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Article

Cyclopalladation of Schiff Bases from Methyl Esters of α-Amino Acids. Unexpected Activation of the O−Me Bond with Formation of a Bianionic Tridentate Metallacycle

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The action of palladium acetate on imines from methyl esters of the α-amino acids glycine, alanine, valine, and tyrosine is herein described. The reactivity of the new metallacycles obtained with phosphines and amines is also described, as well as the synthesis of isoquinolinium salts by insertion of diphenylacetylene into the Pd−C bond. Besides this, the unexpected activation of the Me−O bond of the ester group of the amino acid fragment is also reported, in a process that affords new cyclopalladated derivatives having the metalated molecule as a dianionic (C,N,O) ligand.

Introduction

Cyclometalation reactions were one of the first known examples of C−H bond activation, and cyclopalladated 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, 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]

There is growing interest in the synthesis, reactivity, and applications of organometallic complexes with biologically active ligands such as α-amino acids or biogenic amines,[3] and the term bioorganometallic chemistry is used to describe this research field on the border between biochemistry and organometallic chemistry. α-Amino acids are highly versatile ligands and can afford two classes of compounds: complexes in which the amino acid is coordinated to an organometallic fragment via their donor atoms (amino, carboxylato, or other basic groups) and complexes in which the amino acid is coordinated to the metal through a carbon−metal bond, this last class being comparatively rare. Some C−N chelates have been synthesized by metalation of amino acid derivatives by palladium.[4] The *ortho*-palladated

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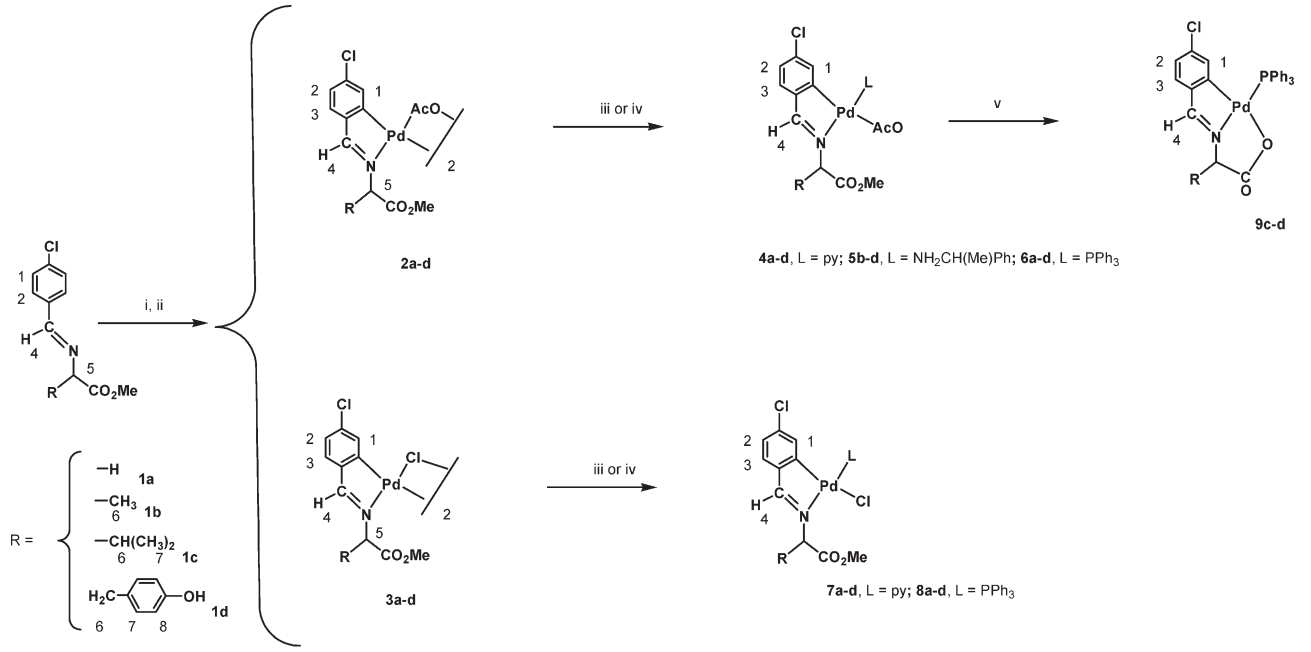
Scheme 1



i) $Pd(AcO)_2$, acetone, 5 days, r.t.
ii) LiCl, acetone, 1h, r.t., for compounds **3**
iii) pyridine-D_5 or methylbenzylamine, $CDCl_3$, r.t., for **4** and **5** respectively
iv) PPh_3, acetone, 1h, r.t.
v) acetone, 24h, reflux

complexes of biologically active ligands are interesting because of their potential cytotoxic activity and because they can be useful precursors to prepare functionalized derivatives that potentially can present important biological effects and that are not easily prepared by other methods.[4,5]

With these precedents in mind, and following our studies on cyclometalation reactions,[6] we focused our attention on the action of palladium acetate on methyl esters of imines from glycine, alanine, valine, and tyrosine and on the reactivity of the metallacycles obtained.

Results and Discussion

Imines **1** were obtained following an analogous procedure to that reported in the literature[7] by condensation of the corresponding amino acid with 4-chlorobenzaldehyde. All attempts to metalate these ligands using, as a metalating agent, mixtures of $PdCl_2$/NaCl/NaAcO, in different reaction conditions, were unsuccesful. Nevertheless, when these Schiff bases were treated with palladium acetate in refluxing acetic acid for 1 h, the corresponding *endo* acetato-bridged five-membered cyclopalladated dimers **2** were obtained. Imines **1c** and **1d** can also afford the *exo*-metallacycles, by activation of an aliphatic carbon−hydrogen bond (imine **1c**) or by activation of an aromatic carbon−hydrogen bond of the tyrosine fragment (imine **1d**); nevertheless overall NMR data showed that only the *endo*-derivative was formed, which is consistent with reports of the strong tendency of imines to form *endo*-metallacycles.[8] The corresponding chloro-bridged cyclopalladated dimers **3** were also isolated by reaction between acetato-bridged dimers and LiCl in acetone.

The ^{1}H NMR spectra of compounds **2** produced broad signals at room temperature, and the spectrum of compound **3a** could not be recorded due to its insolubility. To complete the characterization of the new metallacycles, mononuclear compounds **4** and **7** were obtained in an NMR tube by addition of a few drops of pyridine-D_5 to $CDCl_3$ solutions of **2** or **3**, respectively. It should be noted that complete racemization of the Schiff base takes place during the cyclopalladation reaction, in acetic acid. To evaluate the influence of the reaction conditions in the racemization process, the cyclopalladation reaction was tried using more mild conditions. We found that the imines could also be metalated by carrying out the reaction in acetone at room temperature for 5 days. As expected, under these reaction conditions, the racemization of the imines was not as fast and optically active compounds were obtained for ligands **1b**, **1c**, and **1d** (optical rotation: +22.0, −18.1, and −45.0 for **2b**, **2c**, and **2d**, respectively). To evaluate the ee of **2**, these dinuclear cyclometalated complexes were reacted with (*S*)-(−)-α-methylbenzylamine in an NMR tube, to obtain **5** (Scheme 1).

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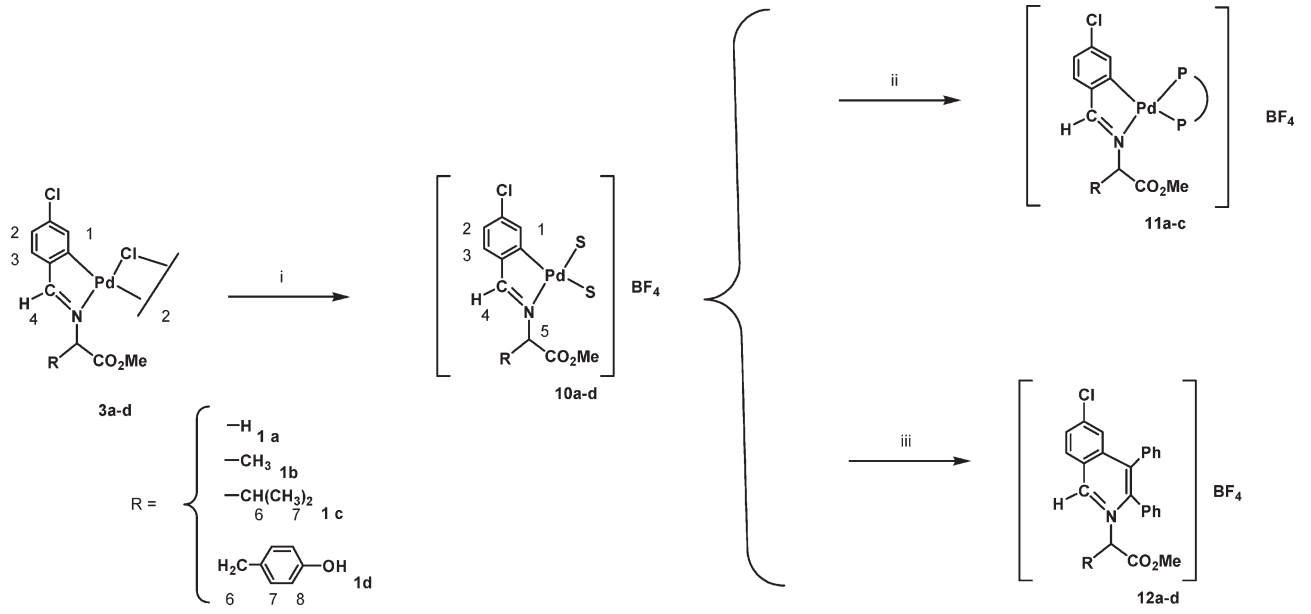
Scheme 2



i) $AgBF_4$, acetone, 1h, r.t.
ii) dppe, acetone, 2h, r.t.
iii) diphenylacetylene, nitromethane, 48h, reflux

The proton NMR spectra of these species show an ee of 40, 85, and 45% for **5b**, **5c**, and **5d**, respectively. This is not an unexpected result bearing in mind the results reported for the racemization of the amino acids.

Generally, free amino acids are difficult to racemize, and some work has been undertaken to develop a simple and economical method for the racemization of optically active amino acids. It is known that heating optically active α-amino acids in the presence of arylaldehydes effects racemization from the intermediate imines. Besides this, the racemization of a wide variety of optically active α-amino acids was found to be greatly accelerated in acetic acid solution in the presence of catalytic amounts of aromatic aldehydes.[9] Reaction of dimers **2** or **3** with PPh_3 afforded the mononuclear complexes $[PdX(C{-}N)(PPh_3)]$, X = AcO or Cl (compounds **6** and **8**, respectively).

All the new cyclometalated compounds obtained were characterized by elemental analysis, IR spectra, and proton NMR spectra. In some cases, 2D-NMR experiments and mass spectra were carried out to complete the characterization. The high-field shift of the aromatic protons of the palladated ring in the proton NMR spectra of complexes **4** and **7** indicates the *cis* disposition of the pyridine relative to the metalated carbon atom. The proton bonded to the chiral carbon atom of the amino acid fragment appears low field shifted, in relation to free ligand, in all compounds containing a chloro ligand in the coordination sphere of the metal. This can be explained by the existence of a C−H···Cl nonconventional hydrogen bond in these complexes. The determination of the crystal structure of compounds **3c** and **8a** (see below) confirmed this interaction. The high-field shift of the aromatic protons of the palladated ring in the triphenylphosphine-containing complexes **6** and **8**, due to the aromatic rings of the phosphine, indicates the *cis* disposition of the phosphorus relative to the metalated carbon atom, and the chemical shift of the phosphorus confirms this arrangement.[10] This arrangement is usual in cyclopalladated compounds containing phosphines.[11] IR spectra of **6** showed $\nu(CO_2)_{asymm}$ and $\nu(CO_2)_{symm}$ separated by 220−250 cm^{-1}, consistent with unidentate acetato coordination.[12]

The structures of **3c** and **8a** were determined by X-ray diffraction (Figures 1 and 2). The asymmetric unit of **3c** presents two independent molecules, which correspond to the *meso* and *rac* forms of compound **3c**. The crystal structures consist of discrete molecules separated by van der Waals distances. The distances between palladium and the coordinated atoms are similar to those reported for analogous compounds (Table 1).[13] In both cases, the

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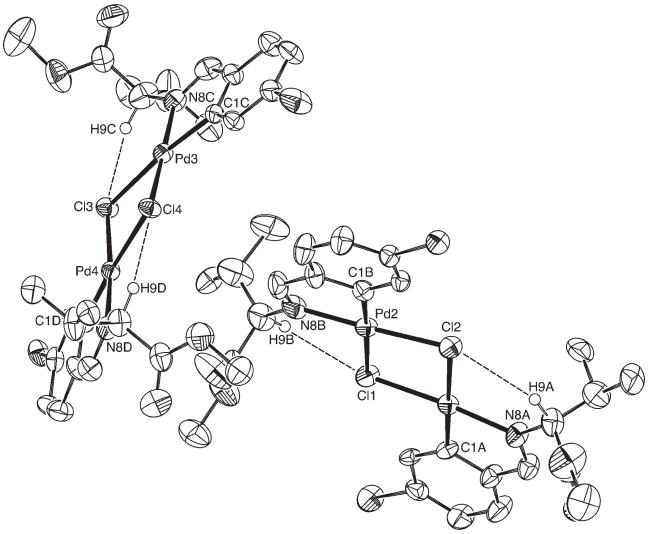

Figure 1. Molecular structure of compound **3c**.

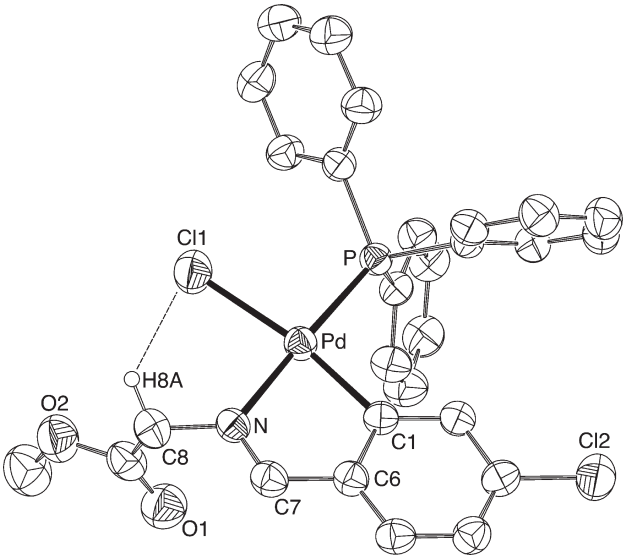

Figure 2. Molecular structure of compound **8a**.

metallacycles that contain the imine functionality are planar and the smallest angle in the coordination sphere of palladium corresponds to the C−Pd−N bite angle, 80.9(3)° for **3c** and 80.57(12)° for **8a**. For the molecules of compound **3c**, the palladium atom is in a square-planar environment, coordinated to one carbon, two chlorine, and one nitrogen atom. The Pd−Cl bonds *trans* to the Pd−C bond are significantly longer than those *trans* to nitrogen, and this can be attributed to the higher *trans* influence of the carbon. An intramolecular C−H···Cl interaction between the proton bonded to the chiral carbon atom of the amino acid fragment and the bridging chlorine atom is observed, with bond distances in the range 2.584−2.661 Å. For compound **8a** the palladium atom is in a square-planar environment, coordinated to carbon, chlorine, nitrogen, and phosphorus atoms. The coordination plane shows a slight tetrahedral distortion, the deviation from the mean plane being 0.014, 0,013, −0.020, 0.017, and −0.010 Å for Pd, C1, N, P, and Cl1, respectively. The phosphorus and nitrogen atoms adopt a *trans* arrangement, the metallacycle contains the C=N bond, and the imine is in the *E*-form. An intramolecular C−H···Cl interaction between one of the protons of the CH_2 group of the amino acid fragment and the chlorine atom bonded to the metal is observed, with a bond distance of 2.645 Å.

There are few reports about the activation of C−O bonds by group 10 transition metal compounds: Milstein et al. have reported the O−Me bond activation of a methoxy-substituted benzyl phosphine, [14a] Colbran et al. have described the O-metalation of 2-(2,5-dimethoxyphenyl)-1,10 phenantroline by palladium(II) with formation of the corresponding O, N,N coordination compound, [14b] and we have reported the activation of an *ortho* O−Me bond of the imine (*E*)-*N*-(2,4,6-trimethoxybenzylidene)-1-phenylethanamine by reacting the cyclopalladated dinuclear complex of this ligand with triphenylphosphine.[10b]

Compounds **9c** and **9d** (Scheme 1), having the metalated molecule as a dianionic (C,N,O) ligand, were unexpectedly obtained by refluxing acetone solutions of the corresponding metallacycles **6c** and **6d** for 24 h. This reaction affords new cyclopalladated derivatives by the activation of the O−Me bond of the ester group of the α-amino acid fragment. These new tridentate metallacycles were characterized by elemental analysis, IR, MS, and NMR spectroscopy, and the structure of **9c** was also determined by X-ray diffraction (Figure 3). The crystal structure consists of discrete molecules separated by van der Waals distances. The distances between palladium and the coordinated atoms are similar to those reported for analogous compounds.[15] The coordination plane shows a slight tetrahedral distortion, the deviation from the mean plane being 0.020, −0.023, −0.016, 0.008, and −0.021 Å for Pd, C1, N, P1, and O1, respectively. The metallacycle that contains the C=N bond is quite planar, the deviation from the mean plane being 0.038, 0,010, −0.039, −0.034, and −0.052 Å for Pd, C6, C7, C1, and N, respectively. In contrast, the cycle formed by Pd, N, C8, C9, and O1 atoms shows a significant distortion from planarity, due to the sp^3 hybridization of O1 and C8 atoms, the deviation from the mean plane being 0.021, −0.104, 0.162, −0.147, and 0.069 Å for Pd, N, C8, C9, and O1, respectively.

Cyclopalladated compounds are valuable intermediates for regioselective organic synthesis, and increasing attention has been paid to insertion of alkynes into the Pd−C bond. This reaction could also afford isoquinoline derivatives, and the synthesis of such derivatives containing the α-amino acid fragment seems interesting to us.[1] It should be noted that *N*-carboxymethylisoquinoline derivatives have been proposed as new carriers for specific brain delivery.[16] Nevertheless, all the attempts to prepare the corresponding isoquinoline

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Table 1. Bond Distances (Å) and Angles (deg) for Compounds 3c, 8a, 9c, and 12b

3c	8a	9c	12b
C1A−Pd1 = 1.986(8)	Pd−C1 = 2.039(3)	Pd1−C1 = 1.951(4)	N1−C10 = 1.323(4)
N8A−Pd1 = 2.033(7)	Pd−N = 2.110(3)	Pd1−N = 2.038(3)	N1−C2 = 1.396(4)
C1B−Pd2 = 1.976(9)	Pd−P = 2.2760(10)	Pd1−O1 = 2.094(3)	N1−C11 = 1.494(4)
N(8B)−Pd(2) = 2.008(8)	Pd−Cl1 = 2.3633(13)	Pd1−P1 = 2.2803(16)	C2−C3 = 1.371(4)
C1C−Pd3 = 1.974(8)	N−C7 = 1.254(4)	O1−C9 = 1.345(5)	C2−C15 = 1.487(4)
N8C−Pd3 = 2.029(8)	N−C8 = 1.453(5)	N−C7 = 1.254(4)	C3−C4 = 1.438(4)
C1D−Pd4 = 1.984(8)	C1−C6 = 1.414(4)	N−C8 = 1.455(4)	C3−C21 = 1.488(4)
N8D−Pd4 = 2.032(8)	C6−C7 = 1.470(5)	C1−C6 = 1.412(5)	C4−C9 = 1.408(4)
Cl1−Pd1 = 2.322(2)	C8−H8A = 0.9700	C6−C7 = 1.435(5)	C9−C10 = 1.397(5)
Cl1−Pd2 = 2.450(2	Cl1−H8A = 2.645	C8−C9 = 1.521(5)	C4−C5 = 1.403(4)
Cl2−Pd2 = 2.331(2)	C1−Pd−N = 80.57(12)	C1−Pd1−N = 81.34(15)	C5−C6 = 1.369(4)
Cl2−Pd1 = 2.458(2)	C1−Pd−P = 97.70(9)	C1−Pd1−O1 = 161.40(13)	C6−Cl1 = 1.734(3)
Cl3−Pd4 = 2.326(2)	N−Pd−P = 177.57(7)	N−Pd1−O1 = 177.10(10)	C11−C12 = 1.520(5)
Cl3−Pd3 = 2.458(2)	C1−Pd−Cl1 = 170.14(9)	C1−Pd1−P1 = 95.78(12)	C11−C13 = 1.526(5)
Cl4−Pd3 = 2.325 (2)	N−Pd−Cl1 = 89.57(8)	N−Pd1−P1 = 177.10(10)	C13−O1 = 1.201(4)
Cl4−Pd4 = 2.464(2)	P−Pd−Cl1 = 92.16(4)	O1−Pd1−P1 = 102.65(9)	C13−O2 = 1.324(4)
Cl1−H9B = 2.594	C7−N−C8 = 119.6(3)	C9−O1−Pd1 = 113.2(2)	O2−C14 = 1.448(5)
Cl2−H9A = 2.661	C7−N−Pd = 113.4(2)	C7−N−C8 = 130.5(3)	C15−C16 = 1.392(5)
Cl3−H9C = 2.584	C8−N−Pd = 126.5(2)	C7−N−Pd1 = 114.8(3)	C21−C22 = 1.389(5)
Cl4−H9D = 2.600	C6−C1−Pd = 111.8(2)	C8−N−Pd1 = 114.6(2)	C10−N1−C2 = 121.3(3)
Pd1−Cl1−Pd2 = 93.90(7)	C1−C6−C7 = 115.0(3)	C6−C1−Pd1 = 111.6(3)	C10−N1−C11 = 120.1(3)
Pd2−Cl2−Pd1 = 93.50(7)	N−C7−C6 = 119.0(3)	C1−C6−C7 = 115.8(3)	C2−N1−C11 = 118.6(3)
Pd4−Cl3−Pd3 = 92.96(7)	N−C8−H8A = 109.8	N−C7−C6 = 115.8(4)	C3−C2−N1 = 119.6(3)
Pd3−Cl4−Pd4 = 92.82(7)	C8−H8A−Cl1 = 116.730	N−C8−C9 = 108.3(3)	C3−C2−C15 = 122.9(3)
C1A−Pd1−N8A = 80.9(3)		O1−C9−C8 = 115.7(3)	N1−C2−C15 = 117.3(3)
C1A−Pd1−Cl1 = 94.7(2)			C2−C3−C4 = 120.2(3)
N8A−Pd1−Cl1 = 175.1(2)			C2−C3−C21 = 119.6(3)
C1A−Pd1−Cl2 = 178.7(3)			C4−C3−C21 = 120.3(3)
N8A−Pd1−Cl2 = 98.6(2)			C5−C4−C9 = 118.8(3)
Cl1−Pd1−Cl2 = 85.89(8)			C5−C4−C3 = 123.4(3)
C1B−Pd2−N8B = 81.5(3)			C9−C4−C3 = 117.8(3)
C1B−Pd2−Cl2 = 95.3(3)			C6−C5−C4 = 118.6(3)
N8B−Pd2−Cl2 = 176.7(2)			C5−C6−Cl1 = 118.6(3)
C1B−Pd2−Cl1 = 176.8(3)			C10−C9−C4 = 119.3(3)
N8B−Pd2−Cl1 = 97.4(2)			N1−C10−C9 = 121.7(3)

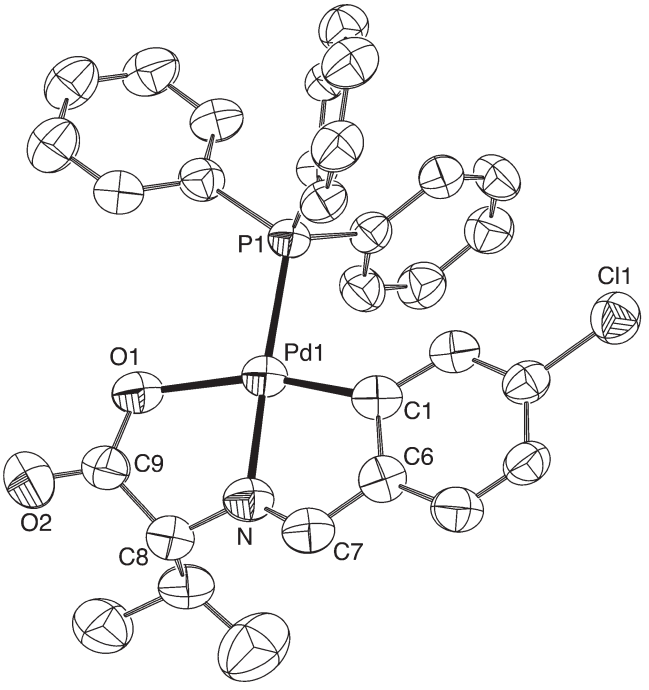

Figure 3. Molecular structure of compound **9c**.

derivatives, in different reaction conditions, by insertion of diphenylacetylene in the Pd−carbon bond of compounds **2** or **3** were unsuccessful.

It is accepted that insertion of alkynes takes place after the alkyne coordination to the metal.[1,17] Thus, cationic species, with solvent molecules as ligands, react more easily with alkynes. This fact prompted us to obtain such ionic compounds in solution. The reactions of halo palladium complexes with silver salts of weakly coordinating anions in solvents with poor donor abilities, especially when they are not thoroughly anhydrous, facilitate the direct synthesis of aqua palladium complexes.[18] Thus, the action of $AgBF_4$ on acetone solutions of the cyclometalated compounds **3** precipitates AgCl, affording solutions containing cyclopalladated ionic species with coordinated water molecules **10a−d** (Scheme 2). These compounds were characterized by NMR spectroscopy. The methinic proton signal appears low field shifted in all compounds, in agreement with the ionic structure proposed. The proton bonded to the chiral atom of the amino acid fragment appears high field shifted in all cases, in relation to compounds **3**, showing that there is no intramolecular hydrogen−chloro bond in these complexes, thus confirming that the chloro ligand has been removed from the coordination sphere of the metal. Besides this, the broadening of the signals assigned to protons 1 and 5 suggests the existence of a fast exchange of the solvent molecules coordinated to palladium. The signals assigned to coordinated water appear in the range 3.69−3.06 and are low field shifted when the spectra are recorded at 220 K, in agreement with previous results.[18]

The addition of 1,2-bis(diphenylphosphino)ethane (dppe), in a 1:1 molar ratio, to an acetone solution of these species affords, as expected, the ionic compounds **11** in good yields.

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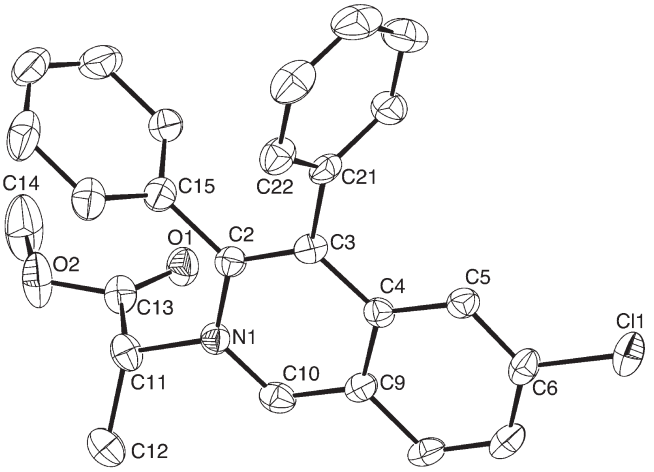

Figure 4. Molecular structure of the organic cation of compound **12b**.

^{1}H and ^{31}P NMR data agree with the ionic stucture proposed for compounds **11**.[19]

More interesting, the reaction of the ionic compounds **10a**−**d** with diphenylacetylene in refluxing nitromethane afforded the isoquinolinium salts **12a**−**d** by insertion of the alkyne into the Pd−C bond (Scheme 2). All these organic compounds were characterized by elemental analysis, IR, MS, and NMR spectroscopy, and the structure of **12b** was also determined by X-ray diffraction (Figure 4), confirming the structure proposed and showing that the bond distances and angles are similar to those reported for related compounds.[20]

In conclusion we have synthesized new metallacycles by cyclopalladation of Schiff bases from the methyl esters of the α-amino acids glycine, alanine, valine, and tyrosine. We also report the unexpected selective activation of the O−Me bond, with formation of a bianionic tridentate metallacycle, as well as the synthesis of isoquinolinium salts by insertion of diphenylacetylene into the Pd−C bond of cyclopalladated ionic complexes.

Experimental Section

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

^{1}H NMR spectra were registered on a Varian Gemini 200, Varian Unity 300, and a Varian Mercury 400 instrument. ^{31}P-{^{1}H} 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 ^{1}H, to 85% H_3PO_4 for ^{31}P, and to C_6F_6 for ^{19}F. Abbreviations used: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad; NMR labeling as shown in schemes. 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. Synthesis of Imines. 4-ClC_6-H_3CH=NCH_2CO_2Me (1a). A mixture of glicine methyl ester hydrochloride (1.0 g, 7.96 mmol), 4-chlorobenzaldehyde (1.120 g, 7.96 mmol), triethylamine (0.806 g, 7.96 mmol), and anhydrous magnesium sulfate (1.5 g, 12.5 mmol) was refluxed for 2 h in dichloromethane. After the reaction mixture was cooled to room temperature, the undissolved materials were removed by filtration, washed with dichloromethane, and discarded. The filtrate was concentrated to dryness on a rotatory evaporator to give a white solid. The white solid was dissolved in benzene and filtered, and the resulting solution was concentrated to dryness on a rotatory evaporator to give compound **1a**, 1.672 g (99%), as a yellow oily material. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K), δ (ppm): 8.26 (s, 1H, H_4), 7.72 (d, 2H, J_{HH} = 8.5, H_2), 7.40 (d, 2H, J_{HH} = 8.5, H_1), 4.41 (s, 2H, CH_2), 3.78 (s, 3H, CO_2Me). IR (KBr), ν (cm^{-1}): ν(C=O) = 1737, ν(C=N) = 1645. MS-CI, m/z: $[M + H]^+$ = 211.0.

4-ClC_6H_3CH=NCH(Me)CO_2Me (1b). A mixture of L-alanine methyl ester hydrochloride (1.0 g, 7.16 mmol), 4-chlorobenzaldehyde (1.003 g, 7.16 mmol), triethylamine (0.723 g, 7.16 mmol), and anhydrous magnesium sulfate (1.5 g, 12.5 mmol) was refluxed for 2 h in dichloromethane. After the reaction mixture was cooled to room temperature, the undissolved materials were removed by filtration, washed with dichloromethane, and discarded. The filtrate was concentrated to dryness on a rotatory evaporator to give an oily material, which was dissolved in benzene and filtered, and the resulting solution was concentrated to dryness on a rotatory evaporator to give compound **1b**, 1.374 g (85%), as a yellow oily material. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K), δ (ppm): 8.27 (s, 1H, H_4), 7.71 (d, 2H, J_{HH} = 8.6, H_2), 7.39 (d, 2H, J_{HH} = 8.6, H_1), 4.16 (q, 1H, J_{HH} = 6.8, H_5), 3.75 (s, 3H, CO_2Me), 1.53 (d, 3H, J_{HH} = 7.0, H_6). IR (cm^{-1}): ν(C=O) = 1733, ν(C=N) = 1647. MS-CI (m/z): $[M + H]^+$ = 225.0. ee = 62%, $[\alpha]_{Na}^{20}$ = −66.6.

4-ClC_6H_3CH=NCH(^{i}Pr)CO_2Me (1c). A mixture of L-valine methyl ester hydrochloride (1.0 g, 5.96 mmol), 4-chlorobenzaldehyde (0.840 g, 7.16 mmol), triethylamine (0.603 g, 5.96 mmol), and anhydrous magnesium sulfate (1.5 g, 12.5 mmol) was refluxed for 2 h in dichloromethane. After the reaction mixture was cooled to room temperature, the undissolved materials were removed by filtration, washed with dichloromethane, and discarded. The filtrate was concentrated to dryness on a rotatory evaporator to give an oily material, which was dissolved in benzene and filtered, and the resulting solution was concentrated to dryness on a rotatory evaporator to give compound **1c**, 1.255 g (83%), as a white oily material. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K), δ (ppm): 8.20 (s, 1H, H_4), 7.73 (d, 2H, J_{HH} = 8.6, H_2), 7.39 (d, 2H, J_{HH} = 8.6, H_1), 3.75 (s, 3H, CO_2Me), 3.67 (d, 1H, J_{HH} = 7.0, H_5), 2.37 (m, 1H, J_{HH} = 7.0, H_6), 0.96 (d, 3H, J_{HH} = 6.8, H_7), 0.93 (d, 3H, J_{HH} = 7.2, $H_{7'}$). IR (cm^{-1}): ν(C=O) = 1728, ν(C=N) = 1645. MS-CI (m/z): $[M + H]^+$ = 254.0. ee = 89%, $[\alpha]_{Na}^{20}$ = −119.7.

4-ClC_6H_3CH=NCH($CH_2C_6H_4$(4′-OH))CO_2Me (1d). A mixture of L-tyrosine methyl ester (1.0 g, 5.20 mmol), 4-chlorobenzaldehyde (0.731 g, 5.20 mmol), and anhydrous magnesium sulfate (1.5 g, 12.5 mmol) was refluxed for 2 h in dichloromethane. After the reaction mixture was cooled to room temperature, the undissolved materials were removed by filtration, washed with dichloromethane, and discarded. The filtrate was concentrated to dryness on a rotatory evaporator to give compound **1d**, 1.255 g (83%), as a white solid (1.619 g, 98%).

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^{1}H NMR (200 MHz, $CDCl_3$, 298 K), δ (ppm): 7.84 (s, 1H, H_4), 7.62 (d, 2H, J_{HH} = 8.4, H_2), 7.36 (d, 2H, J_{HH} = 8.4, H_1), 7.00 (d, 2H, J_{HH} = 8.4, H_7), 6.68 (d, 2H, J_{HH} = 8.4, H_8), 4.10 (dd, 1H, J_{HH} = 8.8, J_{HH} = 5.0, H_5), 3.74 (s, 3H, CO_2Me), 3.28 (dd, 1H, J_{HH} = 13.6, J_{HH} = 5.2, H_6), 3.06 (dd, 1H, J_{HH} = 13.6, J_{HH} = 8.8, $H_{6'}$). IR (cm^{-1}): ν(OH) = 3356, ν(C=O) = 1722, ν(C=N) = 1648. MS-CI (m/z): $[M + H]^+$ = 317.9. ee > 99%, $[\alpha]_{Na}^{20}$ = −270.0.

Cyclometalation Reactions. Synthesis of 2a−d, in Acetone. (μ-OAc)$_2$[Pd{κ^2-(C,N)-4-ClC$_6$H$_3$CH=NCH$_2$CO$_2$Me}]$_2$ (2a). A mixture of imine **1a** (284 mg, 1.34 mmol) and palladium acetate (300 mg, 1.34 mmol) in 35 mL of acetone was stirred at room temperature for 5 days. The resulting suspension was filtered through Celite, and the filtrate was concentrated to dryness on a rotatory evaporator to give a red solid, after addition of diethyl ether. The solid was washed with diethyl ether and dried to obtain **2a**, 312 mg (62% yield). IR (KBr), ν (cm^{-1}): ν (C=O) = 1749, ν(C=N) = 1609, $\nu_a(COO^-)$ = 1582, $\nu_s(COO^-)$ = 1412. MS-MALDI TOF (+) m/z: $[M - OAc]^+$ = 693.1, $[M/2 - OAc]^+$ = 318.2. Anal. Calcd for $C_{24}H_{24}Cl_2N_2O_8Pd_2$: C 38.32, H 3.22, N 3.72. Found: C 38.5, H 3.7, N 3.8.

(μ-OAc)$_2$[Pd{κ^2-(C,N)-4-ClC$_6$H$_3$CH=NCH(Me)CO$_2$Me}]$_2$ (2b). A mixture of imine **1b** (302 mg, 1.34 mmol) and palladium acetate (300 mg, 1.34 mmol) in 35 mL of acetone was stirred at room temperature for 5 days. The resulting suspension was filtered through Celite, the filtrate was concentrated to dryness on a rotatory evaporator, and the solid obtained was eluted through a SiO_2 column, with ethyl acetate−hexane (2:1) as eluent, to obtain **2b** as a yellow solid after addition of diethyl ether, 336 mg (72% yield). IR (KBr), ν (cm^{-1}): ν(C=O) = 1744, ν(C=N) + $\nu_a(COO^-)$ = 1579, $\nu_s(COO^-)$ = 1419. MS-MALDI TOF (+) m/z: $[M - OAc]^+$ = 721.0. Anal. Calcd for $C_{26}H_{28}Cl_2N_2O_8Pd_2$: C 40.02, H 3.61, N 3.59. Found: C 40.0, H 3.7, N 3.6.

(μ-OAc)$_2$[Pd{κ^2-(C,N)-4-ClC$_6$H$_3$CH=NCH(^{i}Pr)CO$_2$Me}]$_2$ (2c). 2c was obtained using the same procedure as that described above for **2b**, from 340 mg (1.34 mmol) of imine **1c**. Yield: 224 mg (40%). IR (KBr), ν (cm^{-1}): ν(C=O) = 1739, ν(C=N) + $\nu_a(COO^-)$ = 1585, $\nu_s(COO^-)$ = 1419. MS-MALDI TOF (+) m/z: $[M - OAc]^+$ = 779.0, $[M/2 - OAc]^+$ = 358.1. Anal. Calcd for $C_{30}H_{36}Cl_2N_2O_8Pd_2$: C 43.08, H 4.34, N 3.27. Found: C 43.3, H 4.4, N 3.3.

(μ-OAc)$_2$[Pd{κ^2-(C,N)-4-ClC$_6$H$_3$CH=NCH(CH$_2$C$_6$H$_4$(4-OH))-CO$_2$Me}]$_2$ (2d). 2d was obtained using the same procedure as that described above from 426 mg (1.34 mmol) of imine **1d**. Yield: 484 mg (75%). IR (KBr), ν (cm^{-1}): ν(C=O) = 1740, ν(C=N) = 1609, $\nu_a(COO^-)$ = 1581, $\nu_s(COO^-)$ = 1419. MS-MALDI TOF (+) m/z: $[M - OAc - HOAc]^+$ = 844.8. Anal. Calcd for $C_{38}H_{36}Cl_2N_2O_{10}Pd_2$: C 47.32, H 3.76, N 2.90. Found: 47.5, H 3.9, N 2.9.

Synthesis of 2a−d, in Acetic Acid. A mixture of imine **1a** (284 mg, 1.34 mmol) and palladium acetate (300 mg, 1.34 mmol) was stirred in 35 mL of refluxing acetic acid for 1 h. The resulting suspension was filtered through Celite, and the filtrate was concentrated to dryness on a vacuum line to give a red solid after addition of diethyl ether, 352 mg (70% yield).

A mixture of imine **1b** (302 mg, 1.34 mmol) and palladium acetate (300 mg, 1.34 mmol) was stirred in 35 mL of refluxing acetic acid for 1 h. The resulting suspension was filtered through Celite, the filtrate was concentrated to dryness on a rotatory evaporator, and the solid obtained was eluted through a SiO_2 column, with ethyl acetate−hexane (2:1) as eluent, to obtain **2b** as a yellow solid after addition of hexane, 366 mg (70% yield).

A mixture of imine **1c** (340 mg, 1.34 mmol) and palladium acetate (300 mg, 1.34 mmol) was stirred in 35 mL of refluxing acetic acid for 1 h. The resulting suspension was filtered through Celite, the filtrate was concentrated to dryness on a rotatory evaporator, and the solid obtained was eluted through a SiO_2 column, with ethyl acetate−hexane (1:1) as eluent, to obtain **2c** as a yellow solid after addition of hexane, 224 mg (40% yield).

A mixture of imine **1d** (4.26 mg, 1.34 mmol) and palladium acetate (300 mg, 1.34 mmol) was stirred in 35 mL of refluxing acetic acid for 1 h. The resulting suspension was filtered through Celite, the filtrate was concentrated to dryness on a rotatory evaporator, and the solid obtained was eluted through a SiO_2 column, with ethyl acetate−hexane (10:4) as eluent, to obtain **2d** as a yellow solid after addition of hexane, 445 mg (69% yield).

Synthesis of 3a−d. (μ-Cl)$_2$[Pd{κ^2-(C,N)-4-ClC$_6$H$_3$CH=NCH$_2$-CO$_2$Me}]$_2$ (3a). A mixture of imine **1a** (284 mg, 1.34 mmol) and palladium acetate (300 mg, 1.34 mmol) in 35 mL of acetone was stirred at room temperature for 5 days. The resulting suspension was filtered, and the filtrate was concentrated to dryness on a rotatory evaporator to give a red solid. The red solid was dissolved in acetone (30 mL). LiCl (2.01 mmol, 85 mg) was added to the solution, and the mixture was stirred at room temperature for 1 h. The resulting solution was concentrated to half volume on a rotatory evaporator, and the yellow solid obtained was filtered and dried to obtain **3a**, 334 mg (71% yield). IR (KBr), ν (cm^{-1}): ν(C=O) = 1744, ν(C=N) = 1621. MS-MALDI TOF (+) m/z: $[M + H]^+$ = 703.7, $[M - Cl]^+$ = 668.7. Anal. Calcd for $C_{20}H_{18}Cl_4N_2O_4Pd_2$: C 34.07, H 2.57, N 3.97. Found: C 34.3, H 2.6, N 3.9.

(μ-Cl)$_2$[Pd{κ^2-(C,N)-4-ClC$_6$H$_3$CH=NCH(Me)CO$_2$Me}]$_2$ (3b). 3b was obtained using the same procedure as that described above from 302 mg (1.34 mmol) of imine **1b**. Yield: 303 mg (72%). ^{1}H NMR (400 MHz, CDCl3, δ ppm): 8.03 (s, 1H, H_4), 7.32 (br s, 1H, H_1), 7.18 (d, 1H, J_{HH} = 7.9, H_3), 7.08 (d, 1H, J_{HH} = 7.9, H_2), 4.66 (br q, 1H, J = 6.9, H_5), 3.82 (s, 3H, CO_2Me), 1.67 (br s, 1H, H_6). IR (KBr), ν (cm^{-1}): ν(C=O) = 1745, ν(C=N) = 1611. MS-MALDI TOF (+) m/z: $[M - Cl]^+$ = 698.9. Anal. Calcd for $C_{22}H_{22}Cl_4N_2O_4Pd_2$: C 36.04, H 3.02, N 3.82. Found: C 36.1, H 3.2, N 3.8.

(μ-Cl)$_2$[Pd{κ^2-(C,N)-4-ClC$_6$H$_3$CH=NCH(^{i}Pr)CO$_2$Me}]$_2$ (3c). A mixture of imine **1c** (340 mg, 1.34 mmol) and palladium acetate (300 mg, 1.34 mmol) in 35 mL of acetone was stirred at room temperature for 5 days. The resulting suspension was filtered, and the filtrate was concentrated to dryness on a rotatory evaporator to give a red solid. The red solid was dissolved in acetone (30 mL). LiCl (2.01 mmol, 85 mg) was added to the solution, and the mixture was stirred at room temperature for 1 h. The resulting solution was concentrated to dryness on a rotatory evaporator, and the solid obtained was eluted through a SiO_2 column, with ethyl acetate−hexane (1:1) as eluent, to obtain **3c** as a yellow solid after addition of hexane, 328 mg (62% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 8.34 (s, 1H, H_4), 7.33 (d, 1H, J_{HH} = 1.8, H_1), 7.21 (d, 1H, J_{HH} = 8.0, H_3), 7.08 (dd, 1H, J_{HH} = 8.0, J_{HH} = 1.9, H_2), 4.57 (d, 1H, J_{HH} = 8.0, H_5), 3.79 (s, 3H, CO_2Me), 2.38 (dh, 1H, J_{HH} = 8.3, J_{HH} = 6.7, H_3), 1.16 (d, 3H, J_{HH} = 6.7, H_7), 1.06 (d, 3H, J_{HH} = 6.6, $H_{7'}$). IR (KBr), ν (cm^{-1}): ν(C=O) = 1742, ν(C=N) = 1602. MS-MALDI TOF (+) m/z: $[M - Cl]^+$ = 755.0. Anal. Calcd for $C_{26}H_{30}Cl_4N_2O_4Pd_2$: C 39.57, H 3.83, N 3.55. Found: C 39.8, H 3.6, N 3.5.

(μ-Cl)$_2$[Pd{κ^2-(C,N)-4-ClC$_6$H$_3$CH=NCH(CH$_2$C$_6$H$_4$(4-OH))-CO$_2$Me}]$_2$ (3d). 3d was obtained using the same procedure as that described above for **3c**, from 426 mg (1.34 mmol) of imine **1d**. Yield: 436 mg (79%). **3d**: ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm, J in Hz): 7.62 (br s, 1H, H_4), 7.34 (br s, 1H, H_1), 7.16 (d, 3H, J_{HH} = 8.3, H_2+H_8), 7.04 (s, 1H, H_2), 6.73 (d, 1H, J_{HH} = 8.1, H_7), 4.59 (br s, 1H, H_5), 3.77 (s, 3H, CO_2Me), 3.51 (dd, 1H, J_{HH} = 14.1, J_{HH} = 7.1, H_6), 3.18 (dd, 1H, J_{HH} = 14.4, J_{HH} = 6.3, $H_{6'}$). IR (KBr), ν (cm^{-1}): ν(C=O) = 1734, ν(C=N) = 1608. MS-MALDI TOF (+) m/z: $[M - Cl]^+$ = 880.9, $[M/2 - Cl]^+$ = 424.0. Anal. Calcd for $C_{34}H_{30}Cl_4N_2O_6Pd_2$: C 44.52, H 3.30, N 3.06. Found: C 45.0, H 3.6, N 3.0.

Mononuclear Amine Derivatives 4, 5, and 7. Synthesis of 4a−d in $CDCl_3$ Solution. The addition of few drops of pyridine-D_5 to a solution of **2** in $CDCl_3$ affords the corresponding mononuclear compounds **4a−d** in solution. **4a**: ^{1}H NMR (200 MHz, $CDCl_3$, 298 K), δ (ppm): 7.95 (s, 1H, H_4), 7.23 (d, 1H, J_{HH} = 8.0, H_3), 7.03 (dd, 1H, J_{HH} = 8.0, J_{HH} = 1.9, H_2), 6.17 (s, 1H, J_{HH} = 1.9, H_1), 4.37 (s, 2H, H_5), 3.83 (s, 3H, CO_2Me), 1.90 (s, 3H, OAc). **4b**: ^{1}H NMR (200 MHz, $CDCl_3$, 298 K), δ(ppm): 8.07 (s, 1H, H_4), 7.24 (d, 1H, J_{HH} = 8.0, H_3), 7.03 (dd, 1H, J_{HH} = 8.0, J_{HH} = 1.9, H_2), 6.11 (s, 1H, J_{HH} = 1.9, H_1), 4.64

(q, 1H, J_{HH} = 7.0, H_5), 3.82 (s, 3H, CO_2Me), 1.88 (s, 3H, OAc), 1.65 (d, 3H, J_{HH} = 7.1, H_6). **4c**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 8.39 (s, 1H, H_4), 7.26 (d, J_{HH} = 8.0, H_3), 7.03 (dd, 1H, J_{HH} = 8.0, J_{HH} = 1.9, H_2), 6.09 (s, 1H, J_{HH} = 1.9, H_1), 4.46 (d, 1H, J_{HH} = 8.4, H_5), 3.79 (s, 3H, CO_2Me), 2.37 (m, 1H, H_6), 1.92 (s, 3H, OAc), 1.15 (d, 3H, J_{HH} = 6.7, H_7), 1.02 (d, 3H, J_{HH} = 6.6, $H_{7'}$). **4d**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 7.66 (s, 1H, H_4), 7.08 (d, 1H, J_{HH} = 7.9, H_3), 7.06 (d, 2H, J_{HH} = 8.3, H_7), 6.97 (dd, 1H, J_{HH} = 7.9, J_{HH} = 1.8, H_2), 6.83 (d, 2H, J_{HH} = 8.3, H_8), 6.05 (d, 1H, J_{HH} = 1.8, H_1), 4.51 (t, 1H, J_{HH} = 6.7, H_5), 3.75 (s, 3H, CO_2Me), 3.39 (dd, 1H, J_{HH} = 14.0, J_{HH} = 7.7, H_6), 3.27 (dd, 1H, J_{HH} = 14.0, J_{HH} = 6.2, $H_{6'}$), 1.88 (s, 3H, OAc).

Synthesis of 5b, 5c, and 5d in $CDCl_3$ Solution. The addition of 0.9 mL (0.8 mL in the case of **2c**) of a solution of (*S*)-(−)-α-methylbenzylamine in $CDCl_3$ (33 mg, 0.27 mmol, in 5 mL of $CDCl_3$) to 0.028 mmol of **2** in $CDCl_3$ affords the corresponding mononuclear compounds **5b**−**d** in solution. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), (*S,S*)-**5b** δ (ppm): 7.99 (s, 1H, H_4), 7.46 (d, 2H, J_{HH} = 8.2, $H_{amine\text{-}ortho}$), 7.38 (t, 2H, J_{HH} = 7.5, $H_{amine\text{-}meta}$), 7.31 (t, 1H, J_{HH} = 7.5, $H_{amine\text{-}para}$), 7.24 (d, 1H, J_{HH} = 8.2, H_3), 7.07 (dd, 1H, J_{HH} = 8.0, J_{HH} = 1.9, H_2), 6.78 (d, 1H, J_{HH} = 1.8, H_1), 4.50 (q, 1H, J_{HH} = 7.2, H_5), 4.15 (m, 1H, H_{amine}), 3.78 (s, 3H, CO_2Me), 3.45 (d, 1H, J_{HH} = 9.4, NH_2), 1.94 (s, 3H, OAc), 1.81 (d, 3H, J_{HH} = 6.8, $H_{amine\text{-}methyl}$), 1.64 (d, 3H, J_{HH} = 7.0, H_6). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), (*R,S*)-**5b**, selected signals, δ (ppm): 8.00 (s, 1H, H_4), 7.06 (dd, 1H, J_{HH} = 8.0, J_{HH} = 1.9, H_2), 6.76 (s, 1H, J_{HH} = 1.8, H_1), 4.54 (q, 1H, J_{HH} = 7.5, H_5), 3.77 (s, 3H, CO_2Me), 3.60 (d, 1H, J_{HH} = 9.4, NH_2), 1.66 (d, 3H, J_{HH} = 7.2, $H_{amine\text{-}methyl}$). NMR (400 MHz, $CDCl_3$, 298 K), (*S,S*)-**5c**, δ (ppm): 8.34 (s, 1H, H_4), 7.45 (d, 2H, J_{HH} = 7.2, $H_{amine\text{-}ortho}$), 7.38 (t, 2H, J_{HH} = 7.5, $H_{amine\text{-}meta}$), 7.31 (t, 1H, J_{HH} = 7.6, $H_{amine\text{-}para}$), 7.25 (m, H_3 + $CHCl_3$), 7.07 (dd, 1H, J_{HH} = 8.0, J_{HH} = 1.7, H_2), 6.76 (d, 1H, J_{HH} = 1.7, H_1), 4.66 (d, 1H, J_{HH} = 8.2, H_5), 4.17 (m, 1H, H_{amine}), 3.77 (s, 3H, CO_2Me), 3.58 (d, 1H, J_{HH} = 8.9, NH_2), 2.37 (m, 3H, J_{HH} = 7.0, H_6), 2.03 (s, 3H, OAc), 1.81 (d, 3H, J_{HH} = 6.8, $H_{amine\text{-}methyl}$), 1.13 (d, 3H, J_{HH} = 6.7, H_7), 1.07 (d, 3H, J_{HH} = 6.6, H_7). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), (*R,S*)-**5c**, selected signals, δ (ppm): 8.36 (s, 1H, H_4), 7.08 (d, 1H, J_{HH} = 8.0, H_2), 6.73 (s, 1H, J_{HH} = 1.7, H_1), 4.69 (d, 1H, J_{HH} = 8.1, H_5) 3.76 (s, 3H, CO_2Me), 3.68 (d, 1H, J_{HH} = 9.2, NH_2), 2.36 (m, 1H, H_6), 2.03 (s, 3H, OAc), 1.81 (d, 3H, J_{HH} = 6.7, $H_{amine\text{-}methyl}$), 1.08 (d, 3H, J_{HH} = 6.6, H_7), 1.02 (d, 3H, J_{HH} = 6.7, $H_{7'}$). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), (*S,S*)-**5d**, δ (ppm): 7.5−6.6 (m, 13H, H_4 + H_{ar}), 3.77 (s, 3H, CO_2Me), 3.58 (d, 1H, J_{HH} = 8.9, NH_2), 3.56 (d, 1H, J_{HH} = 14.9, H_6), 3.34 (dd, 1H, J_{HH} = 14.3, J_{HH} = 4.0, $H_{6'}$), 1.96 (s, 3H, OAc), 1.77 (d, 3H, J_{HH} = 6.7, $H_{amine\text{-}methyl}$). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), (*R,S*)-**5d**, selected signals, δ (ppm): 3.71 (s, 3H, CO_2Me), 3.39 (dd, 1H, J_{HH} = 14.3, J_{HH} = 4.0, H_6), 3.22 (dd, 1H, J_{HH} = 14.2, J_{HH} = 9.5, $H_{6'}$).

Synthesis of 7a−d in $CDCl_3$ Solution. The addition of a few drops of pyridine-D_5 to a solution of **3** in $CDCl_3$ affords the corresponding mononuclear compound **7a**−**d** in solution. **7a**, ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 7.98 (s, 1H, H_4), 7.26 (d, 1H, J_{HH} = 8.0, H_3), 7.07 (dd, 1H, J_{HH} = 8.0, J_{HH} = 2.0, H_2), 6.14 (s, 1H, H_1), 4.72 (s, 2H, H_5), 3.81 (s, 3H, CO_2Me). **7b**, ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 8.16 (s, 1H, H_4), 7.27 (d, 1H, J_{HH} = 8.0, H_3), 7.07 (d, 1H, J_{HH} = 8.0, H_2), 6.09 (s, 1H, H_1), 5.47 (q, 1H, J_{HH} = 6.8, H_5), 3.80 (s, 3H, CO_2Me), 1.67 (d, 3H, J_{HH} = 7.2, H_6). **7c**, ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 8.46 (s, 1H, H_4), 7.30 (d, 1H, J_{HH} = 8.0, H_3), 7.07 (dd, 1H, J_{HH} = 8.0, J_{HH} = 2.0, H_2), 6.06 (s, 1H, H_1), 5.47 (d, 1H, J_{HH} = 8.4, H_5), 3.77 (s, 3H, CO_2Me), 2.37 (m, 1H, J_{HH} = 7.8, J_{HH} = 6.7, H_6), 1.08 (d, 3H, J_{HH} = 6.8, H_7), 1.07 (d, 3H, J_{HH} = 6.4, $H_{7'}$). **7d**, ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 7.76 (s, 1H, H_4), 7.10 (m, 3H, H_3+H_7), 7.01 (dd, 1H, J_{HH} = 8.0, J_{HH} = 1.8, H_2), 6.75 (d, 2H, J_{HH} = 8.4, H_8), 6.03 (d, 1H, J_{HH} = 1.7, H_1), 5.47 (br, 1H, H_5), 3.72 (s, 3H, CO_2Me), 3.56 (dd, 1H, J_{HH} = 13.9, J_{HH} = 6.0, H_6), 3.23 (dd, 1H, J_{HH} = 14.0, J_{HH} = 6.9, $H_{6'}$).

Compounds Containing PPh_3, 6, 8, and 9. **[Pd{κ^2-(C,N)-4-ClC_6H_3CH=NCH_2CO_2Me}(OAc)(PPh_3)] (6a).** A mixture of **2a** (112 mg, 0.15 mmol) and triphenylphosphine (79 mg, 0.30 mmol) in 30 mL of acetone was stirred at room temperature for 1 h. The resulting solution was concentrated to dryness on a rotatory evaporator to give a yellow solid, after addition of diethyl ether The yellow solid obtained was filtered, washed with diethyl ether, and dried under vacuum to obtain **6a**, 180 mg (94% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 8.16 (d, 1H, J_{PH} = 7.2, H_4), 7.76 (m, 6H, PPh_3 *ortho*), 7.43 (m, 9H, PPh_3 *meta* and *para*), 7.21 (d, 1H, J_{HH} = 8.0, H_3), 6.89 (dd, 1H, J_{HH} = 8.0, J_{HH} = 1.9, H_2), 6.33 (dd, 1H, J_{PH} = 5.3, J_{HH} = 1.9, H_1), 4.43 (d, 2H, J_{PH} = 3.5, H_5), 3.77 (s, 3H, CO_2Me), 1.38 (s, 3H, OAc). ^{31}P{^{1}H} NMR (121.4 MHz, CH_2Cl_2, 298 K), δ (ppm): 39.40 (s). IR (KBr), ν (cm^{-1}): ν(C=O) = 1754, ν(C=N) = 1571, $\nu_a(COO^-)$ = 1618, $\nu_s(COO^-)$ = 1374, PPh_3 (q-X sensitive) = 1098. EM-ESI (*m*/*z*): $[M - OAc]^+$ = 580.0. Anal. Calcd for $C_{30}H_{27}ClNO_4PPd$: C 56.44, H 4.26, N 2.19. Found: C 56.6, H 4.4, N 2.2.

[Pd{κ^2-(C,N)-4-ClC_6H_3CH=$NCH(Me)CO_2Me$}(OAc)(PPh_3)] (6b). A mixture of **2b** (190 mg, 0.24 mmol) and triphenylphosphine (128 mg, 0.48 mmol) in 30 mL of acetone was stirred at room temperature for 1 h. The resulting solution was filtered through Celite, and the filtrate was concentrated to dryness on a rotatory evaporator to give a yellow solid after addition of diethyl ether. The yellow solid obtained was filtered, washed with diethyl ether, and dried under vacuum to obtain **6b**, 291 mg (93% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 8.29 (d, 1H, J_{PH} = 7.4, H_4), 7.72−7.80 (m, 6H, PPh_3 *ortho*), 7.35−7.50 (m, 9H, PPh_3 *meta* and *para*), 7.22 (d, 1H, J_{HH} = 8.0, H_3), 6.88 (dd, 1H, J_{HH} = 8.0, J_{HH} = 1.8, H_2), 6.33 (dd, 1H, J_{PH} = 5.4, J_{HH} = 1.8, H_1), 4.77 (qd, 1H, J_{HH} = 7.0, J_{PH} = 3.4, H_5), 3.75 (s, 3H, CO_2Me), 1.61 (d, 3H, J_{HH} = 7.1, H_6), 1.42 (s, 3H, OAc). ^{31}P{^{1}H} NMR (121.4 MHz, CH_2Cl_2, 298 K), δ (ppm): 39.11 (s). IR (KBr), ν (cm^{-1}): ν(C=O) = 1742, ν(C=N) = 1562, $\nu_a(COO^-)$ = 1616, $\nu_s(COO^-)$ = 1366, PPh_3 (q-X sensitive) = 1096. EM-MALDI (*m*/*z*): $[M - OAc]^+$ = 594.1. Anal. Calcd for $C_{31}H_{29}ClNO_4PPd$: C 57.07, H 4.48, N 2.15. Found: C 57.7, H 4.2, N 2.1.

[Pd{κ^2-(C,N)-4-ClC_6H_3CH=$NCH(^iPr)CO_2Me$}(OAc)(PPh_3)] (6c). 6c was obtained using the same procedure as that described above from 125 mg (0.15 mmol) of cyclometalated derivative **2c**. Yield: 132 mg (65%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 8.56 (d, 1H, J_{PH} = 7.72, H_4), 7.72−7.80 (m, 6H, PPh_3, *ortho*), 7.35−7.50 (m, 9H, PPh_3, *meta* and *para*), 7.24 (d, 1H, J_{HH} = 8.0, H_3), 6.88 (dd, 1H, J_{HH} = 8.0, J_{HH} = 1.9, H_2), 6.31 (dd, 1H, J_{PH} = 5.5, J_{HH} = 1.9, H_1), 4.55 (dd, 1H, J_{HH} = 8.3, J_{PH} = 3.1, H_5), 3.74 (s, 3H, CO_2Me), 2.38 (m, 1H, J_{HH} = 8.0, J_{HH} = 6.7, H_6), 1.35 (s, 3H, OAc), 1.11 (d, 3H, J_{HH} = 6.7, H_7), 0.99 (d, 3H, J_{HH} = 6.6, $H_{7'}$). ^{31}P{^{1}H} NMR (121.4 MHz, CH_2Cl_2, 298 K), δ (ppm): 39.25 (s). IR (KBr), ν (cm^{-1}): ν(C=O) = 1736, ν(C=N) = 1570, $\nu_a(COO^-)$ = 1612, $\nu_s(COO^-)$ = 1372, PPh_3 (q-X sensitive) = 1097. EM-MALDI (*m*/*z*): $[M - OAc]^+$ = 620.1. Anal. Calcd for $C_{33}H_{33}ClNO_4PPd$: C 58.25, H 4.89, N 2.06. Found: C 58.6, H 4.9, N 2.0.

[Pd{κ^2-(C,N)-4-ClC_6H_3CH=$NCH(CH_2C_6H_4$(4-OH))CO_2Me}-(OAc)(PPh_3)] (6d). 6d was obtained using the same procedure as that described above from 144 mg (0.15 mmol) of cyclometalated derivative **6d**. Yield: 194 mg (87%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 7.76 (m, 7H, H_4 + PPh_3 *ortho*), 7.34 (m, 9H, PPh_3 *meta* and *para*), 7.03 (m, 3H, H_3, H_7), 6.84 (m, 3H, H_2, H_8), 6.33 (dd, 1H, J_{HP} = 6.5, J_{HH} = 1.8, H_1), 4.60 (m, 1H, H_5), 3.68 (s, 3H, CO_2Me), 3.28 (dd, 1H, J_{HH} = 14.0, J_{HH} = 7.5, H_6), 3.21 (dd, 1H, J_{HH} = 14.0, J_{HH} = 6.5, $H_{6'}$), 1.30 (br s, 3H, OAc). ^{31}P{^{1}H} NMR (121.4 MHz, CH_2Cl_2, 298 K), δ (ppm): 39.50 (s). IR (KBr), ν (cm^{-1}): ν(C=O) = 1741, υ(C=N) = 1573, $\nu_a(COO^-)$ = 1615, $\nu_s(COO^-)$ = 1402, PPh_3 (q-X sensitive) = 1097. EM-MALDI (*m*/*z*): $[M - OAc]^+$ = 686.0. Anal. Calcd for $C_{37}H_{33}ClNO_5PPd$: C 59.69, H 4.47, N 1.88. Found: C 59.8, H 4.5, N 1.9.

[Pd{κ^2-(C,N)-4-ClC_6H_3CH=NCH_2CO_2Me}Cl(PPh_3)] (8a). A mixture of **3a** (112 mg, 0.15 mmol) and triphenylphosphine

(79 mg, 0.30 mmol) in 30 mL of acetone was stirred at room temperature for 2 h. The resulting solution was filtered through Celite and concentrated to dryness on a rotatory evaporator to give a yellow solid after addition of diethyl ether. The yellow solid obtained was filtered, washed with diethyl ether, and dried under vacuum to obtain **8a**, 151 mg (82% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 8.18 (d, 1H, J_{PH} = 7.6, H_4), 7.66−7.75 (m, 6H, PPh_3 *ortho*), 7.34−7.50 (m, 9H, PPh_3 *meta* and *para*), 7.24 (d, 1H, J_{HH} = 8.0, H_3), 6.91 (dd, 1H, J_{HH} = 8.0, J_{HH} = 1.6, H_2), 6.25 (dd, 1H, J_{PH} = 6.0, J_{HH} = 1.6, H_1), 4.83 (d, 2H, J_{PH} = 3.2, H_5), 3.77 (s, 3H, CO_2Me). $^{31}P\{^1H\}$ NMR (121.4 MHz, CH_2Cl_2, 298 K), δ (ppm): 40.48 (*s*). IR (KBr), ν (cm^{-1}): ν(C=O) = 1737, ν(C=N) = 1629, PPh_3 (q-X sensitive) = 1097. EM-MALDI (*m*/*z*): $[M - Cl]^+$ = 579.8, $[M-Cl - Pd]^+$ = 471.9. Anal. Calcd for $C_{28}H_{24}Cl_2NO_2PPd$: C 54.70, H 3.93, N 2.28. Found: C 54.9, H 4.2, N 2.2.

[Pd{κ^2-(C,N)-4-ClC$_6$H$_3$CH=NCH(Me)CO$_2$Me}Cl(PPh$_3$)] (8b). A mixture of **3b** (109 mg, 0.15 mmol) and triphenylphosphine (79 mg, 0.30 mmol) in 30 mL of acetone was stirred at room temperature for 2 h. The resulting solution was filtered through Celite and concentrated to dryness on a rotatory evaporator, and the solid obtained was eluted through a SiO_2 column, with ethyl chloroform−acetone (100:4) as eluent, to obtain **8b** as a yellow solid after addition of diethyl ether, 102 mg (54% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 8.36 (s, 1H, H_4), 7.68−7.77 (m, 6H, PPh_3 *ortho*), 7.35−7.50 (m, 9H, PPh_3 *meta* and *para*), 7.25 (d, 1H, J_{HH} = 8.0, H_3), 6.91 (dd, 1H, J_{HH} = 8.0, J_{HH} = 2.0, H_2), 6.25 (dd, 1H, J_{PH} = 6.0, J_{HH} = 1.6, H_1), 5.71 (dq, 1H, J_{HH} = 7.2, J_{PH} = 3.2, H_5), 3.76 (s, 3H, CO_2Me), 1.64 (d, 3H, J_{HH} = 7.2, H_6). $^{31}P\{^1H\}$ NMR (121.4 MHz, CH_2Cl_2, 298 K), δ (ppm): 40.64 (s). IR (KBr), ν (cm^{-1}): ν(C=O) = 1719, ν(C=N) = 1621, PPh_3 (q-X sensitive) = 1101. EM-MALDI (*m*/*z*): $M - Cl]^+$ = 594.0, $[M - Cl - Pd]^+$ = 486.2. Anal. Calcd for $C_{29}H_{26}Cl_2NO_2PPd$ C 55.39, H 4.17, N 2.23. Found: C 55.3, H 4.4, N 2.2.

[Pd{κ^2-(C,N)-4-ClC$_6$H$_3$CH=NCH(^{i}Pr)CO$_2$Me}Cl(PPh$_3$)] (8c). **8c** was obtained using the same procedure as that described above for the synthesis of **8a**, from 118 mg (0.15 mmol) of cyclometalated derivative **3c**. Yield: 142 mg (72%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 8.68 (d, 1H, J_{PH} = 8.0, H_4), 7.68−7.77 (m, 6H, PPh_3 *ortho*), 7.35−7.50 (m, 9H, PPh_3 *meta* and *para*), 7.28 (d, 1H, J_{HH} = 8.0, H_3), 6.91 (dd, 1H, J_{HH} = 8.0, J_{HH} = 2.0, H_2), 6.25 (dd, 1H, J_{PH} = 6.4, J_{HH} = 2.0, H_1), 5.67 (dd, 1H, J_{HH} = 8.0, J_{PH} = 3.2, H_5), 3.74 (s, 3H, CO_2Me), 2.37 (dh, 1H, J_{HH} = 7.9, J_{HH} = 6.6, H_6), 1.11 (d, 3H, J_{HH} = 6.8, H_7), 1.04 (d, 3H, J_{HH} = 6.8, $H_{7'}$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CH_2Cl_2, 298 K), δ (ppm): 41.15 (s). IR (KBr), ν (cm^{-1}): ν(C=O) = 1723, ν(C=N) = 1615, PPh_3 (q-X sensitive) = 1097. EM-MALDI (*m*/*z*): $[M - Cl]^+$ = 620.4. Anal. Calcd for $C_{31}H_{30}Cl_2NO_2PPd$: C 56.68, H 4.60, N 2.13. Found: C 56.8, H 4.6, N 2.1.

[Pd{κ^2-(C,N)-4-ClC$_6$H$_3$CH=NCH(CH$_2$C$_6$H$_4$(4-OH))CO$_2$Me}-Cl(PPh$_3$)] (8d). 8d was obtained using the same procedure as that described above for the synthesis of **8b**, from 138 mg (0.15 mmol) of cyclometalated derivative **3d**. Yield: 52 mg (24%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 8.11 (d, 1H, J_{PH} = 1.6, H_4), 7.65−7.80 (m, 6H, PPh_3 *ortho*), 7.35−7.50 (m, 9H, PPh_3 *meta* and *para*), 7.12 (d, 2H, J_{HH} = 8.4, H_7), 7.11 (d, 1H, J_{HH} = 8.0, H_3), 6.86 (dd, 1H, J_{HH} = 8.0, J_{HH} = 2.0, H_2), 6.70 (d, 2H, J_{HH} = 8.4, H_8), 6.25 (dd, 1H, J_{PH} = 6.0, J_{HH} = 2.0, H_1), 5.75 (m, 1H, H_5), 5.43 (br s, 1H, OH), 3.65 (s, 3H, CO_2Me), 3.55 (dd, 1H, J_{HH} = 13.6, J_{HH} = 5.4, H_6), 3.11 (dd, 1H, J_{HH} = 13.6, J_{HH} = 8.0, $H_{6'}$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CH_2Cl_2, 298 K), δ (ppm): 41.15 (s). IR (KBr), ν (cm^{-1}): ν(C=O) = 1736, ν(C=N) = 1614, PPh_3 (q-X sensitive) = 1096. EM-MALDI (*m*/*z*): $[M - Cl]^+$ = 686.0, $[M - Cl - Pd]^+$ = 578.1. Anal. Calcd for $C_{35}H_{30}Cl_2NO_3PPd$: C 58.31, H 4.19, N 1.94. Found: C 58.5, H 4.3, N 1.9.

[Pd{κ^3-(C,N,O)-4-ClC$_6$H$_3$CH=NCH(^{i}Pr)CO$_2$}(PPh$_3$)] (9c). **9c** was obtained by refluxing 20 mL of an acetone solution of **6c** (54 mg, 0.09 mmol) for 24 h. The resulting solution was concentrated to dryness on a rotatory evaporator to give a yellow solid. The yellow solid obtained was filtered and recrystallized from dichlorometane−methanol to obtain **9c**, 40 mg (83% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (ppm): 8.03 (dd, 1H, J_{PH} = 10.0, J_{HH} = 1.1, H_4), 7.60−7.80 (m, 6H, PPh_3 *ortho*), 7.48−7.51 (m, 6H, PPh_3 *meta*), 7.37−7.46 (m, 1H, PPh_3 *para*), 7.21 (d, 1H, J_{HH} = 8.2, H_3), 6.96 (dd, 1H, J_{HH} = 8.0, J_{HH} = 2.0, H_2), 5.99 (dd, 1H, J_{PH} = 3.7, J_{HH} = 2.0, H_1), 4.21 (ddd, 1H, J_{PH} = 4.7, J_{HH} = 4.0, J_{HH} = 1.1, H_5), 2.38 (hd, 1H, J_{HH} = 6.9, J_{HH} = 3.7, H_6), 1.21 (d, 3H, J_{HH} = 6.9, H_7), 1.19 (d, 3H, J_{HH} = 6.9, $H_{7'}$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CH_2Cl_2, 298 K), δ (ppm): 32.93(s). EM-ESI (*m*/*z*): 606.05 ($(M + H)^+$. Anal. Calcd for $C_{30}H_{27}ClNO_2PPd$: C 59.42, H 4.49, N 2.31. Found: C 59.3, H 4.4, N 2.3.

[Pd{κ^3-(C,N,O)-4-ClC$_6$H$_3$CH=NCH(CH$_2$C$_6$H$_4$(4-OH))CO$_2$}-(PPh$_3$)] (9d). 9d was obtained by refluxing an acetone solution (20 mL) of **6d** (102 mg, 0.15 mmol) for 24 h. The resulting solution was concentrated to dryness on a rotatory evaporator to give a yellow solid after addition of diethyl ether. The yellow solid obtained was filtered and recrystallized from dichlorometane−diethyl ether to obtain **9d**, 70 mg (70% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 7.64−7.73 (m, 7H, H_4 + PPh_3 *ortho*), 7.48−7.51 (m, 6H, PPh_3 *meta*), 7.38−7.49 (m, 3H, PPh_3 *para*), 6.95 (m, 3H, H_3, H_7), 6.75 (m, 3H, H_2, H_8), 5.98 (dd, 1H, J_{HP} = 3.8, J_{HH} = 1.9, H_1), 4.46 (m, 1H, H_5), 3.10 (m, 2H, H_6). $^{31}P\{^1H\}$ NMR (121.4 MHz, CH_2Cl_2, 298 K), δ (ppm): 32.22 (s). EM-MALDI (*m*/*z*): 670.05 $(M + H)^+$. Anal. Calcd for $C_{34}H_{27}ClNO_3PPd$: C 60.91, H 4.06, N 2.09. Found: C 60.7, H 3.8, N 2.1.

NMR Data of Compounds 10a−d. 10a, ^{1}H NMR (400 MHz, acetone-D_6, 298 K), δ (ppm): 8.36 (s, 1H, H_4), 7.54 (d, 1H, J_{HH} = 8.1, H_3), 7.27 (dd, 1H, J_{HH} = 8.0, J_{HH} = 1.73, H_2), 6.71 (br s, 1H, H_1), 4.46 (s, 2H, H_5), 3.78 (s, 3H, CO_2Me), 3.69 (br s, H_2O). ^{19}F NMR (376.5 MHz, acetone-D_6), δ (ppm): −151.89 (br s, F−^{11}B, 80.9%), −151.84 (br s, F−^{10}B, 19.1%).

10b: ^{1}H NMR (400 MHz, acetone-D_6, 298 K), δ (ppm): 8.42 (s, 1H, H_4), 7.51 (d, 1H, J_{HH} = 7.9, H_3), 7.23 (d, 1H, J_{HH} = 7.9, H_2), 6.90 (br s, 1H, H_1), 4.60 (m, 1H, H_5), 3.79 (s, 3H, CO_2Me), 3.34 (br s, H_2O), 1.70 (d, 3H, J_{HH} = 7.0, H_6). ^{19}F NMR (376.5 MHz, acetone-D_6), δ (ppm): −152.22 (br s, F−^{11}B, 80.9%), −152.17 (br s, F−^{10}B, 19.1%).

10c: ^{1}H NMR (400 MHz, acetone-D_6, 298 K), δ (ppm): 8.52 (s, 1H, H_4), 7.56 (d, 1H, J_{HH} = 8.0, H_3), 7.26 (d, 1H, J_{HH} = 7.6, H_2), 6.84 (br s, 1H, H_1), 4.06 (br s, 1H, H_5), 3.82 (s, 3H, CO_2Me), 3.33 (br s, H_2O), 2.47 (dh, 1H, J_{HH} = 8.6, $J_{HH'}$ = 6.8, H_6), 1.14 (d, 3H, J_{HH} = 6.6, H_7), 1.05 (d, 3H, J_{HH} = 6.6, $H_{7'}$). ^{19}F NMR (376.5 MHz, acetone-D_6), δ (ppm): −152.79 (br s, F−^{11}B, 80.9%), −152.74 (br s, F−^{10}B, 19.1%).

10d: ^{1}H NMR (400 MHz, acetone-D_6, 298 K), δ (ppm): 8.29 (s, 1H, OH), 8.03 (s, 1H, H_4), 7.40 (d, 1H, J_{HH} = 8.0, H_3), 7.25 (d, 2H, J_{HH} = 8.5, H_7), 7.21 (d, 1H, J_{HH} = 7.9, H_2), 6.77 (d, 2H, J_{HH} = 8.5, H_8), 6.69 (br s, 1H, H_1), 4.55 (dd, 1H, $J_{HH'}$ = 9.9, J_{HH} = 4.3, H_5), 3.82 (s, 3H, CO_2Me), 3.41 (dd, 1H, $J_{HH'}$ = 14.1, J_{HH} = 4.4, H_6), 3.19 (dd, 1H, $J_{HH'}$ = 14.3, J_{HH} = 10.0, $H_{6'}$), 3.06 (br s, H_2O). ^{19}F NMR (376.5 MHz, acetone-D_6), δ (ppm): −153.18 (br s, F−^{11}B, 80.9%), −153.12 (br s, F−^{10}B, 19.1%).

[Pd{κ^2-(C,N)-4-ClC$_6$H$_3$CH=NCH$_2$CO$_2$Me}(dppe)]BF$_4$ (11a). A mixture of cyclopalladated compound **3a** (50 mg, 0.07 mmol) and silver tetrafluoroborate (41 mg, 0.21 mmol) was stirred for 1 h in acetone at room temperature. Then the undissolved materials were removed by filtration, washed with acetone, and discarded. 1,2-Bis(diphenylphosphino)ethane (53 mg, 0.13 mmol) was added to the filtrate, and the mixture was stirred for 2 h in acetone at room temperature. The resulting solution was concentrated to dryness on a rotatory evaporator to give compound **11a** after addition of diethyl ether, 95 mg (90%), as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 8.64 (d, 1H, J_{PH} = 7.4, H_4), 7.4−8.1 (m, 21H, 2PPh_2+H_3), 7.17 (dd, 1H, J_{HH} = 8.0, J_{HH} = 2.0, H_2), 6.62 (ddd, 1H, J_{PH} = 7.8, J_{PH} = 5.1, J_{HH} = 2.0, H_1), 4.26 (dd, 1H, J_{PH} = 3.4, J_{PH} = 1.5, H_5), 3.35 (s, 3H, CO_2Me), 2.5−2.9 (m, 4H, 2CH_2). ^{19}F NMR (376.5 MHz, $CDCl_3$), δ (ppm): −151.96 (br s,

F−^{11}B, 80.9%), −151.91 (br s, F−^{10}B, 19.1%). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-D_6) δ: 62.40 (d, J_{PP} = 25.8, $P_{transtoN}$), 45.64 (d, J_{PP} = 25.8, P $P_{transtoC}$). IR (KBr), ν (cm^{-1}): ν(C═O) = 1742, ν(C═N) = 1625, ν(BF_4) = 1071. MS-ESI, m/z: $[M]^+$ = 714.07. Anal. Calcd for $C_{36}H_{33}BClF_4NO_2P_2Pd$: C 53.90, H 4.15, N 1.75. Found: C 53.3, H 4.0, N 1.7.

[Pd{κ^2-(C,N)-4-ClC_6H_3CH═NCH(Me)CO_2Me}(dppe)]BF_4. (11b). 11b was obtained using the same procedure as that described above from 37 mg (0.05 mmol) of cyclopalladated complex **3b**, 30 mg (0.15 mmol) of silver tetrafluoroborate, and 40 mg (0.1 mmol) of 1,2-bis(diphenylphosphino)ethane. Yield: 74 mg (91%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 8.49 (br s, 1H, H_4), 7.3−8.0 (m, 21H, 2PPh_2+H_3), 7.05 (br s, 1H, H_2), 6.53 (br s, 1H, H_1), 4.13 (br s, 1H, H_5), 3.49 (br s, 3H, CO_2Me), 2.3−3.0 (m, 4H, 2CH_2), 1.14 (d, 3H, J_{HH} = 6.1, H_6). ^{19}F NMR (376.5 MHz, $CDCl_3$), δ (ppm): −152.66 (br s, F−^{11}B, 80.9%), −152.61 (br s, F−^{10}B, 19.1%). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-D_6) δ: 62.34 (d, J_{PP} = 26.2, $P_{transtoN}$), 46.95 (d, J_{PP} = 26.2, P $P_{transtoC}$). IR (KBr), ν (cm^{-1}): ν(C═O) = 1739, ν(C═N) = 1611, ν(BF_4) = 1077. MS-MALDI, m/z: $[M - CO_2Me]^+$ = 671.3. Anal. Calcd for $C_{37}H_{35}BClF_4NO_2P_2Pd$: C 54.44, H 4.32, N 1.72. Found: C 54.1, H 4.1, N 1.7.

[Pd{κ^2-(C,N)-4-ClC_6H_3CH═NCH(Me)CO_2Me}(dppe)]BF_4. (11c). 11c was obtained using the same procedure as that described above from 32 mg (0.04 mmol) of cyclopalladated complex **3c**, 23 mg (0.12 mmol) of silver tetrafluoroborate, and 31 mg (0.08 mmol) of 1,2-bis(diphenylphosphino)ethane. Yield: 57 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 8.65 (d, 1H, J_{PH} = 7.5, H_4), 7.4−8.1 (m, 21H, 2PPh_2+H_3), 7.06 (dd, 1H, J_{HH} = 8.0, J_{HH} = 1.9, H_2), 6.53 (ddd, 1H, J_{PH} = 8.0, J_{PH} = 5.3, J_{HH} = 1.9, H_1), 3.73 (dd, 1H, J_{HH} = 9.9, J_{PH} = 2.1, H_5), 3.47 (s, 3H, CO_2Me), 2.7−3.2 (m, 4H, 2CH_2), 2.02 (dh, 1H, J_{HH} = 10.0, J_{HH} = 6.6, H_6), 0.48 (d, 3H, J_{HH} = 6.5, H_7), 0.41 (d, 3H, J_6 = 6.6, H_{HH}). ^{19}F NMR (376.5 MHz, $CDCl_3$), δ (ppm): −156.09 (br s, F−^{11}B, 80.0%), −152.04 (br s, F−^{10}B, 20.0%). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-D_6) δ: 62.28 (d, J_{PP} = 25.7, P_2), 46.12 (d, J_{PP} = 25.6, P_1). IR (cm^{-1}): ν(C═O) = 1735, ν(C═N) = 1609, ν(BF_4) = 1082. EM-MALDI (m/z): $[M - OMe]^+$ = 729.8. Anal. Calcd for $C_{39}H_{39}BClF_4NO_2P_2Pd$: C 55.48, H 4.66, N 1.66. Found: C 55.8, H 4.4, N 1.6.

[2-CH_2CO_2Me-3,4-Ph_2-6-Cl-C_9H_4N]BF_4 (12a). A mixture of cyclopalladated compound **3a** (126 mg, 0.18 mmol) and silver tetrafluoroborate (105 mg, 0.54 mmol) was stirred for 1 h in acetone at room temperature. Then, the undissolved materials were removed by filtration, washed with acetone, and discarded. The resulting solution was concentrated to dryness on a rotatory evaporator, and the solid obtained was dissolved in 35 mL of nitromethane. Diphenylacetylene (112 mg, 0.63 mmol) was added to this solution, and the mixture was refluxed for 48 h. The resulting suspension was filtered through Celite, the filtrate was concentrated to dryness on a rotatory evaporator, and the solid obtained was eluted through a SiO_2 column, with ethyl acetone−chloroform (1:1) as eluent, to obtain **12a** as a white solid, 72 mg (42% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 10.24 (s, 1H, H_4), 8.78 (d, 1H, J_{HH} = 8.8, H_3), 8.19 (d, 1H, J_{HH} = 8.8, J_{HH} = 2.0, H_2), 7.71 (dd, 1H, J_{HH} = 1.9, H_1), 7.45 (br s, 5H, Ph), 7.40 (br s, 5H, Ph), 5.57 (s, 2H, H_5), 3.70 (s, 3H, CO_2Me). ^{19}F NMR (376.5 MHz, $CDCl_3$), δ (ppm): −154.59 (br s, F−^{11}B, 80.9%), −154.03 (br s, F−^{10}B, 19.1%). IR (KBr), ν (cm^{-1}): ν(C═O) = 1742, ν(C═N) = 1629, ν(BF_4) = 1082. MS-ESI, m/z: $[M]^+$ = 388.5. Anal. Calcd for $C_{24}H_{19}BClF_4NO_2$: C 60.60, H 4.03, N 2.94. Found: C 61.1, H 3.8, N 2.9.

[2-CH(Me)CO_2Me-3,4-Ph_2-6-Cl-C_9H_4N]BF_4 (12b). 12b was obtained using the same procedure as that described above from 140 mg (0.18 mmol) of cyclopalladated compound **3b**, 105 mg (0.54 mmol) of silver tetrafluoroborate, and 120 mg (0.67 mmol) of diphenylacetylene. Yield: 130 mg (58%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 10.34 (s, 1H, H_4), 8.85 (d, 1H, J_{HH} = 8.8, H_3), 8.17 (d, 1H, J_{HH} = 8.8, J_{HH} = 2.0, H_2), 7.66 (dd, 1H, J_{HH} = 1.9, J_{para} = 0.6, H_1), 7.50−7.25 (m, 10H, 2Ph), 5.64 (d, 1H, J_{HH} = 7.2, H_5), 3.75 (s, 3H, CO_2Me), 2.14 (d, 3H, J_{HH} = 7.2, H_6). ^{19}F NMR (376.5 MHz, $CDCl_3$), δ (ppm): −151.77 (br s, F−^{11}B, 80.9%), −151.72 (br s, F−^{10}B, 19.1%). IR (KBr), ν (cm^{-1}): ν(C═O) = 1748, ν(C═N) = 1619, ν(BF_4) = 1077. MS-ESI, m/z: $[M]^+$ = 402.5. Anal. Calcd for $C_{25}H_{21}BClF_4NO_2$: C 61.32, H 4.32, N 2.86. Found: C 61.8, H 4.4, N 2.9.

[2-CH(^{i}Pr)CO_2Me-3,4-Ph_2-6-Cl-C_9H_4N]BF_4 (12c). 12c was obtained using the same procedure as that described above from 166 mg (0.21 mmol) of cyclopalladated compound **3c**, 126 mg (0.65 mmol) of silver tetrafluoroborate, and 136 mg (0.76 mmol) of diphenylacetylene. Yield: 165 mg (64%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 10.22 (s, 1H, H_4), 7.90 (d, 1H, J_{HH} = 8.9, H_3), 7.94 (d, 1H, J_{HH} = 8.9, J_{HH} = 1.9, H_2), 7.58 (d, 1H, J_{HH} = 1.9, H_1), 7.50−7.00 (m, 10H, 2Ph), 4.86 (d, 1H, J_{HH} = 10.1, H_5), 3.87 (s, 3H, CO_2Me), 3.08 (dh, 1H, J_{HH} = 10.1, J_{HH} = 6.5, H_6), 1.08 (d, 3H, J_{HH} = 6.5, H_7), 0.88 (d, 3H, J_{HH} = 6.6, $H_{7'}$). ^{19}F NMR (376.5 MHz, $CDCl_3$), δ (ppm): −152.95 (br s, F−^{11}B, 80.9%), −152.89 (br s, F−^{10}B, 19.1%). IR (KBr), ν (cm^{-1}): ν(C═O) = 1738, ν(C═N) = 1619, ν(BF_4) = 1079. MS-ESI, m/z: $[M]^+$ = 431.2. Anal. Calcd for $C_{27}H_{25}BClF_4NO_2$: C 62.63, H 4.87, N 2.87. Found: C 62.2, H 4.6, N 2.9.

[2-CH($CH_2C_6H_4$(4-OH)CO_2Me-3,4-Ph_2-6-Cl-C_9H_4N]BF_4 (12d). 12d was obtained using the same procedure as that described above from 238 mg (0.26 mmol) of cyclopalladated compound **3d**, 152 mg (0.78 mmol) of silver tetrafluoroborate, and 164 mg (0.92 mmol) of diphenylacetylene. Yield: 95 mg (28%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 10.51 (s, 1H, H_4), 8.90 (d, 1H, J_{HH} = 8.9, H_3), 8.21 (dd, 1H, J_{HH} = 8.9, J_{HH} = 1.9, H_2), 7.64 (d, 1H, J_{HH} = 1.9, H_1), 7.30−7.00 (m, 9H, 9Ph), 6.88 (d, 2H, J_{HH} = 8.5, H_7), 6.72 (d, 2H, J_{HH} = 8.5, H_8), 6.63 (dd, 1H, J_{HH} = 7.8, J_{HH} = 1.1, 1Ph), 5.67 (dd, 1H, J_{HH} = 8.4, J_{HH} = 6.9, H_5), 3.82 (s, 3H, CO_2Me), 3.78 (d, 1H, J_{HH} = 6.8, H_6), 3.78 (d, 1H, J_{HH} = 8.5, $H_{6'}$). ^{19}F NMR (376.5 MHz, $CDCl_3$), δ (ppm): −152.05 (br s, F−^{11}B, 80.9%), −152.99 (br s, F−^{10}B, 19.1%). IR (KBr), ν (cm^{-1}): ν(OH) = 3447, ν(C═O) = 1748, ν(C═N) = 1621, ν(BF_4) = 1084. MS-ESI, m/z: $[M]^+$ = 494.5. Anal. Calcd for $C_{31}H_{25}BClF_4NO_3$: C 64.00, H 4.33, N 2.41. Found: C 63.6, H 4.1, N 2.3.

X-ray Structure Analysis. 3c. A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a BrukerAXS ApexII-CCD area detector. Unit-cell parameters were determined from 1908 reflections (2.58° < θ < 26.78°) and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo Kα radiation; 12 370 reflections were measured in the range 1.23° ≤ θ ≤ 26.37°; 10 400 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 SIR97[21] and refined by the full-matrix least-squares method with the SHELX97 computer program,[22] using 12 370 reflections; very negative intensities were not assumed. The function minimized was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + 71.9906P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f', and f'' were taken from International Tables of X-ray Crystallography.[23] 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 atoms that are linked. The final R(on F) factor was 0.076, wR(on $|F|^2$) = 0.146, and goodness of fit = 1.277 for all observed reflections. Number of refined parameters was 697. Max. shift/esd = 0.00, mean shift/esd = 0.00. Max. and min. peaks in final difference synthesis were 1.837 and −2.084 e Å^{-3}, respectively.

8a. A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a MAR345 diffractometer with an image plate detector. Unit-cell parameters were determined from 3930

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Table 2. Crystallographic and Structure Refinement Data for Compounds 3c, 8a, 9c, and 12b

	3c	8a	9c	12b
empirical formula	$C_{26}H_{30}Cl_4N_2O_4Pd_2$	$C_{28}H_{24}Cl_2NO_2PPd\cdot CHCl_3$	$2(C_{30}H_{27}ClNO_2PPd)\cdot H_2O$	$2[(C_{25}H_{21}NO_2)BF_4]\cdot 5H_2$
fw	789.16	734.1	1230.71	1069.46
temperature	100(2) K	293(2) K	293(2) K	90(2) K
wavelength	0.71069 Å	0.71073 Å	0.71073 Å	0.71073 Å
cryst syst, space group	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$
unit cell dimens	a = 11.2943(4) Å	a = 7.938(3) Å	a = 16.343(13) Å	a = 11.962(2) Å
	b = 16.2444(6) Å	b = 11.264(3) Å	b = 8.898(6) Å	b = 26.247(5) Å
	c = 33.4743(13) Å	c = 18.289(6) Å	c = 19.107(8) Å	c = 8.3818(15) Å
	α = 90°	α = 90.93(2)°	α = 90°	α = 90°
	β = 99.710(2)°	β = 96.83(2)°	β = 99.43(4)°	β = 95.933(3)°
	γ = 90°	γ = 107.60(2)°	γ = 90°	γ = 90°
volume	6053.5(4) Å^3	1545.3(9) Å^3	2741(3) Å^3	2617.6(8) Å^3
Z, calcd density	8, 1.732 Mg/m^3	2, 1.578 Mg/m^3	2, 1.491 Mg/m^3	2, 1.357 Mg/m^3
absorp coeff	1.575 mm^{-1}	1.112 mm^{-1}	0.863 mm^{-1}	0.208 mm^{-1}
F(000)	3136	736	1252	1108
cryst size	0.16 × 0.13 × 0.07 mm	0.2 × 0.1 × 0.1 mm	0.2 × 0.1 × 0.1 mm	0.43 × 0.26 × 0.09 mm
θ range for data collection	1.23° to 26.37°	2.80° to 30.64°	2.61° to 32.62°	1.55° to 26.41°
limiting indices	$-14 \le h \le 13$	$-10 \le h \le 9$	$-24 \le h \le 24$	$-14 \le h \le 14$
	$0 \le k \le 20$	$-16 \le k \le 14$	$-11 \le k \le 11$	$-32 \le k \le 32$
	$0 \le l \le 41$	$-24 \le l \le 24$	$-25 \le l \le 28$	$-10 \le l \le 10$
reflns collected/unique	7104/12 370	12 579/6936	24 527/8167	22 166/5367
	[R(int) = 0.0544]	[R(int) = 0.0362]	[R(int) = 0.0460]	[R(int) = 0.0505]
completeness to θ	= 26.37°, 99.9%	= 25.00°, 90.7%	= 25.00°, 92.8%	= 26.41°, 99.9%
absorp corr	semiempirical from equivalents	empirical	empirical	semiempirical from equivalents
max. and min. transmn	0.8977 and 0.7867	0.89 and 0.87	0.92 and 0.90	0.9827 and 0.9209
refinement method	full-matrix least-squares on F^2			
data/restraints/params	12 370/1/697	6936/7/353	8167/10/334	5367/2/348
goodness-of-fit on F^2	1.277	1.093	0.727	1.138
final R indices [$I > 2\sigma(I)$]	R1 = 0.0763	R1 = 0.0436	R1 = 0.0403	R1 = 0.0548
	wR2 = 0.1426	wR2 = 0.1254	wR2 = 0.0704	wR2 = 0.1823
R indices (all data)	R1 = 0.0902	R1 = 0.0495	R1 = 0.1520	R1 = 0.0919
	wR2 = 0.1468	wR2 = 0.1290	wR2 = 0.0878	wR2 = 0.2078
extinction coeff		0.0240(17)		
largest diff peak and hole	1.837 and −2.084 e Å^{-3}	0.852 and −0.519 e Å^{-3}	0.515 and −0.314 e Å^{-3}	1.141 and −0.398 e Å^{-3}

reflections (3° < θ < 31°) and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo Kα radiation; 12 579 reflections were measured in the range 2.80° ≤ θ ≤ 30.64°, 6936 of which were nonequivalent by symmetry (R_{int}(on I) = 0.036); 6075 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 SHELXS computer program,[24] and refined by the full-matrix least-squares method with the SHELX97 computer program,[22] using 125 792 reflections; very negative intensities were not assumed. The function minimized was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0675P)^2 + 0.7493P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f', and f'' were taken from International Tables of X-ray Crystallography.[23] 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 atoms that are linked. The final R(on F) factor was 0.049, wR(on $|F|^2$) = 0.129, and goodness of fit = 1.093 for all observed reflections. Number of refined parameters was 353. Max. shift/esd = 0.00, mean shift/esd = 0.00. Max. and min. peaks in final difference synthesis were 0.852 and −0.519 e Å^{-3}, respectively.

9c. A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a MAR345 diffractometer with image plate detector. Unit-cell parameters were determined from 55 reflections (3° < θ < 31°) and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation; 24 527 reflections were measured in the range 2.61° ≤ θ ≤ 32.62°, 8167 of which were nonequivalent by symmetry (R_{int}(on I) = 0.046); 3093 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Lorentz−polarization but no absorption corrections were made. The structure was solved by direct methods, using the SHELXS computer program,[24] and refined by the full-matrix least-squares method with the SHELX97 computer program,[22] using 24 527 reflections; very negative intensities were not assumed. The function minimized was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0167P)^2]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f', and f'' were taken from International Tables of X-ray Crystallography.[23] 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 atoms that are linked. The final R(on F) factor was 0.040, wR(on $|F|^2$) = 0.070, and goodness of fit = 0.727 for all observed reflections. Number of refined parameters was 334. Max. shift/esd = 0.00, mean shift/esd = 0.00. Max. and min. peaks in final difference synthesis were 0.515 and −0.314 e Å^{-3}, respectively.

12b. A prismatic crystal (0.43 × 0.26 × 0.09 mm) was selected and mounted on a Smart-CCD-1000 Bruker diffractometer. Unit-cell parameters were determined from automatic centering of 25 reflections (2.31° < θ < 26.23°) and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo Kα radiation; 22 166 reflections were measured in the range 1.55 ≤ θ ≤ 26.41, 5367 of which were nonequivalent by symmetry (R_{int}(on I) = 0.050); 3500 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 SHELXS computer program,[24] and refined by the full-matrix least-squares method with the SHELX97 computer program,[22] using 22 166 reflections; very negative intensities were not assumed. The function minimized was $\sum w||F|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0986P)^2 + 1.9906P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f', and f'' were taken from International Tables of X-ray Crystallography.[23] All H atoms were computed and refined, using a riding model, with an isotropic temperature

(24) Sheldrick, G. M. *SHELXS A Program for Automatic Solution of Crystal Structure*; University of Gottingen: Germany, 1997.

factor equal to 1.2 times the equivalent temperature factor of the atoms that are linked. The final R(on F) factor was 0.055, wR(on $|F|^2$) = 0.1823, and goodness of fit = 1.138 for all observed reflections. Number of refined parameters was 348. Max. shift/esd = 0.000, mean shift/esd = 0.00. Max. and min. peaks in final difference synthesis were 1.141 and −0.398 e $Å^{-3}$, respectively.

A summary of the crystallographic data for compounds **2c**, **8a**, **9c**, and **12b** and some details of the refinement are given in Table 2. CCDC-749661, (**3c**) CCDC-749662 (**8a**), CCDC-749663 (**9c**), and CCDC-749664 (**12b**) 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; e-mail: deposit@ccdc.cam.ac.uk.

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