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Determination of the absolute configurations of the epimers of the P-chiral phosphine $Ph_2PCH_2CH_2P^*Ph(L\text{-}(-)\text{-menthyl})$ by use of two-dimensional NMR spectroscopy in combination with a palladium(II) "reporter complex" ☆

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Abstract

The two epimers of the new P-chiral phosphine $Ph_2PCH_2CH_2P^*Ph(L\text{-}(-)\text{-menthyl})$ (**1-Rp** and **1-Sp**) were synthesized by treating Ph_2PH with the diastereomerically pure forms of $Ph(L\text{-}(-)\text{-menthyl})CH{=}CH_2)P$. The palladium(II) complexes $[Pd((S)\text{-}o\text{-}C_6H_4CHMeNMe_2)(\mathbf{1\text{-}Rp})][PF_6]$, **2-Rp**, and $[Pd((S)\text{-}o\text{-}C_6H_4CHMeNMe_2)(\mathbf{1\text{-}Sp})][PF_6]$, **2-Sp**, were obtained by treating the corresponding bisphosphines with $[Pd_2Cl_2((S)\text{-}o\text{-}C_6H_4CHMeNMe_2)_2]$. Each of these complexes exists in the form of two regioisomers differing in the orientation of the chiral phosphine relative to the C-donor. Constraints from close interligand, intramolecular hydrogen–hydrogen contacts within three of these palladium complexes were detected by two-dimensional NOE speetroscopy, and were used to determine the absolute configurations at the chiral phosphorus centers in the $Ph_2PCH_2CH_2PPh(L\text{-}(-)\text{-menthyl})$ isomers. The conformations of the two chelate rings in the more abundant of these isomers were also determined.

Keywords: Chiral phosphine; Absolute configuration; Two-dimensional NMR; Palladium; Solution structure

1. Introduction

Transition metal complexes with chiral bisphosphine ligands play an important role as catalysts in asymmetric synthesis [1]; e.g. the stereospecific hydrogenation of prochiral olefins with rhodium and ruthenium [2–9]. Although most of these catalysts contain phosphine ligands of C_2 symmetry, e.g. chiraphos [3], diop [4] or binap [5], ligands of lower symmetry, i.e. norphos [6], pyraphos [7], ferrocene derivatives [8], or even chelates in which the chirality resides at the phosphorus donor [9], have also been successfully used.

In general, it is of considerable interest to know the absolute configuration of the phosphine employed in order to relate its chirality to that of the product. In the last few years it had been amply demonstrated [10,11] that two-dimensional NMR spectroscopy, notably NOESY, can be used to determine unambiguously the complete stereostructure of metal complexes in solution. When the chirality of a co-ligand is known, this can be used as a "reporter" fragment to determine the absolute configuration of another coordinated molecule. The β-pinene moiety functioning as an π-allyl ligand to Pd(II) was used for this purpose in several instances [11a–11c,11g]. More recently, Bookham and McFarlane [12] have employed rotating frame Overhauser spectroscopy on the cyclometallated unit $Pd(o\text{-}C_6H_4CHMeNMe_2)$ to redetermine the absolute configuration of (+)-chiraphos.

Recent work in this laboratory on tridentate phosphine ligands containing L-(−)-menthyl substituents and chiral centers at the P-atoms, e.g. $PhP(CH_2CH_2PPh(L\text{-Men}))_2$ [13], required the determination of the absolute configuration of the chiral phosphorus atoms produced by treating $PhPH_2$ with the key intermediates $Ph(L\text{-menthyl})(CH{=}CH_2)P$. However, for the determination of the chirality by NMR spectroscopy, it is more convenient to use the bisphosphine because of

☆ Dedicated to Prof. F. Calderazzo.

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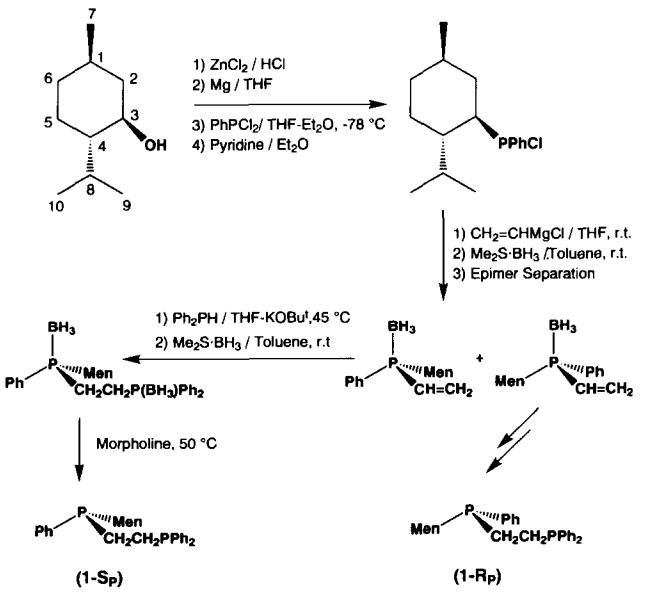
the presence of fewer spins and the possibility of studying square planar complexes instead of the more demanding trigonal-bipyramidal or octahedral compounds favored by the corresponding terdentate ligands. This was accomplished by transforming the vinyl phosphine into the bisphosphine ligand $Ph_2PCH_2CH_2$-PPh(*L*-(−)-menthyl), **1**, which was then combined with the "reporter" fragment 'Pd((S)-*o*-$C_6H_4CHMeNMe_2$)' along the lines suggested by Kyba and Rines [14] and in the studies by Bookham and McFarlane [12]. As the chemical transformations leading to the above trisphosphine do not differ from those used to obtain the bisphosphine, the absolute configurations at their chiral phosphorus centers are expected to be the same. The formation of two regio-isomers of [Pd((S)-*o*-C_6H_4-$CHMeNMe_2$)(Ph(*L*-Men)$PCH_2CH_2PPh_2$)][PF_6] for each of the P-epimers is possible and thus considerable overlap in the ^{1}H-NMR spectrum was expected. Thus the use of a combination of two-dimensional NMR techniques was indicated, as they should provide the necessary NOE information and stereo-specific assignments.

2. Results and discussion

2.1. Preparations

2.1.1. Chiral ligands

The *L*-menthyl substituted chiral bisphosphines were prepared as outlined in Scheme 1. In a first step the menthyl-substituted epimers Ph(*L*-Men)PCl were obtained in the ratio of ca. 3:1 via a Grignard reaction starting from $PhPCl_2$ [15]. This mixture was treated with vinylmagnesium chloride to afford the P-epimeric



Scheme 1.

Ph(*L*-Men)$PCH{=}CH_2$ in a ratio of ca. 2:1. After conversion into the air-stable borane adducts, the pure diastereomers and (Sp)–Ph(*L*-Men)$P(BH_3)(CH{=}CH_2)$ were obtained by column chromatography on silica gel, followed by recrystallization from pentane. Spectral data for these epimers are given in the Experimental details.

After the base-catalyzed addition of the secondary phosphine Ph_2PH to (Rp)– or (Sp)–Ph(*L*-Men)P-$(BH_3)(CH{=}CH_2)$, the products, (Rp)– or (Sp)–Ph(*L*-Men)$P(BH_3)CH_2CH_2$-PPh_2, respectively, were directly converted into the air-stable bisborane adducts (Rp)– or (Sp)–Ph(*L*-Men)$P(BH_3)CH_2CH_2P(BH_3)Ph_2$. The corresponding free bisphosphines were obtained in excellent yields by removing the protecting BH_3 groups with morpholine. The above assignments of the absolute configurations of the vinylphosphines are based on the assumption that their transformation occurs with retention of configuration at the phosphorus centre. This seems reasonable because (i) the P–H bond addition involves only the vinyl group and not the stereogenic quaternary P-center, and (ii) the free phosphine is generated from the borane adduct by a dissociative mechanism [16].

2.1.2. Palladium complexes

The palladium(II) complexes [Pd((S)-*o*-C_6H_4-$CHMeNMe_2$)(Ph(*L*-Men)$PCH_2CH_2PPh_2$))][PF_6], **2-Rp** and **2-Sp**, were prepared by treating the binuclear species [Pd_2Cl_2((S)-*o*-$C_6H_4CHMeNMe_2)_2$] with the phosphines **1-Rp** and **1-Sp**, respectively, and exchanging the anion. These reactions are slow, as the kinetically favored intermediates are the phosphine-bridged species, [Pd_2Cl_2(*o*-$C_4H_4CHMeNMe_2)_2$(μ-(Ph(*L*-Men)$PCH_2CH_2PPh_2$)]. These binuclear species show characteristically small P,P coupling constants, less than 10 Hz, in the ^{31}P-NMR spectra [17], whereas in the mononuclear cations of the type [Pd((S)-*o*-C_6H_4-$CHMeNMe_2$)(P–P)]$^+$ (P–P = chelating bisphosphine) this parameter is usually greater than 25 Hz.

2.2. Absolute configuration of $Ph_2PCH_2CH_2P^*Ph$(*L*-(−)-menthyl)

In order to determine the absolute configurations at the phosphorus centres in the two ligands (Rp)– and (Sp)–Ph(*L*-Men)$PCH_2CH_2PPh_2$, one must be able to discriminate between the four isomers **2a-Rp**, **2b-Rp**, **2a-Sp** and **2b-Sp** below. Note that the stereodescriptors given for the P-centres apply to the free phosphine.

The stereochemical assignment can be made as follows:

(a) The ^{31}P resonances are related to their respective phenyl and menthyl substituents by means of a P,H correlation experiment. This assigns the two chemically inequivalent phosphine sides.

(b) Distance constraints, obtained by two-dimensional NOE spectroscopy, establish whether the menthyl-substituted phosphorus donor is located *cis* or *trans* to the cyclometallated phenyl ring, i.e. **2a-Rp** and **2a-Sp** vs. **2b-Rp** and **2b-Sp**, respectively.

(c) The same spectroscopic method is finally used to decide whether the menthyl substituent resides on the same side of coordination plane as the methine hydrogen of the cyclopalladated nitrogen chelate, i.e. **2a-Rp** and **2b-Sp** as opposed to **2b-Rp** and **2a-Sp**.

The ^{31}P NMR spectrum of the species [Pd((S)-*o*-$C_6H_4CHMeNMe_2$)((Rp)–Ph(*L*-Men)-PCH_2CH_2-PPh_2)][PF_6] shows the presence of two regio-isomers. The ratio between them changes slowly, indicating that isomerization to the thermodynamically stable isomer occurs. Pertinent NMR data are collected in Table 1.

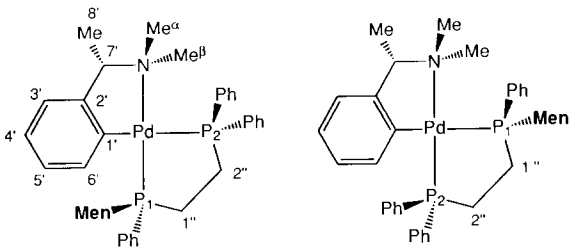
The dominant, more stable isomer will be discussed first. The NOESY spectrum (see Fig. 1) shows that the *ortho*-proton H-6′ on the cyclometallated phenyl ring gives cross-peaks to several of the menthyl protons, e.g. H-3α (s), H-2α (m), H-4β (m) and H-5α (s), establishing a *cis* relationship between the menthyl substituted phosphorus donor, P_1, and the Pd-aryl moiety. Accordingly, its structure can be either **2a-Rp** or **2a-Sp**. Furthermore, the methine proton of the cyclometallated ring, H-7′, exhibits close contacts only to H-3′ and the *ortho*-phenyl protons resonating at δ 7.85. Therefore, this phenyl ring must be placed on the same side of the coordination plane as H-7′. Furthermore, the P,H correlation implies that it is attached to the phosphorus *trans* to the Pd-aryl moiety, i.e. P_2. The stereochemical assignment is completed by the observation that the *ortho* proton at δ 7.85 shows spatial closeness to the isopropyl group of the menthyl moiety, i.e. these groups, *and* H-7′, are all on the same side of the coordination plane. Therefore, the major isomer of [Pd((S)-*o*-$C_6H_4CHMeNMe_2$)((Rp)–Ph(*L*-Men)PCH_2CH_2-PPh_2)][PF_6] can be assigned structure **2a-Rp**. Accordingly, the absolute configuration at P_1 is Sp in the complex and Rp in the free phosphine.

This stereochemical assignment is supported by the analysis of the corresponding spectroscopic results ob-

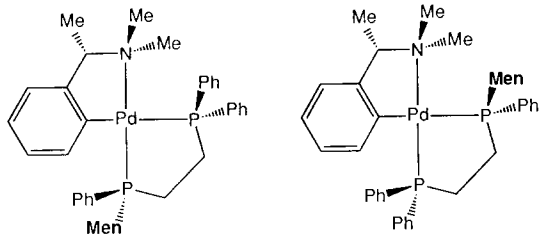
Table 1
NMR data of palladium(II)-complexes [a]

#	**2a-Rp**				**2b-Rp**				**2a-Sp**			
	δC	J(P,C)	Hα	Hβ	δC	J(P,C)	Hα	Hβ	δC	J(P,C)	Hα	Hβ
Aryl-Nitrogen Chelate												
1′	157.15	112.2			156.55	109.9, 1.7			158.81	114.0		
2′	152.30	br [b]			154.98				155.56	1.8, 0.8		
3′	125.00	6.1	7.06		123.04	5.1	7.06		123.35	6.0	7.21	
4′	126.24		7.15		126.2		6.91		126.15	1.0	7.14	
5′	125.62		6.93		125.6		6.50		126.30	7.9, 4.9	7.03	
6′	139.59	9	7.36		138.02	11.2, 2.0	6.56		138.42	8.6, 3.2	7.35	
7′	74.50	br	4.56		77.35	br	3.82		78.30	4.0, 3.0	3.70	
8′	13.0	br		1.37	23.52	br		1.71	26.01			1.85
NMe$^{\alpha}$	51.62	4.0; 1.6	2.80		51.80	br	2.43		51.88	2.5	2.35	
NMe$^{\beta}$	44.05	br		2.02	48.92	br		2.88	49.81	4.0, 0.9		2.45
Phosphine [c]												
P-1	66.6 [d]				46.7 [d]				66.1 [d]			
P-2	44.8 [d]				61.9 [d]				41.4 [d]			
1″	29.2	br	1.67	2.73					21.00	33.8, 19.7	2.92	1.13
2″	28.07	28.7, 7.1	2.57	1.64					27.23	28.8, 7.2	1.58	2.67
Ph^{o}_{1}	135.44	br		8.10			7.57		136.95	12.1	8.23	
$Ph^{o}_{2\alpha}$	134.97	13.4	7.85		134.06	12.2	7.84		131.38	11.3	7.02	
$Ph^{o}_{2\beta}$	131.57	11.2		7.27	133.69	11.9		7.81	135.02	13.7		7.92
L-Menthyl [c]												
1	33.50	11.8	1.42						33.70	9.5	1.30	
2	39.02		2.08	1.06					38.42	7.0	1.81	1.35
3	39.21	24.6	2.55		43.12	br	2.46		37.88	22.8, 1.4	2.97	
4	45.11	1.5		1.32	45.94	4.6		1.41	44.65	1.3		1.38
5	25.04	12.0	1.03	1.54					25.53	10.5	1.02	1.64
6	33.89	1.0	1.62	0.60					33.65	1.6, 0.5	1.67	0.90
7	22.46			0.80	22.27			0.76	22.16			0.90
8	30.00	9.2	2.49		35.45	br	2.74		29.19	9.4	2.80	
9	21.70		0.91		21.70		0.80		21.62		0.71	
10	15.19		0.45		16.74		0.63		16.35		0.40	

[a] recorded in $CDCl_3$ at room temperature. [b] br unresolved multiplet or exchange broadened. [c] additional phenyl resonances, $\delta[J_{(P,C)}]$: **2a-Rp**: 126.22 [34.3], 126.66 [40.7], *ipso*; 129.94 [9.9], 129.65 [9.4], 129.50 [10.4], *meta*; 132.99 [2.2], 132.34 [2.2], 131.29 [2.2], *para*; **2b-Rp**: 129.62 [11.2], 129.46 [9], 129.41 [10], *meta*; 132.54 [2.5], 132.21 [2.5], 130.94 [2.3], *para*; **2a-Sp**: 123.96 [42.0], 125.59 [35.6, 0.8], 129.07 [35.4], *ipso*; 130.15 [10.2], 129.56 [9.7], 129.44 [10.5], *meta*; 133.12 [2.4], 132.72 [2.4], 131.77 [2.4], *para*. [d] δ_P. [e] numbering see scheme 1.



2a-Rp **2b-Rp**



2a-Sp **2b-Sp**

tained for the minor isomer. There are several NOEs between the two N–Me groups and the PPh(*L*-Men) moiety to define the regio-isomer as either **2b-Rp** or **2b-Sp** and their differentiation relies on the stereospecific assignment of the diastereotopic methyl groups at the nitrogen donor. Starting from the methine H-7′ an uninterupted chain of NOEs connects to the N–Me at δ 2.42 and further to the phenyl group whose *ortho* protons resonate at δ 7.56. The second N-methyl substituent at nitrogen shows several NOE crosspeaks of medium intensity to protons of the menthyl moiety. The distance constraints implied by these results are in accordance with structure **2b-Rp**. As expected, the absolute configuration at P_1 is the same as that of the corresponding major isomer **2a-Rp**.

Almost a single regio-isomer was observed for the species [Pd((S)-*o*-$C_6H_4CHMeNMe_2$)((Sp)–Ph(*L*-Men)$PCH_2CH_2PPh_2$)][PF_6]. The procedure for its structural assignment starts again at H-7′. An uninterupted chain of NOEs leads along the metallated phenyl group and further on to the *L*-menthyl substituent and the adjacent phenyl group, defining the regio-isomer as either **2a-Sp** or **2a-Rp**. The assignment of the configuration at the P_1 centre is straightforward because the methyl group Me-8′ exhibits closeness to the isopropyl methyl groups of the *L*-menthyl moiety. Therefore, these two groups have to reside on the same side of the coordination plane, as in isomer **2a-Sp**. Consequently, the absolute configuration in the complex is Rp and Sp in the free ligand.

2.3. Other aspects of the solution structures

2.3.1. Conformation of the cyclometallated chelate ring

A comparison of the NMR data of the three isomeric forms, **2a-Rp**, **2b-Rp** and **2a-Sp**, reveals several interesting facts: (i) the ^{13}C chemical shift of the methyl group Me-8′ varies from 13.0 ppm in **2a-Rp** to 23.5 ppm and 26.0 ppm in **2b-Rp** and **2a-Sp**, respectively. (ii) The ^1H shift of the hydrogen H-7′ in **2b-Rp**, δ 3.82, is similar to that in **2a-Sp**, δ 3.70, but different in **2a-Rp**, 4.56 ppm. (iii) The resonance of H-7′ in **2a-Rp** appears as a quartet, because of coupling with the methyl group, whereas those in **2b-Rp** and **2a-Sp** show a quintet fine-structure because of an additional coupling to the phosphorus spin *trans* to the nitrogen donor. The observed similarity between **2b-Rp** and **2a-Sp** and the difference to **2a-Rp** suggest that the aryl-nitrogen chelate exists in two different conformations in these isomers.

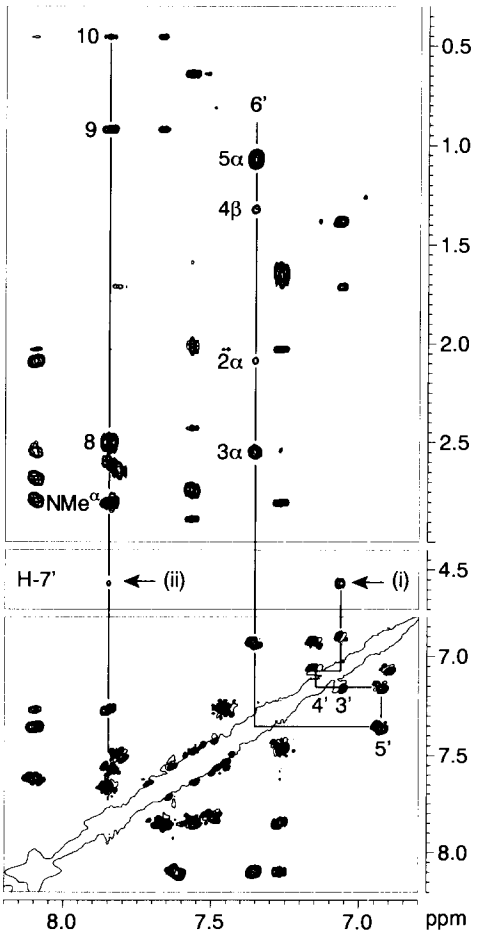


Fig. 1. Part of the 500 MHz NOESY spectrum of [Pd((S)-*o*-$C_6H_4CHMeNMe_2$)(Rp)–Ph(*L*-Men)$PCH_2CH_2PPh_2$)][PF_6] showing (i) the assignment of the regio-isomer starting from H-7′ along the metallated aryl to *L*-menthyl protons and (ii) the determination of the P-chirality from H-7′ to the phenyl resonance and further on to the isopropyl substituent of the *L*-menthyl moiety.

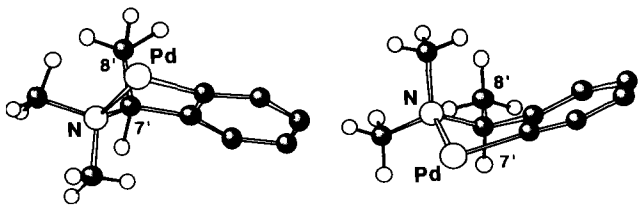


Fig. 2. Models for the two conformations for the cyclometallated chelate rings in **2a-Sp** and **2b-Rp** (left) and **2a-Rp** (right).

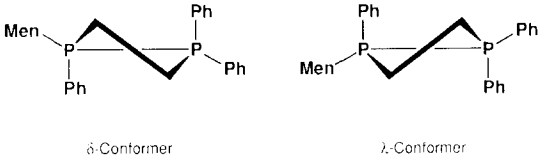
A search for the fragment {M-*o*-aryl-CHMeNMe$_2$} in the Cambridge Structural Data Base indeed shows the occurence of two different conformations, in almost equal abundance in the structurally characterized complexes. In both forms the chelate ring adopts an envelope-type conformation in which the nitrogen atom represents the tip of the envelope, the difference between them being that in one case the Me-8′ group is found in an axial and in the second case in an equatorial position, see Fig. 2.

The assignments of the chelate ring conformations rely on distance constraints obtained from two-dimensional NOE spectroscopy. In the case of the major isomer of [Pd((S)-*o*-C$_6$H$_4$CHMeNMe$_2$)((Rp)–Ph(*L*-Men)PCH$_2$CH$_2$PPh$_2$)][PF$_6$], **2a-Rp**, cross-peak volumes in the NOESY spectrum between Me-8′ and the two diasteromeric N–Me groups are almost equal, indicating two gauche relationships, whereas the NOE between H-7′ and the N-Me groups is selective. These observations are in accordance with a chelate-ring conformation having an equatorial Me-8′ substituent. This assignment is supported by a contact between H-7′ and an *ortho*-phenyl proton across the palladium. For the minor isomer of [Pd((S)-*o*-C$_6$H$_4$CHMeNMe$_2$)((Rp)–Ph(*L*-Men)PCH$_2$CH$_2$PPh$_2$)][PF$_6$], **2b-Rp**, and the major isomer of [Pd((S)-*o*-C$_6$H$_4$CHMeNMe$_2$)((Sp)–Ph(*L*-Men)PCH$_2$CH$_2$PPh$_2$)][PF$_6$], **2a-Sp**, the Me-8′ group is assigned an axial position based on selective NOEs to only one of the N–Me groups. This assignment is further supported for **2a-Sp** in that Me-8′ exhibits a close contact across the palladium to the isopropyl methyl groups of the *L*-menthyl moiety.

2.3.2. *Conformation of the bisphosphine chelate ring*

In the two major isomers, **2a-Rp** and **2a-Sp**, large phosphorus couplings of ca. 55 Hz and 45 Hz are noted for two methylene protons of the phosphine backbones. Values in this range are typical for *trans*-vicinal arrangements of ^{1}H and ^{31}P spins [18] and point to a preferred conformation of the chelate ring which might be either of the λ or δ-type where the hydrogens in question occupy equatorial positions.

Once again, the ambiguity is resolved by considering the close contacts observed by two-dimensional NOE spectroscopy: For [Pd((S)-*o*-C$_6$H$_4$CHMeNMe$_2$)((Rp)–Ph(*L*-Men)PCH$_2$CH$_2$PPh$_2$)][PF$_6$], **2a-Rp**, proximity is found between the *ortho*-protons of the phenyl group adjacent to the *L*-menthyl substituent (i.e. at P$_1$) and the hydrogen at δ 2.93, $J_{(P2,H)} \approx 55$ Hz, establishing a δ-conformation of this chelate ring. Analogous results are obtained for [Pd((S)-*o*-C$_6$H$_4$CHMeNMe$_2$)((Sp)–Ph(*L*-Men)PCH$_2$CH$_2$PPh$_2$)][PF$_6$], **2a-Sp**: As the phosphorus chirality is reversed in the latter complex, the chelate ring must be of the λ-type. The above conformational assignment is supported by analysis of the PPh$_2$-side of the bisphosphine, where specific interactions between the pseudo-equatorial phenyl groups and the second type of equatorial methylene protons are observed. For both complexes **2a-Rp** and **2a-Sp** the *L*-menthyl substituent occupies a pesudo-equatorial position as shown below.



The situation for the minor regio-isomer of [Pd((S)-*o*-C$_6$H$_6$CHMeNMe$_2$)((Rp)–Ph(*L*-Men)PCH$_2$CH$_2$-PPh$_2$)][PF$_6$], **2b-Rp**, is less clear, as *no* large vicinal couplings to ^{31}P are found. This might be either because of a static chelate-ring conformation different from those discussed above, or because of dynamic averaging on the NMR timescale.

In conclusion, it can be noted that the determination of the absolute configuration at the phosphorus center in Ph(*L*-Men)PCH$_2$CH$_2$PPh$_2$ requires only a few NMR experiments, notably two-dimensional NOE spectroscopy, and can be carried out even when more than one regio-isomer is present. In addition, valuable structural information on the complexes in solution might be obtained from the same dataset.

3. Experimental details

3.1. *General considerations*

Analytical results were obtained from the Micro-Analytical Laboratory of the Organic Chemistry Department at ETH-Z. IR-Spectra were recorded on a Perkin-Elmer 883 spectrometer using KBr pellets. NMR spectra of the palladium complexes were recorded on a Bruker AMX 500 spectrometer operating at 500.1, 202.5 and 125.5 MHz for ^{1}H, ^{31}P and ^{13}C, respectively. The two-dimensional NMR experiments such as ^{31}P, ^{1}H heteronuclear COSY [19], ^{13}C, ^{1}H HMQC [20], homonuclear ^{1}H-TOCSY [21], and ^{1}H-NOESY [22] were carried out as described previously [11]. Routine NMR spectra of the organic materials were recorded on Bruker AC 250 and AC 200 instruments at appropriate frequencies. Referencing is rela-

tive to TMS for ^{1}H and ^{13}C, using the solvent resonance as a secondary standard, 7.26 ppm and 77.0 ppm for chloroform, and external 85% H_3PO_4 for ^{31}P. Phosphorus couplings are given in square brackets [].

3.2. Materials

All preparations were carried out under nitrogen or argon using standard Schlenk techniques. Solvents were dried and distilled prior to use. *L*-(−)-menthol, vinyl chloride and $Me_2S \cdot BH_3$ were purchased from Fluka AG. The compounds *L*-menthyl chloride [23], *L*-menthylmagnesium chloride (in refluxing THF) [24], Ph(*L*-menthyl)PCl [15], Ph_2PH [25], and $[Pd_2Cl_2((S)\text{-}o\text{-}C_6H_4CHMeNMe_2)_2]$ [26] were prepared as described previously.

3.2.1. (Rp)–Ph(L-Men)P(BH$_3$)CH=CH$_2$

A solution of CH_2=CHMgCl (70 ml of a ca. 15% THF solution, ca. 123 mmol) was diluted with Et_2O (250 ml) and the resulting pale-yellow slurry was cooled to 0°C in an ice bath. A solution of Ph(*L*-Men)PCl (26.8 g, 94.8 mmol) in Et_2O (150 ml) was added dropwise during 70 min. and the mixture was then allowed to warm slowly to room temperature and was stirred overnight. The ^{31}P NMR spectrum of the reaction mixture showed the presence of two epimers, whose resonances were observed at δ − 14.6 and − 15.3, in ca. 1:2 ratio. The slurry was filtered under argon and MeOH (1.2 ml) added to the stirred filtrate to destroy the excess of the Grignard reagent. The solvents were removed under reduced pressure and the resulting crude phosphine Ph(*L* − Men)PCH=CH_2 was dried under vacuum for ca. 30 min. and then redissolved in toluene (100 ml). The solution was filtered and $Me_2S \cdot BH_3$ (9.0 ml, 95 mmol) was then added during 20 min. to the solution cooled to 0°C. The mixture was then stirred at room temperature for 24 h and MeOH was added. Stirring was continued for another hour and the solution was then evaporated to dryness under reduced pressure. The residue was subjected to chromatography on silica gel with toluene as an eluent. The eluate was evaporated to dryness at less than 40°C under reduced pressure. The crude product was recrystallized from pentane to give 6.04 g (22%) of the optically pure (*R*p)-epimer. IR (KBr): $\nu(BH_3)$ 2384 and 2275 cm^{-1}. Anal. (Calc. for $C_{18}H_{30}BP$): C, 74.97 (75.01); H, 10.23 (10.49)%. ^{1}H NMR ($CDCl_3$): 7.70 (m, 2H, *o*-H); 7.50–7.35 (m, 3H, *m*-H + *p*-H); 6.60 [9.7] (ddd, 1H, C*H*=CH_2); 6.21 [18.0] (ddd, 1H, CH=CH$H_{cis\ to\ P}$); 6.07 [39.4] (ddd, 1H, CH=CH$H_{trans\ to\ P}$); 2.30–2.05 (m, 2H); 1.85–1.50 (m, 3H); 1.40–0.90 (m, 5H); 0.88 (d, 3H, Me); 0.74 (d, 3H, Me); 0.70 (d, 3H, Me). ^{13}C NMR ($CDCl_3$): 133.2 [6.2] (CH_2=); 131.8 [8.2] (*o*-C); 130.4 (*p*-C); 129.9 [55.8] (*i*-C); 129.5 [49.5] (CH=); 128.4 [9,5] (*m*-C); 44.2 (C-4); 36.5 [33.0] (C-3); 35.9 (C-2); 34.1 (C-6); 33.1 [11.6] (C-1); 27.6 [3.9] (C-8); 24.7 [10.7] (C-5); 22.1 (C-7); 21.0 (C-9); 15.3 (C-10).

3.2.2. (Sp)–Ph(L-Men)P(BH$_3$)CH=CH$_2$

After the separation of some optically pure (Rp)–Ph(*L*-Men)PCH=CH_2, the mother liquor was again subjected to chromatography on a silica gel column with toluene/hexane (2:1) as the eluent. The eluate was evaporated to dryness under reduced pressure. The oily residue was dissolved in hexane and the solution cooled to 0°C. The colorless crystals that formed were filtered off, washed with cold hexane (2 × 5 ml), and dried at room temperature in vacuum overnight. Yield: 1.71 g (6%). IR (KBr): $\nu(BH_3)$ 2379 s, 2347 s, 2278 m and 2256 cm^{-1}. Anal. (Calc. for $C_{18}H_{30}BP$): C, 75.03 (75.01); H, 10.23 (10.49)%. ^{31}P NMR ($CDCl_3$): 17.3 br. ^{1}H NMR ($CDCl_3$): 7.80 (m, 2H, *o*-H); 7.50–7.35 (m, 3H, *m*-H + *p*-H); 6.34 (m, 1H, CH=); 6.15–5.85 (m, 2H, CH_2=); 2.25 (m, 1H,); 1.90–0.95 (m, 9H); 0.91 (d, 3H, Me); 0.76 (d, 3H, Me); 0.18 (d, 3H, Me). ^{13}C NMR ($CDCl_3$): 133.1 [5.3] (CH_2=); 131.8 [8.5] (*o*-C); 130.8 [53.2] (*i*-C); 130.5 [2.2] (*p*-C); 128.5 [52.7] (CH=); 128.3 [9.5] (*m*-C); 44.1 [1.6] (C-4); 36.3 (C-2); 36.2 [33.7] (C-3); 34.0 (C-6); 33.3 [11.4] (C-1); 27.8 [4.1] (C-8); 24.6 [11.5] (C-5); 22.2 (C-7); 20.8 (C-9); 14.4 (C-10).

3.2.3. (Rp)–Ph(L-Men)P(BH$_3$)CH$_2$CH$_2$P(BH$_3$)Ph$_2$

(Rp)–Ph(*L*-Men)P(BH_3)CH=CH_2 (4.50 g, 15.6 mmol), Ph_2PH (2.77 ml, 2.92 g, 15.7 mmol) and KO^{t}Bu (0.10 g, 0.9 mmol) were dissolved in THF (40 ml). The orange-red solution was stirred at 45°C for 20 h and MeOH (0.2 mol) then added. The mixture was evaporated to dryness under reduced pressure. The sticky residue was dried at 50°C for 2 h and then redissolved in toluene (50 ml), giving an orange solution. After addition of $Me_2S \cdot BH_3$ (2.5 ml, 26.4 mmol) the mixture was stirred at room temperature for 2 h, during which the solution became pale yellow. Stirring was continued overnight and MeOH (3 ml) was added to destroy the excess of $Me_2S \cdot BH_3$. The mixture was filtered through Celite and the filtrate evaporated to dryness under reduced pressure. The solid residue was recrystallized from toluene/hexane. Yield: 6.90 g (91%). IR (KBr): $\nu(BH_3)$ 2380 vs, 2251 w cm^{-1}. Anal. (Calc. for $C_{20}H_{44}B_2P_2$): C, 74.75 (73.80); H, 9.94 (9.08)%. ^{1}H NMR ($CDCl_3$): 7.80–7.20 (m, 15H, Ph); 2.80–0 (m, 29H, aliphatic + BH_3) of which at δ 0.78 (d, 3H, Me); 0.72 (d, 3H, Me); 0.60 (d, 3H, Me). ^{13}C NMR ($CDCl_3$): 132.4 [8.1] (*o*-C); 132.1 [9.1] (*o*-C); 131.7 [9.3] (*o*-C); 131.2 [2.1] (*p*-C); 131.1 [2.7] (*p*-C); 131.0 [3.1] (*p*-C); 128.7 [9.6] (*m*-C); 128.6 [8.9] (*m*-C); 128.6 [10.8] (*m*-C); 128.4 [54.9] (*i*-C); 127.8 [54.6] (*i*-C); 126.9 [50.8] (*i*-C); 44.0 (C-4); 37.0 [29.5] (C-3); 36.2

(C-2); 33.9 (C-6); 33.0 [10.8] (C-1); 28.2 [3.2] (C-8); 24.6 [11.5] (C-5); 22.0 (C-7); 20.8 (C-9); 19.3 [36.4], 19.2 [31.7] (PCH_2CH_2P); 15.0 (C-10).

3.2.4. (Sp)-Ph(L-Men)P(BH_3)CH_2CH_2P(BH_3)Ph_2

This compound was prepared as described above for the other epimer: (Sp)-Ph(*L*-Men)P(BH_3)CH=CH_2 (1.20 g, 4.15 mmol) yielded 1.61 g product. Yield; 80%. IR (KBr): $\nu(BH_3)$ 2382 vs, 2252 m cm^{-1}. Anal. (Calc. for $C_{30}H_{44}B_2P_2$): C, 73.78 (73.80); H, 8.77 (9.08)%. ^1H NMR ($CDCl_3$): 7.80–7.20 (m, 15H, Ph); 2.70–0 (m, 29H, aliphatic + BH_3) of which at δ 0.89 (d, 3H, Me); 0.74 (d, 3H, Me); 0.05 (d, 3H, Me). ^{13}C NMR ($CDCl_3$): 132.1 [8.4] (*o*-C); 131.8 [8.4] (*o*-C); 131.7 [9.6] (*o*-C); 131.2 [3.9] (*p*-C); 131.0 [2.7] (*p*-C); 130.9 [2.1] (*p*-C); 129.4 [49.3] (*i*-C); 128.7 [9.7] (*m*-C); 128.6 [10.1] (*m*-C); 127.8 [54.6] (*i*-C); 44.1 (C-4); 37.1 [31.3] (C-3); 35.1 (C-2); 33.8 (C-6); 33.1 [10.5] (C-1); 27.8 [4.7] (C-8); 24.4 [11.5] (C-5); 22.1 (C-7); 20.7 (C-9); 18.9 [36.4], 18.1 [34.6] (PCH_2CH_2P); 14.1 (C-10).

3.2.5. (Rp)-Ph(L-Men)$PCH_2CH_2PPh_2$

(Rp)-Ph(*L*-Men)P(BH_3)CH_2CH_2P(BH_3)Ph_2 (1.00 g, 2.05 mmol) was dissolved in morpholine (15 ml) and the solution stirred at 50°C for 24 h. The excess of morpholine was removed under vacuum at room temperature, and the residue extracted with hexane (60 ml). The extract was filtered, and the filtrate concentrated to dryness under reduced pressure. The resulting sticky oil was dried at 60°C under vacuum for several hours. Yield: greater than 95%. The NMR spectra indicated the formation of a pure compound. ^1H NMR ($CDCl_3$): 7.60–7.30 (m, 15H, Ph); 2.94 (m, 1H, C*H*Me_2); 2.50–2.10 (m, 2H); 1.95–0.40 (m, 20H) of which at δ 1.04 (d, 3H, Me); 0.93 (d, 3H, Me); 0.81 (d, 3H, Me). ^{13}C NMR ($CDCl_3$): 138.3 [13.8] (*i*-C); 134.8 [19.8] (*i*-C); 133.3 [19.2] (*o*-C); 132.6 [18.0] (*o*-C); 132.6 [18.2] (*o*-C); 128.4 (*p*-C); 128.3 (*p*-C); 128.2 [6.6] (*m*-C); 127.8 [6.3] (*m*-C); 44.7 [10.3] (C-4); 38.3 [16.9] (C-3); 35.7 [3.1] (C-2); 34.5 (C-6); 33.3 [2.0] (C-8); 27.8 [19.8] (C-1); 25.1 [7.7] (C-5); 24.4 [20.0, 13.8] (PCH_2); 22.3 (C-7); 21.3 (C-9); 18.6 [15.1, 15.1] (PCH_2); 15.1 (C-10).

3.2.6. (Sp)-Ph(L-Men)$PCH_2CH_2PPh_2$

This phosphine was prepared in the way describe for its (Rp)-epimer, above. Yield: greater than 95%. NMR spectra indicate the formation of a pure compound. ^1H NMR ($CDCl_3$): 7.60–7.20 (m, 15H, Ph); 2.70–2.45 (m, 1H); 2.30–1.85 (m, 3H); 1.80–0.20 (m, 19H) of which at δ 0.95 (d, 3H, Me); 0.79 (d, 6H, Me). ^{13}C NMR ($CDCl_3$): 138.3 [13.3] (*i*-C); 138.2 [10.1] (*i*-C); 137.9 [13.6] (*i*-C); 132.7 [18.1] (*o*-C); 132.3 [17.6] (*o*-C); 132.2 [17.7] (*o*-C); 128.5 (*p*-C); 128.3 (*p*-C); 128.2 [6.4] (*m*-C); 128.0 [6.2] (*m*-C); 127.7 (*p*-C); 45.7 [10.7] (C-4); 40.5 [16.7] (C-3); 35.6 [2.8] (C-2); 34.8 (C-6); 33.4 [2.1] (C-8); 27.9 [18.8] (C-1); 25.2 [7.5] (C-5); 24.6 [18.9,12.6] (PCH_2); 22.2 (C-7); 21.3 (C-9); 15.8 [16.1, 16.1] (PCH_2); 14.8 (C-10).

3.2.7. [Pd((S)-o-$C_6H_4CHMeNMe_2$)((Rp)-Ph(L-Men)-$PCH_2CH_2PPh_2$)][PF_6]

A suspension of [Pd_2Cl_2((S)-*o*-$C_6H_4CHMeNMe_2)_2$] (96 mg, 165 μmol) in MeOH (30 ml) was cooled to −78°C in a dry-ice acetone bath and a stock solution of (Rp)-Ph(*L*-Men)$PCH_2CH_2PPh_2$ in MeOH (10 ml, 34.1 mM) was added slowly during 15 min. The mixture was allowed to warm gradually to room temperature; it was observed that the mixture, which was colorless below −20°C, became lightly orange-brown at ca. −10°C and, after 24 h stirring at room temperature some black solid had formed. The mixture was then filtered and $NH_4[PF_6]$ (0.55 g, 3.37 mmol) in H_2O (20 ml) added to the filtrate. The white solid which formed was filtered off and washed with water (3 × 20 ml). Because it was found that the wet solid was soluble in Et_2O, the reaction mixture was extracted with Et_2O (3 × 70 ml). The combined extracts were dried overnight over anhydrous Na_2SO_4, and then filtered. The filtrate was evaporated to dryness under reduced pressure and the residual pale-yellow solid recrystallized from CH_2Cl_2/Et_2O, and then dried at 60°C for 12 h. Yield: 214 mg (76%). IR: $\nu(PF_6^-)$, 838 cm^{-1} (vs). Anal. (calc. for $C_{40}H_{52}F_6NP_3Pd$): C, 56.60 (55.85); H, 6.12 (6.09); N, 1.57 (1.63)%. NMR: see Table 1.

3.2.8. [Pd((S)-o-$C_6H_4CHMeNMe_2$)((Sp)-Ph(L-Men)-$PCH_2CH_2PPh_2$)][PF_6]

A suspension of [Pd_2Cl_2((S)-*o*-$C_6H_4CHMeNMe_2)_2$] (127 mg, 219 μmol) in MeOH (30 ml) was cooled to −78°C in a dry-ice acetone bath. A stock solution of (Sp)-Ph(*L*-Men)$PCH_2CH_2PPh_2$ in MeOH (18.5 ml, 23.9 mM) was added slowly during 20 min. and the reaction mixture then allowed to warm slowly to room temperature, and stirred overnight. The mixture was filtered through Celite, and $NH_4[PF_6]$ (0.78 g, 4.79 mmol) in H_2O (100 ml) was added to the filtrate over 30 min, and the resulting suspension was stirred at room temperature overnight. The pale-yellow solid formed was filtered off, washed with water (2 × 50 ml), and recrystallized form CH_2Cl_2/pentane/Et_2O, and the crystals were dried at 60°C for 4 h over P_2O_5 under vacuum. Yield: 260 mg (69%). IR: $\nu(PF_6^-)$, 838 cm^{-1} (vs). Anal. (Calc. for $C_{40}H_{52}F_6NP_3Pd$): C, 56.00 (55.85); H, 6.09 (6.09); N, 1.52 (1.63)%. NMR: see Table 1.

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