Insertion of Isocyanides across the Pd−C Bond in Alkyl or Aryl Palladium(II) Complexes Bearing Mixed Nitrogen−Sulfur and Nitrogen−Phosphorus Ancillary Ligands. The Mechanism of Reaction

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An exhaustive study dealing with the kinetic and mechanistic behavior of alkyl- and arylpalladium complexes bearing pyridyl−thioethers (NS−R) and quinoline−phosphines (NP) as ancillary ligands when reacting with 2,6-dimethyl isocyanide (DIC) and tosylmethyl isocyanide (TosMIC) was undertaken. In these reactions some differently substituted isocyanides insert into the palladium−carbon bond of alkyl and aryl complexes bearing mixed (NS or NP) ligands. The reactions were carried out under equimolecular conditions since such a restrictive approach allows the determination of the rate constants related to the isocyanide insertion attack. Reactions carried out under nonstoichiometric conditions were also taken into account and the reaction products characterized. Usually the formation of an inserted bis-substituted isocyanide halide derivative of palladium(II) was observed. In a particular case the formation of an imidoyl dimer was detected. The structures of the monoinserted [Pd(NS*t*-Bu)(C(Tol)═NR^2)I] (NS*t*-Bu = 2-(*tert*-butylthiomethyl)pyridine) and of the dimer [Pd(CNR^2)(C(═NR^2)Me)Cl]$_2$ (R^2 = 2,6-Me$_2$C$_6$H$_3$) were reported.

Introduction

The insertion reactions of unsaturated molecules across palladium−carbon bonds represent an extensively studied topic owing to its importance in a remarkable number of metal-mediated organic syntheses.[1,2]

Alkynes,[3] alkenes,[4] allenes,[5] carbon monoxide,[6] and isocyanides[7] are the most widely studied unsaturated molecules when reacting with alkyl−,[5] aryl−,[7] and acyl−palladium complexes.[7a,8] In particular, the reactivity characteristics of carbon monoxide, which, among other properties, reacts in association with alkenes to give copolymers as the result of the catalytic alternate insertion,[9] were studied from both theoretical and experimental points of view.[6] On the contrary, the isoelectronic isocyanides CNR were scarcely investigated despite their steric and electronic properties, which can be easily modulated by taking advantage of the nature of the substituent R.[10] To the best of our knowledge, only two detailed mechanistic studies dealing with insertion in palladium complexes bearing bidentate nitrogen or phosphine ligands have appeared so far in the literature.[7b,11] Thus, our propensity to kinetic investigation and curiosity toward interesting synthetic applications led us to undertake an exhaustive study of the kinetic and mechanistic behavior of alkyl- and arylpalladium complexes bearing pyridyl−thioethers (NS−R) and quinoline−phosphines (NP) as ancillary ligands when reacting with 2,6-dimethyl isocyanide (DIC) and tosylmethyl isocyanide (TosMIC). As a matter of fact, the palladium alkyl derivatives with pyridyl−thioether ligands often display an

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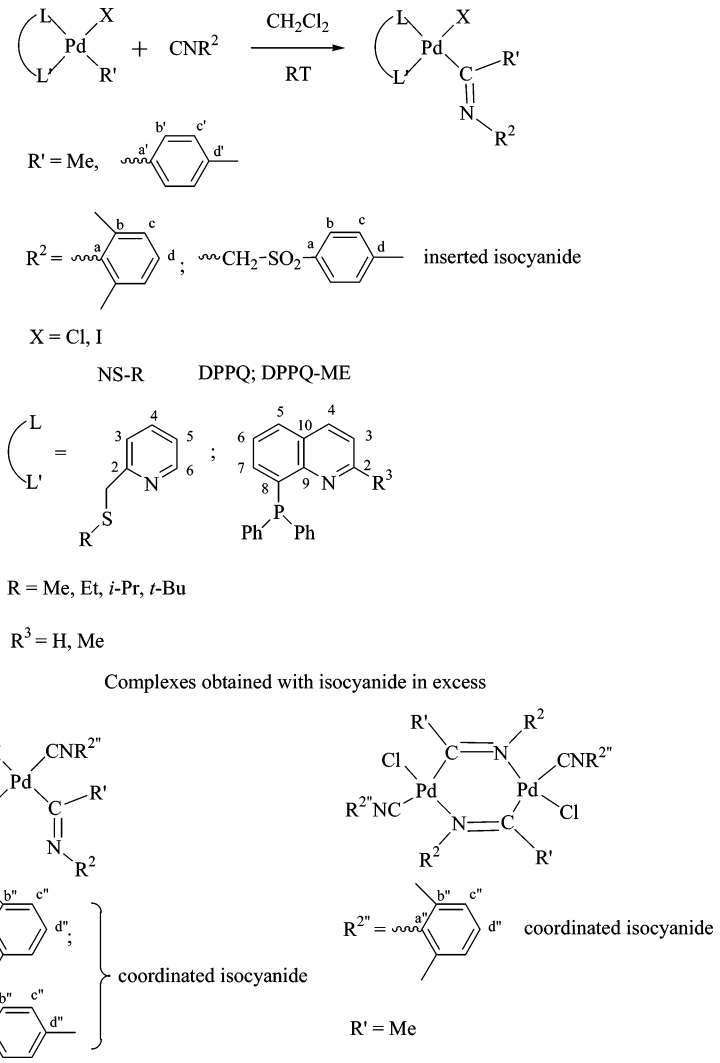
Scheme 1



enhanced reactivity toward insertion reactions,[12] and moreover no investigations were hitherto carried out on alkyl- or arylpalladium complexes bearing *mixed* ancillary ligands. The present study attempts to determine the reaction rates and elucidate the intimate mechanism involved when some differently substituted isocyanides insert into the palladium−carbon bond of alkyl and aryl complexes bearing mixed (NS or NP) ligands. We also aimed at characterizing the compounds produced when a stoichiometric amount or an excess of reacting isocyanide is used. The complexes, the isocyanides involved, and the numbering scheme are reported in Scheme 1.

Results and Discussion

General Considerations. As we have already shown, the structure of the methylpalladium derivatives with mixed bidentate nitrogen−sulfur ligands is determined by the mutual *trans* influence exerted between the alkyl group and the coordinating atoms of the ancillary ligand. Thus, only the geometric isomer with the methyl group lying *trans* to nitrogen (hereafter *trans*) was observed. As a matter of fact, sulfur exerts a *trans* influence higher than nitrogen, and the ensuing *trans* structure is maintained also in the vinyl and butadienyl derivatives, which represent the products of the insertion of activated alkynes across the palladium−carbon bond.[3]

At present, as can be deduced from the NMR and IR spectra, all the complexes in Scheme 1 display only one isomer in solution. On the basis of our experience and knowledge of these systems and on the basis of the resolved structure reported in this paper (*vide post*), we suggest that only the *trans* isomer of the starting complex is present in any studied case (the *trans* influence of phosphorus being considerably higher than that of nitrogen) and that the insertion reactions proceed with retention of configuration.

Insertion Reactions. Preliminary studies carried out by means of NMR technique in $CDCl_3$ confirm that the insertion of isocyanide into the Pd−C bond when performed under stoichiometric conditions proceeds according to the reaction reported in Scheme 1.

As can be deduced from the NMR data reported in the Experimental Section, a general rearrangement of the spectra can be observed upon addition of the isocyanide CNR^2 to a solution of the starting complex [Pd(NS−R)(R′)X] or [Pd(DPPQ)(R′)X]. For instance, in the case of the reaction of the complex [Pd(DPPQ)(Me)Cl] the addition of DIC isocyanide induces the upfield shift of the Qui−H^2 signal (from 10.02 to 9.97 ppm), the downfield shift of the Pd−CH_3 signal (from 0.91

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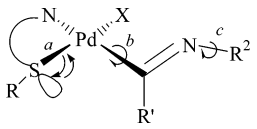
Scheme 2



to 1.83 ppm), and the appearance of the signal at 1.87 ppm attributable to the protons of the methyl substituents of the aromatic ring of DIC isocyanide. The $^{31}P\{H\}$ NMR spectrum displays the upfield shift of the coordinated phosphorus from 39.9 to 22.2 ppm, and the $^{13}C-^{1}H$ HMBC NMR spectrum displays the coupling between the imino carbon $C(CH_3)=N$ (179.1 ppm) and the $C(CH_3)=N$ protons. Furthermore the IR spectrum of the inserted complex displays a strong band at 1622 cm^{-1} attributable to the $\nu_{C=N}$ stretching.

The [Pd(NS−R)(R′)X] derivatives behave similarly if an excess of free ligand is added ([NS−R]:[Pd(NS−R)(R′)X] = 3:1) in order to counteract the displacement of the ligand itself caused by the isocyanide acting as entering rather than inserting nucleophile. Under these experimental conditions the insertion reaction is easily followed by NMR technique, as can be deduced in the case of the reaction between the complex [Pd(NS*t*-Bu)(Tolyl)I] and the tosMIC isocyanide. The signal attributable to the Py−*H*[6] proton undergoes an upfield shift from 9.69 to 9.42 ppm. The $Pd-C_6H_4CH_3$ singlet slightly shifts downfield from 2.25 to 2.32 ppm, and the appearance of a couple of doublets at 5.66 and 5.44 ppm, attributable to the methylene protons of the inserted tosMIC fragment, is also noticed. The $^{13}C\{H\}$ NMR and the $^{13}C-^{1}H$ HMBC NMR spectra together with the IR spectrum ($\nu_{C=N}$ = 1594 cm^{-1}) confirm the insertion. As a matter of fact, the $^{13}C-^{1}H$ HMBC NMR spectrum displays the coupling among the imino-carbon $C(C_6H_3CH_3)=N$ and both the CH_2SO_2 and $H^{b'}$ (tolyl group) protons. These observations can be generalized for any other studied case, as can be deduced from the data in the Experimental Section, where the main NMR and IR features for all the complexes involved in this study are reported in detail.

Fluxional Rearrangement in Solution. The inserted complexes bearing the pyridyl−thioether ligands at RT give rise to a rapid rearrangement in solution due to (a) sulfur absolute configuration inversion, (b) free rotation around the Pd−C bond, and (c) free rotation around the =N−C bond. It is well-known that the absolute configuration inversion of the coordinated sulfur is a low-energy phenomenon;[13] thus at low temperature it is possible to "freeze" this otherwise rapid rearrangement.[3] A further decrease of temperature can also "freeze" the Pd−C rotation (Scheme 2). In this case a couple of rotamers could turn up. Moreover when DIC isocyanide is used as inserting nucleophile, the "freezing" of free rotation of the =N−C bond makes the two methyl *ortho* substituents of phenyl group distinguishable.

The low-temperature (223 K) ^{1}H NMR spectrum in CD_2Cl_2 (see Figure 1SI in Supporting Information) of the complex [Pd(NS−Me)(C(Me)=NR²)Cl] (R^2 = 2,6-$Me_2C_6H_3$) witnesses the formation of a couple of differently populated *endo* and *exo* rotamers.

On the basis of the structural determination (*vide infra*) we suggest that the *exo* rotamer probably represents the most abundant species.

However, we are aware that these rearrangements might also be promoted by ring opening at the pyridine nitrogen of the pyridyl−thioether ligand induced by the remarkable *trans* influence of the carboimine group and the subsequent recoordination, as was observed by other authors.[5c] Moreover, fluxional rearrangements via associative processes promoted by the sulfur lone pair could also be operative.[14] However, a detailed study on these conformational aspects is outside the scope of this paper, and a specific investigation on these problems will be carried out in the future.

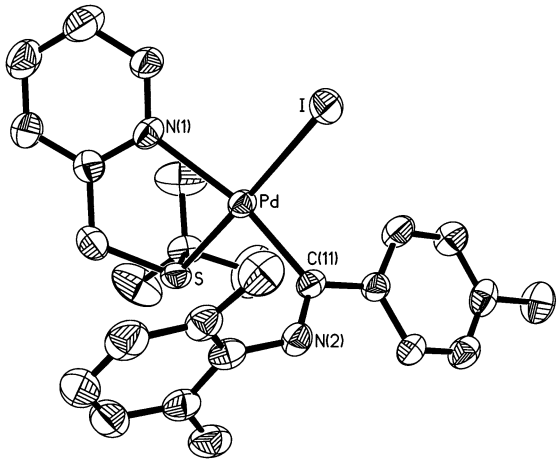


Figure 1. Molecular structure of the complex [Pd(NS*t*-Bu)(C(Tol)=$NC_6H_3Me_2$)I]. Hydrogen atoms are not shown for clarity. Thermal ellipsoids are at the 40% probability level.

At variance with the pyridyl−thioether derivatives, the complexes bearing the flat DPPQ do not obviously give rise to any rotamer.

X-ray Crystal Structure. The ORTEP[15] representation of the neutral complex [Pd(NS*t*-Bu)(C(Tol)=$NC_6H_3Me_2$)I], together with the pertinent labeling scheme is shown in Figure 1. The square-planar environment about Pd shows some tetrahedral distortion; the S−Pd−N "bite" angle is 82.7(2)°, the I−Pd−C(11) angle is 93.4(3)°, and the dihedral angle between the triangles S−Pd−N(1) and I−Pd−C(11) is 11.0° (ideal value 0°). The atoms Pd, S, N(1), I, and C(11) deviate from the main coordination plane by −0.03, −0.16, +0.14, −0.12, and +0.14 Å, respectively. Nevertheless, the sum of the angles about Pd is quite close to 360° (360.7°). The configuration about the double bond of the imino ligand is *Z* (that is, the xylyl and *p*-tolyl moieties of the ligand are *trans* disposed).

The findings of the present investigation have been compared with those stored in the Cambridge Crystallographic Database (CCD).[16] The present compound is structurally similar to the only known complex with the same donor set around Pd ([PdC(*t*-Bu/Me)=C(Me/*t*-Bu)C_6H_4-2-CH_2S-*t*-Bu(C_5H_5N)I]; **7c** in the ref 17; code ZAFDAL).

In particular, the Pd−N bond (2.231(8) Å) is rather long, being the second longest reported so far after 2.240 Å in [PdC(*t*-Bu/Me)=C(Me/*t*-Bu)C_6H_4-2-CH_2S-*t*-Bu(C_5H_5N)I]. Likewise, the relatively long Pd−S (2.306(3) Å) and the relatively short Pd−C (2.005(9) Å) distances also agree with reported data and can be explained in terms of the *trans* influence. In fact, the pyridine ligand and the sulfur atom are faced by a negatively charged σ-bonded C ligand and by an iodide, respectively. The

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trans influence of these bases and the distortion induced by the bulky iodide ligand lead to long Pd−N/Pd−S and short Pd−C bonds. The Pd−I bond (2.642(1) Å) is longer than the corresponding one in [PdC(*t*-Bu/Me)═C(Me/*t*-Bu)C_6H_4-2-CH_2S-*t*-Bu(C_5H_5N)I] (2.632 Å); the latter is also the mean value for the Pd−I distance in more than 300 Pd complexes in the CCD.

As for nonbonding interactions, an examination of the packing diagram does not reveal any significant contact.

Mechanistic Study

Determination of Equilibrium Constants. If an equimolar amount of DIC is added at low temperature (223 K) to a CD_2Cl_2 solution of [Pd(NS−Me)(Me)Cl] ($[Pd]_0 \approx 2 \times 10^{-2}$ mol dm^{-3}), the ensuing ^1H NMR spectrum displays the simultaneous presence of three species, the concentrations of which do not change with time. At different temperatures (240, 255 K), the mutual concentrations of the different species change, but again, no formation of the inserted product [Pd(NS−Me)(C(Me)═$NC_6H_3Me_2$)Cl] is noticed.[18] Apparently, the three species are in a mutual equilibrium. Such a situation however evolves into the inserted complex [Pd(NS−Me)(C(Me)═$NC_6H_3Me_2$)Cl] on increasing the temperature to 298 K. On the basis of a detailed analysis of the NMR spectra and of some chemical deductions (*vide post*), we suggest the following equilibrium network:

$$[Pd(NS-Me)(Me)Cl] + CNR^2 \leftrightarrow [Pd(NS-Me)(CNR^2)(Me)]^+ + Cl^- \qquad K_{Cl} \quad (1)$$

$$[Pd(NS-Me)(Me)Cl] + 2\,CNR^2 \leftrightarrow [Pd(CNR^2)_2(Me)Cl\,] + NS-Me \qquad K_L \quad (2)$$

$$R^2 = 2,6\text{-}Me_2C_6H_3$$

As a matter of fact, the 223 K ^1H NMR spectrum in CD_2Cl_2 of the reaction mixture displays an easily recognizable series of signal. The doublet at 8.51 ppm, the singlet at 3.74 ppm, and the singlet at 1.99 ppm are attributable to H^6 of the pyridine ring, to $-CH_2-$S, and to $-S-CH_3$ protons, respectively, of the uncoordinated NS−Me ligand. The unreacted starting complex displays the Py−H^6 at 9.05 ppm, the $-CH_2-$S AB system at 4.27 ppm, the $-S-CH_3$ signal at 2.40 ppm, and the Pd−CH_3 at 0.67 ppm. The presence of uncoordinated ligand and the absence of any appreciable decomposition suggest the formation of the complex [Pd$(CNR^2)_2$(Me)Cl], which is characterized by the singlet at 0.96 ppm ascribable to Pd−CH_3 and by the singlet at 2.45 ppm related to $C_6H_3(CH_3)_2$ protons. A further substrate that we identify as the [Pd(NS−Me)(CNR^2)(Me)]$^+$ complex is detected in solution with its relevant signals, namely, the doublet at 8.66 ppm (Py−H^6), the signal at 4.50 ppm ($-CH_2-$S), that at 2.13 ppm ($-S-CH_3$), and eventually the broad singlet at 1.00 ppm ascribable to Pd−CH_3 protons. The identification of the nature of the complexes [Pd$(CNR^2)_2$(Me)Cl] and [Pd(NS−Me)(CNR^2)(Me)]$^+$ is also based on their reactivity as will be described later. From the calculated concentrations of all the species present in solution an approximate value of equilibrium constants K_{Cl} and K_L can be estimated. The linear regression of ln K vs $1/T$ according to van't Hoff's equation allows a coarse determination of the equilibrium constants at 298 K. The ensuing values are[19]

$$K_{CL} = [[Pd(NS-Me)(CNR^2)(Me)]^+][Cl^-]/[[Pd(NS-Me)(Me)Cl]][CNR^2] \approx 3.5 \times 10^{-3} \quad (1)$$

$$K_L = [[Pd(CNR^2)_2(Me)Cl]][NS-Me]/[[Pd(NS-Me)(Me)Cl]][CNR^2]^2 \approx 500 \quad (2)$$

Owing to the nucleophilicity of isocyanides, the K_{CL} value sounds very small compared with K_L. However, it is well-known that unsolvated chloride in aprotic solvents acts as a very strong nucleophile.[20]

Kinetic Measurements. Addition under spectrophotometric conditions of an equivalent of isocyanide to a CH_2Cl_2 solution of [Pd(NS−R)(R′)X] ($[Pd]_0 = 2 \times 10^{-4}$ mol dm^{-3}) at RT (298 K) leads to the formation of the inserted complex [Pd(NS−R)(C(R′)═NR^2)X] as unique product. Apparently, the reaction mixture produces only one species, and this fact can be considered a further proof that a fast equilibrium among reactants is operative. Moreover the rate of reaction is strongly influenced by the addition of variable aliquots of the appropriate NS−R ligand and/ or chloride (TEBACl, triethylbutyl ammonium chloride).

In particular, addition of free ligand enhances the rate of reaction; conversely addition of Cl^- induces a decrease in rate. It is apparent that increasing the amount of added ligand leads to a suppression of the equilibrium (2), and the attainment of the asymptotic rate would coincide with the complete suppression of the equilibrium. This condition is easily reached when the free ligand is 10 times the concentration of the starting complex itself, this result being compatible with the value of the calculated equilibrium constant. (Under these conditions the concentration of the starting complex is almost coincident with $[Pd]_0$ since the extent of reaction is about $0.01 \times [Pd]_0$.[21]) Therefore, the overall mechanism of isocyanide insertion can be described by Scheme 3 (the meaning of the symbols **A**, **C**, **C′**, and **D** will be specified further on).

The rate law for the reaction in Scheme 3 is

$$-d[S]/dt = [S][CNR^2](K_{Cl}k_i + k_2[Cl^-])/(K_{Cl}[CNR^2] + [Cl^-]) \quad (3)$$

where

$$[S] = [[Pd(NS-Me)(Me)Cl]] + [[Pd(NS-Me)(CNR^2)(Me)]^+] = [\mathbf{A}] + [\mathbf{C}]$$

In the presence of a strong excess of Cl^- the rate law (3) becomes

$$-d[S]/dt = k_2[S][CNR^2] \quad (4)$$

This expression is easily handled, and thus information on the direct attack of an equimolar amount of isocyanide (second-order condition) on the starting complex can be obtained. It is worth noting that the addition of TEBACl slows down the reaction rate, suggesting that the dechlorinated substrate is

(18) At higher temperature (255 K) traces of the insertion product are observed; however the estimated concentration of the latter is less than 5% of the concentration of the starting complex.

(19) Owing to the very large errors affecting the determination of the concentrations, standard errors of the van't Hoff regression are not reported. Therefore, the equilibrium constant values must be considered as rough estimates of their order of magnitude.

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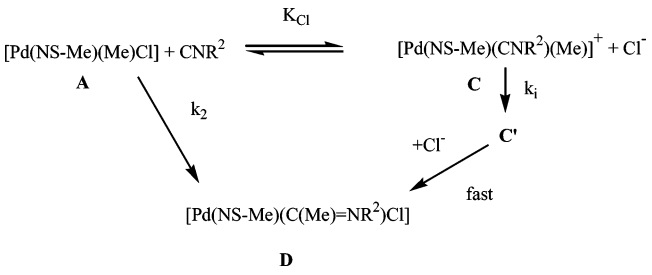
(21) The NSMe species represents the less strongly bonded ligand among all the ligands used in this work. Therefore, its added concentration would represent the limiting concentration also in the case of NS*t*-Bu (DPPQ and DPPQMe are not displaced by isocyanide).

Scheme 3



somewhat more reactive than the chlorinated one. No information can be however obtained about the monomolecular insertion rate k_i since the numerical analysis of eq 3 is rather complicated ($[Cl^-]$ is a function of time) even if an approximate value for K_{Cl} is available.[22] The higher reactivity of the substrate $[Pd(NS-Me)(CNR^2)(Me)]^+$ compared with [Pd(NS−Me)(Me)Cl)] can be traced back to its *cis* structure allowing the facile migration of the methyl group.[23] An indirect confirmation of the proposed mechanism is given by the reactivity behavior of the iodo and DPPQ derivatives. The rates of the reaction of the iodo derivatives are independent of added iodide, while the rates of DPPQ complexes are not affected by the addition of free DPPQ ligand in solution; the reaction rates of complexes containing DPPQ and iodide are independent of both ligand and iodide added. It is well-known that chloride is easily displaced by iodide in Pd(II) planar tetracoordinated substrates, the Cl^-/I^- exchange equilibrium constant being 3/4 orders of magnitude in favor of iodide.[24] Apparently, iodide is not displaced by isocyanide; therefore no equilibria like equilibrium (1) is operative in the case of iodide derivatives. The DPPQ ligand is not displaced either; thus in neither of these cases do equilibria like equilibrium (2) exist. In Table 1 the kinetic data obtained in the presence and in the absence of added ligand or halide for all the studied substrates are reported.

In an attempt at unifying the overall reactivity, we propose an intimate mechanism based on the theory of nucleophilic substitutions on planar tetracoordinated complexes. On the basis of such a theory the entering nucleophile simply replaces the leaving group occupying its position. The key intermediate is a trigonal bipyramid in which the entering, the leaving, and the group *trans* to the leaving group itself occupy the equatorial plane. Scheme 4 suggests the possible paths, which take into account all the possible species involved.

As can be seen in Scheme 4, only the intermediates **B** and **E** can be obtained from the isocyanide attack to the starting complex [Pd(NS−R)(R′)Cl]. **B** gives rise to the inserted product **D** via the cationic *cis* complex **C** when Cl^- is the leaving group

Scheme 4

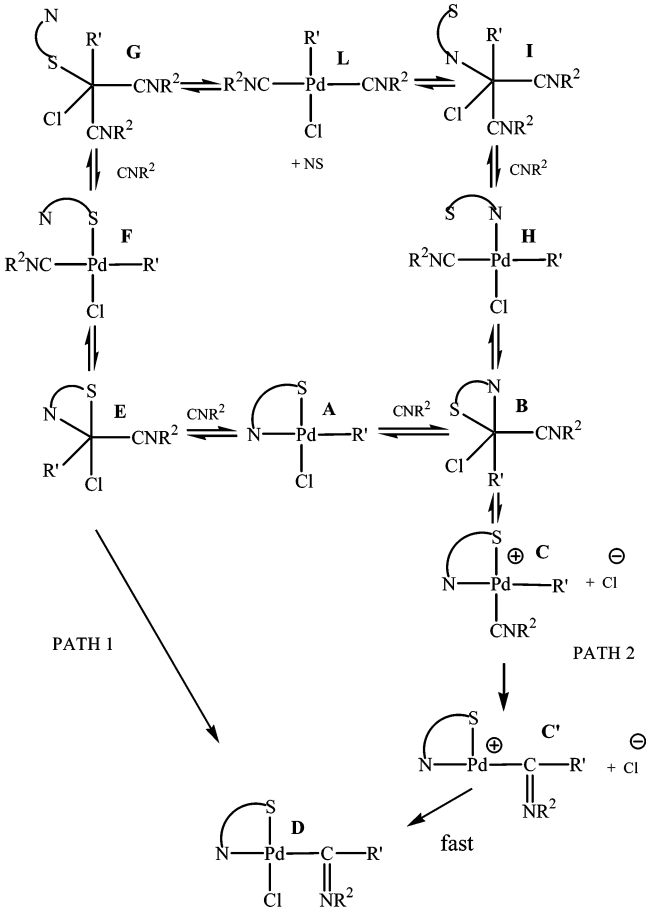


Table 1. Second-Order Rate Constant k_2 (mol^{-1} dm^3 s^{-1}) for the Insertion of the Isocyanides DIC and TosMIC across the Pd−C Bond of Complexes [Pd(L−L′)(R′)X]

	complexes	DIC	TosMIC
1	[Pd(NS−Me)(Me)Cl] + 10 equiv ligand	250 ± 4	too fast
2	[Pd(NS−Me)(Me)Cl] + 10 equiv ligand + 10 equiv Cl^-	65 ± 1	too fast
3	[Pd (NS−Me)(Me)I] + 10equiv ligand	20 ± 1	880 ± 72
4	[Pd (NS−Me)(Me)I] + 10 equiv ligand + 10 equiv I^-	19 ± 2	866 ± 56
5	[Pd(NS*t*-Bu)(Me)Cl] + 10 equiv ligand	100 ± 1	too fast
6	[Pd(NS*t*-Bu)(Me)Cl] + 10 equiv ligand + 10 equiv Cl^-	56.0 ± 0.2	too fast
7	[Pd(NS*t*-Bu)(Me) I] + 10 equiv ligand	18 ± 1	821 ± 51
8	[Pd(NS*t*-Bu)(Me) I] + 10 equiv ligand + 10 equiv I^-	18 ± 3	815 ± 55
9	[Pd(NS−Me)(Tolyl)I] + 10 equiv ligand	433 ± 20	1220 ± 85
10	[Pd(NS−Me)(Tolyl)I] + 10 equiv ligand + 10 equiv I^-	439 ± 26	1205 ± 90
11	[Pd(NS*t*-Bu)(Tolyl)I] + 10 equiv ligand	48 ± 1	540 ± 30
12	[Pd(NS*t*-Bu)(Tolyl)I] + 10 equiv ligand + 10 equiv I^-	50 ± 3	550 ± 38
13	[Pd(DPPQ)(Me)Cl]	1.0 ± 0.1	3. 2 ± 0.5
14	[Pd(DPPQ)(Me)Cl] + 10 equiv Cl^-	0.4 ± 0.1	1.2 ± 0.1
15	[Pd(DPPQ-Me)(Me)Cl]	253 ± 3	1130 ± 20
16	[Pd(DPPQ-Me)(Me)Cl] + 10 equiv Cl^-	236 ± 2	1118 ± 20
17	[Pd(DPPQ)(Me)I]	4.5 ± 0.5	116 ± 1
18	[Pd(DPPQ)(Me)I] + 10 equiv I^-	4.4 ± 0.7	120 ± 5
19	[Pd(DPPQ)(Tolyl)I]	202 ± 1	150 ± 3
20	[Pd(DPPQ)(Tolyl)I] + 10 equiv I^-	200 ± 4	155 ± 7

(path 2). In particular, the reaction sequence **B** → **C** → **C′** → **P** involves intramolecular insertion of isocyanide (**C** → **C′**) to give the cationic coordinatively unsatured intermediate **C′**, which

(22) (a) Strictly speaking, eq 3 turns into eq 4 at very high chloride concentration according to the limit: $\lim (K_{Cl}k_i + k_2[Cl^-])/(K_{Cl}[CNR^2] + [Cl^-]) = k_2$ for $[Cl^-] \rightarrow \infty$. In practice, the amount of added chloride was the concentration at which the rate of reaction levels off to an asymptotic value (k_2). This value is reached even at 3−4 times the concentration of the starting complex [Pd(NSMe)(Me)Cl]. We however decided to add a 10-fold excess in all cases studied in order to ensure the constancy of chloride concentration with time. Moreover, under this condition the extent of reaction for the chloride displacement equilibrium (K_{Cl}) is virtually zero, equilibrium (1) being completely shifted to the left. (b) Analogously to those calculated in the presence of an excess of halide, approximate k_2 values were determined in the absence of added chloride by numerical regression of the absorbance vs time data according to the second-order treatment. Such values are purely indicative since the treatment is obviously inadequate owing to the complexity of the overall reaction mechanism. Nevertheless, the comparison among rates is warranted by the fairly satisfactory fit obtained.

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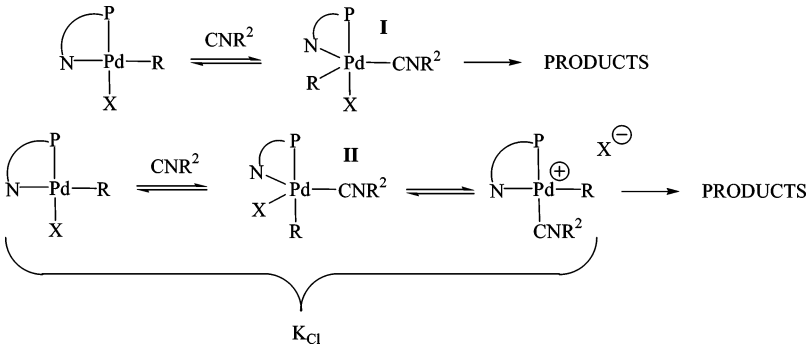
(24) Tobe, M. L.; Burgess, J. In *Inorganic Reactions Mechanisms*; Addison Wesley: New York, 1999.

Scheme 5



rapidly reacts with chloride to yield the final neutral product. Addition of TEBACl clearly suppresses the formation of **C**. In path 1 the leaving group R′ gives rise to complex **D** via direct migration.

The formation of the species **L** is obtained from both the intermediates **B** and **E** passing through the species **H**, **I** and **F**, **G**, respectively. As a matter of fact, the leaving group in **B** could be represented by Cl^- or by the thioetheric sulfur. Analogous considerations can be made when the reaction proceeds via the species **E**. According to the nucleophilic substitution theory, intermediates **G** and **I** would produce *cis*-$[Pd(CNR^2)_2(R')Cl]$ (not reported in Scheme 4), which however quickly isomerizes to the more stable *trans* form **L**.

The following remarks are in order.

(a) The limiting reaction rate is always reached upon addition of the labile ligands (NS−R) and/or halide (Cl^-). Addition of iodide and/or DPPQ ligand does not affect the overall reactivity.

(b) The isocyanide TosMIC is almost always more reactive than the DIC one. This fact can be traced back to the associative nature of the nucleophilic attack, which is strongly influenced by the steric requirement of the species involved coupled with the reduced charge density on the isocyanide carbon,[10] which favors the internal migration of the methyl (or tolyl) group (path 1). However the influence of the steric requirement of the sulfur substituent R, which is probably away from the crowded intermediate, is not so important (entries 2, 6 and 4, 8 in Table 1).

(c) Thanks to its higher basicity and the consequent stronger Pd−C bond, methyl is less efficient than tolyl as a migrating group (entries 10, 4 and 12, 8).

(d) When path 1 is imposed by halide and ligand addition, the nature of the halide is not very important since the halide itself is out of the mechanistic context (Scheme 5) and its influence is limited to a slight difference in the charge density on the metal induced by the different basicity of the halides (entries 2, 4 and 6, 8).

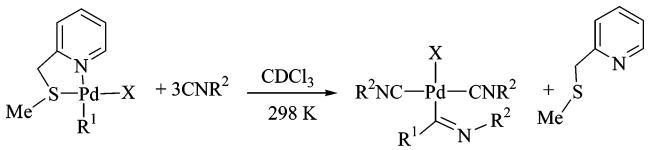
(e) The importance of the steric hindrance on the starting complex arises when *t*-Bu and tolyl groups are both present. In this case a decrease in the absolute and relative reactivity is observed (entries 12 and 8 compared with 10 and 4).

A detailed analysis of the reactivity of the complexes studied must take into account the comparison among NS−R and DPPQ derivatives. The reactivity of phosphine−quinoline substrates is in general (i) not influenced by free ligand addition; (ii) lower than that of their pyridyl−thioether counterparts (entry 16 will be dealt with further on); and (iii) scarcely influenced by addition of free halide.

As for point (i), owing to the efficiency of the phosphine as ligand, addition of free DPPQ does not modify the reactivity of the corresponding complexes since DPPQ is not displaced by the entering isocyanide. As for points (ii) and (iii), they are correlated and represent different aspects of the same chemical behavior, as Scheme 5 shows.

The rigid DPPQ molecule hampers the formation of intermediate **I**, thereby lowering the reactivity of the complex itself (a similar decrease in reactivity was already noticed with DPPQ derivatives when other insertion reactions were studied).[3] Moreover intermediate **II** is probably less stabilized than intermediate **I** due to the mutual *trans* influence exerted by the phosphine and isocyanide in the ensuing cationic species. Thus, the k_2 path becomes predominant even though the k_i path is not impossible (see entries 15 and 16). The enhanced reactivity of DPPQMe derivatives derives from the distortion induced by the methyl substituent in position 2 of the quinoline ring, which somehow makes the formation of the pentacoordinate intermediates easier.[8a,17d]

Reaction in the Presence of Isocyanide in Excess. Complexes Bearing Isocyanide as Substituent and Inserted Moiety. At variance with the DPPQ derivatives, which give rise to isocyanide polyinsertion, the NS−Me complexes react with an excess of isocyanide in $CHCl_3$ at RT according to the following reaction:



R^1 = Me, Tolyl

X = Cl, I

R^2 = 2,6-$Me_2C_6H_3$, CH_2Tosyl

The obtained complexes are stable with the exception of the complex $[Pd(CNR^2)_2(C(Tolyl)=NR^2)I]$ (R^2= CH_2Tosyl), which undergoes fast decomposition. The presence of one single symmetric isomer in solution suggests that the *trans* bis-substituted isocyanide derivative is obtained. For instance, when DIC is reacted with [Pd(NS−Me)(Me)Cl], only a singlet (12H) ascribable to $(CH_3)_2C_6H_3$ protons at 2.41 ppm is detected. The singlets at 2.69 ppm (3H) and at 2.12 ppm (6H) ascribable to (CH_3)−C=N and C=N−$C_6H_3(CH_3)_2$ protons, respectively, confirm the formation of one single isomer. The IR spectrum displays one strong band at 2173 cm^{-1} ($\nu_{C\equiv N}$ of the coordinated isocyanide) and another strong band at 1658 cm^{-1} ($\nu_{C\equiv N}$ inserted isocyanide).

Dimeric Imidoyl Complex. When a 2-fold stoichiometric excess of DIC isocyanide is added to a solution of palladium complexes bearing labile ligands [Pd(LL)(Me)Cl] (LL = NS−R, COD), the reaction mixture yields the dimeric imidoyl derivative $[Pd(CNR^2)(C(=NR^2)Me)Cl]_2$. Crystals suitable for X-ray diffractometric structural determination were grown and

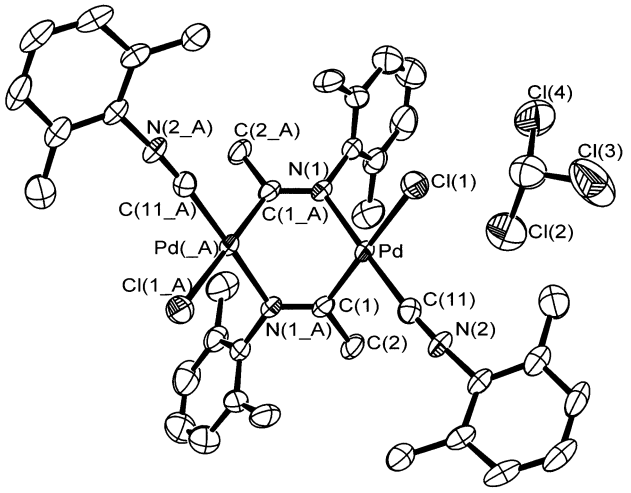


Figure 2. Molecular structure of complex $[Pd(CNR^2)(C(=NR^2)Me)Cl]_2$ ($R^2 = C_6H_3Me_2$). Hydrogen atoms are not shown for clarity. Thermal ellipsoids are at the 40% probability level.

separated from the mother solution, and the resulting structure is reported in Figure 2.

The ORTEP[25] representation of the neutral complex **2** ($[Pd(CNR^2)(C(=NR^2)Me)Cl]_2$; $R^2 = C_6H_3Me_2$), together with the pertinent labeling scheme, is shown in Figure 2, which also shows the solvation chloroform molecule. The molecule is a dimer, in which each Pd atom is coordinated by a chloride ion, by the 2,6-dimethylphenyl isocyanide, and by the 1-(2,6-dimethylphenylimino)ethyl moiety. The latter acts as a bidentate bridging ligand, bonding one Pd center by means of the neutral imine nitrogen and the other one by means of the negatively charged σ-bonded ethyl carbon. This arrangement originates a six-membered, 1,4-dipalladated ring.

Similar cyclic dimers of palladium have already been reported, and in fact a search in the Cambridge Crystallographic Database (CCD)[16] returns about 90 structures, but only in about 20 cases is the bridge made of C or N atoms. To the best of our knowledge, this is the first evidence of the 1-(2,6-dimethylphenylimino)ethyl synthon behaving as bridging. In the majority of already known examples, as well as in complex **2**, the six-membered ring assumes a *twist-boat* arrangement. In the present case, the two Pd atoms are at the "stern" and "prow" positions, 1.06 Å above the mean plane defined by the remaining four atoms, which are coplanar within 0.03 Å. Compared with known structures, the six-membered ring puckering in **2** resembles those found in the CCD entries PZALPD10, KAMQUK, and WERJAF.[26]

The Pd−C (ethyliminophenyl, 1.984(6) Å), Pd−C (isocyanide, 1.953(6) Å), Pd−N (2.088(4) Å), and Pd−Cl (2.389(2) Å) distances about Pd agree with known data. In particular, the Pd−Cl distance is close to the reported mean value (2.329 Å) in the CCD;[26] the same can be said about the Pd−C distance of the isocyanide ligand (mean 1.969 Å). With respect to the bonds involving the bridging ligand, CCD searches for Pd complexes showing σ-bonded C[5c,7c,8b,27] or N-bonded[5c,7c,8b,27,28] ethyliminophenyl donors returned few entries, in which the Pd−C and Pd−N distances vary from 1.976 to 2.042 Å and from 1.989 to 2.085 Å, respectively.

The 2,6-dimethylphenyl moieties of the isocyanide and of the ethylimino ligands make dihedral angles of 77.2° and 38.0°, respectively, with the main coordination plane. The same residues make dihedral angles of 34.3° and 60.4°, respectively, with the best mean plane of the 1,4-dipalladated ring. Finally, the two rings make an angle of 88.7° with each other. The 2,6-dimethylphenyl moiety belonging to the ethylimino donor seems to assume this position in order to minimize the reciprocal steric clashes of its own methyl groups with the methyl group bound to C(1) and with the chloride ligand. A molecular mechanics calculation made by driving the Pd−N(1)−C(3)−C(4) dihedral angle in a range of 40° centered on the solid-state value (−100.4°) indicates that the conformation found in the crystal is in fact the energetically most favorable.[29] As for nonbonding interactions, despite the presence of the solvation chloroform molecule, the examination of the packing diagram does not reveal any significant contact.

As already stated, the formation of the dimer $[Pd(CNR^2)(C(=NR^2)Me)Cl]_2$ was observed *only* when the DIC isocyanide is reacted with palladium methyl derivatives bearing labile ligands. When a 2-fold excess of tosMIC isocyanide is added to a solution of [Pd(LL)(Me)X] (LL = NS−R, COD), the formation of an equimolecular mixture of the complexes $[Pd(LL)(C(=NR^2)Me)X]$ and $[Pd(CNR^2)2(C(=NR^2)Me)X]$ ($R^2 = CH_2SO_2C_6H_4Me$) is observed, and similar behavior is also observed when the reacting complexes contain the tolyl group instead of the methyl one even when the DIC isocyanide is used. The extent of the Pd−N bond length (2.088 Å) might probably be invoked in order to explain the peculiar reactivity leading to the dimeric species. The basicity of the imidoyl nitrogen is considerably weakened by the withdrawing capability of the tosyl group, and the formation of a dative ligand between the electron-poor nitrogen and the palladium in this case is not allowed. When palladium(II) tolyl derivatives were used as starting complexes, no formation of dimeric species was observed either. Again, steric hindrance between bulky vicinal groups will disfavor the formation of a weak Pd−N bond.

As for the fluxional rearrangement of the dimeric complex $[Pd(CNR^2)(C(=NR^2)Me)Cl]_2$ ($R^2 = Me_2C_6H_3$), it is noteworthy that the RT ^{1}H NMR spectrum of the dimer displays two distinguishable singlets ascribable to the $-2,6(CH_3)_2C_6H_3$ methyl groups of the DIC isocyanide (2.40, 2.36 ppm). Apparently the DIC moiety is not allowed to rotate around the

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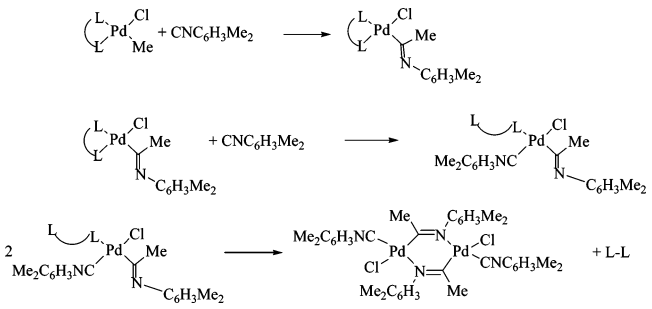
(29) *Spartan '06 for Windows* Version 1.1.0; Wavefunction, Inc.: Irvine, CA, 2006.

Scheme 6



$N-C_6H_3(CH_3)_2$ bond since it is severely hampered by the mutual steric hindrance exerted between substituents in the crowded dimeric structure. In this respect the NOESY spectrum of the dimer $[Pd(CNR^2)(C(=NR^2)Me)Cl]_2$ ($R^2 = C_6H_3Me_2$) clearly displays the spatial correlation between the methyl fragment belonging to the coordinated and that of the inserted isocyanide. Thus, only the signal of the methyl protons of the inserted isocyanide at 2.40 ppm is directly related to the signal of the methyl protons of the coordinated one at 2.52 ppm, while the signal at 2.36 ppm does not display any spatial correlation (see Figure 2SI in Supporting Information).

Similar imidoyl complexes were prepared by some research groups following approaches that take advantage of a coordinative vacancy induced by aryl migration on the Pd−CNR ligand usually promoted by heating the solution mixture containing *trans*-$[Pd(CNR)_2(Ar)X]$, by means of chloro bridge cleavage in dimeric species containing the imidoyl fragment induced by ligand attack,[30] by insertion of isocyanide across the Pd−C ligand in palladacyclo complexes,[31] or by the reaction of the isocyanide complex with aziridines with subsequent deprotonation of bis-carbene species.[32] Interestingly, we have synthesized the complex $[Pd(CNR^2)(C(=NR^2)Me)Cl]_2$ under very mild conditions, and on the basis of our mechanistic observation, we advance the hypothesis that the reaction path to the dimeric species might be summarized by Scheme 6.

Conclusions

The reactivity of several palladium alkyl and aryl substrates bearing pyridyl−thioethers and phosphine−quinolines as ancillary ligands toward two differently substituted isocyanides was investigated. From this study we gathered the following pieces of information.

- Pyridyl−thioether and phosphine−quinoline complexes in the presence of a stoichimetric amount of isocyanide give only the monoinserted derivative analogously to dinitrogen substrates.[5c] This peculiar behavior is unusual since with phosphine derivatives polyinsertion is usually observed.[11]
- Pyridyl−thioether subtrates are more reactive than their phosphine and dinitrogen analogues.[5c,11] It is noteworthy that pyridyl−thioether ligands impart to their alkyl derivatives the highest reactivity that has been hitherto observed in insertion reactions. The reactivity of the DPPQ−Me derivatives reported in this paper should be compared with that of alkyl (or aryl) complexes with pyridyl−thioethers bearing a substituent at the pyridine ring R″NS−R (R″ = Me, Cl) as ligands. The distortion induced by the pyridine substituent makes these substrates very reactive. Unfortunately their very high reaction rates and intrinsic instability due to ligand lability disfavor a detailed study with strong nucleophiles like isocyanates.
- The TosMIC isocyanide is more reactive than DIC due to its reduced steric hindrance at carbon and its enhanced electrophilicity.
- The reaction is scarcely influenced by the nature of the halide. However, when chloride derivatives are used, an excess of Cl^- is added to the reaction mixture in order to suppress the displacement of Cl^- by the added isocyanide.
- Analogously, an excess of NS−R ligand is added in order to suppress its displacement by isocyanide.
- DPPQ−Me derivatives are more reactive than the DPPQ ones due to the distortion induced by the methyl group in position 2 of the quinoline ring in the ground state of the starting complexes.
- On the basis of these pieces of information, a general scheme involving the intimate mechanism was proposed.
- The reaction of methyl or aryl palladium(II) derivatives with a stoichiometric excess of isocyanide was carried out, and the reaction conditions yielding monomeric or dimeric species were carefully investigated.

Experimental Section

Solvents and Reagents. THF and toluene were dried and purified on metallic Na and distilled immediately before use. CH_2Cl_2 and CH_3CN were dried on CaH_2 and distilled before use. Acetone was refluxed and distilled on molecular sieves (3 Å). All other chemicals were commercially available grade products unless otherwise stated.

IR, NMR, and UV−Vis Measurements. The IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer and on a Bruker 300 Avance spectrometer, respectively. The proton and carbon assignments were performed by $^1H-^{13}C$ -HMQC and -HMBC experiments. UV−vis spectra were taken on a Perkin-Elmer Lambda 40 spectrophotometer equipped with a Perkin-Elmer PTP6 (Peltier temperature programmer) apparatus.

Preliminary Studies and Kinetic Measurements. All the insertion reactions were preliminarily analyzed by ^1H NMR technique by dissolving the complex under study in 0.6 mL of $CDCl_3$ ($[complex]_0 \approx 3 \times 10^{-2}$ mol dm^{-3}). An appropriate aliquot of isocyanide was added ($[isocyanide]_0 \approx (3-9) \times 10^{-2}$ mol dm^{-3}), and the reaction was followed to completion by monitoring the signals for the disappearance of the starting complex and the simultaneous appearance of the monoinserted or the inserted-substituted species.

A UV−vis preliminary investigation was also performed with the aim of determining a suitable wavelength. To this purpose, 3 mL of freshly distilled $CHCl_3$ solution of the complex under study ($[complex]_0 \approx 2 \times 10^{-4}$ mol dm^{-3}) and in the case of NS−R derivatives also in the presence of an excess of free ligand ($[NS-R]_0 \approx 2 \times 10^{-3}$ mol dm^{-3}) was placed in a thermostated (25 °C) cell compartment of the UV−vis spectrophotometer, and microaliquots of a concentrated solution of the isocyanide ($[isocyanide]_0 \approx 2 \times 10^{-4}$ mol dm^{-3}) were added. The absorbance change was monitored in the 245−500 nm wavelength interval.

X-ray Analysis. Well-formed crystals of complexes **1** ([Pd(NS*t*-Bu)(C(Tol)=$NC_6H_3Me_2$)I]) and **2** ($[Pd(CNR^2)(C(=NR^2)Me)Cl]_2$), suitable for X-ray work, were placed on the top of a glass capillary and transferred to either a Philips PW-1100 (FEBO System, **1**) or a Nonius MACH3 system (**2**). The latter was generously made available by colleagues at the Department of Environmental Sciences of SUN, Caserta, Italy.

The X-ray diffraction data were collected by the $\omega-2\theta$ technique at 298(2) K, using graphite-monochromated Mo Kα radiation (λ

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= 0.71073 Å (**1**) and λ = 0.70930 (**2**)) and corrected for Lorentz and polarization effects (**1**, **2**) and for absorption factors (**1**). In the case of **2**, the absorption correction was not applied since psi-scans proved that absorption was negligible (transmission between 0.75 and 0.78), probably due to the "cuboid" shape of the specimen. For both complexes, the unit cell parameters were determined by least-squares refinement of the setting angles of 25 well-centered high-angle reflections. Data analysis and cell refinement for **2** were carried out using the programs maXus[33] and SIR 92.[34] Crystal stability was periodically checked by monitoring the intensities of two standard reflections.

The structures of both complexes were solved by means of the direct methods and refined by standard full-matrix least-squares based on F_o^2. The structure solution and refinement were performed by means of the computer programs SHELXTL NT[35] and SHELXL-97[36] using scattering factors incorporated in SHELXL-97. In the last cycles of refinement, all the non-H atoms were allowed to vibrate anisotropically, whereas the H atoms were included in ideal positions and refined as a "riding model". In both structures, the U_{iso} values of hydrogen atoms were set at 1.2 times U_{eq} of the appropriate carrier atom. Crystallographic data and refinement parameters for **1** and **2** are reported in the Supporting information in Tables 1SI and 2SI; no anomalous feature was detected. Tables 3SI and 4SI list relevant bond distances and angles for **1** and **2**, respectively.

Synthesis of the Ligands. The synthesis of the ligands 2-methylthiomethylpyridyne (NS−Me), 2-*tert*-buylthiomethylpyridine (NS*t*-Bu),[37] 8-diphenylphosphanyl-2-methylquinoline (DPPQ−Me),[3] and 8-diphenylphosphanylquinoline (DPPQ)[38] was carried out according to published procedures.

Synthesis of the Complexes [Pd(NS−R)(Me)X]. The synthesis of the title complexes [Pd(NS−R)(Me)X] (R = Me, Et, *i*-Pr, *t*-Bu; X = Cl, I) was carried out according to published procedures.[8a,23]

Synthesis of the Complex [Pd(DPPQ)(Me)Cl]. To 0.1317 g (0.42 mmol) of DPPQ ligand dissolved in 16 mL of anhydrous toluene was added 0.100 g (0.38 mmol) of the complex [Pd(COD)(Me)Cl][39] under inert atmosphere (Ar). The resulting whitish suspension was stirred at RT for 4 h and dried under reduced pressure. The solid residue was dissolved in CH_2Cl_2 (10 mL), treated with activated charcoal, and filtered on a Celite filter. Reduction of the resulting volume under reduced pressure and addition of diethyl ether yielded 0.1615 g (0.342 mmol) of the complex as a white powder. Yield: 90%. ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 10.02 (dd, 1H, J = 1.6 Hz, J = 4.8 Hz, Qui-*H*^{2}), 8.40 (d, 1H, J = 8.3 Hz, Qui-*H*^{4}), 8.08 (d, 1H, J = 8.1 Hz, Qui-*H*^{5}), 7.98 (m, 1H, Qui-*H*^{7}), 7.68 (m, 6H), 7.47 (m, 6H), 0.91 (d, 3H, J = 2.6 Hz, C*H*$_3$-Pd). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K, δ(ppm)): 39.9. Anal. Calcd for $C_{22}H_{19}ClNPPd$: C 56.19, H 4.07, N 2.98. Found: C 56.12, H 4.14, N 3.03.

Synthesis of the Complex [Pd(DPPQ−Me)(Me)Cl]. The title complex was prepared under conditions analogous to those used for the former substrate using DPPQ-Me as ligand. Yield: 85% (whitish microcrystals). ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 8.15 (dd, 1H, J = 1.5, 8.3 Hz, Qui-*H*^{4}), 7.95 (d, 1H, J = 7.9 Hz, Qui-*H*^{3}), 7.66−7.40 (m, 13H aromatic protons), 3.31 (s, 3H, quin-C*H*$_3$), 0.97 (d, 3H, J = 2.9 Hz, C*H*$_3$-Pd). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K, δ(ppm)): 39.3. Anal. Calcd for $C_{23}H_{21}ClNPPd$: C 57.04, H 4.37, N 2.89. Found: C 56.95, H 4.41, N 2.73.

Synthesis of the Complex [Pd(DPPQ)(Me)I]. The title complex was obtained by heterogeneous metathesis of Cl^- with I^- (NaI) under inert atmosphere at RT in CH_2Cl_2 according to established procedures.[23] Yield: 84% (yellow-orange microcrystals). ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 10.41 (dd, 1H, J = 1.6, 4.8 Hz, Qui-*H*^{2}), 8.40 (d, 1H, J = 8.3 Hz, Qui-*H*^{4}), 8.08 (d, 1H, J = 8.1 Hz, Qui-*H*^{5}), 7.97 (m, 1H, Qui-*H*^{7}), 7.66 (m, 6H), 7.50 (m, 6H), 1.12 (d, 3H, J = 2.6 Hz, C*H*$_3$-Pd). ^{31}P{H} NMR ($CDCl_3$, 298 K, δ(ppm)): 35.3. Anal. Calcd for $C_{22}H_{19}INPPd$: C 47.04, H 3.41, N 2.49. Found: C 46.96, H 3.32, N 2.57.

Synthesis of the Complex [Pd(NS−Me)(tolyl)I]. To 0.1431 g (1.03 m.mol) of NS−Me ligand dissolved in 16 mL of anhydrous toluene was added 0.150 g (0.34 mmol) of the complex [Pd(tmeda)(tolyl)I] (tmeda = tetramethylethylenediamine)[40] under inert atmosphere (Ar). The resulting yellow suspension was stirred at RT for 4 h and dried under reduced pressure. The solid residue was dissolved in CH_2Cl_2 (10 mL), treated with activated charcoal, and filtered on a Celite filter. Reduction of the resulting volume under reduced pressure and addition of diethyl ether yielded 0.1262 g (0.272 mmol) of the complex as a pink-yellow powder. Yield: 80%. ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 9.65 (d, 1H, J = 5.4 Hz, Py-*H*^{6}), 7.82 (td, 1H, J = 7.7 Hz, J = 1.7 Hz, H$^4_{pyr}$), 7.47 (d, 1H, J = 7.8 Hz, H$^3_{pyr}$), 7.38 (m, 1H, H$^5_{pyr}$), 7.17 (2H, d, J = 8.0 Hz, H$^{b'}$), 6.85 (d, 2H, J = 8.0 Hz, H$^{c'}$), 4.48 (bs, 1H, pyr-C*H*$_2$-S), 4.18 (bs,-1H, pyr-C*H*$_2$-S), 2.26 (s, 3H, C*H*$_3$C$_6$H$_4$-Pd,), 2.25 (s, 3H, S-C*H*$_3$). Anal. Calcd for $C_{14}H_{16}INPdS$: C 36.26, H 3.48, N 3.02. Found: C 36.39, H 3.52, N 2.96.

The following complexes were prepared under conditions analogous to those of [Pd(NS−Me)(tolyl)I] using the appropriate ligand.

[Pd(NS*t*-Bu)(tolyl)I]. Yield: 81%, pink-yellow powder. ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 9.69 (d, 1H, J = 5.4 Hz, Py-*H*^{6}), 7.79 (td, 1H, J = 7.7 Hz, J = 1.7 Hz, H$^4_{pyr}$), 7.45 (d, 1H, J = 7.8 Hz, H$^3_{pyr}$), 7.33 (m, 1H, H$^5_{pyr}$), 7.21 (d, 2H, J = 8.1 Hz, H$^{b'}$), 6.82 (d, 2H, J = 7.6 Hz, H$^{c'}$), 4.36 (bs, 2H, pyr-C*H*$_2$-S), 2.25 (s, 3H, C*H*$_3$ C$_6$H$_4$-Pd), 1.21 (s, 9H, S-C(C*H*$_3$)$_3$). Anal. Calcd for $C_{17}H_{22}INPdS$: C 40.37, H 4.38, N 2.77. Found: C 40.41, H 4.32, N 2.89.

[Pd(DPPQ)(tolyl)I]. Yield: 81%, pink-yellow powder. ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 10.53 (dd, 1H, Qui-*H*^{2}), 8.44 (d, 1H, J = 8.2 Hz, Qui-*H*^{4}), 8.09 (d, 1H, J = 8.1 Hz, Qui-*H*^{5}), 7.92 (m, 1H, Qui-*H*^{6}), 7.68 (m, 2H, Qui-*H*^{3}, Qui-*H*^{7}), 7.41 (m, 10H, P(C$_6$*H*$_5$)$_2$), 6.92 (d, 2H, J = 6.7 Hz, H$^{b'}$), 6.64 (d, 2H, J = 7.7 Hz, H$^{c'}$), 2.16 (s, 3H, C*H*$_3$ C$_6$H$_4$-Pd). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K, δ(ppm)): 27.4. Anal. Calcd for $C_{28}H_{23}INPPd$: C 52.73, H 3.63, N 2.20. Found: C 52.84, H 3.77, N 2.15.

Synthesis of the Inserted Complexes. DIC Derivatives. Synthesis of the Complex [Pd(NS−Me)(C(=NR^2)Me)Cl], R^2 = 2,6-Me$_2$C$_6$H$_3$. To 0.100 g (0.34 mmol) of [Pd(NS−Me)(Me)Cl] and 0.0947 g of NS−Me dissolved in 9 mL of anhydrous CH_2Cl_2 was added dropwise 0.0446 g (0.34 mmol) of DIC in 2 mL of CH_2Cl_2 under inert atmosphere (Ar). The resulting yellow solution was stirred for 1 h and finally dried under reduced pressure. Diethyl ether was added to the residue, and the ensuing suspension was filtered off, washed twice with small aliquots of diethyl ether to remove the ligand in excess and eventually with pentane, and dried under vacuum at RT; 0.117 g of yellow microcrystals were obtained (yield 81%). ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 9.13 (d, 1H, J = 4.6 Hz, Py-*H*^{6}), 7.77 (td, 1H, J = 7.5 Hz, J = 1.7 Hz, H$^4_{pyr}$), 7.36 (m, 2H, H$^3_{pyr}$, H$^5_{pyr}$), 6.97 (d, 2H, J = 7.3 Hz, H^c), 6.85 (t, 1H, J = 7.4 Hz, H^d), 4.12−3.82 (bd, 2H, pyr-C*H*$_2$-S), 2.55 (s, 3H,

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C(CH_3)=NR^2), 2.34 (s, 6H, (C_6H_3-(CH_3)$_2$)), 1.73 (s, 3H, S-CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K, δ(ppm)): 176.4 (*C*(CH$_3$)=NR^2), 154.4 (C$^2_{pyr}$), 150.8 (C$^6_{pyr}$), 148. 2 (C^b), 138.3 (C$^4_{pyr}$), 128.0 (C^a), 127.8 (C^c), 123.72 (C$^3_{pyr}$), 123.3 (C$^5_{pyr}$), 122.5 (C^d), 45.1 (pyr*C*H$_2$S), 31.8 (C(*C*H$_3$)=NR^2), 20.9 (S-*C*H$_3$), 19.1 (C_6H_3-(*C*H$_3$)$_2$). IR (KBr, cm^{-1}): 1656 $\nu_{C=N}$. Anal. Calcd for $C_{17}H_{21}ClN_2PdS$: C 47.78, H 4.95, N 6.56. Found: C 47.81, H 4.91, N 6.45.

The following complexes were prepared under conditions analogous to those of [Pd(NS−Me)(C(=NR^2)Me)Cl] (R^2 = 2,6-$Me_2C_6H_3$) using the appropriate isocyanide and starting complex.

[Pd(NS−Me)(C(=NR^2)Me)I], R^2 = 2,6-$Me_2C_6H_3$. Yield: 83%, orange-yellow powder. ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 9.48 (d, 1H, J = 4.6 Hz, Py-*H*^{6}), 7.76 (td, 1H, J = 7.5 Hz, J = 1.7 Hz, H$^4_{pyr}$), 7.35 (m, 2H, H$^3_{pyr}$, H$^5_{pyr}$), 6.96 (d, 2H, J = 7.3 Hz, H^c), 6.83 (t, 1H, J = 7.4 Hz, H^d), 4.17 (bs, 2H, pyr-CH_2-S), 2.45 (s, 3H, C(CH_3)=NR^2), 2.28 (s, 6H, (C_6H_3-(CH_3)$_2$)), 2.06 (s, 3H, S-CH_3). IR (KBr, cm^{-1}): 1618 $\nu_{(C=N)}$. Anal. Calcd for $C_{17}H_{21}IN_2PdS$: C 39.36, H 4.08, N 5.40. Found: C 39.45, H 3.99, N 5.29.

[Pd(NS*t*-Bu)(C(=NR^2)Me)Cl], R^2 = 2,6-$Me_2C_6H_3$. Yield: 88%, pale yellow powder. ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 9.13 (d, 1H, J = 4.8 Hz, Py-*H*^{6}), 7.74 (t, 1H, J = 7.7 Hz, H$^4_{pyr}$), 7.31 (m, 2H, H$^3_{pyr}$, H$^5_{pyr}$), 6.95 (d, 2H, J = 7.1 Hz, H^c), 6.86 (m, 1H, H^d), 3.77 (bs, 2H, pyr-CH_2-S)), 2.53 (s, 3H, C(CH_3)=NR), 2.34 (bs, 6H, (C_6H_3-(CH_3)$_2$)), 1.30 (s, 9H, S-C(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K, δ(ppm)): 177.0 (*C*(CH$_3$)=NR^2), 156.3 (C$^2_{pyr}$), 150.1 (C$^6_{pyr}$), 148.1 (C^b), 138.4 (C$^4_{pyr}$), 128.7 (C^a), 127.7 (C^c), 123.5 (C$^3_{pyr}$), 122.2 (C$^5_{pyr}$), 121.6 (C^d), 50.3 (S-*C*(CH$_3$)$_3$), 40.8 (pyr-*C*H$_2$S), 31.9 (C(*C*H$_3$)=NR^2), 30.5 (S−C(*C*H$_3$)$_3$), 19.6 (C_6H_3-(*C*H$_3$)$_2$). IR (KBr, cm^{-1}): 1635 $\nu_{C=N}$. Anal. Calcd for $C_{20}H_{27}ClN_2PdS$: C 51.18, H 5.80, N 5.97. Found: C 51.07, H 5.93, N 6.03.

[Pd(NS*t*-Bu)(C(=NR^2)Me)I], R^2 = 2,6-$Me_2C_6H_3$. Yield: 84%, orange-yellow powder. ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 9.52 (d, 1H, J = 4.8 Hz, Py-*H*^{6}), 7.73 (t, 1H, J = 7.7 Hz, H$^4_{pyr}$), 7.31 (m, 2H, H$^3_{pyr}$, H$^5_{pyr}$), 6.95 (d, 2H, J = 7.1 Hz, H^c), 6.84 (m, 1H, H^d), 4.04 (s, 2H, pyr-CH_2-S)), 2.46 (s, 3H, C(CH_3)=NR^2), 2.32 (s, 6H, (C_6H_3-(CH_3)$_2$)), 1.32 (s, 9H, S-C(CH_3)$_3$). IR (KBr, cm^{-1}): 1633 $\nu_{C=N}$. Anal. Calcd for $C_{20}H_{27}IN_2PdS$: C 42.83, H 4.85, N 4.99. Found: C 42.71, H 4.91, N 4.86.

[Pd(NS−Et)(C(=NR^2)Me)Cl], R^2 = 2,6-$Me_2C_6H_3$. Yield: 86%, pale yellow powder. ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 9.12 (dd, 1H, J = 5.6 Hz, 1.8 Hz, Py-*H*^{6}), 7.75 (td, 1H, J = 7.7 Hz, J = 1.6 Hz, H$^4_{pyr}$), 7.33 (m, 2H, H$^3_{pyr}$, H$^5_{pyr}$), 6.97 (d, 2H, J = 7.4 Hz, H^c), 6.86 (t, 1H, J = 7.3 Hz, H^d), 3.94 (bm, 2H, pyr-CH_2-S), 2.54 (s, 3H, C(CH_3)=NR^2), 2.32 (s, 6H, (C_6H_3-(CH_3)$_2$)), 2.10 (m, 2H, S-CH_2CH$_3$), 1.12 (t, 3H, J = 7.3 Hz, S-CH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K, δ(ppm)): 176.7 (*C*(CH$_3$)=NR^2), 154.9 (C$^2_{pyr}$), 150.6 (C$^6_{pyr}$), 148.4 (C^b), 138.3 (C$^4_{pyr}$), 127.9 (C^a), 127.6 (C^c), 123.6 (C$^3_{pyr}$), 122.9 (C$^5_{pyr}$), 122.4 (C^d), 42.2 (pyr*C*H$_2$S), 31.8 (C(*C*H$_3$)=NR^2), 31.4 (S-*C*H$_2$CH$_3$), 19.4 (C_6H_3-(*C*H$_3$)$_2$), 13.8 (S-CH$_2$*C*H$_3$). IR (KBr, cm^{-1}): 1642 $\nu_{C=N}$. Anal. Calcd for $C_{18}H_{23}ClN_2PdS$: C 48.99, H 5.25, N 6.35. Found: C 49.13, H 5.11, N 6.41.

[Pd(NS*i*-Pr)(C(=NR^2)Me)Cl], R^2 = 2,6-$Me_2C_6H_3$. Yield: 85%, orange-yellow powder. ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 9.11 (d, 1H, J = 5.3 Hz, Py-*H*^{6}), 7.74 (td, 1H, J = 7.7 Hz, J = 1.6 Hz, H$^4_{pyr}$), 7.33 (m, 2H, H$^3_{pyr}$, H$^5_{pyr}$), 6.96 (d, 2H, J = 7.1 Hz, H^c), 6.86 (t, 1H, J = 7.4 Hz, H^d), 3.73 (bs, 2H, pyr-CH_2-S), 2.69 (m, 1H, S-C*H*(CH$_3$)$_2$), 2.52 (s, 3H, C(CH_3)=NR^2), 2.33 (bs, 6H, (C_6H_3-(CH_3)$_2$), 1.30 (bs, 6H, S-CH(CH_3)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K, δ(ppm)): 176.8 (*C*(CH$_3$)NR^2), 155.6 (C$^2_{pyr}$), 150.5 (C$^6_{pyr}$), 148.4 (C^b), 138.3 (C$^4_{pyr}$), 127.5 (C^a), 127.5 (C^c), 123.6 (C$^3_{pyr}$), 122.2 (C$^5_{pyr}$), 122.2 (C^d), 40.9 (pyr*C*H$_2$S), 31.7 (C(*C*H$_3$)=NR^2), 29.6 (S-*C*H(CH$_3$)$_2$), 22.3 (S-CH(*C*H$_3$)$_2$), 19.5 (C_6H_3-(*C*H$_3$)$_2$). IR (KBr, cm^{-1}): 1616 $\nu_{C=N}$. Anal. Calcd for $C_{19}H_{25}ClN_2PdS$: C 50.12, H 5.53, N 6.15. Found: C 50.21, H 5.61, N 6.02.

[Pd(NS−Me)(C(=NR^2)tolyl)I], R^2 = 2,6-$Me_2C_6H_3$. Yield: 91%, orange-yellow powder. ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 9.50 (d, 1H, J = 5.4 Hz, Py-*H*^{6}), 8.02 (d, 2H, J = 8.0 Hz, H$^{b'}$), 7.73 (td, 1H, J = 7.7 Hz, J = 1.7 Hz, H$^4_{pyr}$), 7.33 (m, 2H, H$^3_{pyr}$, H$^5_{pyr}$), 7.15 (d, 2H, J = 8.0 Hz, H$^{c'}$), 7.00 (d, 2H, J = 7.4 Hz, H^c), 6.89 (t, 1H, J = 7.4 Hz, H^d), 3.98 (bs, 2H, pyrCH_2-S), 2.40 (s, 3H, C(C_6H_4CH_3)=NR^2), 2.36 (s, 6H, (C_6H_3-(CH_3)$_2$)), 1.79 (s, 3H, S-CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K, δ(ppm)): 170.5 (*C*(C_6H_4-CH$_3$)NR^2), 154.9 (C$^2_{pyr}$), 153.6 (C$^6_{pyr}$), 148.4 (C^b), 141.2 (C$^{a'}$), 138.6 (C$^{d'}$), 138.1 (C$^4_{pyr}$), 129.3 (C$^{b'}$), 128.2 (C$^{c'}$), 128.2 (C^a), 127.8 (C^c), 124.1 (C$^3_{pyr}$), 123.4 (C$^5_{pyr}$), 122.5 (C^d), 44.4 (pyr*C*H$_2$S), 21.3 (C(C_6H_4*C*H$_3$)=NR^2), 20.5 (S-*C*H$_3$), 20.45 (C_6H_3-(*C*H$_3$)$_2$). IR (KBr, cm^{-1}): 1624 $\nu_{C=N}$. Anal. Calcd for $C_{23}H_{25}IN_2PdS$: C 46.44, H 4.24, N 4.71. Found: C 46.53, H 4.13, N 4.69.

[Pd(NS*t*-Bu)(C(=NR^2)tolyl)I], R^2 = 2,6-$Me_2C_6H_3$. Yield: 90%, orange-yellow powder. ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 9.57 (d, 1H, J = 4.4 Hz, Py-*H*^{6}), 8.24 (d, 2H, J = 7.9 Hz, H$^{b'}$), 7.70 (td, 1H, J = 7.7 Hz, J = 1.7 Hz, H$^4_{pyr}$), 7.27 (m, 2H, H$^3_{pyr}$, H$^5_{pyr}$), 7.14 (d, 2H, J = 8.0 Hz, H$^{c'}$), 6.97 (d, 2H, J = 7.4 Hz, H^c), 6.88 (t, 1H, J = 7.2 Hz, H^d), 3.75 (bs, 2H, pyr-CH_2-S), 2.43 (s, 3H, C(PhCH_3)=NR^2), 2.36 (s, 6H, (C_6H_3-(CH_3)$_2$)), 1.06 (s, 9H, S-C(CH_3)$_3$). ^{13}C-{^{1}H} NMR ($CDCl_3$, 298 K, δ(ppm)): 169.8 (*C*(C_6H_4CH$_3$)=NR^2), 156.7 (C$^2_{pyr}$), 152.9 (C$^6_{pyr}$), 148.1 (C^b), 141.2 (C$^{a'}$), 139.0 (C$^{d'}$), 138.2 (C$^4_{pyr}$), 131.2 (C$^{b'}$), 127.9 (C$^{c'}$), 127.5 (C^a), 127.6 (C^c), 123.8 (C$^3_{pyr}$), 122.2 (C$^5_{pyr}$), 121.8 (C^d), 50.2 ((CH$_3$)$_3$*C*), 40.9 (pyr-*C*H$_2$S), 30.3 (S-C(*C*H$_3$)$_3$), 21.3 (C(C_6H_4*C*H$_3$)=NR^2), 21.1 (C_6H_3-(*C*H$_3$)$_2$). IR (KBr, cm^{-1}): 1608 $\nu_{C=N}$. Anal. Calcd for $C_{26}H_{31}IN_2PdS$: C 49.03, H 4.91, N 4.40. Found: C 48.97, H 4.98, N 4.42.

[Pd(DPPQ)(C(=NR^2)Me)Cl], R^2 = 2,6-$Me_2C_6H_3$. Yield: 88%, pale yellow powder. ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 9.97 (dd, 1H, J = 1.6 Hz, 4.8 Hz, Qui-*H*^{2}), 8.39 (d, 1H, J = 8.3 Hz, Qui-*H*^{4}), 8.06 (d, 1H, J = 8.1 Hz, Qui-*H*^{5}), 7.88 (m, 5H, Qui-*H*^{6}, P(C_6H_2)$_2$), 7.68 (m, 2H, Qui-*H*^{7}, H^3), 7.46 (m, 6H, P(C_6H_2)$_2$), 6.87 (d, 2H, J = 7.4 Hz, H^c), 6.75 (t, 1H, J = 7.3 Hz, H^d), 1.87 (s, 6H, (C_6H_3-(CH_3)$_2$)), 1.83 (d, 3H, J = 1.9 Hz, C(CH_3)=NR^2). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K, δ(ppm)): 178.9 (d, J_{CP} = 11.5 Hz, *C*(CH$_3$)=NR^2), 153.6 (C$^2_{quin}$), 149.9 (C$^9_{quin}$), 149.7 (C$^{10}_{quin}$), 149.5 (C^b), 138.4 (C$^4_{quin}$), 136.4 (C$^6_{quin}$), 134.5 (d, J = 43.9 Hz, C$^8_{quin}$), 134.0 (C$^{P(Ph)}$), 131.5 (d, J_{CP} =2.2 Hz, C$^5_{quin}$,), 131.2 (C$^{P(Ph)}$), 129.2 (C$^{P(Ph)}$), 129.0 (C$^{P(Ph)}$), 127.4 (d, J = 7.1 Hz, C$^7_{quin}$), 127.3 (C^c), 123.0 (C$^3_{quin}$), 121.5 (C^d), 28.3 (d, J_{CP} = 11.0 Hz, C(*C*H$_3$)=NR^2), 18.5 (C_6H_3-(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K, δ(ppm)): 22. 3. IR (KBr, cm^{-1}): 1624 $\nu_{C=N}$. Anal. Calcd for $C_{31}H_{28}ClN_2PPd$: C 61.91, H 4.69, N 4.66. Found: C 62.02, H 4.81, N 4.54.

[Pd(DPPQ−Me)(C(=NR^2)Me)Cl], R^2 = 2,6-$Me_2C_6H_3$. Yield: 86%, pale yellow powder. ^{1}H NMR ($CDCl_3$, 298 K, δ-(ppm)): 8.12 (d, 1H, J = 8.4 Hz, Qui-*H*^{4}), 7.92 (d, 1H, J = 7.7 Hz, Qui-*H*^{3}), 7.79−7.38 (m, 13H, aromatic protons), 6.88 (m 3H, =N-C_6H_3(CH_3)$_2$), 3.26 (s, 3H, quin-CH_3), 1.95 (s, 6H, =N-C_6H_3-(CH_3)$_2$), 1.88 (d, 3H, =N-CH_3, J = 1.8 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K, δ(ppm)): 21.5. IR (KBr, cm^{-1}): 1630 $\nu_{C=N}$. Anal. Calcd for $C_{32}H_{30}ClN_2PPd$: C 62.45, H 4.91, N 4.55. Found: C 62.51, H 4.87, N 4.49.

[Pd(DPPQ)(C(=NR^2)Me)I], R^2 = 2,6-$Me_2C_6H_3$. Yield: 93%, orange-yellow powder. ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 10.36 (d, 1H, J = 4.8 Hz, Qui-*H*^{2}), 8.37 (d, 1H, J = 8.3 Hz, Qui-*H*^{4}), 8.06 (d, 1H, J = 8.1 Hz, Qui-*H*^{5}), 7.88 (m, 5H), 7.64 (m, 2H), 7.48 (m, 6H), 6.85 (d, 2H, J = 7.4 Hz, H^c), 6.74 (t, 1H, J = 7.3 Hz, H^d), 1.87 (s, 6H, (C_6H_3-(CH_3)$_2$)), 1.86 (d, 3H, J = 1.9 Hz, C(CH_3)=NR^2). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K, δ(ppm)): 16.6. IR (KBr, cm^{-1}): 1622 $\nu_{C=N}$. Anal. Calcd for $C_{31}H_{28}IN_2PPd$: C 53.74, H 4.07, N 4.04. Found: C 53.81, H 4.11, N 3.93.

[Pd(DPPQ)(C(=NR^2)tolyl)I], R^2 = 2,6-$Me_2C_6H_3$. Yield: 88%, orange-yellow powder. ^{1}H NMR (CD_2Cl_2, 298 K, δ(ppm)): 10.42 (dd, 1H, J = 1.6 Hz, J = 5.0 Hz, Qui-*H*^{2}), 8.42 (d, 1H, J = 8.2 Hz, Qui-*H*^{4}), 8.05 (d, 1H, J = 8.0 Hz, Qui-*H*^{5}), 7.81 (m,1H, Qui-*H*^{6}), 7.68 (m, 7H, Qui-*H*^{3}, Qui-*H*^{7}, H$_{P(Ph2)}$, 7.45 (m, 2H), 7.30 (m, 3H), 7.03 (d, 2H, J = 8.1 Hz), 6.78 (d, 2H, 7.5 Hz), 6.69 (m, 1H), 6.59 (d, 2H, J = 8.2 Hz), 2.16 (s, 3H, C(C_6H_4CH_3)=NR^2), 1.93 (s, 6H, (C_6H_3-(CH_3)$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K, δ(ppm)): 21.6.

IR (KBr, cm^{-1}): 1611 $\nu_{C=N}$. Anal. Calcd for $C_{37}H_{32}IN_2PPd$: C 57.79, H 4.19, N 3.64. Found: C 57.67, H 4.23, N 3.61.

TosMIC Derivatives. [Pd(NS−Me)(C(=NR²)Me)Cl], R² = CH₂tosyl. Yield: 83%, whitish powder. ^1H NMR ($CDCl_3$, 298 K, δ(ppm)): 9.04 (d, 1H, J = 5.0 Hz, Py-H^6), 7.85 (m, 3H, H^b, $H^4{}_{Pyr}$), 7.49 (d, 1H, J = 7.7 Hz, $H^3{}_{pyr}$), 7.43 (t, 1H, J = 6.5 Hz, $H^5{}_{pyr}$), 7.34 (d, 2H, J = 8.1 Hz, H^c), 5.72−5.19 (bd, 2H, CH_2-SO_2), 4.48−4.11 (bs, 2H, pyr-CH_2-S), 2.54 (s, 3H, CH_3 $C_6H_4SO_2$), 2.45 (s, 3H, C(CH_3)=NR^2), 2.36 (s, 3H, S-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K, δ(ppm)): 179.8 (C(CH_3)=NR^2), 154.9 (C^2), 150.3 (C^6), 144.4 (C^d), 138.8 (C^4), 135.6 (C^c), 129.5 (C^b), 128.8 (C^c), 124.1 (C^3), 123.2 (C^5), 77.1 (CH_2SO_2), 45.6 (CH_2S), 32.1 (C(CH_3)=NR^2), 22.0 (S-CH_3), 21.6 (SO_2 $C_6H_4CH_3$). IR (KBr, cm^{-1}): 1627 $\nu_{C=N}$. Anal. Calcd for $C_{17}H_{21}ClN_2O_2PdS_2$: C 41.55, H 4.31, N 5.70. Found: C 42.44, H 4.45, N 5.61.

[Pd(NS−Me)(C(=NR²)Me)I], R² = CH₂tosyl. Yield: 85%, orange-yellow powder. ^1H NMR ($CDCl_3$, 298 K, δ(ppm)): 9.32 (d, 1H, J = 5.0 Hz, Py-H^6), 7.84 (m, 3H, H^b, $H^4{}_{Pyr}$), 7.48 (d, 1H, J = 7.7 Hz, $H^3{}_{pyr}$), 7.39 (t, 1H, J = 6.5 Hz, $H^5{}_{pyr}$), 7.34 (d, 2H, J = 8.1 Hz, H^c), 5.60 (d, 1H, J = 13.4 Hz, CH_2-SO_2), 5.18 (d, 1H, J = 13.4 Hz, CH_2-SO_2), 4.35 (bs, 2H, pyr-CH_2-S), 2.47 (s, 3H, SO_2-$C_6H_4CH_3$), 2.44 (s, 3H, C(CH_3)=NR), 2.39 (s, 3H, S-CH_3). IR (KBr, cm^{-1}): 1624 $\nu_{C=N}$. Anal. Calcd for $C_{17}H_{21}IN_2O_2PdS_2$: C 35.03, H 3.63, N 4.81. Found: C 35.16, H 3.49, N 4.71.

[Pd(NS*t*-Bu)(C(=NR²)Me)Cl], R² = CH₂tosyl. Yield: 81%, pale yellow powder. ^1H NMR ($CDCl_3$, 298 K, δ(ppm)): 9.03 (d, 1H, J = 5.0 Hz, Py-H^6), 7.88 (d, 2H, J = 8.2 Hz, H^b), 7.82 (td, 1H, J = 7.7 Hz, J = 1.4 Hz, $H^4{}_{pyr}$), 7.45 (d, 1H, J = 7.7 Hz, $H^3{}_{pyr}$), 7.38 (t, 1H, J = 6.5 Hz, $H^5{}_{pyr}$), 7.32 (d, 2H, J = 8.1 Hz,H^c), 5.42 (d, 1H, J = 14.3 Hz, CH_2-SO_2) 5.32 (d, 1H, J = 14.3 Hz, CH_2-SO_2), 4.31 (m, 2H, pyr-CH_2-S), 2.44 (s, 3H, SO_2-$C_6H_4CH_3$), 2.37 (s, 3H, C(CH_3)=NR^2), 1.34 (s, 9H, S-C(CH_3)$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K, δ(ppm)): 186.0 (C(CH_3)=NR^2), 156.3 (C^2), 150.1 (C^6), 144.1 (C^d), 138.8 (C^4), 135.4 (C^c), 129.3 (C^b), 129.0 (C^c), 123.8 (C^3), 121.7 (C^5), 77.1 (CH_2SO_2), 51.2 SC(CH_3)$_3$, 41.0 (CH_2S), 32.9 (C(CH_3)=NR^2), 30.3 (S(CH_3)$_3$), 21.6 (SO_2 $C_6H_4CH_3$). IR (KBr, cm^{-1}): 1625 $\nu_{C=N}$. Anal. Calcd for $C_{20}H_{27}ClN_2O_2PdS_2$: C 45.03, H 5.10, N 5.25. Found: C 44.91, H 5.27, N 5.23.

[Pd(NS*t*-Bu)(C(=NR²)Me)I], R² = CH₂tosyl. Yield: 82%, orange-yellow powder. ^1H NMR ($CDCl_3$, 298 K, δ(ppm)): 9.28 (d, 1H, J = 5.0 Hz, Py-H^6), 7.85 (d, 2H, J = 8.2 Hz, H^b), 7.79 (td, 1H, J = 7.7 Hz, J = 1.4 Hz, $H^4{}_{pyr}$), 7.45 (d, 1H, J = 7.7 Hz, $H^3{}_{pyr}$), 7.32 (m, 3H, $H^5{}_{pyr,}$ H^c), 5.29 (d, 1H, J = 14.2 Hz, CH_2-SO_2), 5.18 (d, 1H, J = 14.2 Hz, CH_2-SO_2), 4.32 (ABsys, 2H 4.38, 4.28, J = 16.8 Hz, pyr-CH_2-S), 2.44 (s, 3H, SO_2-$C_6H_4CH_3$), 2.42 (s, 3H, C(CH_3)=NR^2), 1.30 (s, 9H, S-C(CH_3)$_3$). IR (KBr, cm^{-1}): 1622 $\nu_{C=N}$. Anal. Calcd for $C_{20}H_{27}IN_2O_2PdS_2$: C 38.44, H 4.36, N 4.48. Found: C 38.51, H 4.47, N 4.47.

[Pd(NS−Me)(C(=NR²)tolyl)I], R² = CH₂tosyl. Yield: 85%, orange-yellow powder. ^1H NMR ($CDCl_3$, 298 K, δ(ppm)): 9.48 (d, 1H, J = 5.0 Hz, Py-H^6), 7.96 (d, 2H, J = 8.1 Hz, H^b), 7.92 (d, 2H, J = 8.1 Hz, $H^{b'}$), 7.81 (td, 1H, J = 7.7 Hz, J = 1.5 Hz, $H^4{}_{pyr}$), 7.43 (d, 1H, J = 7.7 Hz, $H^3{}_{pyr}$), 7.37 (m, 3H, $H^5{}_{pyr}$, $H^{c'}$), 7.10 (d, 2H, J = 7.9 Hz, H^c), 5.89−5.35 (bd, 2H, CH_2-SO_2), 4.52−407 (bs, 2H, pyr-CH_2-S), 2.46 (s, 3H, C($C_6H_4CH_3$)=NR^2), 2.34 (s, 3H, SO_2-$C_6H_4CH_3$), 1.9 (bs, 3H, S-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K, δ(ppm)): 168.0 (C($C_6H_4CH_3$)=NR^2), 155.9 (C^2), 153.1 (C^6), 144.4 ($C^{d'}$), 139.5(C^d), 138.5 (C^4), 135.9 ($C^{a'}$), 129.4 ($C^{c'}$), 128.1 ($C^{b'}$), 128.4 (C^c), 124.4 (C^3), 123.4 (C^5), 80.3 (CH_2SO_2), 44.9 (CH_2S), 29.6 ($SO_2C(CH_3)$), 21.6 ($SO_2C_6H_4CH_3$), 21.3 (C($C_6H_4CH_3$)=NR^2), 20.4 (S-CH_3). IR (KBr, cm^{-1}): 1595 $\nu_{C=N}$. Anal. Calcd for $C_{23}H_{25}IN_2O_2PdS_2$: C 41.92, H 3.82, N 4.25. Found: C 41.91, H 3.89, N 4.32.

[Pd(NS*t*-Bu)(C(=NR²)tolyl)I], R² = CH₂tosyl. Yield: 85%, orange-yellow powder. ^1H NMR ($CDCl_3$, 298 K, δ(ppm)): 9.42 (d, 1H, J = 5.0 Hz, Py-H^6), 8.00 (d, 2H, J = 8.1 Hz, H^b), 7.92 (d, 2H, J = 8.1 Hz, $H^{b'}$), 7.81 (td, 1H, J = 7.7 Hz, J = 1.5 Hz, $H^4{}_{pyr}$), 7.44 (d, 1H, J = 7.7 Hz, $H^3{}_{pyr}$), 7.37 (m, 3H, $H^5{}_{pyr}$, H^c), 7.08 (d, 2H, J = 7.9 Hz, H^c), 5.66 (d, 1H, J = 14.3 Hz, CH_2-SO_2), 5.43 (d, 1H, J = 14.3 Hz, CH_2-SO_2), 4.66 (d, 1H, J = 16.7 Hz, pyr-CH_2-S) 4.19 (d, 1H, J = 16.7 Hz, pyr-CH_2-S), 2.43 (s, 3H, SO_2-$C_6H_4CH_3$), 2.32 (s, 3H, C($C_6H_4CH_3$)=NR^2), 1.01 (s, 9H, S-C(CH_3)$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K, δ(ppm)): 181.1 (C($C_6H_4CH_3$)=NR^2), 157.3 (C^2), 152.8 (C^6), 144.1 ($C^{d'}$), 140.9 (C^a), 139.4(C^d), 138.6 (C^4), 135.7 ($C^{a'}$), 130.0 (C^b), 129.3 ($C^{c'}$), 129.1 ($C^{b'}$), 128.2 (C^c), 124. 2 (C^3), 121.9 (C^5), 80.3 (CH_2SO_2), 50.9 (C(CH_3)$_3$), 41.0 (CH_2S), 30.1 (SC-(CH_3)$_3$), 21.6 (SO_2 $C_6H_4CH_3'$), 21.3 (C($C_6H_4CH_3$)=NR^2). IR (KBr, cm^{-1}): 1594 $\nu_{C=N}$. Anal. Calcd for $C_{26}H_{31}IN_2O_2PdS_2$: C 44.55, H 4.46, N 4.00. Found: C 44.61, H 4.38, N 4.12.

[Pd(DPPQ)(C(=NR²)Me)Cl], R² = CH₂tosyl. Yield: 90%, white powder. ^1H NMR ($CDCl_3$, 298 K, δ(ppm)): 9.84 (dd, 1H, J = 1.6 Hz, 4.8 Hz, Qui-H^2), 8.44 (d, 1H, J = 8.3 Hz, Qui-H^4), 8.11 (d, 1H, J = 8.1 Hz, Qui-H^5), 7.86 (m, 1H, Qui-H^6), 7.74 (m, 6H), 7.51 (m, 8H), 7.28 (m, 2H), 5.18 (d, 1H, J = 14.7 Hz, CH_2-SO_2) 4.30 (d, 1H, J = 14.7 Hz, CH_2-SO_2), 2.42 (s, 3H, CH_3- $C_6H_4SO_2$), 2.10 (bs, 3H, C(CH_3)=NR^2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K, δ-(ppm)): 28.1. IR (KBr, cm^{-1}): 1614 $\nu_{C=N}$. Anal. Calcd for $C_{31}H_{28}$-ClN_2O_2PPdS: C 55.95, H 4.24, N 4.21. Found: C 55.79, H 4.37, N 4.15.

[Pd(DPPQ-Me)(C(=NR²)Me)Cl], R² = CH₂tosyl. Yield: 89%, white powder. ^1H NMR ($CDCl_3$, 298 K, δ(ppm)): 8.18 (d,1H, J = 8.5 Hz, Qui-H^4), 7.97 (d, 1H, J = 8.5 Hz, Qui-H^5), 7.89 (m, 1H, Qui-H^6) 7.75−7.42 (m, 14 H, aromatic protons), 7.23 (d, 2H, J = 8.1 Hz, H^c), 5.29 (d, 1H, J = 14.7 Hz, CH_2SO_2), 5.04 (d, 1H, J = 14.7 Hz, CH_2SO_2), 3.28 (s, 3H, quin-CH_3), 2.40 (s, 3H, CH_3PhSO$_2$), 1.89, (s, 3H, C(CH_3)=NR^2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K, δ(ppm)): 27.3. IR (KBr, cm^{-1}): 1626 $\nu_{C=N}$. Anal. Calcd for $C_{32}H_{30}$-ClN_2O_2PPdS: C 56.56, H 4.45, N 4.12. Found: C 56.55, H 4.41, N 4.23.

[Pd(DPPQ)(C(=NR²)Me)I], R² = CH₂tosyl. Yield: 87%, orange-yellow powder. ^1H NMR ($CDCl_3$, 298 K, δ(ppm)): 10.18 (dd, 1H, J = 1.6 Hz, 4.8 Hz, Qui-H^2), 8.43 (d, 1H, J = 8.3 Hz, Qui-H^4), 8.08 (d, 1H, J = 8.1 Hz, Qui-H^5), 7.89 (m, 1H, Qui-H^6), 7.81−7.42 (m, 14H), 5.05 (d, 1H, J = 15.1 Hz, CH_2-SO_2), 4.10 (d, 1H, J = 15.1 Hz, CH_2-SO_2), 2.42 (s, 3H, SO_2 $C_6H_4CH_3$), 2.11 (s, 3H, C(CH_3)=NR^2). $^{31}P\{^1H$ } NMR ($CDCl_3$, 298 K, δ(ppm)): 22.2. IR (KBr, cm^{-1}): 1619 $\nu_{C=N}$. Anal. Calcd for $C_{31}H_{28}IN_2O_2$-$PPdS$: C 49.19, H 3.73, N 3.70. Found: C 49.27, H 3.79, N 3.81.

[Pd(DPPQ)(C(=NR²)tolyl)I], R² = CH₂tosyl. Yield: 90%, orange-yellow powder. ^1H NMR ($CDCl_2$, 298 K, δ(ppm)): 10.31 (dd, 1H, J = 1.6 Hz, J = 5.0 Hz, Qui-H^2), 8.44 (d, 1H, J = 8.2 Hz, Qui-H^4), 8.08 (d, 1H, J = 8.0 Hz, Qui-H^5), 7.78 (m, 3H, $H^{b'}$, Qui-H^7), 7.68 (m, 4H, H^b, Qui-H^3, Qui-H^6), 7.49 (m, 6H, H_{PPh2}), 7.21 (m, 2H, $H^{c'}$), 7.10 (m, 4H, H_{PPh2}), 6.78 (d, 2H, 7.5 Hz, H^c), 5.30 (d, 1H, J = 15.4 Hz, CH_2-SO_2), 4.57 (d, 1H, J = 15.4 Hz, CH_2-SO_2), 2.38 (s, 3H, SO_2-$C_6H_4CH_3$), 2.22 (s, 3H, C($C_6H_4CH_3$)= NR^2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K, δ(ppm)): 184.1 (C(C_6H_4-CH_3)=NR^2), 157.4 ($C^2{}_{quin}$), 150.1 (d, 19.8 Hz, $C^9{}_{quin}$), 143.7 ($C^{d'}$), 140.2 (d, 9.3 Hz, C^a), 138.9 ($C^4{}_{quin}$), 138.2 (C^d), 137.4 ($C^6{}_{quin}$), 135.8 ($C^{a'}$), 133.5 (d, 42 Hz, $C^8{}_{quin}$), 132.9, 132.8, 132.6, 132.4, 132.1 ($C^5{}_{quin}$), 131.5, 130.3, 129.7, 129.6 ($C^{b'}$, C^b), 129.5, 129.1 ($C^{c'}$), 128.6, 128.4 (d, 4.5 Hz, $C^7{}_{quin}$), 127.7 (C^c), 123.6 ($C^3{}_{quin}$), 79.6 (CH_2-SO_2), 21.5 (SO_2-($C_6H_4CH_3$)), 21.1 (C($C_6H_4CH_3$)=NR^2). $^{31}P\{H\}$ NMR ($CDCl_3$, 298 K, δ(ppm)): 22.7. IR (KBr, cm^{-1}): 1593 $\nu_{C=N}$. Anal. Calcd for $C_{37}H_{32}IN_2O_2PPdS$: C 53.35, H 3.87, N 3.36. Found: C 53.26, H 3.79, N 3.43.

Complexes Obtained in the Presence of Isocyanide in Excess. [Pd(CNR²)(C(=NR²)Me)Cl]₂, R² = 2,6-Me₂C₆H₃. To 0.070 g (0.26 mmol) of [Pd(COD)(Me)Cl] in CH_2Cl_2 (10 mL) was added 0.0682 g (0.52mmol; 2 equiv) of DIC isocyanide under inert atmosphere (Ar). The resulting yellowish suspension was stirred for 1 h, dried under vacuum, and treated with diethyl ether (5 mL). The pale yellow solid obtained was washed twice with small aliquots of diethyl ether to remove the COD in excess and

eventually with pentane; 0.0883 g of complex was obtained. Yield: 81%. ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 7.25 (t, 1H, J = 7.4 Hz, H^d), 7.12 (d, 2H, J = 7.4 Hz, H^c), 7.05 (m, 3H, $H^{d''}$, $H^{c''}$), 2.52 (s, 6H, (C_6H_3-(CH_3)$_2$ coordinate isocyanide)), 2.40 (s, 3H, (C_6H_3-(CH_3)$_2$ inserted isocyanide)), 2.36 (s, 3H, (C_6H_3-(CH_3)$_2$ inserted isocyanide)), 2.27 (s, 3H, (C(CH_3)═NR^2)). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K, δ(ppm)): 212.8 (C(CH_3)═NR^2), 145.4 ($C$$NR^2$), 136.1($C^a$), 131.0 ($C^{b'}$), 130.0 ($C^d$), 129.1 ($C^b$), 128.7, 128.4 ($C^{c'}$) 128.0 ($C^c$), 126.2 ($C^{d'}$), 35.0 (C($CH_3$)═$NR^2$), 20.3, 19.4 ($C_6H_4$-($CH_3$)$_2$ inserted), 19.1 (C_6H_4-(CH_3)$_2$ coord). IR (KBr, cm^{-1}): 1563 $\nu_{C=N}$, 2188 $\nu_{C\equiv N}$. Anal. Calcd for $C_{38}H_{42}Cl_2N_4Pd_2$: C 54.43, H 5.05, N 6.68. Found: C 54.57, H 4.98, N 6.71.

[Pd(CNR^2)$_2$(C(═NR^2)Me)Cl], R^2 = 2,6-Me$_2$C$_6$H$_3$. To 0.070 g (0.26 mmol) of [Pd(COD)(Me)Cl] in CH_2Cl_2 (10 mL) was added 0.1023 g (0.78 mmol; 3 equiv) of DIC isocyanide under inert atmosphere (Ar). The resulting yellowish suspension was stirred for 1 h, dried under vacuum, and treated with diethyl ether (5 mL). The pale yellow solid obtained was washed twice with small aliquots of diethyl ether to remove the COD in excess and eventually with pentane; 0.1016 g of complex was obtained. Yield: 71%. ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 7.28 (t, 2H, J = 7.4 Hz, $H^{d''}$), 7.14 (d, 4H, J = 7.5 Hz, $H^{c''}$), 6.89 (m, 3H, H^d, H^c), 2.69 (s, 3H, C(CH_3)═NR^2), 2.41(s, 12H, (C_6H_3-(CH_3)$_2$)$_2$), 2.12 (s, 6H, (C_6H_3-(CH_3)$_2$)). IR (KBr, cm^{-1}): 1660 $\nu_{C=N}$, 2180 $\nu_{C\equiv N}$. Anal. Calcd for $C_{28}H_{30}ClN_3Pd$: C 61.10, H 5.49, N 7.63. Found: C 61.29, H 5.47, N 7.72.

[Pd(CNR^2)$_2$(C(═NR^2)Me)Cl], R^2 = CH$_2$tosyl. The synthesis of the title compound is similar to that of the previously described species. In this case a 3-fold excess of tosMIC isocyanide was used. Yield: 83%, pale yellow powder. ^{1}H NMR ($CDCl_3$, 298 K, δ-(ppm)): 7.88 (d, 4H, J = 8.3 Hz, $H^{b''}$), 7.83 (d, 2H, J = 8.2 Hz, H^b), 7.46 (d, 4H, J = 8.2 Hz, $H^{c''}$), 7.39 (d, 2H, J = 8.0 Hz, H^c), 5.07 (s, 2H, CH_2SO_2), 4.82 (s, 4H, (CH_2SO_2 $C_6H_4CH_3$)$_2$), 2.50 (s, 6H, (SO_2 $C_6H_4CH_3$)$_2$), 2.47 (s, 3H, SO_2-$C_6H_4CH_3$), 2.33 (s, 3H, C(CH_3)═NR^2). IR (KBr, cm^{-1}): 1656 $\nu_{C=N}$, 2224 $\nu_{C\equiv N}$. Anal. Calcd for $C_{28}H_{30}ClN_3O_6PdS_3$: C 45.29, H 4.07, N 5.66. Found: C 45.18, H 3.91, N 5.82.

[Pd(CNR^2)$_2$(C(═NR^2)tolyl)I], R^2 = 2,6-Me$_2$C$_6$H$_3$. To 0.070 g (0.16 mmol) of [Pd(tmeda)(tolyl)I] in CH_2Cl_2 (10 mL) was added 0.0643 g (0.49 mmol; 3 equiv) of DIC isocyanide under inert atmosphere (Ar). The resulting yellowish suspension was stirred for 1 h, dried under vacuum, and treated with diethyl ether (5 mL). The pink-yellow solid obtained was washed twice with small aliquots of diethyl ether to remove the tmeda in excess and eventually with pentane; 0.0908 g of complex was obtained. Yield: 79%. ^{1}H NMR ($CDCl_3$, 298 K, δ(ppm)): 8.21 (d, 2H, J = 7.4 Hz, $H^{b'}$), 7.22 (m, 4H, $H^{c'}$, $H^{d''}$), 7.06 (d, 4H, J = 7.4 Hz, $H^{c''}$), 6.93 (m, 3H, H^c, H^d), 2.43 (s, 3H, C($C_6H_4CH_3$)═NR^2), 2.22 (s, 12H, (C_6H_3-(CH_3)$_2$)$_2$), 2.14 (s, 6H, (C_6H_3-(CH_3)$_2$)). IR (KBr, cm^{-1}): 1624 $\nu_{C=N}$, 2178 $\nu_{C\equiv N}$. Anal. Calcd for $C_{34}H_{34}IN_3O_6PdS_3$: C 44.87, H 3.77, N 4.62. Found: C 45.02, H 3.89, N 4.47.

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Supporting Information Available: Crystallographic data, refinement parameters, bond distances and angles for complex **1** and **2** are reported in Tables 1SI, 2SI, 3SI, and 4SI, respectively. ^{1}H-NMR spectra at 223 and 298 K of complex [Pd(NS−Me)(C(Me)═$NC_6H_3Me_2$)Cl] and the NOESY spectrum of the complex [Pd($CNC_6H_3Me_2$)(C(═$NC_6H_3Me_2$)Me)Cl]$_2$ are reported in Figure 1SI and 2SI, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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