1890 *Organometallics* **1993**, *12*, 1890–1901

# Alkali-Induced Disproportionation of Palladium(II) Tertiary Phosphine Complexes, [$L_2PdCl_2$], to LO and Palladium(0). Key Intermediates in the Biphasic Carbonylation of ArX Catalyzed by [$L_2PdCl_2$]

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*Received February 5, 1993*

Square-planar complexes of divalent palladium, [$L_2PdCl_2$], where L = tertiary phosphine, are active catalysts for the biphasic carbonylation of aromatic halides, including chloroarenes (when L = tricyclohexylphosphine), to the corresponding carboxylic acids. The first step of the process is the aqueous alkali (KOH) induced disproportionation of [$L_2PdCl_2$] to the phosphine oxide and the Pd(0) species, [LPd]. Oxidative addition of aryl halides to the latter, followed by ligand exchange, results in organometallic hydroxo dimers, [$L_2Ar_2Pd_2(\mu\text{-}OH)_2$], **1**–**3**, in high yields. The disproportionation reaction proceeds with *retention* of configuration at phosphorus (demonstrated for L = (*R*)-benzylmethylphenylphosphine). Carbonylation of **1**, Ar = Ph, in the presence of iodobenzene leads to benzoic acid and the aroyl complex [$(ArCO)(PPh_3)Pd(\mu\text{-}I)]_2$, **6**, where Ar = Ph, (complex **7**, Ar = *p*-tolyl, and *p*-toluic acid were similarly formed from **3**, Ar = *p*-tolyl, and *p*-iodotoluene). While complexes **6** and **7** are not prone to facile decarbonylation, they do undergo slow exchange with free carbon monoxide. Reactions of **6** and **7** with aqueous KOH in the presence of the corresponding iodoarenes afford the carboxylic acid anion and the hydroxo complexes **1** and **3**, respectively. These reactions likely involve aroyl bridging palladium dimers as intermediates. The new complexes **1**–**7** exist in solution as mixtures of cis and trans isomers. However, only the trans geometry was found in the X-ray structures of **1** and **6**. Crystallographic data for **1**: space group $P\,2_1/n$, $a = 13.668(3)$ Å, $b = 23.168(7)$ Å, $c = 14.358(3)$ Å, $\alpha = 90.00°$, $\beta = 93.97(2)°$, $\gamma = 90.00°$, $V = 4535.6(2)$ Å$^3$, $Z = 4$, $R = 0.071$, and $R_w = 0.082$. For **6**: space group $P\text{-}1$, $a = 11.413(4)$ Å, $b = 12.597(4)$ Å, $c = 10.494(3)$ Å, $\alpha = 101.37(3)°$, $\beta = 105.22(3)°$, $\gamma = 74.17(3)°$, $V = 1387.7(8)$ Å$^3$, $Z = 1$, $R = 0.039$, and $R_w = 0.035$.

## Introduction

The palladium-catalyzed carbonylation of aryl halides is an important, convenient, and highly effective method for the synthesis of various aromatic compounds including carboxylic acids and their derivatives.[1] The first key step of the catalytic cycle is oxidative addition of the carbon–halogen bond to a coordinatively-unsaturated, electron-rich complex of palladium(0). However, a number of processes successfully employ not just Pd(0) complexes (e.g., [$(Ph_3P)_4Pd$]), but nonorganometallic compounds of divalent Pd as well.[1] Obviously, the latter must be reduced in some manner to a zero-valent palladium species prior to the start of the catalytic cycle with activation and cleavage of the aromatic carbon–halogen bond. Despite their significance in many catalytic reactions, these reduction processes have not been investigated in detail; perhaps the catalytic systems are implied to a priori possess a certain reducing power, as carbonylation reactions are always conducted in the presence of excess CO. One such reaction is the phase-transfer- and palladium-catalyzed hydroxycarbonylation of haloarenes reported by Cassar, Foa, and Gardano (eq 1).[2]

$$ArX \xrightarrow[\text{30\% NaOH-}p\text{-xylene, 95 °C}]{\text{CO (5 atm), [}L_2PdCl_2\text{]/L, }Bu_4N^+I^-} ArCOONa \qquad (1)$$

Ar = different aryls; X = Br, I; L = $PPh_3$

Although a general mechanistic scheme, involving transformations of a zero-valent palladium complex, has been proposed for this useful and convenient carbonylation process,[2] specifics have remained unknown including how the Pd(II) complex is reduced to Pd(0), what zero-valent palladium species are being formed in the course of the reaction, and what carbonyl complexes are key intermediates in the process. In this paper, we wish to report unexpected and novel results obtained by a detailed investigation of the palladium-catalyzed carbonylation of haloarenes in the presence of aqueous alkali. The findings are not only significant for the halide carbonylation reaction but are relevant to other palladium-catalyzed processes.

## Results

While working with bis(trimethylphosphine)palladium dichloride we were surprised to find that this air- and

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**Table I. Carbonylation of Halobenzenes Catalyzed by $[(Ph_3P)_2PdCl_2]$ under Biphasic Conditions**[a]

$$\mathrm{PhX + CO \xrightarrow[[(Ph_3P)_2PdCl_2],\ reflux]{solvent{-}50\%\ KOH} PhCOOK}$$

| X | solvent | 18-crown-6 | time, h | yield, % |
|---|---|---|---|---|
| I | THF | + | 19 | 90 |
| I | THF | + | 24 | 92 |
| I | benzene | – | 20 | 90 |
| I | benzene | – | 24 | 99 |
| I | benzene | + | 18 | 59 |
| Br | THF | + | 23 | 40 |
| Br | benzene | – | 24 | 72 |
| Cl | THF | + | 17 | 0 |
| Cl | benzene | – | 24 | 0 |

[a] Reaction conditions: halobenzene (4 mmol), 50% KOH (3 mL), $[(Ph_3P)_2PdCl_2]$ (0.04 mmol), 18-crown-6 (0.1 mmol if used), organic solvent (10 mL), CO (1 atm).

**Table II. Carbonylation of Iodobenzene Catalyzed by Complexes $[L_2MX_2]$ under Biphasic Conditions**[a]

$$\mathrm{PhI + CO \xrightarrow[[L_2MCl_2],\ reflux]{solvent{-}50\%\ KOH} PhCOOK}$$

| M | L[b] | X | solvent | 18-crown-6 | time, h | yield, % |
|---|---|---|---|---|---|---|
| Pd | $PPh_3$ | Cl | benzene | – | 24 | 99 |
| Pd | $PCy_3$ | Cl | benzene | – | 24 | 92 |
| Pd | $PBu_3$ | Cl | benzene | – | 24 | 23 |
| Pd | $AsPh_3$ | Cl | benzene | – | 24 | 5[c] |
| Pd | $^1/_2$dppe | Cl | THF | + | 19 | 71 |
| Pd | $PMe_3$ | Cl | THF | + | 22 | 67[c] |
| Pt | $PPh_3$ | Cl | benzene | – | 22 | 0[c] |
| Ni | $PPh_3$ | Br | benzene | – | 16 | 0 |
| Ni | $^1/_2$dppp | Cl | benzene | – | 26 | 0 |
| Ni | $^1/_2$dppb | Cl | benzene | – | 24 | 0 |

[a] Reaction conditions as described in Table I. [b] Cy = tricyclohexyl, Bu = *n*-butyl, dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane, dppb = 1,4-bis(diphenylphosphino)butane. [c] The reaction was accompanied by precipitation of Pd(Pt) metal.

**Table III. Carbonylation of Haloarenes Catalyzed by $[(Ph_3P)_2PdCl_2]$ under Biphasic Conditions**[a]

$$\mathrm{ArX + CO \xrightarrow[[(Ph_3P)_2PdCl_2],\ reflux,\ 24\ h]{benzene{-}50\%\ KOH} ArCOOK}$$

| Ar | X | yield, % |
|---|---|---|
| $C_6H_5$ | I | 99 |
| *p*-$CH_3C_6H_4$ | I | 93 |
| *m*-$CH_3C_6H_4$ | I | 90 |
| 1-$C_{10}H_7$ | I | 96 |
| *p*-$ClC_6H_4$ | I | 50[b] |
| *m*-$CH_3OC_6H_4$ | I | 59 |
| *p*-$CH_3OC_6H_4$ | I | 27[c] |
| $C_6H_5$ | Br | 72 |
| *p*-$CH_3C_6H_4$ | Br | 68 |
| 1-$C_{10}H_7$ | Br | 52 |
| 2-$C_{10}H_7$ | Br | 24 |
| $C_6H_5$ | Cl | 0 |

[a] Reaction conditions as described in Table I. [b] The starting halide was recovered in 47% yield. [c] The starting halide was recovered in 65% yield.

moisture-stable, high-melting crystalline Pd(II) complex decomposes immediately upon contact with aqueous alkali (KOH) at ambient temperature to give palladium metal, i.e., a form of palladium in the zero oxidation state. This unexpected, reproducible (in air or under inert atmosphere) observation suggested that other palladium(II) complexes $[L_2PdCl_2]$ (L = tertiary phosphine) are also capable of undergoing reduction to Pd(0) in the presence of the hydroxide anion. Indeed, palladium metal precipitated readily when bis(triphenylphosphine)palladium(II) chloride was heated at 60–80 °C with 20–50% aqueous KOH for 0.5–2 h. Considering eq 1, one could conceive of a number of pathways for the palladium(II) complex conversion to a Pd(0) species. Besides such obvious candidates as CO, $H_2$ (if formed by water gas shift reaction), and the added phosphine, the reducing agents might be tributylamine and 1-butene, resulting from the Hofmann decomposition of tetrabutylammonium cation under biphasic conditions.[3] There is also the possibility of the hydroxide anion inducing the reduction of $[(Ph_3P)_2PdCl_2]$.

**Palladium-Catalyzed Carbonylation of Aryl Halides under Biphasic Conditions.** First, we found that iodobenzene and bromobenzene can be successfully carbonylated in the presence of $[(Ph_3P)_2PdCl_2]$, using alkali stable 18-crown-6 ether instead of tetrabutylammonium iodide as the phase-transfer agent or no phase-transfer catalyst at all. The carbonylation occurs effectively under substantially milder conditions than those described briefly in ref 2. Under such conditions, palladium metal either did not precipitate at all or only in trace quantities. Therefore, there was no need to add extra phosphine or any other "stabilizer" to the reaction mixture. Table I summarizes the results on the carbonylation of halobenzenes, demonstrating that a phase-transfer catalyst is not required in order to achieve good conversion, selectivity, and yield. Hence, the process is biphasic, not phase-transfer catalyzed, in nature.

A number of other phosphine and arsine complexes of divalent nickel, palladium, and platinum were tested for catalytic activity in the biphasic carbonylation of iodobenzene (Table II). Neither nickel nor platinum complexes were active catalysts in this regard. The effectiveness of palladium complexes $[L_2PdCl_2]$ was strongly dependent on ligands L, the efficiency order being $PPh_3 \approx PCy_3 > Ph_2P(CH_2)_2PPh_2 \approx PMe_3 > PBu_3 > AsPh_3$. Deposition of a significant amount of palladium metal at the very early stage of the carbonylation was observed using the (trimethylphosphine) and (triphenylarsine)palladium complexes.

Some other aryl iodides and bromides containing both electron-donating and electron-accepting substituents at the aromatic ring were catalytically converted to the corresponding carboxylic acids in satisfactory to excellent yields (Table III). However, chloroarenes remained unreactive toward carbonylation when $[(Ph_3P)_2PdCl_2]$ was used as the catalyst. It is noteworthy that the catalytic carbonylation of aromatic chlorides is still a challenging problem in organic chemistry. Unlike expensve aryl iodides and bromides, cheap and readily available chloro analogues do not usually undergo carbon–halogen bond cleavage by transition-metal complexes. While there has been some progress in the catalytic functionalization of chloroarenes during the last 3 years,[4–6] a simple, efficient, and inexpensive method for the carbonylation of chloro-

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**Table IV. Carbonylation of Chloroarenes Catalyzed by $[(Cy_3P)_2PdCl_2]$ under Biphasic Conditions**[a]

$$\mathrm{ArCl} + \mathrm{CO} \xrightarrow[{[(Cy_3P)_2PdCl_2],\ \text{reflux}}]{20\%\ \mathrm{KOH}} \mathrm{ArCOOK}$$

| entry | Ar | reactn time, h | catalytic turnover no.[b] |
|---|---|---|---|
| 1 | $C_6H_5$ | 72 | 89 |
| 2 | 1-$C_{10}H_7$ | 72 | 103 |
| 3 | *p*-$CH_3C_6H_4$ | 72 | 116 |
| 4 | *p*-$CH_3C_6H_4$ | 48 | 88 |
| 5 | *m*-$CH_3C_6H_4$ | 48 | 90 |
| 6[c] | *m*-$CH_3C_6H_4$ | 48 | 85 |
| 7 | *o*-$CH_3C_6H_4$ | 48 | 65 |
| 8 | *p*-$CH_3OC_6H_4$ | 48 | 105 |
| 9[d] | *m*-$C_6H_5COC_6H_4$ | 48 | 9 |
| 10 | *p*-$CF_3C_6H_4$ | 48 | 5 |
| 11 | *p*-$CF_3C_6H_4$ | 72 | 7 |
| 12 | *p*-$O_2NC_6H_4$ | 24 | 0 |

[a] Reaction conditions: chloroarene (40 mmol), $[(Cy_3P)_2PdCl_2]$ (0.1 mmol), 20% KOH (10 mL), CO (1 atm). [b] Catalytic turnover numbers, not yields are listed, since the chloroarenes were used as both the reagents and the organic phase. [c] In the presence of 18-crown-6 (0.3 mmol). [d] 10 mmol of *m*-chlorobenzophenone.

arenes is still a desirable goal. Milstein's group[4] reported the homogeneous carbonylation of chloroarenes catalyzed by the expensive and not readily available zero-valent palladium complex $(dippp)_2Pd$ (dippp = 1,3-bis(diisopropylphosphino)propane). Catalytic turnover numbers of 70–100 were obtained in 20 h at 150 °C and $P_{CO}$ = 70–80 psi. A number of chloroarenes were heterogenously alkoxycarbonylated by Basset and co-workers,[6] using a 5% Pd/C commercially available catalyst. The reaction occurred at higher temperature (200 °C, $P_{CO}$ = 3 bar, 50 h), achieving catalytic turnover numbers of 5–350. The paper published by Osborn et al.[5] described kinetic data for the carbonylation of chlorobenzene catalyzed by (tricyclohexylphosphine)palladium complexes in the presence of excess $PCy_3$. Turnover rates of 0.5–1.9 $(mol{\cdot}Pd)^{-1}$ $h^{-1}$ were observed at 180 °C and $P_{CO}$ = 15 bar; however, neither conversions nor yields were reported.[5] It is noteworthy that the catalytically active complex, $[(Cy_3P)_2Pd(Ph)Cl]$, containing *two* phosphine ligands, was shown to undergo a *reversible* carbonylation (compare these data with the results of our mechanistic studies described below).

We have found that neat chloroarenes react with CO and aqueous KOH in the presence of catalytic amounts of $[(Cy_3P)_2PdCl_2]$ to give the corresponding carboxylic acids upon subsequent acidification (a preliminary paper on this subject has been published[7]). The results are presented in Table IV. The reaction proceeds at ca. 100 °C and atmospheric pressure of CO under biphasic conditions and does not require a phase-transfer catalyst (compare entries 5 and 6). The chlorobenzenes were usually used as both substrate and organic phase since they are either liquids or solids melting below 100 °C. This simple technique is superior to that using palladium complexes of expensive sulfonated phosphines for conducting some catalytic reactions (e.g., coupling) in aqueous media.[8] The reactions were effected using either 50% or 20% aqueous solutions of KOH. The (triphenylphosphine)palladium complex catalyzed biphasic carbonylation of iodobenzene and bromobenzene can also be conducted in the absence of an organic solvent (see Experimental Section).

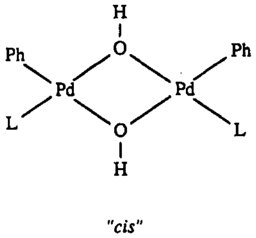
Carboxylic acids were isolated in reasonable to fine yields when chlorobenzenes containing electron-donating or electron-accepting substituents were subjected to carbonylation. Electron-donating substituents (entries 3–8, Table IV) activate the chloroarenes toward carbonylation, whereas electron-withdrawing groups (entries 9–11) exert the opposite trend, with no carbonylation observed in the case of *p*-chloronitrobenzene. Similar trends were reported by Basset and co-workers.[6]

Thus, aryl halides can undergo Pd-catalyzed biphasic carbonylation in the absence of any phase-transfer agent, extra tertiary phosphine, and even organic solvent. These results narrowed substantially the sphere of our quest for the agent which reduces in situ the Pd(II) complexes to a Pd(0) species. Since no reaction of the complex occurred when carbon monoxide was bubbled through a vigorously stirred, refluxing mixture of benzene, water, and $[(Ph_3P)_2PdCl_2]$ for 3 h, one can conclude that it is the hydroxide ion which is responsible for the generation of catalytically active palladium(0) species from the complexes $[L_2PdCl_2]$.

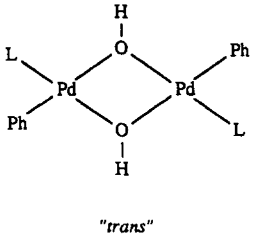
**Reactions of Palladium Complexes $[L_2PdCl_2]$ with Alkali.** Bis(triphenylphosphine)palladium dichloride reacts with $OH^-$ in the presence of iodobenzene to give triphenylphosphine oxide and 1, a new σ-phenyl palladium dimer with two hydroxo bridges (eq 2). The reaction (eq 2) is smooth and clean, leading exclusively to 1 and $OPPh_3$, the byproduct being trace amounts, if any, of palladium metal. Analytically pure complex 1, L = $PPh_3$, was isolated in 75–86% yield and characterized by elemental analysis, IR, $^1H$ and $^{31}P$ NMR spectroscopy (Table V), and a single-crystal X-ray diffraction. The NMR spectra reveal that complex 1 exists in solution as a 4:1 mixture of "trans" and "cis" isomers. The recently reported[9] perhalo analogues of 1, σ-$C_6X_5$ (X = F, Cl), exist in solution only as the trans isomers. The $^{31}P$ NMR spectrum of 1 in benzene or chloroform at room temperature contains two sharp singlets at 33.9 and 33.2 ppm (4:1) which are assigned to the trans and cis isomers, respectively. The high-field region of the $^1H$ NMR spectrum of 1 in $CDCl_3$ contains three (1:8:1) signals at −3.4 (singlet), −1.5 (doublet, *J*(H–P) = 2.9 Hz), and −0.3 (singlet) ppm. The former and the latter resonances arise from the two nonequivalent OH

$$2[L_2PdCl_2]L = PPh_3 + 2PhI + 6KOH \xrightarrow[\text{reflux, 3–5 h}]{\text{benzene–}H_2O} \underset{1}{[LPd(Ph)(\mu\text{-}OH)]_2} + 2LO + 2KI + 4KCl + 2H_2O \quad (2)$$

$$L = PPh_3$$



*"cis"*



*"trans"*

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**Table V. Analytical and Spectral Data for the Complexes $[RPd(PR'_3)(\mu\text{-}X)]_2{\cdot}S$ (1–7)**

| compd | R | R′ | X | S | yield, % | anal. % calcd (found) C | anal. % calcd (found) H | IR $\nu$ (cm$^{-1}$) | $^{31}$P NMR, $\delta$ ($CDCl_3$) [rel integral intens] | $^{1}$H NMR, $\delta$ ($CDCl_3$, 20 °C) |
|---|---|---|---|---|---|---|---|---|---|---|
| **1** | Ph | Ph | OH | $^1/_2CHCl_3$ | 86 | 59.1 (59.5) | 4.4 (4.7) | 3607 (OH) | 20 °C: 33.9 (trans) [4], 33.2 (cis) [1] | −3.4 (s; 0.1H; OH-*cis*); −1.5 (d; 0.8 H; OH-*trans*; $J_{P-H}$ = 2.9 Hz); −0.3 (s; 0.1H; OH-*cis*); 6.6 (m; 3H; 3,4,5-$C_6H_5Pd$); 7.0 (m; 2H; 2,6-$C_6H_5Pd$); 7.1–7.6 (m; 15H; $C_6H_5P$) |
| **2** | Ph | Cy | OH | $C_6H_6$ | 80 | 62.4 (62.7) | 8.1 (8.0) | 3625 (OH) | 20 °C: 37.2 (cis + trans) | −3.3 (s; 0.07H; OH-*cis*); −1.8 (d; 0.86H; OH-*trans*; $J_{P-H}$ = 2.9 Hz); −1.1 (t; 0.07H; OH-*cis*; $J_{P-H}$ = 1.8 Hz); 0.8–2.1 (m; 33H; $C_6H_{11}$); 6.8 (m; 3H; 3,4,5-$C_6H_5$); 7.4 (m; 2H; 2,6-$C_6H_5$) |
| **3** | *p*-Tol | Ph | OH | $CHCl_3$ | 73 | 57.1 (57.4) | 4.4 (4.5) | 3610 (OH) | 20 °C: 33.7 (trans) [4], 33.1 (cis) [1] | −3.4 (s; 0.1H; OH-*cis*); −1.5 (s; 0.8H; OH-*trans*); −0.3 (s; 0.1H; OH-*cis*); 2.05 (s; 3H; $CH_3$); 6.4 (d; 2H; 3,5-$C_6H_4$; $J$ = 7.8 Hz); 6.85 (dd; 2H; 2,6-$C_6H_4$; $J_{H-H}$ = 7.8 Hz; $J_{P-H}$ = 3.2 Hz); 7.1–7.5 (m; 15H; $C_6H_5$) |
| **4** | Ph | Ph | I |  | 78 | 50.3 (50.3) | 3.5 (3.7) |  | −17 °C: 27.9 [1], 27.4 [2] | 6.55 (m; 3H; 3,4,5-$C_6H_5Pd$); 7.0 (m; 2H; 2,6-$C_6H_5Pd$); 7.1–7.5 (m; 15H; $C_6H_5P$) |
| **5** | *p*-Tol | Ph | I |  | 90 | 51.2 (51.1) | 3.8 (4.0) |  | −17 °C: 27.4 [1], 27.0 [2] | 2.0 (s; 3H; $CH_3$); 6.4 (d; 2H; 3,5-$C_6H_4$; $J$ = 7.9 Hz); 6.85 (dd; 2H; 2,6-$C_6H_4$; $J_{H-H}$ = 7.9 Hz; $J_{P-H}$ = 3.2 Hz); 7.1–7.5 (m; 15H; $C_6H_5$) |
| **6**[a] | PhCO | Ph | I | $2C_6H_6$ | 92 | 54.9 (54.7) | 3.9 (3.9) | 1665 (CO) | −7 °C: 24.9 [1], 22.7 [1] | 7.1 (m; 3H; 3,4,5-$C_6H_5CO$); 7.2–7.7 (m; 15H; $C_6H_5P$); 7.8 (m; 2H; 2,6-$C_6H_5CO$) |
| **7**[b] | *p*-TolCO | Ph | I |  | 96 | 50.8 (50.5) | 3.6 (3.6) | 1669 (CO) | −7 °C: 24.6 [1], 22.6 [1] | 2.2 (s; 3H; $CH_3$); 6.9 (d; 2H; 3,5-$C_6H_4CO$; $J$ = 7.9 Hz); 7.1–7.5 (m; 15H; $C_6H_5$); 7.75 (d; 2H; 2,6-$C_6H_4CO$; $J$ = 7.9 Hz) |

[a] $^{13}$C NMR data for **6** prepared with $^{13}CO$ ($\delta$, $CDCl_3$): 20 °C [221.2; d; $J_{P-C}$ = 12.4 Hz]; −17 °C [221.5; d; $J_{P-C}$ = 10.7 Hz; and 221.9; d; $J_{P-C}$ = 10.7 Hz]. [b] $^{13}$C NMR data for **7** prepared with $^{13}CO$ ($\delta$, $CDCl_3$): 20 °C [220.3; d; $J_{P-C}$ = 11.0 Hz]; −17 °C [220.7; d; $J_{P-C}$ = 9.5 Hz; and 221.1; d; $J_{P-C}$ = 10.3 Hz].

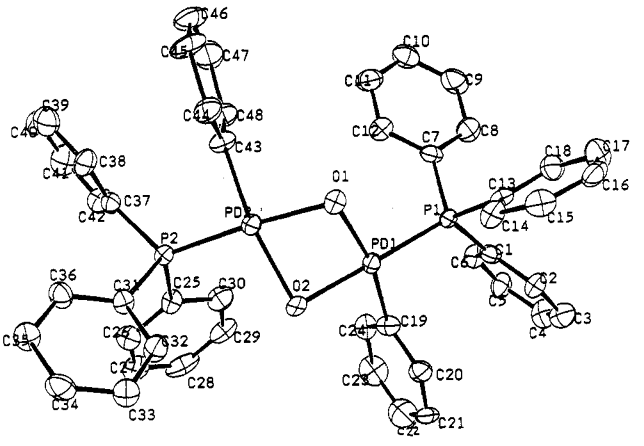

**Figure 1.** Structure of $[Ph_2(PPh_3)_2Pd_2(\mu\text{-}OH)_2]$ in the crystal of **1** showing the atom labeling scheme. Hydrogen atoms omitted for clarity.

groups of the cis isomer. The doublet from coupling to $^{31}$P of the phosphine ligand trans to the OH groups evidently belongs to the trans isomer. The trans geometry for complex **1** was found in the crystalline state by obtaining an X-ray structure of its 1:1 chloroform solvate (Figure 1). Crystallographic data, selected bond distances, and selected bond angles for **1** are listed in Tables VI and VII. A sharp, symmetrical singlet at 33.2 ppm was observed in the solid-state $^{31}$P NMR spectrum of **1**. This result, along with the X-ray diffraction data, indicates that in the solid state complex **1** exists in the trans form. Among the interesting structural features of **1** could be noted the nonplanarity of the four-membered metallacycle (O–Pd–O–Pd torsion angles lie in the range of 35.6–37.3 (3)°). The Pd···Pd separation is 2.983(15) Å. Both Pd–O bonds trans to the $\sigma$-phenyl ligands (2.114(10) and 2.126(10) Å) are slightly elongated in comparison to those trans to the phosphine ligands (2.052(10)–2.085(10) Å), obviously due to the stronger trans influence of the phenyl ligand.

**Table VI. Crystallographic Data for $[Ph_2Pd_2(PPh_3)_2(\mu\text{-}OH)_2]{\cdot}CHCl_3$ (1) and $[(PhCO)_2Pd_2(PPh_3)_2(\mu\text{-}I)_2]{\cdot}2C_6H_6$ (6)**

|  | 1 | 6 |
|---|---|---|
| formula | $C_{49}H_{43}Cl_3O_2P_2Pd_2$ | $C_{62}H_{52}I_2O_2P_2Pd_2$ |
| formula wt | 1044.97 | 1345.54 |
| *a*, Å | 13.668(3) | 11.413(4) |
| *b*, Å | 23.168(7) | 12.597(4) |
| *c*, Å | 14.358(3) | 10.494(3) |
| $\alpha$, deg | 90.00 | 101.37(3) |
| $\beta$, deg | 93.97(2) | 105.22(3) |
| $\gamma$, deg | 90.00 | 74.17(3) |
| space grp | $P2_1/n$ | *P*-1 |
| *Z* | 4 | 1 |
| *V*, Å$^3$ | 4535.6(2) | 1387.7(8) |
| $d_{calc}$, g/cm$^3$ | 1.53 | 1.61 |
| *T*, K | 173 | 166 |
| radiatn | Mo K$\alpha$<br>$\lambda$ = 0.709 30 Å | Mo K$\alpha$<br>$\lambda$ = 0.709 30 Å |
| $\mu$, mm$^{-1}$ | 1.06 | 3.66 |
| *R* ($R_W$), % | 7.1 (8.2) | 3.9 (3.5) |

The tricyclohexylphosphine analogue of **1**, complex **2**, was successfully prepared by treatment of $[(Cy_3P)_2PdCl_2]$ and *chlorobenzene* with KOH in a similar manner. This reaction establishes the metal complex activation of the C–Cl bond in chlorobenzene as the first step for the carbonylation of chloroarenes catalyzed by $[(Cy_3P)_2PdCl_2]$ under biphasic conditions (see above).[7] Unfortunately, attempts to prepare the *p*-tolyl complex $[(CH_3C_6H_4)Pd(PPh_3)(\mu\text{-}OH)]_2$, **3**, in pure form from *p*-iodotoluene and $[(Ph_3P)_2PdCl_2]$ failed by use of the procedure developed for the synthesis of **1**; the $\sigma$-tolyl hydroxo complex

**Table VII. Selected Bond Distances (Å) and Angles (deg) for $[Ph_2(PPh_3)_2Pd_2(\mu\text{-}OH)_2]\cdot CHCl_3$ (1)**

| atom 1 | atom 2 | dist | atom 1 | atom 2 | dist |
|---|---|---|---|---|---|
| Pd(1) | O(1) | 2.114(10) | Pd(1) | P(1) | 2.217(4) |
| Pd(1) | O(2) | 2.085(10) | Pd(2) | P(2) | 2.221(4) |
| Pd(2) | O(1) | 2.052(10) | Pd(1) | C(19) | 1.965(16) |
| Pd(2) | O(2) | 2.126(10) | Pd(2) | C(43) | 2.012(16) |

| atom 1 | atom 2 | atom 3 | angle | atom 1 | atom 2 | atom 3 | angle |
|---|---|---|---|---|---|---|---|
| O(1) | Pd(1) | O(2) | 76.6(4) | P(1) | Pd(1) | O(1) | 102.0(3) |
| O(1) | Pd(2) | O(2) | 77.0(4) | P(1) | Pd(1) | O(2) | 178.6(3) |
| Pd(1) | O(1) | Pd(2) | 91.4(4) | C(43) | Pd(2) | P(2) | 90.3(5) |
| Pd(1) | O(2) | Pd(2) | 90.1(4) | C(43) | Pd(2) | O(2) | 170.2(6) |
| C(19) | Pd(1) | P(1) | 90.0(5) | C(43) | Pd(2) | O(1) | 93.8(6) |
| C(19) | Pd(1) | O(2) | 91.4(5) | P(2) | Pd(2) | O(1) | 175.3(3) |
| C(19) | Pd(1) | O(1) | 167.9(6) | P(2) | Pd(2) | O(2) | 99.0(3) |

**3** was synthesized according to eq 3 (see below).

$$\mathbf{1}\xrightarrow[2.\,p\text{-}CH_3C_6H_4I,\ N_2,\ C_6H_6\text{–}KOH/H_2O]{1.\,p\text{-}CH_3C_6H_4I,\ CO,\ C_6H_6}[p\text{-}CH_3C_6H_4Pd(PPh_3)(\mu\text{-}OH)]_2 \quad (3)$$

**3**

Similar to **1**, complexes **2** and **3** (Table V) exist in solution as mixtures of trans and cis isomers, the ratios being 6:1 and 4:1, respectively. All complexes **1**–**3** exhibited high catalytic activities in the carbonylation of aryl iodides and bromides; however, only **2**, containing bulky, electron-rich phosphine ligands, was effective in the carbonylation of chloroarenes (see ref 5).

Organometallic palladium compounds **1**–**3** are white solids soluble in $CH_2Cl_2$, $CHCl_3$, and hot benzene, sparingly soluble in benzene at room temperature, and almost insoluble in acetone, methanol, and ethanol. Complex **2** is also soluble in petroleum ether, whereas less lipophilic **1** and **3** are not. All these dimers are air- and moisture-stable in the solid state, however, in solution they slowly decompose.

Complexes **1** and **3** are easily converted to the corresponding bridging iodides **4** and **5** by treatment with excess NaI in acetone–dichloromethane–water solutions. When stirred with alkali in a benzene–water biphasic system **4** and **5** can be quantitatively transformed back to **1** and **3**, respectively (eq 4).

$$\underset{\mathbf{1,3}}{[ArPdL(\mu\text{-}OH)]_2}\ \underset{KOH\ (excess)/C_6H_6\text{–}H_2O}{\overset{NaI\ (excess)/Me_2CO\text{–}CH_2Cl_2\text{–}H_2O}{\rightleftharpoons}}\ \underset{\mathbf{4,5}}{[ArPdL(\mu\text{-}I)]_2} \quad (4)$$

$$Ar = C_6H_5\ (\mathbf{1, 4}),\ p\text{-}CH_3C_6H_4\ (\mathbf{3, 5});\ L = PPh_3$$

In contrast to **1**–**3**, but similar to their chloro analogues,[10] iodides **4** and **5** rapidly undergo cis–trans isomerization ($\Delta G^{\ddagger}$ = ca. 13 kcal/mol) in solution as indicated by the variable-temperature (VT) $^{31}P$ NMR experiments. The VT $^{31}P$ NMR spectra of **4** in $CDCl_3$ are shown in Figure 2; an analogous pattern, including the same coalescence temperature and similar chemical shifts, was observed for complex **5**. At the same time, no coalescence was found for **1** in benzene or chloroform even at 60 °C, indicating that the hydroxo bridges between the two palladium atoms are more difficult to cleave than the iodo bridges.

The reaction of $[(Ph_3P)_2PdCl_2]$ with $OH^-$ in the absence of iodo- or bromobenzene under biphasic conditions leads to Pd metal along with triphenylphosphine oxide. Thus, $OH^-$ induces a formal disproportionation of complexes $[L_2PdCl_2]$ to the corresponding phosphine oxide and zero-valent palladium species that can oxidatively add the carbon–halogen bond. The same path is likely to take place in the reduction of $[L_2MCl_2]$ (M = Pd, Pt; L = tertiary phosphine) to the corresponding zero-valent phosphine Pd and Pt complexes by L in the presence of different bases[11] (e.g., $RO^-$,[12-14] $OH^-$,[15,16] and $F^-$[17]). It is noteworthy that all these reduction reactions[12-17] were always conducted in the presence of *excess* free tertiary phosphine. Therefore, it was impossible to conclude umambiguously whether the reduction was effected by *coordinated* or *noncoordinated* phosphine molecules. Our results lead to the following significant conclusion: *the Pd(II) phosphine complexes that are used as catalysts for carbon-*

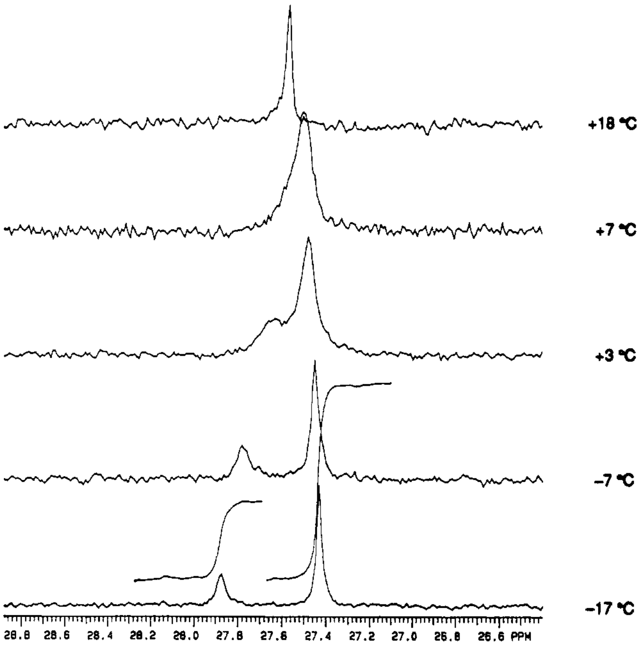

**Figure 2.** The VT $^{31}P$ NMR spectra of **4** in $CDCl_3$.

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[10] Anderson, G. K. *Organometallics* **1983**, *2*, 665.

[11] Oxidation of water-soluble phosphines by Rh(III) in aqueous media occurs under neutral or even acidic conditions. See: Larpent, C.; Dabard, R.; Patin, H. *New. J. Chem.* **1988**, *12*, 907 and references cited therein.

[12] Malatesta, L.; Cenini, S. *Zerovalent Compounds of Metals*; Academic Press: London, 1974.

[13] Hartley, F. R. *Organomet. Chem. Rev. A* **1970**, *6*, 119; *The Chemistry of Platinum and Palladium*; John Wiley and Sons: New York, 1973.

[14] Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1974**, 1205.

[15] Ioele, M.; Ortaggi, G.; Scarsella, M.; Sleiter, G. *Polyhedron* **1991**, *10*, 2475.

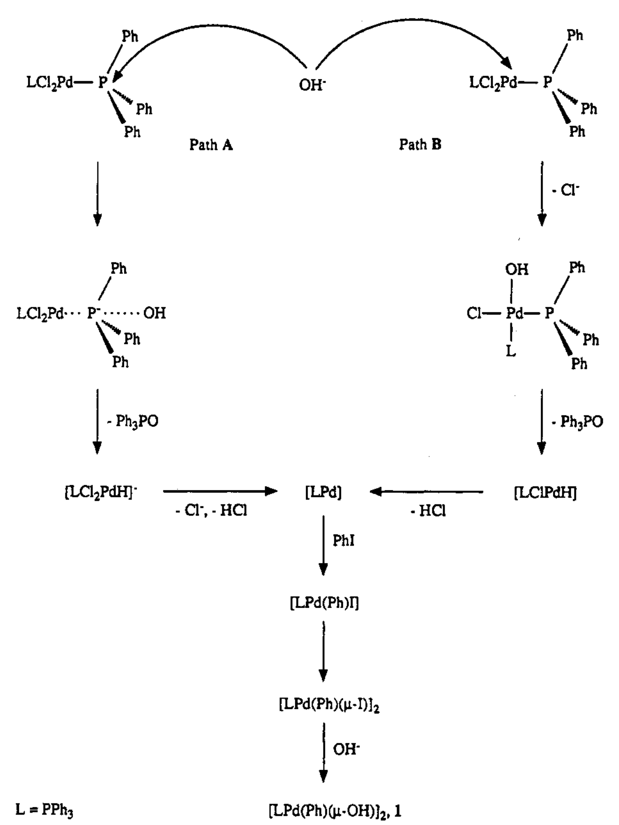
[16] Unlike that claimed by Ioele et al.,[14] the synthesis of $[(Ph_3P)_4M]$ (M = Pd, Pt) from $[(PPh_3)_2MCl_2]$ and excess $PPh_3$ in the aqueous alkali–THF system does not require any phase-transfer catalyst. We have established that these reactions, as well as transformations described in the present paper, are biphasic, not phase transfer catalyzed, in nature.

[17] Mason, M. R.; Verkade, J. G. *Organometallics* **1992**, *11*, 2212.

***ylation and some other reactions, proceedings in the presence of alkali, are reduced to a Pd(0) species not by CO, $H_2$ (if formed by water gas shift reaction), or extra phosphine, etc., but by their own coordinated phosphine ligands which are oxidized to phosphine oxides, with $OH^-$ playing the role as the specific promoter.***

Phosphine complexes of *zero-valent* palladium are evidently required to catalyze a number of important transformations, such as the Heck arylation, carbonylation of organic halides, and various cross-coupling reactions,[1,18,19] including the Suzuki reaction.[20] However, the *added* catalysts for these processes are not necessarily compounds of Pd(0); more convenient to handle, air-stable phosphine complexes of *divalent* palladium, e.g., $[L_2PdX_2]$ (L = tertiary phosphine, X = Cl, Br, AcO), exhibit a similar catalytic activity.[1,18–20] In order to neutralize releasing acid, the reactions are conducted in the presence of excess inorganic (NaOH, NaOAc, $Na_2CO_3$, etc.) or organic (tertiary amines, alkoxides) base, triethylamine being probably the most widely used. It was proposed (ref 19, page 725) that the role of triethylamine is also to reduce the Pd(II) complexes to the catalytically active Pd(0) species. Indeed, it was reported[21] that bis(benzonitrile)dichloropalladium can be reduced by $Et_3N$, $Bu_3N$, and other amines. However, we have found that no reaction occurred when $[(Ph_3P)_2PdCl_2]$ (55 mg) was treated with dry (freshly distilled from sodium) triethylamine (1.1 mL) at 80 °C under $N_2$ for 48 h. The addition of water (15 mg; 10-fold excess) to the reaction mixture changed the reactivity of the complex dramatically. Under the same conditions, palladium metal started precipitating 1 h after the reaction began, and decomposition to palladium black was complete in 2 days. Evidently, the hydroxide anion, which forms on reversible deprotonation of water with $Et_3N$, caused the reduction. All the bases used for the palladium(II)-catalyzed transformations noted above either contain some water or are so hygroscopic that it is very difficult to maintain dryness. The amount of water (the $OH^-$ source) which is sufficient to cause the reduction of a Pd(II) phosphine complex, especially in *catalytic* quantities, is too small to be easily avoided. For instance, if triethylamine containing 0.1% of water is used for a Pd(II)-catalyzed reaction in a common 200:1 ratio to the catalyst, one should take into account that the water present in the reaction mixture is theoretically more than enough to transform all the complex to Pd(0). Therefore, the $OH^-$-promoted disproportionation of the phosphine palladium(II) complexes may be of relevance to a variety of other palladium catalyzed organic reactions, although it is recognized that in selected cases some alkoxide anions[12,13] or organoboron compounds[20] can play the role of the reducing agents. In the very recent article of Mason and Verkade[17] that appeared after the present paper was originally submitted for publication, the reduction of $[L_2PdCl_2]$ by phosphines in the presence of $F^-$ is described. Since the authors stated that their reactions were never performed under rigorously anhydrous conditions,[17] it seems quite possible that at least some part of the Pd(II) was reduced due to the presence of $OH^-$ generated by hydrolysis of the fluoride anion.

**Scheme I**



In principle, two distinct mechanisms are conceivable for the reaction between $[L_2PdCl_2]$ (L = tertiary phosphine) and $OH^-$ (Scheme I). The first mechanism (path A) involves nucleophilic attack of hydroxide ion on the electron-deficient phosphorus atom of the coordinated phosphine ligand. Subsequent extrusion of the phosphine oxide gives rise to the anionic palladium hydride, $[LPd(H)Cl_2]^-$, which then generates highly reactive species, [LPd], upon elimination of $Cl^-$ and HCl in the presence of $OH^-$.[22] This pathway can be regarded as the "inorganic analog" of McEwen's mechanism[23] for alkaline hydrolysis of quaternary phosphonium cations.

The other possible mechanism (path B) includes ligand exchange, i.e., replacement of the chloro ligand for the hydroxo group, followed by reductive elimination of the phosphine oxide from the palladium atom. Deprotonation of the square-planar hydroxo complex may precede the elimination step. Although it was proposed that $OH^-$ [15] and $F^-$ [17] attack the metal rather than the phosphorus atom of $[L_2MCl_2]$ (M = Pd, Pt), no umambiguous evidence was obtained for this proposal.

Mechanisms A and B (Scheme I) can be easily distinguished by studying the stereochemistry of the reaction between $OH^-$ and a complex $[L^*{}_2PdCl_2]$ where L* is an optically active phosphine bearing chirality on the phosphorus atom. If the reaction proceeds via path A then inversion of configuration at phosphorus should take place in the course of the elimination of the phosphine oxide. If the other mechanism (B) is operative, then retention of

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[18] Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.

[19] Collman, J. P.; Hegedus, L.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

[20] Suzuki, A. *Pure Appl. Chem.* **1991**, *63*, 419.

[21] McCrindle, R.; Ferguson, G.; Arsenault, G. J.; McAlees, A. J.; Stephenson, D. K. *J. Chem. Res. Synop.* **1984**, 360.

[22] For examples of reductive elimination of HCl from chloro hydrido transition metal complexes under biphasic or phase-transfer-catalyzed conditions see: (a) Grushin, V. V.; Vymenits, A. B.; Yanovsky, A. I.; Struchkov, Yu. T.; Vol'pin, M. E. *Organometallics* **1991**, *10*, 48. (b) Grushin, V. V.; Vymenits, A. B.; Vol'pin, M. E. *Metalloorg. Khim.* **1990**, *3*, 702. (c) Grushin, V. V.; Vymenits, A. B.; Vol'pin, M. E. *J. Organomet. Chem.* **1990**, *382*, 185. (d) Grushin, V. V.; Akhrem, I. S.; Vol'pin, M. E. *J. Organomet. Chem.* **1989**, *371*, 403.

[23] McEwen, W. E.; Axelrad, G.; Zanger, M.; VanderWerf, C. A. *J. Am. Chem. Soc.* **1965**, *87*, 3948.

**Table VIII. Selected $^1H$ and $^{31}P$ NMR Spectral Data for the Cis and Trans Isomers of the Complex $[L_2PdCl_2]$ (L = (*R*)-Benzylmethylphenylphosphine)**

| | trans isomer (mp 160–162 °C) | | | | cis isomer (mp 168–170 °C) | | | |
|---|---|---|---|---|---|---|---|---|
| NMR[a] | $\delta$ | shape | $^2J$(H–H), Hz | $J$(P–H), Hz | $\delta$ | shape | $^2J$(H–H), Hz | $J$(P–H), Hz |
| $^{31}P\{^1H\}$ | 4.5 | singlet | | | 15.5 | singlet | | |
| $^1H$ | | | | | | | | |
| $CH_3$ | 1.6 | virtual triplet | | 6.9 | 1.3 | doublet | | 9.5 |
| $CH_2$ | 3.3 | doublet of virtual triplets | 14.0 | 8.9 | 3.6 | doublet of doublets | 14.2 | 11.6 |
| | 3.9 | doublet of virtual triplets | 14.0 | 7.4 | 4.2 | doublet of doublets | 14.2 | 10.7 |
| $C_6H_5$ | 6.9–7.8 | multiplets | | | 6.7–7.3 | multiplets | | |

[a] $C_6D_6$ or $CDCl_3$ with TMS as internal standard.

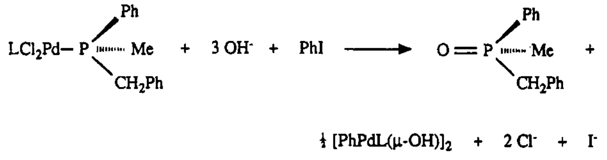
configuration at phosphorus in the phosphine oxide should be observed.

Following the procedure of Kumada and co-workers,[24] we synthesized such a palladium complex of (*R*)-benzylmethylphenylphosphine. The Japanese chemists characterized their compound by elemental analysis, rotation angle ($[\alpha]^{20}_D$ −144.1° (*c* 1.03, $CH_2Cl_2$)) and melting point (165–166 °C); however, no spectral data were reported. We investigated the optically active complex $[((R)\text{-}PhCH_2P(CH_3)Ph)_2PdCl_2]$ by $^1H$ and $^{31}P$ NMR spectroscopy and found that in solution it exists as a mixture of cis and trans isomers (Table VIII), similar to a number of other square-planar Pd and Pt complexes.[25] The trans geometry is indicated by the virtual coupling which gives rise to triplets for the phosphine methyl and methylene groups. Resonances from the same protons of the cis isomer arise as doublets. Both isomers can be isolated in pure form showing no tendency to isomerize in the crystalline state. The cis complex was obtained by slow crystallization resulting from addition of methanol to a concentrated dichloromethane solution of the complex. The trans isomer readily precipitates by treatment of a concentrated benzene solution of the complex with pentane. The isomers equilibrate quite rapidly in solution, with 2–3 h at room temperature usually being sufficient to reach equilibrium. As anticipated, the cis/trans ratio for the equilibrium mixtures depends on the solvent polarity, being 65:35, 40:60, and <3:97 for $CH_2Cl_2$, $CHCl_3$, and benzene, respectively. Evidently, the more polar the media, the higher the concentration of the more polar cis isomer.[25]

The rotation angle for the complex solutions was found to be dependent on the cis/trans ratio. For a freshly prepared solution of the cis isomer the magnitude of $[\alpha]^{20}_D$ was −158.1° (*c* 1.03, $CH_2Cl_2$). Two h later, when the cis–trans equilibrium had been established, the rotation angle reached −152.5° and then remained the same (±0.1°).

The optically active complex $[L^*{}_2PdCl_2]$ (L* = (*R*)-benzylmethylphenylphosphine) was allowed to react with $OH^-$ in the presence of iodobenzene at room temperature. When the reaction reached completion, the clear, pale yellow organic layer was analyzed by $^{31}P$ spectroscopy. The $^{31}P$ NMR spectrum contained two main resonances (ca. 1:1 intensity), i.e., a sharp singlet at 30.7 ppm arising from the phosphine oxide, and a slightly broadened singlet at 15.1 ppm which was assigned to $[PhL^*Pd(\mu\text{-}OH)]_2$. Three other singlet resonances at 14.6, 13.1, and 0.5 ppm were of much lower integral intensity and obviously arose from byproducts. Despite their modest yields, these byproducts prevented the isolation and characterization of the hydroxo organopalladium dimer in pure form. Nonetheless, good evidence was obtained supporting the formation of $[PhL^*Pd(\mu\text{-}OH)]_2$. High-field aromatic multiplets in the $^1H$ NMR spectra (6.5–6.9 ppm) are indicative of the presence of a Pd–Ph bond. Very characteristic resonances at −0.6, −1.6, and −3.4 ppm (ca. 1:7:1) are due to the two isomers (cis and trans) of the complex with bridging OH groups (vide supra). It is likely that the singlet at 14.6 ppm in the $^{31}P$ NMR spectrum belongs to the cis isomer of the dimer, whereas a three to four times more intensive resonance at 15.1 ppm arises from the trans complex.

The benzylmethylphenylphosphine oxide was successfully separated from the other products due to its solubility in water and found to have the *S configuration*[26] (eq 5).



(5)

L = (*R*)-benzylmethylphenylphosphine

This result was reliably reproduced four times: the (*S*)-benzylmethylphenylphosphine oxide of 99.1–99.6% optical purity was always obtained in 50–80% chemical yields.

Since the reaction proceeded with *retention* of configuration at phosphorus, the mechanism (A) involving nucleophilic attack of $OH^-$ on the phosphorus atom (Scheme I) can be ruled out. Interestingly, *cis*-$[L^*{}_2PdCl_2]$ seems to possess a higher reactivity toward the hydroxide anion than the trans isomer, though kinetic data are not available. When the cis complex was added under $N_2$ to the biphasic system benzene/iodobenzene–50% KOH upon stirring, the organic phase turned brown almost immediately, followed by gradual decoloration. Under the same conditions, the trans complex experienced noticeably slower darkening of the benzene layer; however, eventually the same color and chemical composition resulted as that observed for the cis isomer. These observations represent another argument in support of mechanism (B) depicted in Scheme I. Evidently, the substitution of the chloro ligand in a square-planar cis complex $[(R_3P)_2PdCl_2]$ for the hydroxo group should proceed faster than in the trans isomer, due to the strong trans-effect of tertiary phosphine ligands.

**Carbonylation of the Organopalladium Hydroxo Dimers and Related Reactions.** The $\sigma$-phenyl palladium hydroxo dimer **1** readily reacts with CO and PhI in benzene to give the corresponding benzoyl complex **6** along with benzoic acid and trace amounts of biphenyl (eq 6).

Complex **6** was isolated in 92% yield as the benzene solvate and characterized by elemental analysis, $^1H$, $^{31}P$,

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[24] Yamamoto, K.; Kiso, Y.; Ito, R.; Tamao, K.; Kumada, M. *J. Organomet. Chem.* **1981**, *210*, 9.

[25] Anderson, G. K.; Cross, R. J. *Chem. Soc. Rev.* **1980**, *9*, 185.

[26] (a) Korpiun, O.; Lewis, R. A.; Chikos, J.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4842. (b) Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7012.

$$\underset{\mathbf{1}}{[\mathrm{Ph_3P(Ph)Pd}(\mu\text{-OH})]_2} + \mathrm{CO} + \mathrm{PhI} \xrightarrow[20\ ^\circ\mathrm{C}]{\text{benzene}} \underset{\mathbf{6}}{[\mathrm{Ph_3P(PhCO)Pd}(\mu\text{-I})]_2} + \mathrm{PhCOOH} + \mathrm{Ph_2}\ \text{(traces)} \qquad (6)$$

and $^{13}$C (for the same prepared with $^{13}$CO) NMR spectroscopy, IR spectroscopy (Table V), and a single-crystal X-ray diffraction (Figure 3). Selected crystallographic and geometric data for **6** are given in Tables VI and IX, respectively. In contrast to the metallacycle of **1**, the four-membered $\mathrm{Pd_2I_2}$ ring is planar, the Pd···Pd separation being 3.9294(11) Å.

The *p*-toluoyl complex **7** was prepared in a similar manner and characterized by elemental analysis and spectral methods (Table V). Aroyl complexes **6** and **7** can be prepared in quantitative yields by fast direct carbonylation of **4** and **5**, respectively (eq 7). Probably,[10] a toluene solvate of **6** was previously isolated from the reaction between $[\mathrm{Pd_3(CO)_3(PPh_3)_4}]$ and PhI under CO; however, at that time it was characterized as $[\mathrm{PdI(COPh)(PPh_3)}]\cdot$toluene.[27] Both **6** and **7** showed no tendency to undergo facile decarbonylation. After nitrogen was bubbled at room temperature through a toluene solution of $[(p\text{-}\mathrm{CH_3C_6H_4{}^{13}CO})\mathrm{Pd(PPh_3)}(\mu\text{-I})]_2$ for 20 h, less than 5% of **5** formed according to $^1$H NMR, though ca. 15% of the toluoyl complex decomposed to give some unidentified products. The $^{13}$CO-labeled complex **6** was found to undergo a slow (hours at room temperature and atmospheric pressure in benzene) $^{13}$CO/$^{12}$CO exchange with free carbon monoxide (eq 8).

$$\underset{\mathbf{4,\,5}}{[\mathrm{Ph_3P(Ar)Pd}(\mu\text{-I})]_2} + \mathrm{CO} \xrightarrow[1\ \mathrm{atm},\ 20\ ^\circ\mathrm{C},\ 1\text{–}5\ \mathrm{min}]{\mathrm{CDCl_3}} \underset{\mathbf{6,\,7}}{[\mathrm{Ph_3P(ArCO)Pd}(\mu\text{-I})]_2} \qquad (7)$$

$$\mathrm{Ar} = \mathrm{C_6H_5}\ (\mathbf{4},\,\mathbf{6}),\ p\text{-}\mathrm{CH_3C_6H_4}\ (\mathbf{5},\,\mathbf{7})$$

$$[\mathrm{Ph_3P(Ph^{13}CO)Pd}(\mu\text{-I})]_2 \overset{^{12}\mathrm{CO}}{\underset{^{13}\mathrm{CO}}{\rightleftharpoons}} [\mathrm{Ph_3P(Ph^{12}CO)Pd}(\mu\text{-I})]_2 \qquad (8)$$

The exchange was conveniently monitored by $^{13}$C and especially by $^1$H NMR spectroscopy, as the signals from the benzoyl ligand ortho protons (7.8 ppm) arise as a doublet-like resonance for a nonlabeled **6** or as a very characteristic multiplet for the $^{13}$CO-labeled **6**. Accompanied by some decomposition of the benzoyl complex (formation of an insoluble precipitate), the exchange process occurred much more readily than the decarbonylation of **6** and **7** and appreciably more sluggishly than the carbonylation of **4** and **5**. Therefore, an associative mechanism rather than a dissociative path for the exchange should be proposed.

Like the σ-aryl palladium iodo-bridging dimers **4** and **5**, their aroyl analogues **6** and **7** exist in solution as cis and trans isomers interconverting easily at a rate commensurate with the NMR time scale. For instance, the VT$^{31}$P NMR spectra of **6** in chloroform-*d* are shown in Figure 4, and the same behavior was observed for **7**.

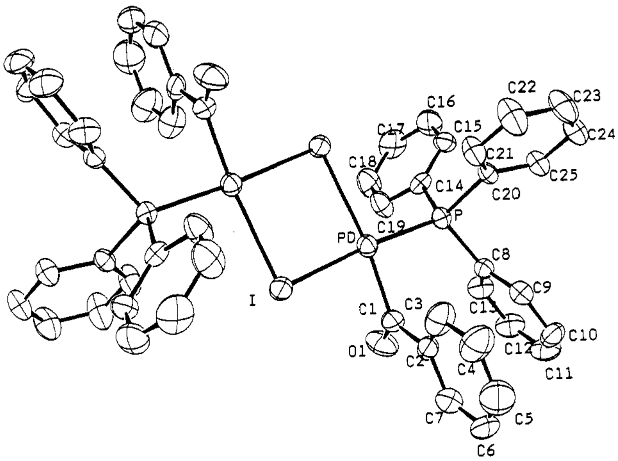

**Figure 3.** Structure of $[(\mathrm{PhCO})_2(\mathrm{PPh_3})_2\mathrm{Pd_2}(\mu\text{-I})_2]$ in the crystal of **6** showing the atom labeling scheme. Hydrogen atoms omitted for clarity.

The reaction of **1** with CO in the absence of iodobenzene instantly resulted in a dark brownish-red, clear solution. The IR spectrum of this solution exhibited three intensive ν(CO) bands at 1911, 1895, and 1877 cm$^{-1}$ and no bands that could be ascribed to a benzoylpalladium species. The $^{31}$P NMR spectra of the same solution contained a number of singlets in the region of 19–30 ppm, relative intensities of which varied from run to run. From these data it seems likely that mixtures of carbonylphosphinepalladium clusters are formed upon the interaction between **1** and CO.

Treatment of the benzoyl complex **6** in benzene with aqueous KOH under $\mathrm{N_2}$ resulted in the benzoate anion and palladium metal deposition. When the same reaction was conducted in the presence of PhI, no palladium metal precipitated, but the hydroxo complex **1** was formed instead, and benzoic acid was again isolated in high yield from the aqueous phase. Similarly, the reaction of **7** with the hydroxide ion and *p*-iodotoluene led to complex **3** (eq 9).

$$\underset{\mathbf{6,\,7}}{[\mathrm{Ph_3P(ArCO)Pd}(\mu\text{-I})]_2} \xrightarrow[20\ ^\circ\mathrm{C},\ 20\text{–}24\ \mathrm{h}]{\mathrm{ArI{-}C_6H_6{-}KOH/H_2O}} \underset{\mathbf{1,\,3}}{[\mathrm{Ph_3P(Ar)Pd}(\mu\text{-OH})]_2} + \mathrm{ArCOOK} \qquad (9)$$

$$\mathrm{Ar} = \mathrm{C_6H_5}\ (\mathbf{1},\,\mathbf{6}),\ p\text{-}\mathrm{CH_3C_6H_4}\ (\mathbf{3},\,\mathbf{7})$$

Although the reaction pathway for the complex **1** catalyzed carbonylation of aryl halides became quite clear after the experiments described above, we attempted to investigate the mechanism in more detail. Unexpectedly, the reaction between **6** and OH$^-$ in the presence of *p*-iodotoluene led not to just benzoic acid and the σ-tolyl palladium hydroxo dimer **3**, but to a 2:1 mixture of benzoic and *p*-toluic acids. Palladium organometallics isolated from the organic layer exhibited a number of singlets (30–35 ppm) in the $^{31}$P NMR spectrum. One could anticipate a similar $^{31}$P NMR spectral pattern for a mixture of complexes $[\mathrm{ArAr(PPh_3)_2Pd_2}(\mu\text{-OH})_2]$, where Ar = $\mathrm{C_6H_5}$ and *p*-$\mathrm{CH_3C_6H_4}$. A mixture of *p*-toluic and benzoic acids (3:2) also formed when the *p*-toluoyl complex **7** was treated with OH$^-$ in the presence of PhI (Scheme II).

To account for the formation of both acids (Scheme II) it can be proposed that, in the course of the reaction of

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[27] Hidai, M.; Hikita, T.; Wada, Y.; Fujikura, Y.; Uchida, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2075.

**Table IX. Selected Bond Distances (Å) and Angles (deg) for $[(PhCO)_2(PPh_3)_2Pd_2(\mu\text{-}I)_2]\cdot 2C_6H_6$ (6)**

| atom 1 | atom 2 | dist | atom 1 | atom 2 | dist |
|---|---|---|---|---|---|
| Pd | I | 2.6862(12) | Pd | C(1) | 1.986(7) |
| Pd′ | I | 2.7658(11) | Pd | P | 2.2850(20) |
| Pd | I′ | 2.7658(11) | C(1) | O(1) | 1.189(8) |

| atom 1 | atom 2 | atom 3 | angle | atom 1 | atom 2 | atom 3 | angle |
|---|---|---|---|---|---|---|---|
| Pd | I | Pd′ | 92.25(3) | I′ | Pd | P | 97.06(6) |
| I | Pd | I′ | 87.75(3) | Pd | C(1) | O(1) | 119.5(5) |
| I | Pd | P | 174.62(5) | Pd | C(1) | C(2) | 116.8(5) |
| I | Pd | C(1) | 87.15(17) | P | Pd | C(1) | 88.25(18) |
| I′ | Pd | C(1) | 172.95(18) | O(1) | C(1) | C(2) | 123.7(6) |

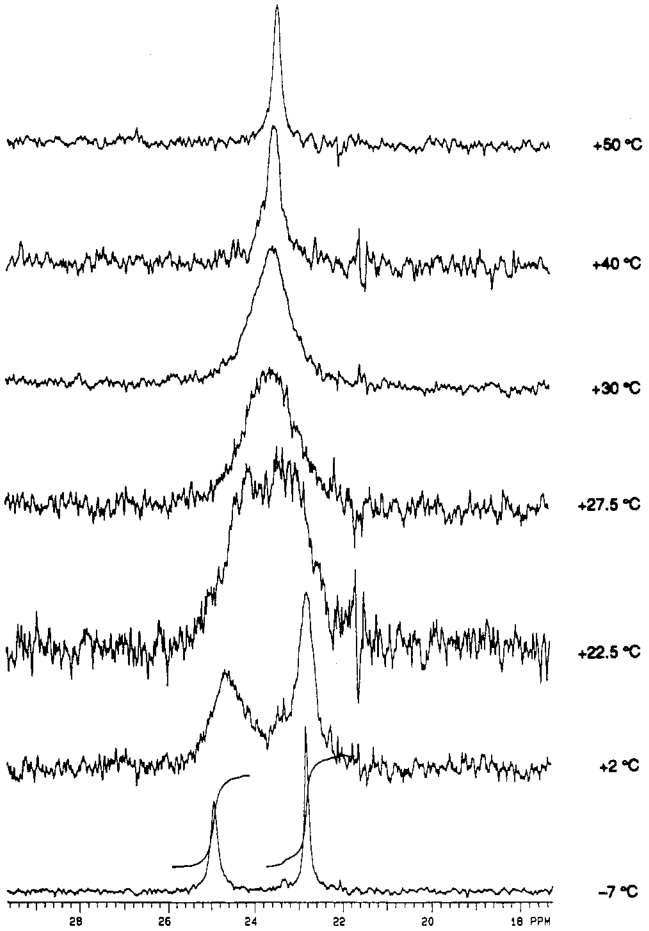
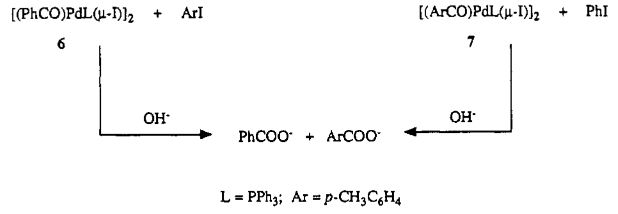


**Figure 4.** The VT$^{31}$P NMR spectra of **6** in $CDCl_3$.

### Scheme II



**6** or **7** with $OH^-$ and ArI, a reversible CO transfer takes place from the as yet unreacted aroyl complex to the already formed σ-aryl complex (eqs 10–12).

$$[PhCOPdL(\mu\text{-}I)]_2 + 4OH^- + 2ArI \rightarrow 2PhCOO^- + [ArPdL(\mu\text{-}I)]_2 + 2I^- + 2H_2O \quad (10)$$

$$[PhCOPdL(\mu\text{-}I)]_2 + [ArPdL(\mu\text{-}I)]_2 \rightleftarrows [PhPdL(\mu\text{-}I)]_2 + [ArCOPdL(\mu\text{-}I)]_2 \quad (11)$$

$$[ArCOPdL(\mu\text{-}I)]_2 + 4OH^- + 2ArI \rightarrow 2ArCOO^- + [ArPdL(\mu\text{-}I)]_2 + 2I^- + 2H_2O \quad (12)$$

$$L = PPh_3;\ Ar = p\text{-}CH_3C_6H_4$$

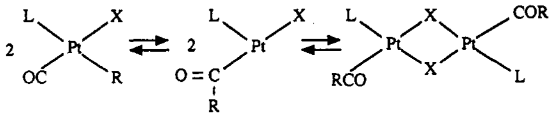
In order to examine this hypothesis, chemical and spectral studies were undertaken. When a dichloromethane solution containing the benzoyl complex **6** and the *p*-tolyl complex **5** in a 1:1 ratio was kept under nitrogen for 2 h and then treated with aqueous KOH, a 1.5:1 mixture of benzoic and *p*-toluic acids was isolated from the aqueous phase. Having been kept under $N_2$ for 5.5 h prior to reacting with alkali, a similarly prepared solution gave a 1.15:1 mixture of benzoic and *p*-toluic acids upon treatment with KOH. Finally, the reaction between KOH and a methylene chloride solution of the toluoyl complex **7** and the phenyl dimer **4** (1:1) that was kept under $N_2$ for 5.5 h led to *p*-toluic and benzoic acids in a 2.3:1 ratio. In each case the presence of the two acids was proved by mass spectrometry, and their ratios were reliably determined by $^1$H NMR spectroscopy.

Besides the chemical evidence some spectral data were obtained in support of the equilibrium (eq 11). Probably, equilibrium 11 involves not only four dimers **4**–**7**, but 10 different compounds $[RR'Pd_2(PPh_3)(\mu\text{-}I)_2]$ where R and R′ can be phenyl, benzoyl, *p*-tolyl, and *p*-toluoyl in all possible combinations, each complex being existent as a mixture of cis and trans isomers. If this is the case, similar complicated patterns of 20 singlet resonances should be theoretically observed in a low-temperature $^{31}$P NMR spectra of mixtures resulted from the equilibration between **4** and **7** and between **5** and **6**. In fact, 19 lines of different intensities were observed in the $^{31}$P NMR spectrum of the sample obtained by dissolving **5** and **6** in $CDCl_3$ and then storing the solution for 18 h under $N_2$ at room temperature. A similar $^{31}$P NMR spectrum was obtained for the sample that was prepared in exactly the same manner with complexes **4** and **7**. The $^{13}$CO-labeled aroyl complexes **6** and **7** were used for the $^{13}$C NMR studies. Again, complicated, not well-resolved, but similar patterns were observed for both solutions (**4** + **7** and **5** + **6**) in $CDCl_3$ 18–20 h after the preparation. The NMR spectra of all these mixtures were measured at -17 °C, i.e., 25–40 °C below the coalescence points which were determined for **4**–**7** earlier.

## Discussion

The obtained data allow us to propose a plausible mechanism for the palladium-catalyzed carbonylation of aryl halides under biphasic conditions. As indicated by the stereochemical study (Scheme I, eq 5), the initial step involves the interface coordination of the hydroxide ion with the transition metal center of square-planar Pd (II) 16-electron complexes, followed by elimination of $Cl^-$, the phosphine oxide, and HCl. Regardless of what order the eliminations take place, the process finally leads to highly reactive complexes [LPd] (L = tertiary phosphine) which probably coordinate slightly with $C_6H_6$, $H_2O$, $OH^-$, and $Cl^-$ of the media. However, such coordination is not sufficient to stabilize these zero-valent Pd complexes toward palladium metal precipitation. The stability of [LPd] is dependent on the nature of the ligand L. The trimethylphosphine and triphenylarsine complexes appeared highly unstable, releasing palladium metal very fast, whereas the complexes bearing tricyclohexylphosphine and tributylphosphine are substantially less prone to decomposition. In the presence of a suitable haloarene the Pd(0) species can undergo oxidative addition of the carbon–halogen bond (Scheme I). Subsequent dimerization and metathesis with $OH^-$ results in the formation of organopalladium dinuclear complexes with bridging hydroxo ligands. It is noteworthy that the replacement of coordinated halogen for hydroxo group in late transition metal complexes is not very common, but known.[28]

Anderson[10,29] has shown that reactions between CO and complexes $[RPdL(\mu\text{-}Cl)]_2$ (R = alkyl, aryl; L = tertiary phosphine) lead smoothly to the corresponding acyl and aroyl dimers $[RCOPdL(\mu\text{-}Cl)]_2$. In the present paper the iodo analogues of the latter were obtained in a similar manner from $[ArPd(PPh_3)(\mu\text{-}I)]_2$, **4** and **5**. The carbonylation likely proceeds via coordination of CO with the palladium atoms and cleavage of the halide bridges. Then the aryl group migrates from palladium to the coordinated carbonyl ligand, and the resulting aroyl complex dimerizes to give the final product. The well-studied equilibrium (eq 13)[29,30] appears to be shifted almost entirely to the aroyl dimer in the case of palladium complexes.

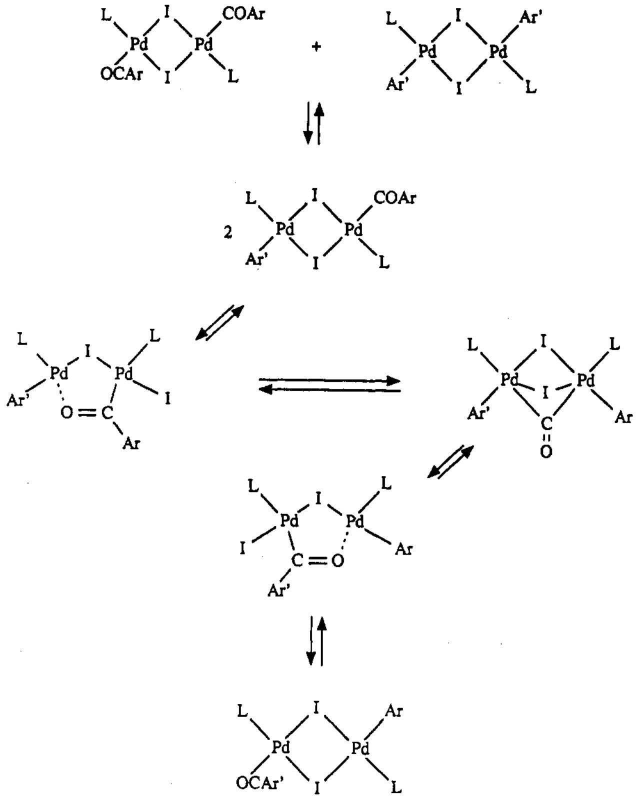


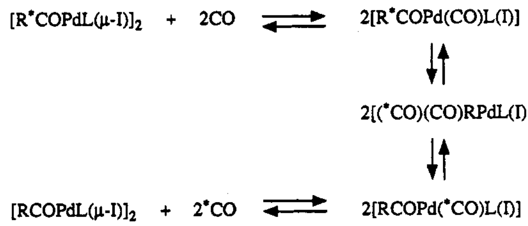
(13)

Unlike stable aroylpalladium complexes with bridging halogeno ligands, their hydroxo analogues readily undergo reductive elimination in the presence of aryl halides to give the carboxylic acid and regenerate the catalytically active zero-valent palladium species [LPd] which immediately undergoes oxidative addition. The $\sigma$-aryl complexes **4** and **5**, resulting from oxidative addition of aryl iodides to $[(Ph_3P)Pd]$, can either react with alkali to give the hydroxo dimers or be converted to the aroyl complexes **6** and **7** in the presence of CO. The aroyl compounds then react with the $OH^-$, giving rise to the carboxylate anion along with $[(Ph_3P)Pd]$ which starts another catalytic cycle. Both reaction sequences are believed to participate in the catalytic process.

Evidently, the aroyl complexes **6** and **7** are not inclined to lose CO converting to **4** and **5**, respectively. Therefore, a dissociative mechanism, involving spontaneous decarbonylation of **6** and **7**, cannot provide a rationale for the $^{13}CO/^{12}CO$ exchange and the CO-transfer from **6** to **5** and from **7** to **4**. The exchange process between $[Ph^{13}CO\text{-}Pd(PPh_3)(\mu\text{-}I)]_2$ and $^{12}CO$ probably occurs via coordination of the two CO molecules with the Pd centers, followed by cleavage of the iodo-bridges and aryl group migration in the formed mononuclear Pd complexes (eq 14).

**Scheme III**





(14)

This mechanism is consistent with the observation of two terminal $\nu$(CO) bands in addition to the band at 1650 cm$^{-1}$ in the solution IR spectrum of $[PhPd(PBu_3)(\mu\text{-}Cl)]_2$ that was treated with CO for 2 h.[10] The bands at 1990 and 2015 cm$^{-1}$ that diminished in intensity upon standing could be ascribed to two isomers of $[PhCOPd(CO)(PBu_3)(Cl)]$ which easily lose CO to give the corresponding stable benzoyl dimer.

Scheme III accounts for the CO-transfer from the aroylpalladium dimers (**6** and **7**) to the $\sigma$-aryl palladium complexes **4** and **5**. A low-energy barrier to the cis–trans isomerisation of complexes **4**–**7** (13–14 kcal/mol, as estimated from the VT$^{31}$P NMR spectra) assures facile exchange between the "monomeric" frameworks of the dimers. Both associative and dissociative paths seem possible for this exchange process and the cis–trans isomerization.[25] The intramolecular replacement of one of the iodo bridges for the bridging aroyl ligand may then occur, followed by migrations of the aryl groups, as described in the literature[31-35] for a number of binuclear transition metal complexes and clusters.

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In conclusion, this investigation has addressed some of the principal questions regarding the pathway for the carbonylation of halides to acids. Not only has evidence accrued for the mechanism of the reduction of Pd(II) to Pd(0) but also for other steps in the process. The importance of the participation of *binuclear* palladium complexes in carbonylation reactions involving *mononuclear* palladium catalysts has been demonstrated, as well as a greater appreciation of concurrent isomerization (cis–trans) and exchange ($^{12}$CO–$^{13}$CO) reactions. These findings are not only of importance to carbonylation reactions, but may be of relevance to other palladium-catalyzed process.

## Experimental Section

Spectral measurements were carried using the following equipment: Varian XL 300 ($^1$H, $^{13}$C, and $^{31}$P NMR), Bruker CXP 180 (solid-state $^{31}$P NMR), Bomem MB-100 (FT-IR), and VG 5050 micromass (mass spectra). A Perkin-Elmer 241 polarimeter was used for optical rotation measurements. Melting point determinations were made on a Fisher-Johns apparatus, and X-ray measurements were made on a Rigaku AFC6S diffractometer. Aryl halides, tertiary phosphines, $^{13}$CO, and other chemicals were purchased from Aldrich, Strem, Organometallics, and MSD Isotopes chemical companies. The palladium complexes [$L_2PdCl_2$] (L = $Ph_3P$,[1,13,18,36] $Ph_3As$,[36] and $^1/_2Ph_2PCH_2CH_2PPh_2$[37]) were prepared as described in the literature, and a similar procedure[13] based on the reaction of aqueous $K_2[PdCl_4]$ with 2.1 equiv of the tertiary phosphine in ethanol under $N_2$ was used for the synthesis of the complexes where L = $Bu_3P$, $Cy_3P$, and $Me_3P$. The preparation of dichlorobis(trimethylphosphine)palladium is described in detail below inasmuch as the general procedure[13] was mistakenly considered inapplicable to the synthesis of this complex.

1. **Preparation of [$(Me_3P)_2PdCl_2$].** A solution of trimethylphosphine (1.39 g; 18.3 mmol) in degassed ethanol (20 mL) was added dropwise to a stirred solution of $K_2[PdCl_4]$ obtained from $PdCl_2$ (1.50 g; 8.5 mmol) and KCl (1.44 g; 19.3 mmol) in water (15 mL) under $N_2$. The mixture was stirred at room temperature for 40 min and then worked up in air. Water (20 mL) was added, and the resulting suspension was extracted with dichloromethane (2 × 100 mL and then 4 × 50 mL). The combined organic solutions were filtered and evaporated to dryness. The remaining solid was dissolved in boiling methanol (ca. 300 mL), and the solution was left at 0–5 °C overnight. Well-shaped, pale yellow crystals of the complex were separated, washed with pentane (3 × 30 mL), and dried under vacuum. The yield of bis(trimethylphosphine)palladium dichloride was 2.4 g (86%). The compound was found to be identical with that obtained by the literature method.[38]

2. **General Procedure for the Palladium-Catalyzed Carbonylation of Aryl Iodides and Bromides under Biphasic Conditions.** Carbon monoxide was slowly bubbled through a vigorously stirred, refluxing mixture of aqueous alkali, organic solvent (benzene or THF), haloarene, dichlorobis(tertiary phosphine)palladium, and 18-crown-6 (if used; see Tables I–III for specifics). The aqueous layer was separated, washed with ether, acidified with 20% HCl, and extracted with ether (3 × 30 mL). The combined ether extracts were dried over $MgSO_4$ and evaporated affording the corresponding carboxylic acid.

3. **General Procedure for the Biphasic Carbonylation of Chloroarenes Catalyzed by [$(Cy_3P)_2PdCl_2$].** Carbon monoxide was slowly bubbled through a vigorously stirred, refluxing mixture of aryl chloride, aqueous alkali, and [$(Cy_3P)_2PdCl_2$] (see Table IV). Water (40 mL) was added, and the aqueous layer was separated from unreacted chloroarene containing palladium complexes, washed with ether, acidified with 20% HCl, and extracted with ether (4 × 40 mL). The combined ether solutions were dried over $MgSO_4$, filtered, and evaporated to give the acid. Unreacted chloroarenes can be recovered by distillation.

4. **Biphasic Carbonylation of Iodobenzene in the Absence of Organic Solvents.** Carbon monoxide was bubbled through a vigorously stirred, refluxing mixture of iodobenzene (1.65 g; 8.1 mmol), 20% KOH (10 mL), and [$(Ph_3P)_2PdCl_2$] (30 mg; 0.04 mmol) for 19 h. Water (20 mL) was added, and the solution was washed with ether and then worked up as described above to give 0.60 g (61%) of benzoic acid, mp 120–122 °C.

5. **Biphasic Carbonylation of Bromobenzene in the Absence of Organic Solvents.** Carbon monoxide was bubbled through a vigorously stirred mixture of bromobenzene (1.26 g; 8.0 mmol), 20% KOH (10 mL), and [$(Ph_3P)_2PdCl_2$] (29 mg; 0.04 mmol) for 18 h. Water (20 mL) and ether (10 mL) were added, and the aqueous phase was worked up in the usual manner. The yield of benzoic acid (mp 121–123 °C) was 0.63 g (64%). The ether solution was concentrated to dryness, the residue was dissolved in pentane, and the pentane solution was filtered through an alumina plug. Removal of pentane under vacuum led to 0.07 g (11%) of biphenyl (mp 67–69 °C) which was identified by GC–MS.

6. **Synthesis of 1.** (a) A vigorously stirred mixture of [$(Ph_3P)_2PdCl_2$] (1.0 g; 1.4 mmol), iodobenzene (0.62 g; 3.0 mmol), benzene (20 mL), KOH (4 g), and water (4 mL) was refluxed under $N_2$ for 3 h. The reaction mixture was worked up in air. The hot organic layer was separated, and the aqueous phase was washed with benzene. The combined benzene solution was filtered through cotton and evaporated to give a solid mixture of 1 and $Ph_3PO$. The mixture was thoroughly washed with acetone (3 × 3 mL) and dried under vacuum. The yield of 1, which is almost insoluble in acetone, was 0.57 g (86%). The complex can be recrystallized with minor losses by addition of pentane to a concentrated solution of 1 in prepurified chloroform. The 1:1 chloroform solvate resulting from the crystallization readily loses 50% of $CHCl_3$ when dried under vacuum. The combined acetone extracts were concentrated to dryness, and the residue was chromatographed on silica gel to give 0.32 g (80%) of triphenylphosphine oxide, mp 157–158 °C.

(b) A mixture of [$(Ph_3P)_2PdCl_2$] (4.0 g; 5.7 mmol), iodobenzene (2.5 g; 12.3 mmol), benzene (80 mL), KOH (8 g), and water (8 mL) was stirred under reflux ($N_2$) for 6 h. The complex was isolated in a 2.1-g (80%) yield as described above.

7. **Biphasic Carbonylation of Iodobenzene Catalyzed by Complex 1.** Carbon monoxide was bubbled through a vigorously stirred, refluxing mixture of 1 (30 mg; 0.03 mmol), iodobenzene (0.91 g; 4.46 mmol), benzene (10 mL), and 50% KOH (4 mL) for 24 h. Benzoic acid (0.49 g; 90%) was isolated from the aqueous layer in the usual manner.

8. **Synthesis of 2.** A stirred mixture of [$(Cy_3P)_2PdCl_2$] (0.36 g; 0.49 mmol), chlorobenzene (6 mL), KOH (2 g), and water (8 mL) was refluxed under $N_2$ for 6 h. The organic layer was separated and evaporated to dryness. The remaining solid was dissolved in benzene, filtered through cotton, evaporated, and treated with acetone to give 0.20 g (80%) of 2 as the 1:1 benzene solvate.

9. **Synthesis of 3.** A mixture of 1 (0.6 g; 0.65 mmol), *p*-iodotoluene (0.58 g; 2.66 mmol), and benzene (15 mL) was degassed by two freeze–pump–thaw cycles and then stirred under 1 atm of CO until all of 1 dissolved. The resulting reddish-brown mixture was kept under CO at room temperature for 17 h and then degassed and stirred under nitrogen with *p*-iodotoluene (0.57 g; 2.62 mmol) and 40% KOH (10 mL) for 27 h. The white precipitate was extracted with warm benzene from the biphasic system (in air). The combined benzene solutions were filtered and evaporated; the residue was washed with acetone (4 × 3 mL) and dissolved in purified chloroform. Slow addition of pentane to the chloroform solution led to crystallization of 3 (0.51 g; 73%) as the 1:1 chloroform solvate.

10. **Synthesis of 4.** A solution of 1 (0.30 g; 0.32 mmol) in dichloromethane (2 mL) was added to a solution of NaI (2.0 g)

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in acetone (9 mL). Then water (1 mL) was added, and the yellow complex 4 was separated, washed with water, acetone, and pentane, and throughly dried under vacuum; the yield of 4 was 0.29 g (78%).

**11. Synthesis of 5.** A solution of 3 (0.10 g; 0.09 mmol) in dichloromethane (1 mL) was treated with NaI (1.0 g) in acetone (6 mL). The mixture immediately turned yellow, and 5 started precipitating. Water (2 mL) was added, and the solid was filtered, washed with acetone, water, acetone, and pentane, and dried under vacuum; the yield was 0.098 g (90%).

**12. Reaction of 4 with Aqueous Alkali.** A mixture of 4 (0.10 g; 0.09 mmol), benzene (6 mL), and 50% KOH (3 mL) was vigorously stirred at room temperature under nitrogen until the yellow complex dissolved and the mixture decolorized (1.5 h). The organic layer was separated, filtered through cotton, and evaporated to give 80 mg (99%) of spectrally pure 1 ($^1$H and $^{31}$P NMR).

**13. Synthesis of 6.** A mixture of 1 (1:1 chloroform solvate; 0.14 g; 0.13 mmol), iodobenzene (0.21 g; 1.03 mmol), and benzene (5 mL) was degassed (two freeze–pump–thaw cycles) and then stirred under 1 atm of CO until all 1 dissolved. The resulting clear, brown solution was kept under CO at room temperature for 24 h. The precipitated benzene solvate of 6 was separated, washed with benzene (2 × 2 mL), ethanol, and pentane, and dried; the yield was 0.168 g (92%).

The combined organic solutions were evaporated, and the remaining oil was dissolved in ether (5 mL) and extracted with 10% KOH. Benzoic acid (17 mg; 53%), mp 119–122 °C, was isolated from the alkali extract in the usual manner. Traces of biphenyl were found in the ether solution after the extraction (GC–MS).

**14. Synthesis of 7.** A mixture of 5 (0.15 g; 0.14 mmol), *p*-iodotoluene (0.15 g; 0.69 mmol), and benzene (2 mL) was degassed and then stirred under CO (1 atm) until 5 dissolved. The resulting solution was kept under CO for 24 h at room temperature. The yellow crystals of 7 were separated, washed with benzene (2 × 2 mL), ethanol, and pentane, and dried under vacuum; the yield was 0.165 g (96%).

**15. Reaction of [((*R*)-PhCH$_2$MePhP)$_2$PdCl$_2$] with Aqueous Alkali and Iodobenzene.** A mixture of *cis*-[((*R*)-PhCH$_2$MePhP)$_2$PdCl$_2$][24] ($[\alpha]^{20}_{\mathrm{D}}$ −152.5° (*c* 1.03, CH$_2$Cl$_2$); 0.11 g; 0.18 mmol), iodobenzene (0.30 g; 1.47 mmol), benzene (6 mL), and KOH (2 g) was vigorously stirred under N$_2$ at room temperature for 16 h. The organic layer was analyzed by $^{31}$P NMR spectroscopy and then extracted with degassed water (13 × 5 mL). The combined aqueous solutions were filtered and evaporated to dryness. The remaining phosphine oxide was dissolved in benzene, and the solution was filtered and evaporated to give 34 mg (81%) of snow-white, spectrally ($^1$H and $^{31}$P NMR) pure (*S*)-benzylmethylphosphine oxide with $[\alpha]^{20}_{\mathrm{D}}$ −51.0° (*c* 2.0, MeOH), corresponding to 99.3% optical purity according to ref. 26 b.

**16. Direct Carbonylation of 4 and 5.** Carbon monoxide was bubbled through a solution or suspension of 4 (5) in CDCl$_3$ at room temperature until a clear, brownish-yellow solution was obtained (2–5 min). The $^1$H NMR spectra of samples thus obtained indicated quantitative conversions of 4 and 5 to 6 and 7, respectively.

**17. Exchange Reaction of $^{13}$CO-Labeled 6 with CO.** A solution of 6 prepared with $^{13}$CO in the usual manner (10 mg) in CDCl$_3$ (1 mL) was stirred under 1 atm of CO in a 200-mL Schlenk tube. The $^1$H and $^{13}$C NMR spectra, obtained 2 h after the reaction was started, indicated no sign of exchange. Stirring of the solution under CO for 20 h longer led to precipitation of an amorphous solid; the liquid phase contained *non*labeled 6 as shown by $^1$H and $^{13}$C NMR spectra.

**18. Reaction of 6 with KOH and Iodobenzene.** A degassed solution of KOH (1 g) in water (1 mL) was added under nitrogen to a mixture of 4 (0.10 g; 0.07 mmol), iodobenzene (0.35 g; 1.7 mmol), and benzene (3 mL). The mixture was stirred under N$_2$ at room temperature until it decolorized (18 h). The organic layer was filtered through cotton and evaporated to dryness. Recrystallization of the residue from chloroform–pentane gave 60 mg (78%) of 1 (identified by $^1$H and $^{31}$P NMR). Benzoic acid was isolated from the aqueous layer in the usual manner and sublimed under vacuum. The yield was 13 mg (72%), mp 121–122 °C.

**19. Reaction of 7 with KOH and Iodobenzene.** A mixture of 7 (0.11 g; 0.09 mmol), iodobenzene (0.17 g; 0.8 mmol), benzene (3 mL), and 50% KOH (3 mL) was stirred at room temperature under N$_2$ until the organic phase decolorized. The $^{31}$P NMR spectrum of the organic phase contained eight singlets in the area of 30–36 ppm. The aqueous layer was worked up in the usual manner to give 21 mg (90%) of a 3:2 mixture of *p*-toluic and benzoic acids (MS, $^1$H NMR).

**20. Reaction between 4, 7, and Alkali.** A solution of 4 (0.096 g; 0.084 mmol) and 7 (0.104 g; 0.084 mmol) in methylene chloride was kept under N$_2$ at room temperature for 5.5 h and then stirred with 20% KOH (5 mL) for 14 h. Usual workup of the aqueous layer gave 14 mg (65%) of a 1.15:1 mixture of *p*-toluic and benzoic acids.

**21. Reaction between 5, 6, and Alkali.** A dichloromethane (20 mL) solution of 5 (0.12 g; 0.10 mmol) and 6 (0.13 g; 0.10 mmol) was kept under nitrogen for 5.5 h and then stirred with 20% KOH (5 mL) for 3 h. The aqueous layer was worked up in the usual manner, affording 16 mg (64%) of a 2.3:1 mixture of benzoic and *p*-toluic acids.

**Acknowledgment.** We are grateful to British Petroleum and to the Natural Sciences and Engineering Research Council of Canada for support of this research. We thank Dr. Corinne Bensimon for the X-ray diffraction studies of complexes 1 and 6 and Mr. Raj Capoor and Dr. Glenn Facey for measuring the solid-state and VT solution $^{31}$P NMR spectra. Dr. J. A. Ripmeester of the National Research Council of Canada is gratefully acknowledged for use of the solid-state NMR facility. We appreciated an exchange of correspondence with Professor J. A. Osborn on this subject.

**Supplementary Material Available:** Full details of the structure solution and tables of atomic coordinates, bond lengths and angles, and thermal parameters for complexes 1 and 6 (23 pages). Ordering information is given on any current masthead page.

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