Insertion of Substituted Alkynes into the Pd−C Bond of Methyl and Vinyl Palladium(II) Complexes Bearing Pyridylthioethers as Ancillary Ligands. The Influence of Ligand Substituents at Pyridine and Sulfur on the Rate of Insertion

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The palladium(II) chloro methyl complexes bearing the bidentate 6-R-C_5H_3N-2-CH_2SR' (RN-SR′; R = H, Me, Cl; R′ = Me, *t*-Bu, Ph) and the potentially terdentate 2,6-$(CH_2SR')_2$-C_5H_3N (S-N-S(R′); R′ = Me, *t*-Bu, Ph) pyridylthioethers as ancillary ligands were synthesized, characterized, and reacted with substituted alkynes ZC≡CZ (Z = COOMe, Z′ = COO*t*-Bu, Z″ = COOEt). The reactions were followed under second-order conditions by ^{1}H NMR technique, and the reaction rates were determined. The corresponding vinyl derivatives were synthesized, and in the case of the complexes [PdCl(ZC=CZMe)(MeN-SPh)] and [PdCl(ZC=CZMe)(C1N-S*t*-Bu)] (Z = COOMe) reaction rates for alkyne insertion yielding the corresponding butadienyl complexes were also determined. The rate of insertion of the second alkyne on the vinyl complex is more than 3 orders of magnitude lower than the first insertion rate in both the studied complexes, thereby allowing easy separation between vinyl and butadienyl derivatives and an easy preparation of mixed butadienyl esters. Furthermore, the reaction rates are strongly dependent on the steric and electronic features of the ancillary ligands. In particular, the distortion of the complex main coordination plane, induced by the substituent in position 6 of the pyridine ring, was found to significantly influence the substrate reactivity. The structures of the mono-inserted vinyl [PdCl(ZC=CZMe)(MeN-S*t*-Bu)] (**1**) and the bis-inserted butadienyl [PdCl((ZC=CZ)$_2$Me)(MeN-S*t*-Bu)] (**2**) complexes were determined by X-ray diffraction, and the persistence of a structural distortion of the complex skeleton was observed. Moreover, the distortion may be related to facile ancillary ligand displacement, a feature that can be exploited for the synthesis of substrates that would not be easily obtained otherwise.

Introduction

We have recently shown that suitable steric and electronic modifications of the pyridylthioether ligands may impart a marked reactivity to the corresponding palladium(II) methyl complexes with respect to the insertion reactions of small unsaturated molecules across the Pd−C bond.[1] Since these kinds of reactions identify an important path to C−C bond formation[2] and therefore represent a current topic in the field of synthetic chemistry and copolymerization reactions,[3] we decided to extend our studies to the insertion reactions of alkynes and in particular to the mechanism governing the stoichiometric mono- and bis-insertion reaction on methyl derivatives of palladium(II) bearing pyridylthioethers as ancillary ligands. Olefin and alkyne insertion

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reactions were first investigated in the 1970s by Maitlis[4] and Clark,[5] who studied the insertion into the Pd−C bond of aryl or methyl palladium complexes, respectively. More recently a number of papers dealing with single and multiple alkyne insertion into the Pd−C bond have appeared in the literature.[6] In the case of aryl derivatives, mono-insertion was achieved by reaction of activated alkynes with neutral complexes, whereas poly-insertion was obtained by the use of solvato species, which often yield cyclic derivatives owing to their labile and reactive vacant coordination site. The latter reaction, however, hampers further insertion.[6,7] The methyl derivatives display a less predictable reactivity, and generally the separation between the mono- and the bis-inserted products is not obvious.[5] Different types of ancillary ligands were also employed in the alkyne insertion reactions. Besides the more usual phosphines, diphosphines, and diazotate amino or pyridine ligands,[4−8] phosphoimines[9] and ferrocene derivatives[10] were used as polydentate ligands.

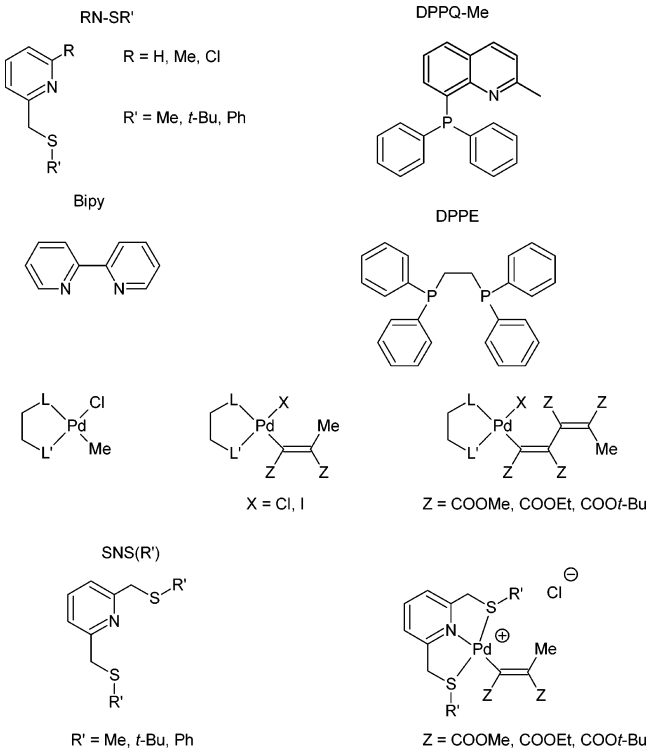
However, it is apparent that the mono- and poly-insertion and in general the reaction degree of advancement are not easily handled since less reactive substrates preferentially give rise to mono-inserted species, whereas the more reactive ones lead to mixtures of mono- and poly-inserted derivatives.

Thus, with the aim of establishing whether the pyridylthioether ligands impart to their palladium methyl substrates an enhanced reactivity analogous to that already observed in the case of entering allenes[1] we decided to extend our study on the reaction of insertion of several activated alkynes across the Pd−C bond. Moreover these insertion reactions go smoothly to completion, and the structure of the product is easily identified. Thus, on the basis of the retention of configuration of the latter (or the lack thereof) and of some other kinetic data, important information about the nature of the intermediate and the involved mechanism becomes available.

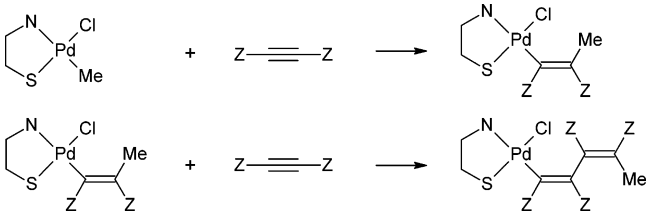
Eventually, on the basis of our knowledge about the coordinating lability of the pyridylthioeter ligands, we programmed the synthesis, by simple metathetic ligand exchange, of a wealth of vinyl and/or butadienyl derivatives that are not easily obtainable otherwise.

The starting alkyl complexes and the ensuing vinyl and butadienyl derivatives together with the employed abbreviations are reported in Scheme 1.

Scheme 1



Scheme 2



Results and Discussion

Synthesis and Solution Behavior of Palladium(II) Vinyl Complexes with Bidentate Pyridylthioethers as Ancillary Ligands. Addition under inert atmosphere of a slight excess of the appropriate alkyne to a solution of palladium(II) pyridylthioether methyl substrates in anhydrous CH_2C1_2 at RT yields quantitatively, promptly, and exclusively the corresponding mono-inserted vinyl complexes (Scheme 2). The reaction could also be carried out under uncontrolled conditions (air and commercial CH_2C1_2), in which case traces of decomposition products render the crystallization process more difficult. Only in the case of the stoichiometric reaction between DMAD (dimethylacetylenedicarboxylate) and [PdCl(Me)(ClN-SPh)] was a mixture of mono- (up to 95%), bis-, and poly-inserted derivatives obtained. On the basis of the X-ray structural determination (vide post) and theoretical and ^{1}H NMR evidence, we suggest that the complex representation in Scheme 2 (the vinyl group in *trans* position to the pyridine nitrogen) agrees with the predominant diastereoisomer (hereafter *trans*)-

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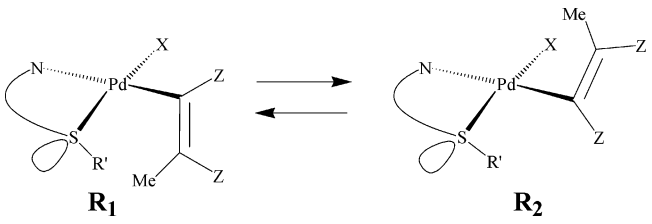
Scheme 3



being present in the solid state and in solution for all the complexes studied. As a matter of fact (i) the ^{1}H NMR spectra of the vinyl derivatives show the presence of only one isomer in solution; (ii) the *trans* influence of sulfur is considerably higher than that of nitrogen; and (iii) all the X-ray diffraction determinations performed in this and in other papers for related methyl species always identify the *trans* isomer.[1a,b]

However, the addition of a small quantity of triethylbenzylammonium chloride (TEBACl) to solutions containing methyl or vinyl derivatives induces a generalized fluxionality, which severely broadens the proton signals; such a phenomenon is ascribed to the establishment of a fast equilibrium between the *trans* and the *cis* isomers promoted by the chloride ion.

Moreover, the peculiar structure of the coordinated vinyl group (which is orthogonal to the main coordination plane) allows the presence of two rotamers, corresponding to the reciprocal positions of the sulfur substituent R′ and the vinyl group itself with respect to the main molecular plane. The low-temperature ^{1}H NMR spectra of these derivatives display the contemporary presence of the two species (Scheme 3). As can be seen in Scheme 3 the existence of the rotamers must be traced back to the rotation of the vinyl fragment around the Pd−C bond since sulfur inversion is already "frozen" at RT, as can be deduced from the presence of signals (two doublets or an AB system) between 4 and 5 ppm due to the diastereotopic endocyclic C$\underline{H}_2$-*S* protons. Usually, inversion of the absolute configuration of sulfur in pyridylthioether palladium complexes is a low-energy process.[11] However, when ligands with a 6-substituted pyridine ring (R = Me, Cl) are involved, it has been noticed that the temperature of inversion of sulfur configuration increases with respect to that of the analogous derivatives bearing ligands with an unsubstituted pyridine. This fact was interpreted on the basis of the weakening of the Pd−N bond generated by distortion of the bond itself with consequent enhancement of the palladium electrophilicity toward the sulfur atom.[1] The distribution between rotamers, summarized in Table 1, is slightly dependent on the steric requirements of the sulfur substituent R. A (^{1}H-2D)-NOESY experiment carried out in $CDCl_3$ at 233 K on the complex [PdCl(ZC═CZMe)(MeN-S*t*-Bu)] indicates that the most abundant rotamer is the *endo* species (**R**$_1$). Such a conclusion can also be advanced for the [PdCl(ZC═CZMe)(ClN-S*t*-Bu)] species, which displays similar behavior in solution and analogous ^{1}H NMR spectrum. No generalization could be drawn for the other species that are present in solution as nonequimolar couples of rotamers and do not display steric characteristics amenable to NOESY experiments.

Table 1. Freezing Temperature and Rotameric Ratio of the Vinyl Derivatives (Z = COOMe)

complex	freezing temperature (K)	rotameric ratio **R**$_1$/**R**$_2$
[PdCl(ZC═CZMe)(HN−SPh)]	243	1.4/1
[PdCl(ZC═CZMe)(MeN−SPh)]	243	1/1
[PdCl(ZC═CZMe)(MeN−S*t*-Bu)]	263	2/1[a]
[PdCl(ZC═CZMe)(ClN−S*t*-Bu)]	243	2.9/1[a]

[a] **R**$_1$ = *endo* rotamer.

With the aim of establishing whether some form of regioselectivity would govern the reaction, the insertion of an asymmetrically substituted alkyne was also studied. Thus, ethyl-4,4,4-trifluoro-2-butynoate (F_3CC≡CCOOEt) was reacted with the complex [PdCl(Me)(MeN-SPh)], leading rapidly to an equally distributed population of isomers. Apparently, the substituent at the unsaturated alkyne carbon does not influence the overall reactivity.

Synthesis and Solution Behavior of Palladium(II) Butadienyl Complexes with Bidentate Pyridylthioethers as Ancillary Ligands. The bis-inserted butadienyl products can be obtained under preparative conditions analogous to the formerly described species by addition of an excess of DMAD to the methyl or vinyl RN-SR′ derivatives (Scheme 2). The choice of the starting complex is strategic, and in this context the most useful substrates are those bearing MeN-SPh or ClN-S*t*-Bu as ancillary ligands. These complexes display a peculiar reactivity that allows facile separation of the required reaction products and an easy control of the reaction degree of advancement, and thus the synthesis of butadienyl derivatives bearing different ester groups Z becomes accessible. Consequently, addition of a 1:5 excess of DMAD to a $CHC1_3$ solution of the complexes [PdCl(Me)(RN-SR′)] or [PdCl(ZC═CZMe)(RN-SR′)] (R = Me, R′ = Ph; R = Cl, R′ = *t*-Bu; Z = COOMe) yields quantitatively the bis-inserted product [PdCl((ZC═CZ)$_2$Me)(RN-SR′)] in 24 h. As will be seen further on, the most reactive substrates are the complexes bearing ClN-SPh as the pyridylthioether ligand; however, such species do not represent the most suitable starting materials, since their intrinsically high reactivity leads often to the formation of poly-inserted derivatives. Conversely, the ligands bearing an unsubstituted pyridine ring (HN-SR′) display a lower reactivity and are not good substrates even toward mono-insertion products, their reactivity being too low in any case. The determination of the rate constants for mono- and bis-insertion will be dealt with further on.

The mono- and bis-inserted complexes undergo a similar fluxional rearrangement in solution. The low-temperature (228 K) ^{1}H NMR spectra in $CDCl_3$ of the latter display the presence of two species that were interpreted as the *exo* and *endo* rotamers, as was suggested in the case of the mono-inserted derivatives.

X-ray Crystal Structures. The molecular structures of [PdCl(ZC═CZMe)(MeN-S*t*-Bu)] (**1**) and [PdCl((ZC═CZ)$_2$Me)(MeN-SPh)] (**2**) and the employed numbering scheme are illustrated as ORTEP[12] drawings, in Figures

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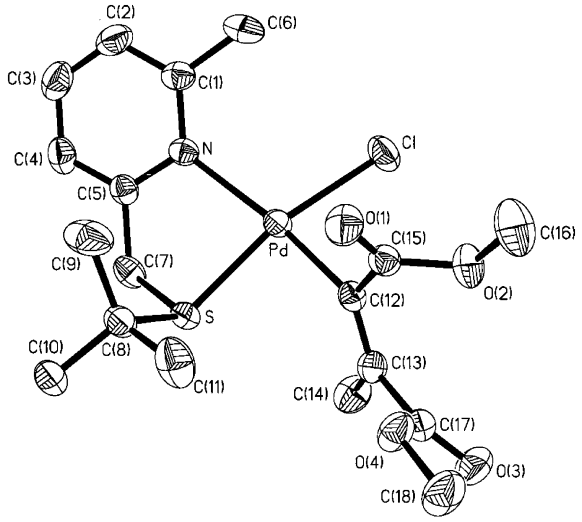

Figure 1. ORTEP representation of complex **1**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are at the 40% probability level.

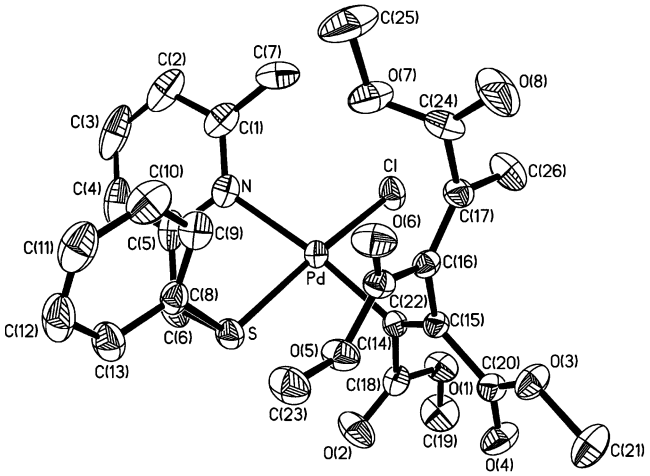

Figure 2. ORTEP representation of complex **2**. Figure settings as for **1**.

1 and 2, respectively. In both complexes the Pd core is surrounded by a tetrahedrally distorted square planar environment, whereas the vinyl and the butadienyl moieties are perpendicular to the main coordination plane. The configuration of complex **2** is *E*,*E* (both sets of ester groups are *cis* disposed). In **1**, the atoms Pd, S, N, Cl, and C(12) deviate from the basal square plane by 0.07, −0.23, 0.19, −0.20, and 0.24 Å. The dihedral angle between the triangles S−Pd−N and Cl−Pd−C(12) is 17.1°, and the angles S−Pd−Cl and Cl−Pd−C(12) measure 164.2(1)° and 85.9(1)°, respectively. In **2**, the atoms Pd, S, N, Cl, and C(14) deviate from the main plane by 0.17, −0.15, 0.14, −0.13, and 0.14 Å. The dihedral angle between the triangles S−Pd−N and Cl−Pd−C(14) is 15.6° and the S−Pd−Cl and Cl−Pd−C(14) measure 164.4(1)° and 90.1(1)°, respectively. The S−Pd−N "bite" angle is 84.2(1)° in **1** and 82.3(1)° in **2**.

A search in the Cambridge Crystallographic Database[13] for similar Pd(II) square planar complexes showing the N_{pyr}, S, Cl, C (N_{pyr} = pyridine nitrogen) donor set returned seven entries;[1a,b,14−16] the bond distances around Pd in **1** and **2** agree with existing data. In particular, the Pd−N bond in **1** (2.206(2) Å) is longer than in **2** (2.148(4) Å), and it is the second longest reported so far, following the one found in ref 1a (2.229(4) Å). The same bond of **2** approaches also the values found in ref 1a, 2.162(5) Å, and in ref 1b, 2.16(1) and 2.17(1) Å. The Pd−S bond in **1** (2.276(1) Å) is shorter than in **2** (2.283(2) Å), and the two distances compare well with those of the complexes described in ref 15, 2.276(1), 2.281(1), and 2.273(1) Å. The bond in **2** is also the third longest after those reported in ref 14 (average value of 2.294 Å). The Pd−Cl distances in **1** and **2** are 2.340(1) and 2.318(2) Å, respectively, and they match those described in ref 1b, 2.340(6) and 2.315(6) Å. The Pd−C distances are 1.986(3) and 1.989(5) Å in **1** and **2**, respectively, and are close to the ones reported for ref 14 (average value of 1.984 Å).

These distances can be explained in terms of the *trans* influence. In both complexes, the pyridine ligand and the sulfur atom are faced by a negatively charged σ-bonded C ligand and by a chloride, respectively. The *trans* influence of these hard bases (combined with the distortion induced by the presence of the pyridine 6-methyl group) leads to long Pd−N and Pd−S and short Pd−C and Pd−Cl bonds. However, the different Pd−N bond length in **1** and **2** cannot be explained only with the greater amount of tetrahedral distortion found in **1**. The Pd−C distances deserve further comment. The σ-bonded C atom in **1** and **2** belongs to an olefin moiety, like in refs 14−16, while it belongs to a methide in refs 1a,b; the shortest Pd−C distance is found in the olefin group (mean value of 1.984 Å for ref 14), the longest in the methide group (2.048(5) Å for ref 1a). This is also due to the *trans* influence. In fact, in the methide group the C donor atom is always *trans* to the pyridine ligand, whereas in the olefin group it is *trans* to a chloride (a softer base).

The chelate pyridine ligand forms a five-membered ring showing an *envelope* (C_s) conformation in both complexes. The atoms participating to the ring other than Pd are N, C(5), C(7), and S in **1** and N, C(5), C(6), and S in **2**. In the former, these atoms do not deviate more than 0.02 Å from the ring mean plane, except sulfur (out by 0.76 Å). In the latter, the deviations are −0.03, 0.07, −0.08, 0.04, and 1.03 Å for Pd, N, C(5), C(6), and S, respectively.

Other sets are defined by the C−C(O)−OMe residues. In **1**, the C(12)−C(15)(=O(1))−O(2)−C(16) and C(13)−C(17)(=O(3))−O(4)−C(18) moieties are defined with the basal plane dihedral angles of 96.7° and 113.6°. In **2** there are four such residues (clockwise from the top in Figure 2: I−IV), which are all approximately perpendicular to the basal plane (dihedral angles of 78.7°, 89.7°, 109.8°, and 105.3° for I−IV, respectively). More planes are defined in **2** by the C(14), C(15), C(16), and C(17) atoms of the alkene ligand and by the phenyl ring bound to sulfur. The former makes a dihedral angle of 85.1° with the basal plane, and the latter makes angles of 109.2° with the basal plane and of 103.7° with the pyridine plane.

As for nonbonding interactions, in **1** the sole detectable interaction involves, within the same molecule, the Pd atom and a hydrogen atom bonded to C(6) (Pd- - -HC(6) distance 2.81 Å, Pd- - -H−C(6) angle 125.5°). In

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Table 2. Second-Order Rate Constants for Reactions 1 (k_I) and 2 (k_{II}) at 298 K

	solvent	complex	k_I (s^{-1} dm^3 mol^{-1})[a]	k_{II} (s^{-1} dm^3 mol^{-1})[b]
1	$CDCl_3$	[PdCl(Me)(HN-SPh)]	1×10^{-4}	
2	$CDCl_3$	[PdCl(Me)(MeN-S*t*-Bu)]	2.1×10^{-3}	
3	$CDCl_3$	[PdCl(Me)(MeN-SPh)]	1×10^{-1}	2.5×10^{-4} [c]
4	$CDCl_3$	[PdCl(Me)(ClN-S*t*-Bu)]	1.17	$\sim 6 \times 10^{-4}$ [c,d]
5	$CDCl_3$	[PdCl(Me)(N-N)] [e]	4.3×10^{-3}	
6	$CDCl_3$	[PdI(Me)(MeN-SPh)]	1.34	
7	Acetone	[PdCl(Me)(MeN-SPh)]	3.2×10^{-2}	
8	CD_3CN	[PdCl(Me)(MeN-SPh)]	5.8×10^{-2}	

[a] Rate of first insertion reaction. [b] Rate of second insertion reaction. [c] Value from second-order half-life expression: $k_{II} = \ln((2B_0 - A_0)/B_0)/(B_0 - A_0)t_{1/2}$ (A_0 and B_0 represent the initial concentrations of complex and alkyne, respectively). [d] Uncertain value due to partially obscured ^{1}H NMR signals. [e] N-N = 6-MeC_5H_3N-2-CH=N-C_6H_4-4-OMe.

2, the packing diagram shows that the pyridine rings are stacked. The separation between the rings is 4.03 Å, compared to 3.40 Å in graphite. A similar, but less efficient, stacking is also observed for the phenyl ring bound to sulfur; the separation is about $^1/_2$ *b*, corresponding to 5.6 Å.

Kinetics and Mechanism of the Alkyne Insertion Reaction. The course of insertion of DMAD (reactions 1, 2) was monitored at 298 K by ^{1}H NMR spectrometry since the UV/vis technique was hampered by the small difference in absorbance between reactants and products. Thus, the reactions were independently followed by mixing the complex under study ([PdCl(Me)(RN-SR′)]$_0 \approx 1.6 \times 10^{-2}$ mol dm^{-3}, [PdCl(Me)(RN-SR′)]$_0$/[DMAD]$_0$ = 1:1.2 for reaction 1 and [PdCl(ZC=CZMe)(RN-SR′)]$_0 \approx 1.6 \times 10^{-2}$ mol dm^{-3}, [PdCl(ZC=CZMe)(RN-SR′)]$_0$/[DMAD]$_0$ = 1:5 for reaction 2) and recording the disappearance of the Pd−C$\underline{H}_3$ proton signal at ~1 ppm (reaction 1) and the appearance or disappearance of the most suitable signals in the case of reaction 2.

$$[\mathrm{PdCl(Me)(RN\text{-}SR')}] + \mathrm{ZC{\equiv}CZ} \rightarrow [\mathrm{PdCl(ZC{=}CZMe)(RN\text{-}SR')}] \quad (k_I) \quad (1)$$

$$[\mathrm{PdCl(ZC{=}CZMe)(RN\text{-}SR')}] + \mathrm{ZC{\equiv}CZ} \rightarrow [\mathrm{PdCl((ZC{=}CZ)_2Me)(RN\text{-}SR')}] \quad (k_{II}) \quad (2)$$

(Z = COOMe)

The rate constants, which are summarized in Table 2, were determined by nonlinear fitting of concentration vs time data by means of the customary integrated second-order rate law or evaluated from the first half-lives under second-order conditions. The second-order conditions were dictated by the peculiar experimental situation (fast reactions and uncertainty in the readability of the NMR spectra owing to problems of mutual scaling among the ensuing signals in the case of pseudo-first-order conditions). Each value represents the average of two or three independent evaluations with an estimated 10% relative error.

It is apparent that (1) the difference between the first and the second insertion rates is large, spanning about 4 orders of magnitude. In other words the Pd-Me derivatives are much more reactive than the vinyl complexes (see entries 3 and 4). (2) The substituent in position 6 of the pyridine ring enhances the reactivity by at least 3 orders of magnitude (see entries 1 and 3). (3) The chloride in position 6 of the pyridine ring imparts a higher reactivity than that of the corresponding substrate bearing the methyl group as pyridine substituent (see entries 2 and 4). (4) The reactivity of the complexes also depends on the substituent at sulfur. The complex bearing the less hindered and more electron-withdrawing phenyl group is markedly more reactive than that with the *t*-Bu moiety (see entries 2 and 3). (5) Complexes bearing different ancillary ligands with analogous chelating capability[17] show an enhanced reactivity if the sulfur atom is present in the complex backbone (see entries 3 and 5). (6) The iodo derivative is more reactive (1 order of magnitude) than its chloro analogue (see entries 3 and 6). (7) The dielectric constant of the solvent does not influence appreciably the rate constants (see entries 3, 7, and 8).

For the sake of completeness, the insertion reaction of DMAD across the Pd−C bond of the complex [PdCl(Me)(MeN-SPh)] was also studied at different temperatures in $CDCl_3$, and the results are summarized in Table 3.

The activation parameters calculated by the reparametrized Eyring equation[18] are $\Delta H^{\ddagger} = 7.7 \pm 1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -6 \pm 5$ cal mol^{-1} K^{-1}.

On the basis of these experimental findings we propose the mechanistic Scheme 4.

Under pre-equilibrium conditions (migration of the methyl group being the rate-determining step), with $1 \gg K_e$[DMAD] the rate law becomes rate = $K_e k_m$[complex][DMAD], where the experimentally determined $k_2 = K_e k_m$.

Scheme 4 directly comes from the well-established theory of nucleophilic substitution of square planar complexes. The pentacoordinate intermediate species displays the alkyne molecule (entering group) lying in the same trigonal plane as the methyl (leaving group) and the pyridine nitrogen (group in *trans* position to the leaving group itself). The rate-determining leaving group migration to the *cis* coplanar alkyne gives rise to the reaction product with retention of configuration, the vinyl group being in *trans* position to the pyridine nitrogen.

It is therefore apparent that the complexity of the composite mechanism undermines any discussion about the real meaning of activation parameters. In particular, no conclusion could be drawn from the low negative value of the activation entropy. Thus, Scheme 4 accounts for the lack of influence of the solvent dielectric constant on the overall reaction rates since no intermediates carrying or producing separation of charges are involved, which would be the case if chloride ions were

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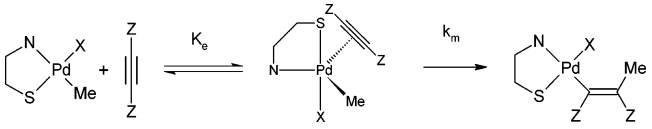
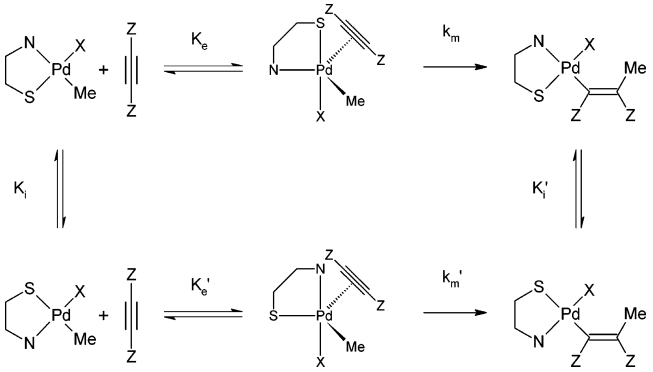
Table 3. Second-Order Rate Constants for Reaction 1 in $CDCl_3$ for the Complex [PdCl(Me)(MeN-SPh)] at Different Temperatures

	T (K)				
	273.15	283.15	298.15	313.15	323.15
k_I ($s^{-1}\,dm^3\,mol^{-1}$)	6.6×10^{-3}	2.67×10^{-2}	1.1×10^{-1}	3.1×10^{-1}	6.8×10^{-1}

Scheme 4



Scheme 5



the leaving group. The difference in reactivity among similarly substituted complexes described in Table 2 arises from the presence of a substituted pyridine ring in the ligand molecule. The induced distortion coupled with adequate electronic effect (i.e., electron-withdrawing capability of sulfur and pyridine substituents) renders the methyl palladium complexes very reactive. These effects were deeply discussed elsewhere,[1] and it is apparent that, despite the fact that distortion would render the starting substrate more similar to a pentacoordinate intermediate, the chemical stability of the complexes is warranted by the flexibility of the chelating ring constituted by the pyridine nitrogen and the two carbon and sulfur sp^3 atoms. As a matter of fact, the complex [PdCl(Me)(N-N)] (N-N = 6-methyl-2-pyridylcarbaldimine) is not particularly reactive despite its having a methyl group in position 6 of the pyridine ring (Table 2). In other words, distortion makes the starting substrate very reactive by enhancing its intrinsic ground state energy and favoring association of alkynes in the first step of reaction (increase of K_e).

However, the reactivity of complexes bearing the ClN-SPh ligand is not immediately explained. It was noticed that the complex [PdCl(Me)(ClN-SPh)] is present in solution as an equilibrium mixture of *cis* and *trans* isomers, the *trans* isomer being predominant ([*trans*]/[*cis*] $\approx$ 10:1), since the 6-chloro-substituted pyridine is less firmly bonded to the metal center.[1b] The presence in solution of a less stabilized and more reactive species would enhance the reactivity of the complex [PdCl(Me)-(ClN-SPh)] toward insertion. Thus, also the present reaction mechanism would be better explained by admitting an alternative path via the more reactive *cis* species, where the methyl group lies in *trans* position with respect to sulfur. Moreover, since iodide displays a higher *trans* effect than the chloride ion, the enhanced reactivity of [PdI(Me)(MeN-SPh)] with respect to its chloride analogue could be explained by invoking the presence in solution of the more reactive *cis* species, as can also be deduced from its ^1H NMR spectrum, which under the same experimental conditions appears considerably more broadened than that of its chloride analogue.[1c] Eventually, addition of chloride ion (TEBACl) to the reaction mixture would catalyze the isomerization between *trans* and *cis* derivatives, giving rise also in this case to the observed rate increment due to the increased rate of formation of the *cis* isomer, a substrate otherwise not available for the insertion reaction.

The overall reaction mechanism should then be described by Scheme 5, the lower part being operative only under the favorable conditions described before. The isomerization constant K_i (in the case of added chloride) is obviously independent of chloride concentration and ionic strength, and its value should be $\ll 1$, as can be deduced from the experimental results and from the consideration that in the case of complex [PdCl(Me)-(ClN-SPh)] (which represents the most favorable case) $K_i \cong 0.1$.

The difference between the k_I and k_{II} values in Table 2 is easily traced back to the increased steric demand of the vinyl with respect to the methyl group and to the shortening with consequent strengthening of the Pd $-$N bond (vide supra). Under these conditions the rate-determining vinyl migration will be depressed due to the lower K_e and k_m values. The insertion reaction of the alkyne across the Pd$-$vinyl bond is also enhanced by the addition of chloride but to a lesser extent than the previously described reactions. Apparently, the faster formation of the more reactive *cis* isomer can hardly affect the reaction rate owing to the higher stabilization of the vinyl with respect to the methyl group (vide supra).

Synthesis, Solution Behavior, and Reactivity of Palladium(II) Vinyl Complexes with Terdentate Pyridylthioethers as Ancillary Ligands. The insertion of the activated alkyne DMAD across the Pd$-$C bond in methyl complexes bearing terdentate pyridylthioether ligands (SNS(R′)) under experimental conditions analogous to those used in the synthesis of the bidentate species yields the mono-inserted vinyl derivatives.

The reaction progress was detected by ^1H NMR technique following the shift of the signal of the methyl group from $\sim$0.8 to $\sim$2.5 ppm upon transfer from the metal to the vinyl moiety. The reactions were monitored under second-order conditions, and the experimental conditions and the half-life times for the insertion of DMAD into different terdentate complexes are listed in Table 4. These half-life times should be taken as raw indicators of reactivity since the mechanistic picture involving these substrates and their insertion reactions is rather complicated and not amenable to a fully fledged kinetic study. In fact, these potentially terdentate complexes are known[1d] to undergo equilibrium displacement of one chelating arm by chloride, leading

Table 4. Molar Ratio and Estimated Half-Life Time for the Insertion Reaction of DMAD into the Pd−Me Bond of Palladium Complexes Bearing Potentially Terdentate Pyridylthioether Ligands

complex	$[Pd]_0/[DMAD]_0$	$t_{1/2}$ (s)
[PdCl(Me)(SNS(Ph))]	$1.06 \times 10^{-2}/1.17 \times 10^{-2}$	90
[PdCl(Me)(SNS(Me))]	$3.04 \times 10^{-2}/3.49 \times 10^{-2}$	410
[PdCl(Me)(SNS(*t*-Bu))]	$3.05 \times 10^{-2}/3.49 \times 10^{-2}$	5200

to neutral bidentate methyl-chloride complexes with a dangling wing. Insertion takes place only on the neutral bidentate species to yield the inserted product, which in turn is in chloride-mediated equilibrium with the corresponding terdentate mono-inserted species. As matter of fact, the terdentate methyl substrate, which is easily obtained by dechloridation with $AgClO_4$ of the bidentate chloro methyl complex, is unreactive. As can be seen, the reactivity of the potentially terdentate ligands is similar to that of 6-methyl-substituted pyridylthioether bidentate derivatives despite their behaving mostly as terdentate moieties in solution.[1d] Only in the case of [PdCl(Me)(SNS(*t*-Bu))] do the bulky *tert*-butyl groups exert a remarkable steric retardation. The most prominent difference between the bidentate and the terdentate derivatives arises from the fact that the latter do not easily give rise to bis-inserted butadienyl species. As a matter of fact, it is noteworthy that the half-life time for the second insertion of DMAD into the complex [PdCl(CZ═CZMe)(SNS(Me))] (Z = COOMe) is about 72 h. Apparently the second insertion reaction is sterically and electronically hampered (the vinyl group is less reactive than the methyl group), and this very fact can be exploited to produce in short time (with a large excess of alkyne) the mono-inserted species, which can be used as starting material in the synthesis of other derivatives (vide post).

Vinyl and Butadienylpyridylthioether Palladium Complexes as Starting Materials. Ligand Exchange. It has been already noticed that the 6-substituted pyridylthioether ligands are easily displaced by monodentate or chelating molecules. Thus, the reaction of allylpyridylthioether derivatives with monodentate amines yields the corresponding unreactive bis-amino species,[17c,19] and the palladium(0) olefin derivatives easily exchange the pyridylthioether ligand with an α-diimine moiety, in any case irrespectively of the apticity of the pyridylthioether ligand itself.[20] It is noteworthy that the lability of the latter ligands and the ease in controlling the insertion degree of advancement when their derivatives are involved could be exploited to synthesize vinyl or butadienyl complexes with ligands that will not impart the adequate reactivity to their methyl derivatives. Thus, the exchange reactions between ligands according to Scheme 6 were performed. The metathetic exchanges were followed in $CDCl_3$ under very mild conditions (complex/ligand = 1:1.02 molar ratio at room temperature). The reactions are fast and complete with all the species studied, as can be seen from the NMR spectra.

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Conclusions

The reactivity and the selectivity toward mono- and bis-insertion reaction of alkynes across the Pd−C bond in pyridylthioether palladium methyl complexes were investigated, and the peculiar behavior of these substrates was confirmed. In particular, the reaction rate in some cases is high and comparable with that of solvento species bearing different ancillary ligands. However, in our complexes no vacant coordinative position is available, and therefore no undesired cyclic species is formed. The modification induced by the ancillary ligand to the geometry of the substrate was confirmed to be very important since the starting complex assumes a distorted configuration similar to that of the reactive intermediate.

On the basis of kinetic and structural investigations a simple mechanism for the reaction under study is proposed that takes into account the electronic and steric features of the sulfur and pyridine substituents and the effect that the substituent *trans* to the pyridine nitrogen exerts on the overall rate. There emerges that the reactivity of the complex [PdCl(Me)(ClN-SPh)] is the highest detected in the case of pyridylthioether complexes and one of the highest found in the literature. However, the stoichiometric reaction of the complex [PdCl(Me)(ClN-SPh)] and DMAD yields a mixture of mono-, bis-, and poly-inserted derivatives, and thus such a substrate is not the best choice as far as the synthesis of intermediates is concerned. The most suitable complexes for mono- and bis-insertion are [PdCl(Me)(MeN-SPh)] and [PdCl(Me)(ClN-S*t*-Bu)], since their reactivity allows the ready formation of [PdCl(ZC═CZMe)(RN-SR′)] at 1:1 complex/alkyne and of [PdCl((CZ═CZ)$_2$Me)-(RN-SR′)] at 1:5 complex/alkyne molar ratios, respectively. Apparently, stoichiometric control of the insertion products is easily achieved.

As a consequence, the synthetic operative conditions allow the formation of mixed butadienyl derivatives bearing different Z groups as butadiene chain substituents whose importance is brought to bear when hydrolysis or *trans*-esterification reactions are involved. The difference in reactivity of the various substituted esters toward such reactions might gain primary importance.[21]

Eventually, these compounds represent an interesting class of starting substrates in the production of vinyl and butadienyl complexes owing to the lability of pyridylthioethers as ancillary ligands.

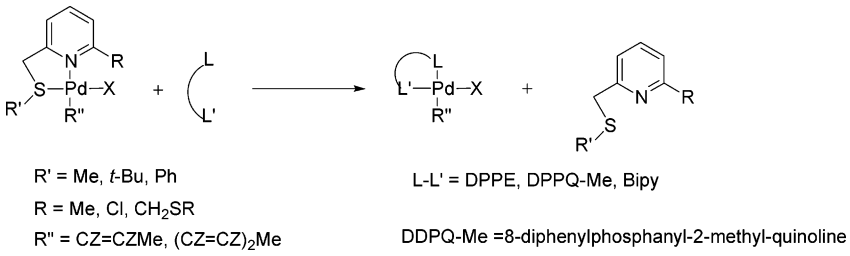
Experimental Section

Solvents and Reagents. CH_2Cl_2 was dried and distilled on CaH_2. 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 $\{^1H-^1H\}$-NOESY experiments 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 assignment was 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.

(21) Kocienski, P. J. In *Protecting Groups*; Georg Thieme Verlag, 2000; p 125.

Scheme 6



Preliminary Studies and Kinetic Measurements: Insertion Reactions. In a typical NMR experiment 1.8×10^{-2} mmol of the complex under study was dissolved in 0.6 mL of $CDCl_3$, and the appropriate alkyne was added in order to produce the molar ratio required by the particular process (1:l or 1:5 for mono- or bis-insertion, respectively). The reaction progress was followed at 298 K by recording selected integrated signals of the reactants and products. The ensuing rate constants were computed from nonlinear regression of the concentration profiles vs time according to the customary second-order rate law or (in the case of the slowest reactions) from the estimated half-life time as $k_2 \approx \ln((2[\mathrm{Alk}]_0 - [\mathrm{Pd}]_0)/[\mathrm{Alk}]_0)/([\mathrm{Alk}]_0 - [\mathrm{Pd}]_0)t_{1/2}$. In one case the asymmetric substituted alkyne 4,4,4-trifluoroacetylene-2-butynoato ($F_3CC{\equiv}CCOOMe$) was also studied in order to gather some information on the regioselectivity of the insertion reaction. However, from the ^1H NMR spectra it can be deduced that the reaction will yield both possible diastereoisomers (Pd(ZC=CZ‴) and Pd(Z‴C=CZ); Z‴ = CF_3, Z = COOMe) in equivalent molar ratio, each species being present as a couple of rotamers (see Results and Discussion).

Metathesis Reactions. The metathetic exchange reaction among ligands was also followed in $CDCl_3$ by NMR technique, and under NMR experimental conditions ($[Pd]_0/[L\text{-}L]_0$, 1:1; $[Pd]_0 \approx 3 \times 10^{-2}$ mol dm^{-3}) all the reactions studied were immediate.

X-ray Analysis. Crystals of **1** and **2** suitable for X-ray analysis were sealed in a glass capillary and mounted on the goniometer head of two different four-circle automated diffractometers equipped with a graphite monochromator in the incident beam (Mo Kα radiation). The crystals of **1** were mounted on a Nicolet Siemens R3m/V; those of **2** on a Philips PW-1100 (FEBO System). The intensities of the diffracted beam were measured at room temperature, and unit cell dimensions were obtained from a least-squares fit of 50 well-centered reflections (for **1**) and 30 reflections (for **2**). Crystal stability was checked periodically by monitoring the intensities of three standard reflections. Data were collected by the $\omega-2\theta$ scan technique and corrected for Lorentz−polarization effects and for absorption. The two structures were solved by the heavy atom method and refined on F^2 by standard full-matrix least squares. In the last cycles of refinement the non-H atoms were allowed to vibrate anisotropically; H atoms were included in ideal positions and refined as riding model. Crystallographic data and reliability factors are reported in Table 5, while Table 6 lists the relevant bond distances and angles for both complexes. The SHELXTL NT[22] computer program was used for structure solution and SHELXL-93 for structure refinement.[23]

Synthesis of the Bidentate and Terdentate Ligands. The synthesis of the ligands 6-chloro-2-*tert*-butylthiomethylpyridine (ClN-S*t*-Bu), 6-chloro-2-phenylthiomethylpyridine (ClN-SPh),[20a] 6-methyl-2-phenylthiomethylpyridine (MeN-SPh), 6-methyl-2-methylthiomethylpyridine (MeN-SMe), 6-methyl-2-*tert*-butylthiomethylpyridine (MeN-S*t*-Bu), 2-phenylthiomethylpyridine (HN-SPh),[17c] 2,6-bis(phenylthiomethyl)-pyridine (S-N-S(Ph)), 2,6-bis(methylthiomethyl)pyridine (S-N-S(Me)), and 2,6-bis(*tert*-butylthiomethyl)pyridine (S-N-S(*t*-Bu))[19,20] was carried out according to published procedures.[17c,19,20] All other chemicals were commercial grade and were purified or dried by standard methods where required.[24]

Table 5. Summary of Crystal and Refinement Data for 1and 2

	1	**2**
empirical formula	$C_{18}H_{26}ClNO_4PdS$	$C_{26}H_{28}ClNO_8PdS$
fw	494.3	656.4
cryst syst; space group	triclinic; $P\bar{1}$ (No. 2)	monoclinic; $P2_1/c$ (No. 14)
a, Å	10.242(2)	10.939(2)
b, Å	10.271(2)	11.314(2)
c, Å	11.162(2)	22.949(5)
α, deg	81.30(3)	
β, deg	69.67(3)	101.84(3)
γ, deg	71.66(3)	
V, Å^3	1044.0(4)	2780(1)
Z; ρ_{calcd}, g cm^{-3}	2; 1.573	4; 1.568
λ, Å; μ, cm^{-1}	0.71073; 11.4	0.71073; 8.9
θ range, deg	3.6−29.5	3.3−26.0
reflns collected	4520	4928
reflns obsd ($I > 2\sigma(I)$)	3656	4769
data/params ratio	4520/235	4928/344
R1[a] (obsd reflns)	0.032	0.051
wR2[b] (obsd reflns)	0.066	0.112
GOF[c] on F^2	0.971	1.361
largest peak, e Å^{-3}	0.82	0.44

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] $GOF = [\sum w(|F_o^2| - |F_c^2|)^2/(N_{obsd} - N_{params})]^{1/2}$.

Table 6. Selected Bond Distances (Å) and Angles (deg) for 1 and 2

1		**2**	
Pd−Cl	2.340(1)	Pd−Cl	2.318(2)
Pd−S	2.276(1)	Pd−S	2.283(2)
Pd−N	2.206(2)	Pd−N	2.148(4)
Pd−C(12)	1.986(3)	Pd−C(14)	1.989(5)
S−C(7)	1.808(3)	S−C(6)	1.825(6)
S−C(8)	1.852(3)	S−C(8)	1.784(5)
C(12)−C(13)	1.334(4)	C(14)−C(15)	1.328(7)
		C(16)−C(17)	1.346(7)
Cl−Pd−S	164.2(1)	Cl−Pd−S	164.4(1)
Cl−Pd−N	103.1(1)	Cl−Pd−N	96.2(1)
Cl−Pd−C(12)	85.9(1)	Cl−Pd−C(14)	90.1(1)
S−Pd−N	84.2(1)	S−Pd−N	82.3(1)
S−Pd−C(12)	88.7(1)	S−Pd- -C(14)	90.9(1)
N−Pd−C(12)	168.6(1)	N−Pd−C(14)	173.1(2)
Pd−S−C(7)	95.3(1)	Pd−S−C(6)	91.2(2)
Pd−S−C(8)	115.2(1)	Pd−S−C(8)	111.0(2)
S−C(7)−C(5)	114.6(2)	S−C(6)−C(5)	112.1(4)
Pd−N−C(1)	127.4(2)	Pd−N−C(1)	127.7(4)
Pd−N−C(5)	114.7(2)	Pd−N−C(5)	112.1(4)
Pd−C(12)−C(13)	127.8(2)	Pd−C(14)−C(15)	123.1(4)
Pd−C(12)−C(15)	109.1(2)	Pd−C(14)−C(18)	112.2(3)

(22) Sheldrick, G. M. *SHELXTL NT*, Version 5.10; Bruker AXS Inc.: Madison, WI, 1999.
(23) Sheldrick, G. M. *SHELXL-93*, Program for the Refinement of Crystal Structures; University of Gottingen: Germany, 1993.
(24) Armarego, W. L. F.; Perrin., D. D. In *Purification of Laboratory Chemicals,* 3rd ed.; Pergamon: New York, 1988.

8-Diphenylphosphanyl-2-methylquinoline (DPPQ-Me). A 2 g (9 mmol) sample of 8-bromo-2-methylquinoline[25] was dissolved in 35 mL of anhydrous THF under inert atmosphere (Ar). To the solution at −78 °C was added dropwise 6.2 mL (9.9 mmol) of *n*-BuLi, and the reaction mixture was stirred for 1 h. Then, 1.62 mL (9 mmol) of chlorodiphenylphosphine was added by a syringe and the solution was brought to room temperature by removing the cooling bath. The resulting solution was stirred at 30 °C for 30 min, and eventually 5 mL of water was added in order to remove the reactants in excess. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and washed twice with a 5% aqueous solution of $NaHCO_3$. The organic phase was separated and dried on $MgSO_4$. Addition of diethyl ether to the concentrated solution yielded the title product, which was filtered off on a gooch, washed with cold diethyl ether, and dried. Yield: 30% (0.9 g, 2.7 mmol, white microcrystals). ^{1}H NMR ($CDCl_3$, T = 295 K, ppm): methyl protons, δ, 2.59 (s, 3H, $C\underline{H}_3$), quinoline protons 7.10 (m, 3H, H^2, H^6, H^7), 8.03 (d, 1H, H^4, J = 9 Hz), 7.66 (d, 1H, H^5, J = 9 Hz), phenyl protons 7.33 (m, 10H).

Synthesis of the Methyl Complexes. All the palladium methyl complexes (Scheme 1) were prepared by addition of the appropriate ligand to a solution of [PdCl(Me)(COD)][26] in toluene or THF under inert atmosphere (N_2) according to published procedures.[1]

The complex [PdI(Me)(MeNS*t*-Bu)] was prepared according to a published procedure by metathetic exchange between [PdCl(Me)(MeNS*t*-Bu)] and NaI.[1c]

Synthesis of the Vinyl Complexes. [PdCl(ZC═CZMe)(MeN−SPh)], Z = COOMe. To 0.1936 g (0.52 mmol) of the complex [PdCl(Me)(MeN-SPh)] dissolved in 30 mL of freshly distilled (CaH_2) CH_2Cl_2 was added 72.3 μL (83.84 mg, 0.59 mmol) of dimethylacetylenedicarboxylate (DMAD) under inert atmosphere (Ar). The reaction mixture was stirred for 4 h at RT, and the resulting yellow solution was concentrated by evaporation under reduced pressure. Addition of diethyl ether caused the precipitation of the title complex as yellow microcrystals, which were filtered off, washed with small aliquots of ether, and dried under vacuum (0.237 g; yield 89%).

^{1}H NMR ($CDCl_3$, T 298 K, ppm): phenyl protons, δ, 7.67 (d, 2H, H_{ortho}, J = 6.8 Hz), 7.36−7.26 (m, 3H, H_{meta}, H_{para}), pyridine protons 7.56 (t, 1H, H^4, J = 7.7), 7.15 (d, 1H, H^3, J = 7.3 Hz), 7.07 (d, 1H, H^5, J = 7.5 Hz), thiomethyl protons 4.99, (d, 1H, Pyr-C$\underline{H}_2$-S, J = 16.0 Hz), 4.34 (d, 1H, Pyr- C$\underline{H}_2$-S, J = 16.0 Hz), carboxylic protons 3.81 (bs, 3H, COOC$\underline{H}_3\alpha$), 3.65 (s, 3H, COOC$\underline{H}_3\beta$), methyl protons 3.15 (s, 3H, Pyr-C$\underline{H}_3$), 2.49 (bs, 3H, ═CC$\underline{H}_3$).

^{1}H NMR ($CDCl_3$, T = 243 K, ppm): phenyl protons, δ, 7.69, 7.67 (d, 2H, H'_{ortho}, H''_{ortho}, J', J'' = 6.4 Hz), 7.41−7.29 (m, 3H, H_{meta}, H_{para}), pyridine protons 7.60 (t, 1H, H^4, J = 7.9 Hz), 7.17 (d, 1H, H^3, J = 7.9 Hz), 7.09 (d, 1H, H^5, J = 7.9 Hz), thiomethyl protons 5.0, 4.98, 4.34, 4.31 (d, 2H, Pyr-C$\underline{H}_2$′-S, Pyr-C$\underline{H}_2$″-S, J' = 15.8, J'' = 16.2 Hz), carboxylic protons 3.87, 3.66 (s, 3H, COOC$\underline{H}_3$′α, COO C$\underline{H}_3$″α), 3.65, 3.64 (s, 3H, COOC$\underline{H}_3$′β, COOC$\underline{H}_3$″β), methyl protons 3.17, 3.13 (s, 3H, Pyr-C$\underline{H}_3$′α, Pyr-C$\underline{H}_3$″α), 2.54, 2.47 (s, 3H, ═CC$\underline{H}_3$′β, ═CC$\underline{H}_3$″β).

Rotameric ratio ≈ l:1 (see Results and Discussion).

^{13}C NMR ($CDCl_3$, T = 298 K, ppm): carboxylic carbons, δ, 171.6 (COOCH$_3$ α), 163.2 (COOCH$_3$ β), pyridine carbons 163.7 (C^6_{pyr}), 155.7 (C^2_{pyr}), 125.6 (C^5_{pyr}), 121.2 (C^3_{pyr}), phenyl carbons 132. 8, 130.9, 130.0, 129.3, vinyl carbons 147.2, 128.3, thiomethyl carbons 50.0 (CH$_2$-S), methyl carbons 52.3, 52.1 (COOCH$_3$α, COOCH$_3\beta$), 27.3 (Pyr-CH$_3$), 21.6 (═CCH$_3$). IR (KBr pellet): $\nu_{C=O}$ 1710.8, 1699.2 cm^{-1}, ν_{CN} 1602.8 cm^{-1}. Anal. Calcd for C_{20} $H_{22}ClNO_4PdS$: C 46.70, H 4.31, N, 2.72. Found: C 46.67, H 4.33, N, 2.62.

The following complexes were prepared under conditions analogous to those of [PdCl(ZC═CZMe)(MeN-SPh)] using the appropriate starting substrates. The reaction time for each complex is reported in parentheses.

Bidentate Complexes. [PdCl(ZC═CZMe)(MeN-SMe)]. (21 h) Yield: 81% (pale yellow microcrystals). ^{1}H NMR ($CDCl_3$, T = 298 K, ppm): pyridine protons, δ, 7.71 (t, 1H, H^4, J = 7 0.7 Hz), 7.26 (d, 1H, H^3, J = 7 0.7 Hz), 7.24 (d, 1H, H^5, J = 7 0.7 Hz), thiomethyl protons 4.53 (broad AB system, 2H, Pyr-C$\underline{H}_2$-S), carboxylic protons 3.84 (s, 3H, COOC$\underline{H}_3\alpha$), 3.68 (s, 3H, COOC$\underline{H}_3\beta$), methyl protons 3.11 (s, 3H, Pyr-C$\underline{H}_3$), 2.49 (bs, 3H, ═CC$\underline{H}_3$), thiomethyl protons 2.32 (bs, 3H, S-C$\underline{H}_3$).

^{1}H NMR ($CDCl_3$, T = 243 K, ppm) major rotamer: pyridine protons, δ, 7.75 (t, $H^{4'}$, J' = 7 0.7 Hz), 7.33 (d, $H^{3'}$, J' = 7.7 Hz), 7.26 (d, $H^{5'}$, J' = 7.7 Hz), thiomethyl protons 4.68, 4.07 (d, Pyr-C$\underline{H}_2$′-S, J_d′ = 16.2 Hz), carboxylic protons 3.87 (s, COOC$\underline{H}_3$′α), 3.68 (s, COOC$\underline{H}_3$′β), methyl protons 3.09 (s, Pyr-C$\underline{H}_3$′), methyl protons 2.46 (s, ═CC$\underline{H}_3$′), methyl protons 2.27 (s, S-C$\underline{H}_3$′).

^{1}H NMR ($CDCl_3$, T = 243 K, ppm) minor rotamer: pyridine protons, δ, 7.74 (t, $H^{4''}$, J'' = 7 0.7 Hz), 7.33 (d, $H^{3''}$, J'' = 7.7 Hz), 7.26 (d, $H^{5''}$, J'' = 7.7 Hz), thiomethyl protons 4.49, 4.44 (AB system, Pyr-C$\underline{H}_2$″-S, J_{AB}″ = 15.1 Hz), carboxylic protons 3.86 (s, COOC$\underline{H}_3$″α), 3.68 (s, 3H, COOC$\underline{H}_3$″β), methyl protons 3.08 (s, Pyr-C$\underline{H}_3$″), methyl protons 2.55 (s, ═CC$\underline{H}_3$″), methyl protons 2.43 (s, S-C$\underline{H}_3$″).

Rotameric ratio ≈ 1.5:1.

IR: (KBr pellet) $\nu_{C=O}$ 1710.4, 1698.2 cm^{-1}, ν_{CN} 1602.8 cm^{-1}. Anal. Calcd for $C_{15}H_{20}ClNO_4PdS$: C 39.84, H 4.46, N 3.10. Found: C 39.93, H 4.48, N 3.01.

[PdCl(ZC═CZMe)(MeN-S*t*-Bu)]. (48 h) Yield: 89% (yellow microcrystals). ^{1}H NMR ($CDCl_3$, T = 298 K, ppm): pyridine protons, δ, 7.68 (t, 1H, H,[4] J = 7.7 Hz), 7.24 (d, 1H, H^3, J = 7.7 Hz), 7.21 (d, 1H, H,[5] J = 7.7 Hz), thiomethyl protons 4.78−4.13 (broad AB system, 2H, Pyr-C$\underline{H}_2$-S), carboxylic protons 3.67 (s, 3H, COOC$\underline{H}_3\alpha$), 3.82 (s, 3H, COOC$\underline{H}_3\beta$), methyl protons 3.15, 3.10 (bs, 3H, Pyr-C$\underline{H}_3$′, Pyr-C$\underline{H}_3$″), 2.62, 2.46 (s, 3H, ═CC$\underline{H}_3$′, ═CC$\underline{H}_3$″), *tert*-butyl protons 1.28, 1.25 (s,9H, S-C(C$\underline{H}_3$)$_3$′, S-C(C$\underline{H}_3$)$_3$″).

^{1}H NMR ($CDCl_3$, T = 323 K, ppm): pyridine protons, δ, 7.67 (t, 1H, H^4, J = 7.7 Hz), 7.24 (d, 1H, H^3, J = 7.7 Hz), 7.20 (d, 1H, H^5, J = 7.9 Hz), thiomethyl protons 4.5 (broad AB system, 2H, Pyr-C$\underline{H}_2$-S), carboxylic protons 3.81 (s, 3H, COOC$\underline{H}_3\alpha$) 3.67 (s, 3H, COOC$\underline{H}_3\beta$), methyl protons 3.14 (s, 3H, Pyr-C$\underline{H}_3$), 2.55 (bs, 3H, ═CC$\underline{H}_3$), *tert*-butyl protons 1.28 (s, 9H, S-C(C$\underline{H}_3$)$_3$).

^{1}H NMR ($CDCl_3$, T = 263 K, ppm) major rotamer: pyridine protons, δ, 7.70 (t, $H^{4'}$, J' = 7.7 Hz), 7.24 (d, $H^{3'}$, J' = 7.7 Hz), 7.20 (d, $H^{5'}$, J' = 7.7 Hz), thiomethyl protons 4.75, 4.10 (d, Pyr-C$\underline{H}_2$′-S, J' = 17.1 Hz), carboxylic protons 3.82 (s, COOC$\underline{H}_3$′α), 3.67 (s, COOC$\underline{H}_3$′β), methyl protons 3.14 (s, Pyr-C$\underline{H}_3$′), 2.62 (s, ═CC$\underline{H}_3$′), *tert*-butyl protons 1.24 (s, S-C(C$\underline{H}_3$)$_3$′).

^{1}H NMR ($CDCl_3$, T = 263 K, ppm) minor rotamer: pyridine protons, δ, 7.71 (t, $H^{4''}$, J'' = 7.7 Hz), 7.24 (d, $H^{3''}$, J'' = 7.7 Hz), 7.20 (d, $H^{5''}$, J'' = 7.7 Hz), thiomethyl protons 4.81, 4.20, (d, Pyr-C$\underline{H}_2$″-S, J'' = 17.3 Hz), carboxylic protons 3.85 (s, COOC$\underline{H}_3$″α), 3.67 (s, COOC$\underline{H}_3$″ β), methyl protons 3.07 (s, Pyr-C$\underline{H}_3$″), 2.46 (s, ═CC$\underline{H}_3$″), *tert*-butyl protons 1.28 (s, S-C(C$\underline{H}_3$)$_3$″).

Rotameric ratio ≈ 2:1.

IR: (KBr pellet) $\nu_{C=O}$ 1711.6 cm^{-1}, ν_{CN} 1597.1 cm^{-1}. Anal. Calcd for $C_{18}H_{26}ClNO_4PdS$: C 43.73, H 5.13, N 2.83. Found: C 43.59, H 5.47, N 2.81.

[PdCl(ZC═CZMe)(HN−SPh)]. (24 h) Yield: 93% (yellow microcrystals). ^{1}H NMR ($CDCl_3$, T = 298 K, ppm): pyridine protons, δ, 9.39 (d, 1H, H^6, J = 6.0 Hz), 7.85 (bt, 1H, H^4), pyridine and phenyl protons 7.49−7.31 (m, 5H, H^3, H^5, H_{ortho}, H_{para}), phenyl protons 7.65 (bs, 2H, H_{meta}), thiomethyl protons 4.73−4.31 (broad AB system, 2H, Pyr-C$\underline{H}_2$-S), carboxylic protons 3.84, 3.37 (s, 3H, COOC$\underline{H}_3$′α, COO C$\underline{H}_3$″α), 3.62 (bs, 3H, COOC$\underline{H}_3\beta$), methyl protons 2.52, 2.04 (bs, 3H, ═CC$\underline{H}_3$′, ═CC$\underline{H}_3$″).

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^{1}H NMR ($CDCl_3$, T = 323 K, ppm): pyridine protons, δ, 9.42 (d, 1H, H^6, J = 4.9 Hz), 7.83 (t, 1H, H^4, J = 7.9 Hz), pyridine and phenyl protons 7.48−7.32 (m, 5H, H^3, H^5, H_{ortho}, H_{para}), phenyl protons 7.67 (d, 2H, H_{meta}, J = 6.1 Hz), thiomethyl protons 4.49 (bs, 2H, Pyr-CH_2-S), carboxylic protons 3.63, (s, 6H, COOC$H_3\alpha$, COOC$H_3\beta$), methyl protons 2.25 (bs, 3H, =CCH_3).

^{1}H NMR ($CDCl_3$, T = 243 K, ppm) major rotamer: pyridine protons, δ, 9.35 (d, H$^{6\prime}$, J' = 6.0 Hz), 7.92 (t, H$^{4\prime}$, J' = 7.6 Hz), pyridine and phenyl protons 7.52−7.32 (m, H$^{3\prime}$, H$^{5\prime}$, H$'_{ortho}$, H$'_{para}$), phenyl protons 7.60 (d, H$'_{meta}$ J' = 6.0 Hz), thiomethyl protons 4.79, 4.35 (d, Pyr-CH_2′-S, J' = 16.8 Hz), carboxylic protons 3.87 (s, COOC$H_3\alpha'$), 3.61 (s, COOC$H_3\beta'$), methyl protons 1.99 (s, =CCH_3′).

^{1}H NMR ($CDCl_3$, T = 243 K, ppm) minor rotamer: pyridine protons, δ, 9.35 (d, H$^{6\prime\prime}$, J = 6.0 Hz), 7.87 (t, H$^{4\prime\prime}$, J'' = 7.6 Hz), pyridine and phenyl protons 7.52−7.32 (m, H$^{3\prime\prime}$, H$^{5\prime\prime}$, H$''_{ortho}$, H$''_{para}$), phenyl protons 7.70 (d, H$''_{meta}$, J'' = 6.0 Hz), thiomethyl potons 4.74, 4.23 (d, Pyr-CH_2″-S, J'' = 16.6 Hz), carboxylic protons 3.63 (s, COOC$H_3\alpha''$), 3.29 (s, COOC$H_3\beta''$), methyl protons 2.52 (s, =CCH_3″).

Rotameric ratio ≈ 1.4:1.

IR: (KBr pellet) $\nu_{C=O}$ 1722.9, 1695.5 cm^{-1}, ν_{CN} 1611.0 cm^{-1}. Anal. Calcd for $C_{19}H_{20}ClNO_4PdS$: C 45.61, H 4.03, N 2.80. Found: C 45.75, H 3.99, N 2.71.

[PdCl(ZC=CZMe)(ClN−S*t*-Bu)]. (0.5 h) Yield: 80% (yellow microcrystals). ^{1}H NMR ($CDCl_3$, T = 298 K, ppm): pyridine protons, δ, 7.78 (t, 1H, H^4, J = 7.6), 7.44 (d, 1H, H^3, J = 7.6 Hz), 7.39 (d, 1H, H^5, J = 7.6 Hz), thiomethyl protons 4.78, 4.18 (bd, bm 2H, Pyr-CH_2′-S, Pyr-CH_2″-S), carboxylic protons 3.82 (s, 3H, COOC$H_3\alpha$), 3.68 (s, 3H, COOC$H_3\beta$), methyl protons 2.65, 2.46 (bs, 3H, =CCH_3′, =C CH_3″), *tert*-butyl protons 1.30 (bs, 9H, S-C(CH_3)$_3$).

^{1}H NMR ($CDCl_3$, T = 243 K, ppm) major rotamer: pyridine protons, δ, 7.83 (t, H$^{4\prime}$, J' = 7.8 Hz), 7 0.46 (d, H$^{5\prime}$, J = 7.8 Hz), 7.44 (d, H$^{3\prime}$, J = 7.8 Hz), thiomethyl protons 4.76, 4.16 (d, Pyr-CH_2′-S, J' = 17.5 Hz), carboxylic protons 3.83 (s, COOC$H_3\alpha'$), 3.66 (s, COOC$H_3\beta'$), methyl protons 2.66 (s, =CCH_3′), *tert*-butyl protons 1.28 (s, S-C(CH_3)$_3$′).

^{1}H NMR ($CDCl_3$, T = 243 K, ppm) minor rotamer: pyridine protons, δ, 7.84 (t, H$^{4\prime\prime}$, J'' = 7.8 Hz), 7 0.46 (d, H$^{5\prime\prime}$, J'' = 7.8 Hz), 7.44 (d, H$^{3\prime\prime}$, J'' = 7.8 Hz), thiomethyl protons 4.82, 4.27 (d, Pyr-CH_2″-S, J'' = 17.6 Hz), carboxylic protons 3.86 (s, COOC$H_3\alpha''$), 3.66 (s, COOC$H_3\beta''$), methyl protons 2.45 (s, =CCH_3″), *tert*-butyl protons 1.32 (s, S-C(CH_3)$_3$″).

Rotameric ratio ≈ 2.9:1.

IR: (KBr pellet) $\nu_{C=O}$ 1701.1 cm^{-1}, ν_{CN} 1591.2 cm^{-1}. Anal. Calcd for $C_{17}H_{24}ClNO_4PdS$: C 42.51, H 5.04, N 2.92. Found: C 42.69, H 4.97, N 2.83.

[PdCl(Z′C=CZ′Me)(MeN−SPh)]; Z′ = COO*t*-Bu. (5 h) Yield: 92% (pale yellow microcrystals). ^{1}H NMR ($CDCl_3$, T = 298 K, ppm): phenyl protons, δ, 7.68 (bs, 2H, H_{ortho}), 7.36−7.25 (bm, 3H, H_{meta}, H_{para}), pyridine protons 7.53 (bt, 1H, H^4), 7.12 (d, 1H, H^5, J = 7.5 Hz), 7.02 (bs, 1H, H^3), thiomethyl protons 4.99, 4.33 (d, bt, 2H, Pyr-CH_2′-S, Pyr-CH_2″-S, J' = 16.0 Hz), methyl protons 3.16 (s, 3H, Pyr-CH_3), methyl protons 2.46, 2.32 (bs, 3H, =CCH_3′, =CCH_3″), *tert*-butyl protons 1.60, 1.49 (bs, 9H, COOC(CH_3)$_3\alpha'$, COOC(CH_3)$_3\alpha''$), 1.45 (s, 9H, COOC-(CH_3)$_3$ β).

^{1}H NMR ($CDCl_3$, T = 328 K, ppm): phenyl protons, δ, 7.68 (d, 2H, H_{ortho}, J = 6.9 Hz), 7.36−7.24 (bm, 3H, H_{meta}, H_{para}), pyridine protons 7.53 (t, 1H, H^4, J = 7.7 Hz), 7.12 (d, 1H, H,^{5} J = 7.7 Hz), 7.02 (d, 1H, H^3, J = 7.7 Hz), thiomethyl protons 4.98, 4.37 (bs, 2H, Pyr-CH_2-S), methyl protons 3.16 (s, 3H, Pyr-CH_3), methyl protons 2.39 (s, 3H, =CCH_3), *tert*-butyl protons 1.55 (bs, 9H, COOC(CH_3)$_3\alpha$) 1.46 (s, 9H, COOC(CH_3)$_3\beta$).

^{1}H NMR ($CDCl_3$, T = 243 K, ppm) major rotamer: phenyl protons, δ, 7 0.73 (d, H$'_{ortho,}$ J' = 6.6 Hz), 7 0.36−7.29 (m, H$'_{meta}$, H$'_{para}$), pyridine protons 7.55 (t, H$^{4\prime}$, J' = 7 0.7 Hz), 7.14 (d, H$^{5\prime}$, J' = 7 0.7 Hz), 7.06 (d, H$^{3\prime}$, J' = 7.7 Hz), thiomethyl protons 4.96, 4.31 (d, Pyr-CH_2′-S, J'=15.7 Hz), methyl protons 3.14 (s, Pyr-CH_3′), methyl protons 2.45 (s, =CCH_3′), *tert*-butyl protons 1.45 (s, COOC(CH_3)$_3\alpha'$), 1.44 (s, COOC(CH_3)$_3\beta'$).

^{1}H NMR ($CDCl_3$, T = 243 K, ppm) minor rotamer: phenyl protons, δ, 7.66 (d, H$''_{ortho}$, J'' = 6.6 Hz), 7.36−7.29 (m, H$''_{meta}$, H$''_{para}$), pyridine protons 7.56 (t, H$^{4\prime\prime}$, J'' = 7 0.7 Hz), 7.15 (d, H$^{5\prime\prime}$, J'' = 7 0.7 Hz), 7.03 (d, H$^{3\prime\prime}$, J'' = 7.7 Hz), thiomethyl protons 5.00, 4.33 (d, Pyr-CH_2″-S, J'' = 16.0 Hz), methyl protons 3.16 (s, Pyr-CH_3″), methyl protons 2.34 (s, =C CH_3″), *tert*-butyl protons 1.61 (s, COOC(CH_3)$_3\alpha''$), 1.42 (s, COOC-(CH_3)$_3\beta''$).

Rotameric ratio ≈ 1:09.

IR: (KBr pellet) $\nu_{C=O}$ 1716.3, 1683.8 cm^{-1}, ν_{CN} 1603.2 cm^{-1}. Anal. Calcd for $C_{26}H_{34}ClNO_4PdS$: C 52.18, H 5.73, N 2.34. Found: C 52.07, H 5.81, N 2.37.

[PdCl(Z″C=CZ″Me) (MeN−SPh)], Z″ = COOEt. (5 h) Yield: 93% (pale yellow microcrystals). ^{1}H NMR ($CDCl_3$, T = 298 K, ppm): phenyl protons, δ, 7.69 (bd, 2H, H_{ortho}), 7.35−7.27 (m, 3H, H_{meta}, H_{para}), pyridine protons 7.55 (t, 1H, H^4, J = 7.8 Hz), 7.14 (d, 1H, H^3, J = 7.8 Hz), 7.06 (d, 1H, H^5, J = 7.8 Hz), thiomethy1 protons 4.99, 4.35 (d, 2H, Pyr-CH_2S, J = 15.6 Hz), ethyl protons 4.22 (bs, 2H, COOCH_2CH$_3\alpha$), 4.10 (d, 2H, COOCH_2CH$_3\beta$, J = 7.2 Hz), 1.35, 1.09 (bs, 3H, COOCH$_2$CH$_3\alpha'$, COOCH$_2$CH$_3$ α''), 1.23 (t, 3H, COOCH$_2$CH$_3\beta$), methyl protons 3.15 (s, 3H, Pyr-CH_3), 2.49 (bs, 3H, =CCH_3).

^{1}H NMR ($CDCl_3$, T = 228 K, ppm): phenyl protons, δ, 7.75, 7.69 (d, 2H, H$'_{meta}$, H$''_{meta}$, J' = J'' = 6.9 Hz), 7.35−7.27 (m, 3H, H_{ortho}, H_{para}), pyridine protons 7.60 (t, 1H, H^4, J = 7.8 Hz), 7.14 (d, 1H, H^3, J = 7.8 Hz), 7.10, 7.09 (d, 1H, H$^{5\prime}$, H$^{5\prime\prime}$, J' = J'' =7.8 Hz), thiomethyl protons 4.99, 4.34, 4.28 (d, 2H, Pyr-CH_2′-S, Pyr-CH_2″-S, J' = J'' = 16.2 Hz), ethyl protons 4.23−3.95 (m, 4H, COOCH_2CH$_3$), 1.41, 0.93 (t, 3H, COOCH$_2$CH$_3\alpha$, J = 7.2 Hz), 1.24,1.23 (t, 3H, COOCH$_2$CH$_3\beta$, J = 7.2 Hz), methyl protons 3.18, 3.14 (s, 3H, Pyr-CH_3′, Pyr-CH_3″), 3.46, 2.54 (s, 3H, =CCH_3′, =CCH_3″).

Isomeric ratio ≈ 1:1.

IR: (KBr pellet) $\nu_{C=O}$ 1709.7 cm^{-1}, ν_{CN} 1601.1 cm^{-1}. Anal. Calcd for $C_{22}H_{26}ClNO_4PdS$: C 48.72, H 4.83, N 2.58. Found: C 48.65, H 4.88, N 2.67.

Terdentate Complexes. [PdCl(ZC=CZMe)(SNS(Me))], Z = COOMe. (3 h) Yield: 89% (fairly unstable pale yellow microcrystals). ^{1}H NMR ($CDCl_3$, T = 298 K, ppm): pyridine protons, δ, 7.97 (t, 1H, H^4, J = 7.7 Hz), 7.75 (d, 2H, H^3, H^5, J = 7.9 Hz), thiomethyl protons 5.10 (s, 4H, Pyr-CH_2-S), carboxylic protons 3.82 (s, 3H, COOC$H_3\alpha$), 3.71 (s, 3H, COOC$H_3\beta$), thiomethyl protons 2.91 (s, 6H, S-CH_3), methyl protons 2.41 (s, 3H, =CCH_3).

IR: (KBr pellet) $\nu_{C=O}$ 1703.1 cm^{-1}, ν_{CN} 1597.8 cm^{-1}. Anal. Calcd for $C_{16}H_{22}C1NO_4PdS_2$: C 38.56, H 4.45, N 2.81. Found: C 38.43, H 4.58, N 2.79.

[PdCl(ZC=CZMe)(SNS(*t*-Bu))]. (11 h) Yield: 94% (pale yellow microcrystals). ^{1}H NMR ($CDCl_3$, T = 298 K, ppm): pyridine protons, δ, 8.18 (d, 2H, H^3, H^5, J = 7.6 Hz), 8.03 (t, 1H, H^4, J = 7.6 Hz), thiomethyl protons 5.19, 4.98 (br AB system, 4H, Pyr-CH_2-S), carboxylic protons 3.79 (s, 3H, COOC$H_3\alpha$), 3.71 (s, 3H, COOC$H_3\beta$), methyl protons 2.36 (s, 3H, =CCH_3), *tert*-butyl protons 1.55 (bs, 9H, S-C(CH_3)$_3$).

^{13}C NMR ($CDCl_3$, T = 298 K, ppm): δ, 172.7, 164.5 (COOCH$_3$), 159.6 (C^6_{pyr},C^2_{pyr}), 146.7, 132.0 (olefin carbons), 141.3 (C^4_{pyr}), 123.6 (C^5_{pyr}, C^3_{pyr}), 56.0 (CH$_2$-S), 52.4, 52.0 (COOCH$_3\alpha$, COOCH$_3$ β), 44.8 (C((CH$_3$)$_3$), 31.0 (C(CH$_3$)$_3$), 23.4 (=CCH_3). IR: (KBr pellet) $\nu_{C=O}$ 1709.7 cm^{-1}, ν_{CN} 1597.6 cm^{-1}. Anal. Calcd for $C_{22}H_{34}ClNO_4PdS_2$: C 45.36, H 5.88, N 2.40. Found: C 45.17, H 5.92, N 2.47.

[PdCl(ZC=CZMe)(SNS(Ph))]. (1 h) Yield: 84% (orange microcrystals). ^{1}H NMR ($CDCl_3$, T = 298 K, ppm): phenyl and pyridine protons, δ, 7.88 (t, 1H, H^4, J = 7.4 Hz), 7.66−7.59 (m, 6H, H_{meta}, H^3, H^5), 7.38−7.31 (m, 6H, H_{ortho}, H_{para}), thiomethyl protons 5.21 (s, 4H, Pyr-CH_2-S), carboxylic protons 3.61 (s, 3H, COOC$H_3\alpha$), 3.52 (s, 3H,COOC$H_3\beta$), methyl protons 2.12 (s, 3H, =CCH_3). IR: (KBr pellet) $\nu_{C=O}$ 1703.1 cm^{-1}, ν_{CN}

1604.4 cm^{-1}. Anal. Calcd for $C_{26}H_{26}ClNO_4PdS_2$: C 50.17, H 4.21, N 2.25. Found: C 50.31, H 4.29, N 2.18.

[PdCl(Z′C=CZ′Me)(SNS(Ph))], Z′ = COO*t*Bu. (1 h) Yield 75% (orange microcrystals). ^1H NMR ($CDCl_3$, T = 298 K, ppm): phenyl and pyridine protons, δ, 7.94 (bt, 1H, H^4), 7. 71−7.65 (m, 4H, H^5, H^3, H_{meta}), 7.34−7.32 (m, 6H, H_{ortho}, H_{para}), thiomethyl protons 5.22 (bs, 4H, Pyr-CH_2-S), methyl protons 1.95 (s, 3H, =CCH_3), *tert*-butyl protons 1.42 (s, 18H, S-C(CH_3)$_3$). IR: (KBr pellet) $\nu_{C=O}$ 1699.2 cm^{-1}, ν_{CN} 1600.8 cm^{-1}. Anal. Calcd for $C_{32}H_{38}ClNO_4PdS_2$: C 54.39, H 5.42, N 1.98. Found: C 54.52, H 5.57, N 1.92.

[PdCl(Z″C=CZ″Me)(SNS(Ph))], Z″ = COOEt. (1 h) Yield 88% (orange microcrystals). ^1H NMR ($CDCl_3$, T = 298 K, ppm): phenyl and pyridine protons, δ, 7.85 (t, 1H, H^4, J = 7. 7 Hz), 7.65 (d, 4H, H_{meta}, J = 6.7 Hz), 7.57 (d, 2H, H^5, H^3, J = 7. 7 Hz), 7.40−7.30 (m, 6H, H_{ortho}, H_{para}), thiomethyl protons 5.17 (bs, 4H, Pyr-CH_2-S), ethyl protons 4.07 (q, 2H, COOCH_2-C$H_3\alpha$, J = 7.1 Hz), 4.04 (q, 2H, COO CH_2C$H_3\beta$, J = 7.1 Hz), methyl protons 2.15 (s, 3H, =CCH_3), 1.21 (t, 3H, COOCH_2-CC$H_3\alpha$, J = 7 Hz), 1.15 (t, 3H, COOCH_2C$H_3\beta$, J = 7.1 Hz). IR: (KBr pellet) $\nu_{C=O}$ 1696.5 cm^{-1}, ν_{CN} 1604.4 cm^{-1}. Anal. Calcd for $C_{28}H_{30}ClNO_4PdS_2$: C 51.69, H 4.65, N 2.15. Found: C 51.57, H 4.61, N 2.19.

Synthesis of Butadienyl Complexes. [PdCl((ZC=CZ)$_2$Me)(MeN(SPh))], Z = COOMe. To a solution of 0.098 g (0.19 mmol) of [PdCl(ZC=CZMe)(MeN-SPh)] in 6 mL of freshly distilled anhydrous CH_2C1_2 was added 69.95 μL (0.57 mmol) of DMAD, and the mixture was stirred at RT for 22 h. The yellow solution was concentrated at reduced pressure, and the title complex was precipitated by addition of diethyl ether. The yellow microcrystals were filtered off, washed with small aliquots of diethyl ether, and dried under vacuum (0.095 g; yield 77%).

^1H NMR ($CDCl_3$, T = 328 K, ppm): phenyl protons, δ, 7.73−7.70 (m, 2H, H_{ortho}), 7.29−7.25 (m, 3H, H_{meta}, H_{para}), pyridine protons 7.47 (t, 1H, H^4, J = 7.7 Hz), 7.05 (d, 1H, H^3, J = 7.7 Hz), 6.96 (d, 1H, H^5, J = 7.7 Hz), thiomethyl protons 4.75 (bs, 2H, Pyr-CH_2-S), carboxylic protons 3.87, 3.86, 3.67 (s, 9H, COOC$H_3\beta$, γ, δ), 3.41 (bs, 3H, COOC$H_3\alpha$), methyl protons 3.10 (s, 3H, Pyr-CH_3), 2.18 (s, 3H, =CCH_3).

^1H NMR ($CDCl_3$, T = 258 K, ppm) major rotamer: phenyl protons, δ, 7.82−7.63 (m, H′$_{ortho}$), 7.40−7.22 (m, H′$_{meta}$, H′$_{para}$), pyridine protons 7.48 (t, $H^{4\prime}$, J' = 7.6 Hz), 7.06 (d, $H^{3\prime}$, J = 7.6 Hz), 6.92 (d, $H^{5\prime}$, J' = 7.6 Hz), thiomethyl protons 5.15, 4.13 (d, Pyr-CH_2′-S, J' = 15.6 Hz), carboxylic protons 3.93, 3.88, 3.62, 2.64 (s, COOCH_3′), methyl protons 3.12 (s, Pyr-CH_3′), 2.41 (s, =CCH_3′).

^1H NMR ($CDCl_3$, T = 258 K, ppm) minor rotamer: phenyl protons, δ, 7.82−7.63 (m, H″$_{ortho}$), 7.40−7.22 (m, H″$_{meta}$, H″$_{para}$), pyridine protons 7.54 (t, $H^{4\prime\prime}$, J'' = 7 0.6 Hz), 7.06 (d, $H^{3\prime\prime}$, J = 7.6 Hz), 7.01 (d, $H^{5\prime\prime}$, J'' = 7.6 Hz), thiomethyl protons 5.60, 4.33 (d, Pyr-CH_2″-S, J'' = 16.2, J'' = 15.6 Hz), carboxylic protons 3.97, 3.88, 3.79, 3.69 (s, COOCH_3″), methyl protons 3.01 (s, Pyr-CH_3″), 2.14 (bs, =CCH_3″).

^{13}C NMR ($CDCl_3$, T = 298 K, ppm): δ, 171.6 (COOCH$_3$), 163.4 (C$^6_{pyr}$), 161.8 (COOCH$_3$), 156.0 (C$^2_{pyr}$), 139.0 (C$^4_{pyr}$), 133.0 (broad, C=C), 130.7, 130.1, 129.1 (phenyl carbons), 125.3(C$^5_{pyr}$), 121.1 (C$^3_{pyr}$), 52.7, 52.5 (COOCH$_3$), 50.8 (broad, CH$_2$-S), 26.4 (Pyr-CH$_3$), 19.4 (broad =CCH$_3$).

Rotameric ratio ≈ 1.4:1.

IR: (KBr pellet) $\nu_{C=O}$ 1736.0, 1709.7, 1689.9 cm^{-1}, ν_{CN} 1604.4 cm^{-1}. Anal. Calcd for $C_{26}H_{28}ClNO_8PdS$: C 47.57, H 4.30, N 2.13. Found: C 47.73, H 4.22, N 2.18.

The following complexes were prepared under conditions analogous to those of [PdCl((ZC=CZ)$_2$Me)(MeN-SPh)] using the appropriate starting substrates. The reaction time for each complex is reported in parentheses.

[PdCl(ZC=CZ-CZ′=CZ′Me)(MeN-SPh)], Z = COOMe, Z′ = COO*t*-Bu. (30 h) Yield: 90% (whitish microcrystals). ^1H NMR ($CDCl_3$, T = 328 K, ppm): phenyl protons, δ, 7.71 (m, 2H, H_{ortho}), 7.30−7.20 (m, 3H, H_{meta}, H_{para}), pyridine protons 7.44 (t, 1H, H^4, J = 7. 7 Hz), 7.03 (d, 1H, H^3, J = 7.7 Hz), 6.92 (bd, 1H, H^5), thiomethyl protons 5.30 (bs, 2H, Pyr-CH_2-S), carboxylic protons 3.85, (s, 3H, COOC$H_3\beta$),3.60 (bs, 3H, COOC$H_3\alpha$), methyl protons 3.10 (s, 3H, Pyr-CH_3), 2.26 (bs, 3H, =CCH_3), *tert*-butyl protons 1.62 (s, 9H, C(CH_3)$_3$), 1.43 (s, 9H, C(CH_3)$_3$).

IR: (KBr pellet) $\nu_{C=O}$ 1709.7 cm^{-1}, ν_{CN} 1606.1 cm^{-1}. Anal. Calcd for $C_{32}H_{40}ClNO_8PdS$: C 51.90, H 4.79, N 1.89. Found: C 51.77, H 4.71, N 1.78.

[PdCl(Z′C=CZ′-CZ=CZMe)(MeN-SPh)], Z′ = COO*t*-Bu, Z = COOMe. (30 h) Yield: 99% (yellow microcrystals). ^1H NMR ($CDCl_3$, T = 298 K, ppm): phenyl protons, δ, 7.77 (m, 2H, H_{ortho}), 7.31−7.22 (bm, 3H, H_{meta}, H_{para}), pyridine protons 7.48 (t, 1H, H^4, J = 7.7 Hz), 7.03 (d, 2H, H^3, H^5, J = 7.7 Hz), thiomethyl protons 5.55, 4.50 (bs, 2H, Pyr-CH_2-S), carboxylic protons 3.86 (s, 3H, COOCH_3), 3.66 (s, 3H, COOCH_3), methyl protons 3.03 (s, 3H, Pyr-CH_3), 2.37 (bs, 3H, =CCH_3), *tert*-butyl protons 1.59 (s, 9H, COOC(CH_3)$_3$ β), 1.28 (bs, 9H, COOC(CH_3)$_3$ α).

IR: (KBr pellet) $\nu_{C=O}$ 1729.4 cm^{-1}, ν_{CN} 1602.0 cm^{-1}. Anal. Calcd for $C_{32}H_{40}ClNO_8PdS$: C 51.90, H 4.79, N 1.89. Found: C 52.03, H 4.68, N 1.93.

Complexes from Ligand Metathesis. [PdCl(ZC=CZMe)-(DPPQ-Me)], Z = COOMe. To a suspension of 0.050 g (0.097 mmol) of [PdCl(ZC=CZMe)(MeN−SPh)] in 6 mL of freshly distilled anhydrous CH_2Cl_2 was added 0.0325 g (0.099 mmol) of DPPQ-Me, and the reaction mixture was stirred for 30 m. The solution was concentrated under reduced pressure, and the complex was precipitated as a whitish solid by addition of diethyl ether. The product was filtered off, washed with small aliquots of diethyl ether, and dried under vacuum (0.058 g, yield 93%). ^1H NMR ($CDCl_3$, T = 298 K, ppm): quinoline protons, δ, 8.17 (d, 1H, H^4, J = 6.5 Hz), 7.78−7.51 (m, 4H), phenyl protons 8.03−7.88 (m, 4H), 7.50−7.37 (m, 6H), carboxylic protons 3.66 (s, 3H, COOCH_3), 3.46 (s, 3H, COOCH_3), methyl protons 3.41 (s, 3H, Pyr-CH_3), 1.85 (s, 3H, =CCH_3). ^{31}P NMR ($CDCl_3$, T = 298 K, ppm): δ, 37.7 (s, 1P). IR: (KBr pellet) $\nu_{C=O}$ 1716.3 cm^{-1}, ν_{CN} 1606.6 cm^{-1}. Anal. Calcd for $C_{29}H_{27}ClNO_4PPd$: C 55.61, H 4.34, N 2.24. Found: C 55.73, H 4.23, N 2.27.

[PdCl((ZC=CZ)$_2$Me)(DPPQ-Me)], Z = COOMe. The synthesis of the title complex is analogous to that of the former species, starting from the appropriate substrate (0.5 h). Yield: 89% (pale yellow microcrystals). ^1H NMR ($CDCl_3$, T = 298 K, ppm): quinoline protons, δ, 8.14 (d, 1H, H,[4] J = 6.5 Hz), quinoline and phenyl protons 7.91−7.38 (m, 14H), carboxylic protons 3.88 (s, 3H, COOCH_3), 3.56 (s, 3H, COOCH_3), 3.37 (s, 3H, COOCH_3), 3.34 (s, 3H, COOCH_3), methyl protons 3.32 (s, 3H, Pyr-CH_3), 2.09 (s, 3H, =CCH_3). ^{31}P NMR ($CDCl_3$, T = 298 K, ppm): δ, 36.3 (s, lP). IR: (KBr pellet) $\nu_{C=O}$ 1724.3, 1699.2 cm^{-1}, ν_{CN} 1604.4 cm^{-1}. Anal. Calcd for $C_{35}H_{33}ClNO_8$-PPd: C 54.70, H 4.33, N 1.82. Found: C 54.57, H 4.39, N 1.87.

The following complexes were separated from the NMR test tube by concentration of the reaction mixture and precipitation with diethyl ether. Each single species was characterized by ^1H NMR and IR spectroscopy but not elementally analyzed.

[PdCl(ZC=CZMe)(DPPE)], Z = COOMe. Yield ≈ 75% (whitish microcrystals). ^1H NMR ($CDCl_3$, T = 298 K, ppm): phenyl protons, δ, 8.07 (m, 2H), 7.72 (m, 6H), 7.59−7.32 (m 14H), carboxylic protons 3.57 (s, 3H, COOCH_3), 3.52 (s, 3H, COOCH_3), methylenic protons 2.75−2.34 (m, 3H), 1.81−1.65 (m, 1H), methyl protons 1.62 (s, 3H, =CCH_3). ^{31}P NMR ($CDCl_3$, T = 298 K, ppm): δ, 55.75 (d, 1P, J = 23.8), 40.01 (d, 1P, J = 23.8). IR: (KBr pe1let) $\nu_{C=O}$ 1709.7 cm^{-1}, ν_{CN} 1591.2 cm^{-1}.

[PdCl((ZC=CZ)$_2$Me)(DPPE)], Z = COOMe. Yield ≈ 70% (whitish microcrystals). ^1H NMR ($CDCl_3$, T = 298 K, ppm): phenyl protons, δ, 7.91 (m, 4H), 7.68 (m, 4H), 7.51−7.18 (m 12H), carboxylic protons 3.75 (s, 3H, COOCH_3), 3.64 (s, 3H, COOCH_3), 3.61 (s, 3H, COOCH_3), 3.13 (s, 3H, COOCH_3), methylenic protons 2.81−2.20 (m, 3H), 1.78−1.62 (m, 1H), methyl protons, 1.65 (s, 3H, =CCH_3). ^{31}P NMR ($CDCl_3$, T =

298 K, ppm): δ, 53.7 (d, 1P, J = 9.3), 44.6 (d, 1P, J = 19.3). IR: (KBr pe1let) $\nu_{C=O}$ 1716.6 cm^{-1}, ν_{CN} 1598.9 cm^{-1}.

[PdCl(ZC═CZMe)(bipy)], Z = COOMe. Yield ≈ 70% (whitish microcrystals). ^1H NMR ($CDCl_3$, T = 298 K, ppm): bipyridyl protons, δ, 9.27, 9.02 (d, 2H, H^2, H^{12}, J = 5.2 Hz), 8.07 (m, 4H, H^4, H^5, H^8, H^9), 7.59 (m, 2H, H^6, H^{10}), carboxylic protons 3.84 (s, 3H, $COOCH_3$), 3.73 (s, 3H, $COOCH_3$), methyl protons 2.51 (s, 3H, ═CCH_3). IR: (KBr pe1let) $\nu_{C=O}$ 1701.7 cm^{-1}, ν_{CN} 1585.2 cm^{-1}.

[PdCl((ZC═CZ)$_2$Me)(bipy)], Z = COOMe. Yield ≈ 70% (whitish microcrystals). ^1H NMR ($CDCl_3$, T = 298 K, ppm): bipyridyl protons, δ, 9.23, 9.03 (d, 2H, H^2, H^{12}, J = 5.2 Hz), 8.04 (m, 4H, H^4, H^5, H^8, H^9), 7.55 (m, 2H, H^6, H^{10}), carboxylic protons 3.90 (s, 3H, $COOCH_3$), 3.74 (s, 3H, $COOCH_3$), 3.71 (s, 3H, $COOCH_3$), 3.33 (s, 3H, $COOCH_3$), methyl protons 2.12 (s, 3H, ═CCH_3). IR: (KBr pe1let) $\nu_{C=O}$ 1736.0, 1729.4, 1689,0 cm^{-1}, ν_{CN} 1601.2 cm^{-1}.

Complex from Halide Metathesis. [PdI(ZC═CZMe)-(MeN-SPh)], Z = COOMe. To a solution of 0.080 g (0.16 mmol) of [PdCl(ZC═CZMe)(MeN-SPh)] in 8 mL of freshly distilled anhydrous CH_2Cl_2 was added 0.145 g (0.96 mmol) of NaI under inert atmosphere (Ar). The heterogeneous mixture was stirred for 1 h, and the pink-orange solution was separated from the undissolved NaCl by filtration. The solution was washed twice with 10 mL of water in a separatory funnel to remove the dissolved inorganic salts and treated with $CaCl_2$ for 2 h. The solid $CaCl_2$ was filtered off, and the solution was concentrated under reduced pressure. Addition of diethyl ether yielded the title product, which was washed with several aliquots of diethyl ether and dried under vacuum (0.076 g, yield 80%). ^1H NMR ($CDCl_3$, T = 298 K, ppm): phenyl protons, δ, 7.63 (bd, 2H, H_{ortho}), 7.31−7.29 (m, 3H, H_{meta}, H_{para}), pyridine protons 7.54 (t, 1H, H^4, J = 7.7 Hz), 7.14 (d, 1H, H^3, J = 7.7 Hz), 7.05 (d, 1H, H^5, J = 7. 7 Hz), thiomethyl protons 5.02 (bs, 1H, Pyr-CH_2-S), 4.32 (bs, 1H, Pyr-CH_2-S), carboxylic protons 3.76 (bs, 3H, $COOCH_3\alpha$), 3.65 (s, 3H, $COOCH_3\beta$), methyl protons 3.20 (s, 3H, Pyr-CH_3), 2.41 (s, 3H, ═CCH_3).

^1H NMR ($CDCl_3$, T = 243 K, ppm) major rotamer: phenyl protons, δ, 7.61 (d, H'_{ortho}), 7.38−7.26 (m, H'_{meta}, H'_{para}), pyridine protons 7.57 (t, $H^{4\prime}$, J' = 7.7 Hz), 7.16 (d, $H^{3\prime}$, J' = 7.7 Hz), 7.08 (d, $H^{5\prime}$, J' = 7.7 Hz), thiomethyl protons 5.08 (d, Pyr-CH_2'-S, J' = 16.1 Hz), 4.31 (d, Pyr-CH_2'-S, J' = 16.1 Hz), carboxylic protons 3.74 (s, $COOCH_3'\alpha$), 3.66 (s, $COOCH_3'\beta$), methyl protons 3.18 (s, Pyr-CH_3'), 2.44 (s, ═CCH_3').

^1H NMR ($CDCl_3$, T = 243 K, ppm) minor rotamer: phenyl protons, δ, 7.64 (d, H''_{ortho}), 7.38−7.26 (m, H''_{meta}, H''_{para}), pyridine protons 7.57 (t, $H^{4\prime\prime}$, J'' = 7.7 Hz), 7.17 (d, $H^{3\prime\prime}$, J'' = 7.7 Hz), 7.09 (d, $H^{5\prime\prime}$, J'' = 7.7 Hz), thiomethyl protons 5.06 (d, Pyr-CH_2''-S, J'' = 15.5 Hz), 4.37 (d, Pyr-CH_2''-S, J'' = 15.5 Hz), carboxylic protons 3.86 (s, $COOCH_3''\alpha$), 3.64 (s, $COOCH_3''\beta$), methyl protons 3.23 (s, Pyr-CH_3''), 2.39 (s, ═CCH_3'').

Rotameric ratio ≈ 1.2:1.

IR: (KBr pellet) $\nu_{C=O}$ 1716.3,1706.1 cm^{-1},ν_{CN} 1599.1 cm^{-1}. Anal. Calcd for $C_{20}H_{22}INO_4PdS$: C 39.65, H 3.66, N 2.31. Found: C 39.63, H 3.71, N 2.28.

Supporting Information Available: Text giving details of the X-ray crystal structure studies and table of crystal structure determination data, atomic coordinates, anisotropic thermal parameters, bond lengths and angles (CIF files) and NOESY graphic output are available free of charge via the Internet at http://pubs.acs.org.

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