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Palladium Iminoacyl Imine Complexes: Strategies toward Imine Insertion§

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The syntheses and characterization of a number of palladium complexes containing imine and/or iminoacyl groups are reported. Our strategies toward the insertion of imines into palladium iminoacyl complexes are outlined. The imine complexes $[Pd(Me)(L_2)\{N(R')=C(H)Ph\}]X$ (where L_2 = dppe, dppp, dppf; R′ = Ph, Me, Bz; and X = BF_4 or OTf) were prepared and fully characterized. $[Pd(Me)(dppe)\{N(Ph)=C(H)Ph\}]BF_4$ (**1**) and $[Pd(Me)(dppp)\{N(Ph)=C(H)Ph\}]OTf$ (**4**) were structurally characterized by X-ray crystallography. The iminoacyl-imine complexes $[Pd\{C(Me)=NXyl\}(L_2)\{\overline{N=C(Me)OCH_2CH_2}\}]BF_4$ (L_2 = dppe, **12**; dppp, **13**) were prepared. The bis-imine complex $[Pd(dppe)\{\overline{N=C(Me)OCH_2CH_2}\}_2][BF_4]_2$ (**14**) resulting from disproportionation of **12** was also prepared and structurally characterized. Protonation of the iminoacyl fragment provided iminoacyl imine complex $[Pd\{C(CH_3)=N(H)Xyl\}(dppe)\{N(Bz)=CPhH\}][BF_4]_2$ (**17**), which was sufficiently stable to be structurally characterized, providing some insight into the coordination of these fragments to palladium.

Introduction

Palladium-catalyzed carbon−carbon bond formation is a well-established methodology for the synthesis of new and valuable organic compounds.[1] More recently efficient methodologies for the coupling of nitrogen, sulfur, and oxygen fragments to carbon have also been established.[2−4] The synthesis of new C−N, C−S, and C−O bonds has great potential for the preparation of new pharmaceuticals and other biologically important species. In the search for new routes to these targets, and by analogy to the copolymerization of olefins and carbon monoxide,[5] there have been some studies on the insertion of imines (R′R″C=NR) into metal−acyl bonds.[6] In 1998, Sen and Arndtsen independently showed the insertion of an imine into palladium−acyl bonds.[7,8] The resulting complexes, however, were unreactive

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§ This article is dedicated to the memory of Dr. Daniela Rais.

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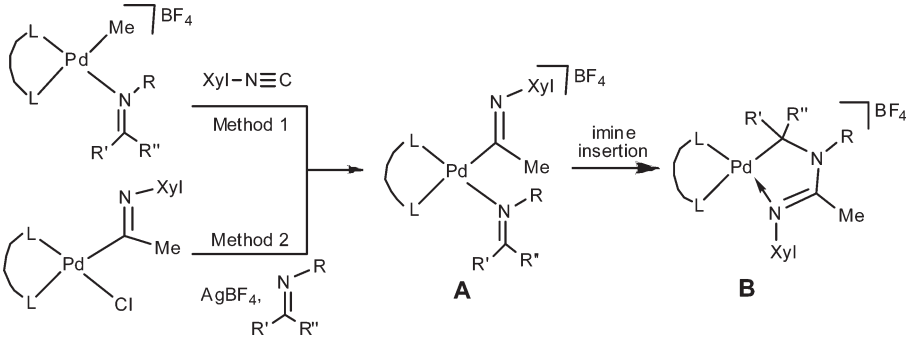
Scheme 1. Two Methodologies for Imine Insertion into the Palladium−Iminoacyl Bond



to further insertion due to the strong chelation of the amide functionality to the metal center. More recently, Arndsten has reviewed this area, showing the wide range of potential reactions that can be performed with this organometallic fragment.[9] On the other hand, Sun reported the first examples of copolymerization of carbon monoxide and imines, providing a novel method for the formation of polypeptides with molecular weights of about 2000 Da.[10] Sun employed $[Co(CH_2Ph)(CO)_4]$ as a precursor, which is initiated by the loss of one molecule of carbon monoxide. The active species subsequently undergoes alternating insertion of imine and carbon monoxide, which is eventually terminated via β-hydride elimination.

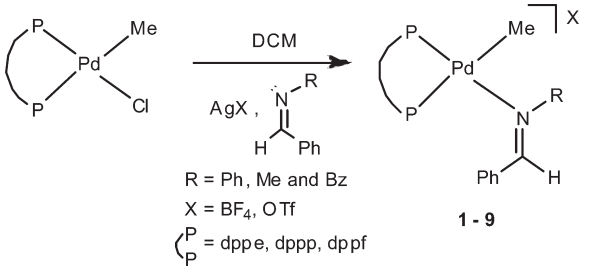
We have previously reported the insertion of olefins into iminoacyl-palladium complexes containing bidentate phosphine ligands.[11] Insertion of imines into the iminoacyl group could provide an alternative route to precursors for the formation of heterocyclic products. Moreover, the products resulting from potential insertion of the imine into the iminoacyl moiety, i.e., amidines, are molecules of great biological interest.[12] We were therefore interested in investigating the potential of imine insertion into palladium−iminoacyl bonds. Herein, we outline our strategies toward imine insertion into palladium−iminoacyl bonds.

Results and Discussion

Two different methodologies were initially envisaged to achieve the iminoacyl-imine species **A**, which could in principle undergo imine insertion into the palladium−iminoacyl bond, forming product **B** (Scheme 1). First, by analogy to the chemistry developed by Sen and Arndtsen,[7,8] a palladium methyl-imine complex was prepared and 1 equiv of isocyanide was subsequently added to the complex. A second method involved initial formation of the iminoacyl complex followed by halide abstraction in the presence of imine.

Method 1: Addition of Isocyanide to Imine Complexes. The first step in our studies toward imine insertion was to synthesize and fully characterize a series of palladium-imine complexes for further reactivity (Scheme 2). The bis-phosphine complexes were targeted since Sen had previously established a greater propensity for imine insertion into

Scheme 2. General Synthesis of the Imine Complexes 1−9



palladium−acyl bonds, where the palladium is coordinated to chelating phosphines rather than to related nitrogen-based ligands. Furthermore, following the publication by Sen and Arndtsen, reporting the insertion of imine into a palladium−acyl bond, a theoretical study by Cavallo was reported.[13] This study confirmed that imine insertion into Pd−acyl bonds is energetically favorable and proceeds via a lower energy barrier when the co-ligands are bis-phosphines in comparison to bis-nitrogen ligands. Cavallo explained that a larger *trans* influence of the phosphines made the bond lengths of both the acyl and imine ligands closer to that of the calculated transition state of the insertion process. This effect reduces the strain on going through the transition state and makes the barrier to insertion lower. This would explain why complexes with bis-nitrogen ligands reported by Arndtsen required elevated temperatures for insertion to take place. The larger driving force for Pd−acyl insertion comes mainly from formation of a strong amido bond. Cavallo confirmed the stability of the σ-bonded coordination mode of the imine over the π-bonded form (π-coordination ca. 20 kcal mol^{-1} higher in energy relative to the σ-coordination mode). Nevertheless, Cavallo further calculated that some π-bonded character is necessary during the final stages of the transition state for insertion. π-Bonding reduces the bond order of the imine, and therefore the complex is closer in energy to the transition state needed for insertion.

A small number of palladium complexes containing imines and chelating phosphines had been previously described by Sen.[7] However their full characterization was not reported. A general method of preparation of the imine complexes is described herein. $[PdCl(Me)L_2]$ (L_2 = dppp, dppe, dppf) was dissolved in CH_2Cl_2. Chloride was then removed by addition of 1 equiv of $AgBF_4$ or AgOTf, in the presence of a slight excess (1.1 equiv) of imine. The resulting AgCl precipitate was removed by filtration, and the product was isolated by addition of hexane and slowly evaporating CH_2Cl_2 under reduced

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Table 1. Isolated Yields of [L_2M(Me)(imine)]X (1−9)

complex[a]	L_2	imine	yield (%)
1	dppe	N(Ph)=CPhH	79
2	dppe	N(Me)=CPhH	78
3	dppe	N(Bz)=CPhH	76
4	dppp	N(Ph)=CPhH	62
5	dppp	N(Ph)=CPhH	73
6	dppp	N(Me)=CPhH	71
7	dppp	N(Bz)=CPhH	68
8	dppf	N(Ph)=CPhH	79
9	dppf	N(Bz)=CPhH	78

[a] Noncoordinating anion is BF_4 except for complex **4**, which is OTf.

pressure. The resulting solid was washed with diethyl ether to remove excess imine. The dppp and dppe products were isolated as white solids, and the dppf products were isolated as analytically pure yellow to orange solids in high yields. The numbering scheme of the prepared complexes is shown in Table 1 together with their isolated yields.

The products (**1**−**9**) were fully characterized by $^{31}P\{^1H\}$ NMR (Table 2), ^1H NMR (Table 3), and IR spectroscopies (Table 3), FAB^+ mass spectrometry, and elemental analysis. Crystallographic studies were carried out on two of the complexes, **1** and **4** (see below).

The $^{31}P\{^1H\}$ NMR spectra of these complexes comprised of a pair of doublets as expected from a *cis* chelating phosphine with two different ligands in the *trans* positions (methyl and imine). The dppe-based complexes are found at lower field chemical shifts with smaller coupling constants compared to the dppp complexes. This is consistent with previously reported data comparing these two chelating phosphines.[14] The chemical shifts and coupling constants for each product are shown in Table 2. The ^1H NMR spectra of compounds **1**−**9** revealed a doublet of doublet signal integrating for three protons, representing the methyl group bound to the palladium (between 0.08 and 0.37 ppm). The proton of the imines, N(R)=C(*H*)Ph was found between 7.84 and 8.52 ppm as a doublet of doublets (with approximate $^4J_{PH}$ = 9.5 and 2.0 Hz, *trans* and *cis* coupling, respectively, to the diphosphine). An additional signal, found between 7.68 and 8.46 ppm (integrating for two protons) in the ^1H NMR spectra of the nine complexes, was observed at lower field chemical shifts than the other aromatic signals. These resonances were assigned to the two *ortho*-protons on the phenyl group of N(R)=CPhH. This assignment was made on the basis of an agostic interaction that is maintained in solution (see below for structural information) and is in accordance with previously reported agostic interactions involving imines' aryl groups.[15−17] An important feature of the reported complexes was the characteristic downfield chemical shift (approximately 1.0−1.5 ppm), in the ^1H NMR spectra, from the corresponding signals for the free imine. The extreme of this

Table 2. $^{31}P\{^1H\}$ NMR Spectroscopic Data for Complexes 1−9

	$^{31}P\{^1H\}$ NMR δ (ppm)		
complex[a]	*trans* to methyl[b]	*trans* to imine[b]	J_{PP} (Hz)
1	57.6	39.1	23
2	57.7	39.9	23
3	57.0	39.7	23
4	23.8	−2.1	51
5[c]	23.1	−2.3	52
6	22.7	0.2	50
7[c]	21.9	0.3	50
8	38.1	19.6	29
9	36.8	19.2	29

[a] Recorded in $CDCl_3$. [b] This assignment was made by comparison with similar complexes such as [L_2Pd(Me)(NCMe)]X; see ref 24b. [c] Recorded in THF.

Table 3. Comparison of ^1H NMR Spectroscopic Data and IR Spectroscopic Data for Imine Complexes[a]

compound[a]	N=C*H* (ppm)	N=CPh *ortho*-H's (ppm)	M−CH_3 (ppm)	C=N (cm^{-1})
N(Ph)=CPhH				1624
1	8.48	8.07	0.54	1606
4	8.05	8.37	0.37	1608
5	8.04	8.37	0.36	1624
8	8.35	8.46	0.41	1607
N(Me)=CPhH				1652
2	8.52	7.94	0.48	1637
6	8.10	7.68	0.35	1645
N(Bz)=CPhH				1643
3	8.62	8.03	0.18	1617
7	7.84	8.15	0.01	1626
9	8.15	8.45	0.08	1626

[a] NMR spectroscopy carried out in $CDCl_3$.

interaction leads to cyclometalation, of which there are many more examples.[18] The IR spectra of these complexes display the characteristic C=N stretching frequency of imines, with reduced frequency relative to the free imine. This is with the exception of complex **5**, which showed no shift in the imine frequency. The IR spectra also revealed characteristic stretches for either the tetrafluoroborate (1057−1069 cm^{-1}) or triflate (1262, 1152, and 1031 cm^{-1}) anions present as counterions in the different complexes. The FAB^+ mass spectra of **1**−**9** showed molecular ion peaks for the expected complexes and fragments corresponding to loss of imine. The molecular composition of the complexes was further confirmed by elemental analysis.

X-ray Crystal Structures of Complexes 1 and 4. Crystals of complexes **1** and **4** suitable for X-ray crystallography were obtained by careful addition of a layer of hexane to a concentrated THF solution of the corresponding complex. The solid state structures of these complexes showed them to be the expected products in each case (Figures 1 and 2, respectively). In both structures the palladium adopts a distorted square-planar geometry with *cis* angles in the ranges 85.83(4)−91.91(9)° and 86.2(4)−94.20(12)° for **1** and **4**, respectively. However, whereas in **4** the metal and the four donor atoms are all coplanar to better than 0.01 Å, in **1** the P(1) phosphorus atom lies ca. 0.26 Å out of the {Pd,P(2),N(1),C(2)} plane (which is coplanar to within ca. 0.01 Å). This is possibly associated with the decreased bite angle of the dppe

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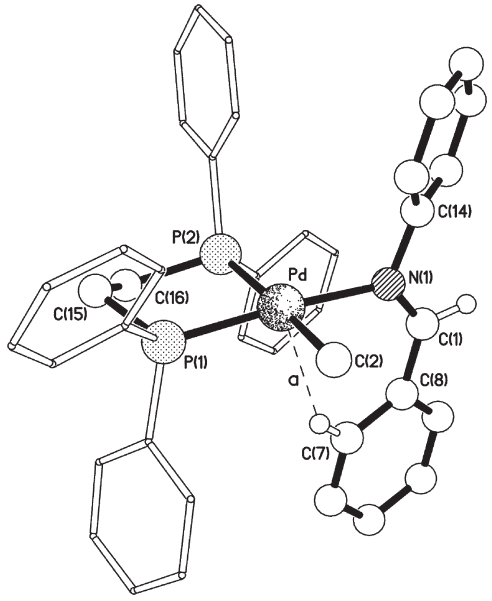


Figure 1. Molecular structure of the cation in **1**. The agostic interaction "**a**" has an H···Pd distance of ca. 2.42 Å.

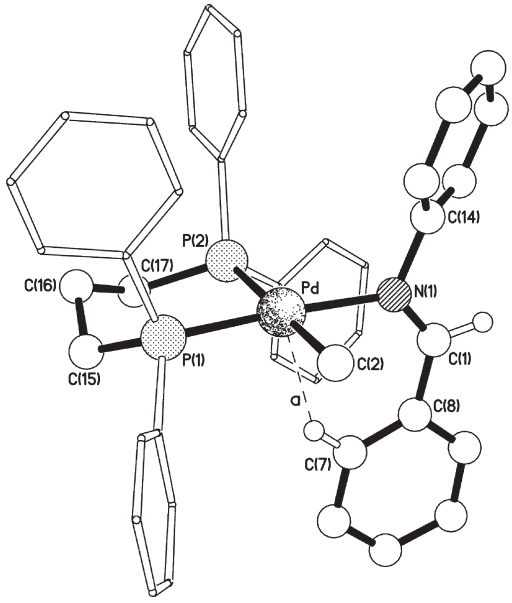


Figure 2. Molecular structure of the cation in **4**. The agostic interaction "**a**" has an H···Pd distance of ca. 2.38 Å.

diphosphine ligand [85.83(4)° with an ethyl linkage] compared to the dppp ligand [94.20(12)° with a propyl linkage].[19] In each structure the Pd−P bond to the phosphorus atom *trans* to the neutral imine donor [Pd−P(1) 2.2221(10) and 2.240(3) Å in **1** and **4**, respectively] is significantly shorter than that *trans* to methyl [Pd−P(2) 2.3381(10) and 2.383(3) Å], reflecting the greater *trans* influence of methyl compared with the imine. The Pd−N bonds to the imine ligands in the two complexes, however, are the same [2.140(3) and 2.133(9) Å in **1** and **4**, respectively]. Interestingly, in both structures one of the *ortho* protons of the C-bound phenyl ring of the imine ligand approaches the metal center in an agostic interaction with H···Pd separations of ca. 2.42 and 2.38 Å in **1** and **4**, respectively,[20] with the H···Pd vectors being inclined in each case by ca. 75° to the respective palladium coordination plane.

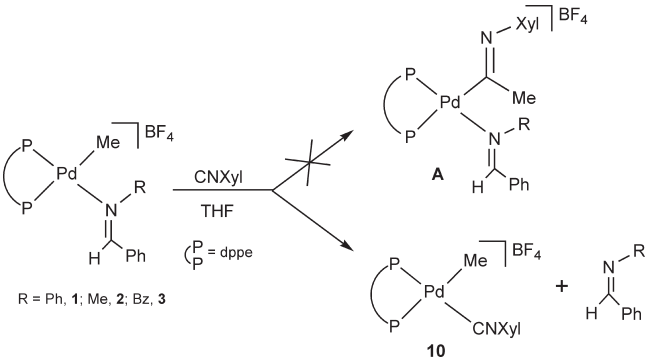
Table 4. Selected Bond Lengths (Å) and Angles (deg) for 1

Pd−P(1)	2.2221(10)	Pd−P(2)	2.3381(10)
Pd−N(1)	2.140(3)	Pd−C(2)	2.128(4)
N(1)−C(1)	1.286(6)		
P(1)−Pd−P(2)	85.83(4)	P(1)−Pd−N(1)	173.54(11)
P(1)−Pd−C(2)	90.59(12)	P(2)−Pd−N(1)	91.91(9)
P(2)−Pd−C(2)	176.11(13)	N(1)−Pd−C(2)	91.82(15)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 4

Pd−P(1)	2.240(3)	Pd−P(2)	2.383(3)
Pd−N(1)	2.133(9)	Pd−C(2)	2.105(13)
N(1)−C(1)	1.259(15)		
P(1)−Pd−P(2)	94.20(12)	P(1)−Pd−N(1)	174.0(3)
P(1)−Pd−C(2)	86.2(4)	P(2)−Pd−N(1)	91.8(3)
P(2)−Pd−C(2)	179.5(4)	N(1)−Pd−C(2)	87.8(4)

Scheme 3. Schematic Representation of the Observed Reactivity of 1−3 with Isocyanide



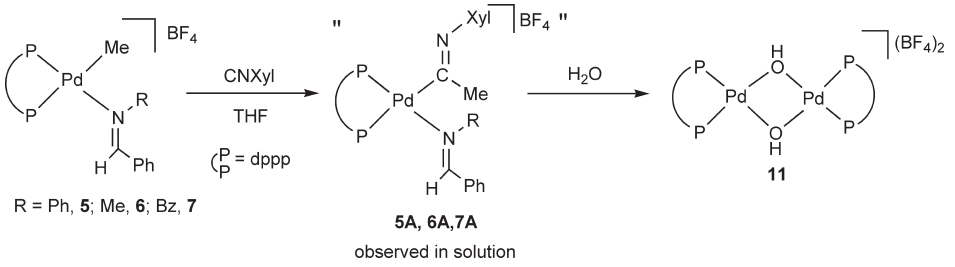
Isocyanide Insertion Reactions. The reactions of complexes **1**−**9** with 2,6-dimethylphenyl isocyanides was subsequently investigated. We hypothesized that the addition of isocyanide should result in the temporary replacement of the imine ligand followed by insertion into the palladium−methyl bond. Once the iminoacyl moiety was formed, the imine would then re-coordinate to the vacant coordination site on the palladium center. Insertion of the imine into the Pd−iminoacyl bond could then occur as shown in Scheme 1.

Complexes containing the dppe ligand are known to exhibit slower (and sometimes differing) reactivity than their dppp analogues.[19] It was therefore decided to carry out the reactions with the dppe complexes first. The slower reactivity perhaps would allow the isolation of the iminoacyl-imine product **A** before reaction to the imine insertion product **B** (Scheme 1). However, instead of either of the expected products, addition of 1 equiv of CNXyl to THF solutions of [Pd(Me)(dppe){N(R)=CPhH}]BF_4 (**1**, **2**, and **3**) led to the formation of [Pd(Me){CNXyl}(dppe)]BF_4 (**10**), where the isocyanide is terminally coordinated (see Scheme 3). The experimental evidence for the formation of this product came from spectroscopic studies. $^{31}P\{^1H\}$ NMR spectroscopy gave the same set of resonances (δ = 59.4(d) and 46.5(d) ppm) for the three reactions, suggesting that the imine was being displaced. The ^1H NMR spectra of the solids isolated from these three reactions (upon addition of hexane to the corresponding reaction mixture) confirmed the absence of resonances associated with the corresponding imine.

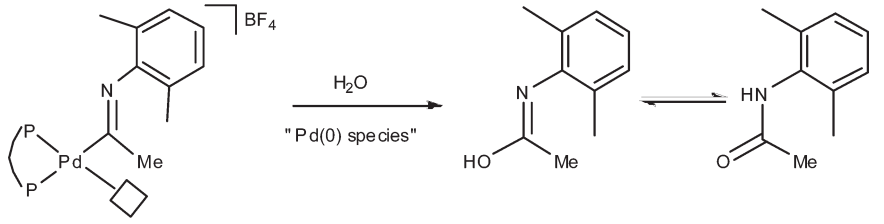
(19) van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741.

(20) The hydrogen atoms involved in these interactions were placed in calculated positions, and for the purpose of calculating the geometries of the interactions their parent C−H distances were normalized to 0.96 Å.

Scheme 4. Reaction of Complexes 5, 6, and 7 with 2,6-Dimethylphenyl Isocyanide



Scheme 5. Diagram Showing the Attack of Water upon the Iminoacyl Group



In addition, a doublet of doublets at 0.77 pm [$^3J_{PHtrans}$ = 6.5 Hz, $^3J_{PHcis}$ = 4.5 Hz] corresponding to the palladium-bound methyl group and a singlet (6 H) at 2.16 ppm, corresponding to the *ortho*-methyl groups of the bound 2,6-dimethylphenyl isocyanide [$C_6H_3(CH_3)_2$], were observed. The IR spectra of the three solids gave a sharp and strong band at 2180 cm^{-1}, which is consistent with a terminally coordinated isocyanide. The FAB^+ mass spectra of the three solids showed a peak at 651 amu corresponding to $[Pd(Me)(CNXyl)(dppe)]^+$.

Complex **10** was also prepared by addition of 1 equiv of $AgBF_4$ to [Pd{C(CH_3)=NXyl}Cl(dppe)].[11] This resulted in the deinsertion of the isocyanide from the iminoacyl fragment, yielding **10**. It was clear that the products resulting from addition of 2,6-dimethylphenyl isocyanide to complexes **1**−**3** were the substitution products and not the desired products **A** and **B** (Scheme 1). Unfortunately, all of our attempts to drive the reaction by heating or addition of excess equivalents of imine proved unsuccessful.

Considering the results obtained with the dppe complexes, it was decided to investigate whether analogous reactions would take place with the corresponding dppp complexes. It is well documented that complexes with dppp are generally more reactive toward insertion than the corresponding dppe analogues.[19] Addition of 1 equiv of CNXyl to THF solutions of the complexes [Pd(Me)(dppp){N(R)=CPhH}]BF_4 (**5**, **6**, and **7**) led to the formation of a new species (within 5 min) in each case. The corresponding new products showed two doublets in the $^{31}P\{^1H\}$ NMR spectra (one of the doublets appeared between 18.5 and 14.2 and the second doublet between 5.8 and 5.5 ppm). In spite of the clean transformation of complexes **5**−**7** into the corresponding new species (tentatively assigned to species **5A**−**7A**; see Scheme 4), the later decomposed over time to the known hydroxo-bridged dimer [Pd(μ-OH)$_2$(dppp)]$(BF_4)_2$ (**11**).[21] This was evident from the singlet resonance at 15.4 ppm in the $^{31}P\{^1H\}$ NMR spectra of the three reactions in addition to a resonance at −2.4 ppm in the ^1H NMR spectra (assigned to the bridging OH groups).

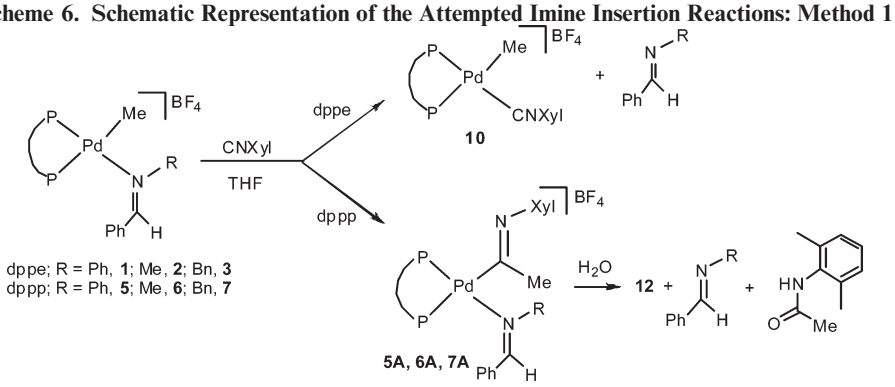
(21) Pisano, C.; Consiglio, G.; Sironi, A.; Moret, M. *J. Chem. Soc., Chem. Commun.* **1991**, 421.

Various attempts were made to isolate products **5A**, **6A**, and **7A** from these reactions, without any contamination of **11**. In most cases the precipitates contained only minor amounts of the desired species. FAB^+ mass spectrometry was unable to provide evidence for the formation of **5A** or **6A**. However, the solid isolated from the methyl imine reaction (**7A**) showed a peak of high intensity at 783 amu corresponding to [Pd{C(CH_3)=NXyl}(dppp){N(Me)=CPhH}]$^+$. Furthermore, although it was not possible to fully determine the identity of these compounds, the ^1H NMR spectra of **5A**−**7A** showed that further reactivity of the corresponding imine with the complex had occurred. Since the metal complex isolated from the above reactions did not contain either the iminoacyl or imine species, it was of interest to identify any organic moieties being eliminated from the complex. With this aim, the reaction solvent was removed from the reaction involving **6**, and the organic material was extracted with diethyl ether and analyzed by GC-MS, which revealed the presence of two major species. The first species corresponded to unreacted imine, confirming that insertion into the corresponding iminoacyl fragment either had not occurred or that the insertion product fragmented, re-forming the starting imine. The second product detected by GC-MS was *N*-(2,6-dimethylphenyl)acetamide (Scheme 5), which formed from the reaction between water and the iminoacyl fragment of the complex. The formation of this product appears to be the driving force for the decomposition of complexes **5A**−**7A**.

Our observations correlate somehow with those of Sen, who had shown that imine insertion into a palladium−acyl bond was efficient only in the case of dppp complexes.[7a] It is also noteworthy that Sen had previously noted significant decomposition in a number of reactions involving insertion of imine into a palladium−acyl bond. From the results discussed above it is clear that the nature of the chelating phosphine has an important influence on the outcome of the reactions under study. These differences are summarized in Scheme 6.

In the case of complexes **1**−**3** (with dppe) substitution of the imine with isocyanide takes place yielding complex **10**, which contains a terminal isocyanide. This can be attributed to two main factors: (a) isocyanide insertions are generally

Scheme 6. Schematic Representation of the Attempted Imine Insertion Reactions: Method 1



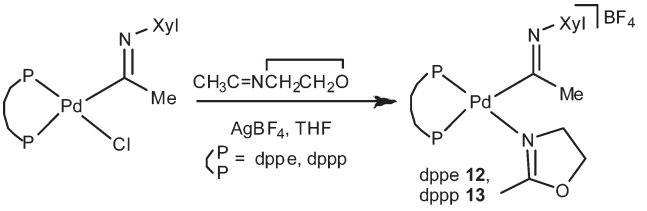
less favored in complexes containing dppe (as compared to other chelating phosphines such as dppp),[11] which has been attributed to differences in bite angles;[19] (b) coordination of imine to the Pd-dppe complex is not as strong as in Pd-dppp complexes.

In contrast, with the dppp complexes, insertion of isocyanide is much more facile, yielding the iminoacyl-imine complexes **5A**, **6A**, and **7A** (detected only in solution). However, these complexes proved to be unstable and readily react with traces of water to yield the hydroxo-bridged dimer **11**.

Method 2: Imine Addition to Iminoacyl Complexes. Despite our efforts, it was evident that method 1 would not yield the desired insertion products. Therefore, a second method involving preparation of the iminoacyl complex prior to addition of imine was investigated (Scheme 1). This sequence of reactivity was perhaps a better method since the iminoacyl fragment was already in place and it would be less likely for the isocyanide fragment to deinsert. This is particularly important with the dppe complexes, which require a strong driving force for insertion of isocyanide into the palladium−methyl bond. We have previously shown that this approach could be utilized to synthesize palladium iminoacyl/imine complexes (complex type **A** in Scheme 1) with dinitrogen ligands such as bipy and $^{t}Bu_2$bipy,[22] although we were unable to provide evidence of insertion of the imine fragment into the palladium−iminoacyl bond in that case.

Some of our preliminary tests using method 2 with the aldimines N(R)=CPhH (where R = Ph, Me, Bz) also gave similar results to those found with method 1 (namely, no insertion was detected, decomposition of the iminoacyl-imine products, etc.). Therefore, our attention moved toward investigating a more strongly coordinating imine to increase the stability of the intermediate species (complexes type **A** in Scheme 1). The reactions of cyclic imine methyloxazaline with [Pd{C(CH_3)=NXyl}Cl(dppe)] and [Pd{C(CH_3)=NXyl}Cl(dppp)] were therefore investigated. In this particular imine, the relative ring strain renders the lone pair of the nitrogen more available for coordinating to the metal, and the release in strain would additionally provide a stronger driving force for insertion. One equivalent of $AgBF_4$ was added to solutions of the iminoacyl complexes [Pd{C(CH_3)=NXyl}Cl(dppe)] and [Pd{C(CH_3)=NXyl}Cl(dppp)][11] in THF in the presence of excess methyloxazaline. The $^{31}P\{^{1}H\}$ NMR spectra indicated quantitative conversion of the starting material into the two new products [(P−P)-Pd{C(Me)=NXyl}(N=C(Me)OCH$_2$CH$_2$)]BF_4 (where P−P = dppe (**12**) and dppp (**13**), respectively) (Scheme 7).

Scheme 7. Synthesis of Iminoacyl-imine Complexes 12 and 13

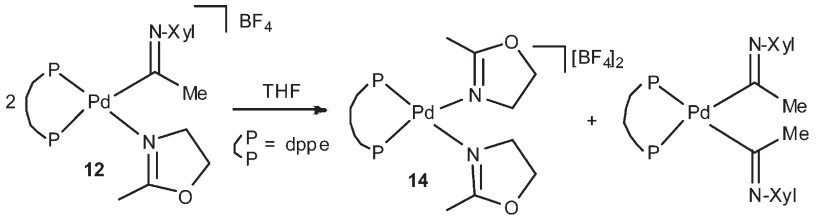


Samples of **12** and **13** were obtained, in good yields, by removing the precipitated AgCl via filtration of the reaction mixture followed by reduction of solvent volume. Addition of hexane to the remaining solution yielded **12** and **13** as pale yellow and white solids, respectively. These complexes were fully characterized by NMR and infrared spectroscopy and by elemental analysis. The ^{1}H NMR spectra of **12** and **13** were consistent with the formation of the expected iminoacyl/imine complexes. The IR spectra of both products showed a reduction in the frequency of the imine C=N stretch as compared to the corresponding free imine. Elemental analyses of these products, were consistent with the expected formulation [Pd{C(CH_3)=NXyl}(dppe)-{N=C(Me)OCH$_2$CH$_2$}]BF_4 (**12**) and [Pd{C(CH_3)=NXyl}-(dppp){N=C(Me)OCH$_2$CH$_2$}]BF_4 (**13**), respectively. Full characterization of these two compounds was encouraging because it provided evidence of imines coordination to iminoacyl complexes.

Since insertion of imine into the palladium−iminoacyl bond was the ultimate goal of these reactions, we were interested in the further reactivity of these complexes. Solutions of **12** and **13** were monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy over time to see if any new products would form. After leaving a solution of **12** for 1 h, a small amount of a new product identified by a singlet at 66.4 ppm was detected in the $^{31}P\{^{1}H\}$ NMR spectrum. When the solution was left for a further 24 h, colorless crystals appeared. An X-ray crystal structure determination performed on these crystals revealed the product to be the disproportionated bis-imine complex, [Pd{N=C(Me)OCH$_2$CH$_2$}$_2$(dppe)][BF_4]$_2$ (**14**), where the iminoacyl fragment has disappeared (Figure 3). The geometry at the palladium center is distorted square planar with *cis* angles in the range 83.63(3)−96.08(9)°, with the metal and the four donor atoms coplanar to within ca. 0.02 Å. Interestingly, the bite angle of the chelating dppe

(22) Owen, G. R.; Vilar, R.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 3025.

Scheme 8. Proposed Method for the Formation of 14



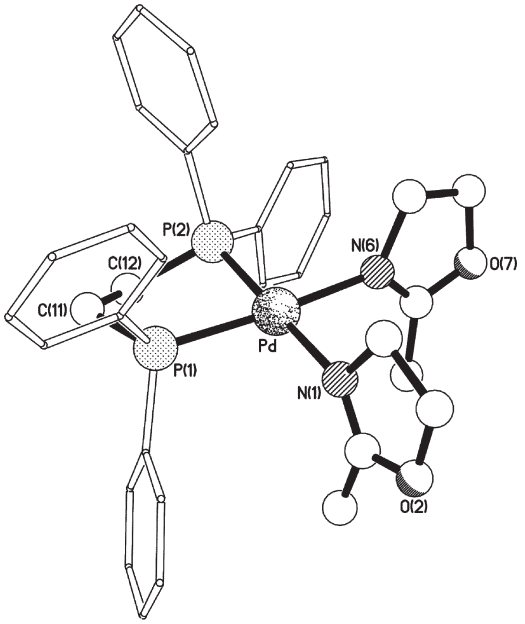


Figure 3. Molecular structure of the dication in **14**.

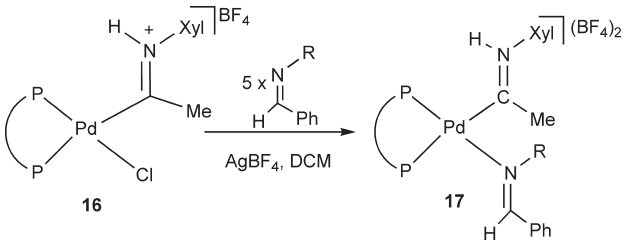
Table 6. Selected Bond Lengths (Å) and Angles (deg) for 14

Pd−P(1)	2.2723(10)	Pd−P(2)	2.2492(10)
Pd−N(1)	2.112(3)	Pd−N(6)	2.090(3)
P(1)−Pd−P(2)	83.63(3)	P(1)−Pd−N(1)	96.08(9)
P(1)−Pd−N(6)	173.96(9)	P(2)−Pd−N(1)	178.42(9)
P(2)−Pd−N(6)	90.35(9)	N(1)−Pd−N(6)	89.95(12)

diphosphine ligand here in **14** [83.63(3)°] is ca. 2° smaller than seen in **1** [85.83(4)°], though there is no obvious reason for this difference. There is evidence for an intramolecular $\pi-\pi$ stacking interaction between the N(6) C_3NO ring and the adjacent phenyl ring bound to P(2) [centroid···centroid and mean interplanar separations ca. 3.83 and 3.60 Å, planes inclined by ca. 21°], but if this is having an effect, it would be to make the bite angle larger. This interaction, however, may explain why the Pd−P(2) [2.2492(1) Å] bond is significantly shorter than that to P(1) [2.2723(10) Å] when the *trans* ligands are otherwise identical. The Pd−N bonds also differ, with that to N(6) [2.090(3) Å] shorter than that to N(1) [2.112(3) Å] so that the shorter Pd−N bond is *trans* to the longer Pd−P bond, and *vice versa*.

The $^{31}P\{^1H\}$ NMR spectrum of the crystalline material gave a singlet at 66.4 ppm, which is the same chemical shift as that previously observed in the reaction mixture. The product presumably precipitated driving the equilibrium of the mixture toward the bis-imine product. The formation of **14** implies that there should be a bis-iminoacyl complex being formed in the mixture (Scheme 8). The $^{31}P\{^1H\}$ NMR spectrum of the resulting mixture revealed many phosphorus signals. Further analysis of the organic material, by GC-MS, confirmed the formation of significant quantities of *N*-(2,6-dimethylphenyl)acetamide, confirming that disproportionation followed by decomposition of complex **12** had occurred in this case. Unfortunately, all of our attempts to drive the insertion of the imine into the palladium−iminoacyl bond in complexes **12** and **13** were unsuccessful.

Scheme 9. Formation of the Protonated Iminoacyl/Imine Complex 17



Protonated Iminoacyl Complexes. A difficultly found with iminoacyl complexes containing phosphine co-ligands is the propensity to undergo deinsertion of isocyanide when there is a weakly coordinated ligand in the fourth coordination site. A method to prevent this from occurring is by protonating the iminoacyl functionality. We have previously reported the synthesis of the protonated compounds [Pd{C(CH$_3$)=NHXyl}Cl(dppe)]OTf (**15**) and [Pd{C(CH$_3$)=NHXyl}Cl(dppe)]BF_4 (**16**)[23] and have shown that removal of the halide does not lead to the deinsertion. Furthermore, protonation of the iminoacyl fragment should in principle make the sp^2 carbon more electrophilic and might favor the insertion of the nucleophilic nitrogen atom of the imine into the palladium−iminoacyl bond. Thus, the reaction of one of these protonated complexes (**16**) with an imine was investigated. Addition of 1 equiv of $AgBF_4$ to a solution of **16** in CH_2Cl_2 in the presence of 1 equiv of N(Bz)=CPhH resulted in the formation of one main new product (ca. 90% of the phosphine-containing compounds) associated to a pair of doublets at 54.4 and 52.2 ppm. A white solid with the formulation [Pd{C(CH$_3$)=N(H)Xyl}(dppe){N(Bz)=CPhH}]$(BF_4)_2$ (**17**) was isolated from the reaction mixture by reduction of the volume followed by addition of hexane (Scheme 9).

The formulation of this white solid was established by spectroscopic, analytic, and structural techniques. The FAB^+ mass spectrum of the solid showed a peak at 932 amu, which corresponds to the molecular mass of complex **17** minus one of the BF_4 counterions. The IR spectrum shows stretches at 3198, 1075, and 1560 cm^{-1}, corresponding to N−H, BF_4, and protonated iminoacyl (C=NH) moieties, respectively. The C=N stretching region of the spectrum

(23) Owen, G. R.; Vilar, R.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 4511.

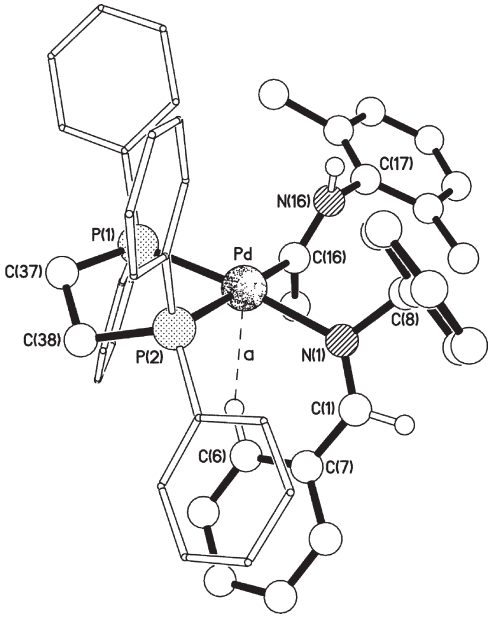


Figure 4. Molecular structure of the dication in **17**. The agostic interaction "**a**" has an H···Pd distance of ca. 2.51 Å.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for 17

Pd−P(1)	2.2723(15)	Pd−P(2)	2.3455(15)
Pd−N(1)	2.102(5)	Pd−C(16)	2.062(6)
N(1)−C(1)	1.283(8)	N(16)−C(16)	1.298(8)
P(1)−Pd−P(2)	84.43(6)	P(1)−Pd−N(1)	173.76(14)
P(1)−Pd−C(16)	92.34(16)	P(2)−Pd−N(1)	95.09(14)
P(2)−Pd−C(16)	175.78(17)	N(1)−Pd−C(16)	87.8(2)

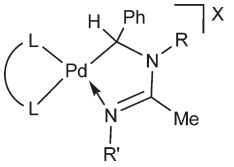


Figure 5. Chelation of the amidine functionality to the fourth coordination site on palladium.

shows a band at 1618 cm^{-1} (cf. 1643 cm^{-1} for the noncoordianted imine). Crystals suitable for X-ray crystallography were obtained by addition of diethyl ether to a concentrated CH_2Cl_2 solution of **17** in the presence of 5 equiv of imine. The palladium coordination geometry in the structure of **17** (Figure 4) is distorted square planar, with the *cis* angles ranging between 84.43(6)° and 95.09(14)° and with the P(1) phosphorus atom lying ca. 0.17 Å out of the {Pd,P(2),N(1), C(16)} plane, which is coplanar to within ca. 0.04 Å. The bite angle of the chelating dppe diphosphine ligand [84.83(6)°] is intermediate between those seen in **1** [85.83(4)°] and **14** [83.63(3)°]. The Pd−P bond *trans* to the iminoacyl ligand [Pd−P(2) 2.3455(15) Å] is significantly longer than that *trans* to the imine [Pd−P(1) 2.2723(15) Å], reflecting the stronger binding of the iminoacyl moiety [Pd−C(16) 2.062(6) Å] compared to the imine unit [Pd−N(1) 2.102(5) Å]. As was seen in the structures of **1** and **4**, one of the *ortho* protons of the C-bound phenyl ring of the imine ligand approaches the metal center in an agostic interaction with an H···Pd separation of ca. 2.51 Å[20] and with the H···Pd vector inclined by ca. 80° to the palladium coordination plane. The same phenyl ring is involved in an intramolecular $\pi-\pi$ stacking interaction with the proximal phenyl ring bound to P(2) [centroid···centroid and mean interplanar separations ca. 3.74 and 3.41 Å, planes inclined by ca. 3°]. Despite a number of attempts, we found no evidence to indicate that insertion of the imine into the palladium−carbon bond had occurred even after prolonged periods of time.

Conclusions

There may be a number of reasons why insertion of imine into the Pd−iminoacyl bond was not observed during the course of our investigations. The amidine product may provide a lower driving force for insertion product in comparison to the corresponding amide.[24] Irrespective of this, the chelation of the amidine functional group to the fourth coordination site on palladium should provide a strong driving force for insertion (Figure 5). A further reason why imine insertion is not observed in the above reactions could originate from lower electrophilicity of the iminoacyl group in comparison to the analogous acyl complexes. This would hinder the attack of the imine at the iminoacyl carbon. Suggs has previously shown that the electrophilicity of iminoacyl groups can be significantly altered by a change in the oxidation state of the transition metal center.[25] This suggests that a subtle change in the electronic environment of the metal center can dramatically alter its reactivity. The protonated iminoacyl complex **17** is certainly more electrophilic at the carbon center and should, in principle, increase its reactivity with the imine; however in this case the driving force to the five-membered chelate (Figure 5) is lost. Additional equivalents of imine were added to the reaction mixtures in an attempt to drive the reactions to the insertion product. Unfortunately this did not lead to any success. The more strongly binding coordination of the cyclic imines showed that stable iminoacyl/imine complexes can be prepared.

In spite of the unsuccessful insertion reactions initially targeted, several interesting results were obtained in the course of these investigations. A series of imine complexes were prepared and fully characterized. The X-ray crystal structures of some of these complexes have revealed strong agostic interactions between the aryl group of the imine and the palladium metal center. These interactions are retained in solution as shown by ^1H NMR spectroscopy. The reaction of these imine complexes with isocyanide has been studied and found to have differing reactivity depending on the nature of the co-ligands. From the analysis of all the attempted reactions it can be concluded that the acyclic aldimine coordination is weak and that attempts to insert the imine via these systems are unlikely to be successful.

A handful of iminoacyl/imine complexes have been prepared and characterized. Our studies have shown that the iminoacyl fragments are susceptible to reaction with water due to the strong driving force of formation of the organic amide product *N*-(2,6-dimethylphenyl)acetamide. Our strategies to hinder the deinsertion of the isocyanide have involved the protonation of the iminoacyl fragment. The protonation reactions have led to the isolation of an iminoacyl/imine complex, which has been confirmed by

(24) Gautier, J. A.; Miocque, M.; Farnoux, C. C. In *The Chemistry of Amidines and Imidates*; Patai, S., Ed.; John Wiley & Sons: London, 1975; p 283.

(25) Suggs, J. W.; Cox, S. D. *Organometallics* **1982**, *1*, 402.

structural characterization. Furthermore, the utilization of more strongly coordinating imines can also allow access to complexes containing both iminoacyl and imine fragments. Although our efforts have not provided an example of an insertion reaction with an imine, a number of possible routes have been explored.

Experimental Section

Materials and Apparatus. All manipulations were carried out in an atmosphere of purified and dry nitrogen using standard Schlenk line techniques unless otherwise stated. Solvents were dried from the appropriate drying agent, degassed, and stored under nitrogen. ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on a JEOL-EX270 spectrometer (270.17, 109.38, 67.94 MHz, respectively) with TMS, H_3PO_4, and TMS, respectively, as internal references. IR spectra were recorded on a Research Series FT-IR using KBr disks in the range 4000−500 cm^{-1}. Mass spectrometry and X-ray crystallography were carried out at Imperial College. Elemental analysis was carried out at the University of North London. The complexes [Pd(Me)Cl(L_2)] (L_2 = dppp, dppe, dppf) were synthesized according to previously reported procedures.[26] The complex [Pd{C(Me)=NXyl}Cl(dppe)] was synthesized using a methodology we recently reported.[11]

[Pd(Me)(dppe)(imine)]BF_4 (1, 2, 3). A degassed solution of imine, RN=CHPh [R = Ph, 0.036 g; R = CH_2Ph, 37.6 μL; R = Me, 24.6 μL (0.20 mmol), in DCM (5 mL)], was added to a solution of [PdCl(Me)(dppe)] (0.100 g, 0.18 mmol) in DCM (15 mL). $AgBF_4$ (0.035 g, 0.18 mmol) was quickly added. The resulting solution was stirred for about 15 min, the precipitated AgCl was removed by filtration, and the resulting complex was isolated by addition of hexane and evaporation of the DCM, resulting in precipitation of a white solid. This was then washed twice with ether to remove any free imine.

1: R = Ph, yield 79%. Anal. Found: C, 61.05; H, 4.76; N, 1.69 ($C_{40}H_{38}NP_2PdBF_4$ requires: C, 60.98; H, 4.86; N, 1.78). IR (ν_{max}/cm^{-1}) (KBr): 1606s, 1589w, 1569w (N=C), 1060vs br (BF_4). ^{31}P{^{1}H} NMR: ($CDCl_3$): δ 57.6 (d, 1P, $^{2}J_{PP}$ = 23 Hz), 39.1 (d, 1P, $^{2}J_{PP}$ = 23 Hz). ^{1}H NMR ($CDCl_3$): δ 0.54 (dd, 3H, PdCH_3, $^{3}J_{PH}$ = 7 Hz, $^{3}J_{PH}$ = 3 Hz), 2.39 [m, 3H, (PCH_2CH_2P)], 2.97 [m, 1H, (PCH_2CH$_2$P)], 7.08−7.74 (m, 28H, 4(PC_6H_5) + 3,4,5-H {N=C(H)C$_6H_5$} + {N(C_6H_5)=C(Ph)H}], 8.07 (d, 2H, 2,6-H {N=C(H)C$_6H_5$}, $^{3}J_{HH}$ = 7 Hz), 8.48 (dd, 1H, {N=C(C_6H_5)H}, $^{4}J_{PH}$ = 10 Hz, $^{4}J_{PH}$ = 2 Hz). MS-FAB$^+$ m/z (rel intensity): 700 (1) [M]$^+$, 519 (13) [M − imine]$^+$, 504 (9) [dppePd]$^+$, 399 (2) [dppe]$^+$.

2; R = Me; yield 78%. Anal. Found: C, 58.05; H, 5.38; N, 1.88 ($C_{35}H_{36}NP_2PdNBF_4.0.2C_4H_{10}O$ requires: C, 58.05; H, 5.17; N, 1.89). IR (ν_{max}/cm^{-1}) (KBr): 1637s, 1571w (N=C), 1052vs br (BF_4). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 57.7 (d, 1P, $^{2}J_{PP}$ = 23 Hz), 39.9 (d, 1P, $^{2}J_{PP}$ = 23 Hz). ^{1}H NMR ($CDCl_3$): δ 0.48 (dd, 3H PdCH_3, $^{3}J_{PH}$ = 7 Hz, $^{3}J_{PH}$ = 3 Hz), 2.35 [m, 3H, (PCH_2CH_2P)], 2.85 [m, 1H, (PCH$_2$CH_2P)], 3.70 (s, 3H, NCH_3), 7.10−7.60 (m, 23H, 4(PC_6H_5) + 3,4,5-H {N=C(H)C$_6H_5$}], 7.94 [d, 2H, 2,6-H {N=C(H)C$_6H_5$}, $^{3}J_{HH}$ = 7 Hz], 8.52 (dd, 1H, {N=C(C_6H_5)H}, $^{4}J_{PH}$ = 11 Hz, $^{4}J_{PH}$ = unresolved]. MS-FAB$^+$ m/z (rel intensity): 638 (65) [M]$^+$, 623 (4) [M − Me]$^+$, 519 (90) [M − imine]$^+$, 504 (33) [dppePd]$^+$.

3; R = CH_2Ph; yield 76%. Anal. Found: C, 61.93; H, 5.40; N, 1.90 ($C_{41}H_{40}NP_2PdNBF_4\cdot0.1(C_{14}H_{13}N)$ requires: C, 61.95; H, 5.06; N, 1.87). IR (ν_{max}/cm^{-1}) (KBr): 1617m, 1575w (N=C), 1052vs br (BF_4). ^{31}P{^{1}H} NMR: ($CDCl_3$): δ 57.0 (d, 1P, $^{2}J_{PP}$ = 23 Hz), 39.7 (d, 1P, $^{2}J_{PP}$ = 23 Hz). ^{1}H NMR ($CDCl_3$): δ 0.18 (dd, 3H, PdCH_3, $^{3}J_{PH}$ = 7 Hz, $^{3}J_{PH}$ = 4 Hz), 2.52 [m, 4H, (PCH_2CH_2P)], 4.75 (d, 1H, NCH_AH$_B$Ph, $^{2}J_{HH}$ = 5 Hz), 4.90 (d, 1H, NCH$_A$$H_B$Ph, $^{2}J_{HH}$ = 5 Hz), 7.11−7.70 (m, 28H, 4(PC_6H_5) + 3,4,5-H {N=C(H)C$_6H_5$} + {N(CH$_2$C$_6H_5$)=C(Ph)H}], 8.03 (d, 2H, 2,6-H {N=C(H)C$_6H_5$}, $^{3}J_{HH}$ = 7 Hz), 8.62 (dd, 1H, {N=C(C_6H_5)H}, $^{4}J_{PH}$ = 10 Hz, $^{4}J_{PH}$ = unresolved). MS-FAB$^+$ m/z (rel intensity): 714 (63) [M − Cl]$^+$, 699 (6) [M − Me]$^+$, 519 (100) [M − imine]$^+$, 504 (33) [dppePd]$^+$.

[Pd(Me)(dppp)(N(Ph)=CPhH)]OTf (4). A degassed solution of N(Ph)=CPhH (0.08 g, 0.44 mmol) in DCM (5 mL) was added to a solution of [PdCl(Me)(dppp)] (0.21 g, 0.37 mmol) in DCM (20 mL). AgOTf (0.11 g, 0.37 mmol) was quickly added. The resulting solution was stirred for about 15 min, the precipitated AgCl was removed by filtration, and the resulting complex was isolated by addition of hexane and evaporation of the DCM, resulting in precipitation of a white solid. This was then washed twice with ether to remove any free imine.

Yield = 62%. Anal. Found: C, 57.04; H, 4.35; N, 1.99 ($C_{42}H_{40}NPdP_2SO_3F_3\cdot0.3CH_2Cl_2$ requires C, 57.11; H, 4.60, N, 1.57). IR (ν_{max}/cm^{-1}) (KBr): 1608m, 1586m, 1569w (N=C), 1486m, 1436m (dppp), 1262s, 1152s, 1031s (OTf). ^{31}P-{^{1}H} NMR: ($CDCl_3$): δ 23.8 (d, 1P, $^{2}J_{PP}$ = 51 Hz), −2.1 (d, 1P, $^{2}J_{PP}$ = 51 Hz). ^{1}H NMR ($CDCl_3$): δ 0.37 [dd, 3H, PdCH_3, $^{3}J_{PH}$ = 6.5 Hz, $^{3}J_{PH}$ = 3.5 Hz], 2.77 [m br, 6H, (PCH_2CH_2CH_2P)], 6.90−7.81 [m, 28H, 4(PC_6H_5) + 3,4,5-H {N=C(H)C$_6H_5$} + {N(C_6H_5)=C(Ph)H}], 8.05 (dd, 1H, { N=C H}, $^{4}J_{PH}$ = 9.5 Hz, $^{4}J_{PH}$ = 2.0 Hz), 8.37 [dd, 2H, 2,6−H {N=C(H)C $_6H_5$}, $^{3}J_{HH}$ = 6.0 Hz, $^{3}J_{HH}$ = unresolved]. MS-FAB$^+$ m/z (rel intensity): 714 (2) [M − Cl]$^+$, 533 (18) [dpppPdMe]$^+$, 518 (3) [(dppp)Pd].

[Pd(Me)(dppp)(imine)]BF_4 (5, 6, 7). A degassed solution of imine RN=CHPh [R = Ph, 0.036 g; R = CH_2Ph, 37.6 μL; R = Me, 24.6 μL; (0.20 mmol), in DCM (5 mL)] was added to a solution of [PdCl(Me)(dppp)] (0.102 g, 0.18 mmol) in DCM (15 mL). $AgBF_4$ (0.035 g, 0.18 mmol) was quickly added. The resulting solution was stirred for about 15 min, the precipitated AgCl was removed by filtration, and the resulting complex was isolated by addition of hexane and evaporation of the DCM, resulting in precipitation of a white solid. This was then washed twice with ether to remove any free imine.

5: R = Ph; yield = 73%. Anal. Found: C, 61.29; H, 4.92; N, 1.68 ($C_{41}H_{40}NPdP_2BF_4$ requires C, 61.41; H, 5.03; N, 1.75). IR (ν_{maz}/cm^{-1}) (KBr): 1624m, 1588w, 1577w (N=C), 1069vs (BF_4). ^{31}P{^{1}H} NMR (THF): δ 23.1 (d, 1P, $^{2}J_{PP}$ = 52 Hz), −2.3 (d, 1P, $^{2}J_{PP}$ = 53 Hz). ^{1}H NMR ($CDCl_3$): δ 0.36 (dd, 3H, PdCH_3, $^{3}J_{PH}$ = 7.0 Hz, $^{3}J_{PH}$ = 4.0 Hz), 2.86 [m br, 6H, (PCH_2CH_2-CH_2P)], 6.91−7.83 (m, 28H, 4(PC_6H_5) + 3,4,5-H {N=C(H)-C$_6H_5$} + {N(C_6H_5)=C(Ph)H}], 8.04 (dd, 1H, {N=C(C_6H_5)H}, $^{4}J_{PH}$ = 9.5 Hz, $^{4}J_{PH}$ = 2.5 Hz), 8.37 [dd, 2H, 2,6-H {N=C(H)C$_6H_5$} $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{HH}$ = unresolved]. MS-FAB$^+$ m/z (rel intensity): 714 (20) [M]$^+$, 698 (4) [M − CH$_3$]$^+$, 533 (65) [M − imine]$^+$, 518 (24) [(dppp)Pd]$^+$.

6: R = Me; yield 71%. Anal. Found: C, 58.39; H, 4.94; N, 1.95 ($C_{36}H_{38}NP_2PdBF_4$ requires: C, 58.44; H, 5.17; N, 1.89). IR (ν_{max}/cm^{-1}) (KBr): 1645s, 1599w, 1578w (N=C), 1482w, 1436m (dppp), 1057s (BF_4). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 22.7 (d, 1P, $^{2}J_{PP}$ = 50 Hz), 0.2 (d, 1P, $^{2}J_{PP}$ = 50 Hz). ^{1}H NMR ($CDCl_3$): δ 0.35 (dd, 3H, PdCH_3, $^{3}J_{PH}$ = 7.0 Hz, $^{3}J_{PH}$ = 3.5 Hz), 1.84 [m, 2H, (PCH$_2$CH_2CH$_2$P)], 2.77 [m, 4H, (PCH_2CH$_2$CH_2P)], 3.44 [s br, 3H, NCH_3], 6.91−7.55 (m, 20 H, 4(PC_6H_5) + 3H {N=C(H)C$_6H_5$}], 7.68 [m, 2H, {N=C(H)C$_6H_5$}], 8.10 (dd, 1H, {N=C(C_6H_5)H}, $^{4}J_{PH}$ = 5.0 Hz, $^{4}J_{PH}$ = 3.0 Hz). MS-FAB$^+$ m/z (rel intensity): 652 (40) [M − Cl]$^+$, 636 (4) [M − Cl − Me]$^+$, 533 (58) [dpppPdMe]$^+$, 518 (17) [dpppPd]$^+$.

7: R = CH_2Ph; yield 68%. Anal. Found: C, 61.05; H, 4.88; N, 1.54 ($C_{42}H_{42}NP_2PdBF_4\cdot1/4CH_2Cl_2$ requires: C, 60.61; H, 5.11; N, 1.67). IR (ν_{max}/cm^{-1}) (KBr): 1626, 1574 (N=C), 1057 (BF_4). ^{31}P{^{1}H} NMR (THF): δ 21.9 (d, 1P, $^{2}J_{PP}$ = 50 Hz), 0.3 (d, 1P, $^{2}J_{PP}$ = 50 Hz). ^{1}H NMR ($CDCl_3$): δ 0.01 (dd, 3H, PdCH_3, $^{3}J_{PH}$ = 6.5 Hz, $^{3}J_{PH}$ = 3.5 Hz), 1.85 [m br, 2H, (PCH$_2$-CH_2CH$_2$P)], 2.85 [m br, 4H, (PCH_2CH$_2$CH_2P)], 4.36 (d, 1H,

(26) (a) Appleton, T. G.; Bennett, M. A.; Tomkins, I. B. *J. Chem. Soc., Dalton Trans.* **1976**, 439. (b) Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K. *Organometallics* **1992**, *11*, 1589.

Table 8. Crystal Data, Data Collection, and Refinement Parameters for Compounds 1, 4, 14, and 17[a]

data	1	4	14	17
formula	$[C_{40}H_{38}NP_2Pd](BF_4)$	$[C_{41}H_{40}NP_2Pd](CF_3SO_3)$	$[C_{34}H_{38}N_2O_2P_2Pd](BF_4)_2$	$[C_{50}H_{50}N_2P_2Pd](BF_4)_2$
solvent		CH_2Cl_2	$C_4H_8O\cdot{}^1/_3H_2O$	$0.75CH_2Cl_2$
fw	787.86	949.08	926.68	1084.57
color, habit	pale yellow prisms	colorless platy needles	yellow prisms	colorless blocky needles
cryst size/mm	$0.77 \times 0.73 \times 0.20$	$0.80 \times 0.45 \times 0.23$	$0.20 \times 0.17 \times 0.13$	$0.60 \times 0.30 \times 0.20$
temp/K	293	293	203	293
cryst syst	monoclinic	orthorhombic	triclinic	monoclinic
space group	$P2_1/n$ (no. 14)	$Pna2_1$ (no. 33)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a/Å	12.6377(13)	12.968(5)	12.0486(7)	20.2999(10)
b/Å	16.066(3)	32.330(3)	13.0469(4)	24.3276(11)
c/Å	18.390(2)	10.5365(12)	13.2701(5)	10.5517(7)
α/deg			91.799(3)	
β/deg	92.298(12)		95.704(6)	104.639(7)
γ/deg			96.529(3)	
V/Å^3	3730.9(9)	4417.5(18)	2060.30(16)	5041.8(5)
Z	4	4	2	4
D_c/g cm^{-3}	1.403	1.427	1.494	1.429
radiation used	Mo Kα	Mo Kα	Cu Kα	Cu Kα
μ/mm^{-1}	0.632	0.712	5.032	4.866
$2\theta_{max}$/deg	50	50	120	120
no. of unique reflns measd	6061	4084	6113	7436
obs, $\lvert F_o\rvert > 4\sigma(\lvert F_o\rvert)$	4646	2634	5457	5046
no. of variables	443	506	555	654
R_1(obs), wR_2(all) [b]	0.042, 0.099	0.059, 0.118	0.036, 0.087	0.059, 0.160

[a] Details in common: graphite-monochromated radiation, refinement based on F^2. [b] $R_1 = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum\lvert F_o\rvert$; $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

NCH_AH_BPh, $^2J_{HH}$ = 14.5 Hz), 4.78 (d, 1H, NCH_AH_BPh, $^2J_{HH}$ = 14.5 Hz), 6.94−7.63 (m, 28H, $4(PC_6H_5)$ + 3,4,5-*H* {N=C(H)C_6H_5} + {N($CH_2C_6H_5$)=C(Ph)H}],), 7.84 [dd, 1H, {N=C(C_6H_5)*H*}, $^4J_{PH}$ = 9 Hz, $^4J_{PH}$ = 2 Hz], 8.15 [dd, 2H, 2,6-*H* {N=C(H)C_6H_5}, $^3J_{HH}$ = 11 Hz, $^3J_{HH}$ = 2 Hz]. MS-FAB$^+$ *m*/*z* (rel intensity): 728 (67) [M]$^+$, 713 (10) [M − CH_3]$^+$, 533 (100) [(dppp)PdMe]$^+$, 518 (43) [(dppp)Pd]$^+$.

[Pd(Me)(dppf)(imine)]BF_4 (8, 9). A degassed solution of imine RN=CHPh [R = Ph, 0.11 g; R = CH_2Ph, 116 μL (0.61 mmol), in DCM (10 mL)] was added to a solution of [PdCl(Me)(dppf)] (0.400 g, 0.56 mmol) in DCM (25 mL). $AgBF_4$ (0.120 g, 0.61 mmol) was added in one portion. The resulting solution was stirred for about 15 min, the precipitated AgCl was removed by filtration, and the resulting complex was isolated by addition of hexane and evaporation of the DCM, resulting in precipitation of a white solid. This was then washed twice with ether to remove any free imine.

8: R = Ph; yield 0.42 g, 79%. IR (ν_{max}/cm^{-1}) (KBr): 1607s, 1598w, 1569w (N=C), 1095, 1058vs br (BF_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 38.1 (d, 1P, $^2J_{PP}$ = 29 Hz), 19.6 (d, 1P, $^2J_{PP}$ = 29 Hz). ^1H NMR ($CDCl_3$): δ 0.41 (dd, 3H, PdCH_3, $^3J_{PH}$ = 6 Hz, $^3J_{PH}$ = 4 Hz), 3.81 [m, 2H, (PC_5H_4)], 4.22 [s, 2H, (PC_5H_4)], 4.48 [d, 2H, (PC_5H_4], 4.67 [s, 2H, (PC_5H_4)], 6.98−7.88 (m, 28H, $4(PC_6H_5)$ + 3,4,5-*H* {N=C(H)C_6H_5} + {N(C_6H_5)=C(Ph)H}], 8.35 [dd, 1H, {N=C(C_6H_5)*H*}, $^4J_{PH}$ = 10.5 Hz, $^4J_{PH}$ = 2.5 Hz], 8.46 [d, 2H, 2,6-*H* {N=C(H)C_6H_5}], $^3J_{HH}$ = 7.5 Hz]. MS-FAB$^+$ *m*/*z* (rel intensity): 858 (15) [M]$^+$, 675 (100) [M − imine]$^+$, 662 (20) [dppePd]$^+$.

9: R = Bz; yield 0.42 g, 78%. Found: C, 61.33; H, 4.58; N, 1.58 ($C_{49}H_{44}NP_2PdFeBF_4$ requires: C, 61.44; H, 4.63; N, 1.46). IR (ν_{max}/cm^{-1}) (KBr): 1626s, 1598w, 1571w (N=C), 1083, 1055vs br (BF_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 36.8 (d, 1P, $^2J_{PP}$ = 29 Hz), 19.2 (d, 1P, $^2J_{PP}$ = 29 Hz). ^1H NMR ($CDCl_3$): δ 0.08 (dd, 3H, PdCH_3, $^3J_{PH}$ = 6 Hz, $^3J_{PH}$ = 2 Hz), 3.81 [s, 1H, (PC_5H_4)], 3.75 [s, 1H, (PC_5H_4)], 4.21 [s, 2H, (PC_5H_4)], 4.48 [m, 3H, (2H, {PC_5H_4}) + (1H, NCH_aH_bPh) overlapping], 4.81 [m, 3H, (2H, {PC_5H_4}) + (1H, NH_aH_bPh) overlapping)], 7.10−7.76 (m, 28H, $4(PC_6H_5)$ + 3,4,5-*H* {N=C(H)C_6H_5} + {N($CH_2C_6H_5$)=C(Ph)H}], 8.15 (dd, 1H, {N=C(C_6H_5)*H*}, $^4J_{PH}$ = 10.5 Hz, $^4J_{PH}$ = 1.5 Hz), 8.45 (d, 2H, 2,6-*H* {N=C(H)C_6H_5}, $^3J_{HH}$ = 7.5 Hz). MS-FAB$^+$ *m*/*z* (rel intensity): 675 (6) [M − imine]$^+$, 660 (5) [dppePd]$^+$.

Synthesis of [Pd(Me)(CNXyl)(dppe)]BF_4 (10). Method 1. To a solution of [PdCl(Me)(dppe)] (0.2 g, 0.36 mmol) in THF (10 mL) was added $AgBF_4$ (0.075 g, 0.38 mmol), followed by CNXyl (0.05 g, 0.38 mmol). The resulting mixture was stirred for 15 min, and then the precipitated AgCl was removed by filtration. The $^{31}P\{^1H\}$ NMR of the filtrate was recorded. $^{31}P\{^1H\}$ NMR (THF): δ 59.0 (d), 46.9 (d).

Method 2. To a solution of [Pd(Me)(dppe){N(Bz)=CPhH}]BF_4 (0.10 g, 0.12 mmol) in THF (10 mL) was added CNXyl (0.017 g, 0.13 mmol). The colorless solution turned yellow over 15 min, after which time the solvent level was reduced to ca. 5 mL under reduced pressure. Hexane (10 mL) was then added to precipitate a yellow solid.

Yield = 0.05 g, 0.06 mmol, 57%. Anal. Found: C, 55.68; H, 4.56; N, 1.83 (calcd for $C_{36}H_{36}NP_2PdBF_4\cdot 0.25AgCl$: C, 55.88; H, 4.69; N, 1.81). IR (ν_{max}/cm^{-1}) (KBr): 2181s (C≡N), 1057br (BF_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 58.5 (d, 1P, $^2J_{PP}$ = 29 Hz), 44.8 (d, 1P, $^2J_{PP}$ = 29 Hz). ^1H NMR ($CDCl_3$): δ 0.77 [dd, 3H, (PdCH_3), $^3J_{PH}$ = 6.5 Hz, $^3J_{PH}$ = 4.5 Hz), 2.16 [s, 6H, {$C_6H_3(CH_3)_2$}], 2.66 [m, 4H, (PCH_2CH_2P)], 7.10 [d, 2H, 3,5-*H* {$C_6H_3(CH_3)_2$}, $^3J_{HH}$ = 7.5 Hz], 7.28 [m, 1H, 4-*H* {$C_6H_3(CH_3)_2$}], 7.58 [m, 20H, $4(PC_6H_5)$]. MS (FAB$^+$) *m*/*z* (rel intensity): 652 (2) [M]$^+$, 519 (3) [(dppe)Pd(Me)]$^+$, 504 (12) [(dppe)Pd]$^+$.

[Pd{C(Me)=NXyl}(dppe)(N=C(Me)OCH_2CH_2)]BF_4 (12). To a solution of [Pd{$C(CH_3)$=NXyl}Cl(dppe)] (**1**) (0.15 g, 0.22 mmol) in THF (20 mL) was added methyloxazaline (18.6 μL, 0.22 mmol). $AgBF_4$ (0.043 g, 0.22 mmol) was then added to the stirring mixture, which resulted in the precipitation of AgCl from the mixture. This precipitate was removed by filtration after 15 min. The solvent level of the filtrate was then reduced to ca. 10 mL, and hexane was added, which resulted in the precipitation of a yellow solid. The solid was then washed with diethyl ether.

Yield = 0.12 g, 0.15 mmol, 66%. Anal. Found: C, 58.28; H, 5.23; N, 3.34 (calcd for $C_{40}H_{43}N_2P_2OBF_4Pd$ requires C, 58.38; H, 5.27; N, 3.40). IR (ν_{max}/cm^{-1}) (KBr): 1662, 1615, 1583 (C=N), 1259 (C−O), 1085, 1057 (BF_4). $^{31}P\{^1H\}$ NMR (THF-d_8): δ 39.5 (d, 1P, $^2J_{PP}$ = 33 Hz), 41.4 (d, 1P, $^2J_{PP}$ = 30 Hz). ^1H NMR (THF-d_8): δ 1.51 [br, dd, Pd{C(CH_3)=NXyl}, $^4J_{PH}$ = unresolved, $^4J_{PH}$ = unresolved], 1.62 [s, 6H, $C_6H_3(CH_3)_2$], 2.04

[s, 3H, N=C(CH_3)], 2.37 [br, m, 4H (PCH_2CH_2P)], 4.00 [m, 2H, NCH_2CH$_2$O], 4.38 [m, 2H, OCH_2CH$_2$N], 6.61 [m, 1H, C$_6H_3$-(CH$_3$)$_2$], 6.75 [m, 2H, C$_6H_3$(CH$_3$)$_2$], 7.45−8.18 [m, 20H, 4(PC$_6H_5$)]. MS-FAB$^+$ *m*/*z* (rel intensity): 650 (10) [M − imine]$^+$, 519 (4) [(dppe)PdMe],$^\cdot$ 504 (5) [(dppe)Pd]$^+$.

[Pd{C(Me)=NXyl}(dppp)(N=C(Me)OCH$_2$CH$_2$)]BF$_4$ (13). To a solution of [Pd{C(CH$_3$)=NXyl}Cl(dppp)] (**2**) (0.09 g, 0.13 mmol) in THF (10 mL) was added methyloxazaline (21 μL, 0.26 mmol). $AgBF_4$ (0.03 g, 0.13 mmol) was then added to the stirring mixture, which resulted in the precipitation of AgCl from the mixture. This precipitate was removed by filtration after 15 min. The solvent level of the filtrate was then reduced to ca. 10 mL, and hexane was added, which resulted in the precipitation of an off-white solid. The solid was then washed with diethyl ether.

Yield = 0.06 g, 0.07 mmol, 55%. Anal. Found: C, 58.72; H, 5.34; N, 3.23 (calcd for $C_{41}H_{45}N_2OP_2BF_4Pd$ requires C, 58.84; H, 5.41; N, 3.35). IR (ν_{max}/cm^{-1}) (KBr): 1664, 1609, 1579 (C=N), 1255 (C−O), 1102, 1057 (BF_4). $^{31}P\{^1H\}$ NMR (THF-d_8): δ 5.4 (br, d, 1P, $^2J_{PP}$ = unresolved), 1.8 (d, 1P, $^2J_{PP}$ = 67 Hz). ^1H NMR (THF-d_8): δ 1.47 [dd, Pd{C(CH_3)=NXy}, $^4J_{PH}$ = 5 Hz, $^4J_{PH}$ = unresolved], 1.63 [s, 6H, C$_6$H$_3$(CH_3)$_2$], 2.06 [s, 3H, N=C(CH_3)], 1.90 [br, m, 2H (PCH$_2$CH_2CH$_2$P)], 2.89 [m, 4H (PCH_2CH$_2$CH_2P)], 3.41 [m, 2H, NCH_2CH$_2$O], 4.02 [m, 2H, OCH_2CH$_2$N], 6.62 [m, 1H, 4-*H* {C$_6H_3$(CH$_3$)$_2$}], 6.74 [m, 2H, 3,5-*H* {C$_6H_3$(CH$_3$)$_2$}], 7.35 [m, 12H, 3,4,5-*H* 4(PC$_6H_5$)], 7.73 [m, 4H, 2,6-*H* 2(PC$_6H_5$)], 8.08 [m, 4H, 2,6-*H* 2(PC$_6H_5$)]. MS-FAB$^+$ *m*/*z* (rel intensity): 664 (18) [M − imine]$^+$, 533 (5) [(dppp)PdMe]$^+$, 518 (9) [(dppp)Pd]$^+$.

[Pd{C(CH$_3$)=N(H)Xyl}(dppe){N(Bz)=CPhH}][BF$_4$]$_2$ (17). To a solution of [Pd{C(CH$_3$)=NHXyl}Cl(dppe)]BF_4 (0.15 g, 0.20 mmol) in DCM (20 mL) was added N(Bz)=CPhH (0.19 mL, 1.0 mmol). $AgBF_4$ (0.045 g, 0.21 mmol) was then added to the stirring mixture, which resulted in the precipitation of AgCl from the mixture. This precipitate was removed by filtration after 15 min. The solvent level of the filtrate was then reduced to ca. 10 mL, and a layer of diethyl ether was carefully added to the reaction mixture. A colorless crystalline solid then precipitated over 2 days.

Yield = 0.18 g, 0.17 mmol, 88%. IR (ν_{max}/cm^{-1}) (KBr): 3198 (N−H), 1616, 1596 (C=N), 1560 (C=NH), 1075 (BF_4). $^{31}P\{^1H\}$ NMR (DCM): δ 54.4 (d, 1P, $^2J_{PP}$ = 20 Hz), 52.2 (d, 1P, $^2J_{PP}$ = 20 Hz). MS-FAB$^+$ *m*/*z* (rel intensity): 932 (2) [M]$^+$, 845 (7) [M − BF_4]$^+$, 650 (96) [M − (BF_4)$_2$]$^+$, 519 (20) [(dppe)PdMe]$^+$, 504 (38) [(dppe)Pd]$^+$.

X-ray Crystallography. Table 8 provides a summary of the crystallographic data for compounds **1**, **4**, **14**, and **17**. Data were collected using Siemens P4 (**1** and **4**) P4/RA (**14**) and Bruker P4 (**17**) diffractometers, and the structures were refined based on F^2 using the SHELXTL and SHELX-97 program systems.[27] The absolute structure of **4** could not be unambiguously determined by either *R*-factor tests [R_1^+ = 0.0586, R_1^- = 0.0587] or the use of the Flack parameter [x^+ = +0.37(17), x^- = +0.63(17)]. CCDC 736713 to 736716.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

(27) *SHELXTL PC version 5.1*, Bruker AXS: Madison, WI, 1997. Sheldrick, G. SHELX-97; Institut Anorg. Chemie: Göttingen, Germany, 1998.