5108 *Organometallics* **2008,** *27,* 5108–5117

Unexpected Structure of Palladacycles Containing Carboxylated Schiff Bases. Synthesis of Some Water-Soluble Metallacycles

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Received July 18, 2008

The action of palladium acetate on carboxylated Schiff bases is herein described. These reactions lead to new metallacycles, some of which are hydrosoluble. Additionally we present the first report of cyclopalladated derivatives having the metalated molecule as a dianionic (C,N,O) bridging ligand between two palladium atoms.

Introduction

Cyclometalation reactions were one of the first known examples of C−H bond activation, and cyclometalated complexes of a wide variety of ligands, containing N, P, As, O, or S as the heteroatom, have been described.[1] The cyclometalation of *N*-donor ligands has been extensively studied and has acquired great interest because of the application of the metallacycles in many areas including organic synthesis, homogeneous catalysis, the design of new metallomesogens and antitumoral drugs, asymmetric synthesis, resolution of racemic ligands, intermolecular aromatic C−H bond activation, or synthesis and reactivity of organometallic complexes with biologically important ligands.[2]

As it is known, water has attracted attention as a potential replacement for organic solvents due to its low cost, nonflammability, and low toxicity and the fact that it is a renewable resource.[3] Moreover, the use of water in combination with hydrophilic homogeneous metal catalysts offers the potential to easily separate and recycle the metal catalyst from organic product streams. There are a limited number of reports on the use of cyclopalladated compounds in Heck,[3h−k] Suzuki,[3h,l−n] Stille,[3h,o] and Sonogashira[3p] couplings in water solution. Recently water-soluble palladacycles have been prepared from sulfonated imines and, in combination with (2-di-*tert*-butylphosphinoethyl)trimethylammonium chloride, have been shown to be active catalysts for the Suzuki coupling. In contrast, the attempts described by these authors to obtain cyclopalladated compounds containing carboxylated imines were unsuccessful.[4] The interest of the metalation of these imines is underlined by the fact that the corresponding metallacycles may be useful catalysts and, in addition, this process can lead to the regiospecific synthesis of *ortho*-substituted carboxylated imines, which can be precursors of pharmaceutical products.[5]

With this precedent in mind,[4] and following our studies on cyclometalation reactions,[2p,u−w] we focused our attention on the action of palladium acetate on carboxylated Schiff bases. These reactions lead to new metallacycles, some of them hydrosoluble. Besides this, cyclopalladated derivatives containing the metalated molecule as a dianionic (C,N,O) bridging ligand between two palladium atoms have been synthesized for the first time.

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10.1021/om8006807 CCC: $40.75 © 2008 American Chemical Society
Publication on Web 09/11/2008

Results and Discussion

Imines can exist as *E* or *Z* isomers, but in general *N*-aldimines adopt the more stable *E* form.[6] Carboxylated Schiff bases may exist in two forms, the ionized (zwitterionic) and the free un-ionized form. Recent studies on these ligands demonstrate that the predominant isomer is by far the un-ionized form.[7]

Cyclometalation of *N*-benzylidenebenzylamines could in principle produce two different five-membered metallacycles, one in which the cycle contains the imine functionality (*endo*) and one in which it does not (*exo*).[8] The tendency to give *endo*-cycles (*endo* effect) is so strong that it allows activation of an aliphatic C−H bond with formation of a six-membered palladacycle in preference to the activation of an aromatic C−H bond with formation of a five-membered *exo*-palladacycle.[9]

The *N*-benzylidenephenylamine ligands **1a**−**1f** were prepared by a condensation reaction of 4-aminobenzoic acid with the corresponding aldehyde.[7] Proton NMR spectra reveal the formation of a single isomer, where the methinic proton signal appears at δ values between 8.3 and 8.8 ppm. Furthermore, 2D NOESY spectra confirm the *E* stereochemistry around the C═N bond, and in addition, no NH signal was detected. Infrared spectra consistently agree with the un-ionized *E* form proposed on the basis of NMR data.

All imines here prepared can afford five-membered *endo*-metallacycles, and this fact prompted us to study the cyclopalladation of the carboxylated imines, under different reaction conditions than those previously reported.[4] When the Schiff bases **1a**−**1f** were treated with palladium acetate in acetic acid, the corresponding acetato cyclopalladated dimers **2a**−**2e** were isolated. Despite varying the reaction conditions, we were unable to metalate ligand **1f**. Nevertheless, this is not an unexpected result and may be due to the fact that the electron-withdrawing nitro group deactivates the aromatic ring to the electrophilic attack of Pd(II).[1,10]

Cyclopalladated derivatives **2a**−**2e** were essentially insoluble in water at pH = 7, but were soluble in pH = 10 buffered media, and no decomposition of these solutions occurred after several hours.

The metalation of imine **1c** could afford two different five-membered *endo*-metallacycles. However, only the activation of the less hindered C−H bond was observed, in agreement with previous results.[8a,b,11]

A noticeable feature of all compounds containing a chlorine substituent in an *ortho* position on the aromatic ring (derivatives of imine **1b**) is the downfield shift of the HC═N proton as compared to the nonsubstituted derivatives, hence indicating a nonconventional hydrogen bond Cl···H−Cl, as found for related palladium and platinum metallacycles.[12]

Slow crystallization of an acetic acid solution of **2c** affords suitable crystals for X-ray structure determination (Figure 1). **2c** is a dinuclear cyclometalated compound with two acetato-bridging ligands. The palladium atom is in a square-planar environment, coordinated to carbon, nitrogen, and two oxygen atoms. The distances between palladium and the coordinated atoms are in accordance with other cyclopalladated compounds (Table 1).[13] As a consequence of the different *trans* influence,[14] the Pd−O bonds having nitrogen atoms in *trans* position [Pd−O(3): 2.0385(16) Å] are significantly shorter than those having a *trans* relationship with respect to the aromatic carbon [Pd−O(4): 2.1492(16) Å]. The five-membered metallacycle is approximately planar, as suggested by the sum of internal angles, which is close to 540°.[15] The palladium−palladium distance of 2.8883(16) Å is in the range observed for other related dimeric palladium complexes.[13]

It should be noted that compound **2c** crystallized with four acetic acid molecules in the crystal lattice, two of which were disordered solvent molecules. Both ordered acetic acid molecules presented hydrogen-bonding interactions with the carboxylic groups of compound **2c**. The distances O(1)−H(1)···O(5) and O(6)−H(6)···O(2) were 2.676(3) and 2.596(3) Å, respectively, which are within the normal range for hydrogen bonds. On the other hand, inter- and intramolecular $\pi-\pi$ stacking interactions add to the stability of the molecular structure. As

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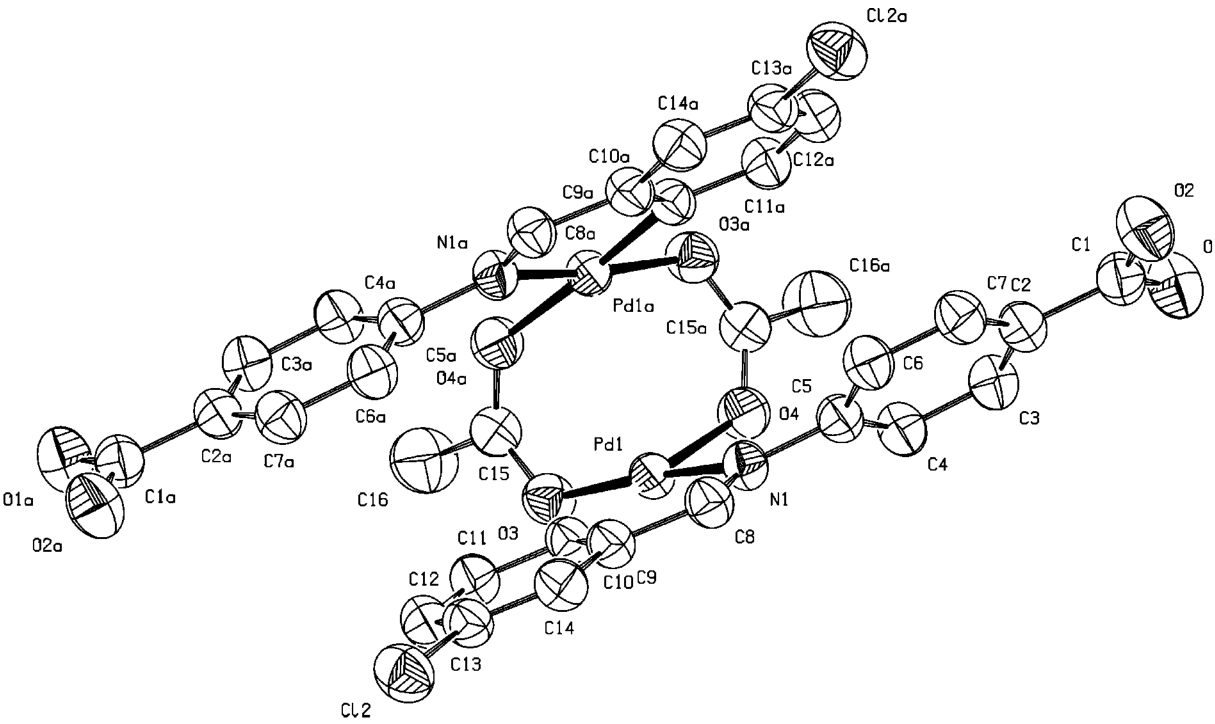

Figure 1. Molecular structure of compound **2c**.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for 2c and 4a

Compound **2c**	
Pd(1)−C(10)	1.956(2)
Pd(1)−O(3)	2.0385(16)
Pd(1)−N(1)	2.0543(18)
Pd(1)−O(4)#1	2.1492(16)
Pd(1)−Pd(1)#1	2.8883(12)
N(1)−C(8)	1.306(3)
C(10)−Pd(1)−O(3)	91.35(8)
C(10)−Pd(1)−N(1)	81.34(8)
O(3)−Pd(1)−O(4)#1	87.09(7)
N(1)−Pd(1)−O(4)#1	100.11(7)
Compound **4a**	
Pd(1)−C(7)	1.990(3)
Pd(1)−N(1)	2.036(3)
Pd(1)−N(14)	2.037(3)
Pd(1)−O(23)#1	2.129(2)
C(7)−Pd(1)−N(1)	93.76(11)
C(7)−Pd(1)−N(14)	81.00(11)
N(1)−Pd(1)−O(23)#1	92.79(9)
N(14)−Pd(1)−O(23)#1	92.49(9)

expected from a folded open-book acetato-bridged compound, both palladacycle rings [plane 1: Pd1, N1, C8, C9, and C10; plane 2: Pd1a, N1a, C8a, C9a, and C10a] are disposed close to each other [centroid-to-centroid distance = 3.817(2) Å, and interplane angle = 30.25°]. Furthermore, compound **2c** exhibits $\pi-\pi$ interactions caused by intermolecular overlapping of the π-conjugated systems of two neighboring *ortho*-metalated rings (C9, C10, C11, C12, C13, and C14) [centroid-to-centroid distance = 3.911(2) Å, and interplane angle = 0.00°].

While compounds **2** were insoluble in water at pH = 7, when an aqueous suspension of these dimers was treated with a large excess of deuterated pyridine (25:1), compounds **3** were obtained in water solution. Proton NMR and mass spectra permit us to propose the zwitterionic form depicted in Scheme 1 for these complexes. The crystal structure of a cyclopalladated cation containing two pyridine molecules by the metal atom has been described.[16a] Regarding the stability of complexes **3** in water solution, proton NMR spectra showed that these compounds remain unaltered for several days.

Dinuclear cyclopalladated derivatives **4** can be synthesized by treatment of the acetato-bridged compounds **2** with pyridine (6:1) at room temperature in methanol (**4a** and **4d**) or $CHCl_3$ solutions (**4b** and **4c**) or in refluxing $CHCl_3$ (**4e**). Proton NMR spectra of $CDCl_3$ solutions of **4**, in the absence of free pyridine, exhibit a complex pattern arising from the different exchange processes in solution involving the labile pyridine ligands and the solvent or water molecules. Compounds **4** are insoluble in water at pH = 7 or 10, but can easily dissolve in water if an excess of pyridine is added to afford **3**. Crystals suitable for X-ray structure determination can be obtained by slow crystallization of chloroform solutions of **4a** and **4d** (Figures 2 and 3).

Surprisingly, the crystal structure determination of **4a** and **4d** revealed dinuclear cyclopalladated complexes where the metalated imine acts as a dianionic bridging ligand between two palladium atoms. The palladium atom is in a square-planar environment, coordinated to carbon, oxygen, and two nitrogen atoms. The distances between palladium and the coordinated atoms are in agreement with those reported for other cyclopalladated compounds (Tables 1 and 2).[16] The angles between adjacent atoms lie in the range 81.00(11)° [C(7)Pd(N14)] and 93.76(11)° [C(7)Pd(N1)] for **4a** and 81.54(9)° [C(7)Pd(N1)] and 96.35(9)° [C(7)Pd(N2)] for **4d**. The five-membered metallacycles are nearly planar, as suggested by the sum of internal angles, which is close to 540° in both metallacycles.[15]

In contrast with the high number of dinuclear cyclometalated compounds described so far with an acetato-bridging ligand in the CSD,[17] the structures here described for compounds **4a**, **4d**,

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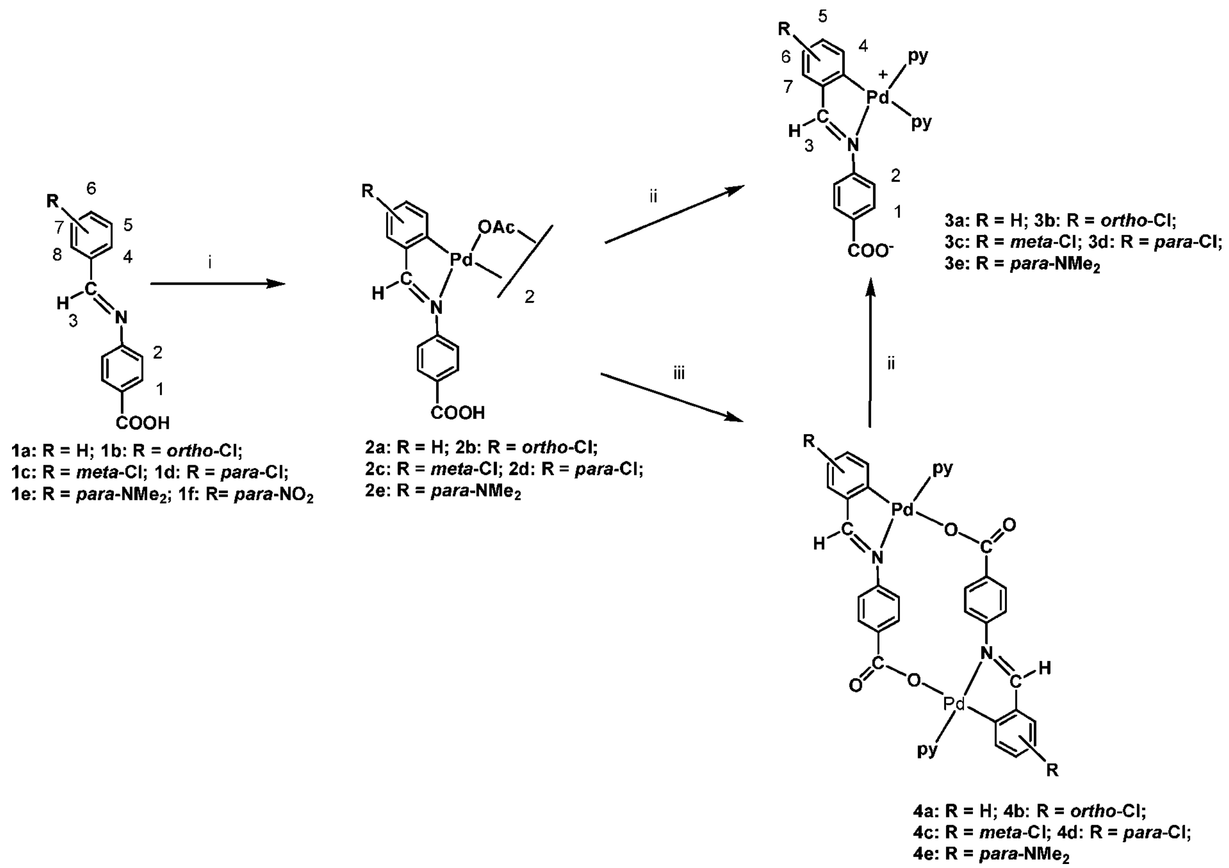
Scheme 1[a]



[a] (i) Pd(OAc)$_2$, acetic acid; (ii) pyridine (25:1), D$_2$O; (iii) pyridine (6:1), methanol (**4a**, **4d**), chloroform (**4b**, **4c**, **4e**).

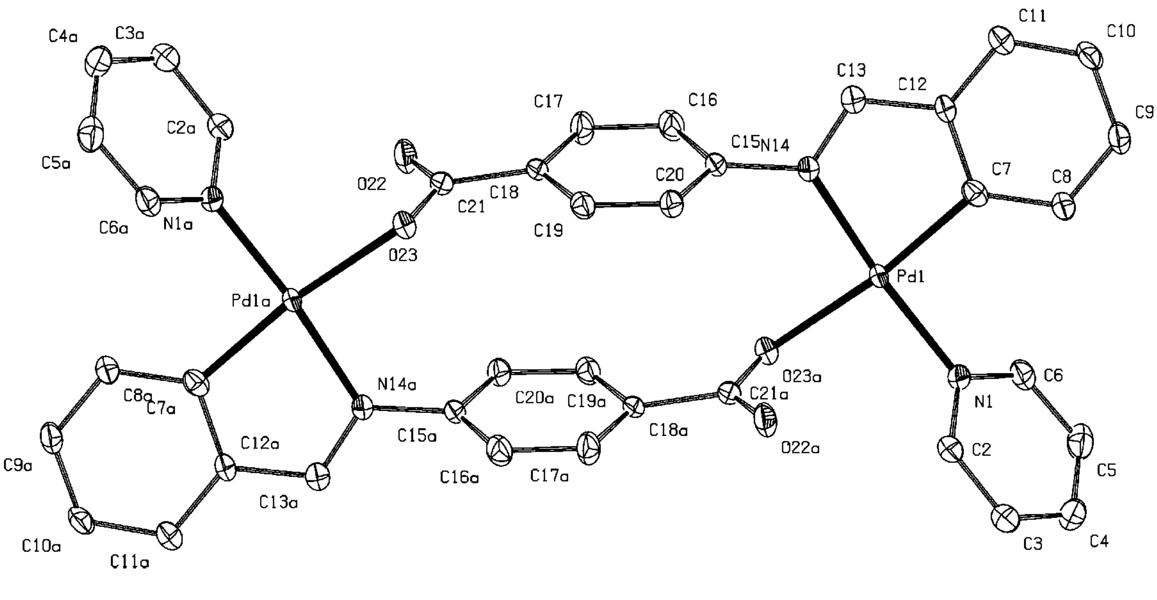


Figure 2. Molecular structure of compound **4a**.

and **5b** (see below) are, to the best of our knowledge, the first cases in which the metalated molecule acts as a dianionic bridging (C,N,O) ligand between two palladium atoms. In the literature only few examples of dinuclear compounds in which the metalated ligand acts as a dianionic bridging ligand are described.[18] In this context it should be noted that cyclopalladated and cycloplatinated compounds containing terdentate (C,N,O), (C,N,S), and (C,N,N) ligands adopt tetranuclear or trinuclear structures, generated by self-assembly of the metalated units.[19] The new structures here described, containing two square-planar palladium atoms, strongly bonded to a dianionic

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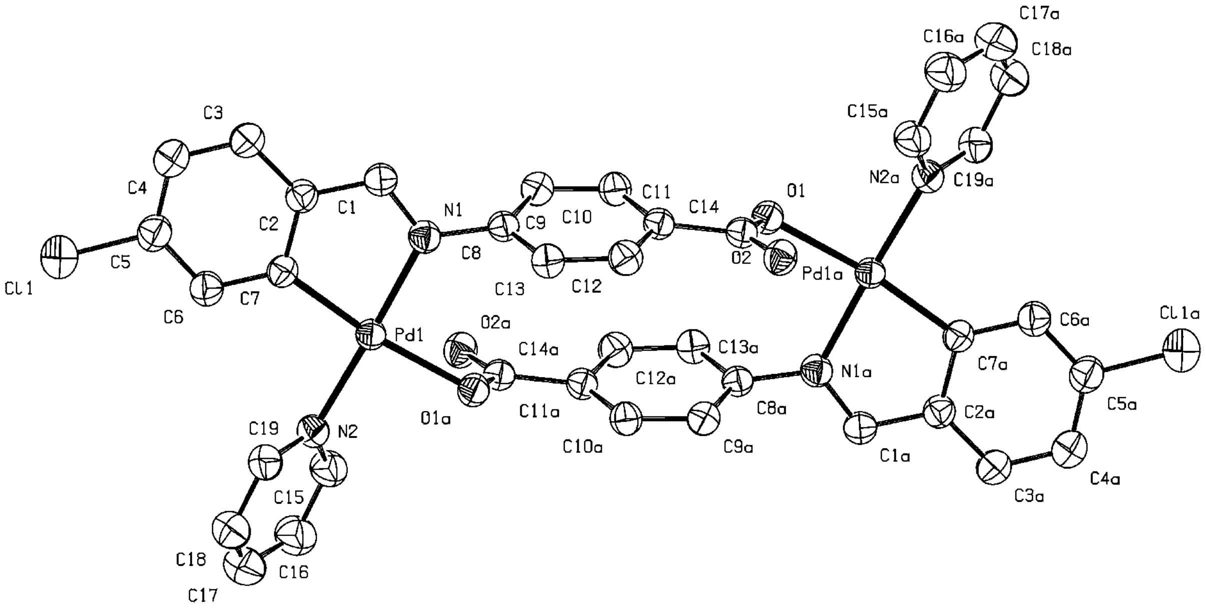

Figure 3. Molecular structure of compound **4d**.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for 4d and 5b

Compound **4d**	
Pd(1)−C(7)	1.974(2)
Pd(1)−N(1)	2.028(2)
Pd(1)−N(2)	2.044(2)
Pd(1)−O(1)	2.1257(17)
O(1)−C(14)#1	1.274(3)
O(2)−C(14)	1.254(3)
C(7)−Pd(1)−N(1)	81.54(9)
C(7)−Pd(1)−N(2)	96.35(9)
N(1)−Pd(1)−O(1)	91.63(7)
N(2)−Pd(1)−O(1)	90.47(7)
C(1)−N(1)−C(8)	119.8(2)
Compound **5b**	
Pd(1)−C(1)	2.012(2)
Pd(1)−N(1)	2.101(2)
Pd(1)−O(1)#1	2.1062(18)
Pd(1)−P(1)	2.2539(11)
O(1)−C(14)	1.286(3)
N(1)−C(7)	1.268(3)
C(1)−Pd(1)−N(1)	81.47(10)
N(1)−Pd(1)−O(1)#1	89.70(8)
C(1)−Pd(1)−P(1)	95.76(8)
O(1)#1−Pd(1)−P(1)	92.98(6)
C(7)−N(1)−C(8)	120.4(2)

imine molecule, and two labile pyridine ligands can be potentially useful new building blocks in supramolecular chemistry. Note that the coordination of the carboxylate group to the palladium atom in compounds **4** and **5** also explains the insolubility of these complexes in water, even at pH = 10.

On the other hand, reaction of dimer **2** with PPh_3 in methanol afforded the dinuclear complex $[Pd(C-N-O)(PPh_3)]_2$, **5**. IR spectra of **4** and **5** showed $\nu(CO_2)_{asymm}$ and $\nu(CO_2)_{symm}$ separated by 220−240 cm^{-1}, consistent with unidentate acetato coordination.[20] In the proton NMR of compounds **5**, the aromatic protons of the palladated ring were high-field shifted, which is ascribed to the *cis* disposition between the phosphine and the metalated carbon,[21] and the HC=N proton was high-field shifted as an indication of the imine *E* form.[22]

Slow crystallization of a $CDCl_3$ solution of **5b** affords crystals suitable for X-ray structure determination. X-ray crystallographic studies of **5b** (Figure 4) confirmed the structure suggested by NMR data, the *E* form adopted by the imine and the *cis* arrangement of the PPh_3 in relation to the palladated carbon. **5b** is a dinuclear cyclopalladated complex containing the metalated imine as a dianionic bridging ligand between two palladium atoms. The palladium atom is in a square-planar environment, coordinated to carbon, nitrogen, oxygen, and phosphorus atoms. The distances between palladium and the coordinated atoms are similar to those reported for other cyclopalladated compounds (Table 2).[16] The angles between adjacent atoms lie in the range 81.47(10)° [C(1)PdN] and 95.76(9)° [C(1)PdP]. The five-membered metallacycle is approximately planar, as suggested by the sum of internal angles, 539.4°, which is close to 540°.[15]

The distance between the methinic proton and the chlorine atom in *ortho* position on the aromatic ring of 2.757 Å confirms the intramolecular interaction between these atoms, suggested by proton NMR spectra (see before).

Crystal structures of compounds **4a**, **4d**, and **5b** reveal intermolecular $\pi-\pi$ stacking interactions among the aromatic moieties derived from 4-aminobenzoic acid [**4a**: centroid-to-centroid distance = 3.984(3) Å, and interplane angle = 0.00°;

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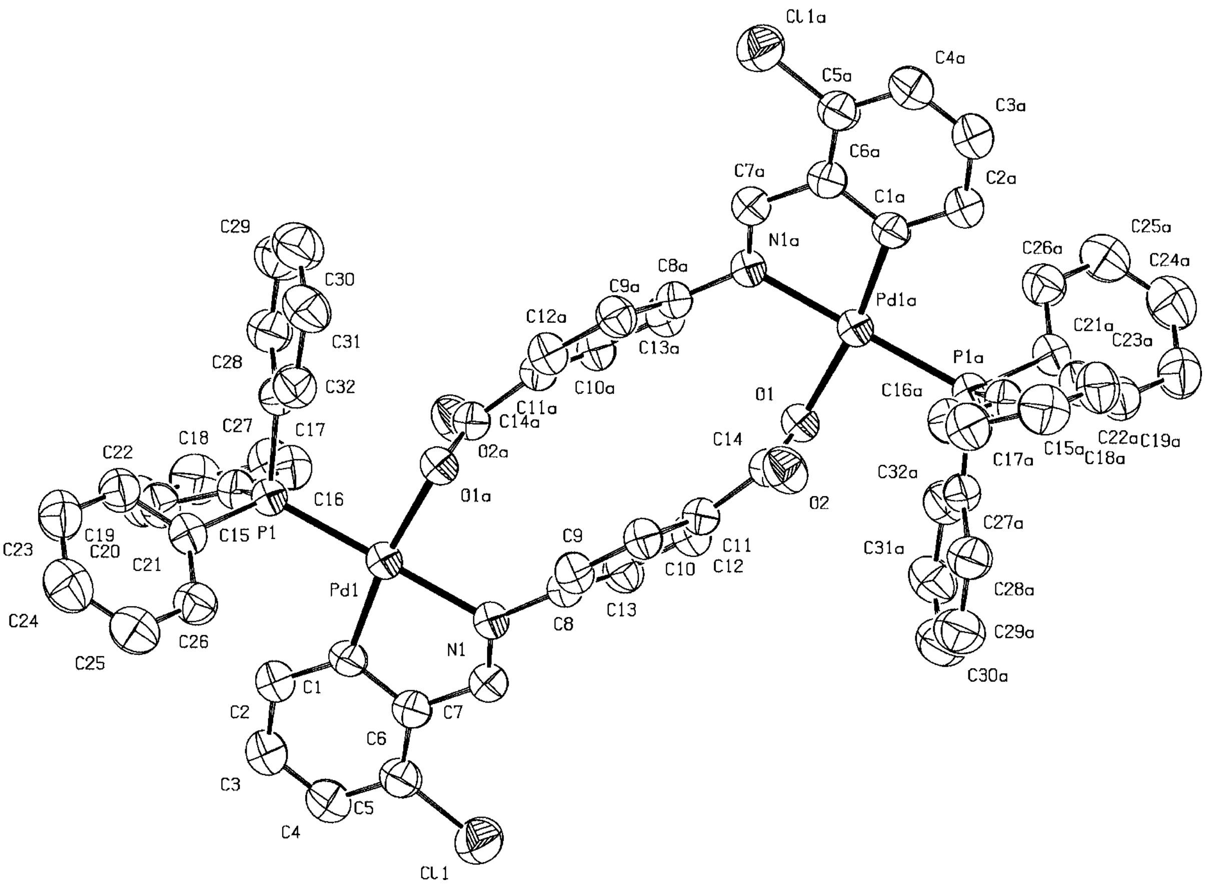

Figure 4. Molecular structure of compound **5b**.

4d: centroid-to-centroid distance = 3.802(2) Å, and interplane angle = 0.00°; and **5b**: centroid-to-centroid distance = 3.790(2) Å, and interplane angle = 0.00°].

It is noteworthy that complexes **2** can also be crystallized from acetic acid solutions of compounds **5** after several days. This is a remarkable result because the acetato ligand coordinates to Pd(II) by replacing the soft PPh_3 ligand, and thus the Pd−P is more labile than Pd−C and Pd−N bonds in acid media, establishing thereby the great stability of the metallacycles here described.

Concluding Remarks

In this contribution we described the action of palladium acetate on carboxylated Schiff bases. These reactions lead to new metallacycles, some of them hydrosoluble. Furthermore, cyclopalladated derivatives containing the metalated molecule as a dianionic bridging ligand between two palladium atoms have been obtained. In contrast with the high number of dinuclear cyclometalated compounds described with an acetato-bridging ligand in the CSD, to the best of our knowledge, the structures here described for compounds **4a**, **4d**, and **5b** are the first cases in which the metalated molecule acts as a dianionic (C,N,O) bridging ligand between two palladium atoms.

Experimental Section

All solvents were dried and degassed by standard methods. All chemicals were of commercial grade and used as received.

^1H NMR spectra were registered on a Varian Unity 300 and a Varian Mercury 400 instruments. $^{31}P\{^1H\}$NMR spectra were recorded on a Bruker DRX 250 spectrometer, operating at 101.26 MHz. Chemical shifts (in ppm) were measured relative to $SiMe_4$ for ^1H and to 85% H_3PO_4 for ^{31}P. Microanalyses were performed by the Servei de Recursos Científics i Tècnics de la Universidad Rovira i Virgili (Tarragona). Infrared spectra were recorded as KBr disks on a FTIR Nicolet 5700 spectrometer. MALDI TOF(+) spectra were recorded on a VOYAGER-DE-RP spectrometer (with a dithranol or a 2,5-dihydroxybenzoic acid matrix). CI spectra were recorded on a ThermoFinnigan TRACE DSQ spectrometer, using NH_3 as reactive gas, and electrospray spectra on an Agilent LC/MSD-TOF spectrometer, equipped with a dual sprayer source using purine (m/z = 121.050873) and HP-0921 (m/z = 922.009798) as internal reference masses.

Preparation of Compounds. Imine 1a. A mixture of 4-aminobenzoic acid (2739 mg, 19.84 mmol), benzaldehyde (2127 mg, 20.04 mmol), glacial acetic acid (two drops), and toluene (150 mL) was refluxed for 4 h. After the reaction mixture was cooled to room temperature, the white solid obtained was filtered, washed with toluene, and recrystallized from methanol to obtain **1a**, 3624 mg (80% yield). ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 8.45 (s, 1H, H^3), 8.15 (d, AA′XX′, 2H, H^1, J_{HH} = 8.6 Hz), 7.93 (d, 2H, H^4, J_{HH} = 8.9 Hz), 7.54−7.48 (m, 3H, $H^5 + H^6$), 7.24 (d, AA′XX′, 2H, H^2, J_{HH} = 8.6 Hz). IR (KBr), ν (cm^{-1}): 1684 (COOH), 1623 (C=N). MS-CI (NH_3), m/z: $[M + H]^+$ = 226.6. Anal. Calcd for $C_{14}H_{11}NO_2$: C 74.65, H 4.92, N 6.22. Found: C 74.2, H 4.9, N 6.4.

Imine 1b. A mixture of 4-aminobenzoic acid (778 mg, 5.67 mmol), 2-chlorobenzaldehyde (904 mg, 6.43 mmol), glacial acetic acid (one drop), and toluene (40 mL) was refluxed for 9 h in a flask connected to a Dean-Stark apparatus. After the reaction mixture was allowed to cool to room temperature, the white solid obtained was filtered, washed with diethyl ether, and dried under vacuum to obtain **1b**, 1302 mg (88% yield). ^1H NMR (400 MHz, DMSO-d_6, 298 K), δ (ppm): 8.87 (*s*, 1H, H^3), 8.17 (d, 1H, H^7, J_{HH} = 7.4 Hz), 8.00 (d, AA′XX′, 2H, H^1, J_{HH} = 8.3 Hz), 7.63−7.56 (m, 2H, $H^4 + H^5$), 7.55−7.47 (m, 1H, H^6), 7.35 (d, AA′XX′, 2H,

H^2, J_{HH} = 8.3 Hz). IR (KBr), ν (cm^{-1}): 1680 (COOH), 1620 (C=N). MS-ESI (+) {H_2O/CH_3OH (1:1)}, *m/z*: [M + H]$^+$ = 260.3. Anal. Calcd for $C_{14}H_{10}ClNO_2$: C 64.75, H 3.88, N 5.39. Found: C 65.6, H 3.4, N 5.4.

Imine 1c. A mixture of 4-aminobenzoic acid (788 mg, 5.75 mmol), 3-chlorobenzaldehyde (911 mg, 6.48 mmol), glacial acetic acid (one drop), and toluene (30 mL) was heated under reflux for 8 h in a flask provided with a Dean-Stark apparatus. After the reaction mixture was cooled to room temperature, the white solid obtained was filtered off, washed with diethyl ether, and dried under vacuum to isolate **1c**, 1329 mg (89% yield). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K), δ (ppm): 8.66 (*s*, 1H, H^3), 8.03−7.96 (m, 3H, H^1 + H^8), 7.92 (d, 1H, H^6, J_{HH} = 7.5 Hz), 7.67−7.54 (m, 2H, H^4 + H^5), 7.34 (d, AA′XX′, 2H, H^2, J_{HH} = 8.5 Hz). IR (KBr), ν (cm^{-1}): 1689 (COOH), 1635 (C=N). MS-ESI (+) {H_2O/CH_3OH (1:1)}, *m/z*: [M + H]$^+$ = 260.4. Anal. Calcd for $C_{14}H_{10}ClNO_2$: C 64.75, H 3.88, N 5.39. Found: C 64.5, H 3.9, N 5.4.

Imine 1d. A mixture of 4-aminobenzoic acid (791 mg, 5.77 mmol), 4-chlorobenzaldehyde (814 mg, 5.79 mmol), glacial acetic acid (one drop) and toluene (40 mL) was refluxed for 24 h in a flask equipped with a Dean−Stark apparatus. After the reaction mixture was cooled to room temperature, the white solid obtained was filtered off, washed with diethyl ether and dried under vacuum to obtain **1d**, 1333 mg (89% yield). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K), δ (ppm): 8.66 (*s*, 1H, H^3), 7.99 (d, AA′XX′, 2H, H^1, J_{HH} = 8.7 Hz), 7.98 (d, 2H, H^5, J_{HH} = 8.4 Hz), 7.62 (d, 2H, H^4, J_{HH} = 8.4 Hz), 7.33 (d, AA′XX′, 2H, H^2, J_{HH} = 8.7 Hz). IR (KBr), ν (cm^{-1}): 1681 (COOH), 1624 (C=N). MS-ESI (+) {H_2O/CH_3OH (1:1)}, *m/z*: [M + H]$^+$ = 260.3. Anal. Calcd for $C_{14}H_{10}ClNO_2$: C 64.75, H 3.88, N 5.39. Found: C 64.5, H 3.8, N 5.4.

Imine 1e. A mixture of 4-aminobenzoic acid (1371 mg, 10.00 mmol) and 4-dimethylamino-benzaldehyde (1491 mg, 9.99 mmol) in ethanol (75 mL) was refluxed for 3 h. After the reaction mixture was cooled to room temperature, the yellow solid obtained was filtered and dried under vacuum to obtain **1e**, 2108 mg (79% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 8.31 (*s*, 1H, H^3), 8.09 (d, AA′XX′, 2H, H^1, J_{HH} = 8.3 Hz), 7.78 (d, 2H, H^4, J_{HH} = 8.9 Hz), 7.21 (d, AA′XX′, 2H, H^2, J_{HH} = 8.3 Hz), 6.74 (d, 2H, H^5, J_{HH} = 9.0 Hz), 3.08 (*s*, 6H, $N(CH_3)_2$). IR (KBr), ν (cm^{-1}): 1681 (COOH), 1625 (C=N). MS-CI (NH_3), *m/z*: [M + H]$^+$ = 269.6, [M + H − $N(CH_3)_2$]$^+$ = 225.6. Anal. Calcd for $C_{16}H_{16}N_2O_2$: C 71.62, H 6.01, N 10.44. Found: C 71.8, H 6.1, N 10.4.

Imine 1f. A mixture of 4-aminobenzoic acid (1377 mg, 10.04 mmol) and 4-nitrobenzaldehyde (1511 mg, 10.00 mmol), glacial acetic acid (one drop), and toluene (75 mL) was refluxed for 3 days in a flask connected to a Dean−Stark apparatus. After the reaction mixture was cooled to room temperature, the yellow solid was recovered by filtration, washed with diethyl ether, and dried under vacuum to obtain **1f**, 2426 mg (89% yield). ^{1}H NMR (400 MHz, acetone-d_6, 298 K), δ (ppm): 8.83 (s, 1H, H^3), 8.41 (d, 2H, H^5, J_{HH} = 8.8 Hz), 8.28 (d, 2H, H^4, J_{HH} = 8.8 Hz), 8.11 (d, AA′XX′, 2H, H^1, J_{HH} = 8.6 Hz), 7.41 (d, AA′XX′, 2H, H^2, J_{HH} = 8.6 Hz). IR (KBr), ν (cm^{-1}): 1681 (COOH), 1630 (C=N). MS-ESI (+) {H_2O/CH_3OH (1:1)}, *m/z*: [M + H]$^+$ = 270.2. Anal. Calcd for $C_{14}H_{10}N_2O_4$: C 62.22, H 3.73, N 10.37. Found: C 62.3, H 3.8, N 10.4.

Cyclometalation Reactions. Metalation of 1a. A mixture of imine **1a** (360 mg, 1.60 mmol) and palladium acetate (349 mg, 1.55 mmol) in 35 mL of glacial acetic acid was stirred at 60 °C for 6 h under nitrogen atmosphere. The orange solid obtained was filtered, washed with ethanol and acetone, and dried under vacuum to obtain **2a**, 505 mg (83% yield). IR (KBr), ν (cm^{-1}): 1700 (COOH), 1570 (COO), 1416 (COO). MS-MALDI TOF (+) (DTH), *m/z*: [M/2 − OAc + DTH]$^+$ = 555.9, [M/2 − OAc]$^+$ = 329.9. Anal. Calcd for $C_{32}H_{26}N_2O_8Pd_2$: C 49.31, H 3.36, N 3.59. Found: C 49.5, H 3.6, N 3.5.

Synthesis of 3a in D$_2$O Solution. The addition of pyridine-d_5 to a suspension of **2a** in D_2O in 25:1 ratio affords the corresponding mononuclear compound **3a**. ^{1}H NMR (400 MHz, D_2O, 298 K), δ (ppm): 8.21 (s, 1H, H^3), 7.58−7.55 (m, 1H, H^7), 7.56 (d, AA′XX′, 2H, H^1, J_{HH} = 8.5 Hz), 7.25 (t, 1H, H^6, J_{HH} = 7.5 Hz), 7.11 (td, 1H, H^5, J_{HH} = 7.6 Hz, J_{HH} = 1.2 Hz), 6.93 (d, 2H, AA′XX′, H^2, J_{HH} = 8.4 Hz), 6.24 (d, 1H, H^4, J_{HH} = 7.7 Hz). MS-ESI (+) {H_2O/CH_3OH (1:1)}, of a chloroform solution with nondeuterated pyridine derivative, *m/z*: [M + H]$^+$ = 488.1, [M + H − py]$^+$ = 409.0.

Metalation of 1b. A mixture of imine **1b** (347 mg, 1.34 mmol) and palladium acetate (300 mg, 1.34 mmol) in 50 mL of glacial acetic acid was stirred at 60 °C for 24 h, and the resulting solution was concentrated at reduced pressure. The orange solid obtained after addition of hexane was filtered and dried under vacuum to obtain **2b**, 536 mg (95% yield). IR (KBr), ν (cm^{-1}): 1700 (COOH), 1574 (COO), 1394 (COO). MS-ESI (+) {H_2O/CH_3OH (1:1)}, *m/z*: [M/2 − OAc + CH_3CN]$^+$ = 407.4, [M/2 − OAc + 2 CH_3CN]$^+$ = 448.4. Anal. Calcd for $C_{32}H_{24}Cl_2N_2O_8Pd_2$: C 45.31, H 2.85, N 3.30. Found: C 45.7, H 2.6, N 3.1.

Synthesis of 3b in D$_2$O Solution. The addition of pyridine-d_5 to a suspension of **2b** in D_2O in 25:1 ratio affords the corresponding mononuclear compound **3b**. ^{1}H NMR (400 MHz, D_2O, 298 K), δ (ppm): 8.40 (s, 1H, H^3), 7.58 (d, AA′XX′, 2H, H^1, J_{HH} = 8.2 Hz), 7.18 (d, 1H, H^6, J_{HH} = 7.7 Hz), 7.06 (t, 1H, H^5, J_{HH} = 7.7 Hz), 6.89 (d, AA′XX′, 2H, H^2, J_{HH} = 8.2 Hz), 6.06 (d, 1H, H^4, J_{HH} = 7.7 Hz). MS-ESI (+) {H_2O/CH_3OH (1:1)}, of a chloroform solution with nondeuterated pyridine derivative, *m/z*: [M + H]$^+$ = 522.0, [M + H − py]$^+$ = 443.0.

Metalation of 1c. A mixture of imine **1c** (174 mg, 0.67 mmol) and palladium acetate (150 mg, 0.67 mmol) in 25 mL of glacial acetic acid was stirred at 60 °C for 6 h under nitrogen, and the resulting solution was concentrated under vacuum. The orange solid obtained after addition of hexane was filtered off, washed with glacial acetic acid, and dried under vacuum to obtain **2c**, 250 mg (88% yield). IR (KBr), ν (cm^{-1}): 1711 (COOH), 1582 (COO), 1416 (COO). MS-ESI (+) {H_2O/CH_3CN (1:1)}, *m/z*: [M/2 − OAc + CH_3CN]$^+$ = 405.3, [M/2 − OAc + 2 CH_3CN]$^+$ = 448.3. Anal. Calcd for $C_{32}H_{24}Cl_2N_2O_8Pd_2$: C 45.31, H 2.85, N 3.30. Found: C 45.6, H 2.6, N 3.4.

Synthesis of 3c in D$_2$O Solution. The addition of pyridine-d_5 to a suspension of **2c** in D_2O in 25:1 ratio affords the corresponding mononuclear compound **3c**. ^{1}H NMR (400 MHz, D_2O, 298 K), δ (ppm): 8.08 (s, 1H, H^3), 7.57 (d, AA′XX′, 2H, H^1, J_{HH} = 8.4 Hz), 7.44 (d, 1H, H^7, J_{HH} = 2.1 Hz), 7.02 (dd, 1H, H^5, J_{HH} = 8.2 Hz, J_{HH} = 2.1 Hz), 6.86 (d, AA′XX′, 2H, H^2, J_{HH} = 8.4 Hz), 6.03 (d, 1H, H^4, J_{HH} = 8.2 Hz). MS-ESI (+) {H_2O/CH_3OH (1:1)}, of a chloroform solution with nondeuterated pyridine derivative, *m/z*: [M + H]$^+$ = 522.0, [M + H − py]$^+$ = 443.0.

Metalation of 1d. A mixture of imine **1d** (349 mg, 1.34 mmol) and palladium acetate (304 mg, 1.35 mmol) in 50 mL of glacial acetic acid was stirred at 60 °C for 6 h under nitrogen, and the resulting solution was concentrated in vacuo. The red solid obtained after addition of hexane was filtered, washed with glacial acetic acid and hexane, and dried under vacuum to obtain **2d**, 486 mg (85% yield). IR (KBr), ν (cm^{-1}): 1718 (COOH), 1585 (COO), 1416 (COO). MS-ESI (+) {H_2O/CH_3CN (1:1)}, *m/z*: [M/2 − OAc + CH_3CN]$^+$ = 407.4, [M/2 − OAc + 2 CH_3CN]$^+$ = 448.4. Anal. Calcd for $C_{32}H_{24}Cl_2N_2O_8Pd_2$: C 45.31, H 2.85, N 3.30. Found: C 45.2, H 2.8, N 3.4.

Synthesis of 3d in D$_2$O Solution. Mononuclear compound **3d** was synthesized by adding pyridine-d_5 to a suspension of **2d** in D_2O in 25:1 ratio. ^{1}H NMR (400 MHz, D_2O, 298 K), δ (ppm): 8.16 (*s*, 1H, H^3), 7.56 (d, AA′XX′, 2H, H^1, J_{HH} = 8.5 Hz), 7.46 (d, 1H, H^7, J_{HH} = 8.1 Hz), 7.23 (dd, 1H, H^6, J_{HH} = 8.0 Hz, J_{HH} = 1.8 Hz), 6.90 (d, AA′XX′, 2H, H^2, J_{HH} = 8.5 Hz), 6.07 (d, 1H, H^4, J_{HH} = 1.8 Hz). MS-ESI (+) {H_2O/CH_3OH (1:1)}, of a chloroform solution with nondeuterated pyridine derivative, *m/z*: $[M + H]^+ = 522.0$, $[M + H - py]^+ = 443.0$.

Metalation of 1e. A mixture of imine **1e** (182 mg, 0.68 mmol) and palladium acetate (152 mg, 0.68 mmol) in 25 mL of glacial acetic acid was stirred at 60 °C for 4 h under nitrogen, and the resulting solution was concentrated in vacuo. The yellow solid obtained after addition of hexane was filtered, washed with hexane, and dried under vacuum to obtain **2e**, 253 mg (86% yield). IR (KBr), ν (cm^{-1}): 1684 (COOH), 1612 (C=N), 1571 (COO), 1419 (COO). MS-MALDI TOF (DTH), *m/z*: $[M/2 - OAc + DTH]^+ = 598.7$, $[M/2 - OAc]^+ = 372.8$. Anal. Calcd for $C_{36}H_{36}N_4O_8Pd_2$: C 49.96, H 4.19, N 6.47. Found: C 49.5, H 4.0, N 6.3.

Synthesis of 3e in D$_2$O Solution. The addition of pyridine-*d*$_5$ to a suspension of **2e** in D$_2$O in 25:1 ratio affords the corresponding mononuclear compound **3e**. ^{1}H NMR (400 MHz, D$_2$O, 298 K), δ (ppm): 8.00 (s, 1H, H^3), 7.54 (d, AA′XX′, 2H, H^1, $J_{HH} = 8.4$ Hz), 7.44 (d, 1H, H^7, $J_{HH} = 8.2$ Hz), 6.90 (d, AA′XX′, 2H, H^2, $J_{HH} = 8.2$ Hz), 6.53 (d, 1H, H^6, $J_{HH} = 8.2$ Hz), 5.34 (d, 1H, H^4, $J_{HH} = 1.6$ Hz), 2.78 (s, 6H, N(CH$_3$)$_2$). MS-ESI (+) {H$_2$O/CH$_3$OH (1:1)}, of a chloroform solution with nondeuterated pyridine derivative, *m/z*: $[M + H]^+ = 531.1$, $[M + H - py]^+ = 452.1$.

Dinuclear Pyridine Derivatives, 4. Compound 4a. A suspension of **2a** (69 mg, 0.09 mmol) in 25 mL of methanol was treated with an excess of pyridine (44 mg, 0.56 mmol). After stirring the mixture at room temperature for 2 h, the resulting precipitate was filtered and washed with further portions of methanol. It gave a beige solid, which upon recrystallization in chloroform led to the desired product **4a**, which was gently powdered in a mortar and thoroughly dried in vacuo (30 mg, 41% yield). IR (KBr), ν (cm^{-1}): 1609 (C=N), 1597 (C=O), 1369 (C−O). Anal. Calcd for $C_{38}H_{28}N_4O_4Pd_2$: C 55.83, H 3.45, N 6.85. Found: C 55.56, H 3.7, N 7.0.

Compound 4b. A mixture containing **2b** (69 mg, 0.08 mmol), an excess of pyridine (45 mg, 0.57 mmol), and 25 mL of chloroform was stirred at ambient temperature for 3 days. The solvent was then removed under reduced pressure, and after addition of diethyl ether, an orange solid was obtained. The product was recovered by filtration and purified by recrystallization in chloroform, leading to yellow crystalline solid **4b**, which was gently ground in an agate mortar and thoroughly dried in vacuo (45 mg, 62% yield). IR (KBr), ν (cm^{-1}): 1604 (C=O), 1384 (C−O). Anal. Calcd for $C_{38}H_{26}Cl_2N_4O_4Pd_2$: C 51.49, H 2.96, N 6.32. Found: C 51.2, H 2.7, N 6.1.

Compound 4c. To an orange suspension of **2c** (93 mg, 0.11 mmol) in chloroform (30 mL) was added an excess of pyridine (52 mg, 0.66 mmol). The reaction was completed after 2 h of stirring. The precipitated solid was filtered, dried under vacuum, and finally redissolved in chloroform. Slow evaporation of the chloroform solution afforded yellow crystals of **4c**, which were pulverized in a mortar and thoroughly dried in vacuo (70 mg, 72% yield). IR (KBr), ν (cm^{-1}): 1597 (C=O), 1370 (C−O). Anal. Calcd for $C_{38}H_{26}Cl_2N_4O_4Pd_2$: C 51.49, H 2.96, N 6.32. Found: C 51.7, H 2.8, N 6.1.

Compound 4d. Compound **4d** was synthesized by adding an excess of pyridine (36 mg, 0.46 mmol) to a suspension of **2d** (65 mg, 0.08 mmol) in 25 mL of methanol. After 1 h of stirring, the beige suspension obtained was filtered off, washed with further portions of methanol, and dried under vacuum. The required product recrystallized from chloroform, affording **4d** as a yellow crystalline solid, which was reduced to powder in an agate mortar and thoroughly dried in vacuo (41 mg, 60% yield). IR (KBr), ν (cm^{-1}): 1607 (C=N), 1598 (C=O), 1366 (C−O). Anal. Calcd for $C_{38}H_{26}Cl_2N_4O_4Pd_2$: C 51.49, H 2.96, N 6.32. Found: C 51.6, H 3.0, N 6.6.

Compound 4e. A brown suspension of **2e** (60 mg, 0.07 mmol) in 25 mL of chloroform was heated under reflux conditions for 1 day with an excess of pyridine (41 mg, 0.52 mmol). After this period, the undissolved materials were removed by filtration and discarded. The deep yellow filtrate was concentrated to dryness on a rotatory evaporator to give an orange solid after adding diethyl ether. The product was filtered off, dried under vacuum, and finally redissolved in chloroform. Slow evaporation of the chloroform solution produced an orange powdery solid, **4e**, which was milled in a mortar and thoroughly dried in vacuo (23 mg, 37% yield). IR (KBr), ν (cm^{-1}): 1567 (C=O), 1348 (C−O). Anal. Calcd for $C_{42}H_{38}N_6O_4Pd_2$: C 55.82, H 4.24, N 9.30. Found: C 55.5, H 4.4, N 9.2.

Compounds Containing PPh$_3$. Compound 5a. A mixture of **2a** (155 mg, 0.20 mmol) and triphenylphosphine (104 mg, 0.40 mmol) in 30 mL of methanol was stirred at room temperature for 2 h. The pale pink solid obtained was filtered, washed with methanol, and dried under vacuum to obtain **5a**, 180 mg (76% yield). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K), δ (ppm): 8.12 (d, 1H, H^3, $J_{HP} = 7.0$ Hz), 7.83 (ddd, 6H, *ortho*-PPh$_3$, $J_{HP} = 11.8$ Hz, $J_{HH} = 8.0$ Hz, $J_{HH} = 1.5$ Hz), 7.42−7.30 (m, 10H, *meta*-PPh$_3$ + *para*-PPh$_3$ + H^7), 7.19 (d, AA′XX′, 2H, H^1, $J_{HH} = 8.5$ Hz), 6.93 (*td*, 1H, H^6, $J_{HH} = 7.3$ Hz, $J_{HH} = 0.9$ Hz), 6.91 (d, AA′XX′, 2H, H^2, $J_{HH} = 8.4$ Hz), 6.62 (td, 1H, H^5, $J_{HH} = 7.3$ Hz, $J_{HH} = 1.2$ Hz), 6.52 (dd, 1H, H^4, $J_{HH} = 7.3$ Hz, $J_{HP} = 5.6$ Hz). ^{31}P{^{1}H} NMR (101 MHz, CH$_2$Cl$_2$, 298 K), δ (ppm): 39.22 (s). IR (KBr), ν (cm^{-1}): 1618 (C=N), 1599 (COO), 1361 (COO), 1096 (coordinated PPh$_3$, X-sensitive mode). MS-MALDI TOF (+) (DHB), *m/z*: $[M + H - PPh_3]^+ = 921.2$, $[M/2 + H]^+ = 592.2$. Anal. Calcd for $C_{64}H_{48}N_2O_4P_2Pd_2$: C 64.93, H 4.09, N 2.37. Found: C 64.8, H 3.9, N 2.4.

Compound 5b. A mixture of **2b** (100 mg, 0.12 mmol) and triphenylphosphine (64 mg, 0.24 mmol) in 40 mL of methanol was stirred at room temperature for 24 h. The white solid obtained was filtered, washed with methanol, and dried under vacuum to obtain **5b**, 116 mg (79% yield). ^{1}H NMR (400 MHz, CDCl$_3$, 298 K), δ (ppm): 8.62 (d, 1H, H^3, $J_{HP} = 7.0$ Hz), 7.84−7.79 (m, 6H, *ortho*-PPh$_3$), 7.42−7.32 (m, 9H, *meta*-PPh$_3$ + *para*-PPh$_3$), 7.18 (d, AA′XX′, 2H, H^1, $J_{HH} = 8.4$ Hz), 6.92 (d, AA′XX′, 2H, H^2, $J_{HH} = 8.4$ Hz), 6.86 (dd, 1H, H^6, $J_{HH} = 7.6$ Hz, $J_{HH} = 0.6$ Hz), 6.54 (*t*, 1H, H^5, $J_{HH} = 7.6$ Hz), 6.40 (dd, 1H, H^4, $J_{HH} = 7.6$ Hz, $J_{HP} = 5.6$ Hz). ^{31}P{^{1}H} NMR (101 MHz, CHCl$_3$, 298 K), δ (ppm): 39.21 (s). IR (KBr), ν (cm^{-1}): 1602 (COO), 1366 (COO), 1096 (coordinated PPh$_3$, X-sensitive mode). MS-MALDI TOF (+) (DTH), *m/z*: $[M - PPh_3 + H]^+ = 990.7$, $[M/2 + H]^+ = 627.8$. Anal. Calcd for $C_{64}H_{46}Cl_2N_2O_4P_2Pd_2$: C 61.36, H 3.70, N 2.24. Found: C 61.5, H 3.7, N 2.1.

Compound 5c. A mixture of **2c** (100 mg, 0.12 mmol) and triphenylphosphine (65 mg, 0.25 mmol) in 40 mL of methanol was stirred at room temperature for 2 h. The white solid obtained was filtered, washed with methanol, and dried under vacuum to obtain **5c**, 122 mg (83% yield). ^{1}H NMR (400 MHz, CDCl$_3$, 298 K), δ (ppm): 8.10 (d, 1H, H^3, $J_{HP} = 7.0$ Hz), 7.80 (dd, 6H, *ortho*-PPh$_3$, $J_{HP} = 11.4$ Hz, $J_{HH} = 7.3$ Hz), 7.44−7.30 (m, 10H, *meta*-PPh$_3$ + *para*-PPh$_3$ + H^7), 7.19 (d, AA′XX′, 2H, H^1, $J_{HH} = 8.3$ Hz), 6.90 (d, AA′XX′, 2H, H^2, $J_{HH} = 8.3$ Hz), 6.61 (dd, 1H, H^5, $J_{HH} = 8.3$ Hz, $J_{HH} = 2.2$ Hz), 6.43 (dd, 1H, H^4, $J_{HH} = 8.3$ Hz, $J_{HP} = 5.1$ Hz). ^{31}P{^{1}H} NMR (101 MHz, CDCl$_3$, 298 K), δ (ppm): 41.24 (s). IR (KBr), ν (cm^{-1}): 1607 (COO), 1358 (COO), 1096 (coordinated PPh$_3$, X-sensitive mode). MS-MALDI TOF (+) (DTH), *m/z*: $[M/2 + H]^+ = 629.9$, $[M - PPh_3 + H]^+ = 992.9$. Anal. Calcd for $C_{64}H_{46}Cl_2N_2O_4P_2Pd_2$: C 61.36, H 3.70, N 2.24. Found: C 61.1, H 3.7, N 2.1.

Compound 5d. A mixture of **2d** (100 mg, 0.12 mmol) and triphenylphosphine (65 mg, 0.24 mmol) in 40 mL of methanol was stirred at room temperature for 1 h. The white solid obtained was filtered, washed with methanol, and dried under vacuum to obtain **5d**, 103 mg (70% yield). ^{1}H NMR (400 MHz, CDCl$_3$, 298 K), δ (ppm): 8.10 (d, 1H, H^3, $J_{HP} = 6.9$ Hz), 7.80 (dd, 6H, *ortho*-PPh$_3$, $J_{HP} = 11.7$ Hz, $J_{HH} = 7.2$ Hz), 7.44−7.34 (m, 9H, *meta*-PPh$_3$ +

Table 3. Crystal Data and Structure Refinement for 2c and 4a

	2c	**4a**
empirical formula	$C_{40}H_{40}Cl_2N_2O_{16}Pd_2 \cdot 4(CH_3COOH)$	$C_{38}H_{18}D_{10}N_4O_4Pd_2 \cdot 2(CDCl_3)$
temperature [K]	203(2)	100(2)
wavelength [Å]	0.71073	0.71069
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	$P\bar{1}$
a [Å]	26.150(12)	12.4786(6)
b [Å]	10.014(3)	8.7293(5)
c [Å]	17.261(7)	19.0202(11)
α [deg]	90	90
β [deg]	90.54(2)	102.347(3)
γ [deg]	90	90
volume [$Å^3$]	4520(3)	2023.94(19)
Z	4	2
calc density [Mg/m^3]	1.600	1.733
abs coeff [mm^{-1}]	0.984	1.332
F(000)	2192	1048
cryst size [mm]	0.2 × 0.09 × 0.09	0.16 × 0.10 × 0.07
no. reflns collected	23 566	29 624
goodness-of-fit on F^2	1.148	1.052
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0356 wR2 = 0.0848	R1 = 0.0302 wR2 = 0.0674
R indices (all data)	R1 = 0.0459 wR2 = 0.0895	R1 = 0.0443 wR2 = 0.0746

Table 4. Crystal Data and Structure Refinement for 4d and 5b

	4d	**5b**
empirical formula	$C_{38}H_{16}D_{10}Cl_2N_4O_4Pd_2 \cdot 4(CDCl_3) \cdot 3(H_2O)$	$C_{68}H_{50}Cl_{14}N_2O_4P_2Pd_2 \cdot 4(CDCl_3)$
temperature [K]	203(2)	203(2)
wavelength [Å]	0.71073	0.71073
cryst syst	monoclinic	triclinic
space group	*C*2/*c*	$P\bar{1}$
a [Å]	30.086(10)	10.808(5)
b [Å]	10.265(2)	12.773(3)
c [Å]	18.179(4)	13.722(5)
α [deg]	90	96.55(3)
β [deg]	97.66(2)	94.76(3)
γ [deg]	90	106.22(2)
Z	4	1
volume [$Å^3$]	5564(2)	1793.9(11)
calc dens [Mg/m^3]	1.693	1.602
abs coeff [mm^{-1}]	1.368	1.116
F(000)	2808	864
cryst size [mm]	0.18 × 0.16 × 0.14	0.09 × 0.08 × 0.05
no. reflns collected	7448	18 764
goodness-of-fit on F^2	1.164	1.083
final *R* indices [$I < 2\sigma(I)$]	R1 = 0.0403 wR2 = 0.1168	R1 = 0.0448 wR2 = 0.1231
R indices (all data)	R1 = 0.0418 wR2 = 0.1180	R1 = 0.0534 wR2 = 0.1277

para-PPh$_3$), 7.23 (d, 1H, H^7, J_{HH} = 8.2 Hz), 7.20 (d, AA′XX′, 2H, H^1, J_{HH} = 8.3 Hz), 6.97−6.94 (m, 3H, H^2 + H^6), 6.42 (dd, 1H, H^4, J_{HP} = 5.5 Hz, J_{HH} = 1.5 Hz). $^{31}P\{^1H\}$ NMR (101 MHz, CHCl$_3$, 298 K), δ (ppm): 38.73 (s). IR (KBr), ν (cm^{-1}): 1598 (COO), 1362 (COO), 1097 (coordinated PPh$_3$, X-sensitive mode). MS-MALDI TOF (+) (DTH), *m*/*z*: $[M - PPh_3 + H]^+$ = 993.6, $[M/2 + H]^+$ = 628.6. Anal. Calcd for $C_{64}H_{46}Cl_2N_2O_4P_2Pd_2$: C 61.36, H 3.70, N 2.24. Found: C 61.2, H 3.6, N 2.0.

Compound 5e. A mixture of **2e** (75 mg, 0.09 mmol) and triphenylphosphine (45 mg, 0.17 mmol) in 40 mL of methanol was stirred at room temperature for 3 h. The yellow solid obtained was filtered, washed with methanol, and dried under vacuum to obtain **5e**, 101 mg (92% yield). ^1H NMR (400 MHz, CDCl$_3$, 298 K), δ (ppm): 7.82 (d, 1H, H^3, J_{HP} = 7.4 Hz), 7.76 (dd, 6H, *ortho*-PPh$_3$, J_{HP} = 11.6 Hz, J_{HH} = 8.0 Hz), 7.31−7.21 (m, 9H, *meta*-PPh$_3$ + *para*-PPh$_3$), 7.08 (m, 3H, H^1 + H^7), 6.80 (d, AA′XX′, 2H, H^2, J_{HH} = 8.0 Hz), 6.94 (dd, 1H, H^6, J_{HH} = 8.6 Hz, J_{HH} = 2.3 Hz), 5.77 (dd, 1H, H^4, J_{HP} = 6.2 Hz, J_{HH} = 2.5 Hz), 2.39 (s, 6H, N(CH$_3$)$_2$). $^{31}P\{^1H\}$ NMR (101 MHz, CHCl$_3$, 298 K), δ (ppm): 39.65 (s). IR (KBr), ν (cm^{-1}): 1569 (COO), 1350 (COO), 1098 (coordinated PPh$_3$, X-sensitive mode). MS-MALDI TOF (+) (DTH), *m*/*z*: $[M - PPh_3 + H]^+$ = 1009.8, $[M/2 + H]^+$ = 635.6. Anal. Calcd for $C_{68}H_{58}N_4O_4P_2Pd_2$: C 64.31, H 4.60, N 4.41. Found: C 64.0, H 4.8, N 4.2.

X-ray Crystallography. The crystal data, data collection, and refinement parameters for the X-ray structures are listed in Tables 3 and 4.

Data were collected for **2c**, **4d**, and **5b** on a MAR345 diffractometer with an image plate detector. Unit-cell parameters were determined from 3506, 830, and 3195 reflections (3° < θ < 31°) for **2c**, **4d**, and **5b** respectively, and refined by least-squares methods. Intensities were collected with graphite-monochromatized Mo Kα radiation. For **2c** 23 566 reflections were measured in the range 2.82 ≤ θ ≤ 32.43, 6394 of which were nonequivalent by symmetry (R_{int} (on *I*) = 0.049); 5475 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Lorentz−polarization but no absorption corrections were made. For **4d** 7448 reflections were measured in the range 2.73 ≤ θ ≤ 31.60; 7035 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. For **5b** 18 764 reflections were measured in the range 2.62 ≤ θ ≤ 32.31, 9654 of which were nonequivalent by symmetry (R_{int} (on *I*) = 0.035); 8055 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Lorentz−polarization and absorption corrections were made.

The structures were solved by direct methods, using the SHELXS computer program, and refined by full-matrix least-squares method with the SHELX97 computer program.[23] For **2c** the function minimized was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0411P)^2 + 1.2034P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$,; *f*, *f*′, and *f*″ were taken from International Tables of X-Ray Crystallography.[24] 3H atoms were located from a difference synthesis and refined with an overall isotropic temperature factor, and 16H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atoms that are linked. The final *R* (on *F*) factor was 0.035, *wR* (on $|F|^2$) = 0.089 and goodness of fit = 1.148 for all observed reflections. Number of refined parameters was 343. Max. shift/esd = 0.00, mean shift/esd = 0.00. Max. and min. peaks in final difference synthesis were 0.576 and −0.395 e Å^{-3}, respectively. For **4d** the function minimized was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0616P)^2 + 6.6461P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$, *f*, *f*′, and *f*″ were taken from International Tables of X-Ray Crystallography.[24] 15H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atoms that are linked. The final *R* (on *F*) factor was 0.040, *wR* (on $|F|^2$) = 0.118 and goodness of fit = 1.164 for all observed reflections. Number of refined parameters was 313. Max. shift/esd = 0.00, mean shift/esd = 0.00. Max. and min. peaks in final difference synthesis were 0.397 and −0.432 e Å^{-3}, respectively. For **5b** the function minimized was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0674P)^2 + 0.5074P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$; *f*, *f*′, and *f*″ were taken from International Tables of X-Ray Crystallography.[24] All H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom that is linked. The final *R* (on *F*) factor was 0.045, *wR* (on $|F|^2$) = 0.123 and goodness of fit = 1.083 for all observed reflections. Number of refined parameters was 425. Max. shift/esd = 0.00, mean shift/esd = 0.00. Max. and min. peaks in final difference synthesis were 0.730 and −0.546 e Å^{-3}, respectively.

Data were collected for **4a** on a BrukerAXS ApexII-CCD area detector diffractometer. Unit-cell parameters were determined from 1874 reflections (2.5° < θ < 25.9°) and refined by least-squares methods. Intensities were collected with graphite-monochromatized

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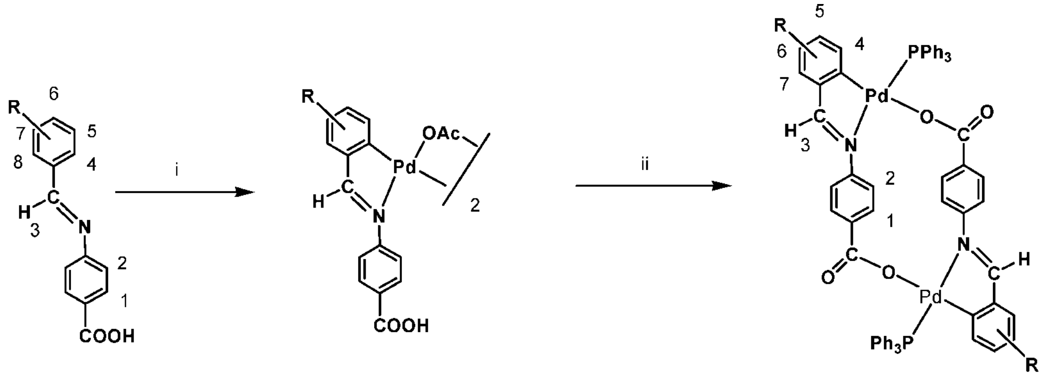
[23] Sheldrick, G. M. *SHELX97, A computer program for determination of crystal structure*; University of Göttingen: Germany, 1997.

[24] *International Tables of X-Ray Crystallography*; Kynoch Press, Birmingham, 1974; Vol. IV, pp 99−100 and 149.

Scheme 2[a]



1a: R = H; **1b**: R = *ortho*-Cl;
1c: R = *meta*-Cl; **1d**: R = *para*-Cl;
1e: R = *para*-NMe$_2$; **1f**: R= *para*-NO$_2$

2a: R = H; **2b**: R = *ortho*-Cl;
2c: R = *meta*-Cl; **2d**: R = *para*-Cl;
2e: R = *para*-NMe$_2$

5a: R = H; **5b**: R = *ortho*-Cl;
5c: R = *meta*-Cl; **5d**: R = *para*-Cl;
5e: R = *para*-NMe$_2$

[a] (i) Pd(OAc)$_2$, acetic acid; (ii) PPh$_3$, MeOH.

Mo Kα radiation, using the $\omega/2\theta$ scan technique; 3988 reflections in the range $1.67 \leq \theta \leq 26.01$ were measured, and 3252 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Lorentz−polarization and absorption corrections were made.

The structure was solved by direct methods, using the SIR97 computer program,[25] and refined by full-matrix least-squares method with the SHELX97 computer program,[23] using 3988 reflections (very negative intensities were not assumed). The function minimized was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0357P)^2 + 2.3916P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$; f, f', and f'' were taken from International Tables of X-Ray Crystallography.[24] All H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom that is linked. The final R (on F) factor was 0.030, wR (on $|F|^2$) = 0.075, and goodness of fit = 1.052 for all observed reflections. Number of refined parameters was 284. Max. shift/esd = 0.002, mean shift/esd = 0.00. Max. and min. peaks in final difference synthesis were 0.962 and −0.897 e Å^{-3}, respectively.

CCDC-689175 (**2c**), CCDC-689176 (**4a**), CCDC-689177 (**4d**), and CCDC-689178 (**5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgment. We thank the Ministerio de Educación y Ciencia for financial suport (project: CTQ2006-02007) and the University of Barcelona for a BRD grant.

OM8006807

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