Synthesis and Structure of New Oxapalladacycles with a Pd−O Bond

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Reaction of the arylpalladium complex [Pd(2-$C_6H_4CH_2OSi$-*t*-$BuMe_2$)(PPh_3)$_2$I] (**9**) with *n*-Bu_4NF gave the oxapalladacycle dimer [Pd(2-$C_6H_4CH_2O$)I(PPh_3)]$_2$ (**7**). Similarly, [Pd(2-$C_6H_4CH_2O$)I($AsPh_3$)]$_2$ (**11**) was obtained by reaction of the arylpalladium complex [Pd(2-$C_6H_4CH_2OSi$-*t*-$BuMe_2$)($AsPh_3$)$_2$I] (**10**) with *n*-Bu_4NF. The structure of dimer **7** was confirmed by single-crystal X-ray diffraction. Reaction of **7** or **11** with the bidentate ligands 1,1′-bis(diphenylphosphino)ferrocene and 1,10-phenanthroline gave the monomeric oxapalladacycle complexes **16** and **17**. Complex **7** inserts *tert*-butyl isocyanide to form 1,1-dimethyl-*N*-1(3*H*)-isobenzofuranylidenethanamine (**18**). Reaction of [Pd(2-C_6H_4R)(PPh_3)$_2$X] (R = CHO, X = Br, **21**; R = CO_2H, X = Br, **24a**; R = CO_2H, X = I, **24b**) with Ag_2CO_3 or Cs_2CO_3/$AgBF_4$ afforded the tetrameric complex [Pd(2-$C_6H_4CO_2$)(PPh_3)]$_4$ (**22**), whose structure was confirmed by X-ray diffraction.

Introduction

Alkoxo and hydroxo complexes of late transition metals are expected to display unusual reactivity as a consequence of the destabilization introduced by the nonbonding interaction between filled orbitals on the metal and on the oxygen.[1] Therefore, due to the central role played by palladium complexes as catalysts in organic synthesis,[2] palladium(II) alkoxide complexes have received particular attention.[3−5] In fact, these complexes have been proposed as intermediates in the important palladium-catalyzed synthesis of aryl ethers from aryl halides and alcohols.[6] Oxapalladacycles are key intermediates in the synthesis of five- to seven-membered-ring heterocycles by the intramolecular nucleophilic substitution of aryl bromides with alcohols.[7,8] An important issue in the formation of C−O bond by this method was the control on the β-hydride elimination.[8a]

Certain palladacycles have been demonstrated to be excellent catalysts for Heck alkenylations and cross-coupling reactions. In particular, the phosphapalladacycles developed by Hermann[9] have found application in a wide variety of transformations.[10] In addition, ortho-palladated triaryl phosphites[11] as well as ortho-metalated imines[12] and oximes[13] have been found to be stable yet active catalysts for the formation of C−C bonds.

As part of our program on the synthesis of stable palladacycles,[14] which might be used as catalysts in a

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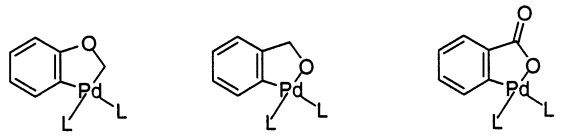
variety of C−C and C−X bond-forming processes, we have synthesized oxapalladacycles of type **I**.[15] These



I **II** **III**

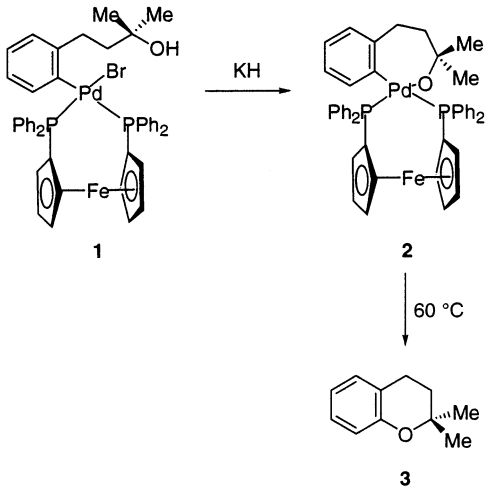
palladacycles are stable complexes that do not undergo reductive elimination to form 2*H*-benzoxete, a high-energy heterocyclic compound.[16] We decided to synthesize isomeric oxapalladacycles **II** with a Pd−O bond, whose decomposition by reductive elimination should be similarly forbidden. However, unlike complexes **I**, oxapalladacycles **II** possess hydrogens at the β-position with respect to the Pd atom and might decompose by β-hydrogen elimination. We also tried to prepare oxapalladacycles of type **III** which may be precursors of benzyne−Pd(0) complexes[17,18] by thermal elimination of CO_2. Herein we report the synthesis of complexes of type **II** and **III** from arylpalladium(II) complexes. Interestingly, complexes of type **II** with monodentate ligands form stable dimers, while complex **III** was isolated as a tetramer.

Oxapalladacycle **2**, a higher homologue of **II**, has been recently shown to undergo reductive elimination under mild conditions. Indeed, the seven-membered-ring oxapalladacycle **2**, prepared by treatment of arylpalladium complex **1** with KH, led to 2,2-dimethylchromane (**3**) by heating at 60 °C in THF-d_8 (Scheme 1).[7c]

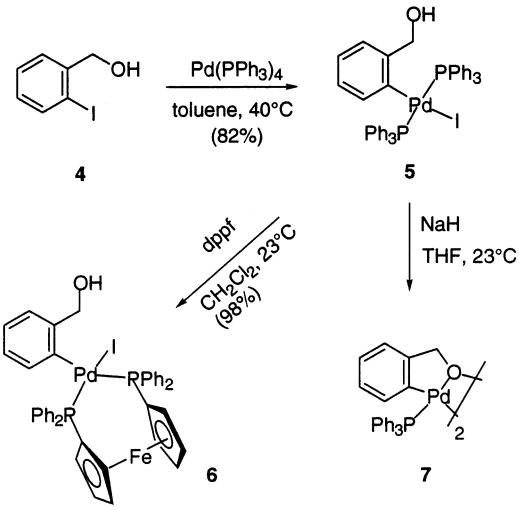
Results and Discussion

Synthesis of Palladacycles II. The synthesis of the desired palladacycles of type **II** was attempted from the oxidative addition product of *o*-iodobenzyl alcohol (**4**) to palladium(0) complexes. Thus, reaction of **4** with Pd(PPh$_3$)$_4$ in toluene at 40 °C led to arylpalladium complex **5** in 82% yield as a white solid (Scheme 2). This complex showed a characteristic singlet at δ 23.03 in the ^{1}P{^{1}H} NMR spectrum ($CDCl_3$), corresponding to a trans arrangement of the phosphine ligands. The hydroxyl proton appeared in the ^{1}H NMR spectrum (C_6D_6) at a rather high field (δ −0.08 ppm). However, this unusual chemical shift is probably merely due to the shielding by one of the phosphine phenyl groups.

Scheme 1



Scheme 2



The ligand exchange reaction of palladium complex **5** with an excess of 1,1′-bis(diphenylphosphino)ferrocene (dppf) gave **6** in 98% yield. This complex shows in the ^{1}H NMR a pattern consistent with the existence of a chirality axis. Thus, the methylene hydrogens of the CH_2OH group give rise to a pair of doublet of doublets (δ 4.72 and 4.03) coupled to the hydroxyl proton, which, in contrast with **5**, appears at δ 2.83. Two doublets were observed in the ^{31}P{^{1}H} NMR spectrum ($CDCl_3$) at δ 27.94 and 8.85 (^3J = 33.3 Hz).

Treatment of complex **5** with K_2CO_3 led to the slow formation of oxapalladacycle **7**, while 4-(dimethylamino)pyridine led only to unchanged starting material. The use of the stronger base NaH allowed for the preparation of **7** in 63% yield (Scheme 2). However, this procedure proved to be somewhat unpredictable, depending on the commercial source of NaH, leading to variable yields and, on occasion, to complete decomposition of the product. For this reason we decided to try the formation of the Pd−O bond under milder conditions by using a silyl ether as the starting material. Thus, we expected that the selective desilylation of a silyl derivative of **5** with a fluoride might lead to the formation of **7** more reproducibly.

Although the trimethylsilyl ether of benzyl alcohol **4** was too labile, the *tert*-butyldimethylsilyl (TBS) deriva-

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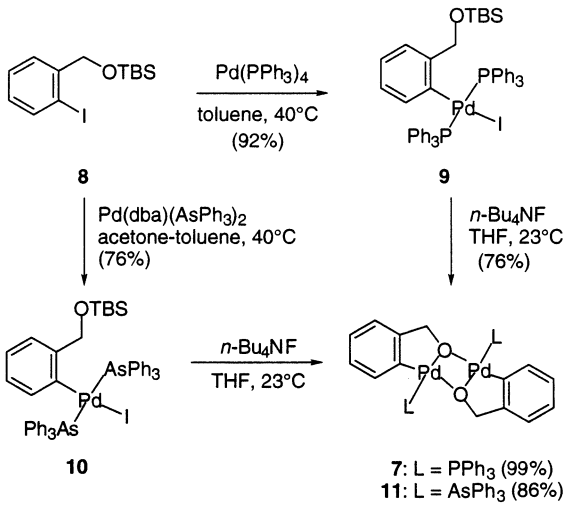
Scheme 3



tive **8** proved to be the substrate of choice. This compound was prepared by silylation under standard conditions in 91% yield (*t*-BuMe$_2$SiCl in DMF at 70 °C, Et$_3$N and DMAP as the bases).[19] Reaction of **8** with Pd(PPh$_3$)$_4$ (toluene, 40 °C) led to complex **9** in 92% yield. Similarly, reaction with Pd(dba)(AsPh$_3$)$_2$ in acetone−toluene at 40 °C afforded **10** (76%) (Scheme 3). Gratifyingly, reaction of **9** with 3 equiv of *n*-Bu$_4$NF (TBAF) in THF at 23 °C for 24 h led to oxapalladacycle **7** in 99% yield. Less soluble KF was not effective and gave only unchanged starting material. Similarly, reaction of **10** with TBAF in THF at 23 °C gave **11** in 86% yield.

The ^{1}H NMR spectrum of **7** corresponded to the formula $(C_{25}H_{21}OPPd)_n$ with only one PPh$_3$ ligand. Thus, the signal at δ 3.66 ppm corresponding to the CH$_2$ appeared as a doublet (J = 2.1 Hz) coupled to ^{31}P. In the ^{13}C{^{1}H} NMR spectrum a carbon signal was also coupled to ^{31}P (^2J = 10.1 Hz). The ^{31}P{^{1}H} NMR spectrum showed a singlet at δ 44.42 ppm. Although a monomeric structure for **7** corresponding to the formula $C_{25}H_{21}OPPd$ with a coordinatively unsaturated Pd center was highly unlikely, the FAB-MS did not allow us to distinguish between dimeric, trimeric, or higher order structures for this complex. Thus, although the peaks corresponding to the dimer (*m*/*z* 949, M$^+$ + 1) were clearly observed, those of the trimer (*m*/*z* 1423, M$^+$ + 1) were also present. Therefore, the X-ray structure of a single pale yellow crystal of **7** was determined, which demonstrated that this complex exists in the solid state as a dimer (Figure 1).

A dimeric structure was also assigned to palladacycle **11**, whose ^{1}H and ^{13}C NMR spectra demonstrated a 1:1 ratio of the organic and AsPh$_3$ ligands. The FAB-MS of **11** also showed peaks at *m*/*z* 1557 (M$^+$, 1) corresponding to the trimer and at *m*/*z* 1039 (M$^+$ + 1) for the dimer. This is consistent with the equilibria shown in Scheme 4 between monomeric, dimeric, and trimeric complexes.

It is important to note that dimers **7** and **11** were formed in the presence of free PPh$_3$ or AsPh$_3$ ligand, which demonstrates that the dimerization by formation of a Pd−O bond trans to the aryl is a highly favorable process. This dimerization could also be explained by

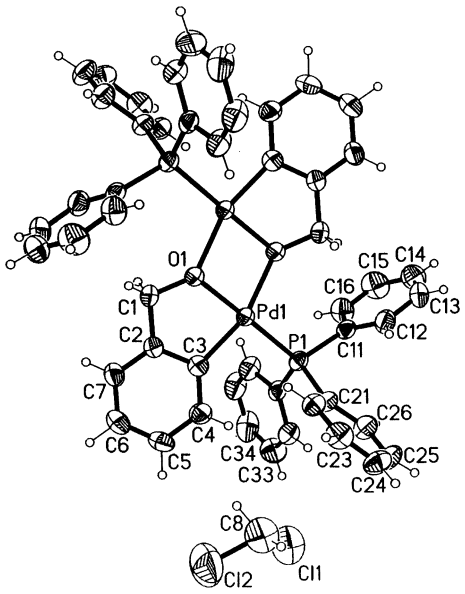
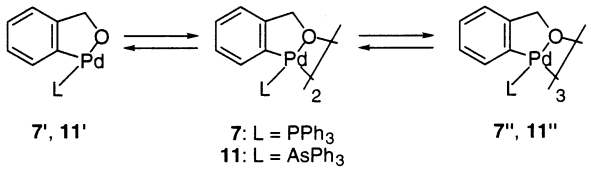


Figure 1. ORTEP drawing of complex **7** (50% probability level). Note the presence of solvating CH_2Cl_2.

Scheme 4



the weakness of the Pd−P and Pd−As bonds trans to the aryl ligand, a phenomenon that has been called "transphobia".[20] Indeed, treatment of **7** with an excess of PPh$_3$ failed to form a monomeric complex with two phosphine ligands. The ^{1}H NMR spectrum (CDCl$_3$) of the reaction mixture showed only a slight broadening of the doublet, corresponding to the methylene hydrogen signal at δ 3.66.

X-ray Structure of 7. An ORTEP drawing of the molecular structure of **7** is depicted in Figure 1. Crystallographic data are listed in Table 1, and significant bond distances and angles are listed in Table 2. This complex presents a dimeric centrosymmetric structure. The metal atom in each palladacycle completes its square-planar coordination sphere with a PPh$_3$ ligand and the O atom of the other metallacycle. The four central atoms (Pd−O−Pd−O) present a rhomboid arrangement. The internal O−Pd−O and Pd−O−Pd angles are 78.38(14) and 101.62(14)°, respectively, and are similar to the ones observed for a related four-membered dipalladacycle in a structurally different complex previously reported.[21] In each monomer, the aromatic ring and the plane determined by the ligands are not parallel, forming a dihedral angle of 13°. The three metal-containing rings form a chairlike structure. The bond distances Pd−C and Pd−O are 1.989(5) and 2.048(3) Å, respectively, in accordance with the values usually encountered in related compounds.[22] The Pd−Pd dis-

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Table 1. Crystal Data for Complexes 7·2CH_2Cl_2 and 22

	7·2CH_2Cl_2	22
mol formula	$C_{52}H_{46}Cl_2O_2P_2Pd_2$	$C_{100}H_{78}O_8P_4Pd_4$
cryst habit	pale yellow prism	pale yellow needle
cryst syst	triclinic	trigonal
a, Å	9.6515(9)	14.9831(13)
b, Å	10.2618(10)	14.9831(13)
c, Å	13.3006(13)	35.257(4)
α, deg	73.5870(10)	90
β, deg	71.9440(10)	90
γ, deg	89.064(2)	120
V, Å^3	1197.7(2)	6854.5(12)
Z	2	3
λ, Å	0.710 73	0.710 73
T, K	296(2)	148(2)
radiation used	Mo Kα	
space group	$P\bar{1}$	$P3_2$
cryst size, mm	0.30 × 0.20 × 0.05	0.10 × 0.08 × 0.08
calcd density, Mg/m^3	1.549	1.391
μ, mm^{-1}	1.081	0.899
abs cor	*ψ* scans	
diffractometer	Bruker-Siemens Smart CCD	
scan method	*ω* scans	
θ range, deg	1.68−23.27	2.72−20.80
limiting indices	$9 \le h \le 10$	$-14 \le h \le 14$
	$-7 \le k \le 11$	$-15 \le k \le 1$
	$-14 \le l \le 13$	$-35 \le l \le 1$
no of rflns measd	4600	12610
no. of indep rflns	3291	6288
R_{int}	0.0399	0.1175
R1[a]	0.0410	0.085
wR2[b]	0.0923	0.2280

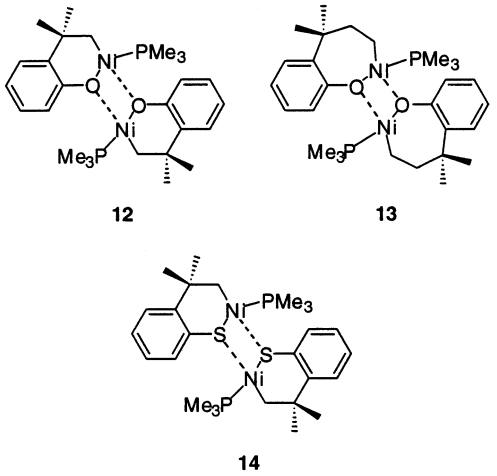
[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 7

	Bond Lengths		
Pd−C(3)	1.989(5)	C(2)−C(3)	1.412(7)
Pd−O(1)	2.048(3)	P(1)−C(21)	1.822(5)
Pd−P(1)	2.225(1)	P(1)−C(31)	1.827(5)
O(1)−C(1)	1.413(6)	P(1)−C(11)	1.841(5)
C(1)−C(2)	1.504(7)		
	Bond Angles		
C(3)−Pd−O(1)	83.56(17)	Pd−P(1)−C(11)	113.25(16)
O(1)−C(1)−C(2)	109.96(42)	Pd−P(1)−C(31)	113.30(16)
C(2)−C(3)−Pd	110.40(35)	C(21)−P(1)−C(31)	108.35(24)
C(1)−C(2)−C(7)	120.02(48)	C(31)−P(1)−C(11)	103.54(23)
C(4)−C(3)−Pd	133.00(41)	C(21)−P(1)−C(11)	102.40(24)
Pd−P(1)−C(21)	114.87(17)		

tance in **7** is ca. 3.22 Å, which is on the same order of the sum of the van der Waals radii (3.26 Å).[23]

Similar dimeric structures have been proposed for complexes **12** and **13**,[24] on the basis of the 1:1 stoichiometric ratio of the $C_{10}H_{12}O$ fragment to the PMe_3 ligand and by analogy to other O-bridging dimeric nickelacycles.[25] Recently, the dimeric structure **14** for the sulfur



analogue of **12** was also proposed on the basis of the spectroscopic data.[26] However, although the dimeric structures were reasonable, trimeric or higher order structures were not rigorously excluded in these cases. Related thianickelacycles and thiaplatinacycles have been demonstrated to exist in the solid state as trimers and dimers, respectively.[27,28]

Reactions of Palladacycles II. Although oxapalladacycles are solids stable to air, they decompose thermally in solution. Thus, heating complex **7** in $CDCl_3$ solution at about 70 °C cleanly gave benzaldehyde. This decomposition probably involves a *β*-hydrogen elimination, through coordinatively unsaturated monomer **7′**, to form the palladium(II) hydride intermediate **15**. This intermediate then undergoes a reductive elimination to form benzaldehyde (Scheme 5).

Ligand substitution from **7** is a facile process. Thus, treatment of **7** with 2 equiv of dppf in CH_2Cl_2 at 23 °C gave complex **16** in 70% yield (Scheme 6). On the other hand, 1,10-phenanthroline (phen) failed to irreversibly displace the phosphine ligand from **7**, leading to reaction mixtures that displayed a single broad signal for the methylene hydrogens at *δ* 4.61. However, displacement of the weaker ligand $AsPh_3$ in **11** by phen led to monomeric complex **17** in 76% yield.

The above results suggested that reaction of dimers **7** or **11** with small unsaturated molecules should be a facile process, resulting in the formation of monomeric complexes or insertion derivatives. In any event, reaction of **7** with *tert*-butyl isocyanide in $CHCl_3$ at 23 °C led to the formation of the known imidate **18**[29] (Scheme 7). This imidate is undoubtedly formed by dissociation of **7** by the isocyanide, followed by insertion and reduc-

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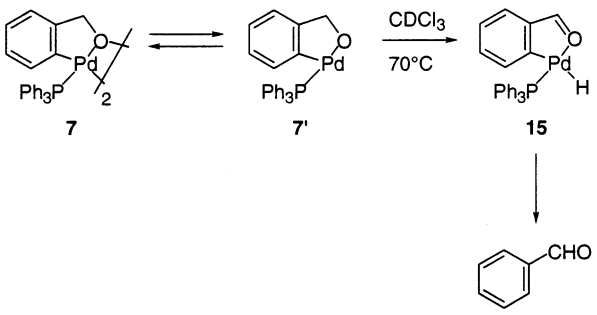
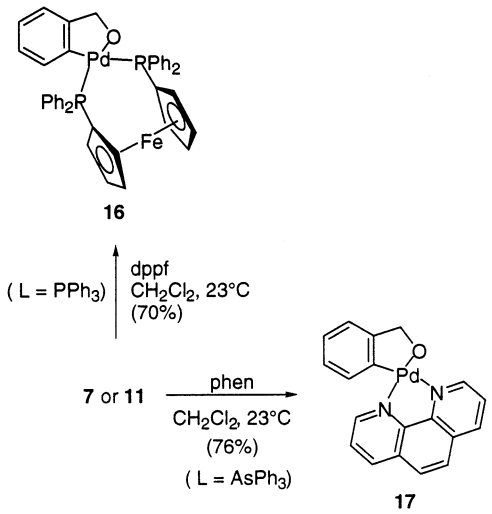
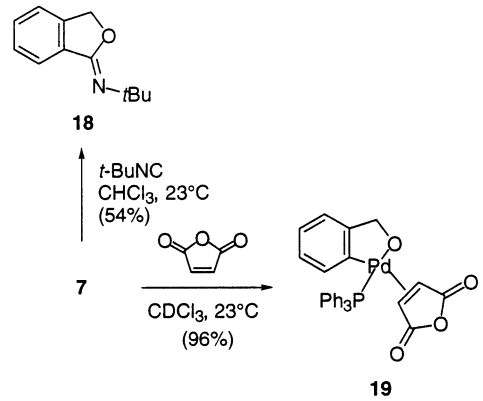
Scheme 5



Scheme 6



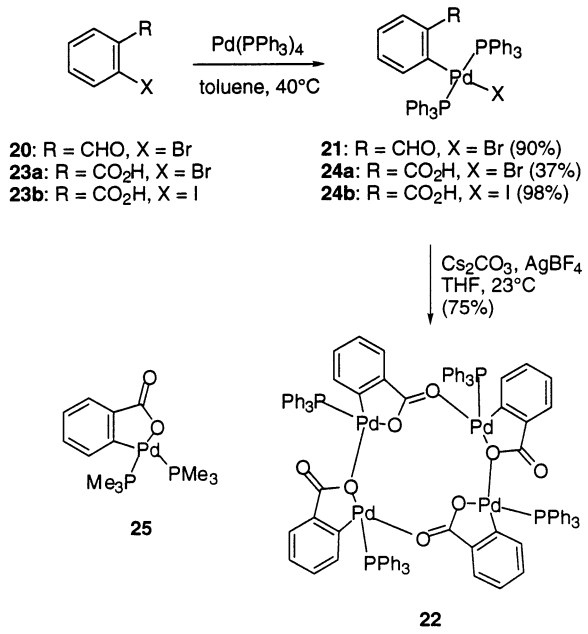
Scheme 7



tive elimination. This facile insertion reaction is in contrast with that observed with palladacycles of type **I**, which failed to undergo an insertion reaction and gave only substitution of a PPh_3 ligand by the isocyanide.[15a,b]

Reaction of **7** with maleic anhydride in $CDCl_3$ for 1 h led to complex **19** in 96% yield (Scheme 6). This complex showed a singlet at δ 48.31 in the $^{31}P\{^1H\}$ NMR spectrum, while the ^1H NMR at 23 °C showed a broad signal at δ 5.84 corresponding to the olefinic hydrogens, which suggests that the maleic anhydride ligands undergoes free rotation at this temperature. The configuration of **19** was assigned as shown, assuming a coordination of the PPh_3 trans to the alkoxide ligand. When the reaction of **7** with maleic anhydride was carried out at higher temperature, a complex mixture of products was obtained.

Scheme 8



Synthesis of Palladacycles III. Reaction of *o*-bromobenzaldehyde (**20**) with $Pd(PPh_3)_4$ gave complex **21** in 90% yield as an air-stable white solid (Scheme 8).[30] Surprisingly, treatment of **21** with Ag_2CO_3 in THF led to a complex in variable yields whose NMR data showed the absence of a formyl group. The ^1H NMR spectrum displayed signals for the aryl (δ 6.88, 6.63, 6.38, and 5.98 ppm) and a multiplet corresponding to a PPh_3. The presence of a single PPh_3 ligand was confirmed by the $^{31}P\{^1H\}$ NMR spectrum, which showed a singlet at δ 45.77 ppm, at a chemical shift similar to that observed for palladacycle dimer **7**. The IR spectrum showed a strong absorption at 1540 cm^{-1}, which suggested the presence of a carboxy group. However, the carbonyl carbon signal was not observed in the ^{13}C NMR, probably due to its very low intensity and the coupling with ^{31}P. The structure of this complex was surprisingly determined as the tetramer **22** on the basis of X-ray diffraction (Figure 2). Interestingly, two different types of monomers are present in the solid state, although the NMR data in $CDCl_3$ in solution correspond to a single species, which indicates that the tetramer is fluxional or dissociates readily in solution.

The oxidation of the formyl group of **21** with Ag_2CO_3 is somewhat surprising, since Ag_2CO_3 is a mild oxidant commonly used for the selective conversion of alcohols into aldehydes.[31] This oxidation might be facilitated by the coordination of the formyl group to the palladium center after abstraction of the bromide by Ag(I).[32]

Complex **22** was also obtained from *o*-bromobenzoic acid (**23a**) by reaction with $Pd(PPh_3)_4$ to give complex **24a** (37%), followed by reaction with Ag_2CO_3 in THF

(30) Complex **29** has been prepared by reaction of bromobenzene with $Pd_2(dba)_3$·dba and PPh_3: Vicente, J.; Abad, J.-A.; Martínez-Viviente, E.; Ramírez de Arellano, M. C. *Organometallics* **2000**, *19*, 752.

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(32) Related stable cationic complexes have been recently prepared from (2-acylphenyl)palladium(II) complexes.[28]

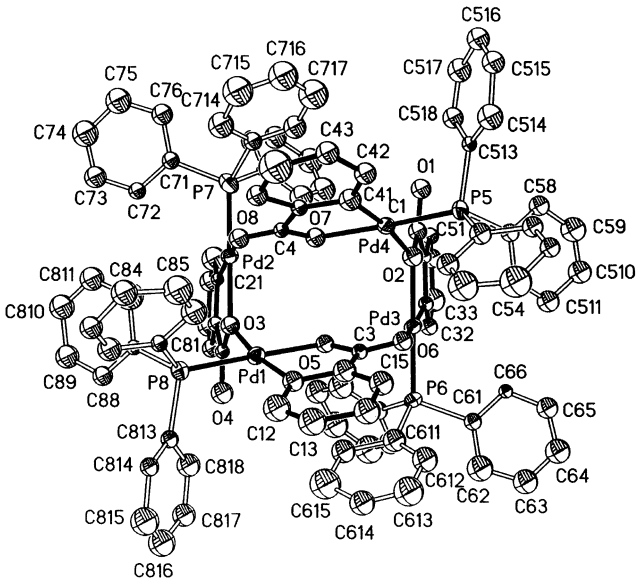

Figure 2. ORTEP drawing of complex **22** (50% probability level).

(Scheme 8). However, the synthesis of **22** by this method was highly dependent on the particular sample of Ag_2CO_3 and the isolated yields varied between 5 and 67%. Reaction of **24a** with $NaHCO_3$ or K_2CO_3 also led to **22**, although the yields were low. Better results were obtained from complex **24b**, which was synthesized in almost quantitative yield by reaction of *o*-iodobenzoic acid (**23b**) with $Pd(PPh_3)_4$. Treatment of **24b** with excess Cs_2CO_3 in THF at 23 °C for 16 h, followed by addition of $AgBF_4$, led to **22** reproducibly in 75% yield. Tetrameric palladacycle **22** decomposed readily upon heating to give black Pd(0) suspensions. However, no pure organic product could be isolated from the reaction mixture. Complex **22** is related to the monomeric palladacycle **25** with two PMe_3 ligands and has been recently prepared by the oxidative addition of phthalic anhydride to $Pd(PMe_3)_2$(styrene) followed by in situ decarbonylation.[33,34]

X-ray Structure of Complex 22. An ORTEP diagram is depicted in Figure 2. Crystallographic data are listed in Table 1, and significant bond distances and angles are listed in Table 3. The molecular structure consists of four palladacycle units arranged in a cyclic tetramer with an approximate C_2 symmetry.[35] Figure 3 shows a simplified diagram of the complex core. Monomers are bonded to their neighbors through two Pd−O bonds, using the metal atoms and O(sp^2) or O(sp^3) atoms for alternate subunits. Thus, two different types of monomers are present. The distances between both pairs of opposite Pd atoms are 5.077 and 5.601 Å. The distances between the centers of opposite aromatic rings are longer than the ones between the corresponding

Table 3. Selected Bond Distances (Å) and Angles (deg) for 22

Bond Lengths			
Pd(1)−C(11)	1.95(3)	C(16)−C(11)	1.40(4)
Pd(1)−O(5)	2.06(2)	C(11)−C(12)	1.49(5)
Pd(1)−O(3)	2.16(2)	C(12)−C(13)	1.30(5)
Pd(1)−P(8)	2.240(9)	C(13)−C(14)	1.41(5)
O(5)−C(3)	1.26(3)	C(14)−C(15)	1.44(5)
C(3)−O(6)	1.24(3)	C(15)−C(16)	1.40(4)
C(3)−C(16)	1.44(4)		

Bond Angles			
P(8)−Pd(1)−O(5)	178.4(6)	Pd(1)−O(3)−Pd(2)	123.0(10)
P(8)−Pd(1)−C(11)	95.6(10)	Pd(1)−O(5)−C(3)	113(2)
P(8)−Pd(1)−O(3)	94.5(6)	O(5)−C(3)−C(16)	115(3)
C(11)−Pd(1)−O(3)	169.8(11)	C(16)−C(11)−C(12)	118(3)
C(11)−Pd(1)−O(5)	82.9(11)	C(16)−C(11)−Pd	109(2)
C(5)−Pd(1)−O(3)	87.0(8)	C(3)−C(16)−C(15)	121(3)
Pd(1)−C(11)−C(12)	133(3)	C(3)−C(16)−C(11)	119(3)
Pd(1)−O(3)−C(2)	121(2)		

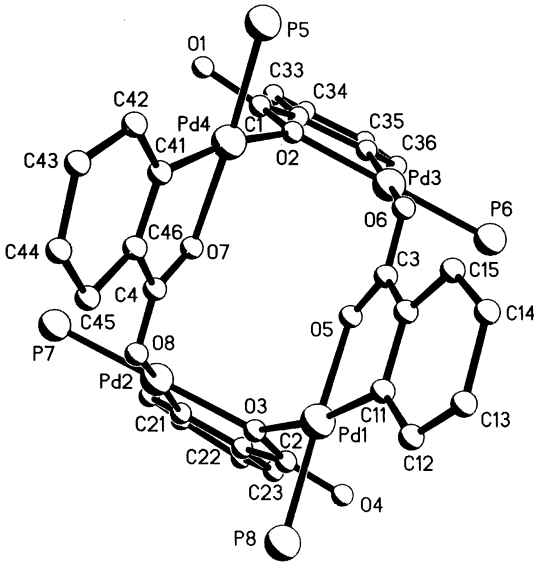

Figure 3. ORTEP representation of complex **22** showing the central macrocyclic core.

metal atoms (5.591 and 6.603 Å, respectively). The four Pd atoms are not coplanar and deviate 1.12−1.13 Å from the mean plane. The benzopalladacycles are arranged alternatively above and below this plane, forming angles of 66.13, 81.10, 63.99, and 81.39°, respectively. Pd−C and Pd−O bond distances lie within the usual values.

Conclusions

We have synthesized new oxapalladacycles with an O−Pd bond by intramolecular displacement of halide ligands by alkoxide or carboxylate. These new palladium complexes with a PPh_3 or $AsPh_3$ neutral ligand exist as dimers (**7** and **11**) or as a tetramer (**22**). The strong trans influence exerted by both aryl and phosphine ligands and the restriction imposed by the coordination of the alkoxide may explain this behavior. Monomeric palladium complexes **16** and **17** were obtained with bidentate ligands.

Although, as expected, oxapalladacycle complexes of type **II** do not undergo reductive elimination, they undergo β-hydride elimination at about 70 °C.

Preparation of benzyne−Pd(0) species by the thermal decarboxylation of **22** as well as catalytic applications of these and related palladacycles are under investigation.

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(34) For a related nickellacycle: Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992.

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Experimental Section

General Considerations. NMR spectra were recorded at 23 °C. Solvents were purified and dried using standard procedures. Chromatographic purifications were carried out using flash grade silica gel with distilled solvents. Trituration involved stirring with the stated solvent, filtering, and washing with the same solvent. All reactions were carried out under an Ar atmosphere.

A correct elemental analysis was not obtained for palladium complexes **6**, **7**, **9**, **11**, **16**, **17**, and **22** due to the presence of traces of ligands as impurities that could not be removed by recrystallization. Complex **19** decomposed at room temperature.

$Pd(PPh_3)_4$[36] and Pd(dba)(bpy)[37] were prepared according to the described procedures.

***trans*-[2-(Hydroxymethyl)phenyl]iodobis(triphenylphosphine)palladium (5).** To a solution of *o*-iodobenzyl alcohol (**4**; 250 mg, 1.06 mmol) in toluene (5 mL) was added $Pd(PPh_3)_4$ (1.12 g, 0.96 mmol), and the resulting solution was briefly sonicated and then heated at 40 °C for 3 h. The solid was filtered and washed with Et_2O to give **5** (680 mg, 82%) as a white solid. This complex was recrystallized from THF−Et_2O. ^1H NMR (200 MHz, C_6D_6): δ 7.30 (m, 12H), 6.83 (br d, J = 7.5 Hz, 1H), 6.55 (m, 18H), 6.35 (d, J = 7.0 Hz, 1H), 6.22 (t, J = 7.0 Hz, 1H), 5.19 (t, J = 7.5 Hz, 1H), 4.19 (d, J = 7.0 Hz, 2H), −0.08 (t, J = 7.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, DEPT): δ 158.35 [t, $J(^{13}C-^{31}P)$ = 2.5 Hz, C], 144.15 [t, $J(^{13}C-^{31}P)$ = 3.4 Hz, C], 134.81 [t, $^2J(^{13}C-^{31}P)$ = 6.1 Hz, PPh_3, CH], 134.02 [t, $J(^{13}C-^{31}P)$ = 4.4 Hz, CH], 131.74 [t, $^1J(^{13}C-^{31}P)$ = 23.2 Hz, PPh_3, C], 129.98 (s, PPh_3, CH), 128.35 (s, CH), 127.84 [t, $^3J(^{13}C-^{31}P)$ = 5.1 Hz, PPh_3, CH], 125.70 (s, CH), 123.51 (s, CH), 68.14 [t, $J(^{13}C-^{31}P)$ = 3.4 Hz, CH_2]. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 23.03. Anal. Calcd for $C_{43}H_{37}IOPdP_2$: C, 59.70; H, 4.31. Found: C, 59.90; H, 4.65.

Author: Please give the missing resonance value in the list of ^{13}C values.

[2-(Hydroxymethyl)phenyl]iodo[1,1′-bis(diphenylphosphino)ferrocene]palladium (6). To a solution of **5** (100 mg, 0.12 mmol) in CH_2Cl_2 (3 mL) was added 1,1′-bis(diphenylphosphino)ferrocene (70 mg, 0.13 mmol) at 23 °C for 1 h. The solvent was evaporated, and the residue was triturated with Et_2O to give **6** (100 mg, 98%) as a yellow solid. ^1H NMR (200 MHz, $CDCl_3$): δ 8.14−7.90 (m, 5H), 7.55 (m, 6H), 7.30 (m, 5H), 7.10 (t, J = 7.0 Hz, 1H), 6.85 (m, 2H), 6.74−6.55 (m, 5H), 5.09 (s, 1H), 4.72 (dd, J = 11.4, 3.0 Hz, 1H), 4.65 (s, 1H), 4.35 (s, 1H), 4.31 (s, 1H), 4.13 (s, 2H), 4.03 (dd, J = 10.5, 10.3 Hz, 1H), 3.69 (s, 1H), 3.59 (s, 1H), 2.83 (dd, J = 9.6, 3.4 Hz, 1H) (the signal at δ 2.83 exchanged with D_2O). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$; DEPT): δ 151.97 [d, $J(^{13}C-^{31}P)$ = 122.0 Hz, C], 144.35 [t, $J(^{13}C-^{31}P)$ = 3.6 Hz, C], 135.45 (m, PPh_2, CH), 134.68 [d, $J(^{13}C-^{31}P)$ = 4.7 Hz, CH], 131.71 (m, PPh_2, CH), 130.28 (m, PPh_2, CH), 129.26 [td, $J(^{13}C-^{31}P)$ = 8.8 Hz, CH], 128.38 (m, PPh_2, CH), 127.02 (m, PPh_2, CH), 126.09 [d, $J(^{13}C-^{31}P)$ = 7.8 Hz, CH], 123.46 (s, PPh_2, CH), 76.35 (m, C), 74.21 (m, CH), 73.29 (m, CH), 72.39 (m, CH), 70.71 (m, CH), 69.58 [t, $J(^{13}C-P)$ = 2.0 Hz, CH_2]. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 27.94 (d, J = 33.2 Hz, 1P), 8.85 (d, J = 33.5 H, 1P).

1-[((*tert*-Butyldimethylsilyl)oxy)methyl]-2-iodobenzene (8). A mixture of **4** (100 mg, 0.42 mmol), chloro-*tert*-butyldimethylsilane (77 mg, 0.51 mmol), DMAP (5 mg, 0.42 mmol), and Et_3N (86 mg, 0.85 mmol) in DMF (10 mL) was heated at 70 °C for 17 h. After being cooled to room temperature, the mixture was partitioned between H_2O and Et_2O. After the usual extractive workup, the solvent was evaporated. The residue was purified by chromatography (hexane) to give **8** (136 mg, 91%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ 7.81 (d, J = 8.1 Hz, 1H), 7.55 (dd, J = 7.7, 1.6 Hz, 1H), 7.41 (t, J = 7.7 Hz, 1H), 6.99 (td, J = 8.1, 1.8 Hz, 1H), 4.66 (s, 2H), 1.00 (s, 9H), 0.17 (s, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 142.87, 138.60, 128.48, 128.11, 127.36, 95.76, 69.35, 25.96, 18.37, −3.01. Anal. Calcd for $C_{13}H_{21}IOSi$: C, 44.83; H, 6.08. Found: C, 44.77; H, 5.78.

(Oxomethylene-1,2-phenylene)(triphenylphosphine)-palladium Dimer (7). A mixture of **9** (1.27 g, 1.30 mmol) and *n*-Bu_4NF (1.19 g, 4.53 mmol) in THF (10 mL) was stirred at 23 °C for 24 h. Precipitated **7** was filtered and washed with Et_2O. The filtrate was evaporated and triturated with THF to give additional **7** (combined yield: 610 mg, 99%), as a pale yellow solid. Crystals of **7** were obtained from a solution of CH_2Cl_2 at −20 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 7.85 (m, 6H), 7.40 (m, 9H), 6.59 (t, J = 7.5 Hz, 1H), 6.19 (m, 2H), 6.06 (t, J = 7.5 Hz, 1H), 3.66 (d, J = 2.1 Hz, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, DEPT): δ 160.14 (s, C), 137.57 [d, $^2J(^{13}C-^{31}P)$ = 10.1 Hz, CH], 135.45 [d, $^3J(^{13}C-^{31}P)$ = 12.7 Hz, PPh_3, CH], 131.38 [d, $^1J(^{13}C-^{31}P)$ = 47.8 Hz, PPh_3, C], 130.48 (br s, PPh_3, CH), 128.30 [d, $^3J(^{13}C-^{31}P)$ = 10.7 Hz, PPh_3, CH], 123.13 (br s, CH), 122.53 (s, CH), 118.94 (s, CH), 75.79 (s, CH_2) (the signal of a quaternary carbon was not observed). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 44.42. MS (FAB$^+$): m/z 1423 (M^+ + 1, trimer, 0.02), 949 (M^+ + 1, dimer, 1), 739, 737 (5), 736 (3), 475 (61) (M^+ + 1, monomer, 4), 474 (46), 473 (24). Anal. Calcd for $C_{50}H_{42}O_2P_2Pd_2 \cdot 0.25CH_2Cl_2$: C, 62.17; H, 4.41. Found: C, 62.28; H, 4.55.

***trans*-[2-(((*tert*-Butyldimethylsilyl)oxy)methyl)phenyl]-iodobis(triphenylphosphine)palladium (9).** To a suspension of $Pd(PPh_3)_4$ (1.32 g, 1.15 mmol) in toluene (10 mL) was added **8** (370 mg, 1.06 mmol), and the mixture was heated at 40 °C for 6 h. The solid was filtered and washed with Et_2O to give **9** (955 mg, 92%) as a pale yellow solid. ^1H NMR (200 MHz, $CDCl_3$): δ 7.50 (m, 12H), 7.40 (m, 18H), 6.85 (d, J = 7.3 Hz, 1H), 6.51 (m, 2H), 6.27 (m, 1H), 4.48 (s, 2H), 0.86 (s, 9H), −0.05 (s, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, DEPT): δ 156.73 (s, C), 143.73 (s, C), 134.80 [d, $^2J(^{13}C-^{31}P)$ = 5.8 Hz, PPh_3, CH], 134.14 [d, $^3J(^{13}C-^{31}P)$ = 3.9 Hz, CH], 131.91 [d, $^1J(^{13}C-^{31}P)$ = 23.1 Hz, PPh_3, C], 129.76 (br s, PPh_3, CH), 127.72 [d, $^3J(^{13}C-^{31}P)$ = 4.2 Hz, PPh_3, CH], 126.40 (br s, CH), 125.30 (s, CH), 122.80 (s, C), 66.79 (s, CH_2), 25.93 (s, 3 CH_3), 18.29 (s, C), −2.78 (s, 2 CH_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 23.16. FAB-MS: m/z 851 (M^+ + 1, 1), 589 (60), 483 (100), 263 (47).

***trans*-[2-(((*tert*-Butyldimethylsilyl)oxy)methyl)phenyl]-iodobis(triphenylarsine)palladium (10).** A mixture of $Pd_2(dba)_3 \cdot dba$ (330 mg, 0.57 mmol) and $AsPh_3$ (790 mg, 2.58 mmol) in acetone (5 mL) was stirred at 23 °C for 3 h to give a precipitate. To the suspension was added **8** (300 mg, 0.86 mmol) and toluene (10 mL), and the mixture was heated at 40 °C for 17 h. The mixture was filtered through Celite, and the filtrate was evaporated. The residue was triturated with Et_2O to give **10** (465 mg, 76%) as a pale yellow solid that was recrystallized from CH_2Cl_2/Et_2O. ^1H NMR (200 MHz, $CDCl_3$): δ 7.35 (m, 30H), 6.88 (d, J = 7.5 Hz, 1H), 6.56 (m, 2H), 6.34 (m, 1H), 4.49 (s, 2H), 0.81 (s, 9H), −0.15 (s, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$; DEPT): δ 147.69 (C), 145.24 (C), 135.06 (CH), 133.93 (CH, $AsPh_3$), 133.65 (C, $AsPh_3$), 129.48 (CH, $AsPh_3$), 128.31 (CH, $AsPh_3$), 126.69 (CH), 125.35 (CH), 123.27 (CH), 66.56 (CH_2), 25.87 (3 CH_3), 19.86 (C), −2.64 (2 CH_3). Anal. Calcd for $C_{49}H_{51}As_2IOPdSi \cdot H_2O$: C, 54.23; H, 4.93. Found: C, 54.07; H, 4.81.

(Oxomethylene-1,2-phenylene)(triphenylarsine)palladium Dimer (11). A mixture of **10** (200 mg, 0.18 mmol) and *n*-Bu_4NF (97 mg, 0.87 mmol) in THF (2 mL) was stirred for 17 h at 23 °C. The solvent was evaporated, and the residue was triturated with 1:3 $CH_2Cl_2-Et_2O$ to give **11** (83 mg, 86%) as a pale yellow solid. ^1H NMR (200 MHz, $CDCl_3$): δ 7.83 (m,

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6H), 7.40 (m, 9H), 6.59 (t, J = 7.5 Hz, 1H), 6.20 (m, 2H), 6.14 (t, J = 7.5 Hz, 1H), 3.83 (s, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, DEPT): δ 160.65 (s, C), 152.75 (s, C), 140.58 (s, CH), 137.76 (s, CH), 134.48 (s, $AsPh_3$, CH), 133.18 (s, $AsPh_3$, C), 130.25 (s, $AsPh_3$, CH), 128.84 (s, $AsPh_3$, CH), 123.25 (s, CH), 122.80 (s, CH), 53.42 (s, CH_2). FAB-MS: m/z 1557 (M^+, 1, trimer), 1039 ($M^+ + 1$, dimer, 1), 825 (8), 519 ($M^+ + 1$, 47, monomer), 154 (100). Anal. Calcd for $C_{50}H_{42}O_2As_2Pd_2 \cdot 0.5CH_2Cl_2$: C, 56.16; H, 4.05. Found: C, 56.43; H, 4.29.

(Oxomethylene-1,2-phenylene)-[1,1′-bis(diphenylphosphino)ferrocene)]palladium (16). A mixture of **7** (25 mg, 0.026 mmol) and dppf (29 mg, 0.052 mmol) in CH_2Cl_2 (2 mL) was stirred at 23 °C for 2 h. The solvent was evaporated, and the residue was triturated with Et_2O to give **16** (28 mg, 70%) as an orange solid. ^1H NMR (300 MHz, $CDCl_3$): δ 7.94 (m, 8H), 7.37. (m, 12H), 7.05 (m, 1H), 6.74 (t, J = 12.5 Hz, 1H), 6.26 (m, 1H), 6.08 (m, 1H), 5.33 (m, 2H), 4.27 (br s, 4H), 4.20 (br s, 2H), 3.92 (br s, 2H). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 35.38 (d, J = 35.4 Hz), 17.62 (d, J = 35.6 Hz).

(Oxomethylene-1,2-phenylene)(1,10-phenanthroline)-palladium (17). A mixture of **11** (20 mg, 0.019 mmol) and 1,10-phenanthroline (8.5 mg, 0.042 mmol) in CH_2Cl_2 (3 mL) was stirred at 23 °C for 17 h. The solvent was evaporated, and the residue was triturated with Et_2O to give **17** (12 mg, 76%) as an orange solid. ^1H NMR (200 MHz, $CDCl_3$): δ 9.50 (d, J = 4.3 Hz, 1H), 9.36 (d, J = 3.9 Hz, 1H), 8.52 (dd, J = 8.1, 1.3 Hz, 1H), 8.47 (dd, J = 8.0, 1.4 Hz, 1H), 7.97 (d, J = 2.0 Hz, 2H), 7.89 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.35 (m, 1H), 7.05 (m, 3H), 5.28 (s, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, DEPT): δ 173.97, 151.35, 150.16, 148.13, 145.02, 139.99, 137.55, 137.51, 131.75, 130.46, 129.65, 127.57, 127.19, 125.54, 125.48, 124.28, 123.77, 106.28, 86.96.

1,1-Dimethyl-*N*-1(3*H*)-isobenzofuranylidenethanamine (18). To a suspension of **7** (50 mg, 0.05 mmol) in $CHCl_3$ (1 mL) was added *tert*-butyl isocyanide (12 mg, 0.14 mmol) to give a clear solution. The solvent was evaporated, and the residue was dissolved in Et_2O. The solution was washed with water (2×), dried (Na_2SO_4 and $MgSO_4$), and evaporated. The oil was purified by chromatography (7:3 hexanes−EtOAc) to give **12** as a white solid (10 mg, 54%).[32] ^1H NMR (200 MHz, $CDCl_3$): δ 7.82 (d, J = 7.5 Hz, 1H), 7.40 (m, 3H), 5.31 (s, 2H), 1.40 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 156.82, 142.32, 131.88, 130.75, 128.11, 123.59, 121.00, 72.15, 53.66, 29.93.

(Maleic anhydride)(oxomethylene-1,2-phenylene)(triphenylphosphine)palladium (19). A suspension of **7** (20 mg, 0.021 mmol) in $CDCl_3$ (0.4 mL) was treated with maleic anhydride (5 mg, 0.051 mmol) at 23 °C for 1 h to give **19** (21 mg, 96%). ^1H NMR (200 MHz, $CDCl_3$): δ 7.70 (m, 6H), 7.36 (m, 9H), 6.95 (t, J = 8.0 Hz, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.44 (t, J = 8.0 Hz, 1H), 6.25 (t, J = 7.4 Hz, 1H), 5.84 (br s, 2H), 5.35 (br s, 2H). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 48.39. FAB-MS m/z 573 ($M^+ + 1$) (16), 475 (23), 339 (40).

***trans*-(2-Formylphenyl)bromobis(triphenylphosphine)-palladium(II) (21).** A mixture of 2-bromobenzaldehyde (**20**; 100 mg, 0.54 mmol) and $Pd(PPh_3)_4$ (567 mg, 0.49 mmol) in toluene (10 mL) was heated at 40 °C for 6 h. The resulting solid was filtered and washed with Et_2O to give **21** (395 mg, 90%) as a pale yellow solid.[33] IR (KBr): 1685 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 9.69 (s, 1H), 7.51 (m, 12H), 7.27 (m, 18H), 6.60 (m, 4H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$; DEPT): δ 194.61 (C), 168.55 (C), 140.18 (C), 135.21 (CH), 134.59 [d, $^2J(^{13}C-^{31}P)$ = 5.8 Hz, PPh_3, CH], 135.07 (CH), 131.26 (CH), 130.81 [d, $^1J(^{13}C-^{31}P)$ = 23.1 Hz, PPh_3, C], 129.91 (br s, PPh_3, CH), 127.93 [d, $^3J(^{13}C-^{31}P)$ = 4.2 Hz, PPh_3, CH], 122.58 (CH). $^{31}P-\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 24.17. Anal. Calcd for $C_{43}H_{35}BrOP_2Pd$: C, 63.29; H, 4.32. Found: C, 63.25; H, 4.40.

***trans*-(2-Carboxyphenyl)bromobis(triphenylphosphine)palladium (24a) and *trans*-(2-Carboxyphenyl)-iodobis(triphenylphosphine)palladium(II) (24b). 24a.** A mixture of 2-bromobenzoic acid (**23a**; 100 mg, 0.50 mmol) and $Pd(PPh_3)_4$ (373 mg, 0.331 mmol) in toluene (5 mL) was heated at 70 °C for 20 h. The resulting solid was filtered and washed with Et_2O to give **24a** (90 mg, 37%) as a yellow solid. ^1H NMR (200 MHz, $CDCl_3$): δ 7.80−7.10 (m, 32H), 6.61 (m, 2H).

24b. A suspension of *o*-iodobenzoic acid (**23b**; 689 mg, 2.78 mmol) and $Pd(PPh_3)_4$ (2.14 g, 1.85 mmol) in toluene (25 mL) was heated at 70 °C for 16 h. The mixture was filtered off, and the solid was washed with Et_2O to yield **24b** (2.14 g, 98%) as a yellow solid. ^1H NMR (300 MHz, DMSO-d_6): δ 7.50−7.24 (m, 31 H), 6.78 (br d, J = 7.5 Hz, 1H), 6.59 (t, J = 7.1 Hz, 1H), 6.39 (t, J = 7.3 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 169.15, 167.59, 134.62 [t, $^2J(^{13}C-^{31}P)$ = 56 Hz; PPh_3], 132.54, 132.08 [t, $^1J(^{13}C-^{31}P)$ = 23 Hz; PPh_3], 130.03 (s, PPh_3), 129.82, 127.92 (br s, PPh_3), 121.98 (two signals are missing or overlapped). ^{31}P NMR (121.5 MHz, DMSO-d_6): δ 22.06. Anal. Calcd for $C_{43}H_{35}IO_2Pd$: C, 58.75; H, 4.01. Found: C, 58.37; H, 3.92.

(Oxycarbonyl-1,2-phenylene)(triphenylphosphine)-palladium Tetramer (22). A suspension of **24b** (60 mg, 0.068 mmol) and Cs_2CO_3 (46 mg, 0.68 mmol) in THF (1 mL) was stirred for 16 h at 23 °C. $AgBF_4$ (7.9 mg, 0.082 mmol) was added, and the reaction mixture was stirred for 1 h at 23 °C. After evaporation of the solvent, CH_2Cl_2 was added, and the resulting suspension was filtered through Celite. The filtrate was evaporated, and the residue was triturated with Et_2O to give **22** (25 mg, 75%) as a white solid. IR (KBr): 1657, 1583, 1564 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.82 (m, 6H), 7.18 (m, 3H), 7.06 (m, 6H), 6.87 (dd, J = 7.6, 1.4 Hz, 1H), 6.63 (t, J = 7.5 Hz, 1H), 6.38 (td, J = 7.6, 1.8 Hz, 1H), 5.98 (dd, J = 6.8, 6.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$; DEPT): δ 145.81 (s, C), 142.16 (s, C), 136.85 [d, $^2J(^{13}C-^{31}P)$ = 13.2 Hz, CH], 135.57 [d, $^2J(^{13}C-^{31}P)$ = 11.2 Hz, PPh_3, CH], 130.55 [d, $^1J(^{13}C-^{31}P)$ = 53.0 Hz, PPh_3, C], 130.22 (s, CH), 129.90 (br s, PPh_3, CH), 130.81 (br s, CH), 127.85 [d, ^3J ($^{13}C-^{31}P$) = 11.0 Hz, PPh_3, CH], 122.59 (s, CH) (the carbonyl signal was not observed). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 45.77.

X-ray Crystallography. Pale yellow crystals of complex **7** suitable for X-ray diffraction studies were obtained by slow evaporation of a CH_2Cl_2 solution at −20 °C under Ar. Colorless monocrystals of complex **22** were obtained from a saturated $CH_2Cl_2-Et_2O$ solution upon cooling from 23 to −20 °C. The crystal dimensions were 0.30 × 0.20 × 0.05 and 0.10 × 0.08 × 0.08 mm for **7** and **22**, respectively. Crystals were mounted on a Bruker-Siemens Smart CCD diffractometer equipped with a low-temperature device and a normal-focus, 2.4 kW sealed-tube X-ray source (molybdenum radiation, λ = 0.71067 Å) operating at 50 kV and 20 mA. For complex **7** data were collected at 296 K over a hemisphere of the reciprocal space by a combination of three exposure sets. The cell parameters were determined by least-squares fit for all reflections collected. Each exposure of 20 s covered 0.3° in ω. The crystal to detector distance was 6.03 cm. For complex **22** data were collected at 148 K over a quadrant of the reciprocal space by a combination of two exposure sets. The unit cell dimensions were determined by least-squares refinement using 121 reflections with $I > 20\sigma$ and $6° < 2\theta < 42°$. The crystal to detector distance was 6.05 cm. Coverage of the unique set was over 92% complete to at least 23° in θ. In both cases the first 50 frames were recollected at the end of the data collection to monitor crystal decays. The intensities were corrected for Lorentz and polarization effects. The structures were solved by Multan and Fourier methods. Full-matrix least-squares refinements were carried out, minimizing $w(F_o^2 - F_c^2)^2$. H atoms were included in their calculated positions. Weighted R factors (R_w) and all goodness of fit values S are based on F^2, and conventional R factors (R) are based on F. Most of the calculations were carried out with SMART software for data collection and reduction and SHELXTL for structure solutions and refinements.

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Supporting Information Available: Tables of X-ray data for complexes **7** and **22** and NMR spectra for **6**, **7**, **9**, **11**, **16**, **17**, **18**, **19**, and **22**. This material is available free of charge via the Internet at http://pubs.acs.org.

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