# Synthesis of Mercury(II) and Palladium(II) Organometallic Derivatives of Terephthaldehyde by Metalation, Transmetalation, Oxidation, and Condensation Reactions. X-ray Crystal Structures of *trans*-[PdCl{$C_6H_3(CO_2H)_2$-2,5}$(PPh_3)_2$]·$Me_2CO$·2MeOH, *trans*-[PdCl{$C_6H_3$(CHO)-2-$(CO_2H)$-5}$(PPh_3)_2$]·$2CH_2Cl_2$, and [Pd{$C_6H_3$(CH=N$C_6H_4NH_2$-4)-2-(CHO)-5}(*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine)]$CF_3SO_3$. Molecular Assemblies through [Pd]−Cl···$HO_2C$−Aryl and [Pd]−Cl···HOMe HO(O)C−Aryl Hydrogen Bonds†

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The organomercurials [HgCl{$C_6H_3(CHO)_2$-2,5}] (**1**) and [Hg{$C_6H_3(CHO)_2$-2,5}$_2$] (**2**) have been prepared by mercuriation of terephthaldehyde. Palladium complexes [PdCl{$C_6H_3(CHO)_2$-2,5}(N-N)] (N-N = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) (**3**) or 2,2′-bipyridine (bpy) (**3′**)) or *trans*-[PdCl{$C_6H_3(CHO)_2$-2,5}$(PPh_3)_2$]·$H_2O$ (**4**) have been obtained by reacting $(Me_4N)_2[Pd_2Cl_6]$ or *trans*-$[PdCl_2(PPh_3)_2]$, respectively, with **1** or **2**. The reaction of potassium permanganate with complexes **3** and **3′** or mercurial **1** results in the selective oxidation of the 5-formyl substituent affording [PdCl{$C_6H_3$(CHO)-2-$(CO_2H)$-5}(N-N)] (N-N = tmeda (**5**), bpy (**5′**)) or, respectively, a mixture whose major component is the fully oxidized [HgCl{$C_6H_3(CO_2H)_2$-2,5}] (**7**) or a mixture of isomers [HgCl{$C_6H_3$(CHO)-2-$(CO_2H)$-5}]/[HgCl{$C_6H_3(CO_2H)$-2-(CHO)}] (**8a**/**8b**) depending on the molar ratio of the reagents. The reaction of mixtures containing **7** or **8** with *trans*-$[PdCl_2(PPh_3)_2]$ give pure *trans*-[PdCl{$C_6H_3(CO_2H)_2$-2,5}$(PPh_3)_2$] (**9**) or *trans*-[PdCl{$C_6H_3$(CHO)-2-$(CO_2H)$-5}$(PPh_3)_2$] (**10**), respectively. Complexes **3** and **3′** react with amines and $NaClO_4$·$H_2O$ or $Tl(CF_3SO_3)$ to give, depending of the reaction conditions, cyclopalladated derivatives [Pd{$C_6H_3$(CH=NR)-2-(CH=NR)-5}(N-N)]$^+$ or [Pd{$C_6H_3$(CH=NR)-2-(CHO)-5}(tmeda)]$^+$. The mercurial **1** reacts with hydroxylamine to give the mercuriated oxime [HgCl{$C_6H_3(CH{=}NOH)_2$-2,5}] (**14**), which reacts with $(Me_4N)_2[Pd_2Cl_6]$ to give the cyclopalladated complex [Pd{$C_6H_3$(CH=NOH)-2-(CH=NOH)-5}($\mu$-Cl)]$_2$ (**15**). From **15** some derivatives have been prepared. Complex **3** reacts with $NH_2OMe$ to give [Pd{$C_6H_3$(CH=NOMe)-2-(CH=NOMe)-5}(tmeda)]$ClO_4$ (**19**). The imine $C_6H_4(CH{=}NTo)_2$-1,4 (To = $C_6H_4$Me-4) reacts with palladium(II) acetate to give the dipalladated imine [Pd{$C_6H_2$(CH=NTo)-2-{Pd($\mu$-OAc)}-4-(CH=NTo)-5}($\mu$-OAc)]$_n$ (**20**). Hydrolysis of **20** in the presence of potassium bromide and bpy results in the formation of [$C_6H_2${PdBr(bpy)}$_2$-1,4-$(CHO)_2$-2,5] (**21**), from which [$C_6H_2${Pd($PPh_3$)(bpy)}$_2$-1,4-$(CHO)_2$-2,5]$(CF_3SO_3)_2$ (**22**) can be prepared. The structures of **9**·$Me_2CO$·1.5MeOH, **10**·$2CH_2Cl_2$ and [Pd{$C_6H_3$(CH=NR)-2-(CHO)-5}(tmeda)]$CF_3SO_3$ (R = $C_6H_4NH_2$-4) (**12c′**) have been determined by X-ray crystallography.

## Introduction

We are currently involved in the synthesis of functionalized organometallic compounds and the study of their reactivity in order to find new types of chemical behavior or applications for organic synthesis. In particular, we have reported 2-amino-,[1] 2-nitro-,[2] 2-formyl-, 2-acetyl-,[3] 2-ethoxymethyl-,[4] and 2-arylazo[5] arylpalladium(II)[5] complexes as well as orthopalla-

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dated imines,[6] primary amines,[7] and phosphonium salts.[8] By reacting some of these complexes with alkynes, different types of organopalladium(II) (*e.g.*, alkyl,[9] vinyl, $\pi$-allyl,[4] 2-vinylaryl,[10] and indenyl[11] derivatives) or organic compounds (indenones, indenols,[3] benzofulvenes,[12] and spirocyclic compounds[3]) have been prepared. We have exploited different synthetic routes to prepare these arylpalladium(II) compounds, such as the oxidative-addition reaction, used for the preparation of 2-aminoaryl derivatives,[1,13] and the orthopalladation process, used for the synthesis of palladated primary amines[7] or phosphonium salts.[8] However, the use of arylmercurials as transmetalating agents has been our choice in many more instances.[4,14−16]

The arylpalladium(II) complexes containing the group $C_6H(OMe)_3$-2,3,4-(CHO)-6 have been among the most fruitful. The presence of the formyl group have been used to prepare other derivatives by condensation of amines or through the Wittig reaction to give orthopalladated imines[6] or 2-vinylarylpalladium(II) complexes, respectively.[10] From the latter, indenyl derivatives have been isolated.[11] The study of the reactivity of these formylaryl complexes has led to the synthesis of indenols and indenones[3] or shown an unprecedented type of rearrangement.[6] These precedents prompted us to prepare palladium(II) derivatives of terephthaldehyde. We report in this paper the mercuriation of terephthaldehyde, the transmetalation to palladium of the 2,5-diformylaryl group, and some condensation reactions (with amines or hydroxilamines) or oxidation reactions of the formyl group in the mercury(II) and palladium(II) derivatives. The resulting functionalized aryl complexes are potentially interesting because of the possibility of forming polymers or oligomers through hydrogen bonds. This way of self-assembling molecules is of great current interest.[17−21] Finally, we have synthesized some dipalladated derivatives of terephthaldehyde.

## Experimental Section

Reactions were carried out at room temperature and without precautions to exclude atmospheric moisture, unless otherwise stated. 3-Nitrobenzyl alcohol was used as the matrix for the FAB mass spectra. Chromatographic separations were performed as previously reported.[3]

**Synthesis of [HgCl{$C_6H_3(CHO)_2$-2,5}] (1).** A solution of HgO (3.05 g, 14.1 mmol) and terephthaldehyde (2.01 g, 14 mmol) in $CF_3SO_3H$ (19 $cm^3$)/water (19 $cm^3$) was stirred for 7 h in an oil bath at 95 °C. After the mixture was cooled down to room temperature, an aqueous solution (100 $cm^3$) of NaCl (15 g, 256 mmol) was added, the suspension stirred overnight, and then the solid filtered, washed with water (300 $cm^3$), air-dried, washed with diethyl ether (150 $cm^3$), and dried again. Evaporation of the ether washings gave unreacted terephthaldehyde (205 mg).The solid was purified by 1,4-dioxane extraction in a Soxhlet apparatus (about 10 h). Partial evaporation of the dioxane (*ca.* 4 $cm^3$) and addition of diethyl ether (40 $cm^3$) gave a white precipitate, which was filtered and air-dried to give **1**. Yield: 2.0 g, 39%. Mp: 250 °C (dec). IR: $\nu$(C=O) 1701 (s), 1670 (s) $cm^{-1}$; $\nu$(Hg−Cl) 328 (w) $cm^{-1}$. $^1$H NMR (200 MHz, DMSO-$d_6$, ppm): 10.19 (s, CHO, 1H), 10.09 (s, CHO, 1H), 8.24 (s, H6, 1H), 8.14 (d, H3, 1H, $^3J_{HH}$ = 7.7 Hz), 7.99 (d, H4, 1H). $^{13}$C{$^1$H} NMR (50 MHz, DMSO-$d_6$, ppm): 194.7 (CHO), 193.4 (CHO), 152.3, 143.5, 139.3 (C1, C2, C5), 138.3, 134.1, 129.6 (C3, C4, C6). Anal. Calcd for $C_8H_5ClHgO_2$: C, 26.03; H, 1.37. Found: C, 25.92; H, 1.30.

Compound **1** was similarly prepared using 60% perchloric acid as the solvent. The mercuriation was conducted behind a protective barricade.

**Synthesis of [Hg{$C_6H_3(CHO)_2$-2,5}$_2$] (2).** A mixture of **1** (1.00 g, 2.71 mmol) and $(Me_4N)Cl$ (358 mg, 3.27 mmol) in acetone (20 $cm^3$) was refluxed for 12 h. Partial evaporation of the solvent (*ca.* 4 $cm^3$) and addition of water (125 $cm^3$) led to the precipitation of a solid, which was filtered and successively washed with water, ethanol, and diethyl ether and air-dried to give **2** as a white solid. Yield: 566 mg, 45% over total mercury. Mp: *ca.* 250 °C (dec). IR: $\nu$(C=O) 1664 (s, br), 1668 (s, br) $cm^{-1}$.$^1$H NMR (200 MHz, DMSO-$d_6$, ppm): 10.43 (s, CHO, 1H), 10.18 (s, CHO, 1H), 8.41 (s br, H6, 1H), 8.24 (d, H3, 1 H), 8.00 (dd, H4, 1H, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 2.0 Hz). $^{13}$C NMR: not soluble enough. Anal. Calcd for $C_{16}H_{10}HgO_4$: C, 41.17; H, 2.16. Found: C, 40.56; H, 2.01. The insolubility of **2** prevented further purification.

**Synthesis of [PdCl{$C_6H_3(CHO)_2$-2,5}(tmeda)] (3).** A mixture of $(Me_4N)_2[Pd_2Cl_4(\mu\text{-}Cl)_2]$ (300 mg, 0.52 mmol), **1** (385 mg, 1.04 mmol), and $(Me_4N)Cl$ (132 mg, 1.2 mmol) in acetone (60 $cm^3$) was stirred for 1 h at room temperature and 5 h at 0 °C and then filtered through Celite. The resulting yellow solution was added to a solution of *N*,*N*′-tetramethylethylenediamine (0.156 $cm^3$, 1.04 mmol) in acetone (6 $cm^3$). After 15 min, the mixture was filtered through Celite. The solvent was removed, and the residue was treated with dichloromethane and filtered over Celite; the resulting solution was washed with water and dried with $MgSO_4$. Partial evaporation of the solvent (*ca.* 4 $cm^3$) and addition of *n*-pentane (20 $cm^3$) led to the precipitation of crude **3** as a yellow precipitate. This product was purified by chromatography through silica gel with dichloromethane and dichloromethane/acetone (1:1). Yield: 310 mg, 76%. Mp: *ca.* 140 °C (dec). IR: $\nu$(C=O) 1660 (m), 1674 (s), 1688 (m), 1700 (s) $cm^{-1}$. IR($CH_2Cl_2$): 1686, 1698 $cm^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$, ppm): 11.23 (s, CHO, 1H), 10.04 (s, CHO, 1H), 8.17 (d, H6, 1H, $^4J_{HH}$ = 1.5 Hz), 7.81 (d, H3, 1H, $^3J_{HH}$ = 7.9 Hz), 7.53 (dd, H4, 1H), 3.1−2.5 (m, $CH_2$, 4H), 2.73 (s, Me, 3H), 2.70 (s, Me, 3H), 2.59 (s, Me, 3H), 2.24 (s, Me, 3H), $^{13}$C{$^1$H} NMR (50 MHz, DMSO-$d_6$, ppm): 196.93 (CHO), 194.12 (CHO), 164.25 (quaternary carbons), 145.10 (quaternary carbon), 137.93 (CH), 136.09 (quaternary carbon), 126.20 (CH), 123.10 (CH), 62.18 ($CH_2$), 57.72 ($CH_2$), 51.73 (Me), 49.37 (Me), 48.00 (Me), 46.69 (Me). FAB MS: *m*/*z* 355 ($M^+$ − Cl, 100), 221 ($M^+$ − Cl − Aryl, 42). Anal. Calcd for

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$C_{14}H_{21}ClN_2O_2Pd$: C, 42.99; H, 5.41; N, 7.16. Found: C, 43.10; H, 5.38; N, 7.11.

**Synthesis of [PdCl{$C_6H_3$(CHO)$_2$-2,5}(bpy)]·$H_2O$ (3′).** A mixture of $(Me_4N)_2[Pd_2Cl_4(\mu\text{-}Cl)_2]$ (300 mg, 0.52 mmol), **1** (385 mg, 1.04 mmol), and $(Me_4N)Cl$ (132 mg, 1.2 mmol) in acetone (60 cm$^3$) was stirred for 1 h at room temperature and 5 h at 0 °C and then filtered through Celite. The resulting yellow solution was added to a solution of 2,2′-bipyridine (163 mg, 1.04 mmol) in acetone (6 cm$^3$). After 15 min, the mixture was filtered through Celite. The solvent was removed, and the residue was recrystallized from dichloromethane/diethyl ether to obtain a precipitate, which was filtered, washed with diethyl ether, and air-dried to give **3′** as a yellow solid. Yield: 370 mg, 78%. Mp: *ca.* 180 °C (dec). IR: $\nu$(C=O) 1682 (s), 1696 (s) cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$, ppm): 11.21 (s, CHO, 1H), 10.07 (s, CHO, 1H), 9.33 (d, bpy, 1H, $^3J_{HH}$ = 5 Hz), 8.32 (d, bpy, 1H, $^3J_{HH}$ = 1.5 Hz), 8.2−7.9 (m, bpy and ArH, 5H), 7.8−7.6 (m, bpy and ArH, 3H), 7.35−7.28 (m, bpy, 1H), 1.59 (s br, $H_2O$, 2H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, ppm): 196.1 (CHO), 193.2 (CHO), 160.8, 156.5, 153.5 (quaternary carbons), 151.3 (CH), 149.7 (CH), 145.5 (quaternary carbon), 139.7 (CH), 139.4 (CH), 138.5 (CH), 137.6 (quaternary carbon), 128.4 (CH), 127.2 (CH), 127.0 (CH), 124.7 (CH), 122.6 (CH), 121.7 (CH). FAB MS: *m*/*z* 431 (M$^+$, 13), 395 (M$^+$ − Cl, 58), 262 (M$^+$ − Cl − Aryl, 100). Anal. Calcd for $C_{18}H_{15}ClN_2O_3Pd$: C, 48.13; H, 3.36; N, 6.24. Found: C, 48.07; H, 2.99; N, 6.06.

**Synthesis of *trans*-[PdCl{$C_6H_3$(CHO)$_2$-2,5}($PPh_3$)$_2$]·$H_2O$ (4).** A mixture of *trans*-$[PdCl_2(PPh_3)_2]$ (300 mg, 0.43 mmol), **1** (189 mg, 0.51 mmol), and $(Me_4N)Cl$ (114 mg, 1.03 mmol) in acetone (30 cm$^3$) was refluxed for 8 h and then filtered through Celite. The solvent was removed, and the residue was recrystallized from dichloromethane/hexane to obtain crude **4** as a yellow solid, which was purified by chromatography through silica gel with dichloromethane/diethyl ether (10:1). Yield: 194 mg, 55%. Mp: 190 °C dec. IR: $\nu$(C=O) 1682 (s, br) cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$, ppm): 10.17 (s, CHO, 1H), 9.47 (s, CHO, 1H), 7.7−7.1 (m, $PPh_3$ and H6, 31H), 7.02 (d, H3, 1H, $^3J_{HH}$ = 6.0 Hz), 6.91 (d, H4, 1H), 1.54 (s br, $H_2O$, 2H). $^{13}$C{$^1$H} NMR (50 MHz, $CDCl_3$, ppm): 194.6 (CHO), 192.4 (CHO), 169.9 (t, C1, $^2J_{PC}$ = 5.6 Hz), 143.7 (t, C2, $^3J_{PC}$ = 2.2 Hz), 138.7 (t, C6, $^3J_{PC}$ = 4.0 Hz), 136.6 (C5), 134.3 (t, *o*-C $PPh_3$, $^2J_{PC}$ = 6.3 Hz), 130.7 (C3 or C4), 130.2 (*p*-C $PPh_3$), 129.9 (*i*-C $PPh_3$, $^1J_{PC}$ = 23.3 Hz), 128.2 (t, *m*-C $PPh_3$, $^3J_{PC}$ = 5.2 Hz), 122.7 (C3 or C4). $^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$, ppm): 24.96 (s). FAB MS: *m*/*z* 798 (M$^+$, 28), 764 (M$^+$ − Cl, 17), 630 (M$^+$ − Cl − Aryl, 99). Anal. Calcd for $C_{44}H_{37}ClO_3P_2Pd$: C, 64.64; H, 4.56. Found: C, 64.68; H, 4.31.

**Synthesis of [PdCl{$C_6H_3$(CHO)-2-($CO_2H$)-5}(tmeda)] (5).** A solution of $KMnO_4$ (162 mg, 1.02 mmol) in an acetone (24 cm$^3$)/water (6 cm$^3$) mixture was added dropwise for 35 min into a solution of **3** (300 mg, 0.77 mmol) in acetone (55 cm$^3$); the dropping funnel was washed with acetone (4 cm$^3$), which was also added to the reaction mixture. The mixture was then stirred for a further 22 h, during which time a brown suspension was formed from the violet solution. A solution of $C_2O_4H_2\cdot 2H_2O$ (129 mg, 1.02 mmol) in acetone (10 cm$^3$)/water (10 cm$^3$) was then added dropwise, and the suspension was stirred for a further 2 h and subsequently filtered over Celite to give a yellow solution. The solvents were partially evaporated (*ca.* 10 cm$^3$) and extracted with $CH_2Cl_2$ (100 cm$^3$). The water phase was extracted again with $CH_2Cl_2$ (2 × 25 cm$^3$). The organic layers were added together, dried over $MgSO_4$, filtered, and partially evaporated (*ca.* 3 cm$^3$). Addition of diethyl ether (30 cm$^3$) and hexane (40 cm$^3$) caused the precipitation of a solid, which was filtered and air-dried to give **5** as a yellow solid. Yield: 141 mg, 45%. Mp: 172 °C. IR: $\nu$(C=O) 1691 (vs), 1668 (vs); $\nu$(Pd−Cl) 323 cm$^{-1}$. $^1$H NMR (300 MHz, DMSO-$d_6$, ppm): 12.97 (s br, $CO_2H$, 1H), 11.24 (s, CHO, 1H), 8.19 (d, H6, 1H, $^4J_{HH}$ = 1.4 Hz), 7.57 (d, H3, 1H, $^3J_{HH}$ = 8.0 Hz), 7.50 (dd, H4, 1H), 2.75−2.50 (m, $CH_2$), 2.58 (s, Me), 2.55 (s, Me), 2.51 (s, Me, 3H), 2.16 (s, Me). $^{13}$C{$^1$H} NMR: not soluble enough. FAB MS: *m*/*z* 371 (M$^+$ − Cl, 32), 221 ($C_6H_{15}N_2Pd$, 15). Anal. Calcd for $C_{14}H_{21}ClN_2O_3Pd$: C, 41.30; H, 5.20; N, 6.88. Found: C, 41.23; H, 5.17; N, 6.81.

**Synthesis of [PdCl{$C_6H_3$(CHO)-2-($CO_2H$)-5}(bpy)] (5′).** This compound was similarly prepared from $KMnO_4$ (148.6 mg, 0.940 mmol) and **3′** (304 mg, 0.705 mmol). After the addition of $C_2O_4H_2\cdot 2H_2O$ (119 mg, 094 mmol), the suspension was stirred for 1 h and filtered over Celite. The solvents were partially evaporated (*ca.* 10 cm$^3$), and a solid precipitated, which was filtered, washed twice with water (10 cm$^3$), air-dried, washed with diethyl ether (10 cm$^3$), and air-dried to give **5′** as a yellow solid. Yield: 134 mg, 43%. Mp: 206 °C. IR: $\nu$(C=O) 1717 (s), 1674 (vs), 1652 (vs) cm$^{-1}$; $\nu$(Pd−Cl) 345 (w) cm$^{-1}$. $^1$H NMR (300 MHz, DMSO-$d_6$, ppm): 13.07 (s br, $CO_2H$, 1H), 11.08 (s, CHO, 1H), 9.02−7.55 (several m, CH, 11H). $^{13}$C{$^1$H} NMR: not soluble enough. FAB MS: *m*/*z* 411 (M$^+$ − Cl, 23), 262 (Pd(bpy), 64). Anal. Calcd for $C_{18}H_{13}ClN_2O_3Pd$: C, 48.35; H, 2.93; N, 6.27. Found: C, 48.17; H, 2.91; N, 6.42.

**Synthesis of [Pd{$C_6H_3$(CHO)-2-($CO_2H$)-5}($PPh_3$)(bpy)]-$CF_3SO_3$ (6).** A solution of K($CF_3SO_3$) (43 mg, 0.23 mmol) and $PPh_3$ (60 mg, 0.23 mmol) in acetone (24 cm$^3$) was added dropwise for 10 min to a suspension of **5′** (103 mg, 0.23 mmol) in acetone (10 cm$^3$). After the addition, the mixture was stirred for a further 2 h. Filtration over Celite yielded a yellow solution, which was evaporated to dryness. The resulting yellow residue was dissolved in 50 cm$^3$ of $CH_2Cl_2$ and washed with 20 cm$^3$ of water. The separated organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo (*ca.* 2 cm$^3$). Addition of 50 cm$^3$ of diethyl ether gave a precipitate, which was filtered and air-dried to give **6** as a yellow solid . Yield: 123 mg, 65%. Mp: 167 °C. IR: $\nu$(C=O) 1679 (s) cm$^{-1}$; $\nu$(SO) 1027 (s), 634 (s) cm$^{-1}$. $^1$H NMR (200 MHz, DMSO-$d_6$, ppm): 13.09 (s br, $CO_2H$, 1H), 10.12 (s, CHO, 1H), 8.76−7.16 (several m, $CH_{arom}$, 26H). $^{31}$P{$^1$H} NMR (121 MHz, DMSO-$d_6$, ppm): 33.1 (s). FAB$^+$ MS: *m*/*z* 674 (M$^+$, 23), 411 (M$^+$ − $PPh_3$, 63), 262 (Pd(bpy), 32). Anal. Calcd for $C_{37}H_{28}F_3N_2O_6PPdS$: C, 53.99; H, 3.43; N, 3.40. Found: C, 53.96; H, 3.52; N, 3.41.

**Synthesis of Crude [HgCl{$C_6H_3$($CO_2H$)$_2$-2,5}] (7).** $KMnO_4$ (684 mg, 3.7 mmol), dissolved in an acetone (72 cm$^3$)/water (18 cm$^3$) mixture, was added dropwise for 25 min to a solution of **1** (1.02 g, 2.77 mmol) in acetone (150 cm$^3$); the dropping funnel was washed with 12 cm$^3$ of acetone, and the solution was also added to the reaction mixture. The mixture was then stirred for a 19 h more, during which time a brown suspension was formed from the violet solution. Aqueous HCl (0.1 M, 38 cm$^3$) was then added, and the suspension was stirred for 1 h and filtered over Celite to give a colorless solution. The solvents were partially evaporated (*ca.* 30 cm$^3$) to give a white precipitate, which was filtered, washed with water, air-dried, washed with ether, and dried again. Using this procedure, 922 mg of crude material was obtained. A Soxhlet extraction with 1,4-dioxane yields an 8:1 molar mixture of **7** and **1** with traces of mono-oxidized products (see Discussion). Yield: 793 mg, 64% (calcd from $^1$H NMR). IR: $\nu$(C=O) 1681 (vs), 1673 (vs) cm$^{-1}$; $\nu$(HgCl) 339 (s) cm$^{-1}$. $^1$H NMR (200 MHz, DMSO-$d_6$, ppm): 13.39 (s br, $CO_2H$, 2H), 8.25 (d, H6, 1H, $^4J_{HH}$ = 1.5 Hz), 8.14 (d, H3, 1H, $^3J_{HH}$ = 8.1 Hz), 7.89 (dd, H4, 1H). Anal. Calcd for $C_8H_5ClHgO_4$: C, 23.95; H, 1.26. Found: C, 24.71; H, 1.34.

**Synthesis of the Mixture [HgCl{$C_6H_3$(CHO)-2-($CO_2H$)-5}]/[HgCl{$C_6H_3$($CO_2H$)-2-(CHO)-5}] (8a/8b).** $KMnO_4$ (286 mg, 1.81 mmol), dissolved in an acetone/water mixture (72/18 cm$^3$), was added dropwise for 3 h to a solution of **1** (1.0 g, 2.71 mmol) in acetone (140 cm$^3$); the dropping funnel was washed with 4 cm$^3$ of acetone, and the solution was also added to the reaction mixture. The mixture was then stirred for a further 30 min, during which time a brown suspension was formed from the violet solution. Aqueous HCl (0.1 M, 18.1 cm$^3$) was then added, and the suspension was stirred for 30 min more and then filtered over Celite. The resulting colorless solution was partially concentrated (*ca.* 20 cm$^3$) to give a suspension, which was filtered, washed with water, air-dried, washed with diethyl ether, and dried again. Using this procedure, 842 mg

of crude material was obtained. A Soxhlet extraction with 1,4-dioxane yields a 1.8/1 ($^1$H NMR) mixture of **8a** and **8b** contaminated with traces of **1**. Yield: 312 mg, *ca*. 30% (calcd from $^1$H NMR). IR: $\nu$(C=O) 1697 (s), 1675 (s) cm$^{-1}$; $\nu$(HgCl) 330 (w) cm$^{-1}$. $^1$H NMR (200 MHz, DMSO-$d_6$, ppm): 13.50 (s br, $CO_2H$, 2H), 10.18 (s, CHO), 10.08 (s, CHO), 8.4−7.8 (several multiplets, aromatic Hs). Anal. Calcd for $C_8H_5ClHgO_3$: C, 24.95; H, 1.31. Found: C, 25.34; H, 1.25.

**Synthesis of *trans*-[PdCl{$C_6H_3(CO_2H)_2$-2,5}($PPh_3$)$_2$] (9).** [$PdCl_2(PPh_3)_2$] (310 mg, 0.44 mmol), crude **7** (276 mg, *ca*. 0.7 mmol), and ($Me_4N$)Cl (156 mg, 1.0 mmol) were mixed in acetone (80 cm$^3$)/1,4-dioxane (10 cm$^3$) and stirred for 5 h at 62 °C. The solvents were then partially evaporated (*ca*. 2 cm$^3$), and $CH_2Cl_2$ (80 cm$^3$) was added, forming a suspension which was filtered, and the resulting solid was air-dried to give **9** as a colorless solid. The yellowish filtered solution was partially evaporated (*ca*. 5 cm$^3$), and the addition of hexane (70 cm$^3$) gave a suspension, which was filtered to give unreacted $PdCl_2(PPh_3)_2$ (57 mg, 18%). The filtered yellow solution was concentrated to dryness, yielding traces of complex **4** (by $^1$H NMR). Yield of 9: 264 mg, 88% (based on reacted [$PdCl_2(PPh_3)_2$]). Mp: 209 °C. IR: $\nu(CO_2)$ 1674 (vs), 1278 (br, s) cm$^{-1}$. $^1$H NMR (300 MHz, DMSO-$d_6$, ppm): 12.50 (s br, $CO_2H$, 2H), 7.72 (s, H6, 1H), 7.52−7.26 (m, $PPh_3$, 30H), 6.93 (d, H3 or H4, 1H, $^3J_{HH}$ = 8.3 Hz), 6.85 (d, H4 or H3, 1H). $^{13}$C{$^1$H} NMR: not soluble enough. $^{31}$P{$^1$H} NMR (121 MHz, DMSO-$d_6$, ppm): 27.4 (s). FAB MS: *m*/*z* 794 (M$^+$ − Cl, 3), 534 (M$^+$ − Cl − $PPh_3$, 9). Anal. Calcd for $C_{44}H_{35}ClO_4P_2Pd$: C, 63.55; H, 4.24. Found: C, 63.46; H, 4.12. Crystals of **9** were grown by slowly cooling (−20 °C) a saturated solution of **9** in *ca*. 1:1:1 (v:v:v) acetone/methanol/dichloromethane solution.

**Synthesis of *trans*-[PdCl{$C_6H_3$(CHO)-2-($CO_2H$)-5}($PPh_3$)$_2$] (10).** *trans*-[$PdCl_2(PPh_3)_2$] (350 mg, 0.5 mmol), the mixture of mercurials **8a/8b** (208 mg, *ca*. 0.54 mmol), and ($Me_4N$)Cl (230 mg, 2.10 mmol) were dissolved in acetone (35 cm$^3$)/1,4-dioxane (10 cm$^3$) and stirred for 4 h at 62 °C. The resulting gray suspension was filtered over Celite, and the yellow solution obtained was evaporated to dryness. The residue was suspended in $CH_2Cl_2$ (20 cm$^3$) and stirred for 2 h. The insoluble solid was filtered off, giving **10** as a yellowish solid. Yield: 162 mg, 40%. Mp: 210° C. IR: $\nu$(C=O) 1715 (s), 1675 (s) cm$^{-1}$. $^1$H NMR (200 MHz, DMSO-$d_6$, ppm): 12.68 (s br, $CO_2H$, 1H), 9.77 (s, CHO, 1H), 7.71 (s, H6, 1H), 7.51−7.29 (m, Ph, 30H), 7.08 (d, H3 or H4, 1H, $^3J_{HH}$ = 8.0 Hz), 6.70 (d, H4 or H3, 1H). $^{13}$C NMR: not soluble enough. $^{31}$P{$^1$H} NMR (121 MHz, DMSO-$d_6$, ppm): 23.3 (s). FAB MS: *m*/*z* 780 (M$^+$ − Cl, 11), 517 (M$^+$ − Cl − $PPh_3$, 56). Anal. Calcd for $C_{44}H_{35}ClO_3P_2Pd$: C, 64.80; H, 4.33. Found: C, 64.63; H, 4.32. Colorless crystals were grown from a hot solution of **10** in methanol and $CH_2Cl_2$ by slowly cooling the solution to room temperature.

**Synthesis of [Pd{$C_6H_3$(CH=NR)-2-(CH=NR)-5}(N-N)]X (11). R = $C_6H_4$Me-4, N-N = tmeda, X = $ClO_4$ (11a).** A mixture of **3** (225 mg, 0.57 mmol), *p*-toluidine (123 mg, 1.15 mmol), $NaClO_4$ (323 mg, 2.30 mmol), and *p*-$MeC_6H_4SO_3H$ (a few crystals) in toluene (70 cm$^3$) was refluxed for 20 h in a Soxhlet containing $CaH_2$ in the extraction thimble. The solvent was then evaporated, and the residue was extracted with dichloromethane and then filtered through Celite to give an orange solution. Partial evaporation of the solvent (*ca*. 4 cm$^3$) and addition of diethyl ether (20 cm$^3$) led to a suspension which was filtered, and the solid was recrystallized from dichloromethane/diethyl ether, washed with diethyl ether, and air-dried to give **11a**·$H_2O$ as an orange solid. Yield: 232 mg, 62%. Mp: 170 °C dec. $\Lambda_M$ (acetone, 5 × 10$^{-4}$ mol L$^{-1}$): 120 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ IR: $\nu$(C=N) 1594 (s, br) cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$, $\delta$): 8.49 (s, CH=N, 1H), 8.00 (s, CH=N, 1H), 7.93 (s, H6, 1H), 7.65 (d, H3, 1H, $^3J_{HH}$ = 7.8 Hz), 7.51 (d, H4, 1H), 7.4−7.1 (m, 2$C_6H_4$Me, 8H), 3.11 (s, NMe, 6H), 3.1−2.6 (m, $CH_2$, 4H), 2.40 (s, CMe, 3H), 2.38 (s, CMe, 3H), 2.17 (s, NMe, 6H), 1.64 (s br, $H_2O$, 2H). Anal. Calcd for $C_{28}H_{37}ClN_4O_5$-Pd: C, 51.62; H, 5.72; N, 8.60. Found: C, 51.41; H, 5.56; N, 8.24.

**R = $C_6H_4Bu^n$-4, N-N = tmeda, X = $ClO_4$ (11b).** This compound was similarly prepared from **3** (215 mg, 0.55 mmol), $NaClO_4$ (309 mg, 2.20 mmol), and *p*-butylaniline (352 $\mu$l, 2.20 mmol) in toluene (70 cm$^3$), 2 h reflux. Yield: 200 mg, 51%. Mp: 200 °C. IR: $\nu$(C=N) 1601 (s) cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$, ppm): 8.49 (s, CH=N, 1H), 8.01 (s, CH=N, 1H), 7.95 (s, H6, 1H), 7.65 (d, H3 or H4, 1H, $^3J_{HH}$ = 7.8 Hz), 7.50 (d, H4 or H3, 1H), 7.31−7.17 (m, $C_6H_4$Bu, 8H), 3.11 (s, NMe, 6H), 3.00 (m, $CH_2$, 2H), 2.74 (m, $CH_2$, 2H), 2.65 (apparent q, $CH_2$, 4H), 2.16 (s, NMe, 6H), 1.62 (m, $CH_2$, 4H), 1.34 (m, $CH_2$, 4H), 0.94 (t, Me, 6H). $^{13}$C{$^1$H} NMR (50 MHz, $CDCl_3$, ppm): 179.4 (CH=N), 158.0 (CH=N), 155.4, 148.7, 148.4, 146.2, 143.9, 141.8, 138.2 (quaternary carbons), 131.2 (CH), 130.0 (CH), 129.5 (2CH), 129.2 (2CH), 126.8 (CH), 123.1 (2CH), 121.1 (2CH), 64.4 ($CH_2$), 60.4 ($CH_2$), 51.6 (NMe), 48.1 (NMe), 35.2 ($CH_2$), 35.1 ($CH_2$), 33.6 ($CH_2$), 33.3 ($CH_2$), 22.3 ($CH_2$), 22.2 ($CH_2$), 13.9 (2Me). FAB$^+$ MS: *m*/*z* 617 (M$^+$ − $ClO_4$, 100). Anal. Calcd for $C_{34}H_{47}ClN_4O_4Pd$: C, 56.91; H, 6.60; N, 7.81. Found: C, 56.85; H, 6.49; N, 7.83.

**R = $C_6H_4Bu^n$-4, N-N = bpy, X = $ClO_4$ (11′b).** This compound was similarly prepared from **3′** (210 mg, 0.49 mmol), $NaClO_4$ (274 mg, 2.1 mmol), *p*-butyl aniline (0.234 cm$^3$, 1.46 mmol), and a few crystals of *p*-$MeC_6H_4SO_3H$ in toluene (70 cm$^3$), reflux. 14 h . Yield: 180 mg, 49%. Mp: 149 °C. IR: $\nu$(C=N) 1596 (s) cm$^{-1}$; $\nu(ClO_4)$, 1086 (vs) cm$^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$, ppm): 8.50 (s, CH=N, 1H), 8.31 (s, CH=N, 1H), 8.59−7.20 (several m, CH, 21H), 2.67 (apparent q, $CH_2$, 4H), 1.62 (m, $CH_2$, 4H), 1.37 (m, $CH_2$, 4H), 0.96 (t, Me, 3H, $^3J_{HH}$ = 7.1 Hz), 0.95 (t, Me, 3H, $^3J_{HH}$ = 7.2 Hz). $^{13}$C{$^1$H} NMR (50 MHz, $CDCl_3$, ppm): 177.4 (CH=N), 157.8 (CH=N), 157.1, 148.9, 148.2, 144.8, 144.5, 142.0, 136.6 (quaternary carbons), 141.1 (CH), 137.0 (CH), 131.8 (CH), 130.2 (CH), 129.9 (2CH), 129.2 (2CH), 129.0 (CH), 126.9 (2CH), 126.8 (CH), 124.2 (2CH), 122.4 (2CH), 121.3 (CH), 35.2 ($CH_2$), 35.1 ($CH_2$), 33.6 ($CH_2$), 33.3 ($CH_2$), 22.3 ($CH_2$), 22.1 ($CH_2$), 13.9 (Me), 13.8 (Me). FAB$^+$ MS: *m*/*z* 657 (M$^+$ − $ClO_4$, 100). Anal. Calcd for $C_{38}H_{39}$-$ClN_4O_4Pd$: C, 60.25; H, 5.19; N, 7.40. Found: C, 60.37; H, 4.95; N, 7.68.

**R = $C_6H_4NH_2$-4, N-N = tmeda, X = $ClO_4$ (11c).** A solution of **3** (112 mg, 0.29 mmol) in acetonitrile (80 cm$^3$) was added dropwise to a solution of $NaClO_4$ (165 mg, 1.18 mmol) and *p*-phenylenediamine (190 mg, 1.76 mmol) in acetonitrile (10 cm$^3$) for 140 min; the mixture was then stirred for a further 17 h, during which time a color change from yellow to orange brown was observed. The suspension was filtered, the resulting solution concentrated to dryness, the residue treated with dichloromethane (50 cm$^3$), and the suspension filtered. The resulting solution was concentrated to dryness, and the red-brown residue was dissolved in dichloromethane/acetone (10/15 cm$^3$). Addition of diethyl ether (25 cm$^3$) gave **11c** as an orange solid. Yield: 57 mg, 31%. Mp: 287 °C (dec). IR: $\nu(NH_2)$ 3450 (m), 3357 (s) cm$^{-1}$; $\nu$(C=N) 1602 (vs) cm$^{-1}$; $\nu(ClO_4)$ 1093 (vs) cm$^{-1}$. $^1$H NMR (200 MHz, DMSO-$d_6$, ppm): 8.74 (s, CH=N, 1H), 8.32 (s, CH=N, 1H), 7.87 (s, H6, 1H), 7.72 (d, H3 or H4, 1H, $^3J_{HH}$ = 7.8 Hz), 7.61 (d, H4 or H3, 1H), 7.21 (d, $CH_{arom}$, 2H, $^3J_{HH}$ = 8.5 Hz), 7.03 (d, $CH_{arom}$, 2H, $^3J_{HH}$ = 8.5 Hz), 6.64 (d, $CH_{arom}$, 2H, $^3J_{HH}$ = 8.5 Hz), 6.61 (d, $CH_{arom}$, 2H, $^3J_{HH}$ = 8.5 Hz), 5.47 (s, $NH_2$, 2H), 5.38 (s, $NH_2$, 2H), 2.99 (s, NMe, 6H), 2.81 (m, $CH_2$, 2H), 2.65 (m, $CH_2$, 2H), 2.14 (s, NMe, 6H). $^{13}$C NMR: not soluble enough. FAB$^+$ MS: *m*/*z* 535 (M$^+$ − $ClO_4$, 100). Anal. Calcd for $C_{26}H_{33}ClN_6O_4Pd$: C, 49.14; H, 5.23; N, 13.23. Found: C, 48.49; H, 5.11; N, 12.62. The low solubility of **11c** prevented further purification.

**R = $C_6H_4NH_2$-4, N-N = bpy, X = $ClO_4$ (11′c).** This compound was similarly prepared from **3′** (206 mg, 0.48 mmol) in acetonitrile (80 cm$^3$), $NaClO_4$ (280 mg, 1.99 mmol), and *p*-phenylenediamine (310 mg, 2.867 mmol) in acetonitrile (18 cm$^3$) Yield: 90 mg, 28%. Mp: 250 °C (dec). IR: $\nu(NH_2)$ 3455 (m), 3357 (s) cm$^{-1}$; $\nu$(C=N) 1608 (vs), 1600 (vs) cm$^{-1}$; $\nu(ClO_4)$

1093 (vs) $cm^{-1}$. $^1H$ NMR (300 MHz, DMSO-$d_6$, ppm): 8.65 (s, CH=N, 1H), 8.56 (s, CH=N, 1H), 8.68−7.65 (several m, $CH_{arom}$, 11H), 7.39 (d, $CH_{arom}$, 2H, $^3J_{HH}$ = 8.7 Hz), 7.19 (d, $CH_{arom}$, 2H, $^3J_{HH}$ = 8.7 Hz), 6.67 (d, $CH_{arom}$, 2H, $^3J_{HH}$ = 8.7 Hz), 6.61 (d, $CH_{arom}$, 2H, $^3J_{HH}$ = 8.7 Hz), 5.68 ($NH_2$, 2H, s), 5.39 ($NH_2$, 2H, s). $^{13}C$ NMR: not soluble enough. $FAB^+$ MS: *m*/*z* 575 ($M^+ - ClO_4$, 6.0). Anal. Calcd for $C_{30}H_{25}ClN_6O_4Pd$: C, 53.45; H, 3.73; N, 12.44. Found: C, 53.28; H, 3.73; N, 11.60.

**Synthesis of [Pd{$C_6H_3$(CH=NR)-2-(CHO)-5}(tmeda)]X (12). R = $C_6H_4$Bu-4, X = $ClO_4$ (12b).** A solution of 3 (210 mg, 0.54 mmol) in acetonitrile (74 $cm^3$) was added dropwise to a solution of $NaClO_4$ (297 mg, 2.11 mmol) and 4-butylaniline (0.085 $cm^3$, 0.53 mmol) in acetonitrile (14 $cm^3$) for 10 min, and the mixture was then stirred for a further 22 h. The acetonitrile was then evaporated, and the residue was dissolved in dichloromethane (50 $cm^3$), filtered over Celite, and concentrated *in vacuo* (*ca*. 8 $cm^3$). Addition of diethyl ether (50 $cm^3$) and filtration of the resulting suspension gave **12b** as a light yellow solid. Yield: 200 mg, 64%. Mp: 111 °C. IR: $\nu$(CO) 1680 (vs) $cm^{-1}$; $\nu$(CN) 1602 (s) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$, ppm): 10.02 (s, CHO, 1H), 8.11 (s, CH=N, 1H), 7.77 (s, H6, 1H), 7.68 (d, H3 or H4, 1H, $^3J_{HH}$ = 7.5 Hz), 7.63 (d, H4 or H3, 1H), 7.30 (d, $CH_{arom}$, 2H, $^3J_{HH}$ = 8.3 Hz), 7.21 (d, $CH_{arom}$, 2H, $^3J_{HH}$ = 8.3 Hz), 3.08 (s, NMe, 6H), 2.79 (m, $CH_2$, 2H), 2.76 (m, $CH_2$, 2H), 2.65 (t, $CH_2$, 2H, $^3J_{HH}$ = 7.8 Hz), 2.16 (s, NMe, 6H), 1.61 (quintuplet, $CH_2$, 2H, $^3J_{HH}$ = 7.8 Hz), 1.35 (sext, $CH_2$, 2H, $^3J_{HH}$ = 7.8 Hz), 0.94 (t, Me, 3H, $^3J_{HH}$ = 7.5 Hz). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, ppm): 192.1 (CHO), 179.6 (CH=N), 155.9, 151.5, 146.0, 144.3, 136.5 (quaternary carbons), 131.2 ($CH_{arom}$, 1C), 130.2 ($CH_{arom}$, 1C), 129.6 ($CH_{arom}$, 2C), 128.4 ($CH_{arom}$), 122.9 ($CH_{arom}$), 64.4 ($CH_2$), 60.5 ($CH_2$), 51.6 (NMe), 48.2 (NMe), 35.1 ($CH_2$), 33.4 ($CH_2$), 22.2 ($CH_2$), 13.9 (Me). $FAB^+$ MS: *m*/*z* 486 ($M^+ - ClO_4$, 100). Anal. Calcd for $C_{24}H_{34}ClN_3O_5Pd$: C, 49.16; H, 5.84; N, 7.17. Found: C, 49.40; H, 5.89; N, 7.08.

**R = $C_6H_4NH_2$-4, X = $ClO_4$ (12c).** A solution of **3** (201 mg, 0.514 mmol) in acetonitrile (50 $cm^3$) was added dropwise to a solution of $NaClO_4$ (108 mg, 0.771 mmol) and *p*-phenylenediamine (56 mg, 0.51 mmol) in acetonitrile (10 $cm^3$) for 70 min. The mixture was then stirred for a further 19 h, during which time a color change from yellow to orange was observed. The acetonitrile was then evaporated, and the residue was dissolved in acetone (30 $cm^3$). The solvents were then evaporated, dichloromethane (30 $cm^3$) was added to the residue, and the suspension was stirred and filtered. The solid was air-dried, washed with water (40 $cm^3$), dichloromethane (10 $cm^3$), and diethyl ether (10 $cm^3$), and air-dried to give **12c** as an orange solid. Yield: 180 mg, 64%. Mp: 212 °C (dec). IR: $\nu(NH_2)$ 3450, 3356 (w) $cm^{-1}$; $\nu$(C=O) 1674 (s) $cm^{-1}$; $\nu$(C=N) 1602 (s) $cm^{-1}$; $\nu(ClO_4)$, 1104 (s) $cm^{-1}$. $^1H$ NMR (300 MHz, DMSO-$d_6$, ppm): 10.09 (s, CHO, 1H), 8.44 (s, CH=N, 1H), 7.89 (s, H6, 1H), 7.75 (s br, H3, H4, 2H), 7.05 (d, $CH_{arom}$, 2H, $^3J_{HH}$ = 8.1 Hz), 6.64 (d, $CH_{arom}$, 2H, $^3J_{HH}$ = 8.1 Hz), 5.51 (s, $NH_2$, 2H), 2.98 (s, NMe, 6H), 2.89 (m, $CH_2$, 2H), 2.67 (m, $CH_2$, 2H), 2.15 (s, NMe, 6H). $^{13}C\{^1H\}$ NMR (50 MHz, DMSO-$d_6$, ppm): 193.6 (CHO), 179.9 (CH=N), 156.4, 152.1, 149.0, 137.5, 135.9 (quaternary carbons), 132.6 ($CH_{arom}$), 130.1 ($CH_{arom}$), 126.4 ($CH_{arom}$), 123.9 ($2CH_{arom}$), 113.4 ($2CH_{arom}$), 63.5 ($CH_2$), 59.6 ($CH_2$), 50.7 (NMe), 47.3 (NMe). $FAB^+$ MS: *m*/*z* 445 ($M^+ - ClO_4$, 100). Anal. Calcd for $C_{20}H_{27}ClN_4O_5Pd$: C, 44.05; H, 4.99; N, 10.27. Found: C, 44.26; H, 4.96; N, 9.47.

**R = $C_6H_4NH_2$-4, X = $CF_3SO_3$ (12c′).** A solution of **3** (202 mg, 0.516 mmol) in acetonitrile (50 $cm^3$) was added dropwise to a solution of Tl($CF_3SO_3$) (212 mg, 0.60 mmol) and *p*-phenylenediamine (56 mg, 0.52 mmol) in acetonitrile (10 $cm^3$) for 15 min, and the mixture was then stirred for a further 18 h, during which time a color change from yellow to orange was observed. The solvent was then evaporated, and the residue was suspended in 100 $cm^3$ of dichloromethane and filtered. The resulting orange solution was partially evaporated (*ca*. 20 $cm^3$), and 15 $cm^3$ of acetone and 40 $cm^3$ of ether were added to give **12c′** as an orange powder. Yield: 238 mg, 83%. Mp: 211 °C (dec). IR: $\nu(NH_2)$ 3444, 3343 (w) $cm^{-1}$; $\nu$(C=O) 1685 (s) $cm^{-1}$; $\nu$(C=N) 1602 (s) $cm^{-1}$; $\nu$(SO) 1025 (s), 636 (s) $cm^{-1}$. $^1H$ NMR (200 MHz, DMSO-$d_6$, ppm): 10.08 (s, CHO, 1H), 8.43 (s, CH=N, 1H), 7.87 (s, H6, 1H), 7.73 (s br, H3, H4, 2H), 7.04 (d, $CH_{arom}$, 2H, $^3J_{HH}$ = 8.5 Hz), 6.63 (d, $CH_{arom}$, 2H), 5.50 (s, $NH_2$, 2H), 2.96 (s, NMe, 6H), 2.87 (m, $CH_2$, 2H), 2.66 (m, $CH_2$, 2H), 2.14 (s, NMe, 6H). $^{13}C\{^1H\}$ NMR: the product decomposes during the experiment. $FAB^+$ MS: *m*/*z* 446 ($M^+ - CF_3SO_3$, 100). Anal. Calcd for $C_{21}H_{27}FN_4O_4PdS$: C, 42.40; H, 4.57; N, 9.42. Found: C, 42.48; H, 4.55; N, 9.25. Orange crystals were grown by diffusion of diethyl ether into a saturated solution of **12c′** in dichloromethane.

**Synthesis of [Pd{$C_6H_3$(CH=N$C_6H_4Bu^n$-4′)-2-(CH=N-$C_6H_4NH_2$-4′)-5}(tmeda)]$ClO_4$ (13).** A solution of **12b** (107 mg, 0.182 mmol) in 25 $cm^3$ of acetonitrile was added dropwise for 15 min to a solution of 1,4-phenylenediamine 7 (59 mg, 0.547 mmol) in 10 $cm^3$ of acetonitrile, and the mixture was then stirred for a further 4 h, during which time the color of the solution changed from yellow to orange. The acetonitrile was then evaporated, and the residue was dissolved in 40 $cm^3$ of dichloromethane, filtered over $MgSO_4$/Celite, and concentrated (*ca*. 5 $cm^3$). Addition of diethyl ether (40 $cm^3$), filtration of the resulting suspension, and air drying gave **13** as an orange solid. Yield: 55 mg, 45%. Mp 245 °C (dec). IR: $\nu(NH_2)$ 3434 (w), 3361 (w) $cm^{-1}$; $\nu$(C=N) 1615 (s), 1608 (s) $cm^{-1}$; $\nu(ClO_4)$ 1091 (s) $cm^{-1}$. $^1H$ NMR (200 MHz, DMSO-$d_6$, ppm): 8.76 (s, CH=N, 1H), 8.43 (s, CH=N, 1H), 7.89 (s, H6, 1H), 7.75 (d, H3 or H4, 1H, $^3J_{HH}$ = 7.9 Hz), 7.63 (d, H4 or H3, 1H), 7.38−7.14 (m, $CH_{arom}$, 6H), 6.62 (d, $CH_{arom}$, 2H, $^3J_{HH}$ = 8.5 Hz), 5.40 (s, $NH_2$, 2H), 3.00 (s, NMe, 6H), 2.92 (m, $CH_2$, 2H), 2.71−2.62 (m, $CH_2$, 4H), 2.08 (s, NMe, 6H), 1.58 (m, $CH_2$, 2H), 1.30 (m, $CH_2$, 2H), 0.90 (t, Me, 3H, $^3J_{HH}$ = 7.2 Hz). $^{13}C$ NMR: not soluble enough. $FAB^+$ MS: *m*/*z* 577 ($M^+ - ClO_4$, 15.3). Anal. Calcd for $C_{30}H_{40}ClN_5O_4Pd$: C, 53.26; H, 5.96; N, 10.35. Found: C, 51.61; H, 5.56; N, 10.25. (See Discussion).

**Synthesis of [HgCl{$C_6H_3$(CH=NOH)$_2$-2,5}] (14).** A solution of $NH_2OH\cdot HCl$ (150 mg, 2.17 mmol) and NaOH (86 mg, 2.17 mmol) in methanol (15 $cm^3$) was added to a suspension of **1** (80 mg, 0.22 mmol) in methanol (5 $cm^3$). The resulting colorless solution was stirred for 15 min, the solvent evaporated, and the residue washed with water and filtered. The resulting solid was air-dried, giving **14** as a white solid. Yield: 72 mg, 83%. Mp: 273 °C (dec.) IR: $\nu$(OH) 3478 (m, br), 3284 (s, br) $cm^{-1}$; $\nu$(C=N) 1682 (m, br), 1584 (m) $cm^{-1}$; $\nu$(HgCl) 326 $cm^{-1}$. $^1H$ NMR (200 MHz, acetone-$d_6$, ppm): 10.93 (s, OH, 1H), 10.51 (s, OH, 1H), 8.31 (s, CH=N, 1H), 8.12 (s, CH=N, 1H), 7.81 (s br, H6, 1H), 7.59 (dd, H4, 1H, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.5 Hz), 7.48 (d, H3, 1H). $^{13}C\{^1H\}$ NMR (50 MHz, acetone-$d_6$, ppm): 151.6 (C=NOH), 148.7 (C=NOH), 139.2, 135.8 (C2, C5), 136.3, 131.4, 127.7 (C3, C4, C6). Anal. Calcd for $C_8H_7ClHgN_2O_2$: C, 24.07; H, 1.77; N, 7.02. Found: C, 24.15; H, 1.72; N, 6.80.

**Synthesis of [Pd{$C_6H_3$(CH=NOH)-2-(CH=NOH)-5}($\mu$-Cl)]$_2$ (15).** A mixture of $(Me_4N)_2[Pd_2Cl_6]$ (292 mg, 0.51 mmol), **14** (406 mg, 1.02 mmol), and $(Me_4N)Cl$ (164 mg, 1.5 mmol) in acetone (90 $cm^3$) was refluxed for 4 h and then filtered through Celite. The solvent was then evaporated, the residue washed with water and filtered, and the resulting solid washed with diethyl ether and air-dried to give **15** as a yellow solid. Yield: 275 mg, 89%. Mp: 280 °C (dec). IR: $\nu$(OH) 3280 (m, br) $cm^{-1}$; $\nu$(C=N) 1631 (m, br) $cm^{-1}$. $^1H$ NMR (200 MHz, DMSO-$d_6$, ppm): 11.34 (br, OH), 8.31 (br), 7.97 (br), 7.25 (br). $^{13}C$ NMR: not soluble enough. Anal. Calcd for $C_8H_7ClN_2O_2Pd$: C, 31.50; H, 2.32; N, 9.19. Found: C, 31.94; H, 2.39; N, 8.80.

**Synthesis of [$(Ph_3P)_2N$][Pd{$C_6H_3$(CH=NOH)-2-(CH=NOH)-5}$Cl_2$] (16).** A mixture of **15** (154 mg, 0.25 mmol) and $[(Ph_3P)_2N]Cl$ (290 mg, 0.50 mmol) in acetone (10 $cm^3$) was stirred until all the solids had dissolved (4 h) and then filtered through Celite. Partial evaporation of the solvent (*ca*. 4 $cm^3$)

and addition of diethyl ether (20 $cm^3$) led to the precipitation of a solid, which was filtered, washed with diethyl ether, and air-dried to give **16** as a yellow solid . Yield: 393 mg, 89%. Mp: 108 °C. $\Lambda_M$ (acetone, $5 \times 10^{-4}$ mol $L^{-1}$): 90 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. $^1H$ NMR (300 MHz, acetone-$d_6$, ppm): 11.40 (s, OH, 1H), 10.42 (br, OH, 1H), 8.02 (d, CH=N, 1H, $^4J_{HH}$ = 1.5 Hz), 7.95 (s, CH=N, 1H), 7.9−7.5 (m, $(Ph_3P)_2N$), H6, 31H), 7.21 (dd, H4, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.5 Hz), 7.12 (d, H3, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, acetone-$d_6$, ppm): 154.4 (C=NOH), 152.9, 144.0, 133.8, 131.8, 125.3, 122.4 (C1−6), 149.5 (C=NOH), 134.0−135.0 (m, $(Ph_3P)_2N$), 132.5−133.5 (m, $(Ph_3P)_2N$), 129.5−130.5 (m, $(Ph_3P)_2N$), 127.9 (dd, C−P, $^1J_{CP}$ = 107.9 Hz, $^3J_{CP}$ = 1.5 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, acetone-$d_6$, ppm): 21.43. Anal. Calcd for $C_{44}H_{37}Cl_2N_3O_2P_2Pd$: C, 60.11; H, 4.25; N, 4.78. Found: C, 60.23; H, 4.15; N, 4.41.

**Synthesis of [Pd{$C_6H_3$(CH=NOH)-2-(CH=NOH)-5}($\mu$-$O_3SCF_3$)]$_2$ (17).** A mixture of **15** (300 mg, 0.49 mmol) and $Tl(CF_3SO_3)$ (348 mg, 0.98 mmol) in acetonitrile (30 $cm^3$) was stirred for 4 h and filtered through Celite. Partial evaporation of the solvent (*ca*. 4 $cm^3$) and addition of diethyl ether (25 $cm^3$) led to the precipitation of a solid, which was filtered, recrystallized from acetone/diethyl ether, washed with diethyl ether, and dried in the oven at 75 °C for 2 days to give **17** as a yellow solid. Yield: 158 mg, 38%. Mp: *ca*. 230 °C (dec). $\Lambda_M$ (acetone, $5 \times 10^{-4}$ mol $L^{-1}$): 62 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. IR: $\nu$(OH) 3198 (s, br) $cm^{-1}$; $\nu$(C=N) 1656 (m), 1628 (m) $cm^{-1}$. $^1H$ NMR (300 MHz, acetone-$d_6$, ppm): 12.17 (s, OH, 1H), 10.86 (s br, OH, 1H), 8.58 (s, CH=N, 1H), 8.43 (s, CH=N, 1H), 7.68 (d, H3 or H4, 1 H, $^3J_{HH}$ = 6.9 Hz), 7.46 (s, H6 1H), 7.17 (d, H4 or 3, 1H, $^3J_{HH}$ = 6.9 Hz). $^1H$ NMR (300 MHz, acetone-$d_6$ with some drops of $D_2O$, ppm): 8.54 (s, HCN, 1H), 8.34 (s, HCN, 1H), 7.59 (d, H3 or H4, 1H, $^3J_{HH}$ = 7.7 Hz), 7.37 (s, H6, 1H), 7.06 (d, H3 or H4, 1H, $^3J_{HH}$ = 7.7 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, acetone-$d_6$, ppm): 162.1 (C=NOH), 156.5 (C=NOH), 148.4, 145.4, 130.1 (C1, C2, C5), 132.8, 130.6, 129.3 (C3, C4, C6), 121.9 (q, $CF_3$, $^1J_{CF}$ = 320 Hz). $^{19}F$ NMR (282 MHz, acetone-$d_6$, ppm): −77.79 (s, $CF_3$). Anal. Calcd for $C_9H_7F_3N_2O_5PdS$: C, 25.82; H, 1.69; N, 6.69; S, 7.66. Found: C, 25.66; H, 1.58; N, 6.72; S, 7.35.

**Synthesis of [Pd{$C_6H_3$(CH=NOH)-2-(CH=NOH)-5}-(bpy)]$CF_3SO_3$ (18).** A mixture of **17** (100 mg, 0.24 mmol) and bpy (37 mg, 0.24 mmol) in acetone (15 $cm^3$) was stirred for 1 h and then filtered through Celite. Partial evaporation of the solvent (*ca*. 4 $cm^3$) and addition of diethyl ether (20 $cm^3$) gave a suspension which was filtered, and the solid was washed with diethyl ether and air-dried to give **18** as a yellow solid. Yield: 94 mg, 68%. Mp: 145 °C. $\Lambda_M$ (acetone, $5 \times 10^{-4}$ mol $L^{-1}$): 96 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. IR: $\nu$(OH) 3354 (m, br) $cm^{-1}$; $\nu$(C=N) 1602 (s) $cm^{-1}$; $\nu$(SO) 638 (vs) $cm^{-1}$. $^1H$ NMR (200 MHz, acetone-$d_6$, −60 °C, ppm): 11.07 (s br, OH, 2H), 9.2−6.5 (several multiplets, $C_6H_3$ and bpy). $^{13}C$ NMR: the compound decomposes during the experiment. Anal. Calcd for $C_{19}H_{15}F_3N_4O_5PdS$: C, 39.70; H, 2.64; N, 9.75. Found: C, 39.54; H, 2.74; N, 9.53.

**Synthesis of [Pd{$C_6H_3$(CH=NOMe)-2-(CH=NOMe)-5}-(tmeda)]$ClO_4$ (19).** A solution of $NH_2OMe$·HCl (213 mg, 2.56 mmol) and NaOH (102 mg, 2.56 mmol) in methanol (15 $cm^3$) was added to a suspension of **3** (100 mg, 0.26 mmol) and $NaClO_4$·$H_2O$ (108 mg, 0.77 mmol) in methanol (15 $cm^3$). The resulting yellow solution was stirred for 2 h, then the solvent was removed, and the residue recrystallized from acetone/diethyl ether to give **19** as a yellow solid, which was filtered, washed with diethyl ether, and air-dried. Yield: 52 mg, 40%. Mp: *ca*. 210 °C (dec). $\Lambda_M$ (acetone, $5 \times 10^{-4}$ mol $L^{-1}$): 127 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. IR: $\nu$(C=N) 1584 (m) $cm^{-1}$; $\nu$(ClO) 1088 (s, br), 624 (s) $cm^{-1}$. $^1H$ NMR (200 MHz, acetone-$d_6$, ppm): 8.66 (s, CH=N, 1H), 8.21 (s, CH=N, 1H), 7.61 (s, H6, 1H), 7.51 (s br, H3, H4, 2H), 4.20 (s, OMe, 3H), 3.94 (s, OMe, 3H), 3.12 (s, $NMe_2$, 6H), 2.89 (s, $NMe_2$, 6H). $^{13}C$ NMR: the compound decomposes during the experiment. Anal. Calcd for $C_{16}H_{27}N_4ClO_6Pd$: C, 37.43; H, 5.34; N, 10.92. Found: C, 37.78; H, 5.17; N, 10.93

**Synthesis of [Pd{$C_6H_2$(CH=NTo)-2-{Pd($\mu$-OAc)}-4-(CH=NTo)-5}($\mu$-OAc)]$_n$ (20).** A mixture of 1,4-$C_6H_4$-(CH=NTo)$_2$ (300 mg, 0.96 mmol) and $Pd(OAc)_2$ (430 mg, 1.92 mmol) in toluene (90 $cm^3$) was refluxed for 4 h in a Soxhlet containing $CaH_2$ in the thimble. The solvent was then evaporated, the residue washed with water and filtered, and the resulting solid washed with acetone, dichloromethane, and diethyl ether and dried in the oven at 75 °C for 2 days to give **20** as a brown solid. Yield: 572 mg, 93%. Mp: 270 °C (dec). IR: $\nu$(C=O) 1578 (vs, br) $cm^{-1}$; $\nu$(C=N) 1560 (vs) $cm^{-1}$. Anal. Calcd for $C_{26}H_{24}N_2O_4Pd_2$: C, 48.70; H, 3.77; N, 4.37. Found: C, 48.69; H, 3.64; N, 4.19.

**Synthesis of [$C_6H_2${PdBr(bpy)}$_2$-1,4-(CHO)$_2$-2,5] (21).** Complex **20** (200 mg, 0.31 mmol), NaBr (320 mg, 3.12 mmol), and AcOH (40 drops) were added to a solution of 2,2′-bipyridine (98 mg, 0,62 mmol) in a 54 $cm^3$ mixture of acetone and water (5:1). The resulting brown suspension was refluxed for 6.5 h to give a solid, which was then filtered, washed with water, acetone, dichloromethane, and diethyl ether, and dried in the oven at 75 °C for 1 day to give **21** as a dark brown solid. Yield: 120 mg, 47%. Mp: 246 °C (dec). IR: $\nu$(C=O) 1666 (vs) $cm^{-1}$. $^1H$ NMR (300 MHz, DMSO-$d_6$, ppm): 10.95 (s, CHO, 2H), 9.20 (d, bpy, 2H, $^3J_{HH}$ = 5 Hz), 8.66 (d, bpy, 4H, $^3J_{HH}$ = 8 Hz), 8.4−8.2 (m, bpy, 4H), 8.0−7.1 (m, bpy, 6H), 7.84 (s, H3, H6, 2H). $^{13}C$ NMR: not soluble enough. Anal. Calcd for $C_{28}H_{20}Br_2N_4O_2Pd_2$: C, 41.15; H, 2.47; N, 6.86. Found: C, 39.90; H, 2.37; N, 6.54. (See Discussion).

**Synthesis of [$C_6H_2${Pd(PPh$_3$)(bpy)}$_2$-1,4-(CHO)$_2$-2,5]-($CF_3SO_3$)$_2$ (22).** A mixture of **21** (150 mg, 0.18 mmol), $PPh_3$ (96 mg, 0.37 mmol), and $K(CF_3SO_3)$ (69 mg, 0.37 mmol) in acetone (30 $cm^3$) was stirred for 30 min and then filtered through Celite to give a yellow solution. Partial evaporation of the solvent (*ca*. 4 $cm^3$) and addition of diethyl ether (20 $cm^3$) led to a suspension which was filtered, and the solid was washed with water and diethyl ether and dried *in vacuo* in a dessicator over $P_2O_5$ for 2 days to give **22** as a yellow solid. Yield: 219 mg, 80%. Mp: 198 °C (dec.). $\Lambda_M$ (acetone, $5 \times 10^{-4}$ mol $L^{-1}$): 174 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. IR: $\nu$(C=O) 1670 (vs) $cm^{-1}$. $^1H$ NMR (300 MHz, DMSO-$d_6$, ppm): 9.65 (s, CHO, 2H), 8.72 (d, bpy, 4H, $^3J_{HH}$ = 8 Hz), 8.3−8.2 (m, bpy, 4H), 7.8−7.1 (m, $C_6H_2$, bpy and $PPh_3$, 40H). $^{13}C$ NMR: not soluble enough. $^{31}P\{^1H\}$ NMR (121 MHz, DMSO-$d_6$, ppm): 32.53. Anal. Calcd for $C_{66}H_{50}F_6N_4O_8P_2Pd_2S_2$: C, 53.56; H, 3.41; N, 3.79. Found: C, 53,54; H, 3,54; N, 3.59.

**Crystal Structures.** Crystals of **9**·$Me_2CO$·1.5MeOH, **10**·$2CH_2Cl_2$, and **12c′** were mounted in inert oil on a glass fiber and transferred to the diffractometer (Siemens P4 with LT2 low-temperature attachment) as summarized in Table 1. The structures were solved by Patterson methods and refined anisotropically on $F^2$ (program SHELXTL).[22]

For compound **9**·$Me_2CO$·1.5MeOH, the unit cell parameters were determined from a least-squares fit of 73 accurately centered reflections (7.2° < 2$\theta$ < 25.04°). Badly resolved electron density near an inversion center was tentatively refined isotropically as a disordered methanol molecule. Hydrogen atoms were included using a riding model or as rigid methyl and hydroxide groups. Hydrogen atoms for the disordered solvent were not considered. Max $\Delta/\sigma$ = 0.006, max $\Delta\rho$ = 1.66 e $Å^3$.

The unit cell parameters of **10**·$2CH_2Cl_2$ were determined from a least-squares fit of 70 accurately centered reflections (10.6° < 2$\theta$ < 25.0°). The hydrogen atom H01 was located in a difference Fourier synthesis and refined with a restrained O−H bond length. Other hydrogen atoms were included using a riding model. Max $\Delta/\sigma$ = 0.003, max $\Delta\rho$ = 0.32 e $Å^3$. The

(22) Sheldrick, G. M. *SHELXL 93*; University of Göttingen: Göttingen, Germany, 1993.

**Table 1. Crystal Data for 9·$Me_2CO$·1.5MeOH, 10·2$CH_2Cl_2$, and 12c′**

| compound | **9**·$Me_2CO$·1.5MeOH | **10**·2$CH_2Cl_2$ | **12c′** |
|---|---|---|---|
| mol formula | $C_{48.5}H_{47}ClO_{6.5}P_2Pd$ | $C_{46}H_{39}Cl_5O_3P_2Pd$ | $C_{21}H_{27}F_3N_4O_4PdS$ |
| mol wt | 937.65 | 985.36 | 594.93 |
| habit | prism | prism | tablet |
| color | colorless | colorless | orange |
| source | liquid diffusion, $Me_2CO$/MeOH | liquid diffusion, $CH_2Cl_2$/MeOH | liquid diffusion, $Et_2O/CH_2Cl_2$ |
| *a*, Å | 11.429(1) | 14.605(1) | 10.786(2) |
| *b*, Å | 11.906(1) | 17.171(1) | 10.998(2) |
| *c*, Å | 18.727(2) | 17.156(2) | 11.140(2) |
| α, deg | 73.27(1) | | 74.991(12) |
| *β*, deg | 73.57(1) | | 75.398(10) |
| *γ*, deg | 69.16(1) | | 82.864(14) |
| *V*, Å$^3$ | 2234.0(1) | 4302.4(6) | 1232.8(4) |
| *Z* | 2 | 4 | 2 |
| *λ*, Å | 0.710 73 | 0.710 73 | 0.710 73 |
| temp, K | 173(2) | 173(2) | 173(2) |
| radiation | Mo Kα | Mo Kα | Mo Kα |
| monochromator | graphite | graphite | graphite |
| space group | $P\bar{1}$ | $Cmc2_1$ | $P\bar{1}$ |
| cryst size, mm | 0.54 × 0.32 × 0.22 | 0.44 × 0.40 × 0.38 | 0.42 × 0.35 × 0.11 |
| abs corr | *ψ*-scans | | |
| max/min transmission, % | 0.960/0.876 | | |
| diffractometer | Siemens P4 | Siemens P4 | Siemens P4 |
| scan method | *ω* | *ω* | *ω* |
| 2*θ* range, deg | 6.2−50.0 | 6.7−50.0 | 6.1−50.0 |
| *h*,*k*,*l* limits | ±*h*, ±*k*, −*l* | +*h*, −*k*, ±*l* | −*h*, ±*k*, ±*l* |
| no. of reflns measd | 13503 | 3945 | 5507 |
| no. of indep reflns | 7813 | 3866 | 4266 |
| $R_{int}$ | 0.018 | 0.013 | 0.021 |
| R1[a] | 0.0370 | 0.0198 | 0.0362 |
| wR2[b] | 0.1065 | 0.0474 | 0.0782 |

[a] $R1 = \sigma||F_o| - |F_c||/\sigma|F_o|$ for reflections with $I > 2\sigma I$. [b] $wR2 = [\sigma[w(F_o^2 - F_c^2)^2]/\sigma[w(F_o^2)^2]]^{0.5}$ 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.



origin was fixed by the method of Flack and Schwarzenbach.[23] The absolute structure was determined (Flack parameter $x = 0.004(18)$).[24]

The unit cell parameters of **12c′** were determined from a least-squares fit of 81 accurately centered reflections (9.4° < 2*θ* < 27.0°). The structure was solved by Patterson methods and refined anisotropically on $F^2$ (program SHELXTL).[22] The triflate anion is disordered over two sites (50% occupancy), as well as the N1−C11−C16−N2 fragment (54% and 46% occupancy). Hydrogen atoms were included using a riding model or as rigid methyl groups. Hydrogen atoms for the N2 amino group were not considered. Max $\Delta/\sigma = 0.001$, max $\Delta\rho = 0.81$ e Å$^3$.

The programs use the neutral atom scattering factors, $\Delta f'$ and $\Delta f''$, and absorption coefficients from the *International Tables for Crystallography* (Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C, Tables 6.1.1.4, 4.2.6.8, and 4.2.4.2, pp 500−502, 219−222, and 193−199, respectively).

## Results and Discussion

**Mercuriation of Terephthaldehyde.** The mercuriation of arenes is the most important method for the synthesis of arylmercurials. These reactions have been studied in great detail, revealing an electrophilic substitution mechanism.[25−29] Normal or activated arenes are easily mercuriated by mercury(II) acetate in alcoholic solvents in the presence of acetic acid.[25,30] Using this method, we have mercuriated 3,4,5-trimethoxy derivatives of benzaldehyde[31] and benzoic acid.[32] Deactivated arenes pose problems which, in some cases, have been solved by using stronger electrophiles and/or high-temperature reactions. The mercuriation of benzoic acid, *o*-dichlorobenzene, benzaldehyde, nitrobenzene, or benzophenone has been achieved using mercury(II) perchlorate in 60−70% perchloric acid at room temperature.[33]

In order to mercuriate terephthaldehyde, we reacted it under these conditions using mercury(II) oxide in 60% aqueous perchloric acid at room temperature, but only traces of the mercuriated compound could be detected. The presence of the two deactivating formyl groups must be responsible for the stronger deactivation of this arene when compared with the ones mentioned above. However, when the same reaction is carried out at 90 °C and the resultant perchloric solution is poured into aqueous sodium chloride, the mercurial [HgCl{$C_6H_3$-$(CHO)_2$-2,5}] (**1**) can be obtained in an acceptable yield (54%) (Scheme 1). However, to handle perchloric solutions at this temperature can be dangerous, and so we have changed the perchloric acid to trifluoromethanesulfonic (triflic) acid, which is much less dangerous, and the triflato ligand possesses a coordination capacity similar to that shown by the perchlorato ligand.[34,35] The reaction was carried out by mixing the arene and HgO in a 1:1 volume mixture of triflic acid and water. After

(23) Flack, H. D.; Schwarzenbach, D. *Acta Crystallogr.* **1988**, *A44*, 499.
(24) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.
(25) Larock, R. C. *Organomercury Compounds in Organic Synthesis. Reactivity and Structure*; Springer-Verlag: Berlin, 1985.
(26) Fung, C. W.; Khorramdel-Vahed, M.; Ranson, R. J.; Roberts, R. M. G. *J. Chem. Soc., Perkin Trans. 2* **1980**, 267.
(27) Damude, L. C.; Dean, P. A. W. *J. Chem. Soc., Chem. Commun.* **1978**, 1083.
(28) Damude, L. C.; Dean, P. A. W. *J. Organomet. Chem.* **1979**, *181*, 1.
(29) Olah, G. A.; Yu, S. H.; Parker, D. G. *J. Org. Chem.* **1976**, *41*, 1983.
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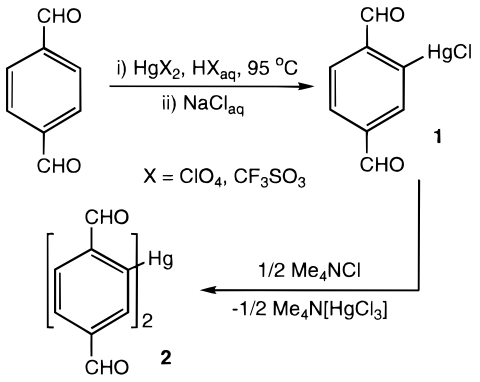
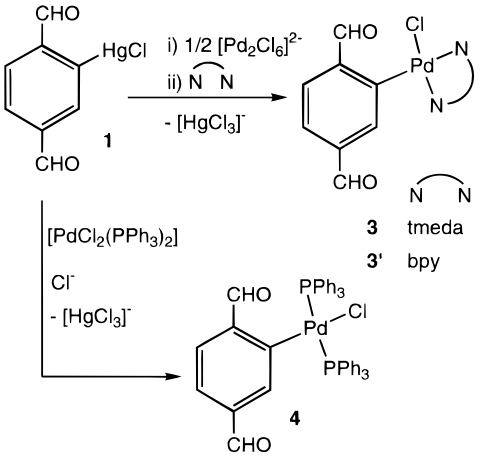
(31) Vicente, J.; Abad, J. A.; Stiakaki, M. A.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1991**, 137.
(32) Vicente, J.; Abad, J. A.; Sandoval, A.; Jones, P. G. *J. Organomet. Chem.* **1992**, *434*, 1.
(33) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5518.
(34) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.
(35) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405.

**Scheme 1**



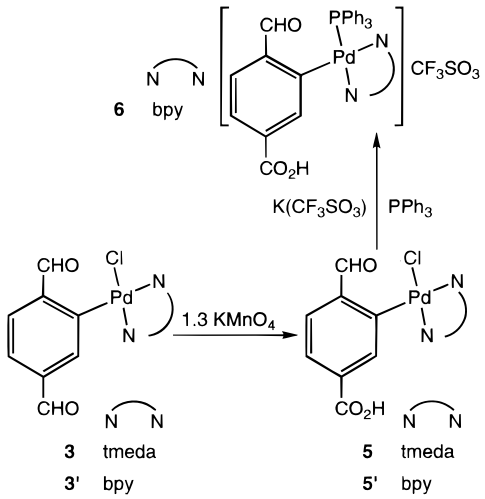

**Scheme 2**




completing the reaction, the mixture was poured into aqueous NaCl in order to exchange the triflato group for chloro to give **1**. Polyhaloarenes have also been mercuriated with mercury(II) trifluoroacetate in trifluoroacetic acid at temperatures ranging from 150 to 240 °C[36,37] or with mercury(II) triflate in trifluoroacetic acid at 73 °C.[38] The mercurial **1** can be symmetrized to the diarylmercurial $[Hg\{C_6H_3(CHO)_2\text{-}2,5\}_2]$ (**2**) by reaction with $(Me_4N)Cl$, exploiting the formation of insoluble $Me_4N[HgCl_3]$ (Scheme 1). We have previously used this reaction in order to obtain other diarylmercurials.[6,32,39]

**Transmetalation Reactions.** The reaction of $(Me_4N)_2[Pd_2Cl_6]$ with **1** in the presence of an excess of $(Me_4N)Cl$ or with **2** in acetone at room temperature or lower led to the formation of $(Me_4N)_2[Pd_2\{C_6H_3(CHO)_2\text{-}2,5\}_2Cl_2(\mu\text{-}Cl)_2]$ which, due to its thermal instability in the solid state, could not be isolated as a pure compound. However, addition of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) or 2,2′-bipyridine (bpy) to these solutions gave complexes $[PdCl\{C_6H_3(CHO)_2\text{-}2,5\}(tmeda)]$ (**3**) or $[PdCl\{C_6H_3(C_6H_3(CHO)_2\text{-}2,5\}(bpy)]$ (**3′**) (Scheme 2). The mercurial **1** reacted with *trans*-$[PdCl_2(PPh_3)_2]$ in boiling acetone, in the presence of $(Me_4N)Cl$, to give *trans*-$[PdCl\{C_6H_3(CHO)_2\text{-}2,5\}(PPh_3)_2]$ (**4**). The transmetalating agent in these processes seems to be the diarylmercurial **2**, formed by the *in situ* symmetrization

**Scheme 3**




of **1** with $(Me_4N)Cl$. When **2** reacts with the palladium(II) chloro complexes, compound **1** is formed which, in turn, is symmetrized again to **2** by the tetraalkylammonium salt. In fact, these transmetalating reactions can also be carried out from **2**, but using half of the mercurial. We have previously used this method in other cases.[39]

**Oxidation Reactions of the Formyl Groups and Transmetalation Reactions.** We studied the $KMnO_4$ oxidation of the formyl substituents of the previously prepared 2,5-diformylphenylmercury(II) and -palladium(II) compounds. Thus, complexes **3** and **3′** react with $KMnO_4$ (1:1.3) to give complexes $[PdCl\{C_6H_3(CHO)\text{-}2\text{-}(CO_2H)\text{-}5\}(tmeda)]$ (**5**) and $[PdCl\{C_6H_3(CHO)\text{-}2\text{-}(CO_2H)\text{-}5\}(bpy)]$ (**5′**), respectively. Complex **5′** reacts with $PPh_3$ and $K(CF_3SO_3)$ to give the derivative $[Pd\{C_6H_3(CHO)\text{-}2\text{-}(CO_2H)\text{-}5\}(PPh_3)(bpy)](CF_3SO_3)$ (**6**) (Scheme 3).

The new mercurial $[HgCl\{C_6H_3(CO_2H)_2\text{-}2,5\}]$ (**7**), in which both CHO substituents have been oxidized, could be obtained by reacting **1** with $KMnO_4$ in a 4:1 acetone/water mixture under the same conditions as for **5** and **5′**. It did not prove possible to form this compound by mercuriation of terephthalic acid (Scheme 4). The product obtained is contaminated with very small amounts of the two mono-oxidized isomers (by NMR spectroscopy). An 1.8:1 mixture of these isomers, $[HgCl\{C_6H_3(CHO)\text{-}2\text{-}(CO_2H)\text{-}5\}]$ (**8a**) and $[HgCl\{C_6H_3(CO_2H)\text{-}2\text{-}(CHO)\}]$ (**8b**), can be obtained by reacting **1** with $KMnO_4$ in a 1:0.67 molar ratio. Crude **7** or the mixture **8a**/**8b** reacted with *trans*-$[PdCl_2(PPh_3)_2]$ and $(Me_4N)Cl$ in a mixture of acetone/1,4-dioxane at 62 °C to give pure *trans*-$[PdCl\{C_6H_3(CO_2H)\text{-}2,5\}(PPh_3)_2]$ (**9**) or *trans*-$[PdCl\{C_6H_3(CHO)\text{-}2\text{-}(CO_2H)\text{-}5\}(PPh_3)_2]$ (**10**), respectively. According to the composition of the mixture of isomers **8a**/**8b** (64/36), the yield obtained in the synthesis of **10** (40%) is only compatible with the asumption that it results from **8a**. Because we have solved the crystal structure of **10** (see below), the structure of **8a** must be that indicated in Scheme 4. We believe that the product from **8b** is insoluble and is separated with the insoluble byproduct $[HgCl_3]^-$ because, in the soluble part of the crude of the reaction, we could not find neither **8b** nor any other P-containing compound in an appreciable amount. The assignment of the substitution pattern in **5** is based on its reaction with $PPh_3$ (1:2) giving **10**.

In these reactions, the 5-CHO group has been oxidized selectively, even when enough $KMnO_4$ for the oxidation

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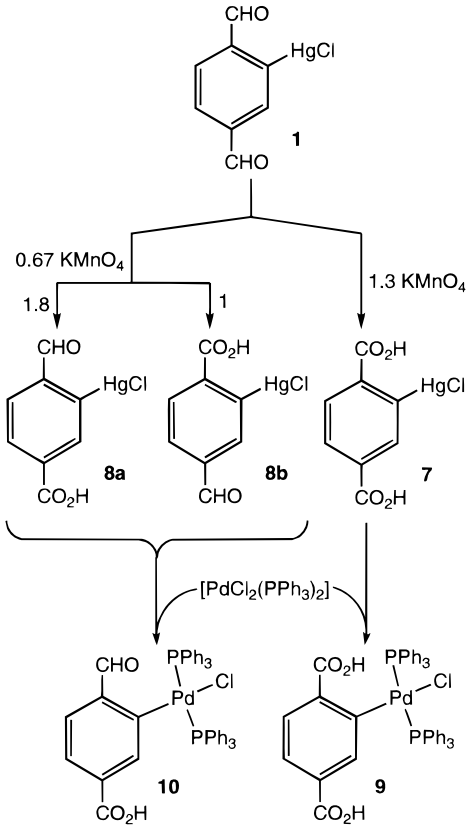
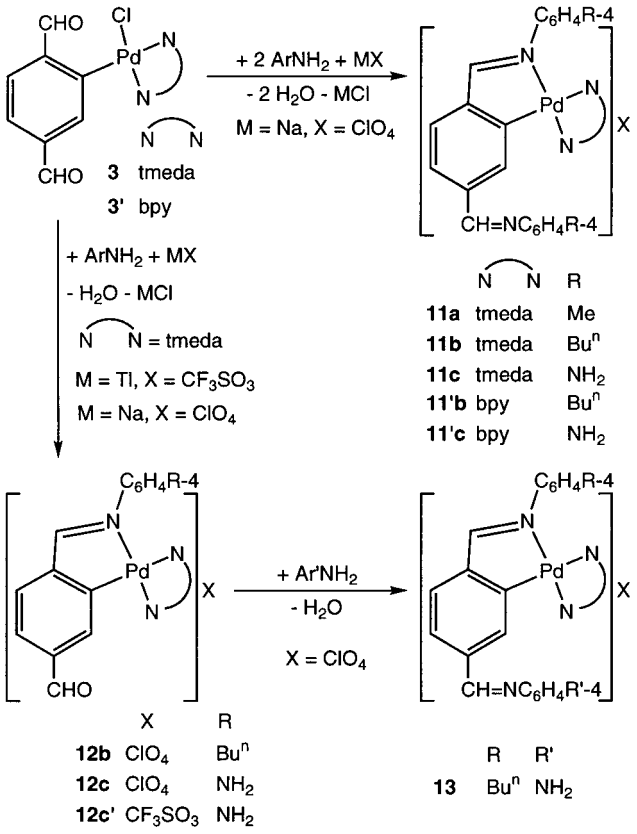
(37) Bertino, R. J.; Deacon, G. B.; Taylor, F. B. *Aust. J. Chem.* **1972**, *25*, 1645.
(38) Deacon, G. B.; Tunaley, D. *J. Organomet. Chem.* **1978**, *156*, 403.
(39) Vicente, J.; Bermúdez, M. D.; Carrión, F. J.; Jones, P. G. *Chem. Ber.* **1996**, *129*, 1395.

**Scheme 4**




**Scheme 5**




of both formyl groups was used. It seems reasonable to assume that $MnO_4^-$ preferentially attacks the carbonyl carbon of the less hindered 5-CHO group in the case of the palladium(II) complexes,[40] while the HgCl group in **1** does not seem to be sufficiently bulky to prevent the oxidation of the 2-CHO substituent. The preferential oxidation of the 5-CHO group in **1** when 1:0.67 molar ratio of **1**:$KMnO_4$ was used also points to the same conclusion. It was not possible to isolate any product from the reaction of complex **4** with $KMnO_4$ because it does not survive the reaction conditions.

**Reactions with Amines.** When complex **3** is reacted with *p*-toluidine in boiling toluene, an ill-defined mixture is obtained. However, addition of sodium perchlorate results in the formation of the cyclometalated cationic compound $[Pd\{C_6H_3(CH{=}NTo)\text{-}2\text{-}(CH{=}NTo)\text{-}5\}(tmeda)](ClO_4)$ (**11a**) (Scheme 5). It is reasonable to assume that the replacement of the chloro ligand by the labile perchlorate anion favors the coordination of the nitrogen atom of the imine group and that this chelating effect is responsible for the formation of **11a**. Compounds $[Pd\{C_6H_3(CH{=}NR)\text{-}2\text{-}(CH{=}NR)\text{-}5\}(N\text{-}N)]ClO_4$ (R = $C_6H_4Bu^n$-4, N-N = tmeda (**11b**), bpy (**11′b**)) were similarly prepared. A slightly different procedure was used for the synthesis of $[Pd\{C_6H_3(CH{=}NR)\text{-}2\text{-}(CH{=}NR)\text{-}5\}(N\text{-}N)]ClO_4$ (R = $C_6H_4NH_2$-4, N-N = tmeda (**11c**), bpy (**11′c**)) in that the reaction was carried out in acetonitrile using an excess of the amine. When the same procedure was followed using a 1:1 palladium(II) to amine molar ratio, the formyl group at the 2 position was selectively transformed into the corresponding imine group, giving complexes $[Pd\{C_6H_3(CH{=}NR)\text{-}2\text{-}(CHO)\text{-}5\}(tmeda)]X$ (X = $ClO_4$, R = $C_6H_4Bu$-4 (**12b**), $C_6H_4NH_2$-4 (**12c**); X = $CF_3SO_3$, R = $C_6H_4NH_2$-4 (**12c′**)) (Scheme 5). This regioselectivity is without a doubt due to the above-mentioned chelating effect and, for this reason, is opposite to that observed in the previous oxidation reactions.

Complexes **12** can be reacted with other amines in order to prepare palladated "mixed" Schiff bases. Thus, **12b** reacts with 1,4-phenylenediamine to give **13** (Scheme 5). Despite the fact that **13** seems to be spectroscopically pure, the carbon analysis is low (see Experimental Section). We do not know if this is due to combustion problems in the analyzer or to the presence of an impurity not detected by NMR.

Cyclopalladated benzylideneimines of aromatic amines are among the best studied cyclopalladated complexes. Cyclopalladation[41,42] is the most frequently used process to prepare these complexes,[43−48] although the exchange

(40) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin/Cummings: Reading, MA, 1972.

(41) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.
(42) Omae, I. *Organometallic Intramolecular-Coordination Compounds*; Elsevier: Amsterdam, The Netherlands, 1986.
(43) Albert, J.; Granell, J.; Moragas, R.; Fontbardia, M.; Solans, X. *J. Organomet. Chem.* **1996**, *522*, 59.
(44) Vila, J. M.; Gayoso, M.; Pereira, T.; Lopez, M.; Alonso, G.; Fernandez, J. J. *J. Organomet. Chem.* **1993**, *445*, 287.
(45) Albert, J.; Granell, J.; Sales, J.; Fontbardia, M.; Solans, X. *Organometallics* **1995**, *14*, 1393.
(46) Vila, J. M.; Gayoso, M.; Pereira, T.; Torres, M. L.; Fernandez, J. J.; Fernandez, A.; Ortigueira, J. M. *J. Organomet. Chem.* **1996**, *506*, 165.
(47) Basuli, F.; Chattopadhyay, P.; Sinha, C. *Polyhedron* **1996**, *15*, 2439.
(48) Lopez, C.; Bosque, R. *J. Organomet. Chem.* **1996**, *524*, 247.

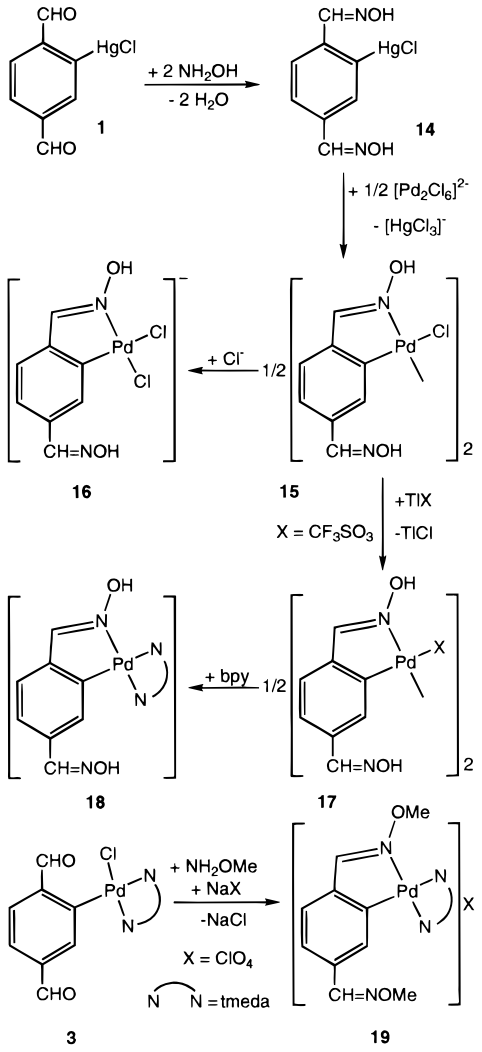
of cyclopalladated ligands has also been utilized.[49,50] Cyclopalladated derivatives of diimines of terephthaldehyde are rare.[44,51] Reaction of terephthaldehyde bis(cyclohexylimine) with palladium(II) acetate failed to give the corresponding cyclopalladated complex, and only the product resulting from the partial hydrolysis $[Pd\{C_6H_3(CH{=}NC_6H_{11})\text{-}2\text{-}(CHO)\text{-}5\}(\mu\text{-}O_2CMe)]_2$ could be isolated. Derivatives of the diimine were isolated by reacting this and similar derivatives with cyclohexylamine. The reaction of $[Pd\{C_6H_3(CH{=}NC_6H_{11})\text{-}2\text{-}(CHO)\text{-}5\}(\mu\text{-}Cl)]_2$ with 2,4,6-trimethylaniline led to the only precedent of our mixed complex **13**.[44] While this manuscript was in preparation, the synthesis of a dipalladated derivative of terephthaldehyde bis(cyclohexylimine) has been reported *via* oxidative addition of the 2,5-dichloro derivative with $[Pd_2(dba)_3]$ (dba = dibenzylidene acetone).[51]

**Reactions with Hydroxylamines.** The mercurial **1** reacts with hydroxylamine to give the mercuriated oxime $[HgCl\{C_6H_3(CH{=}NOH)_2\text{-}2,5\}]$ (**14**). It can be used as transmetalating agent with $(Me_4N)_2[Pd_2Cl_6]$ to give the cyclopalladated complex $[Pd\{C_6H_3(CH{=}NOH)\text{-}2\text{-}(CH{=}NOH)\text{-}5\}(\mu\text{-}Cl)]_2$ (**15**) (Scheme 6). This insoluble material reacts with $[(Ph_3P)_2N]Cl$ to give the soluble anionic complex $[(Ph_3P)_2N][Pd\{C_6H_3(CH{=}NOH)\text{-}2\text{-}(CH{=}NOH)\text{-}5\}Cl_2]$ (**16**) and with $Tl(CF_3SO_3)$ to give the compound $[Pd\{C_6H_3(CH{=}NOH)\text{-}2\text{-}(CH{=}NOH)\text{-}5\}(\mu\text{-}O_3SCF_3)]_2$ (**17**), which, in turn, reacts with bpy yielding $[Pd\{C_6H_3(CH{=}NOH)\text{-}2\text{-}(CH{=}NOH)\text{-}5\}(bpy)]CF_3SO_3$ (**18**).

We have tried to prepare similar compounds by reacting the palladium(II) complexes **3** or **3′** with $NH_2OH$, but we could not separate the mixtures obtained. However, complex **3** reacts cleanly with $NH_2OMe$ to give the expected complex $[Pd\{C_6H_3(CH{=}NOMe)\text{-}2\text{-}(CH{=}NOMe)\text{-}5\}(tmeda)]ClO_4$ (**19**) (Scheme 6).

Palladation of oximes has been achieved by cyclopalladation,[52−58] ligand exchange reactions,[59] or transmetalation reactions using organotin oximes.[60] Therefore, we have discovered two new methods for the synthesis of cyclopalladated aryl oximes: (i) transmetalation using mercury derivatives and (ii) condensation of oximes into orthoformylarylpalladium(II) complexes. Cyclopalladated aryl oximes have found interesting applications in organic synthesis.[58,61−63] As far as we are aware, complexes **15**−**19** are the first cyclopalladated oximes derived from terephthaldehyde, compound **19** being the first cyclometalated *O*-Me oxime and **14** the first mercuriated aryloxime.

**Scheme 6**




**Dipalladation of Terephthaldehyde.** By reacting the diimine $C_6H_4(CH{=}NTo)_2$-1,4 with palladium(II) acetate in boiling toluene (molar ratio 1:2), we obtained an insoluble material whose analytical data suggested it to be the dipalladated imine $[Pd\{C_6H_2(CH{=}NTo)\text{-}2\text{-}\{Pd(\mu\text{-}OAc)\}\text{-}4\text{-}(CH{=}NTo)\text{-}5\}(\mu\text{-}OAc)]_n$ (**20**) (Scheme 7). The same compound can also be obtained when the reaction is carried out using a 1:1 molar ratio. Double palladation on a single phenyl ring is rarely encountered.[54,64−66] Attempts to dipalladate 1,3- and $1,4\text{-}C_6H_4(CH{=}NCy)_2$ resulted in single palladation and hydrolysis of the *meta* imine group, probably due to the solvent used (acetic acid).[44,46] By refluxing a mixture

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(50) Granell, J.; Sainz, D.; Sales, J.; Solans, X.; Font-Altaba, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1785.
(51) Vila, J. M.; Gayoso, M.; Pereira, M. T.; Torres, M. L.; Fernandez, J. J.; Fernandez, A.; Ortigueira, J. M. *Z. Anorg. Allg. Chem.* **1997**, *623*, 844.
(52) Onoue, H.; Minami, K.; Nakagawa, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3480; *Chem. Abstr.* **1971**, *74*, 53979k.
(53) Nielson, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 205.
(54) Phillips, I. G.; Steel, P. J. *J. Organomet. Chem.* **1991**, *410*, 247.
(55) Constable, A. G.; McDonald, W. S.; Sawkins, L. C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 1992.
(56) Grigor, B. A.; Nielson, A. J. *J. Organomet. Chem.* **1977**, *132*, 439.
(57) Carr, K.; Sutherland, J. K. *J. Chem. Soc., Chem. Commun.* **1984**, 1227.
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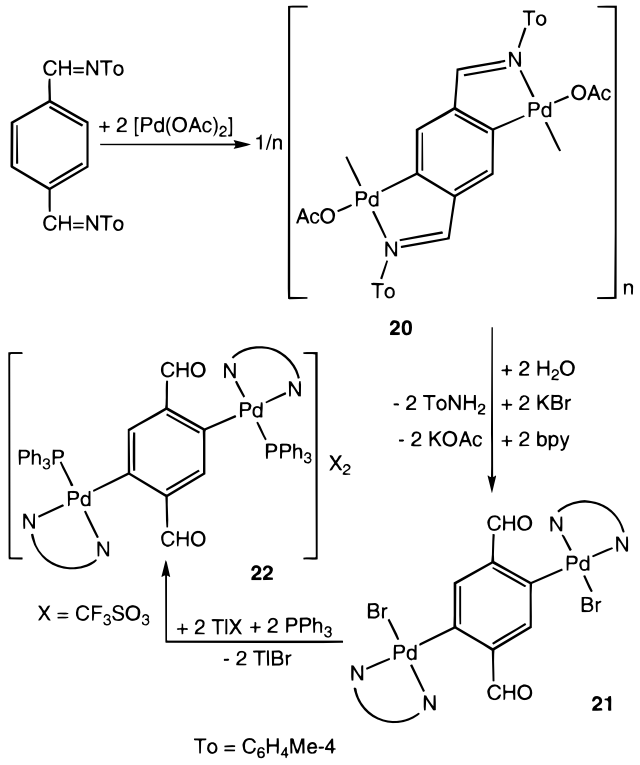
(60) Nishiyama, H.; Matsumoto, M.; Matsumoto, T.; Miura, R.; Itoh, K. *Organometallics* **1985**, *4*, 1911.
(61) Baldwin, J. E.; Nájera, C.; Yus, M. *J. Chem. Soc., Chem. Commun.* **1985**, 126.
(62) Yatsimirsky, A. K.; Kazankov, G. M.; Ryabov, A. D. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1295.
(63) Krooglyak, E. V.; Kazankov, G. M.; Kurzeev, S. A.; Polyakov, V. A.; Semenov, A. N.; Ryabov, A. D. *Inorg. Chem.* **1996**, *35*, 4804.
(64) Chakladar, S.; Paul, P.; Mukherjee, A. K.; Dutta, S. K.; Nanda, K. K.; Podder, D.; Nag, K. *J. Chem. Soc., Dalton Trans.* **1992**, 3119.
(65) Chakladar, S.; Paul, P.; Venkatsubramanian, K.; Nag, K. *J. Chem. Soc., Dalton Trans.* **1991**, 2669.
(66) Chakladar, S.; Paul, P.; Nag, K. *Polyhedron* **1991**, *10*, 1513.

**Scheme 7**




of 1,3-$C_6H_4(CH{=}NR)_2$ (R = Et, Bu, $C_8H_{17}$, benzyl) and palladium(II) acetate in chloroform, dipalladated complexes have been isolated.[65]

The nature of complex **20** requires it to have some degree of polymerization, which accounts for its insolubility. In the above-mentioned derivative of 1,3-$C_6H_4$-$[CH{=}N(C_8H_{17})]_2$, a molecular mass determination in solution showed its tetranuclear nature.[65] Due to the extreme insolubility of **20**, we were not able to prepare any derivative by reacting it with bpy or NaBr and pyridine. However, we did manage to hydrolyze it by reacting it with KBr and bpy (1:10:2) in the presence of an excess of acetic acid in a 5:1 acetone/water mixture. Under these conditions, the diformyl dipalladated compound $[C_6H_2\{PdBr(bpy)\}_2$-1,4-$(CHO)_2$-2,5] (**21**) is obtained. Nevertheless, its insolubility has prevented complete purification. We believe that this compound is slightly contaminated with some metallic palladium(II), as found in similar complexes.[51] However, the reaction of **21** with $PPh_3$ and $KCF_3SO_3$ (1:2:2) affords the more soluble $[C_6H_2\{Pd(PPh_3)(bpy)\}_2$-1,4-$(CHO)_2$-2,5$](CF_3SO_3)_2$ (**22**), which can be isolated as an analytically pure compound (Scheme 7). These compounds are the first reported double-palladated arenes having formyl functions. The hydrolytic process used for their formation allows further applications to other similar cases.

**Structural Studies. Crystal Structures of Complexes 9·$Me_2CO$·1.5MeOH, 10·2$CH_2Cl_2$, and 12c′.** Figures 1−3 show the structures of these complexes and Tables 1−4 give the crystal data and selected bond lengths and angles. The three complexes show the expected square-planar geometry at the metal center, but in **9**·$Me_2CO$·1.5MeOH and **10**·2$CH_2Cl_2$ only slight distortions are observed but in **12c′** the distortion is much greater due to the small bite angle of the five-membered C−N chelate ring (78.5(3)°) and of the tmeda

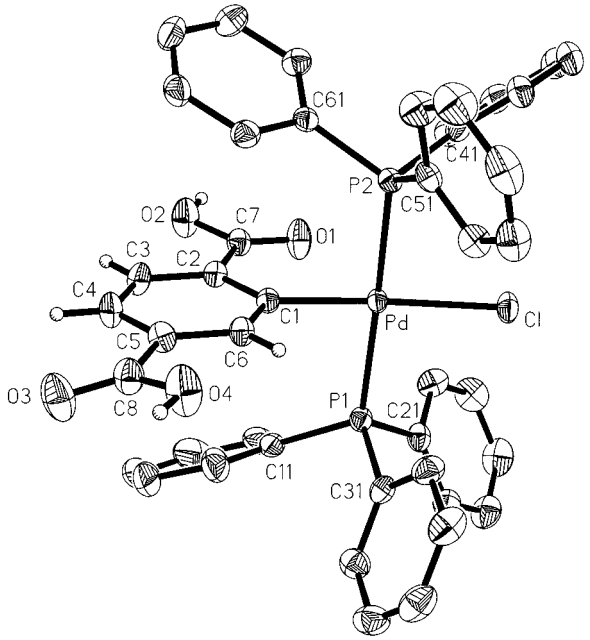



**Figure 1.** ORTEP plot of **9** with the labeling scheme (50% probability ellipsoids).

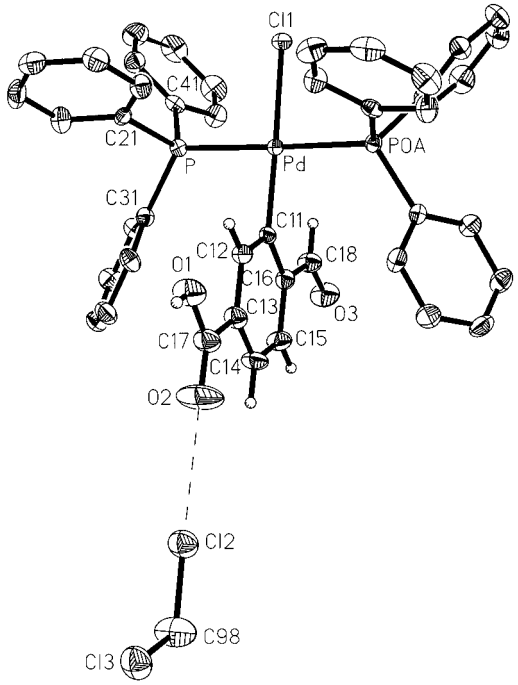



**Figure 2.** ORTEP plot of **10** showing interactions with a dichloromethane molecule (50% probability ellipsoids).

ligand (83.38(12)°). The greater *trans* influence of the aryl ligand compared to that of the N-imine ligand in **12c′** causes the Pd−N(3) bond (2.190(3) Å) to be longer than that of Pd−N(4) (2.112(3) Å).

In spite of the great similarity of complexes **9**·$Me_2$-CO·1.5MeOH and **10**·2$CH_2Cl_2$, the Pd−Cl and Pd−P bond distances are significantly different, although Pd−C distances are essentially identical (2 Å). The Pd−Cl bond distance is shorter in **10**·2$CH_2Cl_2$ (2.3917(8) Å) than in **9**·$Me_2CO$·1.5MeOH (2.4018(8) Å), while the Pd−P bond lengths are longer in **10**·2$CH_2Cl_2$ (2.3482(5) Å) than in **9**·$Me_2CO$·1.5MeOH (2.3205(9), 2.3272(9) Å). It is not reasonable to assume that the slightly different nature of the aryl groups is responsible for the observed differences. In our opinion, such features are due to the

**Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Intermolecular Contacts (Å, deg) for 9·$Me_2CO$·1.5MeOH**

| | | | |
|---|---|---|---|
| **Bond Lengths** | | | |
| Pd−C(1) | 2.000(3) | Pd−P(2) | 2.3205(9) |
| Pd−P(1) | 2.3272(9) | Pd−Cl | 2.4018(8) |
| O(1)−C(7) | 1.208(4) | O(2)−C(7) | 1.332(4) |
| O(3)−C(8) | 1.209(4) | O(4)−C(8) | 1.325(4) |
| C(2)−C(7) | 1.489(5) | C(5)−C(8) | 1.487(5) |
| **Bond Angles** | | | |
| C(1)−Pd−P(2) | 89.66(9) | C(1)−Pd−P(1) | 87.68(9) |
| P(2)−Pd−P(1) | 175.41(3) | C(1)−Pd−Cl | 174.27(9) |
| P(2)−Pd−Cl | 90.83(3) | P(1)−Pd−Cl | 91.44(3) |
| C(6)−C(1)−C(2) | 118.0(3) | O(1)−C(7)−O(2) | 122.1(3) |
| O(1)−C(7)−C(2) | 125.2(3) | O(2)−C(7)−C(2) | 112.7(3) |
| O(3)−C(8)−O(4) | 122.8(3) | O(3)−C(8)−C(5) | 123.2(3) |
| O(4)−C(8)−C(5) | 114.0(3) | | |

**Intermolecular Contacts**[a]

| | | | | | |
|---|---|---|---|---|---|
| O(7)···H(04) | 1.965(19) | O(7)···O(4) | 2.757(4) | O(7)···H(04)−O(4) | 156(4) |
| O(5)···H(02) | 1.846(7) | O(5)···O(2) | 2.627(4) | O(5)···H(02)−O(2) | 154(1) |
| Cl#1···H(05) | 2.439(26) | O(5)···Cl#1 | 3.164 (3) | O(5)−H(05)···Cl#1 | 145(4) |

[a] Symmetry transformations: #1 $-x + 1, y, z$.



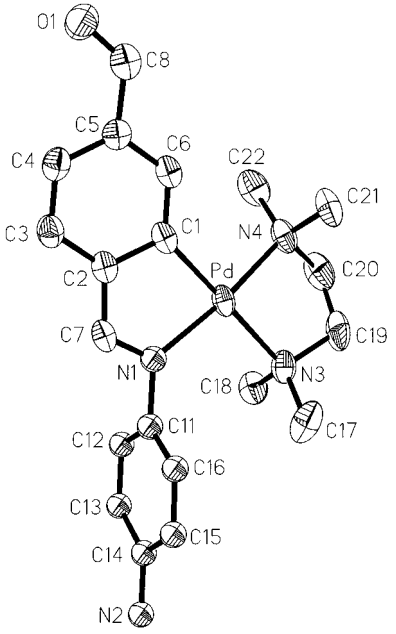



**Figure 3.** ORTEP plot of the anion of compound **12c′** with the labeling scheme (50% probability ellipsoids).

**Table 3. Selected Bond Lengths (Å), Bond Angles (deg), and Intermolecular Contacts for 10·2$CH_2Cl_2$**

| | | | |
|---|---|---|---|
| **Bond Lengths** | | | |
| Pd−C(11) | 1.999(3) | Pd−P | 2.3482(5) |
| Pd−Cl(1) | 2.3917(8) | O(1)−C(17) | 1.316(5) |
| O(2)−C(17) | 1.204(4) | O(3)−C(18) | 1.205(4) |
| C(13)−C(17) | 1.499(5) | C(16)−C(18) | 1.483(5) |
| **Bond Angles** | | | |
| C(11)−Pd−P | 90.42(2) | P−Pd−P#1 | 176.19(4) |
| C(11)−Pd−Cl(1) | 176.80(10) | P−Pd−Cl(1) | 89.48(2) |
| O(2)−C(17)−O(1) | 124.6(4) | O(2)−C(17)−C(13) | 123.1(4) |
| O(1)−C(17)−C(13) | 112.3(3) | O(3)−C(18)−C(16) | 126.4(4) |

**Intermolecular Contacts**[a]

| | | | |
|---|---|---|---|
| O(2)···Cl(2) | 3.042(3) | Cl1#2···H(01) | 2.518 (40) |
| O(1)···Cl1#2 | 3.120 (3) | O(1)−H(01)···Cl1#2 | 168(4) |

[a] Symmetry transformations: #1 $-x + 1, y, z$; #2 $-x + 1, -y + 2, z + 0.5$.

different type of intermolecular interactions. In **10**·2$CH_2Cl_2$, an intermolecular self-assembly is established through hydrogen bonds between the carboxylic group and the chloro ligand (O(1)···Cl(#1), 3.120(3) Å; Cl(#1)···H(1), 2.518(40) Å; O(1)−H(1)···Cl(#1), 168(5)°; see Figures 2 and 4). A similar polymerization, but involving [Pt]Cl···HOAr or [Pt]Cl···$HC_2Ar$, has recently been found in the structure of some arylplatinum complexes.[67,68] In **9**·$Me_2CO$·1.5MeOH, dimers are assembled through four hydrogen bonds established by two bridging molecules of MeOH. Each MeOH molecule acts as a hydrogen bond donor, MeOH···Cl−Pd (O(5)···Cl, 3.164(3) Å; Cl···HO(5), 2.439(26) Å; O(5)−OH(5)···Cl, 145(4)°; see Figure 5) and acceptor C(O)OH···O(H)Me (O(5)···O(2), 2.627(4) Å; O(5)···HO(2), 1.846(7) Å; O(5)−OH(2)···O(2), 153.99(1.24)°; see Figure 5). Additionally, two molecules of acetone are hydrogen bonded to the two remaining $CO_2H$ groups of the dimer (O(7)···O(4), 2.757(4) Å; O(7)···HO(4), 1.965(19) Å; O(7)−OH(4)···O(4), 156.72(4.53)°; see Figure 5).

**Table 4. Selected Bond Lengths (Å) and Angles (deg) for 12c′**

| | | | |
|---|---|---|---|
| **Bond Lengths** | | | |
| Pd−C(1) | 2.014(4) | Pd−N(1) | 2.033(9) |
| Pd−N(1′) | 2.104(10) | Pd−N(4) | 2.112(3) |
| Pd−N(3) | 2.190(3) | O(1)−C(8) | 1.209(5) |
| C(5)−C(8) | 1.476(5) | C(7)−N(1) | 1.218(9) |
| C(7)−N(1′) | 1.351(11) | N(1)−C(11) | 1.448(12) |
| N(2)−C(14) | 1.370(9) | N(1′)−C(11′) | 1.419(13) |
| N(2′)−C(14′) | 1.415(10) | | |
| **Bond Angles** | | | |
| C(1)−Pd−N(1) | 78.5(3) | C(1)−Pd−N(1′) | 83.0(3) |
| C(1)−Pd−N(4) | 97.55(13) | N(1)−Pd−N(3) | 100.6(3) |
| N(1′)−Pd−N(3) | 96.1(3) | N(4)−Pd−N(3) | 83.38(12) |
| C(2)−C(1)−Pd | 111.6(3) | C(1)−C(2)−C(7) | 114.3(3) |
| N(1)−C(7)−C(2) | 115.9(5) | N(1′)−C(7)−C(2) | 121.5(5) |
| O(1)−C(8)−C(5) | 125.3(4) | C(7)−N(1)−Pd | 118.6(5) |
| C(7)−N(1′)−Pd | 107.8(5) | | |

The one-dimensional polymers in **10**·2$CH_2Cl_2$ are assembled in parallel, giving a two-dimensional network in which the metal and the aryl and chloro ligands as well as the $CCl_2$ moieties of the $CH_2Cl_2$ molecules are coplanar (see Figure 6). One of the two $CH_2Cl_2$ molecules associated to each molecule of **10** shows a close C−Cl···O=C(OH)R contact (Cl(2)−O(2), 3.042(3) Å; the sum of the van der Waals radii of Cl and O is 3.20 Å), while the other $CH_2Cl_2$ molecule does not show such an interaction (see Figure 4). A search of the Cambridge

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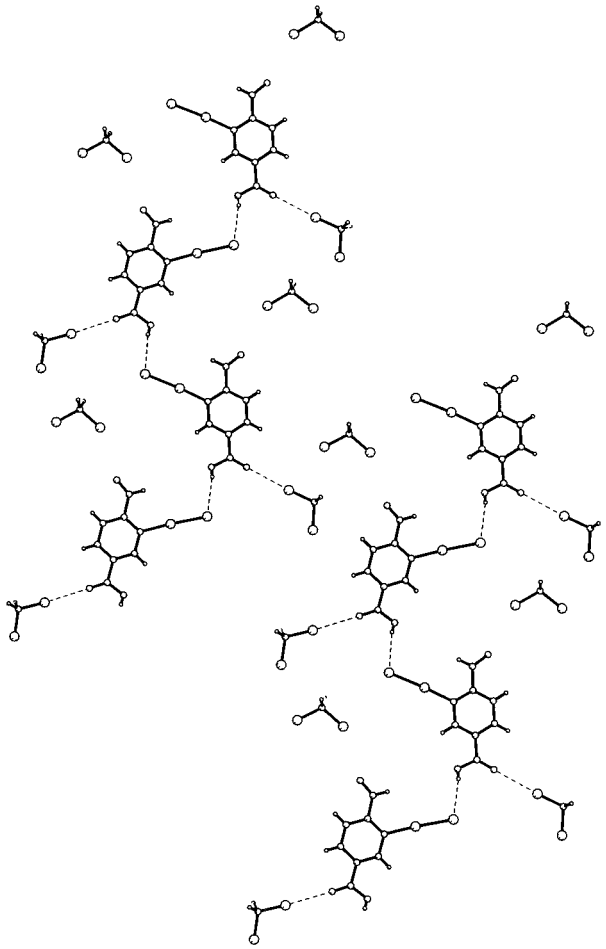

**Figure 4.** Packing diagram of compound **10** showing the hydrogen bonds and O···Cl interactions within the mirror plane. Triphenylphosphine ligands have been omitted for clarity.

Structural Database reveals that C($sp^3$)−Cl···O=C close contacts with a C($sp^3$)−Cl···O=C distance less than 3.20 Å are present in 101 molecules (excluding those in which the CO group is a carbonyl ligand). The mean Cl···O distance is 3.085.[69−71]

**NMR Spectra.** We have used the $^1$H NMR spectral resonances corresponding to the formyl groups (complemented with the above X-ray data) as a tool for proposing the structures of the compounds. Complexes **12**, whose structure must reasonably be that found by X-ray crystallography for **12c′** (see Scheme 5), show two resonances at 10 and 8.44−8.11 ppm. The first disappears in complexes **11** and **13**, while two resonances in the region 8.76−8 ppm are observed. These data allow us to assign the resonance at 10 ppm in **12** to the 5-CHO group and those in the region 8.76−8 ppm to the 2- and 5-CH=NR protons. The resonances assignable to the CHO protons of mercurials **1** and **2** (see Scheme 1) appear at 10.19 and 10.09 and 10.43 and 10.18 ppm, respectively. These values are similar to that of terephthaldehyde (10.14 ppm) and that of the 5-CHO group in **12** (see Scheme 5). However, the palladium(II) complexes **3**, **3′**, and **4** (see Scheme 2) exhibit, in addition to the expected 10 ppm resonance due to the 5-CHO proton, signals at 11.23, 11.21, and 9.47 ppm, respectively. Therefore, contrary to the HgCl and $HgC_6H_3(CHO)_2$-2,5 groups, the PdCl(N-N) and $PdCl(PPh_3)_2$ moieties exert some influence on the chemical shift of the 2-CHO proton, although the PdCl(N-N) group in **3** and **3′** deshields and the $PdCl(PPh_3)_2$ group in **4** slightly shields this proton. Accordingly, the resonances at 11.24 and 11.08 in **5** and **5′** (see Scheme 3), at 10.95 ppm in **21** (see Scheme 7), and at 9.77 ppm in **10** (see Scheme 4) must be assigned to the 2-CHO proton. Furthermore, addition of $PPh_3$ into a solution of complex **5** gives complex **10** (by $^1$H and $^{31}$P NMR). These data prove that the oxidation of complexes **3** and **3′** took place at the 5-CHO group. Complexes **6** (see Scheme 3) and **22** (see Scheme 7) having the $Pd(PPh_3)$(N-N) substituent show the 2-CHO resonance at 10.12 and 9.65 ppm, respectively.

Compounds **3**, **5**, and **19** show four signals corresponding to the $NMe_2$ groups of the tmeda ligand because the rotation around the aryl carbon−palladium bond is restricted at room temperature on the NMR time scale; this behavior is quite commonly observed.[4,72]

Complex **17** could be formulated as a dimer, as done for complex **15** and by analogy to similar cyclopalladated dimers. However, given the low coordinating ability of the triflato group, an alternative formulation could be the coordination of the oxygen or nitrogen atoms of the oxime groups giving oligomers or polymers in the solid state. Unfortunately, attempts to grow single crystals suitable for an X-ray crystallographic study have so far failed. This complex shows a value for the molar conductivity in an acetone solution (62 $\Omega^{-1}$ cm$^2$ mol$^{-1}$) that is too low for an ionic species but too high for a neutral one. It indicates that the solvent partially displaces the triflato anion, giving rise to the establishment of an equilibrium between neutral and cationic species.

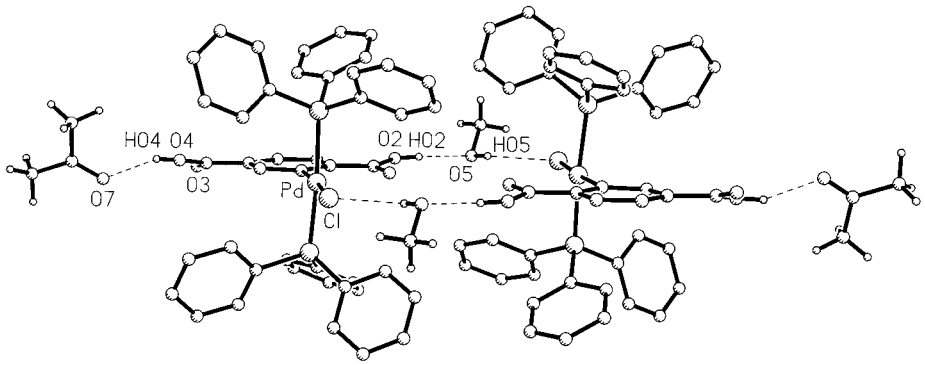


**Figure 5.** Hydrogen bond interactions between **9**, MeOH, and $Me_2CO$. The atoms involved have been labeled. Hydrogen atoms of the phenyl groups have been omitted for clarity.

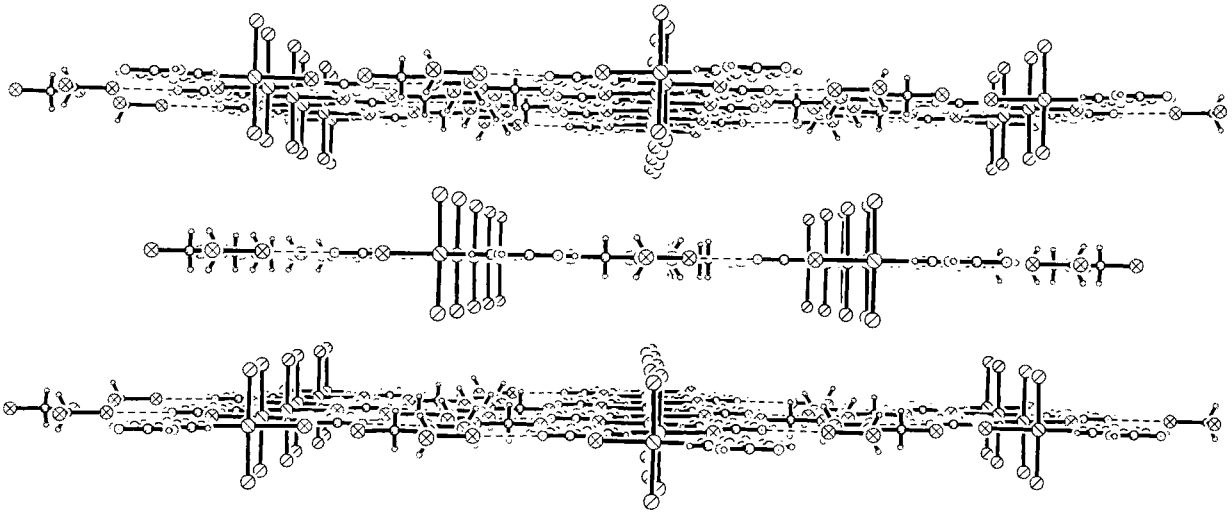

**Figure 6.** A view of the crystal packing of compound **10** along the *c* axis. Phenyl groups of the phosphine ligands have been omitted for clarity.



## Conclusions

We have developed a process which permits the mercuriation of the strongly deactivated terephthaldehyde to give (2,5-diformylphenyl)mercurials. These complexes have been used as transmetalating agents for the synthesis of new arylpalladium(II) complexes containing this functionalized aryl ligand. We have exploited the reactivity of the formyl substituents in order to gain access to new functionalized aryl complexes. Thus, oxidation with $KMnO_4$ takes place selectively at the less hindered formyl group or at both groups, depending on the metal and the reaction conditions. Reactions with amines can be controlled in order to permit the formation of stable orthopalladated mono- and di(homo and hetero)imine complexes. Ortho-mercuriated and -palladated oximes have also been obtained by a condensation reaction for the former and by a transmetalation reaction for the latter. The X-ray crystal structures show interesting self-assembled features. Finally, we designed a synthetic procedure which permits one to isolate dipalladated terephthaldehyde. All of these functionalized aryl complexes open ways to prepare, through other organic reactions, new types of complexes.

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**Supporting Information Available:** X-ray crystallographic files, in CIF format, for compounds **9**, **10**, and **12c′** are available on the Internet only. Access information is given on any current masthead page.

OM970583U

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