Attempts To Prepare Palladium(II) Complexes with the O,C,O Pincer Aryl Ligand $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5†

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The complex $[HgR_2]$ (R = $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5-C^1 (**2**)), obtained by thermal decomposition of $[Hg(O_2CR)_2]$ (**1**), reacts with $Q_2[Pd_2Cl_4(\mu\text{-}Cl)_2]$ to give [Hg(R)Cl] (**3**) and $Q_2[Pd(R)Cl(\mu\text{-}Cl)]_2$ (Q = $(PhCH_2)Ph_3P$ (**4a**), Me_4N (**4b**)), which react (i) with Tl(acac) (1:2, acac = acetylacetonate) to give Q[Pd(R)Cl(O,O-acac)] (Q = $(PhCH_2)Ph_3P$ (**5a**), Me_4N (**5b**)) or (ii) with $AgClO_4$ (1:2) to give $[Pd(\kappa^3\text{-}R)Cl]$ (κ^3-R = κ^3-$C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5-C^1,O,O′ (**6**)), which can also be obtained by reacting **5a** with HBF_4. Complex **6** reacts with *p*-toluidine (1:1, L) to give $[Pd(R)(\mu\text{-}Cl)L]_2$ (**7**). Complex **5b** decomposes in a mixture of acetone/water to give $[Pd(\kappa^2\text{-}R)(O,O\text{-}acac)]$ (κ^2-R = κ^2-$C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5-C^1,O (**8**)), which reacts (i) with neutral monodentate ligands to give [Pd(R)(O,O-acac)L] (L = PPh_3 (**9**), pyridine (py) (**10**), tetrahydrothiophene (**11**)), (ii) with bis(diphenylphosphino)methane (dppm) to give a complex that readily oxidizes to give [Pd(R)(O,O-acac)(dppmO)] (dppmO = monoxide of bis(diphenylphosphino)methane (**12**)), (iii) with 1,10-phenanthroline (phen) to give [Pd(R)(C-acac)(phen)] (**13**), and (iv) with protonated ligands $(HL)ClO_4$ to give **10** (L = py) or *cis*-$[Pd(R)(H_2O)_2(PPh_3)]\cdot H_2O$ (L = PPh_3 (**14**)). Trifluoromethanesulfonic acid ($HOSO_2CF_3$) reacts with **9** and PPh_3 or with **13** to give *trans*-$[Pd(R)(OSO_2CF_3)(PPh_3)_2]$ (**15**) or $[Pd(R)(OSO_2CF_3)(phen)]$ (**16**), respectively. The X-ray crystal structures of **7·2CH_2Cl_2**, **8**, **10**, and **14·H_2O** have been determined.

Introduction

Complexes with the well-known pincer ligand 2,6-bis[(dimethylamino)methyl]phenyl have been shown to be synthetically useful catalysts.[1−4] This and related ligands have been used to prepare complexes with unusual metal oxidation states (e.g. stable Ni(III) complexes),[5,6] with arenonium [7−10] or bridging[11] aryl ligands, as well as bimetallic complexes[10,12] and, in general, complexes with interesting properties.[13−19] Other complexes with X,C,X pincer ligands[20] (X = N,[21,22] P,[23−42] S[43−47]) have also been reported, and some have

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been used as catalysts.[21,22,26,27,31,48−52] The only complexes containing O,C,O pincer ligands have been described while this paper was in preparation. These are tin(IV) complexes containing the ligand C_6H_2[P(O)-(OEt)$_2$]$_2$-1,3-t-Bu-4.[53] We report here the first palladium complex containing an O,C,O pincer ligand ([Pd{C_6-(NO$_2$)$_2$-2,6-(OMe)$_3$-3,4,5}Cl]) as well as other complexes with the same ligand acting as a mono- and dicoordinated group. Among these derivatives there are complexes showing interesting intra- and intermolecular hydrogen bonds as well as complexes with the weakly coordinating ligand CF_3SO_3 and, as far as we are aware, the first organometallic diaquapalladium(II) complex.

We have synthesized a large family of nitroaryl complexes of gold,[54−65] palladium,[66−71] platinum,[72,73] and rhodium,[74−76] using the corresponding mercury derivatives as transmetalating agents. This is the method most frequently employed in the preparation of nitroaryl complexes. Other methods using organolithium or tin derivatives,[77] oxidative-addition reactions,[78−80] arylhydrazonium salts,[81] or direct metalation of arenes[82−84] have more limited applicability. Recently, even the nitration of aryl complexes has been reported.[85,86] Our interest in the synthesis of nitroaryl complexes is based on the great stability of these complexes (allowing, for example, the synthesis of carbonyl arylpalladium(II) complexes[70]) and on the study of the structural properties and the coordination ability of the nitro group. We have shown, for example, that the −I rather than −M effect is observable in most nitroaryl complexes, according to their structures.[57,58,64,66−76] We have studied complexes containing 2-nitro- and 2,4,6-trinitroaryl ligands and shown that, while for the former case the aryl ligand can be mono- or dicoordinated, for the latter the ligand[68−70] can only be monocoordinated. We designed this last type of ligand to see if it can be dicoordinated or act as a pincer. We assumed that the 4-NO$_2$ group could be responsible for the decrease of the 2,6-dinitro groups in coordinating one or both O atoms. For that we designed the ligand C_6(NO$_2$)$_2$-2,6-(OMe)$_3$-3,4,5, which, according to the electron-releasing capacity of the three OMe groups, could help the coordination of

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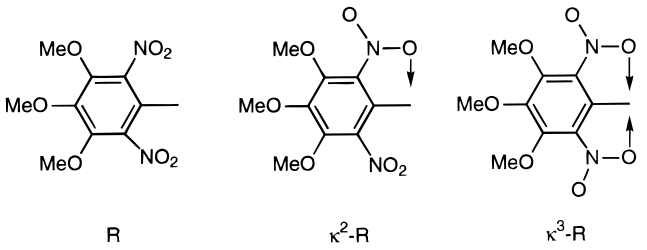
Chart 1



one or both O atoms of the 2,6-dinitro groups (see Chart 1). In this paper we show that our expectations were fulfilled.

Experimental Section

Unless otherwise stated, all reactions were carried out under normal laboratory conditions. The conductivity measurements were made using $\sim 5 \times 10^{-4}$ mol L^{-1} solutions in acetone. 3,4,5-Trimethoxybenzoic acid was purchased from Fluka. The complexes $[Pd_2Cl_4(\mu\text{-}Cl)_2]^{2-}$ [68] and Tl(acac)[87] were prepared as reported. The notation used to designate the different modes of coordination of the aryl groups can be seen in Chart 1. Unless otherwise stated, NMR spectra were recorded on a Varian Unity 300. Chemical shifts are referenced to TMS (^1H and $^{13}C\{^1H\}$) and H_3PO_4 ($^{31}P\{^1H\}$).

Synthesis of 1,2,3-Trinitro-4,5,6-trimethoxybenzene and Mercury(II) 2,6-Dinitro-3,4,5-trimethoxybenzoate (1). 3,4,5-Trimethoxybenzoic acid was added (20 g, 94.25 mmol) in small portions to a well-stirred mixture of concentrated sulfuric (96%, 160 mL) and nitric (60%, 48 mL) acids in a flask placed in a ice−salt bath, at such a rate that the temperature remained at around 10 °C. After 3−4 h without stirring, the mixture was poured into 500 g of crushed ice. The resulting precipitate was filtered after 12 h and washed with cold water to give 8.12 g of a mixture of 2,6-dinitro-3,4,5-trimethoxybenzoic acid and 1,2,3-trimethoxy-4,5,6-trinitrobenzene that was washed with boiling water (100 mL). The insoluble product was identified as 1,2,3-trimethoxy-4,5,6-trinitrobenzene. Yield: 1.8 g, 6.3%. Mp: 153 °C. ^1H NMR ($CDCl_3$): δ 4.08 (s, 3H, MeO), 4.07 (s, 6H, MeO). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 61.99 (MeO-5), 63.20 (MeO-4,6), 129.67 (CNO_2-2), 135.18 (CNO_2-1,3), 148.0 (COMe-4,6), 151.67 (COMe-5). MS: *m*/*z* (%) 303 (M^+, 39), 168 (43), 140 (100), 92 (81), 75 (64), 46 (54). Anal. Calcd for $C_9H_9N_3O_9$: C, 35.65; H, 2.99; N, 13.86. Found: C, 35.91; H, 2.98; N, 13.61.

To the resulting solution was added mercuric acetate (3.33 g, 10.45 mmol) in small portions. The resulting precipitate was collected by filtration, washed with water, and dried in vacuo to give **1** as a yellow solid. Yield: 4.4 g, 12.4% (over the calculated amount of 2,6-dinitro-3,4,5-trimethoxybenzoic acid present in the solution). ^1H NMR (d_6-acetone): δ 4.04 (s, 12H, MeO), 4.09 (s, 6H, MeO). Anal. Calcd for $C_{20}H_{18}HgN_4O_{18}$: C, 29.92; H, 2.26; N, 6.98. Found: C, 29.58; H, 2.13; N, 6.99.

Synthesis of [HgR_2] (2). Compound **1** (4 g, 4.98 mmol) was heated to 180 °C using a glycerin bath. This temperature was maintained until the resulting liquid solidified. After the mixture was cooled, dichloromethane (30 mL) was added and the suspension centrifuged. The decanted yellow dichloromethane solution was purified by passing it through a column of silica gel (8 cm high, 2 cm diameter). The pale yellow solution was concentrated (10 mL) and *n*-hexane added to precipitate **2** as an off-white solid, which was filtered off, washed with hexane, and air-dried. Yield: 1.99 g, 56%. Mp: 250−252 °C. ^1H NMR (d_6-acetone): δ 4.09 (s, 12H, MeO), 4.01 (s, 6H, MeO). $^{13}C\{^1H\}$ NMR (d_6-acetone): δ 61.7 (s, *p*-MeO), 62.7 (s, *m*- MeO), 145.5 (s, *p*-C), 147.1 (s, Hg−C), 148.8 (s, *o*-C), 152.4 (s, *m*-C). Anal. Calcd for $C_{18}H_{18}HgN_4O_{14}$: C, 30.24; H, 2.54; N, 7.84. Found: C, 30.50; H, 2.84; N, 7.72.

Synthesis of [Hg(R)Cl] (3) and [$PPh_3(CH_2Ph)]_2[Pd(R)Cl(\mu\text{-}Cl)]_2$ (4a). A suspension of **2** (2.30 g, 3.22 mmol) and $[PPh_3(CH_2Ph)]_2[Pd_2Cl_4(\mu\text{-}Cl)_2]$ (1.82 g, 1.60 mmol) in acetone (150 mL) was refluxed for 40 min, and the resulting suspension was filtered hot. The solution was used to prepare **3** (solution A). The orange solid was an acetone solvate (by IR) of **4a** (1.9 g). The resulting solution was concentrated (40 mL) to give a solid that was washed with diethyl ether to get a second crop of **4a** (474 mg). Yield: 2.37 g, 87% (assuming the formula **4a·2Me₂CO** like that of the related complex with R = $C_6H_3(NO_2)$-2,4,6).[68] Mp: 215−220 °C. The insolubility of **4a** in organic solvents prevented NMR studies. An unsolvated sample was obtained by heating the solid (70 °C) over 24 h. IR (cm^{-1}): ν(PdCl) 330, 285, 258. Anal. Calcd for $C_{68}H_{62}Cl_4N_4O_{14}P_2Pd_2$: C, 51.83; H, 3.97; N, 3.56. Found: C, 51.53; H, 3.95; N, 3.50.

Solution A was concentrated, and addition of hexane precipitated a solid which was filtered, washed with hexane, and air-dried to give **3** as a off-white solid. Yield: 1.06 g, 67%. Mp: 166−171 °C. ^1H NMR (d_6-acetone): δ 4.10 (s, 6H, MeO), 4.00 (s, 3H, MeO). $^{13}C\{^1H\}$ NMR (d_6-acetone): δ 61.72 (s, *p*-MeO), 62.86 (s, *m*-MeO), 138.43 (s, Hg−C), 143.34 (s, *p*-C), 149.28 (s, *o*-C), 153.07 (s, *m*-C). Anal. Calcd for $C_9H_9ClHgN_2O_7$: C, 21.92; H, 1.84; N, 5.68. Found: C, 22.04; H, 1.66; N, 5.70.

Synthesis of $(NMe_4)_2[Pd(R)Cl(\mu\text{-}Cl)]_2$ (4b). $(NMe_4)_2[Pd_2Cl_4(\mu\text{-}Cl)_2]$ (136 mg, 0.24 mmol) was added to a solution of **2** (306 mg, 0.43 mmol) in acetone (8 mL) solid. After it was stirred for 50 min at room temperature, the solution was concentrated and the suspension filtered. The resulting precipitate was washed with diethyl ether and air-dried to give **4b** as an orange solid. Yield: 205 mg, 94%. Mp: 226−230 °C. The insolubility of **4b** in any solvent prevented NMR studies. IR (cm^{-1}): ν(PdCl) 335, 293, 263. Anal. Calcd for $C_{26}H_{42}Cl_4N_6O_{14}Pd_2$: C, 30.70; H, 4.16; N, 8.26. Found: C, 30.69; H, 4.05; N, 8.26.

Synthesis of Q[Pd(R)Cl(O,O-acac)] (Q = $PPh_3(CH_2Ph)$ (5a), NMe_4 (5b)). Tl(acac) (2:1) was added to a suspension of **4a** (1.90 g, 1.21 mmol) or **4b** (380 mg, 0.37 mmol) in acetone. After 25 min the resulting suspension was filtered through Celite, the resulting solution was concentrated (5 mL), and diethyl ether was added to precipitate **5a** or **5b** as a yellow solid.

5a: yield 1.605 g, 78%. Mp: 172−178 °C. $\Lambda_M = 93\ \Omega^{-1}\ cm^2\ mol^{-1}$. ^1H NMR ($CDCl_3$): δ 1.55 (s, 3H, Me), 1.80 (s, 3H, Me), 3.75 (s, 3H, MeO), 3.87 (s, 6H, MeO), 5.00 (s, 1H, CH), 5.06 (s, 2H, CH_2), 6.97−7.76 [m, 22H, Ph]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.1 (s, Me), 27.1 (s, Me), 30.5 (d, CH_2, $^1J_{P-C} = 47.9$ Hz), 60.9 (s, *p*-MeO), 61.9 (s, *m*-MeO), 99.7 (s, CH), 117.7 (d, C_{ipso}−P, $^1J_{P-C} = 85.8$ Hz), 128.8 (s, *o*-C of $PhCH_2$), 130.2 (d, *o*-C of PhP, $^2J_{P-C} = 12.48$ Hz), 134.3 (d, *m*-C of PhP, $^3J_{P-C} = 9.71$ Hz), 135.0 (s, *p*-C of CH_2Ph), 185.0 (s, CO), 186.1 (s, CO). Anal. Calcd for $C_{39}H_{38}ClN_2O_9PPd$: C, 55.01; H, 4.50; N, 3.29. Found: C, 54.79; H, 4.37; N, 3.28.

5b: yield 305 mg, 71%. Mp: 212−214 °C. $\Lambda_M = 121\ \Omega^{-1}\ cm^2\ mol^{-1}$. ^1H NMR (d_6-acetone): δ 1.73 (s, 3H, Me), 1.76 (s, 3H, Me), 3.43 (s, 12H, NMe_4), 3.87 (s, 3H, *p*-MeO), 3.91 (s, 6H, *m*-MeO), 5.18 (s, 1H, CH). $^{13}C\{^1H\}$ NMR (d_6-acetone): δ 26.2 (s, Me), 27.2 (s, Me), 56.1 (t, NMe_4, $^1J_{C-N} = 4$ Hz), 61.3 (s, MeO), 62.3 (s, MeO), 99.6 (s, CH), 128.2, 143.0, 146.3 (s, quaternary aryl carbons), 185.2 (s, CO), 186.7 (s, CO). Anal. Calcd for $C_{18}H_{28}ClN_3O_9Pd$: C, 37.78; H, 4.93; N, 7.34. Found: C, 37.86; H, 4.83; N, 7.20.

Synthesis of [Pd(κ^3-R)Cl] (6). Method a. $AgClO_4$ (18.4 mg, 0.09 mmol) was added to a suspension of **4a** (70 mg, 0.04 mmol) in acetone (15 mL). After it was stirred for a few minutes, the suspension was filtered through Celite and the resulting solution was evaporated to dryness. Addition of

(87) Vicente, J.; Chicote, M. T. *Inorg. Synth.* **1998**, *32*, 172.

dichloromethane (1 mL) gave first a solution, and immediately **6** precipitated as an intense orange solid. Yield: 20.7 mg, 58%.

Method b. A solution (0.24 mL) of HBF_4 (1.75 mmol) in diethyl ether (54%) was added to a solution of **5a** (1.50 g, 1.77 mmol) in dichloromethane (4 mL). The resulting precipitate was filtered to give **6**. Yield: 0.50 g, 71%. Mp: 259−261 °C. IR (cm^{-1}): ν(PdCl) 293. ^1H NMR ($CDCl_3$): δ 3.87 (s, 3H, *p*-MeO), 4.08 (s, 6H, *m*-MeO). Anal. Calcd for $C_9H_9ClN_2O_7Pd$: C, 27.09; H, 2.27; N, 7.02. Found: C, 27.08; H, 2.31; N, 6.75.

Synthesis of [Pd(R)(μ-Cl)($H_2NC_6H_4$Me-4)]$_2$ (7). Solid p-toluidine (16.3 mg, 0.15 mmol) was added to a suspension of **6** (60.8 mg, 0.15 mmol) in dichloromethane (6 mL). The solution was concentrated (2 mL) and *n*-pentane added to precipitate **7** as a yellow solid. Yield: 53.5 mg, 70%. Mp: 183−185 °C. IR: ν(Pd−Cl) 320, 278 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.22 (s, 3H, Me), 3.81 (d, 3H, MeO, $^3J_{HH}$ = 1.5 Hz, see Discussion), 3.83 (s, 3H, MeO), 3.94 (s, 3H, MeO), 4.94−4.96 (br, 1H, NH_2), 5.08 (s, 1H, NH_2), 6.76−6.97 (m, 4H, *p*-toluidine). Anal. Calcd for $C_{32}H_{36}Cl_2N_6O_{14}Pd_2$: C, 37.97; H, 3.58; N, 8.30. Found: C, 38.03; H, 3.48; N, 8.02. Single crystals of **7·2CH$_2$Cl$_2$** were obtained by slow diffusion of hexane into a solution of **7** in dichloromethane.

Synthesis of [Pd(κ^2-R)(O,O-acac)] (8). Water (15 mL) was added to a solution of **5b** (305 mg, 0,53 mmol) in acetone (5 mL). The resulting precipitate was filtered and air-dried to give **8** as an intensely orange solid. Yield: 200 mg, 82%. Mp: 168 °C dec. ^1H NMR ($CDCl_3$): δ 2.04 (s, 3H, Me), 2.06 (s, 3H, Me), 3.88 (s, 3H, *p*-MeO), 4.04, 4.12 (two s, 3H, *m*-MeO), 5.45 (s, ^1H, CH). Anal. Calcd for $C_{14}H_{16}N_2O_9Pd$: C, 36.34; H, 3.49; N, 6.05. Found: C, 36.27; H, 3.46; N, 6.04. Single crystals of **8** were obtained by slow diffusion of *n*-pentane into a solution of **8** in acetone.

Synthesis of [Pd(R)(O,O-acac)(PPh_3)] (9). PPh_3 (57.2 mg, 0.22 mmol) was added to a solution of **8** (100 mg, 0.22 mmol) in dichloromethane (7 mL). The resulting solution was concentrated (2 mL) and *n*-pentane added to give **9** as a yellow solid. Yield: 131 mg, 83%. Mp: 223−224 °C. ^1H NMR ($CDCl_3$): δ 1.56 (s, 3H, Me), 1.97 (s, 3H, Me), 3.76 (s, 3H, MeO), 3.77 (s, 6H, MeO), 5.33 (s, 1H, CH), 7.31−7.56 (m, 15H, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.39 (s). Anal. Calcd for $C_{32}H_{31}N_2O_9PPd$: C, 53.02; H, 4.31; N, 3.86. Found: C, 53.25; H, 4.26; N, 3.85.

Synthesis of [Pd(R)(O,O-acac)(py)] (10). Method a. Two drops of pyridine were added to a suspension of **8** (50 mg, 0.11 mmol) in dichloromethane (4 mL). The solution was concentrated (2 mL) and diethyl ether added to give **10** as an off-white solid. Yield: 33.8 mg, 58%. Mp: 194−197 °C. ^1H NMR ($CDCl_3$): δ 1.908 (s, 3H, Me), 1.914 (s, 3H, Me), 3.87 (s, 3H, MeO), 3.96 (s, 6H, MeO), 5.33 (s, 1H, CH), 7.26−7.33 (m, 2H, *m*-py), 7.76−7.82 (m, 1H, *p*-py), 8.54−8.57 (m, 2H, *o*-py). Anal. Calcd for $C_{19}H_{21}N_3O_9Pd$: C, 42.12; H, 3.91; N, 7.76. Found: C, 42.26; H, 3.80; N, 7.82.

Method b. A saturated solution of pyridinium perchlorate (24 mg, 0.13 mmol) in water was added to a suspension of **8** (50.2 mg, 0.11 mmol) in acetone (1 mL). After the mixture was stirred for 4 h at room temperature, a solid precipitated, which was filtered and washed with water and then methanol to give **10**. Yield: 44.3 mg, 76%. Single crystals of **10** were obtained by slow diffusion of a solution of **8** in acetone into a solution of pyridinium perchlorate in water.

Synthesis of [Pd(R)(O,O-acac)(tht)] (11). A drop of tetrahydrothiophene was added to a solution of **8** (100 mg, 0.22 mmol) in dichloromethane. The resulting solution was concentrated (2 mL). Addition of diethyl ether gave yellow crystals of complex **11**. Yield: 88.7 mg, 75%. Mp: 172−174 °C. ^1H NMR ($CDCl_3$): δ 1.897 (s, 3H, Me), 1.901 (s, 3H, Me), 2.5−3.6 (m, br, 8H, tht), 3.89 (s, 3H, MeO), 3.99 (s, 6H, MeO), 5.29 (s, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.37 (Me), 27.28 (Me), 30.00 (CH_2), 36.57 (CH_2), 61.10 (MeO), 62.16 (MeO), 100.29 (CH), 127.69, 143.50, 147.10, 147.56 (arylic carbons), 186.02 (CO), 186.32 (CO). Anal. Calcd for $C_{18}H_{24}N_2O_9PdS$: C, 39.25; H, 4.39; N, 5.09, S, 5.82. Found: C, 39.13; H, 4.42; N, 5.04; S, 5.50.

Synthesis of [Pd(R)(O,O-acac)(dppmO)] (dppmO = bis-(diphenylphosphino)methane Monoxide) (12). Bis(diphenylphosphino)methane (66.5 mg, 0.17 mmol) was added to a solution of **8** (80 mg, 0.17 mmol) in dichloromethane (3 mL). The solution was filtered, the resulting solution concentrated (2 mL), and *n*-hexane added to precipitate **12** as a pale yellow solid. Yield: 105.1 mg, 72%. Mp: 177−179 °C. ^1H NMR ($CDCl_3$): δ 1.84 (s, 3H, Me), 1.94 (s, 3H, Me), 3.38 (d, 2H, CH_2, $^2J_{H-P}$ = 9 Hz), 3.68 (s, 3H, MeO), 3.78 (s, 6H, MeO), 5.34 (s, 1H, CH), 7.16−7.69 (m, 20H, Ph), $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −28.31 (d, $^2J_{P-P}$ = 32 Hz), 22.81 (d, P=O, $^2J_{P-P}$ = 32 Hz). Anal. Calcd for $C_{39}H_{38}N_2O_{10}P_2Pd$: C, 54.27; H, 4.44; N, 3.25. Found: C, 54.27; H, 4.35; N, 3.34.

Synthesis of [Pd(R)(C-acac)(phen)] (13). 1,10-Phenanthroline (43 mg, 0.22 mmol) was added to a solution of **8** (100 mg, 0.22 mmol) in dichloromethane (3 mL). The solution was concentrated (2 mL) and diethyl ether added to precipitate **13** as a yellow solid. Yield: 114 mg, 82%. Mp: 205−206 °C. ^1H NMR ($CDCl_3$): δ 2.13 (s, 6H, Me), 4.02 (s, 3H, MeO), 4.10 (s, 6H, MeO), 5.29 (s, 1H, CH), 7.63−9.77 (m, 8H, phen). Anal. Calcd for $C_{26}H_{24}N_4O_9Pd$: C, 48.57; H, 3.76; N, 8.71. Found: C, 48.50; H, 3.76; N, 8.41.

Synthesis of *cis*-[Pd(R)(H_2O)$_2$(PPh_3)]ClO_4·H_2O (14). Solid ($HPPh_3$)ClO_4 (79 mg, 0.22 mmol) was added to a solution of **8** (100 mg, 0.22 mmol) in dichloromethane (3 mL). The solution was concentrated (2 mL) and *n*-pentane added to precipitate **14** as a yellow solid. Yield: 140.5 mg, 85%. Mp: 140−143 °C. Λ_M = 101 Ω^{-1} cm^2 mol^{-1} (acetone). ^1H NMR ($CDCl_3$): δ 2.8−3.4 (br, 4H, H_2O), 3.77 (s, 3H, MeO), 3.79 (s, 6H, MeO), 7.39−7.53 (m, 15H, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.55 (s). Anal. Calcd for $C_{27}H_{30}ClN_2O_{14}PPd$: C, 41.61; H, 3.88; N, 3.59. Found: C, 41.55; H, 3.88; N, 3.59. Single crystals of **14** were obtained by slow diffusion of *n*-pentane into a solution of **14** in chloroform.

Synthesis of [Pd(R)(OSO_2CF_3)(PPh_3)$_2$] (15). PPh_3 (62 mg, 0.24 mmol) and trifluoromethanesulfonic acid (3 drops) were added to a solution of **9** (81 mg, 0.11 mmol) in dichloromethane. After the mixture was stirred for 2 days at room temperature, it was concentrated (2 mL) and diethyl ether added to precipitate **15** as a yellow solid. Yield: 94 mg, 81%. Mp: 190 °C dec. ^1H NMR ($CDCl_3$): δ 3.56 (s, 6H, MeO), 3.61 (s, 3H, MeO), 7.26−7.93 (m, 30H, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19.09 (s). Anal. Calcd for $C_{46}H_{39}F_3N_2O_{10}SP_2Pd$: C, 53.27; H, 3.79; N, 2.70; S, 3.09. Found: C, 53.29; H, 3.84; N, 2.85; S, 2.94.

Synthesis of [Pd(R)(OSO_2CF_3)(phen)] (16). Three drops of trifluoromethanesulfonic acid were added to a solution of **13** (90 mg, 0.14 mmol) in dichloromethane (3 mL). After it was stirred for 30 min, the solution was concentrated (2 mL) and addition of diethyl ether gave **16** as yellow crystals. Yield: 89.5 mg, 91%. Mp: 210 °C dec. ^1H NMR (d_6-acetone): δ 4.00 (s, 3H, MeO), 4.06 (s, 6H, MeO), 7.96−9.04 (m, 8H, phen). Anal. Calcd for $C_{22}H_{17}F_3N_4O_{10}PdS$: C, 38.14; H, 2.47; N, 8.09; S, 4.63. Found: C, 37.57; H, 2.43; N, 7.95; S, 4.55.

X-ray Structure Determinations. Crystals of **7·2CH$_2$Cl$_2$**, **8**, **10**, and **14·H$_2$O** 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 structure of **10** was solved by direct methods and the others by the heavy-atom method and refined anisotropically on F^2 (program SHELXL-97 (**10**), SHELXL-93 (**7·2CH$_2$Cl$_2$**, **8**, and **14·H$_2$O**)).[88,89] For compound **10** unit cell parameters were determined from a least-squares fit of 72 accurately centered

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Table 1. Crystal Data for Compounds 7·2CH_2Cl_2, 8, 10, and 14·H_2O

	7·2CH_2Cl_2	8	10	14·H_2O
mol formula	$C_{34}H_{40}Cl_6N_6O_{14}Pd_2$	$C_{14}H_{16}N_2O_9Pd$	$C_{19}H_{21}N_3O_9Pd$	$C_{27}H_{30}ClN_2O_{14}PPd$
mol wt	1182.22	462.69	541.79	779.35
source	CH_2Cl_2/*n*-hexane liquid diffusion	CH_2Cl_2/*n*-pentane liquid diffusion	acetone/water liquid diffusion	CH_2ClCH_2Cl/*n*-pentane liquid diffusion
descripn	prism	tablet	prism	lath
color	yellow	yellow	pale yellow	yellow
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
a, Å	13.056(2)	7.8605(8)	8.878(2)	33.526(5)
b, Å	9.6249(10)	10.2155(12)	16.194(3)	9.162(2)
c, Å	18.651(2)	11.0542(10)	14.837(3)	23.422(4)
α, deg	72.720(8)			
β, deg	94.684(8)	79.387(8)	92.57(2)	119.125(14)
γ, deg	78.806(8)			
V, Å^3	2335.8(5)	823.83(15)	2131.0(8)	6284.8(18)
Z	2	2	4	8
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73
T, K	173(2)	173(2)	173(2)	173(2)
monochr	graphite	graphite	graphite	graphite
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$C2/c$
cryst size, mm	0.58 × 0.42 × 0.36	0.42 × 0.28 × 0.12	0.73 × 0.20 × 0.16	0.60 × 0.24 × 0.12
μ, mm^{-1}	1.180	1.181	0.928	0.798
abs cor	*ψ* scans	*ψ* scans	*ψ* scans	*ψ* scans
max transmissn, %	0.798	0.963	0.944	0.767
min transmissn, %	0.707	0.765	0.669	0.694
scan method	*ω*	*ω*	*ω*	*ω*
2*θ* range, deg	6.1−50.0	6.2−50.0	6.0−50.0	6.1−50.0
hkl limits	$-h,\pm k,\pm l$	$\pm h,-k,\pm l$	$+h,\pm k,\pm l$	$\pm h,-k,\pm l$
no. of rflns measd	8299	4014	6317	10 320
no. of indep rflns	4107	2877	3102	5515
R_{int}	0.016	0.013	0.028	0.046
R1[a]	0.0214	0.0218	0.0248	0.0462
wR2[b]	0.0560	0.0529	0.0695	0.1198

[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.

reflections (12.8 < 2*θ* < 25.0°). Hydrogen atoms were included using a riding model or as rigid methyl groups. Maximum $\Delta/\sigma = 0.002$; maximum $\Delta\rho = 0.68$ e Å^{-3}. Unit cell parameters of **14·H_2O** were determined from a least-squares fit of 62 accurately centered reflections (6.4 < 2*θ* < 24.7°). The perchlorate anion is disordered over two sites (50% occupancy). A large peak near an inversion center was interpreted as half a disordered water molecule. A second large peak, about 2.1 Å from the one mentioned above, was tentatively identified as a half-occupied water molecule. Solvent hydrogen atoms were not considered. The hydrogen atoms of the coordinated water molecules were located in a difference Fourier synthesis and refined with restrained O−H bond lengths. Other hydrogen atoms were included as rigid methyls or riding. Maximum $\Delta/\sigma = 0.002$; maximum $\Delta\rho = 0.89$ e Å^{-3}. Unit cell parameters of **8** were determined from a least-squares fit of 65 accurately centered reflections (9.3 < 2*θ* < 25.0°). The methyl groups corresponding to C(8) and C(9) are disordered over two sites (50% occupancy). Hydrogen atoms were included using a riding model or as rigid nondisordered methyl groups. Maximum $\Delta/\sigma = 0.001$; maximum $\Delta\rho = 0.40$ e Å^{-3}. Unit cell parameters of **7** were determined from a least-squares fit of 62 accurately centered reflections (8.8 < 2*θ* < 25.2°). Hydrogen atoms were included using a riding model. Maximum $\Delta/\sigma = 0.001$; maximum $\Delta\rho = 0.36$ e Å^{-3}. The programs use the neutral atom scattering factors $\Delta f'$ and $\Delta f''$ and absorption coefficients from ref 90.[90]

Results and Discussion

Synthesis of Bis(2,6-dinitro-3,4,5-trimethoxyphenyl)mercury (2). Slow addition of solid 3,4,5-trimethoxybenzoic acid to a mixture of sulfuric and nitric acid at around 10 °C gives a mixture of 1,2,3-trimethoxy-4,5,6-trinitrobenzene and 1,2-dinitro-3,4,5-trimethoxybenzoic acid. The reaction of this acid with mercuric acetate in water leads to the precipitation of the corresponding mercuric benzoate **1** (see Scheme 1). Decarboxylation of **1** occurs when it is heated at 180 °C to give bis(2,6-dinitro-3,4,5-trimethoxyphenyl)mercury (**2**). Kharash first reported this method for the synthesis of arylmercury compounds, preparing 2,4,6-trinitrophenyl derivatives.[91] Other authors have also employed it to prepare polyfluorophenyl,[92−96] polychlorophenyl,[97] and pentabromophenyl[98] derivatives.

Syntheses of (2,6-Dinitro-3,4,5-trimethoxyphenyl)palladium Complexes. When a 2:1 mixture of **2** and $Q_2[PdCl_2(\mu\text{-}Cl)]_2$ is refluxed in acetone, a transmetalation occurs, giving a mixture of [Hg(R)Cl] (**3**) and $Q_2[Pd(R)Cl(\mu\text{-}Cl)]_2$ (Q = $PPh_3(CH_2Ph)$ (**4a**)) (see Chart 1 and Scheme 2) that can easily be resolved due to the low solubility of **4a** in organic solvents. When $(NMe_4)_2[PdCl_2(\mu\text{-}Cl)]_2$ is reacted with **2**, the reaction occurs at room temperature, giving the insoluble complex $(NMe_4)_2[Pd(R)Cl(\mu\text{-}Cl)]_2$ (**4b**) and the mercurial **3**. A slight

(90) *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. C, Tables 6.1.1.4 (pp 500−502), 4.2.6.8 (pp 219−222), and 4.2.4.2 (pp 193−199).

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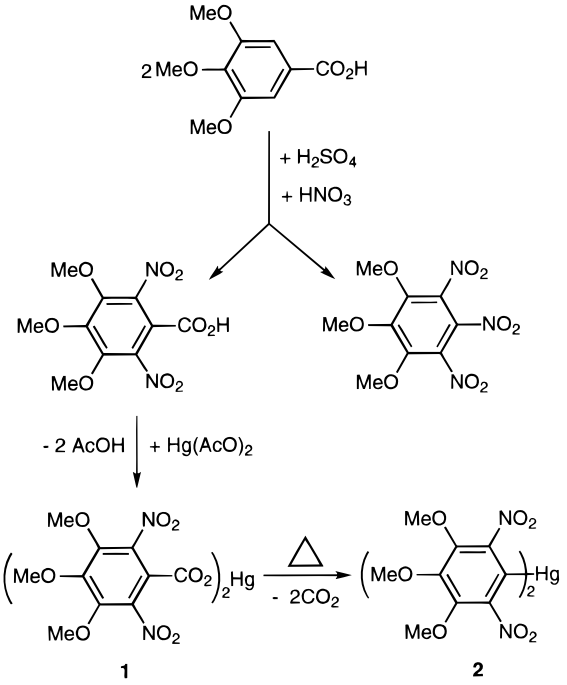
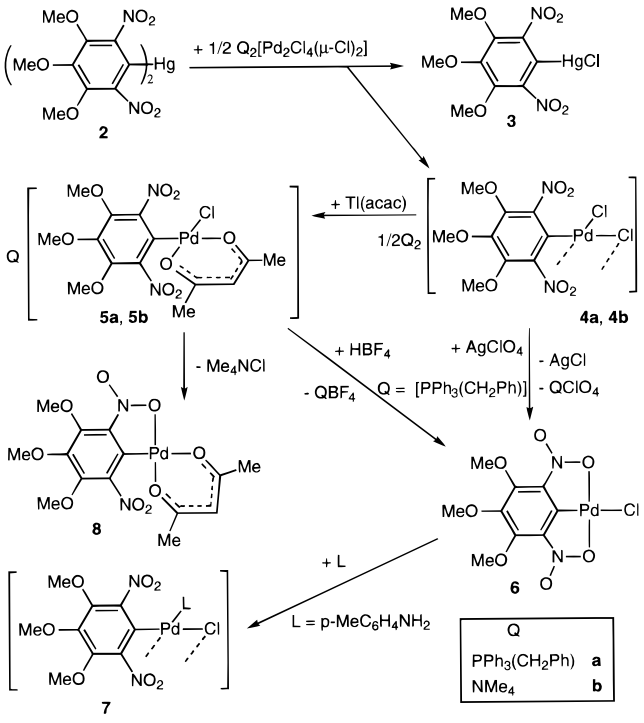
Scheme 1



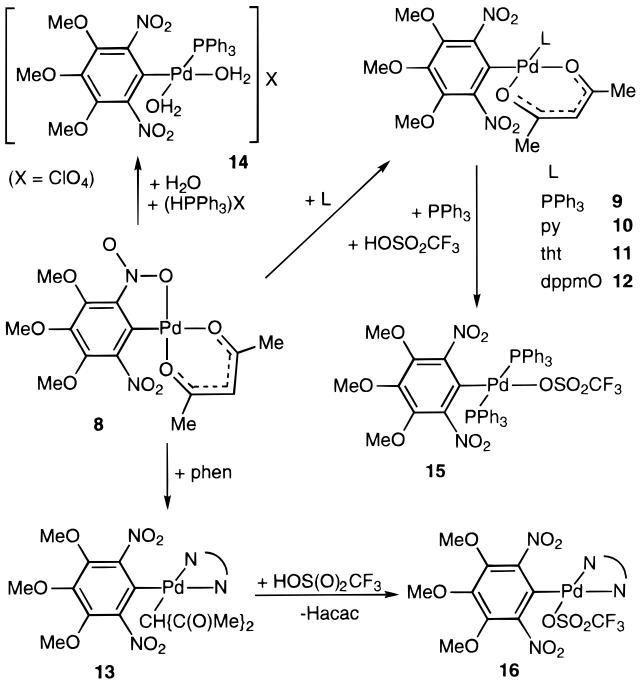
Scheme 2



excess of **2** (about 0.5−1%) over the stoichiometric amount is recommended to avoid contamination of **4a** or **4b** with the corresponding $[PdCl_2(\mu\text{-}Cl)]_2^{2-}$ salt. We have previously reported this synthetic method in the preparation of related nitroaryl palladium complexes.[66,68]

The reaction of **4a** or **4b** with Tl(acac) gives Q[Pd(R)-Cl(O,O-acac)] (Q = $(PhCH_2)Ph_3P$ (**5a**), Me_4N (**5b**)) (see Scheme 2). This result contrasts with that obtained in the reaction between $(NMe_4)_2[Pd(Ar)Cl(\mu\text{-}Cl)]_2$ (Ar = C_6H_3Me-6, NO_2-2) and Tl(acac), which gives the neutral complex [Pd(κ^2-Ar)(O,O-acac)].[71] However, we have been able to obtain the related neutral complex with the ligand κ^2-R (**8**) from **5b** (see below). We are not aware of the previous synthesis of anionic [Pd(R)X(O,O-acac)]$^-$ complexes.

Scheme 3



The complex [Pd(κ^3-R)Cl] (**6**), containing an O,C,O pincer ligand, can be prepared by reacting **4a** with $AgClO_4$ (1:2) or **5a** with HBF_4 (1:1). Complex **6** is the first palladium complex containing an O,C,O pincer ligand. As far as we are aware, the only complexes containing an O,C,O pincer ligand are some recently reported tin derivatives containing the aryl ligand $C_6H_2[P(O)(OEt)_2]_2$-1,3-^{t}Bu-5.[53] Complex **6** is soluble in acetone but only slightly soluble in chlorinated solvents. These solutions decompose to palladium metal when diethyl ether or hydrocarbon solvents are added. Attempts to dissolve **6** in diethyl ether also lead to decomposition. Complex **6** reacts with *p*-toluidine to give the dinuclear complex $[Pd(R)(\mu\text{-}Cl)L]_2$ (L = *p*-toluidine (**7**)) instead of the desired [Pd(κ^2-R)Cl(L)]. It is probable that coordination of one nitro group causes repulsions between the uncoordinated nitro group and the other ligand cis to the aryl group. This problem does not seem to occur in the complex [Pd(κ^2-R)(O,O-acac)] (**8**). This complex is precipitated upon the addition of water to a concentrated solution of **5b** in acetone. Probably, the lower spatial requirement of the oxygen donor atom of the acac ligand in **8** compared with that of chloro or *p*-toluidine ligands is the reason for this different result.

Complex **8** reacts with PPh_3, pyridine (py), tetrahydrothiophene (tht), or bis(diphenylphosphino)methane (1:1) to give the adducts [Pd(R)(O,O-acac)(L)] (L = PPh_3 (**9**), py (**10**), tht (**11**), bis(diphenylphosphino)methane monoxide (dppmO) (**12**)) and with 1,10-phenanthroline to give [Pd(R)(C-acac)(phen)] (**13**) (see Scheme 3). The reaction between **8** and PPh_3 gives **9** even when a 1:2 molar ratio is used. Attempts to prepare complexes with the pincer ligand κ^3-R or κ^2-R from complexes **8**−**10** proved unsuccessful. Thus, the synthesis of [Pd(κ^3-R)-$(PPh_3)]^+$ or [Pd(κ^2-R)X$(PPh_3)]^+$ (X = $OClO_3$ or OSO_2CF_3) was attempted via two different routes. The first was

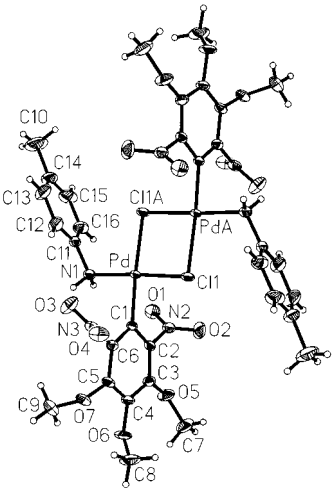


Figure 1. ORTEP plot of **7** with the labeling scheme (50% probability level).

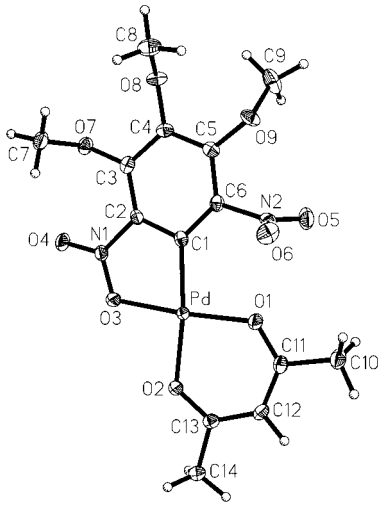


Figure 2. ORTEP plot of **8** with the labeling scheme (50% probability level).

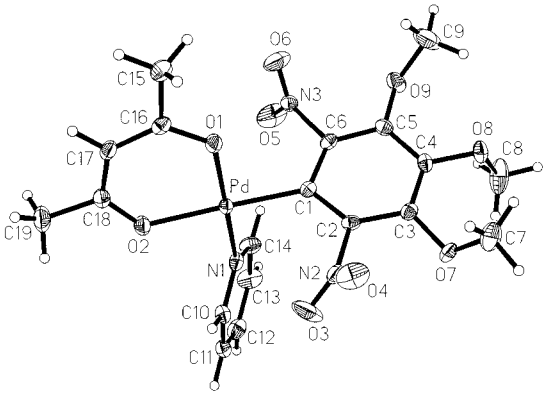


Figure 3. ORTEP plot of **10** with the labeling scheme (50% probability level).

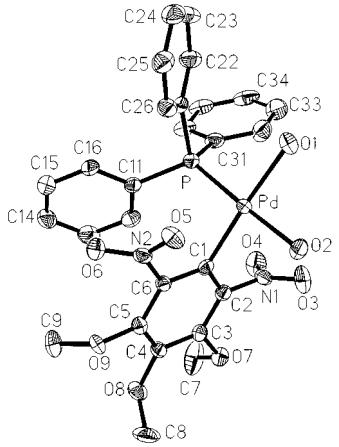


Figure 4. ORTEP plot of **14** with the labeling scheme (50% probability level). Hydrogen atoms are omited for clarity.

the reaction between **8** and $(HPPh_3)ClO_4$. Working under anaerobic conditions, we could only isolate an oil. The complex *cis*-$[Pd(R)(H_2O)_2(PPh_3)]ClO_4 \cdot H_2O$ (**14**) was obtained when working in the air. The second attempt was the reaction between **9** and triflic acid ($HOSO_2CF_3$). When this acid was added to a solution of **9** in dichloromethane, a change of color was observed from yellow to orange. From this mixture we could only obtain an oil. Addition of PPh_3 (PPh_3:Pd = 1:1) gave *trans*-$[Pd(R)(OSO_2CF_3)(PPh_3)_2]$ (**15**). The difficulty of preparing $[Pd(\kappa^3\text{-}R)(PPh_3)]^+$ can be related with the *transphobia* between the aryl and the PPh_3 ligands.[99] The unsuccessful synthesis of $[Pd(\kappa^2\text{-}R)(OSO_2CF_3)(PPh_3)]$ could be due to the repulsion between the PPh_3 and the uncoordinated nitro group.

The reaction between **8** and $(Hpy)ClO_4$ or between **10** and $HClO_4$, designed to prepare $[Pd(\kappa^3\text{-}R)(py)]^+$, gave instead complex **10** or **8**, respectively. The equilibrium **8** + $(Hpy)ClO_4 \rightleftarrows$ **10** + $HClO_4$ can explain these results. Finally, an attempt to prepare $[Pd(\kappa^2\text{-}R)(phen)]CF_3SO_3$, by reacting **13** and triflic acid, gave instead $[Pd(R)(OSO_2CF_3)(phen)]$ (**16**).

Complexes **6** and **8** have an intense orange color which clearly distinguish them from all the other complexes containing the monocoordinated R group, which are yellow or pale orange. It is clear that coordination of one or the two nitro groups is responsible for the color of complexes **6** and **8**. According to this, the yellow solutions obtained when complex **6** is dissolved in acetone or when an stream of CO is passed through an orange dichloromethane solution of **6**, could contain in the first case $[Pd(R)Cl(acetone)_2]$, or $[Pd(R)Cl(CO)_2]$ or $[Pd(R)(\mu\text{-}Cl)(CO)]_2$ in the latter. However, from these solutions only complex **6** could be isolated. The change of color from yellow to orange when triflic acid is added to a solution of **9** in dichloromethane could be indicative of the formation of $[Pd(\kappa^3\text{-}R)(PPh_3)]CF_3SO_3$ or $[Pd(\kappa^2\text{-}R)(OSO_2CF_3)(PPh_3)]$.

Structure of Complexes. The crystal structures of complexes **7**, **8**, **10**, and **14** have been determined (Figures 1-4 and Tables 2−5). In all of them, the palladium atom shows slightly distorted square planar coordination. Complex **7** crystallizes with two molecules of dichloromethane and **14** with one molecule of water. The structure of **7** consists of a chain polymer formed through alternate chloro bridges and intermolecular NH···OMe hydrogen bonds [N(1)−H(2)···O(7C), 2.42 Å; N(1)···O(7C), 3.29 Å; N(1)−H(1)-O(3), 152°] (Figure 5). Additionally, the other hydrogen atom of the amine group establishes an intramolecular hydrogen bond with one oxygen atom of a nitro group (N(1)−H(1)···O(3), 2.30

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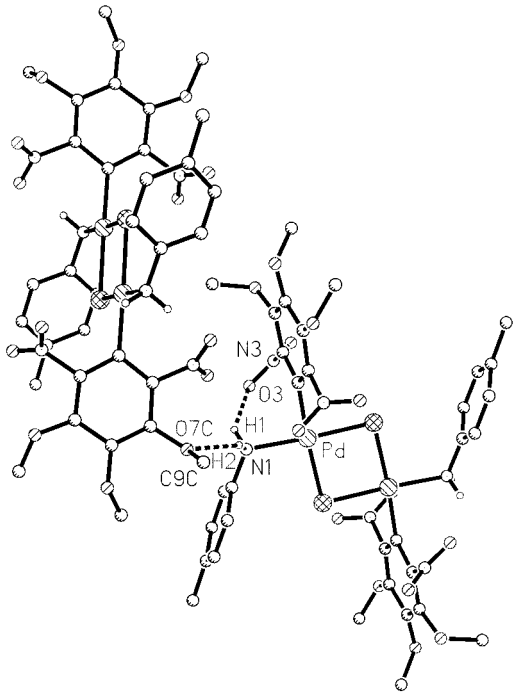

Figure 5. Hydrogen bond interactions in **7**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in Complex 7·2CH_2Cl_2

Pd−C(1)	1.986(2)	Pd−Cl(1)	2.3179(6)
Pd−N(1)	2.076(2)	Pd−Cl(1A)	2.4222(6)
C(1)−Pd−N(1)	87.34(8)	C(1)−Pd−Cl(1)	90.25(6)
N(1)−Pd−Cl(1A)	96.74(5)	Cl(1)−Pd−Cl(1A)	85.67(2)
Pd−Cl(1)−Pd(A)	94.33(2)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) in Complex 8

Pd−C(1)	1.967(2)	O(2)−C(13)	1.278(3)
Pd−O(1)	1.969(2)	O(3)−N(1)	1.290(3)
Pd−O(3)	2.014(2)	O(4)−N(1)	1.209(3)
Pd−O(2)	2.030(2)	O(5)−N(2)	1.218(3)
O(1)−C(11)	1.286(3)	O(6)−N(2)	1.222(3)
C(1)−Pd−O(1)	94.72(8)	O(1)−Pd−O(2)	92.83(7)
C(1)−Pd−O(3)	81.36(8)	O(3)−Pd−O(2)	91.04(7)

Table 4. Selected Bond Lengths (Å) and Angles (deg) in Complex 10

Pd−O(1)	1.9990(18)	Pd−C(1)	2.002(3)
Pd−N(1)	2.021(2)	Pd−O(2)	2.0408(18)
O(1)−Pd−C(1)	88.97(8)	C(1)−Pd−N(1)	91.41(9)
O(1)−Pd−O(2)	93.27(7)	N(1)−Pd−O(2)	86.35(8)

Table 5. Selected Bond Lengths (Å) and Angles (deg) in Complex 14·H_2O

Pd−C(1)	2.035(2)	Pd−O(1)	2.124(4)
Pd−O(2)	2.142(4)	Pd−P	2.228(2)
C(1)−Pd−O(2)	92.4(2)	O(1)−Pd−O(2)	83.5(2)
C(1)−Pd−P	90.41(10)	O(1)−Pd−P	93.7(2)

Å; N(1)−O(3), 2.99 Å; N(1)−H(1)−O(3), 137°). Surprisingly, the N(1)−O(3) and N(1)−O(4) bond distances are almost identical (1.221(3), 1.223(3) Å). In complex **14**, a chain polymer is also formed although only through intermoleculecular OH···OMe hydrogen bonds. The polymerization is achieved via hydrogen bonds connecting each water molecule trans to the phosphine ligand with two methoxy groups each from two neighbor molecules (O(2)−H(03)···O(9A), 2.29 Å; O(2)···O(9A), 2.94 Å; O(2)−H(03)−O(9A), 156°; O(2)−H(04)···O(7B), 2.23 Å; O(2)···O(7B), 2.91 Å; O(2)−H(04)−O(7B), 167°) (Figure 6). Additionally, the other water molecule and one oxygen atom of the perchlorate anion are hydrogen-bonded (because of disorder of the perchlorate anion the O(10A) and O(13′A) atoms are considered: O(1)−H(02)···O(10A), 2.21 Å; O(1)···O(10A), 2.78 Å; O(1)−H(02)−O(10A), 140°; O(1)−H(02)···O(13′A), 2.08 Å; O(1)···O(13′A), 2.71 Å; O(1)−H(02)−O(13′A), 150°). As far as we are aware, only one crystal structure of a diaquapalladium complex, $[Pd(OH_2)_2\{Ph_2P(CH_2)_3PPh_2\}](CF_3SO_3)_2$, has been reported.[100] However, in this complex each cation and its corresponding two anions are intramolecularly hydrogen-bonded instead of forming a polymer like in **14**. Recently, chiral diaqua complexes $[Pd(binap)(H_2O)_2]^{2+}$ have been shown to catalyze asymmetric addition of enol silyl ethers to imines and aldehydes.[101,102] Complex **14** is the first organometallic diaquapalladium(II) complex.

In complex **8**, the molecules are stacked, forming dimers in which the vector formed by the metal atom of one molecule and the center of the aryl ligand of the other molecule has a length of 3.59 Å and forms an angle of 87.2° with the C(1)−C(6) plane (Figure 7).

The Pd−C bond distances are all significantly different. The order is 1.967(2) (**8**) < 1.986(2) (**7**) < 2.002(3) (**10**) < 2.035(2) (**14**) Å. However, given that in **8** and **10** the aryl ligand has the same ligand in a trans position (O-acac), probably the order of trans influence that these data suggest is O-acac ≈ μ-Cl < H_2O. The greater Pd−X bond distance trans to the aryl group (Pd−X_{Ar}) compared to that of the other ligand (Pd−X_L) shows that the aryl group has a greater trans influence than the amine ligand in **7** (Pd−Cl_{Ar}, 2.4222(6) Å; Pd−Cl_{NH_2R}, 2.3179(6) Å), than the O−NO group in **8** (Pd−O_{Ar}, 2.030(2) Å; Pd−O_{ONOAr}, 1.969(2) Å), than py in **10** (Pd−O_{Ar}, 2.0408(18) Å; Pd−O_{py}, 1.9990(18) Å), and than PPh_3 in **14** (Pd−O_{Ar}, 2.142(4) Å; Pd−O_{PPh_3}, 2.124(4) Å).

In complexes **7**, **10**, and **14**, the plane formed by the six carbon atoms of the aryl ligand (C_6 plane) is almost perpendicular to the coordination plane (Pd and the four atoms coordinated to it) (**7**, 81.7°; **10**, 75.4°; **14**, 82.5°), while in **8** both are almost coplanar (1.2°) due to the chelating nature of the aryl ligand. This is also the reason for the almost coplanarity of the C_6 plane and the $CN(1)O_2$ plane (6.5°). The other nitro group in **8** and those of complexes **7**, **10**, and **14** are rotated with respect to its own C_6 plane by an angle in the range 41.9−81.0°. The coordination of the $N(1)O_2$ group in **8** has two other structural consequences: (i) the lengthening of the N(1)−O(Pd) bond distance (1.290(3) Å) in **8** with respect to the other three N−O bonds (N(1)−O(4), 1.209(3) Å; N(2)−O(5), 1.218(3) Å; N(2)−O(6), 1.222(3) Å), which are in the range observed in complexes **7**, **10**, and **14** (1.208(3)−1.230(5) Å) and (ii) the shortening of the C(2)−N(1) bond distance (1.439(3) Å) with respect to the C(6)−N(2) bond length (1.485(3) Å). This is similar to C−N bond distances in complexes **7** (1.465(3), 1.479(3) Å) and **10** (1.477(3), 1.482(4) Å), while

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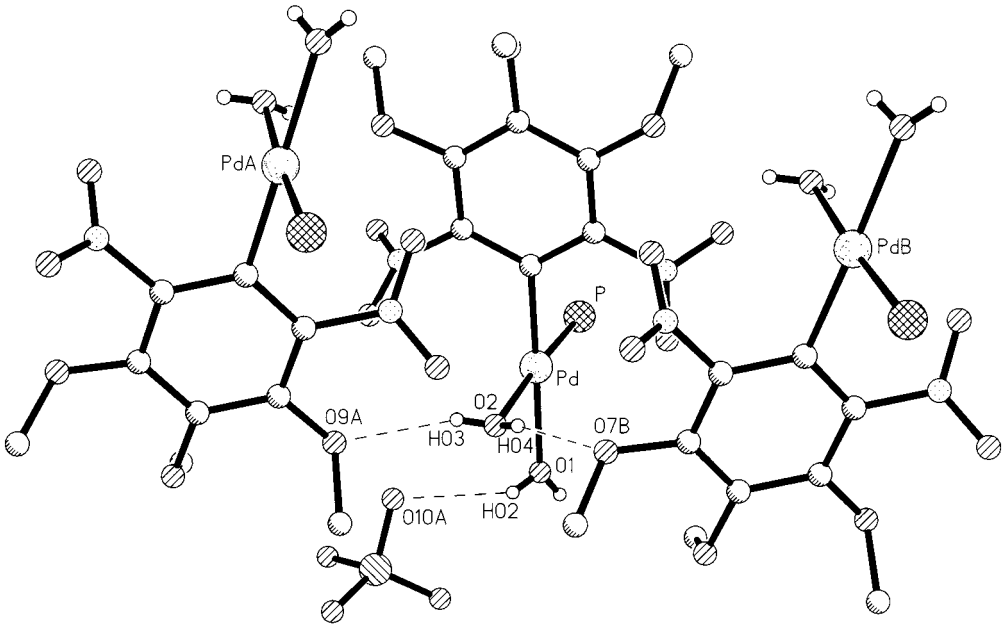

Figure 6. Hydrogen bond interactions in **14**.

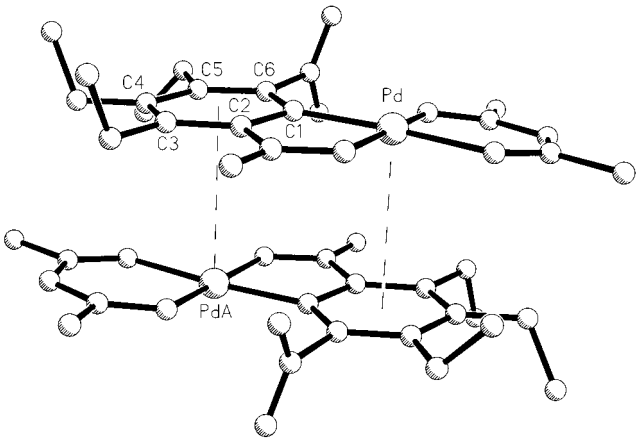

Figure 7. Packing diagram of **8**.

those in **14** (1.435(5), 1.441(5) Å) are similar to C(2)−N(1) in **8**, probably due to the cationic nature of **14**. As we have previously shown, these data suggest that the nitro group exerts an −I rather than −M effect in these metalated aryl rings.[57,58,64,66−76] In fact, the presence in the aryl groups of electron-releasing and -withdrawing groups do not affect significantly the C−C bond distances (range 1.379(3)−1.410(3) Å; in **14** the C−C bond distances have been fixed at 1.39 Å). Additionally, not only is the angle between the C_6 and CNO_2 planes not appropiate for pπ(C) → pπ(N) bonding but also the C−C(NO_2)−C angle is ≥120° when it would be expected to be <120° if the C−N bond were of some multiple character. The −I effect exerted by the nitro group is responsible for C−C(NO_2)−C angles >120° according to the *isovalent hybridization* model proposed by Bent.[103]

Spectroscopic Properties. ^{1}H NMR spectroscopy can be used to determine the mode of coordination of the aryl group in solutions of complexes **1**−**16**. As expected, complex **8** shows three different MeO groups, while the others, except **7**, show two 2:1 singlets according to the structures proposed. In complex **7**, the intermolecular NH···OMe hydrogen bonds (see Figure 5) are responsible for the observation of three resonances due MeO groups. One of these is a doublet with $^3J_{HH}$ = 1.5 Hz because of the coupling through the hydrogen bond between the methyl and NH protons. The NH protons of the amine are not isochronous because of this interaction and, probably too, because of the intermolecular NH···ONO hydrogen bond.

According to the assignment of ν(PdCl) in related nitrophenylpalladium complexes,[66,68−70] the band at 330 (**4a**), 335 (**4b**) cm^{-1} can be assigned to ν(PdCl), corresponding to a terminal chloro ligand, and the bands at 258 (**4a**), 263 (**4b**) and 285 (**4a**), 293 (**4b**) cm^{-1} to ν(PdCl) modes due to bridging chloro ligands. These two bands move to higher frequency (298, 320 cm^{-1}) in complex **7**, probably because it is neutral instead of anionic, and this increases the π-donor ability of the chloro ligand. In complex **6**, the weak band at 293 cm^{-1} can be assigned to ν(PdCl). Similar values have been assigned in *trans*-[PdClR(PPh_3)$_2$] (R = C_6H_3Me-2,NO_2-6) (300 cm^{-1})[66] and [PPh_3(CH_2Ph)][PdRCl_2(CO)] (R = C_6H_3Me-2, NO_2-6) (285 cm^{-1}).[70]

All complexes show a very strong band at around 1520 cm^{-1} corresponding to ν_{asym}(NO_2). Additionally, in all complexes except **6**, a band at around 1350 cm^{-1} is assignable to ν_{sym}(NO_2). According to the lowering of ν_{sym}(NO_2) observed in cyclometalated *o*-nitrophenyl complexes, we assign the strong band observed at 1200 cm^{-1} in complexes **6** and **8** to ν_{sym}(NO_2) of the coordinated nitro groups.

Conclusions

We have prepared one complex with the pincer ligand κ^3-C_6(NO_2)$_2$-2,6-(OMe)$_3$-3,4,5-C^1,O,O′, another one with the chelating ligand κ^2-C_6(NO_2)$_2$-2,6-(OMe)$_3$-3,4,5-C^1,O, and a series of neutral, anionic, and cationic complexes with the monocoordinated ligand C_6(NO_2)$_2$-2,6-(OMe)$_3$-3,4,5-C^1 using the corresponding mercury derivative as transmetalating agent. However, some attempts to prepare other complexes with the pincer and κ^2-chelat-

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ing ligands failed, probably because even poor donor ligands compete with the very weak Pd−O bonds. The presence of the three methoxy groups in the aryl ligand seems to be crucial to success in the synthesis of complexes with the pincer and κ^2-chelating ligands, as previous attempts to prepare 2,4,6-trinitrophenyl complexes with such types of coordination failed. The presence of the nitro and methoxy substituents in the aryl ligand allows the formation of interesting chain polymers through hydrogen bonds.

Acknowledgment. We thank the DGES for financial support and the Ministerio de Educación y Cultura (Spain) for the award of a contract to M.C.R.A.

Supporting Information Available: Tables giving crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles for **7·2CH$_2$Cl$_2$**, **8**, **10**, and **14·H$_2$O** (21 pages). Ordering information is given on any current masthead page.

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