Organometallics **2004,** *23,* 6191−6201 6191

A New Family of P,N Chelates: Stereoselective Synthesis of 2-Pyridyl-2-phospholenes in the Coordination Sphere of Palladium(II) Complexes

François Leca,[†] Christophe Lescop,[†] Loïc Toupet,[‡] and Régis Réau*,[†]

UMR 6509 CNRS-Université de Rennes 1, Institut de Chimie, and Groupe de la Matière
Condensée et des Matériaux, UMR 6626 CNRS-Université de Rennes 1,
Campus de Beaulieu, 35042 Rennes Cedex, France

Received July 2, 2004

The synthesis of Pd(II) complexes **2a**,**c′,** bearing 2-(2-pyridyl)phosphole ligands which act as P,N chelates, is described. Ligands featuring a pendant pyridyl group spontaneously evolve to the corresponding 2-pyridyl-2-phospholene derivatives in the coordination sphere of Pd(II). This isomerization is a stereoselective process, the stereochemistry of the resulting derivatives **3a**,**a′** being established by X-ray diffraction studies. The isomerization of ligands lacking pendant pyridyl groups was accomplished by adding pyridine to the reaction media. High yields were achieved under very mild conditions for ligands possessing different substitution patterns. Multinuclear NMR spectroscopic data and X-ray diffraction studies showed that the stereoselectivity of the process is preserved under these new reaction conditions. The transformation did not occur with free 2-(2-pyridyl)phospholes, even at high temperatures in the presence of pyridine. DFT calculations confirmed that coordination to a Pd(II) center is required to make this isomerization thermodynamically feasible. The isomerization has also been demonstrated with Pt(II) precursors but failed with CuCl, $CuCl_2$, and $ZnCl_2$. The free 2-pyridyl-2-phospholenes **4a**,**c′** were obtained by reacting the complexes **3a**,**c′** with dppe. No inversion of the P atom of the phospholene ring was observed up to 90 °C, indicating that this novel family of P,N chelates is a promising class of ligand for homogeneous catalysis.

Introduction

Heteroditopic P,N chelates have attracted considerable interest in coordination chemistry and homogeneous catalysis for several decades.[1] The success of these mixed-donor ligands arises from the different stereoelectronic properties of the two coordination sites, providing unique reactivity to their metal complexes. For example, P,N chelates can act as hemilabile ligands or induce selective processes, allowing control over the reactivity of the metal centers. Many different N donors (imines, pyridines, quinolines, oxazolines, pyrazolines, oxazines, etc.) have been used for the design of P,N chelates.[1] In contrast, less attention has been paid to the variation of the P donors, the great majority of P,N ligands bearing diarylphosphino fragments. Very recently, derivatives based on other P moieties (Figure 1) have emerged as appealing ligands for important catalytic reactions, including allylic alkylation,[2−5] the Heck reaction,[4] reduction of alkenes or ketones,[6−8] and olefin−CO copolymerization.[9] In these contexts, phospholanes and phospholes have appeared as attractive P donors (derivatives **V**−**VIII**, Figure 1). The electronic and stereochemical properties of these five-membered phosphorus heterocycles are directly related to their degree of unsaturation. First, phospholanes are more electron-rich P-donors than the corresponding phospholes.[10] Second, the phosphorus atom of phospholanes is a stable stereogenic center,[10,11] while that of phospholes inverts rapidly at room temperature, due to the aromatic character of the planar transition-state structure.[10−13]

---

* To whom correspondence should be addressed. Fax: +33 (0)-223236939. Phone: +33 (0)223235784. E-mail: regis.reau@univ-rennes1.fr.

[†] UMR 6509 CNRS.

[‡] UMR 6626 CNRS.

(1) (a) Braunstein, P.; Naud, F. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 680. (b) Helmchem, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, *33*, 336. (c) Drury, W. J., III; Zimmermann, N.; Keenan, M.; Hayashi, M.; Kaiser, S.; Goddard, R.; Pfaltz, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 70. (d) Chelucci, G.; Orru, G.; Pinna, G. A. *Tetrahedron* **2003**, *59*, 9471. (e) Espinet, P.; Soulantica, K. *Coord. Chem. Rev.* **1999**, *193−195*, 499. (f) Braunstein, P.; Knorr, M.; Stern, C. *Coord. Chem. Rev.* **1998**, *178−180*, 9039. (g) Bianchini, C.; Meli, A. *Coord. Chem. Rev.* **2002**, *225*, 35. (h) Guiry, P. J.; Saunders, C. P. *Adv. Synth. Catal.* **2004**, *346*, 497.

(2) Shintani, R.; Lo, M. M−C.; Fu, G.-C. *Org. Lett.* **2000**, 2, *23*, 3695.

(3) Delapierre, G.; Brunel, J. M.; Constantieux, T.; Labande, A.; Lubatti, F.; Buono, G. *Tetrahedron: Asymmetry* **2001**, *12*, 1345.

(4) Gilbertson, S. R.; Genov, D. G.; Rheingold, A. L. *Org. Lett.* **2000**, 2, *18*, 2885.

(5) Zablocka, M.; Koprowski, M.; Donnadieu, B.; Majoral, J.-P.; Achard, M.; Buono, G. *Tetrahedron Lett.* **2003**, *44*, 2413.

(6) Bunlaksananusorn, T.; Polborn, K.; Knochel, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 3941.

(7) Tang, W.; Wang, W.; Zhang, X. *Angew. Chem., Int. Ed.* **2003**, *42*, 943.

(8) Thoumazet, C.; Melaimi, M.; Ricard, L.; Mathey, F.; Le Floch, P. *Organometallics* **2003**, *22*, 1580.

(9) Sauthier, M.; Leca, F.; Toupet, L.; Réau, R. *Organometallics* **2002**, *21*, 1591.

(10) Mathey, F. *Phosphorus−Carbon Heterocyclic Chemistry: The Rise of a New Domain*; Elsevier Science: Oxford, U.K., 2001.

(11) (a) Egan, W.; Tang, R.; Zon, G.; Mislow, K. *J. Am. Chem. Soc*, **1971**, *93*, 6205. (b) Mathey, F. *Chem. Rev.* **1988**, *88*, 429. (c) Quin, L. D. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Pergamon: Oxford, U.K., 1996; p 757.

(12) Nyulászi, L. *Chem. Rev.* **2001**, *101*, 1229.

10.1021/om049510i CCC: $27.50
Publication on Web 11/20/2004

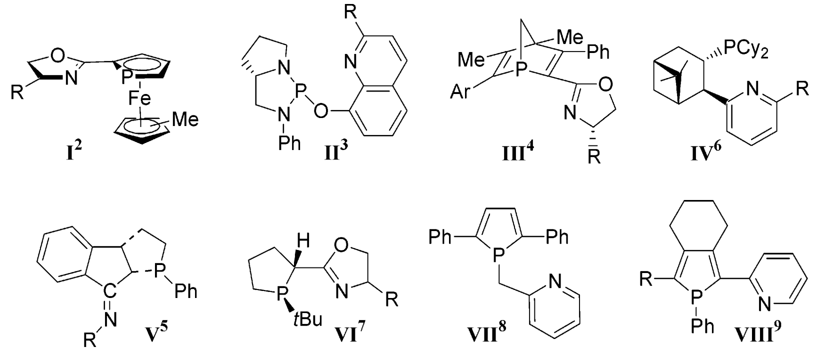
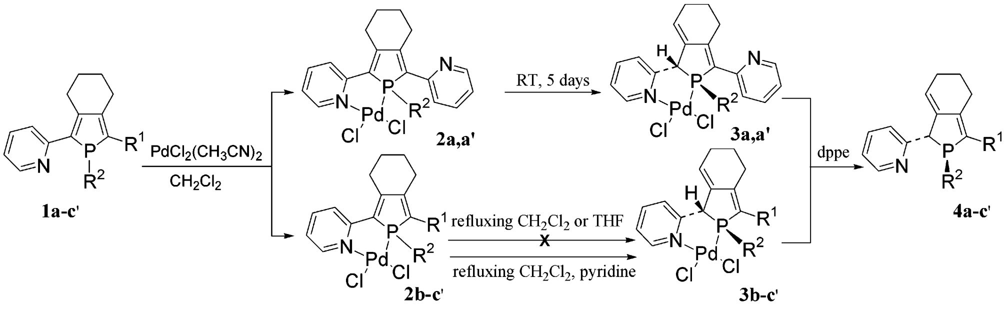


Figure 1. P,N ligands featuring various P moieties.

Scheme 1



	a	a'	b	b'	c	c'
R^1	2-pyridyl	2-pyridyl	phenyl	phenyl	2-thienyl	2-thienyl
R^2	phenyl	cyclohexyl	phenyl	cyclohexyl	phenyl	cyclohexyl

Ligands based on 2-phospholenes, which constitute an interesting "intermediate case", have been poorly investigated due to the somewhat underdeveloped chemistry of this P heterocycle.[10,14,15] In this paper, we report a general and straightforward route to the first P,N chelates featuring 2-phospholene moieties. The key step of this process is a stereoselective base-catalyzed isomerization of a phosphole ring into the corresponding 2-phospholene triggered by coordination to a square-planar Pd(II) or Pt(II) center.[15]

Results and Discussion

The Pd(II) complexes **2a**,**a′**[16] and **2b**,**c′** (Scheme 1) were prepared in excellent yields (Table 1) by reacting the corresponding 2-(2-pyridyl)phospholes[9,17] **1a**−**c** and **1a′**−**c′** with $PdCl_2(CH_3CN)_2$ in CH_2Cl_2 at room temperature. Complexes **2a**−**c** and **2a′**−**c′** exhibit a sharp singlet in their ^{31}P NMR spectra (Table 1); the large downfield ^{31}P NMR coordination chemical shifts (ca. 40 ppm) are consistent with the formation of five-membered palladacycles.[9,17,18] The coordination of the pyridyl group is also indicated by a downfield shift of the ^1H NMR signal, assigned to the H^6 proton of the pyridyl group ($\Delta\delta(H^6)$, 0.9−1.1 ppm). The proposed structures were confirmed by an X-ray diffraction study performed on complex **2c′**[15] (Figure 2a, Table 2). As expected, the almost square-planar Pd(II) center is bonded to **1c′** via the P and N atoms, the coordination sphere of the metal ion being completed by two chloride ligands. The angles and the bond lengths of the metallacycle are consistent

Table 1. Selected Spectroscopic Data[a] for Compounds 2−6

compd	yield (%)	$\delta(^{31}P)$	PCH $\delta(^{13}C)$ (J_{PC})	$\delta(^1H)$ ($^2J_{PH}$)
2a	95	55.2		
2a′	90	73.6		
2b	89	56.2		
2b′	92	72.4		
2c	96	59.1		
2c′	90	69.0		
3a	91	67.3	57.6 (36.6)	4.66 (11.9)
3a′	94	86.5	48.3 (32.7)	4.59 (7.3)
3b	91	69.8	53.7 (36.4)	4.61 (13.0)
3b′	91	84.3	47.7 (32.3)	4.60 (6.2)
3c	88	69.0	57.2 (36.6)	4.56 (10.8)
3c′	87	82.6	48.9 (33.6)	4.63 (8.2)
4a	95	22.7	55.4 (8.1)	4.50 (4.7)
4a′	93	34.9	48.9 (10)	4.51 (m)
4b	92	25.1	56.4 (8.1)	4.22 (4.9)
4b′	90	37.2	48.1 (11)	4.12 (m)
4c	95	22.4	56.0 (8.5)	4.49 (4.6)
4c′	85	36.6	48.8 (11.8)	4.17 (2.3)
5	79	37.3		
6	83	41.2	54.5 (42.9)	4.36 (8.2)

[a] δ values in ppm and *J* values in Hz.

---

(13) Delaire, D.; Dransfeld, A.; Nguyen, M. T.; Vanquinckenborne, L. G. *J. Org. Chem.* **2000**, *65*, 2631.

(14) (a) Deschamps, B.; Ricard, L.; Mathey, F. *Organometallics* **2003**, *22*, 1356. (b) Tran Hyu, N. H.; Mathey, F. *Organometallics* **1994**, *13*, 925. (c) Redwine, K. D.; Nelson, J. H. *Organometallics* **2000**, *19*, 3054. (d) Klärner, F.-G.; Oebels, D.; Sheldrick, W. S. *Chem. Ber.* **1993**, *126*, 473. (e) Wilson, W. L.; Rahn, J. A.; Alcock, N. W.; Fischer, J.; Frederick, J. H.; Nelson, J. H. *Inorg. Chem.* **1994**, *33*, 109. (f) Wilson, W. L.; Fischer, J.; Wasylishen, R. E.; Eichele, K.; Catalano, V. J.; Frederick, J. H.; Nelson, J. H. *Inorg. Chem.* **1996**, *35*, 1486.

(15) For a preliminary account, see: Leca, F.; Sauthier, M.; Le Guennic, B.; Lescop, C.; Toupet, L.; Halet, J.-F.; Réau, R. *Chem. Commun.* **2003**, *14*, 1774.

(16) Leca, F.; Sauthier, M.; Deborde, V.; Toupet, L.; Réau, R. *Chem. Eur. J.* **2003**, *9*, 3785.

(17) Hay, C.; Hissler, M.; Fischmeister, C.; Rault-Berthelot, J.; Toupet, L.; Nuylaszi, L.; Réau, R. *Chem. Eur. J.* **2001**, *7*, 4222.

(18) Fave, C.; Hissler, M.; Sénéchal, K.; Ledoux, I.; Ziss, J.; Réau, R. *Chem. Commun.* **2002**, 1674.

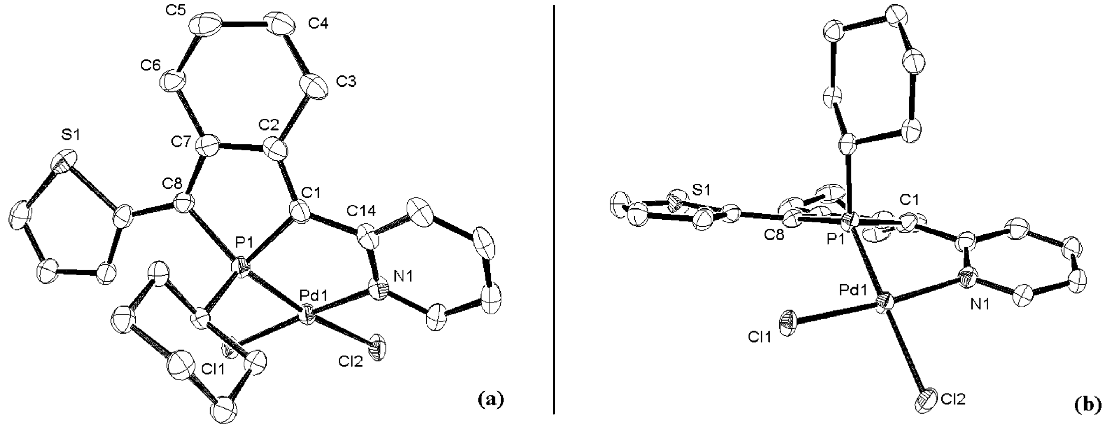


Figure 2. Molecular structure of the Pd(II) complex **2c′** (thermal ellipsoids at 50% probability). Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Pd(II) Complexes 2c′, 3a·1.5CH$_2$Cl$_2$, 3a′·CH$_2$Cl$_2$, and 3c′·0.5CH$_2$Cl$_2$ (M = Pd) and the Pt(II) Complex 6·CH$_2$Cl$_2$ (M = Pt)

	2c′	**3a**·1.5CH$_2$Cl$_2$	**3a′**·CH$_2$Cl$_2$	**3c′**·0.5CH$_2$Cl$_2$	**6**·CH$_2$Cl$_2$
M(1)−P(1)	2.2353(11)	2.2123(10)	2.1929(11)	2.1890(12)	2.1966(15)
M(1)−N(1)	2.076(4)	2.082(3)	2.076(4)	2.0173(4)	2.062(5)
M(1)−Cl(1)	2.3704(11)	2.3665(11)	2.3987(12)	2.3770(16)	2.3727(16)
M(1)−Cl(2)	2.2874(10)	2.2950(11)	2.2858(11)	2.2892(16)	2.2898(19)
P(1)−C(1)	1.794(4)	1.830(4)	1.835(4)	1.838(4)	1.845(6)
C(1)−C(2)	1.354(6)	1.512(5)	1.527(6)	1.522(6)	1.498(8)
C(2)−C(7)	1.483(6)	1.470(5)	1.462(6)	1.465(7)	1.474(9)
C(7)−C(8)	1.369(6)	1.364(5)	1.357(6)	1.351(6)	1.358(8)
C(8)−P(1)	1.819(4)	1.816(4)	1.802(5)	1.803(4)	1.822(6)
C(2)−C(3)	1.504(6)	1.345(5)	1.340(7)	1.342(7)	1.339(9)
C(3)−C(4)	1.527(7)	1.485(6)	1.501(7)	1.466(9)	1.481(10)
C(4)−C(5)	1.513(7)	1.500(6)	1.521(8)	1.538(9)	1.505(12)
C(5)−C(6)	1.528(7)	1.535(6)	1.529(7)	1.506(8)	1.516(10)
C(6)−C(7)	1.505(6)	1.500(5)	1.512(6)	1.500(7)	1.514(8)
C(1)−C(14)	1.461(6)	1.489(5)	1.502(6)	1.510(6)	1.519(8)
P(1)−M(1)−N(1)	83.46(10)	84.64(9)	84.95(11)	85.05(11)	83.50(14)
P(1)−M(1)−Cl(2)	94.10(4)	90.48(4)	87.53(4)	87.84(5)	94.70(6)
Cl(2)−M(1)−Cl(1)	89.79(4)	91.05(4)	91.75(4)	91.99(6)	87.85(7)
Cl(1)−M(1)−N(1)	93.29(10)	93.86(9)	95.61(11)	95.05(11)	94.01(14)
M(1)−P(1)−C(1)	96.84(14)	100.50(13)	104.10(14)	103.59(15)	103.49(19)
C(1)−P(1)−C(8)	92.4(2)	94.20(17)	95.1(2)	94.7(2)	93.1(3)
P(1)−C(1)−C(14)	115.7(3)	111.8(3)	111.1(3)	110.7(3)	107.7(4)
P(1)−C(1)−C(2)	110.6(3)	103.0(3)	104.4(3)	104.0(3)	104.5(4)
C(2)−C(1)−C(14)	131.5(4)	115.4(3)	114.3(4)	112.4(3)	112.5(5)
C(1)−C(2)−C(3)	124.8(4)	124.3(4)	124.5(4)	126.3(5)	125.9(7)
C(1)−C(2)−C(7)	113.4(4)	112.8(3)	113.7(4)	113.3(4)	112.0(5)
C(3)−C(2)−C(7)	121.9(4)	122.8(4)	121.8(4)	120.4(5)	122.1(6)
C(2)−C(3)−C(4)	111.9(4)	122.9(4)	122.7(5)	124.1(6)	121.9(7)

with those reported for related Pd(II) complexes bearing 2-(2-pyridyl)phosphole ligands.[9,16] Notably, the P atom of **2c′** has a highly distorted tetrahedral geometry, while the C(1) carbon atom does not possess a trigonal-planar geometry, despite its sp^2 hybridization (Figure 2b). These data suggest a significant degree of ring strain imposed by the formation of the five-membered metallacycle.

Complexes **2b**,**c′** are stable for weeks in CH$_2$Cl$_2$ solutions at room temperature. In contrast, complexes **2a**,**a′**, which bear a pendant pyridyl group, transform slowly into the new complexes **3a**,**a′** (Scheme 1). The transformation reaches completion after 5 days, and compounds **3a**,**a′** were isolated as air-stable yellow powders in excellent yields (Table 1). High-resolution mass spectrometry and elemental analysis showed that **3a**,**a′** are isomers of their corresponding precursors **2a**,**a′**. They each present one ^{31}P{^{1}H} NMR resonance that is deshielded ($\Delta\delta$ ca. 10 ppm) compared to those of the corresponding phosphole complexes **2a**,**a′**. In addition to the signals expected for coordinated and pendant pyridyl groups, the ^{1}H and ^{13}C NMR spectra of complexes **3a**,**a′** share some intriguing features. Their ^{13}C{^{1}H} NMR spectra show only three signals assignable to the methylene carbon of the fused saturated carbocycle and a doublet due to a PCH moiety (**3a**, 57.6 ppm, J_{PC} = 36.6 Hz; **3a′**, 48.3 ppm, J_{PC} = 32.7 Hz). In the ^{1}H spectra, a multiplet at low field (**3a**, ddd, 1H, 6.26 ppm; **3a′**, m, 1H, 6.26 ppm) indicates the presence of a C=CH fragment. These data reveal a profound modification of the phosphorus heterocycle, and the exact nature of **3a**,**a′**[15] was established by X-ray diffraction studies (Figure 3, Table 2). These new derivatives contain an almost square-planar Pd(II) center linked to two chlorine atoms, a pyridine, and a 2-phospholene ring. Note that the pendant pyridyl group of the ligand does not interact with the metal center (Pd(1)−N(2) distance: **3a**, 5.598(3) Å; **3a′**, 4.444(5) Å). The existence of the phospholene framework is clearly indicated by the tetrahedral geometry about the C(1)

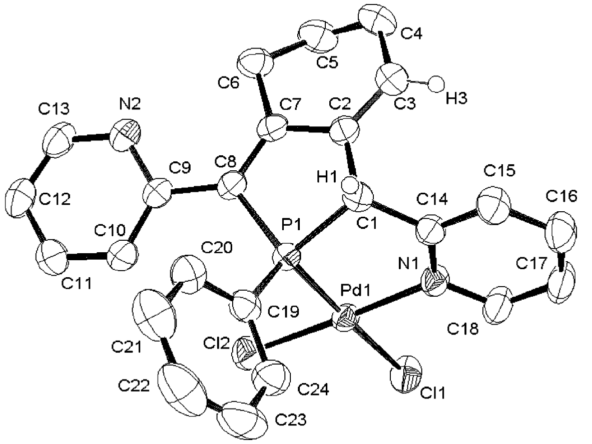


Figure 3. Molecular structure of the Pd(II) complex **3a**·1.5CH$_2$Cl$_2$ (thermal ellipsoids at 50% probability). Hydrogen atoms, except for H(1) and H(3), and dichloromethane molecules have been omitted for clarity.

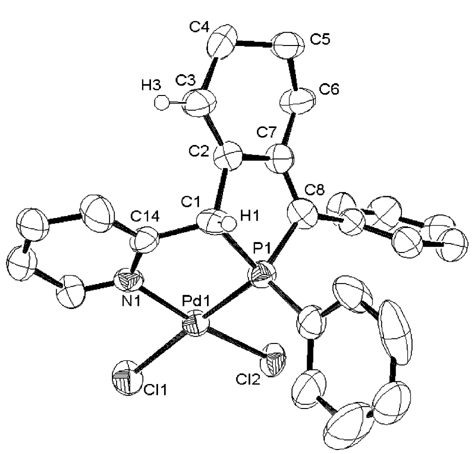


Figure 4. Molecular structure of the Pd(II) complex **3b** (thermal ellipsoids at 50% probability). Hydrogen atoms, except for H(1) and H(3), have been omitted for clarity.

carbon atom and the C(1)−C(2) (**3a**, 1.512(5) Å; **3a′**, 1.527(6) Å) and C(7)−C(8) (**3a**, 1.364(5) Å; **3a′**, 1.357(6) Å) bond distances, which are typical of single and double carbon−carbon links, respectively. The two endocyclic P−C distances (**3a**, 1.830(4) and 1.816(4) Å; **3a′**, 1.835(4) and 1.802(5) Å) are characteristic for single bonds. It is also noteworthy that the C(3) carbon atoms have a planar geometry and that the C(2)−C(3) distances (**3a**, 1.345(5) Å; **3a′**, 1.340(7) Å) are consistent with double bonds. Clearly, the fused carbocycles of **3a**,**a′** are now cyclohexene fragments. These solid-state structural data are in full agreement with the NMR spectroscopic data recorded in solution.

To the best of our knowledge, derivatives **3a**,**a′** are the first P,N chelates to incorporate a 2-phospholene moiety. Furthermore, their syntheses via isomerization of the corresponding 2-(2-pyridyl)phospholes is a very attractive route for several reasons. First, the phosphole precursors are readily available and their substitution pattern can be easily varied.[9,17] Second, the isomerization is not sensitive to the nature of the P substituent, allowing the stereoelectronic properties of the P donor to be tuned. Finally, the [1,3]-hydrogen shift leading to **3a**,**a′** creates a new stereogenic center (the C(1) carbon atom), and the fact that only one diastereoisomer out of the two possible ones is detected by NMR spectroscopy shows that this process is stereoselective. The solid-state studies revealed that the H atom linked to the C(1) atom and the P substituent are in a mutual cis configuration (Figure 3). It was thus of interest to investigate the scope of this synthetic method with the aim of obtaining a family of 2-(2-pyridyl)-2-phospholene ligands.

Complexes **2b**,**b′** and **2c**,**c′** bearing phenyl or 2-thienyl R^1 substituents (Scheme 1) are stable for days in CH$_2$Cl$_2$ and THF solutions at reflux. These results constitute a serious limitation to this new synthetic methodology, since the isomerization process seems dependent on the structure of the ligand. The sole difference between derivatives that undergo (**2a**,**a′**) and those that do not undergo (**2b**,**b′** and **2c**,**c′**) the isomerization is the absence of a pendant pyridyl group in the latter (Scheme 1). This observation prompted us to investigate the fate of complexes **2b**,**b′** and **2c**,**c′** in the presence of pyridine. Indeed, in refluxing CH$_2$Cl$_2$ solutions containing an excess of pyridine, **2b**,**b′** and **2c**,**c′** were transformed quantitatively into the corresponding 2-pyridyl-2-phospholene complexes **3b**,**b′** and **3c**,**c′** after 3 days (Scheme 1). In the presence of a stoichiometric amount of pyridine, the reaction is extremely slow. For example, according to ^{31}P NMR spectroscopy, only 20% of complex **2b** was converted after 2 weeks. In the presence of Et$_3$N and 1,8-diazabycyclo[5.4.0]undec-7-ene complicated mixtures of products were obtained, while with (−)-sparteine or (−)-cinchonidine no reaction was observed.

According to multinuclear NMR spectroscopy, these new complexes **3b**,**b′** and **3c**,**c′** were formed as only one of the two possible diastereoisomers. They exhibited NMR spectroscopic data that are very similar to those recorded for their related analogues **3a**,**a′** (Table 1), strongly supporting the proposed structures. Of particular interest, the $^2J_{\mathrm{PH}}$ values are very similar within a given series (R^2 = Ph, Cy), suggesting that, again, the H atom on C(1) and the P substituent adopt a mutually cis arrangement. To confirm these hypotheses, complexes **3b**,**c′**[15] were subject to X-ray diffraction studies. As expected, **3b**,**c′** are square-planar Pd(II) complexes bearing 2-(2-pyridyl)-2-phospholene ligands and the H atom linked to the C(1) center and the P substituent adopt a mutually cis configuration (Figure 4, Table 2). The structure of **3b** gave high weighted values of R (see the Experimental Section), which precludes a discussion of the metric data. The metric parameters of **3c′** compare well with those of the related complexes **3a**,**a′** (Table 2). Note that the C(1)−C(2) (1.522(6) Å) and C(2)−C(3) (1.342(7) Å) distances are fully consistent with a 3-methylene-2-phospholene framework and that the C(1) carbon atom has a tetrahedral geometry with bond angles ranging from 104.0(3) to 112.4(3)°.

The isomerization of 2-pyridylphospholes into 2-pyridyl-2-phospholenes in the coordination sphere of Pd(II) complexes appears to be a general and powerful synthetic methodology. It is noteworthy that free 2-(2-pyridyl)phospholes **1a**−**c** and **1a′**−**c′** do not isomerize into the corresponding phospholenes in CH$_2$Cl$_2$ and THF solutions containing pyridine at reflux. This result raises questions about the crucial role played by the metal and prompted us to study the isomerization process by DFT calculations for one particular series. This theoretical work[15] revealed that the 2-pyridylphosphole **1a′** is more stable than the 2-pyridyl-2-phospholene **2a′** but that the (2-pyridylphosphole)palla-

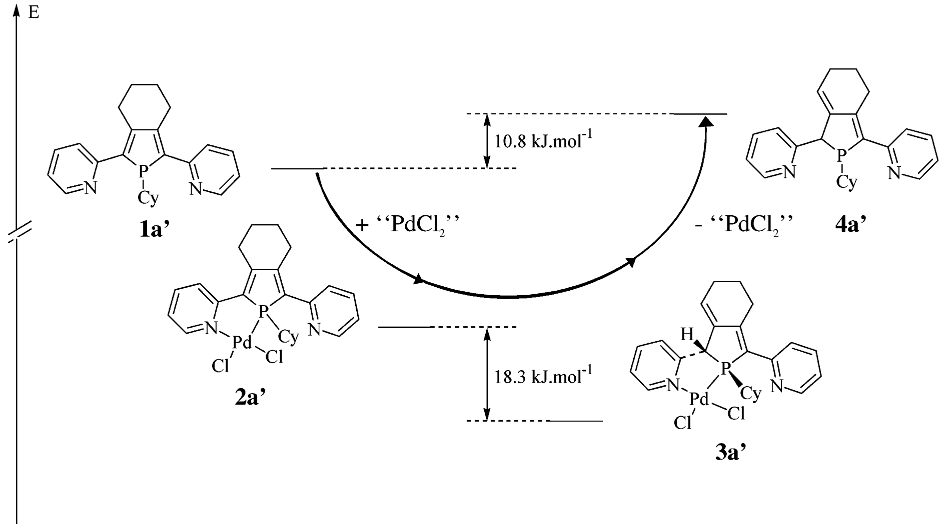
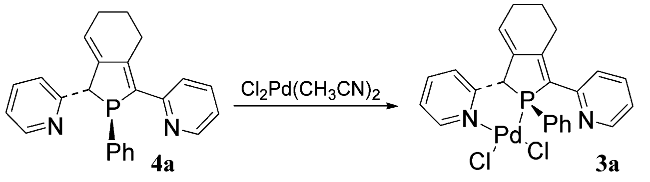


Figure 5. DFT-calculated relative energies of isomers **1a′** and **4a′** and of the corresponding Pd(II) complexes **2a′** and **3a′**.

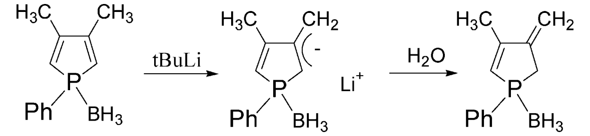
Scheme 2



dium(II) complex **2a′** is less stable than the (2-pyridyl-2-phospholene)palladium(II) complex **3a′** (Figure 5). In other words, coordination to a square-planar d^8 metal center reverses the thermodynamic stability of the two P,N isomers. These calculations agree with the experimental results, which show that the isomerization can take place only in the coordination sphere of the metal, the direct isomerization of phosphole **1a′** into phospholene being a thermodynamically unfavorable process (Figure 5).

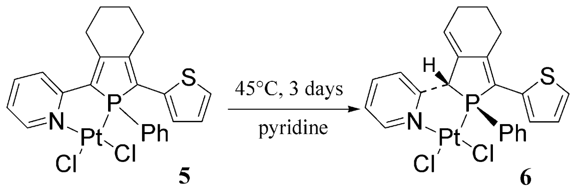
This behavior can be explained tentatively by comparing the solid-state structures of Pd(II) complexes featuring either a 2-pyridylphosphole or a 2-pyridyl-2-phospholene ligand (Scheme 1). As already stated, the distorted geometry of the P(1) and C(1) atoms of coordinated 2-pyridylphospholes revealed a strain, due to the formation of the five-membered metallacycle (Figure 2). In contrast, in the Pd(II) phospholene complexes, the P(1) atom exhibits a geometry close to that of an ideal tetrahedron, as a consequence of the change in hybridization of the C(1) center (Figures 3 and 4). These solid-state data suggest that the strain associated with the metallacycle in phosphole complexes can account for their lower stability compared to that of the phospholene complexes. To reinforce this hypothesis, we investigated the behavior of ligand **4a** (vide infra) possessing two possible chelating moieties (formally a "2-pyridylphospholane" and a "2-pyridylphosphole") with $(CH_3CN)_2PdCl_2$ (Scheme 2). This reaction led exclusively to the formation of complex **3a**. Furthermore, according to ^{31}P NMR spectroscopy, heating **3a** in THF at reflux revealed no fluxional behavior. This experiment clearly shows that coordination of square-planar d^8 metal centers is thermodynamically more favored with 2-pyridyl-2-phospholenes than with 2-pyridylphospholes. It is noteworthy that the DFT calculations also showed that the (2-(2-pyridyl)phospholene)palladium(II) complexes with a cis configuration of the P substituent and the H atom on C(1) are more stable than their trans stereoisomers.[15] Thus, the Pd(II) center plays a double role via the formation of a five-membered metallacycle: it reverses the relative stability of 2-pyridylphospholes vs 2-pyridyl-2-phospholenes, allowing a thermodynamically controlled isomerization, and imposes a stereospecific process.

Scheme 3



Two other examples of isomerization of 3-methylphospholes into 3-methylene-2-phospholenes have already been reported in the literature. The first involves metalation of 3,4-dimethylphosphole (DMPP)−borane adducts, which leads to an intermediate allylic anion, followed by hydrolysis (Scheme 3).[14b] The second involves the thermolysis of Ru(II)−DMPP complexes and proceeds in low yield (ca. 3.9%).[14c] It is also noteworthy that the thermal dimerization of 3,4-dimethylphospholes within the coordination sphere of Pt(II) and Pd(II) to form exomethylenephospholenes is known.[14e,f] Our method offers several advantages compared to these examples. The reaction conditions are very mild (45 °C, presence of a weak base), the yields are almost quantitative, irrespective of the phosphole substitution pattern, and the purification procedure is extremely simple. Furthermore, this process is stereoselective. The main drawback of our method is the requirement for palladium, which is a rather expensive metal. We thus investigated two ways to circumvent this problem. The first is the use of cheaper metals. However, in CH_2Cl_2 solutions containing pyridine, no isomerization was observed in the presence of $ZnCl_2$, CuCl, or $CuCl_2$. The second approach is to perform the isomerization in a catalytic manner, something that could be favored by the hemilabile behavior of P,N donors.[1] According to ^{31}P NMR spectroscopy, addition of 10% of $(CH_3CN)_2PdCl_2$ to a CH_2Cl_2 solution of phosphole **1a** afforded a mixture of **1a** (90%) and complex **2a** (10%). After 3 days at room temperature, this solution contained **1a** (90%) and the

Scheme 4



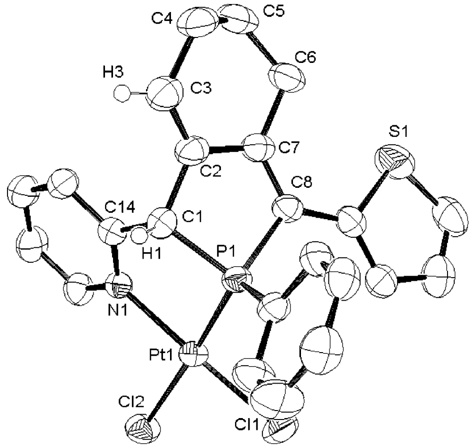


Figure 6. Molecular structure of the Pt(II) complex **6**·CH_2Cl_2 (thermal ellipsoids at 50% probability). Hydrogen atoms, except for H(1) and H(3), and dichloromethane molecules have been omitted for clarity.

phospholene complex **3a** (10%) (Scheme 1). This ratio did not change further upon heating or increasing the reaction time, clearly showing that the isomerization is a stoichiometric process with respect to palladium. Platinum was then investigated as a potential catalyst. First, it was necessary to establish that 2-pyridylphospholes can be transformed into 2-pyridyl-2-phospholenes in the coordination sphere of d^8-Pt(II) complexes. Phosphole **1c** was selected for this study; it reacts rapidly with $PtCl_2(CH_3CN)_2$ in CH_2Cl_2 at room temperature to give complex **5** in 79% yield (Scheme 4). Elemental analysis and high-resolution mass spectrometry support the proposed structure. The downfield ^{31}P NMR coordination chemical shift (ca. 25 ppm) is less pronounced than in the Pd(II) series. However, the coordination of both the P and the N atoms is clear from the large J_{PPt} coupling constant (3704.0 Hz) and the low-field chemical shift of the ^1H NMR signal of the H^6 proton of the pyridyl group (δ 9.88 ppm). Complex **5** could be isomerized quantitatively into **6** in a CH_2Cl_2 solution containing pyridine at reflux (Scheme 4). The allylic moiety could be identified by the presence of a doublet at 4.36 ppm (J_{PH} = 8.2 Hz, PCH) and from a broad resonance at 6.17 ppm (C=CH) in the ^1H spectrum. These data, as well as the other ^1H and ^{13}C NMR data, are consistent with the proposed structure. The cis arrangement of the P substituent and the H atom of the PCH moiety was confirmed by an X-ray diffraction study (Figure 6). The bond lengths and angles of the Pt(II) complex **6** are typical and are similar to those of the related Pd(II) complex **3c′** (Table 2). Thus, the base-promoted stereoselective isomerization of 2-pyridylphospholes into 2-pyridyl-2-phospholenes in the coordination sphere of square-planar d^8 metal centers appears to be a general process. Experiments conducted with a phosphole **1c**/$PtCl_2(CH_3CN)_2$ ratio less than 1 revealed that the isomerization is not a catalytic process with platinum. This feature, also observed with palladium, can be explained by the fact that 2-pyridyl-2-phospholenes are more tightly bonded to the metal centers than the corresponding 2-pyridylphospholes, preventing the ligand exchange step required for a catalytic process.

The next step toward obtaining free 2-(2-pyridyl)-2-phospholenes was their release from the Pd(II) centers. This was easily achieved by addition of 1 equiv of 1,2-(diphenylphosphino)ethane (dppe) to complexes **3a**–**c** and **3a′**–**c′** (Scheme 1). The phospholenes **4a**–**c** and **4a′**–**c** were isolated as air-sensitive powders in excellent yields (Table 1). Their multinuclear NMR spectra showed that they are obtained as single diastereisomers, indicating that the decoordination step proceeds without racemization of the P center. For example, their $^{31}P\{^1H\}$ NMR spectra show a single resonance in the range expected for P-aryl and P-alkyl phospholenes (Table 1).[10,14b] The ^1H and ^{13}C NMR data are typical and support the proposed structures. In the ^{13}C NMR spectra, three singlets for the methylene fragments of the fused carbocycle are observed and a doublet characteristic of a PCH moiety is observed (Table 1). In all cases, the ^1H NMR spectra exhibit a broad resonance corresponding to the C=CH moiety, with chemical shifts ranging from 5.52 to 5.62 ppm.

One further key point was to estimate the inversion barrier at phosphorus for these new types of P,N ligands. It is reasonable to assume that the stereogenic C(1) center of phospholenes **4a**–**c** and **4a′**–**c** will not racemize upon heating in neutral media. Thus, inversion of the P atom should give a new diastereisomer detectable by NMR. We thus investigated the thermal behavior in [D_8]toluene solutions of 1-phenyl-2-pyridyl-2-phospholenes **4a**–**c**, featuring respectively a pyridyl, a phenyl, and a thienyl substituent on the P heterocycle, and 1-cyclohexyl-2-pyridyl-2-phospholene (**4b′**). The samples were gradually heated from 40 to 110 °C, with an isotherm of 1 h every 10 °C, and ^{31}P and ^1H NMR spectra were recorded before and after each temperature ramp. Up to 90 °C no new NMR signals were detected. This result fits with previous studies that have established a high barrier to inversion for phospholenes[10,11a] and shows that P,N chelates **4a**–**c** and **4a′**–**c** are promising P-chiral ligands for homogeneous catalysis. Very interestingly, at 100 °C, derivatives **4a**–**c** and **4a′** cleanly isomerized into the corresponding phospholes, as illustrated in Figure 7 for phospholene **4c**. This process fits nicely with the theoretical data, revealing that free 2-pyridyl-2-phospholenes are thermodynamically less stable than their phosphole isomers.

Conclusion

We have described a general and straightforward route to a new family of P,N chelates featuring a chirogenic P center. This route involves the stereoselective isomerization of Pd(II)-coordinated 2-pyridylphosphole ligands into their corresponding 2-pyridyl-2-phospholene isomers in the presence of pyridine. The role of the metal is to render this isomerization thermodynamically feasible, while the role of the pyridine is very probably to favor the 1,3-shift via the formation

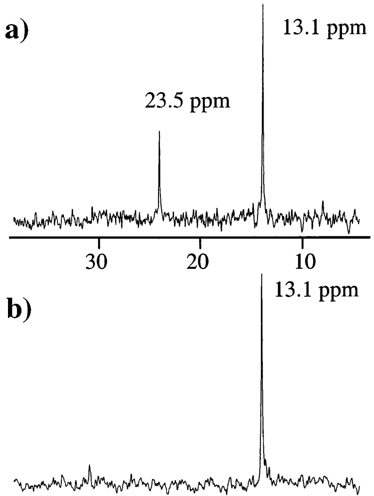


Figure 7. Expansions of the 81.0 MHz $^{31}P\{^{1}H\}$ spectra following isomerization of 2-pyridylphospholene **4c** into 2-pyridylphosphole **1c** at 100 °C: (a) after 2 h; (b) after 12 h.

of an allylic anion. The resolution of racemic 2-pyridyl-2-phospholene derivatives is under intensive investigation.

Experimental Section

General Remarks. All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Commercially available reagents were used as received without further purification. Solvents were freshly distilled under argon from sodium/benzophenone (tetrahydrofuran, diethyl ether) or from phosphorus pentoxide (pentane, dichloromethane, acetonitrile). Complexes **2a**,**a′** were prepared according to ref 16. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AM300, DPX200, and ARX400 spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million (ppm) relative to Me_4Si as external standard. ^{31}P NMR downfield chemical shifts were expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. Assignment of carbon chemical shifts was based on HMBC and HMQC experiments. High-resolution mass spectra were obtained on a Varian MAT 311 or ZabSpec TOF Micromass instrument at the CRMPO, University of Rennes. Elemental analyses were performed by the CRMPO or the Center de Microanalyze du CNRS at Vernaison, France.

[1,5-diphenyl-2-(2-pyridyl)phosphole]PdCl$_2$ (2b). A solution of the 1-phenylphosphole **1b** (0.33 g, 0.90 mmol) in CH_2Cl_2 (5 mL) was added, at room temperature, to a solution of $(CH_3CN)_2PdCl_2$ (0.23 g, 0.90 mmol) in CH_2Cl_2 (10 mL). The solution was stirred for 1 h at room temperature, and the volatile materials were removed under vacuum. The residue was washed with diethyl ether (3 × 10 mL) and dried under vacuum. Complex **2b** was isolated as an air-stable yellow solid (yield 0.43 g, 0.80 mmol, 89%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.40−1.80 (m, 4H; $=CCH_2C\mathit{H}_2$), 2.50−2.75 (m, 2H; $=CCH_2$), 3.02−3.20 (m, 2H; $=CCH_2$), 7.21−7.43 (m, 8H; H arom and H^5 Py), 7.51−7.62 (m, 3H; H arom), 7.73−7.78 (d broad, 1H; H^3 Py), 7.86 (ddd, $^{3}J_{HH}$ = 7.7 and 7.8 Hz, $^{4}J_{HH}$ = 1.6 Hz, 1H; H^4 Py), 9.56 (d, $^{3}J_{H-H}$ = 6.0 Hz, 1H; H^6 Py). $^{13}C\{^{1}H\}$ NMR (50.323 MHz, $CDCl_3$): δ 21.9 (s; $=CCH_2\mathit{C}H_2$), 22.5 (s; $=CCH_2\mathit{C}H_2$), 27.2 (d, J_{PC} = 9.4 Hz; $=C\mathit{C}H_2$), 29.1 (d, J_{PC} = 10.5 Hz; $=C\mathit{C}H_2$), 123.1 (d, J_{PC} = 10.2 Hz; C^3 Py) 123.5 (s; C^5 Py), 128.6 (s; *m*-Ph), 128.8 (s; *p*-Ph), 129.2 (d, J_{PC} = 11.7 Hz, *o*-Ph), 130.7 (d; J_{PC} = 4.7 Hz, *m*-PPh), 132.7 (d, J_{PC} = 2.3 Hz; *p*-PPh), 133.5 (d, J_{PC} = 11.7 Hz; *o*-PPh), 139.3 (s; C^4 Py), 146.5 (d, J_{PC} = 15.1 Hz; $PC{=}C_\beta$), 151.8 (d, J_{PC} = 10.7 Hz; $PC{=}C_\beta$), 153.7 (s; C^6 Py); the C^2 Py, *ipso*-Ph and PCα carbon resonances were not observed. $^{31}P\{^{1}H\}$ NMR (81.014 MHz, $CDCl_3$): δ +56.2. HR-MS (FAB-mNBA): *m*/*z* 520.0209 $[M - Cl]^+$; calcd for $C_{25}H_{22}NPPdCl_2$ 520.0213. Anal. Calcd for $C_{25}H_{22}NPPdCl_2$ (544.753): C, 55.12; H, 4.07; N, 2.57. Found: C, 55.02; H, 4.00; N, 2.49.

[1-cyclohexyl-2-(2-pyridyl)-5-phenylphosphole]PdCl$_2$ (2b′). Following the procedure described for compound **2b,** reaction of 1-cyclohexyl-2-(2-pyridyl)-5-phenylphosphole **(1b′**; 0.35 g, 0.90 mmol) and $(CH_3CN)_2PdCl_2$ (0.23 g, 0.90 mmol) afforded **2b′** as an air-stable yellow solid (yield 0.45 g, 0.82 mmol, 92%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.01−1.19 (m, 3H; CH_2), 1.51−1.87 (m, 12H; CH_2), 2.65−2.83 (m, 3H; CH_2), 3.12 (m, 1H; CH_2), 7.21−7.43 (m, 4H; *p*-H Ph, *m*-H Ph, and H^5 Py), 7.67 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H; H^3 Py), 7.85 (d, $^{3}J_{HH}$ = 7.2 Hz, 2H; *o*-H Ph), 8.05 (dd, $^{3}J_{HH}$ = 8.2 Hz, $^{3}J_{HH}$ = 6.6 Hz, 1H; H^4 Py), 9.63 (d, $^{3}J_{HH}$ = 5.5 Hz, 1H; H^6 Py). $^{13}C\{^{1}H\}$ NMR (50.323 MHz, $CDCl_3$): δ 22.2 (s; $=CCH_2\mathit{C}H_2$), 22.7 (s; $=CCH_2\mathit{C}H_2$), 25.7 (s; $=C\mathit{C}H_2$), 26.7 (d. J_{PC} = 7.2 Hz; CH_2), 26.9 (d, J_{PC} = 9.6 Hz; CH_2), 27.4 (d, J_{PC} = 8.37 Hz; CH_2), 28.1 (d, J_{PC} = 3.9 Hz; CH_2), 29.2 (d, J_{PC} = 9.6 Hz; CH_2), 30.0 (s; $=CCH_2$), 38.5 (d, J_{PC} = 21.7 Hz; PCH), 123.2 (d, J_{PC} = 10.8 Hz; C^3 Py), 123.8 (s; C^5 Py), 128.9 (s; *m*-C Ph), 129.2 (s; *p*-C Ph), 131.2 (d, J_{PC} = 10.8 Hz; *o*-C Ph), 139.9 (s; C^4 Py), 149.8 (d, J_{PC} = 32.6 Hz; $PC_\alpha{=}C$), 151.4 (d, J_{PC} = 10.7 Hz; $PC{=}C_\beta$), 153.0 (d, J_{PC} = 14.8 Hz; C^2 Py), 153.6 (s; C^6 Py), one C_β, one C_α, and the *ipso*-C Ph resonances were not observed. $^{31}P\{^{1}H\}$ NMR (81.014 MHz, $CDCl_3$): δ +72.4. Anal. Calcd for $C_{25}H_{28}NPPdCl_2$ (550.801): C, 54.52; H, 5.12; N, 2.54. Found: C, 55.20; H, 5.01; N, 2.61.

[1-phenyl-2-(2-pyridyl)-5-(2-thienyl)phosphole]PdCl$_2$ (2c). Following the procedure described for compound **2b**, the reaction of 1-phenyl-2-(2-pyridyl)-5-(2-thienyl)phosphole (**1c**; 0.33 g, 0.90 mmol) and $(CH_3CN)_2PdCl_2$ (0.23 g, 0.90 mmol) afforded **2c** as an air-stable red solid (yield 0.48 g, 0.86 mmol, 96%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.72−2.10 (m, 4H; $=CCH_2C\mathit{H}_2$), 2.80 (m, 1H; $=CC\mathit{H}_2$), 2.95 (m, 1H; $=CC\mathit{H}_2$), 3.15 (m, 2H; $=CC\mathit{H}_2$), 7.08 (dd, $^{3}J_{HH}$ = 5.1 and 7.7 Hz; 1H; H^5 Py), 7.32−7.64 (m, 6H; H arom), 7.80−8.04 (m, 4H; H arom), 9.61 (dd broad, $^{3}J_{H-H}$ = 5.1 Hz, $^{5}J_{HH}$ = 0.9 Hz, 1H; H^6 Py). $^{13}C\{^{1}H\}$ NMR (75.469 MHz, CD_2Cl_2): δ 21.9 (s; $=CCH_2\mathit{C}H_2$), 22.8 (s; $=CCH_2\mathit{C}H_2$), 28.4 (d, J_{PC} = 9.2 Hz; $=C\mathit{C}H_2$), 30.2 (d, J_{PC} = 10.4 Hz; $=C\mathit{C}H_2$), 123.9 (s; C^5 Py), 124.0 (d, J_{PC} = 11.0 Hz; C^3 Py), 125.0 (d, J_{PC} = 48.8 Hz; *ipso*-Ph), 128.0 (s; C^4 Thio or C^5 Thio), 129.3 (s; C^4 or C^5 Thio), 129.7 (d, J_{PC} = 12.2 Hz; *m*-Ph), 132.3 (d, J_{PC} = 53.7 Hz; $PC_\alpha{=}C$), 133.9 (d, J_{PC} = 50.6 Hz; $PC_\alpha{=}C$), 133.4 (d, J_{PC} = 2.4 Hz; C^3 Thio), 133.9 (d, J_{PC} = 12.8 Hz; *o*-Ph), 134.5 (d, J_{P-C} = 3.6 Hz; *p*-Ph), 135.5 (d, J_{PC} = 19.5 Hz; C^2 Thio), 140.0 (s; C^4 Py), 148.7 (d, J_{PC} = 14.7 Hz, $PC{=}C_\beta$), 151.9 (d, J_{PC} = 11.0 Hz; C^2 Py), 152.5 (d, J_{PC} = 20.0 Hz; $PC{=}C_\beta$), 153.6 (s; C^6 Py). $^{31}P\{^{1}H\}$ NMR (81.014 MHz, CD_2Cl_2): δ +59.1. HR-MS (FAB-mNBA): *m*/*z* 513.9771 $[M - Cl]^+$, calcd for $C_{23}H_{20}NSPPdCl_2$ 513.9768. Anal. Calcd for $C_{23}H_{20}NSPPdCl_2$: C, 50.16; H, 3.66; N, 2.54. Found: C, 49.98; H, 3.56; N, 2.46.

[1-cyclohexyl-2-(2-pyridyl)-5-(2-thienyl)phosphole]PdCl$_2$ (2c′), Following the procedure described for compound **2b,** reaction of 1-cyclohexyl-2-(2-pyridyl)-5-(2-thienyl)phosphole (**1c′**; 0.34 g, 0.90 mmol) and $(CH_3CN)_2PdCl_2$ (0.23 g, 0.90 mmol) afforded **2c′** as an air-stable red solid (yield 0.45 g, 0.81 mmol, 90%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.80−1.95 (m, 14H; CH_2), 2.60−3.01 (m, 5H; CH_2, CH), 7.25 (dd, $^{3}J_{HH}$ = 3.8 and 5.0 Hz, 1H; H^4 Thio), 7.37 (ddd, $^{3}J_{HH}$ = 6.0 and 7.6 Hz, $^{4}J_{HH}$ = 1.4 Hz, 1H; H^5 Py), 7.57 (dd, $^{3}J_{H-H}$ = 5.0 Hz, $^{4}J_{H-H}$ = 2.8 Hz, 1H; H^3 Thio), 7.62 (d broad, $^{3}J_{HH}$ = 7.4 Hz, 1H; H^3 Py), 8.04 (ddd, $^{3}J_{HH}$ = 7.4 and 7.6 Hz, $^{4}J_{HH}$ = 1.6 Hz, 1H; H^4 Py), 8.34 (d broad, $^{3}J_{HH}$ = 3.8 Hz, 1H; H^5 Thio), 9.59 (d broad, $^{3}J_{HH}$ = 6.0 Hz, 1H; H^6 Py). $^{13}C\{^{1}H\}$ NMR (50.323 MHz, $CDCl_3$): δ 21.9 (s; $=CCH_2\mathit{C}H_2$), 21.8 (s; $=CCH_2\mathit{C}H_2$), 25.7 (d, J_{PC} = 1.5 Hz; CH_2), 26.8 (d, J_{PC} = 11.7 Hz; CH_2), 27.3 (d, J_{PC} = 7.3 Hz; CH_2), 27.3 (d, J_{PC} = 15.5 Hz; CH_2), 28.3 (d, J_{PC} = 7.9 Hz; $=C\mathit{C}H_2$), 29.6

(d, J_{PC} = 10.3 Hz; =C*C*H$_2$), 30.7 (d, J_{PC} = 2.5 Hz; CH$_2$), 39.6 (d, $^1J_{PC}$ = 20.4 Hz; CH), 123.2 (d, $^3J_{PC}$ = 11.0 Hz; C^3 Py), 123.8 (s; C^5 Py), 128.6 (s; C^4 or C^5 Thio), 129.5 (s; C^4 or C^5 Thio), 130.8 (d, J_{PC} = 48.6 Hz, PC$_\alpha$=C), 130.9 (d, J_{PC} = 45.3 Hz; PC$_\alpha$=C), 135.2 (d, J_{PC} = 3.2 Hz; C^3 Thio), 135.6 (d, J_{PC} = 19.5 Hz; C^2 Thio), 140.2 (s; C^4 Py), 148.6 (d, J_{PC} = 13.4 Hz; PC=*C*$_\beta$), 152.5 (d, J_{PC} = 9.5 Hz, PC=*C*$_\beta$), 153.3 (d, J_{PC} = 19.5 Hz, C^2 Py), 153.6 (s; C^6 Py). ^{31}P{^{1}H} NMR (81.014 MHz, CDCl$_3$): δ +69.0. HR-MS (FAB-mNBA): *m/z* 520.0258 [M − Cl]$^+$, calcd for $C_{23}H_{26}NPSPdCl_2$ 520.0253. Anal. Calcd for $C_{23}H_{26}NPSPdCl_2$ (556.827): C, 49.61; H, 4.71; N, 2.52. Found: C, 49.31; H, 4.82; N, 2.61.

[1-phenyl-2,5-bis(2-pyridyl)phosphol-2-ene]PdCl$_2$ (3a). A solution of complex **2a** (0.49 g, 0.90 mmol) in CH$_2$Cl$_2$ (10 mL) was heated at 45 °C for 3 days. The solvent was removed, and the residue was washed with diethyl ether (3 × 10 mL) and dried under vacuum. Complex **3a** was obtained as an air-stable yellow solid (yield 0.45 g, 0.82 mmol, 91%). ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): δ 1.90 (m, 2H; =CCH$_2$*CH$_2$*), 2.30 (m, 2H; =CCH$_2$*CH$_2$*), 2.90 (m, 2H; =C*CH$_2$*), 4.66 (dd, $^2J_{PH}$ = 11.9 Hz, $^3J_{HH}$ = 1.6 Hz, 1H; PCH), 6.26 (ddd, $^3J_{HH}$ = 4.2 and 5.8 Hz, $^4J_{HH}$ = 1.6 Hz, 1H; C=CH), 7.20 (dd, $^3J_{HH}$ = 4.9 and 7.8 Hz, 1H; H^5 Py), 7.33−7.57 (m, 4H; H^5 Py, *m*-Ph, *p*-Ph), 7.66 (m, 2H; H^3 and H^4 Py), 7.82 (d, $^3J_{HH}$ = 8.0 Hz, 1H; H^3 Py), 7.80 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 8.0 Hz, 1H; H^4 Py), 8.09 (ddd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.5 Hz, $^3J_{PH}$ = 12.1 Hz, 2H; *o*-Ph), 8.54 (d, $^3J_{HH}$ = 4.9 Hz, 1H; H^6 Py), 9.77 (d, $^3J_{HH}$ = 5.8 Hz, 1H; H^6 Py). ^{13}C{^{1}H} NMR (75.469 MHz, CD$_2$Cl$_2$): δ 22.1 (s; =CCH$_2$*C*H$_2$), 26.2 (s; =C*C*H$_2$), 28.6 (d, $^3J_{PC}$ = 10.4 Hz; C=C*C*H$_2$), 57.6 (d, J_{PC} = 36.6 Hz; PCH), 123.3 (s; C^5 Py), 124.8 (d, J_{PC} = 12.8 Hz; C^3 Py), 124.9 (s; C^5 Py), 126.9 (s broad; C^3 Py), 127.0 (d, J_{PC} = 51.0 Hz; PC$_\alpha$=C), 129.4 (d, J_{PC} = 12.2 Hz; *m*-Ph), 133.1 (d, J_{PC} = 3.1 Hz; *p*-Ph), 134.4 (d, J_{PC} = 12.8 Hz; *o*-Ph), 134.9 (d, J_{PC} = 4.3 Hz; C=*C*H), 137.0 (s; C^4 Py), 138.7 (d, J_{PC} = 7.9 Hz; PC=*C*$_\beta$), 140.0 (s; C^4 Py), 149.1 (s; C^6 Py), 152.2 (d, J_{PC} = 14.6 Hz; PC−*C*$_\beta$), 154.1 (s; C^6 Py), 157.7 (d, $^2J_{PC}$ = 9.8 Hz; C^2 Py), 163.0 (d, $^2J_{PC}$ = 7.9 Hz; C^2 Py); the *ipso*-Ph resonance was not observed. ^{31}P{^{1}H} NMR (81.014 MHz, CD$_2$Cl$_2$): δ +67.3; HR-MS (FAB-mNBA): *m/z* 511.0168 [M − Cl]$^+$, calcd for $C_{24}H_{21}N_2PCl_2Pd$ 511.0468. Anal. Calcd for $C_{24}H_{21}N_2PCl_2Pd$ (545.74): C, 52.82; H, 3.88; N, 5.13. Found: C, 52.66; H, 3.65; N, 5.22.

[1-cyclohexyl-2,5-bis(2-pyridyl)phosphol-2-ene]PdCl$_2$ (3a′). Following the procedure for complex **3a,** the reaction of **2a′** (0.51 g, 0.90 mmol) afforded **3a′** as an air-stable yellow solid (yield 0.48 g, 0.84 mmol, 94%). ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): δ 0.82−1.95 (m, 8H; CH$_2$), 2.30 (m, 4H; CH$_2$), 2.60−3.15 (m, 5H; CH$_2$, CH Cy), 4.59 (d broad, $^2J_{PH}$ = 7.3 Hz, 1H; PCH), 6.26 (m, 1H; C=CH), 7.23 (dd, $^3J_{HH}$ = 4.9 and 7.6 Hz, 1H; H^5 Py), 7.36 (dd, $^3J_{HH}$ = 5.4 and 7.6 Hz, 1H; H^5 Py), 7.52−7.80 (m, 3H; H^3 Py, H^4 Py), 7.79 (dd, $^3J_{HH}$ = 7.6 and 7.6 Hz, 1H; H^4 Py), 8.59 (s broad, 1H; H^6 Py), 9.40 (d broad, $^3J_{HH}$ = 5.4 Hz, 1H; H^6 Py). ^{13}C{^{1}H} NMR (75.469 MHz, CD$_2$Cl$_2$): δ 21.9 (s; =CCH$_2$*C*H$_2$), 26.0 (s; CH$_2$), 26.2 (s; CH$_2$), 26.8 (d, J_{PC} = 11.8 Hz; *C*H$_2$), 27.1 (d, J_{PC} = 4.3 Hz; CH$_2$), 27.2 (d, J_{PC} = 5.3 Hz; CH$_2$), 27.9 (d, J_{PC} = 9.7 Hz; CH$_2$), 29.1 (d, J_{PC} = 2.3 Hz; CH$_2$), 36.9 (d, $^2J_{PC}$ = 24.7 Hz; P*C*HCH$_2$), 48.3 (d, J_{PC} = 32.7 Hz; PCH), 123.1 (s; C^5 Py), 124.5 (d, J_{PC} = 12.2 Hz; C^3 Py), 124.7 (s; C,^{5} Py), 125.7 (d, J_{PC} = 4.8 Hz; C^3 Py), 127.9 (d, J_{PC} = 44.9 Hz; PC$_\alpha$=C), 133.2 (d, J_{PC} = 5.3 Hz; C=*C*H), 136.5 (s; C^4 Py), 139.7 (d, J_{PC} = 7.8 Hz; PC=*C*$_\beta$), 139.3 (s; C^4 Py), 149.8 (s; C^6 Py), 153.2 (d, J_{PC} = 12.1 Hz; PC−*C*$_\beta$), 153.5 (d, J_{PC} = 9.3 Hz; C^2 Py), 153.9 (s; C^6 Py), 164.2 (d, J_{PC} = 6.8 Hz; C^2 Py. ^{31}P{^{1}H} NMR (81.014 MHz, CD$_2$Cl$_2$): δ +86.5. HR-MS (FAB-mNBA): *m/z* 515.0638 [M − Cl]$^+$, calcd for $C_{24}H_{27}N_2PPdCl_2$. 515.0642. Anal. Calcd for $C_{24}H_{27}N_2PPdCl_2$ (551.788): C, 52.24; H, 4.93; N, 5.08. Found: C, 52.03; H, 4.86; N, 5.16.

[1-phenyl-2-(2-pyridyl)-5-phenylphosphol-2-ene]-PdCl$_2$ (3b). A solution of complex **2b** (0.49 g, 0.90 mmol) and pyridine (1 mL) in CH$_2$Cl$_2$ (20 mL) was heated at 45 °C for 3 days. The volatiles were removed under vacuum, and the residue was washed with diethyl ether (3 × 10 mL) and dried under vacuum. Complex **3b** was isolated as an air-stable yellow solid (yield 0.44 g, 0.82 mmol, 91%). ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): δ 1.71−1.87 (m, 2H; =CCH$_2$*CH$_2$*), 2.23−2.51 (m, 2H; CH$_2$), 2.55−2.73 (m, 2H; CH$_2$), 4.61 (d, $^2J_{PC}$ = 13.0 Hz, 1H; PCH), 6.15 (t broad, 1H; C=CH), 7.28−7.62 (m, 8H; H arom), 7.94−8.10 (m, 4H; H arom), 8.80 (d, $^3J_{HH}$ = 6.6 Hz, 1H; H^4 Py), 9.86 (d, $^3J_{HH}$ = 6.5 Hz, 1H; H^6 Py). ^{13}C{^{1}H} NMR (50.323 MHz, CD$_2$Cl$_2$): δ 22.1 (s; =CCH$_2$*C*H$_2$), 26.1 (s; CH$_2$), 28.2 (s; CH$_2$), 53.7 (d, J_{PC} = 36.4 Hz; PCH), 124.9 (s; C^5 Py), 125.4 (s; C^3 Py), 128.5 (s; *m*-Ph), 128.7 (s; *p*-Ph), 129.4 (d, $^2J_{PC}$ = 7.1 Hz; *o*-Ph), 130.6 (d, J_{PC} = 3.1 Hz; *m*-PPh), 132.6 (d, J_{PC} = 6.1 Hz; C=CH), 133.3 (s; *p*-PPh), 134.4 (d, $^2J_{PC}$ = 12.1 Hz; *o*-PPh), 139.9 (s; C^4 Py), 155.0 (s; C^6 Py), 156.0 (s broad, C^2 Py); the PC$_\alpha$=*C*$_\beta$ and *ipso*-Ph carbon resonances were not observed. ^{31}P{^{1}H} NMR (81.014 MHz, CDCl$_3$): δ +69.8. Anal. Calcd for $C_{25}H_{22}NPPdCl_2$ (544.753) : C, 55.12; H, 4.07; N, 2.57. Found: C, 55.13; H, 4.10; N, 2.59.

[1-cyclohexyl-2-(2-pyridyl)-5-phenylphosphol-2-ene]-PdCl$_2$ (3b′). Following the procedure for complex **3b,** the reaction of **2b′** (0.43 g, 0.80 mmol) afforded **3b′** as an air-stable yellow solid (yield 0.40 g, 0.72 mmol, 91%). ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): δ 1.36−1.52 (m, 2H; CH$_2$), 1.56−1.92 (m, 10H; CH$_2$), 2.21−2.56 (m, 3H; CH$_2$ and CH), 3.01 (m, 2H; CH$_2$), 4.60 (d, $^2J_{PH}$ = 6.2 Hz, 1H; P−CH), 6.25 (m, 1H; CH$_2$C*H*), 7.32−7.54 (m, 4H; H arom), 7.83 (d, $^3J_{HH}$ = 7.4 Hz, 2H; *o*-H Ph), 7.96 (d, $^3J_{HH}$ = 6.4 Hz, 1H; H^3 Py), 8.80 (dd, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 6.4 Hz, 1H; H^4 Py), 9.79 (d, $^3J_{HH}$ = 5.2 Hz; H^6 Py). ^{13}C{^{1}H} NMR (50.323 MHz, CD$_2$Cl$_2$): δ 20.9 (s; =CCH$_2$*C*H$_2$), 25.0 (s; CH$_2$), 25.5 (s; CH$_2$), 25.8 (d, J_{PC} = 11.1 Hz; CH$_2$), 26.0 (d, J_{PC} = 5.12 Hz; CH$_2$), 26.6 (d, J_{PC} = 9.3 Hz; *C*H$_2$), 28.1 (s; C=C*C*H$_2$), 28.9 (s; =C*C*H$_2$), 34.7 (d, J_{PC} = 25.1 Hz; PCH), 47.7 (d, J_{PC} = 32.3 Hz; PCH), 123.2 (d, J_{PC} = 11.9 Hz; C^3 Py), 124.2 (s; C^5 Py), 127.5 (s; *m*-C Ph), 129.3 (s; *p*-C Ph), 129.9 (d, J_{PC} = 3.8 Hz; CH$_2$*C*H), 130.7 (d, $^2J_{PC}$ = 20.1 Hz; PC$_\alpha$=C), 130.8 (d, $^2J_{PC}$ = 5.0 Hz; *o*-C Ph), 131.9 (d, $^1J_{PC}$ = 11.5 Hz; PC=*C*$_\beta$), 138.6 (s; C^4 Py), 151.9 (d, $^2J_{PC}$ = 10.0 Hz; PC−*C*$_\beta$), 152.5 (s; C^6 Py), 163.1 (d, $^2J_{PC}$ = 6.9 Hz; C^2 Py); the *ipso*-C Ph resonance was not observed. ^{31}P{^{1}H} NMR (81.014 MHz, CDCl$_3$): δ +84.3. Anal. Calcd for $C_{25}H_{28}NPPdCl_2$ (550.801) : C, 54.52; H, 5.12; N, 2.54. Found: C, 54.32; H, 5.05; N, 2.59.

[1-phenyl-2-(2-pyridyl)-5-(2-thienyl)phosphol-2-ene]-PdCl$_2$ (3c). Following the procedure for complex **3b,** the reaction of **2c** (0.49 g, 0.90 mmol) afforded **3c** as an air-stable yellow solid (yield 0.43 g, 0.79 mmol, 88%). ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): δ 1.85 (m, 2H; =CCH$_2$*CH$_2$*), 2.25 (m, 2H; C=CCH$_2$*CH$_2$*), 2.92 (m, 2H; CH$_2$), 4.56 (d, $^2J_{PH}$ = 10.8 Hz, 1H; PCH), 6.26 (s broad, 1H; C=CH), 6.92 (dd, $^3J_{HH}$ = 4.2 and 4.5 Hz, 1H; H^5 Py), 7.31−7.60 (m, 6H; H arom), 7.76−8.1 (m, 4H; H arom), 9.79 (d, $^3J_{H-H}$ = 4.5 Hz, 1H; H^6 Py). ^{13}C{^{1}H} NMR (50.323 MHz, CD$_2$Cl$_2$): δ 21.5 (s; =CCH$_2$*C*H$_2$), 25.4 (s; CH$_2$), 28.2 (d, $^3J_{PC}$ = 10.6 Hz; CH$_2$), 57.2 (d, J_{PC} = 36.6 Hz; PCH), 122.0 (d, J_{PC} = 47.8 Hz; *ipso*-Ph), 124.5 (s; C^5 Py), 124.6 (d, J_{PC} = 12.9 Hz; C^3 Py), 126.0 (d, J_{PC} = 49.9 Hz, PC$_\alpha$=C), 127.2 (s; C^4 or C^5 Thio), 127.6 (s; C^4 or C^5 Thio), 129.1 (d, J_{PC} = 12.2 Hz; *m*-Ph), 132.0 (d, J_{P-C} = 4.6 Hz; C^3 Thio), 132.5 (d, J_{PC} = 6.2 Hz; C=*C*H), 133.1 (d, J_{PC} = 2.9 Hz; *p*-Ph), 134.1 (d, J_{PC} = 12.6 Hz; *o*-Ph), 138.1 (d, J_{P-C} = 7.8 Hz; PC=*C*$_\beta$), 139.6 (s; C^4 Py), 150.8 (d, J_{PC} = 12.6 Hz; PC−*C*$_\beta$), 153.8 (s; C^6 Py), 162.3 (d, J_{PC} = 8.1 Hz; C^2 Py); the C^2 thio was not observed. ^{31}P{^{1}H} NMR (81.014 MHz, CD$_2$Cl$_2$): δ +69.0. HR-MS (FAB-mNBA): *m/z* 515.9772 [M − Cl]$^+$, calcd for $C_{23}H_{20}NSPPdCl_2$ 515.9782. Anal. Calcd for $C_{23}H_{21}NSPPdCl_2$ (551.787): C, 50.07; H, 3.84; N, 2.54. Found: C, 50.11; H, 3.89; N, 2.45.

[1-cyclohexyl-2-(2-pyridyl)-5-(2-thienyl)phosphol-2-ene]-PdCl$_2$ (3c′). Following the procedure for complex **3b,** the reaction of **2c′** (0.50 g, 0.90 mmol) afforded **3c′** as an air-stable red solid (yield 0.43 g, 0.78 mmol, 87%). ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): δ 0.82−1.95 (m, 8H; CH$_2$), 2.23 (m, 4H; CH$_2$), 2.70−3.15 (m, 5H; CH$_2$, CH Cy), 4.63 (d broad, $^2J_{PH}$ = 8.2 Hz, 1H; PCH), 6.22 (m, 1H; =CH), 7.11 (m, 1H; H^5 Py), 7.21−7.63 (m, 3H; H arom), 7.74−8.03 (m, 2H; H arom), 9.69 (d, $^3J_{HH}$ = 6.5

Hz, 1H; H^6 Py). ^{13}C{^{1}H} NMR (75.469 MHz, CD$_2$Cl$_2$): δ 21.9 (s; =CCH$_2$*C*H$_2$), 22.8 (s; CH$_2$), 25.8 (d, J_{PC} = 3.0 Hz; CH$_2$), 26.9 (d, J_{PC}= 11.6 Hz; CH$_2$), 27.2 (s; CH$_2$), 28.3 (d, J_{PC} = 8.1 Hz; CH$_2$), 29.7 (d, J_{PC} = 9.0 Hz; CH$_2$), 30.7 (s; CH$_2$), 39.6 (d, J_{PC} = 20.3 Hz; PCH), 48.9 (d, J_{PC} = 33.6 Hz; PCHC=), 124.3 (d, J_{PC} = 11.8 Hz; C^3 Py), 124.8 (s; C^5 Py), 128.3 (s; C^5 Thio), 129.4 (s; C^4 Thio), 131.6 (d, J_{PC} = 4.6 Hz; C^3 Thio), 134.8 (s broad, C=*C*H), 135.9 (d, J_{PC} = 19.0 Hz, C^2 Thio), 138.2 (s broad, PC=C_β), 139.1 (s; C^4 Py), 148.9 (d, J_{PC} = 13.0 Hz; PC−C_β), 153.9 (s; C^6 Py), 164.2 (d, J_{PC} = 6.9 Hz; C^2 Py); the PCα resonance was not observed. ^{31}P{^{1}H} NMR (81.014 MHz, CD$_2$Cl$_2$): δ +82.6. Anal. Calcd for C$_{23}$H$_{26}$NSPPdCl$_2$ (556.827): C, 49.61; H, 4.71; N, 2.52. Found: C, 49.58; H, 4.64; N, 2.44.

1-Phenyl-2,5-bis(2-pyridyl)phosphol-2-ene (4a). To a solution of complex **3a** (0.49 g, 0.90 mmol) in CH$_2$Cl$_2$ was added neat 1,2-(diphenylphosphino)ethane (dppe; 0.36 g, 0.90 mmol). The solution was stirred for 12 h at room temperature, and then the solvent was removed. The residue was extracted with toluene (2 × 10 mL). Evaporation of toluene afforded a residue that was subsequently washed with pentane (3 × 2 mL) and dried under vacuum. **4a** was obtained as a yellow solid (yield 0.31 g, 0.85 mmol, 95%). ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 1.21−1.72 (m, 2H; =CH$_2$C*H*$_2$), 1.75−1.98 (m, 2H; =CCH$_2$), 3.02−3.31 (m, 2H; CH$_2$), 4.50 (dd, $^2J_{PH}$ = 4.7 Hz, $^3J_{HH}$ = 2.0 Hz, 1H; PCH), 5.52 (m, 1H; C=CH), 6.42 (dd, $^3J_{HH}$ = 4.7 Hz, $^3J_{HH}$ = 4.5 Hz, 1H; H^5 Py), 6.58 (m, 1H; H^3 Py), 6.72−7.08 (m, 6H; H arom), 7.38 (d, $^3J_{HH}$ = 7.0 Hz, 1H; H^3 Py), 7.68 (dd, $^3J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 5.0 Hz, 1H; H^4 Py), 7.70 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 5.2 Hz, 1H; H^4 Py), 8.40 (d, $^3J_{HH}$ = 4.7 Hz, 1H; H^6 Py), 8.43 (d, $^3J_{HH}$ = 7.1 Hz, 1H; H^6 Py). ^{13}C{^{1}H} NMR (50.323 MHz, CDCl$_3$): δ 22.3 (s; =CCH$_2$*C*H$_2$), 28.0 (s; CH$_2$), 29.7 (s; CH$_2$), 55.4 (d, J_{PC} = 8.1 Hz; PCH), 121.2 (s; 2 × C^5 Py), 122.6 (d, J_{PC} = 6.9 Hz; C^3 Py), 123.0 (d, J_{PC} = 8.2 Hz; C^3 Py), 128.2 (d, J_{PC} = 7.2 Hz; *m*-Ph), 128.5 (s; C=*C*H), 132.3 (s; *p*-Ph), 133.4 (d, J_{PC} = 13.2 Hz; *o*-Ph), 136.1 (s; C^4 Py), 136.7 (s; C^4 Py), 137.2 (d, J_{PC} = 8.1 Hz; PC_α=C), 141.2 (d, J_{PC} = 7.1 Hz; PC=C_β), 148.9 (s; PC−C_β), 149.9 (s; C^6 Py), 150.2 (s; C^6 Py), 158.2 (d, J_{PC} = 16.8 Hz; C^2 Py), 163.9 (d, J_{PC} = 16.2 Hz; C^2 Py), the *ipso*-Ph carbon resonance was not observed. ^{31}P{^{1}H} NMR (81.014 MHz, CDCl$_3$): δ +22.7. Anal. Calcd for C$_{24}$H$_{21}$N$_2$P (368.420): C, 78.24; H, 5.75; N, 7.60. Found: C. 78.14; H, 5.81; N, 7.56.

1-Cyclohexyl-2,5-bis(2-pyridyl)phosphol-2-ene (4a′). Following the procedure described for compound **4a,** reaction of complex **3a′** (0.43 g, 0.86 mmol) and dppe (0.32 g, 0.86 mmol) afforded compound **4a′** as a yellow solid (yield 0.39 g, 0.79 mmol, 93%). ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 0.92 (m, 3H; CH$_2$), 1.10−1.75 (m, 8H; CH$_2$), 1.95 (m, 5H; CH$_2$, CH Cy), 2.95 (m, 1H; CH$_2$), 4.51 (m, 1H; PCH), 5.62 (m, 1H; C=CH), 6.60 (m, 2H; H^5 Py), 7.02−7.25 (m, 3H; H^4 Py and H^3 Py), 7.47 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.0 Hz, 1H; H^4 Py), 8.50 (m, 2H; H^6 Py). ^{13}C{^{1}H} NMR (50.323 MHz, C$_6$D$_6$): δ 22.5 (s; =CCH$_2$*C*H$_2$), 25.8 (s; CH$_2$), 26.4 (s; CH$_2$), 27.2 (d, J_{PC} = 7.8 Hz; CH$_2$), 27.4 (d, J_{PC} = 10.9 Hz, CH$_2$), 28.0 (s; CH$_2$), 28.8 (d, $^3J_{PC}$ = 9.7 Hz; CH$_2$), 29.8 (d, J_{PC} = 5.9 Hz; CH$_2$), 39.2 (d, J_{PC} = 19.3 Hz; PCH), 48.9 (d, J_{PC} = 10.0 Hz; PCH), 120.9 (d, J_{PC} = 2.3 Hz; C^5 Py), 120.8 (s; C^5 Py), 122.3 (d, J_{PC} = 7.8 Hz; C^3 Py), 123.8 (d, J_{PC} = 8.6 Hz; C^3 Py), 127.9 (s; C=*C*H), 135.3 (s; C^4 Py), 136.0 (s; C^4 Py), 138.2 (d, J_{PC} = 8.6 Hz; PC_α=C), 146.9 (d, J_{PC} = 3.1 Hz; PC=C_β), 149.1 (s; C^6 Py), 149.5 (s; C^6 Py), 149.6 (s; PC−C_β), 158.0 (d, J_{PC} = 18.0 Hz; C^2 Py), 165.9 (d, J_{PC} = 17.2 Hz; C^2 Py). ^{31}P{^{1}H} NMR (81.014 MHz, C$_6$D$_6$): δ +34.9. HR-MS (FAB-mNBA): *m/z* 375.1990 [M + H]$^+$, calcd 375.1990. Anal. Calcd for C$_{24}$H$_{27}$N$_2$P: C, 76.98; H, 7.27; N, 7.48. Found: C, 76.88; H, 7.18; N, 7.56.

1-Phenyl-2-(2-pyridyl)-5-phenylphosphol-2-ene (4b). Following the procedure described for compound **4a,** reaction of complex **3b** (0.46 g, 0.85 mmol) and dppe (0.33 g, 0.85 mmol) afforded compound **4b** as a yellow solid (yield 0.29 g, 0.78 mmol, 92%). ^{1}H NMR (200 MHz, CDCl$_3$): δ 1.51−1.92 (m, 2H; CCH$_2$C*H*$_2$), 2.22−2.38 (m, 2H; CH$_2$), 3.21−3.53 (m, 2H; CH$_2$), 4.22 (d, $^2J_{PH}$ = 4.9 Hz, 1H; PCH), 5.59 (m, 1H; C=CH), 6.92−7.29 (m, 8H; H arom), 7.32−7.63 (m, 5H; H arom), 8.42 (m, 1H; H^6 Py). ^{13}C{^{1}H} NMR (50.323 MHz, CDCl$_3$): δ 22.8 (s; =CCH$_2$*C*H$_2$), 26.2 (s; CH$_2$), 28.5 (s; CH$_2$), 56.4 (d, J_{PC} = 8.1 Hz; PCH), 120.7 (s; C^5 Py), 123.7 (d, J_{PC} = 7.1 Hz; C^3 Py), 126.7 (s; C=*C*H), 128.7 (d, J_{PC} = 7.1 Hz; *m*-Ph), 129.3 (s; *p*-Ph), 129.4 (d, J_{PC} = 4.7 Hz; *m*-Ph), 129.7 (s; *p*-Ph), 130.2 (d, J_{PC} = 19.7 Hz; *o*-Ph), 133.7 (d, J_{PC} = 18.0 Hz; *o*-Ph), 137.1 (s; C^4 Py), 139.2 (d, J_{PC} = 23.1 Hz; PC_α=C), 144.8 (d, J_{PC} = 10.6 Hz; PC=C_β), 148.1 (s; PC−C_β), 149.8 (s; C^6 Py), 164.5 (d, J_{PC} = 16.1 Hz; C^2 Py); the ipso-Ph carbon resonance was not observed. ^{31}P{^{1}H} NMR: δ +25.1. Anal. Calcd for C$_{25}$H$_{22}$NP (367.432): C, 81.72; H, 6.04; N, 3.81. Found: C, 81.62; H, 5.91; N, 3.87.

1-Cyclohexyl-2-(2-pyridyl)-5-phenylphosphol-2-ene (4b′). Following the procedure described for compound **4a**, reaction of complex **3b′** (0.33 g, 0.60 mmol) and dppe (0.18 g, 0.60 mmol) afforded compound **4b′** as a yellow solid (yield 0.19 g, 0.51 mmol, 85%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.02 (m, 4H; CH$_2$), 1.32−1.86 (m, 8H; CH$_2$), 2.52 (m, 4H; CH$_2$, CH Cy), 3.1 (m, 1H; CH$_2$), 4.12 (m, 1H; PCH), 5.44 (m, 1H; CH$_2$C*H*), 7.13 (dd, $^3J_{HH}$ = 4.5 Hz, $^3J_{HH}$ = 7.8 Hz, 1H; H^5 Py), 7.32−7.54 (m, 6H; H arom and H^3 Py), 7.58 (m, 1H; H^4 Py), 8.44 (d, $^3J_{HH}$ = 4.5 Hz, 1H; H^6 Py). ^{13}C{^{1}H} NMR (75.469 MHz, CDCl$_3$): δ 21.3 (s; =CCH$_2$*C*H$_2$), 24.7 (s; CH$_2$), 25.2 (s; CH$_2$), 26.0 (d, J_{P-C} = 2.3 Hz; CH$_2$), 26.1 (s; CH$_2$), 27.8 (d, J_{PC} = 8.7 Hz; *C*H$_2$), 28.1 (s; C=C*C*H$_2$), 28.7 (s; =C*C*H$_2$), 38.0 (d, J_{PC} = 20.9 Hz; P−CH), 48.1 (d, J_{PC} = 11.0 Hz; PCH), 119.0 (s; C^5 Py), 121.7 (d, J_{PC} = 7.6 Hz; C^3 Py), 127.1 (s; *m*-C Ph), 127.7 (s; *p*-C Ph), 125.6 (d, J_{PC} = 2.1 Hz; C=*C*H), 128.2 (d, $^2J_{PC}$ = 9.8 Hz; *o*-C Ph), 135.5 (s; C^4 Py), 141.7 (d, J_{PC} = 9.4 Hz; PC=C_β), 147.8 (s; C^6 Py), 148.4 (s; PC−C_β), 164.2 (d, $^2J_{PC}$ = 16.4 Hz; C^2 Py); the *ipso*-C Ph and PC$_\alpha$= carbon resonances were not observed. ^{31}P{^{1}H} NMR (81.014 MHz, CDCl$_3$): δ +37.2.

1-Phenyl-2-(2-pyridyl)-5-(2-thienyl)phosphol-2-ene (4c). Following the procedure described for compound **4a,** reaction of complex **3c** (0.52 g, 0.95 mmol) and dppe (0.37 g, 0.95 mmol) afforded compound **4c** as a red solid (yield 0.39 g, 0.90 mmol, 95%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.52−1.65 (m, 2H; CCH$_2$C*H*$_2$), 1.94−2.01 (m, 2H; CH$_2$), 2.88−2.98 (m, 2H; C=CH$_2$), 4.49 (dd, $^2J_{PH}$ = 4.6 Hz, $^3J_{HH}$ = 2.1 Hz, 1H; PCH), 5.62 (m, 1H; C=CH), 6.63 (m, 2H; H^5 Py and H^4 Thio), 6.82 (d, $^3J_{HH}$ = 5.1 Hz, 1H; H^3 Py), 6.95−7.15 (m, 5H; *m*-Ph, *p*-Ph, H^3 Thio and H^4 Py), 7.21 (d, $^3J_{HH}$ = 3.5 Hz, 1H; H^5 Thio), 7.71 (ddd, $^2J_{PH}$ = 15.8 Hz, $^3J_{HH}$ = 6.1 Hz, $^4J_{HH}$ = 1.2 Hz, 2H; *o*-Ph), 8.47 (d, $^3J_{HH}$ = 4.6 Hz, 1H; H^6 Py). ^{13}C{^{1}H} NMR (75.469 MHz, CDCl$_3$): δ 22.1 (s; =CCH$_2$*C*H$_2$), 25.4 (s; CH$_2$), 27.9 (s; =CH$_2$), 56.0 (d, J_{PC} = 8.5 Hz; PCH), 120.8 (s; C^5 Py), 121.7 (d, J_{PC} = 7.3 Hz; C^3 Py), 125.5 (d, J_{PC} = 2.1 Hz; C^4 Thio), 127.2 (d, J_{PC} = 7.8 Hz; C=*C*H), 127.7 (d, J_{PC} = 10.1 Hz; C^3 Thio), 128.3 (s; C^5 Thio), 128.6 (d, J_{PC} = 6.5 Hz; *m*-Ph), 129.1 (s; *p*-Ph), 130.8 (d broad, J_{PC} = 15.0 Hz; *ipso*-Ph), 132.6 (d, J_{PC} = 20.1 Hz; *o*-Ph), 136.1 (s; C^4 Py), 140.2 (d, J_{PC} = 22.6 Hz; PC$_\alpha$=C), 144.1 (d, $^2J_{PC}$ = 4.3 Hz; PC=C_β), 148.3 (s; PC−C_β), 149.6 (s; C^6 Py), 164.5 (d, $^2J_{PC}$ = 16.7 Hz; C^2 Py); the C^2 thio carbon resonance was not oberved. ^{31}P{^{1}H} NMR (81.014 MHz, CDCl$_3$): δ +22.4. HR-MS (FAB-mNBA): *m/z* 373.1054 [M$^{\bullet+}$]; calcd 373.1054. Anal. Calcd for C$_{23}$H$_{20}$NPS (373.458): C, 73.97; H, 5.40; N, 3.75. Found: C, 73.91; H, 5.31; N, 3.84.

1-Cyclohexyl-2-(2-pyridyl)-5-(2-thienyl)phosphol-2-ene (4c′). Following the procedure described for compound **4a,** reaction of complex **3c′** (0.38 g, 0.70 mmol) and dppe (0.28 g, 0.70 mmol) afforded compound **4c′** as an orange solid (yield 0.22 g, 0.59 mmol, 85%). ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.82−1.30 (m, 6H; CH$_2$), 1.48−1.85 (m, 6H; CH$_2$), 2.56−2.71 (m, 4H; CH$_2$, CH Cy), 3.18 (m, 1H; CH$_2$), 4.17 (d, $^2J_{PH}$ = 2.3 Hz, 1H; PCH), 5.69 (m, 1H; CH$_2$C*H*), 7.12−7.18 (m, 3H; H^5 Py, H^3 Thio, H^4 Thio), 7.48 (d, $^3J_{HH}$ = 6.3 Hz, 1H; H^3 Py), 7.65 (m, 2H; H^5 Thio and H^4 Py), 8.52 (d, $^3J_{HH}$ = 4.3 Hz, 1H; H^6 Py). ^{13}C{^{1}H} NMR (50.323 MHz, CDCl$_3$): δ 22.5 (s; C=CH$_2$*C*H$_2$), 24.2 (s; CH$_2$), 25.9 (s; CH$_2$), 26.7 (s; CH$_2$), 28.0 (d, J_{PC} = 4.7 Hz; CH$_2$), 28.7 (s; =C*C*H$_2$), 29.0 (s; =C*C*H$_2$), 30.4 (d, J_{PC} = 6.9 Hz; CH$_2$),

Table 3. Summary of Crystal Data and Structure Refinement Details for 2c′, 3a·1.5CH$_2$Cl$_2$, 3a′·CH$_2$Cl$_2$, 3c′·0.5CH$_2$Cl$_2$, and 6·CH$_2$Cl$_2$

	2c′	**3a**·1.5CH$_2$Cl$_2$	**3a′**·CH$_2$Cl$_2$	**3c′**·0.5CH$_2$Cl$_2$	**6**·CH$_2$Cl$_2$
mol formula	$C_{23}H_{26}Cl_2NPPdS$	$C_{25.5}H_{24}Cl_5N_2PPd$	$C_{25}H_{29}Cl_4N_2PPd$	$C_{23.5}H_{26}Cl_3NPPdS$	$C_{24}H_{22}Cl_4NPPtS$
mol wt	556.78	673.08	636.67	598.23	724.35
a (Å)	10.3320(2)	14.985(5)	8.7170(2)	10.866(5)	9.504(5)
b (Å)	17.1370(5)	9.785(5)	16.2360(3)	15.475(5)	17.436(5)
c (Å)	13.1100(4)	37.375(5)	18.9070(4)	16.973(5)	15.476(5)
α (deg)	90	90	90	90	90
β (deg)	106.6950(10)	98.388(5)	90	106.722(5)	96.230(5)
γ (deg)	90	90	90	90	90
V (Å^3)	2223.40(10)	5422(3)	2675.89(10)	2733.3(17)	2549.4(17)
Z	4	8	4	4	4
D_c (g cm^{-3})	1.252	1.661	1.580	1.454	1.887
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$	$P2_12_12_1$	$P2_1/n$	$P2_1/n$
temp (K)	293(2)	293(2)	293(2)	293(2)	293(2)
wavelength Mo Kα (Å)	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69
cryst size (mm)	0.18 × 0.12 × 0.12	0.35 × 0.20 × 0.05	0.38 × 0.36 × 0.36	0.35 × 0.35 × 0.35	0.1 × 0.05 × 0.01
μ (mm^{-1})	1.252	0.953	1.170	1.018	6.082
F(000)	1128	2232	1288	1124	1400
θ limit (deg)	2.01−27.47	3.10−27.49	2.49−27.51	2.92−27.49	3.18−27.48
index ranges *hkl*	$0 \le h \le 13$ $0 \le k \le 22$ $-17 \le l \le 16$	$-19 \le h \le 19$ $-12 \le k \le 10$ $-48 \le l \le 48$	$0 \le h \le 11$ $0 \le k \le 21$ $0 \le l \le 24$	$-14 \le h \le 14$ $-19 \le k \le 20$ $-22 \le l \le 22$	$-12 \le h \le 12$ $-21 \le k \le 22$ $-20 \le l \le 20$
no. of rflns collected	25 726	11 725	30 440	34 847	30 455
no. of indep rflns	5046	6991	3452	12 092	11 191
no. of rflns with $I > 2\sigma(I)$	3887	4216	3351	4972	5027
no. of data/restraints/params	5046/0/263	5167/0/324	3452/0/299	6251/0/298	5841/0/294
goodness of fit on F^2	1.097	1.0499	1.125	1.080	1.154
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0444 wR2 = 0.1039	R1 = 0.0397 wR2 = 0.0909	R1 = 0.0336 wR2 = 0.0860	R1 = 0.0570 wR2 = 0.1687	R1 = 0.0433 wR2 = 0.1079
R indices (all data)	R1 = 0.0662 wR2 = 0.1142	R1 = 0.0546 wR2 = 0.0977	R1 = 0.0350 wR2 = 0.0872	R1 = 0.0709 wR2 = 0.1869	R1 = 0.0517 wR2 = 0.1131
largest diff peak and hole (e Å^{-3})	0.916 and −1.185	0.562 and −0.759	0.697 and −0.862	1.254 and −0.837	1.437 and −3.049

39.4 (d, J_{PC} = 21.8 Hz; PCH), 48.8 (d, J_{PC} = 11.8 Hz; PCH), 121.3 (s; C^5 Py), 122.5 (d, $^3J_{PC}$ = 6.9 Hz; C^3 Py), 123.9 (s; C^4 thio), 125.6 (s; C═*C*H), 127.1 (d, $^3J_{PC}$ = 10.2 Hz; C^3 thio), 127.5 (s; C^5 thio), 137.2 (s; C^4 Py), 149.0 (s; PC−C_β), 149.3 (s; C^6 Py), 165.7 (d, $^2J_{PC}$ = 14.2 Hz; C^2 Py); the C^2 thio, PC_α═C, and PC═C_β carbon resonances were not observed. ^{31}P{^{1}H} NMR (81.014 MHz, CDCl$_3$): δ +36.6.

[1-phenyl-2-(2-pyridyl)-5-(2-thienyl)phosphole]PtCl$_2$ (5). A solution of 1-phenylphosphole **1a** (0.07 g, 0.20 mmol) in CH$_2$Cl$_2$ (5 mL) was added, at room temperature, to a solution of (CH$_3$CN)$_2$PtCl$_2$ (0.09 g, 0.20 mmol) in CH$_2$Cl$_2$ (10 mL). The solution was stirred for 1 h at room temperature, and the volatile materials were removed under vacuum. The residue was washed with diethyl ether (3 × 10 mL) and dried under vacuum. Complex **5** was obtained as an air-stable orange solid (yield 0.10 g, 0,16 mmol, 79%). ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): δ 1.62−2.00 (m, 4H; ═CCH$_2$C*H*$_2$), 2.73−2.60 (m, 2H; ═CCH$_2$), 2.86−3.07 (m, 2H; ═CCH$_2$), 6.26 (d, $^3J_{HH}$ = 4.3 Hz, 1H; H^4 Py), 7.10−7.90 (m, 10H; H arom), 9.88 (d, $^3J_{H-H}$ = 5.8 Hz, 1H; H^6 Py). ^{13}C{^{1}H} NMR (50.323 MHz, CD$_2$Cl$_2$): δ 21.5 (s; ═CCH$_2$*C*H$_2$), 22.4 (s; ═CCH$_2$*C*H$_2$), 27.9 (d, J_{PC} = 9.3 Hz; ═C*C*H$_2$), 29.5 (d, J_{PC} = 10.6 Hz; ═C*C*H$_2$), 123.4 (d, J_{PC} = 9.7 Hz; C^3 Py), 123.5 (s; C^5 Py), 124.3 (d, J_{PC} = 53.7 Hz; *ipso*-Ph), 127.7 (s; C^4 thio or C^5 thio), 128.7 (d, $^3J_{PC}$ = 12.4 Hz; *m*-Ph), 129.1 (s; C^4 or C^5 thio), 130.5 (d, J_{PC} = 60.6 Hz; PC_α═C), 132.6 (d, J_{PC} = 2.9 Hz; C^3 thio), 133.5 (d, J_{PC} = 12.9 Hz; *o*-Ph), 133.9 (d, J_{P-C} = 4.1 Hz; *p*-Ph), 135.3 (d, J_{PC} = 19.4 Hz; C^2 thio), 135.8 (d, J_{PC} = 57.5 Hz; PC_α═C), 138.9 (s; C^4 Py), 150.8 (d, J_{PC} = 12.0 Hz; PC═C_β), 148.3 (d, J_{PC} = 15.8 Hz; PC═C_β), 152.1 (s; C^6 Py), 152.6 (d, J_{PC} = 17.6 Hz; C^2 Py). ^{31}P{^{1}H} NMR (81.014 MHz, CD$_2$Cl$_2$): δ +37.3 (J_{PPt} = 3704.0 Hz). HR-MS (FAB-mNBA): *m/z* 602.0375 [M − Cl]$^+$, calcd for $C_{23}H_{20}NSPPtCl_2$ 602.036 94. Anal. Calcd for $C_{23}H_{20}NSPPtCl_2$: C, 43.20; H, 3.15; N, 2.19. Found: C, 43.12; H, 3.21; N, 2.12.

[1-phenyl-2-(2-pyridyl)-5-(2-thienyl)phosphol-2-ene]-PtCl$_2$ (6). To a solution of **5** (0.051 g, 0.08 mmol) in CH$_2$Cl$_2$ (10 mL) was added an excess of pyridine. The solution was heated at 45 °C and stirred for 3 days. The solvent was removed, and then the residue was washed with diethyl ether (2 × 10 mL) and dried under vacuum. Complex **6** was obtained as an air-stable orange solid (yield 0.042 g, 0.067 mmol, 83%). ^{1}H NMR (200 MHz, CDCl$_3$): δ 1.80−2.05 (m, 4H; ═CCH$_2$C*H*$_2$), 2.90 (m, 2H; CH$_2$), 4.36 (d, $^2J_{PH}$ = 8.2 Hz, 1H; PCH), 6.17 (s broad, 1H; C═CH), 6.87 (m, 1H; H^5 Py), 7.30−7.55 (m, 6H; H arom), 7.70−8.00 (m, 4H; H arom), 10.14 (d, $^3J_{H,H}$ = 5.9 Hz, 1H; H^6 Py). ^{13}C{^{1}H} NMR (50.323 MHz, CD$_2$Cl$_2$): δ 21.0 (s; ═CCH$_2$*C*H$_2$), 24.6 (s; CH$_2$), 27.2 (d, J_{PC} = 9.7 Hz; CH$_2$), 54.5 (d, J_{PC} = 42.9 Hz; PCH), 123.8 (s; C^5 Py), 124.0 (d, J_{PC} = 47.5 Hz; *ipso*-Ph), 126.8 (s; C^4 thio or C^5 thio), 127.0 (s; C^4 thio or C^5 thio), 127.7 (d, J_{PC} = 48.7 Hz; PC_α═C), 128.1 (d, J_{PC} = 12.9 Hz, *m*-Ph), 131.1 (d; J_{PC} = 5.4 Hz, C^3 thio), 131.1 (s; C^3 Py), 131.4 (s; *p*-Ph), 133.0 (d, J_{PC} = 12.2 Hz; *o*-Ph), 133.5 (d, J_{PC} = 16,6 Hz; C═*C*H), 138.2 (s; C^4 Py), 147.1 (d, J_{PC} = 14.3 Hz, PC═C_β), 151.5 (s; C^6 Py), 152.7 (s; PC−C_β), 163.0 (d, J_{PC} = 5.4 Hz; C^2 Py); the C^2 thio resonance was not observed. ^{31}P{^{1}H} NMR (81.014 MHz, CDCl$_3$): δ +41.2 ($^1J_{P-Pt}$ = 3877.5 Hz). Anal. Calcd for $C_{23}H_{20}NSPPtCl_2$: C, 43.20; H, 3.15; N, 2.19. Found: C, 43.09; H, 3.23; N, 2.09.

X-ray Crystallographic Study. Single crystals suitable for X-ray crystal analysis were obtained by diffusion of vapors of pentane into a CH$_2$Cl$_2$ solution of **3a, 3a′**, and **6** at room temperature, by diffusion of diethyl ether into a CH$_2$Cl$_2$ solution of **2c′** and **3c′** at 5 °C, and by slow evaporation of a CH$_2$Cl$_2$ solution of **3b**. Single-crystal data collections were performed at room temperature with a Nonius KappaCCD diffractometer (Center de Diffractométrie, Université de Rennes 1, France), with Mo Kα radiation (λ = 0.710 73 Å). Reflections were indexed, Lorentz−polarization corrected, and integrated by the DENZO program of the KappaCCD software package. The data merging process was performed using the

SCALEPACK program.[19] Structure determinations were performed by direct methods with the solving program SIR97,[20] which revealed all the non-hydrogen atoms. The SHELXL program[21] was used to refine the structures by full-matrix least squares based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters, except for the H(1), H(3), and H(40) hydrogen atoms of **3a**·$1.5CH_2Cl_2$, the H(1) and H(3) hydrogen atoms of **3c′**·$0.5CH_2Cl_2$, and the H(3) hydrogen atom of **6**·CH_2Cl_2, which were located and refined with isotropic displacement parameters. The crystal structure refinement of compound **3b** (R1 = 0.1582) can only be used for the confirmation of the structure. Atomic scattering factors for all atoms were taken from ref 22. Details of crystal data and structural refinements are given in Table 3. CCDC reference numbers 208509−208513 and 236734 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retreving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax (internat.) + 44-1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

Acknowledgment. We thank the Ministère de l'Education Nationale, de la Recherche et de la Technologie, the CNRS, and the Institut Universitaire de France.

Supporting Information Available: X-ray data as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049510I

---

(19) Otwinowski, Z.; Minor, W. In *Methods in Enzymology*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Vol. 276, p 307.

(20) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G., Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32,* 115.

(21) Sheldrick, G. M. SHELX97: Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.

(22) *International Tables for X-ray Crystallography*; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C.