Palladium Complexes of a Novel Family of P,N-Chelates, the 2-(2-Pyridyl)phospholes: Synthesis, Structural Characterization, and Catalytic Activity for Olefin/CO Copolymerization

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2-(2-Pyridyl)phospholes bearing phenyl or cyclohexyl substituents on the phosphorus atom and 2-pyridyl, phenyl, or 2-thienyl groups on the C^5 atom were prepared according to the Fagan−Nugent route. They reacted with (cod)PdClCH$_3$, giving rise to stable complexes **3a**−**c** and **3a′**−**c′** as single diastereoisomers in excellent yields. An X-ray diffraction study performed on complex **3b** featuring a 1-phenyl-2-(2-pyridyl)phosphole ligand revealed a cis configuration of the phosphorus atom and the methyl group. The geometry of the coordinated P atom is highly distorted due to the rigidity of the 1,4-P,N chelate backbone. Complexes **3a**,**a′**, featuring 2,5-bis(2-pyridyl)phosphole ligands, display fluxional behavior. NMR studies revealed an intramolecular exchange between the pendant and coordinated pyridyl groups, showing that 2-(2-pyridyl)phospholes can behave as hemilabile ligands. Treatment of complexes **3a**−**c** and **3a′**−**c′** with 1 equiv of AgSbF$_6$ in CH$_3$CN afforded the corresponding cationic derivatives **4a**−**c** and **4a′**−**c′** as single diastereoisomers. Complexes possessing no pendant pyridyl moiety are air-stable solids that can be isolated in high yield. They are active for the copolymerization of ethylene and CO in CH$_2$Cl$_2$, whereas complex **4a**, bearing the 2-(2-pyridyl)phosphole ligand **2a**, is reduced quantitatively to give the dinuclear $[Pd_2(\mathbf{2a})_2]^{2+}$ complex **6**. The catalytic activities obtained with complexes **4b**,**c and 4b′**,**c′** are among the highest obtained with P,N chelates. The substitution pattern of the 2-(2-pyridyl)-phosphole ligands has an impact on the productivity of the Pd catalysts. *P*-cyclohexylphospholes are more efficient ligands than their *P*-phenyl analogues. Complex **4c**, featuring a 2-(2-pyridyl)-5-(2-thienyl)phosphole ligand, catalyzed the copolymerization of CO and norbornene at 85 °C, affording oligomers with a narrow molecular weight distribution. In methanol, the cationic palladium methyl complex **4c** afforded the bis-chelate $[Pd(\mathbf{2c})_2]^{2+}$ complex **5**, which has been characterized by an X-ray diffraction study. Although the geometry around the palladium atom is distorted, the metric data of complex **5** are similar to those of **3b**.

Introduction

Heteroditopic chelates have attracted considerable interest in coordination chemistry and homogeneous catalysis for several decades.[1] Among them, bidentate P,N-ligands combining σ^3,λ^3-phosphorus and sp^2-hybridized nitrogen donor centers have been particularly studied.[1c−g] Owing to the different stereoelectronic properties of the two coordination sites, they can act as hemilabile ligands and induce selective processes, allowing control over the reactivity of the metal center. Mixed P,N-chelates are also efficient ligands for important catalytic reactions, including reduction,[2a,b] allylic alkylation,[1g] olefin−CO copolymerization,[2c−g] and the Heck reaction.[2h] In several cases, due to their specific properties, catalytic activities or selectivities higher than those observed with diphosphines or dinitrogen donor ligands have been achieved.[3]

Many sp^2-N donors have been used as synthons for the design of P,N-ligands. The most frequently en-

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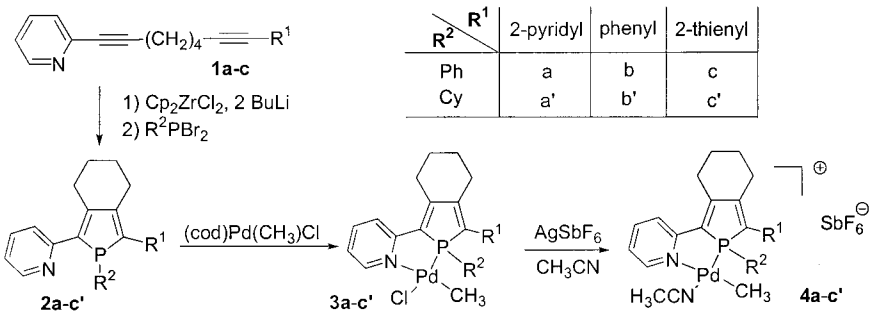
Scheme 1



R^2 \ R^1	2-pyridyl	phenyl	2-thienyl
Ph	a	b	c
Cy	a'	b'	c'

countered N-donors are pyridines, but oxazolines,[1f,g] imines,[2d−f] or pyrazolines[3f,g] have also been quite extensively employed. Less attention has been paid to variation of the phosphorus moiety, the great majority of P,N-ligands bearing diphenylphosphino fragments. This prompted us to prepare new 1,4-P,N chelates incorporating a pyridyl and a phosphole group as potential ligands for homogeneous catalysis. Phospholes act as classical two-electron-donor tertiary phosphines toward late transition metals[4,5] and are versatile synthons for the tailoring of P-ligands in homogeneous catalysis. For example, mono-, di-, or tetraphospholes are efficient ligands for the Rh-catalyzed hydroformylation of olefins[5a−d] and several C−C bond forming processes involving palladium catalysts (allylic alkylation,[5e] olefin−CO copolymerization,[5f] Heck reaction[5g]). Very few P,N-ligands incorporating phospholes have been described and used in homogeneous catalysis.[6] Furthermore, only the dibenzophosphole system has been investigated, and it is well-known that this dibenzoannelated moiety does not display the classical properties of a phosphole but behaves like a diphenylphosphine.[4a,b] Herein, we describe the synthesis of 2-(2-pyridyl)phospholes,[7] their coordination behavior toward neutral and cationic palladium centers, and their use as ligands for olefin−CO copolymerization, a catalytic reaction with numerous potential applications.[1c,8]

Results and Discussion

Synthesis of (2-Pyridyl)phosphole Ligands. (2-Pyridyl)phospholes can be obtained via two different synthetic approaches based on the transformation of the phosphole ring or on ring closure reactions involving zirconacyclopentadienes. Indeed, 2-(2-pyridyl)phospholes were prepared in 1997 by Mathey and co-workers according to the first strategy. Thermolysis of 1-(2-pyridyl)phosphole in the presence of *t*BuOK afforded a 2-(2-pyridyl)phospholide anion, which acts as a nucleophile toward halogenoalkanes, leading to the corresponding 2-(2-pyridyl)phospholes.[9] We have recently reported that oxidative coupling of bis(2-pyridyl)octa-1,7-diyne (**1a**) with zirconocene followed by treatment with $PhPCl_2$ gave rise to 1-phenyl-2,5-bis(2-pyridyl)-phosphole (**2a**) (Scheme 1).[10a] The new 2-(2-pyridyl)-phospholes **2b**,**c** and **2a′**−**c′** described in this study have been obtained using this synthetic approach (the Fagan−Nugent route)[11] which readily allows variation in the nature of the P substituent. For example, 1-cyclohexyl-2,5-bis(2-pyridyl)phosphole (**2a′**) was obtained in 75% yield from diyne **1a** using $CyPBr_2$ (Scheme 1). This method has been extended to unsymmetrical 1,7-diynes in order to prepare 2-(2-pyridyl)phospholes possessing various substituents at the C^5 atom of the phosphole ring. Sonogashira coupling of 1-(2-pyridyl)octa-1,7-diyne with bromobenzene and 2-bromothiophene allowed an efficient and large-scale preparation of differently substituted diynes **1b** (77%) and **1c** (85%), respectively (Scheme 1). Compounds **1b** and **1c** reacted successively with "zirconocene" and dibromophenylphosphine or dibromocyclohexylphosphine to give the corresponding phospholes **2b**,**c** and **2b′**−**c′** (Scheme 1). These derivatives are isolated as air-stable solids after purification

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Table 1. Selected NMR Data[a] and Yields[b] for Ligands 2a−c and 2a′−c′ and Complexes 3a−c, 3a′−c′, 4a−c, and 4a′−4c′

	Pd−CH_3			yield
compd	$\delta(^{31}P\{^1H\})$	$\delta(^1H)$ (J_{PC}, Hz)	$\delta(^{13}C)$ (J_{PC}, Hz)	(%)
2a[10a]	+11.7			73
2a′	+27.9			83
2b	+12.9			75
2b′	+26.9			65
2c	+12.6			83
2c′	+27.7			49
3a	+56.9	0.96 (2.4)	−7.5 (2.4)	88
3a′	+70.4	0.68 (2.4)	−11.0 (2.3)	91
3b	+55.5	0.82 (2.8)	−13.6 (3.3)	95
3b′	+65.2	0.78 (2.7)	−14.3 (3.9)	87
3c	+55.7	0.92 (2.4)	−10.6 (2.4)	91
3c′	+69.8	0.81 (1.3)	−11.4 (0)	91
4a	+56.8	1.00 (broad)	−5.4 (0)	90
4a′	+62.8			86
4b	+55.8	0.72 (1.8)	−12.2 (3.6)	92
4b′	+65.2	0.70 (1.7)	−12.9 (3.9)	95
4c	+57.4	0.85 (2.4)	−9.2 (2.4)	91
4c′	+68.9	0.70 (2.1)	−9.9 (3.3)	91

[a] In CD_2Cl_2 at room temperature, with the exception of compounds **3a** (283 K) and **4a**/**4a′** (CD_2Cl_2/CD_3CN, 218 K). [b] Isolated yields, with the exception of complex **4a′** (spectroscopic yield).

by flash column chromatography in moderate to good yields (Table 1). It is well-known that the stability of phospholes depends on the nature of the P substituent.[4a,b,10c] Phenyl and alkoxy groups[12] are stabilizing substituents, whereas P-alkyl phospholes are generally highly air sensitive due to their ease of oxidation. Our results show that P-alkyl phospholes can be easy-to-handle compounds, provided that the alkyl substituent is sterically demanding. The new phospholes **2b**,**c** and **2a′**−**c′** were characterized by high-resolution mass spectrometry and gave satisfactory elemental analyses. Their multinuclear NMR data are typical[4a,b] and support the proposed structures. The $^{31}P\{^1H\}$ NMR spectra show a single resonance in the range expected for P-aryl and P-alkyl phospholes (Table 1), and four signals are observed at low field in the $^{13}C\{^1H\}$ NMR spectra for the endocyclic carbon atoms of the phosphole ring. The Fagan−Nugent reaction is thus a powerful synthetic route to prepare 2-(2-pyridyl)phospholes with different substitution patterns. The phosphorus substituent (phenyl or cyclohexyl) will directly influence both the steric and electronic properties of the P-donor atom, while the second substituent at the C^5 atom of the phosphole ring (2-pyridyl, phenyl, 2-thienyl) is expected to influence the electronic properties of the N-donor atom via the extended π-conjugated system.[10]

Synthesis and Characterization of [2-(2-Pyridylphosphole)]palladium(II) Complexes. We have investigated the coordination chemistry of 2-(2-pyridyl)-phospholes toward palladium(II) centers with the aim to gain more insight into their coordination behavior and to obtain new catalysts for the copolymerization of olefins with carbon monoxide. This catalytic reaction has attracted considerable attention in the past few years, and much effort has been devoted to the discovery of new catalytic systems and to an understanding of the mechanism.[1c,2e,f,8] Complexes of the type $[Pd(CH_3)(solvent)(L_2)]^+$, L_2 being a chelating ligand, have been widely used as catalytic precursors for this reaction. They are usually prepared from the corresponding neutral chloromethylpalladium derivatives by chlorine abstraction in a coordinating solvent such as acetonitrile. Reaction of 1 equiv of ligands **2a**−**c** and **2a′**−**c′** with Pd(cod)MeCl[13] (cod = 1,5-cycloocta-1,5-diene) afforded the corresponding air-stable complexes **3a**−**c** and **3a′**−**c′** in excellent yield (Scheme 1, Table 1). The large coordination $^{31}P\{^1H\}$ NMR downfield chemical shifts (ca. 40 ppm) are consistent with the formation of a five-membered palladacycle.[5f] In the ^1H NMR spectra, the chemical shift of H^6 of the pyridyl group is also sensitive to coordination with a downfield shift superior to 0.6 ppm.

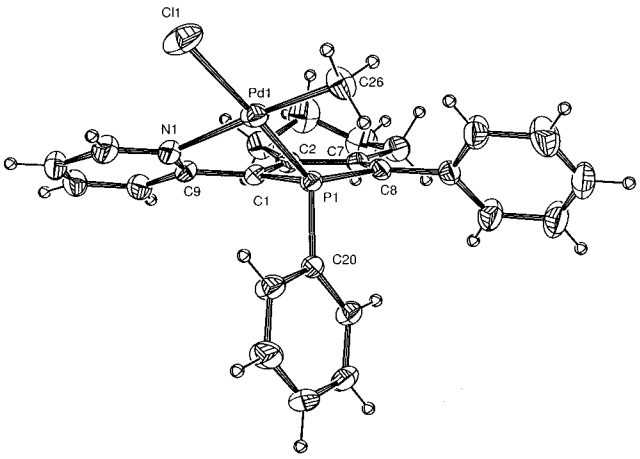

Figure 1. ORTEP view of complex **3b** with atom labeling. Thermal ellipsoids show 40% probability levels.

For complexes **3b**,**c and 3b′**,**c′**, bearing no pendant pyridyl unit, the $^{31}P\{^1H\}$ NMR spectra of the crude reaction mixture contain only one sharp resonance, indicating the formation of a single diastereoisomer. In the ^1H spectra, the methyl group bound to the palladium appears as a doublet with a weak J_{PH} coupling constant (Table 1). The magnitude of these coupling constants is consistent with a cis arrangement of the methyl group and the phosphorus atom. It is noteworthy that the $^{13}C\{^1H\}$ NMR chemical shift of the Pd−CH_3 moiety is more sensitive to the nature of the C^5 substituent (phenyl versus 2-thienyl, $\Delta\delta > 3$ ppm) than to the P substituent (phenyl versus cyclohexyl, $\Delta\delta < 0.8$ ppm) (Table 1). The proposed structures were confirmed by an X-ray diffraction study performed on single crystals of **3b** (Figure 1, Table 2). The coordination sphere around the Pd atom is close to square planar (maximum deviation from the best Pd(1)−N(1)−P(1)−C(26)−Cl(1) plane, 0.03 Å). The five-membered metallacyle adopts a slightly distorted envelope conformation. The Pd(1), N(1), C(9), and C(1) atoms lie almost in the same plane (maximum deviation 0.037 Å) with the P(1) atom being out of this plane (N(1)−C(9)−C(1)−P(1), 21.3°; C(9)−N(1)−Pd(1)−P(1), 26.5°). The angles and the bond lengths of the metallacycle are consistent with known literature values. For example, the chelate bite angle P(1)−Pd(1)−N(1) (82.40(12)°) and the Pd(1)−N(1) (2.197(5) Å) and Pd(1)−P(1) (2.2135(14) Å) distances are similar to values reported for other 1,4-P,N chelates such as (phosphinomethyl)oxazoline (83.69(7)°; 2.058(2),

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 3b and 5

	3b	5		5
Pd(1)−P(1)	2.2135(14)	2.2494(18)	Pd(1)−P(31)	2.260(2)
Pd(1)−N(1)	2.197(5)	2.154(6)	Pd(1)−N(31)	2.119(6)
Pd(1)−C(26)	2.046(5)			
Pd(1)−Cl(1)	2.3356(16)			
N(1)−C(9)	1.357(7)	1.344(9)	N(31)−C(39)	1.320(10)
C(9)−C(1)	1.459(7)	1.453(10)	C(39)−C(31)	1.483(11)
C(1)−C(2)	1.352(7)	1.316(10)	C(31)−C(32)	1.334(11)
C(2)−C(7)	1.481(7)	1.487(11)	C(32)−C(37)	1.481(11)
C(7)−C(8)	1.348(7)	1.349(10)	C(37)−C(38)	1.354(11)
C(8)−P(1)	1.808(5)	1.804(8)	C(38)−P(31)	1.814(8)
P(1)−C(1)	1.798(5)	1.811(7)	P(31)−C(31)	1.794(7)
N(1)−Pd(1)−P(1)	82.40(12)	82.77(16)	N(31)−Pd(1)−P(31)	82.80(17)
N(1)−Pd(1)−Cl(1)	92.99(13)		N(1)−Pd(1)−N(31)	94.4(2)
P(1)−Pd(1)−C(26)	95.41(18)		P(1)−Pd(1)−P(31)	102.64(7)
C(26)−Pd(1)−Cl(1)	89.25(18)			
C(1)−P(1)−C(8)	91.9(2)	92.3(3)	C(31)−P(31)−C(38)	91.7(4)
C(1)−P(1)−C(20)	108.1(2)	109.6(3)	C(31)−P(31)−C(48)	110.8(3)
C(1)−P(1)−Pd(1)	96.24(16)	96.2(2)	C(31)−P(31)−Pd(1)	95.2(2)
C(8)−P(1)−Pd(1)	132.97(16)	128.8(2)	C(38)−P(31)−Pd(1)	128.7(3)
C(8)−P(1)−C(20)	107.7(2)	109.5(4)	C(38)−P(31)−C(48)	107.5(4)
C(20)−P(1)−Pd(1)	113.39(17)	114.6(3)	C(48)−P(31)−Pd(1)	116.9(3)

2.2128(8) Å)[2c] or phosphine-imines (81.37(11)°; 2.224(4), 2.196(2) Å).[2d−f] The Pd(1)−Cl(1) (2.3356(16) Å) and Pd(1)−C(26) (2.046(5) Å) bond lengths are essentially identical with those reported for related Pd complexes.[2c−f] The pyridyl and phosphole rings are not coplanar; however, the twist angle is rather small (21.0°). The inter-ring C(1)−C(9) bond length (1.459(7) Å) is in the range expected for a C(sp^2)−C(sp^2) single bond. The bond lengths and angles of the two endocyclic P−C−C fragments are almost similar (Table 2), and it is noteworthy that the P−C distances (C(1)−P(1), 1.798(5) Å; C(8)−P(1), 1.808(5) Å) approach that of a P−C single bond (1.84 Å). These solid-state data suggest a delocalization involving the dienic moiety of the phosphole ring and the coordinated pyridyl unit. It is well-known that, as observed for classical phosphines, the phosphorus atom of phospholes adopts a tetrahedral geometry upon coordination.[4,5,14] The geometry of the P atom in compound **3b** is highly distorted with unusually large exocyclic C(8)−P(1)−Pd(1) (132.97(16°)) and small endocyclic C(1)−P(1)−Pd(1) (96.24(16)°) angles. In other words, the Pd(1)−P(1)−C(20) plane does not have the traditional perpendicular arrangement with respect to the phosphole ring. This structural feature is probably due to the rigidity of the 1,4-P,N chelate backbone, which contains sp^2-carbon atoms, and shows that the phosphorus atom of phospholes can accommodate severe deviation from an optimal tetrahedral geometry due to the high s character of the P lone pair.[4,15] It is noteworthy that no fluxional behavior has been observed for complexes **3b** and **3c** between 243 and 313 K in CD_2Cl_2 solutions.

In contrast, complexes **3a** and **3a′** possessing a pendant pyridyl arm exhibited fluxional behavior at room temperature. The $^{31}P\{^1H\}$ NMR spectrum of complexes **3a** and **3a′** showed singlets at +57.0 and +70.5 ppm, respectively, at 298 K in CD_2Cl_2 solutions. Only one diastereisomer has been formed, and these chemical shifts are similar to those recorded for related complexes **3b**,**c** and **3b′**,**c′** (Table 1). At 298 K, the $^{13}C\{^1H\}$ NMR signals of complex **3a** are rather broad, preventing the observation of the small J_{PC} coupling constants. The $^{13}C\{^1H\}$ NMR chemical shifts remained almost unchanged on cooling the samples down to 283 K, a temperature for which sharp singlets were observed. At this temperature, the ^{13}C NMR spectrum of complex **3a** shows two sets of signals for the pyridyl moieties and a doublet at −7.8 ppm (J_{PC} = 2.4 Hz) attributed to the Pd−CH_3 moiety. The low magnitude of the coupling constant compares with that of related complexes **3b**,**c** and **3b′**,**c′** (Table 1), in which the P atom and the CH_3 moiety are in a mutual cis positions. The ambient-temperature $^{13}C\{^1H\}$ NMR spectrum of complex **3a′** displays well-resolved lines with two sets of signals for the pyridyl groups and a doublet at −11.0 ppm with a small J_{PC} coupling constant (2.3 Hz) for the Pd−CH_3 fragment. These multinuclear NMR data support the proposed structures (Scheme 1): complexes **3a**,**a′** possess a coordinated and a pendant pyridyl ring, with the phosphorus atom and the coordinated methyl group being in a cis configuration. The ^1H NMR signals of both complexes are broad at room temperature (300 K), suggesting fluxional behavior. The spectra of the two complexes are very similar, and only the results obtained with derivative **3a′** will be described in detail. At 300 K, two multiplets centered at 9.08 and 8.58 ppm are observed for the H^6 atom of the coordinated and noncoordinated pyridyl fragments, respectively. When the temperature was raised to 348 K, line broadening leading to the disappearance of these signals occurred, while at 283 K the ^1H NMR spectrum displays well-resolved signals (Figure 2). These band-shape changes suggested an intramolecular exchange between the pendant and coordinated pyridyl groups (Scheme 2), a phenomenon which has been confirmed by spin transfer saturation experiments performed at room temperature on the two H^6 atoms. However, this fluxional behavior is not a simple exchange of the two pyridines since, according to NMR data (Table 1), the palladium atoms of the two exchanging complexes possess the same stereochemistry (cis-disposed P atom and the CH_3 fragment). In fact, the two exchanging complexes are enantiomers (inversion at the P atom, Scheme 2), which are indistinguishable, since NMR is not sensitive to

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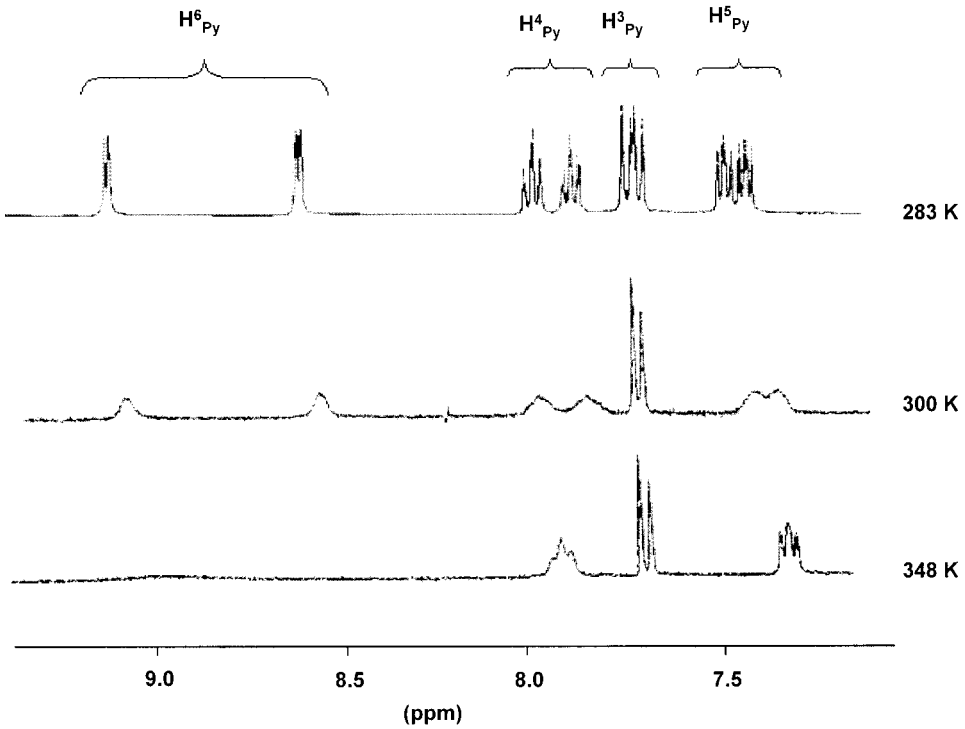
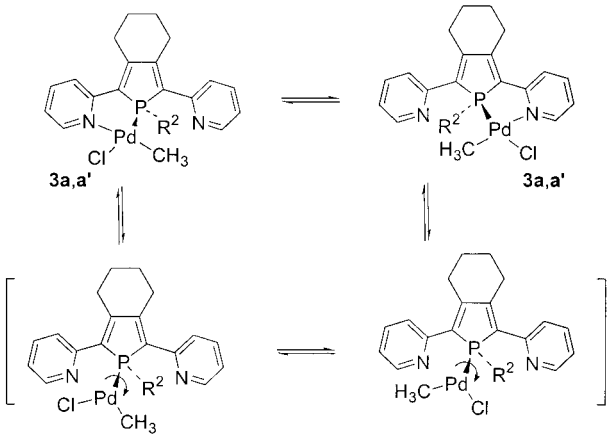


Figure 2. Variable-temperature ^{1}H NMR spectra of complex **3a′** in the pyridine region.

Scheme 2



optical activity. Such hemilabile behavior has recently been encountered with potentially tridentate N,P,N donors such as bis(2-pyridyl)phosphine[16a] or bis(oxazoline) phosphite[16b] ligands. Three possible mechanisms have been proposed to rationalize this dynamic process for Pd(II) complexes.[16b] Two of them imply a tridentate coordination mode of the N,P,N ligand leading to pentacoordinate Pd intermediates. This coordination mode can clearly be discarded for 2,5-bis(2-pyridyl)-phospholes, due to the rigidity of the carbon backbone of these ligands. This can easily be visualized in Figure 1: a nitrogen atom which would replace an ortho C atom of the C(8) phenyl ring cannot bind to the palladium center without decoordination of N(1). The most plausible mechanism for the interconversion of enantiomers of complexes **3a** and **3a′** involves a decoordination of the N donor followed by a rotation around the P−Pd bond and coordination of the second N atom (Scheme 2). These results on neutral Pd(II) complexes show that 2-(2-pyridyl)phospholes undergo stereoselective coordination and that they can act as static or dynamic P,N chelates.

The next step was to prepare the corresponding cationic palladium complexes. Treatment of complexes **3a**−**c′** with 1 equiv of $AgSbF_6$ in CH_3CN afforded derivatives **4a**−**c′** (Scheme 1). In all cases, the $^{31}P\{^1H\}$ NMR spectra of the crude reaction mixtures showed one sharp singlet, indicating the formation of a single diastereoisomer. The $^{31}P\{^1H\}$ NMR chemical shifts are in a similar range for those of their neutral precursors ($\delta\Delta$ < 1.6 ppm, Table 1). Complexes **4b**,**c** and **4b′**,**c′**, with no pendant pyridyl moiety, are air-stable solids that can be isolated in high yields after workup (Table 1). In marked contrast, derivatives **4a** and **4a′** rapidly decomposed in CH_2Cl_2 solutions at room temperature. Addition of acetonitrile lowers the rate of decomposition, and the ^{1}H and $^{13}C\{^1H\}$ NMR of complex **4a** have been recorded in CD_2Cl_2−CD_3CN solutions at low temperature (218 K). This compound has also been characterized by high-resolution mass spectrometry; however, no satisfactory elemental analyses could be obtained. It is noteworthy that, as for its neutral precursor **3a**, complex **4a** exhibits fluxional behavior involving an exchange of the two pyridyl rings. Complex **4a′** is extremely unstable, even in CD_2Cl_2−CD_3CN solutions at low temperature, and was only observed by $^{31}P\{^1H\}$ NMR spectroscopy. The presence of a pendant pyridyl moiety, which exchanges with its coordinated counterpart, appears to be a strong destabilizing factor for cationic palladium(II) complexes featuring 2-(2-pyridyl)phosphole ligands. The ^{1}H and $^{13}C\{^1H\}$ NMR resonances of the Pd−CH_3 moiety of compounds **4a**, **4b**,**c**, and **4b′**,**c′** appeared as doublets at lower field than those of the corresponding neutral complexes (Table 1). The low

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Table 3. Ethylene−CO Copolymerization Catalyzed by Complexes 4b and 4c:[a] Influence of the Temperature, Reaction Time, and Solvent

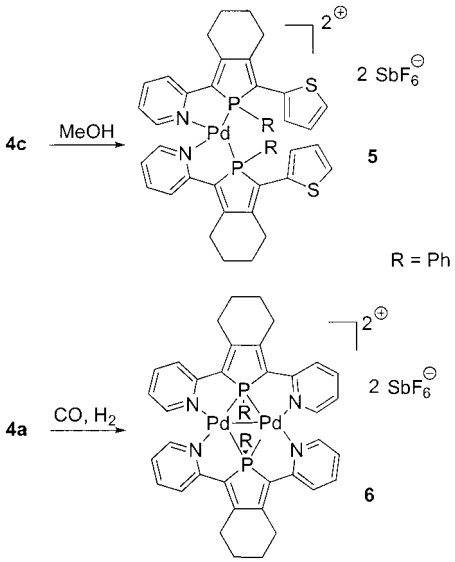
entry	catalyst	*T*/°C	reacn time/h	solvent	g of PK/ g of Pd	TON[b]	TOF[b]
1	**4b**	35	15	CH_2Cl_2	59	112	7
2	**4b**	60	15	CH_2Cl_2	145	276	18
3	**4b**	85	15	CH_2Cl_2	282	536	35
4	**4c**	35	15	CH_2Cl_2	89	169	11
5	**4c**	85	15	CH_2Cl_2	551	1047	70
6	**4c**	85	6	CH_2Cl_2	238	452	75
7	**4c**	85	38[c]	CH_2Cl_2	835	1586	42
8	**4c**	85	6	THF	160	304	51
9	**4c**	85	6	CH_3OH	0	0	0

[a] Reaction conditions: 0.03 mmol of catalyst, initial $p(CO) = 10$ bar, initial p(ethylene) = 10 bar, time 15 h. [b] TON = moles of substrate converted per mole of palladium. TOF = TON per hour. [c] After 15 h, the reactor was pressurized with CO (10 bar) and ethylene (10 bar).

values of the J_{PH} coupling constants (J_{PH} < 2.4 Hz) support a cis arrangement of the phosphorus atom and the methyl group. The coordination of acetonitrile is evidenced by the presence of a single peak in both the ^1H (δ, 2.35−2.37) and $^{13}C\{^1H\}$ (δ, 2.4−2.7) NMR spectra. As observed for the neutral complexes, the $^{13}C\{^1H\}$ NMR chemical shift of the Pd−CH_3 moiety is relatively insensitive to the nature of the P-substituent but is affected by the nature of the C^5 substituent of the phosphole ring (Table 1).

Copolymerization Reactions of Dicationic Palladium Complexes. Ethylene/CO copolymerization experiments have been performed in CH_2Cl_2 under an initial pressure of 20 bar ($p(CO) = p$(ethylene)) in a 150 mL autoclave. The catalytic activity is expressed in grams of polyketone per gram of palladium and turnover frequency (TOF) as moles of substrates converted per mole of Pd per hour. At 35 °C, complexes **4b**,**c** yield insoluble copolymers isolated as gray solids after washing with methanol. Complex **4c** exhibited a higher catalytic activity than **4b** (Table 3, entries 1−4), showing that the nature of the C^5 substituent of the phosphole ring has a notable influence on the productivity of the Pd catalysts. The temperature plays an important role; an increase of the temperature resulted in an enhancement of the catalytic activity for both complexes. At 85 °C, the productivity of complexes **4b**,**c** are ca. 5 times higher than those recorded at 35 °C (Table 3, entries 1−3 and 4 and 5). The influences of the reaction time and of the solvent were examined at 85 °C with complex **4c**, which is the most active catalyst. The turnover frequencies, which give an estimate of the catalytic activity for a given period of time, are very similar for reaction times varying from 6 h (TOF = 75 h^{-1}) to 15 h (TOF = 70 h^{-1}). The small decrease of the TOF for long reaction time can be attributed to the drop of the total pressure during the reaction. These data suggest a negligible decomposition of the active species under these reaction conditions. Repressurization of the autoclave with CO (10 bar) and ethylene (10 bar) after 15 h allowed a further production of copolymers; however, this resulted in an overall lower efficiency (Table 1, entry 7). The nature of the solvent has a marked influence on the productivity of complex **4c**. The amount of copolymer per gram of Pd is substantially more important in CH_2Cl_2 than in THF (Table 3, entries 6−8), while no polymer is formed in MeOH. The absence of

Scheme 3



catalytic activity in MeOH is quite surprising, since this solvent is commonly used for the Pd-catalyzed ethylene/CO copolymerization. In fact, complex **4c** is not stable in MeOH solution at room temperature. A rapid precipitation of "palladium black" occurred, accompanied by the formation of dicationic complex **5** (Scheme 3), isolated in 42% yield (based on **4c**). Derivative **5** is not active for the ethylene/CO copolymerization under the reaction conditions of this study (20 bar, 85 °C). This behavior is quite usual for bis-chelated dicationic palladium(II) complexes of the type $[Pd(L_2)_2]^{2+}$, which are active only in the presence of a proton and/or benzoquinone.[17]

Complex **5** is an air-stable orange solid easily purified by crystallization. Its insolubility in common apolar solvents (pentane, Et_2O) supports an ionic structure. The $^{31}P\{^1H\}$ NMR spectra of derivative **5** exhibits a singlet at +69.7 ppm, an unusually low field for a Pd-coordinated 1-phenylphosphole (for comparison see derivatives **4a**−**c**, Table 1). The simplicity of the $^{13}C\{^1H\}$ NMR spectra is in favor of a highly symmetric structure: one set of signals is recorded for the two 1-phenyl-2-(2-pyridyl)-5-(2-thienyl)phosphole ligands. No signal corresponding to a Pd−CH_3 fragment or a coordinated acetonitrile is observed in the ^1H and $^{13}C\{^1H\}$ NMR spectra. High-resolution mass spectrometry and elemental analysis support the general formula $[Pd(\mathbf{2c})_2]^{2+}(SbF_6^-)_2$. Single crystals of **5** have been grown at room temperature from a 1,2-dichloroethane/toluene solution. The X-ray diffraction study performed on these crystals confirmed the proposed structure; normal van der Waals distances between the dication $[Pd(\mathbf{2c})_2]^{2+}$ (Figure 3a) and the two SbF_6^- counteranions are recorded. The P atoms of the two 2-(2-pyridyl)phosphole ligands **2c** are in a mutually cis configuration. It is noteworthy that this symmetric structure is in accordance with the NMR data; once again, a stereoselective coordination of a 2-(2-pyridyl)phosphole is observed. Complex **5** shows a distorted-square-planar

(17) (a) Milani, B.; Anzilutti, A.; Vicentini, L.; Sessanto o Santi, A.; Zangrando, E.; Geremia, S.; Mestroni, G. *Organometallics* **1997**, *16*, 5064. (b) Bianchini, C.; Lee, H. M.; Barbaro, P.; Meli, A.; Moneti, S.; Vizza, F. *New J. Chem.* **1999**, *23*, 929.

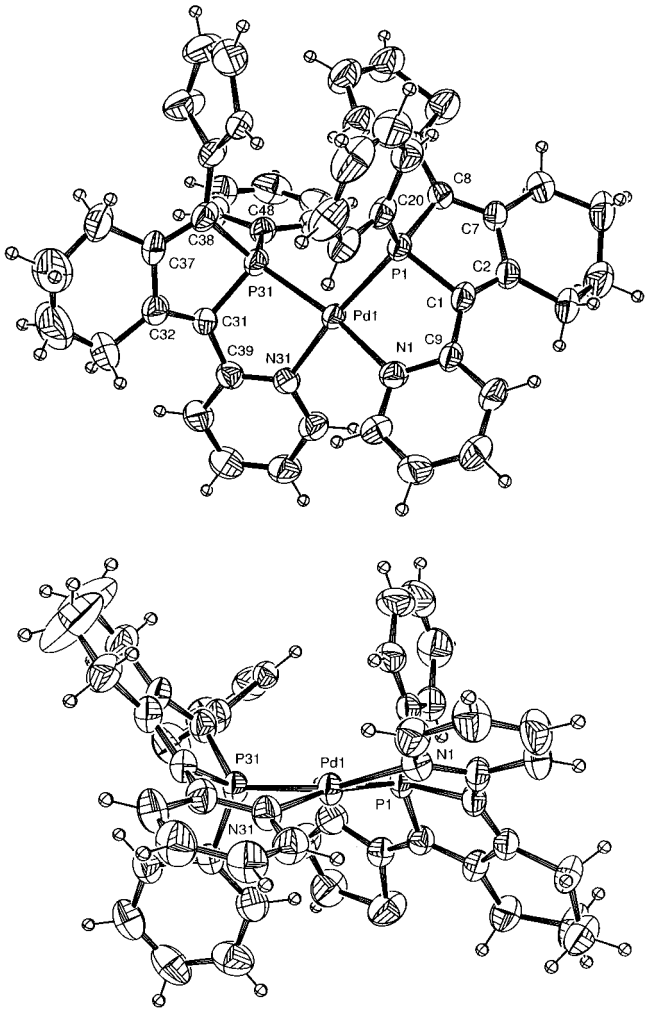


Figure 3. ORTEP view of the dication of complex **5** with atom labeling (top) general view; (bottom) view along the P(1)−Pd(1)−P(31) axis. Thermal ellipsoids show 40% probability levels.

geometry around the palladium atom; the maximum deviation from the best PdN_2P_2 plane reaches 0.206 Å. The angle between the two planes defined, on one hand, by the Pd centers and the coordinated N atoms and, on the other hand, by the Pd centers and the coordinated P atoms attains 10° (Figure 3). This feature, which has already been observed in Pd complexes bearing 2-(phosphinoamino)pyridine ligands,[18] is probably due to the repulsion of the two H^6 hydrogen atoms of the coordinated pyridyl groups (Figure 3). Despite this steric constraint, derivative **5** shares some important structural features with complex **3b** (Figure 1), which bears only one 2-(2-pyridyl)phosphole ligand. For example, the twist angles between the coordinated pyridyl and phosphole rings of **5** are only slightly superior to that of complex **3b** (**3b**, 21.0°; **5**, 25.2−25.6°). As observed for **3b**, the five-membered metallacycles of complex **5** adopt a slightly distorted envelope conformation with the P atoms out of the Pd−N−C−C planes (C−N−Pd−P, 19.1−22.3°; N−C−C−P, 25.2−25.6°), with the geometry around the P atoms being a highly distorted tetrahedron (Table 2). The Pd−N (2.119(6), 2.154(6) Å) and Pd−P distances (2.2494(18), 2.260(2) Å) and the N−Pd−P bite angles (82.77(16), 82.80(17)°) are also almost similar to those recorded for complex **3b** (Table 2). This analogy shows that the structure of the five-membered palladacycle is imposed by the rigidity of the chelating P,N-moiety of 2-(2-pyridyl)phospholes.

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Table 4. Ethylene−CO Copolymerization: Comparison of the Catalytic Activities of Complexes 4a, 4b,c, and 4b′,c′[a]

entry	catalyst	g of PK/g of Pd	TON[b]	TOF[b]
1	**4a**	0		
2	**4b**	135	256	43
3	**4b′**	357	678	113
4	**4c**	238	452	75
5	**4c′**	279	530	88

[a] Reaction conditions: CH_2Cl_2 (20 mL), 0.03 mmol of catalyst, initial p(CO) = 10 bar, initial p(ethylene) = 10 bar, 85 °C, time 6 h. [b] TON = moles of substrate converted per mole of palladium. TOF = TON per hour.

The cationic palladium complexes, except complex **4a′**, which is not stable in solution, have been evaluated for the carbon monoxide−ethylene copolymerization under the optimal reaction conditions determined with complex **4c** (CH_2Cl_2, 85 °C). All the palladium complexes afforded copolymers except for complex **4a**, which bears a pendant pyridyl group (Table 4). Under the catalytic conditions, complex **4a** is reduced quantitatively to give the dinuclear Pd(I) complex **6**[19] (Scheme 3), which is an inactive species. The catalytic activities observed with complexes **4b**,**c** and **4b′**,**c′** are rather low compared to those attained with diphosphines[1c,5f,8a] but are among the highest obtained with P,N-chelates.[3c,8e] Interestingly, the substitution pattern of the 2-(2-pyridyl)-phosphole ligands has an impact on the productivity of the Pd catalysts. *P*-Cyclohexylphospholes are more efficient ligands than their *P*-phenyl-substituted analogues; this trend is more pronounced for 5-phenylphospholes (Table 4, entries 2 and 3) than for 5-(2-thienyl)-phospholes (Table 4, entries 3 and 4). The P substituent influences both the σ-donor ability and the steric demands of the phosphorus center; it is thus rather difficult to rationalize its influence on the catalytic activity of the palladium complexes. The nature of the substituent at the C^5 position of the phosphole ring also has an impact on the catalytic performance (compare entries 2 and 4 and entries 3 and 5, Table 4). It is quite clear that these substituents have no influence on the steric bulk of the metal center; the modulation of the catalytic activity is thus due to electronic factors. It is well-known that thienyl and phenyl groups possess very different electron-donating properties,[20] and we have established that the dienic moiety of the phosphole ring is highly polarizable.[10] Thus, it seems very likely that the substituent at the C^5 position of the phosphole ring influences the donor ability of the pyridyl group. This assumption is supported by the fact that the nature of the C^5 substituent has a notable influence on the NMR data of the Pd−CH_3 moiety from complexes **4b**,**c** and **4b′**,**c′**. It is noteworthy that the presence of an electron-donating thienyl substituent at the C^5 position of the P ring has a positive effect on the catalytic activity in the

(19) Complex **6** has been characterized by an X-ray diffraction study,[7] and its full NMR description will be given in a forthcoming paper on symmetrically bridging phosphines.

(20) Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1997**, *119*, 6575.

P−Ph series (entries 2−4, Table 4) and a negative effect in the P−Cy series (entries 3−5, Table 4). The ethylene/CO copolymers exhibit very low solubility in common organic solvents, preventing gel permeation chromatography (GPC) to determine their exact mass distribution from being undertaken. However, complex **4c** catalyzes the copolymerization of CO and norbornene at 85 °C, affording a white solid soluble in most organic solvents. The molecular weight determined by GPC is 4094, and the low molecular weight distribution ($M_w/M_n = 1.18$) suggests the living polymerization nature of the catalyst.

In conclusion, 2-(2-pyridyl)phospholes possessing different substitution patterns are readily accessible using the Fagan−Nugent route. They coordinate to (chloro)(methyl)palladium(II) centers in a stereoselective way, leading to stable complexes. The palladium complexes of 2-(2-pyridyl)phospholes possessing a pendant pyridyl moiety are fluxional, revealing the hemilabile nature of these P,N-chelates. The catalytic activities observed for the copolymerization of CO and ethylene are rather high for mixed P,N-ligands. The low M_w/M_n value for the norbornene−CO co-oligomers are encouraging, and the use of these catalytic systems to prepare well-controlled block copolymers is under active investigation.

Experimental Section

General Considerations. All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Solvents were freshly distilled under argon from sodium/benzophenone (tetrahydrofuran, diethyl ether, toluene) or from phosphorus pentoxide (pentane, dichloromethane, acetonitrile). Triethylamine was freshly distilled under argon from potassium hydroxide. 2-Bromopyridine, octa-1,7-diyne, Cp_2ZrCl_2, CuI, and *n*-BuLi were obtained from Aldrich Chemical Co. and were used as received. Preparative separations were performed by gravity column chrommatography on silica gel (Merck Geduran 60, 0.063−0.200 mm) or basic alumina (Aldrich, Type 5016A, 150 mesh, 58 Å) in 3.5 × 20 cm columns. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AM300, DPX200, and ARX400 spectrometers. Attribution of carbon atoms is based on HMBC and HMQC experiments. Melting point and decomposition point determinations were performed by using a differential scanning calorimeter (TA-instruments DSC 2010) and a thermogravimetric analyzer (TA-instruments TGA 2050), respectively. High-resolution mass spectra were obtained on a Varian MAT 311 or ZabSpec TOF Micromass instrument at CRMPO, University of Rennes. Elemental analyses were performed by the "Centre de Microanalyze du CNRS" at Vernaison, France.

1-(2-Pyridyl)octa-1,7-diyne. 2-Bromopyridine (0.46 mL, 4.8 mmol) and octa-1,7-diyne (0.74 mL, 5.6 mmol) were added, at room temperature, to a Et_3N solution (15 mL) containing a catalytic amount of $Pd(PPh_3)_2Cl_2$ (0.080 g, 0.11 mmol) and CuI (0.020 g, 0.11 mmol). The heterogeneous yellow mixture was stirred for 12 h at room temperature. A significant amount of precipitate was formed, and the mixture turned brown. The mixture was filtered, and the volatile materials were removed under vacuum. After purification by column chromatography on silica gel (heptane/Et_2O, 40/60, $R_f = 0.40$), 1-(2-pyridyl)-octa-1,7-diyne was obtained as a pale yellow oil (0.46 g, yield 52%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.71 (m, 4 H, C≡CCH$_2$CH_2), 1.93 (t, ^3J = 2.6 Hz, 1 H, C≡CH), 2.23 (m, 2 H, C≡CCH$_2$), 2.46 (m, 2 H, C≡CCH$_2$), 7.15 (ddd, J = 1.3, 4.9 and 7.5 Hz, 1 H, H5 Py), 7.34 (ddd, J = 1.1, 1.3 and 7.8 Hz, 1 H, H3 Py), 7.58 (ddd, ^3J = 1.8, 7.5 and 7.8 Hz, 1 H, H4 Py), 8.51 (ddd, ^3J = 1.1, 1.8 and 4.9 Hz, 1 H, H6 Py). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 18.0, 18.9 (s, C≡CCH$_2$*C*H$_2$), 27.3, 27.5 (s, C≡C*C*H$_2$), 68.6 (s, C≡*C*H), 80.7 (s, C≡*C*−Py), 84.0 (s, *C*≡CH), 90.9 (s, *C*≡C−Py), 122.3 (s, C5 Py), 126.8 (s, C3 Py), 136.0 (s, C4 Py), 143.8 (s, C2 Py), 149.8 (s, C6 Py). HR-MS (EI): *m*/*z* 182.0936 $(M - H)^+$; calcd for $C_{13}H_{12}N$ 182.0970. Anal. Calcd for $C_{13}H_{13}N$ (183.2): C, 85.21; H, 7.15; N, 7.64. Found: C, 85.00; H, 7.04; N, 7.78.

1-Phenyl-8-(2-pyridyl)octa-1,7-diyne (1b). Iodobenzene (0.22 mL, 2.0 mmol) was added, at room temperature, to a Et_3N solution (15 mL) containing 1-(2-pyridyl)octa-1,7-diyne (0.37 g, 2.0 mmol), a catalytic amount of $Pd(PPh_3)_2Cl_2$ (0.014 g, 0.02 mmol), and CuI (0.004 g, 0.02 mmol). The heterogeneous yellow mixture was stirred for 12 h at room temperature. A significant amount of precipitate was formed, and the mixture turned brown. The mixture was filtered, and the volatile materials were removed under vacuum. After purification by column chromatography on silica gel (heptane/Et_2O, 50/50, $R_f = 0.30$), compound **1b** was obtained as a as an yellow oil after purification on silica gel (heptane/Et_2O, 50/50, R_f = 0.30) (0.40 g, yield 77%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.74 (m, 4 H, C≡CCH$_2$CH_2), 2.42 (m, 4 H, C≡CCH$_2$), 7.15 (ddd, J = 1.3, 4.9 and 7.7 Hz, 1 H, H5 Py), 7.20 (m, 3 H, *m*-/*p*-H Ph), 7.32 (m, 3 H, H3 Py and *o*-H), 7.58 (ddd, J = 1.8, 7.5 and 7.5 Hz, 1 H, H4 Py), 8.51 (ddd, J = 0.9, 1.8 and 4.9 Hz, 1 H, H6 Py). ^{13}C{^{1}H} NMR (50.323 MHz, C_6D_6): δ 19.0, 19.1 (s, ≡CCH$_2$*C*H$_2$), 27.5, 27.9 (s, ≡C*C*H$_2$), 80.7 (s, C≡*C*−Py), 81.0 (s, C≡*C*−Ph), 89.7 (s, *C*≡C−Ph or *C*≡C−Py), 90.6 (s, *C*≡C−Ph or *C*≡C−Py), 122.4 (s, C5 Py), 124.0 (s, *i*-C Ph), 126.9 (s, C3 Py), 127.6 (s, *p*-C Ph), 128.2 (s, *m*-C), 131.6 (s, *o*-C), 136.1 (s, C4 Py), 143.8 (s, C2 Py), 149.9 (s, C6 Py). HR-MS (EI): *m*/*z* 259.1365 $(M)^+$; calcd for $C_{19}H_{17}N$ 259.1361. Anal. Calcd for $C_{19}H_{17}N$ (259.1): C, 87.99; H, 6.61; N, 5.40. Found: C, 88.21; H, 6.69; N, 5.55.

1-(2-Pyridyl)-8-(2-thienyl)octa-1,7-diyne (1c). Following the procedure described for the compound **1b**, reaction of 2-iodothiophene (0.22 mL, 2.0 mmol), 1-(2-pyridyl)octa-1,7-diyne (0.37 g, 2.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.03 g, 0.04 mmol), and CuI (0.007 g, 0.04 mmol) afforded **1c** as an orange oil after purification by column chromatography on silica gel (heptane/Et_2O, 50/50, $R_f = 0.20$) (0.45 g, yield 85%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.75 (m, 4 H, C≡CCH$_2$CH_2), 2.46 (m, 4 H, C≡CCH$_2$), 6.89 (dd, J = 3.5 and 5.1 Hz, 1 H, H4 thienyl), 7.08 (dd, J = 1.1 and 5.1 Hz, 1 H, H5 thienyl), 7.12 (dd, ^3J = 1.1 and 3.5 Hz, 1 H, H3 thienyl), 7.15 (ddd, ^3J = 1.0, 4.9, and 7.7 Hz, 1 H, H5 Py), 7.33 (ddd, ^3J = 0.9, 1.0, and 7.7 Hz, 1 H, H3 Py), 7.58 (ddd, ^3J = 1.8, 7.7, and 7.7 Hz, 1 H, H4 Py), 8.51 (ddd, ^3J = 0.9, 1.8, and 4.9 Hz, 1 H, H6 Py). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 19.0, 19.3 (s, C≡CCH$_2$*C*H$_2$), 27.5, 27.7 (s, C≡C*C*H$_2$), 74.1 (s, C≡*C*−thienyl), 80.7 (s, C≡*C*−Py), 90.5 (s, *C*≡C−Py), 93.8 (s, *C*≡C−thienyl), 122.4 (s, C5 Py), 124.0 (s, C2 thienyl), 126.0 (s, C4 thienyl), 126.8 (s, C5 thienyl or C3 Py), 126.9 (s, C5 thienyl or C3 Py), 131.1 (s, C3 thienyl), 136.1 (s, C4 Py), 143.8 (s, C2 Py), 149.9 (s, C6 Py). HR-MS (EI): *m*/*z* 265.0929 $(M)^+$, calcd for $C_{17}H_{15}NS$ 265.0925. Anal. Calcd for $C_{17}H_{15}NS$ (265.4): C, 76.94; H, 5.70; N, 5.28. Found: C, 76.82; H, 5.62; N, 5.32.

1-Cyclohexyl-2,5-bis(2-pyridyl)phosphole (2a′). A solution of BuLi in hexanes (1.6 M, 2.2 mL, 3.5 mmol) was added dropwise to a THF solution (40 mL) of Cp_2ZrCl_2 (0.50 g, 1.72 mmol) and diyne **1a**[10c] (0.45 g, 1.73 mmol) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 12 h, and neat $CyPBr_2$ (0.36 mL, 1.73 mmol) was added. The solution was stirred for 5 h and filtered, and the volatile materials were removed under vacuum. Phosphole **2a′** was isolated as a yellow solid after purification on basic alumina (THF, $R_f = 0.8$) (0.54 g, yield 83%): mp 163 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 0.92 (m, 4 H, CH$_2$), 1.10−1.75 (m, 8 H, CH$_2$), 1.95 (m, 2 H, CH$_2$), 2.71 (m, 3 H, CH$_2$ and PCH), 3.43 (m, 2 H, C=CCH$_2$), 6.60 (ddd, J = 1.0, 4.9 and 7.5 Hz, 2 H, H5 Py), 7.17 (ddd, J = 1.0, 7.5 and 7.7 Hz, 2 H, H4 Py), 7.47 (d broad,

J = 7.7 Hz, 2 H, H3 Py), 8.61 (ddd, J = 1.0, 2.0, and 4.9 Hz, 2 H, H6 Py). $^{13}C\{^1H\}$ NMR (50.323 MHz, C_6D_6): δ 23.5 (s, $=CCH_2CH_2$), 26.4 (s, CH_2 Cy), 28.1 (d, J = 9.7 Hz, CH_2 Cy), 29.1 (s, $=CCH_2$), 30.8 (d, J = 5.9 Hz, CH_2 Cy), 38.0 (d, J = 17.2 Hz, CH Cy), 120.5 (s, C5 Py), 124.0 (d, J = 9.6 Hz, C3 Py), 135.6 (d, J = 1.6 Hz, C4 Py), 143.4 (s, PC_α), 147.9 (d, J = 8.5 Hz, PC_β), 149.6 (s, C6 Py), 157.9 (d, J = 19.1 Hz, C2 Py). $^{31}P\{^1H\}$ NMR (81.014 MHz, CD_2Cl_2): δ 27.9. HR-MS (FAB-*m*NBA): *m*/*z* 375.1990 $(M + H)^+$, calcd for $C_{25}H_{27}N_2P$ 375.1990. Anal. Calcd for $C_{24}H_{27}N_2P$: C, 76.98; H, 7.27; N, 7.48. Found, C, 77.13; H, 7.33; N, 7.38.

1,2-Diphenyl-5-(2-pyridyl)phosphole (2b). By the procedure described for compound **2a′**, the reaction of BuLi (1.6 M, 1.4 mL, 2.20 mmol), Cp_2ZrCl_2 (0.32 g, 1.10 mmol), diyne **1b** (0.28 g, 1.10 mmol), and $PhPBr_2$ (0.25 mL, 1.21 mmol) afforded **2b** as a yellow solid after purification on basic alumina (THF, R_f = 0.90) (0.30 g, yield 75%): mp 177 °C. ^1H NMR (300 MHz, C_6D_6): δ 1.21−1.60 (m, 4 H, $=CCH_2CH_2$), 2.43−2.89 (m, 3 H, $=CCH_2$), 3.51 (m, 1 H, $=CCH_2$), 6.47 (ddd, J = 1.1, 4.9, and 7.5 Hz, 1 H, H5 Py), 6.77−6.86 (m, 3 H, H Ph), 6.96−7.12 (m, 9 H, H3,4 Py and H Ph), 8.50 (ddd, J = 1.0, 1.8, and 4.9 Hz, 1 H, H6 Py). $^{13}C\{^1H\}$ NMR (50.323 MHz, C_6D_6): δ 23.4, 23.6 (s, $=CCH_2CH_2$), 28.2, 29.4 (s, $=CCH_2$), 120.4 (s, C5 Py), 123.5 (d, J = 9.8 Hz, C3 Py), 126.7 (s, *p*-C Ph), 128.6 (s, *m*-C Ph), 128.7 (d, J = 11.0 Hz, *o*-C Ph), 129.2 (d, J = 1.2 Hz, *p*-C Ph), 129.7 (d, J = 9.1 Hz, *m*-C Ph), 133.3 (d, J = 12.8 Hz, *i*-C Ph), 133.9 (d, J = 18.3 Hz, *o*-C Ph), 135.7 (d, J = 1.8 Hz, C4 Py), 137.7 (d, J = 17.7 Hz, *i*-C Ph), 142.4 (d, J = 4.3 Hz, PC_α), 144.4 (d, J = 11.0 Hz, PC_β), 146.4 (d, J = 1.0 Hz, PC_α), 149.3 (d, J = 4.3 Hz, PC_β), 149.7 (d, J = 1.8 Hz, C6 Py), 156.8 (d, J = 20.1 Hz, C2 Py). $^{31}P\{^1H\}$ NMR (81.014 MHz, CD_2Cl_2): δ 12.9. HR-MS (FAB-*m*NBA): *m*/*z* 367.1490 $(M)^+$, calcd for $C_{25}H_{22}NP$ 367.1492. Anal. Calcd for $C_{25}H_{22}NP$: C, 81.72; H, 6.04; N, 3.81. Found: C, 81.44; H, 5.91; N, 3.68.

1-Cyclohexyl-2-phenyl-5-(2-pyridyl)phosphole (2b′). By the procedure described for the compound **2a′**, reaction of BuLi (1.6 M, 1.4 mL, 2.20 mmol), Cp_2ZrCl_2 (0.32 g, 1.10 mmol), diyne **1b** (0.28 g, 1.10 mmol), and $CyPBr_2$ (0.33 mL, 1.20 mmol) afforded **2b′** as a yellow solid after purification on basic alumina (THF, R_f = 0.90) (0.27 g, yield 65%). ^1H NMR (300 MHz, C_6D_6): δ 0.70−2.05 (m, 14 H, CH_2), 2.16 (m, 1 H, CH_2), 2.40−2.89 (m, 3 H, CH_2 and PCH), 3.51 (m, 1 H, $C=CCH_2$), 6.60 (ddd, J = 1.1, 4.9, and 7.3 Hz, 1 H, H5 Py), 7.08−7.31 (m, 4 H, H Ph and H4 Py), 7.47 (ddd, J = 1.0, 1.1, and 7.8 Hz, 1 H, H3 Py), 7.57 (d broad, J = 8.0 Hz, 2 H, *o*-H), 8.60 (ddd, J = 1.0, 1.8, and 4.9 Hz, 1 H, H6 Py). $^{13}C\{^1H\}$ NMR (50.323 MHz, C_6D_6): δ 23.3, 23.4 (s, $=CCH_2CH_2$), 26.1, 27.4, 27.5 (s broad, CH_2 Cy), 27.8, 27.9 (s, $=CCH_2$), 30.0 (d broad, J = 3.1 Hz, CH_2 Cy), 30.3 (d broad, J = 7.0 Hz, CH_2 Cy), 37.2 (d, J = 16.3 Hz, CH Cy), 119.9 (s, C5 Py), 123.3 (d, J = 9.4 Hz, C3 Py), 126.3 (s, *p*-C Ph), 128.4 (s, *m*-C Ph), 129.4 (d, J = 9.4 Hz, *o*-C Ph), 135.4 (d, J = 1.6 Hz, C4 Py), 139.0 (d, J = 18.8 Hz, *i*-C Ph), 141.0 (s, PC_α), 143.8 (d, J = 9.4 Hz, PC_β), 144.4 (d, J = 1.5 Hz, PC_α), 147.7 (d, J = 8.6 Hz, PC_β), 149.6 (d, J = 1.6 Hz, C6 Py), 157.6 (d, J = 18.9 Hz, C2 Py). $^{31}P\{^1H\}$ NMR (81.014 MHz, CD_2Cl_2): δ 26.9. HR-MS (FAB-*m*NBA): *m*/*z* 374.2055 $(M + H)^+$, calcd for $C_{25}H_{29}NP$ 374.2055. Anal. Calcd for $C_{25}H_{28}NP$: C, 80.40; H, 7.56; N, 3.75. Found: C, 80.22; H, 7.41; N, 3.81.

1-Phenyl-2-(2-pyridyl)-5-(2-thienyl)phosphole (2c). By the procedure described for the compound **2a′**, reaction of BuLi (1.6 M, 1.1 mL, 1.75 mmol), Cp_2ZrCl_2 (0.25 g, 0.86 mmol), diyne **1c** (0.23 g, 0.87 mmol), and $PhPBr_2$ (0.23 mL, 1.12 mmol) afforded **2c** an orange solid after purification on basic alumina (THF, R_f = 0.8) (0.27 g, yield 83%): mp 167 °C. ^1H NMR (300 MHz, C_6D_6): δ 1.21−1.62 (m, 4 H, $=CCH_2CH_2$), 2.65 (m, 1 H, $=CCH_2$), 2.87 (m, 2 H, $=CCH_2$), 3.31 (m, 1 H, $=CCH_2$), 6.43 (ddd, J = 1.0, 4.8, and 7.6 Hz, 1 H, H5 Py), 6.68 (ddd, J = 1.2, 3.8, and 4.7 Hz, 1H, H4 thienyl), 6.74−6.90 (m, 4 H, *m*-/*p*-H Ph and H5 thienyl), 6.96 (ddd, J = 1.8, 7.6, and 7.6 Hz, 1 H, H4 Py), 7.19 (d broad, J = 3.8 Hz, 1 H, H3 thienyl), 7.36 (ddd, J = 0.9, 1.0, and 7.6 Hz, 1 H, H3 Py), 7.65 (ddd, J = 1.5, 7.9, and 8.0 Hz, 2 H, *o*-H), 8.47 (ddd, J = 0.9, 1.8, and 4.8 Hz, 1 H, H6 Py). $^{13}C\{^1H\}$ NMR (50.323 MHz, C_6D_6): δ 23.0 (s, $=CCH_2CH_2$), 29.2, 29.8 (s, $=CCH_2$), 120.4 (s, C5 Py), 123.3 (d, J = 9.8 Hz, C3 Py), 125.4 (d, J = 2.4 Hz, C5 thienyl), 126.4 (d, J = 9.8 Hz, C3 thienyl), 127.6 (s, C4 thienyl), 128.9 (d, J = 8.5 Hz, *m*-C Ph), 129.6 (s, *p*-C Ph), 133.9 (d, J = 13.4 Hz, *i*-C Ph), 134.4 (d, J = 18.3 Hz, *o*-C), 135.7 (s, C4 Py), 139.0 (s, PC_α), 140.3 (d, J = 20.0 Hz, C2 thienyl), 142.0 (d, J = 3.8 Hz, PC_α), 144.4 (d, J = 8.5 Hz, PC_β), 149.6 (s, C6 Py), 149.9 (d, J = 8.5 Hz, PC_β), 156.2 (d, J = 19.5 Hz, C2 Py). $^{31}P\{^1H\}$ NMR (81.014 MHz, CD_2Cl_2): δ 12.6. HR-MS (FAB-*m*NBA): *m*/*z* 373.1035 $(M)^+$, calcd for $C_{23}H_{20}NSP$ 373.1054. Anal. Calcd for $C_{23}H_{20}NSP$: C, 73.97; H, 5.40; N, 3.75. Found: C, 74.18; H, 5.49; N, 3.62.

1-Cyclohexyl-2-(2-pyridyl)-5-(2-thienyl)phosphole (2c′). By the procedure described for the compound **2a′**, reaction of BuLi (1.6 M, 1.1 mL, 1.75 mmol), Cp_2ZrCl_2 (0.25 g, 0.86 mmol), diyne **1c** (0.23 g, 0.87 mmol), and $CyPBr_2$ (0.27 g, 1.00 mmol) afforded **2c′** as an orange solid after purification on basic alumina (THF, R_f = 0.90) (0.16 g, yield 49%): mp 100 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 0.70−2.01 (m, 15 H, CH_2), 2.51−3.32 (m, 4 H, CH_2 and PCH), 7.21 (m, 3 H, H5 Py and H3,4 thienyl), 7.22 (d broad, J = 5.0 Hz, 1 H, H5 thienyl), 7.41 (d broad, J = 7.8 Hz, 1 H, H3 Py), 7.80 (ddd, J = 2.0, 7.8, and 7.8 Hz, 1 H, H4 Py), 8.61 (d broad, J = 3.9 Hz, 1 H, H6 Py). $^{13}C\{^1H\}$ NMR (50.323 MHz, C_6D_6): δ 23.4, 23.5 (s, $=CCH_2CH_2$), 26.4 (s, CH_2 Cy), 28.0 (d, J = 8.2 Hz, CH_2 Cy), 28.1 (d, J = 9.5 Hz, CH_2 Cy), 28.8, 29.4 (s, $=CCH_2$), 30.2 (d, J = 5.2 Hz, CH_2 Cy), 30.6 (d, J = 6.8 Hz, CH_2 Cy), 38.6 (d, J = 17.1 Hz, CH Cy), 120.4 (s, C5 Py), 123.9 (d, J = 9.8 Hz, C3 Py), 125.5 (d, J = 2.2 Hz, C5 thienyl), 126.3 (d, J = 9.7 Hz, C3 thienyl), 127.8 (s, C4 thienyl), 135.8 (s, C4 Py), 136.9 (d, J = 2.2 Hz, PC_α), 140.4 (s, PC_α), 140.9 (d, J = 22.7 Hz, C2 thienyl), 144.2 (d, J = 7.6 Hz, PC_β), 148.9 (d, J = 7.1 Hz, PC_β), 149.5 (s, C6 Py), 157.3 (d, J = 19.4 Hz, C2 Py). $^{31}P\{^1H\}$ NMR (81.014 MHz, CD_2Cl_2): δ 27.7. HR-MS (FAB-*m*NBA): *m*/*z* 380.1601 $(M + H)^+$, calcd for $C_{23}H_{27}NSP$ 380.1602. Anal. Calcd for $C_{23}H_{26}NSP$: C, 72.79; H, 6.91; N, 3.69. Found, C, 72.92; H, 6.81; N, 3.89.

[1-phenyl-2,5-bis(2-pyridyl)phosphole]Pd(CH_3)Cl (3a). A CH_2Cl_2 solution (10 mL) of phosphole **2a**[10c] (0.19 g, 0.52 mmol) was added, at room temperature, to a CH_2Cl_2 solution (10 mL) of (COD)Pd(CH_3)(Cl) (0.14 g, 0.52 mmol). The reaction mixture was stirred for 1 h, and the volatile materials were removed under vacuum. The residue was washed with diethyl ether (2 × 10 mL) and dried under vacuum. Complex **3a** was obtained as an air-stable yellow solid (0.24 g, yield 88%). ^1H NMR (300 MHz, CD_2Cl_2, 283 K): δ 0.96 (d, J = 2.4 Hz, 3 H, $PdCH_3$), 1.50−2.10 (m, 4 H, $=CCH_2CH_2$), 2.70−3.31 (m, 4 H, $=CCH_2$), 7.21−7.32 (m, 4 H, CH), 7.09 (ddd, J = 1.0, 4.9, and 7.3 Hz, 1 H, H5 Py), 7.48 (d broad, J = 8.1 Hz, 1 H, H3 Py), 7.56 (d broad, J = 8.1 Hz, 1 H, H3 Py), 7.62−7.72 (m, 3 H, CH), 7.79 (dddd, J = 1.2, 1.7, 7.3, and 8.1 Hz, 1 H, H4 Py), 8.43 (ddd, J = 1.0, 1.7, and 4.9 Hz, 1 H, H6 Py), 9.21 (ddd, J = 1.0, 1.7, and 5.4 Hz, 1 H, H6 Py). $^{13}C\{^1H\}$ NMR (75.469 MHz, CD_2Cl_2, 283 K): δ −7.5 (d, J = 2.4 Hz, $PdCH_3$), 22.4, 23.0 (s, $=CCH_2CH_2$), 28.5 (d, J = 7.3 Hz, $=CCH_2$), 31.1 (d, J = 8.5 Hz, $=CCH_2$), 122.7 (s, C5 Py), 123.1 (d, J = 7.3 Hz, C3 Py), 123.3 (s, C5 Py), 124.1 (d, J = 7.3 Hz, C3 Py), 129.0 (d, J = 47.6 Hz, *i*-C Ph), 129.1 (d, J = 12.1 Hz, C Ph), 131.5 (d, J = 2.4 Hz, C Ph), 133.7 (d, J = 13.4 Hz, C Ph), 137.1, 138.6 (s, C4 Py), 139.0 (d, J = 57.4 Hz, PC_α), 142.0 (d, J = 43.9 Hz, PC_α), 147.9 (d, J = 10.9 Hz, PC_β), 149.8, 151.0 (s, C6 Py), 152.1 (d, J = 15.8 Hz, PC_β), 152.7 (d, J = 13.4 Hz, C2 Py), 152.9 (d, J = 14.6 Hz, C2 Py). $^{31}P\{^1H\}$ NMR (81.014 MHz, CD_2Cl_2): δ 56.9. HR-MS (FAB-*m*NBA): *m*/*z* 509.0150 $(M - CH_3)^+$, calcd for $C_{24}H_{21}N_2ClPPd$ 509.0172. Anal. Calcd for $C_{25}H_{24}N_2PPdCl$: C, 57.16; H, 4.61; N, 5.33. Found: C, 57.36; H, 4.71; N, 5.19.

[1-cyclohexyl-2,5-bis(2-pyridyl)phosphole]Pd(CH_3)Cl (3a′). By the procedure described for the compound **3a**, reaction of phosphole **2a′** (0.30 g, 0.80 mmol) and (COD)Pd(CH_3)(Cl) (0.21 g, 0.80 mmol) afforded **3a′** as an air-stable

orange solid (0.38 g, yield 91%). ^{1}H NMR (300 MHz, CD_2Cl_2, 283 K): δ 0.68 (d, J = 2.4 Hz, 3 H, $PdCH_3$), 0.80−1.30 (m, 4 H, CH_2), 1.45−1.75 (m, 6 H, CH_2), 1.95 (m, 2 H, CH_2), 2.25 (m, 2 H, CH_2), 2.60−2.95 (m, 5 H, CH_2 and CH Cy), 7.19 (ddd, J = 1.0, 4.9, and 7.9 Hz, 1 H, H5 Py), 7.26 (ddd, J = 1.0, 5.4, and 7.9 Hz, 1H, H5 Py), 7.54 (d broad, J = 7.9 Hz, 1 H, H3 Py), 7.57 (d broad, J = 7.9 Hz, 1 H, H3 Py), 7.75 (dddd, J = 1.2, 1.7, 7.9, and 7.9 Hz, 1 H, H4 Py), 7.88 (dddd, J = 1.2, 1.7, 7.9, and 7.9 Hz, 1 H, H4 Py), 8.63 (ddd, J = 1.0, 1.7, and 4.9 Hz, 1 H, H6 Py), 9.24 (d broad, J = 5.4 Hz, 1 H, H6 Py). ^{13}C{^{1}H} NMR (50.323 MHz, CD_2Cl_2): δ −11.0 (d, J = 2.3 Hz, $PdCH_3$), 22.0, 22.7 (s, $=CCH_2CH_2$), 25.8 (d, J = 1.1 Hz, CH_2 Cy), 26.9 (d, J = 11.0 Hz, CH_2 Cy), 27.4 (d, J = 14.6 Hz, CH_2 Cy), 27.5 (d, J = 1.6 Hz, CH_2 Cy), 27.6 (d, J = 6.2 Hz, $=CCH_2$), 30.0 (d, J = 7.8 Hz, $=CCH_2$), 31.2 (d, J = 3.1 Hz, CH_2 Cy), 38.8 (d, J_{P-C} = 22.5 Hz, CH Cy), 122.0 (s, C5 Py), 123.3 (s, C5 Py), 122.4 (d, J = 7.0 Hz, C3 Py), 122.7 (d, J = 7.0 Hz, C3 Py), 136.4 (s, C4 Py), 137.2 (d, J = 48.5 Hz, PC_α), 137.9 (s, C4 Py), 139.1 (d, J = 40.7 Hz, PC_α), 147.4 (d, J = 10.2 Hz, PC_β), 149.5 (s, C6 Py), 150.6 (s, C6 Py), 151.0 (d, J = 9.4 Hz, PC_β), 153.1 (d, J = 16.4 Hz, C2 Py), 153.6 (d, J = 12.5 Hz, C2 Py). ^{31}P{^{1}H} NMR (81.014 MHz, CD_2Cl_2): δ 70.4. HR-MS (FAB-*m*NBA): *m*/*z* 515.0630 $(M - CH_3)^+$, calcd for $C_{24}H_{27}N_2ClPPd$ 515.0635. Anal. Calcd for $C_{25}H_{30}N_2PPdCl$: C, 56.51; H, 5.69; N, 5.27. Found: C, 56.36; H, 5.35; N, 5.20.

[1,2-diphenyl-5-(2-pyridyl)phosphole]Pd(CH_3)Cl (3b). By the procedure described for the compound **3a**, reaction of phosphole **2b** (0.23 g, 0.61 mmol) and (COD)Pd(CH_3)(Cl) (0.16 g, 0.61 mmol) afforded **3b** as an air-stable orange solid (0.30 g, yield 95%). Single crystals suitable for an X-ray diffraction study were grown from a saturated CH_2Cl_2 solution at room temperature. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.82 (d, J = 2.8 Hz, 3 H, $PdCH_3$), 1.45−2.00 (m, 4 H, $=CCH_2CH_2$), 2.71−2.94 (m, 3 H, $=CCH_2$), 3.20 (m, 1 H, $=CCH_2$), 7.10−7.45 (m, 9 H, CH), 7.61 (d broad, J = 7.5 Hz, 1 H, H3 Py), 7.75−7.90 (m, 3 H, CH), 9.33 (ddd, J = 0.7, 1.5, and 5.4 Hz, 1 H, H6 Py). ^{13}C{^{1}H} NMR (75.469 MHz, CD_2Cl_2): δ −13.6 (d, J = 3.3 Hz, $PdCH_3$), 22.2, 22.6 (s, $=CCH_2CH_2$), 27.5 (d, J = 7.8 Hz, $=CCH_2$), 28.7 (d, J = 8.6 Hz, $=CCH_2$), 122.4 (s, C5 Py), 123.1 (d, J = 7.8 Hz, C3 Py), 125.9 (d, J = 43.0, *i*-C Ph), 127.9 (d, J = 1.0 Hz, C Ph), 128.5 (s, C Ph), 128.9 (d, J = 7.2 Hz, C Ph), 129.0 (d, J = 8.8 Hz, C Ph), 131.8 (d, J = 3.1 Hz, C Ph), 133.9 (d, J = 14.9 Hz, C Ph), 134.3 (d, J = 14.1 Hz, *i*-C Ph), 137.6 (d, J = 46.9 Hz, PC_α), 138.0 (d, J = 1.0 Hz, C4 Py), 140.0 (d, J = 46.7 Hz, PC_α), 148.4 (d, J = 11.7 Hz, PC_β), 150.8 (s, C6 Py), 151.0 (d, J = 14.1 Hz, PC_β), 151.7 (d, J = 18.0 Hz, C2 Py). ^{31}P{^{1}H} NMR (81.014 MHz, CD_2Cl_2): δ 55.5. HR-MS (FAB-*m*NBA): *m*/*z* 508.0213 $(M - CH_3)^+$, calcd for $C_{25}H_{22}NClPPd$ 508.0210. Anal. Calcd for $C_{26}H_{25}NPPdCl$: C, 59.56; H, 4.81; N, 2.67. Found: C, 59.44; H, 4.92; N, 2.55.

[1-cyclohexyl-2-phenyl-5-(2-pyridyl)phosphole]Pd(CH_3)Cl (3b′). By the procedure described for the compound **3a**, reaction of phosphole **2b′** (0.19 g, 0.52 mmol) and (COD)Pd(CH_3)(Cl) (0.13 g, 0.52 mmol) afforded **3b′** as an air-stable orange solid (0.24 g, yield 87%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.78 (d, J = 2.7 Hz, 3 H, $PdCH_3$), 0.82−1.15 (m, 4 H, CH_2), 1.40−1.82 (m, 12 H, CH_2), 2.40−2.78 (m, 3 H, CH_2 and CH Cy), 7.23 (ddd, J = 1.3, 5.3, and 7.9 Hz, 1 H, H5 Py), 7.28−7.48 (m, 5 H, CH), 7.57 (d broad, J = 8.1 Hz, 1 H, H3 Py), 7.85 (ddd, J = 1.3, 7.9, and 8.1 Hz, 1 H, H4 Py), 9.28 (d broad, J = 5.3 Hz, 1 H, H6 Py). ^{13}C{^{1}H} NMR (50.323 MHz, CD_2Cl_2): δ −14.3 (d, J = 3.9 Hz, $PdCH_3$), 22.2, 22.5 (s, $=CCH_2CH_2$), 25.7 (d, J = 1.6 Hz, CH_2 Cy), 26.7 (d, J = 10.9 Hz, CH_2 Cy), 26.8 (d, J = 14.1 Hz, CH_2 Cy), 27.3 (d, J = 7.0 Hz, $=CCH_2$), 28.0 (d, J = 7.0 Hz, $=CCH_2$), 28.5 (d, J = 2.3 Hz, CH_2 Cy), 30.5 (d, J = 2.3 Hz, CH_2 Cy), 37.8 (d, J_{P-C} = 22.1 Hz, CH Cy), 122.2 (s, C5 Py), 123.1 (d, J = 7.8 Hz, C3 Py), 128.0 (s, C Ph), 128.8 (s, C Ph), 129.4 (d, J = 3.9 Hz, C Ph), 135.1 (d, J = 13.3, *i*-C Ph), 136.8 (d, J = 42.3 Hz, PC_α), 137.0 (d, J = 41.5 Hz, PC_α), 138.0 (s, C4 Py), 148.7 (d, J = 10.2 Hz, PC_β), 150.4 (d, J = 10.2 Hz, PC_β), 150.8 (s, C6 Py), 152.9 (d, J = 17.2 Hz, C2 Py). ^{31}P{^{1}H} NMR (81.014 MHz, CD_2Cl_2): δ 65.2. Anal. Calcd for $C_{26}H_{31}NPPdCl$: C, 58.88; H, 5.89; N, 2.64. Found: C, 58.73; H, 5.77; N, 2.56.

[1-phenyl-2-(2-pyridyl)-5-(2-thienyl)phosphole]Pd(CH_3)Cl (3c). By the procedure described for the compound **3a**, reaction of phosphole **2c** (0.20 g, 0.54 mmol) and (COD)Pd(CH_3)(Cl) (0.144 g, 0.54 mmol) afforded **3c** as an air-stable orange solid (0.26 g, yield 91%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.92 (d, J = 2.4 Hz, 3 H, $PdCH_3$), 1.50−2.10 (m, 4 H, $=CCH_2CH_2$), 2.70−3.00 (m, 3 H, $=CCH_2$), 3.20 (m, 1 H, $=CCH_2$), 6.85−7.05 (m, 2 H, H Ph), 7.21−7.62 (m, 6 H, H arom), 7.69−7.91 (m, 3 H, H arom), 9.25 (d broad, J = 5.3 Hz, 1 H, H6 Py). ^{13}C{^{1}H} NMR (75.469 MHz, CD_2Cl_2): δ −10.6 (d, J = 2.4 Hz, $PdCH_3$), 21.9, 22.6 (s, $=CCH_2CH_2$), 27.9 (d, J = 8.4 Hz, $=CCH_2$), 29.7 (d, J = 8.6 Hz, $=CCH_2$), 122.4 (s, C5 Py), 123.2 (d, J = 8.6 Hz, C3 Py), 127.1 (d, J = 42.4 Hz, *i*-C Ph), 127.3 (s, C4 or C5 thienyl), 127.4 (C4 or C5 thienyl), 129.0 (d, J = 5.5 Hz, C3 thienyl), 129.0 (d, J = 11.0 Hz, *m*-C Ph), 131.0 (d, J = 47.3 Hz, PC_α), 131.9 (d, J = 2.4 Hz, *p*-C Ph), 134.0 (d, J = 14.9 Hz, *o*-C Ph), 137.1 (d, J = 18.8 Hz, C2 thienyl), 137.9 (d, J = 1.6 Hz, C4 Py), 138.6 (d, J = 47.7 Hz, PC_α), 147.8 (d, J = 13.3 Hz, PC_β), 148.3 (d, J = 10.9 Hz, PC_β), 150.8 (s, C6 Py), 151.7 (d, J = 18.0 Hz, C2 Py). ^{31}P{^{1}H} NMR (81.014 MHz, CD_2Cl_2): δ +55.7. HR-MS (FAB-*m*NBA): *m*/*z* 494.03384 $(M - Cl)^+$, calcd for $C_{24}H_{23}NPSPd$ 494.0333. Anal. Calcd for $C_{24}H_{23}NPSPdCl$: C, 54.35; H, 4.37; N, 2.64. Found, C, 54.28; H, 4.53; N, 2.61.

[1-cyclohexyl-2-(2-pyridyl)-5-(2-thienyl)phosphole]Pd(CH_3)Cl (3c′). By the procedure described for the compound **3a**, reaction of phosphole **2c′** (0.23 g, 0.61 mmol) and (COD)Pd(CH_3)(Cl) (0.161 g, 0.61 mmol) afforded **3c′** as an air-stable orange solid (0.29 g, yield 91%). ^{1}H NMR (200 MHz, CD_2Cl_2): δ 0.81 (d, J = 1.3 Hz, 3 H, $PdCH_3$), 0.70−2.05 (m, 15 H, CH_2), 2.43−2.97 (m, 4 H, CH_2 and PCH), 7.13−7.25 (m, 3 H, H3,4 thienyl and H5 Py), 7.44 (d broad, J = 3.8 Hz, 1 H, H5 thienyl), 7.48 (d broad, J = 7.3 Hz, 1 H, H3 Py), 7.81 (ddd, J = 1.8, 7.3 and 7.3 Hz, 1 H, H4 Py), 9.36 (d broad, J = 4.9 Hz, 1 H, H6 Py). ^{13}C{^{1}H} NMR (75.469 MHz, $CDCl_3$): δ −11.4 (s, $PdCH_3$), 22.0, 22.6 (s, $=CCH_2CH_2$), 25.7 (d, J = 1.6 Hz, CH_2 Cy), 26.8 (d, J = 10.2 Hz, CH_2 Cy), 27.2 (d, J = 5.5 Hz, CH_2 Cy), 27.3 (d, J = 15.6 Hz, CH_2 Cy), 27.8 (d, J = 7.8 Hz, $CH_2=CCH_2$), 29.4 (d, J = 7.8 Hz, $CH_2=CCH_2$), 31.2 (d, J = 3.9 Hz, CH_2 Cy), 38.8 (d, J = 20.3, CH Cy), 122.2 (s, C5 Py), 122.6 (d, J = 7.8 Hz, C3 Py), 125.7, 129.2 (s, C4 and C5 thienyl), 129.1 (d, J = 4.7 Hz, C3 thienyl), 129.8 (d, J = 41.5 Hz, PC_α), 135.3 (d, d, J = 43.8 Hz, PC_α), 137.4 (d, J = 19.6 Hz, C2 thienyl), 138.08 (s, C4 Py), 147.9 (d, J = 10.9 Hz, PC_β), 149.1 (d, J = 8.6 Hz, PC_β), 150.7 (s, C6 Py), 152.9 (d, J = 17.2 Hz, C2 Py). ^{31}P{^{1}H} NMR (81.014 MHz, CD_2Cl_2): δ 69.8. Anal. Calcd for $C_{24}H_{29}NPSPdCl$: C, 53.74; H, 5.44; N, 2.61. Found, C, 53.91; H, 5.55; N, 2.51.

[1-phenyl-2,5-bis(2-pyridyl)phosphole]Pd(CH_3)(CH_3CN)(SbF_6) (4a). Solid $AgSbF_6$ (0.20 g, 0.57 mmol) was added to a CH_3CN/CH_2Cl_2 solution (5 mL/10 mL) of complex **3a** (0.30 g, 0.57 mmol) at room temperature. The mixture was stirred for 0.5 h, and the precipitate of AgCl was filtered off using a plug of Celite. The solvent was removed under vacuum. The residue was precipitated from a CH_2Cl_2/Et_2O mixture and washed with Et_2O (2 × 10 mL). Complex **4c** was isolated as an air- and moisture-sensitive orange solid (0.39 g, yield 90%). ^{1}H NMR (300 MHz, CD_2Cl_2 + CD_3CN, 218 K): δ 1.00 (s broad, 3 H, $PdCH_3$), 1.41−2.08 (m, 4 H, $=CCH_2CH_2$), 2.67−3.35 (m, 4 H, $=CCH_2$), 6.94−7.90 (m, 11 H, H arom), 8.33 (s broad, 1 H, H6 Py), 8.57 (s broad). ^{13}C{^{1}H} NMR (75.469 MHz, CD_2Cl_2 + CD_3CN, 218 K): δ −5.4 (s, $PdCH_3$), 21.6, 22.3 (s, $=CCH_2CH_2$), 28.0 (d, J = 4.7 Hz, $=CCH_2$), 30.3 (d, J = 9.4 Hz, $=CCH_2$), 122.7 (d, J = 7.0 Hz, C3 Py), 122.8 (s, C5 Py), 124.0 (s, C5 Py), 124.4 (d, J = 7.0 Hz, C3 Py), 126.3 (d, J = 52.8, *i*-C Ph), 129.1 (d, J = 11.7 Hz, C Ph), 131.9 (s, C Ph), 133.2 (d, J = 14.1 Hz, C Ph), 137.2 (d, J = 2.3 Hz, C4 Py), 138.6 (d, J = 59.9 Hz, PC_α), 139.4 (s, C4 Py), 140.3 (d, J = 46.9 Hz, PC_α), 148.8 (d, J

= 11.7 Hz, PC_β), 149.6, 151.6 (s, C6 Py), 151.1 (d, J = 16.4 Hz, PC_β), 151.4 (d, J = 12.9 Hz, C2 Py), 152.8 (d, J = 14.6 Hz, C2 Py). $^{31}P\{^1H\}$ NMR (81.014 MHz, CD_2Cl_2 + CD_3CN, 218 K): δ 56.8. HR-MS (FAB-*m*NBA): *m*/*z* 489.0716 (M − CH_3CN − SbF_6)$^+$, calcd for $C_{25}H_{24}N_2PPd$ 489.0722.

[1-cyclohexyl-2,5-bis(2-pyridyl)phosphole]Pd(CH_3)(CH_3CN)(SbF_6) (4a′). By the procedure described for the compound **4a**, reaction of complex **3a′** (0.25 g, 0.47 mmol) and $AgSbF_6$ (0.16 g, 0.47 mmol) afforded **4b** as an extremely sensitive orange solid (0.31 g, yield 86%). $^{31}P\{^1H\}$ NMR (81.014 MHz, CD_2Cl_2 + CD_3CN, 218 K): δ +62.8.

[1,2-diphenyl-5-(2-pyridyl)phosphole]Pd(CH_3)(CH_3CN)(SbF_6) (4b): By the procedure described for the compound **4a**, reaction of complex **3b** (0.30 g, 0.57 mmol) and $AgSbF_6$ (0.20 g, 0.57 mmol) afforded **4b** as an air-stable yellow solid (0.40 g, yield 92%). ^1H NMR (300 MHz, CD_2Cl_2): δ 0.72 (d, J = 1.8 Hz, 3 H, $PdCH_3$), 1.58−2.09 (m, 4 H, =CCH_2CH_2), 2.35 (s, 3H, CH_3CN), 2.55−3.10 (m, 4 H, =CCH_2), 7.72 (m, 2 H, H Ph), 7.20−7.75 (m, 10 H, H arom), 7.91 (dddd, J = 1.4, 1.4, 7.8, and 7.8 Hz, 1 H, H4 Py), 8.57 (d broad, J = 4.9 Hz, 1 H, H6 Py). $^{13}C\{^1H\}$ NMR (50.323 MHz, CD_2Cl_2): δ −12.2 (d, J = 3.6 Hz, $PdCH_3$), 2.7 (s, CH_3CN), 21.9, 22.3 (s, =CCH_2CH_2), 28.0 (d, J = 8.5 Hz, =CCH_2), 29.0 (d, J = 9.7 Hz, =CCH_2), 123.7 (d, J = 47.0 Hz, *i*-C Ph), 124.1 (s, C5 Py), 124.4 (d, J = 8.5 Hz, C3 Py), 128.8 (s, C Ph), 129.1 (s, C Ph), 129.2 (d, J = 3.8 Hz, C Ph), 129.8 (d, J = 12.1 Hz, C Ph), 133.1 (d, J = 3.0 Hz, C Ph), 133.8 (d, J = 13.3 Hz, *i*-C Ph), 134.2 (d, J = 13.3 Hz, C Ph), 139.8 (s, C4 Py), 136.1 (d, J = 52.2 Hz, PC_α), 138.7 (d, J = 49.7 Hz, PC_α), 150.6 (d, J = 12.1 Hz, PC_β), 153.0 (d, J = 14.5 Hz, PC_β), 150.9 (s, C6 Py), 153.5 (d, J = 17.0 Hz, C2 Py). $^{31}P\{^1H\}$ NMR (81.014 MHz, CD_2Cl_2): δ +55.8. HR-MS (FAB-*m*NBA): *m*/*z* 488.0770 (M − CH_3CN − SbF_6)$^+$, calcd for $C_{26}H_{25}NPPd$ 488.0767. Anal. Calcd for $C_{28}H_{28}N_2F_6PPdSb$: C, 43.92; H, 3.69; N, 3.66. Found, C, 44.18; H, 3.82; N, 3.57.

[1-cyclohexyl-2-phenyl-5-(2-pyridyl)phosphole]Pd(CH_3)(CH_3CN)(SbF_6) (4b′). By the procedure described for the compound **4a**, reaction of complex **3b** (0.25 g, 0.47 mmol) and $AgSbF_6$ (0.16 g, 0.47 mmol) afforded **4b′** as an air-stable yellow solid (0.34 g, 95%). ^1H NMR (300 MHz, CD_2Cl_2): δ 0.70 (d, J = 1.7 Hz, 3 H, $PdCH_3$), 0.80−1.20 (m, 4 H, CH_2), 1.51−2.02 (m, 11 H, CH_2), 2.36 (s, 3 H, CH_3CN), 2.42−2.81 (m, 3 H, CH_2 and CH Cy), 3.05 (m, 1 H, CH_2), 7.26 (m, 2 H, CH), 7.35−7.55 (m, 4 H, CH), 7.67 (d broad, J = 7.9 Hz, 1 H, H3 Py), 7.85 (dddd, J = 1.0, 1.9, 7.9, and 7.9 Hz, 1 H, H4 Py), 8.71 (d broad, J = 5.2 Hz, 1 H, H6 Py). $^{13}C\{^1H\}$ NMR (50.323 MHz, CD_2Cl_2): δ −12.9 (d, J = 3.9 Hz, $PdCH_3$), 2.7 (s, CH_3CN), 22.0, 22.2 (s, =CCH_2CH_2), 25.4 (d, J = 1.0 Hz, CH_2 Cy), 26.5 (d, J = 10.9 Hz, CH_2 Cy), 26.8 (d, J = 13.3 Hz, CH_2 Cy), 27.3 (d, J = 7.8 Hz, =CCH_2), 28.1 (d, J = 8.6 Hz, =CCH_2), 28.5 (d, J = 3.1 Hz, CH_2 Cy), 30.6 (s broad, CH_2 Cy), 37.7 (d, J_{P-C} = 24.2 Hz, CH Cy), 120.3 (s, CH_3CN), 123.2 (d, J = 8.6 Hz, C3 Py), 124.2 (s, C5 Py), 128.7 (s, C Ph), 129.1 (s, C Ph), 129.2 (d, J = 4.7 Hz, C Ph), 134.1 (d, J = 12.5, *i*-C Ph), 135.5 (d, J = 46.2 Hz, PC_α), 135.7 (d, J = 44.6 Hz, PC_α), 139.5 (s, C4 Py), 150.1 (d, J = 11.0 Hz, PC_β), 151.1 (s, C6 Py), 151.9 (d, J = 16.4 Hz, C2 Py), 152.2 (d, J = 12.5 Hz, PC_β). $^{31}P\{^1H\}$ NMR (81.014 MHz, CD_2Cl_2): δ 65.2. HR-MS (FAB-*m*NBA): *m*/*z* 494.1240 (M − CH_3CN − SbF_6)$^+$, calcd for $C_{26}H_{31}NPPd$ 494.1229. Anal. Calcd for $C_{28}H_{34}F_6N_2PPdSb$: C, 43.58; H, 4.44; N, 3.63. Found: C, 43.82; H, 4.69; N, 3.42.

[1-phenyl-2-(2-pyridyl)-5-(2-thienyl)phosphole]Pd(CH_3)(CH_3CN)(SbF_6) (4c). By the procedure described for the compound **4a**, reaction of complex **3c** (0.25 g, 0.47 mmol) and $AgSbF_6$ (0.16 g, 0.47 mmol) afforded complex **4c** as an air-stable orange solid (0.33 g, yield 91%). ^1H NMR (200 MHz, CD_2Cl_2): δ 0.85 (d, J = 2.4 Hz, 3 H, $PdCH_3$), 1.51−2.15 (m, 4 H, =CCH_2CH_2), 2.37 (s, 3 H, CH_3CN), 2.70−3.05 (m, 3 H, =CCH_2), 3.18 (m, 1 H, =CCH_2), 6.87 (d broad, J = 3.8 Hz, 1H, H3 thienyl), 6.97 (dd, J = 3.8 and 5.3 Hz, 1 H, H4 thienyl), 7.30−7.52 (m, 5 H, *m*,*p*-H Ph, H5 thienyl, H5 Py), 7.55 (d broad, J = 8.0 Hz, 1 H, H3 Py), 7.70 (dddd, J = 1.5, 1.5, 6.7, and 13.5 Hz, 2 H, *o*-H), 7.91 (ddd, J = 1.3, 8.0, and 8.0 Hz, 1 H, H4 Py), 8.60 (ddd, J = 0.9, 1.3, and 5.5 Hz, 1 H, H6 Py). $^{13}C\{^1H\}$ NMR (50.323 MHz, CD_2Cl_2): δ −9.2 (d, J = 2.4 Hz, $PdCH_3$), 2.4 (s, CH_3CN), 21.7, 22.4 (s, =CCH_2CH_2), 28.0 (d, J = 9.4 Hz, =CCH_2), 29.9 (d, J = 8.6 Hz, =CCH_2), 119.5 (s, CH_3CN), 123.5 (s, C5 Py), 124.1 (d, J = 8.6 Hz, C3 Py), 124.9 (d, J = 48.5 Hz, *i*-C Ph), 127.4 (s, C4 or C5 thienyl), 127.4 (C4 or C5 thienyl), 129.2 (d, J = 5.5 Hz, C3 thienyl), 129.5 (d, J = 11.7 Hz, *m*-C Ph), 129.9 (d, J = 50.3 Hz, PC_α), 132.9 (d, J = 3.1 Hz, *p*-C Ph), 134.1 (d, J = 14.1 Hz, *o*-C Ph), 136.4 (d, J = 18.8 Hz, C2 thienyl), 137.0 (d, J = 45.4 Hz, PC_α),139.3 (s, C4 Py), 149.1 (d, J = 14.1 Hz, PC_β), 150.1 (d, J = 10.9 Hz, PC_β), 150.5 (s, C6 Py), 151.2 (d, J = 16.8 Hz, C2 Py). $^{31}P\{^1H\}$ NMR (81.014 MHz, CD_2Cl_2): δ +57.4. HR-MS (FAB-*m*NBA): *m*/*z* 494.0316 (M − CH_3CN − SbF_6)$^+$, calcd for $C_{24}H_{23}NPSPd$ 494.0333. Anal. Calcd for $C_{26}H_{26}N_2PSPdSbF_6$: C, 40.47; H, 3.40; N, 3.63. Found, C, 40.62; H, 3.72; N, 3.51.

[1-cyclohexyl-2-(2-pyridyl)-5-(2-thienyl)phosphole]Pd(CH_3)(CH_3CN)(SbF_6) (4c′). By the procedure described for the compound **4a**, reaction of complex **3c** (0.33 g, 0.61 mmol) and $AgSbF_6$ (0.21 g, 0.61 mmol) afforded **4c′** as an air-stable orange solid (0.43 g, yield 91%). ^1H NMR (200 MHz, CD_2Cl_2): δ 0.70 (d, J = 2.1 Hz, 3 H, $PdCH_3$), 0.78−1.95 (m, 15 H, CH_2), 2.37 (s, 3 H, CH_3CN), 2.61−3.01 (m, 4 H, CH_2 and PCH), 7.16 (m, 2 H, H3,4 thienyl), 7.42 (ddd, J = 1.1, 4.9, and 7.8 Hz, 1 H, H5 Py), 7.55 (m, 1 H, H5 thienyl), 7.64 (d broad, J = 7.7 Hz, 1 H, H3 Py), 8.05 (dddd, J = 1.4, 1.4, 7.8, and 7.8 Hz, 1 H, H4 Py), 8.60 (d broad, J = 4.9 Hz, 1 H, H6 Py). $^{13}C\{^1H\}$ NMR (50.323 MHz, $CDCl_3$): δ −9.9 (d, J = 3.3 Hz, $PdCH_3$), 2.7 (s, CH_3CN), 21.7, 22.4 (s, =CCH_2CH_2), 25.6 (d, J = 1.1 Hz, CH_2 Cy), 26.6 (d, J = 10.9 Hz, CH_2 Cy), 27.0 (d, J = 5.5 Hz, CH_2 Cy), 27.2 (d, J = 19.7 Hz, CH_2 Cy), 27.9 (d, J = 8.0 Hz, =CCH_2), 29.5 (d, J = 8.5 Hz, =CCH_2), 31.3 (d, J = 2.7 Hz, CH_2 Cy), 38.6 (d, J = 22.2, CH Cy), 120.2 (s, CH_3CN), 123.5 (s, C5 Py), 123.5 (d, J = 8.1 Hz, C3 Py), 127.7, 128.2 (s, C4 and C5 thienyl), 128.5 (d, J = 47.6 Hz, PC_α), 129.2 (d, J = 4.2 Hz, C3 thienyl), 133.7 (d, d, J = 46.2 Hz, PC_α), 136.6 (d, J = 18.8 Hz, C2 thienyl), 139.5 (s, C4 Py), 149.3 (d, J = 12.4 Hz, PC_β), 150.3 (s, C6 Py), 151.1 (d, J = 9.7 Hz, PC_β), 152.4 (d, J = 16.5 Hz, C2 Py). $^{31}P\{^1H\}$ NMR (81.014 MHz, CD_2Cl_2): δ 68.9. HR-MS (FAB-*m*NBA): *m*/*z* 500.0804 (M − CH_3CN − SbF_6)$^+$, calcd for $C_{24}H_{29}NPSPd$ 500.0812. Anal. Calcd for $C_{26}H_{32}N_2PSPdSbF_6$: C, 40.15; H, 4.15; N, 3.60. Found: C, 40.51; H, 4.53; N, 3.45.

Bis[1-Phenyl-2-(2-pyridyl)-5-(2-thienyl)phosphole]Pd(SbF_6^-)$_2$ (5). A MeOH solution (10 mL) of complex **4c** (0.30 g, 0.39 mmol) was stirred at room temperature for 30 min. The dark precipitate was filtered off using a plug of Celite. The solvent was removed under vacuum, and the residue was washed with pentane (3 × 10 mL) and ether (3 × 10 mL). Complex **5** was obtained by crystallization as a deep red solid from a CH_2Cl_2/toluene solution at room temperature (0.21 g, 42% yield). Single crystals suitable for an X-ray diffraction study were grown from a saturated $C_2H_4Cl_2$/toluene solution at −20 °C. ^1H NMR (300 MHz, CD_2Cl_2): δ 2.00 (m, 8H, =CCH_2CH_2), 2.65−2.91 (m, 6H, =CCH_2), 3.20 (m, 2H, =CCH_2), 6.00 (m, 2H), 6.45 (dd, J = 3.5 and 5.0 Hz, 2H, H_4 thienyl), 7.01 (dd, J = 1.0 and 5.0 Hz, 2H), 7.20−8.20 (m, 16 H), 8.50 (s broad, 2H, H6 py). $^{13}C\{^1H\}$ NMR (75.469 MHz, CD_2Cl_2): δ 21.1, 21.7 (s, =CCH_2CH_2), 27.6 (m, =CCH_2), 30.0 (m, =CCH_2), 120.8 (dd, J = 3.0 and 53.2 Hz, *i*-C), 124.3 (m, C3 Py), 125.7 (s, C5 Py), 128.0, 128.7 (s, C4 thienyl and C5 thienyl), 129.4 (m, C3 thienyl), 130.0 (m, *m*-C Ph), 130.1 (s, *p*-C Ph), 132.1 (d, J = 54.0 Hz, C_α), 132.3 (d, = 57.9 Hz, C_α), 133.9 (m, *o*-C Ph), 136.8 (d, J_{PC} = 4.7 Hz, C2 thienyl), 141.6 (s, C4 Py), 150.3 (d, J = 18.0 Hz, C_β), 151.3 (m, C6 Py), 152.8 (m, C_β), 159.2 (m, J = 18.8 Hz, C2 Py). $^{31}P\{^1H\}$ NMR (81.014 MHz, CD_2Cl_2): δ 69.7. HR-MS (FAB-*m*NBA): *m*/*z* 1087.0098 (M − SbF_6^+), calcd for $C_{46}H_{40}N_2P_2S_2PdSbF_6$ 1087.0100. Anal. Calcd for $C_{46}H_{40}N_2P_2S_2PdSb_2F_{12}$: C, 41.70; H, 3.04; N, 2.11. Found, C, 41.21; H, 3.11; N, 2.25.

Table 5. Crystallographic Data for Compounds 3b and 5

	3b	**5**·0.5$C_2H_4Cl_2$·C_7H_8
formula	$C_{26}H_{25}ClNPPd$	$C_{46}H_{40}N_2P_2S_2Sb_2F_{12}$·0.5$C_2H_4Cl_2$·$C_7H_8$
fw	524.29	1464.92
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
temp (K)	293	293
a (Å)	10.229(2)	13.655(10)
b (Å)	14.666(6)	14.991(2)
c (Å)	14.930(4)	16.835(2)
α (deg)	108.89(2)	
β (deg)	97.53(2)	108.48(3)
γ (deg)	90.10(3)	
V (Å^3)	2221(1)	3071(2)
F(000)	1064	1494
Z	4	2
λ(Mo Kα) (Å)	0.710 69	0.710 69
D(calcd) (g cm^{-3})	1.568	1.584
μ(Mo Kα) (cm^{-1})	10.42	15.28
2θ range (deg)	4−54	4−54
no. of data collected	5097	12 920
no. of unique data	4830	7587
no. of params varied	275	645
S	1.033	0.964
R^a	0.0476	0.0735
$R_w{}^b$	0.1236	0.2112
$(\Delta/\rho)_{max}$ (e Å^{-3})	0.800	1.570
$(\Delta/\rho)_{min}$ (e Å^{-3})	−0.1437	−0.971

^{a} $R = \sum||F_o| - |F_o||/\sum|F_o|$. ^{b} $R_w = [\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)^2]^{1/2}$.

Polymerization Procedure. In a typical procedure, the cationic Pd complex (0.03 mmol) was dissolved in CH_2Cl_2 (20 mL) in a Schlenk tube under argon, and the solution was transferred to a 150 mL autoclave equipped with a magnetic stirrer. The reaction mixture was pressurized with CO (10 bar) and ethylene (10 bar) and heated to the desired temperature. The reaction was quenched by release of CO/ethylene pressure. The polymer was isolated by filtration, washed with methanol, dried, and weighed.

Gel permeation chromatographic analysis of CO−norbornene oligomers was performed with THF as the solvent, and the calibration was made with polystyrene standards. The $^{13}C\{^1H\}$ NMR data for the oligomers are in agreement with those of previously described copolymers.[21]

X-ray Structural Analyses. The unit cell constant, space group determination, and data collection were carried out on an automatic CAD4 NONIUS diffractometer with graphite-monochromatized Mo Kα radiation. The cell parameters were obtained by fitting a set of 25 high-θ reflections. After Lorentz and polarization corrections and absorption corrections with ψ scan[22a] the structures were solved with SIR-97,[22b] which reveals non-hydrogen atoms of the structure. During the refinement, a dichloromethane and two partial molecules of toluene appear for compound **5**. After anisotropic refinement, many hydrogen atoms may be found with a difference Fourier map. The entire structures were refined with SHELXL97[22c] by full-matrix least-squares techniques (use of F magnitude; x, y, z, β_{ij} for Pd, P, C, S, Cl, and N atoms; x, y, z in riding mode for H atoms. The structure of **5** shows a statistical disorder (80/20) between S(31) and C(46). ORTEP views were prepared with PLATON98.[21d] All calculations were performed on a Silicon Graphics Indy computer. Selected crystallographic data are listed in Table 5.

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Supporting Information Available: Tables of crystal and intensity collection data, positional and thermal parameters, and interatomic distances and angles for derivatives **3b** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org. Full sets of crystallography data have been deposited with the Cambridge Crystallographic Data Center (CCDC 171791 and 149075 for compounds **3b** and **5**, respectively).

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