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Studies on the Reactivity of Isocyanates and Isothiocyanates with Palladium−Imidoyl Complexes

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The reactions of palladium−iminoacyl complexes with isocyanates (RNCO) and isothiocyanates (RNCS) have been investigated. The reaction of $Pd\{C(Me){=}NXy\}(Cl)(P{-}P)$ (P−P = dppe, **1**; dppp, **2**) with RNCE (E = O, S) in the presence of $AgBF_4$ yields the novel compounds $[\overline{Pd\{C({=}CH_2)N(Xy)C({=}E}){NHR}\}(dppe)][BF_4]$ (E = O and R = Et, **3**; Ph, **4**; E = S and R = Me, **5**; Ph, **6**); the formation of these complexes results from an addition reaction followed by the migration of a proton from the methyl group in the imidoyl fragment to the nitrogen in the RNCE moiety. In contrast, the reaction between $Pd\{C(Ph){=}NXy\}(I)(dppe)$ and RNCO in the presence of $AgBF_4$ yields the addition product $[\overline{Pd\{C(Ph){=}N(Xy)C({=}O)({=}N}Ph)\}(dppe)]$-$[BF_4]$ (**10**). Protonation of the imidoyl group in $Pd\{C(Me){=}NXy\}(Cl)(dppe)$ suppresses the addition reaction when the protonated complex is reacted with RNCS; the products obtained in this case are $[Pd\{C(Me){=}NHXy\}(dppe)(S{=}C{=}NR)][BF_4]_2$ (R = Me, **15**; Ph, **16**).

Introduction

Metal-mediated C−C bond formation processes are employed in several methodologies for the synthesis of novel organic species and polymeric materials. These organometallic reactions involve several different basic transformations such as the insertion of small molecules into metal−carbon bonds (e.g., CO and CNR),[1,2] cross-coupling reactions,[3] or the addition of unsaturated species to organometallic compounds.[4] More recently, there has been increasing interest in finding analogous reactions for the metal-mediated formation of C−N and C−O bonds, one of the most successful processes being the palladium-mediated coupling reactions developed independently by Buchwald[5] and Hartwig.[6] Another potential way of generating new C−N and C−O bonds is by the insertion of imines or ketones into metal−carbon bonds. Despite being an attractive approach, due to the strong tendency of imines to σ-coordinate to metal centers, there are very few examples where this type of transformation has been unambiguously achieved. Recently, Sen[7] and Arndtsen[8] have independently reported the insertion of imines into the palladium−carbon bond of complexes with general formula $[(L{-}L)PdC(Me){=}O]^+$ (where L−L = phen, bipy, dppe, and dppp), providing a new methodology for the formation of C−N bonds.

A different approach to the formation of C−N bonds has been devised by Werner in which the nitrogen atom of a coordinated imidoyl group acts as a nucleophile reacting with the electrophilic carbon of species such as CS_2 and RNCS.[9] Analogous addition reactions have

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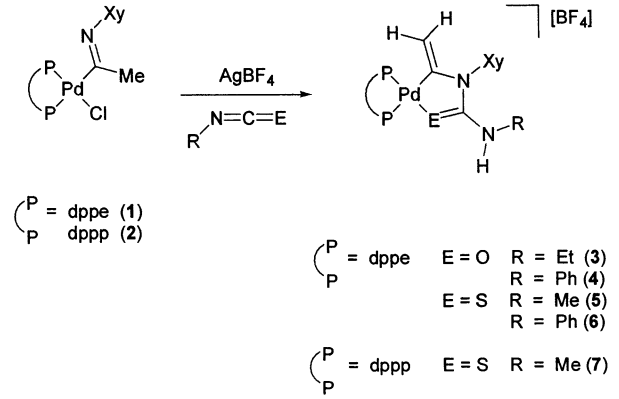
Scheme 1



subsequently been employed by others for the synthesis of organic fragments that contain C–N bonds.[10]

As part of a systematic investigation to discover new organometallic approaches for the formation of C–C and C–N bonds, we have studied the insertion of isocyanides into palladium–carbon bonds followed by the insertion or addition of a second unsaturated species (such as olefins, imines, isocyanates, and isothiocyanates) into the palladium–imidoyl group formed via the first insertion.[11] Herein we report the reactions of Pd{C(Me)=NXy}(Cl)(P–P) and Pd{C(Ph)=NXy}(I)(P–P) (P–P = dppe and dppp) with isocyanates (RNCO) and isothiocyanates (RNCS). In these reactions a series of novel palladium-mediated transformations take place leading to the formation of new C–N bonds.

Results and Discussion

Reaction of Pd{C(Me)=NXy}(Cl)(P–P) with Isocyanates and Isothiocyanates. We have recently reported preliminary results showing that the iminoacyl compound Pd{C(Me)=NXy}(Cl)(dppe) (**1**) reacts with MeNCS in the presence of AgBF$_4$ to yield the new complex $[\overline{\mathrm{Pd\{C({=}CH_2)N(Xy)C({=}S}}\mathrm{)NHMe\}(dppe)][BF_4]}$ (**5**), though this was not structurally characterized.[11] To explore the generality of this reaction and gain a better understanding of its mechanism, the iminoacyl complex **1** was reacted with a series of isocyanates and isothiocyanates.

Following the same synthetic procedure used for the preparation of **5**, 1 equiv of the corresponding isocyanate or isothiocyanate (RNCE where R = Et, Ph and E = O; R = Ph and E = S) was reacted with 1 equiv of **1** in the presence of AgBF$_4$ (see Scheme 1). In each one of the reactions with the three different substrates, the immediate formation of a white precipitate (AgCl) was observed. The course of these reactions was monitored by ^{31}P{^{1}H} NMR spectroscopy, which indicated that with either EtNCO or PhNCS, the quantitative conversion of the starting material to a new product occurred within 10 min of reaction. The ^{31}P{^{1}H} NMR of the new compound in each one of these two cases consisted of a pair of doublets, suggesting the presence of two inequivalent phosphorus centers coupling to each other. On the basis of spectroscopic, analytical, and structural investigations these compounds were characterized as $[\overline{\mathrm{Pd\{C({=}CH_2)N(Xy)C({=}O}}\mathrm{)NHEt\}(dppe)][BF_4]}$ (**3**) and $[\overline{\mathrm{Pd\{C({=}CH_2)N(Xy)C({=}S}}\mathrm{)NHPh\}(dppe)][BF_4]}$ (**6**), respectively. In contrast, the reaction with PhNCO led to the initial formation of two products, each of which showed two doublets in the ^{31}P{^{1}H} NMR spectra. After stirring for 12 h, the complete conversion to only one of the two products was observed (see below for discussion of the relevance of the intermediate species for the proposed mechanism). This final product was characterized as $[\overline{\mathrm{Pd\{C({=}CH_2)N(Xy)C({=}O}}\mathrm{)NHPh\}(dppe)][BF_4]}$ (**4**) on the basis of spectroscopic and analytical evidence.

The ^{31}P{^{1}H} NMR spectra of **3**, **4**, and **6** show an AB pattern associated with the two inequivalent phosphorus atoms from the dppe coordinated to the palladium center (see Scheme 1). The ^{1}H NMR spectra of the three complexes show two signals in the region between 3.9 and 4.8 ppm, characteristic of vinylic protons. These protons appear as doublets of doublets since they couple to the two different phosphorus environments of dppe. The proton on the nitrogen of the former isocyanate or isothiocyanate appears as a singlet between 6.45 and 7.10 ppm, depending on the substrate used. The ^{13}C NMR spectra of the three new complexes are also consistent with the proposed formulation; the resonances for the C=E (E = O, S) carbon atoms of the corresponding products appear as a doublet of doublets due to coupling with both the *cis* and *trans* phosphines (at 164 ppm for E = O and 176 for E = S). The vinylic carbon directly attached to the palladium is strongly coupled to the *trans*-phosphorus, giving a doublet with $^2J_{\mathrm{PC}}$ couplings ranging between 136 and 138 Hz. These coupling constants are larger, though within the same order of magnitude, than the value previously reported for other (phosphine)Pd–C(=CH$_2$) systems.[12] The X-ray crystal structures of two of these complexes (**4** and **6**) (vide infra) were determined and confirmed the proposed formulation.

It is well established that the nature of chelating phosphines has an important influence on the reactivity of metal complexes (e.g., the insertion of CNR or CO into palladium–carbon bonds occurs much more readily when dppp is used instead of dppe).[13] Consequently, it was of interest to investigate whether the reaction of

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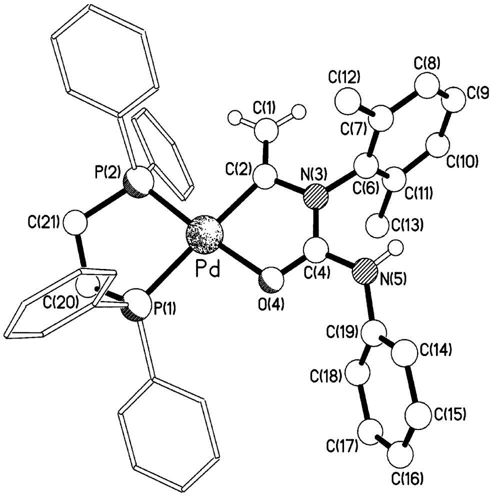

Figure 1. Molecular structure of the cation in **4**.

RNCE (E = S, O) with the coordinated iminoacyl group would be affected by changing the bite angle of the chelating bis-phosphine. For this, the reaction between MeNCS and Pd{C(=NXy)Me}(Cl)(dppp) (**2**) was investigated. Upon mixing the two reagents in a 1:1 ratio in the presence of AgBF$_4$, the immediate formation of a white precipitate (AgCl) was observed. Within 10 min all of **2** had reacted and a new compound formed, as monitored by ^{31}P{^{1}H} NMR spectroscopy. After filtering off the AgCl, reducing the volume of the resulting filtrate, and adding hexane to the mixture, a white solid precipitated, which was characterized as [Pd{C(=CH$_2$)-N(Xy)C(=S)NHMe}(dppp)][BF$_4$] (**7**) on the basis of spectroscopic, analytical, and structural studies. As for compounds **3**−**6**, the ^{31}P{^{1}H} NMR spectrum of **7** shows two doublets, i.e., the expected AB pattern associated with the two inequivalent phosphorus atoms of the coordinated dppp. The vinylic protons appear in the ^{1}H NMR spectrum as doublets of doublets (δ = 3.89 and 4.18 ppm) due to coupling with the two different phosphorus environments. The ^{13}C NMR spectrum shows two doublets of doublets (at 111.5 and 163.5 ppm, respectively) for the vinylic carbons, the latter corresponding to the carbon directly bound to palladium; another doublet of doublets is observed at 175.5 ppm for the carbon of the C=S moiety. The coupling of these carbons to the phosphorus atoms of the phosphine clearly indicates that the organic fragment is coordinated to the palladium center. The elemental analyses and the mass spectrum of **7** (with a molecular peak at 723 amu, which corresponds to **7** − BF$_4$) are also consistent with this formulation. The molecular structure of the compound was determined by X-ray crystallography (see next section), which confirmed the proposed formulation.

The above results indicate that the outcome of the reaction between **1** or **2** and RNCS is the same whether dppe or dppp is used.

Structural Characterization of 4, 6, and 7. A single-crystal X-ray analysis confirmed the structure of **4** (see Figure 1) as being the product resulting from the reaction between the coordinated iminoacyl group of **1** and phenylisocyanate. The geometry at palladium is distorted square planar with *cis* angles at the metal in the range 81.1(2)−98.9(1)°. The coordination plane is slightly twisted, the {PdP$_2$} and {Pd,C(2),O(4)} planes being inclined by ca. 5°. The *C,O* chelate ring has a folded conformation, with the palladium atom lying 0.178 Å out of the plane of the remaining four atoms, which are coplanar to within 0.003 Å. The pattern of bonding to palladium is unexceptional (Table 1) and matches closely to that observed in, for example, bis(trimethylphosphine)(prop-2-en-2-yl-1-carboxylato-*O*)palladium,[14] with the bond to phosphorus *trans* to carbon being more than 0.1 Å longer than that *trans* to oxygen. There are no previously reported examples of related vinylurea *C,O* chelates coordinated to palladium, and as such it is interesting to detail the bonding within this fragment. There is a clear pattern of delocalization in the bonds attached to C(4), whereas C(2)−N(3) is of "normal" single bond length (see Table 1 for bond distances). The 2,6-dimethylphenyl ring is inclined by ca. 84° to the chelate ring, and there is a ca. 45° torsional twist about N(5)−C(19).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 4, Both Independent Molecules of 6 (labeled 6a and 6b, respectively), and 7

	4 [X = O]	**6a** [X = S]	**6b** [X = S]	**7** [X = S]
Pd−C(2)	2.051(5)	2.051(6)	2.058(6)	2.053(6)
Pd−X(4)	2.064(4)	2.2760(17)	2.2894(15)	2.302(2)
Pd−P(1)	2.3416(13)	2.3089(16)	2.3364(16)	2.338(2)
Pd−P(2)	2.2266(14)	2.2807(16)	2.2908(16)	2.287(2)
C(1)−C(2)	1.323(8)	1.339(10)	1.327(10)	1.343(10)
C(2)−N(3)	1.447(7)	1.439(8)	1.463(7)	1.446(9)
N(3)−C(4)	1.353(7)	1.326(9)	1.324(8)	1.346(10)
C(4)−X(4)	1.271(7)	1.706(6)	1.718(6)	1.719(7)
C(4)−N(5)	1.342(8)	1.349(10)	1.345(8)	1.333(10)
C(2)−Pd−X(4)	81.10(18)	84.73(19)	84.31(17)	84.3(2)
C(2)−Pd−P(2)	95.23(15)	100.55(19)	97.07(17)	93.3(2)
X(4)−Pd−P(2)	175.81(12)	170.06(7)	176.11(7)	172.96(8)
C(2)−Pd−P(1)	176.2(2)	174.22(18)	177.41(18)	169.8(2)
X(4)−Pd−P(1)	98.88(11)	90.36(6)	93.99(6)	92.76(6)
P(2)−Pd−P(1)	84.93(5)	84.76(6)	84.75(6)	90.73(6)

Complex **6**, the thio analogue of **4**, crystallizes with two independent molecules in the asymmetric unit, the only significant difference between them being in the torsional twist about the N−C$_6$H$_5$ bond, which is ca. 56° in one molecule and ca. 45° in the other. The bond lengths do not show any major differences (Table 1). The palladium coordination plane in **6** exhibits a tetrahedral distortion similar to that seen in **4**, with the {PdP$_2$} and {Pd,C(2),S(4)} planes inclined to each other by ca. 9° and 4° in the two independent molecules. The vinylthiourea chelate ring has a folded conformation, with the palladium atom lying 0.280 Å [0.388 Å] out of the plane of the remaining four atoms, which are coplanar to within 0.005 Å [0.008 Å] (values for the second independent molecule are given in brackets). The Pd−C(2) and Pd−P(1) bond lengths do not differ markedly from their counterparts in **1**, but the Pd−P(2) distance is significantly increased, reflecting the differing *trans* influence of sulfur vis-à-vis oxygen. Within the "thiourea" fragment there is a slight shortening of the N(3)−C(4) bond length compared with its value in **4**; the C(4)−N(5) distance is unchanged.

The closely related dppp complex **7**, with a methyl substituent at the N(5) position replacing the phenyl

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[14] Kakino, R.; Nagayama, K.; Shimizu, I.; Yamamoto, A. *Chem. Lett.* **1999**, 685.

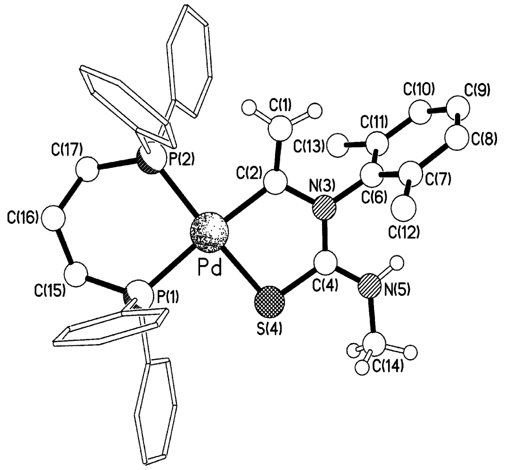
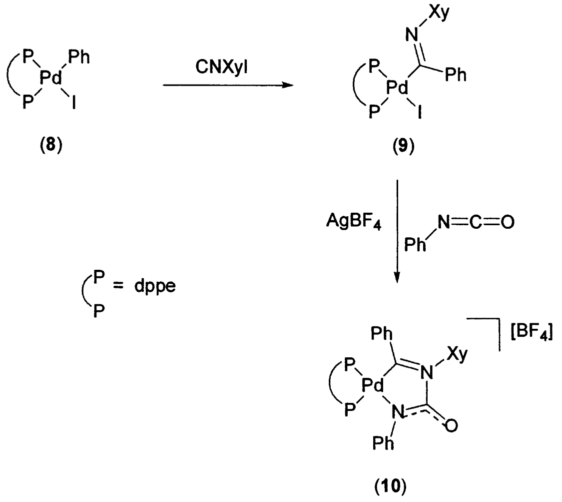


Figure 2. Molecular structure of the cation in **7**.

Scheme 2



group in both **4** and **6**, has a very similar gross structure (see Figure 2). There is a small (ca. 12°) tetrahedral distortion in the palladium coordination plane, and the palladium atom lies 0.241 Å out of the C_2NS chelate ring plane (which is coplanar to within 0.007 Å). The only noteworthy difference in the palladium coordination distances is a slight increase in the length of the bond to the sulfur atom [2.302(2) Å here, cf. 2.276(2) and 2.289(2) Å in **6**]. The geometry of the vinylthiourea fragment (Table 1) is essentially the same as that seen in **6**, but with the N(3)−C(4) linkage reverting to a value closer to that seen in **4** (vide supra).

The analytical, spectroscopic, and structural characterizations of compounds **3**−**7** demonstrate that the reaction between the coordinated iminoacyl fragment and isocyanates (and isothiocyanates) leads to the unprecedented formation of a vinyl-urea coordinated to palladium. The synthesis of this product is likely to be the result of a nucleophilic attack by the nitrogen of the iminoacyl fragment at the electrophilic carbon of the incoming isocyanate (or isothiocyanate) followed by a migration of one of the iminoacyl's methyl protons to the nitrogen of the incoming substrate. A similar mechanism has been proposed by Werner in an analogous reaction with cobalt complexes.[9]

The formation of such an organic fragment opens up the possibility of using this organometallic transformation for the synthesis of a wide range of asymmetric vinyl ureas (and thioureas) as well as the possibility of using these fragments for the synthesis of some drug candidates.[15]

Reaction of RNCE with Pd{C(Ph)═NXy}(I)(P−P). As indicated in the Introduction, the insertion of O-, N-, and S-containing unsaturated species into metal−carbon bonds is a potentially attractive organometallic transformation since it could yield organic precursors for the synthesis of a wide range of heteroatomic organic species. The original motivation to study the reactions between palladium−iminoacyl complexes and R−N═C═E (E = O, S) was to investigate the possibility of these species undergoing an insertion reaction. However, as has been discussed in the previous section, our results indicate that the reactions between the iminoacyl complex **1** and RNCE (R = Me, Ph; E = S; R = Et, Ph; E = O) do not lead to insertion products but to an addition product that involves the migration of one of the iminoacyl's protons to the nitrogen of the isocyanate (or isothiocyanate). It is possible that this proton migration to form the vinyl ureas and thioureas prevents the insertion reaction from occurring. Consequently, to gain a better understanding of these reactions and try to favor the insertion of RNCE into the palladium−carbon bond, it was decided to carry out reactions analogous with the ones discussed in the previous sections but using the complex Pd{C(Ph)═NXy}(I)(dppe) (**9**). The presence of a phenyl group instead of the methyl in the imidoyl group should stop the proton migration and hence modify the reactivity of the system.

The new imidoyl complex **9** was readily prepared by reacting Pd(Ph)(I)(dppe) (**8**) with 1 equiv of CNXy (see Scheme 2). Within 1 h the complete transformation of this species to the CNXy-inserted compound **9** was observed. In contrast to the analogous reaction involving the insertion of isocyanides into palladium−methyl bonds,[11] in this reaction no multiple-insertion products were observed. The new complex **9** was fully characterized by NMR and IR spectroscopies, FAB(+) mass spectrometry, and elemental analysis, which confirmed the formation of the desired product. Particularly characteristic is the IR spectrum, which shows a strong band at 1602 cm^{-1} (C═N) corresponding to inserted isocyanide.

Once it was fully characterized, compound **9** was reacted in situ with 1 equiv of RNCE (R = Ph and E = O; R = Ph, Me and E = S) in the presence of $AgBF_4$. With PhNCO, after the immediate precipitation of AgI, the reaction mixture was stirred for 10 min and then filtered. The $^{31}P\{^1H\}$ NMR spectrum of the mixture showed the presence of only one pair of doublets at 57.5 and 50.4 ppm (consistent with a complex having two different phosphorus centers coupling to each other) shifted relative to the starting materials. Reduction of the solvent to half its volume and careful addition of a

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[15] For examples of asymmetric vinylureas and their use in organic synthesis see: (a) McCusker, J. E.; Main, A. D.; Johnson, K. S.; Grasso, C. A.; McElwee-White, L. *J. Org. Chem.* **2000**, *65*, 5216, and references therein. (b) Murai, T.; Kasai, Y.; Ishihara, H.; Kato, S. *J. Org. Chem.* **1992**, *57*, 5542. (c) Dragovich, P. S.; Barker, J. E.; French, J.; Imbacuan, M.; Kalish, V. J.; Kissinger, C. R.; Knighton, D. R.; Lewis, C. T.; Moomaw, E. W.; Parge, H. E.; Pelletier, L. A. K.; Prins, T. J.; Showalter, R. E.; Tatlock, J. H.; Tucker, K. D.; Villafranca, J. E. *J. Med. Chem.* **1996**, *39*, 1872.

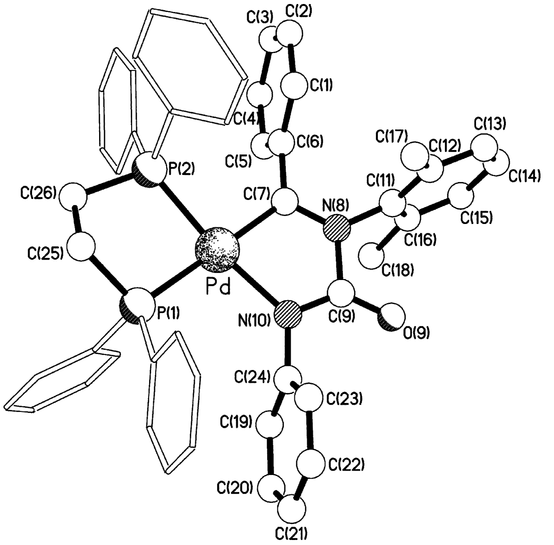


Figure 3. Molecular structure of the cation in **10**.

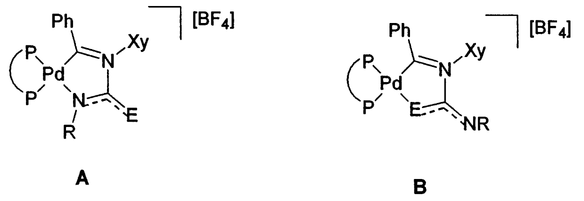
Table 2. Selected Bond Lengths (Å) and Angles (deg) for 10

Pd−C(7)	2.033(6)	Pd−N(10)	2.061(5)
Pd−P(1)	2.3372(13)	Pd−P(2)	2.2618(14)
C(7)−N(8)	1.292(8)	N(8)−C(9)	1.500(7)
C(9)−O(9)	1.216(8)	C(9)−N(10)	1.300(8)
C(7)−Pd−N(10)	79.1(2)	C(7)−Pd−P(2)	95.82(16)
N(10)−Pd−P(2)	171.83(15)	C(7)−Pd−P(1)	177.96(17)
N(10)−Pd−P(1)	101.33(13)	P(2)−Pd−P(1)	83.53(5)

layer of diethyl ether resulted in the formation of a crystalline solid, which on the basis of structural, spectroscopic, and analytical data was formulated as the new palladium complex [Pd{C(Ph)=N(Xy)C(=O)(=NPh)}(dppe)][BF_4] (**10**) (see Scheme 2 and Figure 3). The IR spectrum of **10** shows strong bands characteristic of C=O (1712 cm^{-1}), C=N (1590 cm^{-1}), and BF_4 (1052 cm^{-1}), which supports the above formulation. The molecular peak in the FAB(+) mass spectrum at 830 amu and the elemental analyses are also consistent with the proposed formulation.

To determine the bonding pattern for the new complex **10** and definitively establish its exact nature, a single-crystal X-ray analysis was carried out. This study confirmed **10** to be a palladium complex with a unique *N*,*C* bound chelating urea-type structure (see Figure 3) resulting from the addition of PhNCO to the coordinated imidoyl moiety −C(Ph)=NXy (see Scheme 2). In this compound the geometry at palladium is distorted square planar with *cis* angles in the range 79.1(2)−95.8(1)°, the palladium and its four coordinated atoms being coplanar to within 0.064 Å. The *N*,*C* chelate ring has a folded geometry, with the metal center lying 0.255 Å out of the plane of the remaining four atoms, which are coplanar to within 0.002 Å. The palladium coordination distances are unexceptional, with the Pd−P bond *trans* to carbon being ca. 0.08 Å longer than that *trans* to nitrogen. Within the *N*,*C* chelate ring C(7)−N(8) has "normal" double-bond character and N(8)−C(9) is a long single bond, while both C(9)−N(10) and C(9)−O(9) exhibit significant double-bond character (Table 2). The bonds in the N(10)−C(9)−O(9) fragment can thus be better described as a delocalized system with a partial negative charge (while the nitrogen from the imidoyl fragment holds a partial positive charge). It is noteworthy that there is a significant enlargement of the N(10)−C(9)−O(9) angle [131.9(6)°] compared with N(8)−C(9)−O(9) [115.9(5)°], reflecting a distinct contribution from a resonance hybrid involving a donation of the N(8) "lone pair" into the Ph−N=C=O carbon center.

Scheme 3



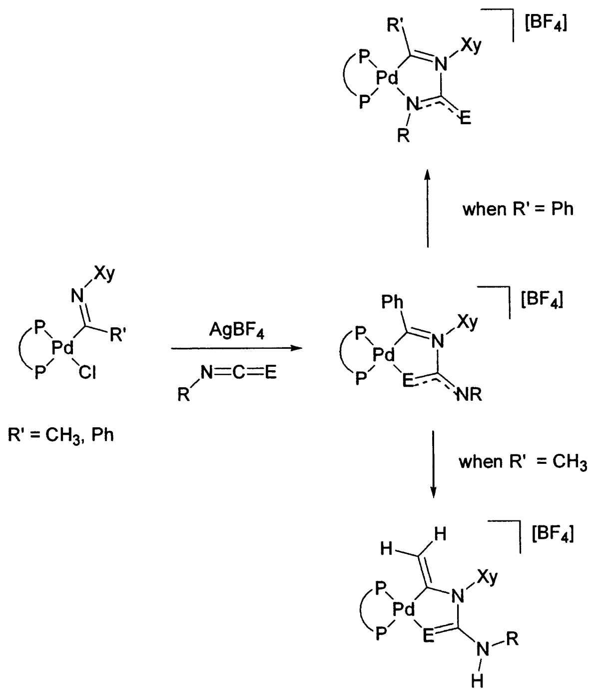
These results indicate that PhNCO does not insert into the palladium−imidoyl bond of **9**. In contrast to the products obtained in the reaction between RNCO and **1**, with complex **9** the proton migration from the imidoyl R group to the nitrogen atom of PhNCO is obviously not observed (since R = Ph and not Me). Instead, a nucleophilic attack from the nitrogen of the imidoyl moiety to the carbon of the isocyanate takes place, generating a new C−N bond, which results in the formation of an asymmetric urea.

To investigate if the coordinated imidoyl fragment would react in an analogous manner with thiocyanates, Pd{C(Ph)=NXy}(I)(P−P) (prepared in situ from **8** and CNXy) was reacted with 1 equiv of RNCS (R = Me, Ph) in the presence of $AgBF_4$. For both isothiocyanates, the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, which showed the quantitative conversion of **9** to a new product (in each one of the two reactions) within 10 min. After filtering the AgI and reducing the volume, the products were precipitated from the corresponding reaction mixtures. On the basis of spectroscopic and analytical techniques these solids were characterized as the addition products [Pd{C(Ph)=N(Xy)C(=S)(=NMe)}(dppe)][BF_4] (**11**) and [Pd{C(Ph)=N(Xy)C(=S)(=NPh)}(dppe)][BF_4] (**12**), respectively.

The $^{31}P\{^1H\}$ NMR spectra of both **11** and **12** consist of a pair of doublets associated with the presence of two inequivalent phosphorus atoms in these complexes. The elemental analyses and FAB(+) mass spectra of both compounds are also consistent with the proposed formulations. It is worth noting that in complexes **10**−**12** there are two potential ways in which the organic moiety can bind to the metal center (see Scheme 3): via the nitrogen (structure A) or via the oxygen/sulfur atom (structure B).

The X-ray crystal structure of **10** has demonstrated that in this compound the coordination is via the nitrogen and not the oxygen atom (which is consistent with the hard−soft properties of the metal and the donor groups). In contrast, in compounds **11** and **12**, coordination to palladium via the softer sulfur atom would be expected on the basis of soft−soft interactions. Although no structural information could be obtained for these compounds, spectroscopic data suggest that this is indeed the favored coordination mode. In particular, the ^1H NMR spectrum of compound **11** provides strong evidence, with the methyl group on the nitrogen of the former methyl isothiocyanate appearing as a

Scheme 4



singlet at $\delta = 3.26$ ppm. If the nitrogen was directly coordinated to the palladium (structure A in Scheme 3), the methyl protons would couple to the two phosphorus atoms of dppe, giving a doublet of doublets instead of the observed singlet.

Proposed Pathway for the Reaction between Palladium−Imidoyl Complexes and RNCE. The results discussed in the previous sections suggest that the reaction between palladium−imidoyl complexes and RNCE (E = O, S) involves a nucleophilic attack of the imidoyl nitrogen on the carbon of the isocyanate (or isothiocyanate). This leads to the formation of species such as **10**−**12**, which are the isolated products when the imidoyl group coordinated to palladium is −C(Ph)=NXy (see Scheme 4). In contrast, the reaction between RNCE and compound **1** (where the imidoyl fragment is −C(Me)=NXy) yields compounds **3**−**7**. It is likely that the formation of these products follows the same reaction path described for compounds **10**−**12**, followed by the migration of one of the iminoacyl methyl protons to the nitrogen of the RNCE group.

Evidence that products analogous to **10**−**12** are intermediates in the syntheses of **3**−**7** comes from the reaction between **1** and PhNCO. As was described above, the formation of an intermediate compound was detected by $^{31}P\{^1H\}$ NMR spectroscopy in the early stages of this reaction. The chemical shifts of the two doublets observed for this intermediate (58.9 and 50.1 ppm) are very similar to those observed for **10** (57.5 and 50.4 ppm). Although we were not able to isolate and purify this species to fully characterize it (due to the fact that it converts to **4**), it is reasonable to assume that an intermediate species analogous to **10** is probably forming in the course of the reaction to obtain complexes **3**−**7** (see Scheme 4).

Protonation of the Iminoacyl Group of Pd{C(Me)=NXy}(Cl)(dppe). To explore further the reactivity of the coordinated imidoyl groups and see under what conditions a potential insertion of RNCE could be favored, it was decided to investigate the effect of protonating the nitrogen of the iminoacyl group of compound **1**. With this the nucleophilicity of the nitrogen atom would be reduced and hence change the reactivity of this fragment.

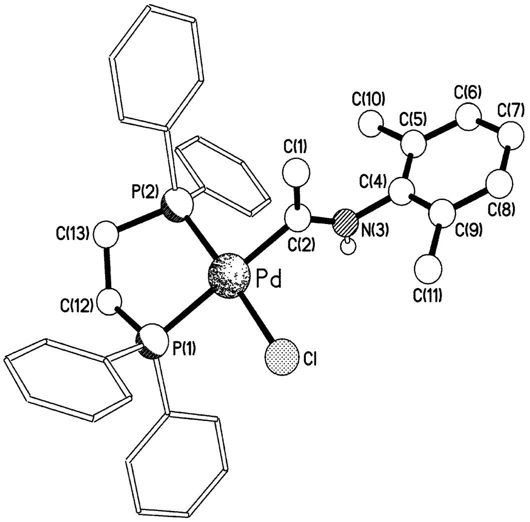
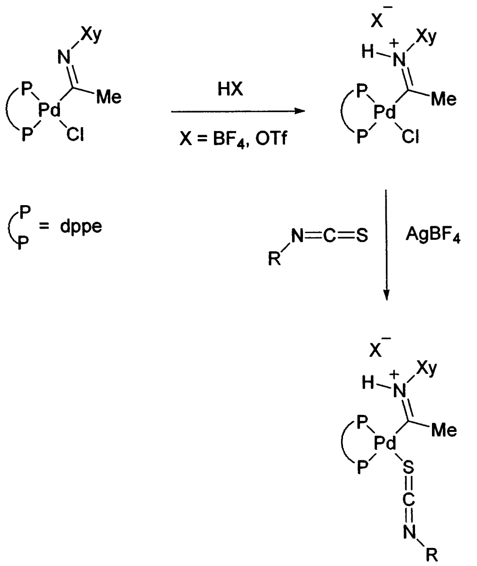


Figure 4. Molecular structure of the cation in **13**.

Scheme 5



The new compounds [Pd{C(Me)=NHXy}(Cl)(dppe)][X] (X = CF_3SO_3, **13**; X = BF_4, **14**) were readily prepared by addition of the corresponding acid to (dppe)Pd{C(Me)=NXy}Cl (see Scheme 5).

These compounds were characterized by spectroscopic, analytical, and structural techniques. Particularly informative is the presence of a singlet at 11.6 ppm (for X = CF_3SO_3) and 11.8 ppm (for X = BF_4) in the ^1H NMR spectra of **13** and **14**, which correspond to the N−H of the protonated iminoacyl groups. To study the structural effects on the iminoacyl complex induced by protonation, both complexes **13** and **14** were analyzed by X-ray crystallography (see Figure 4 for the molecular structure of **13**).

The coordination geometries for both compounds exhibit only small differences (see Table 3), and the protonated iminoacyl moiety has an essentially identical conformation in each case. The only notable difference

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 13 and 14

	13	14		13	14
Pd−C(2)	2.042(4)	2.036(4)	Pd−Cl	2.3338(13)	2.3582(11)
Pd−P(1)	2.3144(12)	2.3260(11)	Pd−P(2)	2.2558(12)	2.2566(11)
C(2)−N(3)	1.291(6)	1.299(6)	N(3)−C(4)	1.468(6)	1.455(6)
C(2)−Pd−P(2)	96.02(13)	96.97(12)	C(2)−Pd−P(1)	176.72(14)	170.84(12)
P(2)−Pd−P(1)	85.66(4)	84.51(4)	C(2)−Pd−Cl	86.82(13)	88.04(12)
P(2)−Pd−Cl	177.16(5)	174.13(4)	P(1)−Pd−Cl	91.49(4)	91.02(4)

between the two cations is in the orientation of the iminoacyl plane with respect to the metal coordination plane (ca. 78° in **13** and ca. 68° in **14**). In **13** the imino N−H group is hydrogen bonded to one of the oxygen atoms of the disordered (60/40) triflate anion: N···O, H···O 2.85, 1.96 Å, N−H···O 170° (major occupancy). In **14** this group is hydrogen bonded to an included water molecule with N···O, H···O 2.72, 1.83 Å and N−H···O 176°; the water protons are involved in hydrogen-bonding interactions to the fluorine atoms of disordered BF_4 anions.

Once the characterization of the protonated compounds was completed, the reaction of **14** with isothiocyanates was investigated. Addition of 1 equiv of MeNCS to **14** in the presence of $AgBF_4$ resulted in the formation of a white precipitate (AgCl) and a clear solution. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, which showed the complete conversion of **14** to a new product ($\delta = 54.4$ and 59.8 ppm) within 15 min. This product was isolated as a white solid and characterized on the basis of spectroscopic and analytic techniques as $[Pd\{C(Me){=}NHXy\}(dppe)(S{=}C{=}NMe)][BF_4]_2$ (**15**). The IR spectrum of this complex showed stretches associated with N−H (3448, 3230 cm^{-1}), terminally coordinated RNCS (2253 cm^{-1}), iminoacyl C═N (1564 cm^{-1}), and BF_4 (1062 cm^{-1}). The ^1H NMR spectrum showed a singlet for the methyl group of the MeNCS moiety, suggesting that the isothiocyanate coordinates via the sulfur (as would be expected) and not via the nitrogen (in which case coupling to the phosphorus of the dppe should be observed). The iminoacyl group in complex **15** remains protonated, as confirmed by a singlet at 12.0 ppm in the ^1H NMR spectrum. The formulation was further confirmed by FAB(+) mass spectrometry and elemental analyses.

The analogous complex $[Pd\{C(Me){=}NHXy\}(dppe)(S{=}C{=}NPh)][BF_4]_2$ (**16**) was prepared by reacting **14** with 1 equiv of PhNCS. As for **15**, the IR spectrum indicates that PhNCS is terminally coordinated to the palladium (2197 cm^{-1}). In the ^1H NMR spectrum a singlet at 11.78 ppm indicates that the iminoacyl group remains protonated. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets ($\delta = 54.6$ and 60.5 ppm) with values very similar to those seen for **15**. The FAB(+) mass spectrum and the elemental analyses are consistent with this formulation.

The results described above indicate that the protonation of **1** (to yield **13** and **14**) does indeed stop the nucleophilic attack by the nitrogen of the iminoacyl fragment to the carbon of the isothiocyanate. However, the desired insertion of isothiocyanate into the metal−carbon bond was not observed under these conditions; instead the terminally coordinated complexes **15** and **16** were obtained. Even after leaving these complexes in solution for prolonged periods of time, no further reactions were observed.

To explore the possibility of inducing the insertion of the coordinated isothiocyanate into the palladium−carbon bond (by adding a second coordinating species), compound **15** was reacted with 1 equiv of CNXy. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, which showed that within 15 min the complete conversion of **15** to a new product occurred. Addition of hexane to the reaction mixture precipitated a white solid, which, on the basis of spectroscopic and analytical data, was characterized as $[Pd\{C(Me){=}NHXy\}(dppe)(CNXy)][BF_4]_2$ (**17**). Clearly, this reaction led to the simple substitution of the coordinated isothiocyanate by isocyanide, and no further reactions were observed.

Conclusions

The results here presented have demonstrated that the insertion of the unsaturated species RNCE (E = O, S) into the Pd−C(R)═NXy bond is not facile. Instead, addition reactions involving the nucleophilic attack of the imidoyl nitrogen atom at the electrophilic carbon center of RNCE occur readily. These reactions have led to the formation of new N−C bonds, resulting in the synthesis of coordinated asymmetric ureas and thioureas which could potentially be interesting organic fragments for the synthesis of more complex structures.[15,16] The products obtained are highly dependent on the nature of the R group in the −C(R)═NXy fragment. When R = CH_3, the addition reaction is followed by the migration of one of the methyl protons to the nitrogen of the incoming RNCE. In the case of R = Ph this migration is not possible, and thus a product resulting from an addition reaction only is obtained. It has also been demonstrated that the nucleophilic attack by the imidoyl nitrogen can be prevented by protonation. This leads to the formation of species where both the imidoyl and RNCE groups are coordinated to the palladium without reacting with each other.

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. All commercially available starting materials were not further purified unless otherwise stated; however all liquid starting materials were dried over molecular sieves and thoroughly degassed by freeze−pump−

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(16) For recent examples where the insertion of isocyanides is a key step in palladium-mediated organic synthesis see: (a) Tanase, T.; Fukushima, T.; Nomura, T.; Yamamoto, Y.; Kobayashi, K. *Inorg. Chem.* **1994**, *33*, 32. (b) Vicente, J.; Abad, J. A.; Shaw, K. F.; Gil-Rubio, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1997**, *16*, 4557. (c) Vicente, J.; Saura-Llamas, I.; Grünwald, C.; Alcaraz, C.; Jones, P. G.; Bautista, D. *Organometallics* **2002**, *21*, 3587. (d) Saluste, C. G.; Whitby, R. J.; Furber, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4156. (e) Curran, D. P.; Du, W. *Org. Lett.* **2002**, *4*, 3215. (f) Vicente, J.; Abad, J. A.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2003**, *22*, 1967.

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_3PO_4, and TMS, respectively, as internal references. IR spectra were recorded on Research Series FT-IR using KBr disks in the range 4000−500 cm^{-1}. Elemental analyses were carried out at the London Metropolitan University. The complexes Pd(Me)(Cl)(COD),[17] Pd(Me)(Cl)(P−P) (P−P = dppp and dppe),[18] Pd{C(Me)=NXy}(Cl)(dppe),[9] Pd{C(Me)=NXy}(Cl)(dppp),[9] and Pd(Ph)(I)(PPh$_3$)$_2$[19] were synthesized according to previously reported procedures.

Synthesis of [Pd{C(=CH$_2$)N(Xy)C(=O)NHEt}(dppe)][BF$_4$] (3). Ethyl isocyanate (13.9 μL, 0.18 mmol) was added to a stirring solution of Pd{C(Me)=NXy}(Cl)(dppe) (0.11 g, 0.16 mmol) in CH_2Cl_2 (20 mL). $AgBF_4$ (0.03 g, 0.17 mmol) was added as a solid to the reaction mixture. AgCl immediately precipitated from the yellow solution. The reaction mixture was stirred for a further 10 min, after which time the AgCl was filtered off. A yellow solid (characterized as **3**) was obtained by concentrating the mixture under reduced pressure (to approximately 10 mL) followed by addition of hexane (10 mL). Yield: 0.08 g; 0.10 mmol; 90%. Anal. Found: C, 55.73; H, 5.00; N, 3.17. Calcd for $C_{39}H_{41}N_2P_2OBF_4Pd\cdot0.5CH_2Cl_2$: C, 55.72; H, 4.97; N, 3.17. IR (ν (KBr)): 3420 (N−H), 3056 (alkene C−H), 1598 (C=O),[20] 1566 s, 1541 s (C=C), 1102, 1058 (BF$_4$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 62.2 (d, 1P, $^2J_{PP}$ = 32 Hz), 42.4 (br d, 1P, $^2J_{PP}$ = 32 Hz). ^{1}H NMR (CDCl$_3$): δ 1.09 (t, 3H, (NCH$_2$CH_3), $^3J_{HH}$ = 7.0 Hz), 2.13 (s, 6H, C$_6$H$_3$(CH_3)$_2$), 2.66 (m, 4H, (PCH_2CH_2P)), 3.33 (q, 2H, HNCH_2CH$_3$, $^3J_{HH}$ = 7.0 Hz), 3.89 [dd, 1H, (dppe)PdC(=CH_2), $^4J_{PH}$ = 19.0 Hz, $^4J_{P'H}$ = 13.0 Hz), 4.85 (dd, 1H, (dppe)PdC(=CH_2), $^4J_{PH}$ = 5.0 Hz, $^4J_{PH}$ = unresolved), 7.12−7−28 (m, 4H, C$_6H_3$(CH$_3$)$_2$ + EtNH), 7.40−7.88 (m, 20H, PC$_6H_5$). ^{13}C{^{1}H} (CDCl$_3$): δ 14.2 (s, NCH$_2$$CH_3$), 17.8 (s, C$_6H_3$($CH_3$)$_2$), 22.5 (br, (P$CH_2CH_2$P)), 31.5 (br, (PCH$_2$$CH_2$P)), 36.6 (s, N$CH_2CH_3$), 103.9 (br, PdC(=$CH_2$)), 125.8−136.8 (several signals assigned to the phenyl rings), 160.7 (dd, (dppe)PdC(=CH$_2$), $^2J_{PCtrans}$ = 138 Hz, $^2J_{PCcis}$ = unresolved), 163.7 (br, (C=O)). MS (FAB$^+$; *m/z* (relative intensity)): 721 (100) [M − BF$_4$]$^+$, 504 (16) [(dppe)Pd]$^+$.

Synthesis of [Pd{C(=CH$_2$)N(Xy)C(=O)NHPh}(dppe)][BF$_4$] (4). Phenyl isocyanate (26.1 μL, 0.24 mmol) was added to a stirring solution of Pd{C(Me)=NXy}(Cl)(dppe) (0.15 g, 0.22 mmol) in CH_2Cl_2 (25 mL). $AgBF_4$ (0.043 g, 0.22 mmol) was added as a solid to the reaction mixture. AgCl immediately precipitated from the yellow solution. The reaction mixture was stirred for a further 10 min. The reaction mixture was left to stir for 12 h, after which time the precipitated AgCl was filtered off to give a clear yellow solution. A yellow product was obtained (and characterized as **4**) by the reduction of the solvent to 10 mL and addition of hexane (15 mL). Yield: 0.13 g; 0.18 mmol; 81%. Anal. Found: C, 60.14; H, 4.93; N, 3.18. Calcd for $C_{43}H_{41}P_2N_2OBF_4Pd$: C, 60.27; H, 4.82; N, 3.27. IR (ν (KBr)): 3321 (N−H), 3056 (alkene C−H), 1593w (C=O),[19] 1555s, 1533s (C=C), 1102, 1064 (BF$_4$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 43.8 (d, 1P, $^2J_{PP}$ = 32 Hz), 62.8 (d, 1P, $^2J_{PP}$ = 32 Hz). ^{1}H NMR (CD$_2$Cl$_2$): δ 2.22 (s, 6H, C$_6$H$_3$(CH_3)$_2$), 2.58 (m, 4H, (PCH_2CH_2P)), 3.48 (dd, 1H, (dppe)PdC(=CH_2), $^4J_{PH}$ = 6.5 Hz, $^4J_{P'H}$ = unresolved], 4.02 (dd, 1H, (dppe)PdC(=CH_2), $^4J_{PH}$ = 18 Hz, $^4J_{PH}$ = 13 Hz), 6.45 (s br, 1H, NH), 7.1−7−78 (m, 28H, C$_6H_3$(CH$_3$)$_2$ + 4 × PC$_6H_5$ + HN(C$_6H_5$)). MS (FAB$^+$; *m/z* (relative intensity): 769 (100) [M − BF$_4$]$^+$, 650 (15) [M − BF$_4$ − {N(Ph)NHC=O)}]$^+$, 504(26) [(dppe)Pd]$^+$.

Synthesis of [Pd{C(=CH$_2$)N(Xy)C(=S)NHPh}(dppe)][BF$_4$] (6). Phenyl isothiocyanate (28.7 μL, 0.24 mmol) was added to a stirring solution of Pd{C(Me)=NXy}(Cl)(dppe) (0.15 g, 0.22 mmol) in CH_2Cl_2 (25 mL). $AgBF_4$ (0.04 g, 0.22 mmol) was added as a solid. AgCl immediately precipitated from the yellow solution, and within 5 min the solution turned pale yellow. The reaction mixture was stirred for a further 10 min, after which time the AgCl was filtered off. A pale yellow solid (characterized as **6**) was obtained by the reduction of the solvent to 10 mL followed by addition of hexane (15 mL). Yield: 0.13 g; 0.15 mmol; 68%. Anal. Found: C, 57.11; H, 4.63; N, 2.92. Calcd for $C_{43}H_{41}N_2P_2SBF_4Pd\cdot0.5CH_2Cl_2$: C, 57.02; H, 4.62; N, 3.06. IR (ν (KBr)): 3448 (N−H), 3054 (alkene C−H), 1592 m, 1534 s (C=C), 1359 (C=S), 1102, 1053 (BF$_4$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 56.9 (d, 1P, $^2J_{PP}$ = 32 Hz), 46.9 (d, 1P, $^2J_{PP}$ = 33 Hz). ^{1}H NMR (CDCl$_3$): δ 2.16 (s, 6H, C$_6$H$_3$(CH_3)$_2$), 2.58 (m, 4H, (PCH_2CH_2P)), 4.10 (m, 1H, PdC(=CH_2)), 4.29 (m, 1H, PdC(=CH_2)), 7.01 (br s, PhNH), 7.17−7−84 (m, 3H, C$_6H_3$(CH$_3$)$_2$, + 20H, 4 × PC$_6H_5$ + 5H, C$_6H_5$). ^{13}C{^{1}H} (CDCl$_3$): δ 17.8 (s, C$_6$H$_3$(CH$_3$)$_2$), 25.8 (br, (PCH$_2$CH$_2$P)), 30.6 (br, (PCH$_2$$CH_2$P)), 113.2 (br, PdC(=$CH_2$)), 126.4−136.4 (several signals assigned to the phenyl rings of dppe and Xy and phenyl group), 163.2 (dd, PdC(=CH$_2$), $^2J_{CPtrans}$ = 136 Hz, $^2J_{CPcis}$ = 2 Hz), 176.4 (dd, (C=S), $^3J_{PC}$ = 14 Hz, $^3J_{PC}$ = 3 Hz). MS (FAB$^+$ *m/z* (relative intensity)): 785 (100) [M − BF$_4$]$^+$, 504 (10) [(dppe)Pd]$^+$.

Synthesis of [Pd{C(=CH$_2$)N(Xy)C(=S)NHMe}(dppp)][BF$_4$] (7). Methyl isothiocyanate (0.016 g, 0.23 mmol) was added to a stirring solution of Pd{C(Me)=NXy}(Cl)(dppp) (0.15 g, 0.21 mmol) in CH_2Cl_2 (25 mL). $AgBF_4$ (0.04 g, 0.21 mmol) was added to the reaction mixture as a solid. AgCl immediately precipitated from the yellow solution. The reaction mixture was stirred for a further 10 min, after which time the AgCl was filtered off. The mixture was concentrated under reduced pressure to 10 mL, and hexane was added until the solution turned cloudy. The solution was then filtered, and then the solvent was removed under reduced pressure. The solid residue was washed with diethyl ether (20 mL) to produce a fine white powder (which was characterized as **7**). Yield: 0.12 g; 0.15 mmol; 69%. Anal. Found: C, 56.68; H, 5.00; N, 3.41. Calcd for $C_{39}H_{41}P_2PdN_2SBF_4$: C, 56.78; H, 5.01; N, 3.41. IR (ν (KBr)): 3386 (N−H), 3054 (alkene C−H), 1560s (C=C), 1262m (C=S), 1099, 1057 (BF$_4$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −1.8 (d, 1P, $^2J_{PP}$ = 63 Hz), 14.0 (d, 1P, $^2J_{PP}$ = 63 Hz). ^{1}H NMR (CDCl$_3$): δ 1.93 (s, 6H, C$_6$H$_3$(CH_3)$_2$), 2.01 (m, 2H, (PCH$_2$CH_2CH$_2$P)), 2.55 (m, 4H, (PCH_2CH$_2$CH_2P)), 2.87 (d, 3H, HNCH_3, $^3J_{HH}$ = 4.5 Hz), 3.89 (dd, 1H, PdC(=CH$_2$), $^4J_{PH}$ = 7.0 Hz, $^4J_{P'H}$ = unresolved), 4.18 (dd, 1H, PdC(=CH_2), $^4J_{PH}$ = 17.5 Hz, $^4J_{P'H}$ = unresolved), 5.39 (m, 1H, CH$_3$NH), 7.12−7−24 (m, 3H, C$_6H_3$(CH$_3$)$_2$), 7.32−7.74 (m, 20H, 4 × PC$_6H_5$). ^{13}C{^{1}H} (CDCl$_3$): δ 17.6 (s, C$_6$H$_3$(CH$_3$)$_2$), 18.7 (s, (PCH$_2$$CH_2CH_2$P)), 24.5 (dd, (P$CH_2CH_2CH_2$P), $^1J_{PC}$ = 25 Hz, $^2J_{P'C}$ = 5 Hz), 28.6 (dd, (PCH$_2$CH$_2$$CH_2$P), $^1J_{PC}$ = 31 Hz, $^2J_{PC}$ = 12 Hz), 32.2 (s, (N-CH$_3$)), 111.5 (dd, PdC(=CH$_2$), $^3J_{PCtrans}$ = 16 Hz, $^3J_{PCcis}$ = 6 Hz), 128.8−136.2 (several signals assigned to the phenyl rings of dppe and Xy group), 163.8 (dd, PdC(=CH$_2$), $^2J_{CPtrans}$ = 138 Hz, $^2J_{CPcis}$ = 5 Hz), 175.5 (dd, (C=S), $^3J_{PC}$ = 14 Hz, $^3J_{PC}$ = 3 Hz). MS (FAB$^+$ *m/z* (relative intensity)): 723 (100) [M − BF$_4$]$^+$, 504 (9) [(dppe)Pd]$^+$.

Synthesis of Pd(Ph)(I)(dppe) (8). 1,2-Bis(diphenylphosphino)ethane (0.95 g, 2.40 mmol) was added to a solution of Pd(Ph)(I)(PPh$_3$)$_2$ (2.0 g, 2.40 mmol) in toluene (65 mL). A precipitate formed after ca. 2 min. The mixture was allowed to stir for 1 h and then filtered. The resulting filtrate was washed with toluene (20 mL) and diethyl ether (20 mL). Yield: 1.25 g; 1.7 mmol; 74%. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 49.5 (d, 1P, $^2J_{PP}$ = 28 Hz), 34.5 (d, 1P, $^2J_{PP}$ = 28 Hz). ^{1}H NMR (CDCl$_3$): δ 2.28 (m, 4H, (PCH_2CH_2P)), 6.67 (m, 3H, (3,4,5-Pd-

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[20] The C=O stretching frequency is unusually low; however, this is not unprecedented for five-membered palladacycles where the oxygen of a carbonyl group coordinates to the metal center. See for example: (a) Brumbaugh, J. S.; Whittle, R. R.; Parvez, M.; Sen, A. *Organometallics* **1990**, *9*, 1735. (b) Markies, B. A.; Rietveld, M. H. P.; Boersman, J.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **1992**, *424*, C12.

C_6H_5)), 7.06 (m, 2H, (2,6-Pd-C_6H_5)), 7.40 (m, 14H, 4 × (3,4,5-P-C_6H_5) + 1 × (2,6-P-C_6H_5)), 7.90 (m, 1 × (2,6-P-C_6H_5)).

Synthesis of Pd{C(Ph)=NXy}(I)(dppe) (9). 2,6-Dimethylphenyl isocyanide (0.06 g, 0.42 mmol) was added to a solution of (dppe)Pd(Ph)I (0.30 g, 0.42 mmol) in THF (30 mL). The resulting mixture was stirred for 2 h. A product was obtained by concentrating the reaction mixture under reduced pressure (to about 10 mL) followed by addition of hexane (20 mL). The resulting pale yellow solid (characterized as **9**) was washed with diethyl ether (20 mL). Yield: 0.32 g; 0.38 mmol; 91%. Anal. Found: C, 58.49; H, 4.50; N, 1.69. Calcd for $C_{41}H_{38}NP_2PdI$: C, 58.62; H, 4.56; N, 1.67. IR (ν (KBr)): 1602m, 1570s (N=C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 41.9 (d, 1P, $^2J_{PP}$ = 43 Hz), 32.2 (d, 1P, $^2J_{PP}$ = 42 Hz). ^1H NMR (CD_2Cl_2): δ 1.87 (s, 6H, $(CH_3)_2C_6H_3NC$), 2.02 (br m, 2H (PCH_2CH_2P)), 2.25 (br m, 2H (PCH_2CH_2P)), 6.60−7.83 (m, 28H, (4 × P-Ph) + ($C_6H_3\{CH_3\}_2$) + (C_6H_5)). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 20.2 (C_6H_3-$(CH_3)_2$), 24.2 (dd, (PCH_2CH_2P), $^1J_{PC}$ = 25 Hz, $^2J_{P'C}$ = 12 Hz), 31.5 [dd, (PCH_2CH_2P), $^1J_{PC}$ = 32 Hz, $^2J_{PC}$ = 24 Hz), 121.4−133.7 (several signals assigned to the phenyl rings of dppe, Xy and Ph groups), 143.2 (dd, PdC{=NR}1-C_6H_5, $^3J_{PC(trans)}$ = 26 Hz, $^3J_{PC(cis)}$ = 15 Hz), 150.6 (dd, PdC{=NR}Ph, $^2J_{PCtrans}$ = 18 Hz, $^2J_{PCcis}$ = 5 Hz). MS (FAB$^+$ m/z (relative intensity)): 840 (97) [M$^+$], 712(10) [M$^+$ − I], 631(11) [(dppe)PdI$^+$].

Synthesis of [Pd{C(Ph)=N(Xy)C(=O)(=NPh)}(dppe)]-[BF$_4$] (10). To a solution of Pd(Ph)(I)(dppe) (0.15 g, 0.21 mmol) in CH_2Cl_2 (20 mL) was added 2,6-dimethylphenyl isocyanide (0.03 g, 0.21 mmol). An immediate color change to orange was observed. The mixture was allowed to stir at room temperature for 1 h to ensure that the isocyanide had inserted. Phenyl isocyanate (23 μL, 0.21 mmol) was then added to the reaction mixture followed by $AgBF_4$ (0.041 g, 0.21 mmol). This resulted in the precipitation of AgI from the solution. The reaction was stirred for a further 10 min and then filtered to removed the AgI. The solvent was then reduced to ca. 15 mL, and hexane was added to precipitate a yellow solid. The yellow solid was washed with two portions of diethyl ether (10 mL) and dried under vacuum. Yield: 0.15 g; 0.16 mmol; 78%. Anal. Found: C, 62.76; H, 4.68; N, 3.08. Calcd for $C_{48}H_{43}N_2P_2BF_4OPd$: C, 62.73; H, 4.72; N, 3.05. IR (ν (KBr)): 1712 (C=O), 1590 (C=N), 1052 (BF_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 57.5 (d, 1P, $^2J_{PP}$ = 34 Hz), 50.4 (d, 1P, $^2J_{PP}$ = 34 Hz). ^1H NMR ($CDCl_3$): δ 2.12 (s, 6H, $C_6H_3(CH_3)_2$), 2.22 (m, 4H, (PCH_2CH_2P)), 6.31−6.97 (m, 13H, PdC(=NXy)(C_6H_5), $C_6H_3(CH_3)_2$, C(O)NPh), 7.46 (m, 20H, 4 × P-(C_6H_5)). MS (FAB$^+$ m/z (relative intensity)): 831 (4) [M − BF_4]$^+$, 712 (100) [M − BF_4 − (PhN=C=O)]$^+$, 581 (26) [(dppe)PdPh]$^+$, 504 (21) [(dppe)Pd]$^+$.

Synthesis of [Pd{C(Ph)=N(Xy)C(=S)(=NMe)}(dppe)]-[BF$_4$] (11). Methyl isothiocyanate (0.02 g, 0.24 mmol) was added to a stirring solution of Pd{C(Ph)=NXy}(I)(dppe) (0.20 g, 0.24 mmol) in THF (25 mL). $AgBF_4$ (0.05 g, 0.24 mmol) was added to the reaction mixture as a solid. AgI immediately precipitated from the bright yellow solution. The reaction mixture was stirred for 10 min, after which time the AgI was filtered off. A yellow solid was obtained by concentrating the filtrate under reduced pressure (to approximately 10 mL) followed by addition of hexane (10 mL). Yield: 0.13 g; 0.15 mmol; 62%. Anal. Found: C, 59.26; H, 4.75; N, 3.16. Calcd for $C_{43}H_{41}N_2P_2SBF_4Pd$: C, 59.16; H, 4.73; N, 3.21. IR (ν (KBr)): 1609 (C=N), 1104, 1056 (BF_4). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 53.7 (d, 1P, $^2J_{PP}$ = 35 Hz), 52.5 (d, 1P, $^2J_{PP}$ = 34 Hz). ^1H NMR (CD_2Cl_2): δ 2.01 (s, 6H, $C_6H_3(CH_3)_2$), 2.38 (m, 4H, (PCH_2CH_2P)), 3.26 (s, 3H, NCH_3), 6.20−7.01 (m, 8H, C(=NR)C_6H_5 + C_6H_3-$(CH_3)_2$), 7.40−7.88 (m, 20H, 4 × PC_6H_5). $^{13}C\{^1H\}$ ($CDCl_3$): δ 18.2 (s, $C_6H_3(CH_3)_2$), 25.5 (dd, (PCH_2CH_2P), $^1J_{CP}$ = 31 Hz, $^2J_{CP'}$ = 16 Hz], 31.9 (br, (PCH_2CH_2P)), 39.8 (s, N(CH_3)), 125.5−133.2 (several signals assigned to the phenyl rings of dppe and Xy), 141.7 (d, PdC-Ph, J_{PC} = 2 Hz), 142.8 (dd, C=S, J_{PC} = 7 Hz, $J_{P'C}$ = 3 Hz). MS (FAB$^+$ m/z (relative intensity)): 785 (22) [M − BF_4]$^+$, 712 (100) [M − BF_4 − {(Me)N=C=S}]$^+$, 581 (29) [(dppe)PdPh]$^+$, 504 (22) [(dppe)Pd].

Synthesis [Pd{C(Ph)=N(Xy)C(=S)(=NPh)}(dppe)][BF$_4$] (12). To a solution of Pd(Ph)(I)(dppe) (0.15 g, 0.21 mmol) in THF (25 mL) was added 2,6-dimethylphenyl isocyanide (0.03 g, 0.21 mmol). An immediate color change to orange was observed. The mixture was allowed to stir at room temperature for 1 h to ensure that the isocyanide had inserted. Phenyl isothiocyanate (25 μL, 0.21 mmol) was then added to the stirring solution followed by $AgBF_4$ (0.041 g, 0.21 mmol). This resulted in the immediate precipitation of AgI from the solution. The reaction was stirred for a further 10 min and then filtered to remove the AgI. The solvent was reduced to ca. 15 mL, and hexane was added to precipitate a yellow solid. This solid was then washed with two portions of diethyl ether (10 mL) and dried under vacuum. Yield: 0.17 g; 0.18 mmol; 87%. Anal. Found: C, 61.62; H, 4.49; N, 3.13. Calcd for $C_{48}H_{43}N_2P_2BF_4SPd$: C, 61.56; H, 4.65; N, 3.00. IR (ν (KBr)): 1579 (C=N), 1055 (BF_4). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 54.2 (d, 1P, $^2J_{PP}$ = 33 Hz), 52.6 (d, 1P, $^2J_{PP}$ = 33 Hz). ^1H NMR (CD_2Cl_2): δ 2.15 (s, 6H, $C_6H_3(CH_3)_2$), 2.44 (m, 4H, (PCH_2CH_2P)), 6.31−7.81 (m, 33H, 4 × P-*Ph*, PdC(=N*Xy*)*Ph*, $C_6H_3(CH_3)_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.5 (s, $C_6H_3(CH_3)_2$), 25.9 (dd, (PCH_2-CH_2P), $^1J_{CP}$ = 28 Hz, $^2J_{CP'}$ = 17 Hz), 32.1 (dd, (PCH_2CH_2P), $^1J_{CP}$ = 39 Hz, $^2J_{CP}$ = 19 Hz), 120.7−133.4 (several signals assigned to the phenyl rings of dppe, Xy, and Ph groups), 142.4 (dd, PdC-Ph, $^2J_{CP(trans)}$ = 68 Hz, $^2J_{CP(cis)}$ = 6 Hz), 147.0 (s, C=S). MS (FAB$^+$ m/z (relative intensity)): 847 (34) [M − BF_4]$^+$, 712 (100) [M − BF_4 − (PhN=C=S)]$^+$, 581 (28) [(dppe)PdPh]$^+$, 504 (23) [(dppe)Pd]$^+$.

Synthesis of [Pd{C(Me)=NHXy}(Cl)(dppe)][OTf] (13). Pd{C(Me)=NXy}(Cl)(dppe) (0.30 g, 0.44 mmol) was dissolved in THF (30 mL) and HOTf (39 μL, 0.44 mmol) added dropwise to this solution. The original yellow color gradually disappeared to yield an almost colorless solution. The reaction mixture was filtered and all the solvent removed under reduced pressure from the filtrate. This resulted in an oil, which upon rapid stirring with diethyl ether (25 mL) yielded a white solid. Yield: 0.24 g; 0.29 mmol; 65%. Anal. Found: C, 54.16; H, 4.62; N, 1.41. Calcd for $C_{37}H_{37}NP_2PdClO_3SF_3\cdot C_4H_8O$: C, 54.19; H, 4.99; N, 1.54. IR (ν (KBr)): 3436 (N−H), 1628, 1570 (C=N), 1290, 1245, 1155, 1105, 1029 (OTf). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 49.5 (d, $^2J_{PP}$ = 23 Hz), 56.9 (d, $^2J_{PP}$ = 23 Hz). ^1H NMR (d_3-MeCN): δ 1.82 (s, 6H, $C_6H_3(CH_3)_2$), 1.90, (dd, 3H, Pd-C(CH_3), $^3J_{PH}$ = 4.5 Hz, $^3J_{P'H}$ = 1.0 Hz) 2.33 (m, 2H, PCH_2CH_2P), 2.78 (m, 2H, PCH_2CH_2P), 7.06 (m, 2H, 3,5-H on Xy group), 7.19 (m, 1H, 4-H on Xy group), 7.60 (m, 12H, P-Ph(3,4,5)), 7.87 (m, 8, P-Ph(2,6)], 11.6 (s, NH). MS (FAB$^+$ m/z (relative intensity)): 688 (83) [M − OTf]$^+$, 652 (12) [(M − OTf − Cl]$^+$, 504 (12) [(dppe)Pd]$^+$.

Synthesis of [Pd{C(Me)=NHXy}(Cl)(dppe)][BF$_4$] (14). Pd{C(=NXy)Me}(Cl)(dppe) (0.50 g, 0.73 mmol) was dissolved in CH_2Cl_2 (30 mL), and HBF_4 [(54 wt % in diethyl ether), 0.10 mL] was added dropwise to this solution. The original yellow color gradually disappeared to yield an almost colorless solution. The reaction mixture was filtered and all the solvent removed under reduced pressure from the filtrate. This resulted in an oil, which upon rapid stirring with diethyl ether (25 mL) yielded a white solid. Yield: 0.47 g; 0.61 mmol; 83%. Anal. Found: C, 55.82; H, 4.95; N, 1.76. Calcd for $C_{36}H_{37}NP_2$-$PdClBF_4$: C, 55.84; H, 4.82; N, 1.81. IR (ν (KBr)): 3448, 3238 (N−H), 1566 (C=N), 1103, 1083, 1054 (BF_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 48.6 (d, $^2J_{PP}$ = 22 Hz), 56.1 (d, $^2J_{PP}$ = 22 Hz). ^1H NMR ($CDCl_3$): δ 1.77 (s, 6H, $C_6H_3(CH_3)_2$), 2.03 (dd, 3H, Pd-C(CH_3), $^3J_{PH}$ = 4.0 Hz, $^3J_{P'H}$ = unresolved), 2.19 (m, 2H, PCH_2CH_2P)), 2.79 (m, 2H, (PCH_2CH_2P)), 6.90 (d, 2H, 3,5-C_6H_3-$(CH_3)_2$, $^3J_{HH}$ = 7.5 Hz), 7.04 (m, 1H, 4-$C_6H_3(CH_3)_2$), 7.53 (m, 12H, P-Ph(3,4,5)), 7.82 (m, 8, P-Ph(2,6)), 11.8 (s, NH). MS (FAB$^+$ m/z (relative intensity)): 688 (100) [M − BF_4]$^+$, 650 (19) [(dppe)PdC(Me)=NXy]$^+$, 504 (18) [(dppe)Pd]$^+$.

Table 4. Crystal Data, Data Collection, and Refinement Parameters for Compounds 4, 6, 7, 10, 13, and 14[a]

	4	6	7
formula	$[C_{43}H_{41}N_2OP_2Pd][BF_4]$	$[C_{43}H_{41}N_2SP_2Pd][BF_4]$	$[C_{39}H_{41}N_2P_2SPd][BF_4]$
solvent		$0.5CH_2Cl_2$	
fw	856.9	915.5	825.0
color, habit	pale yellow needles	colorless blocks	colorless prisms
cryst size/mm	1.00 × 0.25 × 0.23	0.67 × 0.60 × 0.37	0.53 × 0.40 × 0.27
temp/K	203	203	183
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$ (no. 19)	Cc (no. 9)	Cc (no. 9)
a/Å	13.000(2)	18.083(2)	12.780(2)
b/Å	14.578(2)	15.166(2)	18.527(2)
c/Å	20.620(2)	31.243(3)	17.258(2)
β/deg		90.65(1)	107.12(1)
V/Å^3	3907.8(8)	8568(2)	3905.4(8)
Z	4	8[b]	4
D_c/g cm^{-3}	1.457	1.419	1.403
radiation used	Mo Kα	Mo Kα	Mo Kα
μ/mm^{-1}	0.61	0.67	0.66
θ range/deg	2.0−25.0	2.2−25.0	2.0−25.0
no. of unique reflns			
measured	3846	7764	3609
obs, $\lvert F_o\rvert > 4\sigma(\lvert F_o\rvert)$	3374	7192	3389
no. of variables	433	971	426
R_1, wR_2[c]	0.036, 0.074	0.038, 0.085	0.033, 0.077

	10	13	14
formula	$[C_{48}H_{43}N_2OP_2Pd][BF_4]$	$[C_{36}H_{37}NP_2ClPd][CF_3SO_3]$	$[C_{36}H_{37}NP_2ClPd][BF_4]$
solvent		MeCN	H_2O
fw	919.0	877.6	792.3
color, habit	yellow prismatic needles	colorless prismatic needles	colorless platy blocks
cryst size/mm	0.90 × 0.17 × 0.17	0.63 × 0.47 × 0.30	0.30 × 0.20 × 0.20
temp/K	293	293	203
cryst syst	trigonal	monoclinic	monoclinic
space group	$P3_2$ (no. 145)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	12.031(1)	15.167(2)	11.345(2)
b/Å		15.247(2)	17.518(2)
c/Å	26.047(1)	18.550(2)	18.456(2)
β/deg		110.25(1)	104.72(1)
V/Å^3	3264.9(3)	4024.6(9)	3547.6(9)
Z	3	4	4
D_c/g cm^{-3}	1.402	1.448	1.483
radiation used	Cu Kα	Mo Kα	Mo Kα
μ/mm^{-1}	4.59	0.71	0.74
θ range/deg	4.2−64.0	2.0−25.0	2.2−25.0
no. of unique reflns			
measured	3674	7054	6255
obs, $\lvert F_o\rvert > 4\sigma(\lvert F_o\rvert)$	3546	5188	4758
no. of variables	479	454	407
R_1, wR_2[c]	0.031, 0.077	0.045, 0.101	0.041, 0.083

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

Synthesis of [Pd{C(Me)=NHXy}(dppe)(S=C=NMe)][BF$_4$]$_2$ (15). Methyl isothiocyanate (0.01 g, 0.14 mmol) was added to a stirring solution of [Pd{C(Me)NHXy}(Cl)(dppe)][BF$_4$] (0.10 g, 0.13 mmol) in CH_2Cl_2 (20 mL) followed by $AgBF_4$ (0.03 g, 0.14 mmol). AgCl immediately precipitated from the clear solution. The reaction mixture was stirred for 10 min, and then the AgCl was filtered off. The filtrate was then concentrated under reduced pressure (to 10 mL) and hexane (10 mL) added to precipitate **15** as a white product. Yield: 0.06 g; 0.07 mmol; 51%. Anal. Found: C, 55.49; H, 5.93; N, 2.50. Calcd for $C_{38}H_{40}N_2P_2PdSB_2F_8 \cdot 1.75C_6H_{14}$; C, 55.50; H, 6.19; N, 2.66. IR (ν_{max}/cm^{-1}) (KBr): 3448, 3230 (N−H), 2253 (N=C=S), 1564 (C=N), 1062 (BF$_4$). $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 54.4 (d, 1P, $^2J_{PP}$ = 17 Hz), 59.8 (d, 1P, $^2J_{PP}$ = 17 Hz). ^1H NMR (CDCl$_3$): δ 1.80 (s, 6H, $C_6H_3(CH_3)_2$), 2.00 (dd, 3H, Pd{C(CH_3)=NXy}, $^4J_{HH}$ = 4.5 Hz, $^4J_{HH}$ = unresolved), 2.52 (m, 2H, (PCH_2CH$_2$P)), 3.06 (m, 2H, (PCH$_2$CH_2P)), 3.17 (br, 3H, NCH_3), 6.94 (d, 2H, 3,5-*H* {C$_6H_3$(CH$_3$)$_2$}, $^3J_{HH}$ = 7.5 Hz), 7.08 (t, 1H, 4-*H* {C$_6H_3$(CH$_3$)$_2$}, $^3J_{HH}$ = 7.5 Hz), 7.51−7.96 (m, 20H, 4(PC$_6H_5$)), 12.0 (br, 1H, N*H*). MS (FAB$^+$ *m*/*z* (relative intensity)): 723 (55) [M − 2BF$_4$]$^+$, 650 (100) [M − 2BF$_4$ − MeN=C=S]$^+$, 519 (19) [(dppe)PdMe]$^+$, 504 (23) [(dppe)Pd]$^+$.

Synthesis of [Pd{C(Me)=NHXy}(dppe)(S=C=NPh)][BF$_4$]$_2$ (16). Phenyl isothiocyanate (23.2 μL, 0.20 mmol)] was added to a stirring solution of [Pd{C(Me)=NHXy}(Cl)(dppe)][BF$_4$] (0.15 g, 0.20 mmol) in CH_2Cl_2 (20 mL) followed by $AgBF_4$ (0.04 g, 0.195 mmol). AgCl immediately precipitated from the solution. The reaction mixture was stirred for 10 min, after which time the AgCl was filtered off. The filtrate was then concentrated under reduced pressure (to 10 mL) and hexane (10 mL) added to precipitate **16** as a white product. Yield: 0.13 g; 0.15 mmol; 76%. Anal. Found: C, 52.91; H, 4.04; N, 2.26. Calcd for $C_{43}H_{42}N_2P_2PdSB_2F_8$: C, 53.17; H, 4.46; N, 2.95. IR (ν (KBr)): 3239 (N−H), 2197, 2094 (N=C=S),1564 (C=N), 1061 (BF$_4$). $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 54.6 (br d, 1P, $^2J_{PP}$ = unresolved), 60.5 (d, 1P, $^2J_{PP}$ = 18 Hz). ^1H NMR (CDCl$_3$): δ 1.70 (s, 6H, {C$_6$H$_3$(CH_3)$_2$}), 1.93 (br, 3H, PdC(CH_3)), 2.49 (m, 4H, (PCH_2CH_2P)), 6.79−7.96 (m, 28H, 4(PC$_6H_5$) + NC$_6H_5$ + {C$_6H_3$(CH$_3$)$_2$}), 11.78 (br, 1H, N*H*). MS (FAB$^+$ *m*/*z* (relative intensity)): 785 (38) [M − BF$_4$]$^+$, 650 (100) [M − BF$_4$ − PhN=C=S]$^+$, 519 (14) [(dppe)PdMe]$^+$, 504 (24) [(dppe)Pd]$^+$.

Synthesis of [Pd{C(Me)=NHXy}(dppe)(CNXy)][BF$_4$]$_2$ (17). CNXy (0.01 g, 0.09 mmol) was added to a solution of **15** (0.07 g, 0.08 mmol) in CH_2Cl_2 (10 mL). The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, which showed the complete conversion of **15** to a new product after 15 min. After this time, hexane (10 mL) was added to the reaction mixture, precipitating a white solid, which was characterized as **17**. Yield: 0.05 g; 0.05 mmol; 67%. Anal. Found: C, 56.47; H, 4.89; N, 2.85. Calcd for $C_{45}H_{46}N_2P_2B_2F_8Pd$: C, 56.49; H, 4.84; N, 2.93. IR (ν (KBr)): 3216 (N−H), 2199 (N≡C), 1570 (C=N), 1058 (BF_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 54.9 (two overlapping doublets, 2P). ^1H NMR ($CDCl_3$): δ 1.70 (s, 6H, $C_6H_3(CH_3)_2$, terminally coordinated isocyanide), 2.11 (dd, 3H, Pd{C(CH_3)=NXyl}, $^4J_{PH}$ = 4.0 Hz, $^4J_{PH}$ = unresolved), 2.16 (s, 6H, {$C_6H_3(CH_3)_2$}), 2.64 (m, 2H, (PCH_2CH_2P)), 3.04 (m, 2H, (PCH_2CH_2P)), 6.90 (m, 6H, 2{$C_6H_3(CH_3)_2$}), 7.45−7.69 (m, 12H, 3,4,5-*H* (PC_6H_5)), 7.74−7.92 (m, 8H, 2,6-*H* 4(PC_6H_5)), 12.29 (s br, 1H, N*H*). MS (FAB^+ *m*/*z* (relative intensity)): 869 (19) $[M - BF_4]^+$, 650 (100) $[(dppe)PdC\{=NC_6H_3(CH_3)_2\}Me]^+$, 519 (12) $[(dppe)PdMe]^+$, 504 (16) [(dppe)Pd].

Crystal Structure Determination. Table 4 provides a summary of the crystallographic data for compounds **4**, **6**, **7**, **10**, **13**, and **14**. Data were collected on Siemens/Bruker P4 diffractometers using ω-scans, and the structures were refined based on F^2 using the SHELXTL program system.[21] The absolute structures of **4**, **6**, **7**, and **10** were determined by a combination of *R*-factor tests and by use of the Flack parameter [for **4**: $R_1^+ = 0.0358$, $R_1^- = 0.0387$, $x^+ = 0.00(4)$, $x^- = +1.00(4)$; for **6**: $R_1^+ = 0.0376$, $R_1^- = 0.0387$, $x^+ = 0.00(5)$, $x^- = +1.01(5)$; for **7**: $R_1^+ = 0.0333$, $R_1^- = 0.0346$, $x^+ = -0.12(8)$, $x^- = +1.12(8)$; for **10**: $R_1^+ = 0.0311$, $R_1^- = 0.0442$, $x^+ = +0.01(2)$, $x^- = +0.99(2)$]. CCDC 212289−212294.

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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 details, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **4**, **6**, **7**, **10**, **13**, and **14** are available free of charge via the Internet at http://pubs.acs.org.

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[21] *SHELXTL PC version 5.03*; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1994. *SHELXTL PC version 5.1*; Bruker AXS: Madison, WI, 1997.