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Synthesis and Spectral Characterization of Dinuclear Palladium(I) Phenoxides and the Crystal Structure of $Pd_2(dppm)_2(OCOCF_3)_2$

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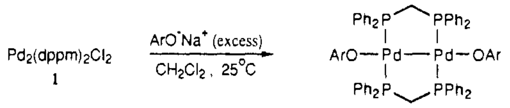
Dinuclear palladium(I) phenoxide compounds $Pd_2(dppm)_2(OAr)_2$ (dppm = bis(diphenylphosphino)methane) and $Pd_2(dmpm)_2(OAr)_2$ (dmpm = bis(dimethylphosphino)methane) have been synthesized from the corresponding dichloro compounds by metathesis with sodium or potassium aryloxides. The trifluoroacetate complex $Pd_2(dppm)_2(OCOCF_3)_2$ also undergoes ligand exchange to yield palladium(I) bisphenoxides. The reactions were followed by ^{31}P NMR spectroscopy, which clearly shows the intermediate chloro-aryloxide compounds $Pd_2(R_2PCH_2PR_2)_2(OAr)Cl$ (R = Ph, Me). The bisphenoxide complexes were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Evidence is presented for hindered rotation about the palladium-oxygen bond in $Pd_2(dmpm)_2(OC_6H_3\text{-}2,6\text{-}Me)_2$. Reaction of the dinuclear compounds $Pd_2(R_2PCH_2PR_2)_2X_2$ (R = Ph, Me) with carbon monoxide resulted in insertion of CO into the metal-metal bond. An X-ray crystal structure of the trifluoroacetate complex $Pd_2(dppm)_2(OCOCF_3)_2$ (**7**) was performed. The complex crystallizes in the monoclinic space group $C2/c$ with $a = 15.870$ (8) Å, $b = 17.212$ (8) Å, $c = 20.364$ (11) Å, $\beta = 102.88$ (5)°, $V = 5423$ (8) Å^3, and $Z = 4$. Refinement with 3276 reflections converged at $R = 0.0422$ and $R_w = 0.0749$. The $Pd_2P_4C_2$ unit is nonplanar with a torsion angle of 44.5° about the metal-metal bond. The carboxylates are monodentate with a cis orientation, giving the molecule overall C_2 symmetry. The Pd-Pd bond distance is 2.594 (2) Å, and the Pd-O distance is 2.191 (4) Å.

Introduction

Transition-metal alkoxides and phenoxides have been extensively studied since the 1950s, particularly those of the early and first-row transition metals.[1] Until the mid 1970s few examples with the heavier group VIII metals were known. More recent work has shown that these compounds are accessible and that the metal-oxygen bonds are thermodynamically stable.[2] Such compounds are of interest, since they are invoked in a number of important catalytic reactions of alcohols and phenol. These include oxalate and carbonate syntheses, hydrogenation of CO, alcohol oxidation and homologation, olefin carboxylation, and others.[3] As part of our general interest in transition-metal phenol chemistry, we report here synthesis of the dinuclear palladium(I) complexes $Pd_2(dppm)_2(OAr)_2$ (**3**)[4] (dppm = bis(diphenylphosphino)methane) from the corresponding dichloride, $Pd_2(dppm)_2Cl_2$ (**1**),[5] or from the bis(trifluoroacetate) complex, $Pd_2(dppm)_2(OCOCF_3)_2$ (**7**).[6] Although several palladium(II) phenoxides are known,[7] the only previously reported palladium(I) phenoxide is the related species $Pd_2(dmpm)_2(OPh)_2$ (dmpm = bis(dimethylphosphino)methane).[8] Synthetic details and further characterization for this class of compound, $Pd_2(dmpm)_2(OAr)_2$ (**6**), are also described. Reaction of the palladium phenoxides with CO is discussed. In addition we report the X-ray crystal structure of the trifluoroacetate complex $Pd_2(dppm)_2(OCOCF_3)_2$, which contains the first structurally characterized example of a nonbridging palladium(I)-oxygen bond.

Results and Discussion

The palladium aryloxides $Pd_2(dppm)_2(OAr)_2$ (**3**) are synthesized from the dichloro compound $Pd_2(dppm)_2Cl_2$ (**1**) by treatment with excess sodium or potassium aryloxide in methylene chloride at room temperature (eq 1). The metathesis is accompanied by a color change from orange to deep red-orange, and the extent of reaction can be conveniently monitored by ^{31}P NMR spectroscopy. Reaction with a stoichiometric quantity of aryloxide



(1)

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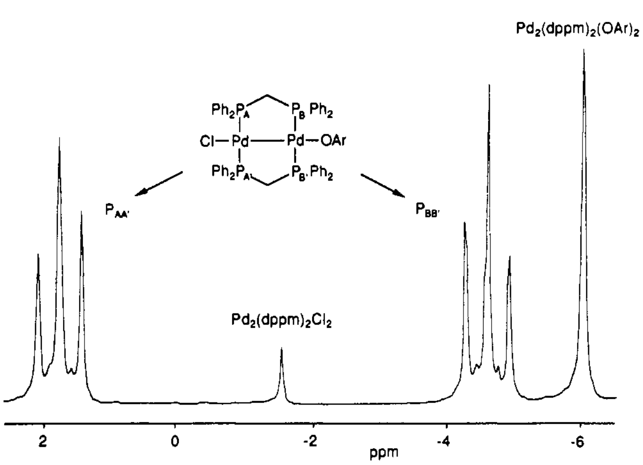

Figure 1. ^{31}P NMR spectrum after addition of sodium 4-*tert*-butylphenoxide to **1**.

produces a mixture of starting material (**1**), bisphenoxide (**3**), and a third compound we have assigned as the monosubstituted product, $Pd_2(dppm)_2(OAr)Cl$ (**2**) (eq 2; Figure 1). Compounds

$$\underset{\mathbf{1}}{\mathrm{Pd_2(dppm)_2Cl_2}} \xrightarrow{2\mathrm{ArO^-Na^+}} \mathbf{1} + \underset{\mathbf{2}}{\mathrm{Pd_2(dppm)_2(OAr)Cl}} + \underset{\mathbf{3}}{\mathrm{Pd_2(dppm)_2(OAr)_2}} \qquad (2)$$

2a,3a Ar = C_6H_5 **2b,3b** Ar = C_6H_4-*p*-F
2c,3c Ar = C_6H_4-*p*-^{t}Bu

2a–c contain two sets of nonequivalent phosphorus and display an AA′BB′ spin pattern that appears as a pair of virtual triplets.[9] Use of excess sodium phenoxide or sodium 4-fluorophenoxide converts dichloride **1** to the bisphenoxides **3a,b**. These reactions appear to be quantitative by ^{31}P NMR spectroscopy. Conversion of **1** to **3c** was more difficult to drive to completion and was often accompanied by some decomposition.

It was discovered that the metathesis reactions are hindered by rigorous exclusion of water. Under dry conditions, substitution proceeds to only a small extent, even when a large excess of aryloxide is employed. Addition of deaerated water or dry phenol greatly increases the degree of substitution. Reactions run on the bench top without special exclusion of air or water also proceed more readily. One possible explanation is that phenol reacts with the metal chloride to liberate HCl (Pd–Cl + PhOH $\rightleftharpoons$ Pd–OPh + HCl), which is then neutralized by aryloxide. Analogous reaction with water would yield Pd–OH, which could then exchange with phenol to give the observed product. Transformations of this type could involve prior protonation of the metal–metal bond[10] or association of ROH with the complex through hydrogen bonding (vide infra).

Attempts to isolate the palladium bisphenoxides by crystallization or precipitation were unsuccessful. Compounds **3a,b** can be isolated, however, if the reaction mixture is filtered twice and evaporated to dryness and the residue stirred vigorously with hexane. The materials were obtained as red powders, which were characterized by ^{31}P, ^{13}C, and ^{1}H NMR (Tables I–III) and IR spectroscopy. The products exhibit a single peak in the ^{31}P NMR spectrum down to −70 °C. Purification of the compounds proved to be problematic. Complexes **3a,b** are stable in methylene chloride at low temperature (−20 °C) for a period of hours, but they decompose slowly at room temperature. The products were less stable in coordinating or polar solvents and had poor solubility in common nonpolar solvents. Attempts to recrystallize the crude materials led to partial decomposition. Elemental analysis of crude **3a** (see Experimental Section) fits the bisphenoxide formulation, but ^{13}C NMR spectroscopy demonstrates that some phenol is also present. If this is taken into account, the analysis is low for carbon and hydrogen. We ascribe this to contamination with small amounts of sodium chloride. Similar problems were encountered with **3b**. Field desorption mass spectroscopy yielded very weak spectra that contained no indication of the molecular ion.

Table I. ^{31}P NMR Data for Palladium Complexes

no.	compd	$\delta(^{31}P)^a$
1	$Pd_2(dppm)_2Cl_2$	−1.4
7	$Pd_2(dppm)_2(CO_2CF_3)_2$	−4.3
2a	$Pd_2(dppm)_2(OC_6H_5)Cl$	2.2, −4.7 (80)^b
2b	$Pd_2(dppm)_2(OC_6H_4\text{-}p\text{-}F)Cl$	2.4, −4.7 (80)^b
2c	$Pd_2(dppm)_2(OC_6H_4\text{-}p\text{-}^tBu)Cl$	2.0, −4.6 (80)^b
3a	$Pd_2(dppm)_2(OC_6H_5)_2$	−5.4
3b	$Pd_2(dppm)_2(OC_6H_4\text{-}p\text{-}F)_2$	−4.8
3c	$Pd_2(dppm)_2(OC_6H_4\text{-}p\text{-}^tBu)_2$	−6.0
12	$Pd_2(dppm)_2(\mu\text{-}^{13}CO)(CO_2CF_3)_2$	22.5 (d, J_{PC} = 7 Hz)
10	$Pd_2(dppm)_2(\mu\text{-}^{13}CO)(OC_6H_5)_2$	20.0 (br)^{c,d}
4	$Pd_2(dmpm)_2Cl_2$	−29.0
5a	$Pd_2(dmpm)_2(OC_6H_5)Cl$	−28.2, −26.2 (75)^b
5c	$Pd_2(dmpm)_2(OC_6H_3\text{-}2,6\text{-}Me)Cl$	−28.4, −27.6^{c,e}
6a	$Pd_2(dmpm)_2(OC_6H_5)_2$	−25.4
6b	$Pd_2(dmpm)_2(OC_6H_4\text{-}p\text{-}F)_2$	−26.1^c
6c	$Pd_2(dmpm)_2(OC_6H_3\text{-}2,6\text{-}Me)_2$	−26.8
11a	$Pd_2(dmpm)_2(\mu\text{-}^{13}CO)(OC_6H_5)_2$	5.4 (d, J_{PC} = 7 Hz)^c
11c	$Pd_2(dmpm)_2(\mu\text{-}^{13}CO)(OC_6H_3\text{-}2,6\text{-}Me)_2$	2.4 (d, J_{PC} = 7 Hz)^c

[a] Shifts are in ppm referenced to 85% H_3PO_4 (δ = 0.00) at 121 MHz; in CD_2Cl_2 at room temperature unless otherwise noted. Data for **1**, **7**, **4**, and **12** compare favorably with literature values.[5f,6,8] [b] Virtual triplets derived from the AA′BB′ spin system. Separation in Hz of outer peaks is given in parentheses. [c] −20 °C. [d] P–C coupling was not resolved. [e] AA′BB′ multiplet.

The related compounds $Pd_2(dmpm)_2(OAr)_2$ (**6**) can also be prepared by the method described above.[11] Reaction of the dichloride, $Pd_2(dmpm)_2Cl_2$ (**4**), with excess aryloxide results in clean conversion to **6** (eq 3). Stoichiometric quantities of phenoxide again generate a mixture of starting material (**4**), bisphenoxide (**6**), and monosubstituted product, $Pd_2(dmpm)_2(OAr)Cl$ (**5**), as shown by ^{31}P NMR spectroscopy (Table I). The nonequivalent phosphorus atoms in **5** appear as two virtual triplets derived from the AA′BB′ spin system. Phenoxide substitution causes an upfield shift in the ^{31}P NMR signal for the dppm complexes, but a downfield shift is observed for the dmpm system. In this case ligand metathesis is not hindered by dry conditions and the reactions are driven to completion by a smaller excess of phenoxide. Synthesis of a 2,6-dimethylphenoxide complex from $Pd_2(dppm)_2Cl_2$ was unsuccessful, but the bisphenoxide **6c** forms readily from $Pd_2(dmpm)_2Cl_2$. This apparently reflects the steric constraints of the dppm dimers. The products **6a–c** were isolated by concentration of the filtered reaction mixture followed by precipitation with pentane and were characterized by ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy (see tables). Decomposition problems were again encountered during attempted recrystallization/purification of these materials, and elemental analyses of the crude products again suggest some contamination with sodium chloride.

$$\underset{\mathbf{4}}{\mathrm{Pd_2(dmpm)_2Cl_2}} \xrightarrow[\mathrm{CH_2Cl_2,\ 25\,^\circ C}]{\mathrm{ArO^-Na^+\ (excess)}} \mathrm{Pd_2(dmpm)_2(OAr)_2} \qquad (3)$$

6a Ar = C_6H_5
6b Ar = C_6H_4-*p*-F
6c Ar = C_6H_4-*p*-^{t}Bu

Low-temperature ^{13}C NMR (−70 °C) spectra of bisphenoxide complexes **3a** and **6a** show one set of signals for the bound phenoxide and a second set for phenol. The signals associated with phenol are temperature and concentration dependent. This may

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(11) The dimers, $Pd_2(dmpm)_2(OAr)_2$, were previously synthesized by metathesis with stoichiometric amounts of aryloxide in THF (see ref 8). In our hands the use of excess aryloxide in CH_2Cl_2 gave better results.

Table II. ^{13}C NMR Data for Palladium Complexes

no.	compd	$\delta(^{13}C)^{a}$ phosphine ligands	other ligands
1	$Pd_2(dppm)_2Cl_2{}^{b}$	133.3, 132.7, 129.9, 127.9 ($C_{o,ip,m}$), 38.4 (qn, CH_2, J_{CP} = 11.0)	
7	$Pd_2(dppm)_2(OCOCF_3)_2{}^{c}$	132.8 (C_o), 132.1 (qn, C_i, J_{CP} = 14.5), 130.3, 128.4 ($C_{p,m}$), 37.1 (qn, CH_2, J_{CP} = 12.2)	160.4 (q, carb, J_{CF} = 34.7), 115.3 (q, CF_3, J_{CF} = 291)
3a	$Pd_2(dppm)_2(OC_6H_5)_2{}^{d,e}$	133.0–127.4 (OPh), 38.9 (m, CH_2)^{f}	PhO, 166.8, 118.8, 111.7 ($C_{i,o,p}$);^{g} PhOH, 158.8, 128.8, 116.9, 115.5 ($C_{i,m,p,o}$)
3b	$Pd_2(dppm)_2(OC_6H_4\text{-}p\text{-}F)_2{}^{d,e}$	133.1–127.5 (OPh), 38.2 (m, CH_2)^{f}	ArO, 152.6 (d, C_p, J_{CF} = 228), 113.6 (d, C_m, J = 20), 161.3, 117.8 ($C_{i,o}$); ArOH, 154.6 (d, C_p, J = 223), 114.8 (d, C_m, J = 23), 154.1, 115.8 ($C_{i,o}$)
12	$Pd_2(dppm)_2(\mu\text{-}^{13}CO)(CO_2CF_3)_2{}^{c}$	133.9, 133.6, 131.2 ($C_{o,o,p}$), 130.9, 129.7 (m, $C_{i,i}$), 128.9 (C_m), 23.1 (m, CH_2)^{f}	228.4 (qn, CO, J_{CP} = 6.4), 160.6 (q, carb, J_{CF} = 35), 116.2 (q, CF_3, J_{CF} = 291)
10	$Pd_2(dppm)_2(\mu\text{-}^{13}CO)(OC_6H_5)_2{}^{b}$	133.7–128.0 (Ph), 22.0 (m, CH_2)^{f}	242.2 (br, CO),^{f} 166.2, 119.7, 113.1 ($C_{i,o,p}$)^{g}
6a	$Pd_2(dmpm)_2(OC_6H_5)_2{}^{h}$	39.3 (qn, CH_2, J_{CP} = 11.8), 15.3 (s, Me)^{f}	170.4, 128.7, 118.3, 111.4 ($C_{i,m,o,p}$)
6b	$Pd_2(dmpm)_2(OC_6H_4\text{-}p\text{-}F)_2{}^{d,e}$	38.6 (m, CH_2), 15.3 (m, Me)^{f}	ArO, 151.9 (d, C_p, J_{CF} = 224), 114.5 (d, C_m, J = 22), 165.4, 117.3 ($C_{i,o}$); ArOH^{i}
6c	$Pd_2(dmpm)_2(OC_6H_3\text{-}2,6\text{-}Me)_2{}^{d}$	38.4 (m, CH_2), 19.1, 10.5 (s, Me)^{f}	168.9, 127.2, 126.4, 111.9 ($C_{i,m,o,p}$), 18.5 (Me)
11a	$Pd_2(dmpm)_2(\mu\text{-}^{13}CO)(OC_6H_5)_2{}^{h}$	23.4 (m, CH_2), 13.3, 12.0 (m, Me)^{f}	250.5 (m, CO),^{f} 169.8, 129.0, 119.2 ($C_{i,m,o}$), 112.0 (C_p)
11c	$Pd_2(dmpm)_2(\mu\text{-}^{13}CO)(OC_6H_3\text{-}2,6\text{-}Me)_2{}^{d}$	24.5 (m, CH_2), 13.7, 11.6 (m, Me)^{f}	248.7 (qn, CO, J_{CP} = 6.4), 174.3, 128.1, 125.7, 114.6 ($C_{i,m,o,p}$), 17.9 (Me)

^{a}Shifts are in ppm, referenced to $SiMe_4$ (δ = 0.00) at 300 MHz. In CD_2Cl_2 except **1** and **7** ($CDCl_3$). Coupling in Hz (qn = quintet). ^{b}–30 °C. ^{c}Room temperature. ^{d}–70 °C. ^{e}Some ArOH present in sample. ^{f}C–P coupling not resolved. $^{g}C_m$ is obscured by phosphine signals. ^{h}–50 °C. ^{i}Signals for 4-fluorophenol are the same as those reported for **3b**.

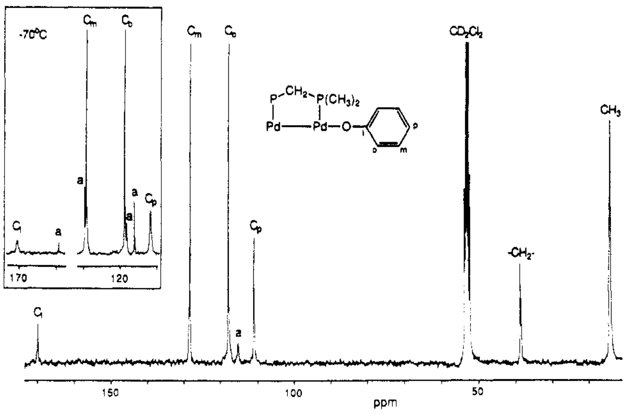

Figure 2. ^{13}C NMR spectrum of $Pd_2(dmpm)_2(OPh)_2$ (**6a**) at –50 °C. Phenol signals are indicated by the letter a. The insert shows resolution of phenol signals at –70 °C.

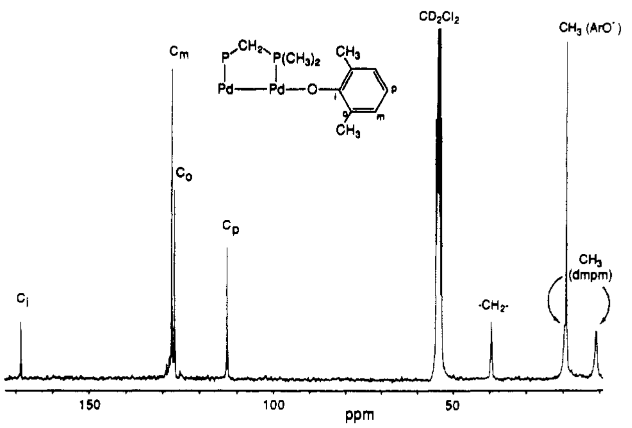

Figure 3. ^{13}C NMR spectrum of $Pd_2(dmpm)_2(OC_6H_3\text{-}2,6\text{-}Me)_2$ (**6c**) at –70 °C. The dmpm methyl signal at 19.1 ppm is more clearly resolved when small amounts of 2,6-dimethylphenol are present.

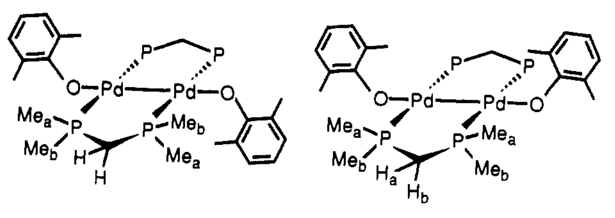

Figure 4. Trans and cis isomers of $Pd_2(dmpm)_2(OC_6H_3\text{-}2,6\text{-}Me_2$ (**6c**).

reflect a rapid equilibrium between free phenol and phenol that is associated with the complex, perhaps through hydrogen bonding.[12] At –70 °C the phenol resonances in **3a** are fairly well resolved and are somewhat shifted from those of phenol in the absence of the palladium complex. Signals for the bound phenoxide and phenol remain distinct up to –10 °C. At higher temperature the signals begin to coalesce but decomposition occurs before averaged signals can be observed. The ^{13}C NMR spectrum of **6a** at –50 and –70 °C is shown in Figure 2. Association of phenol may be a factor in the difficulty of obtaining pure samples. Isolation in the presence of 2 equiv (or an excess) of phenol did not yield pure compounds as might have been expected.

The chemical shifts of the phenoxide carbons in **3a** and **6a** are very similar to those of sodium phenoxide in acetonitrile or tetrabutylammonium phenoxide in methylene chloride but are significantly different from those of phenol.[13] This is consistent with a highly polarized metal–oxygen bond. Surprisingly little NMR data exist in the literature for phenoxide ligands. We are aware of only two other reports on carbon data[14] and have found only a few reports of well-resolved proton spectra.[14,15] The carbon data reported here for phenoxide and phenol are consistent with those reported for Bergman's Rh(I) system.[14b] The chemical shifts

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(12) Such equilibrium between free and hydrogen-bonded phenol was recently described for rhodium(I) aryloxides: Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *J. Am. Chem. Soc.* **1987**, *109*, 6563.

(13) (a) Experimentally obtained ^{13}C NMR data: PhO^-Na^+ (CD_3CN), δ 111.1 (para), 119.5 (ortho), 129.2 (meta), 170.3 (ipso); $PhO^-Bu_4N^+$ (CD_2Cl_2), δ 109.2 (para), 118.6 (ortho), 128.5 (meta), 169.8 (ipso). (b) Literature ^{13}C NMR data for phenol ($CDCl_3$): δ 121.0 (para), 115.4 (ortho), 129.7 (meta), 154.9 (ipso). See: Johnson, L. F.; Jankowski, W. C. *Carbon-13 NMR Spectra*; Wiley: New York, 1972.

(14) (a) Erikson, T. K.; Bryan, J. C.; Mayer, J. M. *Organometallics* **1988**, *7*, 1930. (b) Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *J. Am. Chem. Soc.* **1987**, *109*, 6563.

(15) (a) Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130. (b) Ozawa, F.; Sugimoto, T.; Yuasa, Y.; Santra, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1984**, *3*, 683.

Table III. ^{1}H NMR Data for Palladium Complexes

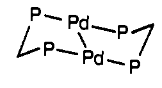
no.	compd	δ(^{1}H)[a] phosphine ligands	other ligands
1	$Pd_2(dppm)_2Cl_2$[b,c]	7.47 (d, H_o, J_{HH} = 7), 7.32 (dd, H_p, J = 7), 7.15 (dd, H_m, J = 7), 4.11 (qn, CH_2, J_{HP} = 4.3)	
7	$Pd_2(dppm)_2(CO_2CF_3)_2$[b,d]	7.5 (br, H_o), 7.38 (dd, H_p, J_{HH} = 7), 7.22 (dd, H_m, J = 7), 4.15 (qn, CH_2, J_{HP} = 4.3)	
3a	$Pd_2(dppm)_2(OC_6H_5)_2$[b,e]	7.7–7.0 (m, Ph)8 4.0 (qn, CH_2, J_{HP} = 4)	6.9–6.6 (dd, H_m), 6.5–6.2 (m, $H_{o,p}$)
4	$Pd_2(dmpm)_2Cl_2$[b,e]	2.73 (qn, CH_2, J_{HP} = 3.8), 1.72 (m, Me)[f,g]	
6a	$Pd_2(dmpm)_2(OC_6H_5)_2$[c,h]	2.54 (qn, CH_2, J_{HP} = 3.7), 1.43 (s, Me)[f]	6.91 (dd, H_m), 6.64 (d, H_o), 6.28 (m, H_p)
6c	$Pd_2(dmpm)_2(OC_6H_3\text{-}2,6\text{-}Me)_2$[c,i]	2.47 (qn, CH_2, J_{HP} = 3.5), 1.35 (s, Me)[f]	6.78 (d, H_m, J_{HH} = 7.5), 6.27 (t, H_p, J_{HH} = 7.5), 2.15 (Me)
6c	$Pd_2(dmpm)_2(OC_6H_3\text{-}2,6\text{-}Me)_2$[c,j]	2.44 (s, CH_2), 1.84, 0.75 (s, Me)[f]	6.72 (d, H_m, J_{HH} = 7.7), 6.23 (t, H_p, J_{HH} = 7.7), 2.15 (Me)
11a	$Pd_2(dmpm)_2(\mu\text{-}^{13}CO)(OC_6H_5)_2$[c,h]	1.60 (qn, CH_2, J_{HP} = 4),[k] 1.43, 1.34 (m, Me)[f]	7.06 (dd, H_m), 6.92 (d, H_o), 6.42 (m, H_p)

[a] Shifts are in ppm, referenced to $SiMe_4$ (δ = 0.00) and were recorded in CD_2Cl_2. [b] Room temperature. [c] 200 MHz. [d] 300 MHz. [e] 90 MHz. [f] H–P coupling not resolved. [g] Compares favorably with reported values.[5] [h] −20 °C. [i] −10 °C. [j] −80 °C. [k] The methylene protons are nonequivalent. The second signal is partially obscured by the methyl at 1.43 ppm.

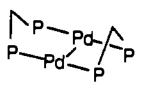
of the phenoxide protons in **3a** and **6a** also compare favorably with values reported for late-transition-metal complexes.[14b,15] Chemical shift differences in NMR data for early-transition-metal phenoxides presumably reflect differences in metal–phenoxide bonding.[14a]

At low temperature the ortho-substituted phenoxide compound **6c** exhibits hindered rotation about the palladium–oxygen bond. The ^{13}C spectrum at −10 °C displays a single peak for the dmpm methyls, but as the temperature is lowered, the phosphine methyl signal broadens and by −70 °C two signals grow in (Figure 3). Nonequivalent phosphine methyls imply restricted rotation about the metal–oxygen bonds (Figure 4). Carbon NMR spectroscopy cannot distinguish between the two isomers (cis and trans), but variable-temperature ^{1}H NMR spectroscopy demonstrates that the trans isomer is selectively frozen out (Table III). As the temperature is lowered, the phosphine methyl signal splits into two but the methylene peak remains a singlet. This is consistent only with the trans isomer that has equivalent methylene protons. Hindered rotation is not observed in the phenoxide complex **6a** at −70 °C although significant broadening of the methyl signal is seen at −90 °C in the ^{13}C spectrum.

An alternative explanation for nonequivalent phosphine methyls involves freezing out the boat–chair equilibration in the palladium–phosphorus–carbon ring system, but if this were operative,



chair



boat

one would also observe nonequivalent methylene protons. We see no evidence of freezing out this ring flipping in the dinuclear palladium dmpm complexes.[16] At low temperature the phenylphosphine compounds $Pd_2(dppm)_2Cl_2$ (**1**) and $Pd_2(dppm)_2(OPh)_2$ (**3a**) exhibit extra aromatic signals in the ^{13}C spectrum, which could be taken as an indication of slow ring flipping. However, proton NMR spectroscopy of **1** demonstrates that the methylene protons remain equivalent at low temperature, which rules out slow ring flipping. Instead, the extra signals could be due to slow rotation of the phenyl rings.

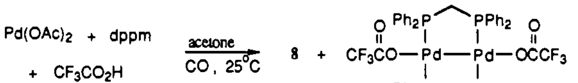
The trifluoroacetate complex $Pd_2(dppm)_2(OCOCF_3)_2$ (**7**) was also reacted with phenoxide in an attempt to identify a better synthetic route to the palladium bisphenoxides **3**. This material has previously been identified as an intermediate in synthesis of the trimer $[Pd_3(\mu_3\text{-}CO)(dppm)_3]^{2+}$ from palladium acetate, dppm, trifluoroacetic acid, and CO.[6] Under our conditions the reaction yielded primarily **7** (~50%) along with a small amount of the palladium(II) monomer $Pd(dppm)(OCOCF_3)_2$ (**8**) (eq 4). The compounds were identified by their NMR spectra (see tables).

Table IV. Selected Bond Distances (Å) for **7**

Pd–Pd′	2.594 (2)	C(21)–F(2)	1.292 (7)
Pd–P(1)	2.309 (2)	C(21)–F(3)	1.307 (8)
Pd–P(2)	2.296 (2)	P(1)–C(7)	1.834 (5)
Pd–O(1)	2.191 (4)	P(2)–C(7)	1.836 (5)
C(20)–O(1)	1.245 (7)	P(1)–C(1)	1.820 (5)
C(20)–O(2)	1.219 (7)	P(1)–C(14)	1.824 (5)
C(20)–C(21)	1.539 (9)	P(2)–C(8)	1.829 (6)
C(21)–F(1)	1.319 (9)	P(2)–C(22)	1.843 (5)

Table V. Selected Bond Angles (deg) for **7**

Pd′–Pd–O(1)	173.3 (1)	C(20)–C(21)–F(1)	112.1 (5)
P(1)–Pd–P(2′)	171.6 (1)	C(20)–C(21)–F(2)	111.1 (5)
P(1)–Pd–O(1)	93.2 (1)	C(20)–C(21)–F(3)	114.5 (6)
P(1)–Pd–Pd′	89.8 (1)	Pd–P(1)–C(7)	112.8 (2)
P(2′)–Pd–O(1)	93.1 (1)	Pd–P(1)–C(1)	116.0 (1)
P(2′)–Pd–Pd′	84.5 (1)	Pd–P(1)–C(14)	114.0 (2)
Pd–O(1)–C(20)	114.3 (4)	Pd′–P(2)–C(7)	104.6 (2)
O(1)–C(20)–O(2)	128.7 (6)	Pd′–P(2)–C(8)	115.4 (2)
O(1)–C(20)–C(21)	114.2 (5)	Pd′–P(2)–C(22)	122.7 (2)
O(2)–C(20)–C(21)	117.0 (5)	P(1)–C(7)–P(2)	106.3 (2)



(4)

7

Compound **7** undergoes metathesis with excess phenoxide to generate $Pd_2(dppm)_2(OPh)_2$ (**3**). Although substitution proceeds more readily here than with the dichloride, product isolation from these reactions was fraught with the same difficulties encountered before. Reaction of **7** with stoichiometric quantities of phenoxide again generates a mixture of compounds **7**, **9**, and **3** (eq 5).

$$7 \xrightarrow{2ArO^-Na^+} 7 + \underset{9}{Pd_2(dppm)_2(CF_3CO_2)(OAr)} + \underset{3}{Pd_2(dppm)_2(OAr)_2} \quad (5)$$

Phosphorus NMR spectroscopy reveals that the nonsymmetrical product, **9**, undergoes an exchange process that renders all the phosphorus equivalent. This could involve inter- or intramolecular exchange of the axial ligands. At first the exchange is slow and the phosphorus atoms appear as two triplets derived from the AA′BB′ spin system. In time the exchange becomes more rapid and the signals eventually coalesce. Lowering the temperature causes the triplets to reemerge, which indicates the coalescence is due to rapid exchange and not rearrangement of **9** to a static symmetrical product. Unfortunately, the results are not sufficiently reproducible to allow careful study and the process is not fully understood.

The infrared spectrum of compound **7** showed the trifluoroacetate ligands to be monodentate. The asymmetric carboxylate

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(16) Slow ring flipping has been examined in some detail for the platinum dimer $[Pt_2(dppm)_2(PPh_3)Cl]^+(PF_6)^-$: Blau, R. J.; Espenson, J. H.; Kim, S.; Jacobson, R. A. *Inorg. Chem.* **1986**, *25*, 757.

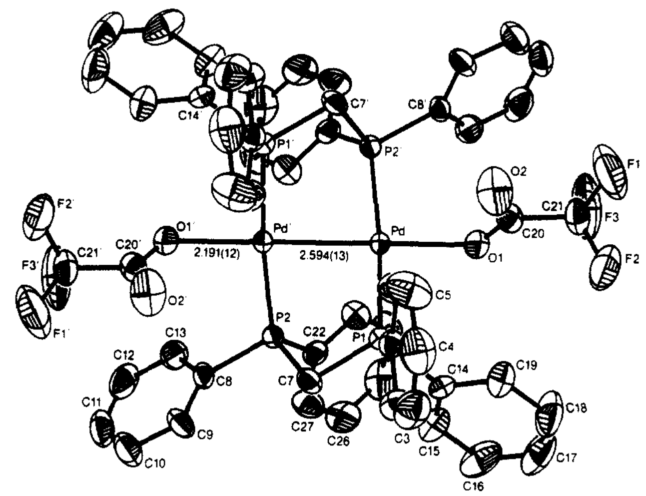


Figure 5. Molecular structure of $Pd_2(dppm)_2(OCOCF_3)_2$ (7) excluding hydrogen atoms.

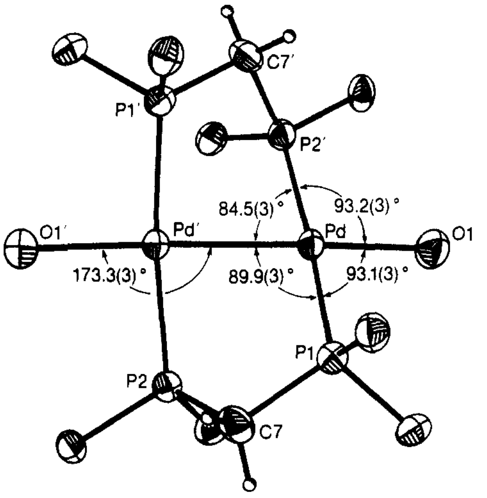


Figure 6. View of the Pd coordination sphere in 7 showing the "twist-boat" configuration.

stretching frequency (1660 cm^{-1}) is somewhat lower than typically found for monodentate trifluoroacetate complexes (1680–1720 cm^{-1}),[17,18] but this could arise from increased electron density on the low-valent metal center.[19] Since 7 is one of only a few complexes with a palladium(I)–oxygen bond,[20] an X-ray structure determination was performed. A suitable crystal of 7 was obtained by slow diffusion of CH_2Cl_2/hexane. Several views of the molecule are shown in Figures 5–7 with selected bond distances and angles in Tables IV and V. This is the first structure that contains an unsupported palladium(I)–oxygen bond.[21] The long distance between Pd and O(2) [3.101 (7) Å] equals the sum of the van der Waals radii (3.10 Å)[22] and rule out any bidentate interaction. The only other structure of a monodentate carboxylate of palladium is $Pd^{II}(COOCH_3)(OCOCH_3)(PPh_3)_2$ in which the Pd–O bond length equals 2.116 (3) Å.[23] The Pd–O bond in 7 [2.191 (4) Å] is longer, as expected from the larger radius of palladium(I) and the trans influence of the metal–metal bond.

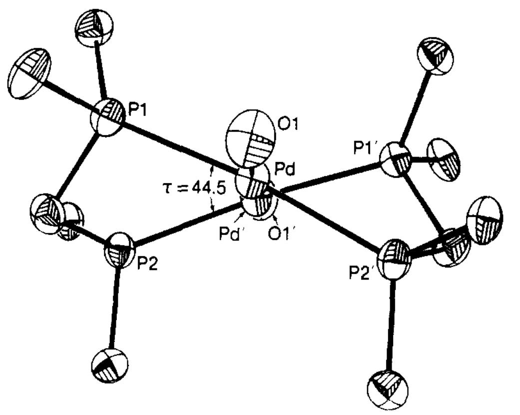
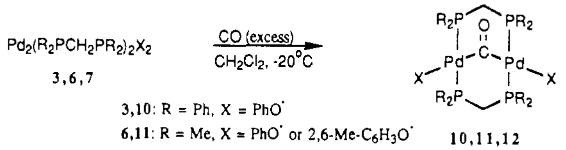


Figure 7. View of 7 along the twisted Pd–Pd axis.

An interesting feature of the structure is the cis orientation of the carboxylates and the "twist-boat" configuration of the palladium–phosphorus–carbon ring system (Figures 6 and 7). This gives the molecule overall C_2 symmetry. The 2-fold axis bisects the metal–metal bond and lies perpendicular to it. Structures of related dppm dimers normally display a "twist-chair" configuration in which the 2-fold axis lies along the metal–metal bond.[24] The importance of steric or crystal packing effects in imposing this difference is unknown. The twist along the Pd–Pd axis is due to antibonding interactions of filled metal d orbitals that are minimized when the torsion angle equals 45°.[25] The twisted conformation also allows the ligands to span a shorter metal–metal bond. The torsion angle in 7 (τ = 44.5°) is larger and the Pd–Pd bond [2.594 (2) Å] is shorter than in other dppm dimers [e.g. $Pd_2(dppm)_2Br_2$, 39° and 2.699 (5) Å; $Pd_2(dppm)_2(SnCl_3)Cl$, 41° and 2.644 (2) Å].[26] These differences may be due to the configuration of the $Pd_2P_4C_2$ ring in 7. Other bond lengths and angles in the structure are within normal ranges.

Reaction of the palladium bisphenoxides **3a**, **6a**, and **6c** with carbon monoxide was studied by ^{31}P and ^{13}C NMR spectroscopy. Conversion of **7** to **12**, which has been previously reported,[6] was included for comparison purposes. The reactions were run with excess CO in methylene chloride at low temperature (eq 6). As



(6)

3,10: R = Ph, X = PhO$^-$
6,11: R = Me, X = PhO$^-$ or 2,6-Me-$C_6H_3O^-$
7,12: R = Ph, X = $CF_3CO_2^-$

the reactions proceed, ^{31}P NMR spectroscopy shows the gradual disappearance of starting material with concurrent growth of a

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(17) Review of trifluoroacetate chemistry: Garner, C. D.; Hughes, B. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 2.

(18) (a) Garner, C. D.; Hughes, B. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 32. (b) Dobson, A.; Moore, D. S.; Robinson, S. D.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 611. (c) Dehand, J.; Mutet, C.; Pfeffer, M. *J. Organomet. Chem.* **1981**, *209*, 255. (d) Clark, H. C.; Goel, A. B.; Goel, S. *Inorg. Chem.* **1979**, *18*, 2803. (e) Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 2134. (f) Jack, T. R.; Powell, J. *Can. J. Chem.* **1975**, *53*, 2558. (g) Klabunde, K. J.; Low, J. Y. F.; Efner, H. F. *J. Am. Chem. Soc.* **1974**, *96*, 1984.

(19) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1974; pp 96–107.

(20) Other examples include the palladium phenoxides discussed in this paper and the palladium(I) tetramer $[Pd_4(CO)_4(OAc)_4]\cdot(AcOH)_2$, which contains bridging acetates: Moiseev, I. I.; Stromnova, T. A.; Vargaftig, M. N.; Mazo, G. J.; Kuzmina, L. G.; Struchov, Y. T. *J. Chem. Soc., Chem. Commun.* **1978**, 27.

(21) The tetramer $[Pd_4(CO)_4(OAc)_4]\cdot(AcOH)_2$, which contains bridging acetates was structurally characterized: Moiseev, I. I.; Stromnova, T. A.; Vargaftig, M. N.; Mazo, G. J.; Kuzmina, L. G.; Struchov, Y. T. *J. Chem. Soc., Chem. Commun.* **1978**, 27.

(22) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 442.

(23) Del Piero, G.; Cesari, M. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2411.

(24) (a) Olmstead, M. M.; Benner, L. S.; Hope, H.; Balch, A. L. *Inorg. Chim. Acta* **1979**, *32*, 193. (b) Manojlovic-Muir, L.; Muir, K. W.; Solomun, T. *J. Organomet. Chem.* **1979**, *179*, 479. (c) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Manojlovic-Muir, L.; Muir, K. W.; Solomun, T.; Seddon, K. R. *Inorg. Chim. Acta* **1977**, *23*, L33. (d) Holloway, G. R.; Penfold, B. R.; Colton, R.; McCormick, M. J. *J. Chem. Soc., Chem. Commun.* **1976**, 485.

(25) (a) Kullberg, M. L.; Lemke, F. R.; Powell, D. R.; Kubiak, C. P. *Inorg. Chem.* **1985**, *24*, 3589. (b) Manojlovic-Muir, L.; Muir, K. W.; Solomun, T. *J. Organomet. Chem.* **1979**, *179*, 479.

(26) (a) Olmstead, M. M.; Benner, L. S.; Hope, H.; Balch, A. L. *Inorg. Chim. Acta* **1979**, *32*, 193. (b) Holloway, R. G.; Penfold, B. R.; Colton, R.; McCormick, M. J. *J. Chem. Soc., Chem. Commun.* **1976**, 485.

new singlet. In each case the phosphorus resonance shifts downfield (by 26–31 ppm) and no intermediates are observed. Use of ^{13}CO produces a doublet in the ^{31}P spectrum (J_{PC} = 7 Hz). Carbon spectra show the terminal ligands, X, to be essentially unchanged. The bridging carbonyl (carbon-13 labeled) appears as a doublet between 226 and 251 ppm with J_{CP} = 6.4 Hz. The phosphine ligands display two methyl/phenyl resonances as expected for A-frame structures, and in each case the methylene carbon is significantly shifted upfield (14–17 ppm). The ^1H NMR spectrum for **11a** shows nonequivalent methylene protons that are shifted upfield. The results are consistent with single insertion of CO into the metal–metal bond to form the corresponding A-frame species.[27] No other carbon signals were observed in these products, which would indicate further incorporation of CO.[28]

The phenoxide complexes **10**, **11a**, and **11b** are not stable at room temperature. Solution IR spectra show a strong band near 1700 cm^{-1}, which is consistent with bridging CO, but additional bands are also present at higher frequency. These grow in time and are presumably from decomposition products. Phosphorus NMR spectroscopy shows that the decomposition proceeds to many products. The fate of phenoxide in these subsequent reactions has not been determined, however GC and GCMS do show the presence of phenol, diphenoxymethane, and in some cases small amounts of biaryl, which could arise from CO insertion into the Pd–O bond with subsequent extrusion of CO_2.[8]

Summary

Dinuclear palladium(I) phenoxides were formed by substitution of chloro or trifluoroacetate ligands. The compounds were isolated and characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Low-temperature carbon NMR spectroscopy indicates some association of free phenol with the complexes. The trifluoroacetate complex $Pd_2(dppm)_2(OCOCF_3)_2$ was synthesized and its solid-state structure determined. It exhibits unusual conformational features in the solid state and contains the first nonbridging palladium(I)–oxygen bond to be structurally characterized. These results add to the growing body of reports regarding electron-rich complexes with metal–oxygen bonds. Spectroscopic results suggest that the palladium phenoxide dimers follow precedent and insert CO into the metal–metal bond.

Experimental Section

General Considerations. All solvents were reagent grade (Aldrich, Baker, Burdick and Jackson, Mallinckrodt) and were used as received unless otherwise noted. Benzonitrile (99%, Aldrich), CO (Matheson), dibenzylideneacetone (99%, Aldrich), 2,6-dimethylphenol (99%, Aldrich), dmpm (Strem), dppm (Strem), 4-fluorophenol (99%, Aldrich), palladium acetate (Strem), palladium chloride (Strem), sodium acetate (99%, Aldrich), sodium chloride (reagent, Baker), and 4-*tert*-butylphenol (99%, Aldrich) were used as received. Phenol (reagent, Mallinckrodt) was dried by azeotropic distillation of a toluene solution followed by distillation of the phenol under N_2. ^1H NMR spectra were recorded on a GE QE 300 or Varian XL 200 spectrometer at 300 and 200 MHz, respectively. ^{31}P and ^{13}C NMR spectra were recorded on a Varian XL 300 spectrometer at 121 and 75 MHz, respectively. ^1H and ^{13}C data are reported in ppm vs Me_4Si (δ = 0.00) with solvent as internal standard. ^{31}P data are reported in ppm vs 85% H_3PO_4 (δ = 0.00) with trimethyl phosphite as external reference. IR spectra were recorded on a Perkin-Elmer Model 598 IR spectrometer. Field desorption mass spectral data were recorded on a Varian MAT 731 spectrometer. Elemental analyses were performed in-house or by Schwarzkopf Microanalytical Laboratory. Reactions were carried out in air unless otherwise noted. Those done in the absence of air were run on the bench top under dry N_2 by using standard Schlenk techniques or in a Vacuum Atmospheres glovebox under Ar. $Pd(NCPh)_2Cl_2$,[29] $Pd_2(dmpm)_2Cl_2$,[30] and $Pd_2(dppm)_2Cl_2$[31] were prepared as described in the literature. Synthesis of $Pd_2(dppm)_2Cl_2$ from $Pd(NCPh)_2Cl_2$, $Pd_2(dba)_3\cdot CHCl_3$, and dppm was found to be the preferred method (dba = dibenzylideneacetone). $Pd_2(dba)_3\cdot dba$ was prepared (95%) by employing the method reported for the diisopropyl complex, $Pd_2(dipdba)_3$ (dipdba = diisopropyldibenzylideneacetone).[32] The product was recrystallized from hot $CHCl_3/Et_2O$ to give $Pd_2(dba)_3\cdot CHCl_3$.

$[Pd(CO)Cl]_n$. The literature procedure[33] was modified by adding a small quantity of H_2O to facilitate reduction of palladium. This gave consistently higher yields. A 500-mL 3-neck flask was charged with 400 mL of $CHCl_3$ and 4 drops of H_2O dissolved in 2 mL of absolute ethanol. After the mixture was purged with N_2 for 30 min, $Pd(NCPh)_2Cl_2$ (1.92 g, 5 mmol) was added and CO bubbled through the solution for 16 h. The light yellow product was collected under N_2 and washed with benzene and petroleum ether. Yield: 0.78 g (92%). IR (KBr): 1970 cm^{-1} (vs).

$Pd_2(dppm)_2(OCOCF_3)_2$ (7).[6] $Pd(OAc)_2$ (0.270 g, 1.2 mmol) and dppm (0.462 g, 1.2 mmol) were dissolved in 20 mL of acetone under N_2. CF_3CO_2H (0.14 g, 1.2 mmol) was added and CO bubbled through the solution at room temperature for 14 h. The solution was filtered and evaporated to dryness, and the residue was left under vacuum for 1 h. The resulting red oil was dissolved in acetone and the product precipitated with toluene and hexane (0.380 g, 52%). Recrystallization from CH_2Cl_2/hexane yielded the compound as orange crystals. IR (KBr): 1660 cm^{-1} (vs, ν_{as}(carboxylate)). ^1H, ^{13}C, and ^{31}P NMR: see tables. The field desorption mass spectrum shows a weak signal for $Pd_2(dppm)_2(OCOCF_3)^+$ with a mass of 1094.6 amu. The parent ion was not observed. Anal. Calcd for $C_{54}H_{44}F_6O_4P_4Pd_2$: C, 53.71; H, 3.67. Found: C, 53.65; H, 3.80.

$Pd(dppm)(OCOCF_3)_2$ (8). **8** was isolated in low yield as an off-white crystalline solid from the filtrate after crystallization of **7**. NMR data compare well with reported values.[6] Anal. Calcd for $C_{29}H_{22}F_6O_4P_2Pd$: C, 48.59; H, 3.09. Found: C, 48.49; H, 3.14.

Sodium Phenoxide, Sodium 4-*tert*-Butylphenoxide, and Sodium 4-Fluorophenoxide. The same method was used for each. THF was dried over Na/benzophenone and distilled. Sodium was cut up under N_2 and washed with dry THF. An excess of Na (10 g, 0.435 mmol) and 300 mL of THF were placed in a 500-mL 3-neck flask fitted with addition funnel and reflux condensor. A THF solution containing dry phenol (20.0 g, 0.213 mol) was added dropwise to the Na/THF under a stream of N_2. After visible gas evolution stopped, the mixture was heated at reflux for 2 h. The excess sodium was removed by filtration under N_2 and the THF removed under vacuum. The resulting white powder was heated under vacuum for 16 h at 70 °C and stored under N_2.

Potassium Phenoxide and Potassium 2,6-Dimethylphenoxide. The same method was used for both. One equivalent of KOH (6.79 g, 0.121 mol) was dissolved in 15 mL of deaerated water, and the mixture was added to a solution of pure phenol (11.4 g, 0.121 mol) and dry THF (110 mL). After the mixture was stirred at room temperature under N_2 for 1 h, the THF and water were removed under vacuum while the mixture was heated at 90 °C. The resulting white solid was left under vacuum at room-temperature overnight, then ground to a powder with mortar and pestle, and further dried under vacuum with heat.

$Pd_2(dppm)_2(OPh)_2$ (3a). $Pd_2(dppm)_2Cl_2$ (210 mg, 0.20 mmol) and phenol (30 mg, 0.32 mmol) were dissolved in CH_2Cl_2 (25 mL). Sodium phenoxide (230 mg, 2.0 mmol) was added and the mixture stirred at room temperature for 15 min. The solution was filtered twice and evaporated to dryness under vacuum. The residue was left under vacuum for 0.5 h and then stirred vigorously with hexane for 1 h. This yielded the crude product as an orange powder (250 mg), which was collected, washed with hexane, and dried under vacuum. The ^{31}P NMR spectrum exhibits a single peak for the product down to −70 °C, but the low-temperature carbon NMR spectrum shows the presence of approximately 3 equiv of phenol in the product. IR (KBr): 1585 (s), 1475 (s), 1439 (m), 1275 (s), 750 (s), 520 (m) cm^{-1}. ^1H, ^{13}C, and ^{31}P NMR: see tables. Anal. Calcd for $C_{62}H_{54}O_2P_4Pd_2\cdot 3(C_6H_5OH)$: C, 66.26; H, 5.00. Found: C, 64.33; H, 4.68. We ascribe the low values for carbon and hydrogen analysis to contamination of the sample with small amounts of sodium chloride.

$Pd_2(dppm)_2(OC_6H_4\text{-}4\text{-}F)_2$ (3b). $Pd_2(dppm)_2Cl_2$ (210 mg, 0.20 mmol) and 4-fluorophenol (34 mg, 0.30 mmol) were dissolved in CH_2Cl_2 (25 mL). Sodium 4-fluorophenoxide (268 mg, 2.0 mmol) was added and the

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(27) For example, see: (a) Besenyei, G.; Lee, C.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1986**, 1750. (b) Kullberg, M. L.; Kubiak, C. P. *Organometallics* **1984**, *3*, 632. (c) Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1983**, 889. (d) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99. (e) Lee, C.; Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 2498. (f) Balch, A. L.; Benner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979**, *18*, 2996. (g) Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 6099.

(28) Kubiak sees evidence for further insertion of CO into the palladium–oxygen bonds of the dmpm complexes $Pd_2(dmpm)_2(OAr)_2$: Kubiak, C. P. Unpublished results. See also ref 8.

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Table VI. Data Collection and Refinement Information for 7

formula	$C_{54}H_{44}F_6O_4P_4Pd_2$	fw	1207.6
space group	$C2/c$	V, Å^3	5423 (8)
a, Å	15.870 (8)	ρ_{calcd}, g cm^{-3}	1.48
b, Å	17.212 (8)	Z	4
c, Å	20.364 (11)	no. of reflcns collcd	3865
α, deg	90.000 (0)	no. of obs reflcns [$F > 3\sigma(F)$]	3276
β, deg	102.88 (5)	R	0.0422
γ, deg	90.000 (0)	R_w	0.0749

mixture stirred at room temperature for 25 min. The product was isolated as described for **3a** and was obtained as a red powder (250 mg). A single peak is seen in the phosphorus NMR of the product, and low-temperature carbon NMR spectroscopy shows the presence of approximately 2 equiv of 4-fluorophenol. ^{13}C and ^{31}P NMR: see tables. Anal. Calcd for $C_{62}H_{52}O_2P_4Pd_2 \cdot 2(4\text{-}F\text{-}C_6H_4OH)$: C, 62.24; H, 4.38. Found: C, 61.00; H, 4.24.

$Pd_2(dppm)_2(OC_6H_4\text{-}4\text{-}{}^tBu)_2$ (3c). This material was made by the method described above for **3a,b** and was characterized in solution by ^{31}P NMR spectroscopy (see Table I). These reactions were typically accompanied by some decomposition. Therefore, isolation of **3c** was never pursued.

$Pd_2(dppm)_2(OAr)Cl$ (2a–c). These materials were generated in equilibrium with compounds **1** and **3**, by reaction of **1** with the appropriate sodium aryloxide, and were characterized by ^{31}P NMR spectroscopy (see Table I).

$Pd_2(dmpm)_2(OPh)_2$ (6a). $Pd_2(dmpm)_2Cl_2$ (150 mg, 0.27 mmol) was dissolved in 10 mL of dry CH_2Cl_2 (distilled from CaH_2) under N_2. Sodium phenoxide (313 mg, 2.7 mmol) was added and the mixture stirred at room temperature under N_2 for 20 min. The solution was filtered twice and concentrated, and dry pentane (from Na/benzophenone) was slowly added. The product precipitated as bright yellow crystals, which were collected and washed with pentane. A second crop was obtained but was of inferior quality and was kept separate. The crystalline material was solvated and lost its crystallinity upon drying. Yield: 110 mg (61%). A single peak is seen in the phosphorus NMR spectrum of the product, and low-temperature carbon NMR spectroscopy indicates the presence of approximately 0.2 equiv of phenol. IR (KBr): 1580 (s), 1470 (s), 1410 (m), 1295 (s), 930 (s), 755 (s), 700 (m), 560 (m) cm^{-1}. ^1H, ^{13}C, and ^{31}P NMR: see tables. Anal. Calcd for $C_{22}H_{38}O_2P_4Pd_2 \cdot 0.2(C_6H_5OH)$: C, 40.38; H, 5.73. Found: C, 39.54; H, 5.63.

$Pd_2(dmpm)_2(OC_6H_4\text{-}4\text{-}F)_2$ (6b). $Pd_2(dmpm)_2Cl_2$ (278 mg, 0.50 mmol) was dissolved in 15 mL of dry CH_2Cl_2 under N_2. Sodium 4-fluorophenoxide (670 mg, 5.0 mmol) was added and the mixture stirred under N_2 for 25 min at room temperature. The product was isolated as described for **6a** and was obtained as a mustard yellow powder. Yield: 260 mg (87%). The ^{31}P NMR spectrum exhibits a single peak, and carbon NMR spectroscopy shows the presence of approximately 0.5 equiv of 4-fluorophenol in the product. ^{13}C and ^{31}P NMR: see tables. Anal. Calcd for $C_{22}H_{36}O_2P_4F_2Pd_2 \cdot 0.5(C_6H_5OH)$: C, 39.34; H, 5.08. Found: C, 38.41; H, 4.90.

$Pd_2(dmpm)_2(OC_6H_3\text{-}2,6\text{-}Me)_2$ (6c). $Pd_2(dmpm)_2Cl_2$ (70 mg, 0.126 mmol) was dissolved in 4 mL of dry CH_2Cl_2 under N_2. Potassium 2,6-dimethylphenoxide (120 mg, 0.749 mmol) was added and the mixture stirred under N_2 for 20 min at room temperature. The product was isolated as described for **6a** and was obtained as a deep red-orange microcrystalline solid. Yield: 80 mg (87%). The product shows a single peak in the phosphorus NMR spectrum, and no appreciable 2,6-dimethylphenol is seen in the carbon NMR spectrum. IR (KBr): 1580 (m), 1450 (s), 1410 (s), 1280 (s), 930 (s), 850 (m), 750 (m), 515 (m) cm^{-1}. ^1H, ^{13}C, and ^{31}P NMR: see tables. Anal. Calcd for $C_{26}H_{46}O_2P_4Pd_2$: C, 42.94; H, 6.37. Found: C, 41.14; H, 6.03.

$Pd_2(dmpm)_2(\mu\text{-}{}^{13}CO)(OPh)_2$ (11a). $Pd_2(dmpm)_2(OPh)_2$ (35 mg, 0.05 mmol) was dissolved in CD_2Cl_2/CH_2Cl_2 (4 mL) and placed in a 5-mm screw-cap NMR tube fitted with a Teflon-lined septum. The solution was cooled to −78 °C and excess ^{13}CO (10 mL) added with a gastight syringe. The temperature was raised to −30 °C and the reaction monitored by ^{31}P NMR spectroscopy. Once phosphorus NMR spectroscopy indicated complete conversion, the product was characterized in solution by ^1H and ^{13}C NMR spectroscopy (see tables). The process was repeated with unlabeled CO for IR characterization. IR (CH_2Cl_2): 1705 (s) cm^{-1}.

$Pd_2(dppm)_2(\mu\text{-}{}^{13}CO)(OPh)_2$ (10), $Pd_2(dmpm)_2(\mu\text{-}{}^{13}CO)(OC_6H_3\text{-}2,6\text{-}Me)_2$ (11b), and $Pd_2(dppm)_2(\mu\text{-}{}^{13}CO)(CF_3CO_2)_2$ (12). These were made by the same method described for **11a** and were characterized in solution by NMR spectroscopy (see tables). IR (in CH_2Cl_2 with unlabeled CO) (cm^{-1}): **10**, 1695 (s); **11b**, 1700 (s); **12**, 1720 (br).

X-ray Data Collection and Structure Determination of 7. A suitable crystal of **7** (0.2 × 0.2 × 0.6 mm) was obtained from CH_2Cl_2/hexane. A summary of crystallographic data and refinement information is given in Table VI. All measurements were made on an automatic Nicolet P3F four-circle diffractometer with graphite-monochromatized Mo Kα radiation (0.71073 Å). The space group was $C2/c$ with monoclinic cell dimensions a = 15.870 (8) Å, b = 17.212 (8) Å, c = 20.364 (11) Å, and β = 102.88 (5)°. The dimensions were determined from a least-squares fit of 15 2θ measurements. Intensities were recorded in the ω–2θ scanning mode up to $2\theta = 45°$ with $h = 0$ to $+17$, $k = 0$ to $+18$, and $l = -21$ to $+21$ resulting in 3865 measured intensities. Background intensities were measured, and two standard reflections were recorded after every 50 measurements. The absorption coefficient was low (8.23 cm^{-1}), and no absorption correction was applied.

Data processing and crystallographic computations were made by using the SHELXTL programs.[34] After reduction of intensities to F values, rejection of structure factors less than $3\sigma(F)$, and averaging equivalent reflections, the number of structure factors was 3297. The structure was solved by direct methods. After atomic coordinates were assigned, the coordinates, temperature factors, and occupational parameters were refined by a least-squares fit of the function $\sum W(|F_o| - |F_c|)^2$, where the weighting function (W) was $1/[\sigma^2(F) + 0.00123F^2]$. This yielded residual indices of $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.0474$ and $R_w = [\sum W(|F_o| - |F_c|)^2/\sum W|F_o|^2]^{1/2} = 0.0918$. An additional 21 structure factors were rejected for which F_o and F_c were in poor agreement. The remaining 3276 structure factors were refined to convergence by using the weighting function $W = 1/[\sigma^2(F) + 0.0037F^2]$, which yielded residual indices of $R = 0.0422$ and $R_w = 0.0749$.

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Supplementary Material Available: A structure determination summary and tables of atomic coordinates, all bond lengths and bond angles, anisotropic temperature factors, and calculated hydrogen coordinates and isotropic thermal parameters (8 pages); a table of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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