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Indirect Formation of Carboxylic Acids via Anhydrides in the Palladium-Catalyzed Hydroxycarbonylation of Aromatic Halides

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Abstract: The carbonylation of $[(Ph_3P)_2Pd_2Ph_2(\mu\text{-OH})_2]$ (**2**) in the presence of PhI results in the quantitative formation of benzoic anhydride and $[(Ph_3P)_2Pd_2(PhCO)_2(\mu\text{-I})_2]$ (**3**). This transformation contributes to some extent to the production of benzoic acid from haloarenes, CO, and alkali, catalyzed by $[(Ph_3P)_2PdCl_2]$, the latter being converted to **2** under the reaction conditions. Phenyl- and benzoylpalladium benzoates are likely key intermediates in the *indirect* formation of the acid, via the anhydride, by the carbonylation of **2**. One such complex, $[L_2Pd(Ph)(PhCOO)]$ (**5**, L = Cy_3P), was isolated from the carbonylation of $[(Cy_3P)_2Pd_2Ph_2(\mu\text{-OH})_2]$ (**4**) in hexane. The related complexes, $[L_2Pd_2Ph_2(\mu\text{-PhCOO})_2]$ (**6**, L = PPh_3; **7**, L = PCy_3), were prepared from benzoic acid and hydroxo complexes **2** and **4**, respectively. Treatment of **6** and **7** with the corresponding phosphine afforded $[L_2Pd(Ph)(PhCOO)]$ (**8**, L = PPh_3; **5**, L = PCy_3). When **6**–**8** were reacted with CO in benzene, benzoic anhydride was readily formed, whereas in the case of **5** both carbonylation and reductive elimination were sluggish. Crystallographic data for **6** (1:2 chloroform solvate): space group *Pccn*, $a = 22.499(4)$ Å, $b = 10.992(3)$ Å, $c = 24.514(6)$ Å, $V = 6062.4(23)$ Å^3, $Z = 4$, $R = 0.056$, and $R_w = 0.038$.

Introduction

The palladium-catalyzed hydroxycarbonylation of haloarenes is an efficient and convenient method for the synthesis of aromatic carboxylic acids.[1] However, little is known about the mechanism of these reactions. The general mechanistic scheme proposed by Cassar[2] (Scheme 1) involves oxidative addition of the carbon–halogen bond to a zero-valent palladium species, followed by carbonylation of the σ-aryl palladium complex and nucleophilic cleavage of the benzoylpalladium intermediate by OH^- under phase-transfer conditions. We have recently studied[3] the hydroxycarbonylation of aryl halides, catalyzed by $[L_2PdCl_2]$ (L = tertiary phosphine) under biphasic conditions in the *absence* of extra L. It has been shown that the mechanism of this catalytic process is rather different and quite complicated as it involves the generation and transformation of *binuclear* palladium complexes with bridging halogeno and hydroxo ligands. Scheme 2 summarizes most of the data obtained from our previous and present studies of the Pd-catalyzed hydroxycarbonylation of halobenzenes. Every single step of the catalytic cycle shown has been performed on a stoichiometric scale with isolation and full characterization of all the organic and organometallic products. First, the Pd(II) complex undergoes alkali-induced intramolecular oxidation–reduction to give a tertiary phosphine oxide and a highly reactive Pd(0) species.[3] Oxidative addition of the carbon–halogen bond to the latter, followed by dimerization results in the formation of a binuclear σ-phenyl palladium complex with bridging iodo (**1**) or (after ligand exchange) hydroxo (**2**) ligands. Both iodo and hydroxo organopalladium dimers readily and irreversibly react with carbon monoxide under very mild conditions (1 atm, room temperature). The reaction between the iodo complex **1** and CO proceeds smoothly, affording the benzoyl complex **3** in quantitative yield. Treatment of **3** with KOH and iodobenzene leads to 2 equiv of benzoate anion, with **1** being totally regenerated. We believe that this catalytic cycle is responsible for the principal contribution to the overall catalytic production of benzoic acid. However, there is another, entirely different catalytic route which also leads to benzoate anion under the same conditions.

If the catalytic biphasic carbonylation is conducted in the presence of concentrated alkali (40–60%), **1** can undergo ligand exchange with OH^- to give **2**. The formation of **2** from **1** and 50% KOH was shown to be very facile even at ambient temperature.[3] In addition, the reaction of $[(Ph_3P)_2PdCl_2]$ with PhI and 50% KOH, in the absence of CO, leads quantitatively to the hydroxo complex **2** which was isolated and fully characterized (including X-ray analysis). When a benzene solution of **2** was treated with CO (1 atm) in the presence of PhI at room temperature, complex **3** precipitated in 92% yield. The extraction of the mother liquor with aqueous alkali, followed by acidification gave benzoic acid in 53% yield.[3] However, as we have found in the present work, the *primary* organic product of the reaction between **2** and CO was *benzoic anhydride*, not benzoic acid which formed upon hydrolysis during the extraction with alkali. We will designate this second catalytic pathway for the formation of benzoic acid via benzoic anhydride as an *indirect* route.[4] The formation of carboxylic acid anhydrides as main or byproducts of some Pd-promoted carbonylations has been reported in a few cases.[5,6] However, except for those processes employing a pre-formed carboxylate anion as nu-

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[1] (a) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation. Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991. (b) For the most recent review on the catalytic carbonylation of chloroarenes see: Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047.

[2] (a) Cassar, L.; Foa, M.; Gardano, A. *J. Organomet. Chem.* **1976**, *121*, C 55. (b) Cassar, L. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 208.

[3] Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 1890.

[4] In order to avoid any semantic misunderstanding, it is worth noting that the formation of $PhCO_2^-$ from the reaction of **3** with alkali might also be "indirect" involving intermediacy of various Pd complexes. For instance, it is conceivable that the iodo ligands of **3** are first replaced by hydroxo groups, followed by reductive elimination of benzoic acid and its neutralization. However, in this case *no* organic intermediates (e.g., anhydride, acid halide, ester, etc.) are presumably formed, which would give the acid upon any subsequent transformation such as hydrolysis. As long as the mechanism of benzoic acid formation from **3** and alkali remains unknown, we suggest that this path for the catalytic production of $PhCOO^-$ be called *direct*, unlike the other route which involves the formation and hydrolysis of benzoic anhydride.

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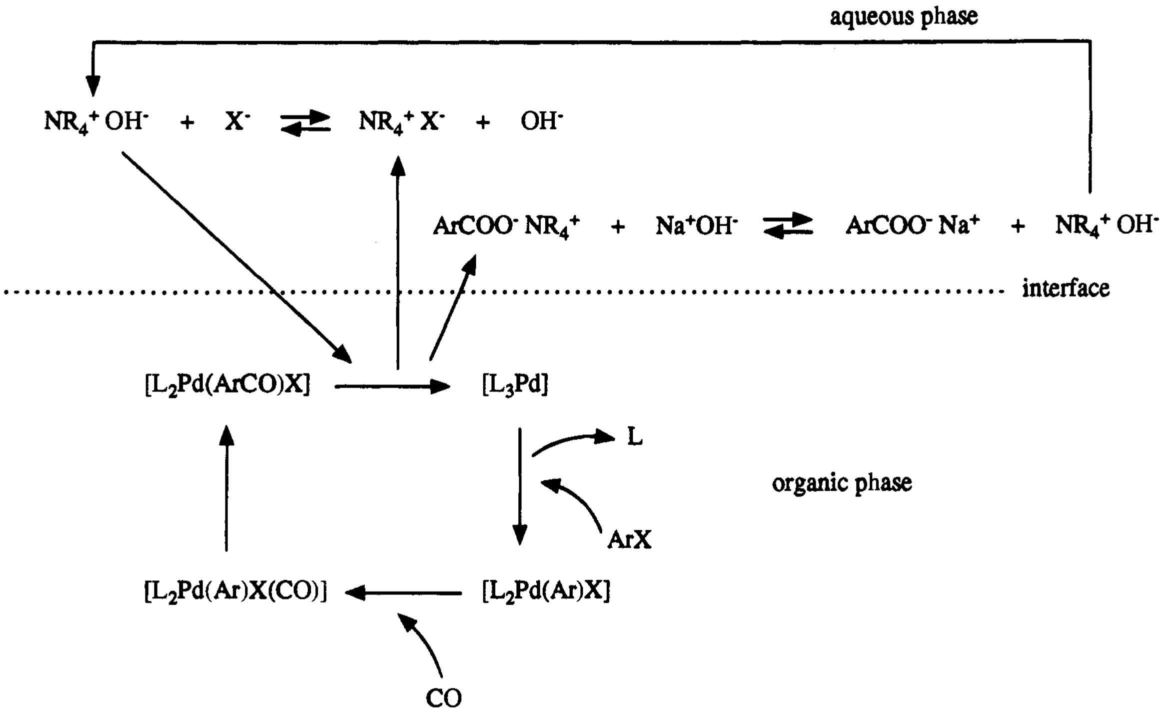
Scheme 1



cleophile (e.g., ref 6), no rationale based on research has been provided for the production of anhydrides in such catalytic reactions under nucleophilic conditions. In the present paper we report the intriguing results of our studies on the indirect production of benzoic acid via benzoic anhydride, during the palladium-catalyzed hydroxycarbonylation of halobenzenes in the presence of alkali. In particular, carbonylation of σ-phenyl hydroxo complexes of palladium results in the formation of benzoic anhydride via clean migratory insertion, followed by reductive elimination.

Results

Carbonylation of [(Ph$_3$P)$_2$Pd$_2$Ph$_2$(μ-OH)$_2$], 2. Treatment of **2** in toluene containing PhI with CO leads to **3** (1:2 toluene solvate) and benzoic anhydride (eq 1). The precipitated **3** was

$$\underset{\mathbf{2}}{[(Ph_3P)_2Pd_2Ph_2(\mu\text{-}OH)_2]} + 4CO + 2PhI \xrightarrow{20\ ^\circ C} \underset{\mathbf{3}}{[(Ph_3P)_2Pd_2(PhCO)_2(\mu\text{-}I)_2]} + (PhCO)_2O + H_2O \quad (1)$$

isolated in 98% yield and found to be identical with an authentic sample (^{1}H and VT ^{31}P NMR).[3] A GC-MS analysis of the mother liquor revealed the presence of benzoic anhydride and trace amounts of benzene, biphenyl, and benzophenone (less than 0.5% of each) and the absence of benzoic acid. The anhydride was also identified by comparison of its ^{1}H, ^{13}C NMR, and IR spectra with those of an authentic material. The yield of benzoic anhydride (95 ± 5%) was determined by ^{1}H NMR with ferrocene as the internal standard.

The carbonylation of **2** also occurred in the absence of iodobenzene to give, in addition to benzoic anhydride, the carbonyl phosphine palladium cluster, of presumed formula [Pd$_3$(CO)$_3$(Ph$_3$P)$_3$], as indicated from its IR[3] and ^{31}P NMR (δ = 32.6 ppm) spectra and the clean conversion to **3** upon treatment with iodobenzene.[7]

For the reaction of **2** with CO, it seemed reasonable to propose intermediate formation of σ-phenyl palladium benzoate complexes which then undergo migratory insertion of CO into the C–Pd bond.[8,9] The resulting benzoyl palladium benzoates might well reductively eliminate benzoic anhydride. Reductive elimination of anhydrides from Pd[8,9] and Ni[10,11] complexes containing both carboxylato and aroyl (or acyl) ligands has been described in the literature. We failed to unequivocally identify intermediates of the reaction between **2** and CO even at low temperatures (see below). However, the proposed σ-phenyl palladium benzoate was successfully isolated when **2** was replaced by its tricyclohexylphosphine analogue, [(Cy$_3$P)$_2$Pd$_2$Ph$_2$(μ-OH)$_2$], **4**.

Carbonylation of [(Cy$_3$P)$_2$Pd$_2$Ph$_2$(μ-OH)$_2$], 4. When CO was bubbled at room temperature through a solution of **4** in hexane for 1.5–2 h, colorless, needle-shaped crystals precipitated while the liquid phase turned red within a few minutes after the carbonylation began. The crystals were isolated (50% yield) by filtration and found to be analytically pure *trans*-benzoatophenylbis(tricyclohexylphosphine)palladium(II), [(Cy$_3$P)$_2$Pd(Ph)(PhCOO)], **5**, as revealed by elemental analyses and ^{1}H, ^{13}C, ^{31}P NMR, and IR spectra.

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(5) (a) Tsuji, J.; Kiji, K.; Imamura, S.; Morikawa, M. *Bull. Chem. Soc. Jpn.* **1964**, *86*, 4350. (b) Chiusoli, G. P.; Cameroni, A. *Chim. Ind. (Milan)* **1964**, *46*, 1063. (c) Nagira, K.; Kikukawa, K.; Wada, F.; Matsuda, T. *J. Org. Chem.* **1980**, *45*, 2365. (d) Fujiwara, Y.; Kawata, I.; Kawauchi, T.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1982**, 132. (e) Cacchi, S.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1985**, *26*, 1109. (f) Ugo, R.; Chiesa, A. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2625. (g) Pri-Bar, I.; Buchman, O. *J. Org. Chem.* **1988**, *53*, 624. (h) Baird, J. M.; Kern, J. R.; Lee, G. R.; Morgans, D. J., Jr.; Sparacino, M. L. *J. Org. Chem.* **1991**, *56*, 1928. (i) Zargarian, D.; Alper, H. *Organometallics* **1991**, *10*, 2914; **1993**, *12*, 712.

(6) Pri-Bar, I.; Alper, H. *J. Org. Chem.* **1989**, *54*, 36 and references cited therein.

(7) Hidai, M.; Hikita, T.; Wada, Y.; Fujikura, Y.; Uchida, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2075.

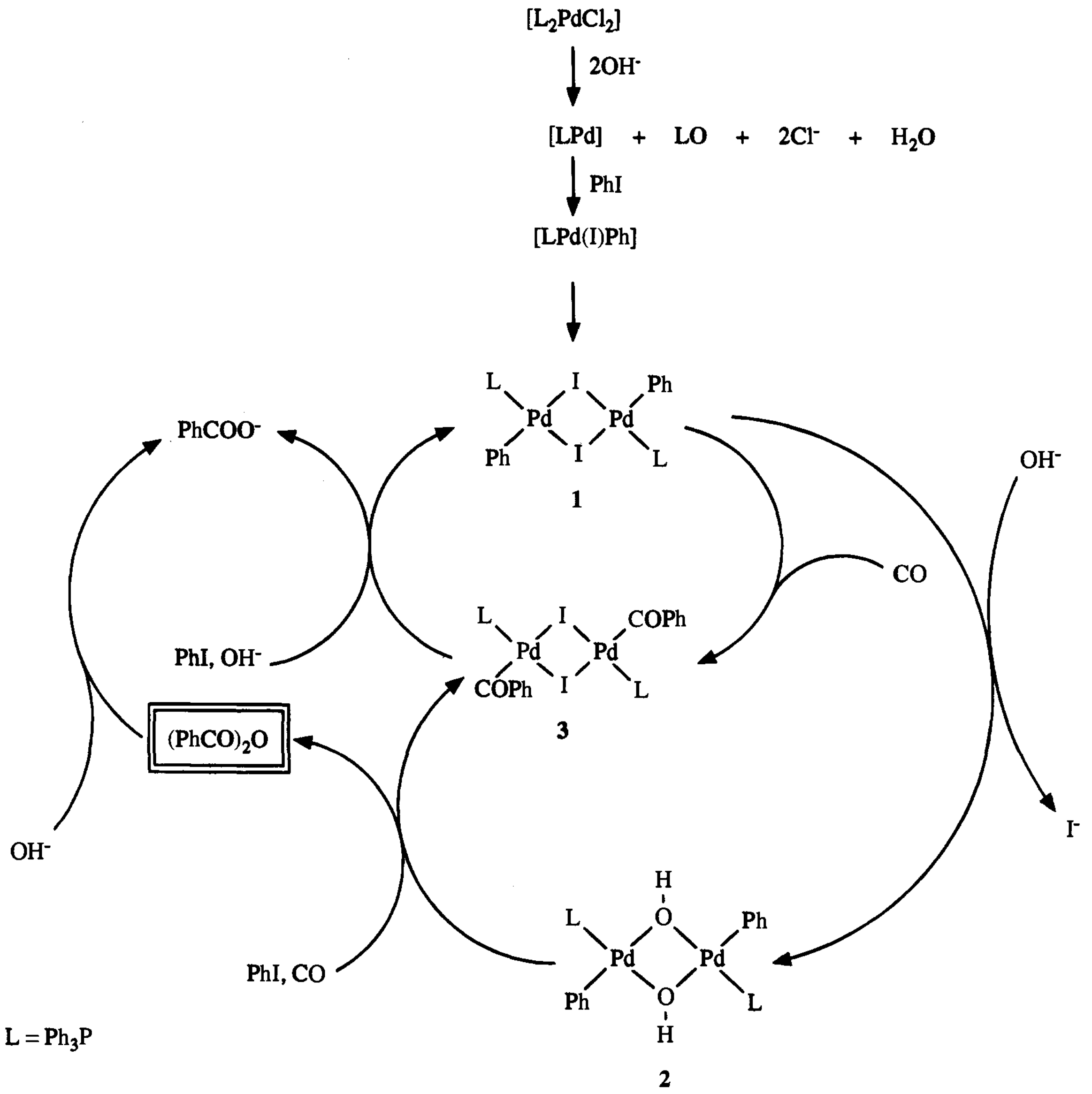
(8) Komiya, S.; Yamamoto, A.; Yamamoto, T. *Chem. Lett.* **1981**, 193.

(9) Osakada, K.; Doh, M.-K.; Ozawa, F.; Yamamoto, A. *Organometallics* **1990**, *9*, 2197.

(10) Yamamoto, T.; Sano, K.; Yamamoto, A. *J. Am. Chem. Soc.* **1987**, *109*, 1092.

(11) Carmona, E.; Gutierrez-Puebla, E.; Marin, J. M.; Monge, A.; Paneque, M.; Poveda, M. L.; Ruiz, C. *J. Am. Chem. Soc.* **1989**, *111*, 2883.

Scheme 2



$$\underset{\mathbf{4}}{[(Cy_3P)_2Pd_2Ph_2(\mu\text{-}OH)_2]} + CO \xrightarrow{20\ ^\circ C} \underset{\mathbf{5}}{[(Cy_3P)_2Pd(Ph)(PhCOO)]} + [Pd] + H_2O \quad (2)$$

Although the formation of Pd(0) is implicated by the stoichiometry of reaction 2, no palladium metal precipitated in the course of the carbonylation. Instead, a carbonyl phosphine palladium cluster of deep red color was isolated from the hexane mother liquor. Unfortunately, our attempts to obtain crystals of this red cluster, suitable for complete X-ray diffraction study, failed. Nevertheless, the quality of a few crystals was sufficient for determination of the cell parameters: a = 24.789(8) Å, b = 29.357(9) Å, c = 14.583(5) Å; α = 98.61(3)°, β = 92.17(3)°, γ = 89.90(3)°; V = 10485(6) Å^3. The ^{1}H, ^{13}C, and ^{31}P NMR spectra of the cluster suggest the presence of only tricyclohexylphosphine and carbonyl ligands. The phosphine ligands are all equivalent at room temperature as only one sharp singlet was observed in the ^{31}P NMR spectrum at 33.3 ppm. A complex multiplet (1.0–2.6 ppm) was the only signal in the ^{1}H NMR spectrum of the cluster, indicating that Cy_3P but no other hydrogen-containing ligands were present in the complex. Although only one singlet at 232.2 ppm was observed in the ^{13}C spectrum of the cluster (^{13}CO was used for the reaction in this case), the IR spectrum (Nujol) revealed the presence of both terminal (2032 and 2021 cm^{-1}) and bridging (1911, 1896, and 1873 cm^{-1}) carbonyl ligands. Interestingly, loss of some CO easily occurred from the red Pd cluster when N_2 was bubbled through its solution in benzene for 15–25 min. The resulting dark-brown species did not bear any terminal carbonyls (IR)[12] exhibiting a quite complex pattern in the ^{13}C (broad peaks at 220–223 ppm) and ^{31}P (singlets at 26, 28, 34, and 36 ppm) NMR spectra. Bubbling CO (or ^{13}CO) through the brown solution resulted in rapid, quantitative recovery of the original red-colored polynuclear palladium complex (^{13}C and ^{31}P NMR and IR spectra), demonstrating the entire reversibility of the CO elimination–addition process. Obviously, the structure of the red cluster could be reliably established only by a detailed single-crystal X-ray diffraction study.

The results described in this and previous sections indicate the complex character of the reactions between **2** or **4** and CO, which involve coordination, migratory insertion, reductive elimination, and even phosphine ligand redistribution processes. However, after isolation and identification of the σ-phenyl palladium benzoate **5**, it became clear that such complexes mediate the formation of benzoic anhydride from **2** or **4** and

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[12] IR (Nujol), cm^{-1}: 1887 (s), 1844 (s), and 1825 (s). A very weak, probably residual band at 2025 cm^{-1} was also observed.

Table 1. Analytical and Spectral Data for the Complexes $[(R_3P)_2Pd(Ph)(PhCOO)]$ (**5**, **8**) and $[(R_3P)_2Pd_2Ph_2(\mu\text{-}PhCOO)_2]\cdot 0.5C_6H_6$ (**6**, **7**)

compd	R	isolated yield,[a] %	anal. % calcd (found) C	anal. % calcd (found) H	IR (Nujol) ν_{CO}, cm^{-1}	^{31}P NMR, δ	^{13}C NMR,[b] δ
5	Cy	83	68.0 (67.9)	8.85 (8.7)	1625, 1334	19.5 (C_6D_6)	170.5 (C_6D_6)
6	Ph	84	66.6 (66.5)	4.6 (4.7)	1598, 1403	30.9 (C_6D_6)	175.1 (C_6D_6)
7	Cy	84	64.6 (64.9)	7.4 (7.6)	1603, 1388	42.5[c] (C_7D_8)	182.8[c] (C_7D_8)
8	Ph	90	71.0 (71.0)	4.9 (5.1)	1609, 1363	23.0 (C_6D_6)	171.2 (C_6D_6)

[a] ^{31}P NMR yields were quantitative in all cases. [b] For complexes prepared with Ph^{13}COOH. [c] Measured at 70 °C (see text).

CO. For this reason, we synthesized a number of phenyl Pd benzoates and studied their reactions with CO.

Synthesis and Characterization of the σ-Phenyl Palladium Benzoato Complexes, $[L_2Pd_2Ph_2(\mu\text{-}PhCOO)_2]$ and $[L_2Pd(Ph)(PhCOO)]$ ($L = Ph_3P$ and Cy_3P). It seemed conceivable to propose a pathway involving migratory insertion of CO into the Pd−C or Pd−O bond of **2** or **4**, followed by reductive elimination to form benzoic acid. The latter then may react with the as yet unreacted σ-phenyl palladium bridging hydroxo dimer to yield the σ-phenyl palladium benzoato complex. Indeed, treatment of a benzene solution of **2** or **4** with 2 equiv of PhCOOH resulted in the immediate and quantitative (^{31}P and ^{1}H NMR) formation of benzoato complexes **6** and **7**, respectively (eq 3).

$$\begin{array}{l}[L_2Pd_2Ph_2(\mu\text{-}OH)_2] + 2PhCOOH \rightarrow \\ L = Ph_3P, (\mathbf{2});\ Cy_3P\ (\mathbf{4}) \\ \qquad\qquad [L_2Pd_2Ph_2(\mu\text{-}PhCOO)_2] + 2H_2O \\ \qquad\qquad L = Ph_3P\ (\mathbf{6});\ Cy_3P\ (\mathbf{7})\end{array} \qquad (3)$$

Both **6** and **7** reacted cleanly with 2 equiv of the corresponding tertiary phosphine to give the *mononuclear* complexes, $[L_2Pd(Ph)(PhCOO)]$ (eq 4), one of them (with $L = Cy_3P$) being totally identical with the above described complex **5** which was previously isolated from reaction 2.

$$\begin{array}{l}[L_2Pd_2Ph_2(\mu\text{-}PhCOO)_2] + 2L \rightarrow \\ L = Ph_3P\ (\mathbf{6});\ Cy_3P\ (\mathbf{7}) \\ \qquad\qquad 2[L_2Pd(Ph)(PhCOO)] \\ \qquad\qquad L = Ph_3P\ (\mathbf{8});\ Cy_3P\ (\mathbf{5})\end{array} \qquad (4)$$

Analytical and spectral data for complexes **5**−**8** are listed in Table 1, except for their ^{1}H NMR spectra which can be found in the Experimental Section. A single-crystal X-ray diffraction study of **6** established the dimeric structure with two square-planar Pd centers and two bridging benzoato ligands *cis* to each other (see Figure 1 and Table 2). Such structures are common in the chemistry of monophosphine carboxylato dimers of divalent nickel, palladium, and platinum, e.g., $[(R_3P)_2M_2X_2(\mu\text{-}R'COO)_2]$, where R and R′ = alkyl or aryl, M = Ni, Pd, or Pt, and X = halogen.[13,14] Similar patterns were observed in the IR spectra of **6** in KBr or Nujol (ν_{CO} = 1598, 1403 cm^{-1}) and in CH_2Cl_2 (ν_{CO} = 1597, 1398 cm^{-1}), indicating that **6** possesses the same dimeric structure in the solid state and in solution. It is also clear from the IR data (Table 1) that **5** and **8** are monomeric species with benzoato ligands coordinated to the metal in η^1-fashion.

Both mononuclear complexes **5** and **8** possess the *trans* geometry as ^{31}P NMR spectra of these complexes display sharp singlets. No signal splitting was observed in the ^{13}C and ^{31}P NMR spectra of **5**−**8** prepared with Ph^{13}COOH, suggesting that the corresponding ^{13}C−^{31}P coupling constants were too small. It is noteworthy that complex **7** exhibited unusual spectral behavior in solution, as was shown by variable-temperature ^{13}C and ^{31}P NMR studies of the compound. Only broad resonances were observed in the NMR spectra of **7** in chloroform, benzene, or toluene at room temperature. These resonances transformed to sharp singlets (see Table 1) upon heating the toluene solution of **7** to 70 °C. Cooling down the sample to −88 °C resulted in a complicated pattern with four singlet resonances of different intensities, in both the ^{13}C and ^{31}P spectra. At the same time, both ^{13}C and ^{31}P NMR spectra of **6**, which is the triphenylphosphine analogue of **7**, consisted of only one sharp singlet in the entire temperature range of −90 to +90 °C.

Carbonylation of the σ-Phenyl Palladium Benzoates 5−8. All carbonylations were performed in standard 5-mm NMR tubes equipped with rubber septum stoppers for bubbling carbon monoxide through the solutions with syringe needles. The reactions were monitored by ^{1}H, ^{13}C, and ^{31}P NMR.

(a) Carbonylation of $[(Cy_3P)_2Pd(Ph)(PhCOO)]$, 5. This complex reacted with carbon monoxide in benzene to give the product of CO insertion into the C−Pd bond, $[(Cy_3P)_2Pd(PhCO)(PhCOO)]$, **9**, which was also prepared independently by reacting $[(Cy_3P)_2Pd]$ with benzoic anhydride (eq 5). The carbonylation of **5** is slow, requiring 7−10 days at ambient temperature and 1 atm of CO for quantitative conversion to **9** with 100% selectivity. In contrast, oxidative addition of benzoic anhydride to $[(Cy_3P)_2Pd]$ was fast (less than 1 h at room temperature), but besides **9**, it gave **5** in ca. 5−10% yield (^{31}P NMR). The formation of **5** was obviously due to decarbonylation in the course of the oxidative addition reaction. A similar minor decarbonylation reaction has been observed by Komiya et al.[8] during the oxidative addition of anhydrides to some Ni(0) complexes. Interestingly, the carbonyl tricyclohexylphosphine Pd(0) cluster, presumably $[(Cy_3P)_3Pd_3(CO)_3]$, which is obtained by treatment of the $[(Cy_3P)_2Pd]$ with CO,[15] also underwent oxidative addition of benzoic anhydride to give **9**. However, this reaction was very sluggish, and only ca. 10% conversion of the cluster to **9** was observed by ^{31}P NMR 1 week after the reaction began.

$$\left.\begin{array}{l}[(Cy_3P)_2Pd(Ph)(PhCOO)] + CO \\ \qquad\mathbf{5} \\ [(Cy_3P)_2Pd] + (PhCO)_2O\end{array}\right] \rightarrow \underset{\mathbf{9}}{[(Cy_3P)_2Pd(PhCO)(PhCOO)]} \qquad (5)$$

All attempts to characterize **9** in pure form resulted in isolation of the product of its formal oxidation, which was formulated as $[(Cy_3P)_2Pd(PhCOO)_2]$ on the basis of the ^{1}H, ^{13}C, and ^{31}P NMR

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(13) Oldham, C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1987; Vol. 2, Chapter 15.6, p 435.

(14) Barnard, C. F. G.; Russell, M. J. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1987; Vol. 5, Chapter 51, p 1099.

(15) Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 2134.

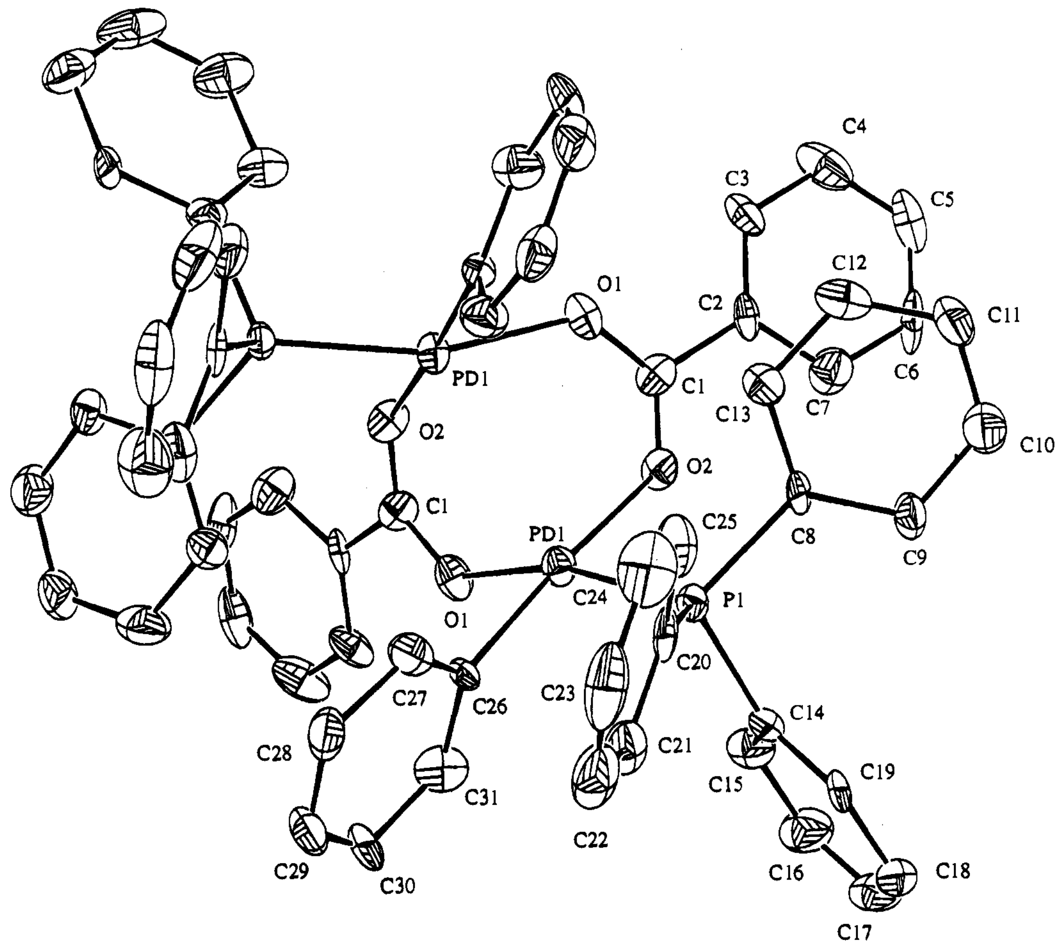

Figure 1. Structure of $[(Ph_3P)_2Pd_2Ph_2(\mu\text{-}PhCO_2)_2]$, **6**, showing the atom-labeling scheme. Selected bond distances (Å): Pd−P, 2.224(3); Pd−O1, 2.128(7); Pd−O2, 2.154(7); Pd−C26, 1.988(9); C1−O1, 1.262(13); C1−O2, 1.239(12). Selected bond angles (deg): P−Pd−O1, 162.76(21); P−Pd−O2, 91.84(20); P−Pd−C26, 88.8(3); O1−Pd−O2, 90.5(3); O1−Pd−C26, 87.2(3); O2−Pd−C26, 174.1(3); Pd−O1−C1, 131.2(7); Pd−O2−C1, 123.4(6); O1−C1−O2, 126.8(10); O1−C1−C2, 115.6(9); O2−C1−C2, 117.5(9).

Table 2. Crystallographic Data for $[(Ph_3P)_2Pd_2Ph_2(\mu\text{-}PhCOO)_2]\cdot 2CHCl_3$ (**6**·$2CHCl_3$)

formula	$C_{64}H_{52}Cl_6O_4P_2Pd_2$
fw	1372.56
cryst shape	rectangular
cryst dimens, mm	0.2 × 0.1 × 0.2
cryst system	orthorhombic
lattice params	
a, Å	22.499(4)
b, Å	10.992(3)
c, Å	24.514(6)
space group	*Pccn*
Z	4
V, Å^3	6062.4(23)
d_{calc}, g/cm^3	1.504
T, K	163
radiation (λ, Å)	Mo Kα (0.70930)
μ, mm^{-1}	0.95
R (R_w), %	5.6 (3.8)

spectra.[16] Nonetheless, complex **9** was characterized in solution by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The *trans* geometry of **9** was established by a ^{31}P NMR spectrum which displayed one singlet (δ = 18.8 ppm) slightly upfield from the resonance of reactant **5**. Such a difference in chemical shifts of **5** and **9** is consistent with the ^{31}P NMR data obtained by Garrou and Heck[17] in their study on the carbonylation of various $[L_2M(Ar)X]$ complexes, where L = tertiary phosphine or arsine, M = Ni, Pd, or Pt, and X = halogen. Two carbonyl resonances at 228.1 and 171.5 ppm were observed in the ^{13}C NMR spectrum of **9** and assigned to the benzoyl and benzoato ligands, respectively. In the ^{1}H NMR spectrum of **9**, there were two downfield doublet-like resonances at 8.7 and 8.8 ppm indicating the presence of two different types of *ortho* phenyl protons in the molecule.

Complex **9** is not susceptible to either decarbonylation or reductive elimination of benzoic anhydride in benzene solution at room temperature. When two selectively carbonyl-labeled samples of **9** were prepared and kept in benzene solution under carbon monoxide at room temperature, no detectable isotope scrambling was observed over a period of 7 days, by monitoring the mixtures by ^{13}C NMR spectroscopy (Scheme 3). Only minor amounts of benzoic anhydride formed (^{13}C NMR, δ = 162.8 ppm) upon heating the solution of $[(Cy_3P)_2Pd(PhCO)(Ph^{13}COO)]$ under CO at 70 °C for 2 h.

(b) Carbonylation of $[(Cy_3P)_2Pd_2Ph_2(PhCOO)_2]$, 7. A dramatic change in reactivity toward CO was observed when passing from the tricyclohexylphosphine mononuclear complex **5** to its dinuclear analogue **7**. Complex **7** underwent 100% conversion in less than 15 min after exposure to CO, whereas it took more than 1 week to quantitatively carbonylate **5** under similar conditions (see above). The main compounds produced by reacting **7** with CO for 1 h were benzoic anhydride, **9**, and

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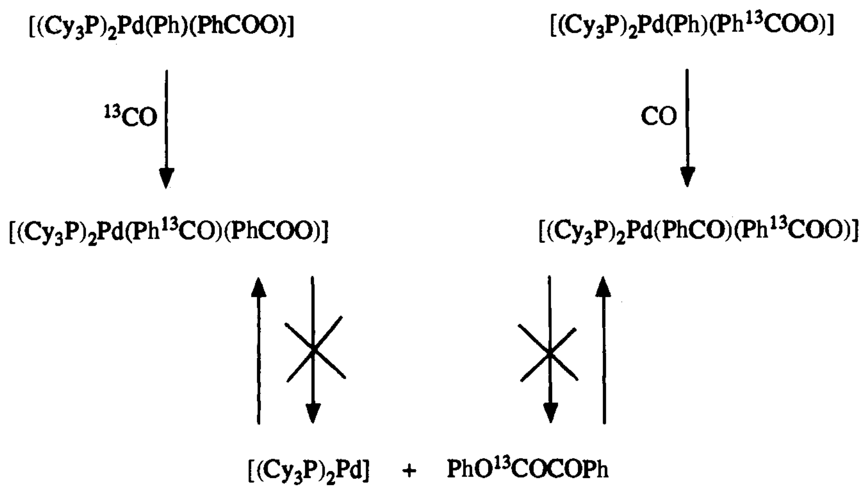
(16) Spectral data for $[(Cy_3P)_2Pd(PhCOO)_2]$: ^{1}H NMR (C_6D_6) δ 1.0–2.5 (m, 66H, Cy), 7.4 (m, 6H, 3,4,5-C_6H_5), 8.6 (d, 4H, 2,6-C_6H_5). ^{13}C NMR ($CDCl_3$) δ 27.1 (s), 28.4 (virtual t, $^2J_{C-P} + {}^4J_{C-P}$ = 10.8 Hz), 30.1 (s), 33.7 (virtual t, $^1J_{C-P} + {}^3J_{C-P}$ = 17.3 Hz), 128.1 (s), 130.2 (s), 130.7 (s), 136.2 (s), 171.2 (s). ^{31}P NMR ($CDCl_3$) δ 23.7. IR (Nujol) ν_{CO} 1632, 1622, 1578 cm^{-1}.

(17) Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115.

Scheme 3



the red cluster Pd compound whose isolation and characterization were described above.

(c) **Carbonylation of [$(Ph_3P)_2Pd(Ph)(PhCOO)$], 8.** As soon as ^{13}CO was introduced into an NMR tube filled with a benzene-d_6 solution of **8** at room temperature, the reaction began, which was followed by ^{13}C and ^{31}P NMR spectroscopy. A new signal appeared at 18.3 ppm in the ^{31}P NMR spectrum within 20 min, due to the formation of [$(Ph_3P)_2Pd(PhCO)(PhCOO)$], **10**. At the same time, the occurrence of two sharp singlets at 227.5 ppm (the benzoyl complex **10**) and 162.8 ppm (benzoic anhydride) was noted in the ^{13}C NMR spectrum of the sample.

$$\underset{\mathbf{8}}{[(Ph_3P)_2Pd(Ph)(PhCOO)]} + CO \rightarrow \underset{\mathbf{10}}{[(Ph_3P)_2Pd(PhCO)(PhCOO)]} \quad (6)$$

$$\underset{\mathbf{10}}{[(Ph_3P)_2Pd(PhCO)(PhCOO)]} \rightarrow (PhCO)_2O + [(Ph_3P)_2Pd] \quad (7)$$

Both carbonylation (eq 6) and reductive elimination (eq 7) progressed until ca. 50% conversion of **8** was reached after 5.5 h, and then the reaction slowed down. This deceleration was accompanied by the appearance and growth in intensity of broad resonances at 17 (^{31}P NMR) and 215 ppm (^{13}C NMR). Hence, we propose that the appreciable retardation of reactions 6 and 7 might be a consequence of the release of free PPh_3 due to decomposition and/or clusterization of [$(Ph_3P)_2Pd$] in the presence of CO (e.g., eq 8). It has been shown that extra PPh_3

$$3[(Ph_3P)_2Pd] + 3CO \rightarrow [(Ph_3P)_3Pd_3(CO)_3] + 3PPh_3 \quad (8)$$

inhibits both carbonylation of [$(Ph_3P)_2Pd(R)X$], where X = halogen,[17] and reductive elimination of ethyl benzoate from [$(Ph_3P)_2Pd(PhCO)(OEt)$].[18] In order to verify this hypothesis, an excess of iodobenzene was added to the "self-frozen" sample. This caused an immediate revival of the reaction with simultaneous replacement of the two broad resonances by sharp singlets at 18.9 and 234.1 ppm in the ^{31}P and ^{13}C NMR spectra, respectively. The signals were clearly due to the formation of [$(Ph_3P)_2Pd(PhCO)I$] which was subsequently isolated and shown to be identical to an authentic sample[17] when the reaction (eq 9) was carried out on a preparative scale. Therefore, suppressing the elimination of PPh_3 from the Pd(0) species by making the latter react with PhI results in the smooth and straightforward

$$\underset{\mathbf{8}}{[(Ph_3P)_2Pd(Ph)(PhCOO)]} + 2CO + PhI \rightarrow [(Ph_3P)_2Pd(PhCO)I] + (PhCO)_2O \quad (9)$$

occurrence of reactions 6 and 7 until quantitative conversion is reached. In fact, conversions of ca. 30% and 100% were found by ^{31}P NMR, when **8** in benzene solution containing excess PhI was treated with CO in the presence (1 equiv) and absence of extra phosphine, respectively.

Despite the fact that complex **10** easily eliminates benzoic anhydride, no exchange between the benzoyl and carboxy carbonyls was observed upon its generation (and decomposition) from the ^{13}C-labeled **8** and CO or a nonlabeled **8** and ^{13}CO.

(d) **Carbonylation of [$(Ph_3P)_2Pd_2Ph_2(\mu\text{-}PhCOO)_2$], 6.** The reaction of **6** with CO is very similar to that of **8**. However, complex **6** exhibits a significantly higher reactivity toward CO than the mononuclear **8**, which is likely due to the lower phosphine to palladium ratio in **6** (see above). In addition, the η^1-benzoato ligand's C=O group in **8** could interact with the metal center, thus retarding carbonylation. Such axial interaction is inconceivable in bridging benzoates. The quantitative formation of benzoic anhydride and the known[3] complex, [$(Ph_3P)_2Pd_2(PhCO)_2(\mu\text{-}I)_2$], took place in ca. 1 h after a toluene solution of **6** and PhI was stirred under CO (eq 10).

$$\underset{\mathbf{6}}{[(Ph_3P)_2Pd_2Ph_2(\mu\text{-}PhCOO)_2]} + 4CO + 2PhI \rightarrow [(Ph_3P)_2Pd_2(PhCO)_2(\mu\text{-}I)_2] + 2(PhCO)_2O \quad (10)$$

Carbonylation reaction 10 proceeds via complex **10** and a carbonyl phosphine Pd cluster ($\delta = 24.7$ ppm), as shown by ^{31}P NMR monitoring of the reaction in the absence of PhI.

Carbonylation of the Hydroxo Complexes 2 and 4 Revisited. Having isolated and/or characterized in solution the phenyl and benzoyl benzoato palladium complexes, **5**–**10**, and studied their properties, we managed to gain a deeper insight into the reactions of **2** and **4** with CO. Figures 2 and 3 show the ^{31}P and ^{13}C NMR spectra obtained 10, 30, and 60 min after ^{13}CO was introduced into the NMR tube filled with a solution of **4** in benzene-d_6. It is clearly seen from the ^{31}P NMR spectra (Figure 2) that **4** (a 1:6 mixture of *cis* and *trans* isomers)[3] reacted completely with carbon monoxide within 10 min to give mostly **5** ($\delta = 19.5$ ppm) and the red cluster ($\delta = 33.3$ ppm, see above). In the corresponding ^{13}C NMR spectrum (Figure 3a), the two major resonances at 170.5 and 232.2 ppm were in line with the formation of **5** and the red carbonyl phosphine cluster, respectively. While the reaction progressed, the in situ generated **5**

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[18] Ozawa, F.; Kawasaki, N.; Okamoto, H.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1987**, *6*, 1640.

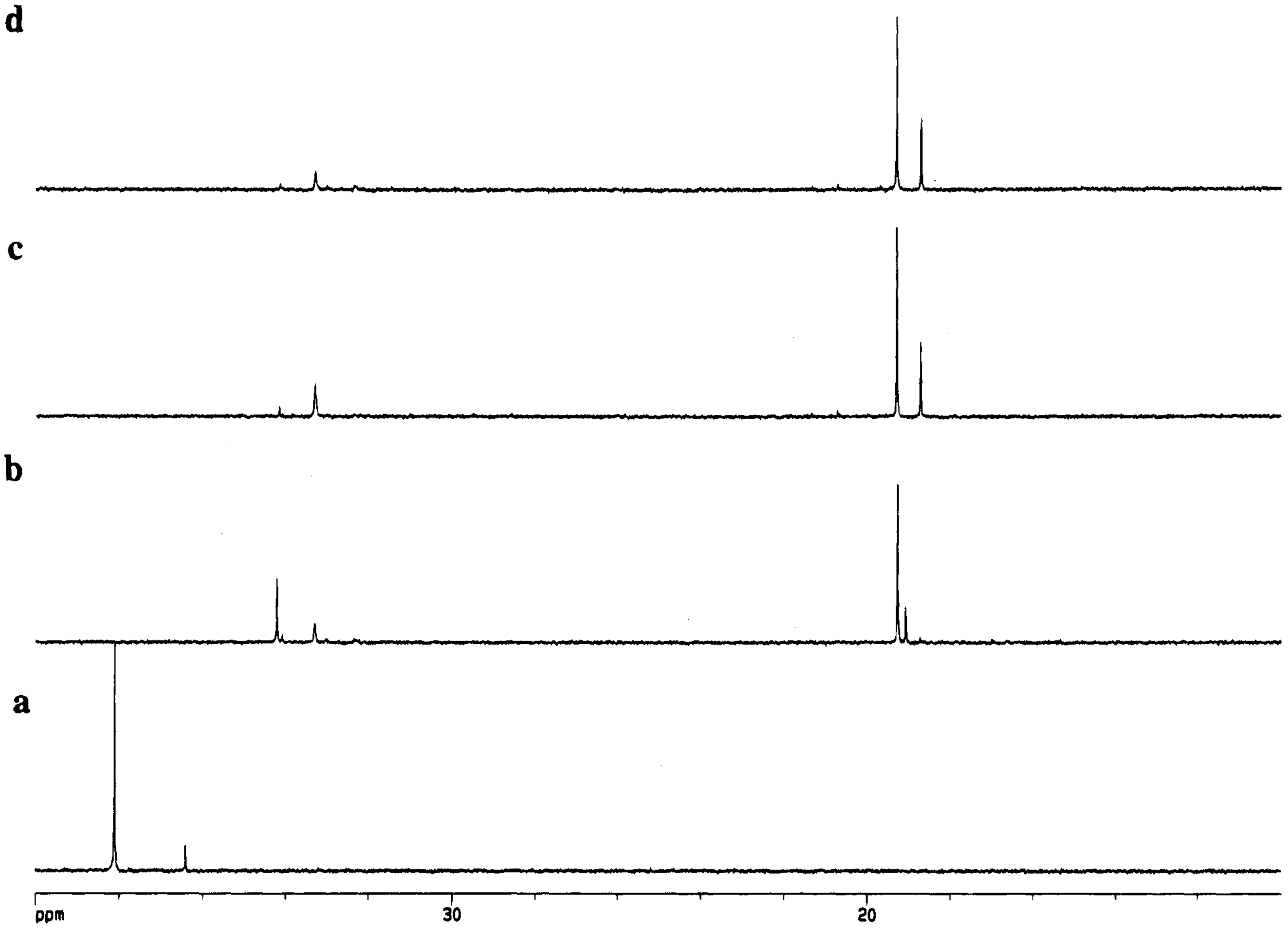

Figure 2. The ^{31}P NMR spectra obtained 0 (a), 10 (b), 30 (c), and 60 min (d) after ^{13}CO was introduced into the NMR tube containing a solution of **4** in benzene-d_6.

underwent partial carbonylation to **9**, as observed by the simultaneous appearance of the singlet at 18.8 ppm in the ^{31}P and two resonances at 171.5 and 228.1 ppm in the ^{13}C NMR spectral patterns (Figure 2, spectra c and d; Figure 3, spectra b and c). No reductive elimination of benzoic anhydride was observed during the first 4–5 h of the reaction. Four days later, however, $(Ph^{13}CO)_2O$ (δ = 162.8 ppm) was formed to a limited extent as shown by ^{13}C NMR spectral analysis of the sample which was kept under ^{13}CO.

At the early stage of the carbonylation of **4** (Figures 2b and 3a) two minor products with δ = 34.2 and 19.1 ppm (^{31}P NMR) and 173.0 and 173.6 ppm (^{13}C NMR) were observed. These unstable species were likely intermediates of the reaction as they disappeared quite rapidly while the carbonylation progressed. Unfortunately, our attempts to characterize intermediate complexes by running the carbonylations of **2** and **4** at lower temperature were unsuccessful. The samples were prepared by placing toluene-d_8 solutions of **2** and **4** in standard 5-mm NMR tubes, cooling the tubes down to −78 °C (acetone–dry ice bath), and bubbling ^{13}CO through the cold solutions for a few minutes. The tubes were then immediately transferred to the thermostated (−80 °C) NMR spectrometer probe. Both ^{13}C and ^{31}P spectra were periodically measured while the temperature was gradually increased. No reaction was observed below −60 and −20 °C for **2** and **4**, respectively. When the reactions started, very complex ^{31}P NMR patterns developed for both carbonylations. In fact, a number of resonances of various intensities were observed in the NMR spectra of the low-temperature reaction mixtures, which might be assigned to complexes **5**–**10** and the above described carbonyl phosphine palladium cluster compounds.

Discussion

As long as σ-aryl palladium dimers with bridging hydroxo ligands can be formed in the process of the hydroxycarbonylation of aryl halides, there is always the possibility for the *indirect* catalytic formation of the carboxylate anion via the corresponding anhydride, followed by its hydrolysis (Scheme 2). The catalytic system depicted in this scheme appeared significantly more complicated than was indicated upon initial consideration. First of all, it seems difficult to determine reliably what proportion of dimer **1** undergoes ligand exchange to produce **2** (which becomes the source of benzoic anhydride), with the rest of **1** being converted to **3** (the source of benzoate anion). Both the carbonylation of **1** resulting in **3** and the ligand exchange yielding **2** are facile processes readily occurring at room temperature and atmospheric pressure.[3] Depending on the reaction conditions, namely, temperature, pressure, concentration of alkali, organic phase, presence or absence of a phase-transfer catalyst or surfactant, the nature of the substrate and phosphine ligands, stirring rate, etc., the formation of **2** might more or less successfully compete with that of **3**. It is believed that the direct rather than indirect formation of benzoate anion would normally make a major contribution to the overall catalytic production of the carboxylic acid. However, since the fact of generation of **2** or **4** under catalytic reaction conditions is now established beyond any doubt,[3] the formation of

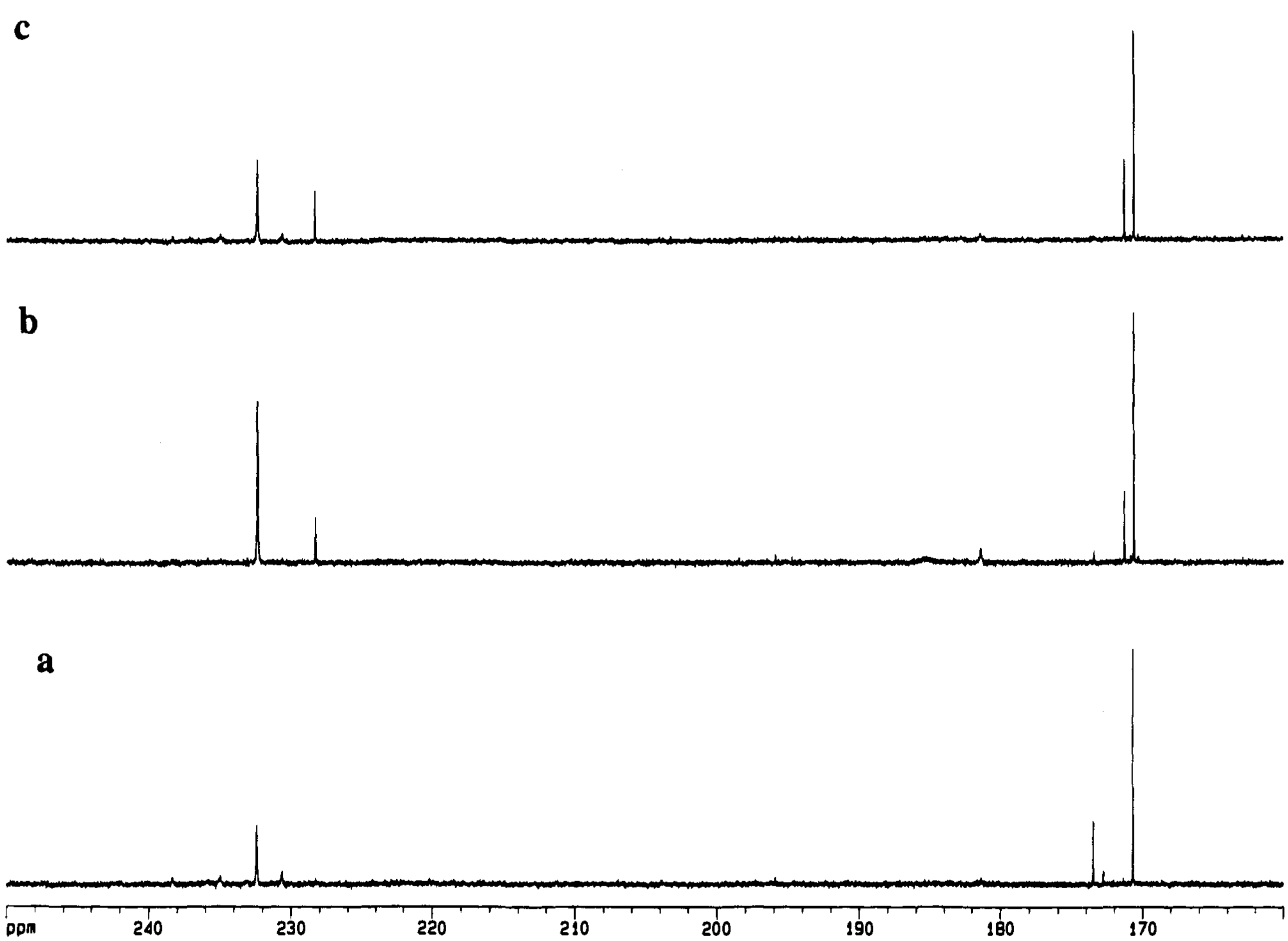

Figure 3. The ^{13}C spectra obtained 10 (a), 30 (b), and 60 min (c) after ^{13}CO was introduced into the NMR tube containing a solution of **4** in benzene-d_6.

PhCOOH via $(PhCO)_2O$ should always be taken into consideration, even if this is not the principal reaction path.

Many palladium-catalyzed carbonylation reactions are conducted in the presence of excess extra phosphine in order to avoid precipitation of palladium metal during the reaction.[1,19] In this case the *mononuclear* σ-phenyl palladium complex, $[L_2Pd(Ph)I]$, is formed upon oxidative addition of PhI to the Pd(0) species, instead of *binuclear* **1**.[19] Nevertheless, the catalytic production of benzoic anhydride cannot be eliminated even in the presence of extra phosphine. Indeed, in the present work we have found that the reaction between $[(Ph_3P)_2Pd(Ph)I]$ and alkali affords **2** and triphenylphosphine in accordance with eq 11. The reaction is accelerated by phase-transfer agents.

$$2[L_2Pd(Ph)I] + 2OH^- \xrightarrow[-2I^-]{} \underset{\mathbf{2}}{[L_2Pd_2Ph_2(\mu\text{-}OH)_2]} + 2L \qquad (11)$$

$$L = PPh_3$$

When the light yellow color of the benzene solution of $[(Ph_3P)_2Pd(Ph)I]$ disappeared after stirring with benzene–50% KOH and catalytic amounts of 18-crown-6 at ambient temperature for 30 min, the organic layer was separated and analyzed by ^{31}P NMR spectroscopy. The spectrum indicated ca. 90–95% conversion of the mononuclear iodo complex (δ = 22.0 ppm) to PPh_3 (δ = −5.5 ppm) and **2** (δ = 33.8 ppm).[3] The latter two resonances were broadened, obviously due to the phosphine ligand exchange process (eq 12). Likewise, broadening of both signals was observed in the ^{31}P NMR spectrum of a 2:1 mixture of PPh_3 and **2** in benzene.

$$\underset{\mathbf{2}}{[(Ph_3P)_2Pd_2Ph_2(\mu\text{-}OH)_2]} + 2Ph_3P \rightleftharpoons 2[(Ph_3P)_2Pd(Ph)OH] \qquad (12)$$

It is worth noting that transformations similar to that depicted in eq 11 have been described in the literature[20,21] for analogous nickel complexes.

Another important question arises as to how carbonylation of the hydroxo organopalladium dimers proceeds. In most cases, carbon monoxide inserts preferentially into the Pd–O rather than the Pd–C bond as the latter is usually stronger.[22] There are some examples, however, where the Pd–C bond is cleaved, while the Pd–O bond present in the same complex remains intact.[23] This is exactly what was observed in the present work when the σ-phenyl palladium benzoates **5**–**8** reacted with CO. However, it was not necessarily the case when carbon monoxide reacted with the hydroxo bridging palladium complexes **2** and **4**. Though no unambiguous proof was obtained for either the Pd–OH or Pd–Ph bond cleavage, we have obtained indirect evidence for CO insertion into the Pd–OH bond.

As described above, the carbonylation of **4** in hexane results in only two Pd-containing products, i.e. **5** and the carbonyl phosphine Pd(0) compound, the red cluster. In benzene, the interaction between **4** and CO eventually gives rise to the same two products. In addition, complex **9** is formed due to the carbonylation of **5**. However, no reductive elimination of

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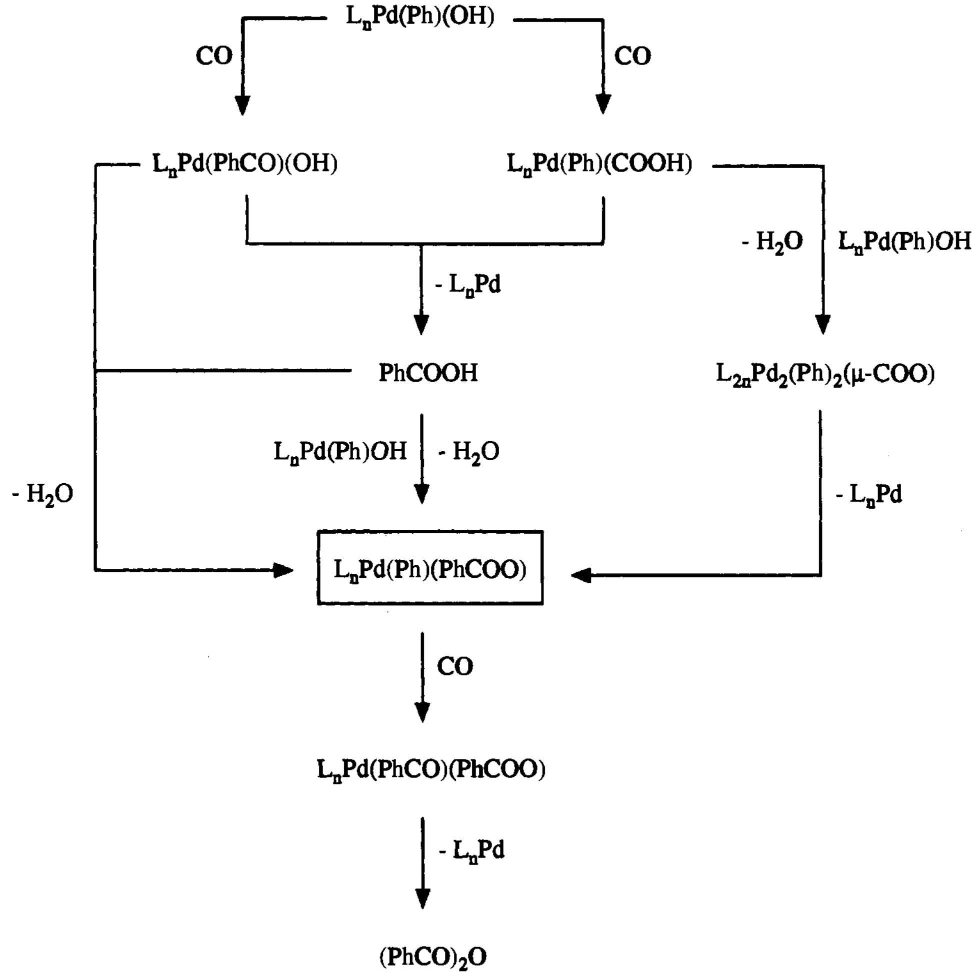
[19] Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.

[20] Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1973**, 1433.

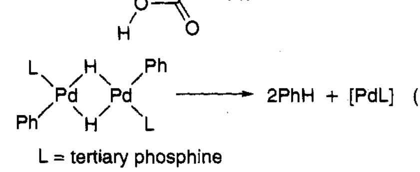
[21] Carmona, E.; Marin, J. M.; Palma, P.; Paneque, M.; Poveda, M. L. *Inorg. Chem.* **1989**, *26*, 1895.

[22] Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.

Scheme 4



benzoic anhydride was observed at ambient temperature during the reaction in either solvent. Since the yield of **5** was approximately 50%, some other reductive elimination process must have taken place so that the red Pd(0) cluster could be generated. Indeed, when **4** was treated with CO in toluene for 2 h, benzene and biphenyl were found (GC-MS) in the liquid phase obtained by vacuum distillation of the reaction mixture at 40–50 °C.[24] Both benzene and biphenyl did not originate from a free-radical reaction, because no bibenzyl was formed in the reaction (GC-MS).[25] It is likely that the formation of benzene was due to reductive elimination from a σ-phenyl palladium hydrido species. The latter might well be formed only if CO inserted into the Pd–OH bond to give the corresponding metallocarboxylic acid, followed by elimination of CO_2 (e.g., eq 13).[26]



(13)

L = tertiary phosphine

The other route for decomposition of the palladocarboxylic acid might be reductive elimination of benzoic acid which, as we have demonstrated, can easily react with as yet unreacted **2** or **4**, to give complexes **6** and **7**, or **5** and **8** upon redistribution of the phosphine ligands. On the other hand, it is also conceivable that the palladocarboxylic acid first condenses with the starting hydroxo complex as described by Bennett and coworkers[27] for platinum complexes (eq 14). Reductive elimination from similar binuclear Pd species with a bridging CO_2 ligand would result in the corresponding benzoato σ-phenyl complex. Scheme 4 summarizes the described options for the generation of benzoato phenyl palladium species from the hydroxo complexes and CO, followed by carbonylation of the Pd–Ph bond and reductive elimination of benzoic anhydride.

$$[L_2Pt(Ph)COOH] + [L_2Pt(Ph)OH] \rightarrow [L_4Pt_2(Ph)_2(\mu\text{-COO})] + H_2O \quad (14)$$

It is known from theoretical calculations[28] that reductive elimination from d^8-complexes should proceed via either a *cis*

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[23] (a) Komiya, S.; Akaki, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130. (b) Kim, Y.-J.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1988**, *7*, 2182. (c) Kim, Y.-J.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096.

[24] Complex **4** is usually isolated as an acetone or benzene solvate.[3] To make sure that no benzene was introduced to the reaction mixture before the carbonylation, **4** was recrystallized from toluene–hexane prior to use in this experiment. The absence of benzene in the thus obtained sample of **4** was confirmed by the ^1H spectrum measured in $CDCl_3$.

[25] Nonhebel, D. C.; Walton, J. C. *Free-Radical Chemistry*; Cambridge University Press: Cambridge, 1974.

[26] Halpern, J. *Comm. Inorg. Chem.* **1981**, *1*, 3. Bennett, M. A. *J. Mol. Catal.* **1987**, *41*, 1.

[27] Bennett, M. A.; Robertson, G. B.; Rokicki, A.; Wickramasingle, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 7098.

[28] Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857.

or a trigonal-planar orientation. Therefore, both dimeric (eq 13) and monomeric, tricoordinate structures of the palladocarboxylic acid should be suitable for the facile reductive elimination of benzoic acid. Moreover, it is likely that because of these requirements to the geometry of d^8-complexes for reductive elimination, binuclear, phosphine-deficient complexes **6** and **7** give benzoic anhydride upon treatment with CO much faster than mononuclear **5** and **8**.

In conclusion, we have established, by the investigations described herein, the pathways by which carboxylic acids are formed from aromatic halides. Of particular significance is the demonstration of an anhydride route as one source of acid formation.

Experimental Section

Spectral measurements were carried out using the following equipment: Varian XL 300 (^{1}H, ^{13}C, and ^{31}P NMR), Bomem MB-100 (FT-IR), and VG 5050 micromass (mass spectra). A Rigaku AFC6S diffractometer was used for single-crystal X-ray diffraction study. All chemicals including tertiary phosphines, ^{13}CO, and Ph^{13}COOH were purchased from Aldrich, Strem, Organometallics, and MSD Isotopes chemical companies. Ferrocene for the spectral determination of the yield of benzoic anhydride was sublimed under vacuum. The palladium complexes **2**,[3] **3**,[3] **4**,[3,29] $[(Ph_3P)_2Pd(PhCO)I]$,[17] $[(Ph_3P)_2Pd(Ph)I]$,[30] and $[(Cy_3P)_2Pd]$[31] were prepared as described in the literature. For monitoring the carbonylations by NMR, a solution of the complex (3−7 mg) in benzene-d_6 or toluene-d_8 was placed under N$_2$ in a standard 5-mm NMR tube fitted with a rubber septum stopper. After CO or ^{13}CO was bubbled through the solution via syringe needle, the tube was immediately placed in the NMR spectrometer.

Carbonylation of 2 in the Presence of PhI. A mixture of **2** (0.27 g, 0.29 mmol), PhI (0.48 g, 2.35 mmol), and toluene (2 mL) was stirred under CO (1 atm) until the solid dissolved (5−10 min) and then kept in a CO atmosphere at ambient temperature for 14 h. A GC-MS analysis of the liquid phase indicated the formation of benzoic anhydride and trace amounts of benzene, biphenyl, and benzophenone. The H$_2$O formed (see eq 1) is by mass balance, as no determination of water was attempted. The well-shaped brown crystals of **3** (1:2 toluene solvate) were separated, washed with benzene (3 × 1 mL), and dried under vacuum. The yield of spectroscopically pure[3] toluene solvate of **3** was 0.38 g (93%). The combined benzene and toluene solutions were evaporated, the residue was dried under vacuum and analyzed by ^{1}H NMR spectroscopy (CDCl$_3$) in the presence of ferrocene (13.3 mg) as the internal standard. From the relative intensities of the signals at 4.15 (s, 16 H, Cp$_2$Fe) and 8.15 ppm (d, 25 H, *ortho* protons of benzoic anhydride) it was concluded that (PhCO)$_2$O was formed in 95 ± 5% yield. Similar results were obtained when iodobenzene was added 1 h after CO was introduced to a mixture of **2** and toluene.

Reaction of 3 with 14% KOH. A 1:2 toluene solvate of **3** (0.18 g, 0.13 mmol) was stirred under N$_2$ with a mixture of KOH (0.5 g), water (3 mL), benzene (3 mL), and PhI (0.15 g, 0.73 mmol) for 22 h. During this time, the dark brown color disappeared and a yellowish microcrystalline solid precipitated. Benzene (4 × 5 mL) was added, and the suspension of the solid in the organic phase was carefully separated from the aqueous layer. The combined organic suspensions were evaporated and the remaining solid was washed with acetone and dried under vacuum. The yield of **1** was 0.14 g (94%). The aqueous layer was filtered, acidified with 10% HCl, and extracted with ether (3 × 20 mL). The combined ether solution were dried over MgSO$_4$ and evaporated. Vacuum sublimation of the residue gave 29.5 mg (93%) of benzoic acid, mp 115−118 °C.

Carbonylation of 4. Carbon monoxide was bubbled through a solution of **4** (100 mg, 0.10 mmol) in hexane (5 mL)[32] for 5 min (the solution turned red), and the mixture was kept under CO at room temperature for 2−4 h. Colorless crystals of **5** were separated, thoroughly washed with hexane, and dried under vacuum. The yield of **5** was 44 mg (49%); see Table 1 for spectral and analytical data. ^{1}H NMR (CDCl$_3$) δ 0.8−2.0 (m, 66 H, Cy), 6.8 (m, 3 H, 3,4,5-C$_6$H$_5$Pd), 7.3 (m, 3 H, 3,4,5-C$_6$H$_5$COOPd), 7.4 (m, 2 H, 2,6-C$_6$H$_5$Pd), 8.0 (m, 2 H, 2,6-C$_6$H$_5$COOPd).

The red mother liquor was kept under CO at −15 °C overnight, filtered, and reduced in volume by bubbling CO through it at room temperature, until the red solid started precipitating. The yield of the red cluster complex was 15 mg. The compound can be stored at room temperature under CO without decomposition for a few weeks.

Synthesis of 6. Benzoic acid (30 mg, 0.25 mmol) was added to a stirring suspension of **2** (0.10 g, 0.11 mmol) in benzene (5 mL). The solids immediately dissolved to give a clear, light yellow solution. Evaporation of the solution and addition of hexane (5 mL) to the residue gave 0.11 g of **6** as yellowish crystals which were washed with hexane and dried under vacuum. Analytical and spectral data for **6** are given in Table 1. ^{1}H NMR (C$_6$D$_6$) δ 6.7−7.6 (m, aromatic H). The ^{13}C-labeled sample of **6** was prepared similarly from **2** and Ph^{13}COOH.

Synthesis of 7. Benzoic acid (30 mg, 0.25 mmol) and **4** (102 mg, 0.11 mmol) were stirred with benzene (6 mL) until the solids dissolved upon slight heating. Isolation of the complex was conducted similarly to that of **6** (see above). ^{1}H NMR (CDCl$_3$) δ 1.0−2.0 (m, 33 H, Cy), 6.8 (br m, 3 H, 3,4,5-C$_6$H$_5$Pd), 7.3 (m, 3 H, 3,4,5-C$_6$H$_5$COOPd), 7.4 (br m, 2 H, 2,6-C$_6$H$_5$Pd), 8.0 (m, 2 H, 2,6-C$_6$H$_5$COOPd). The ^{13}C-labeled sample of **7** was prepared similarly from **4** and Ph^{13}COOH.

Synthesis of 8. Triphenylphosphine (41 mg, 0.16 mmol) was added to a stirring yellow suspension of **6** (81 mg, 0.07 mmol) in benzene (4 mL). The solids dissolved to form a colorless, clear solution. The solution was evaporated to give **8** as colorless crystalline material which was washed with hexane and dried under vacuum. The yield was 103 mg (90%). Analytical and spectral data for **8** are listed in Table 1. ^{1}H NMR (CDCl$_3$) δ 6.2−7.5 (m, aromatic H). The ^{13}C-labeled sample of **8** was prepared from labeled **6**.

Synthesis of 5. Tricyclohexylphosphine (35 mg, 0.13 mmol) was added to an oxygen-free solution of **7** (57 mg, 0.05 mmol) in benzene (8 mL). The solution was evaporated, and the residue was washed with hexane and dried under vacuum. The yield of **5** was 68 mg (83%). The compound was found to be spectroscopically identical (Table 1) with the white crystalline solid obtained by carbonylation of **4** in hexane (see above). The ^{13}C-labeled sample of **5** was synthesized in a similar manner from labeled **7**.

Carbonylation of 6. A mixture of **6** (58 mg, 0.05 mmol), PhI (50 μL), and toluene (1 mL) was stirred under CO until all the solid dissolved (15 min), and then kept under CO at room temperature for 20 h. The dark brown crystals were separated and dried under vacuum, affording 60 mg (90%) of **3**. The ^{1}H NMR analysis of the liquid phase (see above) indicated that benzoic anhydride was formed in quantitative yield.

Carbonylation of 8. A mixture of **8** (52 mg, 0.06 mmol), PhI (50 μL), and toluene (1 mL) was stirred under CO until the solid completely dissolved (20−30 min) and then kept under CO for 13 h. Yellow crystals of $[(Ph_3P)_2Pd(PhCO)I]$ (identical with an authentic sample[17]) were separated and dried under vacuum. The yield of the benzoyl complex was 40 mg (74%). The ^{1}H NMR analysis of the liquid phase in the presence of ferrocene (see above) indicated the formation of benzoic anhydride in 95% yield.

Single Crystal Diffraction Study of 6. Well-shaped, transparent, yellowish crystals of **6**·2CHCl$_3$ were obtained by layering a concen-

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(29) To our surprise, we have recently found that the successful synthesis of **4** from $[(Cy_3P)_2PdCl_2]$, KOH, and PhCl[3] is *strongly* dependent on the quality of chlorobenzene used. The reaction was reproduced as described[3] with only *two* of *six* chlorobenzene samples available in our and neighboring laboratories, although all of these samples were found to be GC-pure. No reaction (dissolution of the $[(Cy_3P)_2PdCl_2]$ accompanied by disappearance of the yellow color) was observed with the other four PhCl samples. Nonetheless, the preparation of **4** was successful with any of the PhCl samples when a phase-transfer agent was added to the reaction mixture. Therefore, we recommend that the synthesis of **4**[3] should be conducted in the presence of catalytic amounts of 18-crown-6 (ca. 5 mol % to the Pd complex).

(30) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 3846.

(31) Grushin, V. V.; Bensimon, C.; Alper, H. *Inorg. Chem.* **1994**, *33*, 4804.

(32) Complex **4** can exist as a benzene or acetone solvate, the former being much more soluble in hexane than the latter. If solubility of a sample of **4** in hexane is too low for the carbonylation, the complex should be dissolved in warm benzene and the solution reduced in volume, treated with hexane, and kept at ca. −10 °C for a few hours. The resulting crystals of the thus obtained benzene solvate of **4** are fairly soluble in hexane.

trated solution of **6** in chloroform with hexane. One of the crystals having approximate dimensions of 0.2 × 0.1 × 0.2 mm was mounted on a glass capillary. The measurements were made at −110 °C with Mo Kα radiation and a graphite monochromator. During the data collection, standard reflections were measured after every 150 reflections to check the stability of the crystal. No crystal decay was noticed. A total of 5081 reflections were measured. The unique set contained 5081 reflections. Using the criteria $I > 2.5\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation derived from the counting statistics, 4024 out of 5081 reflections were used. The data were corrected for Lorentz and polarization effects.[33] An absorption correction (ψ-scan) was made. The minimum and maximum transmission factors were 0.9620 and 0.9958.

The structure was solved by direct method. All the atoms were refined anisotropically except the hydrogens. The hydrogen atoms were found by difference Fourier map. The final cycle of full-matrix least-squares refinement was based on 4024 observed reflections and 353 parameters. Weights based on counting statistics were used. The maximum and minimum peaks on the final Fourier map corresponded to 0.930 and −1.430 e/Å^3, respectively. All the calculations were performed using the NRCVAX crystallographic software package.[34]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for support of this research. Dr. Corinne Bensimon is gratefully acknowledged for the X-ray diffraction study of complex **6**.

Supplementary Material Available: Full textual and tabular details of the structure solution, additional structural diagrams, and the tables of atomic coordinates, bond lengths and angles, and thermal parameters for complex **6** (11 pages); listing of structure factors (27 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA9420151

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(33) Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1978**, *11*, 114.

(34) Gabe, E. J.; Lee, F. L.; Lepage, Y. *J. Appl. Crystallogr.* **1989**, *22*, 384.