Reactions of Electron-Rich Arylpalladium Complexes with Olefins. Origin of the Chelate Effect in Vinylation Catalysis

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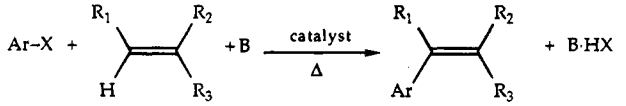
Reaction of (dippp)Pd(Ph)Cl (**1**) with norbornene or styrene yields (dippp)$PdCl_2$ (**8**) and (dippp)Pd(η^2-olefin). Kinetic follow-up reveals fast formation of (dippp)Pd(phenylnorbornyl)-Cl (**10**), followed by its slow decomposition, with $k_{insertion} = 0.50 \times 10^{-3}$ L mol^{-1} s^{-1} and $k_{decomposition} = 0.90 \times 10^{-4}$ s^{-1}. Phenylnorbornane and (with styrene) stilbenes are also formed. Faster reaction is observed with (dppp)Pd(Ph)Br (**2**) and faster still with (dippe)Pd(Cl (**4**) to yield, in the latter case, the stable (dippe)Pd(phenylnorbornyl)Cl (**18**). The rates of these reactions are strongly solvent dependent (DMF ≫ dioxane), are strongly retarded by added Cl^-, and are unaffected by added phosphine, indicating that halide dissociation, followed by olefin coordination and rate-determining olefin insertion, are involved. In contrast, reaction of *trans*-($P^iPr_2{}^nBu)_2$Pd(Ph)X (X = Cl, **5**; X = Br, **6**) with norbornene (or styrene) involves phosphine dissociation and leads to formation of ($P^iPr_2{}^nBu)_2$Pd(H)X. In the case of norbornene, β-carbon elimination of the unobserved intermediate phenylnorbornyl complexes followed by β-H elimination yields 1-methylene-2-phenylcyclohexenes. Complexes of the ligand dippb are unique in that both η^1 and η^2 coordination modes are easily accessible. While reaction products are similar to those obtained with dippp and dippe complexes, dependence of the reaction rate on reaction variables is intermediate between those observed for complexes of chelating and monodentate phosphines. The implications of these findings on catalysis are outlined.

Introduction

Palladium-catalyzed vinylation of aryl halides, the Heck reaction, is one of the most useful synthetic methods for generating carbon–carbon bonds:[1]



A major limitation of this reaction is that aryl chlorides are usually unreactive. We recently developed high-yield carbonylation reactions of aryl chlorides to esters, acids, amides, and aldehydes using Pd(dippp)$_2$ as catalyst (dippp = 1,3-bis(diisopropylphosphino)propane).[2] Extensive studies have shown that this complex is quite unique in its capacity for facile activation of aryl chlorides while forming *cis*-oxidative addition products active in further steps of the catalytic carbonylation cycle.[3]

Encouraged by these results, we tried to perform the Heck reaction between chlorobenzene and styrene using Pd(dippp)$_2$ as a catalyst. Surprisingly, only traces of stilbene were observed under a variety of conditions. However, when the bisphosphine chelate size was enlarged, i.e. when Pd(dippb)$_2$ (dippb = 1,4-bis(diisopropylphosphino)butane) complex was used as a catalyst, high yields of stilbene were observed.[4] Studies of oxidative addition of ArCl to Pd(dippp)$_2$ and Pd(dippb)$_2$ complexes revealed that two different types of products are formed: *cis*-(dippp)Pd(Ar)Cl and *trans*-(η^1-dippb)$_2$-Pd(Ph)Cl.[3] However, the correlation between this result and the difference in catalytic activity of the two systems in the Heck reaction was not clear. In view of the importance of the Heck reaction, we decided to study the chelate effect in steps of the catalytic cycle that succeed the oxidative addition. The first step to be studied is the insertion of olefins into the Pd–Ar bond (Figure 1). We chose norbornene as a substrate in these reactions, since the lack of ability to undergo β-H elimination[5] makes norbornene insertion products more stable, increasing the chances of observing them directly.[6] Another reason is the relative ease of norbornene insertion observed in some studies,[7] probably resulting from the decrease in the strain of the bicyclic skeleton. Styrene was used as a model for olefins, which

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(1) (a) Heck, R.F. *Org. React.* **1982**, *27*, 345. (b) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985; pp 276–287. (c) Heck, R. F. In *Comprehensive Organic Chemistry*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 4, pp 833–863. (d) For a recent example, see: Cabri, W.; Candiani, I.; De Bernardinis, S.; Francalanci, F.; Penco, S. *J. Org. Chem.* **1991**, *56*, 5796.

(2) (a) Ben-David, Y.; Portnoy, M.; Milstein, D. *J. Am. Chem. Soc.* **1989**, *111*, 8742. (b) Ben-David, Y.; Portnoy, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1816.

(3) Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1655.

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(5) (a) Catellani, M.; Chiusoli, G. P. *J. Organomet. Chem.* **1983**, *250*, 509. (b) Catellani, M.; Chiusoli, G. P.; Giroldini, W.; Salerno, G. *J. Organomet. Chem.* **1980**, *199*, C21. (c) Catellani, M.; Chiusoli, G. P. *J. Organomet. Chem.* **1983**, *247*, C59.

(6) (a) Li, C.-S.; Cheng, C.-H.; Liao, F.-L.; Wang, S.-L. *J. Chem. Soc., Chem. Commun.* **1991**, 710. (b) Markies, B. A.; Wijkens, P.; Kooijman, H.; Spek, A. L.; Boersma, J.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1992**, 1420.

(7) (a) Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Roobeek, C. F. *J. Organomet. Chem.* **1992**, *430*, 357. (b) Brown, J. M.; Cooley, N. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1345.

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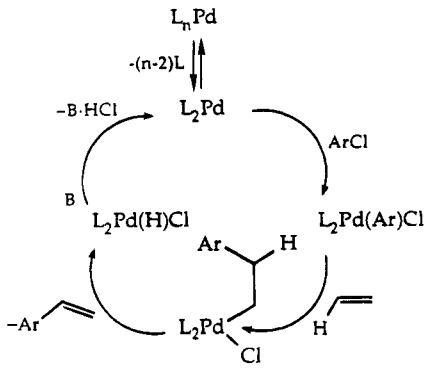


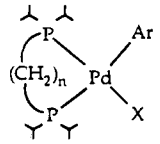
Figure 1.

form insertion products capable of undergoing β-H elimination. The decomposition of insertion products, which is usually a process inseparable from insertion, was studied for both norbornene and styrene.

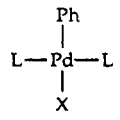
While other studies of olefin arylation clearly demonstrate the effect of chelating ligands on the overall reaction, primarily affecting the product regioselectively,[8] the results reported here clarify the mechanistic pathways and reveal the origin of the chelate effect *at each step*. This has led to an understanding of the macroscopic chelate effect on catalysis.

Results and Discussion

1. Synthesis of $L_2Pd(Ph)Cl$ Complexes (1–7). Attempts to synthesize these complexes by arylation of their dihalide precursors with corresponding Grignard reagents were not very successful, and the complexes were prepared by aryl halide oxidative addition to the corresponding Pd(0) precursors.



1 n = 3, Ar = Ph, X = Cl
2 n = 3, Ar = Ph, X = Br
3 n = 3, Ar = 4MeC(O)C_6H_4, X = Cl
4 n = 2, Ar = Ph, X = Cl

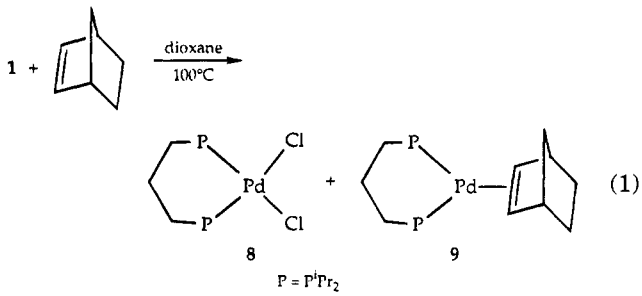


5 L = $^iPr_2{}^n$BuP, X = Cl
6 L = $^iPr_2{}^n$BuP, X = Br
7 L = η^1-$^iPr_2P(CH_2)_4P^iPr_2$, X = Cl

While complexes **1**–**4** are white and **5** and **6** are grayish crystalline solids, **7** is obtained as a very viscous pale yellow oil. All attempts to crystallize it failed.

2. Reactions with Norbornene. a. Reaction of 1 with Norbornene in Dioxane. When **1** is heated at 100 °C in dioxane with a 20-fold excess of norbornene, a very slow reaction takes place. $^{31}P\{^1H\}$ NMR follow-up over several hours reveals the gradual disappearance of complex **1** (two doublets at 11.5 and 29.4 ppm, J = 41.5 Hz) and growth of two new doublets at 12.3 and 36.7 ppm (J = 56.3 Hz) (compound **A**) accompanied by growth of two singlets of equivalent intensity at 29.6 (compound **B**) and 36.0 ppm (compound **C**). The amount of **A** increases to ca. 3% remains almost constant for a while, and then slowly decreases until its complete disappearance at the end of the reaction. The amount of compounds **B** and **C** increases gradually, and after complete disappearance of **1** (ca. 48 h), **B** and **C** are the only complex products remaining. **C** precipitates from the reaction mixture upon cooling, forming colorless prismatic crystals. Spectroscopic analysis of the compound reveals that **C** is (dippp)$PdCl_2$ (**8**).[9] Compound **B** is characterized as (dippp)Pd(η^2-norbornene) (**9**).[10] Isolation of pure **B** from the reaction mixture failed, due to accompanying organic products and to the thermal instability of the complex in the absence of a large excess of norbornene. However, the complex was observed on several other occasions[9b] and was also independently prepared (see Experimental Section).

Equation 1 describes the transformation of the complexes. Since **1** is stable at 100 °C in dioxane, and since



(1)

8 **9**

P = P^iPr_2

neither **8** nor **9** is a direct product of olefin insertion into the Pd–Ar bond, they result from decomposition of the primary insertion product. Complex **A**, which behaves as an intermediate in reaction 1, is likely to be this primary product. Although it was impossible to separate it from the reaction mixture, ^1H NMR of a fraction of the mixture enriched in **A** exhibited three aromatic signals that are assigned to the compound: 6.94 (bt, 7.3 Hz, 1H, H_{para}), 7.07 (t, 7.4 Hz, 2H, H_{meta}), and 7.91 ppm (d, 7.2 Hz, 2H, H_{ortho}). The signal of the ortho proton changes from a triplet in **1** to a doublet here, indicating that the phenyl group is no longer bound to the metal. The downfield shift of the ortho signal hints, however, that the phenyl is located in close proximity to the metal. It is logical, therefore, to suggest that **A** is complex **10**, the direct product of olefin insertion into the Pd–Ph bond of **1**.

Although the stereochemistry of insertion was not proven, all known examples of norbornene insertion into M–Ar bonds result in cis, exo-insertion products.[5,6,7b,10c,11]

Additional proof of the structure of **10** is supplied by the analogous reaction of **4** with norbornene (see below) and by the preparation of the closely related **11** by

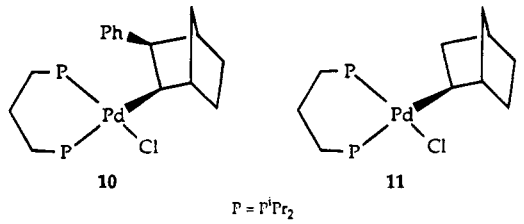
(8) (a) Reference 1d. (b) Ozawa, F.; Kubo, A.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 1417. (c) Cabri, W.; Candiani, I.; Bedeschi, A.; Penco, S.; Santi, R. *J. Org. Chem.* **1992**, *57*, 1481. (d) Cabri, W.; Candiani, I.; Bedeschi, A.; Santi, R. *J. Org. Chem.* **1992**, *57*, 3558.

(9) (a) Portnoy, M.; Frolow, F.; Milstein, D. *Organometallics* **1991**, *10*, 3960. (b) Portnoy, M.; Milstein, D. *Organometallics* **1994**, *13*, 600.

(10) For other (P,P-chelate)Pd(olefin) complexes, see: (a) Krause, J.; Bonrath, W.; Pörschke, K. R. *Organometallics* **1992**, *11*, 1158. (b) Reference 7b. (c) Brown, J. M.; Cooley, N. A. *Organometallics* **1990**, *9*, 353. (d) Carr, N.; Dunne, B. J.; Mole, L.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Dalton Trans* **1991**, 863.

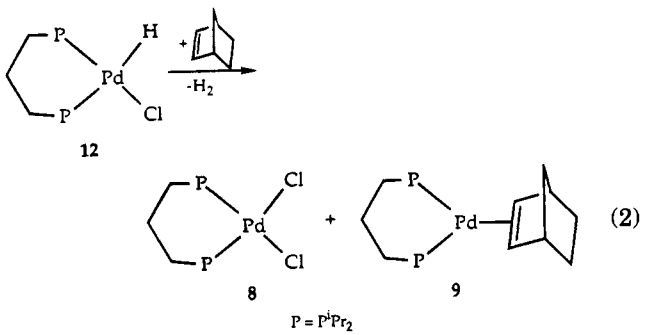
(11) (a) Arcadi, A.; Marinelli, F.; Bernocchi, E.; Cacchi, S.; Ortar, G. *J. Organomet. Chem.* **1989**, *368*, 249. (b) Larock, R. C.; Johnson, P. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1368. (c) Reiser, O.; Weber, M.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1037. (d) Horino, H.; Arai, M.; Inoue, N. *Tetrahedron Lett.* **1974**, *8*, 647.

reacting (norbornyl)MgCl with **8**. In $^{31}P\{^1H\}$ NMR **11**



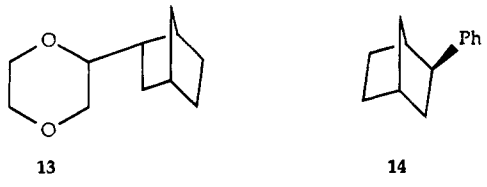
exhibits two doublets (11.1 and 38.0 ppm with $J = 53.0$ Hz). The compound is quantitatively converted into a 1:1 mixture of **8** and **9** upon attempts to separate it from the crude product. The chemical shifts and the coupling constants of **11** are similar to those of **10**, as expected.

11 and **10** differ in stability. While **10** is observable and, thus, relatively stable at 100 °C, **11** decomposes rapidly even at room temperature. The reason for this is that **10** is unable to undergo conventional syn β-hydrogen elimination, while other modes of decomposition of **10** have a higher potential energy barrier. In contrast, **11** decomposes by β-hydrogen elimination, forming the unstable[12] (dippp)Pd(H)Cl (**12**), which is immediately transformed into **8** and **9** (eq 2). **11** is more stable than other palladium bis-phosphine chloro alkyl complexes, because of the strained nature of the alkene that is formed upon β-H elimination.



(2)

In order to understand the decomposition mode of **10**, we analyzed the organic part of the final reaction mixture. While ^1H NMR of the mixture is complex, it is clear that the only olefinic signal observed is that of norbornene. A complex set of aromatic signals is produced. We must assume, therefore, that the organic product of the reaction is saturated and contains a phenyl ring or rings. GCMS analysis shows two major product peaks with M^+ equal to *m/z* 182 and 172, identified according to their fragmentation pattern and ^1H NMR data as **13** and **14**.



Numerous experiments were performed in order to understand the formation modes of **13** and **14**. The intriguing formation of **13** does not seem to be a direct result of reaction 1 but a side process promoted by one

(12) All attempts to prepare **12** resulted in formation of **8** and a Pd(0) complex or metallic Pd.[7b]

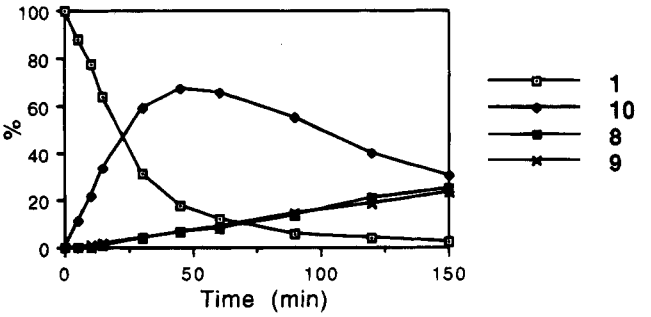
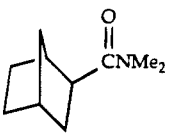


Figure 2. Reaction 1 in DMF at 100 °C according to $^{31}P\{^1H\}$ NMR follow-up ($[1]_{start} = 0.060$ M; $[norbornene]_{start} = 1.2$ M).

of the complexes involved in it. This process is still under investigation and will be reported elsewhere. **14**, which is obtained in ca. 90% yield, results from the reaction of **10** with a hydrogen donor other than dioxane, since when reaction 1 is performed in dioxane-d_8 most of the product is **14**-d_0 and a very small amount of **14**-d_1 is formed. Although the dioxane is thoroughly dried before use, water seems to be a possible hydrogen donor in the reaction. Indeed, addition of a small amount of water enhances the reaction tremendously.[13] Formation of **14** in aqueous dioxane was reported.[11d]

b. Reaction of 1 with Norbornene in DMF. Reaction of **1** with a 20-fold excess of norbornene at 100 °C is much faster in DMF, being complete in less than 2 h, as compared with ca. 48 h in dioxane. Monitoring the reaction by $^{31}P\{^1H\}$ NMR reveals (Figure 2) that the solvent change has a most dramatic effect on the rate of the insertion step. There is rapid formation of **10** (12.6 (d, 56.2 Hz) and 37.7 ppm (d, 56.2 Hz) in $^{31}P\{^1H\}$ NMR), which becomes a dominant complex of the mixture, followed by its decay to form **8** and **9** (37.8 (s) and 29.9 ppm (s) in $^{31}P\{^1H\}$ NMR, respectively). Finally, an ~1:1 mixture of **8** and **9** and a small amount of some byproducts (ca. 10%) are obtained. GCMS analysis of the organic part of the mixture revealed two major compounds: **14** ($M^+ = 172$) and **15**.



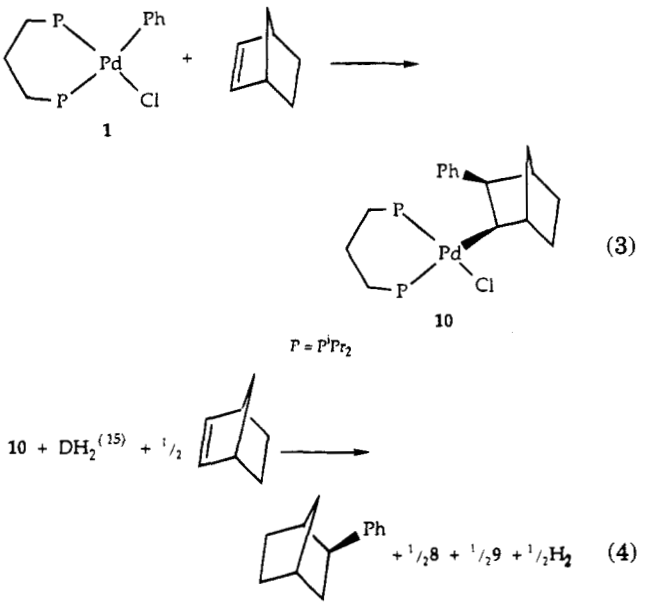
15 is the product of solvent addition to norbornene and does not seem to be connected directly to reaction 1. DMF is likely to be the proton donor responsible for transforming **10** into **14**. Thus, reaction 1 can be divided into two steps: insertion (eq 3) and decomposition (eq 4). Fitting of the kinetic data using the GIT program[14] reveals $k_{insertion} = 0.50 \times 10^{-3}$ L mol^{-1} s^{-1} and $k_{decomposition} = 0.90 \times 10^{-4}$ s^{-1}.

c. Reactions of Complexes 2 and 4 with Norbornene. In an attempt to understand the nature of the transformations shown in (3) and (4), as well as to elucidate the influence of the auxiliary phosphine and halide ligands on them, we performed reactions of

(13) Water seems to enhance both the insertion and decomposition steps. The insertion step is probably enhanced because of greater polarity of the solvent mixture.

(14) Weigert, F. J. *Comput. Chem.* **1987**, *11*, 273.

(15) DH_2 = donor of two hydrogen atoms.

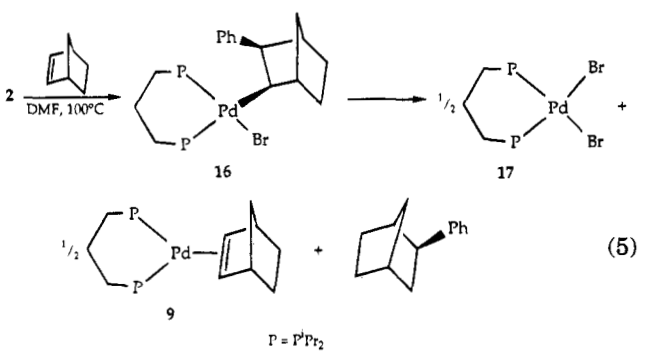


(3)

(4)

complexes **2** and **4** with norbornene under conditions equal to those of reaction of **1**.

Reaction of **2** with a 20-fold excess of norbornene takes practically the same course as that of **1** in both DMF and dioxane. For example, in DMF, $^{31}P\{^1H\}$ NMR follow-up reveals rapid growth of two doublets (10.4 and 35.6 ppm with J = 57.1 Hz) of **16**, followed by rapid decay of **16** to form **17** and **9** (reaction 5).



(5)

The organic products of the reaction are identical with those of reaction 1. However, both steps of the reaction (the insertion and the decomposition) are faster for the bromo complex **2**. The pseudo-first-order rate constant of insertion is increased by a factor of 1.5–2.0.[16] While it is more difficult to estimate the ratio between the rates of decomposition of **10** and **16** in DMF, the maximal concentration of **10** during the reaction is 70% of the total palladium species, whereas the maximal concentration of **16** is below 30%, pointing out that the ratio of decomposition rate constants is greater than the ratio of the insertion rate constants, which is equal to 2. The bromo complex **2** reacts faster in both DMF and dioxane. Reactions 5 and 1 in DMF are also different in the amount of metal complex side products present in the final reaction mixture, these being less than 10% for reaction 1 and 20–25% for reaction 5. Interpretation of these facts will be given in the section discussing the mechanism of insertion.

(16) Here and thereafter, see rate constant comparison in the Experimental Section.

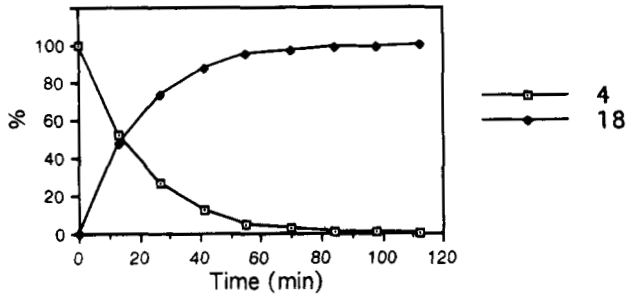
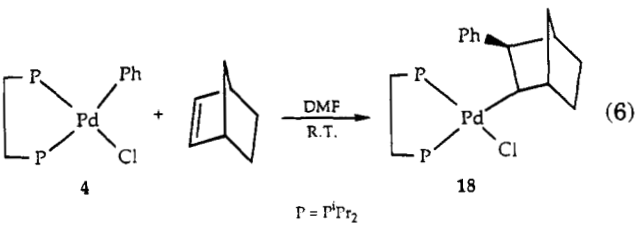


Figure 3. Reaction 6 in DMF at 25 °C according to $^{31}P\{^1H\}$ NMR follow-up ($[4]_{start}$ = 0.060 M, $[\text{norbornene}]_{start}$ = 1.2 M).

Surprising results are obtained when **4** is reacted with excess norbornene in DMF. In contrast to insertion reaction 3, which requires heating, process 6 proceeds at room temperature.

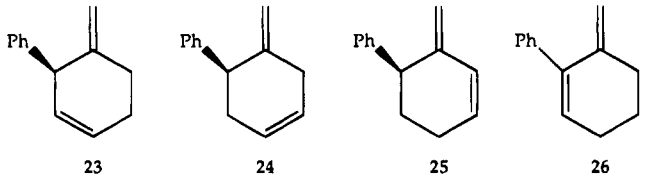


(6)

The rate of insertion for the dippe complex **4** is orders of magnitude higher than that for the dippp complex **1**. Kinetic fitting of the rate data obtained by $^{31}P\{^1H\}$ NMR monitoring of the insertion in DMF (Figure 3) reveals $k_{\text{insertion}} = 0.73 \times 10^{-3}$ L mol^{-1} s^{-1} *at room temperature*. The constant is higher than $k_{\text{insertion}}$ for reaction 3 at 100 °C (!) (under otherwise identical conditions). Even the minimal estimation of the ratio between the insertion rate constants at the same temperature is ca. 260. This dramatic chelate size effect will be discussed later. Complex **18** obtained at room temperature is stable and was isolated and fully characterized. Decomposition of **18** occurs only at elevated temperatures and seems to be slower than that of **10** under similar conditions. $^{31}P\{^1H\}$ NMR exhibits disappearance of the two doublets of **18** (69.3 and 79.4 ppm, J = 27.0 Hz) and formation of singlets of (dippe)$PdCl_2$ (**19**; 103.2 ppm) and (dippe)-Pd(η^2-norbornene) (**20**; 63.2 ppm). The organic products obtained in the final mixture in both DMF and dioxane are the same as those obtained in reactions 1 and 5.

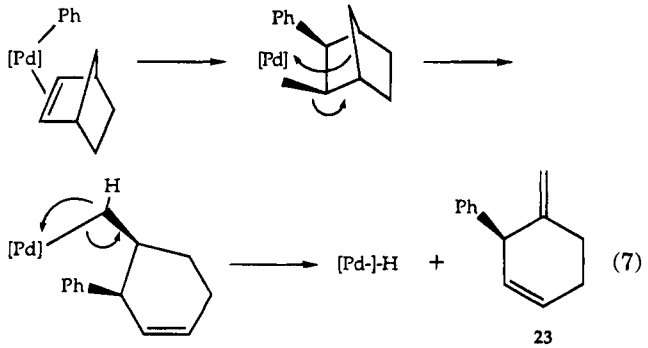
d. Reaction of Complexes 5 and 6 with Norbornene. In order to examine the chelate effect on the insertion process, we investigated the reaction of monodentate complexes **5** and **6** with norbornene. The observed products are entirely different from those obtained with **1**, **2**, and **4**. When **5** or **6** is heated with a 20-fold excess of norbornene in DMF at 100 °C, slow disappearance of the starting material (24.3 (s) and 23.3 ppm (s), respectively, in $^{31}P\{^1H\}$ NMR) is observed, accompanied by growth of a single reaction product (43.5 (s) and 43.3 ppm (s), respectively, in $^{31}P\{^1H\}$ NMR). The products were identified as *trans*-($P^iPr_2{}^nBu)_2Pd(H)Cl$ (**21**) and *trans*-($P^iPr_2{}^nBu)_2Pd(H)Br$ (**22**) by ^{31}P and ^1H NMR and by IR spectroscopy. Except for minor impurities, no other signals were observed during the reaction. GCMS analysis revealed that there is one major organic product with M^+ at m/z 170. While the molecular mass fits the expected product 2-phenylnorbornene, the mass

spectrum is completely different from the one reported.[17] Extensive NMR studies of the fraction containing the major compound, separated by preparative TLC, reveal that three main isomers are present in solution, each containing a phenyl group as well as four vinylic signals. Structures **23–25** are suggested, on the basis of 2D NMR (H–H correlation).



23 **24** **25** **26**

These products probably result from phenyl migration to norbornene, followed by β-carbon elimination (or β C–C cleavage) that opens one of the norbornene rings, followed by β-H elimination (eq 7). Rearrangement of bicyclic systems into monocyclic ones through $\beta-\gamma$ C–C cleavage is a known process.[5c,11a]

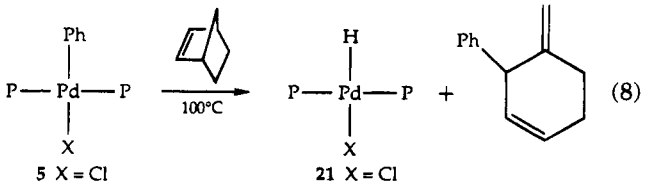


(7)

23

23 seems to be the primary product of the reaction. Its isomerization to **24** and **25** can be easily catalyzed by Pd hydrides **21** and **22** that are present in the reaction mixture. Steric reasons probably prevent the isomerization of the exocyclic double bond, as well as the formation of the more thermodynamically stable **26**.

Other minor organic products are **14**, the product of reductive dimerization of norbornene ((2-norbornyl)-norbornene), and, when the reaction is performed in dioxane, **13**. Although the mixture of organic products is more complex than in the corresponding reactions of **1**, **2**, and **4**, the reaction of **5** or **6** with norbornene can be formulated as shown in (8).



(8)

5 X = Cl
6 X = Br

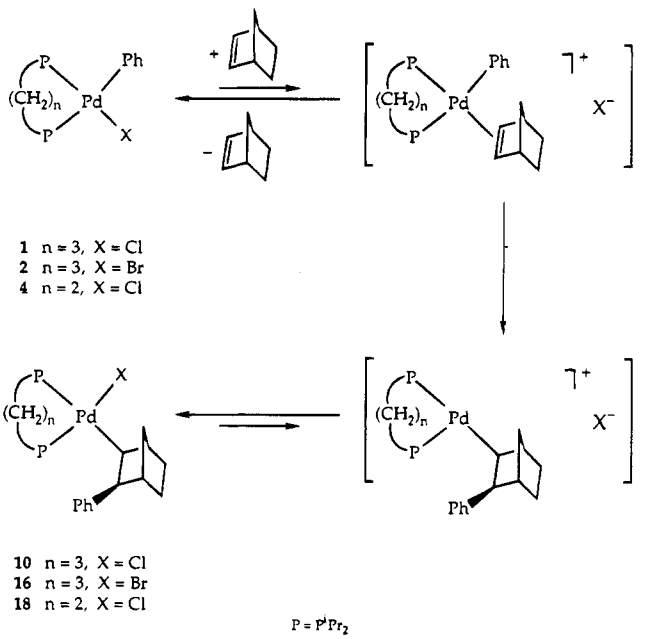
21 X = Cl
22 X = Br

P = $P^iPr_2{}^nBu$

In drastic contrast to reactions 1 and 5, the solvent effect on reaction 8 is small. The rate constant of reaction 8 is 1.7 times faster in DMF than in dioxane (less than $^1/_{100}$ of the rate enhancement in DMF observed with the chelate complexes).

(17) McLafferty, F. W.; Stauffer, D. B. *The Wiley/NBS Registry of Mass Spectral Data*; Wiley-Interscience: New York, 1989; Vol. 1, p 611.

Scheme 1



3. Clarification of Insertion Mechanisms. Our results clearly indicate that the mechanisms of norbornene insertion into the cis chelate complexes and into the trans complexes of the monodentate ligands are entirely different. A number of experiments aimed at clarifying these mechanisms emphasize the difference between the two modes.

When 1 equiv of $P^iPr_2{}^nBu$ is added to reaction 8 in DMF, the rate constant of insertion is decreased by a factor of 12.7! Addition of 2 equiv practically blocks the reaction. Surprisingly, addition of 1 equiv of $P^iPr_2{}^nBu$ to reaction 1 does not alter the reaction rate *at all*!

Addition of 1 equiv of LiCl has an opposite effect on reactions 1 and 8 (in DMF), the rate constant of reaction 1 being decreased by a factor of 5.4, while the rate of reaction 8 (with X = Cl) is almost not affected at all.

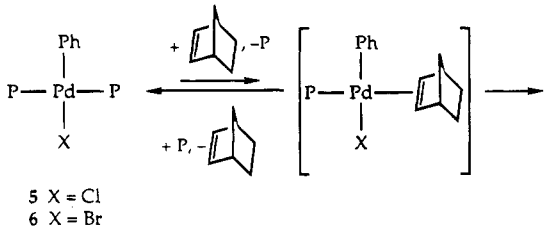
These observations point unequivocally to two different mechanisms of olefin insertion. It is clear that the chelated complexes react through halide dissociation followed by olefin coordination, thus forming a *cationic intermediate*. The migration of Ph to the olefin, followed by fast reassociation of halide, creates a stable Pd–alkyl product of insertion (Scheme 1).

In contrast, reaction of the monodentate ligand complexes proceeds through displacement of the phosphine by olefin, forming a neutral intermediate. Phenyl migration to the olefin creates the tricoordinate unsaturated product **27** (eq 9).

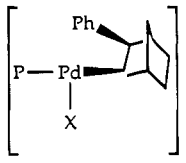
Stabilization of **27** by cis coordination of the phosphine is prevented by steric hindrance. Indeed, $^{31}P\{^1H\}$ NMR of the reaction mixture does not exhibit any cis bis-phosphine pattern. Another possible pathway for the stabilization of **27** is its isomerization to **28** followed by phosphine coordination. However, fast decomposition of **27** through reaction 7 takes place (Scheme 2).

There is ample evidence that β-H elimination processes[18a,b] and probably a β-C elimination process[18c]

(18) (a) Cross, R. J. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 2, Chapter 8. (b) Whitesides, G. M.; Gaasch, J. F.; Stedronsky, R. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258. (c) Ermer, S. P.; Struck, G. E.; Bitler, S. P.; Richards, R.; Bau, R.; Flood, T. C. *Organometallics* **1993**, *12*, 2634.



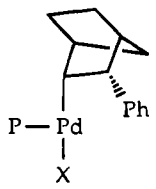
5 X = Cl
6 X = Br



(9)

27

P = P^{i}Pr$_2$^{n}Bu



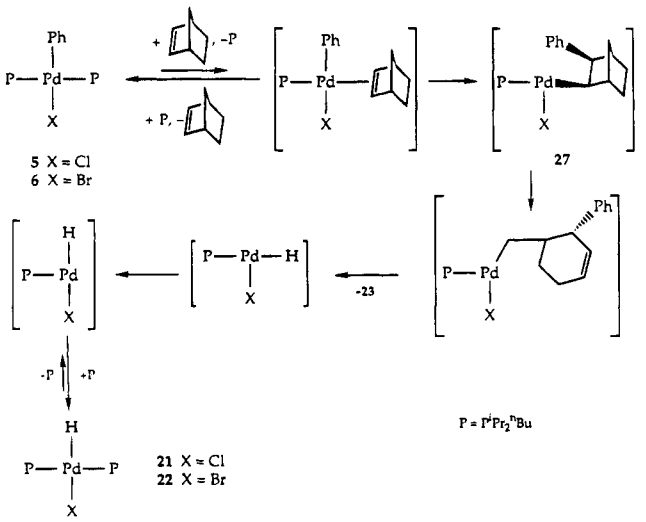
28

are much easier from tricoordinate complexes than from square-planar ones. In agreement with this, the transient T-shaped insertion product **27** undergoes facile decomposition to **23**, while in the square-planar insertion products **10**, **16** and **18**, this pathway is avoided[19] and other modes of decomposition prevail, requiring higher temperatures. Thus, the chelate effect leads both to different modes of olefin insertion and, in the case of norbornene, to different modes of decomposition of the insertion products.

In the case of chelated complexes, the observed processes upon reaction with norbornene can be divided into two parts: insertion and decomposition. While the nature and mechanism of the second part are still not very clear, they are characteristic only of a certain type of olefin and will be studied and discussed elsewhere. However, the insertion part is not restricted to a specific olefin and can serve as a good model for studies of olefin insertion into Pd—Ar bonds. We believe that the rate-determining step is the insertion itself and not the halide—olefin substitution (otherwise, addition of extra halide would not have such a strong effect on the reaction rate). Polar solvents stabilize the ionic intermediate, shifting the equilibrium toward its formation. The greater reaction rate of bromo complexes, as compared to that of their chloro analogues, is probably the result of a higher concentration of the ionic intermediate in solution. Thus, the displacement of halide by olefin is more thermodynamically favorable for bromide than for chloride.[20]

The dramatic effect of chelate ring size on the insertion rate is more puzzling. The bite angle of the chelate can influence the preequilibrium concentration of the ionic intermediate, as well as the kinetics of the migration step (Scheme 1). With regard to the migration process, theoretical studies of olefin insertion into the

Scheme 2



5 X = Cl
6 X = Br

27

P = P^{i}Pr$_2$^{n}Bu

21 X = Cl
22 X = Br

Pt—H bond[21] predict that an increase in the bite angle between the two phosphine ligands makes the ground-state configuration of the starting complex similar to the transition-state geometry, thus lowering the potential energy barrier of the reaction. These theoretical conclusions are supported by experimental data for the hydrido olefin complexes of Pt and Pd.[22] The opposite effect, observed in our case,[23] i.e. increased rate with smaller bite angle, suggests that the chelate size affects the preequilibrium to a larger extent than the migration step kinetics (Scheme 1). The reasons for higher equilibrium concentration of ionic intermediates with smaller chelates can be both electronic and steric. A smaller bite angle of the chelate may increase the basicity on the metal center,[24] stabilizing olefin binding. Coordination of the olefin will also be sterically favored with a smaller chelate. The coplanar olefin conformation required for insertion will also be favored by the less sterically demanding smaller chelate.

Interestingly, examination of the influence of the bite angle between two phosphine moieties on the rate of CO insertion into a Pd—R bond[25] revealed an trend opposite to that observed in our case; i.e., a greater bite angle (equal to larger ring size) promotes the insertion of CO.

In the case of monodentate ligand complexes, process 8 that we observe should be treated as a whole, since no stable intermediate complex is observed en route from complexes **5** and **6** to the products **21** and **22**. The strong influence of excess phosphine on the reaction rate rules out the possibility that phosphine substitution by olefin is rate determining. On the other hand, absence of any observable intermediate after the essentially irreversible phenyl migration step points to this step as rate determining. Indeed, it is very likely that the

(19) Insignificant traces of **23**—**25** are also obtained in these reactions.

(20) Pd^{II}—Cl is generally stronger than Pd^{II}—Br: Hartley, F. R. *The Chemistry of Platinum and Palladium*; Wiley: New York, 1973; pp 240—243.

(21) Thorn, D. L.; Hoffmann, R. *J. Am. Chem.Soc.* **1978**, *100*, 2079.

(22) (a) Mole, L.; Spencer, J. L.; Carr, N.; Orpen, A. G. *Organometallics* **1991**, *10*, 49. (b) Reference 10d.

(23) Although olefin insertion in Pd—Ar may experience a different chelate effect than with Pd—H, the difference is not expected to be very large.

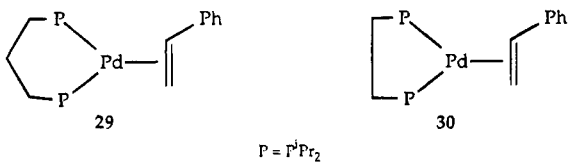
(24) (a) Otsuka, S. *J. Organomet. Chem.* **1980**, *200*, 191. (b) Hoffman, P.; Heiss, H.; Muller, G. *Z. Naturforsch.* **1987**, *B42*, 395. (c) Sowa, J. R., Jr.; Zanotti, V.; Facchin, G.; Angelici, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 160. (d) Sowa, J. R., Jr.; Bonanno, J. B.; Zanotti, V.; Angelici, R. J. *Inorg. Chem.* **1992**, *31*, 1370.

(25) Dekker, G. P. C. M.; Elseiver, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M. *Organometallics* **1992**, *11*, 1598.

tricoordinate complexes in Scheme 2 are very reactive and that the rates of processes involving them are much higher than the rate of insertion of the more saturated square-planar complex. The higher rate of the reaction observed for the bromo complex **6** as compared to that of its chloro analogue **5** probably results from the greater trans effect of the bromo versus chloro ligands.[26] On theoretical grounds, a higher trans effect of the ligand trans to the migrating group lowers the potential barrier and enhances the migration reaction.[27]

4. Reactions of Complexes 1–5 with Styrene. As explained above, norbornene is a good model for studying the insertion of olefins into the Pd–Ar bond, but reactions subsequent to the norbornene insertion are not typical of the majority of olefins. Thus, styrene was also studied.

When complexes **1–6** are reacted with a 20-fold excess of styrene, primary insertion complexes are not observed. Reaction of **1**, **2**, and **4** with styrene converts them quantitatively into 1:1 mixtures of **8** and **29**, **17** and **29**, and **19** and **30**,respectively. **29** and **30** appear



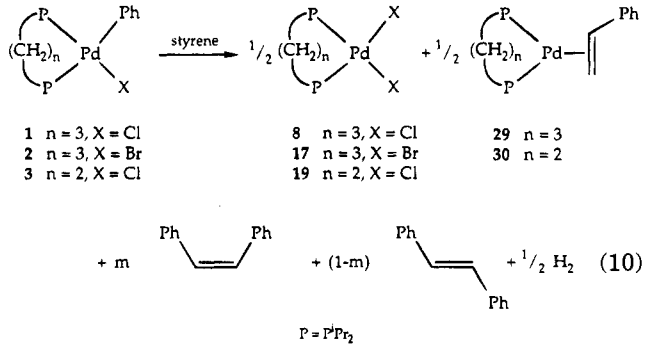
in $^{31}P\{^1H\}$ NMR as sets of two doublets: 23.7 and 33.3 ppm with $J = 8.2$ Hz for **29** and 56.3 and 67.8 ppm with $J = 46.9$ Hz for **30**. These patterns prove that the coordinated olefin is coplanar with the P–Pd–P plane. In this favorable configuration, the olefin is able to significantly reduce the electron density on the metal in the very reactive Pd(bis-phosphine) species through back-donations. The π^* orbital of the coplanar olefin has an appropriate symmetry to match the HOMO of the bent P–Pd–P fragment.[24a,b]

It was impossible to separate the complexes **29** and **30** from excess styrene, but the structure of **29** was proven by an alternative synthesis (see Experimetnal Section).

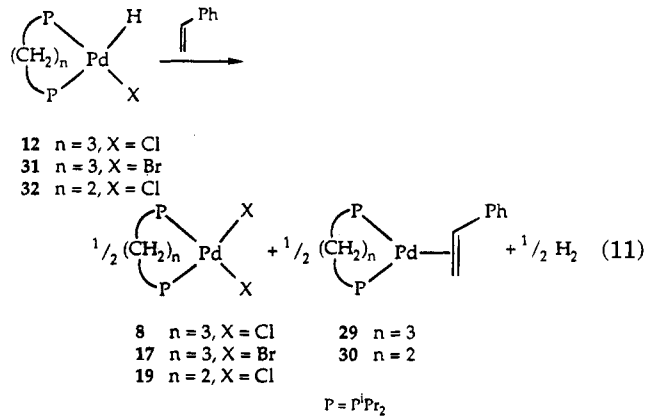
The insertion of styrene is slower than that of norbornene and requires higher temperatures. While experiments with norbornene were usually performed at 100 °C, reactions with styrene were usually run at 140 °C.

Reactions of **1** and **2** in dioxane are very slow, even at 140 °C. As in the case of norbornene, rates higher by some orders of magnitude are observed when DMF is used as a solvent. Another similarity to the norbornene reaction is the fact that **4** reacts much faster than **1** (rate constants differ by a factor of 33.5 in dioxane). Thus, reaction of **4** in dioxane at 140 °C can be completed in ca. 5 h, while in DMF the reaction is completed in less than 1 h.

The organic products of the reaction are *cis*- and *trans*-stilbenes. While with complexes of dippp the cis isomer is the preferred product, a slight preference for the trans isomer is observed with the dippe complex. A small amount of styrene dimerization product (M^+ at *m/z* 208) is observed in the reaction mixtures of the dippp complexes. A small amount of biphenyl is also observed when the reactions were performed in dioxane. These byproducts do not result from the main reaction (10).



We believe that the first step of the reaction is insertion of styrene into the Pd–Ph bond. It is followed by fast β-H elimination, forming a (bis-phosphine)Pd(H)X complex, which immediately undergoes reaction 11 (analogous to reaction 2).



The fact that reaction 10 follows the mechanistic features of norbornene insertion (i.e. greatly enhanced by polar solvents and a decrease in chelate ring size, inhibited by excess halide, and not influenced by extra phosphine) indicates that a similar mechanism, involving rate-determining insertion, is operative in reaction 10.

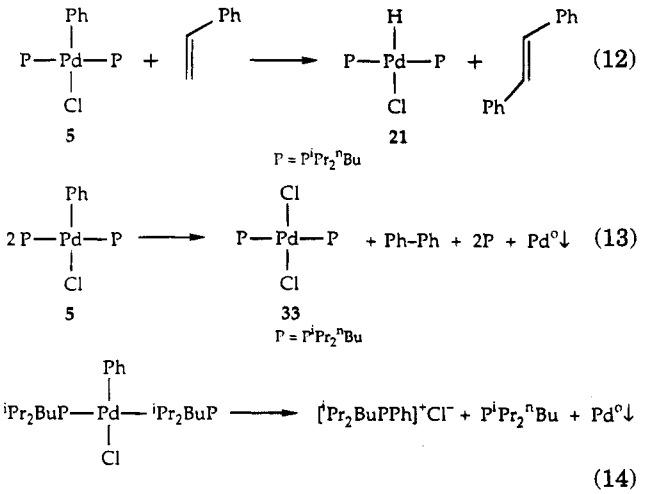
Whereas reaction of **1** with a 20-fold excess of styrene is easily observable in DMF at 140 °C, **3** is practically inert under these conditions and a higher temperature and larger olefin excess are required for its reaction, in accordance with the lower electron density on the migrating group, compatible with the view of migration as an intramolecular nucleophilic attack on the olefin.

Reaction of **5** with styrene proceeds differently. Metal precipitation is usually formed upon heating at 140 °C and, although traces of **21** are observed in this reaction, the major product complex is *trans*-$(P^iPr_2{}^nBu)_2PdCl_2$ (**33**). The phosphonium salt $[^iPr_2{}^nBuPPh]^+Cl^-$ is also detected by $^{31}P\{^1H\}$ NMR. GCMS analysis indicates the presence of a small amount of *trans*-stilbene and a larger amount of biphenyl. Phosphine and phosphine oxide peaks are observed by GCMS as well. Changing the solvent from dioxane to DMF does not significantly alter either the reaction product distribution or the reaction rate. The reaction is very slow, and when

(26) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*; Harper Collins: New York, 1993, pp 543–545.
(27) (a) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7230. (b) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1986**, *108*, 6136.

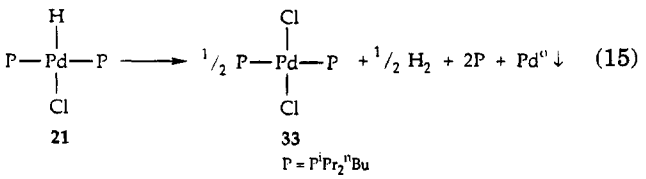
excess phosphine is added, a significant inhibition of the reaction rate is observed, but metal precipitation is prevented.

The direct reaction (insertion + β-H elimination) between styrene and **5** (eq 12) is very slow, and at the temperature required for this reaction (140 °C) some thermal decomposition pathways of **5** take place (eqs 13 and 14).



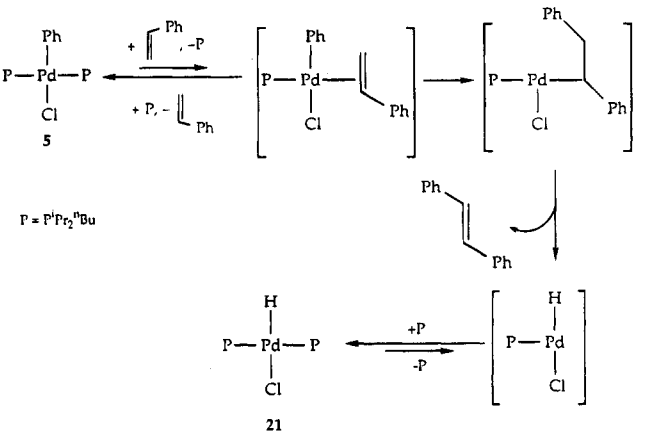
The first decomposition route, (13), probably takes place by a radical mechanism. Reaction 14 can be viewed as a kind of reductive elimination. The Pd(0) complexes formed in these reactions are phosphine deficient and decompose at the operating temperature.

According to $^{31}P\{^1H\}$ NMR follow-up of the reactions, part of **33** is formed by decomposition of **21** at 140 °C (eq 15).



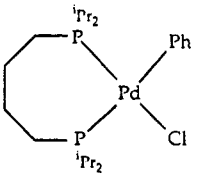
Although it is difficult to analyze reaction 12, because of the multiple decomposition processes accompanying it, it seems to follow the reactivity patterns characteristic of the analogous reaction with norbornene (insensitivity to solvent change, inhibition by extra phosphine). Therefore, the mechanism of insertion suggested for norbornene (eq 9) is also valid for styrene except that in the case of styrene a simple β-H elimination pathway follows the insertion (Scheme 3). It is noteworthy that the only isomer in reaction 12 is the thermodynamically favored *trans*-stilbene. Some studies point out that the cis isomer is kinetically favored,[28] but the possibility that both isomers are primary products of β-H elimination cannot be ruled out. Isomerization of the cis isomer can be catalyzed by the Pd hydride **21**. Metal hydride complexes are well-known isomerization catalysts.[28,29] Obviously, this possibility is absent or, at least, much less pronounced in reactions of chelate complexes where

Scheme 3



palladium hydrides are short-living species. Indeed, reactions of **1**–**4** resulted in mixtures of *cis*- and *trans*-stilbenes.

5. Reaction of 7 with Norbornene. Although complex **7** has a coordination sphere similar to that of **5**, it exists in a dynamic equilibrium with **34**,[3] an analogue of **1** and **4**.



Thus, **7** can adopt two ways for reacting with olefins. Indeed, when it is reacted with a 20-fold excess of norbornene, the reaction products are similar to those obtained in the reactions of **1** and **4**.

7 appears in $^{31}P\{^1H\}$ NMR as a series of peaks between 24.5 and 25.1 ppm and between 3.0 and 3.5 ppm.[30] While **34** can be observed in DMF as two doublets (21.8 and 45.4 ppm with J = 29.9 Hz), being 2–3% of the starting material, this pattern is rarely observed in dioxane, the amount being on the border of the detection limits (less than 1% of the starting material). **34**, which has a higher dipole moment than **7**, is probably better stabilized by polar solvents.

Progress of the reaction is indicated in $^{31}P\{^1H\}$ NMR by the growth of two new singlets at 38.2 and 53.1 ppm (in dioxane, 38.2 and 52.0 ppm). The second signal is known to be due to (dippb)$PdCl_2$ (**35**), while the first is assigned to (dippb)Pd(η^2-norbornene) (**36**). Organic components of the reaction are 2-phenylnorbornane (**14**) and products of solvent addition to norbornene (**13** in dioxane and **15** in DMF). Thus, the products resemble those obtained in reactions of the chelated complexes **1** and **4**.

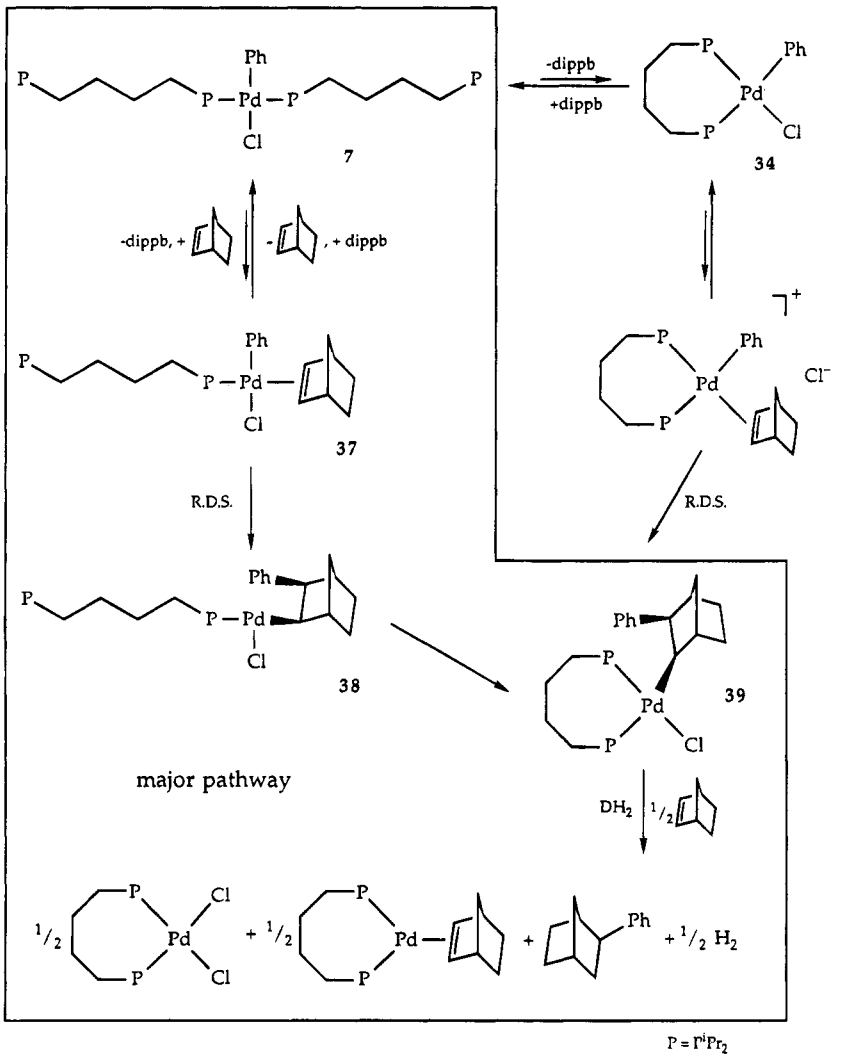
However, dependence of the reaction rate on various changes in reaction conditions is more similar to those observed in the reaction of the monodentate ligand complex **5**. The reaction is slow and requires several days for completion, much as reaction 8. Changing the solvent from dioxane to DMF causes only a moderate rate constant increase by a factor of 2.3. Although the enhancement is greater than that observed in reaction

(28) Reference 1c, p 845.

(29) (a) Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980; pp 31–35. (b) Masters, C. *Homogeneous Transition-Metal Catalysis – A Gentle Art*; Chapman and Hall: London, 1981; pp 70–76.

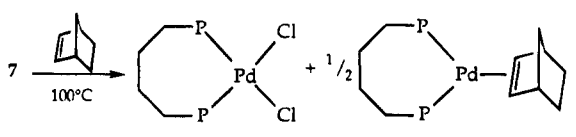
(30) The pattern represents **7** and its oligomers.[3]

Scheme 4



8 (factor of 1.7), it is much closer to it than to the orders of magnitude enhancement observed in the reactions of complexes **1** and **4**.

In the presence of 1 equiv of LiCl, the rate of reaction 16 is mildly inhibited (rate constant is decreased by a factor of 1.7). While excess Cl^- does not influence



$$+ \tfrac{1}{2}\,H_2 + \text{dippb} \quad (16)$$

reaction 8 (monodentate ligand complexes), the rate constant of reaction 1 is decreased by a factor of 5.4 (chelate complexes). Hence, the behavior of reaction 16 is again more similar to the reaction of monodentate ligand complexes than to the reaction of chelate ligand complexes. One interesting observation from these series of experiments is that **34**, the cis isomer of the starting material, has a higher concentration when excess chloride anion is present. Later we will see how this fact fits the mechanism of the reaction.

When 1 equiv of $P^iPr_2{}^nBu$ is added to reaction 16, a mild inhibition of the reaction is observed (the rate constant is decreased by a factor of ca. 1.6). This is strikingly different from the strong inhibition of reaction 8 by an added phosphine. Although mild, retardation of reaction 16 by added phosphine is not observed in reaction 1.

Thus, the mechanism of reaction 16 should explain (1) products similar to those obtained in the reactions of chelate phosphine complexes and (2) kinetics that is similar to that of reactions of monodentate phosphine complexes, although it is shifted slightly toward kinetics of the chelate complexes. Kinetics is established by the rate-determining step and by steps preceding it, while product formation may be altered in steps subsequent to the rate-determining step (RDS). The mechanism presented in Scheme 4 fulfills all the requirements. The rate-determining step of the major pathway is the insertion involving the neutral intermediate **37**, in analogy to the RDS of reaction 8 (Scheme 2). Hence, the whole kinetics of reaction 16 is similar to that of reaction 8 with three major alterations. First, the ligand dippb, although bound in a monodentate mode, has chelating ability. Thus, when an unsaturated **38** is formed, fast chelation stabilizes it, preventing the

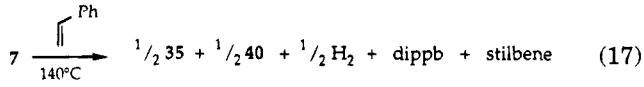
norbornene skeleton rearrangement observed in reaction 8. Intermediate **39** is similar to complexes **10** and **18**, and its decomposition results in formation of **35**, **36**, and **14** in a way analogous to reaction 4.

A second alteration to the simple mechanism of reaction 8 is caused by the free phosphine moieties of the monocoordinated dippb in **7**; i.e., 1 equiv of **7** contains roughly 2 equiv of free phosphine. Thus, when 1 equiv of $P^iPr_2{}^nBu$ is added to the reaction mixture, the phosphine concentration is increased by a factor of 1.5 and not by many orders of magnitude, as is the case of addition of 1 equiv of $P^iPr_2{}^nBu$ to reaction 8. This difference explains why reactions 8 and 16 respond so differently to the added phosphine.

A third alteration of the simple model is the reaction pathway proceeding through the chelated complex **34**. Although minor, the contribution of this bypass can be decreased by using a less polar solvent or by adding Cl^-. This demonstrates the influence of the solvent polarity and chloride concentration on the reaction rate. This influence is stronger than that observed for reaction 8 but significantly milder than for reaction 1, as expected.

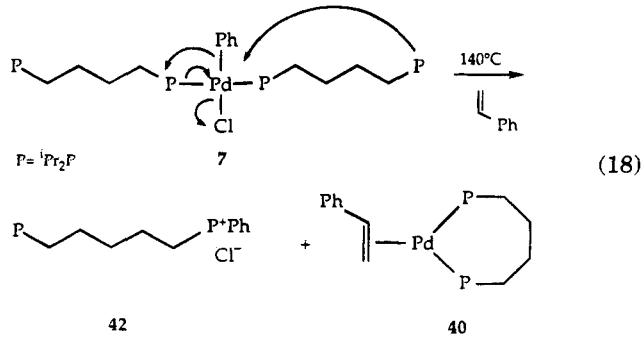
The inhibition of the insertion into **34** by chloride anion causes an increase in the steady-state concentration of this complex, as indeed is observed.

6. Reaction of 7 with Styrene. Reaction of **7** with styrene results in the formation of **35**, (dippb)Pd(η^2-styrene) (**40**; two doublets at 33.6 and 41.4 ppm with J = 21.6 Hz), and a mixture of *cis*- and *trans*-stilbene (according to GCMS analysis). However, $^{31}P\{^1H\}$ NMR reveals that the dichloride complex **35** is formed in a significantly smaller amount relative to the Pd(0) complex **40** than would be likely on the basis of the expected reaction 17.



(17)

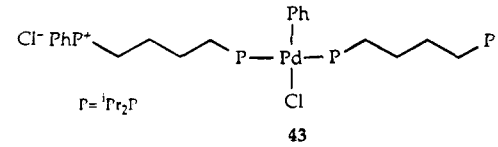
$^{31}P\{^1H\}$ NMR follow-up of the reaction provides a clue to this strange fact. Growth of two peaks at 41.6 and 41.8 ppm usually accompanies growth of Pd(0), although not in a 1:1 ratio. Analysis of the compound associated with these two singlets showed that they are the phosphonium salts $[^iPr_2(^nBu)P^+(Ph)(CH_2)_4P^+(Ph)(^nBu)^iPr_2]Cl^-_2$ (**41**) and $[^iPr_2(^nBu)P^+(Ph)(CH_2)_4P(^nBu)^iPr_2]Cl^-$ (**42**). Thus, we must suggest the competing side reaction 18 that **7** undergoes as a result of the strong heating necessary for carrying out reaction 17.



(18)

The second quaternization of dippb can be similarly achieved through complex **43**.

This pathway lowers the output of stilbene and contributes to the deterioration of the ligands present



43

in solution. Indeed, the amount of stilbenes obtained is smaller than expected.

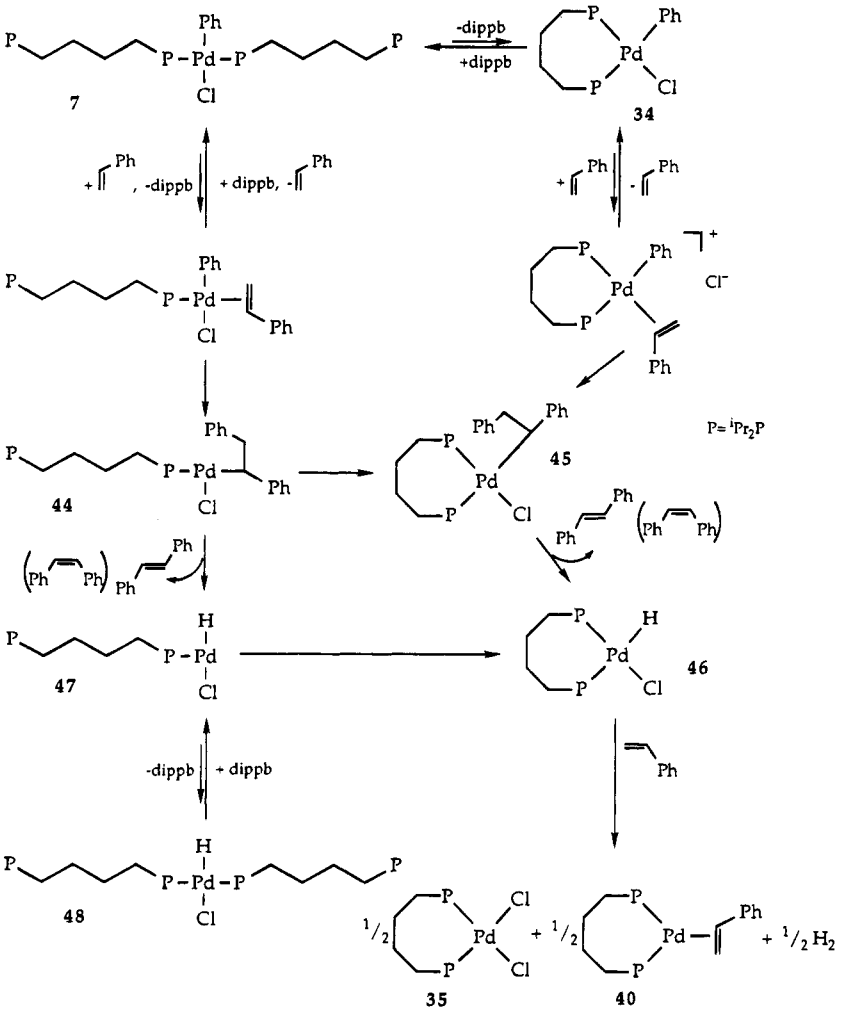
Reaction of **7** with styrene resembles, in many ways, reaction of **5** with this substrate. It is very slow in dioxane and is slightly faster in DMF. Side reactions 14 and 18 form phosphonium salts in a similar way. A major difference is that reaction 18 restores the stabilized Pd(0) complex, while reaction 14 results in the deterioration of Pd-containing species in solution and Pd metal precipitation. While reaction 12 produces *trans*-stilbene exclusively, reactions of the chelated complexes produced considerable amounts of the cis isomer. In this sense, reaction 17 is more similar to reaction 12, since its major organic product is *trans*-stilbene. A small amount of *cis*-stilbene is detected as well. This organic product distribution suggests that some Pd hydrides, having longer lifetimes than Pd hydrides of chelated phosphine complexes, are formed in the reaction mixture. Although these hypothetical species cannot be observed by NMR, their lifetime is sufficient for transforming most of the initially formed *cis*-stilbene into its trans isomer. Assuming that the mechanism of reaction 17 is basically similar to that of reaction 16 and only slightly altered because of the different nature of the two olefins, we can propose a mode in which the suggested Pd hydrides are formed (Scheme 5).

The intermediate **44** formed after phenyl migration to the olefin can be easily transformed into **45**, which undergoes β-H elimination to **46**, followed by irreversible decomposition of **46**. On the other hand, fast β-H elimination from **44** can take place. (Such a process is impossible from **38**, the norbornene-derived analogue of **44**, while β-C elimination from **38** is probably much slower than the predominating, in this case, chelate ring closure into **39**.) The product of elimination, **47**, can be temporarily stabilized by another dippb to give **48**, an analogue of **21**. While the **47**–**48** equilibrium system disappears slowly through chelate ring closure of **47** into **46**, followed by irreversible decomposition of **46**, it probably lives long enough to catalyze stilbene isomerization.

7. Influence of Base on the Reactions of Complexes 1, 2, 5, and 7. Surprisingly, when a secondary or tertiary amine is added to the reaction mixtures of **1**, **2**, **5**, and **7** with norbornene or styrene, the reaction course does not change. Neither deprotonation of **21** nor prevention of formation of the dihalides **8**, **17**, and **35** are observed. A slight inhibition of the reactions takes place, probably as a result of competition between the amine and the olefin for coordination sites on Pd. When sodium acetate is used as a base, reactions of **1** and **2** do not alter at all, while in the reaction of **5** a small amount of the chloro complexes is transferred into acetato species without any major effect on the reaction.

A different effect is caused by acetate on reaction 17. While the reaction rate does not alter, formation of the dichloride is prevented. These results can be explained by the existence of unstable Pd hydrides, which are deprotonated by acetate in preference to the formation

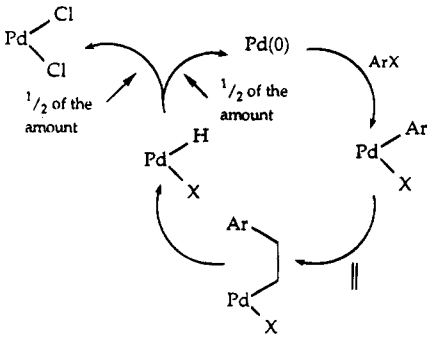
Scheme 5



of **35**. The already proposed complexes **47** and **48** are possible candidates for these hydride species.

8. Olefin Insertion into Pd–Ar Bonds of 1–7 and the Catalysis of the Heck Reaction. Studies performed on the reactions of **1–4** with olefins reveal the reason for the failure of these complexes to promote catalytic Heck reactions of aryl chlorides. According to reaction 1 or similar reactions of other chelated complexes, insertion of an olefin into a Pd–Ar bond (formed in the previous step by oxidative addition of haloarene to the Pd(0) center) would result, following two subsequent steps, in the transformation of half of the Pd amount involved in the reaction into *cis*-dihalide species. Although the second half is restored into Pd(0) which is ready for another catalytic cycle (Scheme 6), deactivation of half of the catalytic potential in each cycle will bring down the reaction rapidly ((bis-phosphine)PdX_2 is completely inert under these reaction conditions). According to this scheme, a maximum of ca. 2 turnovers is expected for such a process ($1 + 1/2 + 1/4 + 1/8 + ...$). Indeed, all attempts to catalyze the reaction of chlorobenzene with styrene, using $Pd(dippp)_2$ as catalyst, result in very low yields (ca. 2 turnovers) and a 1:1 mixture of dippp and **8**. This "leaking" catalytic cycle can be "fixed" by using a reducing agent that will restore the dichloride complex into the catalytic cycle by reducing it into the Pd(0) state. Indeed, this idea led to a successful, base-free aryl chloride vinylation with $Pd(dippp)_2$ as a catalyst and Zn powder as a reducing agent.[31] This unprecedented catalytic process is an excellent example of a new catalytic system development through detailed stoichiometric studies of its isolated steps.

Scheme 6



Studies of olefin insertion into **5** showed that the insertion is strongly inhibited by additional phosphines present in solution. On the other hand, 3–4 equiv of phosphine/Pd is essential for preventing palladium metal precipitation at the temperatures applied in the reaction. The presence of 1–2 equiv of free phosphine in solution during the insertion step slows down this step to a rate that makes effective catalysis impossible. Increasing the temperature did not help, since already

(31) Portnoy, M.; Ben-David, Y.; Milstein, D. *Organometallics* **1993**, *12*, 4734.

at 140 °C side reactions causing decomposition of the catalytically active species overtake the insertion reaction.

Attempts based on $Pd(P^iPr_2{}^nBu)_3$ (generated *in situ*) as a catalyst resulted in less than 1 turnover to stilbene. $^{31}P\{^1H\}$ NMR analysis of the reaction mixture reveals that most of the Pd is present as **5**, not being able to undergo the insertion step. Attempts to catalyze the reaction using only 2 equiv of phosphine/Pd resulted in metal precipitation. Only traces of stilbene are detected in the remaining solution.

The failure of $P^iPr_2{}^nBu$ palladium complexes to catalyze the Heck reaction seems surprising, since many examples of iodo- or bromoarene vinylation catalyzed by $Pd(PPh_3)_4$ are known.[1] However, the lower electron density on *trans*-$Pd(PPh_3)_2(Ar)X$ significantly enhances olefin insertion reactivity. Thus, it is possible that fine tuning of the monodentate phosphine ligands will improve the performance of their complexes in Heck vinylation of chloroarenes.

As was shown above, complex **7** possesses some unique features with regard to olefin insertion into its Pd—Ph bond. The complexes of dippb are also unique in their ability to catalyze the Heck reaction of chloroarenes. One of the features of **7**, the ability to be restored to Pd(0) by a base after styrene insertion and stilbene elimination, correlates well with the catalytic properties of the Pd—dippb system. However, a full explanation of Heck catalysis by dippb complexes of Pd is beyond the scope of this article and will be published in a full paper about Heck vinylation of chloroarenes under basic conditions.

Conclusions

These studies clearly show that steps involved in reactions of olefins with Pd-aryl complexes, i.e. generation of a coordination site, olefin coordination, olefin insertion, and decomposition of the insertion product exhibit a remarkable chelate effect. Different mechanisms and different products are obtained with chelating and with monodentate phosphine. The dippb ligand provides "a bridge" between these two families and offers potential for flexibility in choosing "the lowest resistance pathway" for optimal catalysis.

Among the reactivity trends identified here are the following: (a) chelate complexes react via a cationic intermediate generated by halide dissociation; (b) monodentate complexes react via a neutral intermediate obtained by phosphine dissociation; (c) the rate-determining step in both systems is the insertion itself; (d) the rate of the overall insertion process is the highest with chelating phosphines and is favored by smaller chelates; (e) with dippb complexes, the steps up to and including the actual insertion involve mainly the η^1 coordination mode, whereas subsequent steps are strongly influenced by the chelating mode; (f) because of the instability of Pd—H complexes in which H is trans to P, as compared with complexes in which H is trans to a halide, palladium hydride intermediates containing chelating phosphines disproportionate to Pd(II) dihalide and Pd(0) complexes, providing for a possible "pitfall" in catalysis involving such intermediates.

The relevance of these results to palladium catalysis in general and to the synthetically important Heck reaction in particular is clear.

Since the insertion of olefins into chelated cis complexes proceeds through an ionic intermediate, it can be greatly enhanced by polar solvents. This advantage of the chelate ligand system is, unfortunately, cancelled by the fact that the steps following the insertion deactivate half of the catalytic species in each turnover in such systems. The consequences of this unfortunate process that prevents effective catalysis of the Heck reaction in chelated ligand systems can be overcome by using Zn instead of a base. (Actually, bases were proven useless in the Heck reaction with the dippp ligand system.)

The slowness of olefin insertion with complexes of monodentate ligands hinders effective catalysis of aryl chloride transformations with them. Polar solvents cannot significantly enhance the insertion, since it proceeds through neutral intermediates. On the other hand, excess phosphine (1 or 2 equiv), necessary for preventing metal precipitation under catalytic conditions, inhibits the insertion even more.

In catalysis based on dippb complexes, bimodal (chelate and monodentate) coordinating ability is exhibited, resulting in olefin insertion, which is a crossbreed of the insertion modes of chelate and monodentate ligand systems. The major advantage of this ambient system is the possibility of preventing (by use of a base) the deactivation characteristic of stronger chelating ligand systems, while the chelate effect is maintained in the oxidative-addition reaction and in stabilizing the catalysts.

Experimental Section

1. General Considerations. All procedures with air- and moisture-sensitive compounds were performed in a nitrogen-filled glovebox (Vacuum Atmospheres with an MO-40 purifier) or on a vacuum line using Schlenk techniques. All solvents were reagent grade or better. Pentane, dioxane, and THF (Frutarom) were distilled over sodium/benzophenone ketyl. DMF (Merck) was distilled over barium oxide. Dioxane and DMF was dried over KOH pellets prior to distillation. All solvents were degassed and stored under high-purity nitrogen after the distillation. All deuterated solvents (Aldrich) were stored under high-purity nitrogen on molecular sieves (3 Å). Norbornene, (±)-2-chloronorbornane (Aldrich), chloro- and bromobenzene (Merck), and 4-chloroacetophenone (Fluka) were purchased in the highest available purity and were used as received. Styrene (Merck) was distilled prior to use. $PdCl_2$ was purchased from Alfa. Phosphine ligands[32] as well as $[(\eta^3\text{-}C_4H_9)PdCl]_2$[33] and $(CH_3CN)_2PdCl_2$[34] were prepared according to literature methods. Preparation of Pd(0)—phosphine precursors to complexes **1**—**6** and preparation of **1**, **3**, and **4** were reported earlier.[3]

^1H, ^{31}P, and ^{13}C NMR spectra were recorded at 400, 162, and 100 MHz, respectively, using a Bruker AMX400 spectrometer. ^1H and ^{13}C chemical shifts are reported in ppm downfield from $SiMe_4$ and referenced to the residual solvent-h_1 and all-d solvent peaks, respectively. ^{31}P chemical shifts are in ppm downfield from H_3PO_4 and referenced to an external 85% phosphoric acid sample. Screw-cap 5-mm NMR tubes were used in NMR follow-up experiments.

2. Synthesis. Synthesis of (dippp)$PdCl_2$ (8). A 1.06-g amount of dippp dissolved in 20 mL of THF was added to a

(32) dippp, dippb: Tani, K.; Tanigawa, E.; Tatsubo, Y.; Otsuka, S. *J. Organomet. Chem.* **1985**, *279*, 87. dippe: Fryzuk, M. D.; Jones, T.; Einstein, F. W. B. *Organometallics* **1984**, *3*, 185. P^iPr_2Bu: Reference 3.

(33) Dent, W. T.; Long, R.; Wilkinson, A. J. *J. Chem. Soc.* **1964**, 1585.

(34) Reference 1a, p 17.

vigorously stirred yellow-orange slurry of 1.00 g (1 equiv) of $(CH_3CN)_2PdCl_2$ in 10 mL of THF. The slurry became white immediately and was stirred overnight. Filtration, followed by washing with pentane, yielded 1.651 g (94.4% yield) of a white powder that was identified as **8** by comparison with reported spectroscopic data.[9] The complex could be recrystallized from hot dioxane.

Synthesis of (dippe)PdCl$_2$ (19). The same procedure as for **8** was used but with an equivalent amount of dippe instead of dippp, yielding **19** as a white powder in 95.5% yield: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 100.7 (s); ^1H NMR ($CDCl_3$) δ 2.63 (d heptet, J_{P-H} = 9.8 Hz, J_{H-H} = 7.1 Hz, 4H, CH), 1.91 (d, J_{P-H} = 19.9 Hz, 4H, CH_2), 1.45 (dd, J_{P-H} = 17.8 Hz, J_{H-H} = 7.2 Hz, 12H, CH_3), 1.25 (dd, J_{P-H} = 15.4 Hz, J_{H-H} = 7.0 Hz, 12H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 27.2 (d, J_{P-C} = 27.1 Hz, CH), 22.0 (m, CH_2), 20.1 (s, CH_3), 18.4 (s, CH_3). Anal. Calcd: C, 38.24; H. 7.34, Cl, 16.13. Found: C, 38.34; H. 7.18, Cl, 16.28.

Synthesis of *trans*-(P^{i}Pr$_2$^{n}Bu)$_2$PdCl$_2$ (33). A solution of 1.914 g of P^{i}Pr$_2$^{n}Bu in 20 mL of THF was added to a vigorously stirred yellow-orange slurry of 1.424 g of $(CH_3CN)_2PdCl_2$ in 10 mL of THF. The resulting dark yellow solution was stirred overnight, followed by solvent removal under high vacuum to give 2.823 g of a yellow powder, which was practically pure **33** (97.7% yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 30.3 (s); ^1H NMR ($CDCl_3$) δ 2.41 (t heptet, J_{P-H} = 3.5 Hz, J_{H-H} = 7.0 Hz, 4H, CH), 1.63 (m, 4H, CH_2), 1.58 (m, 4H, CH_2), 1.41 (apparent quintet, $J_{P-H} \approx J_{H-H}$ = 7.3 Hz, 4H, P—CH_2), 1.33 (apparent quartet, $J_{P-H} \approx J_{H-H}$ = 7.3 Hz, 12H, CHCH_3), 1.25 (apparent quartet, $J_{P-H} \approx J_{H-H}$ = 7.1 Hz, 12H, CHCH_3), 0.90 (t, J_{H-H} = 7.3 Hz, 3H, CH_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 27.3 (s, PCH_2CH_2), 25.0 (t, J_{P-C} = 6.7 Hz, CH), 23.2 (t, J_{P-H} = 11.8 Hz, P—CH_2), 19.6 (s, $CHCH_3$), 18.5 (s, $CHCH_3$), 18.5 (d, J_{P-H} = 11.1 Hz, CH_2CH_3), 13.8 (s, CH_2CH_3). Anal. Calcd: C, 45.68; H, 8.81; Cl, 13.48. Found: C, 45.91; H, 8.74; Cl, 13.13.

Synthesis of (dippp)Pd(Ph)Cl (1) from 8. A slurry of 1 g of **8** in 40 mL of dry THF was placed in a three-neck, round-bottom flask equipped with a condensor (connected to argon inlet) and a pressure-equilibrized dropping funnel. A 1.8-mL amount of a 1.2 M solution of PhMgCl in THF was diluted with 10 mL of dry THF and placed in the funnel. The flask was cooled to −30 °C and the Grignard solution added dropwise to the vigorously stirred slurry. On completion of the addition, the mixture was allowed to reach room temperature, stirred for an additional 2 h, and then refluxed for $^1/_2$ h. An almost clear light brown solution was formed. Any excess Grignard reagent was destroyed by addition of 1 mL of a saturated NH_4Cl aqueous solution. The mixture was filtered and the filtrate stripped to dryness and extracted with toluene. The toluene was evaporated and the residue washed with pentane and crystallized twice from toluene by vapor diffusion of pentane. However, the yellowish crystals (ca. 60% yield) contained more than 15% impurity, and thus, preparation of **1** from Pd(0) was preferred.

Synthesis of (dippp)Pd(Ph)Br (2). **2** was prepared in analogy to its chloro analogue **1**[3] using bromobenzene instead of chlorobenzene: $^{31}P\{^1H\}$ NMR (dioxane) δ 9.9 (d, J = 41.9 Hz, 1P), 27.2 (d, J = 41.9 Hz, 1P); ^1H NMR is essentially that reported for **1**;[3] $^{13}C\{^1H\}$ NMR (C_6D_6) δ 156.3 (d, J_{P-C} = 127.1 Hz, C_{ipso}), 136.9 (s, C_{ortho}), 126.9 (d, J_{P-C} = <3.0 Hz, C_{meta}), 122.8 (s, C_{para}), 27.9 (d, J_{P-C} = 30.6 Hz, CH), 25.4 (d, J_{P-C} = 19.9 Hz, CH), 22.2 (d, J_{P-C} = 7.0 Hz, CH_2), 19.2 (dd, J_{P-C} = 23.0 Hz, J_{P-C} = 12.1 Hz, P—CH_2), 16.9 (d, J_{P-C} = 12.7 Hz, P—CH_2), 21.3 (s, CH_3), 20.7 (d, J_{P-C} = 5.5 Hz, CH_3), 18.5 (s, CH_3), 18.1 (s, CH_3). Anal. Calcd: C, 46.73; H, 7.28; Br, 14.80. Found: C, 46.81; H. 7.15; Br, 14.98.

Attempt To Prepare (dippe)Pd(Ph)Cl (4) from 19. When a procedure similar to the synthesis of **1** was applied to **19** instead of **8**, only traces of **4** were detected and the starting material remained mainly unreacted.

Synthesis of 5. Procedure A. In a typical procedure, a solution of 170 mg (0.27 mmol) of Pd(P^{i}Pr$_2$^{n}Bu)$_3$ and 20 equiv of PhCl in 5 mL of dioxane was heated in a pressure bottle to 100 °C for 4 h. Evaporation of the volatiles under high vacuum gave a gray-brown solid. Extraction with a small amount of cold pentane, followed by filtration and pentane evaporation, yielded 121 mg (79%) of the grayish complex **5**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 24.2 (s); ^1H NMR (C_6D_6) δ 7.48 (bd, J_{H-H} = 7.9 Hz, 2H, H_{ortho}), 6.97 (apparent t, J_{H-H} = 7.3 Hz, 2H, H_{meta}), 6.87 (t, J_{H-H} = 7.3 Hz, 1H, H_{para}), 2.42 (t heptet, J_{P-H} = 3.6 Hz, J_{H-H} = 7.0 Hz, 4H, CH), 1.42 (dt, J_{H-H} = 7.9 Hz, J_{P-H} = 7.3 Hz, 12H, CHCH_3), 1.31 (m, 4H, CH_2), 1.23 (m, 4H, CH_2), 1.08 (dt, J_{H-H} = 6.7 Hz, J_{P-H} = 7.0 Hz, 12H, CHCH_3), 1.03 (apparent quintet, J_{P-H} = J_{H-H} = 7.3 Hz, 4H, P—CH_2), 0.78 (t, J_{H-H} = 7.2 Hz, 6H, CH_2CH_3). Anal. Calcd: C, 55.02; H, 9.06; Cl, 6.25. Found: C, 55.32; H, 9.08; Cl, 5.80.

Procedure B. A 1.8-mL amount of a 1.2 M THF solution of PhMgCl was diluted with 10 mL of THF, and the resulting solution was added dropwise into a solution of 1 g of *trans*-(P^{i}Pr$_2$^{n}Bu)$_2$PdCl$_2$ (**33**) in 15 mL of THF under argon. When the addition was complete, a yellow solution had formed. The solution was stirred overnight, upon which it turned brown. Excess Grignard reagent was neutralized with 1 mL of a saturated NH_4Cl aqueous solution. The solvent was evaporated and the residue extracted with toluene. After the extract was dried over $MgSO_4$, the solvent was evaporated again. The brownish solid obtained could be further purified by extraction with pentane as in procedure A, resulting in ca. 95% purity.

Synthesis of 6. **6** was synthesized in analogy to **5** (procedure A) using bromobenzene instead of chlorobenzene. Heating for 2 h was sufficient. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 23.3 (s). ^1H NMR was very similar to that of **5**. Anal. Calcd: C, 51.03; H, 8.40. Found: C, 51.33; H, 8.54.

Synthesis of *trans*-(η^1-dippb)$_2$Pd(Ph)Cl (7). A solution of 55 mg of NaOH in 1.5 mL of methanol was added dropwise to a stirred suspension of 197 mg of $[(2\text{-methylallyl})PdCl]_2$ in 6 mL of MeOH in a 50-mL round-bottom flask under nitrogen. The suspension turned into a pale yellow solution immediately. A 13-mL amount of methanol was added, followed by a solution of 583 mg of dippb in 7 mL of toluene. The bright yellow solution was stirred for 10 min, and then the solvent was stripped off. The resulting lemon yellow powder was transferred to a pressure bottle with 2 mL of dioxane and 2 mL of PhCl and heated to 100 °C overnight, while it was stirred vigorously. The resulting yellow solution was filtered from a small amount of grayish precipitate. Solvent evaporation yielded a yellow oil. $^{31}P\{^1H\}$ NMR exhibits patterns characteristic of **7**.[3]

Synthesis of 2-Norbornylmagnesium Chloride. A 440-mg amount of magnesium and 2 mL of dry THF were placed in a 50-mL three-neck round-bottom flask, equipped with an egg-shaped magnetic bar, a condenser, and a dropping funnel. An argon inlet was connected to the condenser. A solution of 2 g of (±)-*exo*-2-chloronorbornane in 8 mL of dry THF was placed in the dropping funnel, and a small amount (ca. 2 mL) of it was added to the flask. After addition of a few drops of 1,2-dichloroethane and mild heating with a fan, a vigorous reaction started. The contents of the funnel were added dropwise, and on completion of the addition the solution was stirred for 2 h and then refluxed for another 1 h. When this solution stood overnight, insoluble impurities precipitated. The clear solution (ca. 10 mL) was separated, and the concentration was determined to be 1.2 M (86% yield).

In Situ Synthesis of (dippp)Pd(2-norbornyl)Cl (11). Synthesis of (dippp)Pd(η^2-norbornene) (9). Route A. A 500-mg amount of **8** and 80 mL of dry THF were placed in a Schlenk round-bottom flask, equipped with a dropping funnel (under Ar). A 0.92-mL amount of the solution of 2-norbornylmagnesium chloride was diluted by a factor of 10 with dry THF, placed in the funnel, and added dropwise to the vigorously stirred white suspension in the flask at −30 °C. Following completion of the addition the mixture was allowed to reach room temperature and stirred for an additional 2 h. Almost all of the precipiate was dissolved, and the solution changed color to red. Filtration and $^{31}P\{^1H\}$ NMR of the crude

filtrate revealed tha the major component in the solution is **11** (δ 11.1 (d, 53.0 Hz, 1P), 38.0 (d, 53.0 Hz, 1P)), while a minor product is **9** (δ 29.6 (s)). However, upon evaporation of the solvent and extraction with a few milliliters of pentane, all of complex **11** decomposed, and after pentane evaporation 305 mg of yellow solid, identified as pure **9**, was obtained (54% yield). This complex slowly decomposes in the absence of excess norbornene, preventing accurate elemental analysis: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 29.3 (s); ^1H NMR (C_6D_6) δ 3.22 (bd, J_{P-H} = 7.0 Hz, 2H, =CH), 3.07 (bs, 2H, $CH_{bridgehead}$), 1.78 (bd, J_{H-H} = 7.0 Hz, $CHH_{norbornene}$), 1.60–1.75 (m, 4H, P—CH), 1.55 (bd, J_{H-H} = 6.9 Hz, 2H, $CHH_{norbornene}$), 1.45 (m, 2H, PCH_2CH_2), 1.15–1.30 (m, 4H, P—CH_2), 1.13 (dd, J_{P-H} = 14.3 Hz, J_{H-H} = 7.1 Hz, 6H, CH_3), 1.10 (dd, J_{P-H} = 14.1 Hz, J_{H-H} = 7.1 Hz, 6H, CH_3), 0.99 (dd, J_{P-H} = 13.1 Hz, J_{H-H} = 7.1 Hz, 6H, CH_3), 0.94 (dd, J_{P-H} = 12.4 Hz, J_{H-H} = 7.0 Hz, 6H, CH_3), 0.82 (bd, J_{H-H} = 6.8 Hz, 1H, CHH_{bridge}), one of the bridge hydrogen signals is obscured by other signals; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 61.5 (m, =CH), 45.8 (s, $CH_{bridgehead}$), 43.3 (s, CH_2), 30.5 (t, J_{P-C} = 5.9 Hz, $CH_{2\ bridge}$), 26.9 (t, J_{P-C} = 6,7 Hz, P—CH), 24.2 (t,J_{P-C} = 7.5 Hz, PCH_2CH_2), 23.3 (t, J_{P-C} = 4.7 Hz, P—CH_2), 19.4 (t, J_{P-C} = 4.8 Hz, CH_3), 19.3 (t, J_{P-C} = 4.9 Hz, CH_3), 19.1 (t, J_{P-C} = 3.3 Hz, CH_3), 18.6 (t, J_{P-C} = 2.3 Hz, CH_3).

Route B. A solution of 12 mg of $(CH_3CN)_2PdCl_2$ in 1 mL of THF was cooled to −30 °C and added dropwise to a solution of 30 mg (1 equiv) of Pd(dippp)$_2$ and 43 mg (10 equiv) of norbornene in 1 mL of THF at −30 °C. The white precipitate of **8** was filtered off, and $^{31}P\{^1H\}$ NMR revealed that the major species in the filtrate was **9**: δ 29.6 (s).

Synthesis of (dippp)Pd(η^2-styrene) (29). A procedure analogous to the last one, but with 10 equiv of styrene instead of norborene, was employed. $^{31}P\{^1H\}$ NMR revealed that complex **29** was formed: δ 24.5 (d, J_{P-P} = 12.0 Hz), 34.0 (J_{P-P} = 12.0 Hz).

Synthesis and Characterization of 18. A solution of 19 mg of **4** and 76 mg of norbornene (20 equiv) in 0.6 mL of DMF was stirred for 2 h at room temperature, after which clean formation of **18** was observed by $^{31}P\{^1H\}$ NMR. The solvent and excess norbornene were evaporated in vacuo, giving 22 mg of a colorless solid, identified as **18** (95% yield): $^{31}P\{^1H\}$ NMR (DMF-d_7) δ 69.2 (d, J_{P-P} = 27.0 Hz, 1P), 79.2 (d, J_{P-P} = 27.0 Hz, 1P); ^1H NMR ($CDCl_3$) δ 7.88 (dm, J_{H-H} = 7.5 Hz, 2H, H_{ortho}), 7.12 (tm, J_{H-H} = 7.6 Hz, 2H, H_{meta}), 6.99 (tt, J_{H-H} = 7.3 Hz, J_{H-H} = 1.3 Hz, 1H, H_{para}), 2.50 (apparent octet, $J_{P-H} \approx J_{H-H}$ = 7.3 Hz, 1H, P—CH), 2.29 (d heptet, J_{P-H} = 8.8 Hz, J_{H-H} = 7.1 Hz, 1H, P—CH), 2.07 (apparent octet, $J_{P-H} \approx J_{H-H}$ = 7.3 Hz, 1H, PCH), 1.34 (dd, J_{P-H} = 16.3 Hz, J_{H-H} = 7.2 Hz, 3 H, CH_3), 1.29 (dd, J_{P-H} = 16.3 Hz, J_{H-H} = 7.3 Hz, 3H, CH_3), 1.25 (dd, J_{P-H} = 16.4 Hz, J_{H-H} = 7.2 Hz, 3H, CH_3), 1.21 (dd, J_{P-H} = 14.2 Hz, J_{H-H} = 7.0 Hz, 3H, CH_3), 1.11 (dd, J_{P-H} = 11.9 Hz, J_{H-H} = 7.1 Hz, 3H, CH_3), 0.93 (dd, J_{P-H} = 13.4 Hz, J_{H-H} = 7.0 Hz, 3H, CH_3), 0.85 (dd, J_{P-H} = 13.9 Hz, J_{H-H} = 7.0 hz, 3H, CH_3), 0.53 (dd, J_{P-H} = 16.6 Hz, J_{H-H} = 7.2 Hz, 3H, CH_3) (several other signals were observed clearly but not assigned: 2.89 (dt, 9.6 Hz, 1.5 Hz, 1H), 2.39 (dtd, 14.4 Hz, 9.4 Hz, 1.4 Hz, 1H), 1.96 (bs, 1H), 1.08 (dtd, 16.9 Hz, 9.9 Hz, 1.5 Hz, 1H), 1.40–1.86 (six multiplets overlapping, 6H)), two more signals were obscured by the strong methyl double doublets between 1.10 and 1.35 ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 149.7 (dd, J_{P-C} = 9.1 Hz, J_{P-C} = 3.5 Hz, C_{ipso}), 130.0 (s, C_{ortho}), 127.4 (s, C_{meta}), 124.6 (s, C_{para}), 61.0 (dd, J_{P-C} = 3.4 Hz, J_{P-C} = 1.0 Hz, CHPh), 46.7 (d, J_{P-C} = 1.9 Hz, $CH_{bridgehead\ \beta\ to\ Ph}$), 43.8 (s, $CH_{bridgehead\ \beta\ to\ Pd}$), 40.6 (dd, J_{P-C} = 115.6 Hz, J_{P-C} = 2.0 Hz, CHPd), 36.2 (s, CH_2CH_2), 34.5 (dd, J_{P-C} = 11.9 Hz, J_{P-C} = 2.8 Hz, $CH_{2\ bridge}$), 31.3 (s, CH_2CH_2), 26.8 (d, J_{P-C} = 22.2 Hz, P—CH), 25.6 (d, J_{P-C} = 26.4 Hz, P—CH), 24.8 (d, J_{P-C} = 13.6 Hz, P—CH), 24.2 (d, J_{P-C} = 13.8 Hz, P—CH), 23.8 (dd, J_{P-C} = 26.6 Hz, J_{P-C} = 25.4 Hz, P—CH_2), 20.3 (d, J_{P-C} = 3.2 Hz, CH_3), 20.2 (d, J_{P-C} = 5.7 Hz, CH_3), 19.5 (d, J_{P-C} = 6.0 Hz, CH_3), 18.9 (d, J_{P-C} = 3.7 Hz, CH_3), 18.6 (s, CH_3), 18.4 (bs, CH_3), 18.1 (d, J_{P-C} = 2.9 Hz, CH_3), 18.0 (d, J_{P-C} = 2.7 Hz, CH_3), 17.5 (dd, J_{P-C} = 16.1 Hz, J_{P-C} = 9.8 Hz, P—CH_2). Anal. Calcd: C, 56.35; H, 8.17; Cl, 6.17. Found: C, 56.13; H, 8.22; Cl, 6.10.

Characterization of 21. A mixture of 23 mg of **5** with 76 mg of norbornene (20 equiv) in 0.6 mL of dioxane was heated to 100 °C for 3 days. Evaporation under high vacuum overnight yielded a yellow residue containing **21** as a major product: $^{31}P\{^1H\}$ NMR (dioxane) δ 43.6 (s); ^1H NMR (C_6D_6) δ 2.02 (bm, 4H, CH), 1.72 (bm, 4H, CH_2), 1.53 (bm, 4H, CH_2), 1.38 (apparent quintet, $J_{P-H} \approx J_{H-H}$ = 7.3 Hz, 4H, PCH_2), 1.21 (apparent quartet, $J_{P-H} \approx J_{H-H}$ = 7.1 Hz, 12H, $CHCH_3$), 1.10 (apparent quartet, $J_{P-H} \approx J_{H-H}$ = 7.3 Hz, 12H, $CHCH_3$), 0.90 (t, J_{H-H} = 7.3 Hz, 3H, CH_2CH_3), −13.99 (t, J_{P-H} = 3.1 Hz, 1H, Pd—H); IR (neat) ν 2019 cm^{-1}.

Typical Experiment of Olefin Insertion. In a typical experiment, a screw-cap 5-mm NMR tube was loaded with 0.04 mmol of the complex, 0.8 mmol of olefin (20 equiv), and 0.6 mL of solvent (either DMF or dioxane). The tube was kept at the desired temperature and periodically analyzed by $^{31}P\{^1H\}$ NMR. At the end of the experiment, GC and, when required, GCMS analyses were performed.

Additional reagents were sometimes loaded (water, bases, ligands, etc.) in 0.2 mL of solvent at the start of the experiment.

For example, a screw-top 5-mm NMR tube was loaded with 20 mg of **1**, 75 mg of norbornene, and 0.6 mL of DMF. The tube was heated to 100 °C and analyzed by $^{31}P\{^1H\}$NMR after 5, 10, 15, 30, 45, 60, 90, 120, and 150 min. The results of this experiment are presented in Figure 2.

Compounds Observed in the Olefin Insertion Experiments (See Text). 10: $^{31}P\{^1H\}$ NMR (dioxane) δ 12.3 (d, J = 56.3 Hz, 1P), 36.7 (d, J = 56.3 Hz, 1P); ^1H NMR (dioxane-d_8) δ 7.91 (d, J = 7.2 Hz, 2H, H_{ortho}), 7.07 (t, J = 7.4 Hz, 2H, H_{meta}), 6.94 (broad t, J = 7.3 Hz, 1H, H_{para}), other signals are obscured by signals of the other compounds of the reaction mixture, especially by norbornene (>19 equiv excess).

13: MS (m/z) 182 (M^+, 58%), 95 (60%), 87 (100%).

14:[35] MS (m/z) 172 (M^+); ^1H NMR (dioxane-d_8) δ 7.10–7.23 (m), no olefinic signals, aliphatic signals are obscured by signals of the other compounds of the reaction mixture, especially by norbornene (>19 equiv excess).

15: MS (m/z) 167 (M^+, 23%), 95 (78%), 73 (100%), 72 (89%).

16: $^{31}P\{^1H\}$ NMR (DMF) δ 10.4 (d, J = 57.1 Hz, 1P), 35.6 (d, J = 57.1 Hz, 1P).

17: $^{31}P\{^1H\}$ NMR (dioxane) δ 34.6 (s); ^1H NMR ($CDCl_3$) δ 2.97 (apparent octet, $J_{P-H} = J_{H-H}$ = 7.2 Hz, 4H, CH), 2.03 (m, 2H, CH_2), 1.57 (m, 4H, PCH_2), 1.45 (dd, J_{P-H} = 18.6 Hz, J_{H-H} = 7.2 Hz, 12H, CH_3), 1.23 (dd, J_{P-H} = 14.2 Hz, J_{H-H} = 7.0 Hz, 12H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 30.1 (d, J_{P-C} = 31.2 Hz, CH), 22.5 (s, CH_3), 22.2 (s, CH_2), 19.5 (s, CH_3), 16.1 (d, J_{P-C} = 30.6 Hz, PCH_2).

22: $^{31}P\{^1H\}$ NMR (dioxane) δ 43.5 (s); ^1H NMR (C_6D_6) δ −12.79 (t, J = 5.0 Hz, Pd—H), other signals are essentially equivalent to those of **21**.

23–25 (mixture) MS (m/z) 170 (M^+), fragmentation is different from that of 2-phenylnorbornene;[17] ^1H NMR (C_6D_6) δ 7.0–7.6 (number of multiplets, aromatic H); major isomer 5.95 (dm, $J_{H-H(cis)}$ = 8.8 Hz, =CH (endocyclic)), 5.72 (dm, $J_{H-H(cis)}$ = 8.8 Hz, =CH (endocyclic)), 4.76 (bs, =CHH (exocyclic)), 4.67 (t, $J_{H-H(allylic)}$ = 1.5 Hz, =CHH (exocyclic)), and 4.03 (bs, CH (allylic)), two other isomers 5.54 (dm, $J_{H-H(cis)}$ = 10.6 Hz, =CH (endocyclic)), 5.24 (dm, $J_{H-H(cis)}$ = 10.6 Hz, =CH (endocyclic)), 4.73 (t, $J_{H-H(allylic)}$ = 1.7 Hz, =CHH (exocyclic)), 4.59 (bs, =CHH (exocyclic)), 5.32 (dm, $J_{H-H(cis)}$ = 9.3 Hz, =CH (endocyclic)), 4.63 (dm, $J_{H-H(cis)}$ = 9.3 Hz, =CH (endocyclic)), 4.58 (bs, =CHH (exocyclic)), 4.43 (t, $J_{H-H(allylic)}$ = <1.5 Hz, =CHH (exocyclic)), and 3.92 (bd, J = 2.2 Hz, CH (allylic)) (other (aliphatic) signals overlap: 0.7–3 (a number of multiplets)). The connectivity between the hydrogens is also confirmed by 2D H—H correlation NMR.

(35) (a) Reference 11a,b,d. (b) Brunner, H.; Kramler, K. *Synthesis* **1991**, 1121.

30: $^{31}P\{^1H\}$ NMR (DMF) δ 56.3 (d, J = 46.9 Hz, 1P), 67.8 (d, J = 46.9 Hz, 1P).

35: $^{31}P\{^1H\}$ NMR (DMF) δ 53.1 (s); confirmed by preparation from dippb and $(CH_3CN)_2PdCl_2$ that gave a mixture of cis and trans isomers.

40: $^{31}P\{^1H\}$ NMR (DMF) δ 33.6 (d, J = 21.6 Hz, 1P), 41.4 (d, J = 21.6 Hz, 1P).

3. Evaluation of Kinetic Parameters. Kinetic rate constants were calculated from the data, gathered by $^{31}P\{^1H\}$ NMR monitoring of reactions 1 and 6, using the GIT program.[14]

Evaluation of the ratios between rate constants for any two insertion reactions (e.g. the ratio between the rate constants of norbornene insertion into **5** and **6**, ratio between the rate constants of norbornene insertion with and without additional phosphine, etc.) were carried out mathematically, as shown below. Treatment of the kinetics of the two compared processes under pseudo-first-order conditions (large excess of olefin) gives us eqs I and II:

$$\ln[\mathbf{A}]_0 - \ln[\mathbf{A}]_t = k_A t \quad \text{(I)}$$

$$\ln[\mathbf{A}']_0 - \ln[\mathbf{A}']_t = k_{A'} t \quad \text{(II)}$$

where [**A**] and [**A**′] are the concentrations of the starting complexes in the two compared reactions. The indexes 0 and t relate to the concentration at the beginning of the reaction (time = 0) and at time t. Assuming that the insertion cleanly converts complexes **A** and **A**′ into **B** and **B**′, respectively, eqs I and II can be transformed into eqs III and IV:

$$\ln[\mathbf{A}]_0 - \ln([\mathbf{A}]_0 - [\mathbf{B}]_t) = k_A t \quad \text{(III)}$$

$$\ln[\mathbf{A}']_0 - \ln([\mathbf{A}']_0 - [\mathbf{B}']_t) = k_A t \quad \text{(IV)}$$

Thus, the ratio $k_A/k_{A'}$, which we are looking for, is given by eq V:

$$\frac{k_A}{k_{A'}} = \frac{\ln[\mathbf{A}]_0 - \ln[\mathbf{A}]_t}{\ln[\mathbf{A}']_0 - \ln[\mathbf{A}']_t} = \frac{\ln[\mathbf{A}]_0 - \ln([\mathbf{A}]_0 - \ln[\mathbf{B}]_t)}{\ln[\mathbf{A}']_0 - \ln([\mathbf{A}']_0 - \ln[\mathbf{B}']_t)} \quad \text{(V)}$$

If we can define conversions C_t and C'_t as $[\mathbf{B}]_t/[\mathbf{A}]_0$ and $[\mathbf{B}']_t/[\mathbf{A}']_0$, respectively, then

$$\frac{k_A}{k_{A'}} = \frac{\ln[\mathbf{A}]_0 - \ln([\mathbf{A}]_0(1 - C))}{\ln[\mathbf{A}']_0 - \ln([\mathbf{A}']_0(1 - C'))} = \left[\frac{\ln(1 - C)}{\ln(1 - C')}\right] \quad \text{(VI)}$$

Although eq IV shows that $k_A/k_{A'}$ is not dependent on the initial concentrations, our treatment of the reactions as pseudo-first-order processes requires equal initial concentrations of complexes **A** and **A**′, as well as of the substrate olefins. Keeping the conditions of the two reactions equal is essential for a meaningful ratio. However, the time t is excluded from eq VI and, thus, is not important.

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