Organometallics **1990**, *9*, 1405–1413

thioanisole did not affect the kinetics of the reactions, we used the thioethers as they were received from commercial sources. It is necessary to shield the cell from room light, otherwise reactions in the bulk produce unidentified electrochemically active species.

Computer Simulation. The code for the computer simulation of the SW voltammograms is based on the methodology described earlier[2] except that here square waves are employed. Thus in the numerical analysis we define the potential by dividing each square wave period into a sufficiently fine net, typically 14 equal time segments. Potential is held constant for seven time steps and then is stepped to the next value for another seven steps. Current output is computed as the difference between currents at the seventh and fourteenth segment for each period. This simulates the experimentally measured difference in currents between the ends of the first and second half of each square wave. Sweep rate was 0.100 V s^{-1}, corresponding to a square-wave frequency of 25 Hz and square-wave length of 4.00 mV. The rest of the computation proceeds along the lines discussed in our earlier paper.[2] Numerical computation was done using the Adams–Moulton method, with predictor and corrector of order 1 and 2, respectively.[13] As a check of the computation, we examined the case of initial uniform concentration of oxidized acetone complex with either no or full conversion to the sulfide complex and compared the simulation results with the numerical solution obtainable in terms of Laplace transforms.[4] We find for a range of heterogeneous rate constant $k_0/D^{1/2}$ from 30 $s^{-1/2}$ (virtually Nernstian) down to 0.8 $s^{-1/2}$ (below the present range of application) that the results are in good agreement, giving the same shifts in peak potential and the same half-widths and current ratios. The values for the heterogeneous rate constants stated above were found by means of matching experimental and simulated half-widths of the current peaks. These were verified by comparing experimental and computed differences in peak potentials as determined by cyclic voltammetry experiments on these complexes. The code for both the simulation and the Laplace transform solution is provided in the supplementary material (see the paragraph at the end of the paper).

Acknowledgment. We gratefully thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Graduate School of Boston University for support of this research. We thank Professor Janet Osteryoung for helpful comments.

Supplementary Material Available: Code for both the simulation and the Laplace transform solution (4 pages). Ordering information is given on any current masthead page.

---

[13] Shampine, L. F.; Gordon, M. K. *Computer Solution of Ordinary Differential Equations*; W. H. Freeman: San Francisco, 1975.

Five- and Six-Membered Exo-Cyclopalladated Compounds of *N*-Benzylideneamines. Synthesis and X-ray Crystal Structure of $[\overline{PdBr\{p\text{-}MeOC_6H_3(CH_2)_2N}{=}CH(2,6\text{-}Cl_2C_6H_3)\}(PPh_3)]$ and $[PdBr\{C_6H_4CH_2N{=}CH(2,6\text{-}Cl_2C_6H_3)\}(PEt_3)_2]$

Joan Albert, Montserrat Gómez, Jaume Granell, and Joaquim Sales*

Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

Xavier Solans

Departament de Cristal.lografia i Mineralogia, Universitat de Barcelona, Martí i Franquès, s/n 08028 Barcelona, Spain

Received August 14, 1989

The reaction of *N*-(2,6-dichlorobenzylidene)amines, $2,6\text{-}Cl_2C_6H_3CH{=}N(CH_2)_nC_6H_4\text{-}p\text{-}R$ (n = 1, 2; R = H, MeO), with $Pd(AcO)_2$ in refluxing acetic acid has been studied. With *N*-benzylidenebenzylamines (n = 1) exo five-membered derivatives were obtained. From *N*-benzylidene(2-phenylethyl)amines (n = 2) endo five-membered cyclopalladated compounds were formed by oxidative addition of C–Cl bonds of the ligand to Pd(0) formed in situ. Under milder conditions (acetic acid at 80 °C) the exo six-membered compound $[\overline{Pd(AcO)\{p\text{-}MeOC_6H_3(CH_2)_2N}{=}CH(2,6\text{-}Cl_2C_6H_3)\}]_2$ was obtained. All exo derivatives contain the imine ligand in the syn form. By reaction with PR_3 (R = Et, Ph), monophosphine complexes $[\overline{PdX(C^\frown N})(PR_3)]$ and bisphosphine derivatives $[PdX(C^\frown N)(PR_3)_2]$, where the Pd–N bond has been broken, can be obtained. $[\overline{PdBr\{p\text{-}MeOC_6H_3(CH_2)_2N}{=}CH(2,6\text{-}Cl_2C_6H_3)\}(PPh_3)]$ (**6f**) crystallizes in the monoclinic space group $P2_1/n$ with a = 20.321 (4) Å, b = 12.561 (3) Å, c = 12.608 (3) Å, β = 97.50 (2)°, and Z = 4. The exo six-membered ring displays a boat conformation with Pd and C(7) atoms out of the plane defined by the remaining atoms. $[PdBr\{C_6H_4CH_2N{=}CH(2,6\text{-}Cl_2C_6H_3)\}(PEt_3)_2]$ (**9c**) has been characterized by X-ray crystallography; it crystallizes in the monoclinic space group $P2_1/a$ with a = 45.352 (6) Å, b = 8.884 (2) Å, c = 7.556 (2) Å, β = 99.02 (3)°, and Z = 4. The Pd atom has a roughly planar coordination, and the imine ligand is in the anti form.

Introduction

Cyclometalation reactions are a rapidly growing area of organometallic chemistry, in particular cyclopalladation of N-donor ligands.[1] This process represents one of the classic ways to activate C–H bonds in heterosubstituted organic molecules. Cyclopalladated compounds are valuable intermediates for regio- and stereoselective organic synthesis. Carbonylation, vinylation, and halogenation of organic compounds have been reported.[2] The insertion of symmetric and asymmetric alkynes at several cyclometalated complexes has been recently studied.[3] In many

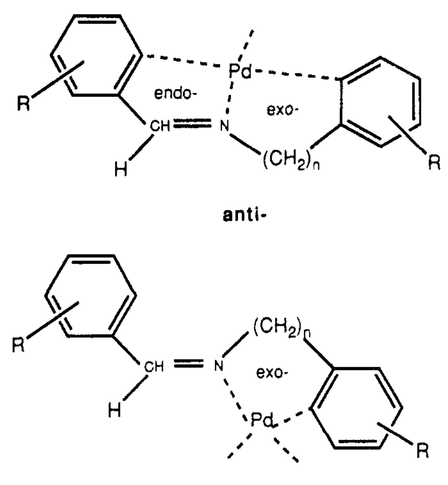
---

[1] (a) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73. (b) Omae, I. *Chem. Rev.* **1979**, *79*, 287. (c) Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem. Rev.* **1986**, *86*, 451. (d) Omae, I. *Coord. Chem. Rev.* **1988**, *83*, 137. (e) Dunina, V. V.; Zalevskaya, O. A.; Potatov, V. M. *Russ. Chem. Rev.* **1988**, *57*, 250.

[2] Ryabov, A. D. *Synthesis* **1985**, 233.

0276-7333/90/2309-1405$02.50/0

Chart I



cases Pd(0) elimination occurs with formation of new heterocyclic compounds. Recently,[4] cyclopalladated compounds have been used as catalysts in the dihydrogen reduction of nitroalkenes and aromatic nitriles to the corresponding amines.

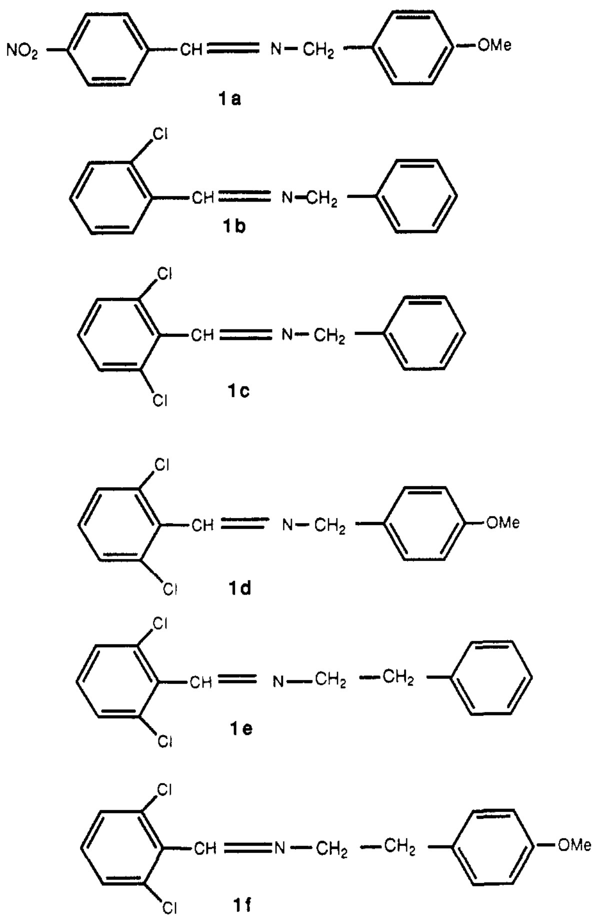
The factors that influence the ease and mode of cyclometalation of N-donor ligands are not thoroughly understood, but the following rules are widely accepted: (i) initial coordination of the ligand to the metal; (ii) electrophilic attack of "Pd^{2+}" on the aromatic carbon atoms; (iii) a strong tendency to form five-membered compounds. But recently, a few six-membered cyclometalated compounds containing Pd–aliphatic carbon bonds have been reported.[5]

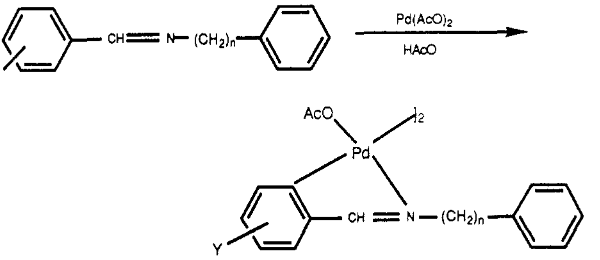
Schiff bases are very suitable ligands with which to study cyclometalation reactions, because they can undergo metalation on different carbon atoms, giving metallocycles with different structures. Thus, from *N*-benzylideneamines, endo and exo metallocycles can be obtained, according to the metalated phenyl ring (Chart I). For $n = 1$, only five-membered compounds can be obtained, but for $n = 2$, metalation of the ethylphenyl ring would give an exo six-membered derivative. The electronic effects of the R substituents can favor electrophilic attack on one of the two phenyl rings.

Schiff bases can exist in two isomeric forms, anti and syn configurations. In general, N-substituted aldimines exist in the solid state and in solution only in the more stable anti form. But in some cases, a significant equilibrium concentration of the less stable syn form has been found.[6] According to the isomer, imines can give different cyclometalated derivatives, i.e., from the anti form, endo and exo cylometalated compounds can be obtained, but from the syn isomer only exo derivatives are formed (Chart I).

Schiff base cyclometalated derivatives, obtained by reaction of palladium salts and the ligand, contain endo five-membered metallocycles, where the imine ligand is in the anti isomer. *N*-Benzylideneanilines ($n = 0$) are easily metalated by $Pd(AcO)_2$, giving the corresponding endo five-membered derivative[7] (eq 1); a slower cyclometalation occurs with electron-withdrawing substituents ($Y = NO_2$).[8] From *N*-benzylidenebenzylamines ($n = 1$), formation of an exo five-membered metallocycle was initially reported,[9] but a reinvestigation of the process showed that only endo derivatives were obtained.[10]

Chart II





(1)

Recently, Dyke et al.[11] have obtained endo and exo derivatives by oxidative addition of *o*-bromobenzylidenebenzylamines on $Pd(dba)_2$; both metallocyles contain the imine ligand in the anti form. From the dibromoimine ($X = X' = Br$), where formation of both metallocycles is possible, only the endo derivative was obtained (Scheme I).

---

(3) (a) Massarani, F.; Pfeffer, M.; van Koten, G. *Organometallics* **1989**, *8*, 871. (b) Wu, G.; Geib, S. J.; Rheingold, A. L.; Heck, R. F. *J. Org. Chem.* **1988**, *53*, 3238.

(4) Bose, A.; Saha, C. R. *J. Mol. Catal.* **1989**, *49*, 271.

(5) (a) Fuchita, Y.; Hiraki, K.; Uchiyama, T. *J. Chem. Soc., Dalton Trans.* **1983**, 897. (b) Newkome, G. R.; Kiefer, G. E.; Frere, Y. A.; Onishi, M.; Gupta, V. K.; Fronczek, F. R. *Organometallics* **1986**, *5*, 348. (c) Albert, J.; Granell, J.; Sales, J.; Solans, X.; Font, M. *Organometallics* **1986**, *5*, 2567.

(6) Tennant, G. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon: Oxford, 1979; Vol 2, Chapter 8.

(7) Onoue, H.; Moritani, I. *J. Organomet. Chem.* **1972**, *43*, 431.

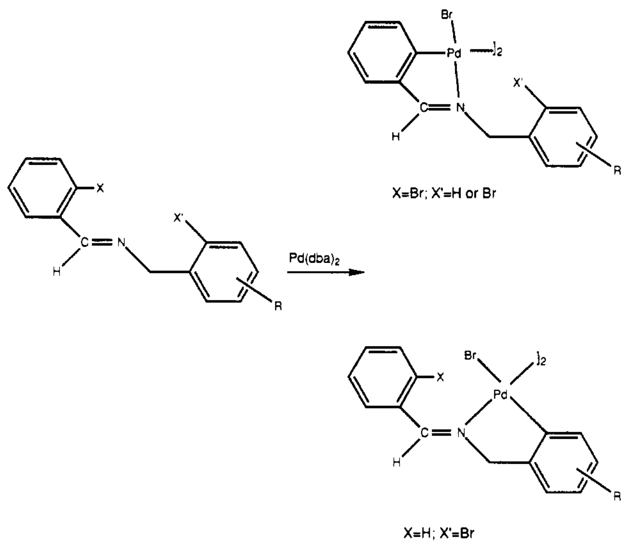
(8) Granell, J.; Sainz, D.; Sales, J.; Solans, X.; Font, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1785.

(9) Thompson, J. M.; Heck, R. F. *J. Org. Chem.* **1975**, *40*, 2667.

(10) Albert, J.; Granell, J.; Sales, J. *J. Organomet. Chem.* **1984**, *273*, 393.

(11) Clark, P. W.; Dyke, S. F.; Smith, G. *J. Organomet. Chem.* **1987**, *330*, 447.

Scheme I



To obtain exo-cyclopalladated derivatives of Schiff bases and to study the effect of the anti–syn isomerization equilibrium in cyclometalation, the *N*-benzylideneamines **1a–f** have been studied (Chart II).

According to the proposed electrophilic substitution mechanism, imine **1a** could afford metalation on the benzylic ring, giving an exo-cyclopalladated derivative. With ortho substituents in the benzal ring, metalation of the other phenyl ring would be favored. Thus, imines **1b–f** with chloro substituents have been studied. Analogous imines with ortho-methyl substituents gave six-membered metallocycles with Pd–aliphatic carbon bonds.[5c] Imines **1b–d** could give exo five-membered derivatives, whereas imines **1e** and **1f** could give exo six-membered cyclometalated complexes. Imines **1d** and **1f** will favor electrophilic attack of Pd on the benzyl or the ethylphenyl ring containing the electron-donating substituent -OMe.

Since the ^{1}H NMR spectra of these imines show that only one isomer is present in solution, we presume that it is the more stable anti form.

Results and Discussion

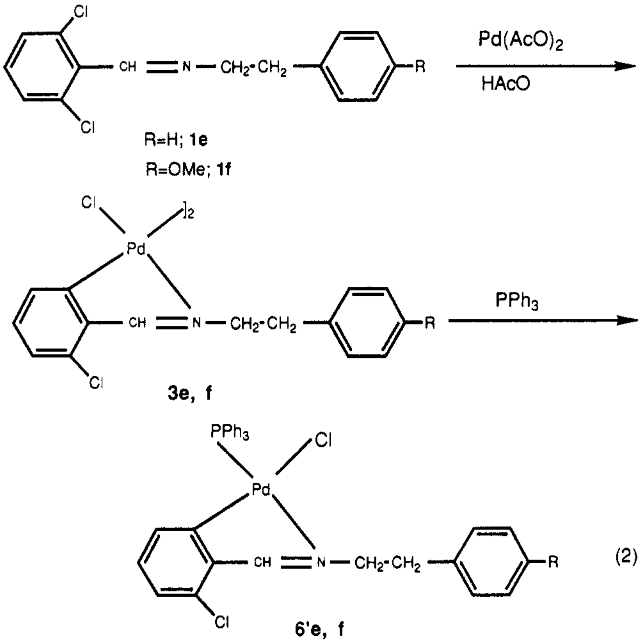
Imines **1a–f** were treated with Pd(AcO)$_2$ in a 2:1 ratio in anhydrous acetic acid under reflux for 45 min. From imine **1a**, the endo acetato-bridge compound **2a** was isolated, where only the benzal ring was metalated; the action of LiBr in acetone gave the corresponding bromo-bridged complex **3a** (Scheme II).

Ryabov has reported[12] that 1-(3,4-dimethoxyphenyl)-2-(4-nitrophenyl)-2-azapropene [3,4-$(OMe)_2C_6H_3CH_2N(CH_3)CH_2C_6H_4NO_2$], which can be metalated on both phenyl rings giving two different complexes, reacts with Pd(AcO)$_2$ in chloroform giving metalation of the electron-rich MeO-substituted phenyl ring, which is activated to electrophilic substitution. When the reaction is carried out in acetic acid, metalation occurs at the nitro-substituted phenyl ring, deactivated to electrophilic attack, but with a Pd–C bond more resistant to acidic hydrolisis. Reaction of **1a** in chloroform gives only the cyclometalated complex **2a**, suggesting that with imines it is not possible to direct the cyclometalation only by changing the electronic effects of the substituents.

With imine **1b**, which contains only one ortho-chloro substituent, the predicted endo bridged compounds **2** and **3** were obtained (Scheme II).

Imines **1c** and **1d**, with two ortho-chloro substituents in the benzal ring, undergo metalation at the benzyl ring giving cyclometallated compounds **4** and **5**, with exo structure, where the imine ligand is in the syn form (see below). Thus, cyclometalation and isomerization of the ligand take place simultaneously (Scheme III). If the reactions between imines **1c** or **1d** and Pd(AcO)$_2$ are carried out in milder conditions (in HAcO, at 60 °C), the same exo derivatives are obtained. It has not been possible to obtain the exo compounds with the imine ligand in the anti form.

Metalation of imines **1e** and **1f** could give exo six-membered cyclometalated compounds. No references of this kind of compounds have been reported before. The action of Pd(AcO)$_2$, in acetic acid under reflux, on these imines led to the endo five-membered compounds **3e** and **3f**, which were characterized as their PPh$_3$ derivatives **6′e** and **6′f** (see below and eq 2).



Obtention of compounds **3e** and **3f** can be explained by oxidative addition of C–Cl bonds to metallic palladium, formed in situ by reduction of the palladium salt by the imine ligand. This is a well-known process that has been proposed in the catalytic olefin arylation from olefins and organic halides.[13] To prevent reduction to Pd(0) and to get metalation of the ethylphenyl ring, the reaction was done in refluxing toluene as solvent, but, as before, only cyclometalated compounds **3** were obtained.

The best results were obtained working in acetic acid at 80 °C for 90 min. In these conditions, a mixture of **5f** and the coordination compound [PdBr$_2$(**1f**)$_2$] were obtained; **5f** can be separated by column chromatography on silica gel (Scheme II).

From imine **1e** only the coordination complex [PdBr$_2$(**1e**)$_2$] was formed. This different result supports the electrophilic attack of the metal on the phenyl ring; imine **1f** contains an electron-donating substituent that favors the metalation process. The yield of **5f** (15–20%) is lower than that obtained with other exo-cyclometalated derivatives that contain five-membered rings. Similarly to compounds **5c** and **5d**, the imine ligand in compound **5f** has

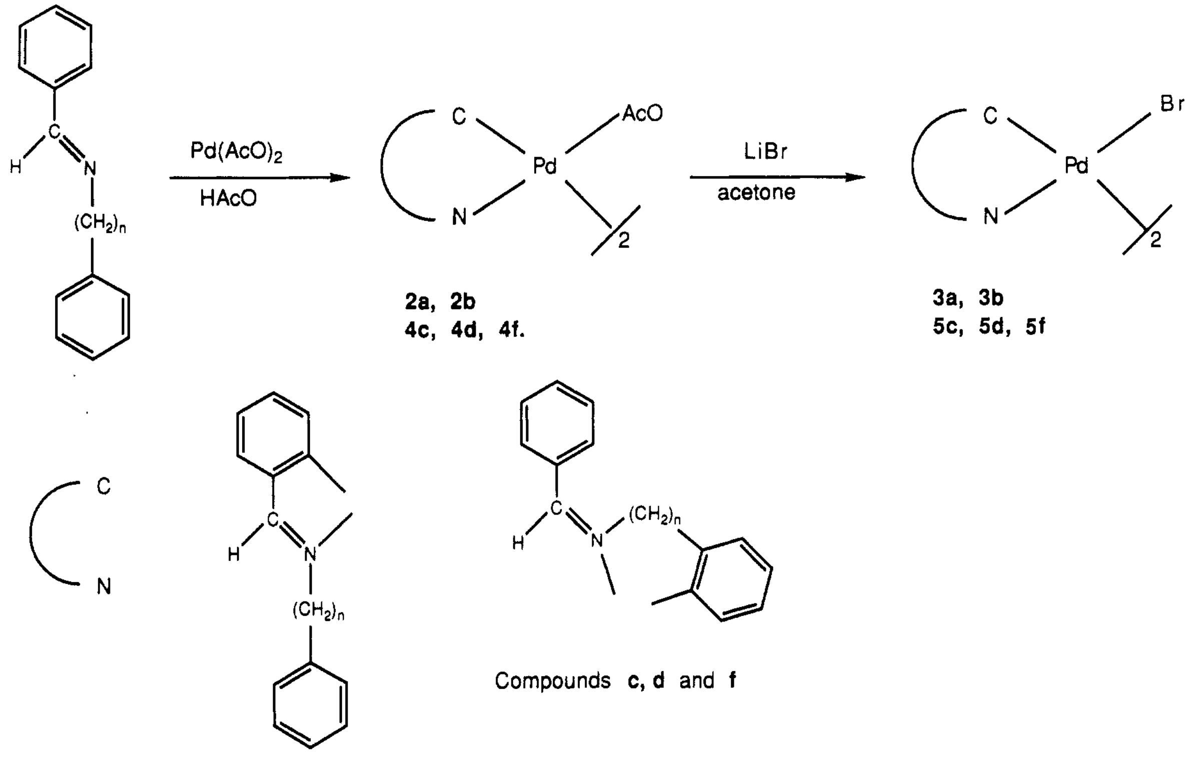
---

(12) Ryabov, A. D. *Inorg. Chem.* **1987**, *26*, 1252.

(13) Heck, R. F. *Org. React.* **1982**, *17*, 345.

(14) Granell, J.; Sales, J.; Vilarrasa, J.; Declerq, J. P.; Germain, G.; Miravitlles, C.; Solans, X. *J. Chem. Soc., Dalton Trans.* **1983**, 2441.

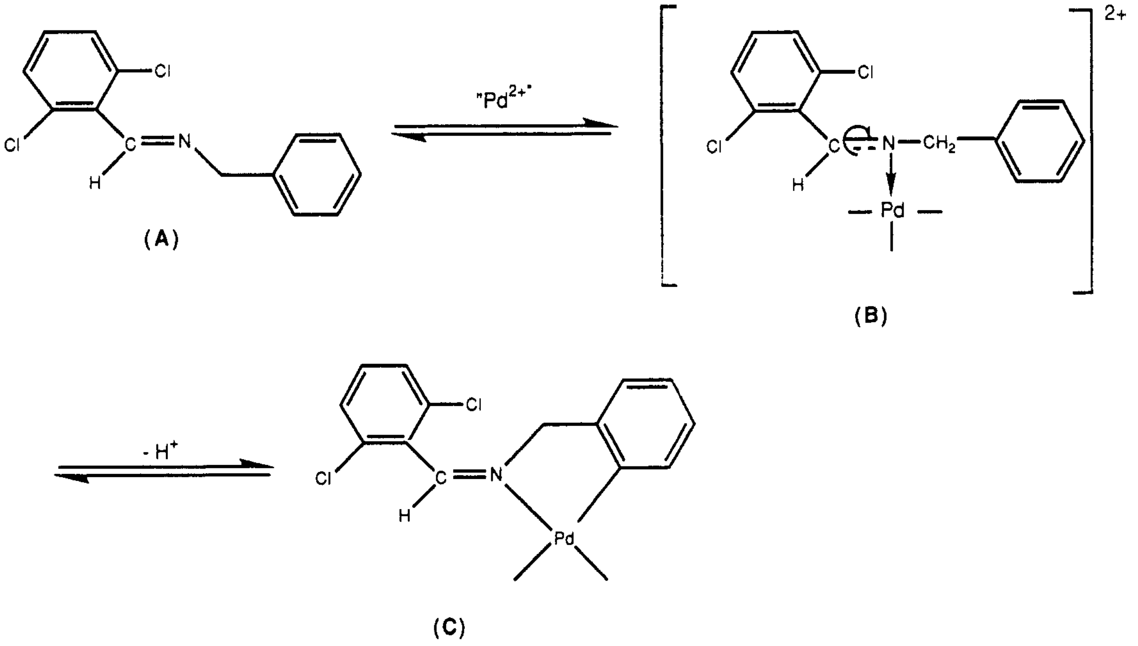
Scheme II



Compounds c, d and f

Compounds a and b

Scheme III



been isomerized to the syn form.

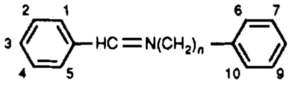
In summary, N-(2,6-dichlorobenzylidene)benzylamines give easily exo five-membered cyclometalated complexes, where the imine ligand is in the syn form. On the other hand, from N-(2,6-dichlorobenzylidene)(2-ethylphenyl)amines, in the usual conditions, endo five-membered derivatives are obtained by oxidative addition of o-C–Cl bonds to Pd(0) formed in situ. Only the MeO-substituted imine **1f**, activated to electrophilic attack, gives under mild conditions the exo six-membered derivatives with the imine ligand in the syn form.

All exo-cyclometalated compounds obtained, **5c**, **5d**, and **5f** have the imine ligand in the syn form, although both isomers, anti and syn, can give exo derivatives. As the free imine is in the anti form, the anti–syn isomerization occurs during the cyclometalation process. This isomerization can be explained by a decrease in the bond order of the C=N— group, produced by coordination of the metal (Scheme III). As ortho-chloro substituents prevent the metalation of the benzal ring, the intermediate B undergoes metalation in the other phenyl ring, giving the exo derivative C. In this complex, the imine is in the syn form in order to decrease the steric repulsion between the 2,6-$Cl_2C_6H_3$ and "PdAcO" groups. If the metalation could take place without isomerization of the imine ligand, the exo-cyclometalated derivatives formed would have the bulky 2,6-

Table I. Proton NMR Data[a]

compd	HC=N	aromatic	aliphatic
1a	8.46 s	8.25 d, ^3J(HH) = 8.9, H_2, H_4 7.91 d, ^3J(HH) = 8.9, H_1, H_5 7.26 d, ^3J(HH) = 8.6, H_6, H_{10} 6.90 d, ^3J(HH) = 8.6, H_7, H_9	4.81 s, CH_2N 3.80 s, CH_3O
2a	*b*	7.93–7.84 br m 7.25–7.07 br m 6.88–6.61 br m	4.35,[c] CH_2N 3.78 s, CH_3O 2.25 s, CH_3COO
6a	8.10 s	7.65–7.27 br m 6.93 d, ^3J(HH) = 8.6, H_7, H_9	5.29 s, CH_2N 3.84 s, CH_3O
9a	9.18 s	8.28 s, H_2 8.03–7.73 br m, H_4, H_5 7.25 d, ^3J(HH) = 8.0, H_6, H_{10} 6.90 d, ^3J(HH) = 8.0, H_7, H_9	4.75 s, CH_2N 3.80 s, CH_3O
1b	8.87 s	8.19–8.07 br m 7.29–7.24 br m	4.88 s, CH_2N
2b	7.61 s	7.27 br m 7.08–7.01 br m	4.28,[c] CH_2N 2.14 s, CH_3COO
6b	8.48 s	6.80 d, ^3J(HH) = 7.0, H_4 6.48–6.30, br m, H_2, H_3 7.84–7.25, br m, $PhCH_2$	5.43 s, CH_2N
7b	8.45 d[d]	7.39–7.26, br m 7.01 br m	5.33 s, CH_2N
9b	8.95 s	7.39–7.22, br m 6.98–6.95, br m	4.85 s, CH_2
1c	8.59 s	7.45–7.23, br m	4.95 s, CH_2N
5c	9.00 br s	7.41–6.94, br m	4.77 br s, CH_2N
6c	9.61 br s	7.95–7.12, br m 6.78–6.33, br m	4.86 br s, CH_2N
7c	9.39 br s	7.56–6.97 br m	4.80 br s, CH_2N
8c	9.63 s	7.88–6.41 br m	4.89 br s, CH_2N
9c	8.60 s	7.36–6.94 br m	5.11 s, CH_2N
1d	8.51 s	7.34–7.24 br m 6.88 d, ^3J(HH) = 8.5, H_7, H_9	4.85 s, CH_2N 3.79 s, CH_3O
5d	8.99 br s	7.41–7.10 br m 6.65–6.59 br m	4.74 br s, CH_2N 3.77 s, CH_3O
6d	9.58 br s	7.95–7.18 br m 6.70 d, ^3J(HH) = 7.0, H_{10} 6.33 dd, ^4J(HH) = 2.4, H_9 5.95 dd, ^4J(HP) = 7.3, H_7	4.81 br s, CH_2N 2.84 s, CH_3O
8d	9.60 s	8.56–6.00 br m	4.83 br s, CH_2N 2.88 s, CH_3O
9d	8.58 s	6.99 d, ^3J(HH) = 8.0, H_{10} 6.91 br s, H_7 6.46 br d, H_9	5.07 s, CH_2N 3.72 s, CH_3O
1f	8.41 s	7.40–7.21 br m 6.9 d, ^3J(HH) = 8.5, H_7, H_9	4.01 t, ^3J(HH) = 7.0, CH_2N 3.08 t, ^3J(HH) = 7.0, CH_2Ph 3.85 s, CH_3O
5f	8.94 br s	6.87 br s, H_7 6.61 d, ^3J(HH) = 8.0, H_{10} 6.39 dd, ^4J(HH) = 2.2, H_9	3.17 br m, CH_2N 3.05 br m, CH_2Ph 3.67 s, CH_3O
6f	9.10 br s	7.55–7.25 br m 6.65 d, ^3J(HH) = 7.0, H_{10} 6.37 dd, ^4J(HH) = 2.4, H_9 6.05 dd, ^4J(HP) = 7.2, H_7	3.21 br m, CH_2CH_2N, CH_3O
8f	9.10 s	8.06–6.10 br m	3.44 br m, CH_2N 3.08 br m, CH_2Ph 3.25 s, CH_3O
9f	8.48 s	7.39–7.18 br m 6.99 d, ^3J(HH) = 8.0, H_{10} 6.85 br s, H_7 6.46 dd, ^4J(HH) = 2.2, H_9	4.04 t, ^3J(HH) = 7.0, CH_2N 3.36 t, ^3J(HH) = 7.0, CH_2Ph 3.71 s, CH_3O
6′e	8.34 d[e]	7.81–7.11 br m 6.80 dd, ^3J(HH) = 7.8, H_4 6.45 t, ^3J(HH) = 7.8, H_3 6.28 br d, H_2	4.17 br m, CH_2N 3.87 br t, CH_2Ph
6′f	8.36 br s	7.70–7.15 br m 6.86–6.81 br m, H_4, H_7, H_9 6.45 t, ^3J(HH) = 7.8, H_3 6.35 br d, H_2	4.14 br t, CH_2N 3.30 br t, CH_2Ph 3.75 s, CH_3O

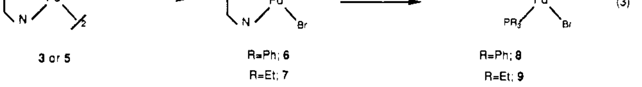
[a] In $CDCl_3$; chemical shifts in ppm with respect to internal $SiMe_4$; coupling constants in Hz; numbering as in



[b] Overlapped with aromatic protons. [c] AB quartet. [d] ^4J(HP) = 7.2. [e] ^4J(HP) = 7.8.

C_6H_3 and "PdAcO" groups on the same side of the iminic C=N bond.

Reactions with Phosphines. To obtain more soluble mononuclear compounds, the action of PEt_3 and PPh_3 on the cyclometalated complexes **3** and **5** has been studied. These reactions will also allow comparison of the relative stabilities of these complexes, since either metallocycles with one phosphine (**6** or **7**) or compounds with two phosphines (**8** or **9**), where the Pd–N bond has been broken, can be obtained (eq 3).



3 or 5

R=Ph; 6
R=Et; 7

R=Ph; 8
R=Et; 9

The stability of the Pd–N bond in the cyclometalated derivatives of *N*-benzylideneamines is very dependent on the basicity of the *N* atom. Thus, while the action of PPh_3 on *N*-benzylideneaniline derivatives gives complexes **8** without a Pd–N bond,[7,8] from *N*-benzylidenebenzylamine derivatives, with a more basic N atom, only cyclometalated complexes **6** were formed.[10] With the more basic phosphine PEt_3, both types of amine derivatives give **9**, where the Pd–N bond has been broken.

Addition of an excess of PEt_3 to acetone solutions of compounds **3** or **5** gives in all cases compounds **9** without Pd–N bonds. However, when PPh_3, less basic and bulkier than PEt_3, is added in excess, the Pd–N bond breaks only for the exo derivatives (compounds **5**), giving **8c**, **8d**, and **8f**. For the endo derivatives **3**, cyclometalated compounds **6a**, **6d**, **6′e**, and **6′f** were obtained. These results agree with the more nucleophilic character of PEt_3 and the lower stability of the exo derivatives. By addition of stoichiometric amounts of phosphine, cyclometalated derivatives **6** and **7** can be obtained.

Characterization. All new compounds obtained are air-stable yellow solids. They are quite soluble in chloroform and acetone and slightly soluble in methanol and diethyl ether. Cyclometalated compounds are, in general, less soluble than compounds containing phosphine.

IR spectra show the typical bands of coordinated phosphines and imines. In compounds with Pd–N bonds, the wavenumbers corresponding to ν(C=N) are smaller than the corresponding to free imines, in agreement with a decrease in bond order due to nitrogen coordination.

Proton NMR spectra are reported in Table I. The chemical shift of methinic protons is a useful tool for the structural characterization of cyclopalladated derivatives. This signal appears high-field shifted (0.3–1.3 ppm) relative to that of free imine in the endo metallocycle **2**, **3**, **6**, and **7** of ligands **1a** and **1b**. This shift results from the expected decrease in the C=N bond order due to nitrogen coordination and agrees with that reported for analogous endocyclic cyclometalated compounds.[7,8,10] For the exo metallocycles **4**–**7** of ligands **1c**, **1d**, and **1f** this peak is low-

Table II. Summary of Crystallographic Data

	6f	9c
formula	$C_{34}H_{29}NOCl_2PBrPd$	$C_{26}H_{40}NP_2Cl_2BrPd$
mol wt	755.8	685.8
syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/a$
a, Å	20.321 (4)	45.352 (6)
b, Å	12.561 (3)	8.884 (2)
c, Å	12.608 (3)	7.556 (2)
β, deg	97.50 (2)	99.02 (3)
V, Å^3	3191 (2)	3007 (2)
d_{calc}, g cm^{-3}	1.573	1.514
Z	4	4
$F(000)$	1512.0	1392.0
cryst size, mm^3	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
μ(Mo Kα), cm^{-1}	21.42	23.10
λ(Mo Kα), Å	0.71069	0.71069
T, °C	25	25
rflctns coll	3263	2350
R	0.031	0.056
R_w	0.031	0.060

field shifted (0.4–1.0 ppm), relative to the corresponding free ligand, and appears as a broad multiplet due to its coupling to both ^{31}P and methilenic protons. After irradiation of the methilenic signals, the peak appears as a doublet, $^4J(PH)$ = 4–5 Hz. This downfield shift can be explained by the paramagnetic anisotropy of the metal.[15] It indicates a close vicinity between Pd and H atoms and suggests a syn form for the ligand, which is in agreement with the existence of long-range coupling between CH_2 and methinic proton, since these hydrogens are in trans position in relation to the C═N bond. The assignment of aromatic signals affords conclusive evidence of the palladation position (see Table I). Aromatic protons of cyclometalated compounds **6**, with PPh_3 ligands, appear highfield shifted. This effect could be caused by a phosphine phenyl ring, according with a cis arrangement of the phosphine and the metalated ring, and in consequence a trans arrangement between phosphorous and nitrogen atoms. The ^{31}P chemical shift of these compounds, 41–43 ppm in five-membered derivatives and 34.4 ppm in six-membered complex **6f**, agrees with this trans arrangement.[16,17]

The chemical shift modifications in the NMR spectra of compounds **8** and **9**, with no Pd–N bond, is in accord with the phenyl ring being metalated. It has not been possible to obtain compounds **8** from endocyclic cyclometalated complexes **3a**, **3b**, **3e**, and **3f**, because an excess of PPh_3 does not break the Pd–N bond in these compounds. In PEt_3-containing compound **9a**, the methinic signal appears 0.8 ppm downfield from free imine, indicating its vicinity to the Pd atom and showing the existence of free rotation around $C_{methinic}$–$C_{aromatic}$ bond. In compound **9b**, this shift is not observed, suggesting that rotation around this bond is hindered, probably by an interaction between the methinic hydrogen and the ortho-chloro substituent.

The downfield shift of iminic protons in compounds **8c**, **8d**, and **8f** can also be attributed to the vicinity of the Pd atom; this interaction is possible only if the imine ligand is in the syn form. Similar interactions have been observed in cyclometalated derivatives of azines.[18] In compounds **9c**, **9d**, and **9f**, no shift is observed for iminic protons, according to the anti form adopted by the ligand (see below). The different behavior of compounds containing PEt_3 and PPh_3 can be explained by steric factors. The reaction of cyclometalated compounds **5** with an excess of phosphine proceeds through compounds $[\overline{\mathrm{Pd}\{p\text{-}\mathrm{RC_6H_3(CH_2)_nN}}{=}\mathrm{CH(2,6\text{-}Cl_2C_6H_3)\}Br(PR'_3)}]$, in which the ligand is in the syn form (see molecular structure of **6f** below). The entrance of a second phosphine in the coordination sphere of palladium breaks the Pd–N bond, and an isomerization process to the anti form can take place. Similar results, showing the influence of the size of phosphines in the structure of cyclometalated compounds, have been reported. Thus, in endocyclic cyclometalated derivatives of imines, the rotation around $C_{methinic}$–$C_{aromatic}$ has been

Table III. Bond Distances (Å) and Angles (deg) for 6f

Bond Distances			
Br–Pd	2.548 (1)	C(16)–C(11)	1.411 (5)
P–Pd	2.263 (1)	C(13)–C(12)	1.426 (5)
C(1)–Pd	2.002 (3)	C(14)–C(13)	1.351 (5)
N(9)–Pd	2.124 (3)	C(15)–C(14)	1.389 (6)
C(51)–P	1.827 (3)	C(16)–C(15)	1.377 (5)
C(61)–P	1.826 (3)	C(52)–C(51)	1.418 (4)
C(71)–P	1.816 (3)	C(56)–C(51)	1.397 (5)
C(13)–Cl(1)	1.728 (4)	C(53)–C(52)	1.400 (5)
C(11)–Cl(2)	1.715 (4)	C(54)–C(53)	1.386 (6)
C(2)–C(1)	1.399 (4)	C(55)–C(54)	1.417 (6)
C(6)–C(1)	1.427 (4)	C(56)–C(55)	1.427 (5)
C(3)–C(2)	1.398 (4)	C(62)–C(61)	1.461 (4)
O(31)–C(3)	1.389 (4)	C(66)–C(61)	1.398 (4)
C(31)–O(31)	1.438 (4)	C(63)–C(62)	1.381 (5)
C(4)–C(3)	1.412 (5)	C(64)–C(63)	1.392 (5)
C(5)–C(4)	1.358 (5)	C(65)–C(64)	1.442 (5)
C(6)–C(5)	1.385 (5)	C(66)–C(65)	1.402 (4)
C(7)–C(6)	1.544 (5)	C(72)–C(71)	1.379 (4)
C(8)–C(7)	1.552 (5)	C(76)–C(71)	1.409 (5)
N(9)–C(8)	1.507 (4)	C(73)–C(72)	1.415 (5)
C(10)–N(9)	1.280 (4)	C(74)–C(73)	1.382 (6)
C(12)–C(10)	1.479 (4)	C(75)–C(74)	1.417 (6)
C(12)–C(11)	1.412 (4)	C(76)–C(75)	1.417 (5)

Bond Angles			
P–Pd–Br	92.9 (1)	C(13)–C(12)–C(11)	114.1 (3)
C(1)–Pd–Br	169.0 (1)	C(10)–C(12)–C(13)	124.0 (3)
C(1)–Pd–P	92.8 (1)	C(10)–C(12)–C(11)	121.1 (4)
N(9)–Pd–Br	90.9 (1)	C(14)–C(13)–C(12)	124.9 (3)
N(9)–Pd–P	171.1 (1)	Cl(1)–C(13)–C(12)	114.3 (3)
N(9)–Pd–C(1)	84.9 (1)	Cl(1)–C(13)–C(14)	120.7 (3)
C(51)–P–Pd	111.3 (1)	C(15)–C(14)–C(13)	119.6 (4)
C(61)–P–Pd	118.1 (1)	C(16)–C(15)–C(14)	118.9 (4)
C(61)–P–C(51)	104.0 (1)	C(15)–C(16)–C(11)	121.3 (4)
C(71)–P–Pd	115.1 (1)	C(52)–C(51)–P	117.2 (3)
C(71)–P–C(51)	104.2 (1)	C(56)–C(51)–P	121.6 (2)
C(71)–P–C(61)	102.7 (1)	C(56)–C(51)–C(52)	121.2 (3)
C(2)–C(1)–Pd	121.4 (2)	C(53)–C(52)–C(51)	119.3 (4)
C(6)–C(1)–Pd	117.9 (2)	C(54)–C(53)–C(52)	119.9 (4)
C(6)–C(1)–C(2)	120.6 (3)	C(55)–C(54)–C(53)	121.5 (4)
C(3)–C(2)–C(1)	117.4 (3)	C(56)–C(55)–C(54)	118.8 (4)
O(31)–C(3)–C(2)	121.9 (3)	C(55)–C(56)–C(51)	119.0 (3)
C(4)–C(3)–C(2)	122.0 (3)	C(62)–C(61)–P	116.0 (2)
C(4)–C(3)–O(31)	116.1 (3)	C(66)–C(61)–P	123.2 (3)
C(3)–O(31)–C(31)	117.6 (4)	C(66)–C(61)–C(62)	119.9 (3)
C(5)–C(4)–C(3)	119.3 (3)	C(63)–C(62)–C(61)	119.1 (3)
C(6)–C(5)–C(4)	121.4 (4)	C(64)–C(63)–C(62)	120.8 (4)
C(5)–C(6)–C(1)	119.3 (3)	C(65)–C(64)–C(63)	120.4 (3)
C(7)–C(6)–C(1)	118.8 (3)	C(66)–C(65)–C(64)	119.1 (3)
C(7)–C(6)–C(5)	121.7 (3)	C(65)–C(66)–C(61)	120.1 (3)
C(8)–C(7)–C(6)	109.4 (3)	C(72)–C(71)–P	119.0 (2)
N(9)–C(8)–C(7)	111.5 (2)	C(76)–C(71)–P	120.5 (2)
C(8)–N(9)–Pd	119.0 (2)	C(76)–C(71)–C(72)	120.6 (3)
C(10)–N(9)–Pd	121.0 (2)	C(73)–C(72)–C(71)	118.8 (4)
C(10)–N(9)–C(8)	120.0 (3)	C(74)–C(73)–C(72)	121.6 (4)
C(12)–C(11)–Cl(2)	116.6 (3)	C(75)–C(74)–C(73)	119.7 (4)
C(16)–C(11)–Cl(2)	122.4 (3)	C(76)–C(75)–C(74)	118.5 (4)
C(16)–C(11)–C(12)	120.9 (3)	C(75)–C(76)–C(71)	120.4 (3)

---

(15) Miller, R. G.; Stauffer, R. D.; Fahey, D. R.; Parnell, D. R. *J. Am. Chem. Soc.* **1970**, *92*, 1511.

(16) Pereira, M. T.; Vila, J. M.; Suarez, A.; Gayoso, E.; Gayoso, M. *Gaz. Chim. Ital.* **1988**, *118*, 783.

(17) In the analogous six-membered cyclopalladated compounds derived from (2,4,6-trimethylbenzylidene)amines, which contain PPh_3 trans to the N atom,[5c] the $\delta(^{31}P)$ is ≈ 35.

(18) Ceder, R.; Granell, J.; Sales, J. *J. Organomet. Chem.* **1986**, *307*, C44.

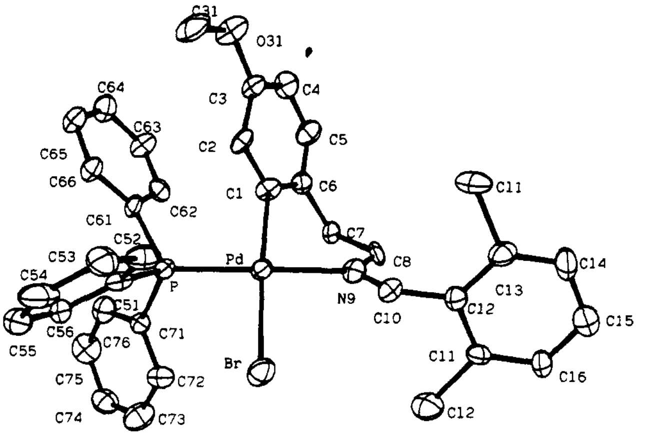


Figure 1. Molecular structure of $[PdBr\{p\text{-}MeOC_6H_3(CH_2)_2N{=}CH(2,6\text{-}Cl_2C_6H_3)(PPh_3)]$ (**6f**).

described for PEt_3-containing compounds but is hindered in the PPh_3 analogues.[8]

The ^{31}P chemical shift of compounds 8 ($\delta \sim 23$) and 9 ($\delta \sim 12$ ppm) is in accord with a trans arrangement of the phosphine ligands.[19]

Molecular Structures of 6f and 9c. To characterize unambiguously the endo six-membered geometry, an X-ray study of **6f** has been undertaken. Bond distances and angles are listed in Tables III and atomic coordinates in Table IV.

The molecular structure of **6f** is shown in Figure 1, with the numbering scheme. The crystal structure consists of discrete molecules separated by van der Waals distances. The Pd atom is in a roughly distorted square-planar environment; it is coordinated to P, Br, and N(9) and C(1) of the imine ligand. The deviations to the plane are as follows: Pd, 0.012 Å; Br, -0,149 Å; P, 0.156 Å; C, -0.200 Å; N, 0.182 Å. The Pd–ligand distances are similar to those found in analogous five-membered cyclometalated compounds.[11] The angles between adjacent atoms in the coordination sphere lie in the range 85.2 (1)–92.9 (1)°. The smallest of these angles is that between the coordinative atoms of the chelated ligand, N(9) and C(1). The six-membered metallocycle has a boat conformation, with Pd (-1.032 Å) and C(7) (-0.708 Å) atoms out of the plane defined by the remaining atoms.[20] It is clearly an exo structure, because the C=N bond is not contained in the cycle. In the other X-ray structure known of a six-membered cyclopalladated compound, $[Pd\{1\text{-}CH_2\text{-}2\text{-}(HC{=}NC_6H_5)\text{-}3,5\text{-}(CH_3)_2C_6H_2\}BrPPh_3]$, the Pd–$C_{aliphatic}$ distance is 2.0060 (5) Å and the metallocycle has a half-skew chair conformation with the Pd atom out of the plane (-1.325 Å).[5c] Another similar six-membered metallocyle compound with known molecular structure is $[RhCl_2(py)_2\{(C_6H_4)\text{-}NHpy\}]$;[21] in this compound the metallocycle, RhN_2C_3, although not truly planar, does not show large deviations from planarity. The Rh atom and the uncoordinated amine nitrogen atom lie below the plane, in what would be described as a boat type configuration for a saturated system. The observed bond lengths are consistent with a significant amount of delocalized π bonding, thus making the $[Rh(C_6H_4)NHpy]$ moiety a formal metallocyclic analogue of anthracene. The C(10)–N(9) distance (1.276 (4) Å) is lengthened due to coordination, but it is not very different from the values found in analogous endo structures.[11,12] The 2,6-$Cl_2C_6H_3$ and $CH_2CH_2C_6H_4$ moieties are in cis position in relation to the C=N bond, in accord with the isomerization process anti–syn of the imine ligand. The imine group is nearly planar, with a torsion angle of -3.39° for C(8)N(9)C(10)C(12). It forms a dihedral angle of 24.10° with the coordination plane of the complex. The dichlorophenyl ring [C(11)–C(13)] is nearly perpendicular to the iminic group, and the N(9)C(10)C(12)C(13) dihedral angle is 94.92°. The other phenyl ring [C(1)–C(6)] forms a dihedral angle of only 24.10° with the concentration plane, as a consequence of the chelating coordination of the ligand.

Table IV. Final Atomic Coordinates (×10^4; Pd and Br ×10^5) of 6f ($B_{eq} = 8\pi^2/3\sum_{ij}U_{ij}A_i^*A_j^*A_iA_j$)

	x/a	y/b	z/c	B_{eq}, Å^2
Pd	39357 (1)	37322 (2)	60413 (2)	3.86 (2)
Br	46672 (2)	23879 (3)	71559 (3)	6.30 (3)
P	3486 (1)	2473 (1)	4883 (1)	3.73 (5)
Cl(1)	1146 (1)	1668 (1)	6092 (1)	8.41 (8)
Cl(2)	3948 (1)	5347 (1)	1807 (1)	7.08 (7)
C(1)	3290 (2)	4845 (3)	5428 (3)	4.12 (19)
C(2)	2606 (2)	4723 (3)	5437 (3)	4.26 (19)
C(3)	2197 (2)	5570 (3)	5054 (3)	4.33 (20)
O(31)	1516 (1)	5552 (3)	5085 (3)	6.85 (18)
C(31)	3761 (2)	-382 (5)	9484 (5)	8.00 (33)
C(4)	2452 (2)	6501 (3)	4632 (4)	5.58 (24)
C(5)	3118 (2)	6602 (4)	4639 (3)	5.55 (23)
C(6)	3550 (2)	5798 (3)	5027 (3)	4.38 (21)
C(7)	4310 (2)	5943 (3)	5130 (3)	4.85 (21)
C(8)	4598 (2)	5994 (3)	6331 (3)	4.90 (21)
N(9)	4422 (1)	5012 (3)	6923 (3)	4.61 (18)
C(10)	4592 (2)	4941 (3)	7934 (3)	4.02 (19)
C(11)	4318 (2)	4369 (3)	1143 (3)	4.53 (21)
C(12)	5012 (2)	4260 (4)	1398 (3)	4.62 (21)
C(13)	5292 (2)	3432 (4)	825 (4)	5.30 (23)
C(14)	4945 (3)	2782 (4)	105 (4)	7.01 (28)
C(15)	4260 (3)	2893 (4)	-112 (4)	5.83 (26)
C(16)	3950 (2)	3656 (5)	431 (4)	6.39 (26)
C(51)	3159 (2)	1360 (4)	5588 (3)	3.95 (19)
C(52)	2903 (2)	1595 (4)	6555 (3)	5.50 (23)
C(53)	2601 (2)	785 (5)	7082 (4)	6.25 (27)
C(54)	2607 (2)	-253 (5)	6708 (5)	7.13 (32)
C(55)	2879 (2)	-510 (4)	5761 (4)	6.01 (26)
C(56)	3152 (2)	323 (3)	5186 (4)	5.03 (22)
C(61)	2793 (2)	2856 (3)	3884 (3)	4.00 (19)
C(62)	2911 (2)	3762 (4)	3207 (3)	5.08 (21)
C(63)	2392 (2)	4155 (4)	2499 (4)	5.75 (24)
C(64)	1753 (2)	3749 (4)	2479 (4)	5.61 (23)
C(65)	1632 (2)	2845 (4)	3132 (4)	5.20 (22)
C(66)	2152 (2)	2448 (4)	3866 (3)	4.77 (21)
C(71)	4059 (2)	1856 (3)	4079 (3)	3.50 (18)
C(72)	4682 (2)	1567 (3)	4562 (4)	4.98 (22)
C(73)	5105 (2)	998 (5)	3957 (5)	7.73 (32)
C(74)	4940 (3)	831 (4)	2872 (4)	6.34 (28)
C(75)	4308 (3)	1152 (4)	2361 (4)	7.04 (28)
C(76)	3871 (2)	1675 (4)	2979 (4)	5.72 (24)

One of the early rules of cyclometalation chemistry, which established that the greater stability of five-membered cyclometalated compounds was due to the fact that their ring size provided the most suitable geometry, is not of general application, since the bond lengths and angles of the six-membered cyclopalladated compound **6f** are not very different from those found in analogous five-membered derivatives and, although the number of known molecular structures of this type of compounds is small, different conformations have been found.[5c,21] Thus, the assumption that metal ions preferring square-planar geometry favor five-membered rings is unnecessarily limiting.

---

[19] Pregosin, P. S. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G.; Quin, L. D. VCH Publishers: Deefield Beach: FL, 1987; Chapter 14.

[20] Least-squares plane given by $-(0.5072)x + (0.5506)y + (0.6630)z = 3.9491$. Deviations: C(1), -0.006 Å; C(6), 0.007 Å; C(8), -0.007 Å; N(9), 0.006 Å.

[21] Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Organometallics* **1985**, *4*, 863.

[22] Albinati, A.; Pregosin, P. S.; Ruedi, R. *Helv. Chim. Acta* **1985**, *68*, 2046.

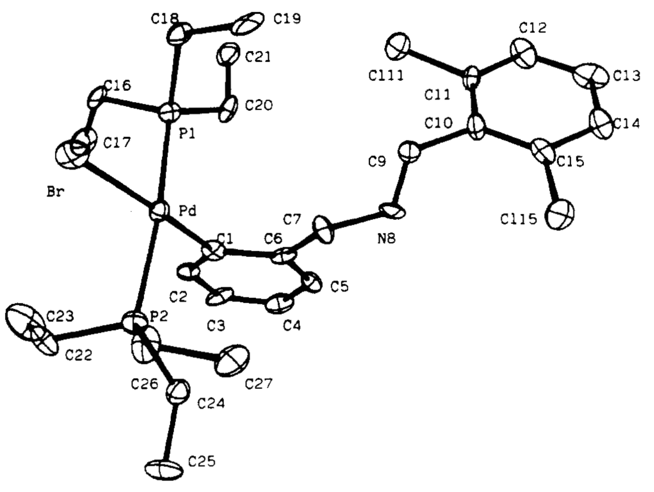


Figure 2. Molecular structure of $[PdBr\{C_6H_4CH_2N{=}CH(2,6\text{-}Cl_2C_6H_3)\}(PEt_3)_2]$ (**9c**).

Table V. Bond Distances (Å) and Angles (deg) for 9c

Bond Distances			
Br–Pd	2.526 (2)	N(8)–C(7)	1.485 (18)
P(1)–Pd	2.318 (4)	C(9)–N(8)	1.222 (19)
P(2)–Pd	2.317 (4)	C(10)–C(9)	1.515 (21)
C(1)–Pd	1.982 (15)	C(11)–C(10)	1.413 (21)
C(16)–P(1)	1.840 (15)	C(15)–C(10)	1.382 (23)
C(18)–P(1)	1.810 (16)	Cl(11)–C(11)	1.740 (15)
C(20)–P(1)	1.813 (18)	C(12)–C(11)	1.375 (21)
C(22)–P(2)	1.788 (16)	C(13)–C(12)	1.450 (28)
C(24)–P(2)	1.825 (17)	C(14)–C(13)	1.357 (27)
C(26)–P(2)	1.804 (18)	C(15)–C(14)	1.399 (23)
C(2)–C(1)	1.394 (21)	Cl(15)–C(15)	1.716 (18)
C(6)–C(1)	1.469 (19)	C(17)–C(16)	1.482 (24)
C(3)–C(2)	1.360 (24)	C(19)–C(18)	1.505 (22)
C(4)–C(3)	1.376 (24)	C(21)–C(20)	1.536 (23)
C(5)–C(4)	1.361 (22)	C(23)–C(22)	1.526 (30)
C(6)–C(5)	1.380 (22)	C(25)–C(24)	1.536 (23)
C(7)–C(6)	1.506 (20)	C(27)–C(26)	1.547 (25)

Bond Angles			
P(1)–Pd–Br	90.6 (1)	C(5)–C(6)–C(1)	119.2 (13)
P(2)–Pd–Br	89.9 (1)	C(7)–C(6)–C(1)	118.3 (13)
P(2)–Pd–P(1)	171.8 (2)	C(7)–C(6)–C(5)	122.5 (13)
C(1)–Pd–Br	176.6 (4)	N(8)–C(7)–C(6)	111.7 (12)
C(1)–Pd–P(1)	89.5 (4)	C(9)–N(8)–C(7)	116.6 (13)
C(1)–Pd–P(2)	89.5 (4)	C(10)–C(9)–N(8)	121.9 (15)
C(16)–P(1)–Pd	109.9 (5)	C(11)–C(10)–C(9)	117.5 (13)
C(18)–P(1)–Pd	116.3 (6)	C(15)–C(10)–C(9)	125.4 (14)
C(18)–P(1)–C(16)	100.8 (7)	C(15)–C(10)–C(11)	117.2 (13)
C(20)–P(1)–Pd	118.5 (5)	Cl(11)–C(11)–C(10)	120.8 (11)
C(20)–P(1)–C(16)	104.9 (8)	C(12)–C(11)–C(10)	123.9 (15)
C(20)–P(1)–C(18)	104.3 (8)	C(12)–C(11)–Cl(11)	115.2 (13)
C(22)–P(2)–Pd	109.7 (6)	C(13)–C(12)–C(11)	116.8 (16)
C(24)–P(2)–Pd	117.9 (6)	C(14)–C(13)–C(12)	119.7 (16)
C(24)–P(2)–C(22)	104.7 (8)	C(15)–C(14)–C(13)	121.7 (17)
C(26)–P(2)–Pd	116.0 (6)	C(14)–C(15)–C(10)	120.7 (16)
C(26)–P(2)–C(22)	101.2 (8)	Cl(15)–C(15)–C(10)	119.4 (11)
C(26)–P(2)–C(24)	105.5 (8)	Cl(15)–C(15)–C(14)	119.4 (14)
C(2)–C(1)–Pd	123.1 (10)	C(17)–C(16)–P(1)	116.5 (11)
C(6)–C(1)–Pd	123.0 (11)	C(19)–C(18)–P(1)	115.2 (11)
C(6)–C(1)–C(2)	113.9 (13)	C(21)–C(20)–P(1)	117.3 (12)
C(3)–C(2)–C(1)	125.1 (14)	C(23)–C(22)–P(2)	113.6 (13)
C(4)–C(3)–C(2)	119.5 (15)	C(25)–C(24)–P(2)	117.3 (13)
C(5)–C(4)–C(3)	119.0 (16)	C(27)–C(26)–P(2)	115.5 (13)
C(6)–C(5)–C(4)	123.0 (14)		

Table VI. Final Atomic Coordinates (×10^4; Pd and Br ×10^5) of 9c ($B_{eq} = 8\pi^2/3\sum_{ij}U_{ij}A_i{}^*A_j{}^*A_iA_j$)

	x/a	y/b	z/c	B_{eq}, Å^2
Pd	34019 (2)	20691 (14)	48523 (16)	2.65 (6)
Br	31210 (4)	35717 (20)	68875 (26)	4.75 (11)
P(1)	3753 (1)	3971 (5)	4924 (6)	3.14 (21)
P(2)	3016 (1)	331 (5)	4412 (6)	3.60 (23)
C(1)	3607 (3)	947 (16)	3131 (20)	2.31 (72)
C(2)	3545 (3)	1164 (17)	1282 (20)	2.98 (81)
C(3)	3672 (4)	381 (18)	50 (21)	3.89 (90)
C(4)	3882 (4)	−708 (20)	615 (23)	4.30 (101)
C(5)	3971 (3)	−911 (18)	2403 (20)	2.90 (79)
C(6)	3843 (3)	−163 (16)	3693 (20)	2.74 (75)
C(7)	3936 (3)	−442 (19)	5668 (18)	3.41 (84)
N(8)	4247 (3)	−1014 (14)	6076 (17)	3.13 (66)
C(9)	4422 (4)	−263 (18)	7107 (21)	3.63 (87)
C(10)	4748 (3)	−699 (18)	7596 (21)	3.48 (84)
C(11)	4964 (3)	373 (16)	7279 (19)	2.71 (75)
Cl(11)	4857 (1)	2161 (6)	6483 (7)	5.54 (26)
C(12)	5267 (3)	130 (24)	7643 (23)	4.69 (101)
C(13)	5364 (4)	8682 (24)	8406 (27)	5.35 (113)
C(14)	5158 (4)	7644 (22)	8710 (21)	4.49 (98)
C(15)	4851 (3)	7925 (21)	8286 (20)	3.88 (83)
Cl(15)	4603 (1)	−3367 (6)	8874 (8)	6.13 (29)
C(16)	3587 (4)	5611 (16)	3653 (23)	3.80 (89)
C(17)	3498 (4)	5402 (21)	1695 (25)	5.77 (115)
C(18)	3880 (4)	4819 (17)	7088 (21)	3.67 (85)
C(19)	4062 (4)	3806 (19)	8436 (23)	5.09 (103)
C(20)	4094 (4)	3587 (18)	4029 (24)	4.05 (91)
C(21)	4310 (3)	4905 (19)	3946 (23)	4.58 (101)
C(22)	2678 (3)	1245 (22)	3445 (24)	4.45 (99)
C(23)	2707 (5)	2162 (29)	1775 (28)	8.42 (147)
C(24)	3052 (4)	−1262 (18)	2935 (23)	3.97 (93)
C(25)	2797 (4)	−2422 (20)	2688 (26)	5.46 (112)
C(26)	2909 (4)	−469 (21)	6412 (22)	4.58 (99)
C(27)	3100 (4)	−1762 (19)	7280 (28)	6.02 (117)

The molecular structure of **9c** has also been determined (Figure 2). Bond distances, angles, and atomic coordinates are given in Tables V and VI. The Pd atom displays a roughly planar coordination. C(1), Br, P(1), and P(2) atoms are nearly in a plane, with the largest deviation for for P(1) and P(2) (0.050 Å), while the Pd atom is 0.116 Å out of this plane. The Pd–C, Pd–Br, and Pd–P distances and related angles are similar to those found in analogous compounds.[14,23] The N atom of the imine ligand is not bonded to the Pd atom, allowing a less crowded structure. The same situation is found for the azobenzene derivative, $[PdCl(C_6H_4N{=}NC_6H_5)(PEt_3)_2]$.[23a] On the other hand, in compounds $[\{PdCl(p\text{-}ClC_6H_3CH{=}N)(PEt_3)_2\}_2]$[14] and $[PdBr(C_6H_4CH{=}NC_6H_5)(PPh_3)_2]$,[8] derived from Schiff bases with endo structures, the Pd atom is pentacoordinated, with Pd–N distances of 2.710 and 2.743 Å, respectively. Although coordination of the N atom to palladium produces a more crowded conformation, the system is stable because the "metallocycle" contains the iminic double bond (endo structure). In the hydrazone derivative $[PdCl(C_6H_4C(CH_3){=}NNHC_6H_5)(PEt_3)_2]$,[23b] there is no Pd–N interaction, but the Pd atom affords pentacoordination by bonding to one hydrogen atom of the methyl group. The metalated phenyl ring [C(1)–C(6)] is perpendicular (92.2 (6)°) to the plane of the complex. The $CH_2C_6H_4$ and $2,3\text{-}Cl_2C_6H_3$ groups are in the trans position relative to the iminic C=N bond, showing that the imine ligand is in the anti form. Thus, the excess of PEt_3 on the cyclometalated compound **5c**, together with the breaking of the Pd–N bond, produces the isomerization of the imine ligand, which recovers the anti form. The NMR spectrum of the analogous compound **8c**, with two PPh_3 molecules, shows that the imine ligand retains the syn form. Probably, the bulkier PPh_3 prevents the isomerization process. The iminic moiety is nearly planar, with a torsion angle of −178.59° for C(7)N(8)C(9)C(10), and forms a dihedral angle of 54.34° with the $2,6\text{-}Cl_2C_6H_3$ ring. The two PEt_3 are trans to each other, and C(20) and C(24) display a

---

[23] (a) Weaver, D. L. *Inorg. Chem.* **1970**, *9*, 2250. (b) Dehand, J.; Fischer, J.; Pfeffer, M.; Mitschler, A.; Zinisus, M. *Inorg. Chem.* **1976**, *15*, 2675.

cis–syn periplanar form with respect to C(1), which produces an increase of C(20)P(1)Pd and C(24)P(2)Pd angles (average value 118.5 (5)°).

Experimental Section

NMR spectra were obtained on a Bruker WP 80 SY (^{1}H, 80.13 MHz; ^{31}P, 32.8 MHz) spectrometer. IR spectra were recorded as KBr disks on a Perkin-Elmer 1330 spectrometer. Microanalyses were performed by the Institut de Quimica Bio-Orgànica de Barcelona (CSIC). Satisfactory analytical data (C, H, and N) were obtained for the new compounds (supplementary material; see the paragraph at the end of the paper).

Materials and Syntheses. Solvents were dried and distilled before use. Imines were prepared according to published methods.[24]

[Pd(RC$_6$H$_3$CH=NCH$_2$C$_6$H$_4$R′-*p*)(AcO)]$_2$ (2a, 2b). A stirred suspension of Pd(AcO)$_2$ (1.0 g, 4.4 mmol) in anhydrous acetic acid (30 mL) was treated with an excess of imine **1a** or **1b** (8.8 mmol) and refluxed for 45 min. The filtrate was concentrated in vacuo, and the solid obtained, after addition of ethanol, was purified by column chromatography over SiO$_2$ with chloroform–methanol (100/1) as eluant; compounds **2** were obtained in 80% yield.

[Pd(RC$_6$H$_3$CH=NCH$_2$C$_6$H$_4$R′-*p*)Br]$_2$ (3a, 3b). A mixture of **2** (0.5 mmol) and LiBr (0.05 g, 0.5 mmol) in ethanol (20 mL) was stirred for 30 min. The precipitate was filtered and recrystallized from CH$_2$Cl$_2$ to give **3** in 80% yield.

[PdBr{*p*-RC$_6$H$_3$CH$_2$N=CH(2,6-Cl$_2$C$_6$H$_3$)}]$_2$ (5c, 5d). A stirred suspension of Pd(AcO)$_2$ (0.45g, 2.0 mmol) in acetic acid (30 mL) was treated with an excess of imine (4.0 mmol) and refluxed for 45 min. The solution was concentrated in vacuo, and the residue obtained was treated with LiBr (0.35 g, 4 mmol) in ethanol for 30 min. The solid obtained was filtered off and purified by column chromatography over SiO$_2$, with chloroform as eluant. Compounds **5c** and **5d** were obtained in 50–60% yield.

[PdBr{*p*-MeOC$_6$H$_3$(CH$_2$)$_2$N=CH(2,6-Cl$_2$C$_6$H$_3$)}]$_2$ (5f). A stirred suspension of Pd(AcO)$_2$ (0.45 g, 2.0 mmol) in acetic acid (30 mL) was treated with an excess of imine **1f** (1.23 g, 4 mmol) at 80 °C for 90 min. The solution obtained was concentrated, and the resulting residue was dissolved in ethanol (20 mL) and treated with LiBr (0.35 g, 4.0 mmol) in ethanol for 30 min, at room temperature. The precipitate formed was filtered off and purified by column chromatography over SiO$_2$, with chloroform as eluant. Compound **5f** was obtained in 20% yield.

[PdCl{2-C$_6$H$_3$ClCH=N(CH$_2$)$_2$C$_6$H$_4$R-*p*}(PPh$_3$)] (6′e, 6′f). A stirred suspension of Pd(AcO)$_2$ (0.45 g, 2.0 mmol) in refluxing acetic acid was treated with an excess of imine (4 mmol) for 4 h. After filtering off the Pd(0) formed, the solution was concentrated in vacuo, and the residue was purified by column chromatography over SiO$_2$, with chloroform as eluant to give compounds **3**. This compound was then refluxed with PPh$_3$ (0.52 g, 2.0 mmol) in acetone for 30 min. The filtrate was concentrated in vacuo, and the solid obtained, after addition of diethyl ether, was purified by column chromatography over SiO$_2$ with CH$_3$OH–CH$_3$Cl (1:100). Compounds **6′** were obtained in 10–15% yield referred to the initial Pd.

[PdBr($\overset{\frown}{\mathrm{C}\,\mathrm{N}}$)(PPh$_3$)$_2$] (8) and [PdBr($\overset{\frown}{\mathrm{C}\,\mathrm{N}}$)(PPh$_3$)] (6). A stirred suspension of compound **5** (0.5 mmol) was treated with PPh$_3$ (0.52 g, 2.0 mmol) in refluxing acetone for 30 min. The solution obtained was concentrated in vacuo, and the solid obtained, after addition of diethyl ether, was purified by recrystallization from CH$_2$Cl$_2$–MeOH. Compounds **8c**, **8d**, and **8f** were obtained in 65–75% yield. Compounds **6a** or **6b** and **6c**, **6d**, or **6f** were obtained analogously (60–70% yield), from compounds **3** and **5**, respectively, and PPh$_3$ (0.25 g, 1.0 mmol). They were purified by column chromatography.

[PdBr($\overset{\frown}{\mathrm{C}\,\mathrm{N}}$)(PEt$_3$)] (7) and [PdBr($\overset{\frown}{\mathrm{C}\,\mathrm{N}}$)(PEt$_3$)$_2$] (9). A mixture of **3** or **5** (0.5 mmol) and PEt$_3$ (1 mmol) in acetone (30 mL) was refluxed for 20 min under nitrogen and then filtered. The filtrate was concentrated in vacuo and the solid obtained, after addition of CH$_3$CH$_2$OH, was purified by column chromatography over SiO$_2$ with chloroform as eluant to afford **7b** or **7c** in 40–50% yield. Compounds **9a** or **9b** and **9c**, **9d**, or **9f** were obtained analogously from compound **3** and **5**, respectively (70–80% yield). They were purified by recrystallization from CH$_2$Cl$_2$–CH$_3$OH.

Crystallographic Studies. A summary of crystallographic data is given in Table II. Crystals were selected and mounted on a Philips PW-1100 four-circle diffractometer. **6f** unit-cell parameters were determined from automatic centring of 25 reflections ($4 < \theta < 12°$) and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo Kα radiation, by using the ω-scan technique, scan width 1°, scan speed 0.03° s^{-1}; 3263 reflections were measured in the range $2 < \theta < 25°$, 2690 of which were assumed as observed applying the condition $I > 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control and significant intensity decay was not observed. Lorentz–polarization and absorption corrections were made (max and min transmission factors 0.97 and 0.83, respectively).

The structure was solved by direct methods using the MULTAN system of computer programs[25] and refined by full-matrix least-squares method, using the SHELX76 computer program.[26] The function minimized was $\sum w||F_o| - |F_c||^2$, where $w = \sigma^{-2}(F_o)$. H atoms were not located. The final R factor was 0.031 ($R_w = 0.031$) for all observed reflections (max shift/esd = 0.05 in y of C(14); max and min peaks in final difference synthesis 0.3 and −0.2 e Å^3).

9c. Unit-cell parameters were determined from automatic centring of 15 reflections ($4 < \theta < 12°$) and refined by least-squares methods. Intensities were collected wuth graphite-monochromatized Mo Kα radiation, using the ω-scan technique, scan width 0.8°, scan speed 0.03° s^{-1}. A total of 2350 reflections were measured in the range $2 < \theta < 25°$, 1805 of which were assumed as observed applying the condition $I > 2.5\sigma(I)$, R_{int} on F was 0.022. Three reflections were measured every 2 h as orientation and intensity control, and significant intensity decay was not observed. Lorentz–polarization, but not absorption, corrections were made. The Pd atom was found from Patterson synthesis, while the remaining non-hydrogen atoms were determined from a subsequent Fourier synthesis. The structure was refined as above.[26] The function minimized was $\sum w||F_o| - |F_c||^2$, where $w = (\sigma^2(F_o) + 0.0033|F_o|^2)^{-1}$, f, f', and f'' were taken from ref 27. Positions of hydrogen atoms were computed and refined with an overall isotropic temperature factor, following a riding model. The final R factor was 0.056 ($R_w = 0.060$) for all observed reflections (max shift/esd = −0.05 in y of C(13); max and min peaks in final difference synthesis 0.4 and −0.3 e Å^{-3}, respectively).

Acknowledgment. We thank the DGICYT (PB 86-575) for financial support.

Registry No. **1a**, 126190-76-9; **1b**, 126190-77-0; **1c**, 126190-78-1; **1d**, 126190-79-2; **1e**, 126190-80-5; **1f**, 126190-81-6; **2a**, 126190-82-7; **2b**, 95029-14-4; **3a**, 126190-96-3; **3b**, 115203-64-0; **5c**, 126190-83-8; **5d**, 126190-84-9; **5f**, 126190-85-0; **6a**, 126190-86-1; **6b**, 115226-45-4; **6c**, 126190-87-2; **6d**, 126216-21-5; **6′e**, 126216-22-6; **6f**, 126190-88-3; **6′f**, 126216-23-7; **7b**, 126190-89-4; **7c**, 126190-90-7; **8c**, 126190-91-8; **8d**, 126190-92-9; **8f**, 126216-24-8; **9a**, 126216-25-9; **9b**, 126253-79-0; **9c**, 126190-93-0; **9d**, 126190-94-1; **9f**, 126190-95-2; Pd(OAc)$_2$, 3375-31-3.

Supplementary Material Available: Tables of elemental analyses, IR data, melting points, and anisotropic thermal parameters for **6f** and **9c** (3 pages); tables of observed and calculated structure factors for **6f** and **9c** (23 pages). Ordering information is given on any current masthead page.

---

[24] Bigelow, L. A.; Eatough, H. *Org. Synth.*: Blatt, A. H. Ed.; Wiley: New York, 1944; Vol. 1, p 80.

[25] Main, P.; Fiske, S. E.; Hull, S. L.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. MULTAN 1984, system of computer programs for crystal structure determination from X-ray diffraction data, University of York and University of Louvain.

[26] Sheldrick, G. M. SHELX, computer program for crystal structure determination, University of Cambridge, 1976.

[27] *International Tables of X-ray Crystallography*, Kynoch: Birmingham, England, 1974; Vol IV, pp 99–100 and 149.