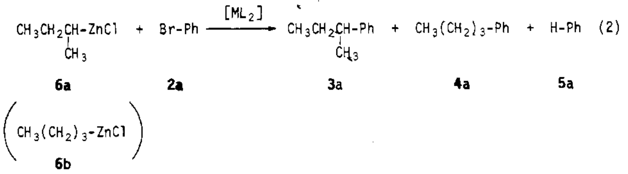
all the bidentate phosphine–palladium complexes, dichloro[1,2-bis(diphenylphosphino)ethane]palladium(II) [$PdCl_2$(dppe)] was almost inactive in the present reactions. Dichloro[1,3-bis(diphenylphosphino)propane]palladium(II) [$PdCl_2$(dppp)] and dichloro[1,4-bis(diphenylphosphino)butane]palladium(II) [$PdCl_2$(dppb)] catalyzed the coupling reaction, but it was accompanied by butyl group isomerization from secondary to primary. The bidentate phosphine–nickel complex, $NiCl_2$(dppp), which has been reported to be the most effective catalyst for the reaction of primary alkyl and simple aryl Grignard reagents,[18] was much less active and less selective than $PdCl_2$(dppf). $NiCl_2(PPh_3)_2$ brought about the reduction of **2a**, producing benzene to a large extent while giving only a small amount (3%) of **3a**, as expected from the results reported previously.[15a]

The palladium–dppf complex also catalyzed the reaction of **1a** with (*E*)-*β*-bromostyrene (**2b**) to produce an essentially quantitative yield of (*E*)-*β*-*sec*-butylstyrene (**3b**) with no byproducts. Use of only 0.01 mol % of the catalyst gave quite a satisfactory result. Here again all of the other catalysts were found to be less active and less selective than $PdCl_2$(dppf), though the yield of **3b** was generally higher than that of **3a**.

The high efficiency of $PdCl_2$(dppf) was also observed in the reaction of 4-bromoanisole (**2c**) and 2-bromotoluene (**2d**), both of which are expected to undergo the cross-coupling reaction with difficulty for electronic[15b] or steric reasons. Thus, $PdCl_2$(dppf) is the only catalyst that gave 4-*sec*-butylanisole (**3c**) and 2-*sec*-butyltoluene (**3d**) with high selectivity in over 50% yield. The nickel catalyst $NiCl_2$(dppp) was found to be fairly effective, but all others were almost inactive for the reaction of **2c** or **2d**. The palladium–dppf complex also catalyzed the cross-coupling of **1a** with 2-bromopropene (**2e**) and 3-trifluorobromobenzene (**2f**), giving the *sec*-butylated products **3e,f** with no isomerization.

The results obtained for the reaction of *n*-butylmagnesium chloride (**1b**) are summarized in Table II. As expected, $PdCl_2$(dppf) was the best catalyst, affording *n*-butylated products selectively in high yield, though the reaction of **1b** was slower than that of **1a**. Other nickel and palladium complexes were all less active.

The phosphine–palladium and –nickel complexes were also examined for the cross-coupling of organozinc reagents, e.g., *sec*-butyl- and *n*-butylzinc chloride (**6a** and **6b**) with bromobenzene (**2a**) (eq 2). Reaction conditions and data obtained are summarized in Table III. $PdCl_2$(dppf) was, here again, the most active and selective catalyst for both the reactions of **6a** and **6b** to give *sec*-butylbenzene (**3a**) and *n*-butylbenzene (**4a**), respectively, in quantitative yields with no byproducts. It may be noted that the reaction of *n*-butylzinc chloride (**6b**) was generally a little more selective than that of *n*-butylmagnesium chloride (**1b**) with palladium catalysts, in accord with Negishi's results.[16]



$$\underset{\mathbf{6a}}{\mathrm{CH_3CH_2\underset{CH_3}{\underset{|}{C}}H\text{-}ZnCl}} + \underset{\mathbf{2a}}{\mathrm{Br\text{-}Ph}} \xrightarrow{[\mathrm{ML_2}]} \underset{\mathbf{3a}}{\mathrm{CH_3CH_2\underset{CH_3}{\underset{|}{C}}H\text{-}Ph}} + \underset{\mathbf{4a}}{\mathrm{CH_3(CH_2)_3\text{-}Ph}} + \underset{\mathbf{5a}}{\mathrm{H\text{-}Ph}} \quad (2)$$

$$\left(\underset{\mathbf{6b}}{\mathrm{CH_3(CH_2)_3\text{-}ZnCl}}\right)$$

**Table III.** Cross-Coupling of Organozinc Chloride (**6**) with Bromobenzene (**2a**) in THF[a]

| catalyst | organozinc chloride (**6**) | reaction time, h | yield, %[b] sec-BuPh (**3a**) | yield, %[b] *n*-BuPh (**4a**) | recovered BrPh (**2a**) |
|---|---|---|---|---|---|
| $PdCl_2$(dppf) | *sec*-BuZnCl | 20 | 100 | 0 | 0 |
| $Pd(PPh_3)_4$ | (**6a**) | 24 | 1 | 2 | 78 |
| $PdCl_2(PPh_3)_2$ | | 22 | 3 | 3 | 87 |
| $PdCl_2$(dppp) | | 22 | 13 | 3 | 79 |
| $NiCl_2(PPh_3)_2$ | | 22 | 1 | 4 | 59 |
| $NiCl_2$(dppp) | | 22 | 45 | 7 | 44 |
| $PdCl_2$(dppf) | *n*-BuZnCl | 22 | | 100 | 0 |
| $PdCl_2(PPh_3)_2$ | (**6b**) | 24 | | 34 | 13 |
| $PdCl_2$(dppp) | | 24 | | 66 | 0 |
| $PdCl_2$(dppb) | | 21 | | 90 | 0 |
| $NiCl_2(PPh_3)_2$ | | 21 | | 42 | 22 |
| $NiCl_2$(dppp) | | 21 | | 3 | 78 |

[a] **6**/**2a** = 2; catalyst/**2a** = $10^{-2}$. The reaction was carried out in THF at room temperature. [b] Determined by GLC using an internal standard.

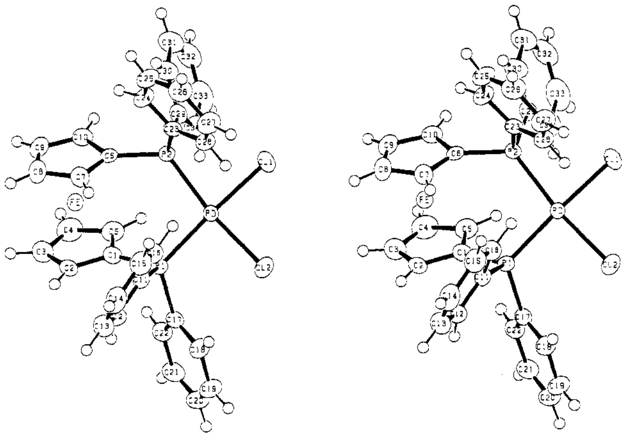


**Figure 1.** Stereoscopic view of $PdCl_2$(dppf).

To summarize, in the reaction of *sec*-butyl Grignard reagent (**1a**) and zinc reagent (**6a**), $PdCl_2$(dppf) is the only catalyst giving exclusively *sec*-butylated derivatives (**3**), and other palladium and nickel complexes induced, as side reactions, isomerization of the butyl group (from secondary to primary) and reduction of organic halides (to form **5**) to some extent. In addition, the coupling reaction with the $PdCl_2$(dppf) catalyst is much faster than that with other catalysts. $PdCl_2$(dppf) is also the most active catalyst for the coupling of *n*-butyl Grignard and *n*-butylzinc reagents. The order of efficiency of palladium catalysts for the cross-coupling reaction is $PdCl_2$(dppf) >> $PdCl_2$(dppb) $\gtrsim$ $PdCl_2$(dppp) > $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$ > $PdCl_2$(dppe). For nickel complexes, $NiCl_2$(dppp) is the most selective, as has been reported,[15,18] but not as selective or active as $PdCl_2$(dppf).

**Structure of $PdCl_2$(dppf).** The structure of $PdCl_2$(dppf) was determined by an X-ray diffraction study. A stereo view of the complex is illustrated together with the numbering scheme in Figure 1[19] and the geometry about the central Pd atom is shown in Figure 2. The environment of the Pd atom is described as square planar with two cis chlorine and two phosphorus atoms. While P1 lies on the $PdCl_2$ plane within 0.01 Å, P2 deviates by 0.21 Å from the plane. The bond distances of Pd–P1 and Pd–P2 are 2.283 (1) and 2.301 (1) Å, respectively. The shorter Pd–P bond involves the phosphorus atom that is closer to the $PdCl_2$ plane. The most conspicuous feature is a large P–Pd–P angle of 99.07 (5)° and a small Cl–Pd–Cl angle of 87.8 (1)°. The opening

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[19] Johnson, C. A. ORTEP-II; Oak Ridge National Laboratory Report ORNL-3794 (2nd revision with supplemental instructions), 1971.

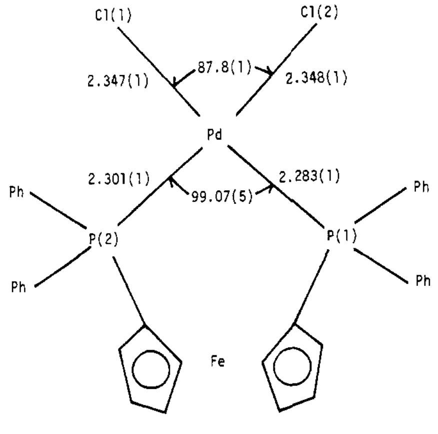
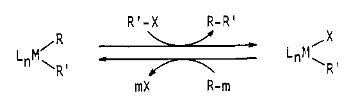
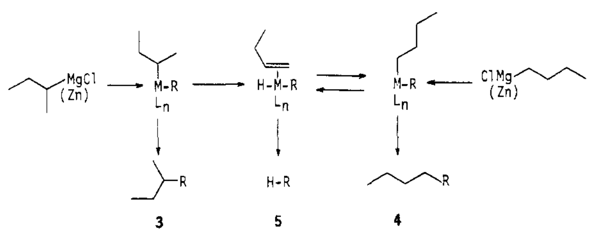


**Figure 2.** Distances (Å) and angles (deg) around central Pd atom.

Scheme II



Scheme III



up of the P–Pd–P bond angle is due to the bulkiness of the dppf moiety, where the two cyclopentadinyl rings are in a staggered conformation with a P–P distance of 3.487 (2) Å. The average distance of the two Pd–P bonds and the two Pd–Cl bonds is 2.292 (1) and 2.348 (1) Å, respectively. It is interesting to compare these angles and average distances with those reported for $\mathrm{PdCl_2}$(dppp) and $\mathrm{PdCl_2}$(dppe).[20] The angles of P–Pd–P and average distances of Pd–P in $\mathrm{PdCl_2}$(dppp) and $\mathrm{PdCl_2}$(dppe) are 90.6 and 85.8°, and 2.247 and 2.230 Å, respectively, and the angles of Cl–Pd–Cl and average distances of Pd–Cl are 90.8 and 94.2°, and 2.355 and 2.359 Å, respectively. Of the three bidentate phosphine–palladium complexes, $\mathrm{PdCl_2}$(dppf) has the largest P–Pd–P angle and the longest P–Pd distances. The P–Pd–P angles are correlated with the Pd–P, Pd–Cl distances and Cl–Pd–Cl angles. An increase of the P–Pd–P angle results in lengthening of the Pd–P bonds and a decrease of the Cl–Pd–Cl angle and Pd–Cl bond distances.

## Discussion

The catalytic cycle of the cross-coupling of organometallic reagents (R–m) with alkenyl or aryl halides and related compounds (R′–X) catalyzed by nickel or palladium complexes may be accommodated within Scheme II.[4,18,21,22] The side reactions, isomerization, and reduction observed for the cross-coupling of *sec*-alkyl reagents are considered to take place by a mechanism involving $\sigma$–$\pi$ interconversions of $\sigma$-alkylmetal intermediates and a hydrido–olefin–metal intermediate by $\beta$-hydride elimination and readdition.[15,23] The $\beta$-hydride elimination is also responsible for the reduction with *n*-alkyl reagents. The mechanism shown in Scheme III illustrates these side reactions for the organometallic reagents with *sec*-butyl and *n*-butyl groups. The results obtained for the present coupling reactions indicate that the palladium complex with the dppf ligand is a catalyst capable of making the reductive elimination of the coupling product much faster than the $\beta$-elimination.

**Table IV.** Angles P–Pd–P and Cl–Pd–Cl in the Complexes $\mathrm{PdCl_2L_2}$ ($\mathrm{L_2}$ = dppf, dppp, dppe) and Their Catalytic Activity in the Reaction of *sec*-Butylmagnesium Chloride (**1a**)

| | angle, deg | | yield, % | | | |
|---|---|---|---|---|---|---|
| $\mathrm{PdCl_2L_2}$ | P–Pd–P | Cl–Pd–Cl | **3a** | **3b** | **3c** | **4a**[a] |
| $\mathrm{PdCl_2}$(dppf) | 99.07 | 87.8 | 95 | 97 | 75 | 92 |
| $\mathrm{PdCl_2}$(dppp) | 90.6[b] | 90.8[b] | 43 | 76 | 4 | 12 |
| $\mathrm{PdCl_2}$(dppe) | 85.8[b] | 94.2[b] | 0-4 | 3 | | 3 |

[a] Reaction of *n*-butylmagnesium chloride (**1b**) with bromobenzene (**2a**). [b] Reported in ref 20.

The inefficiency of the triphenylphosphine–nickel or –palladium complexes used for the coupling of alkyl Grignard reagents may be attributable to the dissociation of triphenylphosphine from the metal, which may promote $\beta$-elimination by forming coordinatively unsaturated species.[24] The possible formation of a *trans*-diorganobis(phosphine)metal intermediate may inhibit the reductive elimination.[25] Since bidentate phosphines are known to stabilize an alkyl–metal moiety against $\beta$-hydride elimination,[24a] the catalysts complexed with a bidentate phosphine are expected to be more efficient than the catalysts with unidentate phosphines.

It is of great significance that the selectivity and the catalytic activity of the palladium complexes with bidentate phosphine ligands are strongly dependent upon the molecular framework lying between the two diphenylphosphino groups in the ligand. The order is dppf >> dppb ≳ dppp >> dppe for all the reactions shown above. The values of the angles P–Pd–P and Cl–Pd–Cl in the three complexes $\mathrm{PdCl_2}$(dppf), $\mathrm{PdCl_2}$(dppp), and $\mathrm{PdCl_2}$(dppe) may well correlate with the catalytic activity and selectivity of the palladium complexes (Table IV); the phosphine ligand that forms the complex having the larger P–Pd–P and smaller Cl–Pd–Cl angles accelerates reductive elimination to form the coupling product selectively. The order of the angle R–Pd–R′ in key intermediates $\mathrm{L_2Pd(R)R'}$ ($\mathrm{L_2}$ = dppf, dppp, dppe) is considered to be parallel to that of the angle Cl–Pd–Cl in $\mathrm{L_2PdCl_2}$, and the smaller angle must be favorable for the coupling of two alkyl groups.

Recently it has been proposed[25] that prior dissociation of a ligand is necessary for reductive elimination from bis(phosphine)dialkylpalladium(II) complexes. If the dissociation mechanism is also operative in the catalytic coupling reactions (see footnote 26, however), the present results may be interpreted to mean that the palladium catalyst with the dppf ligand has a high ability to dissociate one of the diphenylphosphino groups. The unusually large P–Pd–P angle of $\mathrm{PdCl_2}$(dppf) may suggest the presence of serious strain in the chelating system which would be released by the dissociation of the phosphino group.[27]

## Conclusion

Selective cross-coupling of Grignard and organozinc reagents containing secondary and primary alkyl groups has been accom-

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(26) In the catalytic reaction where the dialkylpalladium(II) species is surrounded by a large excess of the organic halide and Grignard reagent, it seems unlikely that the reductive elimination proceeds by the dissociation mechanism. See ref 22b,c and 25a,b.

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plished by use of PdCl$_2$(dppf) as a catalyst. The high selectivity could be ascribed to the large P–Pd–P angle and small Cl–Pd–Cl angle of the palladium complex, which may contribute to accelerating reductive elimination of the diorganopalladium intermediate. The palladium–dppf complex is also expected to be effective for many other catalytic reactions, especially those involving reductive elimination as a crucial step. Indeed, the unique activity of the palladium–dppf catalyst has been demonstrated recently in alkylation of allyl alcohols with Grignard reagents,[28] cross-coupling of aryl Grignard reagents with a 2-methylthiooxazoline,[29] cross-coupling of an alkenylborane with an alkenyl bromide,[30] and reaction of organic halides with carbon monoxide and terminal acetylenes.[31]

## Experimental Section

**General.** Infrared spectra were recorded on a Hitachi EPI-G3 grating infrared spectrometer. $^1$H NMR spectra were determined with a JEOL JNM-MH-100 (100 MHz) spectrometer. Chemical shifts are reported in ppm downfield from Me$_4$Si. GLC analyses were performed on a Shimadzu GC-4B or GC-4C gas chromatograph, equipped with a 3-m column packed with Silicone DC 550 (30% on Celite 545). GLC peak integrals were recorded by using a Shimadzu Chromatopac C-E1B integrator. A Varian Aerograph Model 920, equipped with a 20-ft column packed with Silicone DC 550 (30% on Celite) or PEG 20 M (30% on Celite), was used for isolation and purification of the products.

**Materials.** Except for PdCl$_2$(dppf), phosphine–nickel and –palladium complexes were prepared by known methods. In the following list, the references given after the compounds refer to the source or method of preparation: NiCl$_2$(PPh$_3$)$_2$,[32] NiCl$_2$(dppp),[33] Pd(PPh$_3$)$_4$,[34] PdCl$_2$(PPh$_3$)$_2$,[35] PdCl$_2$(dppe),[20] PdCl$_2$(dppp),[20] and PdCl$_2$(dppb).[36] 2-Bromopropene[37] and (*E*)-$\beta$-bromostyrene[38] were prepared as reported previously. Other organic halides were commercially available and were used without further purification. Grignard reagents were prepared in a standard manner by adding slowly a solution of an organic halide in diethyl ether to magnesium ribbon that had been dried in a rapid stream of dry nitrogen by flaming.

**Preparation of PdCl$_2$(dppf).** To a suspension of 259 mg (1.0 mmol) of dichlorobis(acetonitrile)palladium(II) in 10 mL of benzene was added with stirring a solution of 554 mg (1.0 mmol) of 1,1′-bis(diphenylphosphino)ferrocene[39] (dppf) in 10 mL of benzene. After the solution was stirred at room temperature for 12 h, the reddish brown precipitate formed was collected by filtration, washed with benzene, and dried in vacuo to give 710 mg (97%) of the palladium complex. An analytically pure sample was obtained by recrystallization from chloroform: mp 265 °C dec; IR (KBr) 1480, 1434, 1098, 690, 490 cm$^{-1}$; $^1$H NMR (CDCl$_3$) 4.13–4.23, 4.30–4.41 (m, 8 H), 7.25–7.50, 7.68–8.00 (m, 20 H). Anal. Calcd for C$_{35}$H$_{29}$P$_2$Cl$_5$FePd [PdCl$_2$(dppf)·CHCl$_3$]: C, 49.39; H, 3.43; Cl, 20.83. Found: C, 49.11; H, 3.49; Cl, 21.23.

**Cross-Coupling of Organic Halides with Grignard Reagents. General Procedure.** The reaction conditions and data obtained are listed in Tables I and II. In a 25-mL two-necked flask equipped with a stirring bar, a serum cap, and a three-way stopcock, catalyst (0.04 mmol) was placed. The reaction vessel was filled with argon after evacuation and then charged, at −78 °C, with an organic halide (4 mmol) and a Grignard reagent (8 mmol) in diethyl ether with a syringe through the serum cap. The reaction mixture was stirred at room temperature or 0 °C for a given period of time and hydrolyzed with 10% hydrochloric acid. An appropriate internal standard (normal alkane) was added to the organic layer, which was analyzed by GLC. The organic layer and diethyl ether extracts from the aqueous layer were combined, washed with saturated sodium hydrogen carbonate solution and then water, and dried over anhydrous sodium sulfate. After evaporation of solvent, coupling products were isolated by distillation or column chromatography.

**Cross-Coupling of Bromobenzene with Organozinc Reagents. General Procedure.** *n*-Butylzinc chloride and *sec*-butylzinc chloride were prepared in situ by mixing anhydrous zinc chloride (1.1 eq) in THF with *n*-butyllithium (1.0 eq) in hexane and *sec*-butylmagnesium chloride (1.0 eq) in diethyl ether, respectively. The reaction conditions and data obtained are listed in Table III. In a 50-mL two-necked flask equipped with a stirring bar, a serum cap, and a three-way stopcock a catalyst (0.04 mmol) and anhydrous zinc chloride (9 mmol) were placed. The reaction vessel was filled with argon after evacuation and then charged, at −78 °C, with anhydrous THF (10 mL) and *n*-butyllithium (8 mmol) in hexane or *sec*-butylmagnesium chloride (8 mmol) in diethyl ether with a syringe through the serum cap. To the mixture was then added bromobenzene (4 mmol) at −78 °C. The reaction mixture was stirred at room temperature overnight and hydrolyzed with 10% hydrochloric acid. An appropriate internal standard (normal alkane) was added to the organic layer, which was analyzed by GLC. The following coupling products were identified by spectral (NMR and/or IR) comparison with commercial authentic samples or established spectral and physical data: *n*-butylbenzene,[40] *sec*-butylbenzene,[40] (*E*)-$\beta$-*n*-butylstyrene,[41] (*E*)-$\beta$-*sec*-butylsytrene,[42] and 2,3-dimethyl-1-pentene.[43] Spectral and analytical data of other coupling products are given below.

**4-*sec*-Butylanisole.** Isolated by column chromatography (silica gel/ethyl acetate) and purified by preparative GLC: $^1$H NMR (CCl$_4$) 0.81 (t, $J$ = 7 Hz, 3 H), 1.19 (d, $J$ = 7 Hz, 3 H), 1.55 (quint, $J$ = 7 Hz, 2 H), 2.50 (sext, $J$ = 7 Hz, 1 H), 3.73 (s, 3 H), 6.70, 6.97 (AA′BB′, $J$ = 8 Hz, 4 H); IR (liquid film) 2965, 1519, 1252 cm$^{-1}$. Anal. Calcd for C$_{11}$H$_{16}$O: C, 80.44; H, 9.82. Found: C, 80.44; H, 10.03.

**2-*sec*-Butyltoluene.** Isolated by bulb-to-bulb distillation (90–110 °C (20 mmHg) bath temperature) and purified by preparative GLC: $^1$H NMR (CCl$_4$) 0.85 (t, $J$ = 7 Hz, 3 H), 1.18 (d, $J$ = 7 Hz, 3 H), 1.60 (quint, $J$ = 7 Hz, 2H), 2.30 (s, 3 H), 2.85 (sext, $J$ = 7 Hz, 1 H), 6.89–7.15 (m, 4 H); IR (liquid film) 2970, 1460, 755, 725 cm$^{-1}$. Anal. Calcd for C$_{11}$H$_{16}$: C, 89.12; H, 10.88. Found: C, 88.98; H, 10.86.

**3-*sec*-Butyl-1-trifluoromethylbenzene.** Isolated by bulb-to-bulb distillation (80–100 °C (20 mmHg) bath temperature) and purified by preparative GLC: $^1$H NMR (CCl$_4$) 0.86 (t, $J$ = 7 Hz, 3 H), 1.28 (d, $J$ = 7 Hz, 3 H), 1.65 (quint, $J$ = 7 Hz, 2 H), 2.17 (sext, $J$ = 7 Hz, 1 H), 7.15–7.55 (m, 4 H); IR (liquid film) 2975, 1325, 1165, 1120 cm$^{-1}$. Anal. Calcd for C$_{11}$H$_{13}$F$_3$: C, 65.34; H, 6.78. Found: C, 65.45; H, 6.49.

**X-ray Structure of PdCl$_2$(dppf).** A vermillion crystal (0.21 × 0.15 × 0.32 mm), grown from chloform was used for data collection. **Crystal Data**: C$_{34}$H$_{28}$P$_2$Cl$_2$FePd·CHCl$_3$, $M_r$ = 851.1, monoclinic, space group $P2_1/n$. On the basis of 38 reflections, the following unit cell parameters were obtained: $a$ = 16.872 (5) Å, $b$ = 16.535 (6) Å, $c$ = 12.275 (3) Å, $\beta$ = 93.85 (5)°, $V$ (for $Z$ = 4) = 3417 (2) Å$^3$, $d_{\text{calcd}}$ = 1.65 g cm$^{-3}$, and $\mu$(Mo K$\alpha$) = 14.5 cm$^{-1}$.

Data were collected on an automated Philips PW1100 four circle diffractometer with graphite-monochromated Mo K$\alpha$ radiation (0.7107Å). A total of 4486 reflections were obtained for a $2\theta$ range of 1.5–45°, of which 3544 have $I > 3\sigma(I)$ and were judged observed. Three reference reflections, monitored every 180 min, displayed neither systematic nor significant deviations from their initial intensities. The intensities were corrected for Lorentz and polarization factors, but no absorption correction was applied. The structure was solved by the heavy-atom method. Full-matrix least-squares refinements with anisotropic nonhydrogen and isotropic hydrogen atoms converged to the standard crystallographic residual $R$ of 0.036.[44] Neutral atomic scattering factors of Cromer and Waber were used for all atoms.[45] They were all corrected for the real part of the anomalous dispersion. Additional crystallographic details can be found in the supplemental material.

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**Registry No. 1a**, 15366-08-2; **1b**, 693-04-9; **2a**, 108-86-1; **2b**, 588-72-7; **2c**, 104-92-7; **2d**, 95-46-5; **2e**, 557-93-7; **2f**, 401-78-5; **3a**, 135-98-8; **3b**, 15325-63-0; **3c**, 4917-90-2; **3d**, 1595-16-0; **3e**, 3404-72-6; **3f**, 87922-44-9; **4a**, 104-51-8; **4b**, 6111-82-6; **4c**, 18272-84-9; **6a**, 74133-06-5; **6b**, 42930-39-2; $PdCl_2(dppf)$, 72287-26-4; $Pd(PPh_3)_4$, 14221-01-3; $PdCl_2(PPh_3)_2$, 13965-03-2; $PdCl_2(dppe)$, 19978-61-1; $PdCl_2(dppp)$, 59831-02-6; $PdCl_2(dppb)$, 29964-62-3; $NiCl_2(PPh_3)_2$, 14264-16-5; $NiCl_2(dppp)$, 15629-92-2; dichlorobis(acetonitrile)palladium(II), 14592-56-4.

**Supplementary Material Available:** Fractional coordinates (Table V), bond distances (Table VI), bond angles (Table VII), and observed and calculated structure factors (Table VIII) (10 pages). Ordering information is given on any current masthead page.

# Dinuclear Polyhydrides of Rhenium: Isolation and Characterization of Diamagnetic and Paramagnetic Complexes Containing the $[Re_2H_8]^{n+}$, $[Re_2H_7]^{(n+1)+}$, and $[Re_2H_5]^{(n+1)+}$ Cores ($n$ = 0 or 1) Stabilized by Phosphine, Nitrile, and Isocyanide Ligands

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**Abstract:** The electrochemical oxidation of the dirhenium octahydrides $Re_2(\mu\text{-}H)_4H_4(PR_3)_4$ ($PR_3 = PPh_3$, $PEtPh_2$, or $PEt_2Ph$) and $Re_2(\mu\text{-}H)_4H_4(AsPh_3)_4$ occurs at potentials between −0.15 and −0.40 V vs. SCE, to produce the corresponding paramagnetic, ESR-active monocations. This oxidation has been accomplished chemically in the case of the $PPh_3$ derivative using $Ph_3C^+PF_6^-$ and $C_7H_7^+PF_6^-$ as oxidants, dichloromethane as solvent, and a reaction temperature of 0 °C; the resulting product is $[Re_2(\mu\text{-}H)_4H_4(PPh_3)_4]PF_6$. However, when the reaction with $Ph_3C^+PF_6^-$ is carried out in nitrile solvents, RCN (R = Me, Et, or Ph), then hydride abstraction occurs in preference to oxidation and the diamagnetic complexes $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4(NCR)]PF_6$ are formed. The reaction of $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4(NCMe)]PF_6$ with *t*-BuNC affords the substitution product $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4(CN\text{-}t\text{-}Bu)]PF_6$. The complexes containing the $[Re_2H_7]^+$ moiety have been shown by cyclic voltammetric measurements (on 0.2 M $Bu_4NPF_6$–$CH_2Cl_2$ solutions) to exhibit two quasi-reversible one-electron oxidations (at ca. 0.0 and +0.70 V for the RCN derivatives and +0.19 and +0.94 V vs. SCE for the *t*-BuNC derivative). Oxidation to paramagnetic $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4L](PF_6)_2$ (for L = RCN or *t*-BuNC) has been achieved by using $NO^+PF_6^-$. In contrast to the sluggish reaction of $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ with *t*-BuNC, the oxidized monocation reacts extremely rapidly (in $CH_2Cl_2$ at 0 °C) to give $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$. Like the other polyhydrides this complex possesses two accessible one-electron oxidations, and it may be oxidized chemically to $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2](PF_6)_2$ very easily by using $NO^+PF_6^-$. While the diamagnetic complexes $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4(CN\text{-}t\text{-}Bu)]PF_6$ and $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$ do not react significantly with excess *t*-BuNC within reasonable periods of time, their paramagnetic oxidized congeners do so extremely rapidly, the rhenium(I) complex $[Re(CN\text{-}t\text{-}Bu)_4(PPh_3)_2]PF_6$ and gaseous $H_2$ being the final products of these reactions. The complexes described in this report that contain the $[Re_2H_8]^+$, $[Re_2H_7]^{2+}$, and $[Re_2H_5]^{2+}$ cores constitute very rare examples of isolable radical cations of transition-metal hydrides, the first to be prepared for dimetal polyhydrides. The highly reactive nature of these species, compared to their far less reactive diamagnetic precursors, provides an important extension of the notion that paramagnetic electron-deficient organometallic species exhibit enhanced substitution lability relative to their 18-electron analogues.

Following the recognition that the "agnohydrides" or rhenium, $[ReH_x(PR_3)_2]_2$ ($PR_3 = PPh_3$ or a mixed alkyl-phenyl phosphine),[1] are in reality the dirhenium octahydrides $Re_2(\mu\text{-}H)_4H_4(PR_3)_4$,[2] efforts have been under way to develop the chemistry of this novel series of complexes. In addition to studies directed toward the synthesis of[3] and an understanding of the bonding in[4] these molecules, their reactivity patterns are beginning to attract attention. Of special note are their reactions with organic chlorides[5] and phosphite ligands,[6] in which a dirhenium unit is preserved in the products. In the thermal reaction of $Re_2H_8(PMe_2Ph)_4$ with the phosphite ligand $P(OCH_2)_3CEt$ (abbreviated P′), loss of $H_2$ occurs to give the complex $Re_2(\mu\text{-}H)_3H(PMe_2Ph)_4P'_2$ possessing an unusual asymmetric structure.[6] Protonation of this molecule (using $HBF_4$) gives the symmetric conjugate acid $[Re_2(\mu\text{-}H)_3H_2(PMe_2Ph)_4P'_2]^+$.[6] This work, when taken in conjunction with the recent isolation of complexes of the type $Re_2(\mu\text{-}H)_3H_3(PR_3)_5$, via the photochemical reactions of mononuclear rhenium polyhydrides,[7,8] points to the existence of a variety of dirhenium polyhydride species.

In the present report we describe the isolation and characterization of a range of new complexes containing the $[Re_2H_8]^{n+}$, $[Re_2H_7]^{n+}$, and $[Re_2H_5]^{n+}$ cores, which in the case of $[Re_2H_8]^+$, $[Re_2H_7]^{2+}$, and $[Re_2H_5]^{2+}$ constitute *very rare examples of isolable radical cations of transition-metal hydrides, the first to be prepared for dimetal polyhydrides*.[9] The isolation of the diamagnetic complexes (derivatives containing the $[Re_2H_8]^0$,

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