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Synthesis of Mono-, Di-, and Tripalladated 1,3,5-Benzenetricarboxaldehyde Complexes

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The oxidative addition of 2,4,6-tribromo-1,3,5-benzenetricarboxaldehyde ($C_6(CHO)_3Br_3$) to 1, 2, or 3 equiv of [Pd(dba)$_2$] ([Pd$_2$(dba)$_3$]·dba) and N^N affords, respectively, the mono-, di-, or trinuclear complexes [Pd{$C_6(CHO)_3Br_2$}Br(N^N)] (N^N = tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (**1a**), tbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine (**1b**), bpy = 2,2′-bipyridine, (**1c**)); [{PdBr(N^N)}$_2${μ_2-$C_6(CHO)_3Br$}] (N^N = tmeda (**2a**), tbbpy (**2b**)); or [{PdBr(N^N)}$_3${μ_3-$C_6(CHO)_3$}] (N^N = tmeda (**3a**), tbbpy (**3b**)). The reactions of $C_6(CHO)_3Br_3$ with a mixture of [Pd(dba)$_2$] and PR$_3$ lead, depending on the nature of the phosphine and the molar ratio of the reagents, to the mononuclear *trans*-[Pd{$C_6(CHO)_3Br_2$}Br(PR$_3$)$_2$] (R = Ph (**1d**), R$_3$ = Me$_2$Ph (**1e**)) or the dinuclear [{*trans*-PdBr(PMe$_2$Ph)$_2$}$_2${μ_2-$C_6(CHO)_3Br$}] (**2e**) complex. All attempts to prepare trinuclear phosphine complexes using this method of synthesis have been unsuccessful. However, displacement of the tbbpy ligand in **3b** by an excess of PMe$_3$ affords the trinuclear complex [{*trans*-PdBr(PMe$_3$)$_2$}$_3${μ_3-$C_6(CHO)_3$}] (**3f**). The crystal structures of **1b**, **1d**, **2a**·CDCl$_3$, and **2e** have been determined by X-ray diffraction studies.

Introduction

The chemistry of arylpalladium complexes is a topic of great interest because of the involvement of these compounds in many important palladium-catalyzed carbon–carbon and carbon–heteroatom bond-forming reactions.[1] Suitable substituents ortho to the Pd atom may lead to cyclopalladated compounds,[2–7] influence the reactivity of the complexes,[4–6,8–11] or participate in the formation of organic compounds.[2,4,5,10–13] Consequently, there have been intensive studies of the synthesis of Pd(II) aryl complexes[14,15] and of their reactivity,[2,5–7,9,11,12,15,16] to understand the mechanism of such catalytic or stoichiometric reactions. This rich chemistry of ortho-substituted aryl Pd(II) complexes has prompted us to explore the possibility of synthesizing polypalladated benzene derivatives with functionalized organic substituents ortho to each Pd.

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Although the synthesis and applications of polymetalated derivatives of benzene ($C_6R_{6-n}M_n$, $n = 3-6$) are well-documented, most of them involve representative elements. The element best studied is Hg(II), for which examples with three,[17] four,[18−20] five,[19,21,22] and six[22] metal atoms around a benzene ring have been reported. Hexalithiobenzene has also been described and shown to possess excellent thermodynamic stability.[23] There are also many reports on 1,3,5-trilithiobenzene[20,24] (the use of which to prepare trimetalated Mg, Hg, and Sn derivatives has also been described[24]) and symmetrically 2,4,6-trisubstituted derivatives thereof.[25] 1,3,5-Tris(trimethylstannyl)benzene[26] has been obtained by several routes[20,24,27,28] and has been used in coordination,[29] transmetalation,[20,30] and C−C bond forming reactions.[28,31] 1,3,5-Tris(trimethylgermyl)benzene[32] and hexakis(trimethylgermyl)benzene[33] have also been reported.

As regards transition metal derivatives, the research has been conducted on metal clusters with face-capping arene ligands $\mu^3,\eta^2,\eta^2,\eta^2$ coordinated to three metal atoms such as Co,[34] Ru,[35,36] Rh,[37] and Os.[35,38,39] An unusual $\mu^3,\eta^1,\eta^1,\eta^1$

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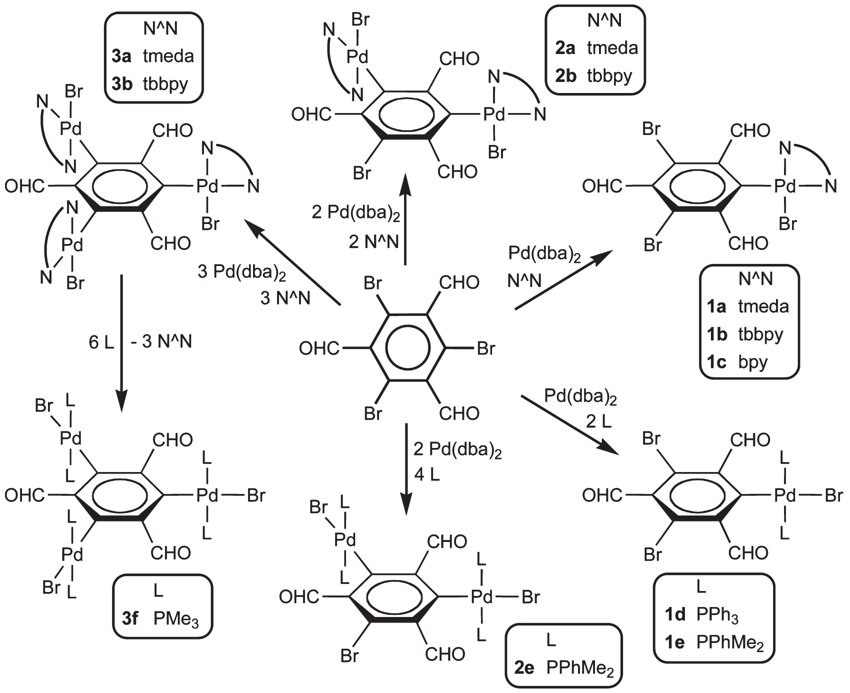
Scheme 1



coordination mode has been described as well.[40] These compounds have been proposed as models for benzene adsorption at a 3-fold site on the surface of a close-packed metal lattice.[38] Very recently, a similar situation has been described for Pd in a μ^3-tripalladium sandwich complex,[41] and there are also reports on Pd3 to Pd5 sheets between polycyclic aromatic hydrocarbon ligands.[42] However, there has been very little research on σ-bonded polymetalated derivatives of benzene with transition metals. Until recently the only examples were 1,3,5-$C_6H_3[Mn(CO)_5]_3$ (**I**),[43] 1,3,5-$C_6H_3[Fe(\eta^5\text{-}Cp)(CO)_2]_3$ (**II**),[43,44] and 1,3,5-$C_6H_3[Fe(\eta^5\text{-}C_5H_4Me)(CO)_2]_3$ (**III**),[45] prepared in two steps involving the reaction of Na[M] ([M] = $[Mn(CO)_5]$, $[Fe(\eta^5\text{-}Cp)(CO)_2]$ or $[Fe(\eta^5\text{-}C_5H_4Me)(CO)_2]$) with 1,3,5-$C_6H_3(COCl)_3$ and subsequent decarbonylation of the resulting 1,3,5-$C_6H_3[C(O)M]_3$ triacyl complexes. Complexes **I** and **II** were later prepared by reaction of 1,3,5-triiodobenzene with 3 equiv of $[KMn(CO)_5]$ or $[Fe(\eta^5\text{-}Cp)(CO)_2]ZnCl$, respectively.[46] In 2001 our group published the first tripalladated benzene derivative, prepared by oxidative addition of 1,3,5-triiodomesitylene to 3 equiv of $[Pd(dba)_2]$ in the presence of chelating N-donor ligands.[47] Shortly after that, another group reported the first 3-fold cyclopalladation of a single benzene ring, 1,3,5-tris(di-2-pyridylamino)benzene.[48] Since then there have been no further reports on the subject, in spite of its potential for the Pd-mediated synthesis of organic polycyclic compounds and in the field of metallodendrimers.[49] With the aim of pursuing these research lines, we decided to explore the possibility of synthesizing tripalladated benzene derivatives with functionalized ortho substituents, and we wish to report here our first successes, involving derivatives of 1,3,5-triformylbenzene.

Results and Discussion

2,4,6-Tribromo-1,3,5-benzenetricarboxaldehyde ($C_6(CHO)_3Br_3$) adds oxidatively to $[Pd(dba)_2]$ ($[Pd_2(dba)_3]\cdot dba$) in the presence of chelating nitrogen donor ligands (N^N) to give mono-, di-, or trinuclear complexes (Scheme 1). Thus, the reaction of equimolecular amounts of the three reagents led to mononuclear complexes $[Pd\{C_6(CHO)_3Br_2\}Br(N^\wedge N)]$ (N^N = tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (**1a**), tbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine (**1b**), bpy = 2,2′-bipyridine (**1c**)) as the major products. However, **1a** was obtained together with the dinuclear complex $[\{PdBr(tmeda\}_2\{\mu_2\text{-}C_6(CHO)_3Br\}]$ (**2a**) and the starting arene, $C_6(CHO)_3Br_3$ (6.5:1:1.8 molar ratio), while **1b** was contaminated with $C_6(CHO)_3Br_3$ (3:1 molar ratio). **1c** was obtained as a single product. Mixtures of products were also formed in most attempts to prepare dinuclear $[\{PdBr(N^\wedge N)\}_2\{\mu_2\text{-}C_6(CHO)_3Br\}]$ (N^N = tmeda (**2a**), tbbpy (**2b**)) or trinuclear $[\{PdBr(N^\wedge N)\}_3\{\mu_3\text{-}C_6(CHO)_3\}]$ (N^N = tmeda (**3a**), tbbpy (**3b**)) complexes. Thus, the reaction of $C_6(CHO)_3Br_3$, $[Pd(dba)_2]$, and N^N in a ca. 1:2:2 molar ratio afforded the dipalladated complex **2a** or **2b** as the major product, together with the corresponding mononuclear and trinuclear complexes (**2a:1a:3a** = 7:4:1 and **2b:1b:3b** = 8:3:1 molar ratios).

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Table 1. Crystal Data for Complexes 1b, 1d, 2a·$CDCl_3$, and 2e·$1^1/_2CH_2Cl_2$

	1b	**1d**	**2a**·$CDCl_3$	**2e**·$1^1/_2CH_2Cl_2$
formula	$C_{27}H_{27}Br_3N_2O_3Pd$	$C_{45}H_{33}Br_3O_3P_2Pd$	$C_{22}H_{35}DBr_3Cl_3N_4O_3Pd_2$	$C_{42.5}H_{50}Br_3Cl_3O_3P_4Pd_2$
M_r	773.64	1029.78	964.44	1291.59
cryst size (mm^3)	0.28 × 0.16 × 0.07	0.35 × 0.30 × 0.15	0.40 × 0.20 × 0.05	0.35 × 0.10 × 0.05
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\overline{1}$
cell constants				
a (Å)	9.0731(9)	13.6265(8)	8.6227(8)	10.9157(11)
b (Å)	19.278(2)	20.8536(12)	21.058(2)	12.8369(12)
c (Å)	16.026(2)	14.1963(8)	18.147(2)	18.423(2)
α (deg)	90	90	90	75.317(4)
β (deg)	104.348(5)	102.804(4)	98.719(4)	80.263(4)
γ (deg)	90	90	90	82.055(4)
V (Å^3), Z	2715.7(5), 4	3933.7(4), 4	3256.8(6), 4	2448.8(4), 2
λ (Å)	0.71073	0.71073	0.71073	0.71073
ρ (calcd) (Mg m^{-3})	1.892	1.739	1.967	1.752
F(000)	1512	2032	1872	1274
T (K)	133	133	133	133
μ (mm^{-1})	5.129	3.642	5.061	3.513
transmissions	0.7153−0.4307	0.6111−0.4896	0.7860−0.4958	0.8439−0.5590
θ range (deg)	1.68−28.28	1.77−30.52	1.49−30.52	1.65−30.51
limiting indices	$-12 \leq h \leq 12$ $-25 \leq k \leq 25$ $-21 \leq l \leq 21$	$-19 \leq h \leq 19$ $-29 \leq k \leq 29$ $-20 \leq l \leq 20$	$-12 \leq h \leq 12$ $-30 \leq k \leq 30$ $-25 \leq l \leq 25$	$-15 \leq h \leq 15$ $-18 \leq k \leq 18$ $-26 \leq l \leq 26$
no. of rflns				
measd	47839	94467	70474	55883
indep	6730	12008	9944	14874
R_{int}	0.1032	0.0315	0.0478	0.0478
abs cor	multiscan	multiscan	multiscan	multiscan
no. of data/restraints/params	6730/20/336	12008/0/487	9944/0/342	14874/51/543
S (F^2)	1.065	1.054	1.122	1.028
R1 ($I > 2(I)$)	0.0385	0.0222	0.0287	0.0429
wR2 (all reflns)	0.0911	0.0506	0.0563	0.1056
largest diff peak (e Å^{-3})	0.876	0.729	1.083	2.043

Similarly, the reaction of $C_6(CHO)_3Br_3$, $[Pd(dba)_2]$, and tbbpy in a 1:3:3 molar ratio gave the trinuclear complex **3b**, together with a small amount of **2b** (5:1 molar ratio). The use of a ca. 1:4:4 molar ratio of the reagents afforded **3b** as a single product, while for tmeda a 9:1 mixture of **3a** and **2a** was obtained. With the ligand bpy, the oxidative addition reaction in a 1:3:3 or even 1:6:6 molar ratio afforded mixtures of two compounds, which according to their ^1H NMR data (in d^6-DMSO) seem to be a dinuclear and a trinuclear complex, but their insolubility in common solvents prevented separation. All the other mixtures could be separated by preparative TLC on silica gel, using as eluent CH_2Cl_2 or mixtures of EtOAc/hexane or CH_2Cl_2/acetone. The order of elution was always, as expected, $C_6(CHO)_3Br_3$ > **1** > **2** > **3**.

The behavior described above contrasts with that reported for 1,3,5-$C_6Me_3I_3$,[47] which reacts with a mixture of $[Pd(dba)_2]$ and tbbpy or bpy to give tripalladated $[\{PdI(N^\wedge N)\}_3(\mu_3\text{-}C_6Me_3)]$, even when substoichiometric amounts of Pd and N^N were used. In contrast, oxidative addition reactions with phosphines instead of chelating N^N ligands occurred in a very similar manner with both 1,3,5-trihalo derivatives. Thus, in the reactions of $C_6(CHO)_3Br_3$ with $[Pd(dba)_2]$ and PPh_3 we could only isolate a mononuclear complex, *trans*-$[Pd\{C_6(CHO)_3Br_2\}Br(PPh_3)_2]$ (**1d**), when a 1:1:2 molar ratio was used. In this reaction, a ca. 1:1 mixture of cis (not observed in the reaction with 1,3,5-$C_6Me_3I_3$) and trans isomers formed, from which the trans isomer could be separated by crystallization. Similar reactions in 1:2:4 or 1:3:6 molar ratios did not afford the corresponding di- or trinuclear complexes, but mixtures of **1d** and $OPPh_3$. However, the use of the more basic and less sterically demanding phosphine PMe_2Ph allowed the synthesis of *trans*-$[Pd\{C_6(CHO)_3Br_2\}Br(PMe_2Ph)_2]$ (**1e**) or [{*trans*-$PdBr(PMe_2Ph)_2\}_2\{\mu_2\text{-}C_6(CHO)_3Br\}]$ (**2e**) when the stoichiometric amounts of $C_6(CHO)_3Br_3$, $[Pd(dba)_2]$, and PMe_2Ph were used. With a 1:3:6 ratio of the reactants, a tripalladated species could not be obtained, but only mixtures of **2e** with other minor unidentified compounds. A final attempt to obtain a tripalladated derivative with phosphine ligands was carried out with the less bulky PMe_3, but the reaction of $C_6(CHO)_3Br_3$ with $[Pd(dba)_2]$ and PMe_3 in a 1:3:6 ratio afforded a complicated mixture of compounds. Nevertheless, the trinuclear complex [{*trans*-$PdBr(PMe_3)_2\}_3\{\mu_3\text{-}C_6(CHO)_3\}]$ (**3f**) could be obtained by displacement of the tbbpy ligand by PMe_3. Therefore, the failure to synthesize **3f** by an oxidative addition reaction does not seem to be due to thermodynamic but to kinetic effects.

Structure of Complexes. The ^1H, ^{13}C, and ^{31}P NMR data of complexes **1**−**3** agree with the structures proposed in Scheme 1. The mononuclear complexes (**1a**−**e**) show the expected spectra for the only possible isomer in **1a**−**c** and for the presence in solution of only the trans isomer of complexes **1d**−**e** (^{31}P NMR). The dinuclear complexes **2a**, **2b**, and **2e** show two 1:2 singlets for the CHO groups in their ^1H and ^{13}C NMR spectra, which is consistent with the presence of a C_2 symmetry axis (confirmed to a reasonable approximation for **2a** in the solid state). The trinuclear PMe_3 complex **3f** shows a single resonance for the CHO groups (^1H and ^{13}C NMR) and for the phosphine ligands (^{31}P NMR), an indication that the molecule has an all trans geometry. In contrast, the other trinuclear complexes **3a** and **3b** show in their NMR spectra a 2:1 pattern for all resonances. This observation is consistent with the structure depicted for these complexes in Scheme 1, where two of the Br atoms lie on one side of the aryl plane, while the third Br atom points to the other side, and implies

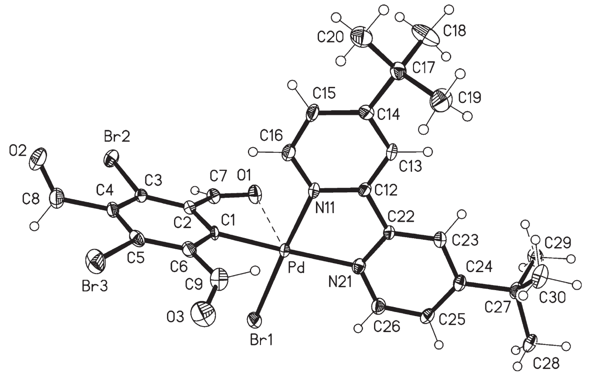

Figure 1. Thermal ellipsoid plot (50% probability level) of **1b**. Selected bond lengths (Å) and angles (deg): Pd−C(1) = 1.994(4), Pd−N(11) = 2.049(4), Pd−N(21) = 2.099(4), Pd−Br(1) = 2.4234(6), Pd···O(1) 2.832(2); C(1)−Pd−N(11) = 95.94(15), C(1)−Pd−Br(1) = 86.02(12), N(11)−Pd−N(21) = 79.59(14), N(21)−Pd−Br(1) = 98.30, C(1)−Pd···O(1) = 72.0(1).

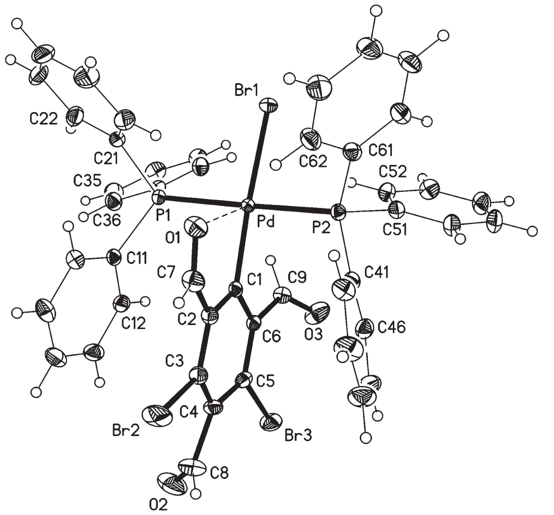

Figure 2. Thermal ellipsoid plot (50% probability level) of **1d**. Selected bond lengths (Å) and angles (deg): Pd−C(1) = 2.0163(15), Pd−P(1) = 2.3426(4), Pd−P(2) = 2.3279(4), Pd−Br(1) = 2.4865(2), Pd···O(1) = 2.8561(13); C(1)−Pd−P(1) = 89.42(4), C(1)−Pd−P(2) = 91.02(4), P(1)−Pd−Br(1) = 91.999(11), P(2)−Pd−Br(1) = 87.891(12), C(1)−Pd···O(1) = 71.29(5).

that the rotation around the Pd−aryl bonds is hindered. No traces of a second isomer were detected, which is consistent with the geometry **2a** and **2b**.

A complete assignment of the aryl ^{13}C chemical shifts has been made (see Table 1 in the Supporting Information). As expected, the ^{13}CHO groups appear highly deshielded (190−202 ppm) and the ^{13}C−Pd nuclei are observed in the range 170−181 ppm for the complexes with N^N ligands and 184−189 ppm for the phosphino complexes. The increase in the number of Pd atoms ortho to a given CHO group (n) deshields the corresponding ^{13}C−CHO nucleus. Thus, for $n = 2$ this resonance appears in the range 147−150 ppm, for $n = 1$ at 137−141 ppm, and for $n = 0$ at values (134−135 ppm) similar to that in $C_6(CHO)_3Br_3$ (138.4 ppm). Finally, the ^{13}C−Br nuclei in complexes **2** (130−133 ppm) are slightly deshielded with respect to those in $C_6(CHO)_3Br_3$ (124.9 ppm), while in complexes **1** they do not shift significantly (124−129 ppm). In spite of the tendencies observed, a simplistic interpretation of these ^{13}C chemical shifts in terms of the electron density should be avoided.[50]

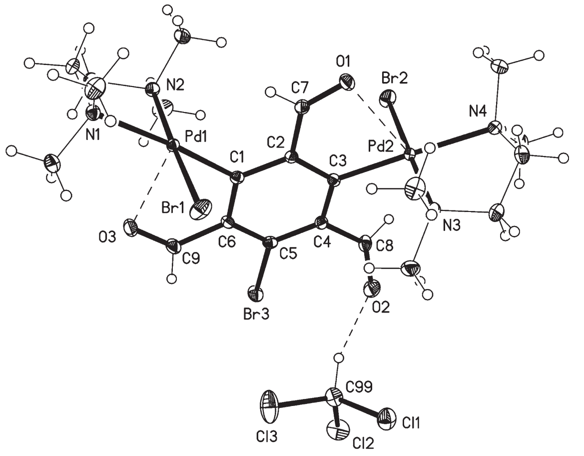

Figure 3. Thermal ellipsoid plot (50% probability level) of **2a**·$CDCl_3$. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) = 1.984(3), Pd(1)−N(1) = 2.165(2), Pd(1)−N(2) = 2.109(2), Pd(1)−Br(1) = 2.4311(4), Pd(1)···O(3) = 2.772(2), Pd(2)−C(3) = 1.971(3); Pd(2)−N(3) = 2.121(3); Pd(2)−N(4) = 2.164 (3), Pd(2)−Br(2) = 2.4313(4), Pd(2)···(O1) = 2.806(2), D(99)···(O2) = 2.35; C(1)−Pd(1)−N(2) = 94.53(10), C(1)−Pd(1)−Br(1) = 87.02(8), N(1)−Pd(1)−N(2) = 84.32(9), N(1)−Pd(1)−Br(1) = 94.47(7), C(1)−Pd(1)···O(3) = 74.20(9), C(3)−Pd(2)−N(3) = 93.79(11), C(3)−Pd(2)−Br(2) = 86.97(8), N(3)−Pd(2)−N(4) = 84.33(10), N(4)−Pd(2)−Br(2) = 94.89(7), C(3)−Pd(2)···O(1) = 73.20(10), C(99)−D(99)···(O2) = 153.

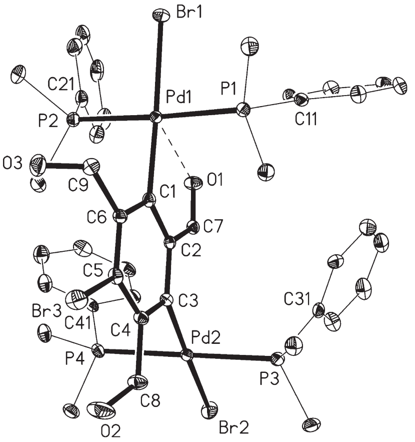

Figure 4. Thermal ellipsoid plot (30% probability level) of **2e**. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) = 2.023(4), Pd(1)−P(1) = 2.3162(11), Pd(1)−P(2) = 2.3152(11), Pd(1)−Br(1) = 2.5049(5), Pd(1)···O(1) = 2.865(3), Pd(2)−C(3) = 2.033(4), Pd(2)−P(3) = 2.3178(11), Pd(2)−P(4) = 2.3315(11), Pd(2)−Br(2) = 2.5080(6); C(1)−Pd(1)−P(1) = 90.41(11), C(1)−Pd(1)−P(2) = 91.97(11), P(1)−Pd(1)−Br(1) = 89.78(3), P(2)−Pd(1)−Br(1) = 87.76(3), C(1)−Pd(1)···O(1) = 70.3(1), C(3)−Pd(2)−P(3) = 90.39(11), C(3)−Pd(2)−Pd(4) = 87.93(11), P(3)−Pd(2)−Br(2) = 91.23(3), P(4)−Pd(2)−Br(2) = 90.55(3).

The ^{31}P NMR spectra of the phosphine complexes **1d**, **1e**, **2e**, **3f** show a single ^{31}P resonance, in agreement with the trans geometry of the complexes. As usual, the ^{31}P chemical shift decreases in the order PPh_3 (δ 21.1 ppm for **1d**) >

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(50) Martínez-Viviente, E.; Pregosin, P. S.; Tschoerner, M. *Magn. Reson. Chem.* **2000**, *38*, 23.

PMe_2Ph (δ −7.5 ppm for **1e** and −10.7 ppm for **2e**) > PMe_3 (δ −18.8 ppm for **3f**).

The crystal and molecular structures of the complexes **1b** (Figure 1), **1d** (Figure 2), **2a**·$CDCl_3$ (Figure 3), and **2e**·$1^1/_2CH_2Cl_2$ (Figure 4) have been determined by X-ray diffraction studies (Table 1). Crystals of apparently good optical quality were also obtained for the PMe_3 complex **3f** and gave diffraction patterns corresponding to a hexagonal cell. However, the structure could only be interpreted as a pseudomerohedral 3-fold twin in space group $P2_1/c$ with $\beta = 120°$. The refinement proved unsatisfactory, with poor *R* values, an impossibly irregular geometry, and considerable areas of residual electron density presumably corresponding to disordered solvent. The qualitative nature of the compound was thus confirmed, but the structure is quantitatively unreliable and we do not present it here.

The four structures solved show somewhat distorted square planar coordination around the Pd atoms. Mean deviations from the best plane through Pd and the four donor atoms are in the range 0.02−0.07 Å [0.021 Å for complex **1b**, 0.069 Å for **1d**, 0.069 Å (Pd1) and 0.023 Å (Pd2) for **2a**, and 0.020 Å (Pd1) and 0.056 Å (Pd2) for **2e**]. Additionally, all complexes show weak interactions between the Pd atoms and the O atoms of the ortho formyl groups, with the sole exception of Pd2 in the dinuclear complex **2e**. The Pd···O distances for these weak interactions are in the range 2.77−2.86 Å (2.832(3) Å for **1b**, 2.8561(13) Å for **1d**, 2.772(2) Å (Pd1···O3) and 2.806(2) Å (Pd2···O1) for **2a**, and 2.865(3) Å (Pd1···O1) for **2e**), lower than the sum of the van der Waals radii (3.15 Å).[51] Clearly these Pd···O interactions do not cause significant deviation from planarity around the Pd atoms.

The Pd−C bond distances show the following order: **2e** [2.033(4) Å (Pd2) and 2.023(4) Å (Pd1)] > **1d** (2.0163(15) Å) > **1b** (1.994(4) Å) > **2a** [1.984(3) Å (Pd1) and 1.971(3) Å (Pd2)]. Although the differences are small, they follow the order of trans influence: Br > tbbpy/tmeda. The slightly longer Pd−C bonds in the dinuclear complex **2e** compared with mononuclear **1d** (both with Br trans to the aryl group) might be due to steric effects. In contrast, the Pd−Br bonds in phosphine complexes **1d** and **2e** are considerably longer [2.4865(2) Å for **1d**, 2.5049(5) Å (Pd1) and 2.5080(6) Å (Pd2) for **2e**] than those in tbbpy and tmeda complexes **1b** (2.4234(6) Å) and **2a** [2.4311(4) Å (Pd1) and 2.4313(4) Å (Pd2)], in agreement with the order of trans influence: aryl ≫ tbbpy/tmeda. Again, the larger Pd−Br distances in the dinuclear complexes **2e** and **2a**, compared with **1d** and **1b**, respectively, might be due to steric effects. Finally, the Pd−N bond distances in **1b** (Pd−N trans to aryl, 2.099(4) Å, Pd−N trans to Br, 2.049(4) Å) and **2a** [Pd−N trans to aryl, 2.165(2) Å (Pd1), 2.164(3) Å (Pd2); Pd−N trans to Br, 2.109(2) Å (Pd1), 2.121(3) Å (Pd2)] also show the order of trans influence aryl > Br and the possible influence of steric effects in the dinuclear complex.

Conclusion

We have synthesized and characterized a novel family of mono-, di-, and tripalladated benzene derivatives and proved that our previous report involving methyl ortho substituents can be extended to complexes with functionalized *ortho*-formyl-benzene, although significant differences in reactivity between the two aryl groups have been established. The potential of the aldehyde functional groups for further synthesis will be investigated.

Experimental Section

NMR spectra (^1H, ^{13}C, and ^{31}P) were recorded on Bruker Avance 200, 300, 400, and 600 spectrometers at room temperature. Chemical shifts are given in ppm (δ) relative to TMS (^1H, ^{13}C) or H_3PO_4 (^{31}P). Infrared spectra were recorded on a Perkin-Elmer 16F-PC-FT spectrometer with Nujol mulls between polyethylene sheets. Melting points were determined on a Reichert apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. All experiments were conducted under a N_2 atmosphere using Schlenk techniques. CH_2Cl_2 was distilled before use. "[Pd(dba)$_2$]"[52] and 1,3,5-tribromo-2,4,6-benzenetricarbaldehyde[53] were prepared according to literature procedures. tbbpy (Aldrich), tmeda (Fluka), bpy (Fluka), PPh_3 (Fluka), PMe_2Ph (Aldrich), and PMe_3 (Aldrich) were used as received.

Synthesis of [Pd{$C_6(CHO)_3Br_2$}Br(tmeda)] (1a). [Pd(dba)$_2$] (144 mg, 0.25 mmol), tmeda (37 μL, 0.25 mmol), and $C_6(CHO)_3Br_3$ (100 mg, 0.25 mmol) were mixed in dry degassed toluene (15 mL). The resulting mixture was stirred at 60 °C for 1 h until the dark red color of [Pd(dba)$_2$] was no longer observed. The brownish suspension was then concentrated in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the resulting solution was evaporated to dryness. Et_2O (15 mL) was added to precipitate a bright yellow solid, which was filtered off and thoroughly washed with Et_2O. The solid obtained is a mixture of complexes **2a**, **1a**, and $C_6(CHO)_3Br_3$ in ca. 1:6.5:2 molar ratio. The products were separated by preparative TLC on silica gel using a mixture of CH_2Cl_2/acetone (5:3) as eluent. The band with Rf = 0.91 was collected, and the product was extracted with acetone (30 mL). Evaporation of the acetone and addition of Et_2O (15 mL) rendered a solid, which was filtered off, thoroughly washed with Et_2O, and dried in vacuo to give **1a** as a yellow solid. Yield: 84 mg (54%). Mp: 214−215 °C. IR: ν(CO) 1697 cm^{-1} (sb). ^1H NMR (400 MHz, $CDCl_3$): δ 10.93 (s, 2H, CHO), 10.18 (s, 1H, CHO), 2.85−2.80 (m, 2H, CH_2), 2.80 (s, 6H, Me), 2.72−2.67 (m, 2H, CH_2), 2.31 (s, 6H, Me). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ 195.2 (2C, CHO), 191.6 (1C, CHO), 173.7 (1C, C1−Pd), 140.9 (2C, *C2*−CHO), 133.4 (1C, *C4*−CHO), 128.1 (2C, C3−Br), 63.1 and 59.4 (1C, CH_2), 51.4 and 49.6 (2C, Me). Anal. Calcd for $C_{15}H_{19}Br_3N_2O_3Pd$: C, 28.99; H, 3.08; N, 4.51. Found: C, 29.06; H, 2.84; N, 4.30.

Synthesis of [Pd{$C_6(CHO)_3Br_2$}Br(tbbpy)] (1b). [Pd(dba)$_2$] (145 mg, 0.25 mmol), tbbpy (68 mg, 0.25 mmol), and $C_6(CHO)_3Br_3$ (100 mg, 0.25 mmol) were mixed under N_2 in dry degassed toluene (15 mL). The resulting mixture was stirred at 60 °C for 10 min until the dark red color of [Pd(dba)$_2$] was no longer observed. Workup as for **1a**, afforded a yellow solid, which was filtered off and thoroughly washed with Et_2O. This solid is a mixture of complex **1b** and $C_6(CHO)_3Br_3$ in 3:1 molar ratio. The products were separated by preparative TLC on silica gel using CH_2Cl_2 as eluent. The band with Rf = 0.3 was collected, and complex **1b** (yellow solid) was isolated as for **1a**. Yield: 111 mg (57%). Single crystals were grown by slow diffusion of Et_2O into a $CDCl_3$ solution of **1b**. Mp: 268−270 °C dec. IR: ν(CO): 1698 cm^{-1} (sb). ^1H NMR (300 MHz, $CDCl_3$): δ 11.11 (s, 2H, CHO), 10.25 (s, 1H, CHO), 9.27 (d, 1H, tbbpy, $^3J_{HH} = 6$ Hz), 7.96 (br s, 2H, tbbpy), 7.57 (dd, 1H, tbbpy, $^3J_{HH} = 6$ Hz, $^4J_{HH} = 2$ Hz), 7.32−7.27 (m, 2H, tbbpy), 1.45 (s, 9H, tBu), 1.38

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(s, 9H, tBu). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 194.7 (2C, CHO), 191.9 (1C, CHO), 170.7 (1C, C1−Pd), 164.5 and 164.4 (1C, C14 and 14′ tbbpy), 156.5 and 154.3 (1C, C12 and 12′ tbbpy), 150.8 and 150.2 (1C, CH16 and 16′ tbbpy), 141.3 (2C, *C2*−CHO), 134.0 (*C3*−CHO), 126.6 (2C, *C3*−Br), 124.6 and 124.3 (1C, CH15 and 15′ tbbpy), 119.2 and 118.5 (1C, CH13 and 13′ tbbpy), 35.8 (2C, *C*Me$_3$), 30.6 and 30.4 (3C, C*Me*$_3$). Anal. Calcd for $C_{27}H_{27}Br_3N_2O_3Pd$: C, 41.92; H, 3.92; N, 3.62. Found: C, 42.30; H, 3.52; N, 3.38

Synthesis of [Pd{$C_6(CHO)_3Br_2$}Br(bpy)] (1c). A mixture of [Pd(dba)$_2$] (112 mg, 0.193 mmol), bpy (31 mg, 0.193 mmol), and $C_6(CHO)_3Br_3$ (70 mg, 0.175 mmol) were mixed under N_2 in dry degassed toluene (15 mL). The resulting mixture was stirred at 60 °C for 30 min until the dark red color of [Pd(dba)$_2$] was no longer observed. Workup as for **1a**, afforded a yellow solid, which was filtered off, thoroughly washed with Et_2O and CH_2Cl_2, and dried in vacuo to give **1c** as a yellow solid. Yield: 78 mg (67%). Mp: 265−266 °C. IR: ν(CO) 1684 (sb) cm^{-1}. ^1H NMR (300 MHz, d^6-DMSO): δ 11.01 (s, 2H, CHO), 10.16 (s, 1H, CHO), 9.13 (d, 1H, bpy, $^3J_{HH}$ = 5 Hz), 8.66−8.82 (m, 2H, bpy), 8.34 (t, 1H, bpy, $^3J_{HH}$ = 8 Hz), 8.3−8.24 (m, 1H, bpy), 7.87−7.82 (m, 1H, bpy), 7.56−7.5 (m, 2H, bpy). $^{13}C\{^1H\}$ NMR (75.4 MHz, d^6-DMSO): δ 193.7 (2C, CHO), 193.4 (1C, CHO), 170.2 (1C, C1−Pd), 155.9 and 154.1 (1C, C12 and 12′ bpy), 150.6 and 149.6 (1C, CH16 and 14′ bpy), 140.6 and 140.4 (1C, CH14 and 14′ bpy), 140.4 (2C, *C2*−CHO), 135.0 (1C, *C4*−CHO), 128.0 and 127.5 (1C, CH15 and 15′ bpy), 124.5 (2C, C3−Br), 123.9 and 123.3 (1C, CH13 and 13′ bpy). Anal. Calcd for $C_{19}H_{11}Br_3N_2O_3Pd$: C, 34.50; H, 1.68; N, 4.24. Found: C, 34.47; H, 1.51; N, 4.13.

Synthesis of *trans*-[Pd{$C_6(CHO)_3Br_2$}Br(PPh_3)$_2$] (1d). A mixture of [Pd(dba)$_2$] (216 mg, 0.375 mmol) and $C_6(CHO)_3Br_3$ (150 mg, 0.375 mmol) was stirred for 2−3 min under N_2 in dry degassed toluene (20 mL) in an ice bath. Then PPh_3 (196 mg, 0.75 mmol) was added, and the resulting mixture was stirred for 50 min under the same conditions. The solvent was then evaporated to dryness, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the resulting solution was concentrated to a small volume. Et_2O (15 mL) was added to precipitate a yellow solid, which was filtered off and thoroughly washed with Et_2O. Recrystallization from CH_2Cl_2/Et_2O gave **1d** as yellow crystals. Yield: 145 mg (37%). Single crystals were grown by slow diffusion of ether into a $CHCl_3$ solution of **1d**. Mp: 241−243 °C dec. IR: ν(CO) 1699 cm^{-1}(sb). ^1H NMR (300 MHz, $CDCl_3$): δ 10.29 (s, 2H, CHO), 9.85 (s, 1H, CHO), 7.63−7.5 (m, 12H, PPh_3), 7.39−7.22 (m, 18H, PPh_3). $^{13}C\{^1H\}$NMR (75.4 MHz, $CDCl_3$): δ 192.8 (s, 2C, CHO), 191.1 (s, 1C, CHO), 188.6 (t, 1C, C1−Pd, $^2J_{PC}$ = 5 Hz), 138.3 (s, 2C, *C2*−CHO), 134.7 (vt, 12C, ortho C's PPh_3, $^2J_{PC}$ + $^4J_{PC}$ = 12 Hz), 133.5 (s, 1C, *C4*−CHO), 130.8 (s, 6C, *para* C's PPh_3), 130.1 (vt, 6C, *ipso* C's PPh_3, $^1J_{PC}$ + $^3J_{PC}$ = 47 Hz), 128.7 (s, 2C, C3−Br), 128.2 (vt, 12C, *meta* C's PPh_3 $^3J_{PC}$ + $^5J_{PC}$ = 10 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 21.1. Anal. Calcd for $C_{45}H_{33}Br_3O_3P_2Pd$: C, 52.48; H, 3.23. Found: C, 52.43; H, 3.28.

Synthesis of *trans*-[Pd{$C_6(CHO)_3Br_2$}Br(PMe_2Ph)$_2$] (1e). A mixture of [Pd(dba)$_2$] (72 mg, 0.125 mmol) and $C_6(CHO)_3Br_3$ (50 mg, 0.125 mmol) was stirred for 2−3 min under N_2 in dry degassed toluene (15 mL) at RT. Then PMe_2Ph (35.5 μL, 0.25 mmol) was added, and the resulting mixture was stirred for 2 h under the same conditions. Workup as for **1d**, afforded an orange solid, which was filtered off and thoroughly washed with Et_2O. Recrystallization from CH_2Cl_2/Et_2O gave **1e** as orange crystals. Yield: 49 mg (50%). Mp: 108 °C. IR: ν(CO) 1698 and 1688 cm^{-1} (sb). ^1H NMR (400 MHz, $CDCl_3$): δ 10.36 (s, 2H, CHO), 9.90 (s, 1H, CHO), 7.2−7.1 (m, 6H, PMe$_2$*Ph*), 7.0−6.95 (m, 4H, PMe$_2$*Ph*), 1.78 (vt, 12H, P*Me*$_2$Ph, $^2J_{PH}$ + $^4J_{PH}$ = 8 Hz). $^{13}C\{^1H\}$NMR (100.6 MHz, $CDCl_3$): δ 193.4 (s, 2C, CHO), 190.9 (s, 1C, CHO), 185.8 (t, 1C, C1−Pd, $^2J_{PC}$ = 6 Hz), 138.7 (s, 2C, *C2*−CHO), 133.2 (vt, 2C, *ipso* C's PMe$_2$*Ph*, $^1J_{PC}$ + $^3J_{PC}$ = 45 Hz), 132.6 (1C, *C4*−CHO), 129.9 (s, 2C, *para* C's PMe$_2$*Ph*), 129.5 (vt, 4C, *ortho* C's PMe$_2$*Ph*, $^2J_{PC}$ + $^4J_{PC}$ = 10 Hz), 128.5 (2C, C3−Br), 128.2 (vt, 4C, *meta* C's PMe$_2$*Ph*, $^3J_{PC}$ + $^5J_{PC}$ = 9 Hz), 13.4 (vt, 4C, P*Me*$_2$Ph, $^1J_{PC}$ + $^3J_{PC}$ = 31 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ −7.5. Anal. Calcd for $C_{25}H_{25}Br_3O_3P_2Pd$: C, 38.42; H, 3.22. Found: C, 38.80; H, 3.25.

Synthesis of [{PdBr(tmeda)}$_2${μ_2-$C_6(CHO)_3Br$}] (2a). [Pd(dba)$_2$] (332 mg, 0.57 mmol), tmeda (86 μL, 0.57 mmol), and $C_6(CHO)_3Br_3$ (100 mg, 0.25 mmol) were mixed in dry degassed toluene (15 mL). The resulting mixture was stirred at 65 °C for 40 min until the dark red color of [Pd(dba)$_2$] was no longer observed. Workup as for **1a**, afforded a bright yellow solid, which was filtered off and thoroughly washed with Et_2O. The solid obtained is a mixture of complexes **3a**, **2a**, and **1a** in a ca. 1:7:4 molar ratio. The products were separated by preparative TLC on silica gel using a mixture of CH_2Cl_2 /acetone (5:3) as eluent. The band with Rf = 0.70 was collected, and complex **2a** (yellow solid) was isolated as in the case for **1a**. Yield: 109 mg (40%). Single crystals of **2a**·$CDCl_3$ were grown by slow diffusion of hexane into a $CHCl_3$ solution of **2a**. Mp: 221−222 °C dec. IR: ν(CO) 1697 (s) and 1676 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 12.11 (s, 1H, CHO), 10.93 (s, 2H, CHO), 2.82 (s, 6H, Me), 2.80 (s, 6H, Me), 2.82−2.75 (m, 4H, CH$_2$), 2.70−2.65 (m, 4H, CH$_2$), 2.30 (s, 6H, Me), 2.28 (s, 6H, Me). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 200.1 (1C, CHO), 195.8 (2C, CHO), 179.5 (2C, C1−Pd), 150.3 (1C, *C2*−CHO), 137.4 (2C, *C3*−CHO), 132.3 (1C, C4−Br), 62.9 and 59.1 (2C, CH$_2$), 51.3 and 51.1 (2C, Me), 49.2 (4C, Me). Anal. Calcd for $C_{21}H_{35}Br_3N_4O_3Pd_2$: C, 29.88; H, 4.18; N, 6.64. Found: C, 30.09; H, 4.22; N, 6.56.

Synthesis of [{PdBr(tbbpy)}$_2${μ_2-$C_6(CHO)_3Br$}] (2b). [Pd(dba)$_2$] (332 mg, 0.575 mmol), tbbpy (154 mg, 0.575 mmol), and $C_6(CHO)_3Br_3$ (100 mg, 0.25 mmol) were mixed under N_2 in dry degassed toluene (15 mL). The resulting mixture was stirred at 60 °C for 15 min until the dark red color of [Pd(dba)$_2$] was no longer observed. Workup as for **1a**, afforded a yellow solid, which was filtered off and thoroughly washed with Et_2O. This solid is a mixture of the complexes **3b**, **2b**, and **1b** in a ca. 1:8:2 molar ratio. The products were separated by preparative TLC on silica gel using a mixture of EtOAc/hexane (2:3) as eluent. The band with Rf = 0.7 was collected, and complex **2b** (yellow solid) was isolated as for **1a** Yield: 140 mg (49%). Mp: 268 °C. IR: ν(CO) 1678 cm^{-1} (sb). ^1H NMR (300 MHz, $CDCl_3$): δ 11.92 (s, 1H, CHO), 11.16 (s, 2H, CHO), 9.24 (d, 2H, tbbpy, $^3J_{HH}$ = 6 Hz), 7.92 (br s, 2H, tbbpy), 7.90 (br s, 2H, tbbpy), 7.59 (d, 2H, tbbpy, $^3J_{HH}$ = 6 Hz), 7.49 (dd, 2H, tbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz), 7.30 (dd, 2H, tbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz), 1.40 (s, 18H, tBu), 1.34 (s, 18H, tBu). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 199.1 (1C, CHO), 196.0 (2C, CHO), 176.1 (2C, C1−Pd), 163.9 and 163.6 (2C, C14 and 14′ tbbpy), 156.0 and 154.4 (2C, C12 and 12′ tbbpy), 151.1 and 150.6 (2C, CH16 and 16′ tbbpy), 150.0 (1C, *C2*−CHO), 138.8 (2C, *C3*−CHO), 130.3 (1C, C4−Br), 124.8 and 123.9 (2C, CH15 and 15′ tbbpy), 118.7 and 118.2 (2C, CH13 and 13′ tbbpy), 35.7 (4C, *C*Me$_3$), 30.6 and 30.4 (6C, C*Me*$_3$). Anal. Calcd for $C_{45}H_{51}Br_3N_4O_3Pd_2$: C, 47.06; H, 4.48; N, 4.88. Found: C, 47.28; H, 4.72; N, 4.92.

Synthesis of [{*trans*-PdBr(PMe_2Ph)$_2$}$_2${μ_2-$C_6(CHO)_3Br$}] (2e). A mixture of [Pd(dba)$_2$] (144 mg, 0.25 mmol) and $C_6(CHO)_3Br_3$ (50 mg, 0.125 mmol) was stirred for 2−3 min under N_2 in dry degassed toluene (15 mL) at RT. Then PMe_2Ph (71 μL, 0.5 mmol) was added, and the resulting mixture was stirred for 2 h under the same conditions. Workup as for **1d**, afforded a brick-red solid, which was filtered off and thoroughly washed with Et_2O. This solid was purified by preparative TLC on silica gel using a mixture of acetone/*n*-hexane (4:1) as eluent. The band with Rf = 0.92 was collected, and the product was extracted with acetone (30 mL). Evaporation of the acetone and recrystallization from CH_2Cl_2/Et_2O gave **2e** as yellow crystals. Yield: 73 mg (50%). Single crystals of **2e**·11/2CH_2Cl_2 were grown by slow diffusion of Et_2O into a $CDCl_3$ solution of **2e**. Mp: 219 °C. IR: ν(CO) 1674 (sb) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 11.18 (t, 1H, CHO, $^5J_{PH}$ = 11 Hz), 10.54 (t, 1H, CHO, $^5J_{PH}$ = 11 Hz), 7.55−7.49 (m, 8H, PMe$_2$*Ph*), 7.35−7.26 (m, 12H, PMe$_2$*Ph*), 1.38 (vt, 12H, P*Me$_2$*Ph, 12 H, $^2J_{PH}$ + $^4J_{PH}$ = 4 Hz), 1.15 (vt, 12H, P*Me$_2$*Ph, 12 H, $^2J_{PH}$ + $^4J_{PH}$ = 4 Hz). ^{13}C{^{1}H}NMR (50.3 MHz, CDCl$_3$): δ 198.4 (s, 1C, CHO), 194.9 (s, 2C, CHO), 184.9 (t, 2C, C1−Pd, $^2J_{PC}$ = 5 Hz), 148.6 (br s, 1C, *C2*−CHO), 137.7 (br s, 2C, *C3*−CHO), 133.5 (vt, 4C, *ipso* C's PMe$_2$*Ph*, $^1J_{PC}$ + $^3J_{PC}$ = 46 Hz), 133.3 (s, 1C, C4−Br), 131.8 (vt, 8C, *ortho* C's PMe$_2$*Ph*, $^2J_{PC}$ + $^4J_{PC}$ = 12 Hz), 130.6 (s, 4C, *para* C's PMe$_2$*Ph*), 128.7 (vt, 8C, *meta* C's PMe$_2$*Ph*, $^3J_{PC}$ + $^5J_{PC}$ = 10 Hz), 15.6 (vt, 4C, P*Me$_2$*Ph, $^1J_{PC}$ + $^3J_{PC}$ = 30 Hz), 14.1 (vt, 4C, P*Me$_2$*Ph, $^1J_{PC}$ + $^3J_{PC}$ = 30 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, CDCl$_3$): δ −10.7. Anal. Calcd for $C_{41}H_{47}Br_3O_3P_4Pd_2$: C, 42.30; H, 4.07. Found: C, 42.62; H, 4.12.

Synthesis of [{PdBr(tmeda)}$_3${μ_3-C$_6$(CHO)$_3$}] (3a). [Pd(dba)$_2$] (588 mg, 1.0 mmol), tmeda (150 μL, 1.0 mmol), and C$_6$(CHO)$_3$Br$_3$ (100 mg, 0.25 mmol) were mixed in dry degassed toluene (15 mL). The resulting mixture was stirred at 60 °C for 2.5 h until the dark red color of [Pd(dba)$_2$] was no longer observed. Workup as for **1a**, afforded a bright yellow solid, which was filtered off and thoroughly washed with Et$_2$O. The solid obtained is a mixture of complex **3a** and **2a** in a ca. 10:1 molar ratio. The products were separated by preparative TLC on silica gel using a mixture of CH$_2$Cl$_2$/acetone (5:3) as eluent. The band with Rf = 0.16 was collected, and complex **3a** (yellow solid) was isolated as for **1a**. Yield: 235 mg (88%). Mp: 230 °C. IR: ν(CO) 1655 cm^{-1} (sb). ^{1}H NMR (600 MHz, CDCl$_3$): δ 11.97 (s, 2H, CHO), 11.77 (s, 1H, CHO), 2.87−2.6 (m, 12H, CH$_2$), 2.80, 2.78, 2.77, 2.34, 2.27, and 2.26 (s, 6H, Me), 2.75−2.6 (m, 12H, CH$_2$). ^{13}C{^{1}H} NMR (150.9 MHz, CDCl$_3$): δ 201.0 (1C, CHO), 200.8 (2C, CHO), 180.3 (1C, C1−Pd), 180.4 (2C, C3−Pd), 147.9 (2C, *C2*−CHO), 147.6 (1C, *C4*−CHO), 63.2 (2C, CH$_2$), 62.9 (1C, CH$_2$), 59.1 (1C, CH$_2$), 59.0 (2C, CH$_2$), 51.6, 51.5, 50.8, 49.5, 49.2, and 49.1 (2C, Me). Anal. Calcd for $C_{27}H_{51}Br_3N_6O_3Pd_3$: C, 30.40; H, 4.82; N, 7.88. Found: C, 30.39; H, 5.0; N,7.51.

Synthesis of [{PdBr(tbbpy)}$_3${μ_3-C$_6$(CHO)$_3$}] (3b). [Pd(dba)$_2$] (562 mg, 0.975 mmol), tbbpy (260 mg, 0.975 mmol), and C$_6$(CHO)$_3$Br$_3$ (100 mg, 0.25 mmol) were mixed under N$_2$ in dry degassed toluene (15 mL). The resulting mixture was stirred at 60 °C for 10 min, until the dark red color of [Pd(dba)$_2$] was no longer observed. Workup as for **1a**, afforded a solid, which was filtered off, thoroughly washed with Et$_2$O, and dried in vacuo to give **3b** as a yellow solid. Yield: 360 mg (94%). Mp: 250−251 °C dec. IR: ν(CO): 1660 cm^{-1} (sb). ^{1}H NMR (400 MHz, CDCl$_3$): δ 11.94 (s, 2H, CHO), 11.88 (s, 1H, CHO), 9.36 (d, 2H, tbbpy, $^3J_{HH}$ = 6 Hz), 9.25 (d, 1H, tbbpy, $^3J_{HH}$ = 6 Hz), 8.02 (d, 1H, tbbpy, $^3J_{HH}$ = 6 Hz), 7.93 (d, 1H, tbbpy, $^4J_{HH}$ = 2 Hz), 7.91−7.88 (m, 5H, tbbpy), 7.72 (d, 2H, tbbpy, $^3J_{HH}$ = 6 Hz), 7.51 (dd, 2H, tbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.48 (dd, 1H, tbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.47 (dd, 1H, tbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.23 (dd, 2H, tbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 1.42 (s, 9H, tBu), 1.41 (s, 18H, tBu), 1.38 (s, 9H, tBu), 1.35 (s, 18H, tBu). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 200.5 (1C, CHO), 199.7 (2C, CHO), 179.8 (1C, C1−Pd), 179.6 (2C, C3−Pd), 163.4 (1C), 163.3 (2C), 162.9 (1C) and 162.9 (2C) (C14 and 14′ tbbpy), 156.3 (2C), 155.5 (1C), 154.6 (1C) and 154.0 (2C) (C12 and 12′ tbbpy), 152.6 (1C), 150.6 (2C), 150.6 (2C) and 150.3 (1C) (CH16 and 16′ tbbpy), 148.2 (1C, *C4*−CHO), 148.0 (2C, *C2*−CHO), 125.4 (1C), 123.8 (2C), 123.6 (2C) and 123.4 (1C) (CH15 and 15′ tbbpy), 118.5 (2C), 118.3 (1C), 117.9 (2C) and 117.9 (1C) (CH13 and 13′ tbbpy), 35.6 (4C, *C*Me$_3$), 35.5 (2C, *C*Me$_3$), 30.5 (6C, C*Me$_3$*), 30.5 (3C, C*Me$_3$*), 30.4 (6C, C*Me$_3$*), 30.4 (3C, C*Me$_3$*). Anal. Calcd for $C_{63}H_{75}Br_3N_6O_3Pd_3$: C, 49.67; H, 4.96; N, 5.52. Found: C, 49.42; H, 5.08; N, 5.31.

Synthesis of [{*trans*-PdBr(PMe$_3$)$_2$}$_3${μ_3-C$_6$(CHO)$_3$}] (3f). Complex **3b** (100 mg, 0.065 mmol) and PMe$_3$ (787 μL of a 1 M solution in toluene, 0.787 mmol) were mixed under N$_2$ in degassed CH$_2$Cl$_2$ (15 mL) and stirred at RT for 20 h. The reaction mixture was then filtered over Celite, and the resulting solution was evaporated to dryness. Et$_2$O (15 mL) was added to precipitate a pale green solid, which was filtered off and thoroughly washed with Et$_2$O. Recrystallization from CH$_2$Cl$_2$/Et$_2$O afforded pale green crystals of **3f**. Yield: 58 mg (75%). Mp: 269 °C. IR: ν(CO) 1658 cm^{-1} (sb). ^{1}H NMR (400 MHz, CDCl$_3$): δ 11.36 (s, 3H, CHO), 1.23 (t, 54H, PMe$_3$, 54H, $^2J_{PH}$ + $^4J_{PH}$ = 4 Hz). ^{13}C{^{1}H}NMR (400 MHz, CDCl$_3$): δ 200.2 (s, 3C, CHO), 187.6 (t, 3C, C1−Pd, $^2J_{PC}$ = 5 Hz), 147.1 (s, 3C, *C2*−CHO), 15.7 (vt, 18C, PMe$_3$, $^1J_{PC}$ + $^3J_{PC}$ = 30 Hz). ^{31}P{^{1}H}NMR (121.4 MHz, CDCl$_3$): δ −18.8. Anal. Calcd for $C_{27}H_{57}Br_3O_3P_3Pd_3$: C, 27.61; H, 4.89. Found: C, 27.60; H, 4.99.

X-ray Structure Determinations. Intensities were registered at low temperature on a Bruker SMART 1000 CCD diffractometer using monochromated Mo Kα radiation (λ = 0.710 73 Å). Absorption corrections were based on multiscans (program SADABS). Structures were refined anisotropically using SHELXL-97.[54] Hydrogen atoms were included using rigid methyl groups or a riding model. *Special features*: In **1b** the atom O(2) is disordered over two positions. For **2e**, both dichloromethane sites are disordered (one over an inversion center).

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Supporting Information Available: Table with ^{13}C NMR data of complexes **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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