Investigations of Benzyl and Aryl Palladium Complexes with Pendant Hydroxy Substituents and Their Transformation into Benzolactones on Carbonylation

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Reactions of 2-hydroxymethylbenzyl halides with $Pd(PPh_3)_4$ afford complexes $Pd(CH_2C_6H_4$-2-CH_2OH-$\kappa^2C^{1\alpha},O)(PPh_3)X$ (X = Br, **3**; X = Cl, **4**) containing bidentate 2-hydroxymethylbenzyl ligands. Further reactions of **3** or **4** with NaH produce the binuclear cyclocondensation product $Pd_2(\mu$-2-$OCH_2C_6H_4CH_2)_2(PPh_3)_2$, **7**, containing a central planar Pd_2O_2 unit incorporated into a system of five fused rings. Compound **7** undergoes phosphine substitution to form related binuclear products $Pd_2(\mu$-2-$OCH_2C_6H_4CH_2)_2(PAr_3)_2$ {Ar = *p*-MeC_6H_4, **8**; *p*-(MeO)-C_6H_4, **9**} but is cleaved by more electron-donating phosphines and by diphosphines to give mononuclear alkoxides $Pd(OCH_2C_6H_4CH_2$-$\kappa^2C^{1\alpha},O)(P-P)$ (P−P = dppf, **10**; dppe, **11**). Compounds **3**, **4**, and **7**−**9** react readily with carbon monoxide to liberate the lactone 3-isochromanone via carbonyl insertion, and the acyl intermediate $PdCl(COCH_2C_6H_4$-2-CH_2-$OH)(PPh_3)$, **12b**, has been studied spectroscopically. Reactions of 2-halogenobenzenealkanols with $Pd(PPh_3)_4$ afford simple derivatives with monodentate aryl ligands, *trans*-$Pd(C_6H_4$-2-$(CH_2)_nOH)(PPh_3)_2X$ (n = 1, X = Br, **15**; n = 2, X = I, **17**) and the known complex (n = 1, X = I, **14**), which on reaction with NaH are also converted into binuclear products $Pd_2(\mu$-2-$O(CH_2)_nC_6H_4)_2(PPh_3)_2$ {n = 1, **19a** (previously reported) and n = 2, **20**}; compound $Pd_2(\mu$-2-$OCH_2C_6H_4)_2\{P(C_6H_4$-4-$OMe)_3\}_2$, **25**, is formed from **19a** by phosphine exchange, and cleavage of **19a** or **20** by diphosphines generates new mononuclear complexes **22**−**24** containing chelating alkoxide ligands. Carbonylations of these arylpalladium derivatives of 2-hydroxyalkylphenyl halides to form the respective benzolactones, phthalide and 3,4-dihydroisocoumarin, have been investigated. Crystal structures of mononuclear compounds **3**, **4**, **14**, and **17**, including intermolecular H-bonding interactions to halogen ligands in the solid state, and of binuclear compounds **7**, **8**, and **25** are reported and discussed. The new complexes are discussed in relation to the mechanism of Pd(0)-catalyzed syntheses of benzolactones from aromatic halo alcohols; in production of 3-isochromanone, the results support a process involving coordination of a hydroxyl group prior to reductive elimination of organic product but with CO insertion into the Pd−C rather than the Pd−O bond.

1. Introduction

Palladium-catalyzed carbonylation is a convenient method for the synthesis of carboxylic acids and esters from organic halides and related substrates.[1] Using this procedure, lactones can be synthesized from organohalogen compounds with adjacent hydroxyl functions.[2] Thus, the benzolactone 3-isochromanone (1,4-dihydro-3*H*-2-benzopyran-3-one), **1**, of industrial interest as a precursor for various pharmaceuticals and plant protection agents, can be prepared from *ortho*-xylylene derivatives, including 2-hydroxymethylbenzyl halides **2**.[3] Catalysis normally requires the presence of an added base (or a basic medium[4]) to remove the hydrogen halide byproduct, and a likely mechanism[1,5] for the process is

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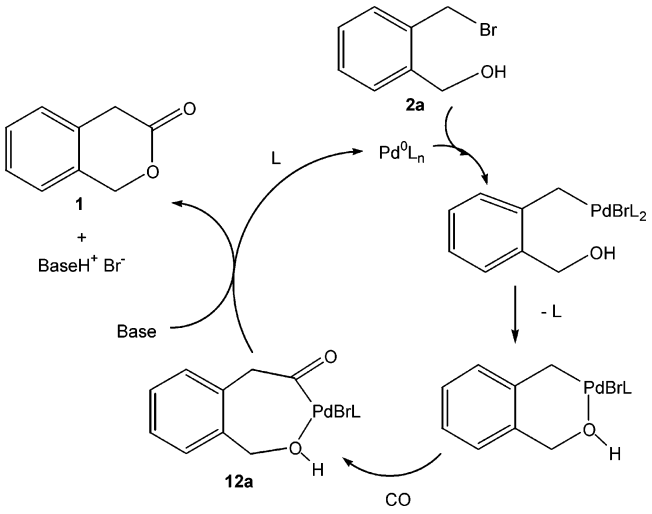
Scheme 1



illustrated in Scheme 1, although none of the steps in an active catalytic system has been directly verified for this substrate; moreover, coordination of the hydroxyl group before reductive elimination of the ester link (cf. refs 5b, 6) and the insertion of CO into the Pd−C rather than the Pd−O bond (cf. ref 7) have not been proven. The nature of the active Pd(0) species is also dependent on the precursor, which may be a Pd(II) compound; when tetrakis(triphenylphosphine)palladium is employed, PdL_n is probably $Pd(PPh_3)_2$.[8]

With the aim of elucidating the steps in the synthesis of 3-isochromanone and related benzolactones, we have undertaken a study of reactions of 2-hydroxymethylbenzyl and 2-hydroxyalkylphenyl halides with palladium(0) species to establish the structures and reactivity of intermediates in their cyclocarbonylation.

2. Results

2.1. Derivatives of 2-Hydroxymethylbenzyl Halides. The palladium-catalyzed reaction of carbon monoxide (1 atm) with 2-hydroxymethylbenzyl bromide **2a** is a route for the synthesis of 3-isochromanone with a reported yield of 71%, although in our hands, using $PdCl_2(PPh_3)_2$ activated by hydrazine as catalyst and K_2CO_3 as base in tetrahydrofuran according to the published procedure,[3] significantly lower conversions were obtained. However, with a catalytic system comprising $Pd(PPh_3)_4$ (2−5 mol %) and $NEt(i\text{-}Pr)_2$ as base, at 60 °C in toluene, we have achieved virtually quantitative conversion to the lactone within 2 h. To understand this process more fully, we therefore investigated reactions of $Pd(PPh_3)_4$ with 2-hydroxymethylbenzyl halides.

2.1.1. Synthesis of Palladium Compounds by Oxidative Addition. Solutions of equimolar amounts of 2-hydroxymethylbenzyl bromide **2a** and tetrakis(triphenylphosphine)palladium in toluene at room temperature produce an off-white precipitate, which can be recrystallized from dichloromethane−petroleum ether to afford pale yellow cubic crystals. This product was characterized as bromo[2-(hydroxymethyl-κO)benzyl-$\kappa C^{1\alpha}$]triphenylphosphinepalladium, **3**, on the basis of elemental analysis, spectroscopic studies, and X-ray diffraction (XRD). NMR spectroscopy supports the 1:1 stoichiometry of triphenylphosphine:hydroxymethylbenzyl ligands and indicates the presence of a unique isomeric species with a single $^{31}P\{^1H\}$ resonance at δ 42.6 ppm in $CDCl_3$ solution (δ 45.7 ppm in solid state); important ^1H resonances include a doublet at δ 2.70 ppm (J_{H-P} 2.5 Hz), assigned to the metal-bound methylene group, a singlet at δ 4.55 ppm from CH_2O, and a broad singlet assignable to the OH group at ca. δ 5.2−5.5 (variable) ppm. The $^{13}C\{^1H\}$ spectrum is also consistent with the formulation, with resonances assignable to $PdCH_2$ and $PdOCH_2$ groups at 32.5 and 64.2 ppm, respectively, in $CDCl_3$ (33.0 and 65.4 ppm in the solid state). The ESI+ mass spectrum (120 °C) does not include a molecular ion but exhibits peaks for binuclear ions $[2M - H_xBr]^+$ (x = 0, 1, 2) and mononuclear fragments, including $[M - H_xBr]^+$. Compound **3** is stable as a solid on exposure to air over many days at ambient temperatures and also stable in solution under an atmosphere of nitrogen, but solutions exposed to air for extended periods decompose, forming black deposits.

In a reaction similar to that described above, 2-hydroxymethylbenzyl chloride **2b** and tetrakis(triphenylphosphine)palladium afford the chlorine analogue chloro[2-(hydroxymethyl-κO)benzyl-$\kappa C^{1\alpha}$]triphenylphosphinepalladium, **4**, isolable as pale yellow crystals. This compound was also characterized by elemental analysis, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra in solution and solid state, and XRD. NMR spectral parameters for compound **4** are similar to those of **3**, providing evidence for one principal isomeric form (see Experimental Section). A broad resonance assignable to the hydroxyl hydrogen is observed in the ^1H NMR spectrum in $CDCl_3$ at variable shifts in the range δ 6−6.7 ppm, and the IR spectrum in Nujol includes a ν(OH) band at ca. 3200 cm^{-1}. The ESI+ mass spectrum shows only a very weak signal for the molecular ion but significant peaks for binuclear ions $[2M - H_xCl]^+$ and mononuclear fragments, including $[M - Cl]^+$.

2.1.2. Crystal Structures of Compounds 3 and 4. Single crystals of nonsolvated **3** and monosolvated **4**·CH_2Cl_2 were obtained by slow diffusion of petroleum ether into a solution of the respective compound in dichloromethane, and these were subjected to analysis by XRD. Figure 1 depicts the derived molecular structures, which are closely related, and selected bond lengths and angles are listed in Table 1.

The geometries around the Pd center are approximately square planar with the rms deviations from the mean plane of Pd and the four coordinating atoms (C, O, P, and halogen) being 0.0313 and 0.1125 Å for compounds **3** and **4**, respectively; angles P−Pd−halogen show the largest deviations from 90° {**3**: P(1)−Pd(1)−Br(1) = 99.44(10)°; **4**: P(1)−Pd(1)−Cl(1) = 100.24(3)°}, with other angles subtended at the metal between *cis* coordinating atoms lying in the range 86−88°. The 2-hydroxymethylbenzyl ligands are C−O chelating and form six-membered palladacycles with boatlike conformations. The isomer obtained, in both cases, contains phosphine *trans* to the hydroxyl group: this places the

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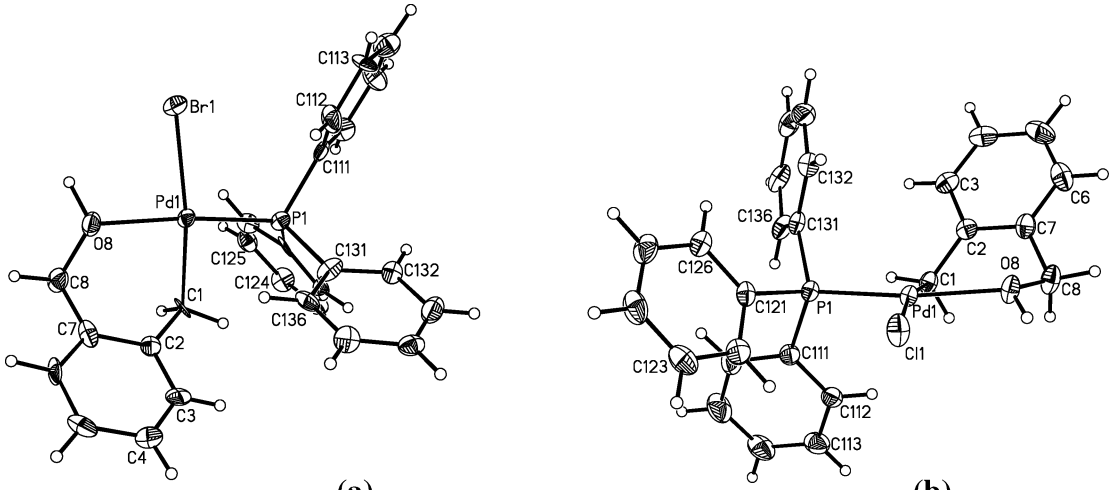

Figure 1. Molecular structures of (a) compound **3**; (b) compound **4** (ellipsoids drawn at the 50% probability level).

Table 1. Selected Bond Lengths [Å] and Angles [deg] of Compounds 3 and 4

	3	**4**
Pd(1)−C(1)	2.067(13)	2.057(3)
Pd(1)−O(8)	2.123(9)	2.1521(18)
Pd(1)−P(1)	2.194(3)	2.2103(7)
Pd(1)−Halogen(1)	2.5056(18)	2.4082(7)
C(1)−C(2)	1.49(2)	1.484(4)
C(2)−C(7)	1.41(2)	1.406(4)
C(7)−C(8)	1.53(2)	1.505(4)
C(8)−O(8)	1.454(19)	1.454(3)
C(1)−Pd(1)−O(8)	86.6(5)	86.66(9)
C(1)−Pd(1)−P(1)	87.7(4)	86.95(8)
O(8)−Pd(1)−P(1)	174.0(3)	171.56(6)
C(1)−Pd(1)−Halogen(1)	171.7(4)	169.44(8)
O(8)−Pd(1)−Halogen(1)	86.2(3)	86.86(5)
P(1)−Pd(1)−Halogen(1)	99.44(10)	100.24(3)
C(2)−C(1)−Pd(1)	110.5(9)	108.84(17
C(8)−O(8)−Pd(1)	122.4(8)	121.22(15)
O(8)−C(8)−C(7)	107.8(12)	108.0(2)

monodentate ligand with the stronger *trans*-influence (PPh_3) opposite the weaker O-donor of the chelate; Pd−P bonds {2.194(3) and 2.2103(7) Å} and Pd−O bonds (2.123(9) and 2.1521(18) Å) are both slightly shorter in compound **3** than in compound **4**. In contrast, the Pd−C bond lengths are virtually the same {2.067(13) and 2.057(3) Å}, although the marginally longer bond in **3** may relate to the larger *trans*-influence of Br compared to Cl. The *ortho*-phenylene planes of the chelating ligands lie at angles of 53.1(4)° and 51.58(8)° to the palladium coordination planes in compounds **3** and **4**, respectively.

There are intermolecular hydrogen-bonding interactions between the coordinated hydroxyl groups and halogen ligands in both compounds **3** and **4**. In compound **3**, the H-bonds to Br have distances H···Br = 2.40 Å and O···Br = 3.232(10) Å and angle O−H···Br = 168.9° and generate a linked chain of complexes with alternating orientations, as illustrated in Figure 2.

In the solvated crystals of compound **4**, there are no significant interactions between the incorporated CH_2Cl_2 and the palladium complexes, but a discrete centrosymmetric binuclear entity is created by dual hydrogen bonds between hydroxyl groups and chlorine ligands on adjacent complexes; see Figure 3, with distances H···Cl = 2.20 Å and O···Cl = 3.016(2) Å and angle O−H···Cl = 164.8°.

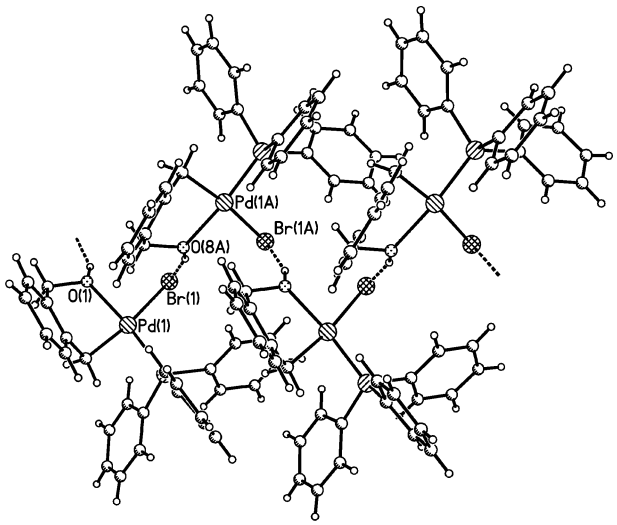

Figure 2. Hydrogen-bonding network in the lattice of compound **3**.

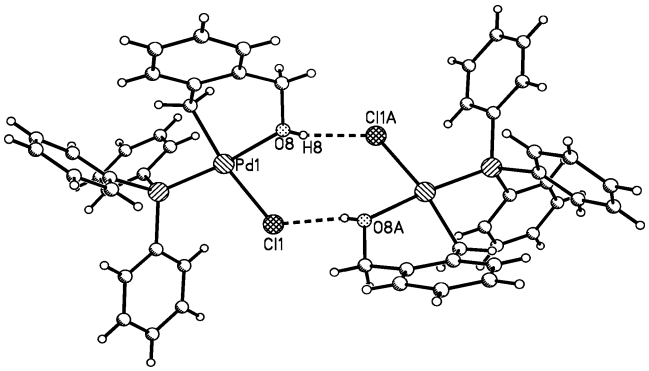

Figure 3. Hydrogen bonding between adjacent molecules of compound **4** in the crystal.

Few examples of palladium alcohol complexes have been structurally characterized, but it is of interest to compare the structure of the reported ionic species [Pd{(2-$HOCH_2CH_2$-κO)C_6H_4-κC^1}(tmeda)]NO_3, **5**, which contains a six-membered chelate ring formed by an arylalcohol ligand and also a bidentate dinitrogen ligand.[9] In compound **5** there is hydrogen-bonding between the

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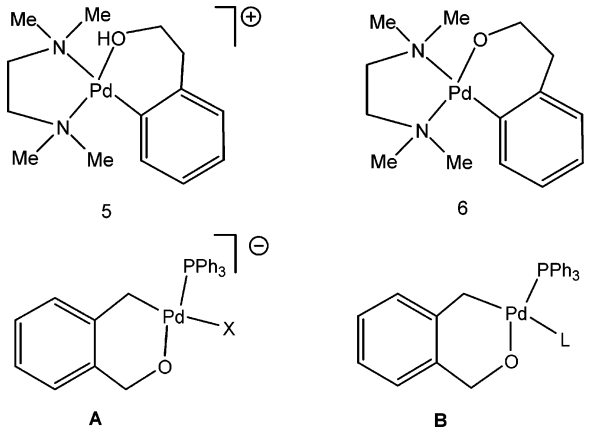
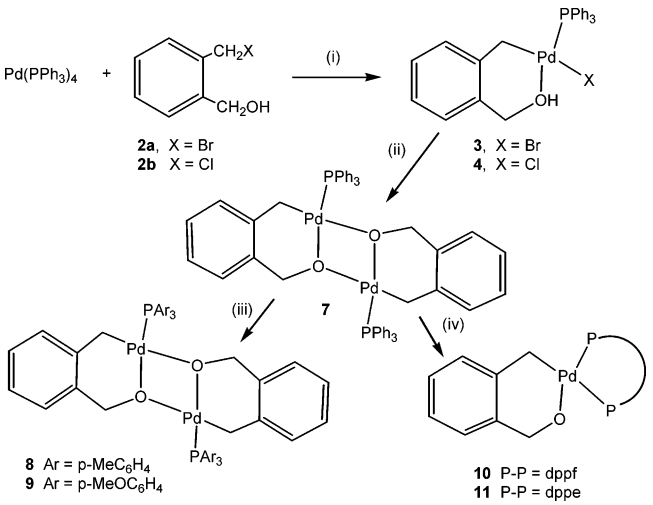
hydroxyl group of the cation and the nitrate anion but no intermolecular interactions. Also, the Pd−O distance of 2.076(4) Å is shorter than those of compounds **3** and **4**, reflecting the positive charge on the ionic complex and the weaker N-donor *trans* ligand.

2.1.3. Deprotonation of Compounds 3 and 4: Formation and Reactions of Binuclear Compound 7. The hydroxyl group in the cationic complex **5** is reported to be weakly acidic, and deprotonation with potassium methoxide forms the neutral alkoxide [Pd{(2-OCH_2CH_2-κO)C_6H_4-κC^1}(tmeda)], **6**, which is stable in the solid state but decomposes slowly in solution.[9] It was also reported that reaction of **5** with pyridine leads to displacement of the coordinated alcohol ligand rather than formation of the alkoxide.[9]



By analogy, simple deprotonation of complex **3** or **4** might produce a chelating benzyl-alkoxide ligand in an anionic complex **A** or, if accompanied by loss of halide in the presence of a 2e-ligand L, may lead to a neutral complex **B**: however, equimolar mixtures of **3** or **4** with noncoordinating bases 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,8-bis(dimethylamino)naphthalene ("Proton sponge") or with ethyldiisopropylamine (the base employed in our catalytic system), in the absence or presence of excess triphenylphosphine, were investigated, but no reaction was observed and only unreacted substrates could be detected and isolated. On the other hand, reaction of **3** or **4** with 1 equiv of sodium hydride occurred readily in the presence of free triphenylphosphine to form the new binuclear complex bis[2-(μ-oxomethyl-κO)benzyl-$\kappa C^{1\alpha}$]bis(triphenylphosphine)-dipalladium, **7**, in ca. 77% isolable yield, by deprotonation and displacement of halide by a bridging alkoxy group (Scheme 2). In the absence of triphenylphosphine, yields of this compound were lower and variable and, although not incorporated in the final product, addition of ca. 1.1 molar equiv of PPh_3 was found to be important for the good yield and reproducibility of this cyclocondensation. Compound **7** was characterized by elemental analysis, spectroscopy, and XRD. The ^{1}H NMR spectrum confirms the 1:1 stoichiometry of phosphine:oxomethylbenzyl ligands and includes resonances at δ 2.36 and 3.34 ppm for $PdCH_2$ and μ-OCH_2 groups, respectively, the latter shifted by over 1 ppm to high field from the hydroxymethyl resonances of the mononuclear precursors (**3**, **4**); also, respective ^{13}C resonances for these methylene groups at δ 25.6 and 68.2 ppm in compound **7** are both significantly shifted from the resonances of

Scheme 2[a]



[a] Reagents and conditions: (i) toluene, RT, 12 h; (ii) NaH, PPh_3, THF, RT, 12 h; (iii) PAr3, toluene, RT, 12 h; (iv) diphosphine (P-P), toluene, RT, 3 h.

compounds **3** and **4**. A singlet resonance at δ 39.7 ppm in the ^{31}P NMR spectrum indicated the presence of only one phosphorus environment, and no changes were observed in the ^{1}H and ^{31}P NMR spectra over the temperature range 25−60 °C. The ESI+ mass spectrum includes a significant peak with $m/z = 999$, assignable to binuclear product **7** as an adduct with Na^+, $[M + Na]^+$. Air-stable solid **7** is insoluble and unreactive to water, used to remove NaCl byproduct; crystallization generally produced solvated materials including water or dichloromethane molecules as shown by elemental and XRD analyses (vide infra).

Compound **7** did not react with excess triphenylphosphine, as evinced from its preparation in the presence of an excess of this ligand, and, similarly, no reaction was observed in solutions at ambient temperature with the sterically demanding ligands trimesitylphosphine or tris(2-methylphenyl)phosphine. However, tris(4-methylphenyl)phosphine and tris(4-methoxyphenyl)phosphine react in toluene with **7**, causing substitution of phosphine ligands to form the new binuclear products $[Pd\{(\mu\text{-}2\text{-}OCH_2\text{-}\kappa O)C_6H_4CH_2\text{-}\kappa C^{1\alpha}\}(PAr_3)]_2$, **8**, Ar = 4-$MeC_6H_4$; **9**, Ar = 4-$MeOC_6H_4$, isolable in good yields. Compounds **8** and **9** were fully characterized by elemental analysis and spectroscopic studies and show little variation in NMR parameters of the bridging organic ligand from those of the closely related parent compound **7**; compound **8** was also subjected to structural analysis by XRD (vide infra). Neither $P(C_6H_4\text{-}4\text{-}Me)_3$ nor $P(C_6H_4\text{-}4\text{-}OMe)_3$ cleave the alkoxy bridge. The more electron-rich, monodentate ligands PMe_3 and PMe_2Ph react to a greater extent with compound **7**, and, although the final products were unstable and incompletely characterized, it appears that cleavage of the binuclear structure does occur.

Alkoxy-bridge cleavage was clearly established in the reactions of compound **7** with the bidentate diphosphine ligands 1,1′-bis(diphenylphosphino)ferrocene (dppf) and 1,2-bis(diphenylphosphino)ethane (dppe), from which the mononuclear products Pd{(2-OCH_2-κO)$C_6H_4CH_2$-$\kappa C^{1\alpha}$}(dppf), **10**, and Pd{(2-OCH_2-κO)$C_6H_4CH_2$-$\kappa C^{1\alpha}$}-(dppe), **11**, were isolated; see Scheme 2. These compounds were characterized as solvated crystalline solids

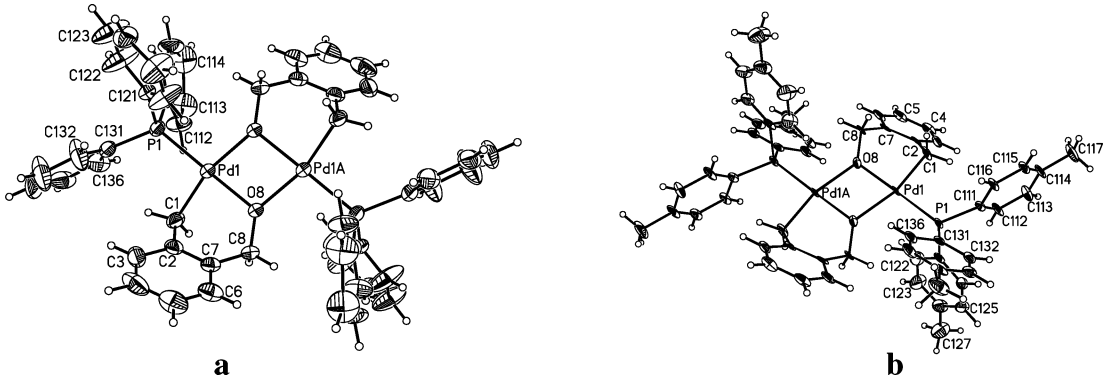


Figure 4. Molecular structures of (a) compound **7** (ellipsoids drawn at the 40% probability level); (b) compound **8** (ellipsoids drawn at the 50% probability level).

Table 2. Selected Bond Lengths [Å] and Angles [deg] of Compounds 7 and 8

	7	**8**
Pd(1)−C(1)	2.034(6)	2.064(11)
Pd(1)−O(8)	2.082(4)	2.044(7)
Pd(1)−O(8)A	2.128(4)	2.146(7)
Pd(1)−P(1)	2.2283(15)	2.227(3)
C(1)−C(2)	1.472(9)	1.457(16)
C(2)−C(7)	1.398(9)	1.425(16)
C(7)−C(8)	1.505(9)	1.493(17)
C(8)−O(8)	1.402(7)	1.420(12)
C(1)−Pd(1)−O(8)	87.1(2)	89.7(4)
C(1)−Pd(1)−O(8)A	164.4(2)	165.2(4)
O(8)−Pd(1)−O(8)A	77.30(16)	75.6(3)
C(1)−Pd(1)−P(1)	93.99(18)	91.0(3)
O(8)−Pd(1)−P(1)	178.45(13)	178.3(2)
O(8)A−Pd(1)−P(1)	101.58(11)	103.8(2)
Pd(1)−O(8)−Pd(1)A	102.70(16)	104.4(3)
C(2)−C(1)−Pd(1)	104.8(4)	108.6(7)
C(7)−C(2)−C(1)	119.4(6)	122.1(11)
C(2)−C(7)−C(8)	119.1(5)	117.9(9)
O(8)−C(8)−C(7)	111.2(5)	109.3(9)
C(8)−O(8)−Pd(1)	121.4(3)	121.2(6)
C(8)−O(8)−Pd(1)A	134.2(4)	133.5(6)

by elemental analysis, by ESI+ mass spectra, which gave molecular ions, and by NMR spectra. Two doublets are present in the $^{31}P\{^1H\}$ NMR spectra, assignable to the two, mutually coupled, inequivalent *cis* P-nuclei of the chelating diphosphine ligands, and the ^1H NMR spectra show resonances with appropriate shifts and relative intensities assignable to the bidentate oxomethylbenzyl and diphosphine entities. Solutions of both compounds **10** and **11** in chlorinated solvents decompose over several hours so that crystals suitable for analysis by XRD could not be grown. Attempts to react compound **7** with the bidentate nitrogen ligands *N,N,N′,N′*-tetramethyl-1,2-ethanediamine (tmeda) and 1,10-phenathroline (phen) at temperatures between 20 and 50 °C were unsuccessful, leading only to recovery of starting materials.

2.1.4. Crystal Structures of Compounds 7 and 8. Solvated single crystals **7**·CH_2Cl_2 and **8**·CH_2Cl_2 were obtained from dichloromethane/petroleum ether and subjected to analysis by XRD.

Discrete binuclear molecules of **7** and **8** were identified, as depicted in Figure 4, with negligible interaction between the complexes and dichloromethane. Selected geometrical parameters are listed in Table 2. Both compounds have related centrosymmetric structures, comprising a central planar rhomboid, PdOPdO, with Pd−O distances 2.082(4) and 2.128(4) Å in complex **7,** and 2.044(7) and 2.146(7) Å in complex **8**; the Pd−O bond *trans* to phosphine is longer in compound **7**, containing PPh_3, whereas the other Pd−O bond is marginally shorter. Each bridging alkoxy arm is part of a boat-shaped, six-membered ring which chelates a Pd(II) center with a Pd−C distance of 2.034(6) Å in **7** and 2.064(11) Å in **8**. The coordination sphere around Pd is completed by a phosphine ligand with virtually identical Pd−P bond lengths in both compounds: 2.2283(15) Å in **7** and 2.227(3) Å in **8**. The geometry around each Pd atom is distorted square-planar with the four angles varying in the range 75−104°, the largest being P(1)−Pd−O(8)A {101.58(11)° in **7**; 103.8(2)° in **8**}, but the sum of the angles around each Pd is 359.97° in **7** and 360.1° in **8**, indicating near planarity of the coordination sphere; this planarity essentially extends over the eight central atoms, $Pd_2O_2P_2C_2$. The *ortho*-xylylene units are also planar, and the angles of these aromatic planes to the coordination plane are 67.06(15)° and 53.6(4)° in **7** and **8**, respectively. Overall the five fused rings form an extended chairlike arrangement, shown in Figure 5.

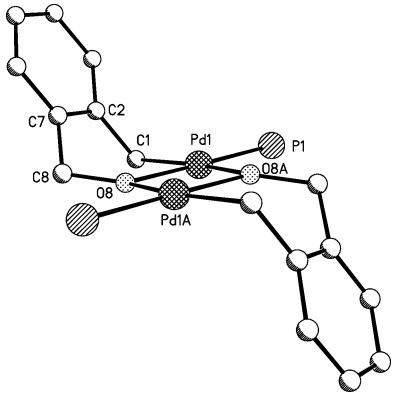


Figure 5. Structure around the five fused rings at the center of compound **7**.

The structures of **7** and **8** are related to that of the reported[10] aryl-alkoxy derivative [Pd{(μ-2-OCH_2-κO)-C_6H_4-κC^1}(PPh_3)]$_2$, **17a**, which contains five-membered C−O chelate rings and is discussed below. Diaryloxy-bridged organopalladium dimers have been reported by Hartwig and co-workers:[11] the structurally character-

(10) Fernández-Rivas, C.; Cárdenas, D. J.; Martin-Matute, B.; Monge, A.; Gutiérrez-Puebla, E.; Echavarren, A. M. *Organometallics* **2001**, *20*, 2998.

(11) Mann, G.; Shelby, Q.; Roy, A. H.; Hartwig, J. F. *Organometallics* **2003**, *22*, 2775. Mann, G.; Incarvito, C.; Rheingold, A. L.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 3224.

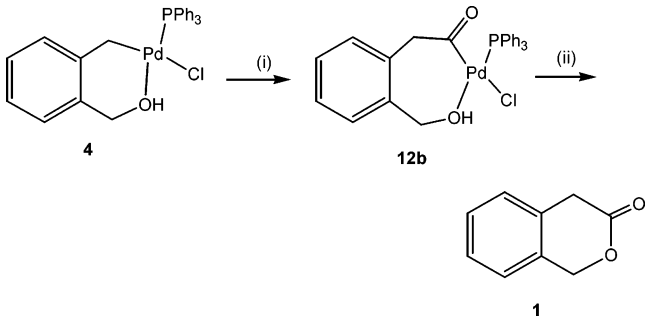
ized di-*tert*-butylferrocenylphosphine derivative [Pd(μ-OC_6H_4-4-OMe)(C_6H_4-4-Me){PBu^t_2(Fc)}]$_2$ contains two planar, four-coordinate Pd centers with large P−Pd−O angles of 102.9°, comparable to those in **7** and **8**, but the central Pd_2O_2 ring adopts a nonplanar, puckered geometry.[11]

2.1.5. Carbonylation of Palladium Complexes Derived from 2-Hydroxymethylbenzyl Halides. Carbon monoxide at atmospheric pressure reacts over 0.5−2 h with mononuclear compounds **3** and **4** or binuclear **7** in tetrahydrofuran to give intense yellow-orange colored solutions from which 3-isochromanone can be isolated in high yields, accompanied by palladium residues which rapidly turn black in the solid state. Therefore, the palladacycles in these complexes must form insertion products with CO (cf. Scheme 1) but, even under these mild conditions, undergo facile subsequent reductive elimination of lactone. On the other hand, the mononuclear diphosphine complexes with the deprotonated 2-oxomethylbenzyl ligands, **10** and **11**, failed to react with CO under the same experimental conditions.

The nature of the insertion product in the above reaction of complex **4** with CO was subjected to further investigation. After 20 min, the reaction mixture was rapidly cooled to −78 °C and palladium-containing products present were collected after precipitation by addition of petroleum ether. The IR spectrum of the resulting yellow solid included a strong band at 1707 cm^{-1} (KBr disk) assignable to a carbonyl function; reported vibrational frequencies of the acyl group in phenylacetyl complexes Pd($COCH_2C_6H_5$)X(PPh_3)$_2$ are 1670 cm^{-1} (X = Cl in CD_2Cl_2)[12] and 1696 cm^{-1} (X = Br in Nujol).[13] Monitoring the IR spectra of solutions of the yellow product in CH_2Cl_2 showed that this band (1709 cm^{-1}) completely decayed over 20−30 min at ambient temperature with the concomitant growth of a band at 1750 cm^{-1} from 3-isochromanone. This instability of the insertion product in solution prevented the isolation of analytically pure samples or the growth of crystals suitable for XRD. However, NMR studies on freshly prepared solutions were informative: a ^{31}P resonance occurred at δ27.4 ppm, shifted 14 ppm to low frequency of that in complex **4**; the ^{1}H NMR spectrum included resonances at δ 4.16 and 4.01 ppm assignable to hydrogen nuclei of the two *ortho*-methylene groups, both significantly shifted from resonances expected for a $PdCH_2$ system and consistent with the presence of PdO(H)CH_2 and $PdCOCH_2$ groupings {cf. $PdCOCH_2$: δ 3.4 ppm in Pd($COCH_2C_6H_5$)Cl(PPh_3)$_2$;[12] δ 3.9 ppm in Pd($COCH_2C_6H_5$)Cl(PEt_3)$_2$[14]}. This evidence supports the formation of acyl complex Pd{(2-$HOCH_2$-κO)$C_6H_4CH_2$CO}Cl(PPh_3), **12b**, by insertion of CO into the Pd−C rather than the Pd−O bond (Scheme 3). The EI mass spectrum of **12b** showed a peak at m/z = 551, $[M - 1]^+$.

2.2. Derivatives of 2-Halogenobenzenealkanols. For comparison with the studies of benzylpalladium compounds derived from 2-hydroxymethylbenzyl halides **2**, we have investigated the properties of related arylpalladium compounds derived from 2-halogenobenzenemethanol and -ethanol.

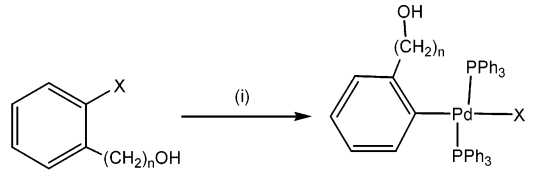
Scheme 3[a]



4 **12b** **1**

[a] Reagents and conditions: (i) CO (1 atm), THF, RT, 20 min; (ii) THF, RT, <26 min.

Scheme 4[a]



13a n = 1, X = I
13b n = 1, X = Br
16 n = 2, X = I

14 n = 1, X = I (see ref.10)
15 n = 1, X = Br
17 n = 2, X = I

[a] Reagents and conditions: (i) Pd(PPh_3)$_4$, toluene; (a) X = I, RT, 12 h; (b) X = Br, 70 °C, 48 h.

2.2.1. Products of Oxidative Addition to Pd(0). Echavarren and co-workers[10] have reported that 2-iodobenzenemethanol **13a** reacts with tetrakis(triphenylphosphine)palladium at 40 °C to form *trans*-[2-(hydroxymethyl)phenyl]iodobis(triphenylphosphine)-palladium, **14**, in good yield: in addition to **14**, we have also obtained the bromo analogue, PdBr(C_6H_4-2-CH_2OH)(PPh_3)$_2$, **15**, by reaction of 2-bromobenzenemethanol **13b** and Pd(PPh_3)$_4$ at 70 °C. Similarly (see Scheme 4), we found that 2-iodobenzeneethanol **16** adds oxidatively to Pd(PPh_3)$_4$ at ambient temperature to form *trans*-Pd(C_6H_4-2-CH_2CH_2OH)I(PPh_3)$_2$, **17**, but that the corresponding reaction of 2-bromobenzeneethanol with Pd(PPh_3)$_4$ requires temperatures > 80 °C and under these conditions decomposition of the initial product occurs so that it was not possible to obtain pure samples of the bromo analogue, *trans*-PdBr(C_6H_4-2-CH_2CH_2OH)(PPh_3)$_2$. The new compounds have been characterized by elemental analyses and by NMR and mass spectra, with **15** showing closely similar NMR parameters to those reported[10] for compound **14**. Related products, described in the literature, include the structurally characterized PdBr(C_6H_4-2-CH_2CH_2OH)(tmeda), **18,** containing a chelating diamine ligand,[9] and a complex with a longer side-chain alcohol, PdBr(C_6H_4-2-$CH_2CH_2CMe_2$-OH)(dppf),[15] containing a chelating diphosphine, but both compounds have a *cis* arrangement of aryl and bromide ligands. Products **14**, **15**, and **17** contain Pd−aryl bonds and, as confirmed by crystal structure determinations of **14** and **17**, possess uncoordinated hydroxyl groups; five- or six-membered C−O chelate systems are not formed by displacement of a phosphine ligand, in contrast to the facile formation of oxapalladacycles in the benzylpalladium derivatives **3** and **4** under similar or milder reaction conditions.

(12) Gaviño, R.; Pellegrini, S.; Castanet, Y.; Mortreux, A.; Mentré, O. *Appl. Catal. A* **2001**, *217*, 91.
(13) Kudo, K.; Sato, M.; Hidai, M.; Uchida, Y. *Bull. Chem. Soc. Jap.* **1973**, *46*, 2820.
(14) Becker, Y.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 838.
(15) (a) Palucki, M.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 10333. (b) Widenhoefer, R. A.; Zhong, H. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6787.

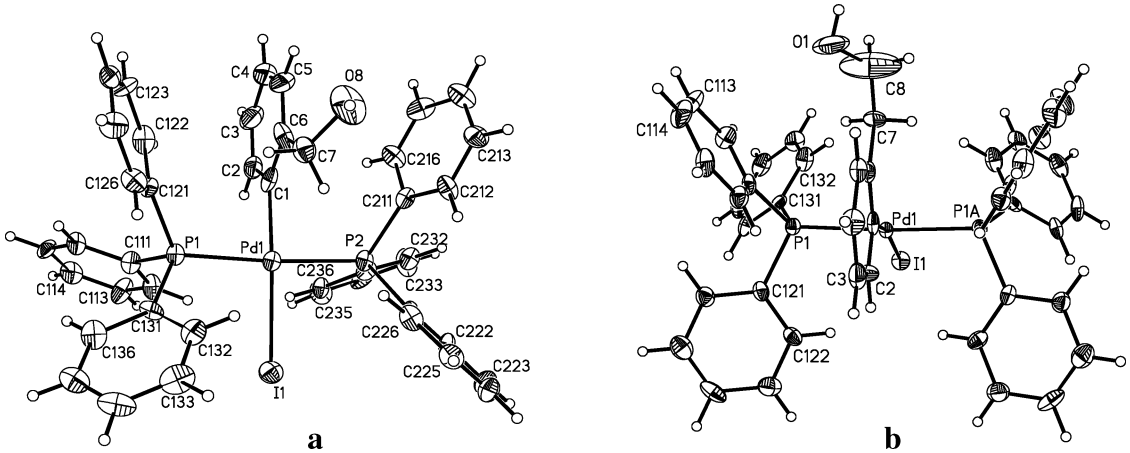


Figure 6. Molecular structures of (a) compound **14**; (b) compound **17** (ellipsoids drawn at the 50% probability level).

Table 3. Selected Bond Lengths [Å] and Angles [deg] of Compounds 14 and 17

	14	**17**
Pd(1)−C(1)	2.030(11)	2.007(11)
Pd(1)−P(2)	2.330(3)	2.3355(19)
Pd(1)−P(1)	2.336(3)	2.3355(19)
Pd(1)−I(1)	2.6900(12)	2.7067(11)
C(1)−C(6)	1.385(15)	1.391(16)
C(1)−C(2)	1.452(14)	1.386(16)
C(6)−C(7)	1.448(15)	1.518(15)
C(7)−C(8)	-	1.40(2)
C(7)−O(8)	1.486(13)	-
C(8)−O(1)	-	1.323(12)
C(1)−Pd(1)−P(2)	88.1(3)	87.61(5)
C(1)−Pd(1)−P(1)	87.8(3)	87.61(5)
P(2)−Pd(1)−P(1)	175.84(10)	174.39(11)
C(1)−Pd(1)−I(1)	167.1(3)	167.0(3)
P(2)−Pd(1)−I(1)	90.11(7)	92.66(5)
P(1)−Pd(1)−I(1)	94.03(7)	92.66(5)
C(2)−C(1)−Pd(1)	116.0(8)	116.9(9)
C(6)−C(1)−Pd(1)	124.3(8)	124.5(9)
C(1)−C(6)−C(7)	118.3(11)	118.9(10)
C(6)−C(7)−O(8)	112.5(9)	−
C(6)−C(7)−C(8)	-	119.9(12)
C(7)−C(8)−O(1)	-	128.5(13)

2.2.2. Crystal Structures of Compounds 14 and 17. Solvated crystals **14**·CH_2Cl_2 and **17**·$2CH_2Cl_2$, obtained from solutions in dichloromethane/petroleum ether, were subjected to analysis by XRD. Derived structures and atomic numbering of individual molecules are shown in Figure 6, and Table 3 lists important geometrical parameters.[16]

Molecules **14** and **17** are *trans* square planar, with planarity being supported by the sum of the four angles, 360.0° and 360.54°, respectively, but with angles P−Pd−I > 90° and angles C−Pd−P < 90°. Unlike **14**, the molecular structure of **17** includes a mirror plane, containing the *ortho*-phenylene ring, which bisects the P−Pd−P angle, with the OH group lying just off this plane, resulting in 50% disorder. Pd−P, Pd−I, and Pd−C bond lengths are similar in both complexes. The Pd−C(aryl) bonds are shorter than the Pd−C(benzyl) bonds of complexes **3** and **4**, and the two *trans*-Pd−P bonds in **14** and **17** are longer than the Pd−P bonds *trans* to OH in the chelated complexes. In **14** or **17**, respectively, the aromatic rings lie approximately {85.8-(3)°}or precisely perpendicular to the coordination plane; the hydroxyl groups point away from the palladium center and do not interact with the metal. In **14**, the hydrogen atom of the hydroxyl group could not be located from the X-ray data, but there is a close contact between this oxygen and the C(5)−H(5) unit of the aryl ligand {O···C(5) 2.863(17) Å; O···H(5) 2.56 Å; angle O−H(5)−C(5) 98.7°}; there are no significant interactions between the OH group and atoms on neighboring molecules, with the separation O···I being >5 Å. In contrast, the terminal hydroxyl group on the longer side-chain of **17** shows evidence for intermolecular hydrogen bonding to an iodide ligand on an adjacent molecule {H···I 2.72 Å, O···I 3.493(13) Å, angle O−H···I 153.3°} to form a linked chain; see Figure 7: it may be noted that *intramolecular* hydrogen bonding has been reported between OH and Br in PdBr(C_6H_4-2-CH_2CH_2-OH)(tmeda), **18**.[9] The crystal structures of complexes **14** and **17** present no clear explanation for the relatively high field ^{1}H NMR shift (δ ∼0 ppm) of the hydroxyl groups, but these are surrounded by phenyl rings of the triphenylphosphine ligands and could be magnetically shielded by these ligands in solution.

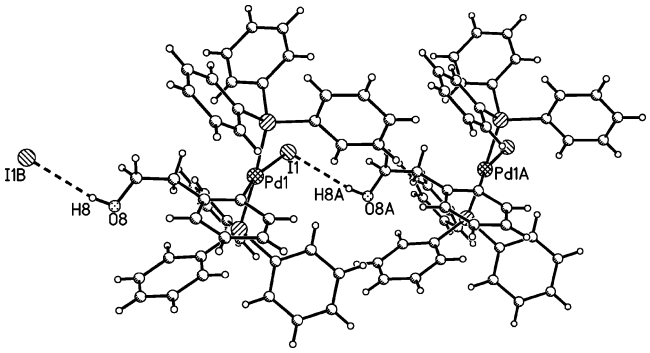
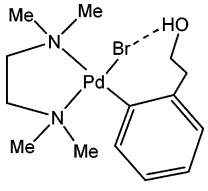


Figure 7. Hydrogen-bonding network in the lattice of compound **17**.



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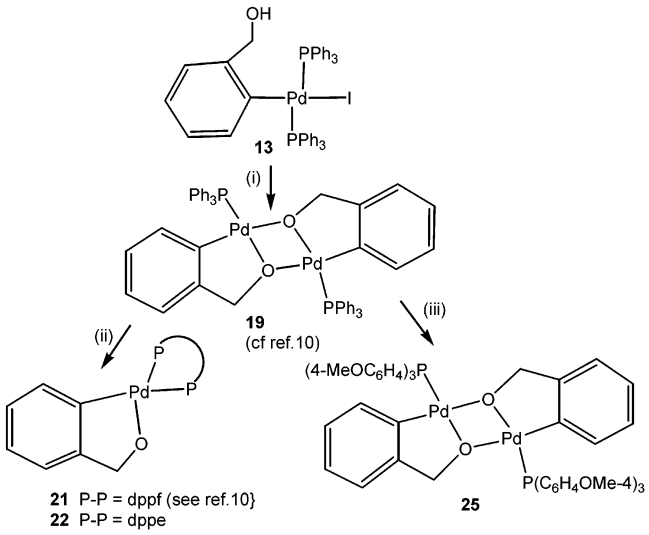
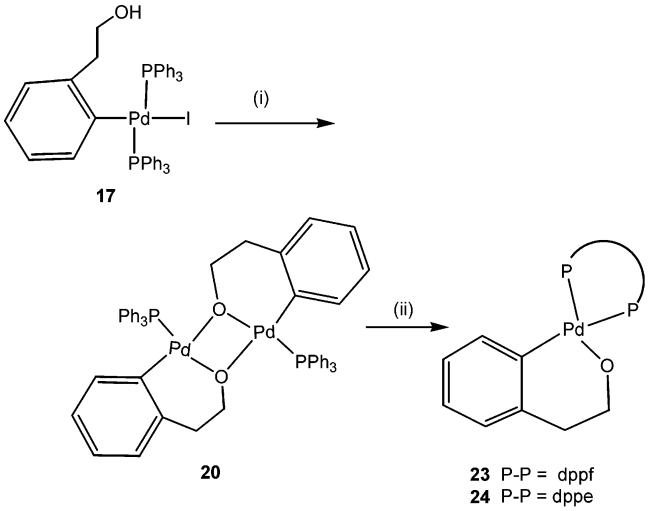
2.2.3. Formation and Reactions of Binuclear Oxoarylpalladium Complexes. The mononuclear complex **14** has previously been transformed via a silyl derivative or, reportedly less reliably, by direct depro-

Scheme 5[a]



[a] Reagents and conditions: (i) NaH, PPh_3, THF, RT, 12 h; (ii) diphosphine, toluene, RT, 13 h; (iii) $P(OC_6H_4OMe\text{-}4)_3$, toluene, RT, 12 h.

Scheme 6[a]



[a] Reagents and conditions: (i) NaH, PPh_3, THF, RT, 12; (ii) diphosphine, toluene, RT, 4 h.

tonation using NaH, into the binuclear compound **19**,[10] which is a precatalyst for some Heck and cross-coupling reactions;[17] we found the synthesis of **19** from **14** using NaH to be successful in the presence of free triphenylphoshine, as in preparation of **7** (see Scheme 5). The crystal structure of compound **19** has been reported and is related to that of the benzyl compound **7** formed from hydroxymethylbenzyl halides, but contains five- rather than six-membered C−O chelating ligands.[10]

Deprotonation of complex **17** afforded the binuclear compound **20** (Scheme 6), which was characterized analytically and spectroscopically, but it is less stable

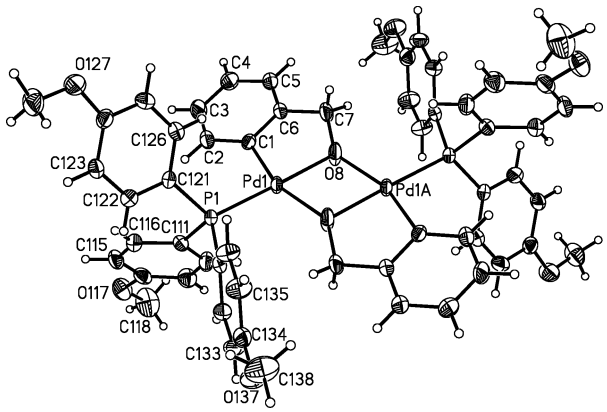


Figure 8. Molecular structures of compound **25** (ellipsoids drawn at the 50% probability level).

in solution than compounds **7** and **19**; solutions of **20** visibly darkened over 2−3 h, precipitating palladium residues, so that single crystals suitable for structural determination by XRD were not obtainable. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR and ESI+ mass spectra of **20** are in accord with a dimeric structure containing six-membered bridging oxapalladacycles, isomeric with **7** but containing aryl−palladium bonds and two linked methylene units in the rings, which should lead to a different conformation around the Pd centers.

As reported by Echavarren and co-workers,[10] **19** reacts with dppf to form the mononuclear oxopalladacyclic compound **21**, an arylpalladium analogue of the benzylic derivative **10**, and we have also characterized an analogous derivative, **22**, formed by cleavage of **19** with dppe at ambient temperature (Scheme 5). Similarly, **20**, containing the larger oxopalladacycles, reacts with dppf and dppe to form the corresponding mononuclear complexes **23** and **24** (Scheme 6). Complexes **22**−**24** are stable in the solid state and were characterized by elemental analysis, ^1H and $^{31}P\{^1H\}$ NMR, and mass spectra, but solutions decompose within hours so that $^{13}C\{^1H\}$ NMR spectra or crystals suitable for XRD were not obtained. It should be noted that compounds of this type are potential intermediates in the palladium-catalyzed formation of aryl ethers by thermal reductive elimination of a C−O bond,[18] as demonstrated by the complex Pd[2-{$OCMe_2CH_2CH_2$-κO}C_6H_4-κC^1]-(dppf) isolated by Buchwald et al.,[15] and this is one possible decomposition path for compounds **22**−**24**.

Although the monodentate phosphines $P(C_6H_4\text{-}4\text{-}Me)_3$ and $P(C_6H_4\text{-}4\text{-}OMe)_3$ will replace PPh_3 in **7** to form new binuclear compounds **8** and **9**, NMR studies indicated that neither of these phosphines reacted readily at ambient temperature with **20** and that only $P(C_6H_4\text{-}4\text{-}OMe)_3$ reacted with **19** to form the tri(4-methoxyphenyl)-phosphine product **25**, which was isolated and characterized. A solvated crystal, **25**·$4CH_2Cl_2$, was analyzed by XRD, and the derived molecular structure is depicted in Figure 8 with selected geometrical parameters given in Table 4. The structure of **25** is very similar to that reported[10] for the triphenylphosphine analogue, **19**, and the presence of $P(C_6H_4\text{-}4\text{-}OMe)_3$ ligands causes negligible changes to the geometry.

2.2.4. Carbonylation of Palladium Complexes Derived from 2-Halogenobenzenealkanols. The

(16) A nonsolvated crystal of **17** {triclinic, $P\bar{1}$, a = 10.848(2) Å, b = 14.295(3) Å, c = 24.476(5) Å, α = 75.34(2)°, β = 88.90(2)°, γ = 89.17-(2)°} was also analyzed by XRD establishing the presence of molecules very similar to that of Figure 8: the lattice contained two independent molecules per unit cell, one with disorder at the hydroxyl group, but refinement of the data gave high final R factors {indices [$I>2\sigma(I)$]: R1 = 0.1129, wR2 = 0.2677; all indices R1 = 0.1260, wR2 = 0.2702}. See Supporting Information.

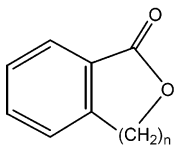
(17) Muñoz, M. P.; Martín-Matute, B.; Fernández-Rivas, C.; Cárdenas, D. J.; Echavarren, A. M. *Adv. Synth. Catal.* **2001**, *343*, 338.

(18) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131.

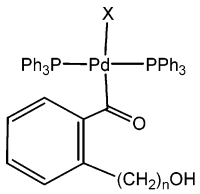
Table 4. Selected Bond Lengths [Å] and Angles [deg] of Compound 25

Pd(1)−C(1)	1.994(4)	O(8)−Pd(1)−O(8)A	78.37(13))
Pd(1)−O(8)	2.051(3)	C(1)−Pd(1)−P(1)	96.11(12)
Pd(1)−O(8)A	2.114(3)	O(8)−Pd(1)−P(1)	178.42(11)
Pd(1)−P(1)	2.2250(11)	O(8)A−Pd(1)−P(1)	102.46(8)
[Pd(1)−Pd(1)A]	[3.2287(7)]	Pd(1)−O(8)−Pd(1)A	101.63(13)
C(1)−C(6)	1.409(6)	C(6)−C(1)−Pd(1)	110.1(3)
C(6)−C(7)	1.511(6)	C(1)−C(6)−C(7)	117.7(4)
C(7)−O(8)	1.367(6)	O(8)−C(7)−C(6)	109.9(4)
C(1)−Pd(1)−O(8)	83.00(14)	C(7)−O(8)−Pd(1)	111.5(3)
C(1)−Pd(1)−O(8)A	161.23(14)	C(7)−O(8)−Pd(1)A	138.3(3)

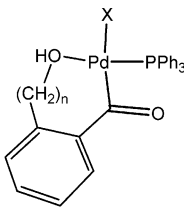
aryl-palladium complexes derived from 2-halogenobenzenealkanols **13** and **16** show similar reactivity to the related benzyl derivatives on exposure to carbon monoxide. At atmospheric pressure and ambient temperature, CO reacts completely with the simple monodentate aryl compounds **14**, **15**, and **17** in tetrahydrofuran solutions within 0.5−1 h to form the corresponding lactone, phthalide {1(3*H*)-isobenzofuranone}, **26a**,[3,19] or 3,4-dihydroisocoumarin (3,4-dihydro-1*H*-2-benzopyran-1-one), **26b**,[9] with characteristic IR, NMR, and GC-MS properties. Carbonylated palladium species, precipitated from these reactions at −78°C, exhibited IR spectra containing ν(CO) bands assignable to aroyl species, but these bands decayed completely within 5−15 min after redissolving the solids in CH_2Cl_2 at ambient temperature, accompanied by the growth of bands of the respective lactone **26a** or **26b** (see Experimental Section). It may be concluded that the intermediates in these processes are simple aroyl compounds, probably **27a**,**b**, or **c** (or possibly monophosphine complexes **28** with coordinated hydroxy group), which undergo a facile reductive elimination of lactone by intramolecular alcoholysis of the aroyl function.



26a n = 1
26b n = 2



27a X = I , n = 1
27b X = Br, n = 1
27c X = I, n = 2



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We also found that both binuclear triphenylphosphine complexes **19** and **20** react readily with CO under ambient conditions to form lactones **26a** and **26b**, respectively. However, the mononuclear complex Pd{(2-OCH_2-κO)C_6H_4-κC^1}(dppe), **22**, containing bidentate alkoxy-aryl and diphosphine ligands, showed no evidence of reaction with CO at atmospheric pressure during 1 h.

3. Discussion

In line with reported reactions of benzylic halides,[20] both bromo and chloro compounds **2a**,**b** readily undergo oxidative addition to tetrakis(triphenylphosphine)-palladium, but, in the isolable products **3** and **4**, respectively, the alcoholic function of the *ortho*-hydroxymethyl substituent also coordinates to the palladium to form a six-membered oxapalladacycle with the displacement of a phosphine ligand. Also, in accord with known reactivities of aryl halides,[21] the aromatic iodides **13a** and **16** add oxidatively to $Pd(PPh_3)_4$ at ambient temperature, whereas the bromide **13b** reacts at 70 °C and an even higher temperature is required for complete reaction of the bromo analogue of **16**, preventing isolation of pure product. In the characterized products, **14**, **15**, and **17**, the hydroxy group of the *ortho*-hydroxymethyl or -ethyl substituent is not coordinated so that five- or six-membered oxapalladacycles are not so readily formed for these arylpalladium derivatives.

Reactions of carbon monoxide at atmospheric pressure and room temperature with the benzyl- or aryl-palladium products of oxidative addition give quantitative conversion to the corresponding lactone, **1**, **26a**, or **26b**, and spectroscopic studies indicate that the insertion of CO occurs into the Pd−C bond to form a labile acyl or aroyl intermediate. This pathway is to be expected for the monodentate aryl compounds **14**, **15**, and **17**, but the alternative insertion into the Pd−O bond of the coordinated OH group in **3** or **4**, to form an alkoxycarbonyl intermediate, is possible and this mechanism has been previously proposed for the formation of lactone **26b** from the chelated 2-hydroxyethylphenyl ligand in [Pd{(2-$HOCH_2CH_2$-κO)C_6H_4-κC^1}(tmeda)]NO_3, **5**.[9] However, notable differences between **5** and the monophosphine complexes **3** and **4** are the positive charge and the presence of a chelating nitrogen ligand in the former complex. It is also of interest that a recent theoretical study of the iron-catalyzed [2+2+1] cycloaddition of diazabutadiene, ethylene, and carbon monoxide to form lactam supports preferential insertion of CO into an Fe−C rather than an Fe−N bond.[22]

Carbonylations under mild conditions (1 atm, RT) of binuclear products **7**, **19**, and **20** readily produce the corresponding lactones, but in these cases no evidence for the nature of intermediates has been adduced and CO insertion into either the Pd−C or Pd−O bond could take place, although the latter bond is initially part of a bridging alkoxy system. In contrast to these facile reactions, the neutral, mononuclear complexes **10**, **11**, and **22** containing bidentate alkoxy-benzyl or -aryl and diphosphine ligands, formed by cleavage of the binuclear compounds with dppe or dppf, show no reaction with CO under the same mild conditions. Low or zero reactivity of palladium catalysts containing dppe ligands for carbonylation of halo alcohols has previously been noted by Stille and was explained by assuming that a necessary fifth coordination site on palladium was blocked by the hydroxy group;[3] this is not the case with the four-coordinate complexes **10**, **11**, and **22**, and there must be an alternative explanation for the retarding effect of the diphosphine ligands in these species.

Mechanisms for insertion of CO into M−R or M−OR bonds of group 10 metals have been the subject of several theoretical and experimental studies,[5−7,23−31] with reaction at an M−OR bond (R = alkyl) generally being more favored by the larger metals if both ligands

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are present,[7] although aryloxide bonds are less reactive.[30] A possible pathway is an associative process to form a five-coordinate intermediate within which migratory insertion occurs, and this appears to apply for some Ni(II) species.[7] An alternative mechanism involves displacement of a ligand in the square plane by CO to form a four-coordinate *cis*-carbonyl species before migratory insertion, although the migration step may be assisted by the displaced ligand remaining in a more loosely bound state;[7,26] studies suggest that a pathway of this type becomes more favored for Pd(II) and Pt(II) complexes. Assuming the latter mechanism applies, the displaced ligand for complexes **3**, **4**, **14**, **15**, and **17** could be halide, to form a more active cationic species {cf. studies on $MRCl(PMe_3)_2$[5b,25]}, or triphenylphosphine, to form a neutral species.[31] However, for complexes **3** and **4** displacement of the chelating hydroxy group, *trans* to phosphine, seems more likely, possibly with this group remaining weakly coordinated in an apical site during reaction; removal of the Pd−O bond from the square plane will also explain the formation of acyl rather than alkoxycarbonyl intermediates which might have been expected from these Pd(II) complexes. It is also possible that in complexes **14**, **15**, and **17** the hydroxyl group on the *ortho*-substituent of the aromatic ring assists in the migratory process and could remain coordinated to the palladium in the aroyl product prior to reductive elimination of lactone; if this occurs, the insertion intermediates detected by IR spectroscopy may not contain two phosphine ligands as depicted in **27** but include a coordinated alcohol function, as in **28**. Considering the binuclear compounds **7**, **19**, and **20**, the alkoxy bridges may be cleaved by addition of CO to form a four-coordinate mononuclear complex, and this would place CO *cis* to the alkoxy group so that reaction might proceed via alkoxycarbonyl prior to rapid elimination of lactone. However, Pd(II) complexes are prone to ready isomerization so that formation of an acyl/aroyl ligand cannot be ruled out.

The lack of reaction of the diphosphine complexes **10**, **11**, and **22** with CO under mild conditions is in apparent contrast with literature reports on reactivity of diphosphine palladium and platinum complexes containing both alkyl and alkoxy ligands. Thus, Pt(OMe)Me(dppe) reacts with CO at low pressures and temperatures by insertion into the Pt−O bond,[27] and facile insertions of CO into the Pd−O bond of complexes Pd(OCHRR′)Me(dppe)[28] and Pd(OMe)Me{(S,S)-bdpp}[29] lead to liberation of methyl esters. Also, methyl(alkoxy)palladium[30a] and even simple methylpalladium[26] complexes containing N−N or N−O chelating ligands undergo carbonylation very readily; for the latter compounds, theoretical studies support the formation of a square pyramidal carbonyl intermediate with a long apical bond to one chelate arm.[26] However, CO insertions into the Pd−C bond of simple, neutral diphosphine complexes PdMeCl(P−P) (P−P = dppe, dppp, dppb, or dppf) do require pressures above atmospheric and the acetyl products decarbonylate in the absence of CO; rates of insertion decrease with diphosphine in the order dppb ≥ dppp ≥ dppf ≫ dppe, so that the complex containing dppe, with the smallest bite angle and poorest backbone flexibility, is significantly the least reactive.[23] If the mechanism involves displacement of one arm of the bidentate diphosphine from the square plane before alkyl migration (cf. ref 7b), this would be least favorable for dppe. Cationic species $[PdMe(P-P)L]^+$, with a readily substituted, weakly coordinating ligand L, are more reactive to CO insertion,[23−25] but again reaction is slowest when P−P = dppe.[23] Therefore, the low reactivity of complexes **11** and **22** containing dppe ligands is not inconsistent with observations on related complexes, although complex **10**, containing dppf, might be expected to more reactive. A theoretical study has indicated that the preferred pathway for migration of a methoxy ligand to a coordinated CO involves rotation about the metal−oxygen bond so that an oxygen lone pair of electrons can participate in O−C bond formation;[7] the ring conformations of the alkoxy-benzyl or -aryl chelates in complexes **10**, **11**, and **22** are likely to prevent the optimum orientation of orbitals for migration of the alkoxy group, and this factor may be deactivating with respect to Pd−O insertion; additionally, the geometrical restrictions of these chelates may also hamper the pathway for Pd−C insertion.

There is good evidence that the final steps in formation of ester from acylpalladium complexes, and alcohol, in the presence of base, generally involve the coordination of alcohol, deprotonation, and subsequent reductive elimination of alkoxy group with the acyl ligand.[5,6] An inverse reductive elimination of alkyl and alkoxycarbonyl ligands occurs when CO preferentially inserts into the M−O of an alkoxy(alkyl)complex.[28−30] Therefore, coordination of both oxygen and carbon donor ligands is normally required before final alcoholysis. The benzyl and aryl palladium complexes **3**, **4**, **7**, **19**, and **20** described in this paper contain a *cis*-alcohol or -alkoxy function coordinated to the metal or, in the case of aryl compounds **14**, **15**, and **17**, an adjacent hydroxyl group that can readily be coordinated; the presence of these Pd−O bonds will explain the ready formation of lactone from the carbonyl inserted intermediates derived from all these complexes.

The characterization of complexes **3** and **4** containing the bidentate 2-hydroxymethylbenzyl ligand and spectroscopic identification of the acyl compound **12b** support the mechanism shown in Scheme 1 as the primary pathway for the palladium-catalyzed synthesis of 3-isochromanone from *2*-hydroxymethylbenzyl halides. The facile chelation of the hydroxyl group supports Pd−O bond formation in the catalytic cycle; as in the isolated derivatives, this bond probably forms prior to carbonyl insertion, but under catalytic conditions it is possible

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that the interaction occurs during, or even after, migration of the benzyl group to coordinated CO. Since the isolated binuclear derivative **7** is formed in appreciable amounts only in the presence of hydride and not with amine bases, it is less likely to be involved in the catalytic cycle in which $NEt(i\text{-}Pr)_2$ is the added base. However, **7** is readily transformed by CO into 3-isochromanone and is itself an active catalyst precursor.

The isolated arylpalladium complexes **14**, **15**, and **17** are also readily transformed into the corresponding lactones on reaction with CO, and they are probably the initial oxidative-addition intermediates in the catalytic carbonylations of 2-halogenobenzenealkanols by Pd(0) in the presence of PPh_3; insertion of CO occurs readily into the aryl−palladium bond in the absence of a Pd−O bond, although subsequent coordination of the neighboring hydroxyl group is very likely to precede lactone formation. Binuclear products, **19** and **20**, although unlikely to be involved in the basic catalytic cycle, are also readily carbonylated to form lactone and can act as precursors of mononuclear catalysts. However, complexes **10**, **11**, and **21**−**24**, which contain bidentate diphosphine and chelating, formally dinegative, alkoxyalkyl or -aryl ligands, do not react readily with CO to form the corresponding lactone and are inactive as catalysts for lactone formation from the parent halo alcohols.

4. Experimental Section

4.1. General Procedures. Reactions and operations involving palladium compounds were conducted under an atmosphere of dry, oxygen-free nitrogen or argon gas, using Schlenk techniques. Solvents were dried, using sodium (toluene), sodium-benzophenone (diethyl ether, tetrahydrofuran, petroleum ether), calcium hydride (dichloromethane), or sodium hydroxide (dimethyl sulfoxide) and freshly distilled before use. Light petroleum ether had a boiling range of 60−80 °C. Tetrakis(triphenylphosphine)palladium[32] and 2-iodobenzeneethanol[33] were prepared by literature methods, and other reagents were obtained commercially (Aldrich Chemicals or Syngenta, Grangemouth, UK) and used as supplied. NMR spectra were recorded on a Bruker DPX 400 spectrometer (at ca. 17 °C) using $SiMe_4$ as internal reference for 400.1 MHz ^1H and 100.6 MHz $^{13}C\{^1H\}$ spectra and 85% H_3PO_4 as external reference for 162.0 MHz $^{31}P\{^1H\}$ spectra; many assignments of ^1H and ^{13}C resonances were aided by HMQC, NOE, and DEPT measurements. Solid-state NMR spectra were run by the EPSRC service at the University of Durham, UK. IR spectra were recorded using a Perkin-Elmer 1600 series FTIR spectrophotometer. EI/ESI mass spectra were measured on an upgraded VG MS9 instrument. GC-MS spectra were recorded on a Hewlett-Packard HP6890 gas chromatograph with a HP5MS (30 m × 0.25 mm) capillary column coupled to a Hewlett-Packard HP5973 quadrupole mass filter (EI, high-energy dynode/electron multiplier detector). Elemental CHN analyses were carried out at Heriot-Watt University.

4.2. Synthesis and Characterization. 2-(Hydroxymethyl)benzyl Bromide, 2a. 1,2-Benzenedimethanol (2.5 g, 18.1 mmol) was dissolved in toluene (35 cm^3). The solution was heated to 70 °C, and 48% HBr (2.3 cm^3) was added dropwise over 5 min. The mixture was stirred at 70 °C for 3 h, cooled to RT, neutralized with sodium carbonate solution, and then extracted with diethyl ether (3 × 20 cm^3). The combined organic phases were washed with water (40 cm^3) and dried ($MgSO_4$). After filtration the solution was evaporated to dryness in vacuo to give the title compound as a white, waxy solid (3.0 g, 82%). NMR ($CDCl_3$) δ_H/ppm: 2.08 (br s, 1H, O*H*), 4.64 (s, 2H, CH_2Br), 4.84 (br s, 2H, CH_2O), 7.35 (m, 4H, C_6H_4).

2-(Hydroxymethyl)benzyl Chloride, 2b. 1,2-Benzenedimethanol (6.03 g, 43.6 mmol) was dissolved in toluene (65 cm^3). The solution was heated to 70 °C, and concentrated HCl (6.1 cm^3) was added dropwise over 5 min. The mixture was then stirred at 70 °C for 2 h and cooled to RT. Workup as above gave the title compound as a white, waxy solid (6.35 g, 93%). NMR ($CDCl_3$) δ_H/ppm: 1.83 (t, J = 5.8 Hz, 1H, O*H*) 4.73 (br s, 2H, CH_2Cl), 4.84 (br d, J = 5.8 Hz, 2H, CH_2O), 7.37 (m, 4H, C_6H_4).

Bromo[2-(hydroxymethyl-κ*O*)benzyl-κ*C*$^{1\alpha}$](triphenylphosphine)palladium, 3. 2-(Hydroxymethyl)benzyl bromide (**2a**) (0.25 g, 1.24 mmol) dissolved in toluene (10 cm^3) was added dropwise to a stirred suspension of tetrakis(triphenylphosphine)palladium(0) (1.43 g, 1.24 mmol) in toluene (60 cm^3) and the mixture stirred at RT for 12 h. The solid product was collected by filtration, washed with diethyl ether (3 × 20 cm^3), and dried in vacuo to give the title compound as an amorphous, off-white solid (605 mg, 86%). Crystallization from dichloromethane and light petroleum ether gave yellow cubes, mp 168−171 °C (dec). Found: C, 54.96; H, 4.28; $C_{26}H_{24}$BrOPPd requires C, 54.81; H, 4.25. NMR ($CDCl_3$) δ_H/ppm: 2.79 (d, J_{HP} = 2.6 Hz, 2H, PdCH_2), 4.53 (d, J_{HP} = 2.1 Hz, 2H, CH_2O), ca. 5.5 (vbr s, 1H, O*H*) 6.19 (d, J = 7.6 Hz, 1H, C_6H_4, *H-6*), 6.96 (t, J = 7.3 Hz, 1H, C_6H_4, *H-5*), 7.01−7.11 (m, 2H, C_6H_4, *H-3, 4*), 7.37−7.50 (m, 9H, PPh_3, *m, p*-C*H*), 7.62−7.70, (m, 6H, PPh_3, *o*-C*H*); δ_C/ppm: 33.0 (Pd*C*H_2), 64.2 (d, J_{CP} = 5.9 Hz, *C*H_2O), 124.9 (C_6H_4, *C*H-*4*), 127.7−128.9 (C_6H_4, *C*H-*3,5,6*), 128.3 (d, $J_{CP} \approx$ 11 Hz, PPh_3, *m-C*H), 130.6 (PPh_3, *p-C*H), 131.1 (d, J_{CP} = 53.0 Hz, quat.-C, PPh_3, *ipso-C*), 134.5 (d, J_{CP} = 11.6 Hz, PPh_3, *o-C*H),138.8 (quat.-C, C_6H_4, *C-2*), 141.0 ((d, J_{CP} = 4 Hz, quat.-C, C_6H_4, *C-1*); δ_P/ppm: 42.6 (s). MS (ESI+): *m/z* 1051−1065 {max. 1056, 50%, (2M − H_xBr)}, 484−494 {max. 488, 60%, (M − H_xBr)}; $C_{26}H_{24}$BrOPPd requires 568.

Chloro[2-(hydroxymethyl-κ*O*)benzyl-κ*C*$^{1\alpha}$](triphenylphosphine)palladium, 4. 2-(Hydroxymethyl)benzyl chloride (**2b**) (0.25 g, 1.6 mmol) dissolved in toluene (10 cm^3) was added dropwise to a stirred suspension of tetrakis(triphenylphosphine)palladium(0) (1.65 g, 1.43 mmol) in toluene (60 cm^3), and the mixture was stirred at RT for 12 h. The solid product was collected by filtration, washed with diethyl ether (3 × 20 cm^3), and dried in vacuo to give the title compound as an amorphous, off-white solid (640 mg, 76%). Recrystallization from dichloromethane and petroleum ether gave pale yellow cubes, mp 192−197 °C (dec). Found: C, 59.16; H, 4.54. $C_{26}H_{24}$ClOPPd requires C, 59.45; H, 4.60. NMR ($CDCl_3$) δ_H/ppm: 2.70 (d, J_{HP} = 2.9 Hz, 2H, PdCH_2), 4.45 (br s, 2H, CH_2O), 6.20 (d, J = 7.7 Hz, 1H, C_6H_4, *H-6*), ca. 6.7 (v br, 1H, O*H*), 6.93 (dt, J = 1.6 and 7.4 Hz, 1H, C_6H_4, *H-5*), 6.98 (m, 1H, C_6H_4, *H-3*), 7.05 (∼tt, J = 1.1 and 7.3 Hz, 1H, C_6H_4, *H-4*), 7.3−7.5 (m, 9H, PPh_3, *m, p*-C*H*), 7.6−7.7 (m, 6H, PPh_3, *o*-C*H*); δ_C/ppm: 30.6 (Pd*C*H_2), 63.6 (*C*H_2O), 124.7 (C_6H_4, *C*H-*4*), 127.6 (d, J_{CP} = 2.0 Hz, C_6H_4, *C*H-*6*), 128.3 (d, J_{CP} = 11.0 Hz, PPh_3, *m-C*H), 128.8 (br, C_6H_4, *C*H-*3, 5*), 130.6 (d, J_{CP} = 2.5 Hz, PPh_3, *p-C*H), ∼130.9 (d, $J_{CP} \approx$ 55 Hz, quat.-C, PPh_3, *ipso-C*), 134.5 (d, J_{CP} = 11.7 Hz, PPh_3, *o-C*H), 139.1 (quat.-C, C_6H_4, *C-2*), 141.5 (d, J_{CP} = 3.0 Hz, quat.-C, C_6H_4, *C-1*); δ_P/ppm: 41.4 (s). MS (EI+): *m/z* 525 (M + 1) (6%); (ESI+) *m/z* 1007−1023 {max. 1013, 100%, (2M − H_xCl)}; $C_{26}H_{24}$ClOPPd requires 524.

Reaction of Chloro[2-(hydroxymethyl-κ*O*)benzyl-κ*C*$^{1\alpha}$](triphenylphosphine)palladium (4) with Carbon Monoxide. Carbon monoxide was bubbled through a solution of chloro[2-(hydroxymethyl)benzyl](triphenylphosphine)-palladium (**4**) (150 mg, 0.286 mmol) in tetrahydrofuran (20 cm^3) for 20 min. Petroleum ether (40 cm^3) was quickly added, via syringe, and the reaction mixture was cooled to −78 °C. The precipitate was collected by filtration and dried in vacuo, to give an amorphous yellow-orange solid, comprising mainly

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chloro[2-(hydroxymethyl-κO)phenylacetyl-$\kappa C^{1\beta}$](triphenylphosphine)palladium (**12b**) (134 mg, 85%). NMR (CD_2Cl_2); δ_H/ppm: 4.01 (s, 2H, CH_2CO), 4.16 (s, 2H, CH_2O), 6.17 (d, J = 7.6 Hz, C_6H_4, *H-6*), 6.95−7.25 (complex, 3H, C_6H_4, *H-3*−*5*), 7.4−7.8 (complex, 15H, PPh_3); δ_P/ppm: 27.4 (s). MS (EI+): *m/z* 551 (M − 1); $C_{27}H_{24}ClO_2PPd$ requires 552. IR ν_{max}(CO)/cm^{-1}: 1707 (KBr); 1709 (CH_2Cl_2). In dichloromethane, compound **12** decomposes completely within 26 min at RT to form 3-isochromanone (IR: ν_{max}(CO) 1750 cm^{-1}).

Bis[2-(μ-oxomethyl-κO)benzyl-κC$^{1\alpha}$]bis(triphenylphosphine)dipalladium, 7. NaH (60% dispersion in mineral oil; 60 mg, 1.51 mmol) was added to a suspension of chloro[2-(hydroxymethyl)benzyl-$\kappa C^{1\alpha}$,κO](triphenylphosphine)-palladium (**4**) (790 mg, 1.50 mmol) and triphenylphosphine (435 mg, 1.66 mmol) in THF (40 cm^3). The suspension was stirred at RT for 12 h. Liberation of hydrogen gas occurred, and a pale green precipitate formed. The precipitate was collected by filtration, washed with H_2O (3 × 30 cm^3) to remove NaCl and with diethyl ether (3 × 10 mL), and then dried in vacuo to give the title compound as a microcrystalline, pale green solid (570 mg, 77%). Recrystallization from dichloromethane and light petroleum ether afforded pale yellow crystals. Found: C, 62.64; H, 4.92. $C_{52}H_{46}O_2P_2Pd_2{\cdot}H_2O$ requires C, 62.72; H, 4.86. NMR ($CDCl_3$): δ_H/ppm: 2.36 (d, J_{HP} = 5.4 Hz, 4H, PdCH_2), 3.34 (d, J_{HP} = 4.2 Hz, 4H, CH_2O), 6.18 (m, 2H, C_6H_4, *H-3*), 6.27 (m, 2H, C_6H_4, *H-6*), 6.72 (m, 4H, C_6H_4, *H-4, 5*), 7.42−7.50 (m, 18H, PPh_3, *m*, *p*-C*H*), 7.85 (m, 12H, PPh_3, *o*-C*H*); δ_C/ppm: 25.6, (d, J_{CP} = 4.4 Hz, Pd*C*H$_2$), 68.2 (*C*H$_2$O), 122.9 (C_6H_4, *C*H-*4 or 5*), 126.0 (C_6H_4, *C*H-*6*),126.7 (C_6H_4, *C*H-*5 or 4*), 127.1 (C_6H_4, *C*H-*3*), 128.4 (d, J_{CP} = 10.5 Hz, PPh_3, *m*-*C*H), 130.3 (d, J_{CP} = 2.1 Hz, PPh_3, *p*-*C*H), 132.1 (d, J_{CP} = 46.6 Hz, PPh_3, *ipso-C*), 134.8 (d, J_{CP} = 12.5 Hz, PPh_3, *o*-*C*H), 143.8 (d, J_{CP} = 1.3 Hz, quat.-C, C_6H_4, *C-1 or 2*), 146.9 (quat.-C, C_6H_4, *C-2 or 1*); δ_P/ppm: 39.6 (s). MS (ESI+): *m/z* 999 (M + Na) (84%), 476 (55%); $C_{52}H_{46}O_2P_2Pd_2$ requires 976.

Bis[2-(μ-oxomethyl-κO)benzyl-κC$^{1\alpha}$]bis[tris(4-methylphenyl)phosphine)]dipalladium, 8. Tris(4-methylphenyl)phosphine (**9**) (376 mg, 1.24 mmol) in toluene (10 cm^3) was added dropwise to a suspension of bis[2-(μ-oxomethyl-κO)-benzyl-$\kappa C^{1\alpha}$]bis(triphenylphosphine)dipalladium (**7**) (301 mg, 0.31 mmol) in toluene (10 cm^3). The mixture was stirred for 12 h at RT to form a homogeneous, olive-green solution. After partial removal of solvent at reduced pressure the resulting precipitate was collected by filtration, washed with H_2O (2 × 20 cm^3), followed by diethyl ether (3 × 20 cm^3), and dried in vacuo to give the title compound (272 mg, 83%) as a pale green solid. Found: C, 64.31; H, 5.40. $C_{58}H_{58}O_2P_2Pd_2{\cdot}H_2O$ requires C, 64.51; H, 5.60. NMR ($CDCl_3$); δ_H/ppm: 2.38 (br s, 4H, PdCH_2), 2.42 (s, 18H, CH_3), 3.40 (d, J_{HP} = 3.8 Hz, 4H, CH_2O), 6.24 (d, J = 7 Hz, 2H, C_6H_4, *H-3*), 6.40 (d, J = 8.5 Hz, 2H, C_6H_4, *H-6*), 6.75 (m, 4H, C_6H_4, *H-4, 5*), 7.26 (m, 12H, PC_6H_4, *m*-C*H*), 7.80 (m, 12H, PC_6H_4, *o*-C*H*); δ_C/ppm: 21.4 (*C*H$_3$), 25.4 (d, J_{CP} = 4.0 Hz, Pd*C*H$_2$), 68.2 (*C*H$_2$O), 122.6 (C_6H_4, *C*H-*4* or *5*), 125.9 (C_6H_4, *C*H-*6*), 126.5 (C_6H_4, *C*H-*5* or *4*), 127.1 (C_6H_4, *C*H-3), 129.1 (d, J_{CP} = 11.3 Hz, PC_6H_4Me, *m*-*C*H), 129.2 (d, $J_{CP} \approx$ 48 Hz, PC_6H_4Me, *ipso-C*P),134.7 (d, J_{CP} = 12.7 Hz, PC_6H_4Me, o-*C*H), 140.3 (quat.-C, PC_6H_4Me, *p*-*C*Me), 144.3 (quat.-C, C_6H_4, *C-1* or *2*), 147.0 (quat.-C, C_6H_4, *C-2* or *1*), δ_P/ppm: 37.5 (s). MS (ESI+): *m/z* 529.5 (1/2M) (100%); $C_{58}H_{58}O_2P_2Pd_2$ requires 1060.2.

Bis[2-(μ-oxomethyl-κO)benzyl-κC$^{1\alpha}$]bis[tris(4-methoxyphenyl)phosphine]dipalladium, 9. Tris(4-methoxyphenyl)phosphine (350 mg, 1.0 mmol) in toluene (10 cm^3) was added dropwise to a suspension of bis[2-(μ-oxomethyl-κO)-benzyl-$\kappa C^{1\alpha}$]bis(triphenylphosphine)dipalladium (**7**) (301 mg, 0.31 mmol) in toluene (10 cm^3). The mixture was stirred for 12 h at RT to form a homogeneous, pale green solution. After partial removal of solvent under reduced pressure the resulting off-white precipitate was collected by filtration, washed with H_2O (2 × 20 cm^3), followed by diethyl ether (3 × 20 cm^3), and dried in vacuo to give the title compound (219 mg, 61%). The product was recrystallized from dichloromethane/light petroleum. Found: C, 57.13; H, 4.85. $C_{58}H_{58}O_8P_2Pd_2{\cdot}CH_2Cl_2$ requires C, 57.02; H, 4.87. NMR ($CDCl_3$); δ_H/ppm: 2.36 (d, J_{HP} = 5.0 Hz, 4H, PdCH_2), 3.39 (d, J_{HP} = 3.8 Hz, 4H, CH_2O), 3.84 (s, 18H, CH_3), 6.22 (d, J = 8.2 Hz, 2H, C_6H_4, *H-3*), 6.38 (d, J = 7.1 Hz, 2H, C_6H_4, *H-6*), 6.73 (m, 4H, C_6H_4, *H-4, 5*), 6.95 (d, J = 8.8 Hz, 12H, PC_6H_4O, *m*-C*H*), 7.74, (dd, J = 8.8 and 10.6 Hz, 12H, PC_6H_4O, *o*-C*H*); δ_C/ppm: 25.5 (d, J_{CP} = 3.8 Hz, Pd*C*H$_2$), 55.3 (*C*H$_3$O), 68.3 (*C*H$_2$O), 113.9 (d, J_{CP} = 11.5 Hz, PC_6H_4OMe, *m*-*C*H), 122.6 (C_6H_4, *C-4* or *5*), 124.0 (d, J_{CP} = 51.4 Hz, PC_6H_4OMe, *ipso-C*P), 126.0 (C_6H_4, *C-6*), 126.6 (C_6H_4, *C-5* or *4*), 127.2 (C_6H_4, *C-3*), 136.2 (d, J_{CP} = 13.9 Hz, PC_6H_4OMe, *o*-*C*H), 144.4 (quat.-C, C_6H_4, *C-1* or *2*), 147.0 (quat.-C, C_6H_4, *C-2* or *1*), 161.1 (d, J_{CP} = 2.0 Hz, PC_6H_4OMe, *p*-*C*OMe); δ_P/ppm: 35.5, (s). MS (ESI+): *m/z* 1179 (M + Na) (99%); $C_{58}H_{58}O_8P_2Pd_2$ requires 1156.

[1,1′-Bis(diphenylphosphino)ferrocene-κ^2*P*,*P*′][(2-oxomethyl-κ*O*)benzyl-κ*C*$^{1\alpha}$]benzyl-κ*C*$^{1\alpha}$]palladium, 10. 1,1′-Bis(diphenylphosphino)ferrocene (1.15 g, 2.07 mmol) in toluene (20 cm^3) was added dropwise to a suspension of bis[2-(μ-oxomethyl-κO)benzyl-$\kappa C^{1\alpha}$]bis(triphenylphosphine)dipalladium, **7** (509 mg, 0.52 mmol), in toluene (40 cm^3). The mixture, which immediately became a homogeneous orange solution, was stirred for 3 h to produce a bright yellow-orange solid precipitate. This solid was collected by filtration, washed with H_2O (2 × 20 cm^3), followed by diethyl ether (3 × 20 cm^3), and dried in vacuo to give the title compound (323 mg, 40%). A purified sample for analysis was obtained by expeditious recrystallization from dichloromethane/light petroleum. Found: C, 61.97; H, 4.45. $C_{42}H_{36}FeOP_2Pd.0.5CH_2Cl_2$ requires C, 61.99; H, 4.53. NMR (CD_2Cl_2); δ_H/ppm: 2.72 (dd, J_{HP} = 6.8 and 9.7 Hz, 2H, PdCH_2), 3.69 (br ∼t, 2H, C_5H_4), 4.20 (br ∼t, 2H, C_5H_4), 4.32 (br ∼t, 2H, C_5H_4), 4.35 (br ∼t, 2H, C_5H_4), 4.47 (d, J = 6.5 Hz, 2H, CH_2O), 6.31 (d, J = 7.2 Hz, 1H, C_6H_4, *H-3* or *6*), 6.90 (m, 2H, C_6H_4, *H-4*, *5*), 7.05 (d, J = 6.9 Hz, 1H, C_6H_4, *H-6* or *3*), 7.3−7.5 (m, 12H, PPh_2, *m, p*-C*H*), 7.67−7.85 (m, 8H, PPh_2, *o*-C*H*); δ_P/ppm: 16.2 (d, J_{PP} = 38.0 Hz), 34.2 (d, J_{PP} = 38.0 Hz). MS (ESI+): *m/z* 780.5 (M); $C_{42}H_{36}FeOP_2Pd$ requires 780.

[1,2-Bis(diphenylphosphino)ethane-κ^2*P*,*P*′][2-(oxomethyl-κ*O*)benzyl-κ*C*$^{1\alpha}$]palladium, 11. 1,2-Bis(diphenylphosphino)ethane (1.11 g, 2.79 mmol) in toluene (20 cm^3) was added dropwise to a suspension of bis[2-(μ-oxomethyl-κO)benzyl-$\kappa C^{1\alpha}$]-bis(triphenylphosphine)dipalladium, **7** (678 mg, 0.69 mmol), in toluene (40 cm^3). The mixture was stirred for 3 h at RT to form a creamy-white suspension. The white solid was collected by filtration, washed with H_2O (2 × 20 cm^3), followed by diethyl ether (3 × 20 cm^3), and dried in vacuo to give the title compound (749 mg, 86%). Found: C, 64.25; H, 5.01. $C_{34}H_{32}OP_2Pd{\cdot}1/2H_2O$ requires C, 64.41; H, 5.25. NMR ($CDCl_3$): δ_H/ppm: 2.11 (m, 2H, dppe, CH_2), 2.29 (m, 2H, dppe, CH_2), 2.80 (dd, J_{HP} = 5.3 and 10.3 Hz, 2H, PdCH_2), 4.78 (br s, 2H, CH_2O), 6.14 (d, J = 7.1 Hz, 1H, C_6H_4, *H-3* or *6*), 6.88 (m, 2H, C_6H_4, *H-4, 5*), 7.17 (m, 1H, C_6H_4, *H-6* or *3*), 7.29−7.37 and 7.43−7.61 (complex, 16H, PPh_2, C*H*), 7.82 (m, 4H, PPh_2, C*H*); δ_P/ppm: 33.8 (d, J_{PP} = 29.4 Hz), 55.7 (d, J_{PP}= 29.4 Hz). MS (ESI+): *m/z* 624 (M) (100%); $C_{34}H_{32}OP_2Pd$ requires 624.

***trans*-[2-(Hydroxymethyl)phenyl]iodobis(triphenylphosphine)palladium, 14 (cf. ref 10).** 2-Iodobenzenemethanol, **13a** (0.5 g, 2.14 mmol), dissolved in toluene (20 cm^3), was added dropwise to a stirred suspension of tetrakis(triphenylphosphine)palladium (2.47 g, 2.14 mmol) in toluene (80 cm^3) and the mixture stirred at room temperature for 12 h. Approximately one-third of the solvent was removed in vacuo and replaced with petroleum ether (30 cm^3), and the mixture cooled in a refrigerator. The resultant precipitate was collected, washed with diethyl ether (3 × 20 cm^3), and dried in vacuo to give the title compound as a yellowish solid (1.13 g, 61%). Further recrystallization from dichloromethane/light petroleum ether afforded yellow crystals. Found: C, 55.32; H, 4.07. $C_{43}H_{37}IOP_2Pd.CH_2Cl_2$ requires C, 55.63; H, 4.14. NMR

($CDCl_3$): δ_H/ppm: 0.01 (t, J = 6.8 Hz 1H, O*H*), 4.16 (d, J = 6.8 Hz, 2H, CH_2O), 6.41 (d, J = 7.6 Hz, 1H, C_6H_4, *H-3*), 6.46 (t, J = 7.1 Hz, 1H, C_6H_4, *H-5*), 6.62 (t, J = 7.6 Hz, 1H, C_6H_4, *H-4*), 7.05 (m, 1H, C_6H_4, *H-6*), 7.21−7.28 (m, 12H PPh_3), 7.30−7.37 (m, 6H PPh_3), 7.41−7.48 (m, 12H, PPh_3); δ_C/ppm: 68.2, (t, J_{CP} = 3.5 Hz, *C*H_2O), 123.5 (C_6H_4, *C*H-*4*), 125.7 (C_6H_4, *C*H-*5*), 127.9 (t, J_{CP} = 5.0 Hz, PPh_3, *m-C*H), 128.4 (C_6H_4, *C*H-*3*), 130.0 (PPh_3, *p-C*H), 131.8 (t, J_{CP} = 23.2 Hz, PPh_3, *ipso-C*), 134.0 (t, J_{CP} = 4.2 Hz, C_6H_4, *C*H-*6*), 134.8 (t, J_{CP} = 6.3 Hz, PPh_3, *o-C*H), 144.2 (quat.-C, C_6H_4, *C-2*), 158.4 (quat.-C, C_6H_4, Pd*C-1*); δ_P/ppm: 23.8, (s). MS (ESI+): *m/z* 737 {M − I}; $C_{43}H_{37}IOP_2Pd$ requires 864.

***trans*-[2-(Hydroxymethyl)phenyl]bromobis(triphenylphosphine)palladium, 15.** 2-Bromobenzenemethanol, **13b** (0.25 g, 1.34 mmol), was dissolved in toluene (10 cm^3) and added dropwise to a stirred suspension of tetrakis(triphenylphosphine)palladium, **1** (1.54 g, 1.33 mmol), in toluene (60 cm^3). The suspension was stirred at 70 °C for 48 h. Approximately one-third of the solvent was removed in vacuo and replaced with 40 mL of petroleum ether, and the mixture was cooled in a refrigerator. The resultant precipitate was collected, washed with diethyl ether (3 × 20 cm^3), and dried in vacuo to give the title compound as a yellowish solid (627 mg, 58%); this was recrystallized from dichloromethane/light petroleum ether to give yellow crystals; mp 265 °C (dec). Found: C, 58.35; H, 4.27. $C_{43}H_{37}BrOP_2Pd.CH_2Cl_2$ requires C, 58.53; H, 4.35. NMR ($CDCl_3$); δ_H/ppm: 0.04 (t, J = 6.8 Hz 1H, O*H*), 4.16 (d, J = 6.6 Hz, 2H, CH_2O), 6.43 (m, 2H, C_6H_4, *H-3*, *5*), 6.62 (t, J = 7.3 Hz, 1H, C_6H_4, *H-4*), 7.03 (m, 1H, C_6H_4, *H-6*), 7.25 (m, 12H PPh_3, *m-*C*H*), 7.34 (m, 6H PPh_3, *p-*C*H*), 7.45 (m, 12H, PPh_3, *o-*C*H*); δ_C/ppm: 68.6, (t, J_{CP} = 3.4, *C*H_2O), 123.4 (C_6H_4, *C*H-*4*), 125.7 (C_6H_4, *C*H-*5*), 127.9 (t, J_{CP} = 5.1 Hz, PPh_3, *m-C*H), 128.1 (C_6H_4, *C*H-*3*), 130.0 (PPh_3, *p-C*H), 131.2 (t, J_{CP} = 22.9 Hz, PPh_3, *ipso-C*), 134.3 (t, J_{CP} = 4 Hz, C_6H_4, *C*H-*6*), 134.6 (t, J_{CP} = 6.3 Hz, PPh_3, *o-C*H), 144.1 (quat.-C, C_6H_4, *C-2*), 155.7 (t, J_{CP} = 3.5 Hz, quat.-C, C_6H_4, Pd*C-1*); δ_P/ppm: 24.8, (s). MS (ESI+) *m/z* 732−743 (M − Br) (100%); $C_{43}H_{37}BrOP_2Pd$ requires 816.

[2-(Hydroxyethyl)phenyl]iodobis(triphenylphosphine)-palladium, 17. 2-Iodobenzeneethanol, **16** (0.75 g, 3.02 mmol), in toluene (20 cm^3) was added dropwise to a stirred suspension of tetrakis(triphenylphosphine)palladium (3.50 g, 3.03 mmol) in toluene (150 cm^3). The mixture was stirred at RT for 12 h and then refrigerated to aid crystallization. The resultant precipitate was collected by filtration, washed with diethyl ether (3 × 20 cm^3), and dried in vacuo to give the title compound as a white solid (1.135 g, 43%). Recrystallization from dichloromethane and light petroleum ether afforded colorless needles. Found: C, 55.52; H, 4.27. $C_{44}H_{39}IOP_2Pd.CH_2Cl_2$ requires C, 56.07; H, 4.29. NMR ($CDCl_3$); δ_H/ppm: 0.38 (t, J_{HH} = 6.0 Hz 1H, O*H*), 2.56 (t, J_{HH} = 6.8 Hz, 2H, C$H_2$$CH_2$O), 3.29 (∼q (dt), J = 6.0 and 6.8 Hz, 2H, CH_2CH_2O), 6.28 (br d, J = 7.6 Hz, 1H, C_6H_4, *H-3*), 6.36 (t, J = 7.5 Hz, 1H, C_6H_4, *H-5*), 6.57 (t, J = 7.2 Hz, 1H, C_6H_4, *H-4*), 6.92 (m, 1H, C_6H_4, *H-6*), 7.24 (m, 12H, PPh_3, *m-*C*H*), 7.33 (m, 6H, PPh_3, *p-*C*H*), 7.43 (m, 12H, PPh_3, *o-*C*H*); δ_C/ppm: 42.2 (*C*$H_2$$CH_2$O), 61.4, (*C*$H_2$O), 123.2 ($C_6H_4$, *C*H-*4*), 124.8 ($C_6H_4$, *C*H-*5*), 127.8 (t, J_{CP} = 4.9 Hz, PPh_3, *m-C*H), 129.4 (C_6H_4, *C*H-*3*), 129.9 (PPh_3, *p-C*H), 131.9 (t, J_{CP} = 22.6 Hz, PPh_3, *ipso-C*P), 135.0 (t, J_{CP} = 6.4 Hz, PPh_3, *o-C*H), 136.0 (t, J_{CP} ∼ 5 Hz, C_6H_4, *C*H-*6*), 141.4 (quat.-C, C_6H_4, *C-2*), 159.7 (quat.-C, C_6H_4, Pd*C-1*); δ_P/ppm: 23.2, (s); MS (ESI+): *m/z* 751 (M − I); $C_{44}H_{39}IOP_2Pd$ requires 878.

Reactions of Complexes 14, 15, and 17 with Carbon Monoxide. (a) *trans*-[2-(Hydroxymethyl)phenyl]iodobis(triphenylphosphine)palladium, **14** (250 mg, 0.29 mmol), was dissolved in tetrahydrofuran (20 cm^3). Carbon monoxide was then bubbled though the solution for 30 min. Light petroleum ether (40 cm^3) was quickly added via syringe, and the reaction mixture was cooled to −78 °C. The resultant precipitate was collected by filtration and dried in vacuo, to give an amorphous yellow solid (186 mg), containing a carbonylated product, tentatively identified as *trans*-[2-(hydroxymethyl)benzoyl]-iodobis(triphenylphosphine)palladium, **27a** (or related aroyl derivative). IR: ν_{max}(CO)/cm^{-1} 1659, 1633 (KBr); 1633 (CH_2Cl_2). Further purification or spectroscopic characterization was prevented by instability in solution. In dichloromethane at RT, this product decomposes completely within 15 min to form phthalide (IR: ν_{max}(CO) 1765 cm^{-1}).

(b) Under similar reactions conditions, *trans*-[2-(hydroxymethyl)phenyl]bromobis(triphenylphosphine)palladium, **15** (200 mg, 0.24 mmol), with CO gave a yellow solid (171 mg), assumed to contain *trans*-[2-(hydroxymethyl)benzoyl]bromobis-(triphenylphosphine)palladium, **27b**. IR: ν_{max}(CO)/cm^{-1} 1636 (KBr); 1636 (CH_2Cl_2). This product similarly decomposes in dichloromethane to form phthalide.

(c) Similarly, *trans*-[2-(hydroxyethyl)phenyl]iodobis(triphenylphosphine)palladium, **17** (150 mg, 0.17 mmol), gave a yellow solid (95 mg), assumed to contain *trans*-[2-(hydroxyethyl)-benzoyl]iodobis(triphenylphosphine)palladium, **27c**. IR: ν_{max}-(CO)/cm^{-1} 1651 (KBr); 1652 (CH_2Cl_2). In dichloromethane at RT, this product decomposes completely within 5 min to form 3,4-dihydroisocoumarin (IR: ν_{max}(CO) 1722 cm^{-1}).

Bis[2-(*μ*-oxomethyl-*κO*)phenyl-*κC*^{1}]bis(triphenylphosphine)dipalladium, 19 (cf. ref 10). NaH (60% dispersion in mineral oil; 10.0 mg, 0.25 mmol) was added to a suspension of *trans*-[2-(hydroxymethyl)phenyl]iodobis(triphenylphosphine)-palladium, **14** (212 mg, 0.245 mmol), and triphenylphosphine (71 mg, 0.27 mmol) in tetrahydrofuran (20 cm^3), and the mixture was stirred at RT for 12 h. The liberation of hydrogen gas occurred, and a pale green precipitate formed. The precipitate was collected by filtration, washed with H_2O (3 × 5 cm^3), to remove NaCl, followed by diethyl ether (3 × 10 mL), and finally dried in vacuo to give the title compound as a microcrystalline, pale green solid (68 mg, 58%). Recrystallization from dichloromethane/light petroleum ether afforded pale yellow crystals. Found: C, 61.74; H, 4.34. $C_{50}H_{42}O_2P_2Pd_2{\cdot}H_2O$ requires C, 62.06; H, 4.58. Spectral data as reported in ref 10.

[1,2-Bis(diphenylphosphino)ethane-*κ*^{2}*P,P′*][2-(oxomethyl-*κO*)phenyl-*κC*^{1}]palladium, 22. 1,2-bis(diphenylphosphino)ethane (840 mg, 2.11 mmol) in toluene (20 cm^3) was added dropwise to a suspension of bis[2-(*μ*-oxomethyl-k*O*)-phenyl-k*C*^{1}]bis(triphenylphosphine)dipalladium, **19a** (500 mg, 0.53 mmol), in toluene (55 cm^3) and the mixture stirred for 13 h at RT. The creamy-white precipitate was collected by filtration, washed with H_2O (2 × 20 cm^3), followed by diethyl ether (3 × 20 cm^3), and dried in vacuo to give the title product as a white solid (508 mg, 79%). Found: C, 63.14; H, 4.54. $C_{33}H_{30}OP_2Pd{\cdot}H_2O$ requires C, 63.02; H, 5.13. NMR ($CDCl_3$); δ_H/ppm: 2.20 (m, 2H, dppe, CH_2), 2.42 (m, 2H, dppe, CH_2), 5.70 (br s, 2H, CH_2O), 6.47 (∼t, J = 7.4 Hz, 1H, C_6H_4), 6.66 (m, 1H, C_6H_4), 6.86 (t, J = 7.4 Hz, 1H, C_6H_4), ∼7.2 (m, 1H, C_6H_4), 7.40 (m, 12H, PPh_2), 7.88 (m, 4H, PPh_2), 8.06 (m, 4H, PPh_2); δ_P/ppm: 34.0 (d, J_{PP} = 27.1 Hz), 55.7 (d, J_{PP} = 27.1 Hz). MS (ESI+): *m/z* 1209−21 (max. 1216, 100%), 606−616 (max. 610, 86%, M); $C_{33}H_{30}OP_2Pd$ requires 610.

Bis[2-(*μ*-2-oxoethyl-*κO*)phenyl-*κC*^{1}]bis(triphenylphosphine)dipalladium, 20. NaH (60% dispersion in mineral oil; 14.4 mg, 0.360 mmol) was added to a suspension of [2-(hydroxyethyl)phenyl]iodobis(triphenylphosphine)palladium, **17** (316 mg, 0.36 mmol), and triphenylphosphine (103.9 mg, 0.40 mmol) in THF (20 cm^3), and the mixture was stirred at RT for 12 h. Liberation of hydrogen gas occurred, and a pale green solid precipitated. The solid was collected by filtration, washed with H_2O (3 × 5 cm^3) to remove NaCl, then with diethyl ether (3 × 10 mL), and finally dried in vacuo to give the title compound as a microcrystalline, pale green solid (100 mg, 57%). Recrystallization from dichloromethane and light petroleum ether afforded colorless cubic crystals. Found: C, 63.68; H, 5.28. $C_{52}H_{46}O_2P_2Pd_2$ requires C, 63.88; H, 4.74. NMR ($CDCl_3$); δ_H/ppm: 2.72 (br d, 8H, CH_2CH_2), 6.21 (∼dt, J = 1.8

Table 5. Crystal and Structure Refinement Data.

	3	(**4**·CH_2Cl_2)$_2$	**7**·CH_2Cl_2	**8**·CH_2Cl_2	**14**·CH_2Cl_2	**17**·2CH_2Cl_2	**25**·4CH_2Cl_2
empirical formula	$C_{26}H_{24}BrOPPd$	$C_{54}H_{52}Cl_6O_2P_2Pd_2$	$C_{53}H_{48}Cl_2O_2P_2Pd_2$	$C_{59}H_{60}Cl_2O_2P_2Pd_2$	$C_{44}H_{39}Cl_2IOP_2Pd_2$	$C_{46}H_{43}Cl_4IOP_2Pd_2$	$C_{60}H_{62}Cl_8O_8P_2Pd_2$
fw	569.73	1220.40	1062.59	1146.72	949.89	1048.84	1469.44
cryst syst	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic	triclinic
space group	*Pna*2(1)	*P*2/*c*	*P*2(1)/*n*	$P\bar{1}$	*P*2(1)/*n*	*Pbcm*	$P\bar{1}$
unit cell dimensions/Å, deg	$a = 7.6260(16)$	$a = 12.8727(14)$	$a = 12.0474(12)$	$a = 8.782(5)$	$a = 11.878(5)$	$a = 10.360(1)$	$a = 10.3038(11)$
	$b = 28.235(4)$	$b = 10.9950(10)$	$b = 15.569(2)$	$b = 12.163(5)$	$b = 14.902(4)$	$b = 18.713(5)$	$b = 11.9421(14)$
	$c = 10.4316(17)$	$c = 19.490(3$	$c = 13.581(2)$	$c = 12.816(5)$	$c = 22.507(7))$	$c = 23.102(3)$	$c = 14.743(2)$
	$\alpha = \beta = \gamma = 90$	$\alpha = \gamma = 90$	$\alpha = \gamma = 90$	$\alpha = 99.900(5)$	$\alpha = \gamma = 90$	$\alpha = \beta = \gamma = 90$	$\alpha = 67.594(9)$
		$\beta = 106.921(14)$	$\beta = 112.960(9)$	$\beta = 95.560(5)$	$\beta = 95.42(4)$		$\beta = 71.833(11)$
				$\gamma = 103.680(5)$			$\gamma = 89.336(11)$
volume/Å^3	2246.2(7)	2639.2(5)	2345.4(5)	1296.7(10)	3966(2)	4478.7(14)	1581.6(3)
Z	4	2	2	1	4	4	1
density (calcd)/Mg/m^3	1.685	1.536	1.505	1.468	1.591	1.555	1.543
absorp coeff/mm^{-1}	2.692	1.086	0.989	0.901	1.496	1.448	1.009
F(000)	1136	1232	1076.0	586	1896	2096	744
cryst size/mm^3	0.78 × 0.22	0.74 × 0.24	0.52 × 0.46	0.34 × 0.32	0.42 × 0.12	0.56 × 0.52	0.40 × 0.28
	× 0.08	× 0.14	× 0.38	× 0.16	× 0.08	× 0.44	× 0.10
θ range for data	2.08 to	2.15 to	2.09 to	2.59 to	1.87 to	1.97 to	1.90 to
collection/deg	24.99	25.00	25.01	25.00	25.01	25.00	25.00
index ranges	$-1 \le h \le 9$	$-1 \le h \le 15$	$-1 \le h \le 14$	$-10 \le h \le 0$	$-1 \le h \le 14$	$-1 \le h \le 12$	$-12 \le h \le 1$
	$-33 \le k \le 1$	$-13 \le k \le 1$	$-1 \le k \le 18$	$-13 \le k \le 14$	$-1 \le k \le 17$	$-1 \le k \le 22$	$-13 \le k \le 13$
	$-1 \le l \le 12$	$-23 \le l \le 22$	$-16 \le l \le 15$	$-15 \le l \le 15$	$-26 \le l \le 26$	$-1 \le l \le 27$	$-17 \le l \le 17$
no. of reflns collected	2809	5914	5136	4838	8668	4978	6348
no. of indep reflns	2327	4647	4125	4466	6931	3988	5373
	[*R*(int) = 0.0577]	[*R*(int) = 0.0393]	[*R*(int) =0.0584]	[*R*(int) = 0.0649]	[*R*(int) = 0.0753]	[*R*(int) = 0.0687]	[*R*(int) = 0.0386]
completeness to max. θ/%	99.9	100.0	99.8	97.7	99.3	98.3	96.3
max./min. transmn	0.9898/0.7584	0.7890/0.6943	0.7179/0.6699	0.8939/0.730	0.9151/ 0.6594	0.6312/ 0.5378	0.8751/0.7617
no. of data/restraints/ params	2327/7/271	4647/0/316	4125/2/312	4466/6/325	6931/12/460	3988/2/268	5373/0/37
goodness-of-fit on F^2	1.069	1.035	0.980	2.078	1.008	1.013	1.059
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0613	R1 = 0.0292	R1 = 0.0510	R1 = 0.1055	R1 = 0.0748	R1 = 0.0626	R1 = 0.0435
	wR2 = 0.1661	wR2 = 0.0721	wR2 = 0.1213	wR2 = 0.2570	wR2 = 0.1731	wR2 = 0.1417	wR2 = 0.1061
R indices (all data)	R1 = 0.0701,	R1 = 0.0343	R1 = 0.0801	R1 = 0.1179	R1 = 0.1329	R1 = 0.0975	R1 = 0.0544
	wR2 = 0.1732	wR2 = 0.0754	wR2 = 0.1396	wR2 = 0.2678	wR2 = 0.2064	wR2 = 0.1621	wR2 = 0.1119
largest diff peak and hole/e Å^{-3}	2.011 and −4.024	0.616 and −0.445	0.656 and −0.999	4.395 and −5.489	1.305 and −2.275	2.236 and −1.258	0.727 and −0.902

and 7.35 Hz, 2H, C_6H_4, C*H-6*), 6.56 (m, 6H, C_6H_4, C*H-3*, *4, 5*), 7.18 (m, 12H, PPh_3, *m*-C*H*), 7.31 (m, 6H, PPh_3, *p*-C*H*), 7.53 (m, 12H, PPh_3, *o*-C*H*); δ_C/ppm: 48.0 (*C*H_2), 65.2 (*C*H_2O), 122.7 (C_6H_4, *C*H), 123.3 (d, J_{CP} = 4.4. Hz, C_6H_4, *C*H), 125.3 (C_6H_4, *C*H), 128.1 (d, J_{CP} = 10.6 Hz, PPh_3, *m-C*H), 130.1 (d, J_{CP} = 2.2 Hz, PPh_3, *p-C*H), 131.6 (d, J_{CP} = 48.0 Hz, PPh_3, *ipso-C*), 134.6 (d, J_{CP} = 11.3 Hz, PPh_3, *o-C*H), 138.2 (d, J_{CP} = 12.7 Hz, C_6H_4, *C*H-*6*), 141.1 (quat.-C, C_6H_4, *C-1* or *2*), 146.7 (d, J_{CP} = 5.6 Hz, quat.-C, C_6H_4, *C-1* or *2*); δ_P/ppm: 35.6 (s). MS (ESI+): *m/z* 978 (M + 2); $C_{52}H_{46}O_2P_2Pd_2$ requires 976.

[1,1′-Bis(diphenylphosphino)ferrocene-κ^2*P,P′*][2-(2-oxoethyl-κ*O*)phenyl-κ*C*^{1}]palladium, 23. 1,1′-Bis(diphenylphosphino)ferrocene (358 mg, 0.65 mmol) in toluene (10 cm^3) was added dropwise to a suspension of bis[2-(*μ*-2-oxoethyl-κ*O*)-phenyl-κ*C*^{1}]bis(triphenylphosphine)dipalladium, **20** (158 mg, 0.162 mmol), in toluene (10 cm^3), and the mixture was stirred for 4 h at RT. The resulting yellow-orange solid was collected by filtration, washed with diethyl ether (3 × 10 cm^3), and dried in vacuo to give the title compound (177 mg, 70%). Found: C, 64.18; H, 5.02. $C_{42}H_{36}FeOP_2Pd$ requires C, 64.59; H, 4.65. NMR ($CDCl_3$); δ_H/ppm: 3.11 (vbr s, 2H, C*H*$_2$CH$_2$O), 3.51 (br s, 2H, C_5H_4), 3.60 (vbr s, 2H, C*H*$_2$O), 4.14 (br s, 2H, C_5H_4), 4.47 (br s, 2H, C_5H_4), 4.73 (br s, 2H, C_5H_4), 6.24 (br m, 1H, C_6H_4), 6.64 (m, 2H, C_6H_4), 6.79 (m, 1H, C_6H_4), 7.10 (m, 4H, PPh_2), 7.26 (m, 4H, PPh_2), 7.45 (br m, 8H, PPh_2), 8.06 (br m, 4H, PPh_2); δ_P/ppm: 9.0 (d, J_{PP} = 35.2 Hz), 33.0 (d, J_{PP} = 35.3 Hz). MS (ESI+): *m/z* 780.7 (M); $C_{42}H_{36}FeOP_2Pd$ requires 780.

[1,2-Bis(diphenylphosphino)ethane-κ^2*P,P′*][2-(2-oxoethyl-κ*O*)phenyl-κ*C*^{1}]palladium, 24. 1,2-Bis(diphenylphosphino)ethane (450 mg, 1.13 mmol) in toluene (10 cm^3) was added dropwise to a suspension of bis[2-(*μ*-2-oxoethyl-κ*O*)-phenyl-κ*C*^{1}]bis(triphenylphosphine)dipalladium, **20** (276 mg, 0.282 mmol), in toluene (15 cm^3), and the mixture was stirred for 3 h at RT to form a creamy-white suspension. The white solid was collected by filtration, washed with diethyl ether (3 × 10 cm^3), and dried in vacuo to give the title compound (241 mg, 68%). Found: C, 65.39; H, 5.20. $C_{34}H_{32}OP_2Pd$ requires C, 65.34; H, 5.16. NMR ($CDCl_3$); δ_H/ppm: 2.05−2.6 (m, 4H, dppe C*H*$_2$), 3.05 (m, 2H, C*H*$_2$CH$_2$O), 3.83 (m, 2H, C*H*$_2$O), 6.40 (m, 1H, C_6H_4), 6.54 (m, 1H, C_6H_4), ∼6.77 (m, 1H, C_6H_4), ∼7.15 (m, 1H, C_6H_4), 7.2−7.6 (m, 12H, PPh_2), 7.7−7.9 (m, 4H, PPh_2), 8.0−8.17, (m, 4H, PPh_2); δ_P/ppm: 31.2 (d, J_{PP} = 28.0 Hz), 50.5 (d, J_{PP} = 28.0 Hz). MS (ESI+): *m/z* 624.7 (M); $C_{34}H_{32}OP_2Pd$ requires 624.

Bis[2-(*μ*-oxomethyl-κ*O*)phenyl-κ*C*^{1}]bis[tris(4-methoxyphenyl)phosphine]dipalladium, 25. Tris(4-methoxyphenyl)phosphine (275 mg, 0.78 mmol) in toluene (15 cm^3) was added dropwise to a suspension of bis[2-(*μ*-oxomethyl-κ*O*)-phenyl-κ*C*^{1}]bis(triphenylphosphine)dipalladium, **19** (185 mg, 0.195 mmol), in toluene (15 cm^3), and the mixture was stirred for 12 h at RT. The resulting homogeneous, pale green solution was reduced to 67% volume by distillation under reduced pressure, and light petroleum ether (20 cm^3) was added. The white precipitate produced was collected by filtration, washed with H_2O (2 × 10 cm^3), followed by diethyl ether (3 × 20 cm^3), and dried in vacuo to give the title compound (171 mg, 78%). Found: C, 58.66; H, 4.89. $C_{56}H_{54}O_8P_2Pd_2 \cdot H_2O$ requires C, 58.60; H, 4.92. NMR ($CDCl_3$); δ_H/ppm: 3.73 (s, 4H, C*H*$_2$O), 3.81 (s, 18H, OC*H*$_3$), 6.11 (t, *J* = 6.6 Hz, 2H, C_6H_4, *H-6*), 6.24 (m, 4H, C_6H_4, *H-3*, *5*), 6.61 (t, *J* = 7.4 Hz, 2H, C_6H_4, *H-4*), 6.88 (∼d, *J* ≈ 8 Hz, 12H, PC_6H_4O, *m*-C*H*), 7.77 (dd, *J* = 8.6 and 11.1 Hz, 12H, PC_6H_4O, *o*-C*H*); δ_C/ppm: 55.3 (*C*H_3O), 76.0 (*C*H_2O), 113.8 (d, J_{CP} = 11.8 Hz, PC_6H_4OMe, *m*-*C*H), 118.8 (C_6H_4, *C*H-*3* or *5*), 122.4 (C_6H_4, *C*H-*4*), 123.1 (d, J_{CP} = 5.7 Hz, C_6H_4, *C*H-*5* or *3*), 123.1 (d, J_{CP} = 52.3 Hz, PC_6H_4OMe, *ipso-C*P), 136.9 (d, J_{CP} = 14.1 Hz, PC_6H_4OMe, *o-C*H) 137.7 (d, J_{CP} = 10.1 Hz, C_6H_4, *C*H-*6*), 143.6 (d, J_{CP} = 6.4 Hz, quat.-C, C_6H_4, *C-2*), 160.4 (d, J_{CP} = 2.8 Hz, quat.-C, C_6H_4, Pd*C-1*), 161.4 (d, J_{CP} = 1.7 Hz, quat.-C, PC_6H_4OMe, *p-C*O); δ_P/ppm: 41.5 (s). MS (ESI+): *m/z* 1130.7 (M + 2), 564.6 (0.5M); $C_{56}H_{54}O_8P_2Pd_2$ requires 1128.

Typical Catalytic Carbonylation Reaction: Carbonylation of 2-(Hydroxymethyl)benzyl Bromide. 2-(Hydroxymethyl)benzyl bromide, **2a** (250 mg, 1.24 mmol), was added to a solution of ethyldiisopropylamine (0.48 mL, 2.74 mmol) and tetrakis(triphenylphosphine)palladium(0) (72 mg, 0.062 mmol) in toluene (20 cm^3). The vessel was immersed in a water bath and heated to 60 °C, and CO (1 atm) was passed through the mixture for 2 h to form a bright yellow homogeneous solution. The mixture was acidified with dilute HCl and filtered, and the soluble products were extracted into petroleum ether. The organic phase was dried with magnesium sulfate and filtered through a coarse sinter. GC-MS analysis of the sample showed quantitative conversion to 3-isochromanone **1**, which was identified by comparison with an authentic sample: NMR ($CDCl_3$); δ_H/ppm: 3.75 (s, 2H, C*H*$_2$CO), 5.35 (s, 2H, C*H*$_2$O), 7.15−7.4 (m, 4H, Ar-*H*). IR (CH_2Cl_2): ν_{max}(CO)/cm^{-1} 1750.

4.3. X-ray Data Collection and Crystal Structure Determination. Single crystals of compounds were grown by slow diffusion of light petroleum into solutions of the complex in dichloromethane at −15 °C. Crystals were mounted on a glass fiber and data collected with a Siemens P4 diffractometer. All data sets were collected with Mo Kα radiation (0.7107 Å) at 160 K with cooling by an Oxford Cryosystems cryostream. Absorption was corrected for using psi-scans, and structure refinement was by full matrix least squares against F^2.[34] For all structures, H atoms were constrained to idealized geometries; the hydroxyl hydrogen atoms were found in the difference map but drifted to unrealistic distances during refinement and so were constrained. In **7**, the disordered CH_2Cl_2 solvent was treated as 20/80% occupancy of both Cl atoms, each over two sites. In **8**, the anisotropy of C8 was restrained and the disordered CH_2Cl_2 solvent was modeled with one Cl atom over three sites. In **25**, one disordered CH_2Cl_2 had one Cl atom over three sites and the C atom over two sites. A summary of the data from the crystal structure determinations is given in Table 5.

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Supporting Information Available: Tables of X-ray data for complexes **3**, **4**, **7**, **8**, **14**, **17** (solvated and unsolvated crystals), and **25.** This material is available free of charge via the Internet at http://pubs.acs.org.

OM049131P

(34) *Siemens XSCANS*, Version 2.2; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1996. Sheldrick, G. M. *SHELXTL*, Version 5.10; Bruker AXS Inc.: Madison, WI, 1997.