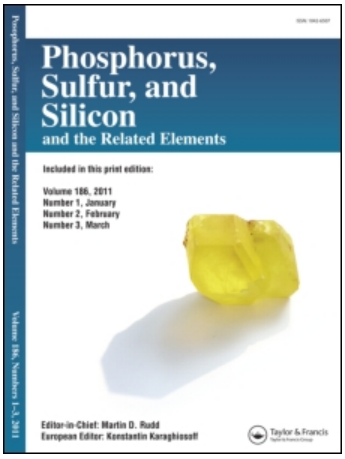

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MENTHYL-SUBSTITUTED ORGANO-PHOSPHORUS-COMPOUNDS. VII[1]: FLUORINATED COMPOUNDS AND DERIVATIVES

Matthias Gruber[a]; Reinhard Schmutzler[a]; Michael Ackermann[b]; Jürgen Seega[b]; Gerhard Hägele[b]
[a] Institut für Anorganische und Analytische Chemie, Technische Universität, Braunschweig, FRG [b] Institut für Anorganische Chemie und Strukturchemie der Universität Düsseldorf, Universitätsstr. 1, Düsseldorf, FRG

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MENTHYL-SUBSTITUTED ORGANO-PHOSPHORUS-COMPOUNDS. VII[1]: FLUORINATED COMPOUNDS AND DERIVATIVES

MATTHIAS GRUBER and REINHARD SCHMUTZLER†
Institut für Anorganische und Analytische Chemie, Technische Universität, Hagenring 30, 3300 Braunschweig, FRG

MICHAEL ACKERMANN, JÜRGEN SEEGA and GERHARD HÄGELE
Institut für Anorganische Chemie und Strukturchemie der Universität Düsseldorf, Universitätsstr. 1, 4000 Düsseldorf 1, FRG

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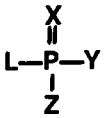
Key words: Menthylphosphorus compounds; phosphorus-fluorine compounds; menthylphosphonic acid; chirality; NMR.

The synthesis of a series of compounds, containing the (−)-menthyl group, bonded to tri-, tetra- and penta-coordinate phosphorus is described. Specifically, the formation of (−)-menthyltetrafluorophosphorane is described, based on the oxidative addition of (−)-menthyl fluoride to phosphorus trifluoride or by the oxidation-reduction reaction between (−)-menthyldichlorophosphine and arsenic trifluoride. The hydrolysis of (−)-menthyltetrafluorophosphorane was found to proceed stepwise, with formation of (−)-menthylphosphonofluoridic acid and, and ultimately, (−)-menthylphosphonic acid. ^{1}H-, ^{13}C-, ^{19}F- and ^{31}P-NMR techniques were used to establish molecular structures of (−)-menthyl-substituted phosphorus compounds. Particular attention is drawn towards the chiral discrimination of geminal fluorine pairs in (−)-menthyl-$P(X)F_2$ (X = :, O, S) compounds, giving rise to ABX spin systems in the $^{19}F\{H\}$- and $^{31}P\{H\}$-NMR spectra.

INTRODUCTION

In previous publications[1,2] of this series we have described menthyl-substituted phosphorus compounds of the general type I, where L stands for the (−)-menthyl,

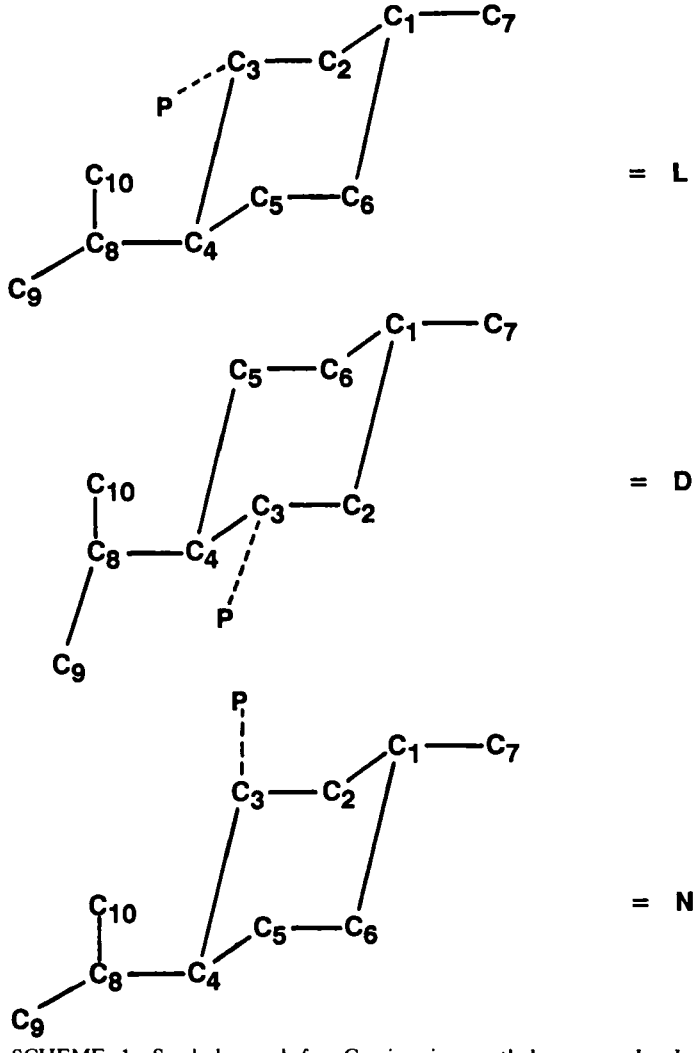


I X = :, O, S

Y, Z = Cl, Alkyl, Aryl, L, D

† Author to whom correspondence should be addressed.

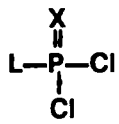
D for the (+)-menthyl, and N for the (−)-neo-menthyl group, as shown in Scheme **1**:



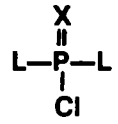
SCHEME 1 Symbols used for C-epimeric menthyl groups: L = L-Menthyl = (−)-Menthyl, D = D-Menthyl = (+)-Menthyl, N = (−)-Neomenthyl.

Our special interest was in the chlorinated compounds of types II–V, as well as in derivatives of tertiary phosphines of type VI.

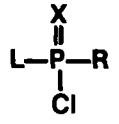
For these compounds pro-chiral (II), chiral (III, VI), pseudo-prochiral (IV) and pseudo-chiral (V) phosphorus centers are characteristic. Based on the X-ray crystal structure determinations of compounds III-c-4, III-c-5, IV-c, V-c and VI-c, and on detailed 1D- and 2D-NMR studies, using nuclei such as ^{1}H, ^{13}C and ^{31}P[1,2,3] we have succeeded in obtaining rotamer- and P-epimer-specific sets of parameters. Our findings should allow us, in the future, to deduce molecular



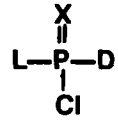
II a X = :
II b X = O
II c X = S



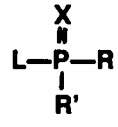
IV a X = :
IV b X = O
IV c X = S



III a X = :
III b X = O
III c X = S
III--1 R = CH_3
III--2 R = C_2H_5
III--3 R = l-C_3H_7
III--4 R = t-C_4H_9
III--5 R = C_6H_5



V a X = :
V b X = O
V c X = S



VI a X = :
VI b X = O
VI c X = S
R = CH_3
R' = C_6H_5

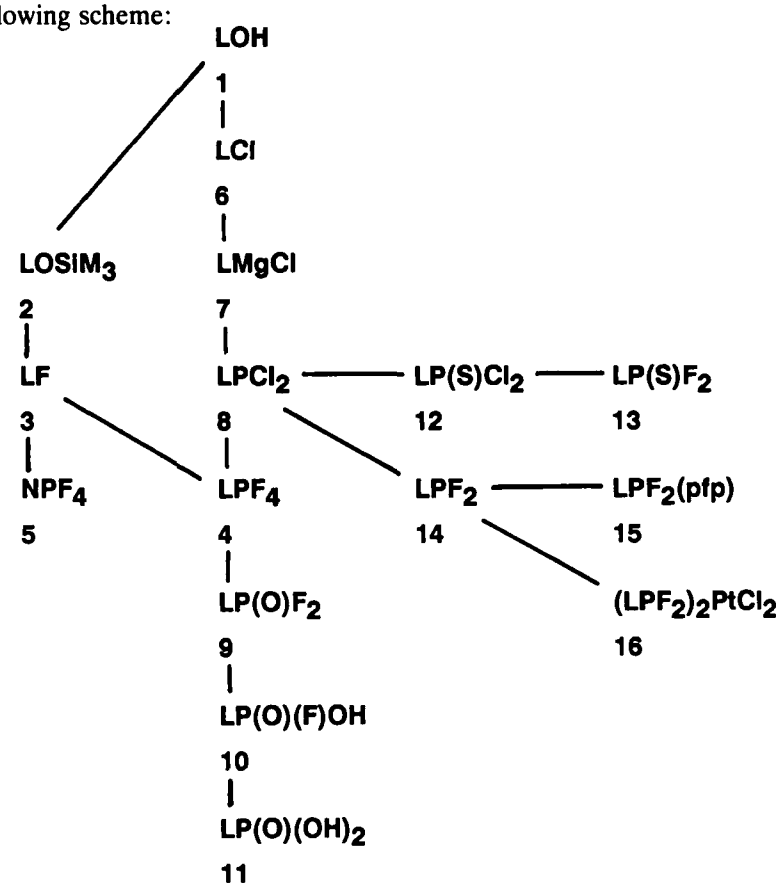
geometries of a given class of compounds without the use of X-ray crystallography.

We have found, furthermore, that the size of the alkyl groups, R and R', has a profound influence on the equilibria between the rotamers and on the population of the P-epimeric pairs in III and VI. Further elaborating on these findings we were interested in the influence of highly electronegative substituents, X and Y, in I on the characteristic shift and coupling parameters of the L-menthyl group, serving as a NMR probe. If the chlorine in II-V is replaced by fluorine the coupling constants, $^nJ_{FH}$, $^nJ_{FC}$ and $^nJ_{PF}$ of the resultant compounds, which are affected by their stereochemistry, should provide further insight into the conformation of these model substances. It is to be expected that the C-chiral menthyl group will permit a differentiation between the geminal fluorine atoms,

thus furnishing the coupling constant, $^2J_{FF}$, which cannot be obtained in the case of achiral compounds. The method of chiral differentiation was also considered as a means of characterizing phosphorane structures.

SYNTHETIC INVESTIGATIONS

In this publication a series of previously unknown (−)-menthyl-phosphorus-fluorine compounds of type II (F instead of Cl) were synthesized, in accord with the following scheme:



SCHEME 2 Reaction sequences

The required starting material, (−)-menthyl fluoride, **3** was formed in accord with Equations (1) and (2), via the reaction of the trimethylsilyl ether, **2** with phenyltetrafluorophosphorane:

$$\underset{1}{LOH} + (CH_3)_3SiCl/[(CH_3)_3Si]_2NH \rightarrow \underset{2}{LOSi(CH_3)_3} \quad (1)$$

$$\underset{2}{LOSi(CH_3)_3} + C_6H_5PF_4 \rightarrow \underset{3}{LF} \quad (2)$$

This type of reaction has been employed successfully in the synthesis of 1-adamantyl fluoride.[4]

Initially we attempted to synthesize (−)-menthyltetrafluorophosphorane, **4** by what may be termed the oxidative addition of (−)-menthyl fluoride, **3** to phosphorus trifluoride, as illustrated in Equation (3):

$$\underset{\mathbf{3}}{LF} + PF_3 + \text{cat. } C_6H_5PF_4 \longrightarrow \underset{\mathbf{4}}{LPF_4} \quad (+ \underset{\mathbf{5}}{NPF_4}) \tag{3}$$

It was found that this reaction did not produce pure (−)-menthyl-tetrafluorophosphorane, **4**. Because of partial C-epimerization the two epimeric forms (−)-menthyltetrafluorophosphorane, **4** and (−)-neo-menthyltetrafluorophosphorane, **5** were formed. In contrast to the analogous addition of 1-adamantyl fluoride to phosphorus trifluoride, **4** and **5** were formed only in small yields.

Fortunately, an alternative synthetic approach, not requiring the use of (−)-menthyl fluoride, **3** led to the formation of (−)-menthyltetrafluorophosphorane, **4**. Following known procedures[5–7] (−)-menthol, **1** was converted to (−)-menthyldichlorophosphine, **8** which, upon oxidative fluorination[8] according to Equation (4), gave (−)-menthyltetrafluorophosphorane, **4**:

$$3\,\underset{\mathbf{8}}{LPCl_2} + 4\,AsF_3 \longrightarrow 3\,\underset{\mathbf{4}}{LPF_4} + 2\,As + 2\,AsCl_3 \tag{4}$$

(−)-Menthyltetrafluorophosphorane, **4** reacts smoothly with hexamethyldisiloxane as do the other fluorophosphoranes[9] to produce (−)-menthylphosphonic difluoride, **9**, as shown in Equation (5).

$$\underset{\mathbf{4}}{LPF_4} + [(CH_3)_3Si]_2O \longrightarrow \underset{\mathbf{9}}{LP(O)F_2} + 2\,(CH_3)_3SiF \tag{5}$$

Since our interest was directed towards phosphonic acids bearing chiral and bulky substituents we attempted to hydrolyse the phosphorane, **4** with formation of (−)-menthylphosphonic acid, **11**. This type of reaction is common with fluorophosphoranes.[10,15d]

Surprisingly, a stable intermediate, the hitherto unknown (−)-menthylphosphonofluoridic acid, **10** was obtained (Equations (6*a*) and (6*b*)).

$$\underset{\mathbf{4}}{LPF_4} + H_2O \longrightarrow \underset{\mathbf{9}}{LP(O)F_2} + 2\,HF \tag{6a}$$

$$\underset{\mathbf{9}}{LP(O)F_2} + H_2O \longrightarrow \underset{\mathbf{10}}{LP(O)(F)OH} + HF \tag{6b}$$

Under more vigorous conditions, **10** could be converted to **11** in low yield

(Equation (7)):

$$\underset{\mathbf{10}}{LP(O)(F)OH} + H_2O \longrightarrow \underset{\mathbf{11}}{LP(O)(OH)_2} + HF \qquad (7)$$

(−)-Menthyldichlorophosphine, **8**, was found to react smoothly with sodium fluoride in anhydrous acetonitrile in the presence of the crown ether, 15-crown-5, to form (−)-menthyldifluorophosphine, **14** (Equation (8)):

$$\underset{\mathbf{8}}{LPCl_2} + 2\ NaF/CH_3CN \longrightarrow \underset{\mathbf{14}}{LPF_2} + 2\ NaCl \qquad (8)$$

For reasons of spectroscopic comparison the phosphonothioic difluoride, **13** was desired. The compound could be synthesized by chlorine-fluorine exchange in **12**,[11] using sodium fluoride in acetonitrile as a fluorinating agent (Equation (9)):

$$\underset{\mathbf{8}}{LPCl_2} + 1/8\ S_8/SnCl_4 \longrightarrow \underset{\mathbf{12}}{LP(S)Cl_2} \qquad (9a)$$

$$\underset{\mathbf{12}}{LP(S)Cl_2} + 2\ NaF/CH_3CN \longrightarrow \underset{\mathbf{13}}{LP(S)F_2} + 2\ NaCl \qquad (9b)$$

In analogy to other phosphorus(III)-fluorine compounds[12] the difluorophosphine, **14** was found to undergo an oxidative addition reaction with hexafluoroacetone, producing a perfluoropinacolylphosphorane, **15** (Equation (10)):

$$\underset{\mathbf{14}}{LPF_2} + 2\ (CF_3)_2CO \longrightarrow \underset{\mathbf{15}}{\text{L(F)(F)P(O)C(CF}_3\text{)}_2\text{OC(CF}_3\text{)}_2\text{O}} \qquad (10)$$

(−)-Menthyldifluorophosphine, **14** was found to exhibit reactivity typical of difluorophosphines.[13] Thus a platinum(II)-complex, **16** could readily be obtained in the reaction of **14** with the cyclo-octadiene complex, (COD)$PtCl_2$ (COD = 1,5-cyclooctadiene) (Equation (11)).

$$\underset{\mathbf{14}}{2\ LPF_2} + (COD)PtCl_2 \longrightarrow COD + \underset{\mathbf{16}}{trans\text{-}Pt(LPF_2)_2Cl_2} \qquad (11)$$

The magnitude of the phosphorus-phosphorus coupling constant $^2J_{PP}$[14] suggests that **16** is present in the cis-configuration.

NUCLEAR MAGNETIC RESONANCE INVESTIGATIONS

^{19}F- and $^{19}F\{^1H\}$-NMR-studies

The ^{1}H-decoupled ^{19}F-NMR spectra of the series, LPF_2, **14**, $LP(O)F_2$, **9** and $LP(S)F_2$, **13** display typical ABX features (A, B = ^{19}F; X = ^{31}P). The relative signs of coupling constants of type $^nJ_{FH}$, $^nJ_{FF}$ and $^nJ_{PF}$ were not determined explicitly. The relevant data for chemical shifts and absolute values of coupling constants are listed in Table I:

TABLE I

^{19}F-NMR: Chemical shift data δ_F (ppm) and coupling constants $^1J_{PF}$, $^2J_{FF}$, $^3J_{FH}$ (Hz) of compounds: **14** (−)-menthyldifluorophosphine, **9** (−)-menthylphosphonic difluoride, **13** (−)-menthylphosphonothioic difluoride, (10% solutions in $CDCl_3$). For references, see text. a) not observed.

Compound: $LP(X)F_2$	**14** X:	**9** O	**13** S
δ_{F_A}	−105.1	−63.0	−43.0
$^1J_{PF_A}$	1169	1167	1194
$^3J_{F_AH_{3\text{-}ax}}$	6.9	2.7	4.5
δ_{F_B}	−111.6	−69.5	−51.3
$^1J_{PF_B}$	1172	1154	1176
$^3J_{F_BH_{3\text{-}ax}}$	16.5	a	a
$^2J_{F_AF_B}$	172	106	54

The chiral differentiation of the geminal fluorine atoms is represented by the difference Δ in their chemical shifts:

$$\Delta = \delta_{F_A} - \delta_{F_B} \tag{12}$$

For the compound of trivalent phosphorus, **14** we have found Δ = 6.5 ppm, while in the case of the phosphonic difluoride, **9** shift differences of 6.5 ppm, and for the phosphonothioic difluoride, **13** of 8.3 ppm have been observed. The geminal interfluorine coupling constant, $^2J_{FF}$ has been determined as 172, 106, and 54 Hz for compounds **14**, **9**, and **13**, respectively. Thus, the strongest coupling effects were noted in the case of (−)-menthyldifluorophosphine, **14**.

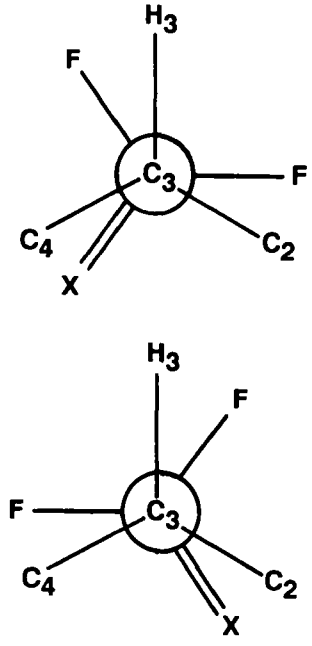
A second parameter, L is defined to describe the chiral differentiation of geminal fluorine pairs by

$$L = |^1J_{PF_A}| - |^1J_{PF_B}| \tag{13}$$

An increase of L is observed in the series **14**, **9** and **13** showing numerical values of −6, +13 and +18 Hz.

In the proton-coupled ^{19}F NMR spectrum of (−)-menthyldifluorophosphine, **14** fine structure, due to coupling between the low-field fluorine F_A and a unique proton M in an ABMX system was observed. Double resonance and 2D-NMR

studies have shown that this fine structure is the result of coupling between F_A and the $H_{3\text{-ax}}$ atom of the (−)-menthyl group. For the high-field fluorine atom F_B in ABMX a comparable coupling, $^3J_{FH}$ is resolved for the compound of trivalent phosphorus, **14** only, but not for **9** and **13**. These findings suggest that the following rotamers are preferred:



SCHEME 3 Rotameric forms.

Some useful conclusions may be derived for compounds of type $LP(X)F_2$:

$$|^1J_{PF_A}| < |^1J_{PF_B}| \quad \text{for } X = :$$

$$|^1J_{PF_A}| > |^1J_{PF_B}| \quad \text{for } X = O, S$$

$$|^3H_{F_AH_{3\text{-ax}}}| < |^3J_{F_BH_{3\text{-ax}}}| \quad \text{for } X = :$$

$$|^3J_{F_AH_{3\text{-ax}}}| > |^3J_{F_BH_{3\text{-ax}}}| \quad \text{for } X = O, S$$

The fluorine resonances cannot be assigned absolutely and conclusively to the alternative structures, at the present time.

(−)-Menthyltetrafluorophosphorane, **4** is undergoing fast pseudorotation at room temperature, in accord with expectation.[15] All four fluorine atoms are apparently equivalent, with $\delta_F = -53.1$ ppm, at ambient temperature. A series of ^{19}F-NMR spectra was recorded, varying the temperature between 273 K and 183 K in increments of 10 K. Only slight broading and no coalescense was observed at the lowest temperature accessible with our instrumentation.

For the perfluoropinacolyl derivative, **15**, even at room temperature, a rigid ground state structure was observed. The assignment of shift values $\delta_{F(axial)} = -58.8$ ppm and $\delta_{F(equatorial)} = -49.9$ ppm is based on previously known analogous cases.[12] For the trifluoromethyl groups of the perfluoropinacolyl

group an $A_3B_3C_3D_3X$ (A, B, C, D = ^{19}F; X = ^{31}P) type spectrum was expected but the room temperature ^{19}F NMR spectra could not be assigned unambiguously and conclusively. Two broad multiplets, centered at -67.7 ppm and -68.5 ppm, were observed for the CF_3 groups.

As a result of the isotopic distribution of platinum a superimposition of the AB regions of $[ABX]_2M$ (M = Pt) systems may be expected in the ^{19}F-NMR spectrum of **16**. In fact, only simple ABX spectra were observed and it follows directly that $|^2J_{PP}| \ll |^1J_{PF}|$ and $|^4J_{FF}| \ll |^1J_{PF}|$. Thus, the presence of a platinum complex is ruled out, as very large values for $^2J_{PP}$ would be expected.[14]

$^{13}C\{^1H\}$-NMR investigations

The ^{13}C NMR resonances have been assigned on the basis of the principles discussed in detail in References 2 and 3. Coupling between ^{19}F and ^{13}C of the menthyl skeleton has been resolved only for the C_3 atoms. Results are given in Tables IIa and IIb.

TABLE IIa

^{13}C-NMR: Chemical shift δ_C (ppm) for compounds: **2**, **4**, **9–11**, and **13–16** (10% solution in $CDCl_3$; for **2**, 20%). For references, see text.

	Compound:								
	2	**4**	**9**	**10**	**11**	**13**	**14**	**15**	**16**
C_1	31.79	32.89	32.46	32.74	32.81	32.44	30.25	33.08	33.10
C_2	45.62	34.90	34.35	34.92	35.30	34.83	32.52	36.47	33.86
C_3	72.59	47.82	38.09	37.67	37.87	45.03	47.90	49.30	46.87
C_4	50.19	43.50	42.56	42.90	43.14	43.31	42.38	43.73	43.47
C_5	23.16	23.63	23.94	24.19	24.39	23.67	24.87	24.75	24.90
C_6	34.70	34.23	33.96	34.39	34.67	34.10	34.59	34.12	34.18
C_7	22.32	22.17	21.95	22.27	22.50	22.21	22.56	22.19	22.42
C_8	25.39	29.95	29.59	28.94	28.56	29.32	29.30	30.22	30.19
C_9	16.05	15.24	15.11	15.21	15.39	15.00	15.60	15.99	15.70
C_{10}	21.25	21.41	21.28	21.50	21.67	21.51	21.48	21.47	21.76

TABLE IIb

^{13}C-NMR: Coupling constants $^nJ_{PC}$ and $^2J_{FC}$ (Hz) for compounds **4**, **9–11**, and **13–16** (10% solutions in $CDCl_3$). a) The X-part of an ABMX-system was observed. Averaged coupling constants $^2J_{FC}$ in **14** ca. 6 Hz, in **16** ca. 15 Hz. b) This second order spectrum could not be fully analysed up to now.

		Compound							
n		**4**	**9**	**10**	**11**	**13**	**14**	**15**	**16**
		$^nJ_{PC}$ coupling constants:							
3	C_1	21.2	17.4	16.7	16.0	17.4	6.8	20.3	17.0
2	C_2	7.4	—	—	—	—	5.7	—	—
1	C_3	175.0	133.6	140.5	140.3	95.5	37.4	154.3	43.6
2	C_4	—	—	—	—	—	12.0	—	—
3	C_5	24.8	19.9	18.6	17.1	19.5	7.2	24.2	14.6
3	C_8	—	—	—	—	—	15.6	—	3.3
		$^2J_{FC}$ coupling constants:							
2	C_3	13.2	12.2	16.6	—	11.2	a,b	b	a,b

^1H- and $^{31}P\{^1H\}$-NMR investigations

In the absence of detailed 2D-NMR experiments only parts of the ^1H resonance region can be assigned to the stereochemically relevant hydrogen atoms in the menthyl group. As has previously been shown[1-3] the resonances due to the methyl groups in the menthyl system are readily assigned, and relevant data are listed in Table III.

TABLE III

^1H-NMR: Chemical shift data, δ_H (ppm) and coupling constants, $^3J_{HH}$ (Hz) for the methyl groups, 7, 9 and 10 of (−)-menthyl-substituted phosphorus compounds (10% solutions in $CDCl_3$). The spectra were recorded at 400 MHz. The assignment of the methyl groups was confirmed by C,H-COSY for **11** and **13** in other cases it is suggested, by analogy to References 1–3. For references see text.

Comp.:	Chemical shift data δ_H Methyl groups			Coupling constants $^3J_{HH}$		
	7	9	10	7	9	10
5	0.9614	0.9614	0.8473	6.70	6.70	6.96
9	0.9562	0.8448	0.9906	6.79	6.44	6.83
10	0.925	0.811	0.949	6.86	6.54	6.79
11	0.8946	0.7832	0.9109	6.33	6.63	6.68
13	0.9519	0.8134	0.9724	6.47	6.91	6.82
14	0.9711	0.8875	0.9794	6.82	6.63	6.88
15	0.9571	0.7995	0.9662	6.81	6.97	6.80
16	0.9945	0.9782	0.9529	6.67	6.44	6.82

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EXPERIMENTAL

General remarks: The usual precautions with regard to exclusion of air and moisture were observed throughout the course of this work. Solvents were dried by standard procedures[16].

NMR measurements were made, using a BRUKER AM 200 NMR spectrometer, at 200 MHz (^1H), 188 MHz (^{19}F), and 81 MHz (^{31}P), and an AM 400 NMR spectrometer, at 400 MHz (^1H) and 101 MHz (^{31}P), respectively. If not otherwise stated 10% solutions in $CDCl_3$ were used for recording NMR spectra. References were int. TMS (^1H), int. $CDCl_3$ (^{13}C), ext. C_6F_6 (^{19}F), ext. 85% H_3PO_4 (^{31}P). Multiplicity of NMR spectra: s = singlet; d = doublet; t = triplet; q = quartet; qt = quintet.

Mass spectra were recorded on a Finnigan MAT 8430 instrument (direct inlet system; 70 eV). Compound **10** was characterized by chemical ionization mass spectrometry (CI-MS), using ammonia as a reagent gas.

Preparation of (−)-menthyltrimethylsilyl ether, **2.** Trimethylchlorosilane (34.5 g 0.32 mole) was added dropwise to a solution of 50 g (0.32 mole) of (−)-menthol, **1** in 25.6 g (0.16 mole) of hexamethyldisilazane during 30 min. The reaction mixture was magnetically stirred at 130°C for 12 h. After it had been allowed to cool to room temperature the ammonium chloride formed was removed by filtration, and the filtrate was fractionally distilled. Yield: 67.8 g (93%) of **2**. B.p. 83°C (3.5 mm) (Lit.[17]).

^1H-NMR data: δ_H 0.01 ppm (s, $Si(CH_3)_3$); δ_H 3.38 ppm (dt, $H_{3\text{-ax}}$); δ_H 0.881 ppm (d), $^3J_{HH}$ 7.53 Hz; δ_H 0.879 ppm (d), $^3J_{HH}$ 6.55 Hz; δ_H 0.672 ppm (d), $^3J_{HH}$ 6.93 Hz; 3 methyl groups from (−)-menthyl skeleton, no stereospecific assignment possible.

Reaction of (−)-menthyltrimethylsilyl ether, **2** *with phenyltetrafluorophosphorane: formation of (−)-menthyl fluoride,* **3.** At room temperature 63.5 g (0.28 mole) of (−)-menthyltrimethylsilyl ether, **2** were added dropwise with magnetic stirring to 54.3 g (0.3 mole) of phenyltetrafluorophosphorane during 1 h. The reaction mixture was subsequently stirred for 12 h at room temperature. A saturated aqueous solution of sodium carbonate (1000 ml) was then added, followed by extraction with 500 ml of diethyl-ether. Upon fractional distillation 17.2 g (39%) of **3** was obtained. B.p. 51°C (10 mm) (Lit.[18]).

^{1}H-NMR data (C_6D_6): δ_H 4.15 ppm (m, $H_{3\text{-ax}}$); $^2J_{FH_{3\text{-ax}}}$ 50 Hz

^{19}F-NMR data (recorded on a JEOL JNMC 60 HL instrument at 56.4 MHz; neat): δ_F −175.7 ppm (d); $^2J_{FH_{3\text{-ax}}}$ 50 Hz.

Reaction of **3** *with phosphorus trifluoride in the presence of $C_6H_5PF_4$: formation of a mixture of (−)-menthyltetrafluorophosphorane,* **4** *and (−)-neomenthyltetrafluorophosphorane,* **5.** The experiment was conducted in a 250 ml glass tube, fitted with a TEFLON® stopcock. In this tube were placed 8.86 g (0.06 mole) of **3** and 1.29 g (0.007 mole) of phenyltetrafluorophosphorane.[16c] After cooling to liquid nitrogen temperature 6.0 g (0.068 mole) of phosphorus trifluoride was condensed into the tube. The reaction mixture was allowed to warm up to room temperature (1 h), and was magnetically stirred for 4 h. The colour of the initially colourless solution had then changed to dark red. The tube was subsequently evacuated to 10^{-4} mm (−100°C) and 5.0 g (0.0557 mole) of phosphorus trifluoride were recovered. The less volatile liquid was fractionally distilled, and 1.8 g of a mixture of **4** and **5** (b.r. 35–38°C, 2.5 mm) was obtained.

^{1}H-NMR data ($CDCl_3$): δ_H 0.5–2.1 ppm (m, **4** and **5**). Impurities: δ_H 7.5–7.9 ppm (m, $C_6H_5P(O)F_2$).

^{19}F-NMR data (recorded on a JEOL JN MC 60 HL instrument at 56.4 MHz; neat): δ_F − 53.7 ppm (d); $^1J_{PF}$ 1034 Hz (**4**); relative intensity (I_{rel}) 2; δ_F − 55.0 ppm (d); $^1J_{PF}$ 1030 Hz (**5**); I_{rel} 1;

Impurities: δ_F − 46.7 ppm (d); $^1J_{PF}$ 1030 Hz; I_{rel} 1; δ_F − 65.6 ppm (d); $^1J_{PF}$ 1096 Hz; ($C_6H_5P(O)F_2$); I_{rel} 5.

^{31}P-{^{1}H}-NMR data: δ_P − 28.8 ppm (qt); $^1J_{PF}$ 1030 Hz (**4** and **5**). Impurity: δ_P 11.0 ppm (t); $^1J_{PF}$ 1100 Hz ($C_6H_5P(O)F_2$).

Similar mixtures of products, including small amounts of the desired tetrafluorophosphorane, **4** were obtained when the reaction of **3** with PF_3 was conducted in the presence of PF_5 and CH_3PF_4.

Synthesis of (−)-menthyldichlorophosphine, **8;** The synthesis was conducted using procedures described in the literature.[8,15e] (−)-Menthyl chloride, **6** was prepared from (−)-menthol, **1** and $ZnCl_2$/37% HCl.[5]

A Grignard reagent, **7**, prepared from 133.5 g (0.76 mole) of **6** and 22.3 g (0.92 mole) of magnesium turnings,[6] was allowed to react with 100 g (0.73 mole) phosphorus trichloride.[7] The dichlorophosphine, **8** was obtained in 46% yield (84.4 g). B.p. 92°C (1 mm) (Lit.:[7] yield 77% B.p. 92°C (1.2 mm)).

^{1}H-NMR data ($CDCl_3$): δ_H 0.5–2.3 ppm (m), (−)-menthyl group.

^{31}P{^{1}H}-NMR data ($CDCl_3$): δ_P 209.7 ppm (s); Lit.,[7] δ_P 209.0 ppm.

Reaction of **8** *with arsenic trifluoride: synthesis of (−)-menthyl-tetrafluorophosphorane,* **4.** Arsenic trifluoride (9.13 g; 0.069 mole) was added dropwise with magnetic stirring to 11.0 g (0.046 mole) of **8** over 15 min. The colour changed from an initial brown to black. Stirring was continued for 1 h at room temperature. The product was obtained upon distillation through a 10 cm Vigreux still as a colourless fuming liquid. Yield 7.2 g (64%) of **4**. B.p. 93°C (22 mm).

$C_{10}H_{19}F_4P$ (246.23). Found: C, 50.84; H, 7.76; F, 29.60. Calc.: C, 48.78; H, 7.78; F, 30.86. MS (25°C): 226 ($M - HF^+$)(31%); 107 (PF_4^+)(68%).

^{1}H-NMR data ($CDCl_3$): δ_H 0.7–2.4 ppm (m), (−) menthyl group.

^{19}F-NMR data ($CDCl_3$): δ_F −53.1 ppm (dd); $^1J_{PF}$ 1024 Hz; $^3J_{FH_{3\text{-ax}}}$ 6.3 Hz;

^{31}P{^{1}H}-NMR data ($CDCl_3$); δ_P −30.3 ppm (qt); $^1J_{PF}$ 1024 Hz.

Reaction of (−)-menthyltetrafluorophosphorane, **4** *with hexamethyldisiloxane: preparation of (−)-menthylphosphonic difluoride,* **9.** (−)-Menthyltetrafluorophosphorane, **4** (11.8 g; 0.05 mole) was placed into a two-necked flask, fitted with a pressure-equalizing dropping funnel, and a reflux condenser, protected by a drying tube. After addition of 6.35 g (0.04 mole) of hexamethyldisiloxane[9] over 20 min the reaction mixture was stirred magnetically overnight, and was then distilled through a 10 cm Vigreux still. Yield 7.6 g (71%) of **9**. B.p. 86°C (3.5 mm).

$C_{10}H_{19}F_2OP$ (224.23). Found: C, 53.78; H, 8.53; F, 16.80. Calc.: C, 53.57; H, 8.54; F, 16.95. MS (25°C): 224 (M^+) (26%).

^{1}H-NMR data ($CDCl_3$): δ_H 0.7–2.3 ppm (m, (−)-menthyl group).

^{19}F-NMR data ($CDCl_3$): δ_{F_A} −63.0 ppm (ddd); $^1J_{PF_A}$ 1167 Hz; $^3J_{F_AH_{3\text{-ax}}}$ 2.7 Hz; δ_{F_B} −69.5 ppm (dd); $^1J_{PF_B}$ 1154 Hz; $^3J_{F_BH_{3\text{-ax}}}$ not resolved; $^2J_{F_AF_B}$ 106 Hz.

^{31}P-{^{1}H}-NMR data ($CDCl_3$): δ_P 27.8 ppm (dd); $^1J_{PF_A}$ 1167 Hz; $^1J_{PF_B}$ 1155 Hz.

Reaction of (−)-menthyltetrafluorophosphorane, **4** *with water: synthesis of (−)-menthylphosphonofluoridic acid,* **10.** *(−)-Menthyltetrafluorophosphorane,* **4** (19 *g*; 0.077 mole) was stirred with excess water for 24 h at room temperature. The reaction mixture was extracted with 50 ml of dichloromethane. Upon evaporation of the dichloromethane a milky, viscous product was left which was dissolved in 10 ml of toluene. Upon cooling to −20°C (overnight) white crystals of **10** were formed which were collected by filtration and dried in vacuo. Yield 5.9 g (34%) of **10.** M.p. 90°C.

$C_{10}H_{20}FO_2P$ (222.23). Found: C, 54.11; H, 8.88; F, 8.50; P, 13.70. Calc.: C, 54.04; H, 9.07; F, 8.55; P, 13.94. MS (90°C; NH_3 positive CI-MS): 240 $(M + NH_4^+)$ (100%) (100°C; NH_3 negative CI-MS): 221 (M-H) (100%).

Titration of **10** with 0.1 m tetramethylammonium hydroxide (using a fully automated PC-guided AUTO-T[19] titration apparatus): 93.124 mg of **10**, dissolved in 40 ml H_2O (doubly distilled); found: 4.21 ml, calc.: 4.19 ml. The equivalence point at pH 7.07, is characteristic of this strong monobasic acid.

^{1}H-NMR data ($CDCl_3$): δ_H 0.7–2.3 ppm (m, (−)-menthyl group); δ_H 12.47 ppm (s, OH); δ_H 0.949 ppm (d, CH_3-10); $^3J_{HH}$ 6.79 Hz; δ_H 0.925 ppm (d, CH_3-7); $^3J_{HH}$ 6.86 Hz; δ_H 0.811 ppm (d, CH_3-9); $^3J_{HH}$ 6.54 Hz.

^{19}F-NMR data ($CDCl_3$): δ_F −60.1 ppm (d); $^1J_{PF}$ 1070 Hz.

^{31}P{^{1}H}-NMR data ($CDCl_3$): δ_P 35.1 ppm (d); $^1J_{PF}$ 1071 Hz.

Reaction of (−)-menthylphosphonofluoridic acid, **10** *with water: synthesis of (−)-menthylphosphonic acid,* **11.** (−)-Menthylphosphonofluoridic acid, **10** (3.0 g; 0.0135 mole) was stirred in 40 ml of water in a round-bottom flask, fitted with a reflux condenser, at 70°C, for 24 h. The resulting mixture was allowed to cool to room temperature, and was extracted with five 10 ml portions of dichloromethane. The volume of the extract was reduced to 10 ml, and **11** was precipitated as a colourless solid upon cooling of the solution to −20°C overnight. Yield: 0.8 g (27%); m.p. 127°C.

$C_{10}H_{21}O_3P$ (220.25). Found: C, 54.72; H, 9.57; P, 14.02. Calc.: C, 54.53; H, 9.61; P, 14.06. MS (130°C): 220 (M^+) (74)%.

Titration of **11** with 0.1 m tetramethylammonium hydroxide (using an AUTO-T instrument[19]): 74.10 mg of **11**, dissolved in 40 ml H_2O (doubly distilled), equivalence points at: pH 7.19, found: 3.38 ml, calc.: 3.38 ml, pH 10.25, found: 6.82 ml, calc.: 6.76 ml.

^{1}H-NMR data ($CDCl_3$): δ_H 0.7–2.4 ppm (m, (−)-menthyl group); δ_H 10.5 ppm (s, OH); δ_H 0.911 ppm (d, CH_3-10); $^3J_{HH}$ 6.68 Hz; δ_H 0.895 ppm (d, CH_3-7); $^3J_{HH}$ 6.33 Hz; δ_H 0.783, ppm (d, CH_3-9); $^3J_{HH}$ 6.63 Hz.

^{31}P{^{1}H}-NMR data ($CDCl_3$): δ_P 36.65 ppm (s).

Preparation of (−)-menthyldifluorophosphine, **14.** (−)-Menthyldichlorophosphine, **8** (10.2 g; 0.042 mole) was added to a suspension of 7.0 g (0.16 mole) of sodium fluoride in 40 ml of acetonitrile in the presence of 0.32 g (0.0013 mole) of the crown ether 15-crown-5. The reaction mixture was stirred magnetically for 3d at 80°C, was then allowed to cool to room temperature, and was filtered and fractionally distilled through a 10 cm Vigreux column. The product, **14** was obtained as a colourless, fuming liquid. Yield 6.34 g (72%); b.p. 94°C (21 mm).

$C_{10}H_{19}F_2P$ (208.23). Found: C, 57.64; H, 9.15; F, 18.00. Calc.: C, 57.68; H, 9.20; F, 18.25. MS (25°C): 208 (M^+) (1%).

^{1}H-NMR data ($CDCl_3$): δ_H 0.8–2.3 ppm (m, ((−)-menthyl group).

^{19}F-NMR data ($CDCl_3$): δ_{F_A} −105.1 ppm (ddd); $^1J_{PF_A}$ 1169 Hz; $^3J_{F_AH_{3-ax}}$ 6.9 Hz; δ_{F_B} −111.6 ppm (ddd); $^1J_{PF_B}$ 1172 Hz; $^3J_{F_BH_{3-ax}}$ 16.5 Hz; $^2J_{F_AF_B}$ 172 Hz.

^{31}P{^{1}H}-NMR data ($CDCl_3$): δ_P 241.9 ppm (dd); $^1J_{PF_A}$ 1163 Hz; $^1J_{PF_B}$ 1168 Hz.

Preparation of (−)-menthylphosphonothioic dichloride, **12.** A procedure adapted from that described in the literature[2b] was employed. A mixture, consisting of 38.0 g (0.16 mole) of **8**, 5.5 g (0.17 g-atoms) of sulphur, and 0.5 ml of tin tetrachloride was heated with magnetic stirring for 3 h at 130°C, and was subsequently distilled in vacuo. Yield of **12**, 36.5 g (85%); b.p. 130–135°C (0.6 mm) (Lit.:[2b] yield 37%; b.p. 138–141°C (0.3–0.4 mm).

^{31}P{^{1}H}-NMR data (recorded on a JEOL JNMC 60 HL instrument at 24.6 MHz; neat): δ_P 100.4 ppm (s); Lit.:[2b] δ_P 101.6 ppm.

Reaction of (−)-menthylphosphonothioic dichloride, **12** *with sodium fluoride: preparation of (−)-menthylphosphonothioic difluoride,* **13.** A mixture of 16.5 g (0.06 mole) (−)-menthylphosphonothioic dichloride, **12** and 0.35 g of the crown ether, 15-crown-5 was added with magnetic stirring to a suspension of 10 g (0.24 mole) of sodium fluoride in acetonitrile. After 1 h the colour of the reaction mixture turned yellow. After 24 h stirring the reaction mixture was allowed to cool to room

temperature, was filtered, and was distilled through a 10 cm Vigreux column, to give a colourless liquid. Yield of **13** 10.3 g (71%); b.p. 78°C (2 mm).

$C_{10}H_{19}F_2PS$ (240.30). Found: C, 50.16; H, 8.03; F, 16.0. Calc.: C, 49.98; H, 7.97; F, 15.81. MS (25°C): 240 (M^+) (4%).

^{1}H-NMR data ($CDCl_3$): δ_H 0.7–2.3 ppm (m, (−)-menthyl group).

^{19}F-NMR data ($CDCl_3$): δ_{F_A} −43.0 ppm (ddd); $^1J_{PF_A}$ 1194 Hz; $^3J_{F_AH_{3\text{-}ax}}$ 4.5 Hz; δ_{F_B} −51.3 ppm (dd); $^1J_{PF_B}$ 1176 Hz; $^3J_{F_BH_{3\text{-}ax}}$ not resolved; $^2J_{F_AF_B}$ 54 Hz.

^{31}P-{^{1}H}-NMR data ($CDCl_3$): δ_P 118.8 ppm (dd); $^1J_{PF_A}$ 1186 Hz; $^1J_{PF_B}$ 1168 Hz.

Reaction of (−)-menthyldifluorophosphine, **14** *with hexafluoroacetone: synthesis of (−)-menthyldifluoro-perfluoropinacolyl-phosphorane,* **15.** A mixture of 1.64 g (0.008 mole) of **14** and 2.81 g (0.017 mole) of hexafluoroacetone was condensed via a vacuum line into a heavy wall glass tube, fitted with a TEFLON^R stopcock. The reaction mixture was allowed to warm up to room temperature, and was stirred magnetically for 24 h. Upon attempted recovery by pumping in vacuo the product **15** solidified. The crude solid was sublimed at 50°C (1 mm). Yield 3.93 g (92%); m.p. 48°C.

$C_{16}H_{19}F_{14}O_2P$ (540.28). Found: C, 36.15; H, 3.78; F, 48.7. Calc.: C, 35.57; H, 3.54; F, 49.23. MS (70°C): 540 (M^+) (4%); 401 ($M - Men^+$)(100%).

^{1}H-NMR data ($CDCl_3$): δ_H 0.7–2.5 ppm (m, (−)-menthyl group).

^{19}F-NMR data ($CDCl_3$): δ_{F_A} −49.9 ppm (dd); $^1J_{PF_A}$ 1021 Hz; δ_{F_B} −58.8 ppm (dd); $^1J_{PF_B}$ 1032 Hz; $^2J_{F_AF_B}$ 72 Hz; δ_F −67.7 ppm (m, 2 CF_3 groups); δ_F −68.5 ppm (m, 2 CF_3 groups).

^{31}P{^{1}H}-NMR data ($CDCl_3$): δ_P −13.3 ppm (dd); $^1J_{PF_A}$ 1013 Hz; $^1J_{PF_B}$ 1023 Hz.

Reaction of **14** *with dichlorocyclooctadiene-platinum(II): preparation of cis-dichloro-bis(−)-menthyldifluorophosphine-platinum(II),* **16.** A solution of 0.611 g (0.0293 mole) of **14** in 10 ml of dichloromethane was combined with a solution of 0.542 g (0.00145 mole) of dichloro-cyclooctadiene-platinum(II) in 10 ml of dichloromethane. The volume of the reaction mixture was reduced in vacuo by about half. Upon cooling to −20°C (overnight) the complex **16** crystallized. Yield 0.841 g (85%); m.p. 137–140°C.

$C_{20}H_{38}Cl_2F_4P_2Pt$ (682.46). Found: C, 35.40; H, 5.60; F, 11.2. Calc.: C, 35.20; H, 5.61; F, 11.14. MS (100°C): 645 ($M - HCl^+$) (1.4%); (based on ^{195}Pt as the most abundant isotope).

^{1}H-NMR data ($CDCl_3$): δ_H 0.8–3.1 ppm (m, (−)-menthyl group).

^{19}F-NMR data ($CDCl_3$): δ_{F_A} −71.5 ppm; $^1J_{PF_A}$ 1169 Hz; $^2J_{PtF_A}$ 501 Hz; δ_{F_B} −76.5 ppm; $^1J_{PF_B}$ 1161 Hz; $^2J_{PtF_B}$ 500 Hz.

^{31}P{^{1}H}-NMR data ($CDCl_3$): δ_P 161.5 ppm (t); $^1J_{PF}$ 1170 Hz; $^1J_{PtP}$ 4961 Hz.

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