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Influence of Chelating Phosphines on the Insertion of Isocyanides into Palladium−Methyl Bonds in (P−P)Pd(Me)Cl Complexes and Their Further Reaction with Olefins and Isothiocyanates

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A systematic study of the insertion reactions between (P−P)Pd(Me)Cl (where P−P = dppe, dppp, dppf) and CNR (where R = 2,6-dimethylphenyl, *tert*-butyl) is presented. The results have demonstrated that the insertion of CNR into the Pd−Me bond is highly dependent on the nature of the chelating phosphine. For the more strained complex formed with dppe, the insertion of isocyanides is slower and multiple insertion is not observed. This is in contrast to (dppp)Pd(Me)Cl, which reacts readily with isocyanides to produce single-, double-, and multiple-inserted products. Results analogous to those of dppp have been observed for the complexes with dppf, although the reactions are more controllable, indicating a less reactive complex. In an attempt to establish some structure−reactivity correlations, structural characterizations of (dppe)Pd{C(Me)═NXyl}Cl (**1**) and (dppp)Pd{(C═NXyl)(C(Me)═NXyl)}-Cl (**3**) have been carried out. The structural parameters obtained are consistent with the observed reactivity. The reactions between (dppe)Pd{C(Me)═NXyl}Cl and unsaturated (olefins and isothiocyanates) species have also been studied. While norbornadiene (a strained diolefin) inserts into the palladium−iminoacyl bond, an addition is observed when reacting **1** with isothiocyanates.

Introduction

The insertion of small molecules such as carbon monoxide, isocyanides, and alkenes into transition-metal−carbon bonds is an attractive organometallic reaction, since it leads to the formation of new C−C bonds.[1] Such insertions are found in a wide range of catalytic transformations, and hence, there has been widespread interest in their study. In recent years a large number of these studies have concentrated on the insertion of carbon monoxide into metal−carbon[2] bonds, since this process plays a crucial role in the copolymerization of this molecule with alkenes.[3] Another species that readily inserts into metal−carbon bonds is isocyanide (CNR),[4] which is generally regarded as a better σ donor and weaker π acceptor than CO. In contrast to carbon monoxide, the electronic and steric properties of isocyanides can be easily modified by changing their substituent group. This feature allows the fine tuning of their reactivity and also the properties of the products formed, making isocyanides versatile starting materials in organometallic chemistry. Moreover, isocyanides can multiply insert into metal−carbon bonds, leading to the synthesis of a wider range of products such as heterocyclic and oligomeric compounds.[5]

More specifically, the insertion of isocyanides occurs readily into palladium−carbon bonds.[6] The products obtained from such reactions are highly dependent on the nature of the ligands coordinated to the palladium center and the properties of the isocyanide's R group. Since the 1970s a large number of studies have been carried out to understand the nature of this organometallic transformation.[7] More recently, there has been increased interest in using the insertion of isocyanides

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into palladium–carbon bonds as one of several steps for the synthesis of a wider range of organic materials. For example, Whitby has recently reported the synthesis of amidines by palladium-catalyzed couplings of amines, aryl halides, and isocyanides.[8] Also of interest is the multiple insertion of isocyanides into palladium–carbon bonds, since this can lead to the formation of a wide range of products such as helical polyisocyanides and heterocyclic compounds.[9]

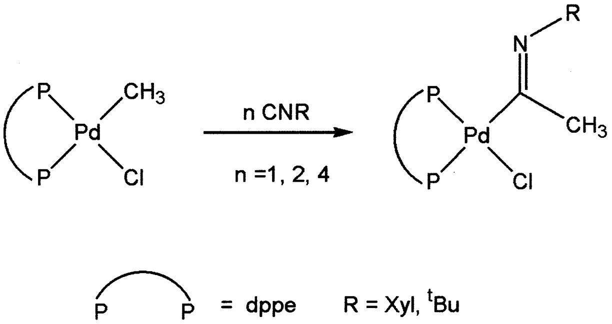
A potentially attractive organometallic transformation would be the alternating insertion of isocyanides and alkenes into palladium–metal bonds to produce polyimines. Although the analogous reaction with carbon monoxide and alkenes (to produce polyketones) is well documented,[3] there are very few examples of insertion reactions of unsaturated hydrocarbons into palladium–iminoacyl bonds.[10] The relative lack of such alternated insertion reactions might be a consequence of the difficulties in controlling the multiple insertion of isocyanides, which prevents the second species from reacting.

Herein we present a systematic study of the reactions between (P–P)Pd(Me)Cl (where P–P = dppe, dppp, dppf) and CNR (where R = 2,6-dimethylphenyl, *tert*-butyl). Although the reactivity of these palladium–methyl complexes has been thoroughly studied before, surprisingly, there has not been a prior systematic study on their reactions with isocyanides. The reactions between the iminoacyl products, obtained upon isocyanide insertion, and unsaturated species such as olefins and isothiocyanates has also been studied, and some preliminary results are presented.

Results and Discussion

Insertion of 2,6-Dimethylphenyl Isocyanide into Palladium–Methyl Bonds. When 1 equiv of 2,6-dimethylphenyl isocyanide was added to a solution of (dppe)Pd(Me)Cl in THF at room temperature, a gradual color change from colorless to yellow was observed. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, which showed, after 1 h, the conversion of approximately 10% of the starting material (δ 59.3 (d), 30.2 (d) ppm) to a new product (δ 39.1 (d), 27.3 (d) ppm); this later proved to be the mono-insertion compound (dppe)-Pd{C(=NXyl)Me}Cl (**1**) (see Scheme 1). The reaction mixture was monitored over a period of 24 h, and no further changes were observed. To force the conversion of all the starting material to the mono-insertion product **1**, the reaction was repeated, adding 2 equiv of CNXyl. This resulted in the quantitative conversion of (dppe)-Pd(Me)Cl into **1** after 2 h. The mono-insertion product **1** was isolated as a yellow solid in 83% yield and fully characterized by ^1H and $^{31}P\{^1H\}$ NMR and IR spectroscopy, mass spectrometry, elemental analyses, and X-ray crystallography (vide infra).

Scheme 1



To explore the influence of the phosphine's bite angle in the isocyanide insertion (which has proven to be very important in the insertion of other species into metal–carbon bonds[14]), analogous reactions were carried out using (dppp)Pd(Me)Cl and (dppf)Pd(Me)Cl (both of which have larger P–Pd–P angles). When 1 equiv of 2,6-dimethylphenyl isocyanide was added to (dppp)Pd-(Me)Cl in THF, a rapid color change from colorless to yellow was observed. After 1 h the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed the presence of three species, corresponding to starting material (15%) and two new pairs of doublets (at δ 7.8 (d), −6.6 (d) ppm and δ 16.0 (d), −4.7 (d) ppm). The two new products were isolated and characterized as the mono-insertion product (dppp)Pd{C(=NR)Me}Cl (**2**) (present in 25% amount in the reaction mixture) and the double-insertion product (dppp)Pd{C(=NR)C(=NR)Me}Cl (**3**) (present in 60% amount in the reaction mixture). Interestingly, further studies showed that using CH_2Cl_2 as the solvent in this reaction favored the mono-insertion product **2** (which was isolated in 67% yield) in favor of **3**. To favor the formation of the bis-insertion product **3**, 2 equiv of CNXyl was added to a solution of (dppp)Pd(Me)Cl in THF (see Scheme 2). In contrast to the behavior observed for (dppe)Pd(Me)Cl, this reaction led to the quantitative formation of the bis-insertion product **3**. Both **2** and **3** were fully characterized on the basis of NMR and IR spectroscopy, FAB(+) mass spectrometry, and elemental analysis (see Table 1). **3** was also characterized by X-ray crystallography (vide infra).

In the case of (dppf)Pd(Me)Cl, reaction with 1 equiv of CNXyl led to the formation of (dppf)Pd{(C=NXyl)-Me}Cl (**5**) in high yields (as monitored by ^{31}P NMR

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Scheme 2

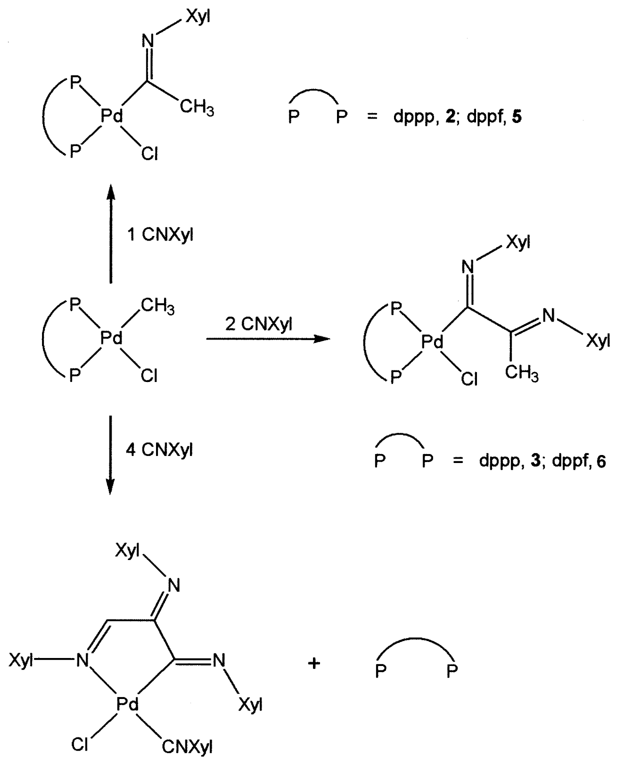
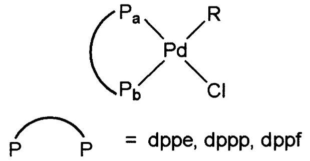


Table 1. Selected NMR Values for Starting Materials and Insertion Products[a]



compd	^{1}H NMR (Pd−CH$_3$ or Pd−C(=NR)$_n$−CH$_3$ δ [J(P$_a$−H), J(P$_b$−H)]	^{31}P{^{1}H} NMR δ	^2J(P−P)
(dppe)Pd(Me)Cl[b]	0.64 (dd) [3,8]	59.6 (d) 32.0 (d)	27
(dppp)Pd(Me)Cl[b]	0.62 (dd) [4, 8]	26.9 (d) −5.8 (d)	60
(dppf)Pd(Me)Cl[b]	0.79 (dd) [4, 8]	37.8 (d) 8.8 (d)	39
1	1.68 (dd) [1, 5]	39.1 (d) 27.3 (d)	37
2	1.61 (dd) [ur,[d] 4]	7.8 (d) −6.6 (d)	67
5	1.65 (dd) [2, 5]	23.6 (d) 9.1 (d)	52
7	2.29 (dd) [ur,[d] 3]	40.5 (d) 19.5 (d)	46
8	2.25 (s)[c]	25.1 (d) 6.9 (d)	59
3	2.04 (s)	16.0 (d) −4.7 (d)	67
6	2.03 (s)	28.3 (d) 9.0 (d)	47

[a] δ values are given in ppm and J values in Hz. [b] Value taken from ref 15. [c] Broad peak. [d] ur = unresolved coupling.

spectroscopy). When the reaction was repeated with 2 equiv of CNXyl, the bis-insertion product (dppf)Pd{(C=NXyl)(C(Me)=NXyl)}Cl (**6**) was obtained (see Scheme 2). This complex was found to be unstable both in solution and in the solid state, leading to the formation of non-phosphine-containing palladium compounds (as demonstrated by ^{31}P NMR studies, which revealed the presence of free phosphine as the unique product). Despite this, compound **6** was isolated and characterized on the basis of NMR and IR spectroscopy, mass spectrometry, and elemental analyses.

From Table 1 it can be seen that, upon insertion of CNXyl into the Pd−Me bond, the phosphorus resonances of (P−P)Pd(Me)Cl (P−P = dppe, dppp, dppf) shift to lower frequencies. Such shifts are less pronounced for the phosphorus trans to the R group, which is consistent with the results obtained previously by van Leeuwen in analogous carbonylation reactions.[15] The ^2J(P−P) coupling constant increases on going from (P−P)Pd(Me)Cl to the corresponding insertion products (see Table 1), which again follows the same trend observed previously in the analogous carbonylation reactions. The insertion products were also characterized by ^{1}H NMR spectroscopy, which showed, in the case of the mono-insertion compounds, a measurable H−P coupling between the protons of the iminoacyl's methyl and the cis and trans phosphorus atoms of the phosphine (resulting in doublets of doublets with ^4J(P$_a$−H) and ^4J(P$_b$−H) ranging from 3.5 to 5.0 Hz and from 1.0 to 1.5 Hz, respectively).

The results so far presented suggest that the chelating phosphines in (P−P)Pd(Me)Cl play a very important role in determining the nature of the insertion products. The results indicate that (dppp)Pd(Me)Cl and (dppf)Pd(Me)Cl are much more reactive toward insertion of CNXyl than is (dppe)Pd(Me)Cl. A similar trend has been previously observed for the insertion of other species (such as CO) into these palladium−methyl complexes. Theoretical[16] and experimental[17] studies have suggested that the bite angle, relative flexibility, and electronic properties of the phosphines determine the reactivity of the complexes toward the insertion of various substrates (e.g. CO and CNR). To obtain a structural insight into the reactivity differences of the complexes under study toward isocyanides, it was of interest to obtain the crystal structures of the mono- and bis-insertion products **1** and **3**. Since in these compounds the R groups around the phosphorus of dppe and dppp are the same, the geometrical parameters are likely to play a more important role than the electronic effects—hence the interest in getting structural insight into these specific products.

Crystals of **1** suitable for an X-ray crystallographic study were grown by vapor diffusion of petroleum ether (40−60 °C) into a THF solution of the complex. The geometry at palladium is square planar (Figure 1), though the metal and its four coordinated atoms are planar to within only 0.07 Å, the deviation from planarity being a consequence of a ca. 5° twist of the Pd−P(1)−P(2) plane with respect to that formed by Pd−C(1)−Cl. The cis angles range between 85.25(4) and 94.19(4)°, the most acute being associated with the bite of the chelat-

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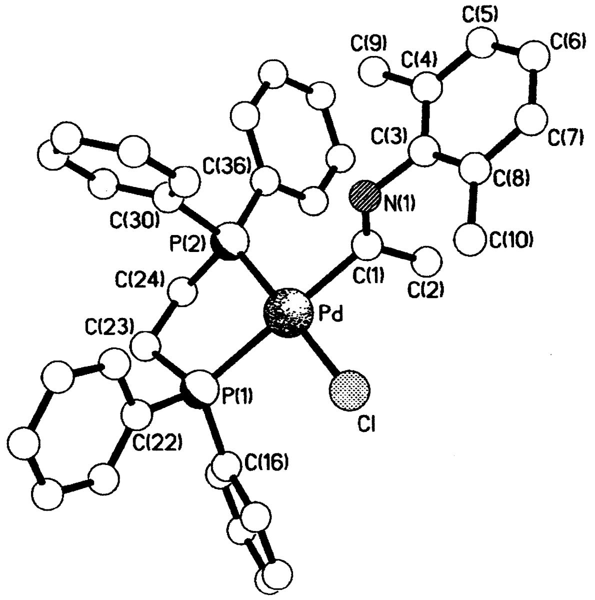

Figure 1. Molecular structure of **1**. Selected bond lengths (Å) and angles (deg); Pd−Cl = 2.3741(12), Pd−P(1) = 2.3738(10), Pd−P(2) = 2.2336(10), Pd−C(1) = 2.039(3), C(1)−N(1) = 1.251(5); C(1)−Pd−P(2) = 92.47(10), C(1)−Pd−P(1) = 176.09(11), P(2)−Pd−P(1) = 85.25(4), C(1)−Pd−Cl = 88.28(11), P(2)−Pd−Cl = 176.27(5), P(1)−Pd−Cl = 94.19(4).

ing phosphine; the C(1)−Pd−Cl angle is 88.28(11)° (vide infra). The five-membered chelate ring has an envelope conformation with C(23) and C(24) lying +0.17 and +0.79 Å, respectively, out of the Pd−P(1)−P(2) plane. The iminoacyl fragment has its 2,6-dimethylphenyl ring oriented approximately orthogonally (ca. 85°) to the N(1)−C(1)−C(2) plane, favoring C−H···N(pπ) interactions[18] between the C(9) and C(10) methyl hydrogen atoms and N(1); there is a ca. 3° rotation about the C=N double bond. There is an intramolecular C−H···π stabilizing interaction (2.81 Å) between one of the C(9) methyl hydrogen atoms and the C(36)-containing phenyl ring. There is also an intermolecular C−H···π interaction (2.73 Å) between the *p*-C−H of the C(22)-based phenyl ring in one molecule and the 2,6-dimethylphenyl ring of a centrosymmetric counterpart; there are no other intermolecular interactions of note.

The single-crystal structure analysis of **3** confirmed it to be the desired double-inserted complex shown in Figure 2. The geometry at palladium is square planar, the coordination sphere being planar to within 0.02 Å. The cis angles, however, range between 85.88(13) and 96.80(13)°, the most acute angle being associated with C(1)−Pd−Cl (contracted by ca. 2.5° compared to that in **1**, vide supra). The Pd−P distances are noticeably different, with Pd−P(1) being 0.134 Å longer than Pd−P(2), reflecting the stronger trans influence of the iminoacyl carbon vis-à-vis chloride. The two imino linkages within the bis(iminoacyl) ligand are gauche with respect to each other, the torsional twists along the C(3)···C(11) backbone being ca. 70, 180, 50, 179, and 77°, respectively. The coordinated bis(iminoacyl) moiety can be described as having a trans N=CC=N conformation with anti substituents at both imine nitrogens (i.e. with the aryl group of the second inserted isocyanide cis to the palladium center). The geometry adopted by this moiety in **3** is analogous to the most stable conformation observed for free α-diimines (suggesting why, despite the potential steric repulsions, the aryl group is found cis to the palladium center and not trans). This is in contrast to the mono-insertion product **1**, where the isocyanide inserts to give a product with the aryl group trans to the palladium center (which minimizes steric repulsions). Both of these conformations are in agreement with previously reported data.[4e]

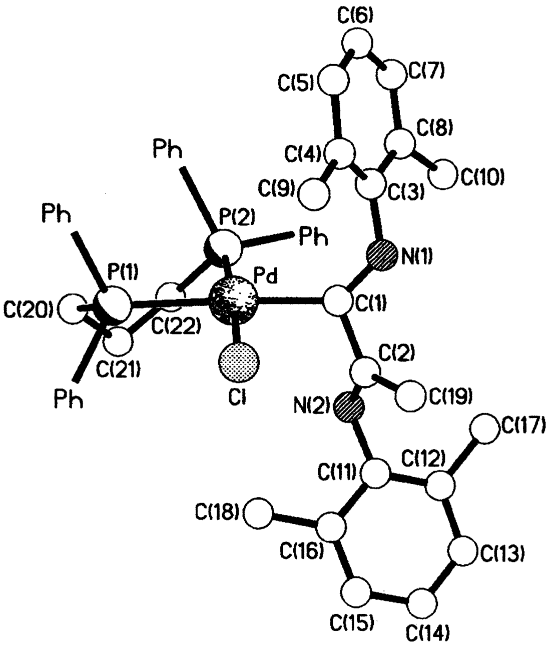

Figure 2. Molecular structure of **3**. The phosphine phenyl rings have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−Cl = 2.379(2), Pd−P(1) = 2.3811(14), Pd−P(2) = 2.247(2), Pd−C(1) = 2.058(5), C(1)−N(1) = 1.271(6), C(2)−N(2) = 1.284(6); C(1)−Pd−P(2) = 96.80(13), C(1)−Pd−Cl = 85.88(13), P(2)−Pd−Cl = 176.80(6), C(1)−Pd−P(1) = 174.10(13), P(2)−Pd−P(1) = 89.10(5), Cl−Pd−P(1) = 88.24(5).

It is well-known that isocyanides can multiply insert into metal−carbon bonds[9] (in contrast to carbon monoxide). Since the doubly inserted products **3** and **6** had been obtained in the course of these investigations, it was of interest to determine what sort of species would be formed upon reacting (P−P)Pd(Me)Cl with an excess of isocyanide. Hence, solutions of (P−P)Pd(Me)Cl were treated with 4 equiv of CNXyl. In the case of (dppe)Pd(Me)Cl this reaction led to the formation of the mono-insertion product **1** only. The reaction was monitored by ^{31}P NMR spectroscopy over 24 h, and no further products were formed, indicating the lack of reactivity of this complex toward multiple insertion. In contrast, when 4 equiv of CNXyl was added to (dppp)Pd(Me)Cl and the mixture monitored by ^{31}P{^{1}H} NMR spectroscopy, the mono- and bis-inserted products **2** and **3** were not detected. The reaction mixture turned dark orange, and the ^{31}P{^{1}H} NMR spectrum after 3 h showed only one singlet at −16.1 ppm, which corresponds to free dppp. Reduction of the solvent under vacuum led to the precipitation of a deep red solid, which was formulated

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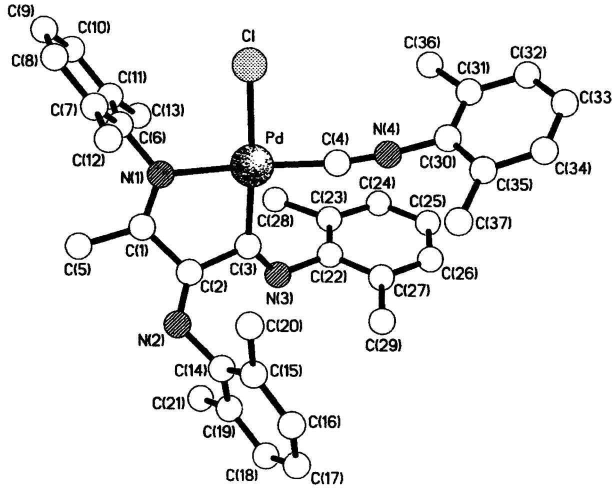

Figure 3. Molecular structure of **4**. Selected bond lengths (Å): Pd−Cl = 2.4005(13), Pd−N(1) = 2.085(4), Pd−C(3) = 1.975(5), Pd−C(4) = 1.924(5).

as the multiple-insertion product (CNXyl)Pd{(C=NXyl)(C=NXyl)(C(Me)=NXyl)}Cl (**4**) (see Scheme 2) on the basis of IR, ^{1}H NMR, mass spectrometry, and elemental analysis. The analogous iodide structure has been reported previously by Yamamoto, who reacted Pd(PPh_3)$_2$(Me)I with an excess of CNXyl.[19] To confirm the formulation of **4**, a single-crystal X-ray analysis was carried out (see Figure 3). Crystals of this compound have included dichloromethane solvent, though the conformation of the complex does not differ significantly from that of its iodide counterpart reported previously.

Similarly, the addition of 4 equiv of CNXyl to (dppf)Pd(Me)Cl leads to the complete displacement of the chelating phosphine and the consequent formation of phosphine-free products (as demonstrated by ^{31}P{^{1}H} NMR spectroscopy). The free-phosphine product formed is analogous to that obtained with (dppp)Pd(Me)Cl.

Insertion of *tert*-Butyl Isocyanide into Palladium−Methyl Bonds. Once the influence of the phosphine had been studied, our attention turned to the nature of the isocyanide: specifically, the insertion of the more basic CN^{t}Bu isocyanide into the palladium−carbon bond of (P−P)Pd(Me)Cl (P−P = dppe, dppp, dppf). When 1 equiv of CN^{t}Bu was added to (dppe)Pd(Me)Cl in THF, approximately 50% of the starting material reacted to yield the mono-insertion product [(dppe)Pd{C(Me)=N^{t}Bu}Cl] (**7**). Addition of a further 1 equiv of CN^{t}Bu to the reaction mixture led to the complete conversion of (dppe)Pd(Me)Cl to the mono-insertion product **7**. As with CNXyl, no evidence for further insertion was observed (even after long reaction times).

In contrast to the relative lack of reactivity of (dppe)Pd(Me)Cl toward insertion, when the analogous reaction between (dppp)Pd(Me)Cl and 1 equiv of CN^{t}Bu was carried out, the formation of a complex mixture was observed by ^{31}P{^{1}H} NMR spectroscopy (which proved very difficult to separate and fully characterize). In an attempt to drive the reaction to a single product, a further 1 equiv of isocyanide was added. As expected, the addition of the extra CNR indeed simplified the ^{31}P{^{1}H} NMR spectrum to two pairs of doublets, indicating the formation of only two phosphorus-containing compounds (which could be detected during the first $^1/_2$ h of the reaction). The chemical shifts of such products (5.4 (d) and −6.8 (d) ppm, $J = 76$ Hz; 17.3 (d) and −5.1 (d), $J = 56$ Hz) are remarkably similar to those observed for the mono- and bis-insertion species **2** and **3** (see Table 1), suggesting the formation of the analogous complexes with CN^{t}Bu. Unfortunately, full characterization of these two products was prevented by their instability both in solution and in the solid state.

Analogous insertion reactions were carried out between (dppf)Pd(Me)Cl and CN^{t}Bu. When 1 equiv of isocyanide was added to the palladium complex, the quantitative formation of the mono-insertion product [(dppf)Pd{C(Me)=N^{t}Bu}Cl] (**8**) was observed. In an attempt to obtain the corresponding bis-insertion product (analogous to **6**), (dppf)Pd(Me)Cl was reacted with 2 equiv of CN^{t}Bu. The reaction was monitored by ^{31}P{^{1}H} NMR, which showed the gradual disappearance of the starting material and the production of free phosphine. This suggests that multiple insertion of CN^{t}Bu must be occurring and free-phosphine products similar to **4** are being formed. No further characterization of these products was attempted.

As for the reactions with CNXyl, upon insertion of CN^{t}Bu into (P−P)Pd(Me)Cl a shift of the phosphine resonances in the ^{31}P{^{1}H} NMR spectra to lower frequencies is observed (see Table 1). Again, such shifts are more pronounced for the phosphorus cis to the R group than for the trans.

Insertion of Norbornadiene into Palladium−Iminoacyl bonds. The systematic study of isocyanide insertion into (P−P)Pd(Me)Cl provided the required background to investigate the possibility of further insertion of alkenes into the palladium−iminoacyl bonds. While the insertion of olefins into palladium−acyl bonds is a well-established process, there are very few reported examples of the analogous insertions into palladium−iminoacyl bonds (among which are the papers by Vrieze[10a] and Takahashi[10b]). Such organometallic transformations could lead to the copolymerization of alkenes and isocyanides, yielding polyimines.

The possible insertion of norbornadiene (which due to its strained nature has proven to undergo insertion reactions readily[20]) into the palladium−iminoacyl compound **1** was then investigated. This complex was chosen, since our previous studies demonstrated it to be stable and not prone to multiple isocyanide insertion (which would complicate the study of alkene insertion). One equivalent of norbornadiene was added to a solution of (dppe)Pd{C(Me)=NXyl}Cl in THF. The reaction mixture was monitored by ^{31}P{^{1}H} NMR spectroscopy for a period of 24 h, and no changes were observed (even when an excess of norbornadiene was added). Since the targeted insertion reaction was not observed under these conditions, 1 equiv of $AgBF_4$ (to remove the chloride from **1** and produce a vacant site for substrate coordination) was added to the reaction mixture. Immediately after the addition, a white precipitate was

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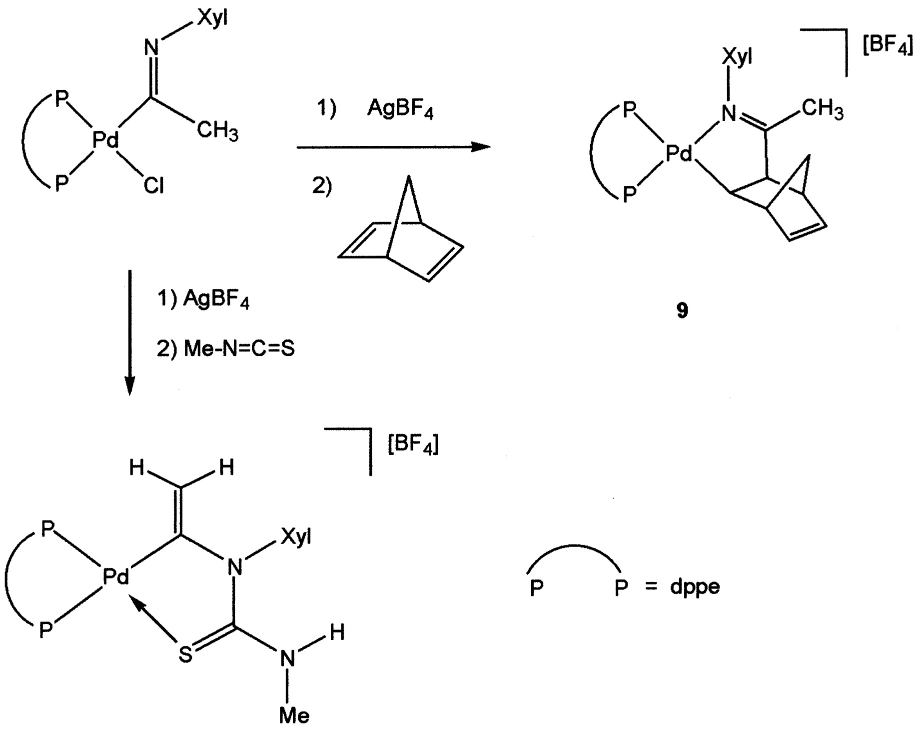
Scheme 3



9

10

formed (AgCl) followed by a change in the color of the reaction mixture (from yellow to colorless). The $^{31}P\{^1H\}$ NMR spectrum of this mixture demonstrated the quantitative conversion of **1** to a new product after approximately 15 min (at 34.5 (d), 53.0 (d) ppm). This product was isolated and characterized on the basis of analytical and spectroscopic techniques as $[(dppe)Pd(C_7H_8C({=}NC_6H_3(CH_3)_2)CH_3][BF_4]$ (**9**) (see Scheme 3). The AB pattern in the $^{31}P\{^1H\}$ NMR spectrum is consistent with this formulation, as is the presence of strong stretches at 1612 and 1472 cm^{-1} in the IR spectrum, which can be assigned to the C=N and the strained C=C bonds, respectively. The ^1H NMR spectrum clearly indicated the presence of each one of the proton environments with the expected coupling and integration (see the Experimental Section for detailed assignments). Particularly indicative for this formulation are the olefinic protons (H_c and H_d) and that bound to the carbon directly attached to the palladium center, H_a (which shows a coupling to the phosphorus atoms of the bis-phosphine). Another important feature of the ^1H NMR that indicates the insertion of norbornadiene is the disappearance of the H−P coupling between the iminoacyl's methyl protons and the phosphine. The formulation was further confirmed by FAB(+) mass spectrometric analyses (which showed the presence of a peak at 742 amu corresponding to the cationic part of the proposed species) and elemental analyses. Complex **9** is analogous to the complex reported by Vrieze on inserting norbornadiene into the palladium−iminoacyl bond of (N−N)Pd{C(Me)=NXyl}Cl (where N−N = bipy, phen; X = Cl, Br, I).[10a] The insertion reaction reported for the (N−N)Pd(R)Cl complexes seems to be more facile than for the compounds here reported (since for the former chloride removal is not needed for the insertion reaction to occur). This can be attributed to the more labile Pd−N bond (compared to the Pd−P bond), which, upon temporary dissociation, allows the substrate to coordinate to the metal center and subsequently insert into the Pd−C bond.

Reaction of Complex 1 with Isothiocyanates. To broaden our investigations on the reactivity of palladium−iminoacyl complexes with unsaturated species, the reaction between **1** and methyl isothiocyanate was studied. Our initial aim was to investigate the possibility of inserting the isothiocyanate into the palladium−iminoacyl bond, by which a new route for C−N or C−S bond formation (depending on the insertion process) would be established. When 1 equiv of MeN=C=S was reacted with 1 equiv of the iminoacyl complex **1** in the presence of $AgBF_4$, the immediate formation of a white precipitate (AgCl) and color change (from yellow to colorless) were observed. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, which indicated the quantitative formation of a new product within the first 10 min of reaction. No further changes were observed on stirring the mixture for a few hours. The product was isolated, and its characterization indicated that, instead of an insertion reaction, the isothiocyanate had undergone an addition to the iminoacyl group, yielding $[(dppe)Pd\{C({=}CH_2)N(Xyl)C({=}S)NHMe\}][BF_4]$ (**10**) (see Scheme 3). To the best of our knowledge, this seems to be the first example of such a reaction on a palladium center. Structural characterization of this complex has not been possible, due to the poor quality of the crystals obtained. Despite this, NMR and IR spectroscopy together with FAB(+) mass spectrometry and elemental analyses provide enough evidence to confirm the proposed formulation of **10** as a result of the addition of methyl isothiocyanate to the iminoacyl group of **1**. The $^{31}P\{^1H\}$ NMR spectrum of **10** shows the expected AB pattern due to the two nonequivalent phosphorus atoms.

The ^{1}H NMR spectrum indicates the presence of the vinylic protons (coupling to the two different phosphorus environments) as doublets of doublets at 3.9 and 4.3 ppm. The protons corresponding to the methyl of the former iminoacyl group appear at 3.1 ppm as a doublet (due to the coupling to the N−H proton). A broad quartet at 5.9 ppm can be assigned to the proton on the nitrogen of the former isothiocyanate. The protons corresponding to the Xyl and dppe groups are integrated correctly for this formulation (see the Experimental Section for a complete assignment). The ^{13}C NMR spectrum is also consistent with the proposed formulation for **10**; a doublet of doublets at 176.4 ppm can be assigned to the C═S carbon, which couples to both the cis and trans phosphines. The resonances for the two vinylic carbons appear at 162.8 ppm (for the carbon directly linked to the palladium) and 110.9 ppm. The vinylic carbon directly attached to the palladium is strongly coupled to the trans phosphorus, giving a doublet with $^2J_{PC} = 136$ Hz. This coupling constant is larger (though within the same order of magnitude) than the values previously reported for other (phosphine)Pd−*C*(═CH_2) systems.[21] The formulation was further confirmed by FAB(+) mass spectrometry and elemental analyses.

Conclusions

The systematic study of the insertion of CNR (R = Xyl, ^{t}Bu) into the palladium−methyl bond of (P−P)Pd(Me)Cl (P−P = dppe, dppp, dppf) has been carried out. The results have demonstrated that the insertion is highly dependent on the nature of the chelating phosphine. For the more strained complex formed with dppe, the insertion of isocyanides is slower and multiple insertion is not observed. This is in contrast to the high reactivity of (dppp)Pd(Me)Cl, which readily reacts with isocyanides to produce multiply inserted products (even when only 1 equiv of CNR is present). Similar results have been observed for the complexes with dppf, although the reactions are more controllable, indicating a less reactive complex (in comparison to the dppp one). These results are consistent with the previously observed reactivity trend (dppp ≈ dppf ≫ dppe) in carbonylation reactions. The structural characterization of **1** and **3** has provided a unique structural insight into this reactivity trend. The P−Pd−P angle in **3** (i.e. P−P = dppp) is larger than in the dppe complex **1**. Consequently, the R−Pd−Cl angle is smaller for dppp than dppe, which allows closer proximity of the reacting species. Moreover, dppp with a longer alkyl backbone provides much more flexibility to the systems which, presumably, reduces the energy of the transition state (as occurs with carbonylation reactions). In the case of dppf, the bite angle is larger than for the other phosphines (although in this case the electronic effects due to the dppf−Cp rings are likely to play important roles in controlling the reactivity at the palladium center).

The studies presented here have also demonstrated the possibility of inserting olefins (particularly the strained norbornadiene) into the palladium−iminoacyl bond. This could have interesting implications for potential isocyanide/olefin copolymerization reactions. Further studies in this area are currently being carried out. In contrast to the reaction with norbornadiene, the reaction with the more reactive unsaturated substrate MeN═C═S leads to the formation of a product resulting from addition of the isothiocyanate and the coordinated iminoacyl. In the future we hope to be able to favor the insertion (instead of addition) of isothiocyanates into the palladium−iminoacyl bond.

Experimental Section

Materials and Apparatus. All manipulations were carried out under 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. All commercially available solid starting materials were not further purified. All liquid starting materials were dried over molecular sieves and thoroughly degassed by freeze−pump−thaw prior to use. ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on a JEOL-EX270 spectrometer (270.17, 109.38, and 67.94 MHz, respectively) with TMS, H_2PO_4, and TMS, respectively, as internal references. IR spectra were recorded on a Research Series FT-IR instrument using KBr disks in the range 4000−500 cm^{-1}. Mass spectroscopy and X-ray crystallography were carried out at Imperial College. Elemental analysis was carried out at the University of North London. The complexes (COD)$PdCl_2$,[11] (COD)PdMeCl,[12] and L_2PdMeCl (L_2 = dppp, dppe, dppf)[13] were synthesized according to previously reported procedures.

Synthesis of (dppe)Pd{C(Me)═NXyl}Cl (1). 2,6-Dimethylphenyl isocyanide (0.052 g, 0.40 mmol) was added to a solution of (dppe)PdMeCl (0.111 g, 0.20 mmol) in THF (30 mL). The resulting mixture was stirred for 2 h. The product was isolated by removing the solvent under reduced pressure and washing the remaining solid with diethyl ether and cold THF. Yield: 0.12 g; 0.17 mmol; 83%. Anal. Found: C, 62.82; H, 5.29; N, 2.04. Calcd for $C_{36}H_{36}NP_2PdCl$: C, 62.82; H, 5.36; N, 1.98. IR (ν (KBr)): 1617, 1583 (N═C). $^{31}P\{^1H\}$ NMR ($(CD_3)_2C{=}O$): δ 39.1 (d, 1P, $^2J_{PP} = 37$ Hz), 27.3 (d, 1P, $^2J_{PP} = 37$ Hz). ^{1}H NMR ($(CD_3)_2C{=}O$): δ 1.68 (dd, 3H, PdC(═NR)CH_3, $^4J_{PH} = 5$ Hz, $^4J_{PH} = 1$ Hz), 1.75 (s, 6H, $(CH_3)_2C_6H_3NC$), 2.33 (m, 2H, PCH_2CH_2P), 2.65 (m, 2H, PCH_2CH_2P), 6.61 (dd, 1H, 4-H $C_6H_3(CH_3)_2$, $^3J_{HH} = 8$ Hz, $^3J_{HH} = 7$ Hz), 6.74 (2 overlapping d, 2H, 3,5-H $C_6H_3(CH_3)_2$, $^3J_{HH} = 8$ Hz), 7.51 (m, 12H, P−Ph(3,4,5)), 8.60 (m, 8H, P−Ph(2,6), $^3J_{HH} \approx 3$ Hz). MS (FAB$^+$; *m*/*z* (relative intensity)): 686 (7) [M]$^+$, 650(3) [M − Cl]$^+$, 539(2) [(dppe)PdCl]$^+$.

Synthesis of (dppp)Pd{C(Me)═NXyl}Cl (2). 2,6-Dimethylphenyl isocyanide (0.026 g, 0.20 mmol) was added slowly to a solution of (dppp)Pd(Me)Cl (0.114 g, 0.20 mmol) in CH_2Cl_2 (30 mL). The resulting solution was stirred for 1 h. A mixture of products was obtained (as detected by $^{31}P\{^1H\}$ NMR), including starting material and the bis-inserted isocyanide. All volatiles from the reaction mixture were removed under reduced pressure, and the remaining product was washed with ether to remove the bis-inserted product. The resulting solid was dissolved in THF, and a pure sample of **2** was precipitated as a yellow solid upon addition of hexane, separating it from the remaining starting material. Yield: 0.09 g; 0.13 mmol; 67%. Anal. Found: C, 59.75; H, 5.00; N, 1.71. Calcd for $C_{37}H_{38}NP_2PdCl\cdot 0.7CH_2Cl_2$: C, 59.58; H, 5.23; N, 1.84. IR (ν (KBr)): 1614, 1582 (N═C). $^{31}P\{^1H\}$ NMR (THF): δ 7.8 (d, 1P, $^3J_{PP} = 67$ Hz), −6.6 (d, 1P, $^3J_{PP} = 67$ Hz). ^{1}H NMR ($CDCl_3$): δ 1.61 (dd, 3H, PdC(═NR)CH_3, $^4J_{PH} = 3.5$ Hz, $^4J_{PH}$ unresolved), 1.74 (s, 6H, $C_6H_3(CH_3)_2$), 1.82 (m, 4H, $PCH_2CH_2CH_2P$), 2.40 (m, 2H, $PCH_2CH_2CH_2P$), 6.72 (m, 3H, $C_6H_3(CH_3)_2$), 7.35(m, 12H, P−Ph(3,4,5)), 7.78 (m, 8H, P−Ph(2,6)). MS (FAB$^+$; *m*/*z* (relative intensity)): 702 (4) [M$^+$], 664 (7) [M$^+$ − Cl], 518 (11) [Pd(dppp)]$^+$.

Synthesis of (dppp)Pd{(C═NXyl)(C(Me)═NXyl)}Cl (3). 2,6-Dimethylphenyl isocyanide (0.026 g, 0.20 mmol) was added to a solution of (dppp)PdMeCl (0.057 g, 0.10 mmol) in THF

(30 mL). The resulting mixture was stirred for 20 min. The solvent was removed under reduced pressure and the remaining solid recrystallized from a diethyl ether/hexane mixture to yield pure **4** as a yellow crystalline solid. Yield: 0.07 g; 0.08 mmol; 85%. Anal. Found: C, 66.31; H, 5.82; N, 3.28. Calcd for $C_{46}H_{47}N_2P_2PdCl$: C, 66.43; H, 5.70; N, 3.37. IR (ν (KBr)): 1613, 1582 (N=C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 16.0 (d, 1P, $^2J_{PP} = 67$ Hz), −4.7 (d, 1P, $^2J_{PP} = 67$ Hz). ^1H NMR ($CDCl_3$): δ 1.81 (br s, 6H, $C_6H_3(CH_3)_2$), 1.92 (m, 4H, $PCH_2CH_2CH_2P$), 2.04 (s, 3H, PdC(=NR)CH_3), 2.27 (m, 2H, $PCH_2CH_2CH_2P$), 2.33 (br s, 6H, $C_6H_3(CH_3)_2$), 6.77−7.52 (m, 26H, aromatic H). MS (FAB$^+$; *m/z* (relative intensity)): 795 (2) [M − Cl]$^+$, 702(3) [M − CNXyl]$^+$, 664 (3) [M − (CNR) − Cl]$^+$, 535 (1) [(dppp)PdMe]$^+$, 518 (4) [(dppp)Pd]$^+$.

Synthesis of (NCXyl)Pd{(C=NXyl)(C=NXyl)[C(Me)=NXyl)]Cl (4). 2,6-Dimethylphenyl isocyanide (0.09 g, 0.73 mmol) was added to a solution of (dppp)PdMeCl (0.10 g, 0.18 mmol) in THF (30 mL). The resulting mixture was stirred for 3 h. The resulting red solution was evaporated to dryness, and the product was extracted with small portions of diethyl ether (3 × 10 mL). Hexane solvent was then added to the solution, and the diethyl ether was slowly removed under reduced pressure to give a red microcrystalline solid. Yield: 0.07 g: 0.10 mmol: 57%. Anal. Found: C, 65.05; H, 5.81; N, 8.21. Calcd for $C_{37}H_{39}N_4PdCl$: C, 65.20; H, 5.77; N, 8.22. IR (ν): 2194 (C≡N), 1643, 1590 (N=C). ^1H NMR ($CDCl_3$): δ 1.69 (s, 6H, $C_6H_3(CH_3)_2$, terminally coordinated), 2.08 (s, 6H, $C_6H_3(CH_3)_2$), 2.16 (s, 6H, $C_6H_3(CH_3)_2$), 2.26 (s, 3H, C(=NR)CH_3), 2.38 (s, 6H, $C_6H_3(CH_3)_2$), 6.33 (m, 1H, $C_6H_3(CH_3)_2$), 6.67 (m, 2H, $C_6H_3(CH_3)_2$), 6.83−7.20 (m, 9H, $C_6H_3(CH_3)_2$). MS (FAB$^+$; *m/z* (relative intensity)): 680 (3) [M]$^+$, 645 (24) [M − Cl]$^+$, 549 (11) [M − CNR]$^+$.

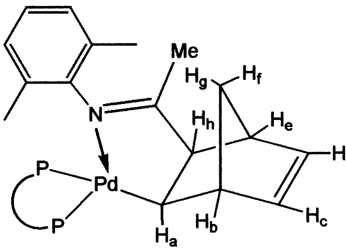
Synthesis of (dppf)Pd{C(Me)=NXyl}Cl (5). 2,6-Dimethylphenyl isocyanide (0.013 g, 0.10 mmol) was added to a solution of (dppf)PdMeCl (0.071 g, 0.10 mmol) in CH_2Cl_2 (30 mL). The resulting mixture was stirred for 2 h, resulting in the mono-inserted product and a small amount of bis-inserted product and starting material (as detected by $^{31}P\{^1H\}$ NMR). The solvent was removed under reduced pressure, and the resulting solid was washed (to remove the bis-inserted product) with diethyl ether. The crude product was recrystallized from THF and hexane, yielding **5** as an orange solid. Yield: 0.053 g: 0.06 mmol; 64%. Anal. Found: C, 62.63; H, 4.91; N, 1.61. Calcd for $C_{44}H_{40}NP_2PdFeCl$: C, 62.70; H, 4.74; N, 1.66. IR (ν; KBr): 1627, 1583 (N=C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 23.6 (d, 1P, $^2J_{PP} = 52$ Hz), 9.1 (d, 1P, $^2J_{PP} = 52$ Hz). ^1H NMR (CD_2Cl_2): δ 1.65 (dd, 3H, PdC(=NR)CH_3, $^3J_{PH} = 5.0$ Hz, $^3J_{PH} = 1.5$ Hz), 1.71 (s, 6H, $(CH_3)_2C_6H_3NC$), 3.59 (br d, 2H, (2′,5′)$C_5H_4PPh_2$, $^3J_{PH} = 2.0$ Hz), 4.16 (br s, 2H, (3′,4′)$C_5H_4PPh_2$), 4.44 (br s, (3,4)$C_5H_4PPh_2$), 4.69 (br d, 2H, (2,5)$C_5H_4PPh_2$, $^3J_{PH} = 2.0$ Hz), 6.69 (m, 1H, (4)-$C_6H_3(CH_3)_2$), 6.77 (m, 2H, (3,5)$C_6H_3(CH_3)_2$), 7.24−8.03 (m, 20H, PPh). MS (FAB$^+$; *m/z* (relative intensity)): 806 (100) [M − Cl]$^+$, 697 (11) [(dppf)PdCl]$^+$, 660 (58) [Pd(dppf)]$^+$.

Synthesis of (dppf)Pd{(C=NXyl)(C(Me)=NXyl)}Cl (6). A solution of 2,6-dimethylphenyl isocyanide (0.088 g, 0.68 mmol) in CH_2Cl_2 (20 mL) was added slowly to a solution of (dppf)PdMeCl (0.24 g, 0.34 mmol) in CH_2Cl_2 (40 mL). The resulting solution was stirred for 1 h and analyzed by ^{31}P NMR spectroscopy, which showed the formation of a mixture of products (corresponding to starting material, **5**, and the new product **6**). The solvent was removed under reduced pressure, and the resulting solid was washed with diethyl ether. The solution contained **6** together with some free phosphine. The solution was concentrated under reduced pressure and left to stand for 1 h, upon which time **6** precipitated as a yellow solid. Yield: 0.17 g; 0.17 mmol; 51%. Anal. Found: C, 65.82; H, 5.35; N, 2.35. Calcd for $C_{53}H_{49}N_2P_2PdFeCl \cdot 0.5C_4H_{10}O$ (the added solvent was detected by ^1H NMR spectroscopy): C, 65.36; H, 5.39; N, 2.77. IR (ν; KBr): 1618, 1585 (N=C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 28.3 (d, 1P, $^2J_{PP} = 47$ Hz), 9.0 (d, 1P, $^2J_{PP} = 47$ Hz). ^1H NMR (CD_2Cl_2): δ 1.75 (s, 6H, $(CH_3)_2C_6H_3$), 2.03 (s, 3H, PdC(=NR)CH_3), 2.32 (s, 6H, $(CH_3)_2C_6H_3$), 3.09 (br, 2H, (2′,5′)$C_5H_4PPh_2$), 4.02 (br, 2H, (3′,4′)$C_5H_4PPh_2$), 4.43 (br, 4H, $C_5H_4PPh_2$), 6.82−7.87 (m, 26H, aromatic H). MS (FAB$^+$; *m/z* (relative intensity)): 937 (2) [M − Cl]$^+$, 806 (15) [(dppf)Pd(CNR)Me]$^+$, 675 (5) [(dppf)PdMe]$^+$, 660 (6) [Pd(dppf)]$^+$.

Synthesis of [(dppe)Pd{C(Me)=N^{t}Bu}Cl] (7). *tert*-Butyl isocyanide (81.4 μL, 0.72 mmol) was added to a solution of (dppe)PdMeCl (0.20 g, 0.36 mmol) in THF. The resulting solution was stirred for 2 h. The solvent was removed under reduced pressure and the remaining solid washed with diethyl ether and recrystallized from a THF/hexane mixture to yield pure **7**. Yield: 0.17 g; 0.27 mmol; 74%. Anal. Found: C, 58.70; H, 5.29; N, 2.08. Calcd for $C_{32}H_{36}NP_2PdCl \cdot H_2O$ (the added solvent, which was detected by ^1H NMR spectroscopy, could not be removed even after the sample was left under vacuum for several days): C, 58.55; H, 5.83; N, 2.13. IR (ν; KBr): 1637, 1587 (N=C). $^{31}P\{^1H\}$ NMR (THF-d_6): δ 40.5 (d, 1P, $^2J_{PP} = 46$ Hz), 19.5 (d, 1P, $^2J_{PP} = 46$ Hz). ^1H NMR (CD_2Cl_2): δ 1.04 (s, 9H, $(CH_3)_3NC$), 1.50 (m, 2H, PCH_2CH_2P), 2.29 (dd, PdC(=NR)CH_3, 3H, $^3J_{PH} = 2.5$ Hz, $^3J_{PH}$ unresolved), 2.45 (m, 2H, PCH_2CH_2P), 7.30−8.03 (m, P−Ph, 20H). MS (FAB$^+$; *m/z* (relative intensity)): 640 (8) [M]$^+$, 602 (8) [M − Cl]$^+$, 539 (2) [(dppe)PdCl]$^+$, 504 (5) [(dppe)Pd]$^+$.

Synthesis of [(dppf)Pd{C(Me)=N^{t}Bu}Cl] (8). *tert*-Butyl isocyanide (12.9 μL, 0.10 mmol) was added to a solution of (dppf)PdMeCl (0.143 g, 0.20 mmol) in THF (30 mL), and the reaction mixture was stirred for 5 h. The crude product was isolated by evaporation of all volatiles. This was washed with diethyl ether (20 mL) to remove a small quantity of a purple uncharacterized side product. The crude solid was recrystallized from THF and hexanes, yielding an orange solid. Yield: 0.12 g; 0.15 mmol; 77%. Anal. Found: C, 60.49; H, 4.97; N, 1.73. Calcd for $C_{40}H_{40}NP_2PdFeCl$: C, 60.48; H, 5.07; N, 1.76. IR (ν; KBr): 1661 (C=N). $^{31}P\{^1H\}$ NMR (THF-d_8): δ 25.1 (d, 1P, $^2J_{PP} = 59$ Hz), 6.9 (d, 1P, $^2J_{PP} = 59$ Hz). ^1H NMR (THF-d_8): δ 1.26 (s, $(CH_3)_3NC$, 9H), 2.25 (s, 3H, PdC(=NR)CH_3), 3.42 (br, 2H, (2′,5′)$C_5H_4PPh_2$), 4.11 (br, 2H, (3′,4′)$C_5H_4PPh_2$), 4.60, (m, (3,4)$C_5H_4PPh_2$ + (2,5)$C_5H_4PPh_2$), 7.09−8.29 (m, 20H, P−Ph). MS (FAB$^+$; *m/z* (relative intensity)): 794 (1) [M]$^+$, 758 (4) [M − Cl]$^+$, 695 (2) [(dppf)PdCl]$^+$, 660 (18) [(dppf)Pd]$^+$.

Synthesis of [(dppe)Pd{C_7H_8C(=N$C_6H_3(CH_3)_2$}CH_3]-[BF_4] (9). Bicyclo[2.2.1]hepta-2,5-diene (i.e. norbornadiene) (16.1 μL, 0.15 mmol) was added to a stirred solution of (dppe)-Pd{C(Me)=NXyl}Cl (0.10 g, 0.15 mmol) in THF (20 mL). To the resulting reaction mixture was added 1 equiv of $AgBF_4$ (0.03 g, 0.15 mmol) as a solid in one portion. Immediate formation of AgCl was observed along with a change in the solution's color (from yellow to colorless). The reaction mixture was stirred for 15 min, after which time the precipitated AgCl was filtered off. The remaining reaction mixture was stirred for a further 10 min. A white product was obtained by reducing the reaction mixture's volume (under vacuum) to ca. 5 mL followed by addition of hexane (10 mL).



Yield: 0.09 g; 0.12 mmol; 81%. Anal. Found: C, 57.09; H, 5.01; N, 1.52. Calcd for $C_{42}H_{44}NPdBF_4 \cdot CH_2Cl_2$: C, 57.20; H, 5.13; N, 1.55. IR (ν; KBr): 1612 (C=N), 1472 (C=C), 1100, 1058 (BF_4). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 34.5 (d, 1P, $^2J_{PP} = 29$ Hz), 53.0 (d, 1P, $^2J_{PP} = 30$ Hz). ^1H NMR (CD_2Cl_2): δ 1.20 (dd, 1H,

H_a, $^{3}J_{PH} = 9.5$ Hz, $^{3}J_{PH}$ unresolved), 1.75 (s, 3H, C(═NR)CH_3), 1.92 (s, 3H, $C_6H_3(CH_3)_2$), 1.96 (s, 3H, $C_6H_3(CH_3)_2$), 2.26 (m, 1H, H_h), 2.32 (br, 2H, $H_f + H_g$), 2.80 (dd, 1H, H_b, $^{3}J_{PH}$ unresolved), 3.19 (s, 1H, H_e), 5.63 (dd, 1H, H_c, $^{3}J_{PH} = 5.0$ Hz, $^{3}J_{PH} = 2.5$ Hz), 6.08 (dd, 1H, H_d, $^{3}J_{PH} = 5.0$ Hz, $^{3}J_{PH} = 2.5$ Hz), 6.43 (d, 1H, $C_6H_3(CH_3)_2$, $^{3}J_{HH} = 7.5$ Hz), 6.56 (d, 1H, $C_6H_3(CH_3)_2$, $^{3}J_{HH} = 7.5$ Hz), 6.67 (τ, 1H, $C_6H_3(CH_3)_2$), 7.04−7.89 (m, 20H, 4 × P−Ph). MS (FAB$^+$; *m*/*z* (relative intensity)): 742 (24) $[M - BF_4]^+$, 676 (5) $[M - BF_4 - C_5H_6]^+$, 504 (4) $[Pd(dppe)]^+$.

Synthesis of [(dppe)Pd{C(═CH$_2$)N(Xyl)C(═S)NHMe}][BF$_4$] (10). Methyl isothiocyanate (0.018 g, 0.24 mmol) was added to a stirred solution of (dppe)Pd{C(Me)═NXyl}Cl (0.15 g, 0.22 mmol) in CH_2Cl_2 (25 mL). $AgBF_4$ (0.04 g, 0.22 mmol) was added in one portion. The AgCl salt immediately precipitated from the yellow solution, and within 5 min the solution turned clear. The reaction mixture was left for a further 10 min, and then the AgCl was filtered off. The white product was obtained by the reduction of the solvent to 10 mL and addition of hexane (15 mL). Yield: 0.13 g; 0.16 mmol; 73%. Anal. Found: C, 56.27; H, 4.84; N, 3.54. Calcd for $C_{38}H_{39}N_2P_2SBF_4Pd$: C, 56.28; H, 4.85; N, 3.45. IR (ν; KBr): 3448 (N−H), 3055 (alkene C−H), 1560 s (C═C), 1262 m (C═S), 1102, 1058 (BF_4). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 46.9 (d, 1P, $^{2}J_{PP} = 33$ Hz), 56.6 (d, 1P, $^{2}J_{PP} = 33$ Hz). ^{1}H NMR ($CDCl_3$): δ 2.00 (s, 6H, $C_6H_3(CH_3)_2$), 2.55 (m, 4H, PCH_2CH_2P), 3.05 (d, 3H, HNCH_3, $^{3}J_{HH} = 4.5$ Hz), 3.91 (τ, 1H, PdC(═CH_2) cis to Pd, $^{4}J_{PH} = 6.5$ Hz), 4.29 (τ, 1H, PdC(═CH_2) trans to Pd, $^{4}J_{PH} = 16.0$ Hz), 5.94 (br q, CH_3NH, $^{3}J_{HH} = 4.5$ Hz), 7.10−7−24 (m, 3H, $C_6H_3(CH_3)_2$), 7.40−7.83 (m, 20H, 4 × PC_6H_5). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 17.6, 25.9 (dd, PCH_2CH_2P), $^{1}J_{PC} = 29$ Hz, $^{2}J_{PC} = 11$ Hz), 30.7 (dd, PCH_2CH_2P, $^{1}J_{PC} = 34$ Hz, $^{2}J_{PC} = 18$ Hz), 32.9 (s, N−CH_3), 111.0 (br, PdC(═CH_2)), 127.3−136.2 (several signals assigned to the phenyl rings of dppe and Xyl group), 162.8 (dd, Pd*C*(═CH$_2$), $^{2}J_{CPtrans} = 136$ Hz, $^{2}J_{CPcis}$ unresolved), 176.4 (dd, C═S, $^{3}J_{PC} = 16$ Hz, $^{3}J_{PC}$ unresolved). MS (FAB$^+$; *m*/*z* (relative intensity)): 723 (31) $[M]^+$, 504 (4) $[(dppe)Pd]^+$.

Crystal Structure Determinations. Data for all three compounds were collected on Bruker P4 diffractometers with graphite-monochromated Mo or Cu Kα radiation as indicated and using ω-scans.

Crystal Data for 1: $C_{36}H_{36}NP_2ClPd$, $M_r = 686.5$, triclinic, $P\bar{1}$ (No. 2), $a = 11.363(2)$ Å, $b = 11.787(2)$ Å, $c = 14.186(4)$ Å, $\alpha = 112.85(2)°$, $\beta = 103.79(2)°$, $\gamma = 102.60(1)°$, $V = 1594.6(6)$ Å^3, $Z = 2$, $D_c = 1.430$ g cm^{-3}, μ(Mo Kα) = 0.79 mm^{-1}, $T = 293$ K, clear prisms; 5350 independent measured reflections, F^2 refinement, R1 = 0.036, wR2 = 0.080, 4384 independent observed reflections ($|F_o| > 4\sigma(|F_o|)$, $2\theta \le 50°$), 322 parameters. CCDC 191378.

Crystal Data for 3: $C_{46}H_{47}N_2P_2ClPd{\cdot}C_4H_8O$, $M_r = 903.8$, triclinic, $P\bar{1}$ (No. 2), $a = 13.541(4)$ Å, $b = 13.597(2)$ Å, $c = 13.671(3)$ Å, $\alpha = 92.46(1)°$, $\beta = 110.99(2)°$, $\gamma = 103.70(2)°$, $V = 2260.4(9)$ Å^3, $Z = 2$, $D_c = 1.328$ g cm^{-3}, μ(Mo Kα) = 0.58 mm^{-1}, $T = 293$ K, yellow prisms; 7739 independent measured reflections, F^2 refinement, R1 = 0.050, wR2 = 0.109, 5778 independent observed reflections ($|F_o| > 4\sigma(|F_o|)$, $2\theta \le 50°$), 490 parameters. CCDC 191379.

Crystal Data for 4: $C_{37}H_{39}N_4ClPd{\cdot}CH_2Cl_2$, $M_r = 766.5$, triclinic, $P\bar{1}$ (No. 2), $a = 11.674(1)$ Å, $b = 12.391(1)$ Å, $c = 14.779(1)$ Å, $\alpha = 70.45(1)°$, $\beta = 83.80(1)°$, $\gamma = 69.17(1)°$, $V = 1882.7(2)$ Å^3, $Z = 2$, $D_c = 1.352$ g cm^{-3}, μ(Cu Kα) = 6.17 mm^{-1}, $T = 293$ K, orange prisms; 5474 independent measured reflections, F^2 refinement, R1 = 0.048, wR2 = 0.120, 4676 independent observed absorption-corrected reflections ($|F_o| > 4\sigma(|F_o|)$, $2\theta \le 120°$), 416 parameters. CCDC 191380.

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Supporting Information Available: Details about the X-ray crystal structures, including ORTEP diagrams and tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **1**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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