Ligand-Induced and Thermally-Induced Orthometalation of the Bis(ylide) Ligand $[Ph_3P{=}C(H)]_2CO$. Generation of the C,C-Chelating Group C_6H_4-2-PPh_2C((H)$COCH_2PPh_3$

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The dinuclear complex $[Pd(\mu\text{-Cl})\{[C(H)PPh_3]_2CO\}]_2(ClO_4)_2$ (**2c**) undergoes thermal rearrangement in refluxing NCMe, giving the dinuclear orthometalated derivative $[Pd(\mu\text{-Cl})(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)]_2(ClO_4)_2$ (**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_2C(H)$COCH_2PPh_3$) 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 $[Pd(\mu\text{-Cl})\{[C(H)PPh_3]_2CO\}]_2(ClO_4)_2$ (**2c**) under very mild conditions. For instance, complex **2c** reacts with PPh_3 or $PPhMe_2$ in CH_2Cl_2 at room temperature to give $[PdCl(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)(PR_3)](ClO_4)$ (PR_3 = PPh_3 **8**, $PPhMe_2$ **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 $[PdCl(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)(L)](ClO_4)$ (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 $[Pd\{[C(H)PPh_3]_2CO\}(NCMe)_2](ClO_4)_2$ (**3c**). **3c** reacts with py or dppm giving $[Pd\{[C(H)PPh_3]_2CO\}(L)_2](ClO_4)_2$ (L = py **10**, L_2 = dppm **11**), which is transformed into $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)(L_2)](ClO_4)$ (L = py **12**, L_2 = dppm **13a** + dppm-O **13b**) by refluxing in NCMe. However, complex **3c** reacts with PPh_3, dppe, or phen in CH_2Cl_2 at room temperature giving $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)(L_2)](ClO_4)$ (L_2 = PPh_3, NCMe **14**, dppe **15**, phen **16**). Complex **3c** is not transformed into its corresponding orthometalated derivative $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)(NCMe)_2](ClO_4)_2$ (**17**) by refluxing in NCMe, but **17** can be obtained by treatment of **4c** with $TlClO_4$ in NCMe. The orthometalation reaction of the bis(ylide) ligand can even occur spontaneously. The acetate-bridged dimer $[Pd(\mu\text{-}OOCCH_3)\{[C(H)PPh_3]_2CO\}]_2(ClO_4)_2$ (**18**) transforms spontaneously at room temperature into the mixed orthometalated bis(ylide)complex $[(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)Pd(\mu\text{-}OOCCH_3)_2Pd\{[C(H)PPh_3]_2CO\}](ClO_4)_2$ (**19**). The crystal structure of $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)(PPh_3)(NCMe)](ClO_4)_2$ (**14**) has been determined and reveals the presence of an orthometalated C_6H_4-2-PPh_2 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.[1] In recent papers, we have described a selection of the chemistry of Pd^{II} and Pt^{II} with α-stabilized ylides, such as $Ph_3P{=}C(H)COR$ (R = Me, Ph, OMe, NMe_2) and $Ph_3P{=}C(H)CN$.[2−7] Throughout these studies, we have observed the

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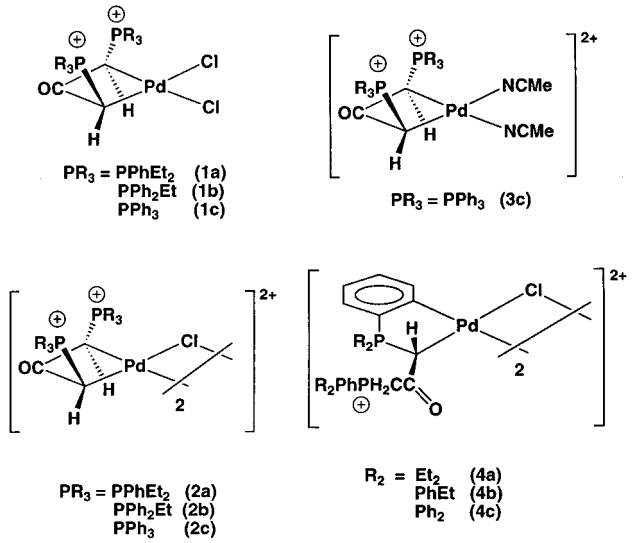
ability of these ylides to behave as ambidentate ligands (except for the NMe_2 derivative[7]), and it has been demonstrated that control can be exerted over the bonding modes: that given an organometallic substrate the coordination mode of a given ylide can be predicted and, conversely, a substrate can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

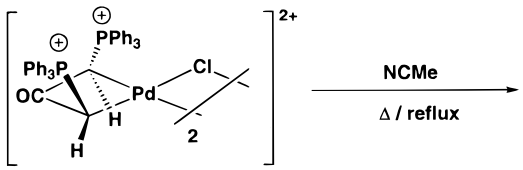
More recent studies are focused on the reactivity of palladium complexes with bis(ylides) such as $Ph_3P{=}C(H)COC(H){=}PPh_3$. In a first communication[8] we have described the synthesis of palladium(II) complexes in which this bis(ylide) acts as a C,C-chelate through the two ylidic carbon atoms. Through subsequent study we have now found an interesting reactivity of these chelates, namely, the rearrangement of the C,C-coordinated ligand $[C(H)PPh_3]_2CO$ to give the orthometalated unit C_6H_4-2-$PPh_2C(H)COCH_2PPh_3$, 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_2Cl_2, room temperature). Due to the intrisic interest of reactions involving C−H activation[9] and also due to the fact that the number of C,C-orthometalated complexes is relatively scarce[10−20] compared with other C,X-cyclometalated (X = heteroatom) derivatives,[9,21] 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

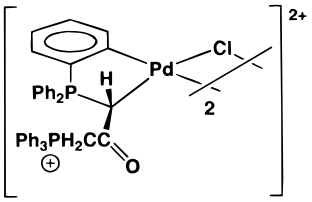
Thermally-Induced Orthometalations. The prolonged reflux in NCMe (8 h) of a suspension of the yellow dimer $[Pd(\mu\text{-}Cl)\{[C(H)PPh_3]_2CO\}]_2(ClO_4)_2$ (**2c**) affords an orange solution from which the orthometalated dinuclear complex $[Pd(\mu\text{-}Cl)(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)](ClO_4)_2$ (**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^{-1}, suggesting the presence of the $Pd(\mu\text{-}Cl)_2Pd$ unit, and a strong absorption at 1648 cm^{-1} attributed to the carbonyl group. This latter absorption is shifted to higher energies with respect to that in the starting product **2c** (1617 cm^{-1}),[8] 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**.

Chart 1





(2c)



(4c) (1)

The ^1H 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 $^2J_{P-H}$ around 4 Hz and $^4J_{P-H}$ 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 $^{13}C\{^1H\}$ 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 $Pd-C_{orthometalated}$ bond, since this region (155−164 ppm) is characteristic of this kind of bond.[14,17a,20] 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[2−7] ($^1J_{P-C} = 66.8$ Hz, $^3J_{P-C} = 8.8$ Hz). The $^{31}P\{^1H\}$ 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[22] 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, $[PhEt_2PCH_2COCH_2PPhEt_2]Cl_2$ and $[Ph_2EtPCH_2COCH_2PPh_2Et]Cl_2$, by reaction of the corresponding phosphine and 1,3-dichloroacetone (2:1 molar ratio) in $CHCl_3$ (see Experimental Section). Following the same experimental method described for the synthesis of **1c** and **2c**[8] (see Experimental Section), we have synthesized the neutral derivatives $Cl_2Pd\{[CH(PR_3)]_2CO\}$ ($PR_3 = PPhEt_2$ **1a**, PPh_2Et **1b**) and the dinuclear $[Pd(\mu\text{-}Cl)\{[CH(PR_3)]_2CO\}]_2(ClO_4)_2$ ($PR_3 = PPhEt_2$ **2a**, PPh_2Et **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 ^{31}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 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.[13]

As has been pointed out,[9,17,21,23−26a] 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_3 fragments lie on the same side of the molecular plane[8] promote the orthometalation. In addition, in the crystal structure of the dinuclear derivative $[Pd(\mu\text{-}Cl)\{[C(H)PPh_3]_2CO\}]_2(ClO_4)_2$ (**2c**),[8] 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.[26b] Thus, we think that the driving force for orthometalation in our complexes is the simultaneous presence of a four-membered cycle (ring strain) and one bulky PPh_3 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_3 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 ($PPhEt_2$, 136°),[27] does not show orthometalation at all, while complex **2b** (PPh_2Et, 140°)[27] shows only partial conversion, both under the same conditions in which **2c** (PPh_3, 145°)[27] 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 ^1H and $^{31}P\{^1H\}$ 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 $NCCD_3$ is fully dissociated into the monomer $[PdCl\{[C(H)PPh_3]_2CO\}(NCCD_3)]^+$, characterized by its NMR spectra (see Experimental Section); (b) the neutral complex **1c**, when dissolved in $NCCD_3$,

(22) Complex **4c** reacts with $Hg(OOCCH_3)_2$ to give the trinuclear derivative $[Pd_2(\mu\text{-}Cl)_2(C_6H_4\text{-}2\text{-}PPh_2C(H)COC(H)PPh_3)_2(\mu\text{-}Hg)](ClO_4)_2$, and the X-ray crystal structure of this complex reveals the anti disposition of the cyclometalated rings. Falvello, L. R.; Fernández, S.; Navarro, R.; Urriolabeitia, E. P. Manuscript submitted to *Inorg. Chem.*

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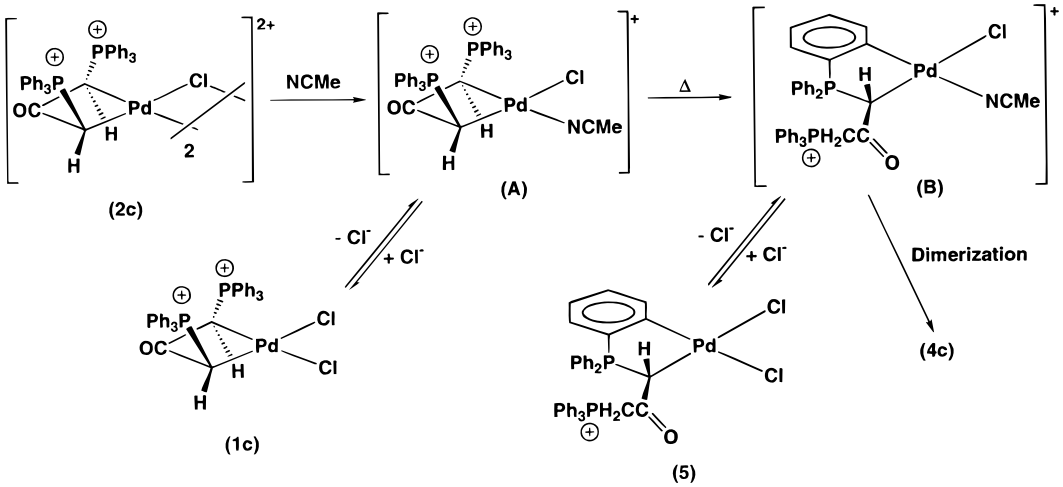
Scheme 1



exists as an equilibrium mixture between the neutral form **1c** and the cationic form $[PdCl\{[C(H)PPh_3]_2CO\}(NCCD_3)]^+$; (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 $NCCD_3$ 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 $[PdCl\{[C(H)PPh_3]_2CO\}(NCCD_3)]^+$ (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_2O) 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 $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)(NCMe)_2]^{2+}$ (**17**) (which can easily be obtained by reaction of **4c** with $TlClO_4$ 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^- ligands are not simple spectators in this reaction.

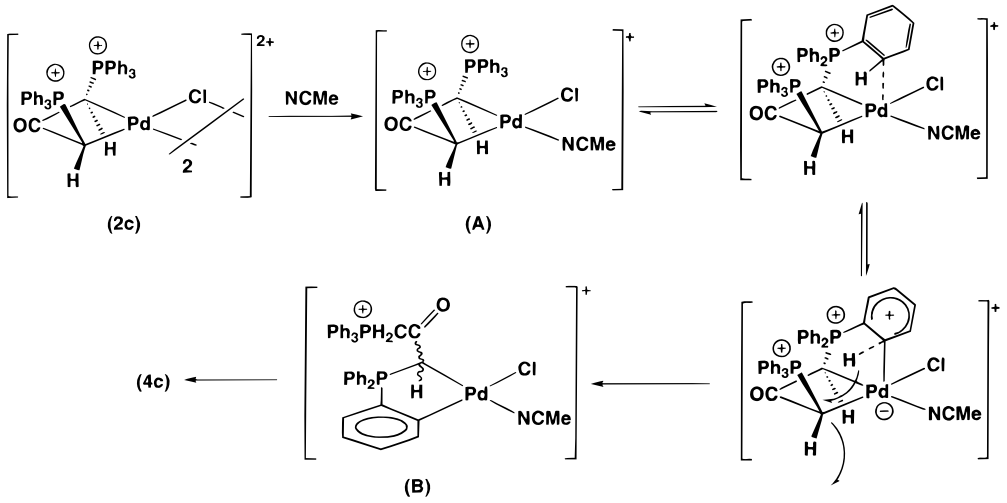
There are two generally accepted mechanisms for C−H bond activation by palladium(II): oxidative addition resulting from nucleophilic attack by the metal on the phenyl ring and electrophilic substitution in the aromatic ring. Although there are known examples in which the Pd(II) center behaves as a nucleophile,[9] 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 ($PPhEt_2$ 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.[17] 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**.

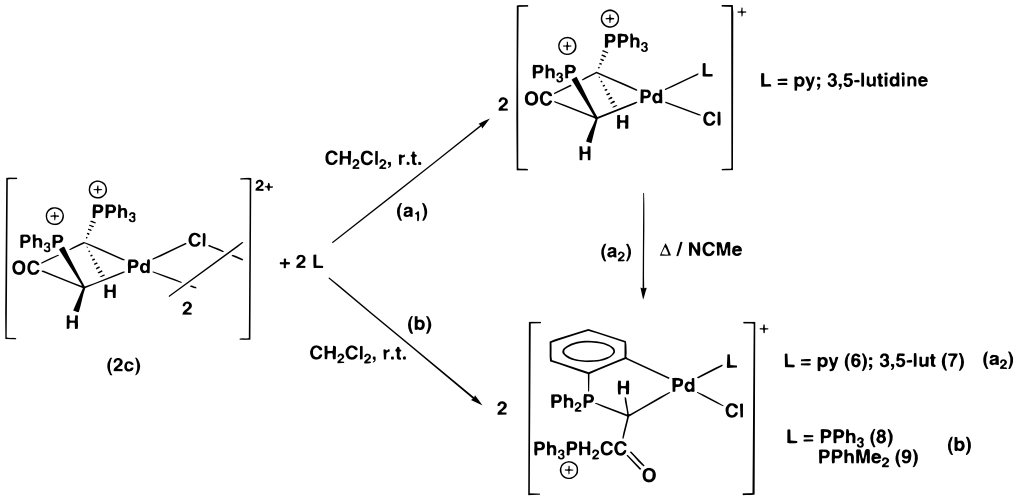
The generation of the phosphonium group in the final product can be rationalized in two different ways. One of these is that shown in Scheme 2 involving an intramolecular acid−base reaction and is similar to that described in the orthometalation of bis(*N*-aryliminophosphoranyl)alkanides of Pd(II) and Pt(II).[17a] 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[18] complex $\{PtCl_2[C(H)COMe(PPh_2\text{-}o\text{-}C_6H_4)]\}^-$ (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_2CO_3 did not show an appreciable decrease in yield; (b) the orthometalation of the ylide−phosphonium salt $[Ph_3P{=}C(H)COCH_2PPh_3]ClO_4$ 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 base-assisted); (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,C-chelating bis(ylide) ligand $[C(H)PPh_3]_2CO$ generates the C,C-chelating $[C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3]$ ligand through an electrophilic substitution at the phenyl ring and an intramolecular acid−base reaction. The driving

Scheme 2



Scheme 3



force for this reaction seems to be related to the steric repulsions between the two PPh_3 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[8] 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 $[PdCl\{[C(H)PPh_3]_2CO\}L]ClO_4$ (see Scheme 3, path a_1). 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_3 (PPh_3, $PPhMe_2$) in CH_2Cl_2 at room temperature results in the formation of the cationic orthometalated derivatives $[PdCl(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)L]ClO_4$ (L = PPh_3 **8**, $PPhMe_2$ **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,C-bis(ylide) complexes.[8] On the other hand, the Pd−Cl stretch appears in the 270 cm^{-1} region, suggesting that the Cl ligand is trans to the orthometalated carbon atom.[28] The ^1H NMR spectra show the presence of the CH_2P 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_3 ligand. The magnitudes of the coupling constants strongly suggest that the PR_3 ligand is trans to the ylidic carbon atom. Additional evidence for this stereochemistry can be found in the $^{13}C\{^1H\}$ NMR spectrum of **8**. There, the orthometalated carbon atom (C_1) appears at 163.86 ppm as a doublet ($^2J_{P-C}$ = 20 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.[17a] Moreover, the $^{31}P\{^1H\}$ NMR spectra of **8** and **9** show the same pattern of resonances (with the expected difference in

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

the chemical shift of the PR_3 ligand), in which the P atom in the ring appears as a doublet of doublets by coupling with the trans-PR_3 ligand and with the phosphonium group. Finally, the $^1H-^1H$ NOESY spectrum of complex **9** shows a strong NOE interaction between the Me resonances of the $PPhMe_2$ ligand (1.57 and 1.37 ppm) and the H_6 proton of the orthometalated C_6H_4 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_3 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.[29]

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 $C(H)PPh_3$ group located in the cis position, and the molecule remains stable toward orthometalation.[8] However, the volume occupied by ligands such as phosphines is considerably larger and such ligands could crowd the two cis ylidic $C(H)PPh_3$ 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_3), and the reactions with larger amines (NEt_3) are more complicated since they involve deprotonation of the CH_2PPh_3 group generated.

The synthesis of the complexes $[PdCl(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)L]ClO_4$ (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,C-chelating 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_2).

The reaction of **2c** with PPh_3 has been followed by NMR spectroscopy. A solution of **2c** in CD_2Cl_2 was mixed with PPh_3 (1:2 molar ratio), and the ^1H NMR spectrum of the mixture was measured at 183 K 5 min after mixing (the time needed for locking and shimming). This ^1H 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 ($^2J_{P-H}$ = 6.2 Hz, $^4J_{P-H}$ = 3.4 Hz) and a doublet of doublets of doublets at 2.64 ppm ($^3J_{P-H}$ = 11.4 Hz, $^2J_{P-H}$ = 5.0 Hz, $^4J_{P-H}$ = 2.3 Hz). These two resonances could indicate the presence of the intermediate complex $[PdCl\{[C(H)PPh_3]_2CO\}(PPh_3)]ClO_4$, since the first resonance would correspond to the ylidic proton cis to the PPh_3 ligand and the second to the ylidic proton trans to the PPh_3 group. Moreover, the $^{31}P\{^1H\}$ 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**.

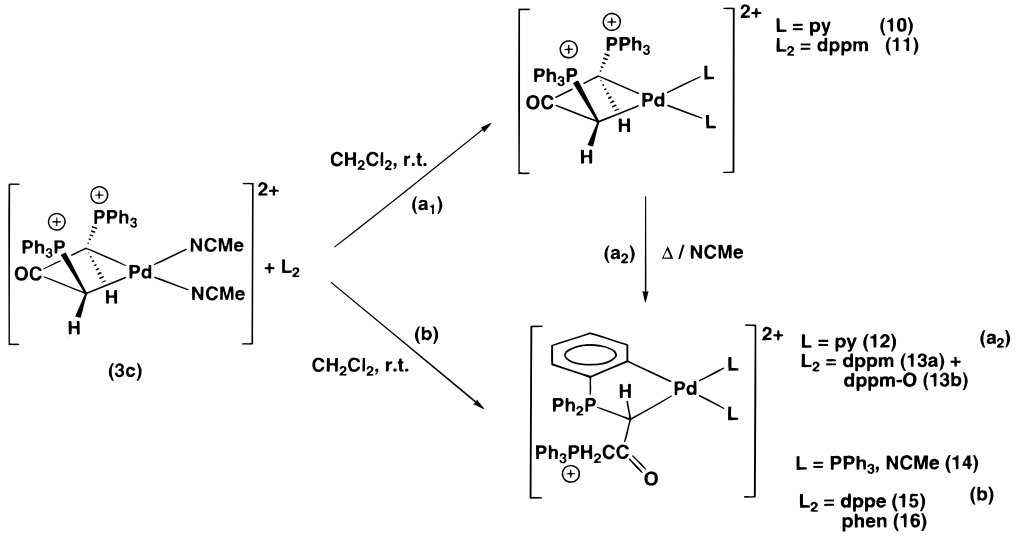
We reported in the first section that complex **3c** does not undergo thermal orthometalation. Prompted by the results obtained in the synthesis of **8** and **9**, we have explored the reactivity of this complex toward different neutral monodentate and bidentate ligands. The reaction of **3c** with 2 equiv of pyridine results in the formation of the bis(ylide) derivative $[Pd\{[C(H)PPh_3]_2CO\}(py)_2](ClO_4)_2$ (**10**), which was characterized by its analytical and spectroscopic data (see Experimental Section). In accord with the foregoing discussion of the complexes $[PdCl\{[C(H)PPh_3]_2CO\}(py)]ClO_4$ (see preceding paragraphs), complex **10** is stable toward orthometalation since the steric repulsion between the pyridine ligands and the ylidic $C(H)PPh_3$ fragments is not severe. More interesting is the reaction between **3c** and dppm ($Ph_2PCH_2PPh_2$) in 1:1 molar ratio (CH_2Cl_2, 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 $^{31}P\{^1H\}$ 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[30] 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 ^1H 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 quintuplet 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_2 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**[8] the value of the bite angle is about 68° and for dppm-chelating complexes a typical

(29) Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127, and references therein.

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

Scheme 4



value of this angle[30] 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$_6$H$_4$-2-PPh$_2$C(H)COCH$_2$PPh$_3$)(py)$_2$](ClO$_4$)$_2$ (**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 ^{31}P{^{1}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$_6$H$_4$-2-PPh$_2$C(H)COCH$_2$PPh$_3$)(dppm)](ClO$_4$)$_2$ (**13a**), since the two high-field resonances signal the presence of the P,P-chelating dppm ligand[30] 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 four-memebered ring has been transformed into a five-membered ring, giving [Pd(C$_6$H$_4$-2-PPh$_2$C(H)COCH$_2$-PPh$_3$)(dppm-O)](ClO$_4$)$_2$ (**13b**). Similar aerobic oxidations of the dppm ligand have been described[29] for C,N-orthometalated complexes of Pd(II) such as [Pd(C$_6$H$_4$N=NPh-2)(η^2-dppmO)]SbF$_6$. 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;[31] 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).

(31) Pearson, R. G. *Inorg. Chem.* **1973**, *12*, 712.

The reaction of **3c** with other monodentate or bidentate ligands follows different trends. The reaction of **3c** with PPh$_3$ (1:1 molar ratio) in CH$_2$Cl$_2$ at room temperature results in the formation of [Pd(C$_6$H$_4$-2-PPh$_2$C(H)-COCH$_2$PPh$_3$)(PPh$_3$)(NCMe)](ClO$_4$)$_2$ (**14**), even if the reaction is performed in the presence of an excess of PPh$_3$. On the other hand, the reaction of **3c** with dppe or phen (1:1 molar ratio) in CH$_2$Cl$_2$ at room temperature affords the dicationic derivatives [Pd(C$_6$H$_4$-2-PPh$_2$C(H)-COCH$_2$PPh$_3$)(L$_2$)](ClO$_4$)$_2$ (L$_2$ = 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 ^{1}H NMR spectrum of **16** was carried out with the help of the ^{1}H−^{1}H NOESY spectrum), and further characterization is provided by the determination of the crystal structure of complex **14**·2CHCl$_3$.

Crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a solution of **14** in CHCl$_3$. 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 $P\bar{1}$ 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$_3$ 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$_3$ 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,[29] as are the Pd−C(ylide) bond distance [Pd − C(57) = 2.161(8) Å],[2,5,7] the Pd−P bond distance [2.315-(2) Å],[29] and the Pd−N bond distance [2.091(7) Å].[29] Other internal structural parameters of the orthometalated ligand, the PPh$_3$ 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

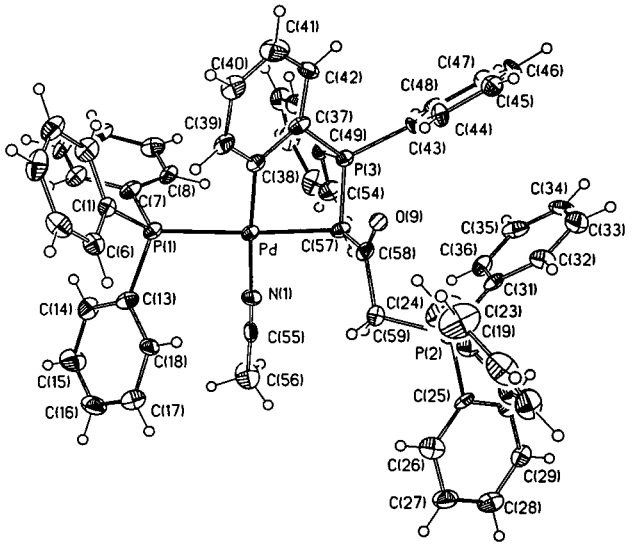


Figure 1. Thermal ellipsoid plot of the organometallic $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)(PPh_3)(NCMe)]^{2+}$ cation. Atoms are drawn at the 50% probability level.

Table 1. Crystal Data and Structure Refinement for $14\cdot 2CHCl_3$

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 $\alpha = 79.150(10)°$ $b = 13.299(2)$ Å $\beta = 86.530(10)°$ $c = 25.154(3)$ Å $\gamma = 73.900(10)°$
volume	3059.9(7) Å^3
Z	2
density (calcd)	1.548 Mg/m^3
abs coeff	0.788 mm^{-1}
$F(000)$	1448
cryst size	0.26 × 0.12 × 0.09 mm
θ range for data collection	2.09−22.50°
index ranges	$0 \le h \le 10$, $-13 \le k \le 14$, $-27 \le l \le 27$
reflns collected	8619
ind reflns	8008 ($R_{int} = 0.0574$)
abs correction	ψ-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^2[a]	1.025
R indices $[I > 2\sigma(I)]$[b]	R1 = 0.0617, wR2 = 0.1279
largest diff peak and hole	0.990 and −1.819 eÅ^{-3}

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

is, coordination of PPh_3 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_3 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 $14\cdot 2CHCl_3$

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°)[32,33] leaves the two groups in close proximity (similar to the case of PPh_3), 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_α groups adjacent to the nitrogen of the phen ligand.

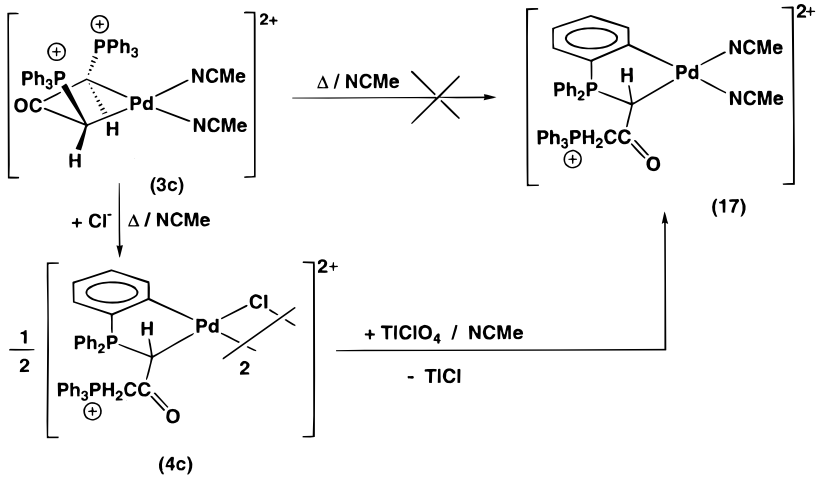
It should be noted that the presence of large substituents on the donor atom of the incoming ligand is also important (for instance, two phenyl groups on the P atoms of dppe), since the absence of substituents on the donor atoms, even if they give a sufficient ring size to promote the orthometalation, could result in no orthometalation. We have a clear example of this in the reaction of **2c** with Tlacac,[8] which results in the formation of $[Pd\{[C(H)PPh_3]_2CO\}(acac\text{-}O,O')]ClO_4$ 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 $TlClO_4$ (1:2 molar ratio) in NCMe, as indicated in Scheme 5.

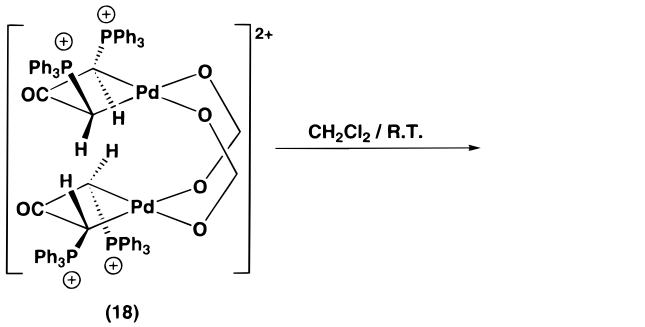
The orthometalation can also be produced spontaneously, without thermal induction or addition of ligands. The dinuclear complex $[Pd(\mu\text{-}OOCMe)\{[C(H)PPh_3]_2CO\}]_2(ClO_4)_2$ (**18**)[8] evolves spontaneously in CH_2Cl_2 at room temperature, resulting in the formation of $[(C_6H_4\text{-}$

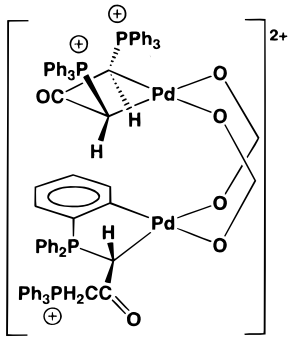
(32) Oberhauser, W.; Bachmann, C.; Stampfl, T.; Haid, R.; Brüggeller, P. *Polyhedron* **1997**, *16*, 2827.
(33) Wu, B.; Zhang, W.; Huang, X.; Wu, X.; Yu, S. *Polyhedron* **1997**, *16*, 801.

Scheme 5



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





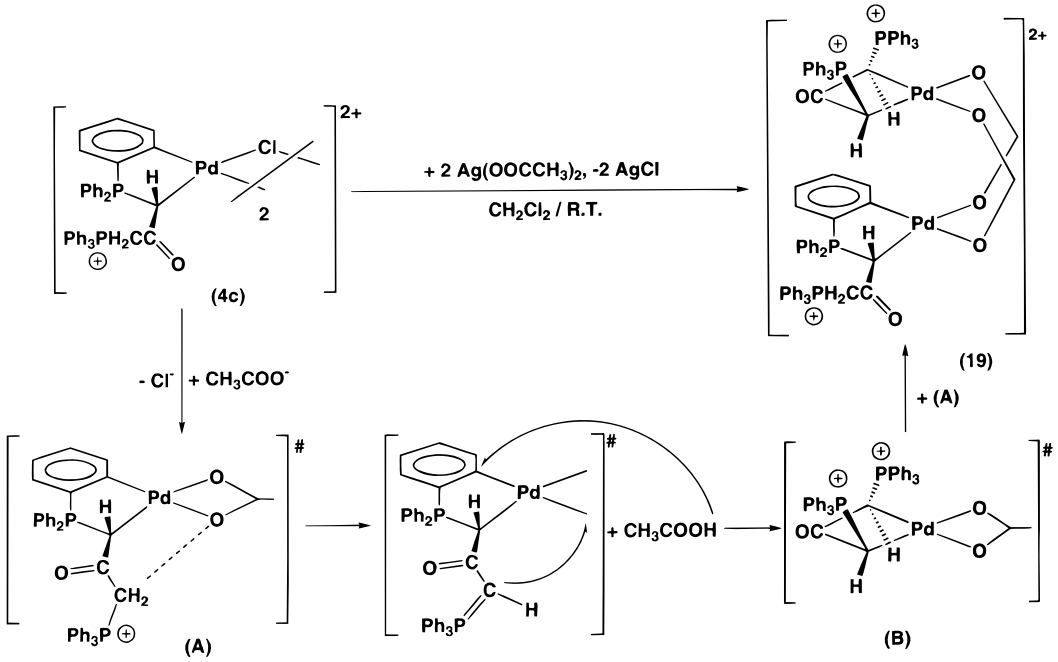
(2)

characterization of this compound has been carried out on the basis of its analytical and spectroscopic data. The ^1H NMR spectrum of **19** shows characteristic resonances for the CH_2PPh_3 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 $^{31}P\{^1H\}$ 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 $^1H\{^{31}P\}$ spectra and selective irradiation of all P resonances. More structural information can be obtained from the $^1H-^1H$ 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_3 groups to the outer side. In the orthometalated ligand, the ylidic proton is also directed inward and the bulky $COCH_2$-PPh_3 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 $[Ph_3P{=}C(H)COCH_2PPh_3]ClO_4$,[8] 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 $Ag(OOCCH_3)$ in a noncoordinating solvent such as CH_2Cl_2. 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.

Scheme 6



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 $[C(H)PPh_3]_2CO$ 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_2, 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^{-1}) were recorded on a Perkin-Elmer 883 infrared spectrophotometer from Nujol mulls between polyethylene sheets. ^1H (300.13 MHz), $^{13}C\{^1H\}$ (75.47 MHz), and $^{31}P\{^1H\}$ (121.49 MHz) NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 solutions at room temperature (unless otherwise stated) on a Bruker ARX-300 spectrometer; ^1H and $^{13}C\{^1H\}$ were referenced using the solvent signal as internal standard, and $^{31}P\{^1H\}$ was externally referenced to H_3PO_4 (85%). The two-dimensional $^1H-^1H$ 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 × 1024 matrix and then transformed into 1024 × 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_2Cl_2 solutions. Electrical conductivity measurements were performed in acetone solutions with concentrations of about 5 × 10^{-4} M with a Philips PW 9509 conductivity cell.

The starting bis(ylide) complexes *cis*-$PdCl_2[\{C(H)PPh_3\}_2CO]$ (**1c**), $\{Pd(\mu\text{-}Cl)[\{C(H)PPh_3\}_2CO]\}_2(ClO_4)_2$ (**2c**), $\{Pd[\{C(H)PPh_3\}_2CO](NCMe)_2\}(ClO_4)_2$ (**3c**), and $\{Pd(\mu\text{-}OAc)[\{C(H)PPh_3\}_2CO]\}_2(ClO_4)_2$ (**18**) were prepared according to published methods.[8]

Preparation of Phosphonium Salts. $[Et_2PhPCH_2COCH_2PPhEt_2]Cl_2$. To a solution of $ClCH_2COCH_2Cl$ (2.000 g, 15.75 mmol) in 35 mL of deoxygenated $CHCl_3$ under nitrogen was added $PPhEt_2$ (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 $Et_2O/CHCl_3$ 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 $Et_2O/CHCl_3$ (3 × 10 mL), and dried in vacuo. Obtained: 6.115 g (84% yield). The product crystallizes as a monohydrate.

Anal. Calcd. for $C_{23}H_{34}Cl_2OP_2\cdot OH_2$ (477.39 g/mol): C, 57.86; H, 7.60. Found: C, 57.42; H, 7.59. IR (ν, cm^{-1}): 1714 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 7.90 (m, 2H, H_o, Ph), 7.57 (m, 3H, $H_m + H_p$, Ph), 5.51 (d, 2H, CH_2, $^2J_{P-H} = 9$ Hz), 2.74 (m, 4H, CH_2CH_3), 1.19 (dt, 6H, CH_2CH_3, $^3J_{P-H} = 20$ Hz, $^3J_{H-H} = 7$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.52.

(34) Wolsey, W. C. *J. Chem. Educ.* **1973**, *50*, A335.

[EtPh₂PCH₂COCH₂PPh₂Et]Cl₂. To a solution of $ClCH_2COCH_2Cl$ (2.000 g, 15.75 mmol) in 35 mL of deoxygenated $CHCl_3$ under nitrogen was added PPh_2Et (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_2O. 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_2O (3 × 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 (ν, cm^{-1}): 1716 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 7.85 (m, 4H, H_o, Ph), 7.60 (m, 6H, $H_m + H_p$, Ph), 6.02 (s, br, 2H, CH_2), 3.17 (m, 2H, CH_2CH_3), 1.20 (br, 3H, CH_2CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.12.

Cl₂Pd{[C(H)PPhEt₂]₂CO} (1a). To a solution of $Pd(OAc)_2$ (0.3000 g, 1.336 mmol) in CH_2Cl_2 (35 mL) was added $[Et_2PhPCH_2COCH_2PPhEt_2]Cl_2$ (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_2O (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_2Cl_2/Et_2O, giving deep yellow crystals of **1a**·$0.75CH_2Cl_2$, which were used in analytical and spectroscopic measurements. The amount of CH_2Cl_2 of crystallization was determined by ^1H 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 [$(M - Cl)^+$, 35%]. IR (ν, cm^{-1}): 1599 (ν_{CO}); 277, 260 (ν_{Pd-Cl}). ^1H NMR ($CDCl_3$): δ 7.92 (m, 2H, H_o, Ph), 7.60 (m, 3H, $H_m + H_p$, Ph), 3.25 (d, 1H, CH, $^2J_{P-H}$ = 6 Hz), 2.98 (m, 2H, CH_2CH_3), 2.76 (m, 1H, CH_2CH_3), 2.63 (m, 1H, CH_2CH_3), 1.21 (dt, 3H, CH_2CH_3, $^3J_{P-H}$ = 19 Hz, $^3J_{H-H}$ = 7.6 Hz), 1.14 (dt, 3H, CH_2CH_3, $^3J_{P-H}$ = 19 Hz, $^3J_{H-H}$ = 7.6 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 33.82.

Cl₂Pd{[C(H)PPh₂Et]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**·$0.6CH_2Cl_2$, which were used in analytical and spectroscopic measurements. The amount of CH_2Cl_2 of crystallization was determined by ^1H NMR integration.

Anal. Calcd for $C_{31}H_{32}Cl_2OP_2Pd \cdot 0.6CH_2Cl_2$ (710.81 g/mol): C, 53.39; H, 4.70. Found: C, 53.33; H, 4.39. MS [*m*/*z*, %]: 625 [$(M - Cl)^+$, 28]. IR (ν, cm^{-1}): 1604 (ν_{CO}); 286, 274 (ν_{Pd-Cl}). ^1H NMR ($CDCl_3$): δ 7.95 (m, 2H, Ph), 7.79−7.52 (m, 6H, Ph), 7.40 (m, 2H, Ph), 3.61 (d, 1H, CH, $^2J_{P-H}$ = 6.6 Hz), 3.39 (m, 1H, CH_2CH_3), 2.87 (m, 1H, CH_2CH_3), 1.11 (dt, 3H, CH_2CH_3, $^3J_{P-H}$ = 19 Hz, $^3J_{H-H}$ = 7.5 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.11.

[Pd(μ-Cl){[C(H)PPhEt₂]₂CO}]₂(ClO₄)₂ (2a). To a solution of **1a** (0.300 g, 0.532 mmol) in CH_2Cl_2 (40 mL) was added $AgClO_4$ (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_2O (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 (ν, cm^{-1}): 1614 (ν_{CO}); 270, 248 (ν_{Pd-Cl}). ^1H NMR ($CDCl_3$): δ 7.81 (m, 2H, H_o, Ph), 7.61 (m, 1H, H_p, Ph), 7.52 (m, 2H, H_m, Ph), 3.66 (br, 1H, CH), 2.49 (m, 4H, CH_2CH_3), 1.17 (br m, 6H, CH_2CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 33.24.

[Pd(μ-Cl){[C(H)PPh₂Et]₂CO}]₂(ClO₄)₂ (2b). Complex **2b** was obtained as a yellow solid similarly to **2a** starting from **1b** (0.300 g, 0.455 mmol) and $AgClO_4$ (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 (ν, cm^{-1}): 1621 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 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_2CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 28.81.

[Pd(C₆H₄-2-PPh₂C(H)COCH₂PPh₃)(μ-Cl)]₂(ClO₄)₂ (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_2O (40 mL) and continuous stirring **4c** was obtained as an orange solid, which was filtered, washed with additional Et_2O (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 $C_{78}H_{64}Cl_4O_{10}P_4Pd_2$ (1639.87 g/mol): C, 57.13; H, 3.93. Found: C, 57.17; H, 3.99. MS [*m*/*z*, %]: 1541 [$(M_2 - ClO_4)^+$, 25]. IR (ν, cm^{-1}): 1648 (ν_{CO}), 278 (ν_{Pd-Cl}). ^1H NMR (CD_2Cl_2): δ 7.78−7.48 (m, Ph), 7.14−7.12 (m, C_6H_4), 5.30 (dd, CH_2P, maj), 5.21 (dd, CH_2P, min), 4.98 (dd, CH_2P, min, $^2J_{H-H}$ = 17.3 Hz, $^2J_{P-H}$ = 14.1 Hz), 4.78 (pseudo t, CH_2P, maj, $^2J_{H-H} \cong {}^2J_{P-H}$ = 15 Hz), 4.58 (dd, CH, min, $^2J_{P-H}$ = 3.9 Hz, $^4J_{P-H}$ = 2.5 Hz), 4.52 (dd, CH, maj, $^2J_{P-H}$ = 4.3 Hz, $^4J_{P-H}$ = 2.7 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 22.84 (d, min, $C_6H_4PPh_2$, $^4J_{P-P}$ = 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_2PPh_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 190.87 (t, CO, min, $^2J_{P-C}$ = 7 Hz), 190.36 (t, CO, maj, $^2J_{P-C}$ = 6.4 Hz), 157.58 (d, C_1, C_6H_4, maj, $^2J_{P-C}$ = 18.8 Hz), 157.49 (d, C_1, C_6H_4, min, $^2J_{P-C}$ = 18.8 Hz), 137−120 (Ph + C_6H_4, both isomers), 43.76 (br d, CH_2, min, $^1J_{P-C}$ = 49.2 Hz), 38.85 (dd, CH_2, maj, $^1J_{P-C}$ = 57.5 Hz, $^3J_{P-C}$ = 10.5 Hz), 31.35 (dd, CH-ylide, maj, $^1J_{P-C}$ = 66.8 Hz, $^3J_{P-C}$ = 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 $^{31}P\{^1H\}$ NMR spectroscopy. The resonances attributed to **4b** are as follows (CD_2Cl_2): δ 33.39 (d, $^4J_{P-P}$ = 6.5 Hz, C_6H_4-2-PPhEt), 33.15 (d, $^4J_{P-P}$ = 6 Hz, C_6H_4-2-PPhEt), 32.07 (d, $^4J_{P-P}$ = 7 Hz, C_6H_4-2-PPhEt), 26.67 (d, CH_2PPh_3), 26.51 (d, CH_2PPh_3), 26.23 (d, CH_2PPh_3).

NMR Experiments. Characterization of the Equilibria. (a) The NMR spectra of **2c** in $NCCD_3$ show resonances corresponding exclusively to the cationic monomer $[PdCl\{[C(H)PPh_3]_2CO\}(NCCD_3)]^+ClO_4^-$. ^1H: δ 7.76−7.51 (m, 30 H, Ph), 4.16 (d, 1H, CH-ylide, $^2J_{P-H}$ = 6 Hz), 4.12 (d, 1H, CH-ylide, $^2J_{P-H}$ = 3.3 Hz). $^{31}P\{^1H\}$: δ 26.30 (d, 1P, $^4J_{P-P}$ = 10 Hz), 24.90 (d, 1P). (b) The NMR spectra of **1c** in $NCCD_3$ 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 ^1H, δ 3.92 (d, 1H, CH-ylide, $^2J_{P-H}$ = 7.5 Hz); $^{31}P\{^1H\}$, δ 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 $NCCD_3$ 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 $NCCD_3$ solutions (a) and (b) described above were heated at a temperature of 80 °C for 8 h, and after cooling, the ^1H and $^{31}P\{^1H\}$ NMR spectra were measured in the same solvent. Experiment (a) showed a conversion of 100% of the starting product **2c** into the monomer $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)Cl(NCCD_3)]^+$. The resonances attributed to this compound are ^1H, δ 7.73−7.51 (m, 25H, Ph), 7.36−7.17 (m, 4H, C_6H_4), 6.01 (dd, 1H, CH_2PPh_3, $^2J_{H-H}$ = 16.5 Hz, $^2J_{P-H}$ = 10.2 Hz), 4.62 (pseudo t, 1H, CH_2-

PPh_3, $^2J_{H-H} \cong {}^2J_{P-H} = 16$ Hz), 4.56 (d, 1H, CH-ylide, $^2J_{P-H} = 4.2$ Hz); $^{31}P\{^1H\}$ NMR, δ 25.29 (d, $^4J_{P-P} = 6.2$ 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 $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2\text{-}PPh_3)Cl(NCCD_3)]^+$ but slightly shifted, probably due to the presence of a fast equilibrium with **5**.

$[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)Cl_2]$ (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 (ν, cm^{-1}): 1636 (ν_{CO}), 277 (ν_{Pd-Cl}). ^1H NMR (CD_2Cl_2): δ 8.00−7.43 (m, 26H, C_6H_4 + Ph), 7.02 (m, 3H, C_6H_4), 6.49 (br t, 1H, CH_2P), 4.64 (br s, 1H, CH-ylide), 4.37 (pseudo t, 1H, CH_2P, $^2J_{H-H} \cong {}^2J_{P-H} = 15.3$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 23.35 (d), 20.75 (d, $^4J_{P-P} = 7.3$ Hz).

$[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)Cl(py)](ClO_4)$ (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_2O (40 mL) and continuous stirring **6** was obtained as a white solid, which was filtered, washed with additional Et_2O (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$^+$, 15]. IR (ν, cm^{-1}): 1645 (ν_{CO}), 278 (ν_{Pd-Cl}). ^1H NMR ($CDCl_3$): δ 8.04 (d, 2H, $H_2 + H_6$, py, $^3J_{H-H} = 5.1$ Hz), 7.83−7.43 (m, 26H, Ph + H_4 (py)), 7.23 (m, 2H, $H_3 + H_5$, py), 7.15−6.96 (m, 3H, C_6H_4), 6.23 (d, 1H, H_6, C_6H_4, $^3J_{H-H} = 7.2$ Hz), 6.12 (dd, 1H, CH_2P, $^2J_{H-H} = 15.3$ Hz, $^2J_{P-H} = 10.5$ Hz), 4.71 (pseudo t, CH_2P, 1H, $^2J_{H-H} \cong {}^2J_{P-H} = 16$ Hz), 4.58 (dd, 1H, CH-ylide, $^2J_{P-H} = 6$ Hz, $^4J_{P-H} = 2.7$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.17 (d, $^4J_{P-P} = 6.2$ Hz), 21.42 (d).

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

Anal. Calcd for $C_{46}H_{41}Cl_2NO_5P_2Pd$ (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$^+$, 20]. IR (ν, cm^{-1}): 1647 (ν_{CO}), 263 (ν_{Pd-Cl}). ^1H NMR (CD_2Cl_2): δ 7.93−7.39 (m, 28 H, Ph + NC_5H_3), 7.18−7.04 (m, 3H, C_6H_4), 6.33 (d, 1H, H_6, C_6H_4, $^3J_{H-H} = 7.5$ Hz), 6.09 (dd, 1H, CH_2P, $^2J_{H-H} = 16$ Hz, $^2J_{P-H} = 10.5$ Hz), 4.51 (dd, 1H, CH-ylide, $^2J_{P-H} = 6.6$ Hz, $^4J_{P-H} = 2.4$ Hz), 4.44 (dd, CH_2P, 1H, $^2J_{P-H} = 14$ Hz), 2.18 (s, 6H, Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 22.76 (d, $^4J_{P-P} = 6.2$ Hz), 21.19 (d).

$[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)Cl(PPh_3)](ClO_4)$ (8). To a solution of complex **2c** (0.186 g, 0.113 mmol) in CH_2Cl_2 (20 mL) was added PPh_3 (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_2O (20 mL), and air-dried. Obtained: 0.140 g (56% yield). Recrystallization of **8** from CH_2Cl_2/Et_2O gave colorless crystals of **8**·0.5CH_2Cl_2, which were used for analytical and spectroscopic measurements. The amount of CH_2Cl_2 was determined by ^1H 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$^+$, 100]. IR (ν, cm^{-1}): 1628 (ν_{CO}), 270 (ν_{Pd-Cl}). ^1H NMR (CD_2Cl_2): δ 7.79−7.15 (m, 40H, Ph), 7.03 (m, 1H, C_6H_4), 6.85 (m, 1H, C_6H_4), 6.55 (m, 2H, C_6H_4), 5.86 (dd, 1H, CH_2P, $^2J_{H-H} = 17.1$ Hz, $^2J_{P-H} = 11.4$ Hz), 5.00 (td, 1H, CH-ylide, $^2J_{P-H} = {}^3J_{P-H} = 8.2$ Hz, $^4J_{P-H} = 1.6$ Hz), 4.80 (dd, CH_2P, 1H, $^2J_{P-H} = 13.3$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 31.60 (d, Pd−PPh_3, $^3J_{P-P} = 13.8$ Hz), 21.00 (d, CH_2PPh_3, $^4J_{P-P} = 7.8$ Hz), 17.02 (dd, C_6H_4-2- PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (the carbonyl and ylidic carbons were not observed): δ 163.86 (d, C_1, C_6H_4, $^2J_{P-C} = 20$ Hz), 138.87, 131.12, 129.62, 129.14, 124.17 (C_6H_4), 134−127 (Ph), 125.23 (d, C_{ipso}, Ph, $^1J_{P-C} = 90$ Hz), 118.66 (d, C_{ipso}, Ph, $^1J_{P-C} = 89$ Hz), 37.93 (dd, CH_2, $^1J_{P-C} = 56$ Hz, $^3J_{P-C} = 14$ Hz).

$[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)Cl(PPhMe_2)](ClO_4)$ (9). Complex **9** was obtained similarly to **8** starting from **2c** (0.442 g, 0.269 mmol) and $PPhMe_2$ (76 μL, 0.54 mmol). Obtained: 0.372 g (72% yield).

Anal. Calcd for $C_{47}H_{43}Cl_2O_5P_3Pd$ (958.08 g/mol): C, 58.92; H, 4.52. Found: C, 58.85; H, 4.46. MS [*m*/*z*, %]: 857 [M$^+$, 100]. IR (ν, cm^{-1}): 1627 (ν_{CO}), 257 (ν_{Pd-Cl}). ^1H NMR (CD_2Cl_2): δ 7.83−7.33 (m, 30 H, Ph), 7.14−6.96 (m, 3H, C_6H_4), 6.82 (m, 1H, C_6H_4), 5.79 (dd, 1H, CH_2P, $^2J_{H-H} = 17.1$ Hz, $^2J_{P-H} = 11.1$ Hz), 4.76 (td, 1H, CH-ylide, $^2J_{P-H} = {}^3J_{P-H} = 8.7$ Hz, $^4J_{P-H} = 2.3$ Hz), 4.63 (dd, CH_2P, 1H, $^2J_{P-H} = 13.8$ Hz), 1.57 (d, CH_3, 3H, $^2J_{P-H} = 10.5$ Hz), 1.37 (d, CH_3, 3H, $^2J_{P-H} = 10.1$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 21.22 (d, CH_2PPh_3, $^4J_{P-P} = 7.5$ Hz), 15.13 (dd, C_6H_4-2- PPh_2), 0.95 (d, Pd−$PPhMe_2$, $^3J_{P-P} = 13.7$ Hz).

$[Pd\{[CH(PPh_3)]_2CO\}(py)_2](ClO_4)_2$ (10). To a solution of complex **3c** (0.151 g, 0.156 mmol) in CH_2Cl_2 (20 mL) was added pyridine (51 μL, 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_2O (10 mL), giving **10** as a white solid, which was filtered, washed with Et_2O (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_4)$^+$, 60]. IR (ν, cm^{-1}): 1614, 1607 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 8.76 (d, 2H, H_o, py, $^3J_{H-H} = 5.1$ Hz), 7.97−7.21 (m, 16 H, Ph + H_p(py)), 6.87 (t, 2H, H_m, py, $^3J_{H-H} \cong 6$ Hz), 4.99 (d, 1H, CH ylide, $^2J_{P-H} = 3.9$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 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_2Cl_2 (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_2O (10 mL), giving **11** as a white solid, which was filtered, washed with Et_2O (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 (ν, cm^{-1}): 1589 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 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_2-dppm, $^2J_{H-H} = 15.3$ Hz, $^2J_{P-H} = 10.8$ Hz), 4.02 (dt, 1H, CH_2-dppm, $^2J_{H-H} = 15.3$ Hz, $^2J_{P-H} = 9.6$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 22.40 (virtual t, bis(ylide), $^3J_{P-P} = 4.4$ Hz), −25.54 (virtual t, dppm).

$[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)(py)_2](ClO_4)_2$ (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_2O (30 mL) and continuous stirring **12** was obtained as a white solid, which was filtered, washed with additional Et_2O (20 mL), and air-dried. Obtained: 0.144 g (73% yield). Recrystallization of **12** from CH_2Cl_2/*n*-hexane gave colorless crystals of **12**·0.25CH_2Cl_2, which were used for analytical and spectroscopic measurements. The amount of CH_2Cl_2 was determined by ^1H 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_4)$^+$, 10]. IR (ν, cm^{-1}): 1652 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 8.71 (d, 2H, H_o, py, $^3J_{H-H} = 5.1$ Hz), 8.31 (d, 2H, H_o, py, $^3J_{H-H} = 4.8$ Hz), 7.91−7.18 (m, 31 H, Ph + H_m + H_p(py)), 7.01 (m, 2H, C_6H_4), 6.78 (m, 1H, C_6H_4), 6.57 (d, 1H, C_6H_4, $^3J_{H-H} = 7.2$ Hz), 5.43 (dd, 1H, CH_2P, $^2J_{H-H}$

≅ $^2J_{P-H}$ = 16.8 Hz), 4.60 (d, 1H, CH-ylide, $^2J_{P-H}$ = 3.9 Hz), 4.17 (dd, CH_2P, 1H, $^2J_{P-H}$ = 10.2 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.80 (d, $^4J_{P-P}$ = 10.7 Hz), 20.97 (d).

Attempted Orthometalation of [Pd{[CH(PPh$_3$)]$_2$CO}(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_2O (30 mL) and continuous stirring a white solid was obtained, which was filtered, washed with additional Et_2O (20 mL), air-dried, and identified spectroscopically as a mixture of [Pd(C$_6$H$_4$-2-PPh$_2$C(H)COCH$_2$PPh$_3$)(Ph$_2$PCH$_2$PPh$_2$-*P,P′*)](ClO$_4$)$_2$ (**13a**) and[Pd(C$_6$H$_4$-2-PPh$_2$C(H)COCH$_2$PPh$_3$)(Ph$_2$PCH$_2$P(O)Ph$_2$-*P,O*)](ClO$_4$)$_2$ (**13b**). Obtained: 0.168 g.

^1H NMR (CD_2Cl_2): (**13a**) δ 5.57−5.51 (m, 1H, CH-ylide), 4.91−4.70 (m, 2H, CH_2PPh_3 + dppm), 4.29 (dd, 1H, CH_2PPh_3, $^2J_{H-H}$ = 18 Hz, $^2J_{P-H}$ = 13.5 Hz), 4.15−3.98 (m, 1H, dppm); (**13b**) δ 5.37 (dd, 1H, CH_2PPh_3, $^2J_{H-H}$ = 17.7 Hz, $^2J_{P-H}$ = 13.8 Hz), 5.12 (dd, 1H, CH_2PPh_3, $^2J_{H-H}$ = 17.7 Hz, $^2J_{P-H}$ = 11.1 Hz), 4.33 (d, 1H, CH-ylide, $^2J_{P-H}$ = 13.5 Hz), 3.75 (dt, CH_2-dppm, $^2J_{H-H}$ = 15 Hz, $^2J_{P-H}$ = 10 Hz), 3.53 (dt, CH_2-dppm, $^2J_{H-H}$ = 15 Hz, $^2J_{P-H}$ = 11 Hz).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): (**13a**) δ 23.55 (ddd, 1P, C$_6$H$_4$-2-PPh$_2$, $^3J_{P-P}$ = 33.9 Hz, $^3J_{P-P}$ = 16.1 Hz, $^4J_{P-P}$ = 8.9 Hz), 21.49 (d, 1P, CH_2PPh_3, $^4J_{P-P}$ = 8.9 Hz), −14.43 (dd, 1P PPh$_2$ *cis*-to-CH-ylide, $^2J_{P-P}$ = 59.4 Hz, $^3J_{P-P}$ = 16.1 Hz), −29.19 (dd, 1P, PPh$_2$ *trans*-to-CH-ylide, $^2J_{P-P}$ = 59.4 Hz, $^3J_{P-P}$ = 33.9 Hz); (**13b**) δ 59.14 (d, 1P, P=O, $^2J_{P-P}$ = 24.8 Hz), 25.41 (dd, 1P, Pd−PPh$_2$, $^3J_{P-P}$ = 17.7 Hz), 21.36 (d, CH_2PPh_3, $^4J_{P-P}$ = 8.9 Hz), 17.15 (dd, 1P, C$_6$H$_4$-2-PPh$_2$).

[Pd(C$_6$H$_4$-2-PPh$_2$C(H)COCH$_2$PPh$_3$)(NCMe)(PPh$_3$)](ClO$_4$)$_2$ (14). To a solution of **3c** (0.150 g, 0.155 mmol) in CH_2Cl_2 (20 mL) was added PPh_3 (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_2O (30 mL) was added. By continuous stirring, **14** was obtained as a white solid, which was filtered, washed with Et_2O (10 mL), and air-dried. Obtained: 0.135 g (73% yield). Recrystallization of **14** from CH_2Cl_2/*n*-hexane gave colorless crystals of **14**·0.75CH_2Cl_2, which were used for analytical and spectroscopic measurements. The amount of CH_2Cl_2 was determined by ^1H NMR integration.

Anal. Calcd for $C_{59}H_{50}Cl_2NO_9P_3Pd$·0.75$CH_2Cl_2$ (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$_4$)$^+$, 20]. IR (ν, cm^{-1}): 2319, 2291 (ν_{CN}), 1640 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 8.01−7.95 (m, 2H, Ph), 7.69−7.28 (m, 38H, Ph), 7.05 (m, 1H, C$_6$H$_4$), 6.94 (m, 1H, C$_6$H$_4$), 6.67 (m, 2H, C$_6$H$_4$), 5.54 (br m, 1H, CH-ylide), 5.37 (pseudo t, 1H, CH_2P, $^2J_{H-H}$ ≅ $^2J_{P-H}$ = 16.8 Hz), 4.96 (dd, 1H, CH_2P, $^2J_{P-H}$ = 10.8 Hz), 1.86 (s, 3H, NCMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.84 (d, Pd−PPh$_3$, $^3J_{P-P}$ = 15.2 Hz), 22.73 (d, CH_2PPh_3, $^4J_{P-P}$ = 8 Hz), 17.45 (dd, C$_6$H$_4$-2-PPh$_2$).

[Pd(C$_6$H$_4$-2-PPh$_2$C(H)COCH$_2$PPh$_3$)(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 $C_{65}H_{56}Cl_2O_9P_4Pd$ (1282.36 g/mol): C, 60.88; H, 4.40. Found: C, 60.52; H, 4.34. MS [*m*/*z*, %]: 1181 [(M − ClO$_4$)$^+$, 12]. IR (ν, cm^{-1}): 1642 (ν_{CO}). ^1H NMR ($CDCl_3$): δ 7.91−6.87 (m, 46H, Ph + C$_6$H$_4$), 6.76 (t, 1H, C$_6$H$_4$, $^3J_{H-H}$ = 7.8 Hz), 6.68 (d, 1H, C$_6$H$_4$, $^3J_{H-H}$ = 7.2 Hz), 6.64 (d, 1H, C$_6$H$_4$, $^3J_{H-H}$ = 7.8 Hz), 5.10 (dd, 1H, CH-ylide, $^2J_{P-H}$ = 10.2 Hz, $^3J_{P-H}$ = 6.3 Hz), 4.02 (dd, 1H, CH_2P, $^2J_{H-H}$ = 18 Hz, $^2J_{P-H}$ = 13.8 Hz), 3.52 (dd, 1H, CH_2P, $^2J_{P-H}$ = 10.2 Hz), 3.16, 2.71, 2.52, 2.31 (4m, 4H, CH_2-dppe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 55.03 (dd, 1P, P-dppe-*cis*-to-C-ylide, $^3J_{P-P}$ = 16.8 Hz, $^3J_{P-P}$ (dppe) = 23.4 Hz), 43.67 (dd, 1P, P-dppe-*trans*-to-C-ylide, $^3J_{P-P}$ = 31.8 Hz, $^3J_{P-P}$ (dppe) = 23.4 Hz), 24.13 (ddd, C$_6$H$_4$-2-PPh$_2$, $^4J_{P-P}$ = 9 Hz), 22.23 (d, CH_2PPh_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 193.46 (t, CO, $^2J_{P-C}$ = 5 Hz), 169.25 (ddd, C$_1$, C$_6$H$_4$, $^2J_{Ptrans-C}$ = 125 Hz, $^2J_{Pcis-C}$ = 29 Hz, $^2J_{P-C}$ = 6 Hz), 138−117 (Ph + C$_6$H$_4$), 47.12 (t, CH-ylide, $^1J_{P-C}$ ≅ $^2J_{Ptrans-C}$ = 55 Hz), 39.11 (dd, CH_2, dppe, $^1J_{P-C}$ = 60 Hz, $^2J_{P-C}$ = 11 Hz), 37.73 (dd, CH_2, dppe, $^1J_{P-C}$ = 53 Hz, $^2J_{P-C}$ = 17 Hz), 28.02 (dt, CH_2PPh_3, $^1J_{P-C}$ = 36 Hz, $^3J_{P-C}$ ≅ $^4J_{P-C}$ = 11 Hz).

[Pd(C$_6$H$_4$-2-PPh$_2$C(H)COCH$_2$PPh$_3$)(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 (ν, cm^{-1}): 1620 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 9.77 (dd, 1H, H$_\alpha$, phen, $^3J_{\alpha\beta}$ = 5 Hz, $^4J_{\alpha\gamma}$ = 1.1 Hz), 9.00 (dd, 1H, H$_{\alpha'}$, phen, $^3J_{\alpha'\beta'}$ = 4.5 Hz, $^4J_{\alpha'\gamma'}$ = 1 Hz), 8.62 (dd, 1H, H$_{\gamma'}$, phen, $^3J_{\gamma'\beta'}$ = 8.2 Hz), 8.51 (dd, 1H, H$_\gamma$, phen, $^3J_{\gamma\beta}$ = 8.2 Hz), 8.09 (dd, 1H, H$_\beta$, phen), 8.01−7.96 (AB spin system, 2H, H$_\delta$ + H$_{\delta'}$, phen, $^3J_{H-H}$ = 8.9 Hz), 7.96 (dd, 1H, H$_{\beta'}$, phen), 7.91−7.84 (m, 2H, Ph), 7.71 (d, 1H, H$_6$, C$_6$H$_4$, $^3J_{H-H}$ = 7.7 Hz), 7.63−7.26 (m, 26H, Ph + C$_6$H$_4$), 5.38 (dd, 1H, CH_2P, $^2J_{H-H}$ = 17.8 Hz, $^2J_{P-H}$ = 12.1 Hz), 5.35 (pseudo t, 1H, CH-ylide, $^2J_{P-H}$ ≅ $^4J_{P-H}$ = 1.6 Hz), 5.16 (dd, 1H, CH_2P, $^2J_{P-H}$ = 12.3 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 21.43 (d, $^4J_{P-P}$ = 10.3 Hz), 20.32 (d). This complex was insufficiently soluble for ^{13}C NMR measurements.

[Pd(C$_6$H$_4$-2-PPh$_2$C(H)COCH$_2$PPh$_3$)(NCMe)$_2$](ClO$_4$)$_2$ (17). To a solution of **4c** (0.300 g, 0.182 mmol) in NCMe (20 mL) was added $TlClO_4$ (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_2O (30 mL) was added. By continuous stirring, complex **17** was obtained as a white solid, which was filtered, washed with Et_2O (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$_4$)$^+$, 55]. IR (ν, cm^{-1}): 2319, 2291 (ν_{CN}), 1653 (ν_{CO}). ^1H NMR ($CDCl_3$/213 K): δ 7.78−7.09 (m, 29H, Ph + C$_6$H$_4$), 5.08 (br m, 1H, CH-ylide), 5.02, 4.98 (br AB spin system, CH_2P, $^2J_{H-H}$ = 13 Hz), 2.41 (s, 3H, NCMe), 2.28 (s, 3H, NCMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$/213 K): δ 23.82 (br s), 21.81 (br s).

[(C$_6$H$_4$-2-PPh$_2$C(H)COCH$_2$PPh$_3$)Pd(μ-Ac)$_2$Pd{[C(H)PPh$_3$]$_2$CO}](ClO$_4$)$_2$ (19). A solution of complex **18** in CH_2Cl_2 (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_2O (25 mL), filtered, and air-dried. The yield is quantitative. Recrystallization of **19** from CH_2Cl_2/*n*-hexane gave colorless crystals of **19**·0.5CH_2Cl_2, which were used for analytical and spectroscopic measurements. The amount of CH_2Cl_2 was determined by ^1H NMR integration.

Anal. Calcd for $C_{82}H_{70}Cl_2O_{14}P_4Pd_2$·0.5$CH_2Cl_2$ (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 (ν, cm^{-1}): 1640−1565 (broad absorption,ν_{CO}, ylide and acetate). ^1H NMR (CD_2Cl_2): δ 7.85−7.28 (m, 58H, Ph + C$_6$H$_4$), 6.81 (td, 1H, C$_6$H$_4$, $^3J_{H-H}$ = 7.8 Hz, $^5J_{P-H}$ = 2.9 Hz), 5.74 (ddd, 1H, CH_2P, $^2J_{H-H}$ = 17.8 Hz, $^2J_{P-H}$ = 9.5 Hz, $^4J_{P-H}$ = 1.2 Hz), 5.50 (dd, 1H, CH_2P, $^2J_{P-H}$ = 15 Hz), 4.70 (pseudo t, 1H, CH-ylide (orthom), $^2J_{P-H}$ ≅ $^4J_{P-H}$ = 3.1 Hz), 2.99 (d, 1H, CH-bis(ylide), $^2J_{P-H}$ = 5.1 Hz), 2.85 (dd, 1H, CH-bis(ylide), $^2J_{P-H}$ = 5.6 Hz, $^4J_{P-H}$ = 0.8 Hz), 1.45 (s, 3H, Me), 0.60 (s, 3H, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.14 (d, $^4J_{P-P}$ = 8.8 Hz, P in orthom ring), 25.74, 25.54 (AB spin system, bis(ylide), $^4J_{P-P}$ = 8.5 Hz), 22.23 (d, CH_2PPh_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 195.88 (t, *C*OCH$_2$, $^2J_{P-C}$ = 4 Hz), 192.50 (dd, *C*O-bisylide, $^2J_{P-C}$ = 7 Hz, $^2J_{P'-C}$ = 4 Hz), 181.08 (s, COO$^-$), 180.62 (s, COO$^-$), 155.36 (d, C$_1$, C$_6$H$_4$, $^2J_{P-C}$ = 22 Hz), 136.61−119.79 (m, Ph + C$_6$H$_4$), 52.41 (dd, Pd−CH in ring, $^1J_{P-C}$ = 54 Hz, $^3J_{P-C}$ = 14 Hz), 41.03 (dd, Pd−CH bis(ylide), $^1J_{P-C}$ = 58 Hz, $^3J_{P-C}$ = 10 Hz), 39.74 (dd, CH_2P, $^1J_{P-C}$ = 60 Hz, $^3J_{P-C}$ = 12 Hz), 39.45 (dd, Pd−CH bis(ylide), $^1J_{P-C}$ = 58 Hz, $^3J_{P-C}$ = 10 Hz), 24.48 (s, CH_3), 23.13 (s, CH_3).

Crystallography. Data Collection. Crystals suitable for X-ray measurements were grown by slow diffusion of a $CHCl_3$ solution of **14** into *n*-hexane at room temperature. A pale

yellow crystal of **14**·2$CHCl_3$ 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 $21.9° \leq 2\theta \leq 31.9°$. For intensity data collection, pure ω 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[35] were based on azimuthal scans of 13 reflections, 9 of which had the Eulerian angle χ near 90°. The other four reflections used for this purpose had their bisecting-position χ values distributed in the range 16−60°.

Structure Solution and Refinement. The structure was solved and developed by Patterson and Fourier methods.[36] 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 $CHCl_3$ 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_o^2, and all reflections were used in the least-squares calculation.[37] 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.[38]

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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**·2$CHCl_3$ (9 pages). Ordering information is given on any current masthead page.

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(35) 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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