Synthesis and Characterization of a Novel Chiral Phosphole and Its Derivatives

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Received November 13, 2000

A novel chiral and enantiomerically pure phosphole with two (−)-menthyl groups at the 2- and 5-positions of the phosphole ring is prepared in two steps, starting from (−)-menthylacetylene, in 67% overall yield. This is the first example of a chiral phosphole in which chiral substituents attach directly to the carbon atoms of the phosphole ring. The phosphole was characterized by X-ray crystallography, and its solid-state structure has no symmetry, with an envelope-like bent structure for the five-membered ring. The phosphole was readily oxidized into the corresponding phosphole oxide, and reaction with MCl_2(cod) (M = Pt, Pd) led to two chiral phosphole−transition-metal complexes, *trans*-MCl_2(phosphole)$_2$, quantitatively. Treatment of the phosphole with metallic lithium in THF cleaved the exocyclic P−Ph bond to give a chiral lithium phospholide with retention of the two (−)-menthyl substituents. The lithium phospholide was converted into a chiral diphosphole in 62% yield by reaction with $BrCH_2CH_2Br$ and into a chiral monophosphaferrocene in 85% yield by reaction with [(η^6-mesitylene)FeCp]PF_6. A reaction of the phosphole with $Mn_2(CO)_{10}$ in refluxing xylene gave a chiral phosphacymantrene in 84% yield.

Introduction

Phospholes and their anionic derivatives (phospholides; phospholyl anions) show a variety of coordination modes as ligands to transition metals, and thus, they are a very attractive subject of organotransition-metal chemistry.[1] By the pioneering works of Mathey and other researchers,[1] the versatile potential of these species as multifunctional ligands has been demonstrated. However, their steric modifications have been limited so far.[2] We started this project with the intention of introducing chirality onto the phosphole. Reported chiral phospholes are still very few, and to the best of our knowledge, all of them possess the chiral substituents on their phosphorus atoms.[3] Conversion of phospholes into the corresponding phospholyl anions (or phosphametallocenes) is accompanied by cleavage of exocyclic P−C bonds; thus, the chiral groups in these phospholes will be lost during the transformation process. Gladiali and co-workers reported phospholes with two fused naphthalene units, whose frameworks are similar to that of BINAP.[2a] In these molecules, atropisomeric chirality based on the binaphthyl skeletons is not stable at room temperature, and thus the phosphole is *not* isolated in an optically active form. Here we wish to report the first example of a chiral phosphole, in which chiral substituent (−)-menthyl groups attach directly to the carbon atoms of the phosphole ring, and two of its transition-metal complexes. The chiral phosphole can be transformed into the corresponding phospholide and chiral phosphametallocenes by conventional methods. During all these transformation processes, the (−)-menthyl groups were retained and, thus, all the products were obtained in chiral and enantiomerically pure forms. Recently, Ganter[4] and Fu[5] reported several enantiomerically pure planar chiral phosphaferrocenes with unsymmetrically substituted phospholides. They started syntheses of the complexes from racemic precursors and resolved the racemates either by derivatization into diastereomers using chiral auxiliaries[4a] or by chiral HPLC.[5] On the other hand, the chiral phosphametallocenes prepared from our chiral phosphole were obtained in enantiomerically pure forms without resolution.

Results and Discussion

Preparation and Characterization of a Chiral Phosphole and Its Oxide. The chiral phosphole **1** was obtained as a colorless crystalline solid in two steps starting from (−)-menthylacetylene,[6] as shown in Scheme 1.

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[1] Reviews: (a) Mathey, F.; Fischer, J.; Nelson, J. H. *Struct. Bonding* **1983**, *55*, 153. (b) Mathey, F. *New J. Chem.* **1987**, *11*, 585. (c) Mathey, F. *Chem. Rev.* **1988**, *88*, 429. (d) Mathey, F. *J. Organomet. Chem.* **1990**, *400*, 149.

[2] (a) Dore, A.; Fabbri, D.; Gladiali, S.; De Lucchi, O. *J. Chem. Soc., Chem. Commun.* **1993**, 1124. (b) Carmichael, D.; Ricard, L.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1167. (c) Forissier, K.; Ricard, L.; Carmichael, D.; Mathey, F. *Chem. Commun.* **1999**, 1273.

[3] For examples of phospholes with chiral P-substituents, see: (a) Dang, T. P.; Poulin, J. C.; Kagan, H. B. *J. Organomet. Chem.* **1975**, *91*, 105. (b) Brunet, J. J.; Gomez, M.; Hajouji, H.; Neibecker, D. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *85*, 207. (c) Toth, I.; Elsevier, C. J.; de Vries, J. G.; Bakos, J.; Smets, W. J. J.; Spek, A. L. *J. Organomet. Chem.* **1997**, *540*, 15. (d) Schenk, W. A.; Stubbe, M.; Hagel, M. *J. Organomet. Chem.* **1998**, *560*, 257.

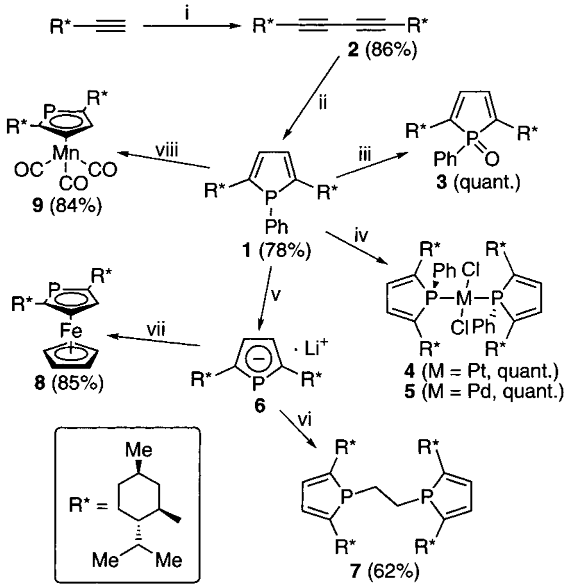
[4] (a) Ganter, C.; Brassar, L.; Ganter, B. *Tetrahedron: Asymmetry* **1997**, *8*, 2607. (b) Ganter, C.; Glinsböckel, C.; Ganter, B. *Eur. J. Inorg. Chem.* **1998**, 1153. (c) Ganter, C.; Kaulen, C.; Englert, U. *Organometallics* **1999**, *18*, 5444.

[5] (a) Qiao, S.; Hoic, D. A.; Fu, G. C. *Organometallics* **1998**, *17*, 773. (b) Qiao, S.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 4168.

[6] Spence, J. D.; Wyatt, J. K.; Bender, D. M.; Moss, D. K.; Nantz, M. H. *J. Org. Chem.* **1996**, *61*, 4014.

10.1021/om000952d CCC: $20.00 © 2001 American Chemical Society
Publication on Web 02/02/2001

Scheme 1[a]



[a] Reagents and conditions: (i) CuCl, TMEDA, O_2, 50 °C in acetone; (ii) $PhPH_2$, BuLi, THF$-C_6H_6$ reflux, then H_2O; (iii) H_2O_2; (iv) MCl_2(cod) in $CHCl_3$ (for Pt) or in CH_2Cl_2 (for Pd); (v) Li (excess) in THF; (vi) $BrCH_2CH_2Br$ in THF; (vii) $[(\eta^6$-mesitylene)FeCp]PF_6 (2 equiv) in THF; (viii) $Mn_2(CO)_{10}$, xylene reflux.

The (−)-menthylacetylene was oxidatively coupled by a well-known copper-promoted reaction[7] to give 1,4-bis-((−)-menthyl)-1,3-butadiyne (**2**) in 86% yield. The diyne **2** underwent cycloaddition with $PhPH_2$ according to a reported procedure using a catalytic amount of butyllithium;[8] however, the product was obtained as a complex mixture of uncharacterized species with a trace amount of **1** (<1% by ^{31}P NMR). After modification of the reaction conditions, it was found that reaction of **2** with 3 equiv of PhPHLi, which was generated in situ from $PhPH_2$ and butyllithium, in a THF$-C_6H_6$ mixture at reflux temperature for 1.5 h followed by hydrolysis gave the chiral phosphole **1**, which was isolated in pure form in 78% yield by column chromatography over SiO_2 (with hexane/$CHCl_3$ = 10/1) under nitrogen. The phosphole is air sensitive in solution but is air stable in the crystalline form and can be stored under air for several months without oxidation. Single-crystal X-ray analysis of **1** (Figure 1 and Tables 1 and 2) revealed that the solid-state structure of the phosphole was asymmetric, with an envelope-like bent phosphole ring in which the $C_\alpha-C_\beta$ distance is 1.335 Å (mean value) and the $C_\beta-C_\beta$ distance is 1.465 Å. The difference between the two values, 0.13 Å, is quite large compared to those of the other structurally characterized phospholes,[9] indicating weaker electronic delocalization (less aromatic) in **1**. This is in clear contrast to the recent reports by Quin on the enhancement of aromaticity of phospholes by bulky P substituents.[10] The effect of electron delocalization (aromaticity) in the phospholes can be quantitatively compared using an index developed by Bird.[11]

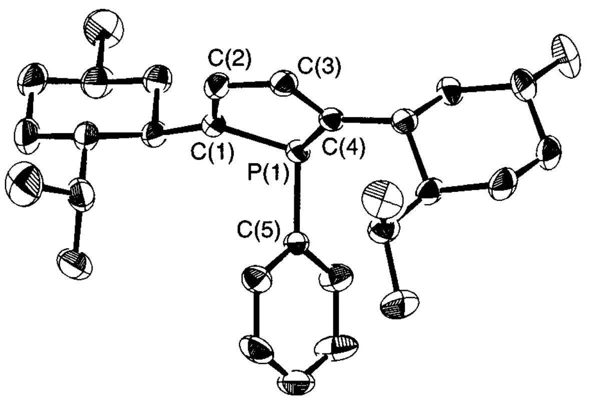


Figure 1. Crystal structure of **1** with thermal ellipsoids at the 30% probability level. All hydrogen atoms are omitted for clarity.

The Bird index of **1** was calculated to be 15.2, which is one of the smallest values reported to date for phospholes,[10c,11b] indicating the low aromaticity of **1**.

On the other hand, the phosphole **1** showed a rapid isomerization process in solution with inversion at the phosphorus center.[12] Thus, in the ^{1}H NMR spectra **1** showed time-averaged signals and was observed as a pseudo-C_2-symmetric molecule at and above room temperature. Lowering the temperature decoalesced the resonance of the two diastereotopic β-hydrogens into the partially overlapped eight lines of an ABX pattern (coupled with the phosphorus) at and below −10 °C (see Figure 2). The thermodynamic parameter of the fluxional process at 10 °C (coalescence temperature of the β-hydrogen signals at 500 MHz) was calculated to be $\Delta G^\ddagger = 14.4 \pm 0.3$ kcal mol^{-1}, and the value is somewhat lower than those reported for other phospholes.[12]

The phosphole was readily oxidized by H_2O_2 treatment to give the corresponding phosphole oxide **3** quantitatively as a colorless crystalline solid. The oxide **3** did not show the fractional process observed for **1**; **3** showed a clearly resolved pair of diastereotopic β-H resonances in the ^{1}H NMR spectrum. In accordance with the observed weak aromaticity in **1**, the bond lengths in the phosphole ring of **3** ($C_\alpha-C_\beta$ = 1.320 Å (mean value) and $C_\beta-C_\beta$ = 1.492 Å; from X-ray structure determination, see Figure 3 and Tables 1 and 2) are only slightly different from those in **1**.

Although both **1** and **3** possess a strong dienic character, they are completely inert toward Diels−Alder cycloaddition: no reaction was observed after stirring a toluene solution of either **1** or **3** at 100 °C in the presence of maleic anhydride for 10 h. This unusual stability of **1** and **3** may be ascribed to steric protection by the fairly bulky menthyl groups.[1c]

Phosphole Complexes of Platinum and Palladium. As shown in Figure 1, the phosphorus atom in **1** retains distorted-tetrahedral geometry (including an

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(8) Märkl, G.; Potthast, R. *Angew. Chem.* **1967**, *79*, 58.

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(10) (a) Quin, L. D.; Keglevich, G.; Ionkin, A. S.; Kalgutkar, R.; Szalontai, G. *J. Org. Chem.* **1996**, *61*, 7801. (b) Nyulaszi, L.; Keglevich, G.; Quin, L. D. *J. Org. Chem.* **1996**, *61*, 7808. (c) Keglevich, G.; Böcskei, Z.; Keserü, G. M.; Újszászy, K.; Quin, L. D. *J. Am. Chem. Soc.* **1997**, *119*, 5095.

(11) (a) Bird, C. W. *Tetrahedron* **1985**, *41*, 1409. (b) Bird, C. W. *Tetrahedron* **1990**, *46*, 5697.

(12) (a) Egan, W.; Tang, R.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 1442. (b) Egan, W.; Tang, R.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1971**, *93*, 6205.

Table 1. Crystallographic Data for 1 and 3−5

	1	**3**	**4**	**5**
formula	$C_{30}H_{45}P$	$C_{30}H_{45}OP$	$C_{60}H_{90}Cl_2P_2Pt$	$C_{60}H_{90}Cl_2P_2Pd$
fw	436.66	452.66	1139.31	1050.62
color, habit	colorless, prismatic	colorless, prismatic	pale yellow, prismatic	yellow, plate
cryst size (mm)	0.12 × 0.30 × 0.30	0.22 × 0.36 × 0.50	0.07 × 0.22 × 0.28	0.08 × 0.28 × 0.42
cryst syst	triclinic	orthorhombic	orthorhombic	orthorhombic
space group	$P1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	8.238(2)	16.669(4)	23.137(4)	23.153(10)
b (Å)	13.294(3)	24.818(3)	25.592(3)	25.56(1)
c (Å)	6.504(3)	6.798(4)	9.792(4)	9.80(1)
α (deg)	91.03(3)			
β (deg)	93.39(3)			
γ (deg)	101.90(2)			
V (Å^3)	695.5(4)	1812(1)	5798(2)	5796(7)
Z	1	4	4	4
D_{calcd} (g cm^{-3})	1.042	1.069	1.305	1.204
μ (cm^{-1})	1.12	1.16	25.93	5.03
F_{000}	240.00	992.00	2368.00	2240.00
$2\theta_{max}$ (deg)	55	55	55	55
total no. of data	3420	3690	7377	7386
no. of unique data	3199		7376	7384
no. of obsd data	1768 ($I > 3.00\sigma(I)$)	2435 ($I > 3.00\sigma(I)$)	4379 ($I > 3.00\sigma(I)$)	2570 ($I > 3.00\sigma(I)$)
no. of variables	416	425	587	586
R,[a] R_w[b]	0.040, 0.039	0.041, 0.040	0.041, 0.049	0.074, 0.094
GOF	1.40	1.52	1.07	1.98
residual ρ (e Å^{-3})	+0.16, −0.12	+0.23, −0.19	+1.61, −0.65	+1.63, −1.41

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1 and 3

	1	**3**
Bond Distances		
P(1)−C(1)	1.822(4)	1.813(4)
P(1)−C(4)	1.815(5)	1.792(3)
C(1)−C(2)	1.333(7)	1.314(5)
C(2)−C(3)	1.465(7)	1.492(5)
C(3)−C(4)	1.337(7)	1.326(5)
P(1)−O(1)		1.489(3)
Bond Angles		
C(1)−P(1)−C(4)	91.5(2)	93.9(2)
C(1)−P(1)−C(5)	109.2(2)	103.9(2)
C(4)−P(1)−C(5)	105.7(2)	107.8(2)
O(1)−P(1)−C(1)		118.1(2)
O(1)−P(1)−C(4)		118.5(1)
O(1)−P(1)−C(5)		112.4(2)

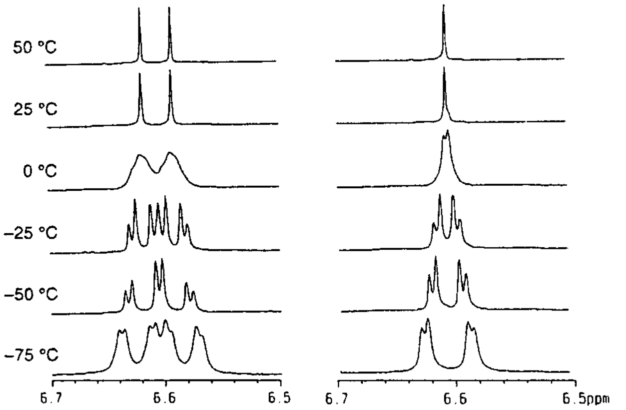

Figure 2. Variable-temperature ^{1}H NMR spectra of **1** in the β-hydrogen region at 500 MHz in toluene-d_8 (^{31}P-coupled, left; ^{31}P-decoupled, right).

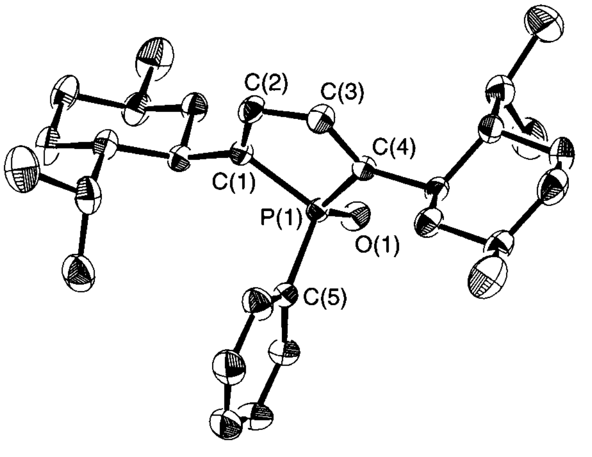

Figure 3. Crystal structure of **3** with thermal ellipsoids at the 30% probability level. All hydrogen atoms are omitted for clarity.

unseen lone pair on the phosphorus), and thus, certain σ-basicity is expected for **1**. The phosphole **1** was allowed to react with 0.5 equiv of $PtCl_2$(cod) in chloroform at 60 °C to give the phosphole complex *trans*-$PtCl_2$(**1**)$_2$ (**4**) quantitatively as a pale yellow crystalline solid. Crystals of **4** were grown from acetone/dichloromethane, and the solid-state structure was clarified by X-ray crystallography (Figure 4). Selected crystallographic data are summarized in Table 1, and selected bond lengths and angles are listed in Table 3. Complex **4** has a trans geometry with an almost perfect square-planar structure; the sum of the four angles at Pt involving Cl(1), Cl(2), P(1), and P(2) are 359.9(3)°. As shown in Figure 4, the phosphole **1** is extremely sterically demanding and constructs a unique chiral pocket around the platinum center. The steric bulkiness of the phosphole ligand should be a reason for the preference of trans geometry in **4**. Because of the weak electronic delocalization in **1**, the σ-basicity of **1** should be as strong as that of normal tertiary phosphines. Indeed, the Pt−P bond length in **4** (2.318(3) and 2.309(3) Å) is within the range observed for the analogous *trans*-P−Pt−P complex with triethylphosphine (Pt−P = 2.298(18) Å):[13,14a] i.e., **1** has potential as a rare example of chiral monodentate phosphines. In the ^{1}H NMR spectrum of **4** in $CDCl_3$, the β-hydrogens of the coordinating phospholes

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(13) Messmer, G. G.; Amma, E. L. *Inorg. Chem.* **1966**, *5*, 1775.

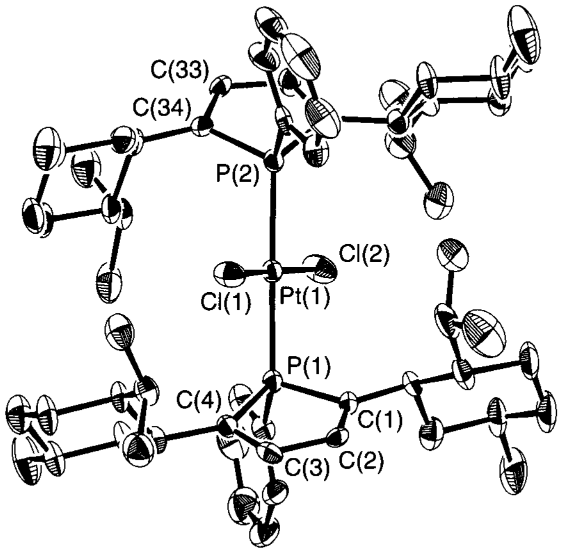

Figure 4. Crystal structure of **4** with thermal ellipsoids at the 30% probability level. All hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 4 and 5

	4 (M = Pt)	**5** (M = Pd)
Bond Distances		
M(1)−Cl(1)	2.296(3)	2.280(7)
M(1)−Cl(2)	2.301(3)	2.271(7)
M(1)−P(1)	2.318(3)	2.353(7)
M(1)−P(2)	2.309(3)	2.325(7)
C(1)−C(2)	1.36(2)	1.39(3)
C(2)−C(3)	1.49(2)	1.50(3)
C(3)−C(4)	1.31(2)	1.30(3)
C(31)−C(32)	1.33(1)	1.35(3)
C(32)−C(33)	1.48(2)	1.54(3)
C(33)−C(34)	1.31(1)	1.25(3)
Bond Angles		
Cl(1)−M(1)−P(1)	87.7(1)	89.0(2)
Cl(1)−M(1)−P(2)	91.8(1)	90.9(2)
Cl(2)−M(1)−P(1)	91.7(1)	90.7(2)
Cl(2)−M(1)−P(2)	88.7(1)	89.3(2)
C(1)−P(1)−C(4)	93.1(5)	92(1)
C(31)−P(2)−C(34)	92.8(5)	90(2)

were observed as a pair of AB doublets which were virtually coupled with two phosphorus atoms. This observation is consistent with retention of the trans geometry of **4** in the solution. The ^{31}P NMR spectrum of **4** showed a pair of satellite signals with $J_{Pt-P} = 2535$ Hz. The overall geometry of the coordinating phospholes in **4** is very similar to that of the phosphole moiety in the oxide **3**.

The analogous palladium complex *trans*-$PdCl_2(\mathbf{1})_2$ (**5**) was quantitatively prepared from $PdCl_2$(cod) and 2.2 equiv of **1** and isolated as a yellow crystalline solid.[14b] Crystals of **5** were grown from acetone/dichloromethane, and an X-ray single-crystal diffraction study was performed. Although the obtained final structure (Figure 5) has some uncertainty because of the poorly formed crystals, the complex **5** is isostructural with the platinum complex **4**.

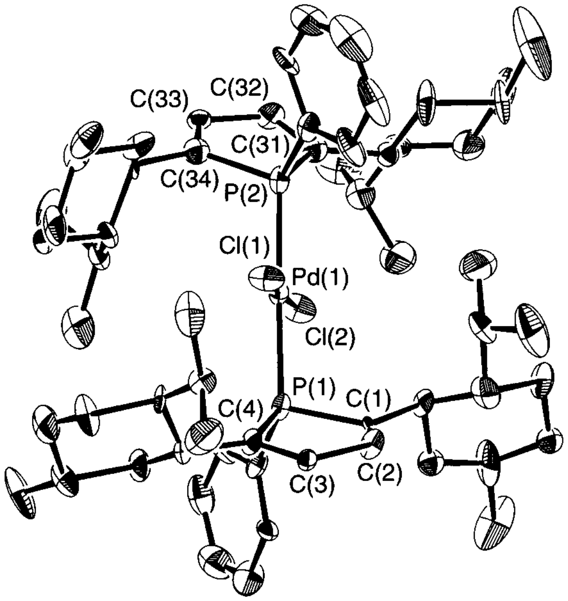

Figure 5. Crystal structure of **5** with thermal ellipsoids at the 30% probability level. All hydrogen atoms are omitted for clarity.

Preparation of a Chiral Phospholyl Anion and Chiral Phosphametallocenes. The phosphole **1** can be converted into the corresponding chiral phospholide in a conventional manner.[15] The phosphole **1** was dissolved in THF and treated with excess metallic lithium at room temperature to cleave the Ph−P bond, giving an equimolar mixture of the lithium phospholide **6** and PhLi. The latter was selectively killed by $AlCl_3$ treatment,[16] and the remaining **6** was reacted with 0.5 equiv of $BrCH_2CH_2Br$ to give the chiral diphosphole **7**,[17] which was isolated as colorless crystals by preparative TLC over SiO_2 (with hexane) under Ar in 62% yield.

Two representative chiral phosphametallocenes, phosphaferrocene and phosphacymantrene, were prepared from **1**. The mixture of **6** and PhLi, which was generated as above,[15] was reacted with 2 equiv of $[(\eta^6\text{-mesitylene})\text{FeCp}]PF_6$[18] in THF at reflux temperature. The chiral monophosphaferrocene **8** was isolated in pure form by chromatography over SiO_2 (with hexane) under Ar as a red-orange solid in 85% yield. The chiral phosphacymantrene **9** was prepared directly from **1** and $Mn_2(CO)_{10}$ in refluxing xylene in 84% yield as an air-sensitive yellow solid with a low melting point.[19] During the transformation into the phosphametallocenes, the chiral (−)-menthyl substituents in **1** were retained on the phospholyl cycles. Thus, the two β-hydrogens on the phosphacyclopentadienyl ligand in both **8** and **9** are diastereotopic and are detected as two clearly separated resonances in the ^{1}H NMR spectrum.

Concluding Remarks

A novel chiral phosphole which has two (−)-menthyl groups on the two α-carbons of the phosphole ring was

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(14) Analogous platinum and palladium species with sterically compact phospholes, $MCl_2(\text{phosphole})_2$ (M = Pt, Pd), showed only cis isomers in the solid state; see: (a) Holt, M. S.; Nelson, J. H.; Alcock, N. W. *Inorg. Chem.* **1986**, *25*, 2288. (b) MacDougall, J. J.; Nelson, J. H.; Mathey, F.; Mayerle, J. J. *Inorg. Chem.* **1980**, *19*, 709.

(15) Braye, E. H.; Caplier, I.; Saussez, R. *Tetrahedron* **1971**, *27*, 5523.

(16) Mathey, F.; de Lauzon, G. *Organomet. Synth.* **1986**, *3*, 259.

(17) Charrier, C.; Maigrot, N.; Mathey, F. *Organometallics* **1987**, *6*, 586.

(18) Roberts, R. M. G.; Wells, A. S. *Inorg. Chim. Acta* **1986**, *112*, 171.

(19) Mathey, F. *Tetrahedron Lett.* **1976**, 4155.

prepared and characterized by X-ray crystallography and NMR spectroscopy. The (−)-menthyl substituents are fairly sterically demanding, which reduces the reactivity of the phosphole and its oxide toward cycloaddition with maleic anhydride. The phosphole can be conveniently converted into a variety of chiral species, such as lithium phospholide, phosphaferrocene, phosphacymantrene, and diphosphole. All these products were obtained in chiral and enantiomerically pure forms. Hence, the chiral phosphole has been demonstrated as a novel chiral building block. Most of the new compounds possess lone pairs on the phosphorus atoms and are potential ligands for transition metals. Applications of these compounds for asymmetric reactions will be the next subject of this study.

Experimental Section

General Considerations. All anaerobic and/or moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox techniques under prepurified argon. Tetrahydrofuran, Et_2O, and benzene were distilled from benzophenone−ketyl under nitrogen prior to use. Dichloromethane was distilled from CaH_2 under nitrogen prior to use. MeOH and EtOH were distilled from the corresponding magnesium alkoxides and stored in glass flasks with Teflon stopcocks under nitrogen. (−)-Menthylacetylene,[6] $PhPH_2$,[20] $PdCl_2(cod)$,[21] $PtCl_2(cod)$,[22] and $[(\eta^6$-mesitylene)FeCp]PF_6[23] were synthesized as reported. ^{n}BuLi in hexane was obtained from Kanto Chemicals. CuCl and hydrogen peroxide (30%) were purchased from Wako Pure Chemical Industries. *N*,*N*,*N′*,*N′*-tetramethylethylendiamine (TMEDA), MnO_2, 1,2-dibromoethane, lithium wire, and $Mn_2(CO)_{10}$ were purchased from Aldrich Chemical Co. and used as received. $AlCl_3$ was purchased from Nacalai Tesque and purified by sublimation prior to use. Reaction progress was monitored by analytical thin-layer chromatography (TLC) using 0.25 mm Merck F-254 silica gel glass plates. Visualization of the TLC plates was achieved by UV illumination. NMR spectra were recorded on a JEOL JNM LA500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{31}P, 202 MHz). ^{1}H and ^{13}C chemical shifts are reported in ppm downfield of internal tetramethylsilane. ^{31}P NMR chemical shifts are externally referenced to 85% H_3PO_4. Optical rotations were measured on a JASCO DIP-370 polarimeter. X-ray crystallographic data were collected at 296 K on a Rigaku AFC7S diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å).

1,4-Bis((−)-menthyl)-1,3-butadiyne (2). A mixture of (−)-menthylacetylene (8.36 g, 50.9 mmol), CuCl (10.1 g, 102 mmol), and *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (15.4 mL, 102 mmol) in acetone (70 mL) was stirred at 50 °C for 1 h with constant oxygen bubbling. The heterogeneous mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The resulting residue was diluted with hexane, and the hexane solution was washed successively with saturated NaCl, 10% HCl, and saturated $NaHCO_3$. The organic layer was dried over anhydrous $MgSO_4$ and then concentrated under reduced pressure. The crude product was chromatographed on silica gel using hexane as an eluent to give the title compound in pure form. Yield: 7.14 g (21.9 mmol, 86%). An analytically pure sample was obtained by recrystallization from hot MeOH. Mp: 77−78 °C. ^{1}H NMR ($CDCl_3$, 24 °C): δ 0.76 (d, $J = 6.8$ Hz, 6H), 0.82−0.97 (m, 4H), 0.87 (d, $J = 6.6$ Hz, 6H), 0.92 (d, $J = 6.8$ Hz, 6H), 1.11 (q, $J = 12.2$ Hz, 2H), 1.20 (tt, $J = 11.2$ and 2.9 Hz, 2H), 1.26−1.36 (m, 2H), 1.59−1.63 (m, 2H), 1.67−1.72 (m, 2H), 1.98 (dq, $J = 12.9$ and 3.0 Hz, 2H), 2.18−2.26 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 15.70, 21.34, 22.21, 24.07, 28.81, 32.43, 34.05, 34.70, 42.06, 47.22, 66.17, 80.96. $[\alpha]^{20}_D = -71.7°$ (*c* 1.01, $CHCl_3$). Anal. Calcd for $C_{24}H_{38}$: C, 88.27; H, 11.73. Found: C, 88.07; H, 11.70.

1-Phenyl-2,5-bis((−)-menthyl)phosphole (1). A solution of *n*-butyllithium in hexane (1.66 mol/L, 12.9 mL, 21.4 mmol) was added dropwise to a solution of $PhPH_2$ (2.36 mL, 21.4 mmol) in THF−C_6H_6 (80 mL, 1:1 mixture) at 0 °C. The resulting yellow solution was added dropwise to a THF (20 mL) solution of the diyne **2** (2.33 g, 7.13 mmol) by means of cannula transfer. After the addition, the wine red mixture was heated to reflux for 1.5 h to give a reddish brown suspension. This suspension was quenched with water (ca. 1.5 mL), and the mixture was evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel (elution with 10/1 hexane/$CHCl_3$) under nitrogen and then further purified by recrystallization from hot EtOH to give the analytically pure compound as colorless crystals. A crystal for X-ray structure determination was obtained by recrystallization from dichloromethane−EtOH. Yield: 2.44 g (5.56 mmol, 78%). Mp: 118−120 °C. ^{1}H NMR (toluene-d_8, 100 °C): δ 0.65−0.82 (m, 20H), 0.93 (qd, $J = 12.3$ and 3.3 Hz, 2H), 1.01 (br, 2H), 1.16 (br, 4H), 1.54−1.61 (m, 4H), 1.79 (dq, $J = 13.1$ and 2.4 Hz, 2H), 1.98−2.04 (m, 2H), 2.38 (qd, $J = 11.2$ and 3.5 Hz, 2H), 6.52 (d, $J = 12.8$ Hz, 2H), 6.96−7.06 (m, 3H), 7.37−7.40 (m, 2H). ^{31}P{^{1}H} NMR (toluene-d_8, 100 °C): δ 5.60 (s). $[\alpha]^{20}_D = -167°$ (*c* 1.01, $CHCl_3$). Anal. Calcd for $C_{30}H_{45}P$: C, 82.52; H, 10.39. Found: C, 82.41; H, 10.60.

1-Phenyl-2,5-bis((−)-menthyl)phosphole oxide (3). To a solution of **1** in acetone was added an aqueous solution of hydrogen peroxide (30%) dropwise with stirring at room temperature. After 1 h, the remaining H_2O_2 was decomposed with a small amount of MnO_2. TLC analysis indicated the quantitative conversion of **1** to the oxide. The mixture was evaporated to dryness under reduced pressure. The residue was extracted with $CHCl_3$, and the organic layer was dried over anhydrous $MgSO_4$. After filtration, the filtrate was evaporated to dryness and the crude material was purified by short-path silica gel column chromatography (EtOAc as an eluent) to give a slightly yellow solid. An analytically pure sample was obtained by recrystallization from hot EtOH. A crystal for X-ray structure determination was obtained by recrystallization from dichloromethane−EtOH. Mp: 228−230 °C. ^{1}H NMR ($CDCl_3$, 22 °C): δ 0.28 (d, $J = 7.1$ Hz, 3H), 0.41 (d, $J = 6.8$ Hz, 3H), 0.67−0.95 (m, 18H), 1.15−1.30 (m, 2H), 1.35 (q, $J = 12.4$ Hz, 1H), 1.42−1.50 (m, 2H), 1.54−1.66 (m, 5H), 1.85 (sept of d, $J = 6.8$ and 2.0 Hz, 1H), 2.02−2.06 (m, 1H), 2.12−2.20 (m, 1H), 2.31−2.40 (m, 1H), 6.43 (dd, $J = 26.9$ and 3.7 Hz, 1H), 6.51 (dd, $J = 26.6$ and 3.7 Hz, 1H), 7.40−7.43 (m, 2H), 7.47−7.50 (m, 1H), 7.78 (dd, $J = 11.5$ and 1.5 Hz, 1H), 7.80 (d, $J = 11.7$ Hz, 1H). ^{31}P{^{1}H} NMR ($CDCl_3$, 23 °C): δ 43.8 (s). $[\alpha]^{20}_D = -228°$ (*c* 1.01, $CHCl_3$). Anal. Calcd for $C_{30}H_{45}OP$: C, 79.60; H, 10.02. Found: C, 79.31; H, 9.84.

***trans*-Dichlorobis[1-phenyl-2,5-bis((−)-menthyl)phosphole]platinum(II) (4).** A 1:2.2 mixture of $PtCl_2(cod)$ and **1** in $CHCl_3$ was stirred for 1 h at 60 °C; then all the volatiles were removed under reduced pressure. An analytically pure sample, which was suitable for X-ray structure determination, was obtained by recrystallization from dichloromethane−acetone. Mp: 275−277 °C. ^{1}H NMR ($CDCl_3$, 27 °C): δ 0.32 (d, $J = 6.8$ Hz, 6H), 0.36−0.44 (m, 2H), 0.53 (d, $J = 6.5$ Hz, 6H), 0.58−0.68 (m, 2H), 0.72−0.75 (m, 12H), 0.89−0.98 (m, 16H), 1.02−1.06 (m, 6H), 1.16 (q, $J = 12.6$ Hz, 2H), 1.37 (d, $J = 13.1$ Hz, 2H), 1.50−1.56 (m, 6H), 1.74−1.78 (m, 4H), 1.84−1.87 (m, 2H), 1.97−2.07 (m, 4H), 2.72−2.81 (m, 4H), 3.07 (d, $J = 12.5$ Hz, 2H), 6.49 (vt of d, $J = 15.4$ and 2.8 Hz, 2H), 6.65 (vt of d, $J = 15.2$ and 2.8 Hz, 2H), 7.23−7.26 (m, 4H), 7.35 (t, $J = 7.3$ Hz, 2H), 7.81 (m, 4H). ^{31}P{^{1}H} NMR ($CDCl_3$, 27 °C): δ 30.0

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(J_{Pt-P} = 2535 Hz). $[\alpha]^{20}_D = -409°$ (*c* 1.00, $CHCl_3$). Anal. Calcd for $C_{60}H_{90}Cl_2P_2Pt$: C, 63.25; H, 7.96. Found: C, 63.07; H, 8.03.

***trans*-Dichlorobis[1-phenyl-2,5-bis((−)-menthyl)phosphole]palladium(II) (5)**. A 1:2.2 mixture of $PdCl_2$(cod) and **1** in CH_2Cl_2 was stirred for 20 min at room temperature; then all the volatiles were removed under reduced pressure. An analytically pure sample, which was suitable for X-ray structure determination, was obtained by slow diffusion of acetone into a concentrated dichloromethane solution of the complex at room temperature. Mp: 259−263 °C. ^1H NMR ($CDCl_3$, 26 °C): δ 0.29 (d, J = 6.8 Hz, 6H), 0.50 (q, J = 12.6 Hz, 2H), 0.59 (d, J = 6.6 Hz, 6H), 0.64−0.69 (m, 2H), 0.71 (d, J = 7.1 Hz, 6H), 0.77 (d, J = 6.7 Hz, 6H), 0.84−1.08 (m, 10H), 0.89 (d, J = 7.0 Hz, 6H), 0.94 (d, J = 6.5 Hz, 6H), 1.17 (q, J = 12.9 Hz, 2H), 1.51−1.61 (m, 8H), 1.73−1.77 (m, 6H), 1.94−2.05 (m, 4H), 2.69−2.81 (m, 4H), 3.10 (d, J = 13.3 Hz, 2H), 6.48 (vt of d, J = 15.1 and 3.2 Hz, 2H), 6.64 (vt of d, J = 14.8 and 3.2 Hz, 2H), 7.23 (d, J = 7.5 Hz, 4H), 7.35 (t, J = 7.3 Hz, 2H), 7.76 (dd, J = 12.7 and 6.0 Hz, 4H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 26 °C): δ 32.0 (s). $[\alpha]^{20}_D = -428°$ (*c* 1.00, $CHCl_3$). Anal. Calcd for $C_{60}H_{90}Cl_2P_2Pd$: C, 68.59; H, 8.63. Found: C, 68.35; H, 8.78.

1,2-Bis[2,5-bis((−)-menthyl)phospholyl]ethane (7). Lithium metal (27.8 mg, 4.00 mmol) was added to a solution of **1** (437 mg, 1.00 mmol) in THF at room temperature. The mixture was stirred until disappearance of **1** (checked by TLC). The mixture was filtered by a glass filter and added to anhydrous $AlCl_3$ (44.0 mg, 0.333 mmol) at 0 °C. After the mixture was stirred for 30 min, a THF solution of 1,2-dibromoethane (93.9 mg, 0.50 mmol) was added at this temperature, and the mixture was allowed to reach room temperature and stirred for 30 min. The resulting yellow mixture was concentrated in vacuo, and the crude product was purified by preparative TLC (elution with hexane) under an argon atmosphere to give the title compound. Yield: 231 mg (0.309 mmol, 62%). An analytically pure sample was obtained by recrystallization from hot EtOH. Mp: 113−115 °C. ^1H NMR (toluene-d_8, 90 °C): δ 0.82 (d, J = 6.8 Hz, 12H), 0.87−1.12 (m, 40H), 1.32−1.42 (m, 8H), 1.66−1.73 (m, 8H), 1.96−2.02 (m, 8H), 2.50−2.57 (m, 4H), 6.57 (vt, J = 6.9 Hz, 4H). $^{31}P\{^1H\}$ NMR (toluene-d_8, 90 °C): δ −22.5 (s). $[\alpha]^{20}_D = +280°$ (*c* 1.00, $CHCl_3$). Anal. Calcd for $C_{50}H_{84}P_2$: C, 80.38; H, 11.33. Found: C, 79.86; H, 11.32.

(η^5-Cyclopentadienyl)[η^5-2,5-bis((−)-menthyl)phosphacyclopentadienyl]iron(II) (8). Lithium metal (34.7 mg, 5.00 mmol) was added to a solution of **1** (218 mg, 0.500 mmol) in THF at room temperature. The mixture was stirred until disappearance of **1** (checked by TLC). The mixture was added to [(η^6-mesitylene)FeCp]PF_6 (386 mg, 1.00 mmol) at reflux temperature, and the mixture was stirred overnight. After it was cooled, the mixture was concentrated in vacuo. The resulting crude product was extracted with benzene and filtered through Celite. The mixture was evaporated to dryness under reduced pressure, and the crude product was chromatographed over SiO_2 (elution with hexane) under an argon atmosphere to give the desired compound in pure form. Yield: 205 mg (0.426 mmol, 85%). Mp: 98−100 °C. ^1H NMR ($CDCl_3$, 26 °C): δ 0.69−1.14 (m, 26H), 1.35−1.42 (m, 2H), 1.58−1.62 (m, 2H), 1.70−1.82 (m, 4H), 1.84−1.92 (m, 3H), 2.03 (m, 1H), 4.28 (s, 5H), 4.87 (dd, J = 5.5 and 2.8 Hz, 1H), 4.95 (dd, J = 4.8 and J = 2.8 Hz, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 27 °C): δ −63.6 (s). $[\alpha]^{20}_D = -180°$ (*c* 0.667, $CHCl_3$). Anal. Calcd for $C_{29}H_{45}PFe$: C, 72.49; H, 9.44. Found: C, 72.43; H, 9.54.

Tricarbonyl[η^5-2,5-bis((−)-menthyl)phosphacyclopentadienyl]manganese(I) (9). A mixture of **1** (218 mg, 0.500 mmol) and $Mn_2(CO)_{10}$ (195 mg, 0.500 mmol) in xylene was refluxed for 2 days. The resulting red solution was concentrated under reduced pressure, and the crude product was purified by preparative TLC (elution with hexane) under an argon atmosphere to give the yellow oily compound. Yield: 209 mg (0.419 mmol, 84%). An analytically pure sample was obtained by distillation onto a cold finger under reduced pressure. Mp: 43−45 °C. ^1H NMR ($CDCl_3$, 26 °C): δ 0.77−1.03 (m, 26H), 1.31−1.41 (m, 2H), 1.52 (dq, J = 12.8 and 3.0 Hz, 1H), 1.62−1.75 (m, 5H), 1.82−1.94 (m, 4H), 5.16 (dd, J = 3.7 and 3.0 Hz, 1H), 5.48 (dd, J = 4.8 and 3.0 Hz, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 27 °C): δ −6.31 (s). $[\alpha]^{20}_D = -123°$ (*c* 0.509, $CHCl_3$). Anal. Calcd for $C_{27}H_{40}O_3PMn$: C, 65.05; H, 8.09. Found: C, 65.20; H, 8.13.

X-ray Structure Determination of 1 and 3−5. Suitable crystals were obtained by recrystallization (see above). Crystal data and other details of the structure analyses are summarized in Table 1 and the Supporting Information. Crystals of suitable size were mounted on glass fibers and then transferred to a goniostat for characterization and data collection. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied for **1** and **3** (coefficient 7.73700e-07 for **1**; 8.97400e-07 for **3**). The structures were solved by direct methods (SIR92) and expanded using Fourier techniques. In the final cycles of refinement, the non-hydrogen atoms were varied with anisotropic thermal parameters and the hydrogen atoms were varied with isotropic thermal parameters. All calculations were performed using the TEXSAN[24] crystallographic software package of Molecular Structure Corp.

Acknowledgment. This work was supported by "Research for the Future" Program (the Japan Society for the Promotion of Science), a Grant-in-Aid for Scientific Research (the Ministry of Education, Japan), and Mitsubishi Chemical Corporation Fund (to M. O.). K. Y. thanks the Japan Society for the Promotion of Science for the award of a fellowship for graduate students.

Supporting Information Available: Tables of crystallographic data for **1** and **3−5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000952D

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[24] TEXSAN: Crystal Structure Analysis Package; Molecular Structure Corp., The Woodlands, TX, 1985 and 1992.