Divergent Behavior in the Cyclopalladation of Phosphorus Ylides and Iminophosphoranes

David Aguilar, Miguel Angel Aragüés, Raquel Bielsa, Elena Serrano, Rafael Navarro, and Esteban P. Urriolabeitia*

Departamento de Compuestos Organometálicos, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

Received March 26, 2007

The cyclopalladation of the stabilized iminophosphoranes $Ph_3P{=}NC(O)C_6H_4R$ (R = H **1a**, 4-OMe **1b**, 3-OMe **1c**, 2-Me **1d**, 3-Me **1e**) results in the regioselective activation of the ortho CH bond of the benzamide ring, giving *exo*-[Pd(μ-Cl){*C,N*-C_6H_3(R){C(O)N=PPh_3-2}}]$_2$ (R = H **2a**, 5-OMe **2b**, 4-OMe **2c**, 3-Me **2d**, 4-Me **2e**). The palladated ligand behaves as a strong C,N-chelating group and cannot be easily displaced by other chelating ligands. This is clear from the reaction of **2c** with Tl(acac), py, or $AgClO_4$/L∧L, which gives [Pd(acac){*C,N*-C_6H_3(MeO-4){C(O)N=PPh_3-2}}] (**3c**), [PdCl{*C,N*-C_6H_3(MeO-4){C(O)N=PPh_3-2}}(py)] (**4c**), or [Pd{*C,N*-C_6H_3(MeO-4){C(O)N=PPh_3-2}}(L∧L)]ClO_4 (L∧L = dppe **5c**, bipy **6c**, phen **7c**). However, $Pd(OAc)_2$ reacts with the ylides $Ph_3P{=}CHC(O)C_6H_4R$ (R = H **8a**, 3-OMe **8b**, 2,5-$(OMe)_2$ **8c**) to give the C,C-orthometalated complexes [Pd(μ-Cl){*C,C*-[C_6H_4(PPh_2CHC(O)C_6H_4R)-2]}] (R = H **9a**, 3-OMe **9b**, 2,5-$(OMe)_2$ **9c**), which are also regioselectively obtained. The C,C-metalated chelate is very stable, as shown by the reactions of **9b** with Tl(acac), PPh_3, and $AgClO_4$/L∧L. The X-ray structures of **2d** and **9b** have been determined. Unexpectedly, the reaction of $Pd(OAc)_2$ with the ylide [$Ph_3P{=}CHC(O)C_6H_3$-2,4-$(OMe)_2$] (**16**) gives the polymer [(μ-Cl)Pd{C_6H_4(PPh_2*C*H−C(*O*)-C_6H_2-3,5-$(OMe)_2$)-2}-κ-C,C,C,O)Pd(μ-Cl)]$_n$ (**17**) as a result of a double palladation, giving two types of metalacycles: in one of them, the Pd atom is bonded to the ylidic Cα atom and has activated an ortho C(Ph)−H bond of the PPh_3 group; in the other one, the Pd atom is bonded to the carbonyl oxygen and has activated an ortho C−H bond of the $C_6H_3(OMe)_2$ unit. This tetradentate ylide ligand is remarkably stable.

Introduction

The activation of C−H bonds in organic compounds promoted by transition metals is one of the most important research topics nowadays.[1] This is because this process is a mandatory key step in their functionalization,[2] and its relevance is emphasized in the functionalization of hydrocarbons.[2f,i] Due to the almost ubiquitous nature of the C−H bond, it is usual to find two or more C−H bonds in the same compound, able to be activated. These bonds can be of the same or of different nature (for instance, alkyl Csp^3−H versus aryl Csp^2−H), and these differences could determine the orientation of the metalation. For example, it is well established that C_{aryl}−H bond activations are more easily promoted than those of C_{alkyl}−H bonds, even though C_{aryl}−H bonds (about 110 kcal/mol) are stronger than C_{alkyl}−H bonds (about 100 kcal/mol).[3] When several C−H bonds of the same nature are present on a molecule (for instance, aryl rings), the metalation can be easily directed to a given position by introduction of ancillary coordinating groups. In these cases, the metalation is produced at the ortho position with respect to the ancillary group,[4] and the compounds thus obtained are known as orthometalated derivatives.[1j] The functionalization of such substrates, promoted by transition metals, is quite selective, and the usefulness of the orthometalation reaction in metal-mediated organic synthesis is well recognized.[2a,b,g,5] However, even in the presence of directing groups, some substrates show quasi-equivalent metalation

* Corresponding author. Fax: (+34) 976761187. E-mail: esteban@unizar.es.

(1) Recent reviews: (a) Shilov, A. E.; Shul'pin, G. B. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*; Kluwer Academic Publishers: Dordretch, Germany, 2000. (b) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2437. (c) Doye, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 3351. (d) Slugovc, C.; Padilla-Martínez, I.; Sirol, S.; Carmona, E. *Coord. Chem. Rev.* **2001**, *213*, 129. (e) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (f) Jones, W. D. *Acc. Chem. Res.* **2003**, *36*, 140. (g) Periana, R. A.; Mironov, O.; Taube, D.; Bhalla, G.; Jones, C. J. *Science* **2003**, *301*, 814. (h) Fekl, U.; Goldberg, K. I. *Adv. Inorg. Chem.* **2003**, *54*, 259. (i) Crabtree, R. H. *J. Organomet. Chem.* **2004**, *689*, 4083. (j) Omae, I. *Coord. Chem. Rev.* **2004**, *248*, 995. (k) Goldberg, K. I., Goldman, A. S., Eds. In *Organometallic C-H Bond Activation*; *Activation and Functionalization of C-H Bonds*; ACS Symposium Series 885; American Chemical Society: Washington, DC, 2004. (l) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 351. (m) Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471. (n) Carmona, E.; Paneque, M.; Santos, L. L.; Salazar, V. *Coord. Chem. Rev.* **2005**, *249*, 1729.

(2) Recent reviews: (a) Dupont, J.; Pfeffer, M.; Spencer, J. *Eur. J. Inorg. Chem.* **2001**, 1917. (b) Rietling, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731. (c) Kakiuchi, F.; Chatani, N. *Adv. Synth. Catal.* **2003**, *345*, 1077. (d) Bedford, R. B. *Chem. Commun.* **2003**, 1787. (e) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (f) Periana, R. A.; Bhalla, G.; Tenn, W. J., III; Young, K. J. H.; Liu, X. Y.; Mironov, O.; Jones, C. J.; Ziatdinov, V. R. *J. Mol. Catal. A: Chem.* **2004**, *220*, 7. (g) Dupont, J.; Consorti, C.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527. (h) Park, Y. J.; Jun, C. H. *Bull. Korean Chem. Soc.* **2005**, *26*, 871. (i) Jones, W. D. *Inorg. Chem.* **2005**, *44*, 4475. (j) Hashmi, A. S. K.; Salathé, R.; Frost, T. M.; Schwarz, L.; Choi, J. H. *Appl. Catal. A: Gen.* **2005**, *291*, 238. (k) De Vos, D. E.; Sels, B. F. *Angew. Chem., Int. Ed.* **2005**, *44*, 30. (l) Godula, K.; Sames, D. *Science* **2006**, *312*, 67.

(3) (a) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91. (b) Castelhano, A. L.; Griller, D. *J. Am. Chem. Soc.* **1982**, *104*, 3655. (c) Tian, Z.; Fattahi, A.; Lis, L.; Kass, S. R. *J. Am. Chem. Soc.* **2006**, *128*, 17087.

(4) (a) Clegg, W.; Dale, S. H.; Hevia, E.; Honeyman, G. W.; Mulvey, R. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 2370. (b) Clegg, W.; Dale, S. H.; Harrington, R. W.; Hevia, E.; Honeyman, G. W.; Mulvey, R. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 2374.

10.1021/om7002877 CCC: $37.00
Publication on Web 06/01/2007

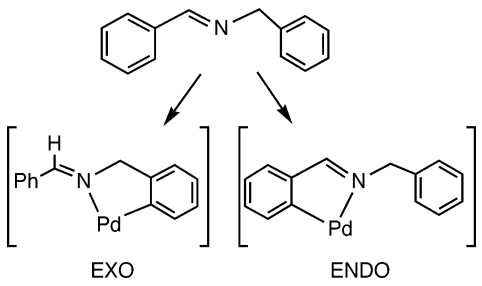


Figure 1. Possible cyclopalladation positions on benzylidene−benzylamines.

positions. A typical case is the palladation of benzylidene−benzylamines [$C_6H_5C(H)$═$NCH_2C_6H_5$]. These substrates usually form *endo* metallacycles—that is, the C═N double bond is *endocyclic*—while the *exo* metalation is obtained only if the *endo* is strongly disfavored for steric or electronic reasons.[6] This fact limits further reactivity of the starting substrate since only *endo* functionalization could be obtained (Figure 1).

Following our current research work on C−H bond activations on phosphorus ylides[7] and iminophosphoranes,[8] we have studied the metalation of two closely related types of compounds: the stabilized iminophosphoranes [Ph_3P═$NC(O)$-$C_6H_{5-n}R_n$] and the stabilized phenacyl ylides [Ph_3P═$CHC(O)$-$C_6H_{5-n}R_n$]. The metalation of phosphorus ylides is a known process,[7,9] and in all cases the Ph−P ring is activated, giving—not strictly speaking—*endo* complexes. However, the metalation of the phenacyl ylide [Ph_3P═$CHC(O)Ph$] promoted by Pd^{II} complexes has not been fully characterized, and that induced by Pt^{II} complexes[10] still presents some ambiguities about the *endo*/*exo* character of the metalation. On the other hand, the metalation of iminophosphoranes is still scarcely represented,[11] in spite of notable recent contributions, all examples sharing in common that the metalation gives *endo* derivatives. In this context, the only *exo* derivative has been obtained through an oxidative addition process.[11m] Thus, it seems that there is a clear preference for the *endo* metalation. The present work aims to shed light on and to obtain additional information about the factors governing the preference of such *endo* cyclopalladation in the afore-mentioned derivatives.

Results and Discussion

1. Synthesis of Iminophosphorane Complexes. The iminophosphoranes [Ph_3P═$N-C(O)-C_6H_4R_n$] (R_n = H **1a**, 4-OMe **1b**, 3-OMe **1c**, 2-Me **1d**, 3-Me **1e**, 4-NO_2 **1f**) have been prepared as air-stable solids following reported methods,[12] by reaction of the corresponding benzamide $H_2NC(O)C_6H_4R_n$ with PPh_3 and bis(^{t}Bu-azocarboxylate). The IR spectra of **1a**−**f** show a strong band in the range 1580−1620 cm^{-1}, due to the carbonyl stretch, and another strong absorption in the 1310−1340 cm^{-1} region, due to the P═N stretch. The absorption due to the carbonyl stretch clearly appears at lower energies than expected (around 1720 cm^{-1}), due to the conjugation of the C═O bond with the P═N bond. The delocalization of the density charge in the P−N−C−O bond system is responsible for the stability of these

(5) (a) Murai, S. Ed. *Topics in Organometallic Chemistry*, Vol. 3; Springer: New York, 1999. (b) Farina, V. *Adv. Synth. Catal.* **2004**, *346*, 1553. (c) Beletskaya, I. P.; Cheprakov, A. V. *J. Organomet. Chem.* **2004**, *689*, 4055. (d) Schlummer, B.; Scholz, U. *Adv. Synth. Catal.* **2004**, *346*, 1599. (e) Kalyani, D.; Deprez, N. R.; Desai, L. V.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 7330. (f) Zapf, A.; Beller, M. *Chem. Commun.* **2005**, 431. (g) Vicente, J.; Abad, J. A.; López-Sáez, M. J.; Jones, P. G. *Organometallics* **2006**, *25*, 1851. (h) Hull, K. L.; Lanni, E. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 14047. (i) Dick, A. R.; Sanford, M. S. *Tetrahedron* **2006**, *62*, 2439.

(6) (a) Keuseman, K. J.; Smoliakova, I. P.; Dunina, V. V. *Organometallics* **2005**, *24*, 4159. (b) Gorunova, O. N.; Keuseman, K. J.; Goebel, B. M.; Kataeva, N. A.; Churakov, A. V.; Kuz'mina, L. G.; Dunina, V. V.; Smoliakova, I. P. *J. Organomet. Chem.* **2004**, *689*, 2382. (c) Crespo, M.; Evangelio, E. *J. Organomet. Chem.* **2004**, *689*, 1956. (d) Albert, J.; Cadena, J. M.; González, A.; Granell, J.; Solans, X.; Font-Bardia, M. *Chem. Commun.* **2003**, 528. (e) Castro-Juiz, S.; López-Torres, M.; Fernández, A.; Mosteiro, R.; Suárez, A.; Vila, J. M.; Fernández, J. J. *Polyhedron* **2001**, *20*, 2925. (f) Albert, J.; Bosque, R.; Granell, J.; Tavera, R. *Polyhedron* **2001**, *20*, 3225.(g) Gómez, M.; Granell, J.; Martínez M. *Eur. J. Inorg. Chem.* **2000**, 217. (h) Gómez, M.; Granell, J.; Martínez, M. *J. Chem. Soc., Dalton Trans.* **1998**, 37. (i) Albert, J.; Granell, J.; Luque, A.; Font-Bardía, M.; Solans, X. *J. Organomet. Chem.* **1997**, *545*−*546*, 131. (j) Gómez, M.; Granell, J.; Martínez, M. *Organometallics* **1997**, *16*, 2539. (k) Albert, J.; Granell, J.; Moragas, R.; Font-Bardía, M.; Solans, X. *J. Organomet. Chem.* **1996**, *522*, 59. (l) Crespo, M.; Solans, X.; Font-Bardía, M. *J. Organomet. Chem.* **1996**, *518*, 105. (m) Crespo, M.; Solans, X.; Font-Bardía, M. *J. Organomet. Chem.* **1996**, *509*, 29. (n) Albert, J.; Granell, J.; Sales, J.; Font-Bardía, M.; Solans, X. *Organometallics* **1995**, *14*, 1393. (o) De Munno, G.; Ghedini, M.; Neve, F. *Inorg. Chim. Acta* **1995**, *239*, 155. (p) Barro, J.; Granell, J.; Sainz, D.; Sales, J.; Font-Bardía, M.; Solans, X. *J. Organomet. Chem.* **1993**, *456*, 147. (q) Navarro-Ranninger, C.; López-Solera, I.; Álvarez-Valdés, A.; Rodríguez-Ramos, J. H.; Masaguer, J. R.; García-Ruano, J. L. *Organometallics* **1993**, *12*, 4104. (r) Albert, J.; Ceder, R. M.; Gómez, M.; Granell, J.; Sales, J. *Organometallics* **1992**, *11*, 1536. (s) Albert, J.; Gómez, M.; Granell, J.; Sales, J.; Solans, X. *Organometallics* **1990**, *9*, 1405. (t) Albert, J.; Granell, J.; Sales, J.; Solans, X.; Font-Altaba, M. *Organometallics* **1986**, *5*, 2567.

(7) (a) Navarro, R.; Urriolabeitia, E. P. *J. Chem. Soc., Dalton Trans.* **1999**, 4111, and references therein. (b) Falvello, L. R.; Fernández, S.; Navarro, R.; Rueda, A.; Urriolabeitia, E. P. *Organometallics* **1998**, *17*, 5887. (c) Falvello, L. R.; Fernández, S.; Navarro, R.; Urriolabeitia, E. P. *Inorg. Chem.* **1999**, *38*, 2455. (d) Fernández, S.; Navarro, R.; Urriolabeitia, E. P. *J. Organomet. Chem.* **2000**, *602*, 151. (e) Larraz, C.; Navarro, R.; Urriolabeitia, E. P. *New J. Chem.* **2000**, *24*, 623. (f) Falvello, L. R.; Fernández, S.; Larraz, C.; Navarro, R.; Urriolabeitia, E. P. *Organometallics* **2001**, *20*, 1424. (g) Gracia, C.; Marco, G.; Navarro, R.; Romero, P.; Soler, T.; Urriolabeitia, E. P. *Organometallics* **2003**, *22*, 4910. (h) Serrano, E.; Vallés, C.; Carbó, J. J.; Lledós, A.; Soler, T.; Navarro, R.; Urriolabeitia, E. P. *Organometallics* **2006**, *25*, 4653.

(8) Bielsa, R.; Larrea, A.; Navarro, R.; Soler, T.; Urriolabeitia, E. P. *Eur. J. Inorg. Chem.* **2005**, 1724.

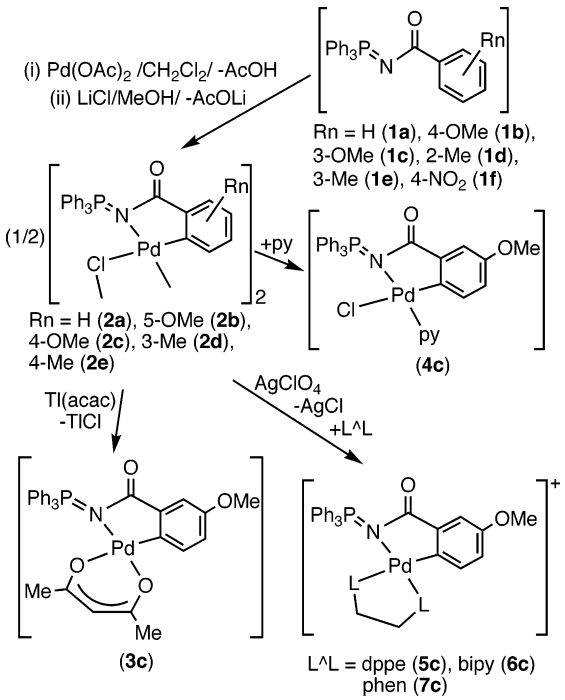
(9) (a) Rüba, E.; Mereiter, K.; Schmid, R.; Kirchner, K.; Bustelo, E.; Puerta, M. C.; Valerga, P. *Organometallics* **2002**, *21*, 2912. (b) O'Connor, J. M.; Bunker, K. D. *J. Organomet. Chem.* **2003**, *671*, 1. (c) Onitsuka, K.; Nishii, M.; Matsushima, Y.; Takahashi, S. *Organometallics* **2004**, *23*, 5630. (d) Petz, W.; Kutschera, C.; Neumüller, B. *Organometallics* **2005**, *24*, 5038. (e) Canac, Y.; Conejero, S.; Soleilhavoup, M.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2006**, *128*, 459. (f) Kawachi, A.; Yoshioka, T.; Yamamoto, Y. *Organometallics* **2006**, *25*, 2390. (g) Vicente, J.; Chicote, M. T.; Fernández-Baeza, J. *J. Organomet. Chem.* **1989**, *364*, 407. (h) Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G.; Bembenek, E. *Organometallics* **1994**, *13*, 1243. (i) Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G. *Inorg. Chem.* **1995**, *34*, 5441.

(10) Teagle, J. A.; Burmeister, J. L. *Inorg. Chim. Acta* **1986**, *118*, 65.

(11) (a) Stuckwish, C. G. *J. Org. Chem.* **1976**, *41*, 1173. (b) Alper, H. *J. Organomet. Chem.* **1977**, *127*, 385. (c) Nusshär, D.; Weller, F.; Dehnicke, K. Z. *Anorg. Allg. Chem.* **1993**, *619*, 1121. (d) Steiner, A.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1752. (e) Avis, M. W.; Vrieze, K.; Ernsting, J. M.; Elsevier, C. J.; Veldman, N.; Spek, A. L.; Katti, K. V.; Barnes, C. L. *Organometallics* **1996**, *15*, 2376. (f) Avis, M. W.; van der Boom, M. E.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L. *J. Organomet. Chem.* **1997**, *527*, 263. (g) Wingerter, S.; Gornitzka, H.; Bertrand, G.; Stalke, D. *Eur. J. Inorg. Chem.* **1999**, 173. (h) Lesson, M. A.; Nicholson, B. K.; Olsen, M. R. *J. Organomet. Chem.* **1999**, *579*, 243. (i) Wingerter, S.; Gornitzka, H.; Bertermann, R.; Pandey, S. K.; Rocha, J.; Stalke, D. *Organometallics* **2000**, *19*, 3890. (j) Wingerter, S.; Pfeiffer, M.; Stey, T.; Bolboaca, M.; Kiefer, W.; Chandrasekhar, V.; Stalke, D. *Organometallics* **2001**, *20*, 2730. (k) Jones, N. D.; Lin, G.; Gossage, R. A.; McDonald, R.; Cavell, R. G. *Organometallics* **2003**, *22*, 2832. (l) Wei, P.; Chan, K. T. K.; Stephan, D. W. *Dalton Trans.* **2003**, 3804. (m) Vicente, J.; Abad, J. A.; Clemente, R.; López-Serrano, J.; Ramírez de Arellano, M. C.; Jones, P. G.; Bautista, D. *Organometallics* **2003**, *22*, 4248. (n) Chan, K. T. K.; Spencer, L. P.; Masuda, J. D.; McCahill, J. S. J.; Wei, P.; Stephan, D. W. *Organometallics* **2004**, *23*, 381. (o) Cadierno, V.; Díez, J.; García-Álvarez, J.; Gimeno, J. *Organometallics* **2005**, *24*, 2801. (p) Wang, Z. X.; Qi, C. Y. *Dalton Trans.* **2005**, 996. (q) Fang, M.; Jones, N. D.; Ferguson, M. J.; McDonald, R.; Cavell, R. G. *Angew. Chem., Int. Ed.* **2005**, *44*, 2005. (r) Boubekeur, L.; Ricard, L.; Mézailles, N.; Demange, M.; Auffrant, A.; Le Floch, P. *Organometallics* **2006**, *25*, 3091.

(12) Bittner, S.; Assaf, Y.; Krief, P.; Pomerantz, M.; Ziemnicka, B. T.; Smith, C. G. *J. Org. Chem.* **1985**, *50*, 1712.

Scheme 1. Synthesis and Reactivity of Orthopalladated Iminophosphoranes



compounds and can also be inferred from the ^{31}P NMR spectra. These spectra show a single peak at about 19−22 ppm, a position shifted to low field with respect to that observed in other nonstabilized systems (about 0−6 ppm) and showing the lower shielding of the P atom in the stabilized compounds due to delocalization. These results are similar to those observed in other stabilized systems.[12−14]

The reactivity of **1a**−**f** toward $Pd(OAc)_2$ (OAc = acetate) has been investigated. Thus, the treatment of $Pd(OAc)_2$ with **1a**−**e** (1:1 molar ratio, Scheme 1) in refluxing CH_2Cl_2 and further reaction of the acetate intermediate with excess LiCl in methanol gives the cyclopalladated complexes **2a**−**e**. Surprisingly, the metalation has been produced at the ortho C−H bond of the benzamide group, giving the *exo* derivative, instead of the expected *endo* metalation at the P−Ph groups.[8,11b,m] The reaction proceeds with yields ranging from low to excellent, and no *endo* isomers have been detected, showing that the process can be considered to be regioselective. In the presence of substituents at the meta position (**1c**, **1e**) two different CH bonds can be activated, but only the less hindered isomer is obtained; that is, the metalation is produced selectively at the 6 position on the starting material. The metalation of **1d** also gives a single isomer showing that the palladation of a C_{aryl}−H bond forming a five-membered metallacycle is really more favorable than the palladation of a C_{alkyl}−H bond forming a six-membered ring, as expected. Only when the benzamide ring is strongly deactivated by the presence of the nitro group (**1f**) does the reaction not proceed, and no metalation has been observed in the studied conditions.

The characterization of **2a**−**e** has been carried out on the basis of their spectroscopic parameters. The N-bonding of the iminophosphorane can be inferred from their IR spectra, due to the simultaneous observation of an increase in the position of the carbonyl stretch (regions from 1580−1620 to 1640−1650 cm^{-1}) and a decrease in that of the P═N stretch (regions from 1310−1340 to 1280−1310 cm^{-1}). The low-frequency shift of the P═N stretch reflects unambiguously the coordination of the N atom through the lone pair, while the high-frequency shift of the carbonyl stretch is related to the loss of conjugation of the C═O and the P═N bonds.[14] The NMR spectra of **2a**−**e** show that the C−H bond activation and the subsequent metalation have occurred at the benzamide ring. For instance, the ^{1}H NMR spectrum of **2a** shows three signals due to the PPh_3 protons (7.3−8.0 ppm region; relative intensity 6:3:6) and another three signals (6.7−7.2 ppm region; relative intensity 1:1:2) due to the C_6H_4 group. Similar conclusions can be derived from the analysis of **2b**−**e** (see Experimental Section and SI). On the other hand, the $^{13}C\{^1H\}$ NMR spectra show, in addition to the signals due to the Ph_3P═NC(O) unit, six different peaks in the aromatic region due to the metalated aryl fragment. Among them, the metalated carbon atom C_1 appears in the 139−146 ppm region. Finally, the $^{31}P\{^1H\}$ NMR spectra show, in all studied cases, a single peak in the range 29.0−32.0 ppm. This implies a moderate downfield shift after metalation, and this fact is consistent with the N-bonding of the iminophosphorane. Moreover, the position of this peak also suggests that the *endo* metalation has not occurred, since in that case an even stronger downfield shift must be expected, the ^{31}P peak appearing at about 50 ppm.[8,11m]

It is quite remarkable the regioselective *exo* palladation of the benzamide ring, instead of the, in principle, more stable *endo* metalation. One of the main arguments to explain why the *endo* metalation is more favored than the *exo* is based on electronic factors, more explicitly the metalloaromaticity.[15] This phenomenon, which can be defined such as the presence of a partial aromatic character in metallacycles, could be originated in *endo* compounds due to the presence in the palladacycle of two conjugated double bonds, the C═C double bond of the metalated aryl and the iminic P═N bond, and the appropriate filled d orbitals of the Pd atom.[15] Obviously, this conjugation cannot be established in the *exo* derivatives. The presence of a certain degree of aromaticity is accompanied by a resonance energy stabilization, and the *endo* complexes become energetically more favorable than the *exo*.[6q] It is clear that the metalation of **1a**−**e** to give stable *exo* **2a**−**e** must be driven by additional factors that counterbalance this stabilization by delocalization.

A plausible explanation can be given assuming that the mechanism of palladation occurs through electrophilic substitution at the aromatic ring.[16] If the metalation occurs at the benzamide ring, in a solvent such as CH_2Cl_2, this means that this ring is more electron-rich than those of the P−Ph groups. Why? We can consider the resonant forms shown in Figure 2: one of them is neutral and the other two are zwitterionic. In a polar solvent (CH_2Cl_2) the two zwitterionic forms are favored, meaning that the phosphorus atom is supporting a high positive formal charge (near +1) and that the phenyl rings at this P atom should be strongly deactivated. In addition, and due to the delocalization, the formal negative charge is shifted to the N−C−O fragment, and this accumulation of negative charge produces a, comparatively, more electron-rich benzamide ring. The amide substituent (usually a strong deactivating group) is thus operating as an activating group and drives the metalation to the benzamide ring. The deactivating nature of the amide group and relative low affinity of aryl amides to be metalated

(13) Falvello, L. R.; Fernández, S.; García, M. M.; Navarro, R.; Urriolabeitia, E. P. *J. Chem. Soc., Dalton Trans.* **1998**, 3745.
(14) Falvello, L. R.; García, M. M.; Lázaro, I.; Navarro, R.; Urriolabeitia, E. P. *New J. Chem.* **1999**, *23*, 227.
(15) Ghedini, M.; Aiello, I.; Crispini, A.; Golemme, A.; La Deda, M.; Pucci, D. *Coord. Chem. Rev.* **2006**, *250*, 1373, and references therein.
(16) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.

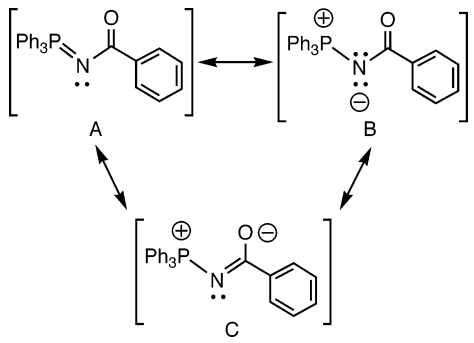


Figure 2. Resonant forms of the keto-stabilized iminophosphoranes.

can be inferred from a careful inspection of the reported structures at the Cambridge Crystallographic Database.[17] From 633 structures found at the CCDC including a five-membered metallacycle Pd−N−C−C_{aryl}, only nine (1.4%) contain an amide group Pd−N−C(O)−C_{aryl}. This fact is clearly related with the deactivating nature of the amide group and makes the *exo* metalation presented here more relevant.

Additional arguments in favor of the charge separation and the localization of a formal negative charge over the nitrogen as important factors in the metalation of the amide ring can be obtained from the following observations. First, the metalation of pyridinium ylides and betaines derived from benzamide has been reported,[18] and the C−H bond activation has been produced at the benzamide ring. This reaction seems to be general, and the reactants show a similar charge separation to our iminophosphoranes. On the other hand, the metalation of benzamide derivatives has been reported,[19] and all described complexes share a common feature: the C,N-benzamidate ligand acts as a dianion, one negative charge centered at the metalated carbon and the other one at the nitrogen (amide) atom. Very few reports show an orthometalated benzamide ring as a monoanionic ligand. Curiously, in those cases the ligand is coordinated as a C,O-chelate instead of as a C,N-chelate.[20]

The reactivity of the dinuclear derivatives **2** has been studied (Scheme 1). All results show that the C,N-orthopalladated iminophosphoranes behave as strong chelating ligands, as do other classical C,N derivatives. Complex **2c** reacts with Tlacac (1:2 molar ratio) to give [Pd(acac){*C*,*N*-C_6H_3(MeO-4){C(O)N═PPh_3-2}}] (**3c**), with an excess of py to give [PdCl{*C*,*N*-C_6H_3(MeO-4){C(O)N═PPh_3-2}}(py)] (**4c**), and with $AgClO_4$ and chelating ligands (1:2:2 molar ratio) to give [Pd{*C*,*N*-C_6H_3(MeO-4){C(O)N═PPh_3-2}}(L∧L)]ClO_4 (L∧L = dppe **5c**, bipy **6c**, phen **7c**). The IR spectrum of **3c** shows the typical absorptions of the chelating acac ligand (1582, 1513 cm^{-1}), and the ^1H and $^{31}P\{^1H\}$ NMR spectra show clearly that the *exo*-palladated iminophosphorane ligand remains unaffected. The cleavage of the dinuclear μ-Cl complex **2c** with neutral L ligands could give two geometric isomers, L trans N or L trans C,[8] although usually only one isomer is observed (L trans N).[21] The reaction of **2c** with excess py (1:4 molar ratio) gives **4c** as a single isomer. When stoichiometric amounts of py are used, a mixture of **2c** and **4c** is obtained, showing that the palladated group is not displaced by an excess of incoming L ligand. The pyridine ligand is bonded trans to the iminic N atom, as expected.[21] This fact is observed in the ^1H NMR spectrum, since the chemical shift of the H_6 proton in the metalated ring of **4c** has been high-field shifted, with respect to its position in **2c**, due the anisotropic shielding of the cis-bonded pyridine ligand.[21] The characterization of **5c**−**7c** lies in the following key features. The $^{31}P\{^1H\}$ NMR spectrum of **5c** shows three different signals, corresponding to the three P atoms of the molecule. One of the peaks (21.09 ppm) shows the presence of the *exo*-metalated ligand, while the other two (39.96 and 61.90 ppm) are typical of chelating dppe. The $^{31}P\{^1H\}$ NMR spectra of **6c** and **7c** show a single peak in each case (22.98 and 22.91 ppm), whose chemical shifts show the maintenance of the *exo* metalation. The ^1H NMR spectra of **6c** and **7c** show, in addition to ligand peaks, eight different signals due to the phen or bipy ligands, meaning that these groups are N,N-bonded.

In conclusion, the palladation of iminophosphoranes Ph_3P═NC(O)Aryl is regioselective and gives five-membered *exo* metallacycles. This type of metalation is quite unusual. In addition, the resulting palladacycles show a high stability, as it can be inferred from their reactivity toward different ligands.

2. Synthesis of Ylide Complexes. The metalation of ylides $Ph_3ZCHC(O)Ph$ (Z = P, As) and $Bu_3PCHC(O)Ph$ using Pd(II) and Pt(II) complexes was described some years ago.[10,18] The ylide $Bu_3PCHC(O)Ph$ reacts with Pd(II) substrates at the benzoyl group, while $Ph_3AsCHC(O)Ph$ does not metalate at all. The results obtained with Pt complexes and the ylide $Ph_3PCHC(O)Ph$ were not conclusive about the position of platination (*back-door* versus *front-door*).[10] The palladation of $Ph_3PCHC(O)Ph$ has been reported in a previous work,[18a] and it was characterized as [Pd(μ-Cl){*C*,*C*-C_6H_4(C(O)CHPPh_3-2}]$_2$, that is, metalated at the benzoyl ring, but very few conclusive structural data were given.

The similarity between phosphoylides and iminophosphoranes,[22] the results described in the preceding section, and the fact that the hypothetical palladation/platination of $Ph_3PCHC(O)Ph$ have been poorly characterized[18a] have prompted us to study the competitive metalation of different phenacyl P-ylides, aiming to determine the similitude or complementarity of the reactivity patterns. In addition, the study of the activation of C−H bonds on P-ylides is still an active research area.[23]

The ylides Ph_3P═CHC(O)Aryl (Aryl = Ph **8a**, 3-$MeOC_6H_4$ **8b**, 2,5-$(MeO)_2C_6H_3$ **8c**) were prepared following the method reported by Ramirez et al.[24] in two steps. The reaction of the corresponding phenacyl bromide with PPh_3 gives the phospho-

(17) Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380.

(18) (a) Dias, S. A.; Downs, A. W.; McWhinnie, W. R. *J. Chem. Soc., Dalton Trans.* **1975**, 162. (b) Dias, S. A.; Downs, A. W.; McWhinnie, W. R. *Inorg. Chem. Nucl. Lett.* **1974**, *10*, 233. (c) Chia, L. Y.; Dias, S. A.; McWhinnie, W. R. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1263.

(19) (a) Hedden, D.; Roundhill, D. M.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 5014. (b) Hedden, D.; Roundhill, D. M.; Fultz, W. C.; Rheingold, A. L. *Organometallics* **1986**, *5*, 336. (c) Palenik, G. J.; Giordano, T. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1175. (d) Failes, T. W. Hall, M. D.; Hambley, T. W. *Dalton Trans.* **2003**, 1596. (e) Hursthouse, M. B.; Mazid, M. A.; Robinson, S. D.; Sahajpal, A. *Chem. Commun.* **1991**, 1146. (f) Hursthouse, M. B.; Mazid, M. A.; Robinson, S. D.; Sahajpal, A. *J. Chem. Soc., Dalton Trans.* **1993**, 2835. (g) Das, A.; Basuli, F.; Falvello, L. R.; Bhattacharya, S. *Inorg. Chem.* **2001**, *40*, 4085. (h) Bacchi, A.; Carcelli, M.; Costa, M.; Pelagatti, P.; Pelizzi, C.; Pelizzi, G. *J. Chem. Soc., Dalton Trans.* **1996**, 4239.

(20) (a) Vicente, J.; Abad, J. A.; Shaw, K. F.; Gil-Rubio, J.; Ramírez de Arellano, M. C. *Organometallics* **1997**, *16*, 4557. (b) Kametani, Y.; Satoh, T.; Miura, M.; Nomura, M. *Tetrahedron Lett.* **2000**, *41*, 2655. (c) Shabashov, D.; Daugulis, O. *Org. Lett.* **2006**, *8*, 4947.

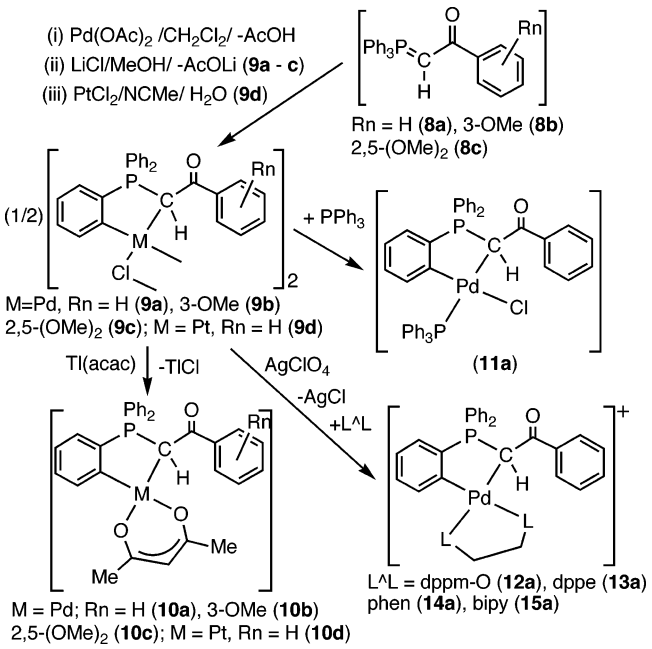
(21) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; New, L. *J. Chem. Soc., Dalton Trans.* **1978**, 1940.

(22) Johnson, A. W.; Kaska, W. C.; Starzewski, K. A. O.; Dixon, D. A. *Ylides and Imines of Phosphorus*; John Wiley and Sons: New York, 1993.

(23) Selected recent references: (a) Onitsuka, K.; Nishii, M.; Matsushima, Y.; Takahashi, S. *Organometallics* **2004**, *23*, 5630. (b) Kubo, K.; Jones, N. D.; Ferguson, M. J.; McDonald, R.; Cavell, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 5314. (c) Petz, W.; Kutschera, C.; Neumüller, B. *Organometallics* **2005**, *24*, 5038. (d) Kawachi, A.; Yoshioka, T.; Yamamoto, Y. *Organometallics* **2006**, *25*, 2390. (e) Vignolle, J.; Donnadieu, B.; Bourissou, D.; Soleilhavoup, M.; Bertrand, G. *J. Am. Chem. Soc.* **2006**, *128*, 14810.

(24) Ramírez, F.; Dershowitz, S. *J. Org. Chem.* **1957**, *22*, 41.

Scheme 2. Synthesis and Reactivity of Orthopalladated Phenacyl P-Ylides



nium salt, which reacts with a weak base in $MeOH/H_2O$, allowing the isolation of ylides **8a**−**c** as compounds stable to air and moisture. The characterization of **8b** and **8c** follows the expected patterns: (i) the carbonyl stretch appears in the IR spectra around 1510 cm^{-1}; (ii) the methine proton appears in the ^1H NMR spectra as a doublet with a large $^2J_{PH}$ coupling constant (around 25 Hz); (iii) the $^{31}P\{^1H\}$ NMR spectra show a single peak in each case at about 15 ppm. All these facts are typical for carbonyl-stabilized ylides.[7a] Ylides **8a**−**c** react with $Pd(OAc)_2$ (1:1 molar ratio) in CH_2Cl_2, and further treatment of the acetate intermediate with excess LiCl in methanol gives the palladated complexes **9a**−**c** (see Scheme 2). It is interesting to note that no decomposition is observed during the first stages of the reaction, giving **9a**−**c** in high yields.

The IR spectra of **9a**−**c** show a strong absorption in the range 1614−1629 cm^{-1}, which has been shifted to higher frequency with respect to the starting ylides **8a**−**c** (range 1504−1525 cm^{-1}), meaning that the ylides are C-bonded to the palladium center.[7a] The $^{31}P\{^1H\}$ NMR spectra of **9a**−**c** show two singlet resonances in each case (range 17−22 ppm), which are shifted to low field with respect to the parent ylides **8a**−**c** (range 15−17 ppm), in good agreement with the C-bonding of the ylides. The presence of two lines of different intensity on each spectrum can be originated from the presence of two diastereoisomers (*RR/SS* and *RS/SR*), as a result of the C-bonding of the ylide and the dinuclear nature of **9a**−**c**. The metalation of a phenyl group of the PPh_3 unit is evident from the ^1H NMR spectra of **9a**−**c**, since the resonances assigned to the protons of the CC(O)Ph fragment can still be observed, while the expected 6:3:6 pattern of the H_o:H_p:H_m protons of the PPh_3 group has disappeared. A new pattern of signals of intensity 1:1:1:1:4:2:4 is observed, partially overlapped due to the presence of the two diastereoisomers.

The full characterization of the [Pd{*C*,*C*-C_6H_4($PPh_2CHC(O)$-Ph)-2}] moiety has been carried out on the corresponding *O*,*O*′-acetylacetonate derivatives **10a**−**c**, obtained by reaction of **9a**−**c** with the stoichiometric amount of Tl(acac) (Scheme 2). The ^1H NMR spectra of **10a**−**c** show, in addition to the expected peaks assigned to the acac ligand or the methoxy groups, well-defined signals attributed to the PdC_6H_4, $C(O)C_6H_mR_n$, and PPh_2 protons. The same features have been observed in the $^{13}C\{^1H\}$ NMR spectra, where six different resonances are attributed to the carbon atoms of the PdC_6H_4 group. All these facts are in very good agreement with the structures depicted in Scheme 2, in which the metalated unit is, unambiguously, the PPh_3 fragment.

These results are in clear contrast with those reported previously,[18a] in which it was stated that the palladation of $Ph_3P{=}CHC(O)Ph$ gives the dinuclear orthometalated [Pd(μ-Cl)-{*C*,*C*-$C_6H_4(C(O)CHPPh_3)$-2}]$_2$. Since our reaction conditions [$Pd(OAc)_2$, ylide, CH_2Cl_2, reflux] were quite different from those described in the original contribution [$PdCl_2$, NaOAc, ylide, MeOH, reflux], we have carried out an experiment in the original conditions. After extraction of the solid insoluble in MeOH, the $^{31}P\{^1H\}$ NMR spectrum of the extract shows peaks corresponding to free ylide (15.92 ppm), $O{=}PPh_3$ (29.79 ppm), and **9a** (17.76 and 19.55 ppm, see SI) in a 1.2:0.17:2.98 molar ratio. Thus, in our hands, the material described originally by McWhinnie et al. was actually the product of metalation at the PPh_3 unit (**9a**).

We have also reinvestigated the platination of the stabilized ylide [$Ph_3P{=}CHC(O)Ph$], in order to ascertain the true nature of the resulting product and the actual position of metalation.[10] However, when the experiment was performed following the original conditions [$PtCl_2$, ylide, 1:3 molar ratio, NCMe, reflux, 3 h], the starting ylide was recovered and the decomposition of the platinum salt was clearly observed. A slight modification of the original method gives improved results. Thus, when a mixture of $PtCl_2$ and the ylide (1:1 molar ratio) was refluxed in NCMe for 24 h, complex **9d** (see Scheme 2) could be isolated in pure form after exhaustive washing of the crude reaction product to eliminate phosphonium salt. The presence of the cycloplatinated ligand [Pt{*C*,*C*-$C_6H_4(PPh_2CHC(O)Ph)$-2}] is unambiguously stated in the ^1H NMR spectrum of the acetylacetonate **10d**, obtained from reaction of **9d** with Tlacac (1:2 molar ratio). There, the observed pattern of resonances of **9d** is very similar to that described for **9a** and shows three different peaks due to the C(O)Ph protons, four different peaks assigned to the PtC_6H_4 unit, and the expected signals for the PPh_2 group.

Thus, although the reaction conditions are not strictly the same as those reported previously, in our hands the platination of the ylide $Ph_3P{=}CHC(O)Ph$ is produced at the PPh_3 group, as for the analogous palladium derivatives. It seems that the metalation of the ylides is also a general reaction, but with the opposite regioselectivity of that found for the stabilized iminophosphoranes.

Further reactivity of complexes **9a**−**c** shows the stability of the C,C-palladacycle. The reaction of **9a** with PPh_3 (1:2 molar ratio) affords **11a**, while treatment of **9a** with $AgClO_4$ and chelating L∧L ligands (1:2:2 molar ratio) gives the mononuclear dicationic [Pd{*C*,*C*-$C_6H_4(PPh_2CHC(O)Ph)$-2}(L∧L)]ClO_4 complexes (L∧L = dppm-O **12a**, dppe **13a**, phen **14a**, bipy **15a**). In all cases the [$C_6H_4PPh_2CH$] unit remains C,C-bonded to the Pd atom, even if the reaction is performed in presence of an excess of ligand. Complex **11a** shows the PPh_3 ligand bonded trans to the ylidic C atom, in accord with the data obtained from the $^{31}P\{^1H\}$ NMR spectrum and their comparison with related arrangements.[7b] The characterization of complexes **13a** and **14a** is straightforward from their corresponding NMR spectra. Full assignment of the signals due to the phen, C(O)-C_6H_5, and Pd(C_6H_4) fragments was performed with the help of COSY, 1D-NOESY, and ROESY experiments. In addition, the $^{31}P\{^1H\}$ NMR spectrum of **12a** shows that the dppm ligand

Scheme 3. Unexpected Reactivity of Phosphorus Ylide 16

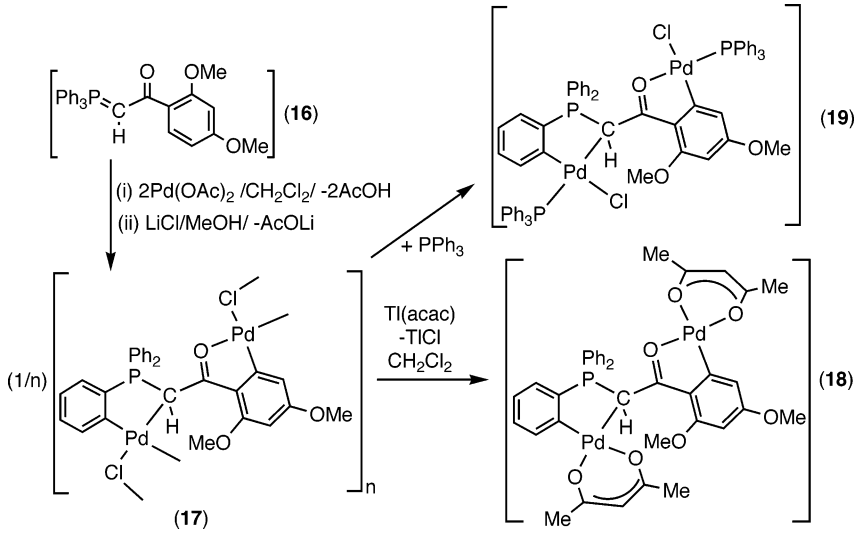


Table 1. Crystal Data and Structure Refinement for Compounds 2d and 9b·2CHCl$_3$

	2d	**9b**·2CHCl$_3$
empirical formula	$C_{52}H_{42}Cl_2N_2O_2P_2Pd_2$	$C_{56}H_{46}Cl_8O_4P_2Pd_2$
fw	1072.52	1341.27
temp (K)	100(2)	100(2)
radiation (λ, Å)	0.71073	0.71073
cryst syst	monoclinic	triclinic
space group	$P2(1)/c$	$P\bar{1}$
a (Å)	14.5611(4)	9.010(4)
b (Å)	9.8108(2)	9.1801(6)
c (Å)	16.4092(4)	17.024(4)
α (deg)		93.230(13)
β (deg)	108.644(3)	103.86(3)
γ (deg)		99.287(18)
V (Å^3)	2221.14(9)	1342.6(7)
Z	2	1
D_{calc} (Mg/m^3)	1.604	1.659
μ (mm^{-1})	1.047	1.174
cryst size (mm^3)	0.39 × 0.16 × 0.02	0.19 × 0.11 × 0.02
no. of reflns collected	16 269	8974
no. of indep reflns	4495 (R_{int} = 0.0425)	4332 (R_{int} = 0.0408)
no. of data/restraints/params	4495/0/281	4332/0/326
goodness-of-fit on F^2	0.931	0.960
final R indices [$I > 2\sigma(I)$]	R1 = 0.0277, wR2 = 0.0582	R1 = 0.0324, wR2 = 0.0479
R indices (all data)	R1 = 0.0486, wR2 = 0.0613	R1 = 0.0591, wR2 = 0.0503
largest diff peak, hole (e·Å^{-3})	0.744 and −0.606	0.578 and −0.604

has been mono-oxidized, since no signals are found at high field and since a resonance at 58.20 ppm clearly indicates the presence of the P(O)Ph$_2$ unit. This type of oxidation has already been reported,[7b,25] and a similar arrangement—the O atom trans to the palladated C atom—is also here proposed.

The metalation of the stabilized ylides **8a**−**c** has taken place at the phenyls of the PPh$_3$ unit, in spite of the presence of one or even two activating methoxy groups at the benzoyl ring. This fact has been unambiguously established through the spectroscopic characterization of derivatives **9a**−**15a** and through the X-ray structure determination of **9b** (see below). In additon, this result is in good agreement with those reported previously for direct palladation of P-ylides,[7,10] since in all reported cases the phenylic C−H bonds at the phosphonium group are easily activated. Following our previous reasoning, these results imply that, in these ylides, the phenyl rings at the PPh$_3$ fragment are more electron-rich than that at the benzoyl unit, assuming an electrophilic mechanism for the aromatic substitution, and show that the carbonyl group actually behaves as a strong deactivating group, even in the presence of two methoxy substituents. In complexes **9a**−**15a** the metalation can be considered, not strictly speaking, to be an *endo* metalation, since the P−Cα bond belongs to the palladacycle, and this seems to be the most represented arrangement. As far as we know, only one example of *exo*-cyclometalated ylide—the C═PR$_3$ double bond projecting out of the metallacycle—has been reported.[26] There, the formation of the ylide is produced by nucleophilic attack of PMe$_3$ at the C(alkylidene) of the transient nickelacyle [Ni(C$_6$H$_4$CMe$_2$-CH)Cl(PMe$_3$)]. Clearly, the formation of the ylide is produced after the metalation, then it cannot be properly considered as an example of direct ylide metalation.

However, it can be argued that the metalation at the benzoyl ring on compound **8c** is not very favored, since the 2 position is blocked by one OMe group and the 6 position is sterically hindered by the presence of the 5-OMe substituent. Due to these facts, we have prepared the less hindered ylide Ph$_3$P═CHC-

(25) Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127.

(26) (a) Beldarraín, T. R.; Nicasio, M. C.; Paneque, M.; Poveda, M. L.; Carmona, E. *Gazz. Chim. Ital.* **1994**, *124*, 341. (b) Carmona, E.; Gutiérrez-Puebla, E.; Monge, A.; Paneque, M.; Poveda, M. L. *J. Chem. Soc., Chem. Commun.* **1991**, 148.

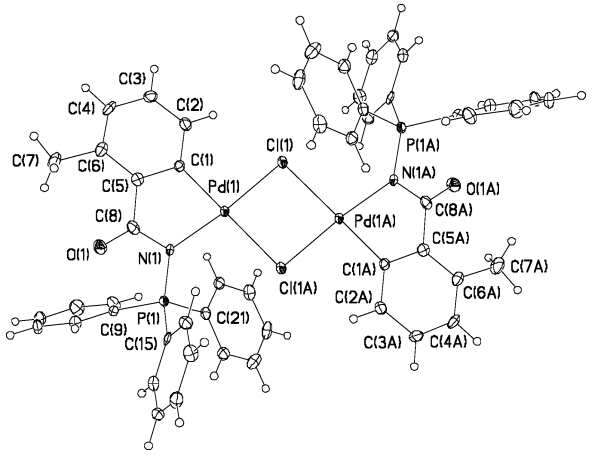


Figure 3. Thermal ellipsoid drawing of complex **2d**. Ellipsoids representing non-H atoms are drawn at the 50% probability level.

(O)C_6H_3(OMe)-2,4 (**16**), following reported procedures,[24] and studied its palladation reactions. The treatment of **16** with Pd(OAc)$_2$ (see Experimental Section, Scheme 3 and SI) under the same experimental conditions as those described for **9a**−**c** (5 h of reflux were used instead of 4 h in order to improve the reaction yield) gives the polymeric complex **17**. The analytic data of **17** show that the reaction has not occurred in the same way as that described for complexes **9**, since two units PdCl are present by each ylide group. In accord with this, we have proposed the stoichiometry shown in Scheme 3, which has been confirmed in subsequent reactions. The extreme insolubility of **17** prevents a complete characterization, and more soluble derivatives have been obtained through the synthesis of the acetylacetonate **18** or formation of the adduct of PPh_3 (**19**), all reactions shown in Scheme 3. The ^{1}H NMR spectrum of **18** shows very clearly the presence of two different acac ligands for each ylide unit, confirming the stoichiometry of **17**, and also shows the absence of two protons in the ylide ligand, showing that two C−H bond activations have been produced in **16**. Thus, two doublets ($^4J_{HH}$ = 2.5 Hz) at 6.10 and 6.49 ppm are assigned to the protons at the 4 and 6 positions of the palladated C_6H_2 aryl group, while four different resonances at 6.99, 7.10, 7.30, and 7.91 ppm are attributed to the PdC_6H_4 moiety. In addition, peaks corresponding to the PPh_2 unit are also observed. The relative intensity of these three sets of resonances is 2:4:10. This pattern can be easily explained considering that the Pd atom has activated the 6 position of the benzoyl ring and one of the ortho C−H bonds of the PPh_3 moiety in **16**. Similar conclusions can be derived from the analysis of the ^{13}C{^{1}H} (APT) NMR spectrum of **18**. There, in addition to the expected signals assigned to the two palladated aryl rings, the O-bonding of the ylide can be inferred from the observation of a strongly deshielded carbonyl peak (213.00 ppm). Moreover, the IR spectrum of **18** gives an additional proof of the O-coordination, since the ν_{CO} of the ylide carbonyl ligand is found at the lowest energy among the complexes reported here (1568 cm^{-1}), only slightly higher than the value found in the free ylide (1517 cm^{-1}). All these facts are in very good agreement with the structure depicted for **18** in Scheme 3. The spectroscopic characterization of complex **19** also agrees with the structure shown in Scheme 3 (see Experimental Section).

The synthesis of complexes **17**−**19** is very noteworthy, since they contain an ylide-bridging ligand in which a double C−H bond activation has occurred and because the ylide is acting in a very rare coordination mode (C,C,C,O-tetradentate). In light of the preceding results, mainly the synthesis of **9c**, it seems sensible to assume that the first C−H bond activation is produced at the PPh_3 group and that the presence of two methoxy substituents at the 2- and 4-positions of the benzoyl ring counterbalances the deactivating effect of the carbonyl group and leaves a nonsterically hindered ortho C−H bond, able to be activated. The C_{aryl},O-orthometalation is known in Pd(II) chemistry, although it is one of the less represented bonding modes,[1j,2a,g] and, as far as we know, no examples have been reported using ylides as substrates.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 2d

Pd(1)−C(1)	1.962(3)	Pd(1)−N(1)	2.043(2)
Pd(1)−Cl(1)	2.3270(6)	Pd(1)−Cl(1A)	2.4646(8)
P(1)−N(1)	1.629(2)	P(1)−C(21)	1.788(3)
P(1)−C(15)	1.793(3)	P(1)−C(9)	1.812(3)
N(1)−C(8)	1.393(4)	O(1)−C(8)	1.228(3)
C(5)−C(8)	1.489(4)	C(6)−C(7)	1.504(4)
C(1)−C(2)	1.387(4)	C(1)−C(5)	1.400(4)
C(2)−C(3)	1.376(4)	C(3)−C(4)	1.382(4)
C(4)−C(6)	1.380(4)	C(5)−C(6)	1.408(4)
C(1)−Pd(1)−N(1)	80.44(10)	C(1)−Pd(1)−Cl(1)	94.20(8)
N(1)−Pd(1)−Cl(1)	174.61(7)	C(1)−Pd(1)−Cl(1A)	173.24(8)
N(1)−Pd(1)−Cl(1A)	99.18(7)	Cl(1)−Pd(1)−Cl(1A)	86.06(2)
Pd(1)−Cl(1)−Pd(1A)	93.94(2)	C(8)−N(1)−P(1)	117.20(17)
C(8)−N(1)−Pd(1)	111.19(16)	P(1)−N(1)−Pd(1)	130.98(14)
O(1)−C(8)−N(1)	123.3(3)	O(1)−C(8)−C(5)	125.5(3)
N(1)−C(8)−C(5)	111.1(2)		

3. X-ray Crystal Structure of Complexes 2d and 9b. A drawing of complex **2d** is shown in Figure 3, relevant crystallographic parameters are given in Table 1, and selected bond distances and angles are collected in Table 2. The structure shows a dinuclear complex, with two fragments, [Pd{C_6H_3-(C(O)NPPh_3)-2-Me-3}], bridged by two Cl ligands. The relative arrangement of the two cyclometalated unit is trans, probably in order to minimize steric repulsions between the two bulky PPh_3 units. Each Pd atom is located in a slightly distorted square-planar environment, surrounded by the orthometalated C(1) atom, the iminic N(1) atom, and the two bridging chloride ligands, confirming the *exo* metalation of the iminophosphorane.

The Pd(1)−C(1) bond distance [1.962(3) Å] is identical, within experimental error, to those found in other palladated iminophosphoranes. For instance, the distance found in [PdCl(C_6H_4(PPh_2=N−C(O)-2-py)-2)] is 1.976(3) Å,[8] while those found in [Pd(C_6H_4(PPh_2=NC_6H_4Me-4′)-2)(μ-OAc)]$_2$ are 1.964(3) and 1.959(3) Å.[11m] However, the Pd(1)−N(1) bond distance [2.043(2) Å] is slightly longer than that found in [PdCl(C_6H_4-(PPh_2=N−C(O)-2-py)-2)] [1.997(2) Å], while it is identical, within experimental error, to those reported in [Pd(C_6H_4-(PPh_2=NC_6H_4Me-4′)-2)(μ-OAc)]$_2$ [2.050(2) and 2.051(2) Å] and [Pd(C_6H_4(PPh_2=NC_6H_4Me-4′)-2)(tmeda)]ClO_4 [2.055(2) Å].[11m] All these facts reflect similar environments to those reported previously, even though the metalated carbon belongs to P−Ph group or to a benzamido group. The Pd(1)−Cl(1) and Pd−Cl(1A) bonds are quite different, reflecting the different trans influence of the carbon and nitrogen atoms. The internal parameters of the metalated ligand have been compared with those found in other iminophosphoranes derived from benzamide.[27] Thus, the P(1)−N(1) bond distance [1.629(2) Å] is identical, within experimental error, to that found in free Ph_3P=N−C(O)Ph [1.626(3) Å].[27a] The effect of the coordination and subsequent loss of conjugation is more evident on the NCO fragment. The N(1)−C(8) bond distance [1.393(4) Å] is longer

(27) (a) Bar, I.; Bernstein, J. *Acta Crystallogr., Sect. B* **1980**, *36*, 1962. (b) López-Ortíz, F.; Peláez-Arango, E.; Palacios, F.; Barluenga, J.; García-Granda, S.; Tejerina, B.; García-Fernández, A. *J. Org. Chem.* **1994**, *59*, 1984.

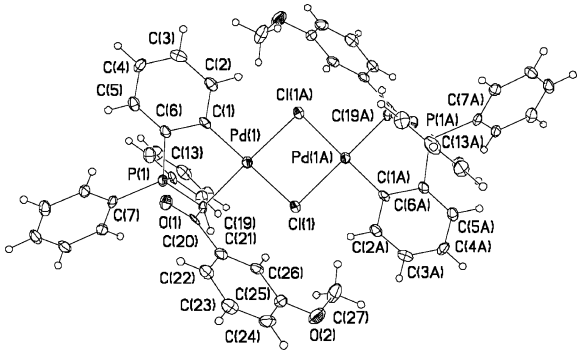


Figure 4. Thermal ellipsoid drawing of complex **9b**. Ellipsoids representing non-H atoms are drawn at the 50% probability level.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 9b·2CHCl$_3$

Pd(1)−C(1)	1.977(4)	Pd(1)−C(19)	2.090(3)
Pd(1)−Cl(1A)	2.3804(14)	Pd(1)−Cl(1)	2.4443(13)
P(1)−C(19)	1.777(4)	P(1)−C(6)	1.775(4)
P(1)−C(13)	1.802(4)	P(1)−C(7)	1.811(4)
C(1)−C(2)	1.395(5)	C(1)−C(6)	1.411(4)
C(2)−C(3)	1.391(5)	C(3)−C(4)	1.377(5)
C(4)−C(5)	1.392(5)	C(5)−C(6)	1.381(5)
C(19)−C(20)	1.488(4)	C(20)−O(1)	1.233(4)
C(20)−C(21)	1.517(5)		
C(1)−Pd(1)−C(19)	87.52(15)	C(1)−Pd(1)−Cl(1A)	93.31(11)
C(19)−Pd(1)−Cl(1×bb)	177.94(10)	C(1)−Pd(1)−Cl(1)	170.81(10)
C(19)−Pd(1)−Cl(1)	93.51(11)	Cl(1A)−Pd(1)−Cl(1)	85.97(5)
Pd(1A)−Cl(1)−Pd(1)	94.03(5)	C(20)−C(19)−P(1)	113.1(3)
C(20)−C(19)−Pd(1)	109.8(2)	P(1)−C(19)−Pd(1)	99.14(17)
O(1)−C(20)−C(19)	120.8(4)	O(1)−C(20)−C(21)	119.5(3)
C(19)−C(20)−C(21)	119.7(3)		

than that found in the free ligand [1.353(5) Å], meaning that this bond has been relaxed, while the C(8)−O(1) bond distance [1.228(3) Å] is shorter than that observed in Ph$_3$P═N−C(O)Ph [1.245(5) Å].[27a] Then, the N-bonding of the ligand fixes the density charge at the N atom and breaks the conjugation in the NCO system, increasing the participation of the A and B resonant forms in the bonding description (Figure 2). Other internal parameters are as usual and do not merit further comment.

With respect to compound **9b**, a drawing is shown in Figure 4, relevant crystallographic parameters are given in Table 1, and selected bond distances and angles are collected in Table 3. The structure also shows a trans dinuclear complex, but now the two fragments bridged by two chlorine ligands are [Pd(C$_6$H$_4$(PPh$_2$CHC(O)C$_6$H$_4$-3-OMe)-2)]. The metalation at the Ph rings of the PPh$_3$ unit is thus confirmed, in good agreement with the NMR data. Each Pd atom is located in a square-planar environment, surrounded by the palladated C(1) atom, the ylidic C(19) atom, and the two bridging Cl ligands.

The Pd(1)−C(1) bond distance [1.977(4) Å] is statistically identical to that found in **2d** and falls at the low end of the usual range of Pd−C bond distances found for metalated ylides [1.998(3)−2.012(10) Å],[7b,c,9h] and the same conclusion can be derived from the comparison of the Pd(1)−C(19) bond distance [2.090(3) Å] with respect to published examples [range 2.083(9)−2.161(8) Å]. The Pd(1)−Cl(1) and Pd−Cl(1A) bonds are also different, reflecting the very different trans influence of the two types of carbon atoms. The comparison of internal bond distances and angles of the metalated ylide with respect to the free ylide[28] follows the expected pattern. Thus, the P−Cα bond is clearly elongated in **9b** [P(1)−C(19) = 1.777(4) Å] with respect to the value found in Ph$_3$P═CHC(O)Ph [1.71 Å], as well as the Cα−Cβ bond distance [C(19)−C(20) = 1.488(4) Å vs 1.39 Å in ref 28], while the Cβ−O bond distance is shorter in **9b** [C(20)−O(1) = 1.233(4) Å] than in the free ylide [1.26 Å]. All these data are also in good agreement with the loss of conjugation by coordination. Finally, and it has been noted in other keto-stabilized ylides,[29] the P−O intramolecular distance [2.902 Å] is shorter than the sum of the van der Waals radii [3.32 Å],[30] and the value of the dihedral angle PCCO is 17.0°. Other internal parameters of the metalated ylide ligand do not deviate from published values and are not relevant.

Conclusion

The palladation of iminophosphoranes Ph$_3$P═NC(O)Aryl is regioselective and gives five-membered *exo* metallacycles of high stability. Several factors, such as the metalloaromaticity or the charge distribution, could be responsible for the orientation of the reaction. In this particular case, the selectivity observed seems to be more closely related with the charge distribution in the ligand than with other factors.

In summary, the palladation of stabilized phosphoylides Ph$_3$P═CHC(O)Aryl occurs regioselectively at the phenyl rings of the PPh$_3$ group. The same behavior is observed for the cycloplatination reaction, in the reported conditions. Only when the benzoyl ring is activated with at least two methoxy substituents is the metalation of the two aryl rings competitive. Here we have obtained one case in which the two palladations are present at the same time. These results are in clear contrast with those reported for the iminophosphoranes Ph$_3$P═NC(O)-Aryl, in spite of the resemblance of the two ligands. Factors such as the metalloaromaticity, the charge distribution, and the structure of the starting materials, among others, are responsible for the delicate counterbalance that drives the final orientation of the reaction.

Experimental Section

Safety note: *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared, and they should be handled with great caution. See: *J. Chem. Educ.* **1973**, *50*, A335−A337.

Synthesis of 2a. To a solution of Pd(OAc)$_2$ (0.500 g, 1.31 mmol) in CH$_2$Cl$_2$ (20 mL) was added **1a** (0.294 g, 1.31 mmol), and the resulting solution was refluxed for 2 h. At this point some decomposition is evident. After cooling, the black suspension was filtered over Celite, giving an orange solution. This clear solution was evaporated to dryness, and the oily residue was redissolved in MeOH (20 mL). To this solution was added an excess of anhydrous LiCl (0.222 g, 5.24 mmol), and the stirring was prolongued at rt for 20 h. During this time a yellow solid (**2a**) precipitated, which was filtered, washed with additional MeOH (10 mL) and Et$_2$O (40 mL), and dried by suction. Yield: 0.205 g (30.0%). Anal. Calc for C$_{50}$H$_{38}$Cl$_2$N$_2$O$_2$P$_2$Pd$_2$ (1044.55): C, 57.49; H, 3.67; N, 2.68. Found: C, 57.37; H, 4.01; N, 2.58. MS (FAB+): *m*/*z* (%) 487 [(M/2 − Cl)$^+$, 28%]. IR (ν, cm^{-1}): 1654 (ν_{CO}), 1284 (ν_{NP}). ^{1}H NMR (CDCl$_3$): δ 6.77−6.80 (m, 2H, H$_5$, H$_6$), 6.90 (t, 1H, H$_4$, $^3J_{HH}$ = 7.5), 7.15 (d, 1H, H$_3$, $^3J_{HH}$ = 7.5), 7.33−7.38 (m, 6H, H$_m$,

(28) Shao, M.; Jin, X.; Tang, Y.; Huang, Q.; Huang, Y. *Tetrahedron Lett.* **1982**, *23*, 5343.

(29) (a) Lledós, A.; Carbó, J. J.; Urriolabeitia, E. P. *Inorg. Chem.* **2001**, *40*, 4913. (b) Lledós, A.; Carbó, J. J.; Navarro, R.; Urriolabeitia, E. P. *Inorg. Chim. Acta* **2004**, *357*, 1444. (c) Serrano, E.; Vallés, C.; Carbó, J. J.; Lledós, A.; Soler, T.; Navarro, R.; Urriolabeitia, E. P. *Organometallics* **2006**, *25*, 4653.

(30) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

PPh_3), 7.43−7.46 (m, 3H, H_p, PPh_3), 7.89−7.94 (m, 6H, H_o, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.20.

Synthesis of 2d. Compound **2d** was prepared following the same synthetic method as that reported for **2a**. Thus, $Pd(OAc)_2$ (0.280 g, 1.26 mmol) was reacted with **1d** (0.500 g, 1.26 mmol) and LiCl (0.210 g, 5.06 mmol) to give **2d** as a yellow solid. Yield: 0.224 g, (33.0%). Anal. Calc for $C_{52}H_{42}Cl_2N_2O_2P_2Pd_2$ (1072.60): C, 58.23; H, 3.95; N, 2.61. Found: C, 58.40; H, 4.07; N, 2.56. MS (FAB+): *m*/*z* (%) 500 [$(M/2 - Cl)^+$, 22%]. IR (ν, cm^{-1}): 1646 (ν_{CO}), 1307 (ν_{NP}). ^1H NMR ($CDCl_3$): δ 2.20 (s, 3H, Me), 6.65−6.80 (m, 3H, H_4, H_5, H_6), 7.33−7.36 (m, 6H, H_m, PPh_3), 7.41−7.45 (m, 3H, H_p, PPh_3), 7.88−7.93 (m, 6H, H_o, PPh_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 19.52 (Me), 125.80 (d, $^1J_{PC}$ = 101.7, C_i, PPh_3), 127.75, (C_6H_4), 128.55 (C_6H_4), 129.02 (d, $^3J_{PC}$ = 12.9, C_m, PPh_3), 131.60 (C_6H_4), 133.14 (d, $^4J_{PC}$ = 2.2, C_p, PPh_3), 134.06 (d, $^2J_{PC}$ = 10.1, C_o, PPh_3), 136.07 (d, $^3J_{PC}$ = 13.0, C_2, C_6H_4), 140.02 (d, $^4J_{PC}$ = 2.7, C_3, C_6H_4), 145.09 (C_1, C_6H_4), 181.65 (d, $^2J_{PC}$ = 6.9, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.31.

Synthesis of 3c. To a solution of **2c** (0.295 g, 0.270 mmol) in CH_2Cl_2 (20 mL) was added Tl(acac) (0.162 g, 0.530 mmol), resulting in the immediate precipitation of TlCl. This suspension was stirred for 1 h at 25 °C and then filtered over Celite. The clear yellow solution was evaporated to dryness and the residue treated with cold *n*-pentane (10 mL), to give **3c** as a yellow solid. Yield: 0.192 g (58.4%). Anal. Calc for $C_{31}H_{28}NO_4PPd$ (615.94): C, 60.45; H, 4.58; N, 2.27. Found: C, 59.95; H, 4.29; N, 1.97. IR (ν, cm^{-1}): 1650 (ν_{CO}), 1582, 1513 (ν_{CO}, acac) 1267 (ν_{NP}). ^1H NMR ($CDCl_3$): δ 0.98 (s, 3H, Me, acac), 1.88 (s, 3H, Me, acac), 3.65 (s, 3H, OMe), 4.93 (s, 1H, CH, acac), 6.79 (dd, 1H, H_5, C_6H_4, $^3J_{HH}$ = 8.3, $^4J_{HH}$ = 2.9), 6.87 (d, 1H, H_3, C_6H_4, $^4J_{HH}$ = 2.9), 7.40−7.45 (m, 7H, H_6 + H_m, PPh_3), 7.49−7.53 (m, 3H, H_p, PPh_3), 7.93−7.97 (m, 6H, H_o, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 28.04.

Synthesis of 4c. To a solution of **2c** (0.301 g, 0.27 mmol) in CH_2Cl_2 (10 mL) was added an excess of py (87.56 μL, 1.08 mmol), and the resulting yellow solution was stirred for 30 min at rt. After the reaction time, the solvent was evaporated to dryness and the residue treated with cold *n*-hexane (15 mL) to give **4c** as a yellow solid. Yield: 0.199 g (57.8%). Anal. Calc for $C_{31}H_{26}ClN_2O_2PPd$ (631.39): C, 58.97; H, 4.15; N, 4.44. Found: C, 59.45; H, 4.34; N, 4.56. MS (FAB+): *m*/*z* (%) 595 (100%) [$(M - Cl)^+$]. IR (ν, cm^{-1}): 1644 (ν_{CO}), 1582, 1513 (ν_{CO}, acac), 1273 (ν_{NP}). ^1H NMR ($CDCl_3$): δ 3.65 (s, 3H, OMe), 6.10 (d, 1H, H_6, $^3J_{HH}$ = 8.4), 6.56 (dd, 1H, H_5, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 3.0), 6.94 (d, 1H, H_3, $^4J_{HH}$ = 3.0), 7.23−7.26 (m, 2H, H_m, py), 7.43−7.47 (m, 6H, H_m, PPh_3), 7.49−7.52 (m, 3H, H_p, PPh_3), 7.65−7.70 (m, 1H, H_p, py), 8.01−8.06 (m, 6H, H_o, PPh_3), 8.78 (dd, 2H, H_o, py, $^3J_{HH}$ = 6.2, $^4J_{HH}$ = 1.2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.82.

Synthesis of 9a. To a solution of **8a** (1.00 g, 2.63 mmol) in CH_2Cl_2 (10 mL) was added $Pd(OAc)_2$ (0.59 g, 2.63 mmol), and the resulting brown solution was refluxed for 4 h. Then the solvent was evaporated to dryness, and the yellow residue was redissolved in MeOH (15 mL), treated with an excess of LiCl (0.44 g, 10.52 mmol). and further stirred for 30 min at rt. During this time **9a** precipitated as a yellow solid, which was filtered, washed with additional MeOH (5 mL) and Et_2O (20 mL), and dried by suction. Yield: 0.61 g, (45%). The NMR characterization of **9a** showed that it was a mixture of two diastereoisomers in 2.5:1 molar ratio. Anal. Calc for $C_{52}H_{40}Cl_2O_2P_2Pd_2$ (1042.60): C, 59.91; H, 3.87. Found: C, 58.97; H, 4.02. MS (MALDI) [*m*/*z*, (%)]: 485.1 (30%) $[M/2 - Cl]^+$. IR (ν, cm^{-1}): 1625 (ν_{CO}). ^1H NMR (dmso-d_6): δ 5.13 (s, CHP, major), 5.41 (s, CHP, minor) 7.13−7.25 (m, C_6H_4), 7.37−7.42 (m, H_m, PhCO minor + C_6H_4), 7.46−7.49 (m, H_m, PhCO major), 7.51−7.91 (m, PPh_2+C_6H_4), 7.94−7.98 (m, PPh_2), 8.04 (d, H_o, PhCO major, $^3J_{HH}$ = 7.2), 8.17 (d, H_o, PhCO minor, $^3J_{HH}$ = 7.6). $^{31}P\{^1H\}$ NMR (dmso-d_6): δ 17.71 (major), 19.53 (minor).

Synthesis of 9b. Compound **9b** was prepared following the same synthetic method as that reported for **9a**. Thus, **8b** (0.070 g, 0.17 mmol) was reacted with $Pd(OAc)_2$ (0.038 g, 0.17 mmol) in CH_2Cl_2 and with LiCl (0.029 g, 0.68 mmol) in MeOH (15 mL) to give **9b** as a yellow solid. Yield: 0.085 g (91%). **9b** was characterized by NMR as a mixture of diastereoisomers in 1.3:1 molar ratio. Anal. Calc for $C_{54}H_{44}Cl_2O_4P_2Pd_2$ (1102.6): C, 58.82; H, 4.02. Found: C, 59.32; H, 4.03. MS (MALDI) [*m*/*z*, (%)]: 1066.2 (8%) $[M - Cl - H]^+$. IR (ν, cm^{-1}): 1627 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 3.57 (s, OMe, major), 3.60 (s, OMe, minor), 4.74 (s, CHP, minor), 4.83 (d, CHP, major, $^2J_{PH}$ = 2.3), 6.72−7.93 (m, Ph, major + minor).$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 17.92 (s, major), 19.50 (s, minor).

Synthesis of 9c. Compound **9c** was prepared following the same synthetic method as that reported for **9a**. Thus, **8c** (0.16 g, 0.36 mmol) was reacted with $Pd(OAc)_2$ (0.082 g, 0.36 mmol) in CH_2Cl_2 and with LiCl (0.061 g, 1.44 mmol) in MeOH (15 mL) to give **9c** as a yellow solid. Yield: 0.165 g (77%). **9c** was characterized by NMR as a mixture of diastereoiosmers in 1.25:1 molar ratio. Anal. Calc for $C_{56}H_{48}Cl_2O_6P_2Pd_2$ (1162.65): C, 57.85; H, 4.16. Found: C, 58.03; H, 4.26. MS (MALDI) [*m*/*z*, (%)]: 1127 (11%) $[M - Cl]^+$. IR (ν, cm^{-1}): 1626 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 3.47 (s, OMe, minor), 3.53 (s, OMe, major), 3.61 (s, OMe, major), 3.75 (m, OMe, minor), 5.10 (d, CHP, major, $^2J_{PH}$ = 4.0), 5.29 (s, CHP, minor), 6.69−6.80 (m, H_3 + H_4, C_6H_4, major + minor), 6.97−7.47 (m, H_6, major + minor, Ph+C_6H_4, major + minor), 7.84−7.85 (m, H_o, PPh_2, major + minor). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.38 (minor), 21.90 (major).

Synthesis of 10a. Compound **10a** was prepared following the same synthetic method as that reported for **3c**. Thus, **9a** (0.200 g, 0.190 mmol) was reacted with Tl(acac) (0.120 g, 0.38 mmol) in CH_2Cl_2 to give **10a** as a yellow solid. Yield: 0.101 g (46.4%). Anal. Calc for $C_{31}H_{27}O_3PPd$ (584.95): C, 63.65; H, 4.65. Found: C, 64.24; H, 4.48. MS (MALDI) [*m*/*z*, (%)]: 485 (100%) $[(M - acac)^+]$. IR (ν, cm^{-1}): 1625 (ν_{CO}), 1564, 1514 (ν_{CO}, acac). ^1H NMR ($CDCl_3$): δ 1.70 (s, 3H, CH_3, acac), 1.89 (s, 3H, CH_3, acac), 4.80 (d, 1H, CHP, $^2J_{PH}$ = 3.3), 5.11 (s, 1H, CH, acac), 7.04−7.12 (m, 1H, C_6H_4), 7.12−7.18 (m, 1H, C_6H_4), 7.20−7.22 (m, 1H, C_6H_4), 7.25−7.31 (m, 2H, H_m, PhCO), 7.33−7.42 (m, 3H, H_p (PhCO) + H_m (PPh_2)), 7.42−7.51 (m, 2H, H_m, PPh_2), 7.50−7.57 (m, 2H, H_p (PPh_2)),7.63−7.68 (m, 1H, C_6H_4), 7.89−7.96 (m, 4H, H_o, PPh_2), 8.15 (d, 2H, H_o, PhCO, $^3J_{HH}$ = 9.6). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.20.

Synthesis of 10b. Compound **10b** was prepared following the same synthetic method as that reported for **3c**. Thus, **9b** (0.06 g, 0.054 mmol) was reacted with Tl(acac) (0.033 g, 0.109 mmol) in CH_2Cl_2 to give **10b** as a yellow solid. Yield: 0.031 g (46.3%). Anal. Calc for $C_{32}H_{29}O_4PPd$ (614.95): C, 62.50; H, 4.75. Found: C, 62.00; H, 4.75. MS (MALDI) [*m*/*z*, (%)]: 515.0 (67%) $[(M - acac)^+]$. IR (ν, cm^{-1}): 1618 (ν_{CO}), 1564, 1515 (ν_{CO}, acac). ^1H NMR ($CDCl_3$): δ 1.73 (s, 3H, CH_3, acac), 1.88 (s, 3H, CH_3, acac), 3.72 (s, 3H, OMe), 4.78 (d, 1H, CHP, $^2J_{PH}$ = 3.6), 5.11 (s, 1H, CH, acac), 6.91 (dd, 1H, H_4, C_6H_4O, $^3J_{HH}$ = 9.0, $^4J_{HH}$ = 2.0), 7.07 (m, 1H, H_5, C_6H_4), 7.15−7.23 (m, 3H, H_5 (C_6H_4O) + H_3, H_4 (C_6H_4)), 7.38 (m, 2H, H_m, PPh_2), 7.43−7.54 (m, 4H, H_m (PPh_2) + H_p (PPh_2)), 7.64−7.67 (m, 2H, H_2 + H_6, C_6H_4O + C_6H_4), 7.77−7.82 (m, 3H, H_o (PPh_2) + H_6 (C_6H_4O)), 7.89 (m, 2H, H_o, PPh_2). $^{13}C\{^1H\}$ NMR

($CDCl_3$): δ 27.81 (CH_3, acac), 27.96 (CH_3, acac), 35.50 (d, CHP, $^1J_{PC}$ = 65.6), 55.44 (OMe), 99.46 (s, CH-acac), 113.07 (d, C_2, C_6H_4O, $^4J_{PC}$ = 1.5), 118.23 (C_4, C_6H_4O), 121.82 (d, C_6, C_6H_4O, $^4J_{PC}$ = 1.1), 124.57 (d, C_5, C_6H_4, $^4J_{PC}$ = 13.3), 126.13 (d, C_{ipso}, PPh_2, $^1J_{PC}$ = 70.0), 127.47 (d, C_{ipso}, PPh_2, $^1J_{PC}$ = 57.56), 125.49 (C_5, C_6H_4O), 128.55 (d, C_m, PPh_2, $^3J_{PC}$ = 11.4), 128.67 (d, C_m, PPh_2, $^3J_{PC}$ = 11.7), 129.56 (d, C_3, C_6H_4, $^2J_{PC}$ = 15.7), 130.12 (d, C_4, C_6H_4, $^3J_{PC}$ = 3.5), 132.38 (d, C_p, PPh_2, $^4J_{PC}$ = 2.7), 132.50 (d, C_p, PPh_2, $^4J_{PC}$ = 2.8), 132.95 (d, C_o, PPh_2, $^2J_{PC}$ = 8.9), 133.67 (d, C_6, C_6H_4, $^3J_{PC}$ = 15.4), 134.49 (d, C_o, PPh_2, $^2J_{PC}$ = 9.9), 138.03 (d, C_2, C_6H_4, $^1J_{PC}$ = 117.53), 139.94 (d, C_1, C_6H_4O, $^3J_{PC}$ = 8.8), 159.28 (C_3, C_6H_4O), 159.32 (d, C_1, C_6H_4, $^2J_{PC}$ = 21.1), 186.20 (CO, acac), 186.84 (CO, acac), 194.9 (d, C = O, $^2J_{PC}$ = 3.7). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.86.

Synthesis of 11a. To a suspension of **9a** (0.20 g, 0.19 mmol) in CH_2Cl_2 (15 mL) was added PPh_3 (0.10 g, 0.38 mmol). The initial yellow suspension gradually dissolved, and after 30 min stirring at rt the resulting solution was filtered over a Celite pad in order to remove any residual insoluble solid. The clear solution was evaporated to dryness, and the treatment of the oily residue with Et_2O (30 mL) gave **11a** as a yellow solid. Yield: 0.250 g, (81.3%). Anal. Calc for $C_{44}H_{35}ClOP_2Pd$ (783.60): C, 67.44; H, 4.50. Found: C, 67.30; H, 4.84. MS (FAB+) [*m*/*z*, (%)]: 747 (15%) $[M - Cl]^+$. IR (ν, cm^{-1}): 1610 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 5.43 (s, 1H, CHP), 6.45 (s, 2H, C_6H_4), 6.79−6.84 (m, 1H, C_6H_4), 7.07−7.11 (m, 6H, H_m, PPh_3), 7.15 (m, 1H, C_6H_4), 7.18−7.25 (m, 9H, $H_o + H_p$, PPh_3), 7.27−7.38 (m, 5H, H_m, PPh_2, $H_m + H_p$, (PhCO)), 7.43−7.60 (m, 4H, $H_m + H_p + H_p$, PPh_2), 7.78 (m, 2H, H_o, PPh_2), 7.96−7.80 (m, 2H, H_o, PPh_2), 8.36 (d, 2H, H_o, PhCO, $^3J_{HH}$ = 7.2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 14.57 (d, 1P, C_6H_4-2-PPh_2, $^3J_{PP}$ = 17.7), 31.45 (d, 1P, Pd−PPh_3).

Synthesis of 12a. To a suspension of **9a** (0.20 g, 0.19 mmol) in THF (20 mL) was added $AgClO_4$ (0.08 g, 0.38 mmol). The resulting mixture was stirred for 30 min at 25 °C with exclusion of light and then filtered over Celite. To the freshly prepared solution of the bis-solvate was added dppm (0.15 g, 0.38 mmol), and the resulting solution was stirred at 25 °C for 4 h. After the reaction time, the solvent was evaporated to dryness and the residue treated with Et_2O (25 mL) to give **12a** as an orange solid. Yield: 0.240 g (63.2%). Anal. Calc for $C_{51}H_{42}ClO_6P_3Pd$ (985.76): C, 62.10; H, 4.30. Found: C, 62.20; H, 4.24. MS (FAB+) [*m*/*z*, (%)]: 886 (45%) $[M - ClO_4]^+$. IR (ν, cm^{-1}): 1614 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 3.45−3.54 (m, 1H, CH_2, dppm), 3.60−3.69 (m, 1H, CH_2, dppm), 5.33 (dd, 1H, CHP, $^3J_{PH}$ = 8.0, $^2J_{PH}$ = 3.2), 6.63−6.71 (m, 2H, C_6H_4), 6.98 (m, 1H, C_6H_4), 7.08−7.43 (m, 25H, PhCO + PPh_2 + C_6H_4), 7.48−7.58 (m, 4H, $H_m(PPh_2) + H_p(PPh_2) + H_p$(PhCO)), 7.68 (t, 1H, H_p, PPh_2, $^3J_{HH}$ = 7.6), 7.74 (m, 2H, H_o, PPh_2), 7.93 (m, 2H, H_o, PPh_2), 8.30 (d, 2H, H_o, PhCO, $^3J_{HH}$ = 7.2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 15.32 (d, 1P, $C_6H_4PPh_2$, $^3J_{PP}$ = 19.6), 24.95 (dd, 1P, $PdPPh_2$, dppm), 58.20 (d, 1P, Ph_2P═O, dppm, $^2J_{PP}$ = 25.1).

Synthesis of 14a. Complex **14a** was prepared following the same experimental method as that reported for **12a**. Thus, **9a** (0.20 g, 0.19 mmol) was reacted, in THF, with $AgClO_4$ (0.080 g, 0.38 mmol) and 1,10-phen (0.076 g, 0.38 mmol) to give **14a** as a yellow solid. Yield: 0.190 g (65.2%). Anal. Calc for $C_{38}H_{28}ClN_2O_5PPd$ (765.51): C, 59.62; H, 3.89; N, 3.66. Found: C, 59.61; H, 3.32; N, 3.82. MS (FAB+) [*m*/*z*, (%)]: 665 (100%) $[M - ClO_4]^+$. IR (ν, cm^{-1}): 1634 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 5.13 (s, 1H, CHP), 7.25−7.37 (m, 5H, H_3, H_4, H_5 (C_6H_4) + H_m (PhCO)), 7.41−7.62 (m, 9H, H_β, H_δ, $H_{\delta'}$ (phen) + H_6 (C_6H_4) + H_p (PhCO) + H_m (PPh_2)), 7.81−7.92 (m, 9H, $H_{\beta'}$ (phen) + H_o (PhCO) + H_o, H_p (PPh_2)), 8.34 (dd, 1H, H_γ, phen, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 1.2), 8.52 (dd, 1H, $H_{\gamma'}$, phen, $^3J_{HH'}$ = 8.0, $^4J_{HH'}$ = 1.2), 8.69 (d, 1H, H_α, phen, $^3J_{HH}$ = 4.4), 8.95 (dd, 1H, $H_{\alpha'}$, phen, $^3J_{HH}$ = 4.8). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 19.43.

Synthesis of 16. Compound **16** was prepared following the same synthetic method as that reported for **8b** or **8c** Thus, PPh_3 (1.062 g, 4.05 mmol) was reacted with $BrCH_2C(O)C_6H_3$-2,4-$(OMe)_2$ (0.350 g, 1.35 mmol) in refluxing CH_2Cl_2 (24 h) to give the corresponding phosphonium salt in 95.3% yield. IR (ν, cm^{-1}): 1644 (ν_{CO}) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.79 (s, 3H, OMe), 4.00 (s, 3H, OMe), 5.91 (d, 2H, CH_2P, $^2J_{PH}$ = 10.8), 6.40 (d, 1H, H_3, $^4J_{HH}$ = 2), 6.44 (dd, 1H, H_5, $^3J_{HH}$ = 8.8), 7.56−7.61 (m, 6H, H_m, PPh_3), 7.68 (t, 3H, H_p, PPh_3, $^3J_{HH}$ = 7.6), 7.76 (d, 1H, H_6), 7.82 (dd, 6H, H_o, PPh_3, $^3J_{PH}$ = 12.8, $^3J_{HH}$ = 8.0). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.59. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 41.54 (d, CH_2P, $^1J_{PC}$ = 60.0), 55.83 (OMe), 56.82 (OMe), 98.32 (C_3), 106.46 (C_5), 118.55 (d, C_1, $^3J_{PC}$ = 4.3), 119.42 (d, C_i, PPh_3, $^1J_{PC}$ = 89.0), 123.24 (C_4), 130.12 (d, C_m, PPh_3, $^3J_{PC}$ = 13.0), 133.64 (C_6), 134.0 (d, C_o, PPh_3, $^2J_{PC}$ = 10.5), 134.5 (d, C_p, PPh_3, $^4J_{PC}$ = 3.0), 162.36 (C_4), 166.57 (C_2), 189.16 (d, C═O, $^2J_{PC}$ = 6.6). Anal. Calc for $C_{28}H_{26}BrO_3P$ (521.12): C, 64.50; H, 5.03. Found: C, 64.40 H, 5.47. In a second step, the phosphonium salt (0.200 g, 0.384 mmol) was reacted with KOH (0.032 g, 0.576 mmol) in methanol/water (10 mL/10 mL) to give **8c** as a white solid. Yield: 0.067 g (39.4%). Anal. Calc for $C_{28}H_{25}O_3P$ (440.21): C, 76.34; H, 5.72. Found: C, 76.85 H, 5.73. IR (ν, cm^{-1}): 1517 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 3.74 (s, 3H, OMe), 3.79 (s, 3H, OMe), 4.65 (d, 1H, CHP, $^2J_{PH}$ = 29.2), 6.40 (s, br, 1H, H_3), 6.43 (dd, 1H, H_5, $^3J_{HH}$ = 8.8, $^4J_{HH}$ = 2.4), 7.40−7.36 (m, 6H, H_m, PPh_3), 7.46 (t, 3H, H_p, PPh_3, $^3J_{HH}$ = 6.8), 7.67 (dd, 6H, H_o, PPh_3, $^3J_{PH}$ = 12.4, $^3J_{HH}$ = 7.2). 7.86 (d, 1H, H_6, $^3J_{HH}$ = 8.4), $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 15.32. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 54.74 (d, CHP, $^1J_{PC}$ = 108.1), 55.38 (OMe), 55.82 (OMe), 98.87 (C_3), 104.10 (C_5), 124.15 (d, C_1, $^3J_{PC}$ = 13.8), 127.66 (d, C_i, PPh_3, $^1J_{PC}$ = 90.8), 128.74 (d, C_m, PPh_3, $^3J_{PC}$ = 12.2), 131.43 (C_6), 131.77 (d, C_p, PPh_3, $^4J_{PC}$ = 2.7), 133.21 (d, C_o, PPh_3, $^2J_{PC}$ = 10.0), 159.10 (C_4), 161.41 (C_2), 182.56 (d, C═O, $^2J_{PC}$ = 2.2).

Synthesis of 17. A solution of **16** (0.100 g, 0.227 mmol) and $Pd(OAc)_2$ (0.102 g, 0.454 mmol) in CH_2Cl_2 (20 mL) was refluxed under Ar for 5 h. After the reaction time, the cold solution was filtered over Celite in order to remove some black Pd^0 formed. The clear yellow solution was evaporated to dryness, and the residue was redissolved in 15 mL of MeOH and treated with an excess of anhydrous LiCl (0.077 g, 1.8 mmol). Subsequent stirring at room temperature gave complex **17** as a yellow precipitate, which was filtered, washed with cold MeOH (2 mL) and Et_2O (10 mL), and air-dried. Yield: 0.151 g (83.2%). Anal. Calc for $[C_{28}H_{23}Cl_2O_3PPd_2]_n$ (722.17)$_n$: C, 46.57; H, 3.21. Found: C, 46.58; H, 3.74. IR (ν, cm^{-1}): 1637 (ν_{CO}). This polymeric compound was not adequately soluble in the usual organic solvents, preventing accurate NMR measurements. Instead, it was characterized through its reactivity.

Synthesis of 18. To a suspension of **17** (0.067 g, 0.094 mmol) in 15 mL of CH_2Cl_2 was added Tl(acac) (0.056 g, 0.187 mmol), resulting in an immediate change of the color of the suspension (yellow to gray). The resulting mixture was stirred at room temperature for 30 min, then filtered over Celite. The pale yellow solution was evaporated to dryness. The treatment of the yellow residue with cold *n*-hexane (5 mL) gave **18** as a pale yellow solid. Yield: 0.067 g (85.2%). Anal. Calc for $C_{38}H_{37}O_7PPd_2$ (849.56): C, 53.73; H, 4.39. Found: C, 53.60; H, 4.21. MS (MALDI+) [*m*/*z*, (%)]: 750 (10%) $[M - acac]^+$. IR (ν, cm^{-1}): 1586 (ν_{CO}), 1568, 1514 (ν_{CO}, acac). ^1H NMR

($CDCl_3$): δ 1.46 (s, 3H, CH_3, acac), 1.99 (s, 3H, CH_3, acac), 2.01 (s, 3H, CH_3, acac), 2.04 (s, 3H, CH_3, acac), 3.88 (s, 3H, OMe), 3.93 (s, 3H, OMe), 5.16 (s, 1H, CH, acac), 5.29 (s, 1H, CH, acac), 5.45 (d, 1H, CHP, $^2J_{PH} = 5.0$), 6.10 (d, 1H, H_6, C_6H_2, $^4J_{HH} = 2.5$), 6.49 (d, 1H, H_4, C_6H_2), 6.99 (t, 1H, H_3, C_6H_4, $^3J_{PH} = {}^3J_{HH} = 7.5$), 7.10 (tdd, 1H, H_4, C_6H_4, $^3J_{HH} = {}^3J_{HH} = 7.5$, $^4J_{PH} = 4.5$, $^4J_{HH} = 1.0$), 7.30 (m, 1H, H_5, C_6H_4), 7.48 (td, 2H, H_m, PPh_2, $^3J_{HH} = 8$, $^4J_{PH} = 3.5$), 7.56−7.59 (m, 3H, $H_m + H_p$, PPh_2), 7.66 (td, 1H, H_p, PPh_2, $^3J_{HH} = 7.0$, $^5J_{PH} = 2.0$), 7.76 (dd, 2H, H_o, PPh_2, $^3J_{PH} = 12$), 7.91 (d, 1H, H_6, C_6H_4, $^3J_{HH} = 7.8$), 8.03 (dd, 2H, H_o, PPh_2, $^3J_{PH} = 13$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (the signals due to the carbon atoms C_2 (C_6H_2 group) and one CO (acac group) were not observed): δ 27.41 (CH_3, acac), 27.46 (CH_3, acac), 27.81 (CH_3, acac), 27.90 (CH_3, acac), 31.73 (d, CHP, $^1J_{PC} = 60.8$), 55.42 (OMe), 55.65 (OMe), 95.17 (C_4, C_6H_2) 99,08 (CH, acac), 100.12 (CH, acac), 105.73 (C_6, C_6H_2), 124.46 (d, 1H, C_4, C_6H_4, $^3J_{PC} = 12.8$), 126.10 (d, C_i, PPh_2, $^1J_{PC} = 90.4$), 126.40 (d, C_i, PPh_2, $^1J_{PC} = 69.6$), 128.20 (d, C_m, PPh_2, $^3J_{PC} = 12.9$), 128.32 (d, C_m, PPh_2, $^3J_{PC} = 11.5$), 129.32 (d, C_3, C_6H_4, $^2J_{PC} = 11.5$), 129.86 (d, C_5, C_6H_4, $^4J_{PC} = 3.1$), 132.26 (d, C_p, PPh_2, $^4J_{PC} = 3.2$), 132.72 (d, C_p, PPh_2, $^4J_{PC} = 2.7$), 132.82 (d, C_o, PPh_2, $^2J_{PC} = 9.7$), 133.87 (d, C_6, C_6H_4, $^3J_{PC} = 15.2$), 136.16 (d, C_2, C_6H_4, $^1J_{PC} = 113.2$), 136.35 (d, C_o, PPh_2, $^2J_{PC} = 10.7$), 158.24 (d, C_1, C_6H_4, $^2J_{PC} = 20.1$), 160.78 (C_5, C_6H_2), 161.92 (C_1, C_6H_2), 162.49 (C_3, C_6H_2), 185.07 (CO, acac), 187.03 (CO, acac), 188.18 (CO, acac), 213.00 (d, C═O, $^2J_{PC} = 4.9$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.04.

Synthesis of 19. To a suspension of **17** (0.100 g, 0.138 mmol) in 15 mL of CH_2Cl_2 was added PPh_3 (0.073 g, 0.277 mmol). The initial yellow suspension gradually dissolved, and in few minutes a pale yellow solution was obtained. This solution was stirred at room temperature for an additional 30 min and then filtered over Celite to remove any trace of insoluble materials. The clear yellow solution thus obtained was evaporated to dryness. Treatment of the yellow residue with cold *n*-hexane (5 mL) and further stirring gave **19** as a pale yellow solid. Yield: 0.146 g (84.6%). Complex **19** was recrystallized from CH_2Cl_2/*n*-hexane to give pale yellow crystals of **19**·0.5CH_2Cl_2, which were used for analytic and spectroscopic measurements. The amount of CH_2Cl_2 was quoted by ^1H NMR. Anal. Calc for $[C_{64}H_{53}Cl_2O_3P_3Pd_2]$·0.5$CH_2Cl_2$ (1289.22): C, 60.09; H, 4.22. Found: C, 59.92; H, 4.18. MS (MALDI+) [*m*/*z*, (%)]: 1211.0 (25%) $[M - Cl]^+$. IR (ν, cm^{-1}): 1584 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 2.74 (s, 3H, OMe), 3.80 (s, 3H, OMe), 5.46 (br, 2H, CHP + H_3, C_6H_2), 5.83 (s, 1H, H_5, C_6H_2), 6.43 (t, 1H, H_3, C_6H_4, $^3J_{PH} = {}^3J_{HH} = 7.4$), 7.10 (m, 1H, H_4, C_6H_4), 6.95 (t, 1H, H_5, C_6H_4, $^3J_{HH} = 8.0$), 7.10−7.64 (m, 39H, $H_6(C_6H_4)$ + Ph), 8.41 (br, 2H, H_o, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 15.9 (d, 1P, C_6H_4-2-PPh_2, $^3J_{PP} = 12.9$), 32.91 (s, br, 1P, Pd−PPh_3), 46.55 (s, br, 1P, Pd−PPh_3).

Crystal Structure Determination and Data Collection of 2d and 9b·2CHCl₃. Crystals of **2d** of adequate quality for X-ray measurements were grown by vapor diffusion of Et_2O into a CH_2Cl_2 solution of **2d** at 25 °C, while crystals of **9b**·2$CHCl_3$ were obtained by cooling a $CHCl_3$ solution of **9b** at low temperature (−18 °C) and standing for several days. All the crystals readily lose solvent; thus they were always handled in the mother liquor. A single crystal of each compound was very quickly mounted at the end of a quartz fiber in a random orientation, covered with magic oil, and placed under the cold stream of nitrogen. Data collection was performed at 100 K on an Oxford Diffraction Xcalibur2 diffractometer using graphite-monocromated Mo Kα radiation ($\lambda = 0.71073$ Å). A hemisphere of data was collected on the basis of three ω-scan or ϕ-scan runs. The diffraction frames were integrated using the program CrysAlis RED,[31] and the integrated intensities were corrected for absorption with SADABS.[32]

Structure Solution and Refinement. The structures were solved and developed by Patterson and Fourier methods.[33] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed at idealized positions and treated as riding atoms. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent atom. The structures were refined to F_o^2, and all reflections were used in the least-squares calculations.[34]

Acknowledgment. Funding by the Dirección General de Investigación Científica y Técnica (DGICYT) (Spain, Project CTQ2005-01037) is gratefully acknowledged. R.B. thanks Ministerio de Educación y Ciencia (Spain), and D.A. and E.S. thank Diputación General de Aragón (Spain) for respective research grants. E.P.U. thanks Prof. Michel Pfeffer for stimulating and helpful discussions.

Supporting Information Available: Complete experimental section with all preparative details, spectroscopic data, and references of the synthesis previously described. Tables giving complete data collection parameters, atomic coordinates, bond distances and angles, and thermal parameters for **2d** and **9b**·2$CHCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM7002877

(31) *CrysAlis RED*, Version 1.171.27p8; Oxford Diffraction Ltd., 2005.
(32) Sheldrick, G. M. *SADABS*, Empirical absorption correction program; Göttingen University, 1996.
(33) Sheldrick, G. M. *SHELXS-86*. *Acta Crystallogr*. **1990**, *A46*, 467.
(34) Sheldrick, G. M. *SHELXL-97*, FORTRAN program for the refinement of crystal structures from diffraction data; Göttingen University, 1997. Molecular graphics were done using the commercial package *SHELXTL-PLUS*, Release 5.05/V; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1996.