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Synthesis of the new chiral tridentate ligand bis(pyrid-2-ylethyl) menthylphosphine and its use in the palladium-catalyzed allylic alkylations

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Abstract

We describe the synthesis of a new asymmetric *P*,*N*,*N*′-tridentate ligand (bis(pyrid-2-ylethyl) menthylphosphine, BPEMP), containing two pyridyl rings and (1*S*,2*R*,5*S*)-menthylphosphino group. The ligand is obtained in five steps from natural abundant *l*-menthol. The coordination behavior of the ligand toward cationic (allylic)Pd(II) moiety and its first application in palladium-catalyzed asymmetric allylic alkylation are presented. Crystallographic and spectroscopic analyses reveal that $[(\eta^3\text{-allylic})\text{Pd(BPEMP)}]^+$ complex forms only one isomer in the solid state as well as in solution.

Keywords: Palladium; Chiral tridentate ligand; Allylic alkylation; Asymmetric induction

1. Introduction

The development of transition metal complexes containing chiral ligands to catalyze asymmetric organic reactions represents one of the most important achievements of modern organometallic chemistry, and high selective catalysts are now available to catalyze an impressive range of reactions. Progress in asymmetric catalysis relies on the design of new chiral ligands. The vast majority of these ligands exhibiting high enantioselectivity have been prepared by taking advantage of elaborated asymmetric molecules as starting materials; the synthesis of these optically pure starting materials often involves tedious routes that are limited to only one antipode or require a resolution step. Consequently, difficult and specialized procedures involved in preparing these ligands limit their synthetic potential. Thus, special efforts have been devoted toward the synthesis of easily accessible ligands based on high natural abundant materials [1]. Along these lines, we designed a new chiral tridentate ligand (bis(pyrid-2-ylethyl) menthylphosphine), abbreviated BPEMP (Chart 1), which was obtained in five steps from inexpensive *l*-menthol. It has been recognized that chiral tridentate ligands generally form a deeper chiral concave pocket around the metal center than the corresponding chiral bidentate ligands [2].

In this ligand, we envisioned that due to chiral (1*S*,2*R*,5*S*)-menthyl group, the two labile pyridyl groups become diastereotopic, so as to make its metal complexes asymmetric. In addition, this heteroatomic donor ligand possesses both "hard" nitrogen and "soft" phosphorus centers. Such heterofunctional ligands containing soft and hard donor sites are of considerable current interest in connection with the development of novel homogeneous catalysts [3]. For example, the previously reported bis(pyrid-2-ylethyl) cyclohexylphosphine, which is closely related to BPEMP, is a promising ligand for palladium-catalyzed dimerization of isoprene with carbon dioxide [3b]. This tridentate ligand was found to be more effective than tricyclohexyl-phosphine in the transformation; it is conceivable

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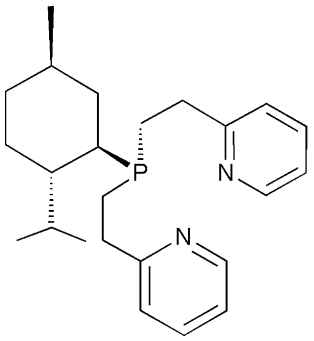


BPEMP

Chart 1.

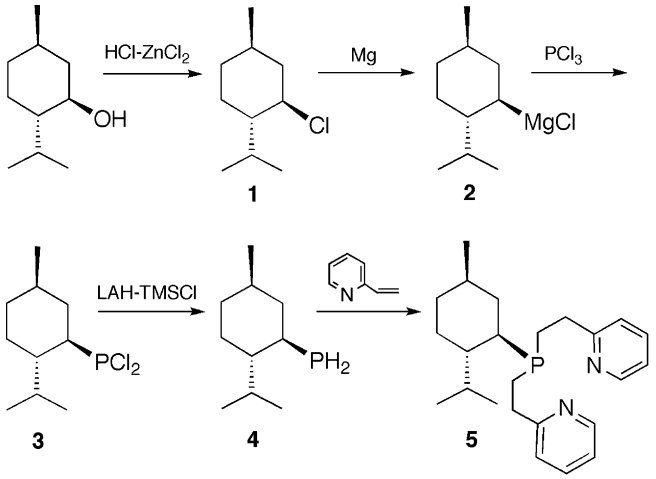
that the pyridyl groups coupled with the cyclohexylphosphine moiety activate an intermediate η-allyl palladium complex. Hence, we set out exploring the application of BPEMP to a palladium catalyzed allylation reaction.

In this paper, we report (1) the ready synthesis of new BPEMP ligand, (2) its subsequent application in the asymmetric catalytic bond forming reaction, and (3) the synthesis and structure of the cationic Pd-allyl intermediate containing BPEMP.

2. Results and discussion

2.1. Synthesis of BPEMP (5)

We have synthesized this ligand through the route shown in Scheme 1. The (−)-menthyl chloride (**1**) was obtained in 84% yield from (1*R*,2*S*,5*R*)-(−)-menthol [4]. Treatment of **1** with a moderate excess of Mg in THF at 70 °C gave the Grignard reagent **2**, which then was reacted with PCl_3 to give menthyldichlorophosphine (**3**) [5a]. Initially, the reduction of **3** was carried out using Ph_2SiH_2 as reducing reagent [6], but this method did not lead to the desired product **4**; no reaction occurred up to 200 °C.



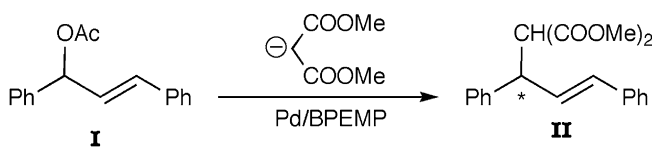
Scheme 1.

However, the reduction of **3** with $LiAlH_4$ in the presence of trimethylsilyl chloride proceeded in a straightforward manner to produce **4** in reasonable yield (70%) [7]. The tridentate ligand (**5**) was prepared from **4** by adaptation of a method described by Toto and Doi for the synthesis of (pyrid-2-ylethyl)diphenylphosphine [8]. Thus subsequent treatment of **4** with 2 equiv. of distilled 2-vinylpyridine in the presence of catalytic amounts of glacial acetic acid resulted in the formation of **5** (BPEMP). The product **5** is high-boiling (ca. 200 °C at 0.05 mmHg), air-sensitive liquid that was characterized by spectroscopic analyses. In the ^1H NMR, besides the resonances for the menthyl group, the resonances for the pyrid-2-ylethyl groups are observed. The pyridine protons resonate between δ 6.8 and 8.5 ppm. Two sets of the ethylene resonances for the pyrid-2-ylethyl groups are observed between δ 2 and 3 ppm. In addition, the P-CH_2CH_2-py peaks occur at δ 35.8 ($J_{P-C} = 21$ Hz) and 36.4 ppm ($J_{P-C} = 13$ Hz), respectively in the ^{13}C NMR spectrum. These results indicate that the two pyridyl groups become diastereotopic; the presence of the chiral menthyl group imparts asymmetry to the molecule and hence inequivalence of the two pyridyl groups of the ligand. The $^{31}P\{^1H\}$ NMR spectrum of the ligand **5** shows one singlet at −22.3 ppm.

2.2. Allylic substitution with BPEMP-palladium catalyst

Next, the effectiveness of the ligand **5** in palladium catalyzed allylation reactions was tested. Asymmetric catalytic bond forming reactions promoted by palladium complexes containing chiral ligands have become an indispensable tool in synthetic chemistry [9]. Especially the racemic (*E*)-1,3-diphenyl-3-acetoxyprop-1-ene (**I**) has been usually used as a model molecule in enantioselective palladium catalyzed nucleophilic allylic substitution (Scheme 2) [10].

The catalytic runs were carried out using the allylic dimmer complex, $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, as precatalyst and sodium dimethyl malonate as nucleophile under the typical experimental conditions defined in Table 1. The chemical identity of the alkylated product (**II**) was checked by NMR. THF, toluene, CH_3CN, and CH_2Cl_2 were examined as solvent; the optimum activity was obtained in THF solution. As can be seen, the highest ee (53%) was found to be achieved at 0 °C (entry 5), while it decreased at −20 °C (entry 6). Interestingly the Pd/ligand ratio influences both the optical and product yields (entries 10, 12); the 1:4 ratio is highly efficient in this case. Asymmetric induction exceeds 50% in this system, although it has been recognized that the monodentate chiral ligand derived from (1*R*,2*S*,5*R*)-(−)-



Scheme 2.

Table 1
Results of asymmetric allylic alkylation of **I** with dimethyl malonate catalyzed by $[PdCl(C_3H_5)]_2$/BPEMP

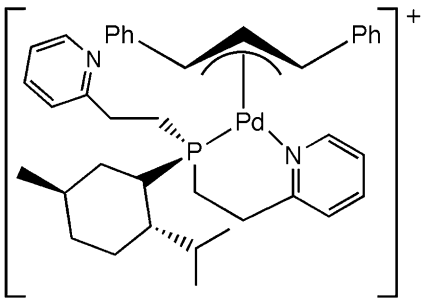
Entry	Ratio	Solvent	Conditions		Yield (%)	ee II (%)
	Pd/BPEMP/**I**		*t* (h)	*T* (°C)		
1	1/4/100	CH_2Cl_2	48	r.t.	36	26
2	1/4/100	CH_2Cl_2	8	0	13	32
3	1/4/100	THF	24	r.t.	80	22
4	1/4/100	THF	8	r.t.	71	26
5	1/4/100	THF	24	0	63	53
6	1/4/100	THF	72	−20	57	21
7	1/4/100	Toluene	24	r.t.	70	12
8	1/4/100	CH_3CN	5	r.t.	10	20
9	1/2/100	THF	24	r.t.	47	23
10	1/2/100	THF	24	0	24	28
11	1/6/100	THF	24	r.t.	56	20
12	1/6/100	THF	24	0	27	15

menthol is ineffective as asymmetric ligand [5]. Thus, the P–N chelation effect of BPEMP may play a crucial role in the present asymmetric induction reaction.

2.3. Complex formation and crystal structure

In order to define the structure of a key intermediate in the present reaction as well as the conformational properties of the ligand **5**, $[(\eta^3\text{-allylic})Pd(BPEMP)]^+$ complex was prepared from $Pd_2(dba)_3$, BPEMP, and (*E*)-1,3-diphenyl-3-acetoxyprop-1-ene. The resulting complex **6** (Chart 2) was isolated as its hexafluorophosphate salt. The study of the solid-state and solution characteristics of such 1,3-diphenylallyl-Pd complexes has attracted considerable interest in recent decades [11].

The complex **6** was crystallized from CH_2Cl_2/ethanol, and an ORTEP plot of the cation is shown in Fig. 1. The more important bond lengths and bond angles are given in Table 2. A summary of the crystallographic data is given in Table 3 (see Section 4). Interestingly unlike analogous π-allyl palladium complexes containing chiral chelating ligands [9,12], no diastereoisomers were observed for **6**; only the 'exo' isomer (the central C-atom of the allyl moiety points toward the menthyl group) exists in the solid state. The X-ray analysis shows the existence of both the chelating and uncoordinated pyridyl moiety together with



6

Chart 2.

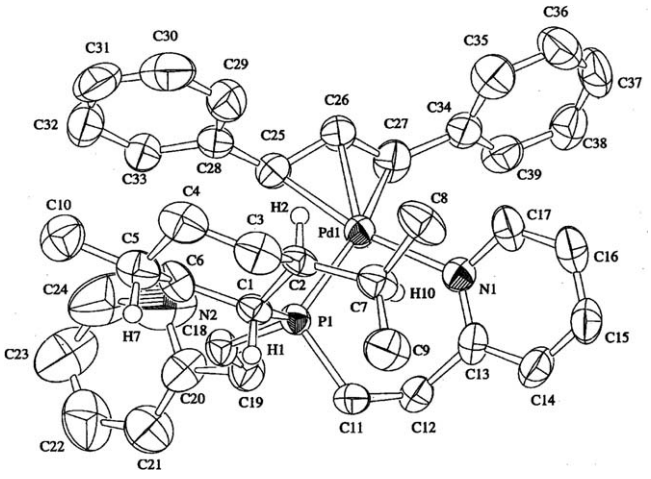


Fig. 1. Molecular structure of **6**.

Table 2
Interatomic distances (Å) and angles (°) for **6**

Distances			
Pd1–P1	2.302(2)	Pd1–N1	2.122(7)
Pd1–C25	2.161(8)	Pd1–C26	2.173(7)
Pd1–C27	2.279(9)	P1–C11	1.843(8)
C25–C26	1.42(1)	C25–C28	1.46(1)
C26–C27	1.36(1)	C27–C34	1.49(1)
Angles			
P1–Pd1–N1	93.3(2)	P1–Pd1–C25	99.9(2)
P1–Pd1–C27	155.8(3)	N1–Pd1–C27	101.4(3)
C25–Pd1–C26	38.4(3)	C25–Pd1–C27	65.9(3)
C26–Pd1–C27	35.5(3)	Pd1–N1–C13	125.0(6)
C25–C26–C27	120.5(10)	Pd1–C25–C26	71.3(4)

the π-allyl ligand. As expected for $[Pd^{II}(allyl)]$ complexes of this type, the local coordination geometry is distorted square planar, with the P, N, and C atoms of the allyl group making up the ligand coordination sphere [12,13]. The six-membered chelating ring adapts a boat-like structure, which is similar to a π-allyl Pd(II) complex containing a N,N-donor ligand [9b]. The Pd1–N1 distance of 2.122(7) Å is slightly shorter than that reported for $[Pd(\eta^3\text{-PhCHCHCHPh})(TMEDA)]^+$ (**A**, 2.161(3) Å) [11a]. Furthermore, the Pd1–P1 bond length of 2.302(2) Å is also shorter than that of 2.342(1) Å in the related bis(triphenylphosphine) complex $[Pd(\eta^3\text{-PhCHCHCHPh})(PPh_3)_2]^+$ (**B**) [14]. These observations demonstrate that the P, N donors of BPEMP are attached rigidly to the central metal.

Although the bond lengths and bond angles of the $(\eta^3$-allylic)Pd core are within the expected range reported for several related complexes involving π-allyl ligands, there are some features in the structure of **6** that are worthy of note. The significantly smaller C25–Pd–C27 angle (65.9(3)°) in **6** versus that in **A** (67.4(2)°) coincides with longer Pd–C bond distances observed in the former. This included angle is found to be intermediate between **A** and **B** (64.9(2)°). The Pd–C bond to the terminal allylic C-atom *trans* to the P-atom is significantly longer than that to the C-atom *trans* to the N-atom (Pd1–C27 = 2.279(9) Å,

Table 3
Summary of crystal data for **6**

Empirical formula	$C_{39}H_{48}F_6N_2P_2Pd$
Formula weight	827.16
Temperature	23 °C
Crystal dimensions	$0.30 \times 0.18 \times 0.15$ mm
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (# 19)
Lattice type	Primitive
Lattice parameters	
a (Å)	17.667(4)
b (Å)	20.585(6)
c (Å)	10.892(3)
β (°)	106.34(5)
V (Å^3)	3960(1)
Z value	4
D_{calcd} (g/cm^3)	1.387
$F(000)$	1704.00
μ(Mo Kα) (cm^{-1})	6.07
Number of reflections used for unit cell determination (2θ range)	25 (28.3–30.0°)
2θ max (°)	60.0
Scan rate	16.0°/min (in ω) (up to 3 scans)
Number of reflections measured	Total: 6479 Unique: 6352 ($R_{int} = 0.206$)
Number of reflections (all, $2\theta < 60.02°$)	6327
Number of variables	451
Residuals: R; Rw	0.130; 0.167
Goodness-of-fit	1.32

Pd1–C25 = 2.161(8) Å). This is an expression of the higher *trans* influence of the phosphine ligand [15]. For the P,N-ligand systems developed by Pfaltz and Helmchen [16], and Brown et al. [17], it is generally agreed that the nucleophilic attack takes place preferentially at the allyl terminus *trans* to phosphorus. Thus, attack at this position allows one to rationalize the observed enantiomer in the catalytic experiment.

A detailed NMR assignment for the complex was made by comparison and by analogy with the NMR data for the related π-allyl palladium complexes containing P,N-heterodonating ligands [9,12] and the ligand BPEMP itself. The $^{31}P\{^1H\}$ NMR spectrum at room temperature shows only one sharp resonance, which is shifted downfield by about 70 ppm with respect to that of **5**, verifying that the phosphorus atom is coordinated to the metal center in solution. On the other hand, the ^1H NMR spectrum of **6** reveals a broad doublet centered at about 8.45 ppm, assignable to the proton resonances of the 6-position of the pyridyl rings. This value was sifted downfield by only 0.04 ppm with respect to that of **5** and we were unable to distinguish unequivocally between the free and the coordinated pyridine in the ^1H NMR spectrum, thus suggesting that the pyridine group is weakly coordinated in solution. Taking into account the hemilabile character of BPEMP ligand, these behaviors are not unexpected. The allyl moiety gives only one set of signals in the ^{13}C NMR spectrum (68.77, C25; 75.26, C27; 109.87, C26), which is in accord with the X-ray diffraction data. Namely complex **6** forms only one isomer in solution as well as in the solid state.

3. Conclusion

We have shown that a new asymmetric *P*,*N*,*N*′-tridentate ligand (BPEMP) incorporating two pyridyl rings and (1*S*,2*R*,5*S*)-menthylphosphino group is easily obtained in five steps from natural abundant *l*-menthol. The application of the resulting ligand in the asymmetric Pd-catalyzed allylic alkylation led to the formation of the alkylated product with enantiomeric excesses up to 53% ee. Since the menthyl group is generally regarded as ineffective chiral auxiliary for asymmetric ligands, the discriminative coordination of one of the pyridyl rings in BPEMP is considered as the source of asymmetric induction.

The chirality on this new ligand can be readily fine-tuned by incorporating different chiral groups. Thus, the present simple synthetic approach allows the preparation of a great variety of chiral tridentate ligands having a breadth of electronic and steric properties.

4. Experimental

4.1. General procedures

Unless otherwise noted, all manipulations were conducted using standard Schlenk techniques under purified argon or nitrogen. Commercially available reagent grade chemicals were used as such without any further purification. All solvents were dried by standard methods and were stored under argon. The new compounds were characterized by IR, ^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR spectroscopy. C–H COSY decoupling experiment was used to gain additional structure information. All NMR spectra were recorded on a JEOL-JNM-270 spectrometer. $^{31}P\{^1H\}$ NMR peak positions were referenced to external PPh_3. (−)-Menthyl chloride [4], menthyldichlorophosphine [5a], (*E*)-1,3-diphenyl-3-acetoxyprop-1-ene [18], and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ [19] were prepared according to the published methods.

4.2. Synthesis of menthylphosphine (*4*)

A two-necked, round-bottomed flask equipped with a gas inlet, a dropping funnel, and a stirrer was flushed with N_2. The flask was charged with $LiAlH_4$ (5.51 g, 145 mmol) suspended in THF (74 ml), which was cooled to −60 °C. Under rapid stirring, trimethylsilyl chloride (18.4 ml, 145 mmol) was added slowly to the flask from the dropping funnel. After the addition was complete, the mixture was allowed to warm to room temperature and was stirred for 120 min. It was then cooled to −60 °C once more, whereupon menthyldichlorophosphine (**3**, 11.1 g, 46 mmol) in THF (110 ml) was carefully added. After the addition was complete, the mixture was allowed to warm to room temperature and was stirred for 36 h. The resulting mixture was treated with water (37 ml) and aq NaOH (1 M, 74 ml), and then extracted with diethyl ether (3×100 ml). The combined organic layers were evaporated under reduced

pressure. Fractional distillation of the crude product gave menthylphosphine (**4**, 5.54 g, 70% yield, 102 °C/18 mmHg).

^{1}H NMR (270 MHz, C_6D_6): $\delta = 2.99$ (ddd, $^3J_{H-H} = 5.5$ Hz, $^2J_{H-H} = 12.2$ Hz, $^1J_{P-H} = 55.8$ Hz, 1H, P*H*), 2.29 (ddd, $^3J_{H-H} = 5.5$ Hz, $^2J_{H-H} = 12.2$ Hz, $^1J_{P-H} = 55.8$ Hz, 1H, P*H*), 2.09 (m, 1H, C*H*$(CH_3)_2$), 0.60–1.80 (m, 9H, ring protons of the menthyl group), 0.85 (d, 3H, $^3J_{H-H} = 6.9$ Hz, CH(C*H*$_3)_2$), 0.79 (d, 3H, $^3J_{H-H} = 6.3$ Hz, C*H*$_3$), 0.71 (d, 3H, $^3J_{H-H} = 6.9$ Hz, CH(C*H*$_3)_2$).

^{13}C NMR (C_6D_6): $\delta = 48.1$ (*C*HCH$(CH_3)_2$), 46.7 (PCH*C*H$_2$), 35.4 (CH_3CH*C*H$_2$), 34.0 (P*C*H), 30.2 (CH_3*C*H), 29.4 (($CH_3)_2$*C*H), 25.3 (($CH_3)_2$CHCH*C*H$_2$), 22.5 (*C*H$_3$), 21.7 ((CH$_3)_2$CH), 15.2 ((CH$_3)_2$CH).

^{31}P NMR (C_6D_6): $\delta = -116.3$.

4.3. Synthesis of BPEMP (5)

A Schlenk flask equipped with a condenser and a stirrer was flushed with N_2. The flask was charged with menthylphosphine (**4**, 5.49 g, 32 mmol), glacial acetic acid (0.70 ml), and distilled 2-vinylpyridine (8.76 ml, 81 mmol). The solution was heated with stirring at 150 °C for 8 h. The crude mixture was dissolved in methanol (30 ml) and made basic with solid potassium carbonate. The precipitate was removed by suction filtration through Celite and the filtrate was concentrated under vacuum to give a viscous oil. Fractional distillation of the crude product gave BPEMP (**5**, 6.15 g, 50% yield, ca. 200 °C/0.05 mmHg) as a yellow viscous oil. The compound was found to be air-sensitive and had to be stored under N_2.

^{1}H NMR (270 MHz, C_6D_6): $\delta = 8.40 - 8.60$ (m, 2H, H6 of pyridyl ring), 6.65–7.30 (m, 6H, pyridyl ring), 2.80–3.15 (m, 4H, PCH$_2$C*H*$_2$-py) 2.73 (m, 1H, C*H*$(CH_3)_2$), 0.60–2.15 (m, 13H, ring protons of the menthyl group and PC*H*$_2$-CH$_2$-py), 0.84 (d, 3H, $^3J_{H-H} = 6.9$ Hz, CH(C*H*$_3)_2$), 0.84 (d, 3H, $^3J_{H-H} = 6.9$ Hz, C*H*$_3$), 0.83 (d, 3H, $^3J_{H-H} = 6.9$ Hz, CH(C*H*$_3)_2$).

^{13}C NMR (C_6D_6): $\delta = 162.6 - 120.9$ (C_5H_4N), 44.9–22.0 (ring carbons of the menthyl group, *C*H$(CH_3)_2$, and P*C*H$_2$CH$_2$-py), 36.4 (PCH$_2$*C*H$_2$-py), 35.8 (PCH$_2$*C*H$_2$-py), 22.7 (*C*H$_3$), 21.6 ((CH$_3)_2$CH), 15.3 ((CH$_3)_2$CH).

^{31}P NMR (C_6D_6): $\delta = -22.3$.

IR (neat): 2951, 2923, 1591, 1568, 1472, 1434, 771, 750.

4.4. Enantioselective Pd-catalyzed allylic alkylation

Experiments were carried out at different temperatures, different reaction times, and different catalyst concentrations in various kinds of solvents as reported in Table 1. A typical procedure is as follows. The catalytic precursor was generated in situ from [Pd(η^3-C_3H_5)Cl]$_2$ (3.1 mg, 0.0086 mmol) and BPEMP (**5**, 13.1 mg, 0.0344 mmol) in THF (3.0 ml) for 40 min before adding a solution of (*E*)-1,3-diphenyl-3-acetoxyprop-1-ene (**I**, 0.200 g, 0.80 mmol) in THF (1.0 ml). In a separate flask, dimethyl malonate (0.19 ml, 1.65 mmol) was added to a slurry of hexane-washed sodium hydride (38 mg, 1.59 mmol) in THF (3.0 ml). To the resulting clear solution of sodium dimethyl malonate was added the former by a syringe, and the combined mixture was stirred at 0 °C for 24 h. The reaction mixture was partitioned between ether and water. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and then concentrated in vacuo. The residue was purified by a column chromatography (SiO_2; *n*-hexane/ethyl acetate (15/1)) to give the alkylated product (**II**, 63%). The chemical identity of the product was checked by NMR. Evaluation of the optical yields was performed by HPLC using a commercial CHIRALCEL OD column.

4.5. Synthesis of [Pd(η^3-PhCHCHCHPh)(BPEMP)]$^+PF_6^-$ (6)

A Schlenk flask equipped with a stirrer was flushed with N_2. The flask was charged with BPEMP (**5**, 76 mg, 0.199 mmol), $Pd_2(dba)_3$ (92 mg, 0.100 mmol), and dry CH_2Cl_2 (10 ml). To the resulting solution was added (*E*)-1,3-diphenyl-3-acetoxyprop-1-ene (**I**, 50 mg, 0.199 mmol), and the combined mixture was stirred at room temperature for 30 min. During this period the solution changed from dark purple to dark green. The solvent was removed at reduced pressure, and the remaining content was washed with *n*-hexane (15 ml × 3). To the residue was added KPF_6 (50 mg, 0.27 mmol) and acetone (5 ml), and the mixture was stirred at room temperature for 12 h. After removal of the solvent under reduced pressure, the residual mixture was washed with *n*-hexane (15 ml × 3) and then extracted with CH_2Cl_2. The solution was filtered through a filter paper and the resulting orange solution was evaporated to dryness. The residue was recrystallized (CH_2Cl_2/ethanol) in a refrigerator. Compound **6** was obtained as a yellow plate (107 mg, 63%).

^{1}H NMR (270 MHz, C_6D_6): $\delta = 8.34 - 8.50$ (m, 2H, H6 of pyridyl ring), 7.13–7.80 (m, 16H, CH_{arom}), 6.61–6.81 (m, 1H, PhCHC*H*CHPh), 5.64–5.76 (m, 1H, PhC*H*CHCHPh (*trans* to P)), 4.83–4.93 (m, 1H, PhCHCHC*H*Ph (*trans* to N)), 3.00–3.27 (m, 4H, PCH$_2$C*H*$_2$-py) 2.78–2.85 (m, 1H, C*H*$(CH_3)_2$), 0.42–1.81 (m, 18H, ring protons of the menthyl group, PC*H*$_2$CH$_2$-py, CH(C*H*$_3)_2$, and C*H*$_3$).

^{13}C NMR (C_6D_6): $\delta = 143.2 - 128.3$ (py and Ph), 109.9 (C26), 75.3 (C27), 68.8 (C25), 44.6–24.7 (ring carbons of the menthyl group, *C*H$(CH_3)_2$, and P*C*H$_2$CH$_2$-py), 36.3 (PCH$_2$*C*H$_2$-py), 35.9 (PCH$_2$*C*H$_2$-py), 22.5 (*C*H$_3$), 21.7 ((CH$_3)_2$CH), 15.5 ((CH$_3)_2$CH).

^{31}P NMR ($CDCl_3$): $\delta = 50.7$.

IR (KBr): 3059, 3026, 2958, 2869, 1737, 1651, 1624, 1603, 1575, 1494, 1449, 1339, 1189, 1099, 1017, 984, 838.

4.6. X-ray crystal structure analysis of 6

A simple crystal of **6** was mounted on a glass fiber. All measurements were made on a Rigaku AFC-7R diffractometer by using Mo Kα radiation ($\lambda = 0.71069$ Å) with $\mu = 6.07$ cm^{-1} and $F(000) = 1704.00$ Å. The unit-cell parameters were obtained from a least-squares refinement

using the setting angles of 25 carefully centered reflections in the range $28.3° \leqq 2\theta \leqq 30.0°$. The parameters used during the collection of diffraction data are given in Table 3. The structure was solved and expanded by using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

CCDC reference number 291390. See http://www.rsc.org/suppdata/dt/b2/b209624m/ for crystallographic data in CIF or other electronic format.

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