

**Mixed Triply and Doubly Bridged Dinuclear  
Palladium(II) Cyclometalated Compounds. Crystal and  
Molecular Structures of  
[1,3-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>]( $\mu$ -O<sub>2</sub>CMe)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]  
and [1,4-{Pd[2,3,4-  
(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>](Cl)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>( $\mu$ -Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)]**

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Reaction of the Schiff base ligand 1,3-[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**1**) with palladium(II) acetate in toluene gave the doubly cyclometalated complex [1,3-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>]( $\mu$ -O<sub>2</sub>CMe)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>] (**2**), in which the two palladium atoms are intramolecularly bonded by acetato bridging ligands. The crystal structure of **2** is given. Reaction of the Schiff base ligand 1,4-[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**6**) with palladium(II) acetate under similar reaction conditions yielded the cyclometalated complex [1,4-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>]( $\mu$ -O<sub>2</sub>CMe)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sub>n</sub> (**7**), probably of polymeric nature. Reaction of **2** and **7** with aqueous sodium chloride gave the chloro-bridged complexes [1,3-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>]( $\mu$ -Cl)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sub>2</sub> (**3**) and [1,4-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>]( $\mu$ -Cl)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sub>2</sub> (**8**), respectively, after a metathesis reaction. Treatment of complex **2** with Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub> (dppp) in a 1:1 molar ratio gave the dinuclear cyclometalated complex [1,3-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>](OAc)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>( $\mu$ -Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)] (**4**), in which the metal atoms are bonded by the diphosphine ligand. Treatment of the chloro-bridged complex **3** with dppp in a 1:2 molar ratio gave the dinuclear cyclometalated complex [1,3-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>](Cl)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>( $\mu$ -Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)] (**5**), with the palladium atoms intramolecularly bridged by the diphosphine. The complex showed a fluxional behavior in solution, with the cyclometalated moieties adopting a cis/trans arrangement. Reaction of the chloro-bridged complex **8** with dppp in a 1:2 molar ratio yielded the mixture of complexes [1,4-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>](Cl)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>( $\mu$ -Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)] (**9**) and [1,4-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>](Cl)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>( $\mu$ -Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)]<sub>2</sub> (**10**), of which only **9** was isolated pure. Compound **9** showed a structure and solution behavior similar to those of **5**; however, the structure of **10** was not unambiguously established. The crystal structure of **9** is also reported.

### Introduction

Cyclometalated compounds have aroused great interest due to the many applications they present in, for example, organic and organometallic chemistry<sup>1,2</sup> or in the synthesis of bioactive compounds,<sup>3,4</sup> and they have

been extensively reviewed.<sup>5–9</sup> More recently we have reported their use in promoting new coordination environments.<sup>10,11</sup>

In the majority of cases, cyclometalation involves the coordination of one metal atom per organic ligand; however, a relatively large number of examples with

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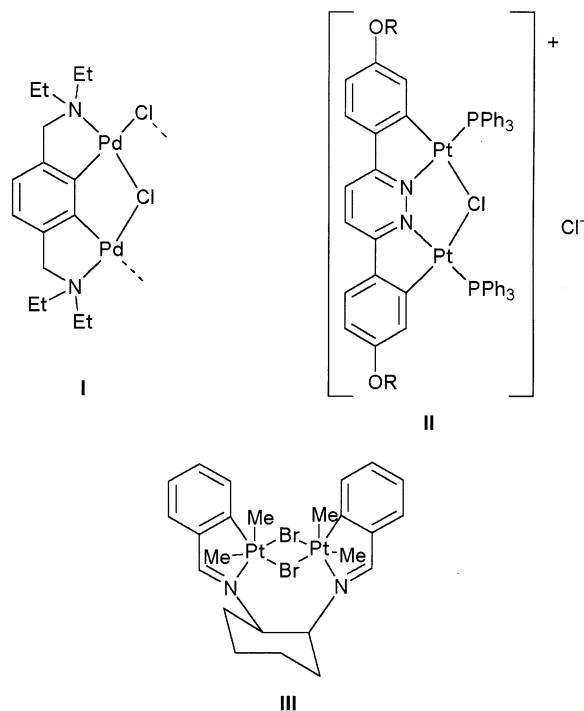
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**Figure 1.**

doubly cyclometalated ligands are known.<sup>12–33</sup> Much less common are those compounds in which the two metal atoms bonded to the organic moiety are also intramolecularly linked through a second ligand. Since the first compound of this kind was reported by Trofimenko (**I**; see Figure 1),<sup>24</sup> little work has been done on this subject. With the purpose of promoting formation of the intramolecular bridge the geometric characteristics of the cyclometalated ligand must be carefully selected. Thus, the ligand may be either rigid enough to hold the metalated atoms close together and induce intramolecular coordination (**I** and **II**)<sup>24,34</sup> or sufficiently

flexible to bring near both metal centers (**III**),<sup>13</sup> hence promoting intramolecular bridging.

In past years we have been interested in the double cyclometalation of Schiff base ligands derived from 1,4-phenylenediamine.<sup>35,36</sup> In these complexes, the relative position of the metal atoms did not allow the formation of the intramolecular bridge. Therefore, with this in mind we designed the more flexible ligands 1,3-[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**1**) and 1,4-[2,3,4-(MeO)<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**6**) to achieve intramolecular coordination of the metal atoms via a second ligand. Reaction of **1** with palladium(II) acetate gave the doubly cyclometalated complex **2**, in which both palladium atoms were intramolecularly bonded by the acetato bridging ligands, which was characterized crystallographically. However, the reaction of **6** with palladium(II) acetate under analogous conditions also gave a doubly cyclometalated complex, but probably of polymeric nature. We also report the reactivity of the complexes with the tertiary diposphine Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>-PPh<sub>2</sub> (dppp) which revealed the tendency of the complexes to undergo intramolecular coordination. The X-ray crystal structure of one of these complexes is also described.

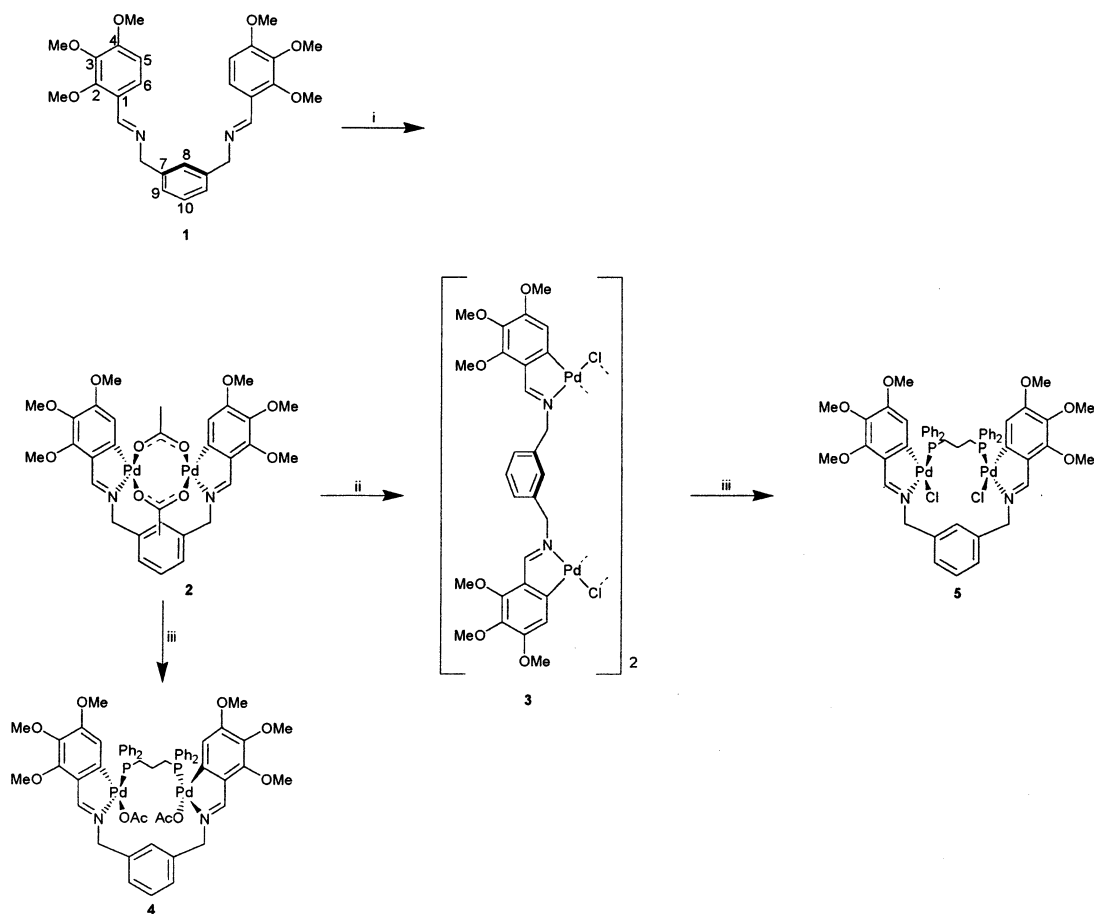
## Results and Discussion

For the convenience of the reader the compounds and reactions are shown in Schemes 1 and 2. The compounds described in this paper were characterized by elemental analysis (C, H, N), IR spectroscopy, <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H}, and (in part) <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy, and FAB mass spectrometry (data are given in the Experimental Section).

Reaction of the Schiff base ligand 1,3-[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**1**) with palladium(II) acetate in toluene gave the doubly cyclometalated complex [1,3-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>](*μ*-O<sub>2</sub>CMe)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>] (**2**), which was fully characterized. The IR spectrum of **2** showed the  $\nu(\text{C}=\text{N})$  stretch at 1600 cm<sup>-1</sup>, shifted to lower wavenumbers (as compared to the free ligand) due to N-coordination of the imine.<sup>37,38</sup> The IR spectrum also showed strong bands assigned to the symmetric and asymmetric  $\nu(\text{COO})$  vibrations, in agreement with those expected for bridging acetate ligands<sup>39</sup> (see Experimental Section). The resonance corresponding to the HC=N proton in the <sup>1</sup>H NMR spectrum was shifted to lower frequency consequent upon coordination of the imine group to the palladium atom via the lone pair of the nitrogen resonances unequivocally showed that metalation had taken place at the C6 carbon atoms. The presence of only one set of signals for the HC=N and aromatic protons was indicative of the symmetric nature

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Scheme 1<sup>a</sup>

<sup>a</sup> Legend: (i) Pd(AcO)<sub>2</sub> (toluene); (ii) NaCl (acetone/water); (iii) dppp (chloroform).

of the complex, showing that double metalation had taken place. A noticeable feature of the <sup>1</sup>H NMR spectrum was the low-field shift of the H8 resonance (as compared to the free ligand **1**) by 1.1 ppm. We believe this is due to approximation of the deshielding zone of the HC=N groups to the H8 proton compelled by the bridging acetate ligands. The <sup>1</sup>H NMR of ligand **1** showed a singlet resonance for the four CH<sub>2</sub> protons. However, two doublet signals ( $\delta$  5.05, 4.55;  $J(\text{HH}) = 15.6$  Hz) were assigned to the diastereotopic CH<sub>2</sub> protons in the <sup>1</sup>H NMR spectrum of **2**. This was due to the lower symmetry of **2**. The acetato-bridged complexes showed the characteristic open-book geometry,<sup>41–46</sup> for which two different dispositions are possible, syn and anti (Figure 2), with equivalent (anti) and nonequivalent (syn) MeCOO groups, that give rise to one and two MeCOO signals in the <sup>1</sup>H NMR spectrum, respectively.

The <sup>1</sup>H NMR spectrum of **2** showed two singlets at  $\delta$  2.23 and 1.26 assigned to the nonequivalent MeCOO

resonances as proof of a syn geometry,<sup>27</sup> imposed by linkage of the C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub> group to both nitrogen imine atoms. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **2** showed the high-frequency shift of the resonances corresponding to the HC=N, C6, and C1 carbons, confirming that metalation had occurred.<sup>47</sup>

The reaction of the Schiff base ligand 1,4-[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**6**) with palladium(II) acetate under similar reaction conditions yielded the complex [1,4-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>]( $\mu$ -O<sub>2</sub>-CMe)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sub>n</sub> (**7**). The IR spectrum showed features similar to those described for complex **2**. Likewise, the <sup>1</sup>H NMR spectrum showed the low-frequency shift of the singlet resonance corresponding to the HC=N protons and the absence of the H6 signal, indicating double metalation had occurred. This was confirmed by the shift toward higher frequency of the HC=N, C6, and C1 resonances in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. However, two broad signals at  $\delta$  4.39 and 3.65 were assigned to the CH<sub>2</sub> protons, and the <sup>1</sup>H NMR spectrum showed only one resonance for the MeCOO protons,  $\delta$  2.08; the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum showed two signals for the MeCOO and MeCOO carbons,  $\delta$  24.3 and 181.0, respectively, as expected for an anti conformation. These data preclude a dinuclear formulation analogous to the one described for complex **2**, which would require a syn arrangement. A tetranuclear formulation, similar to those reported for other doubly cyclometalated com-

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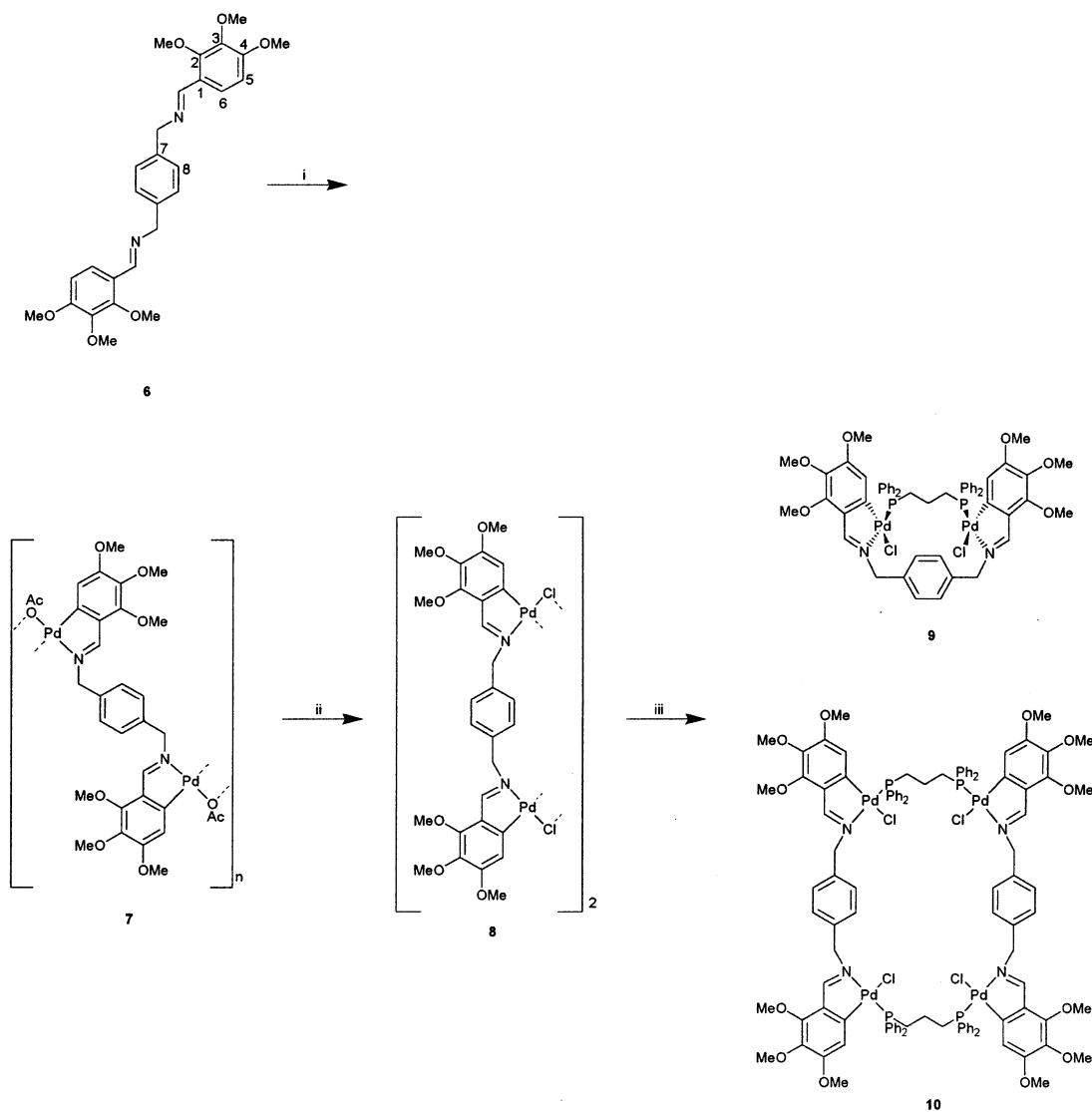
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Scheme 2<sup>a</sup>

<sup>a</sup> Legend: (i) Pd(AcO)<sub>2</sub> (toluene); (ii) NaCl (acetone/water); (iii) dppp (chloroform).

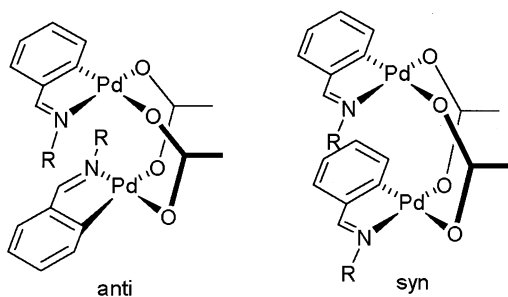


Figure 2.

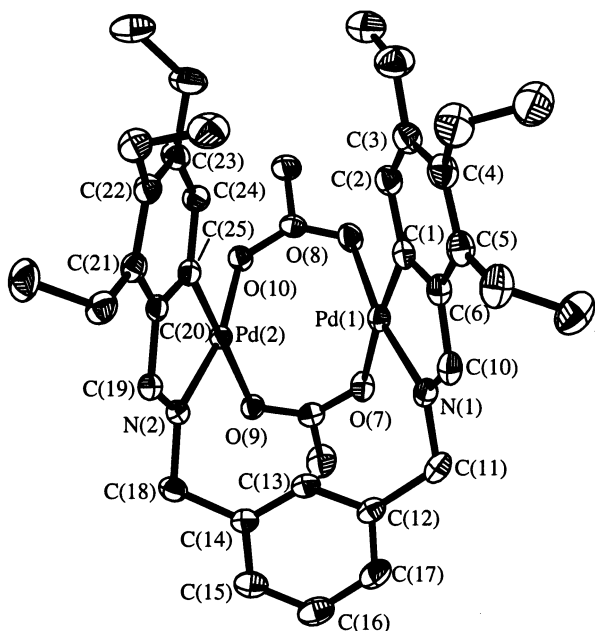
plexes,<sup>27</sup> may also be rejected, because it would require a relative syn disposition. Furthermore, the FAB mass spectrum of 7 did not show peaks assignable to a dinuclear or tetranuclear formulation; therefore, we suggest the anti disposition should be formulated as a polymeric or oligomeric species.

**Crystal Structure of [1,3-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>](μ-O<sub>2</sub>CMe)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]}<sub>2</sub> (2).** Suitable crystals of complex 2 were grown by slowly evaporating a *n*-hexane/dichloromethane solution at room temperature. The molecular structure is shown in Figure 3. Crystal data are given in Table 1, and selected bond distances

and angles with estimated standard deviations are shown in Table 2.

The crystal structure consists of discrete molecules separated by van der Waals distances. The asymmetric unit comprises two molecules with similar structures, of which only one will be discussed.

The molecular structure consists of the doubly cyclometalated Schiff base ligand 1 with the two metal centers bridged by two acetato ligands and with the two metalated phenyl rings in an open-book disposition. Although a large number of crystal structures of dinuclear acetato-bridged cyclometalated complexes have been reported, examples of a syn disposition remained unknown. Each palladium atom is bonded, in a slightly distorted square planar geometry, to one carbon atom of the phenyl ring and one imine nitrogen atom of the Schiff base ligand and to two oxygen atoms of the bridging acetato ligands. The Pd(1)–Pd(2) bond distance of 3.0748(5) Å is slightly longer than values reported for related complexes<sup>41</sup> and can be regarded as non-bonding. The sum of angles around the palladium atoms is approximately 360°. The angles between adjacent atoms in the coordination sphere are close to the



**Figure 3.** Molecular structure of [1,3-{Pd[2,3,4-(MeO)<sub>3</sub>-C<sub>6</sub>H<sub>1</sub>C(H)=NCH<sub>2</sub>]}(μ-O<sub>2</sub>CMe)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>] (**2**), with the labeling scheme. Only one of the two independent molecules is shown. Hydrogen atoms have been omitted for clarity.

**Table 1. Crystallographic Data for Complexes 2 and 9**

	<b>2</b>	<b>9</b>
empirical formula	C <sub>32</sub> H <sub>36</sub> N <sub>2</sub> O <sub>10</sub> Pd <sub>2</sub>	C <sub>58</sub> H <sub>62</sub> N <sub>2</sub> O <sub>6</sub> Cl <sub>8</sub> P <sub>2</sub> Pd <sub>2</sub>
fw	821.43	1441.44
<i>T</i> (K)	293(2)	173(2)
<i>λ</i> (Å)	0.710 73	0.710 73
cryst syst	orthorhombic	orthorhombic
space group	<i>Pbcn</i>	<i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i>
<i>a</i> (Å)	22.731(1)	14.389(1)
<i>b</i> (Å)	22.896(1)	18.384(1)
<i>c</i> (Å)	24.918(1)	23.815(1)
<i>V</i> (Å <sup>3</sup> )	12968(1)	6300(1)
<i>Z</i>	16	4
<i>μ</i> (mm <sup>-1</sup> )	1.169	1.010
max, min transmissn	0.80, 0.65	0.82, 0.72
<i>ρ</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.683	1.520
<i>θ</i> range (deg)	1.26–28.49	2.40–28.30
no. of rflns collected	68 271	44 226
no. of indep rflns	16 086 ( <i>R</i> <sub>int</sub> = 0.074)	15 617 ( <i>R</i> <sub>int</sub> = 0.039)
<i>R</i> 1 <sup>a</sup>	0.0494	0.0366
w <i>R</i> 2 <sup>b</sup>	0.1041	0.0776
abs structure param		-0.02(2)

<sup>a</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$  ( $F > 4\sigma(F)$ ). <sup>b</sup>  $wR2 = [\sum (w(F_o^2 - F_c^2))^2 / \sum w(F_o^2)^2]^{1/2}$  (all data).

expected value of 90°; the most noticeable distortion corresponds to the C(1)–Pd(1)–N(1) and C(25)–Pd(2)–N(2) angles of 81.6(2) and 81.4(2)°, respectively, consequent upon chelation. The Pd(1)–C(1) and Pd(2)–C(25) bond distances of 1.983(5) and 1.967(4) Å, respectively, are somewhat shorter than the values predicted from their covalent radii<sup>48</sup> but similar to values found earlier.<sup>41,45</sup> However, the Pd(1)–N(1) and Pd(2)–N(2) bond lengths of 2.031(4) and 2.027(4) Å, respectively, are in agreement with the value based on the sum of covalent radii for nitrogen and palladium<sup>48</sup> and similar to values

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2**

Pd(1)–C(1)	1.983(5)	Pd(2)–C(25)	1.967(4)
Pd(1)–N(1)	2.031(4)	Pd(2)–N(2)	2.027(4)
Pd(1)–O(7)	2.150(3)	Pd(2)–O(9)	2.160(3)
Pd(1)–O(8)	2.048(3)	Pd(2)–O(10)	2.034(3)
C(1)–C(6)	1.403(7)	C(25)–C(20)	1.399(6)
C(6)–C(10)	1.448(7)	C(20)–C(19)	1.440(6)
C(10)–N(1)	1.305(6)	C(19)–N(2)	1.295(6)
N(1)–C(11)	1.467(6)	N(2)–C(18)	1.471(6)
C(11)–C(12)	1.506(7)	C(18)–C(14)	1.490(7)
C(1)–Pd(1)–N(1)	81.4(2)	C(25)–Pd(2)–N(2)	81.6(2)
C(1)–Pd(1)–O(8)	91.9(2)	C(25)–Pd(2)–O(10)	91.6(2)
N(1)–Pd(1)–O(8)	169.7(1)	N(2)–Pd(2)–O(10)	167.2(1)
C(1)–Pd(1)–O(7)	175.1(2)	C(25)–Pd(2)–O(9)	177.7(2)
N(1)–Pd(1)–O(7)	94.9(2)	N(2)–Pd(2)–O(9)	96.2(1)
O(8)–Pd(1)–O(7)	91.3(1)	O(10)–Pd(2)–O(9)	90.7(1)
C(1)–C(6)–C(10)	114.0(4)	C(25)–C(20)–C(19)	114.1(4)
C(6)–C(10)–N(1)	117.1(5)	C(20)–C(19)–N(2)	117.4(4)
C(10)–N(1)–C(11)	119.6(4)	C(19)–N(2)–C(18)	120.2(4)
N(1)–C(11)–C(12)	114.7(4)	N(2)–C(18)–C(14)	111.5(4)

previously reported.<sup>41,45</sup> The differing Pd(1)–O(8) and Pd(1)–O(7) (2.048(3) and 2.150(3) Å, respectively) and Pd(2)–O(10) and Pd(2)–O(9) (2.034(4) and 2.160(3) Å, respectively) bond distances reflect the higher trans influence of the aryl carbon as compared to the imine nitrogen atom. The geometry about the palladium atoms is planar (plane 1, Pd(1), C(1), N(1), O(7), O(8); plane 2, Pd(2), C(25), N(2), O(9), O(10); rms = 0.0478 and 0.0937 Å, respectively) and coplanar with the cyclometalated rings (plane 3, Pd(1), C(1), C(6), C(10), N(1); plane 4, Pd(2), C(25), C(20), C(19), N(2); rms = 0.0046 and 0.0139 Å, respectively) (angles: plane 1/3 = 3.8°; 2/4 = 5.5°). The angle between the coordination planes is 42.1°, considerably larger than the values reported for acetato-bridged complexes with anti geometry.<sup>41,45</sup> This is probably due to the geometrical constraint imposed by the coordination of the palladium atoms to the same Schiff base ligand.

The reactions of **2** and **7** with aqueous sodium chloride gave the chloro-bridged complexes [1,3-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>]}(μ-Cl)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sub>2</sub> (**3**) and [1,4-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>]}(μ-Cl)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sub>2</sub> (**8**), respectively. The IR spectra of the complexes showed the absence of the ν(COO) bands. The <sup>1</sup>H NMR spectra showed only one set of resonances for the imine and phenyl protons, indicating double metalation of the ligand. The CH<sub>2</sub> resonances appeared as two broad signals at δ 4.98, 4.67 and δ 4.96, 4.70 for complexes **3** and **8**, respectively. The FAB mass spectra of both complexes showed peaks at 1548 and 1513 amu whose isotopic patterns were in agreement with the [M]<sup>+</sup> and [M – Cl]<sup>+</sup> fragments, based on a tetranuclear formulation, although the [M]<sup>+</sup> peaks were of relatively low intensity. Therefore, the data fit with the proposed tetranuclear formulation, similar to that reported by us for related doubly cyclometalated complexes.<sup>35</sup>

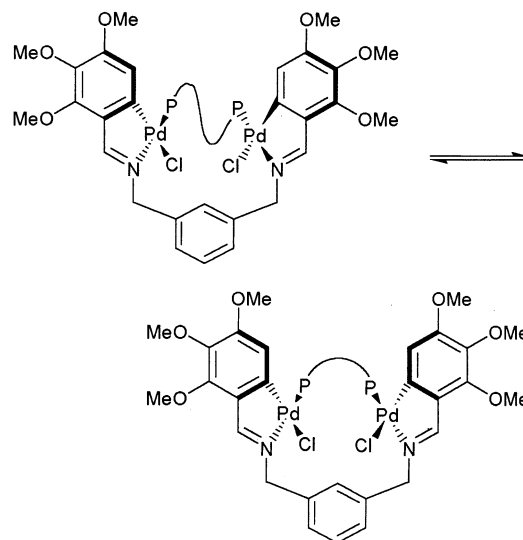
Reaction of complex **2** with Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub> (dppp) in a 1:1 molar ratio gave the dinuclear cyclometalated complex [1,3-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>]}(OAc)}<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>(μ-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)] (**4**). The IR spectrum of **4** showed two strong bands at 1580 s and 1380 s cm<sup>-1</sup>, assigned to the ν<sub>as</sub>(COO) and ν<sub>s</sub>(COO) vibrations, in agreement with those expected for monodentate acetate ligands.<sup>39</sup> The <sup>1</sup>H NMR spectra showed coupling of the HC=N and the H5 resonances to the phosphorus nucleus (δ 8.46 and 5.72, *J*(HP) = 7.3 and 5.4 Hz,

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respectively), and in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, the phosphorus resonance appeared as a singlet at δ 30.7, in accordance with the symmetric nature of the complex. These findings and the low-frequency shift of the resonance assigned to the C4–OMe group, due to shielding by a phenyl ring from the phosphine, were in agreement with a phosphorus trans to nitrogen arrangement.<sup>49–51</sup> The resonances corresponding to the diastereotopic CH<sub>2</sub> protons (consequent upon the formation of the intramolecular bridge) appeared at δ 5.08 and 4.46 as a doublet and a doublet of doublets, respectively, the latter showing coupling to the phosphorus nucleus (*J*(HP) = 5.4 Hz). Only one signal, at δ 1.91, was assigned to the MeCO<sub>2</sub> acetate protons. The FAB mass spectrum showed a set of peaks at 1173 amu assignable to the [M – OAc]<sup>+</sup> fragment. The conductivity measurements carried out in dry acetonitrile have shown the compound to be a nonelectrolyte.

Treatment of the chloro-bridged complex [1,3-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>](*μ*-Cl)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sub>2</sub> (**3**) with dppp in a 1:2 molar ratio gave the dinuclear cyclometalated complex [1,3-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>](Cl)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(*μ*-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)] (**5**). The IR and <sup>1</sup>H NMR spectra of the complex showed features similar to those described for **4** (except for the absence of the acetato ligands), with the most noticeable difference corresponding to the absence of the CH<sub>2</sub> resonances and the low-field shift of the H8 signal (δ 8.29), which appeared close to the position observed in the spectrum of the acetato-bridged compound **2**. However, the <sup>1</sup>H NMR spectrum recorded at 50 °C showed a broad resonance at δ 5.20 assigned to the CH<sub>2</sub> protons. Bearing this in mind, we decided to record the spectra at lower temperatures. This showed the progressive broadening and splitting of the signals corresponding to the HC=N, H8, H5, CH<sub>2</sub>, and C4–OMe resonances, indicating the existence of two isomers at –50 °C. The HC=N and H5 signals (at δ 8.65, 8.48 and δ 5.87, 5.62, respectively) showed coupling to the phosphorus nuclei. The CH<sub>2</sub> resonances appeared as doublets at δ 6.05 and 5.93 and at δ 4.30 as a multiplet. This assumption was confirmed by the presence of two singlet signals at δ 33.2 and 32.6, in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (–50 °C). The spectroscopic features of both isomers were similar and, consequently, their structural features. Therefore, we propose the equilibrium depicted in Figure 4, in which the metalated moieties adopt alternatively a cis and trans disposition. For compound **5** a relative proportion of isomers of 1:1.5 was observed with a *T<sub>c</sub>* value of 20 °C. The energy difference between both isomers was 74.1 kJ mol<sup>–1</sup>.

A similar equilibrium may be proposed for complex **4**. However, the <sup>1</sup>H NMR spectra did not change upon lowering the temperature. Although the <sup>1</sup>H NMR data do not exclude either one of the two possible cis or trans geometries, we tentatively propose that the bulky nature of the acetato ligand, as compared to chlorine, hinders the cis disposition. The FAB mass spectrum of **5** showed peaks at 1186 and 1151 amu assignable to



**Figure 4.**

the [M]<sup>+</sup> and [M – Cl]<sup>+</sup> fragments, respectively, whose isotopic patterns were in agreement with the proposed dinuclear formulation.

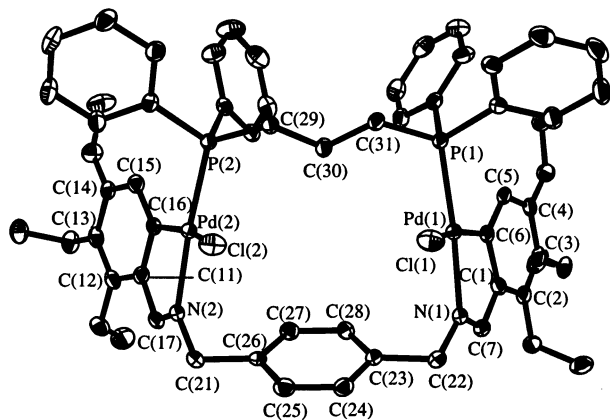
Reaction of the chloro-bridged complex [1,4-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>](*μ*-Cl)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sub>2</sub> (**8**) with dpbb in a 1:2 molar ratio yielded the mixture of complexes [1,4-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>](Cl)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(*μ*-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)] (**9**) and [1,4-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>](Cl)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(*μ*-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)]<sub>2</sub> (**10**). Complex **9** was isolated from the mixture by column chromatography (elution with dichloromethane/ethanol (1.2%)); however, we were unable to obtain complex **10** pure. A mixture enriched in **10** (**9**:**10** = 0.25:1) was prepared by column chromatography using dichloromethane/ethanol (0.4%). The IR and <sup>1</sup>H NMR spectra of **9** were similar to those of **5**, with the HC=N band shifted to lower frequency and the HC=N and H5 resonances coupled to the phosphorus nuclei. However, the <sup>1</sup>H NMR spectrum showed two broad resonances at δ 5.70, 4.57 assigned to the CH<sub>2</sub> protons. NMR low-temperature experiments were carried out with a chloroform solution of **9**. These suggested a behavior similar to that described for complex **5**. The <sup>1</sup>H NMR spectrum at –50 °C showed the presence of two isomers. This was confirmed by the <sup>31</sup>P{<sup>1</sup>H} spectrum at the same temperature, which showed the presence of two singlet resonances at δ 33.4 and 32.9. In view of the similarity shown by the spectra of **5** and **9**, we propose a similar structure and solution behavior for both complexes. For compound **9** a relative proportion of isomers of 1:2.5 was observed with a *T<sub>c</sub>* value of 50 °C. The energy difference between both isomers was 76.8 kJ mol<sup>–1</sup>. However, the structure of complex **10** is uncertain. The <sup>1</sup>H NMR of **10** showed the HC=N and H5 resonances at δ 8.19 and 5.73 (*J*(HP) = 7.8 and 5.9 Hz), respectively. The signal corresponding to the CH<sub>2</sub> protons appeared as a somewhat broad singlet, at δ 5.13, due to the change in symmetry (vide supra). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum showed only one singlet. In view of these results we tentatively propose for complex **10** a tetranuclear structure similar to that reported by us for other doubly cyclometalated complexes.<sup>10</sup>

[1,4-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>HC(H)=NCH<sub>2</sub>](Cl)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-(*μ*-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)] (**9**). Suitable crystals of complex

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(51) Bosque, R.; Granell, J.; Sales, J.; Fon-Bardiá, M.; Solans, X. *Organometallics* **1995**, *14*, 1393.



**Figure 5.** Molecular structure of  $[1,4\text{-}\{\text{Pd}[2,3,4\text{-}(\text{MeO})_3\text{C}_6\text{-HC(H)=NCH}_2\text{]}(\text{Cl})\}_2\text{C}_6\text{H}_4(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)]$  (**9**), with the labeling scheme. Hydrogen atoms and solvate molecules have been omitted for clarity.

**Table 3. Selected Bond Lengths (Å) and Angles (deg) for 9**

Pd(1)–C(6)	2.025(4)	Pd(2)–C(16)	2.016(3)
Pd(1)–N(1)	2.089(3)	Pd(2)–N(2)	2.095(3)
Pd(1)–P(1)	2.2626(9)	Pd(2)–P(2)	2.2516(9)
Pd(1)–Cl(1)	2.369(1)	Pd(2)–Cl(2)	2.377(1)
C(6)–C(1)	1.425(5)	C(16)–C(11)	1.413(5)
C(1)–C(7)	1.435(6)	C(11)–C(17)	1.435(5)
C(7)–N(1)	1.281(5)	C(17)–N(2)	1.283(5)
N(1)–C(22)	1.455(5)	N(2)–C(21)	1.450(5)
C(22)–C(23)	1.518(5)	C(21)–C(26)	1.519(5)
C(6)–Pd(1)–N(1)	81.2(1)	C(16)–Pd(2)–N(2)	80.7(1)
C(6)–Pd(1)–P(1)	100.7(1)	C(16)–Pd(2)–P(2)	98.1(1)
N(1)–Pd(1)–P(1)	175.98(8)	N(2)–Pd(2)–P(2)	174.51(8)
C(6)–Pd(1)–Cl(1)	166.3(1)	C(16)–Pd(2)–Cl(2)	166.1(1)
N(1)–Pd(1)–Cl(1)	91.79(9)	N(2)–Pd(2)–Cl(2)	93.99(9)
P(1)–Pd(1)–Cl(1)	87.11(3)	P(2)–Pd(2)–Cl(2)	88.43(3)
C(6)–C(1)–C(7)	116.5(3)	C(16)–C(11)–C(17)	116.1(3)
C(1)–C(7)–N(1)	118.0(3)	C(11)–C(17)–N(2)	117.9(3)
C(7)–N(1)–C(22)	120.5(3)	C(17)–N(2)–C(21)	121.2(3)
N(1)–C(22)–C(23)	111.9(3)	N(2)–C(21)–C(26)	111.8(3)

**9** were grown by slowly evaporating a *n*-hexane/dichloromethane solution at room temperature. The molecular structure is shown in Figure 5. Crystal data are given in Table 1, and selected bond distances and angles with estimated standard deviations are shown in Table 3.

The crystal comprises one molecule of **9** and three dichloromethane solvate molecules.

The molecular structure consists of the doubly cyclometalated Schiff base ligand **6**. Each palladium atom is bonded, in a slightly distorted square-planar geometry, to one carbon atom of the phenyl ring and to one imine nitrogen atom of the Schiff base ligand and to one chloro ligand and a phosphorus atom of the tertiary phosphine dppp, which bridges the two metallic centers. The sum of angles about the palladium atoms is approximately 360°, with the most noteworthy distortions corresponding to the C(6)–Pd(1)–N(1) and C(6)–Pd(1)–N(1) angles of 81.2(1) and 80.7(1)°, consequent upon chelation. The Pd(1)–C(6) and Pd(2)–C(16) bond distances of 2.025(4) and 2.016(3) Å, respectively, are similar to values found earlier.<sup>52,53</sup> The Pd(1)–N(1) and

Pd(2)–N(2) bond lengths of 2.089(3) and 2.095(3) Å, respectively, show the high trans influence of the phosphine phosphorus as compared to oxygen (Pd–N distances of 2.031(4) and 2.027(4) Å for complex **2**). The Pd–P and Pd–Cl bond distances are also within the expected values.<sup>53</sup>

The geometry about the palladium atoms is square planar, slightly twisted toward tetrahedral (plane 1 Pd(1), C(6), N(1), Cl(1), P(1), rms = 0.125 Å, maximum deviation from the least-squares plane 0.169 Å for C(6); plane 2 Pd(2), C(16), N(2), Cl(2), P(2), rms = 0.144 Å, maximum deviation from the least-squares plane 0.199 Å for C(16)).

The angle between the coordination planes (plane 1 and plane 2) is 49.7°, similar to that shown by complex **2**. The two cyclometalated moieties, the central phenyl ring (C(23)–C(28)), and the dppp phosphine define a molecular box (Pd–Pd distance of 6.498(1) Å). However, none of the dichloromethane solvent molecules were located inside the cavity.

## Conclusions

We have shown that potentially [C,N,C,N] tetradentate Schiff base ligands may be doubly cyclometalated to render species in which the metalated N–(benzylidene) moieties are linked to the central amine phenyl ring via –CH<sub>2</sub>– groups. The flexibility awarded by the methylenes makes it possible for the metal centers to be brought close together, allowing bidentate ligands, such as the acetate ion and tertiary diphosphine ligands, to bridge the palladium atoms, yielding intramolecular bridged dinuclear compounds. In the case of the diphosphines, cis and trans arrangements are possible, as shown by variable-temperature NMR spectroscopy. We are currently in the process of detailing further the characteristics of this equilibrium system.

## Experimental Section

Solvents were purified by standard methods.<sup>54</sup> Chemicals were reagent grade. Microanalyses were carried out using a Carlo Erba elemental analyzer, Model 1108. IR spectra were recorded as Nujol mulls or polyethylene disks on a Perkin-Elmer 1330 instrument and on a Mattson spectrophotometer. NMR spectra were obtained as CDCl<sub>3</sub> or (CD<sub>3</sub>)<sub>2</sub>SO solutions and referenced to SiMe<sub>4</sub> (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}) or 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P{<sup>1</sup>H}) and were recorded on a Bruker AC-200F spectrometer. All chemical shifts were reported downfield from standards. The FAB mass spectra were recorded using a VG Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol was used as the matrix. Conductivity measurements were made on a CRISON GLP 32 conductivimeter using 10<sup>–3</sup> mol dm<sup>–3</sup> solutions in dry acetonitrile.

The syntheses of the Schiff bases 1,3-[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**1**) and 1,4-[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**6**) were performed by heating chloroform solutions of the appropriate quantities of 2,3,4-trimethoxybenzaldehyde and *m*-xylylenediamine or *p*-xylylenediamine, respectively, in a Dean–Stark apparatus under reflux.

Schiff base **1**: yield 90%. Anal. Found: C, 67.9; H, 6.6; N, 5.5. Calcd for C<sub>28</sub>H<sub>32</sub>N<sub>2</sub>O<sub>6</sub>: C, 68.3; H, 6.6; N, 5.7. IR: ν(C=N), 1635 cm<sup>–1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, δ in ppm, *J* in Hz): 8.66 (s, 2H, H<sub>i</sub>), 7.73 (d, 2H, H<sub>6</sub>, *J*(H<sub>5</sub>H<sub>6</sub>) = 8.8), 7.26 (m, 4H, H<sub>8</sub>, H<sub>9</sub>, H<sub>10</sub>), 6.65 (d, 2H, H<sub>5</sub>), 4.80 (s, 4H, CH<sub>2</sub>), 3.90

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(s, 6H, MeO), 3.86 (s, 6H, MeO), 3.84 (s, 6H, MeO). <sup>13</sup>C{<sup>1</sup>H} NMR (50.28 MHz, CDCl<sub>3</sub>, δ in ppm): 157.4 (C=N); 155.9, 153.9 (C2, C4); 141.7, 139.8 (C3, C7); 128.5, 127.5, 126.5 (C8, C9, C10); 122.7 (C1); 122.4 (C6); 107.7 (C5); 65.4 (CH<sub>2</sub>); 61.9, 60.9, 56.0 (MeO). FAB-MS: *m/z* 493 [M]<sup>+</sup>.

Schiff base **6**: yield 90%. Anal. Found: C, 68.0; H, 6.3; N, 5.5. Calcd for C<sub>28</sub>H<sub>32</sub>N<sub>2</sub>O<sub>6</sub>: C, 68.3; H, 6.6; N, 5.7. IR: ν(C=N), 1635 s cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, δ in ppm, *J* in Hz): 8.66 (s, 2H, H<sub>i</sub>), 7.74 (d, 2H, H<sub>6</sub>, *J*(H<sub>5</sub>H<sub>6</sub>) = 8.8), 7.31 (s, 4H, H<sub>8</sub>), 6.71 (d, 2H, H<sub>5</sub>), 4.80 (s, 4H, CH<sub>2</sub>), 3.94 (s, 6H, MeO), 3.90 (s, 6H, MeO), 3.89 (s, 6H, MeO). <sup>13</sup>C{<sup>1</sup>H} NMR (50.28 MHz, CDCl<sub>3</sub>, δ in ppm): 157.4 (C=N); 155.9, 153.9 (C2, C4); 141.7 (C7); 138.3 (C3); 128.1 (C8); 122.7 (C1); 122.4 (C6); 107.7 (C5); 65.2 (CH<sub>2</sub>); 61.9, 60.9, 56.0 (MeO). FAB-MS: *m/z* 493 [M]<sup>+</sup>.

**Synthesis of [1,3-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>]}(μ-O<sub>2</sub>CMe)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]}<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (2).** 1,3-[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>]}<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**1**; 33 mg, 0.67 mmol) and palladium(II) acetate (30 mg, 0.45 mmol) were added to 50 cm<sup>3</sup> of toluene to give a dark red solution. After it was heated at 60 °C for 4 h under argon, the solution was cooled and filtered through Celite to remove the small amount of black palladium formed. The solvent was then removed under vacuum and the required product recrystallized from dichloromethane/*n*-hexane. Yield: 0.49 g, 80%. Anal. Found: C, 46.4; H, 4.3; N, 3.2. Calcd for C<sub>32</sub>H<sub>36</sub>N<sub>2</sub>Pd<sub>2</sub>O<sub>10</sub>: C, 46.8; H, 4.4; N, 3.4. IR: ν<sub>as</sub>(COO), 1570 s; ν<sub>s</sub>(COO), 1415 s; ν(C=N), 1600 m sh cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, δ in ppm, *J* in Hz): 8.10 (s, 2H, H<sub>i</sub>), 8.35 (s, 1H, H<sub>8</sub>), 7.22 (t, 1H, H<sub>10</sub>, *J*(H<sub>9</sub>H<sub>10</sub>) = 6.8), 7.03 (d, 2H, H<sub>9</sub>), 6.13 (s, 2H, H<sub>5</sub>), 5.05 (d, 2H, CH(a)<sub>2</sub>, *J*(H(a)H(b)) = 15.6), 4.55 (d, 2H, CH(b)<sub>2</sub>), 3.92 (s, 6H, MeO), 3.79 (s, 6H, MeO), 3.69 (s, 6H, MeO), 2.23 (s, 3H, MeCO<sub>2</sub>), 1.26 (s, 3H, MeCO<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (50.28 MHz, CDCl<sub>3</sub>, δ in ppm): 181.5, 179.6 (MeCO<sub>2</sub>); 172.2 (C=N); 154.5, 151.1, 151.0 (C2, C4, C6); 138.0, 137.7 (C3, C7); 135.6 (C8); 130.5 (C1); 127.6, 123.8 (C9, C10); 111.1 (C5); 62.0 (CH<sub>2</sub>); 61.6, 60.8, 55.8 (MeO); 24.1, 23.3 (MeCO<sub>2</sub>). FAB-MS: *m/z* 822 [M]<sup>+</sup>, 763 [M - OAc]<sup>+</sup>, 597 [(1-H)Pd]<sup>+</sup>.

**Synthesis of [1,3-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>]}(μ-Cl)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]}<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (3).** An aqueous solution of NaCl (ca. 10<sup>-2</sup> M) was added dropwise to **2** (40 mg, 0.49 mmol) in acetone (ca. 25 cm<sup>3</sup>). A yellow solid immediately formed. After the mixture was stirred for 5 h, the solid was filtered off, washed with water and cold acetone, and dried in vacuo. Yield: 0.32 g, 86%. Anal. Found: C, 43.3; H, 4.0; N, 3.6. Calcd for C<sub>56</sub>H<sub>60</sub>N<sub>4</sub>Pd<sub>4</sub>O<sub>12</sub>Cl<sub>4</sub>: C, 43.4; H, 3.9; N, 3.6. IR: ν(C=N), 1600 s cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, *d*<sub>6</sub>-DMSO, δ in ppm, *J* in Hz): 8.29 (br, 2H, H<sub>i</sub>), 7.40 (m, 4H, H<sub>8</sub>, H<sub>9</sub>, H<sub>10</sub>), 6.93 (br, 2H, H<sub>5</sub>), 4.98, 4.67 (br, 4H, CH<sub>2</sub>), 3.80 (s, 6H, MeO), 3.74 (s, 6H, MeO), 3.65 (s, 6H, MeO). FAB-MS: *m/z* 1548 [M]<sup>+</sup>, 1513 [M - Cl]<sup>+</sup>, 1371 [M - 2Cl - Pd]<sup>+</sup>, 739 [(1-H)2Pd(X)]<sup>+</sup>.

**Synthesis of [1,3-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>]}(OAc)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(μ-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (4).** To a suspension of **2** (200 mg, 0.24 mmol) in chloroform (ca. 15 cm<sup>3</sup>) was added Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub> (100 mg, 0.243 mmol). The mixture was stirred for 12 h at room temperature. The resulting solution was chromatographed on silica gel. Elution with dichloromethane/ethanol (0.4%) afforded the desired complex, which was recrystallized from dichloromethane/*n*-hexane to give a yellow solid. Yield: 0.15 g, 50%. Anal. Found: C, 57.0; H, 4.8; N, 2.3. Calcd for C<sub>59</sub>H<sub>62</sub>N<sub>2</sub>Pd<sub>2</sub>O<sub>10</sub>P<sub>2</sub>: C, 57.4; H, 5.1; N, 2.3. IR: ν<sub>as</sub>(COO), 1580 s; ν<sub>s</sub>(COO), 1380 s; ν(C=N), 1605 s cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, δ in ppm, *J* in Hz): 8.46 (d, 2H, H<sub>i</sub>, *J*(H<sub>i</sub>P) = 7.3), 5.72 (d, 2H, H<sub>5</sub>, *J*(H<sub>5</sub>P) = 5.4), 5.08 (d, 2H, CH(a)<sub>2</sub>, *J*(H(a)H(b)) = 12.7), 4.46 (dd, 2H, CH<sub>2</sub>(b), *J*(H(b)P) = 5.4), 3.91 (s, 6H, MeO), 3.68 (s, 6H, MeO), 2.97 (s, 6H, C(4)-MeO), 1.91 (s, 6H, MeCO<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (80.96 MHz, CDCl<sub>3</sub>, δ in ppm): 30.7 s. <sup>13</sup>C{<sup>1</sup>H} NMR (50.28 MHz, CDCl<sub>3</sub>, δ in ppm, *J* in Hz): 176.7 (MeCO<sub>2</sub>); 172.2 (d, C=N, *J*(CP) = 4.3); 154.8, 152.5, 151.8 (C2, C4, C6); 138.5, 137.6 (C3, C7); 133.8 (C1); 131.5, 127.7 (C8, C9, C10); 116.9 (d, C5, *J*(C5P) = 11.4); 60.8 (CH<sub>2</sub>); 61.8, 60.7, 55.2 (MeO); 23.3 (MeCO<sub>2</sub>); P-phenyl appear

at C<sub>6</sub> 134.6 d, *J*(PC) = 11.4 Hz; C<sub>m</sub> 128.5 d, *J*(PC) = 10.6 Hz; PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P, 30.5 m; PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P, 22.0. FAB-MS: *m/z* 1173 [M - OAc]<sup>+</sup>, 763 [M - phosphine - OAc]<sup>+</sup>, 597 [M - phosphine - 2OAc - Pd]<sup>+</sup>.

**Synthesis of [1,3-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>]}(Cl)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(μ-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (5).** To a suspension of **2** (200 mg, 0.13 mmol) in chloroform (ca. 15 cm<sup>3</sup>) was added Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub> (106 mg, 0.26 mmol). The mixture was stirred for 12 h at room temperature. The resulting solution was chromatographed on silica gel. Elution with dichloromethane/ethanol (0.8%) afforded the desired complex, which was recrystallized from dichloromethane/*n*-hexane to give a yellow solid. Yield: 0.15 g, 50%. Anal. Found: C, 56.0; H, 4.6; N, 2.4. Calcd for C<sub>55</sub>H<sub>56</sub>N<sub>2</sub>Pd<sub>2</sub>O<sub>6</sub>Cl<sub>2</sub>P<sub>2</sub>: C, 55.7; H, 4.8; N, 2.4. IR: ν(C=N), 1605 s cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, δ in ppm, *J* in Hz, room temperature): 8.51 (d, 2H, H<sub>i</sub>, *J*(H<sub>i</sub>P) = 8.3), 8.29 (s, 1H, H<sub>8</sub>), 5.81 (d, 2H, H<sub>5</sub>, *J*(H<sub>5</sub>P) = 5.9), 5.20 (br, 4H, CH<sub>2</sub> (50 °C)), 3.92 (s, 6H, MeO), 3.72 (s, 6H, MeO), 2.87 (s, 6H, C(4)-MeO). <sup>31</sup>P{<sup>1</sup>H} NMR (80.96 MHz, CDCl<sub>3</sub>, δ in ppm): 32.9 s. <sup>13</sup>C{<sup>1</sup>H} NMR (50.28 MHz, CDCl<sub>3</sub>, δ in ppm): 172.2 (d, C=N, *J*(CP) = 4.2); 154.7, 152.2 (C2, C6); 154.5 (d, C4, *J*(CP) = 6.4); 139.1, 137.4 (C3, C7); 136.7 (C1); 131.5, 128.5, 127.5 (C8, C9, C10); 117.2 (C5, *J*(C5P) = 12.0); 59.9 (CH<sub>2</sub>); 61.9, 60.7, 54.9 (MeO); P-phenyl, C<sub>6</sub> 133.7 d, *J*(PC) = 12.8 Hz; C<sub>m</sub> 128.4 d, *J*(PC) = 10.6 Hz; C<sub>p</sub> 130.6 d; PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P, 31.6 (dd, *J*(PC) = 34.0, 5.6); PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P, 20.8. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, δ in ppm, *J* in Hz, 223 K): 8.65 d, 8.48 d (d, 4H, H<sub>i</sub>, *J*(H<sub>i</sub>P) = 7.8), 8.49, 8.08 (s, 2H, H<sub>8</sub>), 5.87, 5.62 (d, 2H, H<sub>5</sub>, *J*(H<sub>5</sub>P) = 6.3, 5.3), 6.05 (d, 2H, CH(a)<sub>2</sub>, *J*(H(a)H(b)) = 11.2), 5.93 (d, 2H, CH(a)<sub>2</sub>, *J*(H(a)H(b)) = 11.2), 4.30 (m, 4H, CH(b)<sub>2</sub>), 3.92 (s, 12H, MeO), 3.73 (s, 12H, MeO), 2.87, 2.70 (s, 12H, C(4)-MeO). <sup>31</sup>P{<sup>1</sup>H} NMR (80.96 MHz, CDCl<sub>3</sub>, δ in ppm): 33.2, 32.6 s. FAB-MS: *m/z* 1186 [M]<sup>+</sup>, 1151 [M - Cl]<sup>+</sup>, 739 [M - phosphine - Cl]<sup>+</sup>, 663 [M - phosphine - Cl - Pd]<sup>+</sup>, 597 [M - phosphine - 2Cl - Pd]<sup>+</sup>.

**[1,4-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>]}(μ-O<sub>2</sub>CMe)<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>]}<sub>n</sub> (7).** Complex **7** was synthesized as an orange solid using a procedure similar to that described for complex **2**. Yield: 80%. Anal. Found: C, 46.5; H, 3.9; N, 3.5. Calcd for [C<sub>32</sub>H<sub>36</sub>N<sub>2</sub>-Pd<sub>2</sub>O<sub>10</sub>]<sub>n</sub>: C, 46.8; H, 4.4; N, 3.4. IR: ν<sub>as</sub>(COO), 1570 s; ν<sub>s</sub>(COO), 1415 s; ν(C=N), 1600 m sh cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, δ in ppm, *J* in Hz): 7.42 (s, 2H, H<sub>i</sub>), 7.15, 7.12 (s, 4H, H<sub>8</sub>), 6.40 (s, 2H, H<sub>5</sub>), 4.39, 3.65 (br, 4H, CH<sub>2</sub>), 3.85 (s, 6H, MeO), 3.78 (s, 12H, MeO), 2.08 (s, 6H, MeCO<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (50.28 MHz, CDCl<sub>3</sub>, δ in ppm): 181.0 (MeCO<sub>2</sub>); 169.1 (C=N); 154.5, 151.7, 151.4 (C2, C4, C6); 137.8, 135.9 (C3, C7); 131.0 (C1); 129.2 (C8); 110.3 (C5); 61.3 (CH<sub>2</sub>); 61.8, 61.0, 56.0 (MeO); 24.3 (MeCO<sub>2</sub>). FAB-MS: *m/z* 763 [M - OAc]<sup>+</sup> (M = C<sub>32</sub>H<sub>36</sub>N<sub>2</sub>-Pd<sub>2</sub>O<sub>10</sub>).

**Synthesis of [1,4-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>]}(μ-Cl)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]}<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (8).** Complex **8** was synthesized as a yellow solid using a procedure similar to that described for complex **3**. Yield: 92%. Anal. Found: C, 43.9; H, 4.0; N, 3.8. Calcd for C<sub>56</sub>H<sub>60</sub>N<sub>4</sub>Pd<sub>4</sub>O<sub>12</sub>Cl<sub>4</sub>: C, 43.4; H, 3.9; N, 3.6. IR: ν(C=N), 1600 s cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, *d*<sub>6</sub>-DMSO, δ in ppm, *J* in Hz): 8.05 (s, 2H, H<sub>i</sub>), 7.54 (s, 4H, H<sub>8</sub>), 6.60 (s, 2H, H<sub>5</sub>), 4.96, 4.67 (br, 4H, CH<sub>2</sub>), 3.95 (s, 6H, MeO), 3.88 (s, 6H, MeO), 3.76 (s, 6H, MeO). <sup>13</sup>C{<sup>1</sup>H} NMR (50.28 MHz, CDCl<sub>3</sub>, δ in ppm): 172.2 (C=N); 154.8, 151.5, 150.5 (C2, C4, C6); 138.1, 137.0 (C3, C7); 131.3 (C1); 129.1 (C8); 112.0 (C5); 61.7 (CH<sub>2</sub>); 61.8, 60.9, 56.2 (MeO). FAB-MS: *m/z* 1548 [M]<sup>+</sup>, 1513 [M - Cl]<sup>+</sup>.

**Synthesis of [1,4-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>]}(Cl)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(μ-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(μ-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (9) and [1,4-{Pd[2,3,4-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(H)=NCH<sub>2</sub>]}(Cl)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(μ-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(μ-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (10).** To a suspension of **8** (200 mg, 0.129 mmol) in chloroform (ca. 15 cm<sup>3</sup>) was added Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub> (106 mg, 0.258 mmol). The mixture was stirred for 12 h at room temperature. The resulting solution was chromatographed on silica gel. Elution with dichloromethane/ethanol (1.2%) afforded complex **9**, which was recrystallized from dichloromethane/*n*-hexane to give a yellow solid. Elution with dichloromethane/ethanol



(0.4%) afforded a mixture of complexes **9** and **10** (molar ratio 0.25:1, calculated from NMR data), which was recrystallized from dichloromethane/*n*-hexane to give a yellow solid.

**Complex 9:** Yield: 25%. Anal. Found: C, 55.52; H, 4.71; N, 2.41. Calcd for  $C_{55}H_{56}N_2Pd_2O_6Cl_2P_2$ : C, 55.7; H, 4.8; N, 2.4. IR:  $\nu(C=N)$  1610  $s\text{ cm}^{-1}$ .  $^1H$  NMR (200 MHz,  $CDCl_3$ ,  $\delta$  in ppm,  $J$  in Hz): 8.47 (d, 2H, H<sub>i</sub>,  $J(H_iP) = 7.8$ ), 7.55 (s, 4H, H8), 5.73 (d, 2H, H5,  $J(H5P) = 5.8$ ), 5.70, 4.57 (br, 4H, CH<sub>2</sub>), 3.98 (s, 6H, MeO), 3.74 (s, 6H, MeO), 2.84 (s, 6H, C(4)-MeO).  $^{31}P\{^1H\}$  NMR (80.96 MHz,  $CDCl_3$ ,  $\delta$  in ppm) 32.9 s.  $^{13}C\{^1H\}$  NMR (50.28 MHz,  $CDCl_3$ ,  $\delta$  in ppm): 170.9 (C=N); 155.1, 154.6, 152.2 (C2, C4, C6); 137.5, 136.5 (C3, C7); 129.2 (C8); 117.2 (C5); 62.5 (CH<sub>2</sub>); 61.9, 60.7, 54.9 (MeO); P-phenyl C<sub>o</sub> 133.7 d,  $J(PC) = 12.8$  Hz; C<sub>m</sub> 128.4 d,  $J(PC) = 10.2$  Hz; C<sub>p</sub> 131.4 d;  $PCH_2CH_2CH_2P$ , 29.6 m;  $PCH_2CH_2CH_2P$ , 18.9.  $^1H$  NMR (200 MHz,  $CDCl_3$ ,  $\delta$  in ppm,  $J$  in Hz, 223 K): 8.47 (d, 2H, H<sub>i</sub>,  $J(H_iP) = 7.8$ ), 7.60, 7.51 (s, 4H, H8), 5.70 (m, 4H, H5, CH(a)<sub>2</sub>), 4.57 (m, 2H, CH(b)<sub>2</sub>), 3.98, 3.96 (s, 6H, MeO), 3.98, 3.76, 3.96, 3.73 (s, 6H, MeO), 2.78, 2.73 (s, 6H, C(4)-MeO).  $^{31}P\{^1H\}$  NMR (80.96 MHz,  $CDCl_3$ ,  $\delta$  in ppm) 33.4, 32.9 s.

**Complex 10:** Yield: 30%. IR:  $\nu(C=N)$  1610  $s\text{ cm}^{-1}$ .  $^1H$  NMR (200 MHz,  $CDCl_3$ ,  $\delta$  in ppm,  $J$  in Hz): 8.19 (d, 2H, H<sub>i</sub>,  $J(H_iP) = 7.8$ ), 7.46 (s, 4H, H8), 5.73 (d, 2H, H5,  $J(H5P) = 5.9$ ), 5.13 (s, 4H, CH<sub>2</sub>), 3.79 (s, 6H, MeO), 3.62 (s, 6H, MeO), 2.87 (s, 6H, C(4)-MeO).  $^{31}P\{^1H\}$  NMR (80.96 MHz,  $CDCl_3$ ,  $\delta$  in ppm): 33.4 s.  $^{13}C\{^1H\}$  NMR (50.28 MHz,  $CDCl_3$ ,  $\delta$  in ppm): 171.8 (C=N); 154.6, 153.8, 152.0 (C2, C4, C6); 137.4, 137.2 (C3, C7); 129.6 (C8); 117.1 (C5); 60.1 (CH<sub>2</sub>); 61.8, 60.6, 55.2 (MeO); P-phenyl C<sub>o</sub> 133.9 d,  $J(PC) = 12.8$  Hz; C<sub>m</sub> 128.6d,  $J(PC) = 10.1$  Hz; C<sub>p</sub> 130.8 d;  $PCH_2CH_2CH_2P$  30.1 m;  $PCH_2CH_2CH_2P$  20.8.

**X-ray Crystallography.** Three-dimensional X-ray data were collected on a Siemens Smart CCD diffractometer by the

$\omega$  scan method using graphite-monochromated Mo K $\alpha$  radiation. All the measured reflections were corrected for Lorentz and polarization effects and for absorption by semiempirical methods based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined by full-matrix least squares on  $F^2$ . Hydrogen atoms were included in calculated positions. Refinement converged at a final R1 = 0.0494 and 0.0366 (for complexes **2** and **9**, respectively, observed data,  $F$ ) and wR2 = 0.1041 and 0.0776 (for complexes **2** and **9**, respectively, unique data,  $F^2$ ), with allowance for thermal anisotropy of all non-hydrogen atoms. The structure solution and refinement were carried out using the program package SHELX-97.<sup>55</sup>

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**Supporting Information Available:** Crystallographic data (excluding structure factors) for structures **2** and **9** reported in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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