# Ligand-Induced and Thermally-Induced Orthometalation of the Bis(ylide) Ligand [Ph<sub>3</sub>P=C(H)]<sub>2</sub>CO. Generation of the C,C-Chelating Group C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C((H)COCH<sub>2</sub>PPh<sub>3</sub>

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The dinuclear complex  $[Pd(\mu-Cl){[C(H)PPh_3]_2CO}]_2(ClO_4)_2$  (**2c**) undergoes thermal rearrangement in refluxing NCMe, giving the dinuclear orthometalated derivative [Pd( $\mu$ -Cl)- $(C_6H_4-2-PPh_2C(H)COCH_2PPh_3)]_2(ClO_4)_2$  (4c) as a mixture of two diastereoisomers (*RR/SS*) and RS/SR). The orthometalation proceeds through an electrophilic substitution pathway, and the formation of the C,C-chelating ligand ( $C_6H_4$ -2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>) results from an intramolecular acid-base reaction in which the proton generated in the orthometalation reaction is captured by an ylide group. A decrease in the cone angle of the phosphonium group dramatically reduces the conversion of the bis(ylide) ligand into the orthometalated ligand. The orthometalation reaction can also be induced by ligand addition to the dimer  $[Pd(\mu-Cl){[C(H)PPh_3]_2CO}]_2(ClO_4)_2$  (**2c**) under very mild conditions. For instance, complex **2c** reacts with PPh<sub>3</sub> or PPhMe<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature to give  $[PdCl(C_6H_4-2 PPh_2C(H)COCH_2PPh_3)(PR_3)](ClO_4)$  (PR<sub>3</sub> = PPh<sub>3</sub> **8**, PPhMe<sub>2</sub> **9**). Less sterically hindered ligands such as pyridine or 3,5-lutidine react with 2c to give in a first step the bis(ylide) complexes  $[PdCl{[C(H)PPh_3]_2CO}(L)](ClO_4)$  (L = py; 3,5-lut), which are transformed into the corresponding orthometalated derivatives [PdCl(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>)(L)](ClO<sub>4</sub>) (L = py 6, 3.5-lut 7) by thermal treatment in refluxing NCMe. This different behavior is explained on the grounds of the different steric requirements of the incoming ligand (phosphine/pyridine). Similar behavior has been observed for the complex  $[Pd{[C(H)PPh_3]_2} CO_{1}(NCMe)_{2}(CIO_{4})_{2}$  (3c). 3c reacts with py or dppm giving  $[Pd_{1}(C(H)PPh_{3})_{2}CO_{1}(L)_{2}(CIO_{4})_{2}$  $(L = py 10, L_2 = dppm 11)$ , which is transformed into  $[Pd(C_6H_4-2-PPh_2C(H)COCH_2PPh_3) (L_2)$ ](ClO<sub>4</sub>) (L = py 12, L<sub>2</sub> = dppm 13a + dppm-O 13b) by refluxing in NCMe. However, complex 3c reacts with PPh<sub>3</sub>, dppe, or phen in CH<sub>2</sub>Cl<sub>2</sub> at room temperature giving [Pd-(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>)(L<sub>2</sub>)](ClO<sub>4</sub>) (L<sub>2</sub> = PPh<sub>3</sub>, NCMe **14**, dppe **15**, phen **16**). Complex **3c** is not transformed into its corresponding orthometalated derivative  $[Pd(C_6H_4-2 PPh_2C(H)COCH_2PPh_3)(NCMe)_2](ClO_4)_2$  (17) by refluxing in NCMe, but 17 can be obtained by treatment of 4c with TlClO<sub>4</sub> in NCMe. The orthometalation reaction of the bis(ylide) ligand can even occur spontaneously. The acetate-bridged dimer  $[Pd(\mu - OOCCH_3) \{ [C(H)PPh_3]_2 \}$  $CO_{1}^{2}(ClO_{4})_{2}$  (18) transforms spontaneously at room temperature into the mixed orthometalated bis(ylide)complex [(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>)Pd(*u*-OOCCH<sub>3</sub>)<sub>2</sub>Pd{[C(H)PPh<sub>3</sub>]<sub>2</sub>CO}]-(ClO<sub>4</sub>)<sub>2</sub> (**19**). The crystal structure of [Pd(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>)(PPh<sub>3</sub>)(NCMe)](ClO<sub>4</sub>)<sub>2</sub> (14) has been determined and reveals the presence of an orthometalated  $C_6H_4$ -2-PPh<sub>2</sub> unit, a C-linked ylide Pd-C(H), and a phosphonium fragment  $CH_2PPh_3$ . The phosphine group is coordinated cis to the orthometalated carbon atom.

## Introduction

Ylides of phosphorus are now recognized as a class of extremely powerful ligand systems that form complexes with both main group and transition metals.<sup>1</sup> In recent papers, we have described a selection of the chemistry of  $Pd^{II}$  and  $Pt^{II}$  with  $\alpha$ -stabilized ylides, such as  $Ph_3P=$ 

C(H)COR (R = Me, Ph, OMe, NMe<sub>2</sub>) and Ph<sub>3</sub>P=C(H)-CN.<sup>2-7</sup> Throughout these studies, we have observed the

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ability of these ylides to behave as ambidentate ligands (except for the  $NMe_2$  derivative<sup>7</sup>), and it has been demonstrated that control can be exerted over the bonding modes: that given an organometallic substrate the coordination mode of a given ylide can be predicted and, conversely, a substrate can be designed to obtain a given bonding mode.

More recent studies are focused on the reactivity of palladium complexes with bis(vlides) such as  $Ph_3P=$  $C(H)COC(H) = PPh_3$ . In a first communication<sup>8</sup> we have described the synthesis of palladium(II) complexes in which this bis(ylide) acts as a C,C-chelate through the two ylidic carbon atoms. Through subsequent study we have now found an interesting reactivity of these chelates, namely, the rearrangement of the C,Ccoordinated ligand [C(H)PPh<sub>3</sub>]<sub>2</sub>CO to give the orthometalated unit  $C_6H_4$ -2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>, which is linked to the metal center through an aromatic carbon atom and through an ylidic carbon atom. This C-H activation can be induced either thermally (refluxing NCMe) or by addition of auxiliary ligands under very mild conditions (CH<sub>2</sub>Cl<sub>2</sub>, room temperature). Due to the intrisic interest of reactions involving C-H activation<sup>9</sup> and also due to the fact that the number of C,Corthometalated complexes is relatively scarce<sup>10-20</sup> compared with other C,X-cyclometalated (X = heteroatom) derivatives,<sup>9,21</sup> we have performed a systematic study of this particular C-H activation in bis(ylide) complexes. Even though the orthometalation of ylides has been known for several years, 10-13,15,18 we are not aware of a mechanistic proposal for this reaction, nor of a study of the influence of different parameters on this process. To shed light on these questions, we report here our first results with this previously unexplored chemistry.

### **Results and Discussion**

**Thermally-Induced Orthometalations.** The prolonged reflux in NCMe (8 h) of a suspension of the yellow dimer  $[Pd(\mu-Cl){[C(H)PPh_3]_2CO}]_2(ClO_4)_2$  (**2c**) affords an orange solution from which the orthometalated dinuclear complex  $[Pd(\mu-Cl)(C_6H_4-2-PPh_2C(H)-$ 

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 $COCH_2PPh_3$ ]( $ClO_4$ )<sub>2</sub> (**4c**) can be isolated in good yield (see Chart 1 and eq 1). The mass spectrum of **4c** 



confirms its dinuclear nature, through the observation of a peak of medium intensity at 1541 amu, which corresponds to the dinuclear dicationic fragment plus one  $ClO_4^-$  group. The IR spectrum of **4c** shows a broad absorption at 278 cm<sup>-1</sup>, suggesting the presence of the  $Pd(\mu-Cl)_2Pd$  unit, and a strong absorption at 1648 cm<sup>-1</sup> attributed to the carbonyl group. This latter absorption is shifted to higher energies with respect to that in the starting product **2c** (1617 cm<sup>-1</sup>),<sup>8</sup> and this shift agrees with the change in the chemical environment of the carbonyl group on passing from the bis(ylide) in **2c** to the ylide–phosphonium in **4c**.

The <sup>1</sup>H NMR spectrum of **4c** shows, as expected, two identical sets of signals (molar ratio 1.77:1) corresponding to the two possible diastereoisomers (*RR/SS* and *RS/SR*). Although the reaction is slightly stereoselective (de = 27.8%), we have not been able to determine the absolute configurations in the major isomer. The observed pattern of signals reveals the presence of an ylide C-bonded to the Pd center and of a phosphonium group. The resonances attributed to the methine protons appear as doublet of doublets at 4.58 and 4.52 ppm with coupling constants <sup>2</sup>*J*<sub>P-H</sub> around 4 Hz and <sup>4</sup>*J*<sub>P-H</sub> around

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2.5 Hz, this fact also showing the inequivalence of the phosphorus atoms. On the other hand, the resonances assigned to the  $CH_2PPh_3$  protons appear as AB spin systems coupled with the adjacent P nucleus. The <sup>13</sup>C-<sup>1</sup>H} NMR spectrum of **4c** also shows two sets of signals. The carbonyl group appears in both isomers as a triplet. Two doublet resonances at 157.58 (major isomer) and 157.49 (minor isomer) ppm signal the existence of the Pd–C<sub>orthometalated</sub> bond, since this region (155–164 ppm) is characteristic of this kind of bond.<sup>14,17a,20</sup> The ylidic carbon atom of the major isomer appears at 31.35 ppm as a doublet of doublets with characteristic coupling constants for a C-bonded ylide<sup>2-7</sup> ( ${}^{1}J_{P-C} = 66.8$  Hz,  ${}^{3}J_{P-C}$ = 8.8 Hz). The  ${}^{31}P{}^{1}H$  NMR spectrum shows two AB spin sytems, as expected for two diastereoisomers with two chemically inequivalent P atoms each.

The presence of only two sets of signals in the NMR spectra also reveals that only one geometrical isomer (anti or syn) is present. Although with the current data it is not possible to deduce which geometrical isomer has been obtained, further reactivity of this complex<sup>22</sup> has shown that 4c is actually obtained as the anti isomer.

To elucidate the nature of this orthometalation reaction, we have studied the influence of several parameters on the global process. The influence of the phosphonium group, the solvent, the temperature, the net charge of the starting complex, and the addition of halide ligands have been examined.

Two new phosphonium salts have been obtained, [PhEt<sub>2</sub>PCH<sub>2</sub>COCH<sub>2</sub>PPhEt<sub>2</sub>]Cl<sub>2</sub> and [Ph<sub>2</sub>EtPCH<sub>2</sub>COCH<sub>2</sub>-PPh<sub>2</sub>Et]Cl<sub>2</sub>, by reaction of the corresponding phosphine and 1,3-dichloroacetone (2:1 molar ratio) in CHCl<sub>3</sub> (see Experimental Section). Following the same experimental method described for the synthesis of 1c and 2c<sup>8</sup> (see Experimental Section), we have synthesized the neutral derivatives  $Cl_2Pd\{[CH(PR_3)]_2CO]\}$  (PR<sub>3</sub> = PPhEt<sub>2</sub> 1a, PPh<sub>2</sub>Et **1b**) and the dinuclear  $[Pd(\mu-Cl){[CH(PR_3)]_2}$ - $CO_{1}$  (ClO<sub>4</sub>)<sub>2</sub> (PR<sub>3</sub> = PPhEt<sub>2</sub> **2a**, PPh<sub>2</sub>Et **2b**) (see Chart 1). Complexes 2a and 2b were subjected to the same experimental conditions which produced the orthometalation of 2c to give 4c (NCMe, reflux, 8 h). After the reaction and usual workup, complex 2a did not show evidence of transformation and was recovered in almost quantitative yields. However, the refluxing of complex **2b** afforded a mixture in which were identified the starting product **2b** together with some of the possible isomers of the resulting product 4b (now there are four chiral centers in the molecule). The approximate conversion was 50% based on the integrals of the <sup>31</sup>P resonances (see Experimental Section).

The importance of the solvent in the development of the reaction is not negligible. Other solvents were tried instead of NCMe, with negative results. The use of coordinating solvents but with lower boiling points such as MeOH or acetone resulted in the recovery of the starting product **2c**. On the other hand, the use of high boiling point solvents without coordinating ability such as toluene resulted in the decomposition of the starting product 2c and formation of black palladium. Only with

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a polar solvent with high coordinating strength and an intermediate boiling point (80 °C) such as NCMe does the orthometalation reaction proceed. These results are similar to those described by Vicente et al.<sup>13</sup>

As has been pointed out,<sup>9,17,21,23–26a</sup> the orthometalation reaction of a given ligand requires the concurrence of several factors such as the presence of bulky groups in the donor atom or the existence of some degree of flexibility in the ligand to be orthometalated. In addition, the existence of ring strain in four-membered metallocycles could also be responsible for the orthometalation and transformation of these sterically hindered rings into the more stable five-membered cycles. We think that this last factor especially applies to our case. The bulky phenyl groups on both P atoms of the C,C-chelated bis(ylide) ligand and the fact that both PPh<sub>3</sub> fragments lie on the same side of the molecular plane<sup>8</sup> promote the orthometalation. In addition, in the crystal structure of the dinuclear derivative  $[Pd(\mu-Cl) \{ [C(H)PPh_3]_2CO \} \}_2(ClO_4)_2$  (2c),<sup>8</sup> one ortho H atom of one phenyl group is in close proximity to the palladium(II) center and is most likely to orthometalate; however, we must note that even if this proximity is a prerequisite. this "nonbonding" interaction is not the true intermediate stage in the C–H bond activation process.<sup>26b</sup> Thus, we think that the driving force for orthometalation in our complexes is the simultaneous presence of a fourmembered cycle (ring strain) and one bulky PPh<sub>3</sub> group supported at each donor ylidic carbon atom (steric hindrance).

The reactivity of complexes 2a and 2b provides additional proof, since a decrease in the cone angle of the PR<sub>3</sub> group at the ylidic carbon atom results in a gradual quench of the orthometalation reaction. Complex **2a**, which possesses the phosphine with the smallest cone angle (PPhEt<sub>2</sub>, 136°),<sup>27</sup> does not show orthometalation at all, while complex 2b (PPh<sub>2</sub>Et, 140°)<sup>27</sup> shows only partial conversion, both under the same conditions in which 2c (PPh<sub>3</sub>, 145°)<sup>27</sup> orthometalates in 100% spectroscopic yield. The importance of steric effects in the orthometalation reaction will be proved definitively in the next section (see Ligand-Induced Orthometalations).

We have also compared the reactivity of complexes 1c (neutral). 2c (dinuclear, dicationic), and 3c (mononuclear, dicationic) under the same conditions (NCMe, reflux, 8 h) aiming to determine the influence of the net charge of the starting compound on the orthometalation reaction. The reactions were followed by <sup>1</sup>H and <sup>31</sup>P-<sup>1</sup>H} NMR spectroscopy (see Experimental Section). Similar conversions were obtained for complexes 1c and **2c**, and these results can be rationalized taking into account the following observations: (a) the dinuclear complex 2c in NCCD<sub>3</sub> is fully dissociated into the monomer [PdCl{[C(H)PPh<sub>3</sub>]<sub>2</sub>CO}(NCCD<sub>3</sub>)]<sup>+</sup>, characterized by its NMR spectra (see Experimental Section); (b) the neutral complex 1c, when dissolved in NCCD<sub>3</sub>,

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<sup>(22)</sup> Complex **4c** reacts with Hg(OOCCH<sub>3</sub>)<sub>2</sub> to give the trinuclear derivative  $[Pd_2(\mu-Cl)_2(C_6H_4-2-PPh_2C(H)COC(H)PPh_3)_2(\mu-Hg)](ClO_4)_2$ , and the X-ray crystal structure of this complex reveals the anti disposition of the cyclometalated rings. Falvello, L. R.; Fernández, S.; Rev. 1989, 93, 155. (b) Dupont, J.; Beydoun, N.; Pfeffer, M. J. Chem. Navarro, R.; Urriolabeitia, E. P. Manuscript submitted to Inorg. Chem.

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exists as an equilibrium mixture between the neutral form 1c and the cationic form [PdCl{[C(H)PPh<sub>3</sub>]<sub>2</sub>CO}- $(NCCD_3)$ ]<sup>+</sup>; (c) the existence of a true equilibrium between these two forms was established by measurement of the NMR spectra of 1c at different temperatures and by addition of LiCl to an NCCD<sub>3</sub> solution of **2c**. All these facts are compiled in Scheme 1. Thus, the "active species" in the orthometalation reaction of 1c and 2c is the monocationic complex [PdCl{[C(H)PPh<sub>3</sub>]<sub>2</sub>CO}-(NCCD<sub>3</sub>)]<sup>+</sup> (named A in Scheme 1), which orthometalates to give the monocationic solvate **B**. This solvate **B** can dimerize to give 4c by addition of a precipitating agent (Et<sub>2</sub>O) or, through reaction with  $Cl^-$ , can give 5. It is worth noting that the reaction of **3c** in refluxing NCMe does not afford the corresponding orthometalated  $[Pd(C_6H_4-2-PPh_2C(H)COCH_2PPh_3)(NCMe)_2]^{2+}$  (17) (which can easily be obtained by reaction of 4c with TlClO<sub>4</sub> in NCMe; see Scheme 5) and that the starting product is recovered at the end of the reaction. We are unaware of the reasons for this behavior, but it seems that the Cl<sup>-</sup> ligands are not simple spectators in this reaction.

There are two generally accepted mechanisms for C-H bond activation by palladium(II): oxidative addition resulting from nucleophilic attack by the metal on the phenyl ring and electrophilic substitution in the aromatic ring. Although there are known examples in which the Pd(II) center behaves as a nucleophile,<sup>9</sup> most reports of cyclopalladation describe this reaction as an electrophilic substitution. In some cases, alteration of the electron density at the aromatic ring or the metal center provides evidence for this mechanism. In our case, the results obtained with complexes 2a, 2b, and 2c can be related with an electrophilic substitution mechanism, since a decrease in the basicity of the phosphine (PPhEt<sub>2</sub> in  $2a > PPh_2Et$  in  $2b > PPh_3$  in 2c) would result in a decrease in the electron-donating capacity of the ylidic carbon in the respective complexes and, consequently, in a more favorable setting for electrophilic attack by the metal center following the sequence 2c > 2b > 2a. However, this argument is not a definitive proof for this mechanism, since the decrease in the electron density at the metal center follows the same order as the increase of the cone angle of the phosphine, as already described (see above).

Another argument in favor of electrophilic substitution is the fact that these reactions are often assisted by coordinated or free bases.<sup>17</sup> In our case, we have an internal base in the form of two ylidic C atoms of the C,C-chelate bis(ylide) ligand, which can capture the proton resulting from the C–H bond activation. With these data we propose the mechanism shown in Scheme 2 for the orthometalation of complex **2c**. The reaction begins with the cleavage of the halide bridging system and formation of the "active species" **A**, in which the electrophilic attack by the metal on the phenyl group takes place. The proton resulting from the C–H bond activation is captured by one of the basic ylidic fragments, giving the species **B**, which contains a phosphonium group. Dimerization of **B** results in the formation of **4c**.

The generation of the phosphonium group in the final product can be rationalized in two different ways. One of these is that shown in Scheme 2 involving an intramolecular acid-base reaction and is similar to that described in the orthometalation of bis(N-aryliminophosphoranyl)alkanides of Pd(II) and Pt(II).<sup>17a</sup> The other route would involve the presence of HCl, which protonates the metal center; transfer of this proton to one ylidic group would be followed by elimination of a phosphonium fragment, oxidative addition of the phenylic C-H bond, and reductive elimination of HCl, as has been described for the formation of the anionic<sup>18</sup> complex  ${PtCl_2[C(H)COMe(PPh_2-o-C_6H_4)]}^-$  (that is, the C-H activation takes place after the formation of the phosphonium group). However, although this second alternative could explain the role of the Cl- ligands (see above), we propose the first pathway due to the following facts: (a) the orthometalation reaction performed in the presence of K<sub>2</sub>CO<sub>3</sub> did not show an appreciable decrease in yield; (b) the orthometalation of the ylidephosphonium salt [Ph<sub>3</sub>P=C(H)COCH<sub>2</sub>PPh<sub>3</sub>]ClO<sub>4</sub> was attempted with a variety of Pd(II) precursors, but it was always unsuccessful even in the presence of external bases (thus, the reaction is intramolecularly baseassisted); (c) if HCl were formed during the reaction, its elimination under the reaction conditions used (reflux/air) would be especially favorable.

In conclusion, the thermal orthometalation of the C,Cchelating bis(ylide) ligand  $[C(H)PPh_3]_2CO$  generates the C,C-chelating  $[C_6H_4-2-PPh_2C(H)COCH_2PPh_3]$  ligand through an electrophilic substitution at the phenyl ring and an intramolecular acid—base reaction. The driving



force for this reaction seems to be related to the steric repulsions between the two PPh<sub>3</sub> fragments in the chelating bis(ylide) group and to the transformation of a four-membered ring into a five-membered ring. Moreover, the orthometalation can be promoted under very mild conditions by the addition of ligands. As will be described in the following section, we have also studied the reactivity of complexes 2c and 3c toward a variety of neutral mono- and bidentate ligands.

**Ligand-Induced Orthometalations.** In a previous paper<sup>8</sup> we described the reactivity of the dinuclear complex **2c** toward different neutral monodentate ligands L (1:2 molar ratio,  $CH_2Cl_2$ , room temperature) such as pyridine, lutidine, and phosphorus ylides. These reactions resulted in the cleavage of the halide bridging system and formation of the mononuclear derivatives [PdCl{[C(H)PPh<sub>3</sub>]<sub>2</sub>CO}L]ClO<sub>4</sub> (see Scheme 3, path a<sub>1</sub>). The reactivity of **2c** with other neutral monodentate ligands such as phosphines shows a very different behavior.

The reaction of 2c with 2 equiv of phosphines PR<sub>3</sub> (PPh<sub>3</sub>, PPhMe<sub>2</sub>) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature results in the formation of the cationic orthometalated derivatives [PdCl(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>)L]ClO<sub>4</sub> (L = PPh<sub>3</sub> **8**, PPhMe<sub>2</sub> **9**) in very good yields (see Scheme 3, path b). The spectroscopic data of **8** and **9** are in keeping

with the proposed structure in Scheme 3. The IR spectra show the carbonyl absorption at about 1630  $cm^{-1}$ , shifted to higher energies with respect to that in C,Cbis(ylide) complexes.8 On the other hand, the Pd-Cl stretch appears in the 270 cm<sup>-1</sup> region, suggesting that the Cl ligand is trans to the orthometalated carbon atom.<sup>28</sup> The <sup>1</sup>H NMR spectra show the presence of the CH<sub>2</sub>P group as an AB spin system coupled to the P atom of the phosphonium group and also show the CH ylidic proton as a triplet of doublets. The shape of the latter signal means that this proton is coupled with the adjacent P atom in the ring, with the phosphonium atom and with the P atom of the PR<sub>3</sub> ligand. The magnitudes of the coupling constants strongly suggest that the PR<sub>3</sub> ligand is trans to the ylidic carbon atom. Additional evidence for this stereochemistry can be found in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **8**. There, the orthometalated carbon atom (C1) appears at 163.86 ppm as a doublet  $(^{2}J_{P-C} = 20 \text{ Hz})$  by coupling with the P atom in the ring, while a coupling with a trans phosphine should give a coupling constant of about 110-130 Hz.<sup>17a</sup> Moreover, the  ${}^{31}P{}^{1}H$  NMR spectra of **8** and **9** show the same pattern of resonances (with the expected difference in

<sup>(28)</sup> Crociani, B.; Boschi, T.; Pietropaolo, R.; Belluco, U. J. Chem. Soc. (A) 1970, 531.

the chemical shift of the PR<sub>3</sub> ligand), in which the P atom in the ring appears as a doublet of doublets by coupling with the trans-PR<sub>3</sub> ligand and with the phosphonium group. Finally, the <sup>1</sup>H<sup>-1</sup>H NOESY spectrum of complex **9** shows a strong NOE interaction between the Me resonances of the PPhMe<sub>2</sub> ligand (1.57 and 1.37 ppm) and the H<sub>6</sub> proton of the orthometalated C<sub>6</sub>H<sub>4</sub> group (6.82 ppm), indicating their proximity and hence their relative cis disposition. All of these data support the structure shown in Scheme 3 for **8** and **9** in which the PR<sub>3</sub> ligand is trans to the ylidic C atom, in line with the *transphobia* of the phosphine ligands to coordinate trans to an orthometalated carbon atom.<sup>29</sup>

The different behavior observed in the reaction of 2c with pyridines and with phosphines can be related to steric effects. Ligands such as pyridine, which can be accommodated in a plane perpendicular to the molecular plane, do not exert a considerable influence upon the ylidic C(H)PPh<sub>3</sub> group located in the cis position, and the molecule remains stable toward orthometalation.<sup>8</sup> However, the volume occupied by ligands such as phosphines is considerably larger and such ligands could crowd the two cis ylidic C(H)PPh3 fragments. As a result, the molecule evolves to give a less hindered situation via orthometalation. Differences in the nature of the donor atom (N versus P) do not seem to play an important role here since, as we will see later, we have been able to obtain complexes with P donor ligands and the C,C-chelating bis(ylide) (complex 11) and orthometalated complexes with N donor ligands (complex 16), and these differences can be explained taking into account only steric factors. We have not tried reactions with smaller phosphines (PMe<sub>3</sub>), and the reactions with larger amines (NEt<sub>3</sub>) are more complicated since they involve deprotonation of the CH<sub>2</sub>PPh<sub>3</sub> group generated.

The synthesis of the complexes  $[PdCl(C_6H_4-2-PPh_2C-(H)COCH_2PPh_3)L]ClO_4$  (L = py **6**, 3,5-lutidine **7**) can be accomplished in three ways: (a) by reaction of **4c** with the appropriate amount of ligand; (b) by refluxing complex **2c** in NCMe in the presence of an excess of ligand; and (c) by refluxing the corresponding C,Cchelating bis(ylide) complexes  $[PdCl\{[C(H)PPh_3]_2CO\}L] ClO_4$  in NCMe. In our experience, the best results have been obtained using method (c), and this method is described in the Experimental Section (see also Scheme 3, path a<sub>2</sub>).

The reaction of 2c with PPh<sub>3</sub> has been followed by NMR spectroscopy. A solution of 2c in  $CD_2Cl_2$  was mixed with PPh<sub>3</sub> (1:2 molar ratio), and the <sup>1</sup>H NMR spectrum of the mixture was measured at 183 K 5 min after mixing (the time needed for locking and shimming). This <sup>1</sup>H NMR spectrum shows, in addition to the resonances for 8, two new resonances of very weak intensity: a doublet of doublets at 3.72 ppm ( $^{2}J_{P-H} =$ 6.2 Hz,  ${}^{4}J_{P-H} = 3.4$  Hz) and a doublet of doublets of doublets at 2.64 ppm ( ${}^{3}J_{P-H} = 11.4$  Hz,  ${}^{2}J_{P-H} = 5.0$  Hz,  ${}^{4}J_{\rm P-H}$  = 2.3 Hz). These two resonances could indicate the presence of the intermediate complex [PdCl{[C(H)-PPh<sub>3</sub>]<sub>2</sub>CO}(PPh<sub>3</sub>)]ClO<sub>4</sub>, since the first resonance would correspond to the ylidic proton cis to the PPh<sub>3</sub> ligand and the second to the ylidic proton trans to the PPh<sub>3</sub> group. Moreover, the  ${}^{31}P{}^{1}H{}$  NMR spectrum of this

mixture shows the presence of three resonances at 31.45  $(Pd-PPh_3)$ , 26.75, and 23.67 ppm (bis(ylide)), which are consistent with the proposed intermediate. On warming this solution to room temperature, these resonances disappear and only the resonances attributed to **8** are observed. Thus, the reaction begins with the cleavage of the halide bridging system, giving the intermediate  $[PdCl\{[C(H)PPh_3]_2CO\}(PPh_3)]ClO_4$ , which is very unstable and undergoes internal metalation to give **8**, and it is sensible to assume that this metalation occurs through a mechanism similar to that described for **2c**.

We reported in the first section that complex **3c** does not undergo thermal orthometalation. Prompted by the results obtained in the synthesis of 8 and 9, we have explored the reactivity of this complex toward different neutral monodentate and bidentate ligands. The reaction of 3c with 2 equiv of pyridine results in the formation of the bis(ylide) derivative [Pd{[C(H)PPh<sub>3</sub>]<sub>2</sub>- $CO_{2}(py)_{2}(ClO_{4})_{2}$  (10), which was characterized by its analytical and spectroscopic data (see Experimental Section). In accord with the foregoing discussion of the complexes [PdCl{[C(H)PPh<sub>3</sub>]<sub>2</sub>CO}(py)]ClO<sub>4</sub> (see preceding paragraphs), complex 10 is stable toward orthometalation since the steric repulsion between the pyridine ligands and the ylidic C(H)PPh<sub>3</sub> fragments is not severe. More interesting is the reaction between **3c** and dppm (Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>) in 1:1 molar ratio (CH<sub>2</sub>Cl<sub>2</sub>, room temperature), which results in the formation of [Pd- $\{[C(H)PPh_3]_2CO\}(dppm)](ClO_4)_2$  (11) (see Scheme 4, path  $a_1$ ). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **11** shows only two resonance triplets at 22.40 and -25.54 ppm. This spectrum shows that the molecule has high symmetry since the two P atoms of the dppm ligand (-25.54 ppm) are equivalent, as are the two P atoms of the bis(ylide) ligand (22.40 ppm). The location of the dppm resonances at high field shows that this ligand is coordinated as a P,P-chelate<sup>30</sup> and, thus, that the bis(ylide) ligand acts as a C,C-chelate. The triplet shape of each signal results from virtual coupling between the P atoms of the spin system. The <sup>1</sup>H NMR spectrum of **11** confirms the proposed structure (see Scheme 4) and shows the presence of three resonances of relative intensity 2:1:1. The resonance at lowest field (5.16 ppm) is attributed to the ylidic CH protons and appears as a false guintuplet due to virtual coupling with the four P atoms present in the molecule. The other two resonances at higher field (4.83 and 4.02 ppm) are attributed to the CH<sub>2</sub> protons of the dppm, and each signal appears as a doublet of triplets (an AB spin system coupled to two equivalent P atoms).

From these data it is clear that the nature of the donor atom is not determinative for the orthometalation, since with both trans P- and N-donor atoms the resulting bis(ylide) complexes **10** and **11** are stable toward orthometalation. An explanation for the stability of **10** has been given in the preceding paragraphs, and we think that the stability of complex **11** can be explained by taking into account that both ligands (the bis(ylide) and the dppm) are chelates and that both chelates are four-membered rings; hence they show small bite angles (for instance, for complex **2c**<sup>8</sup> the value of the bite angle is about 68° and for dppm-chelating complexes a typical

<sup>(30)</sup> Falvello, L. R.; Forniés, J.; Navarro, R.; Rueda, A.; Urriolabeitia, E. P. *Organometallics* **1996**, *15*, 309, and references therein.



value of this angle<sup>30</sup> is about 74°). Thus, the interactions between the Ph groups of the dppm ligand and the ylidic fragments  $C(H)PPh_3$  are not strong enough to promote the orthometalation.

As has been described for the syntheses of complexes 6 and 7, the synthesis of the orthometalated complexes derived from 10 and 11 can be carried out by refluxing these complexes (10 and 11) in NCMe (see Scheme 4, path  $a_2$ ). The refluxing of **10** in NCMe gives [Pd(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>)(py)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**12**), which is characterized on the basis of its analytical and spectroscopic data (see Experimental Section). However, prolonged reflux of 11 in NCMe does not afford a single product but a mixture of two products as can be inferred from the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the crude reaction mixture, which gives two sets of resonances. One set of resonances appears at 23.55 (ddd), 21.49 (d), -14.43 (dd), and -29.19 (dd) and is attributed to the orthometalated [Pd(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>)(dppm)]-(ClO<sub>4</sub>)<sub>2</sub> (13a), since the two high-field resonances signal the presence of the P,P-chelating dppm ligand<sup>30</sup> and the signals at 23.55 and 21.49 ppm are characteristic of the orthometalated group. The second set of signals appears at 59.14 (d), 25.41 (dd), 21.36 (d), and 17.15 (dd). The absence of resonances at high field and the presence of a peak at 59.14 ppm show that one of the P atoms of the dppm ligand has been oxidized and the fourmemebered ring has been transformed into a fivemembered ring, giving  $[Pd(C_6H_4-2-PPh_2C(H)COCH_2-$ PPh<sub>3</sub>)(dppm-O)](ClO<sub>4</sub>)<sub>2</sub> (13b). Similar aerobic oxidations of the dppm ligand have been described<sup>29</sup> for C,Northometalated complexes of Pd(II) such as [Pd(C<sub>6</sub>H<sub>4</sub>N= NPh-2)( $\eta^2$ -dppmO)]SbF<sub>6</sub>. In the latter, oxidation has occurred at the P atom trans to the aryl group. By analogy to this compound, we propose the same structure for 13b; that is, the oxygen atom is trans to the arylic carbon atom. In addition, this arrangement of ligands matches that expected from consideration of the antisymbiotic effect;<sup>31</sup> that is, the hardest donor atom of the dppmO ligand (the oxygen) is trans to the softer donor atom of the orthometalated group (the arylic carbon).

The reaction of 3c with other monodentate or bidentate ligands follows different trends. The reaction of 3c with PPh<sub>3</sub> (1:1 molar ratio) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature results in the formation of [Pd(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)-COCH<sub>2</sub>PPh<sub>3</sub>)(PPh<sub>3</sub>)(NCMe)](ClO<sub>4</sub>)<sub>2</sub> (14), even if the reaction is performed in the presence of an excess of PPh<sub>3</sub>. On the other hand, the reaction of **3c** with dppe or phen (1:1 molar ratio) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature affords the dicationic derivatives [Pd(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)- $COCH_2PPh_3)(L_2)](ClO_4)_2$  (L<sub>2</sub> = dppe **15**, phen **16**) in very good yields (see Scheme 4, path b). The analytical and spectroscopic data of complexes 14-16 are in good agreement with the proposed structures in Scheme 4 (complete assignment of the resonances in the <sup>1</sup>H NMR spectrum of 16 was carried out with the help of the <sup>1</sup>H-<sup>1</sup>H NOESY spectrum), and further characterization is provided by the determination of the crystal structure of complex 14.2CHCl<sub>3</sub>.

Crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a solution of **14** in CHCl<sub>3</sub>. A drawing of the organometallic cation is shown in Figure 1, relevant crystallographic parameters are given in Table 1, and selected bond distances and angles are collected in Table 2. The complex crystallizes in the triclinic space group  $P\overline{1}$  with Z = 2. Thus, although only one enantiomer is shown in Figure 1, the crystal as a whole is racemic. The palladium atom is located in a distorted square-planar environment, surrounded by the P atom of the PPh<sub>3</sub> ligand, the N atom of the NCMe ligand, and the two carbon atoms of the orthometalated ligand, one arylic [C(38)] and one ylidic [C(57)]. As was expected on the basis of the transphobic effect, the PPh<sub>3</sub> ligand is coordinated trans to the ylidic carbon. The Pd-C(aryl) bond distance [Pd - C(38) = 1.999(8) Å] is similar to those reported in the literature for this kind of bond,<sup>29</sup> as are the Pd-C(ylide) bond distance [Pd - $C(57) = 2.161(8) \text{ Å}]_{,2,5,7}$  the Pd-P bond distance [2.315-(2) Å],<sup>29</sup> and the Pd–N bond distance [2.091(7) Å].<sup>29</sup> Other internal structural parameters of the orthometalated ligand, the PPh<sub>3</sub> group, and the NCMe ligand are unremarkable.

The synthesis of complex **14** can be rationalized in the same way as was done for complexes **8** and **9**; that

<sup>(31)</sup> Pearson, R. G. Inorg. Chem. 1973, 12, 712.



**Figure 1.** Thermal ellipsoid plot of the organometallic [Pd- $(C_6H_4$ -2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>)(PPh<sub>3</sub>)(NCMe)]<sup>2+</sup> cation. Atoms are drawn at the 50% probability level.

Table 1.	<b>Crystal Data and Structure Refinement</b>				
for 14·2CHCl <sub>3</sub>					

empirical formula	$C_{61}H_{52}Cl_8NO_9P_3Pd$
fw	1425.95
temp	150(1) K
wavelength	0.710 73 Å
cryst system	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 9.6940(10)$ Å $\alpha = 79.150(10)^{\circ}$
	$b = 13.299(2)$ Å $\beta = 86.530(10)^{\circ}$
	$c = 25.154(3) \text{ Å}$ $\gamma = 73.900(10)^{\circ}$
volume	3059.9(7) Å <sup>3</sup>
Ζ	2
density (calcd)	1.548 Mg/m <sup>3</sup>
abs coeff	$0.788 \text{ mm}^{-1}$
<i>F</i> (000)	1448
cryst size	$0.26\times0.12\times0.09~mm$
$\theta$ range for data collection	$2.09-22.50^{\circ}$
index ranges	$0\leq h\leq 10,-13\leq k\leq 14,$
-	$-27 \leq l \leq 27$
reflns collected	8619
ind reflns	8008 ( $R_{\rm int} = 0.0574$ )
abs correction	$\psi$ -scan
max. and min. transmission	0.932 and 0.821
refinement method	full-matrix least-squares on $F^2$
no. of data/restrains/params	8008/0/748
goodness-of-fit on F <sup>2</sup> a	1.025
<i>R</i> indices $[I > 2\sigma(I)]^b$	R1 = 0.0617, wR2 = 0.1279
largest diff peak and hole	0.990 and $-1.819 \text{ e}\text{\AA}^{-3}$

<sup>*a*</sup> Goodness-of-fit =  $[\sum w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$ . <sup>*b*</sup> R1=  $\sum (|F_o| - |F_c|)/\sum |F_o|$ . wR2 =  $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ .

is, coordination of PPh<sub>3</sub> to the starting complex **3c** leaves the phenyl groups of the phosphine in close proximity to the ylidic fragments  $C(H)PPh_3$  and promotes the orthometalation in order to minimize steric repulsions. Regardless of where the phosphine attacks **3c**, only one isomer is obtained in the final product **14**, which is, as predicted by the *transphobic* effect, that containing PPh<sub>3</sub> trans to the ylidic carbon and cis to the arylic carbon (see the crystal structure of **14**). The synthesis of **15** and **16** under mild conditions provides strong evidence in favor of the importance of steric repulsions in the promotion of the orthometalation reaction. Both complexes are obtained by reaction of **3c** with chelating ligands which contain substituents on the donor atom and which, once coordinated, form five-membered rings.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 14·2CHCl<sub>3</sub>

	( 8	0	
Pd-C(38)	1.999(8)	Pd-N(1)	2.091(7)
Pd-C(57)	2.161(8)	Pd-P(1)	2.315(2)
P(2)-C(31)	1.766(8)	P(2)-C(19)	1.784(8)
P(2)-C(25)	1.795(8)	P(2)-C(59)	1.801(7)
P(3)-C(57)	1.764(7)	P(3)-C(43)	1.778(7)
P(3)-C(37)	1.801(8)	P(3)-C(49)	1.808(8)
C(37)-C(38)	1.405(11)	C(38)-C(39)	1.390(10)
N(1)-C(55)	1.129(10)	C(55)-C(56)	1.456(12)
C(57)-C(58)	1.456(11)	C(58)-O(9)	1.212(9)
C(58)-C(59)	1.533(10)		
C(38)-Pd-N(1)	173.3(3)	C(38)-Pd-C(57)	86.7(3)
N(1) - Pd - C(57)	88.4(3)	C(38) - Pd - P(1)	93.8(2)
N(1)-Pd-P(1)	90.59(19)	C(57) - Pd - P(1)	174.2(2)
N(1)-C(55)-C(56)	177.5(9)	C(58)-C(57)-P(3)	118.7(6)
C(58)-C(57)-Pd	107.2(5)	O(9) - C(58) - C(57)	124.9(7)
O(9)-C(58)-C(59)	119.5(7)	C(57)-C(58)-C(59	) 115.6(7)
C(58)-C(59)-P(2)	113.4(5)		

The fact that either an N-donor ligand or a P-donor ligand can promote the same reaction means that the nature of the donor atom does not have a decisive influence on the overall process. However, the fact that the dppm ligand does not promote orthometalation at room temperature (synthesis of 11), while dppe does under the same conditions (synthesis of 15), means that the ring size is critical. Thus, the phenyl groups on the P atoms and the ylidic units are "far apart" in 11 and the molecule is "stable" toward orthometalation, while in the case of dppe the increase in the bite angle of the ligand (average value 86°)<sup>32,33</sup> leaves the two groups in close proximity (similar to the case of PPh<sub>3</sub>), and the orthometalation can easily be induced, giving 15. The same reasoning applies to the synthesis of 16, although in this case the interaction must be between the ylidic groups and the  $C_2-H_{\alpha}$  groups adjacent to the nitrogen of the phen ligand.

It should be noted that the presence of large substituents on the donor atom of the incoming ligand is also important (for instance, two phenyl groups on the P atoms of dppe), since the absence of substituents on the donor atoms, even if they give a sufficient ring size to promote the orthometalation, could result in no orthometalation. We have a clear example of this in the reaction of 2c with Tlacac,<sup>8</sup> which results in the formation of  $[Pd\{[C(H)PPh_3]_2CO\}(acac-O,O')]ClO_4$  without contamination by other products. Thus, the combination of an appropriate ring size and large substituents on the donor atom are mandatory requirements for the induction of the orthometalation.

We have already mentioned that complex **3c** does not undergo internal metalation by refluxing in NCMe, but the corresponding orthometalated complex **17** can be obtained by treating **4c** with TlClO<sub>4</sub> (1:2 molar ratio) in NCMe, as indicated in Scheme 5.

The orthometalation can also be produced spontaneously, without thermal induction or addition of ligands. The dinuclear complex  $[Pd(\mu-OOCMe)\{[C(H)PPh_3]_2-CO\}]_2(ClO_4)_2$  (**18**)<sup>8</sup> evolves spontaneously in CH<sub>2</sub>Cl<sub>2</sub> at room temperature, resulting in the formation of  $[(C_6H_4-COCMe)]_2(ClO_4)_2$ 

<sup>(32)</sup> Oberhauser, W.; Bachmann, C.; Stampfl, T.; Haid, R.; Brüggeller, P. Polyhedron 1997, 16, 2827.

<sup>(33)</sup> Wu, B.; Zhang, W.; Huang, X.; Wu, X.; Yu, S. *Polyhedron* **1997**, *16*, 801.



 $2-PPh_2C(H)COCH_2PPh_3)Pd(\mu-OOCMe)_2Pd\{[C(H)PPh_3]_2-CO\}](ClO_4)_2$  (**19**) in quantitative yield (see eq 2). The



characterization of this compound has been carried out on the basis of its analytical and spectroscopic data. The <sup>1</sup>H NMR spectrum of **19** shows characteristic resonances for the CH<sub>2</sub>PPh<sub>3</sub> group (5.74 ppm, ddd; 5.50, dd) and for the ylidic C(H) proton in the ring (4.70, pseudo triplet). In addition, two doublets at 2.99 and 2.85 ppm reveal the presence of the bis(ylide) ligand. The resonances attributed to the acetate ligands appear at 1.45 and 0.60 ppm, at unusually high fields, probably due to the anisotropic shielding of the methyl moieties by the phenyl groups. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows the presence of two AB spin systems, one of them (25.74 and 25.54 ppm) assigned to the bis(ylide) group and the other one (30.14 and 22.23 ppm) to the orthometalated ligand. These assignments were confirmed by measurement of the  ${}^{1}H{}^{31}P{}$  spectra and selective irradiation of all P resonances. More structural information can be

obtained from the <sup>1</sup>H-<sup>1</sup>H NOESY spectrum of **19**. In this spectrum, a strong NOE interaction is observed between the resonance at 2.99 ppm and that at 4.70 ppm, showing the proximity of one ylidic proton of the chelating bis(ylide) and the ylidic proton in the ring of the orthometalated ligand. This proximity suggests that the stereochemistry of 19 is that shown in eq 2. The acetate ligands adopt an "open-book" structure, bridging the two palladium atoms, and there is a bis(ylide) ligand chelating one palladium and an orthometalated ligand chelating the other palladium. In additon, the hydrogen atoms of the bis(ylide) ligand should be directed to the inner side of the complex and the bulky PPh<sub>3</sub> groups to the outer side. In the orthometalated ligand, the ylidic proton is also directed inward and the bulky COCH2-PPh<sub>3</sub> group outward, resulting in minimization of the steric repulsions between the bulky substituents. The NOESY spectrum also shows a NOE interaction between the highest-field acetate resonance (0.60 ppm) and the phenyl groups, confirming the suggestion of the anisotropic shielding mentioned earlier.

The transformation of **18** to **19** has two striking characteristics. The first is the spontaneity of the reaction, since in this case neither incoming ligands nor heating is required to promote the orthometalation. The steric crowding in **18**, which can be considered as the kinetic isomer in the reaction of  $Pd(OAc)_2$  with  $[Ph_3P=C(H)COCH_2PPh_3]ClO_4$ ,<sup>8</sup> appears to be the sole driving force for the orthometalation. The second noteworthy feature is that the thermodynamic isomer **19** contains only one orthometalated group. We have attempted the orthometalation of the remaining bis(ylide) ligand in **19** by refluxing in THF or NCMe, but in all cases the dimer **19** was recovered. Thus, **19** is remarkably stable and does not show any tendency to further transform.

Other reactions were attempted for the synthesis of the expected acetate-bridging orthometalated compound. The most obvious of them is the replacement of the chloride-bridging ligands in **4c** by acetate ligands through the reaction of **4c** with Ag(OOCCH<sub>3</sub>) in a noncoordinating solvent such as CH<sub>2</sub>Cl<sub>2</sub>. Surprisingly, the reaction product contains complex **19** exclusively; thus at some point in the reaction one of the orthometalated ligands has reverted to the bis(ylide); that is, we have induced the reversibility of the cyclometalation.



We propose the reaction pathway shown in Scheme 6 to explain the reversibility of the orthometalation. In a first step, the reaction of 4c with silver acetate in a noncoordinating solvent would produce the precipitation of AgCl and the generation of two vacant sites which could immediately be occupied by the acetate ligand (A). The proximity of the acetate ligands and the phosphonium moiety could result in an interaction between one oxygen and the H atoms of the  $CH_2P$  group and subsequent deprotonation of the latter, giving a free ylidic fragment and acetic acid. The coordination of the ylide generated and protonation of the C(aryl)–Pd bond results in the formation of species **B**, which can be recombinated with **A** to give complex **19**.

As a general conclusion, the orthometalation of the bis(ylide) ligand [C(H)PPh<sub>3</sub>]<sub>2</sub>CO can be induced by addition of bulky ligands under very mild conditions, this reaction being controlled by steric factors. Moreover, if the steric crowding in the starting compound is important, the orthometalation can occur spontaneously. Another important conclusion is that the orthometalation can be reversed through an intermediate in which a second ylide is generated. We have now focused our efforts on the stabilization of compounds in which the orthometalated phosphonium ligand is transformed into a new group in which the orthometalated unit is preserved and which also contains an ylide fragment.

### **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 ref 34.

**General Procedures.** Solvents were dried and distilled under nitrogen before use: diethyl ether and tetrahydrofuran over benzophenone ketyl, dichloromethane and chloroform over  $P_2O_5$ , acetonitrile over CaH<sub>2</sub>, methanol over magnesium and *n*-hexane and toluene over sodium. Elemental analyses were carried out on a Perkin-Elmer 240-B microanalyzer. Infrared spectra (4000-200 cm<sup>-1</sup>) were recorded on a Perkin-Elmer 883 infrared spectrophotometer from Nujol mulls between polyethylene sheets. 1H (300.13 MHz), 13C{1H} (75.47 MHz), and <sup>31</sup>P{<sup>1</sup>H} (121.49 MHz) NMR spectra were recorded in CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub> solutions at room temperature (unless otherwise stated) on a Bruker ARX-300 spectrometer; <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} were referenced using the solvent signal as internal standard, and  ${}^{31}P{}^{1}H{}$  was externally referenced to  $H_3PO_4$  (85%). The two-dimensional <sup>1</sup>H-<sup>1</sup>H NOESY experiments for complexes 9, 16, and 19 were performed at a measuring frequency of 300.13 MHz. The data were acquired in a phase-sensitive mode into a 512  $\times$  1024 matrix and then transformed into 1024  $\times$ 1024 points using a sine window in each dimension. The mixing time was 400 ms. Mass spectra (positive ion FAB) were recorded on a V. G. Autospec spectrometer from CH<sub>2</sub>Cl<sub>2</sub> solutions. Electrical conductivity measurements were performed in acetone solutions with concentrations of about 5 imes10<sup>-4</sup> M with a Philips PW 9509 conductivity cell.

The starting bis(ylide) complexes *cis*-PdCl<sub>2</sub>[{C(H)PPh<sub>3</sub>}<sub>2</sub>CO] (**1c**), {Pd( $\mu$ -Cl)[{C(H)PPh<sub>3</sub>}<sub>2</sub>CO]}<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (**2c**), {Pd[{C(H)PPh<sub>3</sub>}<sub>2</sub>-CO](NCMe)<sub>2</sub>}(ClO<sub>4</sub>)<sub>2</sub> (**3c**), and {Pd( $\mu$ -OAc)[{C(H)PPh<sub>3</sub>}<sub>2</sub>CO]}<sub>2</sub>-(ClO<sub>4</sub>)<sub>2</sub> (**18**) were prepared according to published methods.<sup>8</sup>

**Preparation of Phosphonium Salts.** [Et<sub>2</sub>PhPCH<sub>2</sub>COCH<sub>2</sub>-**PPhEt**<sub>2</sub>]Cl<sub>2</sub>. To a solution of ClCH<sub>2</sub>COCH<sub>2</sub>Cl (2.000 g, 15.75 mmol) in 35 mL of deoxygenated CHCl<sub>3</sub> under nitrogen was added PPhEt<sub>2</sub> (6.86 mL, 39.4 mmol) in one portion. After an initial period in which the mixture warmed gently, it was allowed to reach room temperature, then refluxed for 1 h, and again stirred at room temperature overnight. The resulting solution was added to 200 mL of an Et<sub>2</sub>O/CHCl<sub>3</sub> mixture (10: 1). An oily material was formed, which was subjected to vigorous stirring until a white solid was obtained. This solid was filtered, washed with additional portions of a mixture of Et<sub>2</sub>O/CHCl<sub>3</sub> (3  $\times$  10 mL), and dried in vacuo. Obtained: 6.115 g (84% yield). The product crystallizes as a monohydrate.

Anal. Calcd. for C<sub>23</sub>H<sub>34</sub>Cl<sub>2</sub>OP<sub>2</sub>·OH<sub>2</sub> (477.39 g/mol): C, 57.86; H, 7.60. Found: C, 57.42; H, 7.59. IR ( $\nu$ , cm<sup>-1</sup>): 1714 ( $\nu$ <sub>CO</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.90 (m, 2H, H<sub>0</sub>, Ph), 7.57 (m, 3H, H<sub>m</sub> + H<sub>p</sub>, Ph), 5.51 (d, 2H, CH<sub>2</sub>, <sup>2</sup>J<sub>P-H</sub> = 9 Hz), 2.74 (m, 4H, CH<sub>2</sub>CH<sub>3</sub>), 1.19 (dt, 6H, CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J<sub>P-H</sub> = 20 Hz, <sup>3</sup>J<sub>H-H</sub> = 7 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  30.52. **[EtPh<sub>2</sub>PCH<sub>2</sub>COCH<sub>2</sub>PPh<sub>2</sub>Et]Cl<sub>2</sub>.** To a solution of ClCH<sub>2</sub>-COCH<sub>2</sub>Cl (2.000 g, 15.75 mmol) in 35 mL of deoxygenated CHCl<sub>3</sub> under nitrogen was added PPh<sub>2</sub>Et (8.11 mL, 39.4 mmol) in one portion. The resulting mixture was refluxed for 3 h and stirred overnight at room temperature. The resulting solution was added to 200 mL of anhydrous Et<sub>2</sub>O. An oily material was formed, which was subjected to vigorous stirring until a white solid was obtained. This solid was filtered, washed with additional portions of Et<sub>2</sub>O (3  $\times$  10 mL), and dried in vacuo. Obtained: 7.285 g (83% yield). The product crystallizes as a dihydrate.

Anal. Calcd for  $C_{31}H_{34}Cl_2OP_2 \cdot 2OH_2$  (591.47 g/mol): C, 62.95; H, 6.47. Found: C, 63.35; H, 5.99. IR ( $\nu$ , cm<sup>-1</sup>): 1716 ( $\nu_{CO}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.85 (m, 4H, H<sub>o</sub>, Ph), 7.60 (m, 6H, H<sub>m</sub> + H<sub>p</sub>, Ph), 6.02 (s, br, 2H, CH<sub>2</sub>), 3.17 (m, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.20 (br, 3H, CH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  25.12.

Cl<sub>2</sub>Pd{[C(H)PPhEt<sub>2</sub>]<sub>2</sub>CO} (1a). To a solution of Pd(OAc)<sub>2</sub> (0.3000 g, 1.336 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (35 mL) was added [Et<sub>2</sub>-PhPCH<sub>2</sub>COCH<sub>2</sub>PPhEt<sub>2</sub>]Cl<sub>2</sub> (0.614 g, 1.336 mmol). The initial orange solution evolved to give a yellow solution, which was stirred at room temperature for 4 h. The solvent was then evaporated to dryness and the residue treated with Et<sub>2</sub>O (30 mL). Continuous stirring gave 1a as a yellow solid, which was filtered and air-dried. Obtained: 0.637 g (85% yield). Crude 1a was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O, giving deep yellow crystals of 1a·0.75CH<sub>2</sub>Cl<sub>2</sub>, which were used in analytical and spectroscopic measurements. The amount of CH<sub>2</sub>Cl<sub>2</sub> of crystallization was determined by <sup>1</sup>H NMR integration.

Anal. Calcd for  $C_{23}H_{32}Cl_2OP_2Pd \cdot 0.75CH_2Cl_2$  (627.46 g/mol): C, 45.46; H, 5.38. Found: C, 45.49; H, 4.97. MS [*m/z*, %]: 529 [(M - Cl)<sup>+</sup>, 35%]. IR ( $\nu$ , cm<sup>-1</sup>): 1599 ( $\nu_{CO}$ ); 277, 260 ( $\nu_{Pd-Cl}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.92 (m, 2H, H<sub>o</sub>, Ph), 7.60 (m, 3H, H<sub>m</sub> + H<sub>p</sub>, Ph), 3.25 (d, 1H, CH, <sup>2</sup>J<sub>P-H</sub> = 6 Hz), 2.98 (m, 2H, CH<sub>2</sub>CH<sub>3</sub>), 2.76 (m, 1H, CH<sub>2</sub>CH<sub>3</sub>), 2.63 (m, 1H, CH<sub>2</sub>CH<sub>3</sub>), 1.21 (dt, 3H, CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J<sub>P-H</sub> = 19 Hz, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz), 1.14 (dt, 3H, CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J<sub>P-H</sub> = 19 Hz, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  33.82.

 $Cl_2Pd\{[C(H)PPh_2Et]_2CO\}$  (1b). Complex 1b was obtained as a yellow solid similarly to 1a starting from Pd(OAc)\_2 (0.300 g, 1.336 mmol) and the phosphonium salt [EtPh\_2PCH\_2COCH\_2PPh\_2Et]Cl\_2 (0.742 g, 1.336 mmol). Obtained: 0.720 g (82% yield). Crude 1b was recrystallized from CH\_2Cl\_2/Et\_2O giving deep yellow crystals of  $1b\cdot 0.6CH_2Cl_2$ , which were used in analytical and spectroscopic measurements. The amount of CH\_2Cl\_2 of crystallization was determined by <sup>1</sup>H NMR integration.

Anal. Calcd for C<sub>31</sub>H<sub>32</sub>Cl<sub>2</sub>OP<sub>2</sub>Pd·0.6CH<sub>2</sub>Cl<sub>2</sub> (710.81 g/mol): C, 53.39; H, 4.70. Found: C, 53.33; H, 4.39. MS [*m*/*z*, %]: 625 [(M - Cl)<sup>+</sup>, 28]. IR ( $\nu$ , cm<sup>-1</sup>): 1604 ( $\nu$ <sub>CO</sub>); 286, 274 ( $\nu$ <sub>Pd-Cl</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.95 (m, 2H, Ph), 7.79–7.52 (m, 6H, Ph), 7.40 (m, 2H, Ph), 3.61 (d, 1H, CH, <sup>2</sup>J<sub>P-H</sub> = 6.6 Hz), 3.39 (m, 1H, CH<sub>2</sub>CH<sub>3</sub>), 2.87 (m, 1H, CH<sub>2</sub>CH<sub>3</sub>), 1.11 (dt, 3H, CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J<sub>P-H</sub> = 19 Hz, <sup>3</sup>J<sub>H-H</sub> = 7.5 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  30.11.

 $[Pd(\mu-Cl){[C(H)PPhEt_2]_2CO}]_2(ClO_4)_2$  (2a). To a solution of 1a (0.300 g, 0.532 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) was added AgClO<sub>4</sub> (0.111 g, 0.535 mmol). This suspension was stirred at room temperature for 4 h and filtered. The resulting orange solution was evaporated to dryness and the residue treated with Et<sub>2</sub>O (30 mL), giving 2a as a yellow solid, which was filtered and air-dried. Obtained: 0.279 g (83% yield).

Anal. Calcd for  $C_{46}H_{64}Cl_4O_{10}P_4Pd_2$  (1255.52 g/mol): C, 44.00; H, 5.14. Found: C, 43.67; H, 4.88. IR ( $\nu$ , cm<sup>-1</sup>): 1614 ( $\nu_{CO}$ ); 270, 248 ( $\nu_{Pd-Cl}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.81 (m, 2H, H<sub>o</sub>, Ph), 7.61 (m, 1H, H<sub>p</sub>, Ph), 7.52 (m, 2H, H<sub>m</sub>, Ph), 3.66 (br, 1H, CH), 2.49 (m, 4H, CH<sub>2</sub>CH<sub>3</sub>), 1.17 (br m, 6H, CH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  33.24.

 $[Pd(\mu-Cl){[C(H)PPh_2Et]_2CO}]_2(ClO_4)_2$  (2b). Complex 2b was obtained as a yellow solid similarly to 2a starting from 1b (0.300 g, 0.455 mmol) and AgClO<sub>4</sub> (0.095 g, 0.46 mmol). Obtained: 0.292 g (89% yield).

Anal. Calcd for  $C_{62}H_{64}Cl_4O_{10}P_4Pd_2$  (1447.69 g/mol): C, 51.44; H, 4.46. Found: C, 50.64; H, 3.84. IR  $(\nu,\,cm^{-1})$ : 1621  $(\nu_{CO})$ .  $^{1}H$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.87–7.48 (m, 10H, Ph), 3.92 (d, 1H, CH,  $^2J_{P-H}$  = 3.7 Hz), 2.54 (m, 2H, CH\_2CH\_3), 1.08 (br m, 3H, CH<sub>2</sub>CH\_3).  $^{31}P\{^{1}H\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  28.81.

[Pd(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>)( $\mu$ -Cl)]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (4c). A suspension of complex 2c (0.200 g, 0.122 mmol) in NCMe (20 mL) was refluxed for 8 h. During this time, the initial yellow suspension gradually dissolved and gave an orange solution. Once cooled, this solution was evaporated to small volume (3 mL). By addition of Et<sub>2</sub>O (40 mL) and continuous stirring 4c was obtained as an orange solid, which was filtered, washed with additional Et<sub>2</sub>O (20 mL), air-dried, and identified spectroscopically as a mixture of the diastereomers (*RR/SS*) and (*RS/SR*) in molar ratio 1.77:1 (major:minor). Obtained: 0.188 g (94% yield).

Anal. Calcd for C<sub>78</sub>H<sub>64</sub>Cl<sub>4</sub>O<sub>10</sub>P<sub>4</sub>Pd<sub>2</sub> (1639.87 g/mol): C, 57.13; H, 3.93. Found: C, 57.17; H, 3.99. MS [m/z, %]: 1541 [(M<sub>2</sub> ClO<sub>4</sub>)<sup>+</sup>, 25]. IR ( $\nu$ , cm<sup>-1</sup>): 1648 ( $\nu$ <sub>CO</sub>), 278 ( $\nu$ <sub>Pd-Cl</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>-Cl<sub>2</sub>):  $\delta$  7.78–7.48 (m, Ph), 7.14–7.12 (m, C<sub>6</sub>H<sub>4</sub>), 5.30 (dd, CH<sub>2</sub>P, maj), 5.21 (dd, CH<sub>2</sub>P, min), 4.98 (dd, CH<sub>2</sub>P, min,  ${}^{2}J_{H-H} = 17.3$ Hz,  ${}^{2}J_{P-H} = 14.1$  Hz), 4.78 (pseudo t, CH<sub>2</sub>P, maj,  ${}^{2}J_{H-H} \simeq {}^{2}J_{P-H}$ = 15 Hz), 4.58 (dd, CH, min,  ${}^{2}J_{P-H}$  = 3.9 Hz,  ${}^{4}J_{P-H}$  = 2.5 Hz), 4.52 (dd, CH, maj,  ${}^{2}J_{P-H} = 4.3$  Hz,  ${}^{4}J_{P-H} = 2.7$  Hz).  ${}^{31}P{}^{1}H{}$ NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  22.84 (d, min, C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>, <sup>4</sup>J<sub>P-P</sub> = 7 Hz), 21.68 (d, maj,  $C_6H_4PPh_2$ ,  ${}^4J_{P-P} = 9$  Hz), 21.21 (d, maj,  $CH_2PPh_3$ ), 21.14 (d, min, CH<sub>2</sub>PPh<sub>3</sub>).  ${}^{13}C{}^{1}H$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  190.87 (t, CO, min,  ${}^{2}J_{P-C} = 7$  Hz), 190.36 (t, CO, maj,  ${}^{2}J_{P-C} = 6.4$  Hz), 157.58 (d, C<sub>1</sub>, C<sub>6</sub>H<sub>4</sub>, maj,  ${}^{2}J_{P-C} = 18.8$  Hz), 157.49 (d, C<sub>1</sub>, C<sub>6</sub>H<sub>4</sub>, min,  ${}^{2}J_{P-C} = 18.8$  Hz), 137–120 (Ph + C<sub>6</sub>H<sub>4</sub>, both isomers), 43.76 (br d, CH<sub>2</sub>, min,  ${}^{1}J_{P-C} =$  49.2 Hz), 38.85 (dd, CH<sub>2</sub>, maj,  ${}^{1}J_{P-C} = 57.5$  Hz,  ${}^{3}J_{P-C} = 10.5$  Hz), 31.35 (dd, CH-ylide, maj,  ${}^{1}J_{P-C} = 66.8$  Hz,  ${}^{3}J_{P-C} = 8.8$  Hz).

Attempts at Orthometalation of Complexes 2a and 2b. Complex 2a was refluxed in NCMe under the same conditions as those described for 2c. At the end of the reaction and after the usual workup, the NMR spectra of the solid obtained showed that the starting product 2a had been recovered in almost quantitative yield. In the same way, complex 2b was refluxed in NCMe for 8 h. At the end of the reaction a mixture of 2b and 4b (three diastereoisomers) was identified by <sup>31</sup>P-{<sup>1</sup>H} NMR spectroscopy. The resonances attributed to 4b are as follows (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  33.39 (d, <sup>4</sup>J<sub>P-P</sub> = 6.5 Hz, C<sub>6</sub>H<sub>4</sub>-2-PPhEt), 33.15 (d, <sup>4</sup>J<sub>P-P</sub> = 6 Hz, C<sub>6</sub>H<sub>4</sub>-2-PPhEt), 32.07 (d, <sup>4</sup>J<sub>P-P</sub> = 7 Hz, C<sub>6</sub>H<sub>4</sub>-2-PPhEt), 26.67 (d, CH<sub>2</sub>PPh<sub>3</sub>), 26.51 (d, CH<sub>2</sub>PPh<sub>3</sub>), 26.23 (d, CH<sub>2</sub>PPh<sub>3</sub>).

NMR Experiments. Characterization of the Equilibria. (a) The NMR spectra of 2c in NCCD<sub>3</sub> show resonances corresponding exclusively to the cationic monomer [PdCl{[C(H)-PPh<sub>3</sub>]<sub>2</sub>CO}(NCCD<sub>3</sub>)]<sup>+</sup>ClO<sub>4</sub><sup>-</sup>. <sup>1</sup>H: δ 7.76-7.51 (m, 30 H, Ph), 4.16 (d, 1H, CH-ylide,  ${}^{2}J_{P-H} = 6$  Hz), 4.12 (d, 1H, CH-ylide,  ${}^{2}J_{P-H} = 3.3 \text{ Hz}$ ).  ${}^{31}P{}^{1}H{}$ :  $\delta 26.30 \text{ (d, 1P, } {}^{4}J_{P-P} = 10 \text{ Hz}), 24.90 \text{ Hz}$ (d, 1P). (b) The NMR spectra of 1c in NCCD<sub>3</sub> show resonances corresponding to a mixture of 1c and the cationic monomer  $[PdCl{[C(H)PPh_3]_2CO}(NCCD_3)]^+ClO_4^-$  in molar ratio (1c: cation) = 2.6:1. The resonances attributed to 1c are <sup>1</sup>H,  $\delta$  3.92 (d, 1H, CH-ylide,  ${}^{2}J_{P-H} = 7.5 \text{ Hz}$ );  ${}^{31}P{}^{1}H$ },  $\delta$  26.31 (s). When this mixture was heated to 313 K, the molar ratio (1c:cation) changed to 3.9:1. (c) The addition of LiCl to a solution of 2c in NCCD<sub>3</sub> and subsequent measurement of the NMR spectra showed the presence of the mixture 1c:cation in molar ratio (1c:cation) = 2.6:1.

**Orthometalation Reactions.** The NCCD<sub>3</sub> solutions (a) and (b) described above were heated at a temperature of 80 °C for 8 h, and after cooling, the <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were measured in the same solvent. Experiment (a) showed a conversion of 100% of the starting product **2c** into the monomer [Pd(C<sub>6</sub>H<sub>4</sub>-2·PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>)Cl(NCCD<sub>3</sub>)]<sup>+</sup>. The resonances attributed to this compound are <sup>1</sup>H,  $\delta$  7.73–7.51 (m, 25H, Ph), 7.36–7.17 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 6.01 (dd, 1H, CH<sub>2</sub>PPh<sub>3</sub>, <sup>2</sup>J<sub>H-H</sub> = 16.5 Hz, <sup>2</sup>J<sub>P-H</sub> = 10.2 Hz), 4.62 (pseudo t, 1H, CH<sub>2</sub>-

PPh<sub>3</sub>,  ${}^{2}J_{H-H} \cong {}^{2}J_{P-H} = 16$  Hz), 4.56 (d, 1H, CH-ylide,  ${}^{2}J_{P-H} = 4.2$  Hz);  ${}^{31}P{}^{1}H$  NMR,  $\delta$  25.29 (d,  ${}^{4}J_{P-P} = 6.2$  Hz), 22.33 (d). Experiment (b) also showed a 100% conversion of the starting product **1c** into a compound with the same pattern of resonances as has the monomer [Pd(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>-PPh<sub>3</sub>)Cl(NCCD<sub>3</sub>)]<sup>+</sup> but slightly shifted, probably due to the presence of a fast equilibrium with **5**.

[Pd(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>)Cl<sub>2</sub>] (5). To a solution of 4c (0.553 g, 0.337 mmol) in acetone (20 mL) was added an excess of LiCl (0.200 g, 4.72 mmol), and the resulting solution was stirred at room temperature for 12 h. During this time complex 5 precipitated as a yellow solid, which was filtered, washed with small portions of acetone (5 mL), and air-dried. Obtained: 0.220 g (43% yield). The washings were evaporated to dryness and treated with MeOH (10 mL), giving a second crop of 5. Obtained: 0.088 g (net yield 61%).

Anal. Calcd for  $C_{39}H_{32}Cl_2OP_2Pd$  (755.94 g/mol): C, 61.97; H, 4.27. Found: C, 61.94; H, 4.17. IR ( $\nu$ , cm<sup>-1</sup>): 1636 ( $\nu_{CO}$ ), 277 ( $\nu_{Pd-Cl}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.00–7.43 (m, 26H, C<sub>6</sub>H<sub>4</sub> + Ph), 7.02 (m, 3H, C<sub>6</sub>H<sub>4</sub>), 6.49 (br t, 1H, CH<sub>2</sub>P), 4.64 (br s, 1H, CH-ylide), 4.37 (pseudo t, 1H, CH<sub>2</sub>P, <sup>2</sup>J<sub>H-H</sub>  $\cong$  <sup>2</sup>J<sub>P-H</sub> = 15.3 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  23.35 (d), 20.75 (d, <sup>4</sup>J<sub>P-P</sub> = 7.3 Hz).

 $[Pd(C_6H_4-2-PPh_2C(H)COCH_2PPh_3)Cl(py)](ClO_4)$  (6). A solution of  $[PdCl\{[C(H)PPh_3]_2CO\}(py)]ClO_4$  (0.243 g, 0.270 mmol) in NCMe (20 mL) was refluxed for 8 h. After cooling, this solution was evaporated to small volume (3 mL). By addition of Et<sub>2</sub>O (40 mL) and continuous stirring **6** was obtained as a white solid, which was filtered, washed with additional Et<sub>2</sub>O (20 mL), and air-dried. Obtained: 0.160 g (67% yield).

Anal. Calcd for  $C_{44}H_{37}Cl_2NO_5P_2Pd$  (899.04 g/mol): C, 58.78; H, 4.15; N, 1.56. Found: C, 58.31; H, 4.19; N, 1.30. MS [*m*/*z*, %]: 798 [M<sup>+</sup>, 15]. IR ( $\nu$ , cm<sup>-1</sup>): 1645 ( $\nu_{CO}$ ), 278 ( $\nu_{Pd-Cl}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.04 (d, 2H, H<sub>2</sub> + H<sub>6</sub>, py, <sup>3</sup>*J*<sub>H-H</sub> = 5.1 Hz), 7.83–7.43 (m, 26H, Ph + H<sub>4</sub> (py)), 7.23 (m, 2H, H<sub>3</sub> + H<sub>5</sub>, py), 7.15–6.96 (m, 3H, C<sub>6</sub>H<sub>4</sub>), 6.23 (d, 1H, H<sub>6</sub>, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>*J*<sub>H-H</sub> = 7.2 Hz), 6.12 (dd, 1H, CH<sub>2</sub>P, <sup>2</sup>*J*<sub>H-H</sub> = 15.3 Hz, <sup>2</sup>*J*<sub>P-H</sub> = 10.5 Hz), 4.71 (pseudo t, CH<sub>2</sub>P, 1H, <sup>2</sup>*J*<sub>H-H</sub>  $\cong$  <sup>2</sup>*J*<sub>P-H</sub> = 16 Hz), 4.58 (dd, 1H, CH-ylide, <sup>2</sup>*J*<sub>P-H</sub> = 6 Hz, <sup>4</sup>*J*<sub>P-H</sub> = 2.7 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  23.17 (d, <sup>4</sup>*J*<sub>P-P</sub> = 6.2 Hz), 21.42 (d).

 $\label{eq:constraint} \begin{array}{l} \mbox{Pd}(C_6H_4\mbox{-}2\mbox{-}PPh_2C(H)COCH_2PPh_3)Cl(3,5\mbox{-}lutidine)](Cl-O_4) (7). Complex 7 was obtained similarly to 6 starting from [PdCl{[C(H)PPh_3]_2CO}(3,5\mbox{-}lutidine)]ClO_4 (0.339 g, 0.365 mmol). Obtained: 0.270 g (82% yield). \end{array}$ 

Anal. Calcd for C<sub>46</sub>H<sub>41</sub>Cl<sub>2</sub>NO<sub>5</sub>P<sub>2</sub>Pd (927.09 g/mol): C, 59.59; H, 4.46; N, 1.51. Found: C, 59.45; H, 4.14; N, 1.75. MS [*m/z*, %]: 826 [M<sup>+</sup>, 20]. IR ( $\nu$ , cm<sup>-1</sup>): 1647 ( $\nu$ <sub>CO</sub>), 263 ( $\nu$ <sub>Pd-Cl</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.93–7.39 (m, 28 H, Ph + NC<sub>5</sub>H<sub>3</sub>), 7.18–7.04 (m, 3H, C<sub>6</sub>H<sub>4</sub>), 6.33 (d, 1H, H<sub>6</sub>, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>*J*<sub>H-H</sub> = 7.5 Hz), 6.09 (dd, 1H, CH<sub>2</sub>P, <sup>2</sup>*J*<sub>H-H</sub> = 16 Hz, <sup>2</sup>*J*<sub>P-H</sub> = 10.5 Hz), 4.51 (dd, 1H, CH-ylide, <sup>2</sup>*J*<sub>P-H</sub> = 6.6 Hz, <sup>4</sup>*J*<sub>P-H</sub> = 2.4 Hz), 4.44 (dd, CH<sub>2</sub>P, 1H, <sup>2</sup>*J*<sub>P-H</sub> = 14 Hz), 2.18 (s, 6H, Me). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  22.76 (d, <sup>4</sup>*J*<sub>P-P</sub> = 6.2 Hz), 21.19 (d).

[Pd(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>)Cl(PPh<sub>3</sub>)](ClO<sub>4</sub>) (8). To a solution of complex 2c (0.186 g, 0.113 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added PPh<sub>3</sub> (0.059 g, 0.23 mmol), and the resulting solution was stirred for 6 h at room temperature. The solvent was evaporated to dryness and the residue treated with MeOH (10 mL), giving 8 as a white solid, which was filtered, washed with additional MeOH (5 mL), and Et<sub>2</sub>O (20 mL), and air-dried. Obtained: 0.140 g (56% yield). Recrystallization of 8 from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O gave colorless crystals of 8·0.5CH<sub>2</sub>Cl<sub>2</sub>, which were used for analytical and spectroscopic measurements. The amount of CH<sub>2</sub>Cl<sub>2</sub> was determined by <sup>1</sup>H NMR integration.

Anal. Calcd for  $C_{57}H_{47}Cl_2O_5P_3Pd \cdot 0.5CH_2Cl_2$  (1124.69 g/mol): C, 61.40; H, 4.30. Found: C, 61.33; H, 4.20. MS [*m*/*z*, %]: 981 [M<sup>+</sup>, 100]. IR ( $\nu$ , cm<sup>-1</sup>): 1628 ( $\nu$ <sub>CO</sub>), 270 ( $\nu$ <sub>Pd-Cl</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.79–7.15 (m, 40H, Ph), 7.03 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 6.85 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 6.55 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 5.86 (dd, 1H, CH<sub>2</sub>P, <sup>2</sup>J<sub>H-H</sub> = 17.1 Hz, <sup>2</sup>J<sub>P-H</sub> = 11.4 Hz), 5.00 (td, 1H, CH-ylide, <sup>2</sup>J<sub>P-H</sub>)

 $= {}^{3}J_{P-H} = 8.2 \text{ Hz}, {}^{4}J_{P-H} = 1.6 \text{ Hz}), 4.80 \text{ (dd, CH}_{2}P, 1H, {}^{2}J_{P-H} \\ = 13.3 \text{ Hz}), {}^{31}P\{{}^{1}H\} \text{ NMR (CD}_{2}Cl_{2}); \delta 31.60 \text{ (d, Pd}-PPh_{3}, {}^{3}J_{P-P} \\ = 13.8 \text{ Hz}), 21.00 \text{ (d, CH}_{2}PPh_{3}, {}^{4}J_{P-P} = 7.8 \text{ Hz}), 17.02 \text{ (dd, } \\ C_{6}H_{4}\text{-}2\text{-}PPh_{2}). {}^{13}C\{{}^{1}H\} \text{ NMR (CDCl}_{3}) \text{ (the carbonyl and ylidic carbons were not observed): } \delta 163.86 \text{ (d, C}_{1}, C_{6}H_{4}, {}^{2}J_{P-C} = 20 \\ \text{Hz}), 138.87, 131.12, 129.62, 129.14, 124.17 \text{ (C}_{6}H_{4}), 134-127 \\ \text{ (Ph), } 125.23 \text{ (d, } C_{ipso}, Ph, {}^{1}J_{P-C} = 90 \text{ Hz}), 118.66 \text{ (d, } C_{ipso}, Ph, \\ {}^{1}J_{P-C} = 89 \text{ Hz}), 37.93 \text{ (dd, CH}_{2}, {}^{1}J_{P-C} = 56 \text{ Hz}, {}^{3}J_{P-C} = 14 \text{ Hz}).$ 

[Pd(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>)Cl(PPhMe<sub>2</sub>)](ClO<sub>4</sub>) (9). Complex 9 was obtained similarly to 8 starting from 2c (0.442 g, 0.269 mmol) and PPhMe<sub>2</sub> (76  $\mu$ L, 0.54 mmol). Obtained: 0.372 g (72% yield).

Anal. Calcd for C<sub>47</sub>H<sub>43</sub>Cl<sub>2</sub>O<sub>5</sub>P<sub>3</sub>Pd (958.08 g/mol): C, 58.92; H, 4.52. Found: C, 58.85; H, 4.46. MS [*m*/*z*, %]: 857 [M<sup>+</sup>, 100]. IR ( $\nu$ , cm<sup>-1</sup>): 1627 ( $\nu$ <sub>CO</sub>), 257 ( $\nu$ <sub>Pd-Cl</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.83–7.33 (m, 30 H, Ph), 7.14–6.96 (m, 3H, C<sub>6</sub>H<sub>4</sub>), 6.82 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 5.79 (dd, 1H, CH<sub>2</sub>P, <sup>2</sup>J<sub>H-H</sub> = 17.1 Hz, <sup>2</sup>J<sub>P-H</sub> = 11.1 Hz), 4.76 (td, 1H, CH-ylide, <sup>2</sup>J<sub>P-H</sub> = <sup>3</sup>J<sub>P-H</sub> = 8.7 Hz, <sup>4</sup>J<sub>P-H</sub> = 2.3 Hz), 4.63 (dd, CH<sub>2</sub>P, 1H, <sup>2</sup>J<sub>P-H</sub> = 13.8 Hz), 1.57 (d, CH<sub>3</sub>, 3H, <sup>2</sup>J<sub>P-H</sub> = 10.5 Hz), 1.37 (d, CH<sub>3</sub>, 3H, <sup>2</sup>J<sub>P-H</sub> = 10.1 Hz). <sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  21.22 (d, CH<sub>2</sub>PPh<sub>3</sub>, <sup>4</sup>J<sub>P-P</sub> = 7.5 Hz), 15.13 (dd, C<sub>6</sub>H<sub>4</sub>-2- PPh<sub>2</sub>), 0.95 (d, Pd-PPhMe<sub>2</sub>, <sup>3</sup>J<sub>P-P</sub> = 13.7 Hz).

[Pd{[CH(PPh<sub>3</sub>)]<sub>2</sub>CO}(py)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (10). To a solution of complex **3c** (0.151 g, 0.156 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added pyridine (51  $\mu$ L, 0.63 mmol), and the resulting solution was stirred for 1 h at room temperature. The solvent was evaporated to dryness and the residue treated with Et<sub>2</sub>O (10 mL), giving **10** as a white solid, which was filtered, washed with Et<sub>2</sub>O (20 mL), and air-dried. Obtained: 0.110 g (68% yield).

Anal. Calcd for  $C_{49}H_{42}Cl_2N_2O_9P_2Pd\cdot 0.25CH_2Cl_2$  (1063.37 g/mol): C, 55.63; H, 4.02; N, 2.63. Found: C, 55.37; H, 3.81; N, 2.79. MS [*m*/*z*, %]: 783 [(M - 2py-ClO<sub>4</sub>)<sup>+</sup>, 60]. IR ( $\nu$ , cm<sup>-1</sup>): 1614, 1607 ( $\nu_{CO}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.76 (d, 2H, H<sub>o</sub>, py, <sup>3</sup>J<sub>H-H</sub> = 5.1 Hz), 7.97-7.21 (m, 16 H, Ph + H<sub>p</sub>(py)), 6.87 (t, 2H, H<sub>m</sub>, py, <sup>3</sup>J<sub>H-H</sub>  $\cong$  6 Hz), 4.99 (d, 1H, CH ylide, <sup>2</sup>J<sub>P-H</sub> = 3.9 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  24.83.

 $[Pd{[CH(PPh_3)]_2CO}(dppm)](ClO_4)_2$  (11). To a solution of complex 3c (0.200 g, 0.207 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added dppm (0.079 g, 0.21 mmol), and the resulting solution was stirred for 1 h at room temperature. The solvent was evaporated to dryness and the residue treated with Et<sub>2</sub>O (10 mL), giving 11 as a white solid, which was filtered, washed with Et<sub>2</sub>O (15 mL), and air-dried. Obtained: 0.240 g (92% yield).

Anal. Calcd for  $C_{64}H_{54}Cl_2O_9P_4Pd$  (1268.33 g/mol): C, 60.61; H, 4.29. Found: C, 60.47; H, 4.22. MS [m/z, %]: 1169  $[(M - ClO_4)^+, 20]$ , 1067  $[(M - 2ClO_4 + H)^+, 100]$ . IR  $(\nu, \text{ cm}^{-1})$ : 1589  $(\nu_{CO})$ . <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.80–6.87 (m, 50H, Ph), 5.16 (virtual q, 2H, CH-ylide,  $J_{P-H} = 1.8$  Hz), 4.83 (dt, 1H, CH<sub>2</sub>-dppm, <sup>2</sup> $J_{H-H} = 15.3$  Hz, <sup>2</sup> $J_{P-H} = 10.8$  Hz), 4.02 (dt, 1H, CH<sub>2</sub>-dppm, <sup>2</sup> $J_{H-H} = 15.3$  Hz, <sup>2</sup> $J_{P-H} = 9.6$  Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  22.40 (virtual t, bis(ylide), <sup>3</sup> $J_{P-P} = 4.4$  Hz), -25.54 (virtual t, dppm).

 $[Pd(C_6H_4-2-PPh_2C(H)COCH_2PPh_3)(py)_2](ClO_4)_2$  (12). A solution of complex 10 (0.197 g, 0.189 mmol) in NCMe (15 mL) was refluxed for 8 h. After cooling, this solution was evaporated to dryness. By addition of Et<sub>2</sub>O (30 mL) and continuous stirring 12 was obtained as a white solid, which was filtered, washed with additional Et<sub>2</sub>O (20 mL), and air-dried. Obtained: 0.144 g (73% yield). Recrystallization of 12 from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane gave colorless crystals of  $12 \cdot 0.25$ CH<sub>2</sub>Cl<sub>2</sub>, which were used for analytical and spectroscopic measurements. The amount of CH<sub>2</sub>Cl<sub>2</sub> was determined by <sup>1</sup>H NMR integration.

Anal. Calcd for  $C_{49}H_{42}Cl_2N_2O_9P_2Pd\cdot 0.25CH_2Cl_2$  (1063.37 g/mol): C, 55.63; H, 4.02; N, 2.63. Found: C, 55.46; H, 3.70; N, 2.78. MS [*m*/*z*, %]: 864 [(M – py–ClO<sub>4</sub>)<sup>+</sup>, 10]. IR ( $\nu$ , cm<sup>-1</sup>): 1652 ( $\nu_{CO}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.71 (d, 2H, H<sub>0</sub>, py, <sup>3</sup>*J*<sub>H-H</sub> = 5.1 Hz), 8.31 (d, 2H, H<sub>0</sub>, py, <sup>3</sup>*J*<sub>H-H</sub> = 4.8 Hz), 7.91–7.18 (m, 31 H, Ph + H<sub>m</sub> + H<sub>p</sub>(py)), 7.01 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 6.78 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 6.57 (d, 1H, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>*J*<sub>H-H</sub> = 7.2 Hz), 5.43 (dd, 1H, CH<sub>2</sub>P, <sup>2</sup>*J*<sub>H-H</sub>

 $\simeq {}^{2}J_{P-H} = 16.8$  Hz), 4.60 (d, 1H, CH-ylide,  ${}^{2}J_{P-H} = 3.9$  Hz), 4.17 (dd, CH<sub>2</sub>P, 1H,  ${}^{2}J_{P-H} = 10.2$  Hz).  ${}^{31}P{}^{1}H{}$  NMR (CDCl<sub>3</sub>):  $\delta$  22.80 (d,  ${}^{4}J_{P-P} = 10.7$  Hz), 20.97 (d).

Attempted Orthometalation of  $[Pd{[CH(PPh_3)]_2CO}-(dppm)](ClO_4)_2$  (11). A solution of complex 11 (0.262 g, 0.207 mmol) in NCMe (15 mL) was refluxed for 8 h. After cooling, this solution was evaporated to dryness. By addition of Et<sub>2</sub>O (30 mL) and continuous stirring a white solid was obtained, which was filtered, washed with additional Et<sub>2</sub>O (20 mL), airdried, and identified spectroscopically as a mixture of [Pd-(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>)(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>-P,P)](ClO<sub>4</sub>)<sub>2</sub> (13a) and[Pd(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>)(Ph<sub>2</sub>PCH<sub>2</sub>PCH<sub>2</sub>P(O)Ph<sub>2</sub>-P,O)]-(ClO<sub>4</sub>)<sub>2</sub> (13b). Obtained: 0.168 g.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): **(13a)**  $\delta$  5.57–5.51 (m, 1H, CH-ylide), 4.91–4.70 (m, 2H, CH<sub>2</sub>PPh<sub>3</sub> + dppm), 4.29 (dd, 1H, CH<sub>2</sub>PPh<sub>3</sub>, <sup>2</sup>J<sub>H-H</sub> = 18 Hz, <sup>2</sup>J<sub>P-H</sub> = 13.5 Hz), 4.15–3.98 (m, 1H, dppm); **(13b)**  $\delta$  5.37 (dd, 1H, CH<sub>2</sub>PPh<sub>3</sub>, <sup>2</sup>J<sub>H-H</sub> = 17.7 Hz, <sup>2</sup>J<sub>P-H</sub> = 13.8 Hz), 5.12 (dd, 1H, CH<sub>2</sub>PPh<sub>3</sub>, <sup>2</sup>J<sub>H-H</sub> = 17.7 Hz, <sup>2</sup>J<sub>P-H</sub> = 11.1 Hz), 4.33 (d, 1H, CH-ylide, <sup>2</sup>J<sub>P-H</sub> = 13.5 Hz), 3.75 (dt, CH<sub>2</sub>dppm, <sup>2</sup>J<sub>H-H</sub> = 15 Hz, <sup>2</sup>J<sub>P-H</sub> = 10 Hz), 3.53 (dt, CH<sub>2</sub>-dppm, <sup>2</sup>J<sub>H-H</sub> = 15 Hz, <sup>2</sup>J<sub>P-H</sub> = 11 Hz).

 $^{31}{\rm P}\{^{1}{\rm H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): (**13a**)  $\delta$  23.55 (ddd, 1P, C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>,  $^{3}J_{\rm P-P}=$  33.9 Hz,  $^{3}J_{\rm P-P}=$  16.1 Hz,  $^{4}J_{\rm P-P}=$  8.9 Hz), 21.49 (d, 1P, CH<sub>2</sub>PPh<sub>3</sub>,  $^{4}J_{\rm P-P}=$  8.9 Hz), -14.43 (dd, 1P PPh<sub>2</sub> *cis*-to-CH-ylide,  $^{2}J_{\rm P-P}=$  59.4 Hz,  $^{3}J_{\rm P-P}=$  16.1 Hz), -29.19 (dd, 1P, PPh<sub>2</sub> *trans*-to-CH-ylide,  $^{2}J_{\rm P-P}=$  59.4 Hz,  $^{3}J_{\rm P-P}=$  33.9 Hz); (**13b**)  $\delta$  59.14 (d, 1P, P=O,  $^{2}J_{\rm P-P}=$  24.8 Hz), 25.41 (dd, 1P, Pd–PPh<sub>2</sub>,  $^{3}J_{\rm P-P}=$  17.7 Hz), 21.36 (d, CH<sub>2</sub>PPh<sub>3</sub>,  $^{4}J_{\rm P-P}=$  8.9 Hz), 17.15 (dd, 1P, C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>).

[Pd(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>)(NCMe)(PPh<sub>3</sub>)]-(ClO<sub>4</sub>)<sub>2</sub> (14). To a solution of 3c (0.150 g, 0.155 mmol) in CH<sub>2</sub>-Cl<sub>2</sub> (20 mL) was added PPh<sub>3</sub> (0.040 g, 0.16 mmol), and the resulting solution was stirred for 24 h at room temperature. This clear solution was evaporated to small volume (2 mL), and Et<sub>2</sub>O (30 mL) was added. By continuous stirring, 14 was obtained as a white solid, which was filtered, washed with Et<sub>2</sub>O (10 mL), and air-dried. Obtained: 0.135 g (73% yield). Recrystallization of 14 from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane gave colorless crystals of 14·0.75CH<sub>2</sub>Cl<sub>2</sub>, which were used for analytical and spectroscopic measurements. The amount of CH<sub>2</sub>Cl<sub>2</sub> was determined by <sup>1</sup>H NMR integration.

Anal. Calcd for  $C_{59}H_{50}Cl_2NO_9P_3Pd\cdot 0.75CH_2Cl_2$  (1250.97 g/mol): C, 57.36; H, 4.15; N, 1.11. Found: C, 57.12; H, 4.17; N, 1.09. MS [*m*/*z*, %]: 1045 [(M - NCMe-ClO<sub>4</sub>)<sup>+</sup>, 20]. IR ( $\nu$ , cm<sup>-1</sup>): 2319, 2291 ( $\nu_{CN}$ ), 1640 ( $\nu_{CO}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.01–7.95 (m, 2H, Ph), 7.69–7.28 (m, 38H, Ph), 7.05 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 6.94 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 6.67 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 5.54 (br m, 1H, CH-ylide), 5.37 (pseudo t, 1H, CH<sub>2</sub>P, <sup>2</sup>J<sub>H-H</sub>  $\cong$  <sup>2</sup>J<sub>P-H</sub> = 16.8 Hz), 4.96 (dd, 1H, CH<sub>2</sub>P, <sup>2</sup>J<sub>P-H</sub> = 10.8 Hz), 1.86 (s, 3H, NCMe). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  30.84 (d, Pd–PPh<sub>3</sub>, <sup>3</sup>J<sub>P-P</sub> = 15.2 Hz), 22.73 (d, CH<sub>2</sub>PPh<sub>3</sub>, <sup>4</sup>J<sub>P-P</sub> = 8 Hz), 17.45 (dd, C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>).

 $[Pd(C_6H_4-2-PPh_2C(H)COCH_2PPh_3)(dppe)](ClO_4)_2$  (15). Complex 15 was obtained in a similar way to that described for 14 starting from 3c (0.200 g, 0.207 mmol) and dppe (0.081 g, 0.21 mmol). Obtained: 0.238 g (90% yield).

Anal. Calcd for C<sub>65</sub>H<sub>56</sub>Cl<sub>2</sub>O<sub>9</sub>P<sub>4</sub>Pd (1282.36 g/mol): C, 60.88; H, 4.40. Found: C, 60.52; H, 4.34. MS [m/z, %]: 1181 [(M - $ClO_4$ )<sup>+</sup>, 12]. IR ( $\nu$ , cm<sup>-1</sup>): 1642 ( $\nu_{CO}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.91– 6.87 (m, 46H, Ph + C<sub>6</sub>H<sub>4</sub>), 6.76 (t, 1H, C<sub>6</sub>H<sub>4</sub>,  ${}^{3}J_{H-H} = 7.8$  Hz), 6.68 (d, 1H, C<sub>6</sub>H<sub>4</sub>,  ${}^{3}J_{H-H} = 7.2$  Hz), 6.64 (d, 1H, C<sub>6</sub>H<sub>4</sub>,  ${}^{3}J_{H-H} =$ 7.8 Hz), 5.10 (dd, 1H, CH-ylide,  ${}^{2}J_{P-H} = 10.2$  Hz,  ${}^{3}J_{P-H} = 6.3$ Hz), 4.02 (dd, 1H, CH<sub>2</sub>P,  ${}^{2}J_{H-H} = 18$  Hz,  ${}^{2}J_{P-H} = 13.8$  Hz), 3.52 (dd, 1H, CH<sub>2</sub>P,  ${}^{2}J_{P-H} = 10.2$  Hz), 3.16, 2.71, 2.52, 2.31 (4m, 4H, CH<sub>2</sub>-dppe). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 55.03 (dd, 1P, P-dppe-*cis*-to-C-ylide,  ${}^{3}J_{P-P} = 16.8$  Hz,  ${}^{3}J_{P-P}$  (dppe) = 23.4 Hz), 43.67 (dd, 1P, P-dppe-*trans*-to-C-ylide,  ${}^{3}J_{P-P} = 31.8$  Hz,  ${}^{3}J_{P-P}$ (dppe) = 23.4 Hz), 24.13 (ddd,  $\tilde{C}_6H_4$ -2-PPh<sub>2</sub>,  ${}^4J_{P-P} = 9$  Hz), 22.23 (d, CH<sub>2</sub>PPh<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  193.46 (t, CO,  ${}^{2}J_{P-C} = 5$  Hz), 169.25 (ddd, C<sub>1</sub>, C<sub>6</sub>H<sub>4</sub>,  ${}^{2}J_{Ptrans-C} = 125$  Hz,  ${}^{2}J_{Pcis-C}$ = 29 Hz,  ${}^{2}J_{P-C}$  = 6 Hz), 138–117 (Ph + C<sub>6</sub>H<sub>4</sub>), 47.12 (t, CHylide,  ${}^{1}J_{P-C} \simeq {}^{2}J_{Ptrans-C} = 55$  Hz), 39.11 (dd, CH<sub>2</sub>, dppe,  ${}^{1}J_{P-C}$  = 60 Hz,  ${}^{2}J_{P-C}$  = 11 Hz), 37.73 (dd, CH<sub>2</sub>, dppe,  ${}^{1}J_{P-C}$  = 53 Hz,  ${}^{2}J_{P-C}$  = 17 Hz), 28.02 (dt, CH<sub>2</sub>PPh<sub>3</sub>,  ${}^{1}J_{P-C}$  = 36 Hz,  ${}^{3}J_{P-C} \approx {}^{4}J_{P-C}$  = 11 Hz).

 $[Pd(C_6H_4-2-PPh_2C(H)COCH_2PPh_3)(phen)](ClO_4)_2$  (16). Complex 16 was obtained in a way similar to that described for 14, starting from 3c (0.130 g, 0.134 mmol) and 1,10-phen (0.024 g, 0.13 mmol). Obtained: 0.100 g (70% yield).

Anal. Calcd for  $C_{51}H_{40}Cl_2N_2O_9P_2Pd$  (1064.14 g/mol): C, 57.56; H, 3.79; N, 2.63. Found: C, 57.58; H, 3.43; N, 2.83. IR ( $\nu$ , cm<sup>-1</sup>): 1620 ( $\nu_{CO}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  9.77 (dd, 1H, H<sub>a</sub>, phen,  ${}^{3}J_{\alpha\beta} = 5$  Hz,  ${}^{4}J_{\alpha\gamma} = 1.1$  Hz), 9.00 (dd, 1H, H<sub>a</sub>', phen,  ${}^{3}J_{\alpha'\beta'} = 4.5$  Hz,  ${}^{4}J_{\alpha'\gamma'} = 1$  Hz), 8.62 (dd, 1H, H<sub>\gamma'</sub>, phen,  ${}^{3}J_{\gamma'\beta'} = 8.2$ Hz), 8.51 (dd, 1H, H<sub>\gamma</sub>, phen,  ${}^{3}J_{\gamma\beta} = 8.2$  Hz), 8.09 (dd, 1H, H<sub>β</sub>, phen), 8.01–7.96 (AB spin system, 2H, H<sub>δ</sub> + H<sub>δ'</sub>, phen,  ${}^{3}J_{H-H} = 8.9$  Hz), 7.96 (dd, 1H, H<sub>β</sub>', phen), 7.91–7.84 (m, 2H, Ph), 7.71 (d, 1H, H<sub>6</sub>, C<sub>6</sub>H<sub>4</sub>,  ${}^{3}J_{H-H} = 7.7$  Hz), 7.63–7.26 (m, 26H, Ph + C<sub>6</sub>H<sub>4</sub>), 5.38 (dd, 1H, CH<sub>2</sub>P,  ${}^{2}J_{H-H} = 17.8$  Hz,  ${}^{2}J_{P-H} = 12.1$ Hz), 5.35 (pseudo t, 1H, CH-ylide,  ${}^{2}J_{P-H} \cong {}^{4}J_{P-H} = 1.6$  Hz), 5.16 (dd, 1H, CH<sub>2</sub>P,  ${}^{2}J_{P-H} = 12.3$  Hz).  ${}^{31}P{}^{1}H{}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  21.43 (d,  ${}^{4}J_{P-P} = 10.3$  Hz), 20.32 (d). This complex was insufficiently soluble for  ${}^{13}C$  NMR measurements.

[Pd(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>)(NCMe)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (17). To a solution of 4c (0.300 g, 0.182 mmol) in NCMe (20 mL) was added TlClO<sub>4</sub> (0.110 g, 0.365 mmol). The resulting suspension was stirred for 12 h at room temperature and filtered through Celite. The clear solution was evaporated to small volume (2 mL), and Et<sub>2</sub>O (30 mL) was added. By continuous stirring, complex 17 was obtained as a white solid, which was filtered, washed with Et<sub>2</sub>O (10 mL), and air-dried. Obtained: 0.307 g (87% yield).

Anal. Calcd for  $C_{43}H_{38}Cl_2N_2O_9P_2Pd$  (966.04 g/mol): C, 53.46; H, 3.96; N, 2.90. Found: C, 52.95; H, 3.62; N, 2.89. MS [*m/z*, %]: 783 [(M - 2NCMe-ClO<sub>4</sub>)<sup>+</sup>, 55]. IR ( $\nu$ , cm<sup>-1</sup>): 2319, 2291 ( $\nu_{CN}$ ), 1653 ( $\nu_{CO}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>/213 K):  $\delta$  7.78–7.09 (m, 29H, Ph + C<sub>6</sub>H<sub>4</sub>), 5.08 (br m, 1H, CH-ylide), 5.02, 4.98 (br AB spin system, CH<sub>2</sub>P, <sup>2</sup>J<sub>H-H</sub> = 13 Hz), 2.41 (s, 3H, NCMe), 2.28 (s, 3H, NCMe). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>/213 K):  $\delta$  23.82 (br s), 21.81 (br s).

[(C<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>C(H)COCH<sub>2</sub>PPh<sub>3</sub>)Pd( $\mu$ -Ac)<sub>2</sub>Pd{[C(H)-PPh<sub>3</sub>]<sub>2</sub>CO}](ClO<sub>4</sub>)<sub>2</sub> (19). A solution of complex 18 in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was stirred at room temperature for 48 h. At the end of the reaction the solvent was evaporated to dryness, and the orange 19 was collected with Et<sub>2</sub>O (25 mL), filtered, and airdried. The yield is quantitative. Recrystallization of 19 from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane gave colorless crystals of 19·0.5CH<sub>2</sub>Cl<sub>2</sub>, which were used for analytical and spectroscopic measurements. The amount of CH<sub>2</sub>Cl<sub>2</sub> was determined by <sup>1</sup>H NMR integration.

Anal. Calcd for C82H70Cl2O14P4Pd2.0.5CH2Cl2 (1729.52 g/mol): C, 57.29; H, 4.13. Found: C, 56.94; H, 4.09. MS [m/z, %]: 1587 [(M\_2 - ClO\_4)^+, 10]. IR ( $\nu,\,cm^{-1}$ ): 1640–1565 (broad absorption,  $\nu_{CO}$ , ylide and acetate). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.85-7.28 (m, 58H, Ph + C<sub>6</sub>H<sub>4</sub>), 6.81 (td, 1H, C<sub>6</sub>H<sub>4</sub>,  ${}^{3}J_{H-H} = 7.8$  Hz,  ${}^{5}J_{P-H} = 2.9$  Hz), 5.74 (ddd, 1H, CH<sub>2</sub>P,  ${}^{2}J_{H-H} = 17.8$  Hz,  ${}^{2}J_{P-H}$ = 9.5 Hz,  ${}^{4}J_{P-H}$  = 1.2 Hz), 5.50 (dd, 1H, CH<sub>2</sub>P,  ${}^{2}J_{P-H}$  = 15 Hz), 4.70 (pseudo t, 1H, CH-ylide (orthom),  ${}^{2}J_{P-H} \simeq {}^{4}J_{P-H} =$ 3.1 Hz), 2.99 (d, 1H, CH-bis(ylide),  ${}^{2}J_{P-H} = 5.1$  Hz), 2.85 (dd, 1H, CH-bis(ylide),  ${}^{2}J_{P-H} = 5.6$  Hz,  ${}^{4}J_{P-H} = 0.8$  Hz), 1.45 (s, 3H, Me), 0.60 (s, 3H, Me). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 30.14 (d,  ${}^{4}J_{P-P} = 8.8$  Hz, P in orthom ring), 25.74, 25.54 (AB spin system, bis(ylide),  ${}^{4}J_{P-P} = 8.5$  Hz), 22.23 (d, CH<sub>2</sub>PPh<sub>3</sub>).  ${}^{13}C{}^{1}H{}^{1}NMR$ (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  195.88 (t, COCH<sub>2</sub>, <sup>2</sup>J<sub>P-C</sub> = 4 Hz), 192.50 (dd, CObisylide,  ${}^{2}J_{P-C} = 7$  Hz,  ${}^{2}J_{P'-C} = 4$  Hz), 181.08 (s, COO<sup>-</sup>), 180.62 (s, COO<sup>-</sup>), 155.36 (d, C<sub>1</sub>, C<sub>6</sub>H<sub>4</sub>,  ${}^{2}J_{P-C} = 22$  Hz), 136.61–119.79 (m, Ph + C<sub>6</sub>H<sub>4</sub>), 52.41 (dd, Pd–CH in ring,  ${}^{1}J_{P-C} = 54$  Hz,  ${}^{3}J_{P-C} = 14$  Hz), 41.03 (dd, Pd–CH bis(ylide),  ${}^{1}J_{P-C} = 58$  Hz,  ${}^{3}J_{P-C} = 10$  Hz), 39.74 (dd, CH<sub>2</sub>P,  ${}^{1}J_{P-C} = 60$  Hz,  ${}^{3}J_{P-C} = 12$ Hz), 39.45 (dd, Pd–CH bis(ylide),  ${}^{1}J_{P-C} = 58$  Hz,  ${}^{3}J_{P-C} = 10$ Hz), 24.48 (s, CH<sub>3</sub>), 23.13 (s, CH<sub>3</sub>).

**Crystallography. Data Collection.** Crystals suitable for X-ray measurements were grown by slow diffusion of a CHCl<sub>3</sub> solution of **14** into *n*-hexane at room temperature. A pale

yellow crystal of 14.2CHCl3 was mounted on a quartz fiber and covered with epoxy. Normal procedures were used for the determination of the unit cell constants and for the measurement of intensity data. After preliminary indexing and transformation of the cell to a conventional setting, axial photographs were taken of the *a*-, *b*-, and *c*-axes to verify the Laue symmetry and lattice dimensions. Accurate unit cell dimensions were determined from 25 centered reflections in the range  $21.9^{\circ} \le 2\theta \le 31.9^{\circ}$ . For intensity data collection, pure  $\omega$  scans were used with  $\Delta \omega = 1.25 + 0.35 \tan \theta$ . Three monitor reflections were measured after every 3 h of beam time, and the orientation of the crystal was checked after every 500 intensity measurements. Absorption corrections<sup>35</sup> were based on azimuthal scans of 13 reflections, 9 of which had the Eulerian angle  $\chi$  near 90°. The other four reflections used for this purpose had their bisecting-position  $\chi$  values distributed in the range 16-60°.

**Structure Solution and Refinement.** The structure was solved and developed by Patterson and Fourier methods.<sup>36</sup> All non-hydrogen atoms were assigned anisotropic displacement parameters. The hydrogen atoms of the aromatic groups and of the  $CH_2$  and CH moieties were constrained to idealized geometries, and the isotropic displacement parameter of each of these hydrogen atoms was set to a value of 1.2 times the equivalent isotropic displacement parameter of its parent carbon atom. The hydrogen atoms of the  $CH_3$  group were also

constrained to idealized geometries, and the isotropic displacement parameter of each of these hydrogen atoms was set to a value of 1.5 times the equivalent isotropic displacement parameter of its parent carbon atom (C56). The parameters for the two interstitial CHCl<sub>3</sub> molecules did not show signs of either static or dynamic disorder; the hydrogens atoms of these groups were omitted from the model. The data-to-parameter ratio in the final refinement was 10.7. The structure was refined to  $F_0^2$ , and all reflections were used in the least-squares calculation.<sup>37</sup> The residuals and other pertinent parameters are summarized in Table 1. Crystallographic calculations were done on a Local Area VAXCluster (VAX/VMS V5.5-2). Data reduction was done by the program XCAD4B.<sup>38</sup>

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**Supporting Information Available:** Tables of crystal data and structure refinement details, atomic coordinates, bond distances and angles, and anisotropic displacement parameters for compound **14**·2CHCl<sub>3</sub> (9 pages). Ordering information is given on any current masthead page.

#### OM980625U

<sup>(35)</sup> Absorption corrections and molecular graphics were done using the commercial package *SHELXTL-PLUS*, Release 4.21/V; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

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