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2-Pyridyl-2-phospholenes: New P,N ligands for the palladium-catalyzed isoprene telomerization

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Abstract

2-(2-Pyridyl)-2-phospholenes are efficient ligands for the palladium-catalyzed telomerization of isoprene with diethylamine. Good selectivities for the tail-to-head or tail-to-tail aminoterpenes are achieved on optimization of the ligand substituents and of the reaction conditions, such as the nature of the catalyst precursor and of the solvent. Moreover, excellent catalytic activities are achieved on photochemical activation or addition of acidic co-catalysts.

Keywords: Telomerization; Isoprene; Phospholene; P,N ligands; Palladium; Homogeneous catalysis; Photochemical reactions

1. Introduction

Telomerization allows the synthesis of functionalized oligomers from dienes and a nucleophile in a 100% atom efficient manner. The first publication describing the synthesis of functionalized linear octadienes via telomerization of 1,3-butadiene with nucleophiles appeared in 1967 [1,2]. Since then, many catalytic systems have been studied; the most efficient are palladium complexes bearing phosphine or carbene ligands [3–7]. The telomerization of other dienes has been poorly investigated despite the great interest in the resulting telomers. For example, with isoprene, natural products, such as functionalized C_{10} terpenes, could be synthesized. However, due to the nonsymmetrical structure of the diene, four isomers can be formed, of which only the head-to-tail telomer **4** is a natural terpene (Fig. 1). The nature of the Pd ligand (e.g., mono- or di-phosphines, P,N-donors) can influence the product distribution; however, none of them allows good selectivities for the target compound **4** [8–11]. For instance, in most cases palladium/phosphine complexes give the tail-to-tail **1** or tail-to-head **3** products (Fig. 1). Hence the search for new ligands able to induce a good selectivity in one of the telomers **1**–**4** remains a challenge in this field.

We have recently reported the synthesis of the first family of P,N-chelates bearing a 2-phospholene moiety [12,13]. The fact that the electronic properties of this P-ring are different from those of the well-known phosphole or phospholane heterocycles prompted us to evaluate these novel P,N-donors for palladium-catalyzed isoprene telomerization. In this paper we present a detailed study including the optimization of the catalytic parameters and variation of the ligand structure. We also describe an unprecedented activation of the catalytic system on photochemical activation.

2. Results and discussion

We have recently reported that (2-pyridyl)-2-phospholenes **8a**–**c** can be obtained from the corresponding (2-pyridyl)phospholes **5a**–**c** via a three-step process involving: (i) coordination of **5a**–**c** to a Pd(II)-center, (ii) addition of a base such as pyridine, and (iii) release of **8a**–**c** on addition of 1,2-diphenylphosphinoethane (dppe) (Scheme 1) [12,13]. The role of the base is to catalyze the [1,3]-H shift via the formation of an allylic anion. Note that this step is very slow, requiring a large excess of pyridine and long reaction times (ca. 2–3 days) in refluxing CH_2Cl_2 [12,13].

Because we wanted to investigate the Pd-catalyzed telomerization of isoprene with diethylamine, it was of interest

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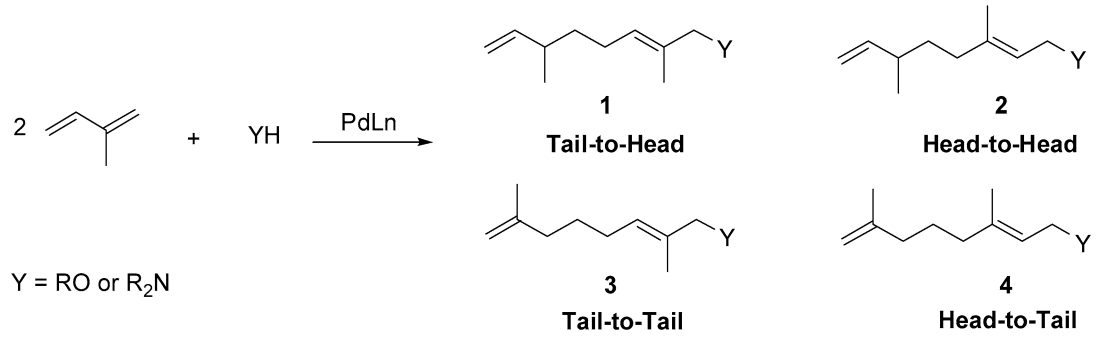
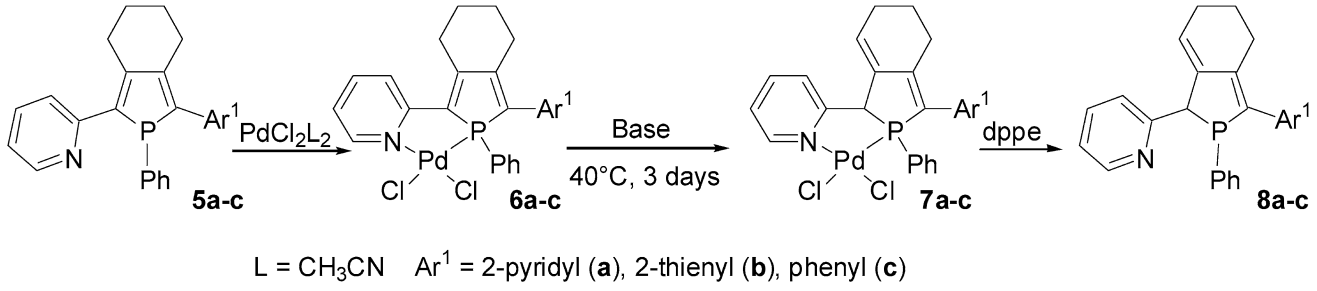
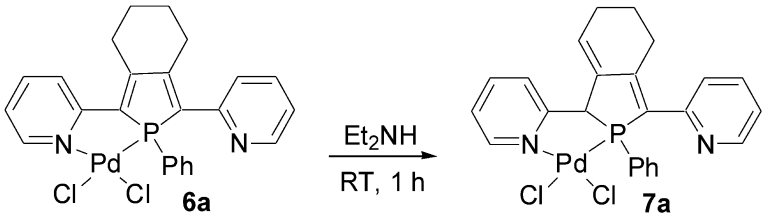


Fig. 1. Products of telomerization of isoprene with nucleophiles.



Scheme 1. Synthesis of 2-pyridyl-2-phospholenes **8a**–**c**.



Scheme 2. Reaction between diethylamine and Pd(II) complex **6a**.

to know whether this base can also promote the isomerization process depicted in Scheme 1. Indeed, in presence of one equivalent of diethylamine, complex **6a** gives quantitatively the corresponding [2-pyridyl-2-phospholene]Pd(II) complex **7a** within 1 h at room temperature in dichloromethane (Scheme 2). Hence diethylamine is by far the most efficient base for promoting phosphole–phospholene isomerization. This result suggests that phosphole-complexes **6** could be used as precursors of the corresponding phospholene complexes **7** in the isoprene-diethylamine telomerization. This is an appealing possibility avoiding the stepwise preparation of 2-pyridylphospholene ligands (Scheme 1). To check this hypothesis, the performance of the 2-pyridylphospholes **5a**,**b** and of their 2-pyridyl-2-phospholene isomers **8a**,**b** (Scheme 1) in the Pd-catalyzed telomerization were compared. The reactions were conducted at 40 °C over 48 h. The catalytic systems are formed in situ by reacting $(CH_3CN)_2PdCl_2$ with one equivalent of the P,N-ligands.

The yields and selectivities obtained with the phosphole ligands **5a** and **5b** are very similar to those recorded with their phospholene analogues **8a** and **8b** (Table 1). These data confirm that under the catalytic reaction conditions, isomerization is rapid and the catalytic species is a palladium complex bearing a 2-pyridyl-2-phospholenes ligand. Hence it is possible to conduct this study using 2-pyridylphospholes, which are easily available on a gram scale, as precursors of 2-pyridylphospholenes.

Table 1
Activities and selectivities of complexes (**5a**,**b**)$PdCl_2$ and (**8a**,**b**)$PdCl_2$. See Scheme 1 for structure numbering

Entry	Ligand	Solvent	Yield (%)	**1** (%)	**2** (%)	**3** (%)	**4** (%)
1	**5a**	CH_3CN	54	40	21	26.5	12.5
2	**8a**	CH_3CN	48	43.5	26	23.5	7
3	**5b**	CH_3CN	40	41	10	27	22
4	**8b**	CH_3CN	38	40	7	36	17

General conditions: 0.025 mmol of ligand and metallic precursor, 40 °C, 48 h. Yields are determined by GC.

The nature of the pyridylphospholene ligand influences the catalytic activity and product distribution. The yields are higher with di(2-pyridyl)phospholene **8a** (48%) than with (2-pyridyl)-(2-thienyl)phospholene **8b** (38%). With this latter ligand, the selectivity for the head-to-tail telomere **4** is higher (Table 1, entries 2 and 4), although in both cases the major product is the derivative **1**. The next step was to optimize the reaction conditions (i.e., solvent, metallic salts, temperature) to improve both the catalytic activity and the selectivity. In a first round of ex-

Table 2
Effect of solvent and temperature on yields and product distribution using catalytic precursor **6a**

Entry	Solvent	Yield (%)	**1** (%)	**2** (%)	**3** (%)	**4** (%)
5	CH_3CN	54	40	20.5	27	12.5
6	THF	8	5	3	92	0
7	CH_3CN[a]	15	46	12	34	8
8	CH_3CN/THF	16	58	0	42	0

General conditions: 0.025 mmol of ligand and metallic precursor, 40 °C, 48 h. Yields are determined by GC, $T = 60$ °C, 48 h.

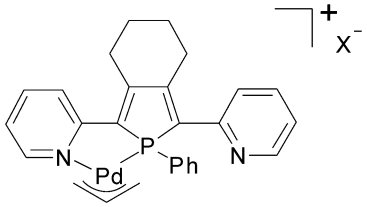


Fig. 2. [(**5a**)Pd(allyl)]$^+X^-$ complexes **9**.

periments, ligand **8a**, which is the most efficient, was used. Its phosphole precursor **5a** was reacted with $(CH_3CN)_2PdCl_2$ in dichloromethane for 1 h, affording complex **6a** (Scheme 1). Then dichloromethane was replaced by the desired solvent. The influence of several solvents was evaluated for a temperature of 40 °C for a reaction time of 48 h. No reaction occurs using methanol, toluene, or dichloromethane as solvent. The formation of telomers is observed only in a coordinating solvent, such as THF and CH_3CN. The yield decreases considerably when using THF instead of CH_3CN (Table 2, entries 5 and 6); however, the catalytic system is more selective in THF. It gives the tail-to-tail telomer **3** as the major product, whereas in CH_3CN a mixture of the four telomers is isolated (Table 2, entry 5). The nature of the coordinated solvent plays thus a crucial role in activity and selectivity. This is nicely illustrated by the fact that when an equivolume of THF and CH_3CN is used, the yield is still low, and the main products are the isomers **1** and **3** (Table 2, entry 8). Note that increasing the temperature results in lowering the yield, with the main products remaining almost similar. A catalytic run was conducted in ionic liquid medium using a cationic complex and butyl-methyl-imidazolium salts. The yield was about 15% after 48 h without profound variation of the selectivity. These experiments clearly show that only coordinated solvents allow good activity, and that the best temperature for this reaction is 40 °C.

The final parameter studied was the nature of the metallic salts. The (**5a**)$NiBr_2$, (**5a**)$PtCl_2$, and (**5a**)RuCpCl complexes are totally inactive in the conditions described below. With Cl^- or BF_4^- as the counter-anion, the allylic palladium complex **9** gave a very low yield in CH_3CN (3–4%; Table 3) compared with the $PdCl_2$-complex **6a** (54%). However, the catalytic activity increased when using THF (Table 3, entries 9–12). In this solvent, the nature of the counter-anion strongly influences the yields (Table 3, entries 10–14), as has been observed for allylic palladium complexes bearing carbene ligands [7].

Table 3
Catalytic experiments conducted with complexes **9**

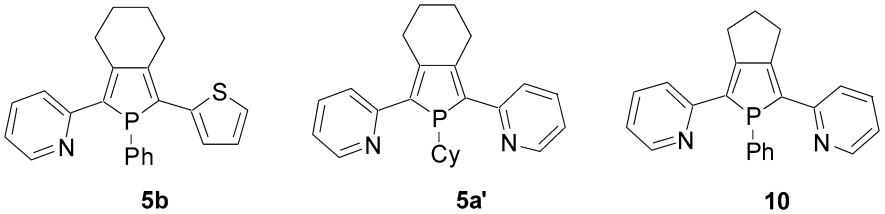
Entry	X^-	Solvent	Yield (%)	**1** (%)	**2** (%)	**3** (%)	**4** (%)
9	Cl^-	CH_3CN	4	57	0	43	0
10	Cl^-	THF	20	2.5	5.0	92.5	0
11	BF_4^-	CH_3CN	3	38	32	19	12
12	BF_4^-	THF	48	32	3.5	37	27
13	SbF_6^-	THF	1	64	0	36	0
14	OTf^-	THF	7	43.5	27	29.5	0

General conditions: 0.025 mmol of **9**, 40 °C, 48 h. Yields are determined by GC.

The counter-anion has a dramatic influence on the product distribution. With Cl^-, the tail-to-tail telomer **3** is the major product (Table 3, entry 10), as observed using the $PdCl_2$ precursor **6a**. Very interestingly, with BF_4^-, a rather high amount of the natural isomer **4** was obtained (Table 3, entry 12). This result is promising, because it can be expected that further variations of the ligand structure will allow an increase in this selectivity.

In this preliminary study with ligand **5a**, we have shown the importance of the solvent and of the counter-anion depending on the metallic precursor used. With $PdCl_2(CH_3CN)_2$, the use of a coordinated solvent, such as THF or acetonitrile, is required, whereas with the allylic palladium complex **9**, Cl^- and BF_4^- counter-anions are needed.

In these optimized conditions, we evaluated the behavior of different ligands in which electronic and steric properties were been varied by modifying the substitution pattern of the phosphole ring. Ligands **5b**, **5a′**, and **10** (Fig. 3) were selected as phospholene precursors. The phosphorus substituent (phenyl vs. cyclohexyl) will directly influence both the steric and electronic properties of the P-donor atom, whereas the second substituent at the C^5-atom of the phosphole ring (2-pyridyl versus 2-thienyl) is expected to influence the electronic properties of the N-donor atom via the extended π-conjugated system [14,15]. Finally, the size of the fused saturated carbocycle (six-membered vs. five-membered) is expected to influence the steric bulk of the ligands. We have previously reported that these variations can modify the behavior of Pd complexes during catalytic processes [16].



5b **5a'** **10**

Fig. 3. 2-Pyridylphosphole precursors of phospholene ligands tested in telomerization.

Table 4
Reaction in presence of ligand precursors **5b** and **10**

Entry	Ligand	Metal	Solvent	Yield (%)	**1** (%)	**2** (%)	**3** (%)	**4** (%)
16	**5b**	$PdCl_2(CH_3CN)_2$	CH_3CN	40	41	10	27	22
17	**5b**	$PdCl_2(CH_3CN)_2$	THF	4	12	3	85	0
18	**5b**	$PdCl_2(CH_3CN)_2$	THF	7	0	7	93	0
19	**10**	$PdCl_2(CH_3CN)_2$	CH_3CN	65	43	20	22	15
20	**10**	$PdCl_2(CH_3CN)_2$	THF	5	25	3	72	0
21	**10**	Pd(allyl)Cl	THF	8	5	6	89	0
22	**10**	Pd(allyl)Cl[a]	THF	11	5	7	88	0
23	**10**	$PdCl_2(CH_3CN)_2$[a]	THF	6	10	0	90	0

General conditions: 0.025 mmol of ligand and metallic precursor, 40 °C, 48 h. Yields are determined by GC.
[a] $T = 60$ °C, 48 h.

Table 5
Catalytic reaction using $[(\mathbf{5a})Pd(CH_3CN)]^{2+}2BF_4^-$

Entry	Complex	Yield (%)	**1** (%)	**2** (%)	**3** (%)	**4** (%)
24	$[(\mathbf{5a})Pd(CH_3CN)]^{2+}2BF_4^-$	30	51	0	49	0
25[a]	$[(\mathbf{5a})Pd(CH_3CN)]^{2+}2BF_4^-$	82	31	13	23	33

General conditions: 0.025 mmol of ligand and metallic precursor, 40 °C, 48 h. Yields are determined by GC.
[a] $T = 40$ °C, 7 days.

In the same reaction conditions, the yields obtained with **5b** (Table 4, entries 16–18) are lower than those observed with di(2-pyridyl)phosphole **5a** (ca. 54%). The selectivity is similar for both systems. Moreover, no catalytic activity has been detected with the complex $[(\mathbf{5b})Pd(allyl)]^+Cl^-$. Experiments with **5a**′ showed yields down to 3%. These results can be explained by the presence of a bulky substituent on the phosphorus atom, which disfavors the coordination of isoprene on metallic center or the diethylamine nucleophilic attack.

Ligand **5a**, bearing two 2-pyridyl moieties and one phenyl fragment on a P atom, is the most efficient ligand in the presence of palladium salts for telomerization of isoprene. Interestingly, the yield is further increased using ligand **10** (65 vs. 54% for **5a**) in acetonitrile. Unfortunately, the four telomers are formed, with **1** being the major product (43%). Variations of solvent or metallic precursors do not allow an increase in selectivity for one of these telomers.

To avoid the abstraction step of the chlorine on the $PdCl_2$ complex, which can be a difficult step, we decided to use another palladium salt, namely $[Pd(CH_3CN)_4]^{2+}2[BF_4^-]$, which contains four labile acetonitrile ligands. In each experiment, only one equivalent of ligand **5a** was added to $[Pd(CH_3CN)_4]^{2+}2[BF_4^-]$. In THF, the yield reached 30% after 48 h, and only two telomers, **1** and **3**, are formed in equal amounts. If the reaction mixture were stirred during 7 days, then the yield would increase to 82%, but the product distribution would be completely different. The four isomers **1**–**4** are produced; the head-to-tail telomer **4** is the major product (Table 5, entry 25). In conclusion, this new palladium precursor affords active but nonselective catalysts.

The addition of acidic co-catalysts to the reaction media could strongly drive variations in activity and selectivity [17]. Thus, the influence of acetic acid (20 eq.) and $BF_3{\cdot}OEt_2$ (20 eq.) in the reaction mixture was evaluated (Table 6). Adding acetic acid, the yield reached 90%, and the main product was telomer **1** (Table 6, entry 26). But the most interesting result was obtained with $BF_3{\cdot}OEt_2$. With this Lewis acid, only one telomer was formed (Table 6, entry 27). These results clearly show a considerably enhanced yield and selectivity using an acidic co-catalyst, in agreement with results reported by Keim [17].

Table 6
Influence of addition of an acidic co-catalyst

Entry	Co-catalyst	Yield (%)	**1** (%)	**2** (%)	**3** (%)	**4** (%)
26	CH_3CO_2H	90	52	16	32	0
27	$BF_3{\cdot}OEt_2$	35	100	0	0	0

General conditions: 0.025 mmol of ligand **5a** and $[Pd(CH_3CN)_4]^{2+}2BF_4^-$, 20 eq. of acidic co-catalyst. $T = 40$ °C, 48 h.

Table 7
Catalysis under UV with **5a**

Entry	Metal	Solvent	Yield (%)	**1** (%)	**2** (%)	**3** (%)	**4** (%)
28	$Pd(CH_3CN)_4{}^{2+}2BF_4^-$	THF	91	46	20	18	17
29	$PdCl_2(CH_3CN)_2$	DCM	8	100	0	0	0
30	$Pd(CH_3CN)_4{}^{2+}2BF_4^-$	CH_3CN	30	40	43	16	0
31	$Pd(CH_3CN)_4{}^{2+}2SbF_6^-$	THF	75	38.5	21	22.5	18

General condition: 0.025 mmol of ligand **5a** and $[Pd(CH_3CN)_4]^{2+}2BF_4^-$, 48 h under UV lamp.

Finally, we were able to develop a catalytic system for isoprene telomerization under photochemical activation. This work was motivated by the fact that the 2-pyridylphosphole ligands are chromophores exhibiting broad absorption in the UV–vis range [15]. Photoinduced electron transfer could drive some catalytic reaction in the solid state [18,19] or could be used for the synthesis of complex molecules [20,21]. Recently, Bach et al. described efficient organocatalytic enantioselective reactions performed under photochemical conditions, suggesting that photochemical routes also could be used in catalysis [22]. In our case, we expected that on irradiation, activation of the Pd-complexes could occur. Indeed, under UV irradiation, the yield obtained with complex $[(\mathbf{5a})Pd(CH_3CN)_2]^{2+}2BF_4^-$ (91%) was far superior to that recorded without irradiation (8%). Note that under irradiation with $[Pd(CH_3CN)_4]^{2+}2BF_4^-$, the yield was very low (ca. 3%). The results reported in Table 7 show that the catalytic system was always more active under UV–vis activation than under thermal activation. The best catalytic system was obtained in THF at 40 °C in 48 h (91% yield, compared with a 30% yield under thermal activation) with a selectivity in favor of **1** (46%, entry 28). Activities dropped when acetonitrile or another counter-anion was used in the same conditions (entries 30 and 31). To the best of our knowledge, this is the first report of a photochemical activation of a catalytic system for telomerization.

3. Conclusion

We have described new and efficient catalysts bearing 2-pyridyl-2-phospholenes ligands for the telomerization of isoprene and diethylamine. We have demonstrated that diethylamine can induce a rapid quantitative isomerization of

2-pyridylphospholes in 2-pyridyl-2-phospholenes under mild conditions in the coordination sphere of palladium. Catalytic studies show the crucial role played by the solvent and metallic salts. Coordinating solvents were needed to obtain good yields, generally directed toward telomer **1** (tail-to-head coupling) and **3** (tail-to-tail coupling). Unfortunately, telomer **4** (the natural product) was obtained at only 32% in the presence of complex $[(\mathbf{5a})Pd(CH_3CN)_2]^{2+}2BF_4^-$. High activity could be reached in the presence of acidic cocatalyst, such as acetic acid. In the same way, the use of $BF_3{\cdot}OEt_2$ enables achievement of high selectivity in **1**. We have shown the first UV-activation of a catalytic system for this reaction. This latter feature holds much promise, because the ligand will influence the catalytic center not only by its steric and electronic properties, but also by the nature of the ligand–metal charge transfer. Complementary research is in progress to further explore this unique catalytic system based on ligands that are also chromophores.

4. Experimental

4.1. 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, diethylether, toluene) or from phosphorus pentoxide (dichloromethane, acetonitrile). ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker model AM300 and DPX200 spectrometers. ^1H and ^{13}C NMR chemical shifts were reported in parts per million (ppm) relative to Me_4Si as an 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 atoms was based on HMBC and HMQC experiments. High-resolution mass spectra were obtained on a Varian MAT 311 or ZabSpec TOF Micromass at the CRMPO, University of Rennes. Elemental analyses were performed by the CRMPO or the Center de Microanalyse du CNRS, Vernaison, France.

4.2. Standard procedure for isoprene telomerization

A solution of 0.025 mmol of the ligand in dichloromethane was added to a solution of the metallic precursor (0.025 mmol) in dichloromethane. The mixture was stirred for 2 h, after which the solvent was removed. Then the solvent used for the catalytic test was added. After 30 min of stirring, an excess of isoprene (0.5 mL) and diethylamine (0.5 mL) were injected into the reaction mixture. The reaction was stirred for 48 h at 40 °C, after which flash chromatography was done to stop the reaction and the liquid filtrate was injected in GC–MS.

4.3. [1-Phenyl-2,5-di(2-pyridyl)phosphole]Pd(allyl)BF_4^- 9

A solution of 1-phenylphosphole **5a** (0.33 g, 0.90 mmol) in dichloromethane (5 mL) was added to a solution of $[Pd(allyl)Cl]_2$ (0.08 g, 0.45 mmol) in dichloromethane (3 mL). Then one equivalent of silver tetrafluoroborate $AgBF_4$ was added to the reaction mixture. The solution was filtered on Celite, and the solvent was removed. The product was washed with diethyl ether (2×5 mL), affording **9** as an air-stable yellow solid (yield, 0.51 g, 0.86 mmol, 96%). ^1H NMR (200 MHz, $CDCl_3$): $\delta =$ 1.83 (m, 6H; CH_2 and syn-H allyl), 2.92 (d, $^3J_{H-H} = 18.8$ Hz, 2H; anti-H allyl), 3.36 (d, $^3J_{H-H} = 12.5$ Hz, 2H; anti-H allyl), 4.24 (m, 4H; CH_2), 5.9 (broad s, 1H; H allyl), 7.26–7.34 (m, 6H; arom-H Ph and H^5 Py), 7.41–7.58 (m, 3H; H^3 Py), 7.88 (t, $^3J_{H-H} = 7.4$ Hz, 2H; H^4 Py), 8,67 (d, $^3J_{H-H} = 4.8$ Hz, 2H; H^6 Py). $^{13}C\{^1H\}$ NMR (50.323 MHz, $CDCl_3$): $\delta = 22.5$ (s, $C{=}CCH_2CH_2$), 22.3 (d, $J_{P-C} = 2.4$ Hz, $C{=}CCH_2$), 52.4 (s, $CH{=}CH_2$), 123.4 (s, C^5 Py), 124.3 (d, $J_{P-C} = 6.73$ Hz, C^3 Py), 126.9 (d, $J_{P-C} = 43.0$ Hz, ipso-C Ph), 129.5 (d, $J_{P-C} = 11.4$ Hz, m-C Ph), 131.7 (s, CH_2CH allyl), 131.8 (s, p-C Ph), 133.7 (d, $J_{P-C} = 13.5$ Hz, o-C Ph), 138.6 (s, C^4 Py), 140.0 (d, $J_{P-C} = 47.6$ Hz, $PC^{\alpha}{=}C$), 151.1 (d, $J_{P-C} = 11.0$ Hz, C^2 Py), 152.7 (s, C^6 Py), 153.1 (d, $J_{P-C} = 21.8$ Hz, $PC{=}C^{\beta}$). $^{31}P\{^1H\}$ NMR (81.014 MHz, $CDCl_3$): $\delta = +49.7$; HR–MS (ESI) m/z: 515.0879 [M^+]. Calcd. for $C_{27}H_{26}N_2PPdBF_4$: 515.0877; elemental analysis (%) calcd. for $C_{27}H_{26}N_2PPdBF_4$(515.0879): C 53.81, H 4.35, N 4.65; found: C 53.85, H 4.32, N 4.62.

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