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First Representative of Optically Active *P*-L-Menthyl-Substituted (Aminomethyl)phosphine and Its Borane and Metal Complexes

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The first representative of 1,5-diaza-3,7-diphosphacyclooctanes (**1**) with chiral L-menthyl substituents on the phosphorus atoms was obtained by condensation of L-menthylphosphine with formaldehyde and *p*-toluidine. This optically active cyclic bisphosphine readily forms a stable P,P-complex with borane (**2**) and P,P-chelate complexes with platinum(II) (**3**) and palladium(II) dichloride (**4**). The structure of the bisphosphine **1** in solution was elucidated by employing a variety of 1D/2D NMR correlation experiments, and the molecular structure of complex **3** was studied by X-ray crystallography.

Introduction

Menthyl derivatives play an important role in the synthesis of optically active compounds,[1] and tertiary *P*-menthylphosphines continue to draw attention as useful ligands for different transition-metal-catalyzed reactions.[1−6] The attractive feature of the menthyl unit is the proximity of one asymmetric carbon atom and an isopropyl group to the phosphorus donor center, which may lead to an increase in the regio- and stereoselectivity of the catalysts on the basis of various menthylphosphines.[1] Some catalysts on the basis of various menthylphosphines indeed provide high regioselectivity[1,5] and high or satisfactory stereoselectivity, in particular in catalytic asymmetric C−C or P−C bond formation.[1,2,7] To date, dozens of menthylphosphines have been synthesized, but only a few bisphosphines with chiral menthyl groups on each phosphorus atom are described. All of them are acyclic and contain two dimenthylphosphino groups linked by an organic backbone.[1,6,8] We have already shown that Mannich-type condensation of primary amines, formaldehyde, and primary or secondary phosphines is a very effective approach to the design of various P,N-containing heterocycles, in particular eight-membered P,P-chelating bisphosphines, namely, 1,5-diaza-3,7-diphosphacyclooctanes,[9] including ones with chiral substituents on the nitrogen atoms.[10] Nevertheless, the products of the condensation of amines with L-menthylphosphine[11] and formaldehyde or with bis(hydroxymethyl)-L-menthylphosphine[12] have not been described yet even though both phosphines have been known for more than 10 years.[11,12] We have, therefore, used this approach for the synthesis of the first representative of 1,5-diaza-3,7-diphosphacyclooctanes with asymmetrical groups on the phosphorus atoms, namely, 3,7-di-L-menthyl-1,5-di-*p*-tolyl-1,5-diaza-3,7-diphosphacyclooctane (**1**).

Experimental Section

All manipulations were carried out by standard high-vacuum and dry-nitrogen techniques. ^{1}H NMR spectra (Bruker Avance-600, 30 °C, standard, 600.00 MHz): Me_4Si. ^{13}C NMR spectra (Bruker Avance-400, standard, 100.57 MHz): internal solvent. ^{31}P NMR spectra (Bruker Avance-600, 242.937 MHz; BrukerAvance-DRX 400, 162 MHz; CXP-100, 36.47 MHz; standard): external 85% H_3PO_4. ^{15}N NMR spectra (Bruker Avance-600, 60.81 MHz): CH_3CN (^{15}N δ 239.5 ppm). 1D ^{1}H ROESY spectra of **1** and **2** and nuclear Overhauser enhancements (NOEs) were obtained in

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(1) Brunner, H.; Janura, M. *Synthesis* **1998**, 45–55.
(2) Minato, M.; Kaneko, T.; Masauji, Sh.; Ito, T. *J. Organomet. Chem.* **2006**, *691*, 2483–2488.
(3) Bartik, T.; Ding, H.; Bartik, B.; Hanson, B. E. *J. Mol. Catal. A: Chem.* **1995**, *98*, 117–122.
(4) Munoz, B.; Marinetti, A.; Ruiz, A.; Castillon, S.; Claver, C. *Inorg. Chem. Commun.* **2005**, *8*, 1113–1115.
(5) Kawashima, Y.; Okano, K.; Nozaki, K.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 347–355.
(6) Brunner, H.; Ziegler, J. *J. Organomet. Chem.* **1990**, *397*, C25–C27.
(7) Blank, N. F.; McBroom, K. C.; Glueck, D. S.; Kassel, W. S.; Rheingold, A. L. *Organometallics* **2006**, *25*, 1742–1748.
(8) Hoehn, A.; Wolf, J. German Patent DE 19544448, 1997.
(9) Arbuzov, B. A.; Nikonov, G. N. *Adv. Heterocycl. Chem.* **1994**, *61*, 59–138.
(10) Karasik, A. A.; Naumov, R. N.; Sinyashin, O. G.; Belov, G. P.; Novikova, H. V.; Lönnecke, P.; Hey-Hawkins, E. *Dalton Trans.* **2003**, 2209–2214.
(11) Marinetti, A.; Buzin, F.-X.; Ricard, L. *Tetrahedron* **1997**, *53*, 4363–4370.
(12) Brunner, H.; Rosenboem, S. *Monatsh. Chem.* **2000**, *131*, 1371–1382.

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$CDCl_3$ at 288 K. Low-temperature NMR experiments were carried out in CD_2Cl_2. The positive-ion fast atom bombardment (FAB_{pos}) mass spectra were obtained on a ZAB-HSQ-VG instrument from Analytical Manchester. The IR spectra were obtained on a IFG 113 V spectrometer. The specific rotation was determined on a Perkin-Elmer model 341 polarimeter at 589 nm. L-Menthylphosphine was obtained by the reported method.[11] $[MCl_2(COD)]$ was prepared according to the literature.[13] $BH_3(THF)$ (THF = tetrahydrofuran) is commercially available.

3,7-Di-L-menthyl-1,5-di-*p*-tolyl-1,5-diaza-3,7-diphosphacyclooctane (1). A mixture of L-menthylphosphine (1.04 g, 6.04 mmol) and paraformaldehyde (0.36 g, 12 mmol) was stirred at 110 °C until homogenization. The bis(hydroxymethyl)-L-menthylphosphine obtained (6.0 mmol) was dissolved in dry ethanol (10 mL), and a solution of *p*-toluidine (0.65 g, 6.02 mmol) in dry ethanol (7 mL) was added. The mixture was stirred at 80 °C for 3 h and then at room temperature overnight. The precipitate formed was filtered off, washed carefully with ethanol, and dried at 0.05 Torr for 3 h. Yield of **1**: 1.45 g (80%). Mp: 170 °C. Anal. Calcd for $C_{38}H_{60}N_2P_2$ [606.84]: C, 75.24; H, 9.90; N, 4.62; P, 10.23. Found: C, 75.08; H, 10.26; N, 4.27; P, 9.76. ^{1}H NMR ($CDCl_3$): δ_H 6.95 (d, 2H, J = 8.6 Hz, H-15), 6.41 (d, 2H, J = 8.6 Hz, H-14), 4.37 (dd, 1H, J = 7.1 and 15.2 Hz, H-12$_{eq}$), 4.23 (dd, 1H, J = 4.8 and 15.2 Hz, H-11$_{eq}$), 3.70 (dd, 1H, J = 1.0 and 15.2 Hz, H-11$_{ax}$), 3.56 (dd, 1H, J = 2.9 and 15.2 Hz, H-12$_{ax}$), 2.70 (m, 1H, H-7), 2.19 (s, 3H, Me-17), 1.84 (d, 1H, J = 11.9 Hz, H-3$_{eq}$), 1.84 (d, 1H, J = 11.9 Hz, H-4$_{eq}$), 1.78 (d, 1H, J = 12.8 Hz, H-6$_{eq}$), 1.68 (m, 1H, H-1), 1.41 (dd, 1H, J = 11.9 and 11.9 Hz, H-2), 1.38 (m, 1H, H-5), 1.17 (ddd, 1H, J = 11.9, 11.9, and 11.9 Hz, H-3$_{ax}$), 1.04 (ddd, 1H, J = 12.4, 12.4, and 12.4 Hz, H-6$_{ax}$), 1.00 (d, 3H, J = 7.1 Hz, Me-9), 0.98 (m, 1H, H-4$_{ax}$), 0.93 (d, 3H, J = 6.7 Hz, Me-10), 0.76 (d, 3H, J = 6.7 Hz, Me-8). ^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 143.7 (C-13), 130.3 (C-16), 129.6 (C-15), 113.1 (br, C-14), 56.6 (d, $^1J_{CP}$ = 26.5 Hz, C-11), 52.1 (d, $^1J_{CP}$ = 29.3 Hz, C-12), 44.8 (d, $^2J_{CP}$ = 8.8 Hz, C-2), 40.4 (d, $^1J_{CP}$ = 19.3 Hz, C-1), 35.5 (C-6), 35.1 (C-4), 33.9 (C-5), 27.9 (d, $^3J_{CP}$ = 23.2 Hz, C-7), 25.3 (d, $^3J_{CP}$ = 5.5 Hz, C-3), 22.5 (C-10), 21.5 (C-9), 20.1 (C-17), 15.0 (C-8). ^{31}P{^{1}H} NMR (C_6D_6): δ_P −50.72. ^{15}N NMR ($CDCl_3$): δ_N 53.0. $[\alpha]_D^{20}$: −52.4 (*c* 0.65 g/100 mL, CH_2Cl_2).

3,7-Di-L-menthyl-1,5-di-*p*-tolyl-1,5-diaza-3,7-diphosphacyclooctane *P*,*P*-Bisborane (2). A 1 M borane−THF solution in THF (0.22 mL, 0.22 mmol) was added to a solution of **1** (0.0648 g, 0.107 mmol) in dry benzene (3 mL) at 0 °C under stirring. The reaction mixture was stirred at 0 °C for 30 min and then at ambient temperature for 1 h. The precipitate formed was filtered off, washed with benzene, and dried. Yield of **2**: 0.062 g (90%). Mp: 124 °C. Anal. Calcd for $C_{38}H_{66}B_2N_2P_2$ [634.51]: C, 71.93; H, 10.48; N, 4.41; P, 9.76. Found: C, 71.92; H, 10.41; N, 4.50; P, 9.14. ^{1}H NMR ($CDCl_3$): δ_H 7.09 (d, $^3J_{HH}$ = 8.1 Hz, 2H, C^{15}H), 7.03 (d, $^3J_{HH}$ = 8.1 Hz, 2H, C^{14}H), 4.45 (dd, $^2J_{HH}$ = 15.7 Hz, $^2J_{PH}$ = 4.8 Hz, 1H, C^{11}H$_e$), 4.35 (dd, $^2J_{HH}$ = 15.2 Hz, $^2J_{PH}$ = 2.4 Hz, 1H, C^{12}H$_e$), 3.78 (dd, $^2J_{HH}$ = 15.7 Hz, $^2J_{PH}$ = 6.2 Hz, 1H, C^{11}H$_a$), 3.60 (dd, $^2J_{HH}$ = 15.2 Hz, $^2J_{PH}$ = 6.7 Hz, 1H, C^{12}H$_a$), 2.28 (s, 3H, C^{17}H), 1.91 (dddd, 1H, J = 11.4, 11.4, 11.4, and 2.4 Hz, C^{1}H), 1.72 (br s, C^{7}H), 1.68−1.76 (m, C^{3}H$_{eq}$, C^{4}H$_{eq}$) (total intensity 3H), 1.64 (br d, 1H, J = 12.4 Hz, C^{6}H$_{eq}$), 1.58 (br d, 1H, J = 11.4 Hz, C^{2}H$_{ax}$), 1.27 (m, 1H, C^{5}H$_{ax}$), 1.13 (dddd, 1H, J = 12.4, 12.4, 12.4, and 5.7 Hz, C^{6}H$_{ax}$), 1.02 (dddd, 1H, J = 12.4, 12.4, 12.4, and 3.3 Hz, C^{3}H$_{ax}$), 0.91 (dddd, 1H, J = 12.8, 12.8, 12.8, and 2.8 Hz, C^{4}H$_{ax}$), 0.85 (d, 3H, $^3J_{HH}$ = 6.7 Hz, C^{10}H$_3$), 0.78 (d, $^3J_{HH}$ = 6.7 Hz, C^{10}H), 0.77 (d, $^3J_{HH}$ = 7.6 Hz, C^{8}H) (total intensity 6H), 0.47 (v br m, 3H, BH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 147.4 (d, $^3J_{CP}$ = 2.2 Hz, C^{13}), 130.9 (s, C^{16}), 129.4 (s, C^{15}), 118.9 (s, C^{14}), 54.0 (d, $^1J_{CP}$ = 28.2 Hz, C^{11}), 50.4 (d, $^1J_{CP}$ = 37.0 Hz, C^{12}), 43.8 (s, C^2), 36.6 (d, $^1J_{CP}$ = 22.1 Hz, C^1), 35.3 (s, C^6), 34.1 (s, C^4), 33.5 (d, $^3J_{CP}$ = 10.0 Hz, C^5), 29.1 (d, $^3J_{CP}$ = 2.8 Hz, C^7), 25.0 (d, $^3J_{CP}$ = 11.1 Hz, C^3), 22.3 (s, C^{10}), 21.2 (s, C^9), 20.5 (s, C^{17}), 15.7 (s, C^8). ^{31}P{^{1}H} NMR (THF): δ_P 27.0 (br s). ^{15}N NMR ($CDCl_3$): δ_N 41.0. $[\alpha]_D^{20}$: −80.0 (*c* 0.1367 g/100 mL, $CHCl_3$).

***cis*-Dichloro(3,7-di-L-menthyl-1,5-di-*p*-tolyl-1,5-diaza-3,7-diphosphacyclooctane)platinum(II) (3).** A solution of (cyclooctadiene)-platinum(II) dichloride (0.0560 g, 0.15 mmol) in methylene dichloride (5 mL) was added to a solution of **1** (0.0908 g, 0.15 mmol) in methylene dichloride (10 mL). The reaction mixture was stirred at ambient temperature for 4 h, the solvent was removed in vacuo, and acetonitrile was added to the residue. The precipitate formed was filtered off, washed with acetonitrile, and dried at 0.1 Torr for 3 h. Yield of **3**: 0.058 g (45%), Mp: 171 °C. Anal. Calcd for $C_{38}H_{60}Cl_2N_2P_2Pt$ [872.83]: C, 52.29; H, 6.92; N, 3.20; P, 7.10. Found: C, 51.82; H, 7.06; N, 3.02; P, 6.88. ^{1}H NMR ($CDCl_3$): δ_H 7.20 (d, $^3J_{HH}$ = 6.8 Hz, 4H, C^{15}H), 6.97 (d, $^3J_{HH}$ = 6.8 Hz, 4H, C^{14}H), 3.71−4.10 (m, 8H, C^{11}H/C^{12}H), 3.22−3.59 (m, 2H, C^{7}H), 2.33 (s, 6H, C^{17}H$_3$), 1.92−2.05 (m, 2H, CH$_{ment}$), 1.70−1.82 (m, 4H, CH$_{ment}$), 1.45−1.67 (m, 8H, CH$_{ment}$), 1.25−1.34 (m, 2H, CH$_{ment}$), 1.12−1.24 (m, 2H, CH$_{ment}$), 0.82−1.05 (m, 18H, C^{8}H$_3$/C^{9}H$_3$/C^{10}H$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P −6.80 ($^1J_{PtP}$ = 3150 Hz). IR (Nujol, PE, cm^{-1}): 286 (br), 307 (br, ν_{Pt-Cl}). $[\alpha]_D^{20}$: −47.5. (*c* 1.05 g/100 mL, CH_2Cl_2).

Monocrystals of **3** suitable for X-ray crystal structure analysis were grown from dichloromethane by the slow evaporation of the solvent from the solution of **3**. The crystals obtained were drawn out of the mother liquor and were cautiously dried under atmospheric pressure for 0.5 h without additional washing. Mp: 170 °C (the loss of CH_2Cl_2 was observed at 88−90 °C). Anal. Calcd for $C_{38}H_{60}Cl_2N_2P_2Pt\cdot 2CH_2Cl_2$ [1042.70]: C, 46.08; H, 6.14; N, 2.68; P, 5.94. Found: C, 46.52; H, 6.39; N, 2.98; P, 6.21. ^{1}H NMR ($CDCl_3$): δ_H 7.20 (d, $^3J_{HH}$ = 6.8 Hz, 4H, C^{15}H), 6.97 (d, $^3J_{HH}$ = 6.8 Hz, 4H, C^{14}H), 5.29 (s, 4H, CH_2Cl_2), 3.70−4.10 (m, 8H, C^{11}H/C^{12}H), 3.21−3.60 (m, 2H, C^{7}H), 2.33 (s, 6H, C^{17}H$_3$), 1.24−1.34 (m, 2H, CH$_{ment}$), 1.12−1.24 (m, 2H, CH$_{ment}$), 0.81−1.05 (m, 18H, C^{8}H$_3$/C^{9}H$_3$/C^{10}H$_3$).

***cis*-Dichloro(3,7-di-L-menthyl-1,5-di-*p*-tolyl-1,5-diaza-3,7-diphosphacyclooctane)palladium(II) (4).** Complex **4** was prepared like **3** from **1** (0.0567 g, 0.094 mmol) and (cyclooctadiene)palladium(II) dichloride (0.0267 g, 0.094 mmol), except that the nonvolatile residue was washed with diethyl ether. Yield of **4**: 46%. Mp: 152 °C. Anal. Calcd for $C_{38}H_{60}Cl_2N_2P_2Pd$ [784.17]: C, 58.20; H, 7.71; N, 3.57; P, 7.89; Cl, 9.04. Found: C, 58.14; H, 8.01; N, 3.67; P, 7.45; Cl, 8.67. ^{1}H NMR ($CDCl_3$): δ_H 7.20 (d, $^3J_{HH}$ = 7.8 Hz, 4H, C^{15}H), 6.96 (d, $^3J_{HH}$ = 7.8 Hz, 4H, C^{14}H), 3.92 (d, $^2J_{HH}$ = 14.1 Hz, 2H, C^{11}H$_B$), 3.86 (d, $^2J_{HH}$ = 13.9 Hz, 2H, C^{12}H$_B$), 3.71 (d, $^2J_{HH}$ = 13.9 Hz, 2H, C^{12}H$_A$), 3.62 (dd, $^2J_{HH}$ = 14.1 Hz, $^2J_{PH}$ = 2.1 Hz, 2H, C^{11}H$_A$), 2.84−2.95 (m, 2H, C^{7}H), 2.32 (s, 6H, C^{17}H$_3$), 1.87−1.96 (m, 2H, CH$_{ment}$), 1.70−1.82 (m, 6H, CH$_{ment}$), 1.56−1.66 (m, 2H, CH$_{ment}$), 1.15−1.27 (m, 2H, CH$_{ment}$), 0.99 (d, $^3J_{HH}$ = 5.8 Hz, C^{10}H$_3$), 0.95 (d, $^3J_{HH}$ = 6.3 Hz, C^{9}H$_3$ or C^{8}H$_3$), 0.92 (d, $^3J_{HH}$ = 6.3 Hz, C^{8}H$_3$ or C^{9}H$_3$), 0.82−1.09 (m, CH$_{ment}$) (total intensity 24H). ^{31}P{^{1}H} NMR (CH_2Cl_2): δ_P 13.81. IR (nujol, PE, cm^{-1}): 275 (br), 294 (br, ν_{Pd-Cl}). $[\alpha]_D^{20}$: −75.1 (*c* 1.10 g/100 mL, CH_2Cl_2).

X-ray Crystal Structure Analysis. Crystal data for **3** were obtained with an Xcalibur-S diffractometer (Varian) using Mo Kα radiation (λ = 0.710 73 Å) and ω-scan rotation. Data reduction was performed with *CrysAlis Pro*[14] including the program *SCALE3 ABSPACK*[15] for empirical absorption correction. The structure was solved by direct methods, and the refinement of all non-hydrogen atoms was performed with *SHELX97*.[16] All hydrogen atoms were calculated on idealized

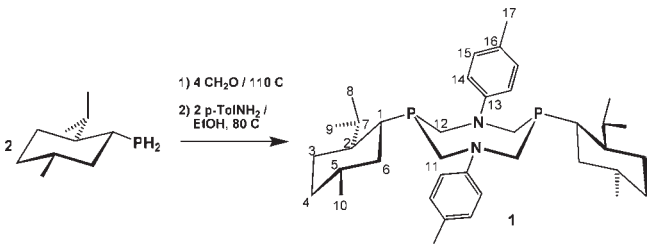
(13) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1990**, *28*, 346–349.

(14) *CrysAlis Pro: Data collection and data reduction software package*, Varian, Inc.: Palo Alto, CA, **2006**.

(15) *SCALE3 ABSPACK: Empirical absorption correction using spherical harmonics*; Oxford Diffraction: Oxford, U.K., **2006**.

(16) *SHELX97* (includes *SHELXS97* and *SHELXL97*): Sheldrick, G. M. *SHELX97: Programs for Crystal Structure Analysis*, release 97-2; University of Göttingen, Göttingen, Germany; **1997**.

Scheme 1



positions using a riding model. Structure figures were generated with ORTEP.[17] A single crystal of **3** was grown from dichloromethane: $C_{38}H_{60}Cl_2N_2P_2Pt \cdot 2CH_2Cl_2$, M = 1042.66 g mol^{-1}, a = 8.1017(1) Å, b = 21.4564(2) Å, c = 25.1560(2) Å, α = 90°, β = 90°, γ = 90°, V = 4372.95(8) Å^3, ρ_{calcd} = 1.584 g cm^{-3}, colorless crystal 0.40 × 0.20 × 0.20 mm, μ = 3.680 mm^{-1}, Z = 4, orthorhombic, space group $P2_12_12_1$, T = 130 K, absolute structure parameter x = −0.014(2), 142 867 reflections collected, 13 363 independent reflections (R_{int} = 0.0337), 468 refined parameters, R1 = 0.0176, wR2 = 0.0367 for $I > 2\sigma(I)$, R1 = 0.0199, wR2 = 0.0380 (all reflections), max residual electron density 1.20 and −0.81 e Å^{-3}.

Results and Discussion

Bis(hydroxymethyl)-L-menthylphosphine was obtained from L-menthylphosphine according to the known method.[12] Its condensation with *p*-toluidine in ethanol gives **1** in 80% yield as an air-stable microcrystalline solid (Scheme 1).

1 is easily soluble in benzene, dichloromethane, and chloroform. Its mass spectrum (FAB_{pos}) showed a molecular ion peak with m/z 606 and peaks with m/z 467 and 668, which are attributable to the loss of one menthyl group by the molecular ion of **1** and the molecular ion peak with a potassium cation and a sodium cation. The specific rotation value $[\alpha]_D^{20}$ of **1** is −52.4.

Complete structure determination of **1** was accomplished by a variety of 1D/2D NMR correlation experiments (COSY, HSQC, ^{1}H−^{13}C/^{1}H−^{15}N/^{1}H−^{31}P HMBC, and 1D DPFGNOE).[18,19] Half of the heterocycle can be easily deduced from internuclear connectivities (see the Supporting Information) on the basis of scalar spin−spin couplings and NOEs (Figure 1). The methylene groups of the heterocycle are nonequivalent in the ^{1}H and ^{13}C NMR spectra because of the presence of asymmetric substituents on the phosphorus atoms (Figure 1). At the same time, there is only one signal in the ^{31}P NMR spectrum (a narrow singlet at δ_P −50.7 ppm) and one ^{15}N NMR peak (δ_N 53 ppm) in ^{1}H−^{15}N HMBC spectrum of **1**, as expected because of the C_2 symmetry of the whole molecule (C_2 symmetry operation around the axis, which is perpendicular to the PNPN plane).

Moreover, the NMR data also suggest high symmetry of the 3D structure of **1** that might be a result of its symmetrical conformation or of the fast mutual exchange between two nonsymmetrical forms. The search for energy minimum conformations (MM2 and hf/6-31g)[20] results in the structure presented in Figure 2, which is strongly supported by a

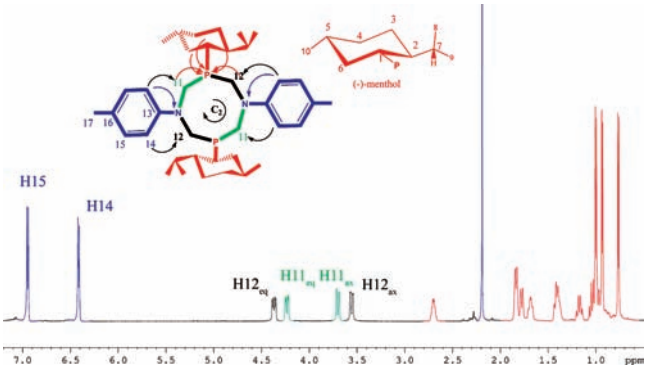


Figure 1. ^{1}H NMR spectrum of **1** ($CDCl_3$ at T = 303 K) and its structure with the principal HMBC [from protons to phosphorus (red) and to nitrogen (blue)] and NOE (black) correlations.

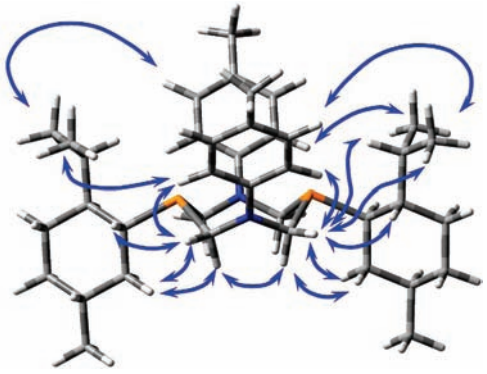


Figure 2. 3D structure of **1** with principal NOEs.

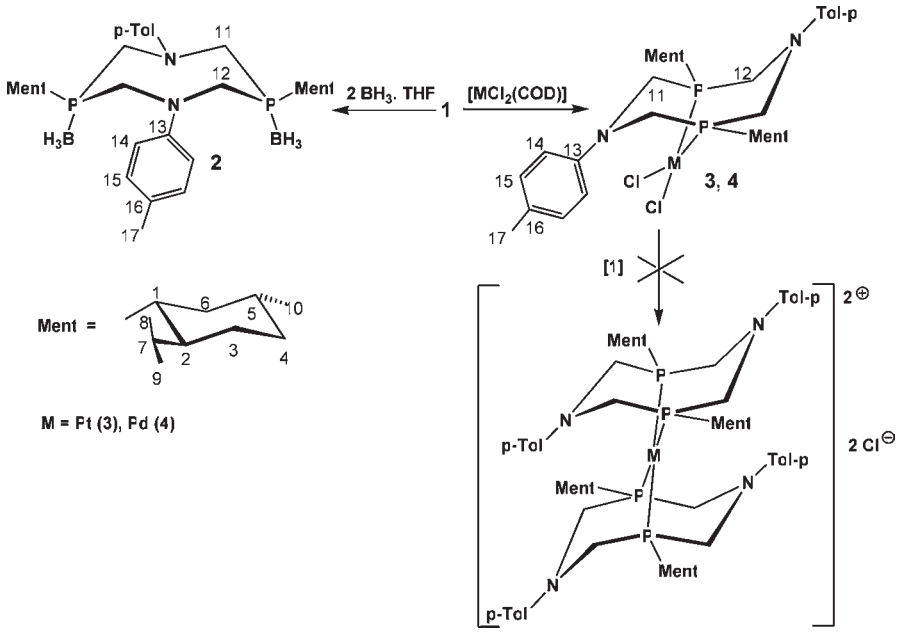
number of stereoselective proton−proton NOEs (see the Supporting Information).

Thus, in solution the eight-membered cycle of **1** adopts the chair−chair conformation with equatorial positions of the menthyl substituents. Their isopropyl groups, lone pairs of electrons of the phosphorus atoms, and N-aromatic groups are oriented approximately in the same direction relative to the PNPN plane. Analogous conformations were earlier found for various *P*-aryl-1,5-diaza-3,7-diphosphacyclooctanes on the basis of essentially different stereospecific coupling constant values $^2J_{PH}$ for equatorial and axial protons and confirmed by the X-ray analysis data.[10,21,22] However, the direct confirmation of this heterocycle's conformation is especially important for **1** because the difference between $^2J_{PH}$ values of equatorial and axial protons at C^{11} (4.8 and 1.0 Hz, accordingly) is low and less informative in comparison with most of the earlier studied 1,5-diaza-3,7-diphosphacyclooctanes.[21,22]

As has been expected, the presence of bulky alkyl substituents on the phosphorus atoms of **1** does not essentially change its complexation properties in comparison with the earlier described diazadiphosphacyclooctanes.[10,22] Treatment of **1** with 2 equiv of the borane−THF complex in benzene leads to the formation of the relatively stable complex **2** containing two borane units coordinated by the

(17) ORTEP3 for Windows: Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565–565.
(18) Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon: Cambridge, U.K., 1988; pp 183−245.
(19) Rahman, A.-ur *One and Two Dimensional NMR Spectroscopy*; Elsevier: Amsterdam, The Netherlands, 1989; pp 406−416.
(20) Haigh, C. W.; Mallion, R. B. *Prog. NMR Spectrosc.* **1980**, *13*, 303–344.
(21) Märkl, G.; Jin, G. Yu.; Schörner, Ch. *Tetrahedron Lett.* **1980**, *21*, 1409–1412.
(22) Karasik, A. A.; Naumov, R. N.; Balueva, A. S.; Spiridonova, Yu. S.; Golodkov, O. N.; Novikova, H. V.; Belov, G. P.; Katsyuba, S. A.; Vandyukova, E. E.; Lonnecke, P.; Hey-Hawkins, E.; Sinyashin, O. G. *Heteroat. Chem.* **2006**, *17*, 499–513.

Scheme 2



phosphorus atoms (Scheme 2). Complex **2** is easily soluble in chloroform and THF. The specific rotation value $[\alpha]_D^{20}$ of **2** is −80. The ^{31}P NMR spectrum of **2** shows one slightly broadened singlet ($\Delta\nu_{1/2}$ = 60 Hz) of four-coordinated phosphorus atoms at δ_P 27.0 ppm, whereas the ^{1}H NMR spectrum indicates retention of the ligand structure and the symmetrical structure of complex **2** in solution. The main changes are observed for signals of the heterocyclic methylene groups and reflect the change of the coordination of the phosphorus atoms due to the disappearance of the lone electron pair's anisotropic effect, but the inequivalence of different methylene groups is also observed, as in the spectra of bisphosphine **1**. A number of the NOEs (Supporting Information, Table 1) indicate retention of the predominant chair−chair conformation of the eight-membered cycle of **2**.

The cyclic bisphosphine **1** also readily reacts with 1 equiv of *cis*-1,5-cyclooctadieneplatinum(II) and *cis*-1,5-cyclooctadienepalladium(II) dichloride in dichloromethane to give stable complexes **3** and **4** of the composition $[MCl_2(L)]$ [L = **1**, M = Pt (**3**), Pd (**4**); Scheme 2]. Specific rotation values $[\alpha]_D^{20}$ of complexes **3** and **4** are −47.5 and −75.1, respectively. The presence of two broad bands for the M−Cl vibrations at 286 and 307 cm^{-1} for **3** and at 275 and 294 cm^{-1} for **4** in the FTIR spectra is evidence of the cis square-planar coordination of the central ions. The ^{31}P NMR spectra of complexes **3** and **4** show extremely broad signals ($\Delta\nu_{1/2}$ > 250 Hz) at δ_P −6.8 and 13.8 ppm, respectively. The coupling constant $^1J_{PtP}$ of the platinum complex **3** of 3150 Hz confirms the cis configuration of the platinum ion.[22,23] The ^{1}H NMR spectra (particularly the spectrum of complex **3**) also show broad lines (Figure 3a). The strong broadening of the signals in the ^{1}H and ^{31}P NMR spectra of the palladium complex **4** and, in particular, of the platinum complex **3** is probably caused by a conformational exchange in solution, which is near intermediate on the NMR time scale.

To prove this hypothesis, DNMR experiments with **3** were carried out. A decrease of the temperature led to additional broadening of the lines, particularly of the signals corresponding to the heterocyclic fragment, and then at ca. 223 K, a collapse was observed in the ^{1}H NMR spectrum (Figure 3b). Finally, at 188 K the ^{1}H NMR spectrum of **3** corresponded to the slow exchange regime on the NMR time scale (Figure 3c). The most important finding is that the number of signals in the ^{1}H NMR spectrum is doubled in comparison with the spectrum at 293 K; e.g., there are proton signals of four N−CH_2−P and two tolyl moieties. Thus, a low-temperature spectrum of **3** corresponds to the conformation that lacks any symmetry. Most likely, it is a chair−boat conformation, where all N−CH_2−P fragments become nonequivalent because of the presence of chiral substituents on the phosphorus atoms and different positions of the methylene groups in the "halves" ("chair"- and "boat"-like) of the heterocycle relative to the central ion (Figure 4), so that the signals of protons at atoms C(11) and C(11′) and atoms C(12) and C(12′) are observed separately (Figure 3c) as eight partially overlapped multiplets. The different environments of two *p*-tolyl groups in this conformation (Figure 4) lead to the nonequivalence of their protons at atoms C(14) and C(14′), C(15) and C(15′), and C(17) and C(17′), so six signals (two AB systems in the aromatic part of the spectrum and two singlets of the methyl groups) are observed for these substituents (Figure 3c).

At 293 K, the signals of only two N−CH_2−P fragments and one *p*-tolyl group are observed as a result of the faster mutual exchange between two possible chair−boat conformations (Figures 3a and 4).

These results are fully supported by the solid-state data. The structure of complex **3** was investigated by X-ray analysis (Figure 5). Single crystals of **3** were obtained as a solvate with two molecules of dichloromethane. It should be mentioned that this solvate is not very stable and that washing with acetonitrile or prolonged drying gives solvent-free microcrystalline **3**. The platinum ion has cis square-planar coordination, and the P,P-chelating ligand has a chair−boat

(23) Alt, H. G.; Baumgartner, R. R.; Brune, H. A. *Chem. Ber.* **1986**, *119*, 1694–1703.

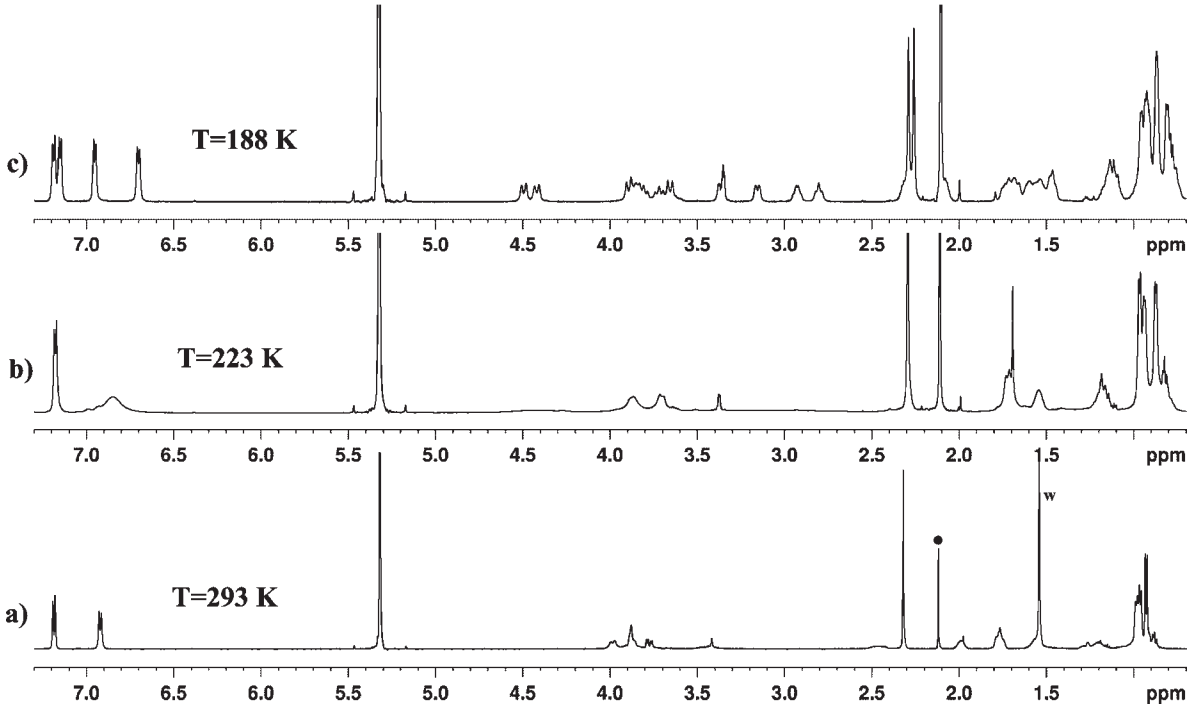


Figure 3. ^{1}H NMR spectra of **3** in CD_2Cl_2 at different temperatures [impurities marked as follows: w, H_2O; ●, $(CH_3)_2CO$].

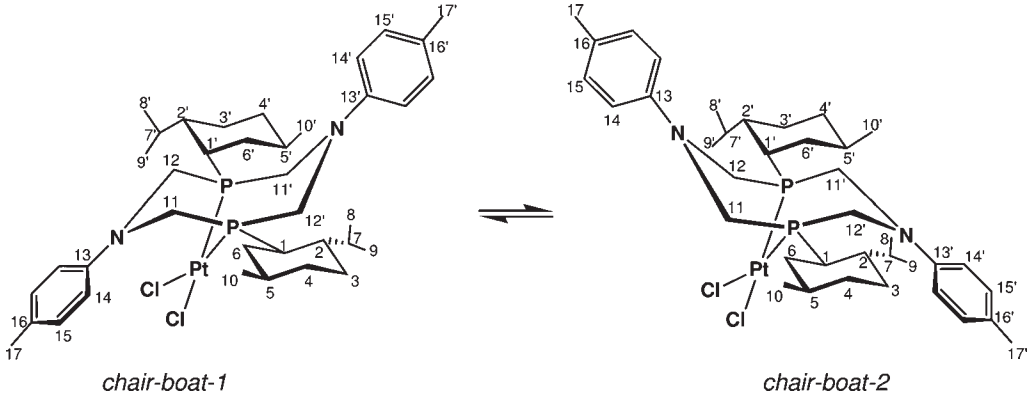


Figure 4. Scheme of the conformational exchange in solutions of complex **3**.

conformation, which is typical for transition-metal complexes of 1,5-diaza-3,7-diphosphacyclooctanes.[10,22] This conformation always leads to the presence of more- and less-shielded sides of the central ion, but in the case of **3**, the total asymmetry of the complex is increased by the different orientations of the menthyl substituents. The isopropyl group of one of the menthyl substituents is directed to the same side as the platinum ion and is located in close proximity to it so that the distances Pt(1)···C(28) and Pt(1)···H(28) are only 4.044(2) and 3.138(2) Å, whereas the corresponding group of the other substituent is directed to the opposite side. The nitrogen atoms have different coordinations: N(2), which is closer to the platinum ion, is coordinated in a nearly trigonal-planar fashion (the sum of the C−N−C bond angles is 354.2°) as a result of conjugation with the π system of the aromatic substituent on this atom,[22,24,25] but the remote atom N(1) is coordinated in a trigonal-pyramidal fashion (the sum of the C−N−C bond angles is 343.8°) and its lone pair of electrons is apparently not conjugated with the π system of the tolyl substituent. The planar coordination of both nitrogen atoms is typically observed for *N*-aryl-substituted 1,5-diaza-3,7-diphosphacyclooctanes as a result of n−π conjugation;[22,24,25] in most of their metal complexes, at least one of the nitrogen atoms (and sometimes both of them[25]) is also trigonal-planar.[22,25,26] On the contrary, the pyramidal coordination of both nitrogen atoms in metal complexes of these *N*-aryl-substituted ligands is rare and, to date, has been observed by X-ray analysis only in the case of dichloro(1,5-di-3′,5′-dicarboxyphenyl-3,7-dimesityl-1,5-diaza-3,7-diphosphacyclooctane)platinum(II) because of the steric interaction of bulky substituents on phosphorus and nitrogen atoms.[22] Probably the sp^3 hybridization of the atom

(24) Arbuzov, B. A.; Erastov, O. A.; Nikonov, G. N.; Litvinov, I. A.; Yufit, D. S.; Struchkov, Yu. T. *Dokl. Acad. Nauk SSSR* **1981**, *257*, 127–131.
(25) Kane, J. C.; Wong, E. H.; Yap, G. P. A.; Rheingold, A. L. *Polyhedron* **1999**, *18*, 1183–1188.
(26) Karasik, A. A.; Bobrov, S. V.; Nikonov, G. N.; Pisarevskii, A. P.; Litvinov, I. A.; Dokuchaev, A. S.; Struchkov, Yu. T.; Enikeev, K. M. *Russ. J. Coord. Chem.* **1995**, *21*, 574–584.

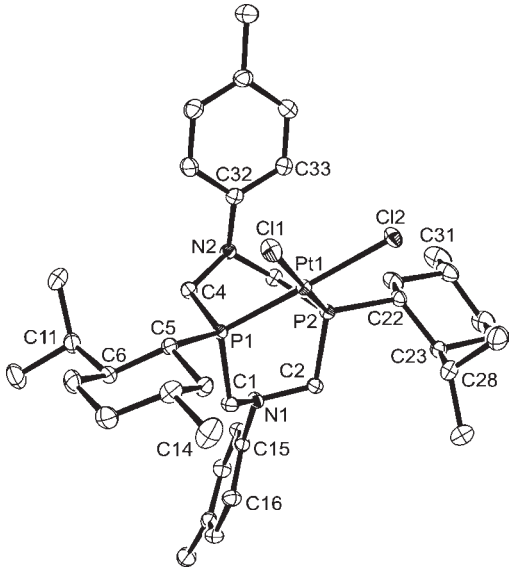


Figure 5. Molecular structure of complex **3**. The solvent molecules and hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50% probability.

N(1) of complex **3** is also the result of the steric interaction of its tolyl substituent with the bulky menthyl group on the phosphorus atom. The relatively short contact between one of the isopropyl groups and the metal ion creates an asymmetry of the transition-metal ion environment and restricts rotation around the exocyclic P−C bond.

An attempt to synthesize the ionic complex of composition $[PtL_2]Cl_2$ (L = **1**) by using a **1**−*cis*-1,5-cyclooctadieneplatinum(II) ratio of 2:1 was unsuccessful. The ^{31}P NMR spectrum of the reaction mixture showed only signals of unreacted ligand **1** and complex **3**, which was isolated from the reaction mixture. Apparently, the presence of the menthyl substituents on the phosphorus atoms does not prevent the formation of *cis*-P,P-chelate metal complexes, but these groups are too bulky for the formation of the cationic bischelate complex $[PtL_2]^{2+}$, which is formed with *P*-phenyl-substituted 1,5-diaza-3,7-diphosphacyclooctanes.[26]

Conclusions

The successful synthesis of the first representative of *P*-L-menthyl-substituted (aminomethyl)phosphine and its borane and chelate metal complexes indicates that L-menthylphosphine is a useful key reagent for the convenient preparation of various (aminomethyl)phosphine ligands with chiral groups on the phosphorus atoms. These ligands are potentially interesting for enantioselective catalytic systems.

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Supporting Information Available: 1D and 2D spectra for compounds **1**−**4**, tables of observed NOE's for compounds **1** and **2**, and X-ray crystallographic data of complex **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.