(Cyclohexylmethylphenylphosphine)[(1-η^1:6−8-η^3)-octa-2,6-diene-1,8-diyl]palladium(II) as a Model for Key Intermediates in Enantioselective Reactions of 1,3-Butadiene Catalyzed by Palladium(0)

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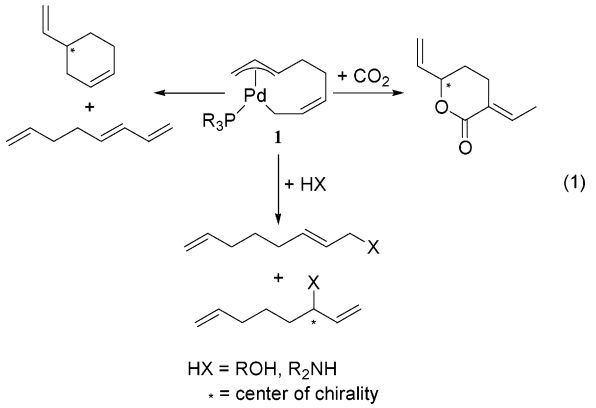
(Cyclohexylmethylphenylphosphine)[(1-η^1:6−8-η^3)-octa-2,6-diene-1,8-diyl]palladium(II) (**1**) was synthesized from bis(η^3-propenyl)palladium(II) and 1,3-butadiene in the presence of racemic cyclohexylmethylphenylphosphine (**2**) and exists in the form of two diastereomeric pairs of enantiomers **1a**,**b**. The diastereomers have been fully characterized by NMR spectroscopic methods, with special focus on their stereochemistry. The molecular structure of **1b** was determined by X-ray crystallography and confirmed the results of the NMR investigation: in both diastereomers the C_8H_{12} chains exhibit the same rigid topology and thus represent an inherent chiral element in these intermediates originating from butadiene coupling. This is an essential prerequisite for subsequent enantioselective transformations of complexes of type **1**.

Introduction

Phosphine(η^1:η^3-octadienediyl)palladium(II) complexes **1** have been said to be the primary reaction products of 1,3-butadiene coupling at a palladium(0) center in the presence of stabilizing phosphine ligands.[1] Although 20 years ago they were identified as playing a key role as common intermediates in telomerization, codimerization, and cooligomerization reactions, only very little is known about their stereochemical abilities (eq 1).[2] In those cases, where the final organic products of these reactions contain a center of chirality, in particular when cyclic products are formed, it is of considerable interest to obtain them in an enantiopure form by enantioselective catalysis. One strategy of asymmetric induction in the catalytic system may be a stereoselective 1,3-butadiene coupling step, which, when proceeding under stereocontrol by chiral phosphine ligands, should lead to diastereopure phosphine(η^1:η^3-octadienediyl)palladium(II) intermediates. Here, we report in detail on the stereochemical properties of an intermediate of this type, in which a racemic ligand, the Horner type cyclohexylmethylphenylphosphine (**2**) is coordinated. The topology of the resulting diastereomers **1a**,**b** has been fully analyzed by NMR spectroscopy as well as by XRD, in the case of diastereomer **1b**. Displaying permanent chirality, the C_8H_{12} chain represents an inherent chiral element in these intermediates, which gives rise to a potential stereocontrol in the aforementioned catalytic reactions.



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Results and Discussion

The title compound has been prepared analogously to the synthesis of the PMe_3 derivative reported in the literature,[3] by reacting bis(η^3-propenyl)palladium(II) at room temperature in liquid 1,3-butadiene for 1 week in the presence of a stoichiometric amount of phosphine **2** (eq 2).

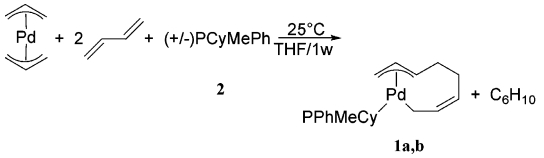

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Table 1. Crystallographic Data for Complex 1b

empirical formula	$C_{21}H_{31}PPd$
formula wt	420.87
T (K)	200(2)
radiation (Å)	0.710 73
cryst syst	monoclinic
Space group	$C2/c$ (No. 15)
Z	8
a (Å)	18.1315(14)
b (Å)	14.5984(14)
c (Å)	16.3494(14)
β (deg)	114.317(2)
V (Å^3)	3943.6(6)
ρ_{calcd} (g cm^{-3})	1.418
μ (mm^{-1})	1.021
cryst color	yellow
cryst size (mm^3)	0.15 × 0.15 × 0.3
θ_{max} (deg)	28.36
no. of rflns collected/ unique/obsd	20 337/4797 (R(int) = 0.0653)/ 3459
no. of restraints/params	0/226
goodness of fit on F^2	1.031
final R1	0.0381
final R_w	0.0665
max/min in diff map (e Å^{-3})	+0.489/−0.571

The reaction product has the form of an amorphous pale yellow powder, which decomposes in the absence of butadiene above −10 °C and in solution above −30 °C. It consists of a mixture of the two diastereomers **1a**,**b** in a 1:1 ratio, determined by integration of the two resonances present in the ^{31}P NMR spectrum (vide infra). Recrystallization from a mixture of THF and butadiene at −78 °C affords, after several weeks, crystals of **1b** suitable for X-ray analysis.

X-ray Crystal Structure of 1b. 1b crystallizes as a racemate in the form of yellow needles which belong to the centrosymmetric space group $C2/c$ (No. 15) in the monoclinic crystal system (Table 1). The elementary cell includes eight formula units, each having C_1 symmetry. The atoms P, C1, C6, and C8 and the central Pd atom span a "best fit" coordination plane cp with an average deviation from planarity of 0.09 Å. Correspondingly, the coordination geometry at the Pd center in **1b** is best described as slightly distorted square plane, which is expected for a complex with a d^8 electronic configuration.

(a) C_8H_{12} Chain Part. The torsion angles of the carbon atoms C1−C2−C3−C4 and C5−C6−C7−C8 of the C_8H_{12} chain amount to −2.1° and +176.2°, respectively, and thus show that the C_8H_{12} chain consists of two planar C_4 subunits corresponding to two butadiene molecules they are emanating from (Figure 1, Table 2). The C_4 subunit that consists of the carbon atoms C1−C4 (C_4^{1-4}) bearing the η^1-allylic group with a double bond between C2−C3 exhibits a Z configuration, while the C_4 subunit consisting of C5−C8 (C_4^{5-8}) and bearing the η^3-allylic group shows a syn configuration.[4,5] The single bond between the atoms C4 and C5 that connects both C_4 subunits is the longest bond in the overall C_8H_{12} chain. Both meso protons, H21 of the η^1-allylic group and H71 of the η^3-allylic group, point toward the same direction with respect to the coordination plane cp. The descriptor H$^{21/71}$-syn thus defines the positions of the two C_4 subunits relative to each other. The (η^1:η^3-C_8H_{12})-Pd^{II} fragment in **1b** is of C_1 symmetry and is isostructural with its analogues in the corresponding Pt and Ni complexes [(PMe$_3$)(η^1:η^3-C_8H_{12})Pt^{II}][6] and [(PMe$_3$)(η^1:η^3-2,6-Me$_2$C$_8$H$_{10}$)Ni^{II}].[7] The only X-ray structure of an analogous palladium complex reported in the literature, the trimethylphosphine derivative [(PMe$_3$)(η^1:η^3-C_8H_{10})-Pd^{II}],[8] shows enantiomeric disorder, with different enantiomers occupying equivalent lattice positions.[9]

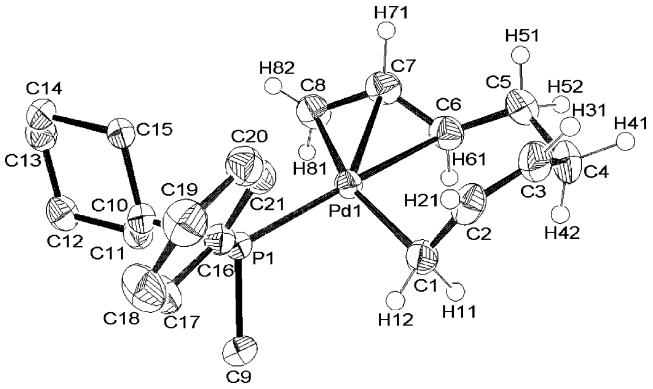

Figure 1. ORTEP drawing of the X-ray crystal structure of **1b**. All atoms (except H) are shown with 50% probability thermal ellipsoids. The mapped H atoms are localized and isotropically refined. The [(*S*)-P,(*R*)-C6] enantiomer (vide infra) is depicted.

Table 2. Selected Structural Parameters (Angles (deg) and Distances (Å), with Standard Deviations in Parentheses for 1b

σ^b	0.0905	τ_1^c	+176.2
		τ_2^c	−2.1
C1−Pd−C6	94.5(1)	C6−Pd−C8	66.9(1)
C1−Pd−P	90.5(1)	C10−P−C9	101.8(1)
P−Pd−C8	107.2(1)	C10−P−C16	101.0
Pd−C1	2.127(3)	C9−cp^a	−1.571
Pd−C6	2.252(3)	C10−cp^a	−0.013
Pd−C7	2.181(3)	C16−cp^a	+1.292
Pd−C8	2.210(3)	H21−cp^a	+1.937
Pd−P	2.271(1)	H12−cp^a	−0.229
C2−C3	1.340(5)	H82−cp^a	+0.282
C4−C5	1.558(6)	H11−cp^a	−0.941
C6−C7	1.379(5)	H81−cp^a	−0.982
C7−C8	1.398(5)		

^{a} cp is the "best fit" plane spanned by the atoms P, C1, C6, C8, and Pd. ^{b} σ is the mean feviation (Å) of the atoms P, C1, C6, C8, and Pd from the coordination plane cp. ^{c} τ_1 is the torsion angle for the atoms C1−C2−C3−C4, and τ_2 is the torsion angle for the atoms C5−C6−C7−C8.

(b) P-Ligand Part. The distance between the phosphorus atom and the palladium atom in **1b** is 0.027 Å longer than in [(PMe$_3$)(η^1:η^3-C_8H_{10})Pd^{II}], due to the increased steric interactions between the C_8H_{12} chain and the more space-filling phosphine ligand in **1b**. The crystal structure consists of only one rotational isomer of the phosphine ligand, as the P−Pd bond with the three substituents at the phosphorus atom adopt defi-

(3) (a) Schick, K.-P. Dissertation, Ruhr-Universität Bochum, 1982. (b) Schenker, G. Dissertation, Ruhr-Universität Bochum, 1984.

(4) In accordance with the literature, the term syn for the η^3-allyl part of the C_8H_{12} chain refers to the position of the connected methylene group with respect to the meso proton.

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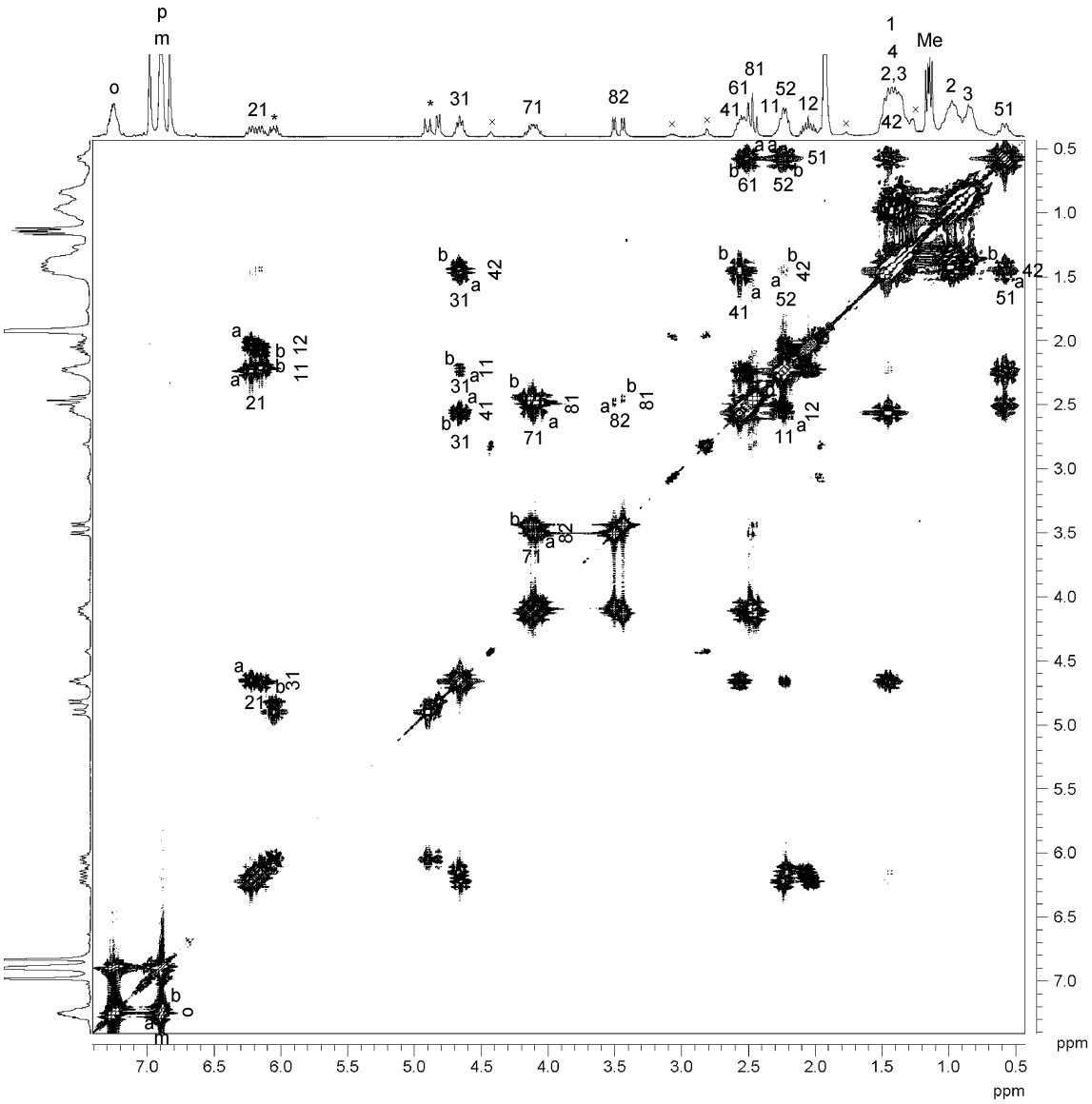


Figure 2. H,H-DQF-COSY spectrum of a mixture of **1a** and **1b** in toluene-d_8 at −50 °C: (×) decomposition products not determined; (*) 1,3-butadiene. The denotation of the protons of the C_8H_{12} chain refer to the X-ray structure. H_o, H_m, H_p, H1−H4, and HMe are the protons of the phosphine ligand (see also the NMR numbering scheme in the Experimental Section).

nite positions. The sterically most demanding substituent, the cyclohexyl group, occupies a position nearly in the coordination plane cp, which is reflected by the very small distance of 0.013 Å between C10 and cp (Table 2). Accordingly, the two remaining substituents, the phenyl and methyl groups, occupy positions which are located nearby symmetrically at opposite sides of the coordination plane, which is shown by almost the same values for the angles C10−P−C9 and C10−P−C16.

NMR Studies on a Mixture of 1a and 1b. To determine the topology of diastereomers **1a**,**b** in solution**,** 2D-NMR spectroscopic techniques were applied. NMR experiments which afford longer total acquisition times, such as ^{13}C and the 2D experiments, required a temperature of −50 °C in toluene-d_8. This was found to be the best compromise to avoid thermal decomposition while having sufficiant solubility.

(a) Assignment for 1a,b. With two sharp singlets at δ +29.5 and +27.0 ppm in a 1:1 ratio the ^{31}P NMR spectrum displays a doubled set of resonances compared to the spectra of analogous phosphine(η^1:η^3-octadienediyl)palladium(II) complexes with achiral phosphine ligands. Correspondingly, most of the 17 resonances expected for the $^{13}C\{^1H\}$ NMR spectrum are doubled, in particular those of the C_8H_{12} chain and the resonances of all carbon atoms adjacent to phosphorus. The 46 signals which are expected for two sets of signals in the ^1H NMR spectrum are not all observed, because most signals are overlapping. Separation and subsequent assignment of the resonances to one of the sets succeeds via H,H-COSY (Figure 2) and 2D-NOESY (Figure 3) for all protons of the C_8H_{12} chain and for all protons in α- and β-positions with respect to phosphorus of the phosphine ligand: in particular, the methyl protons (HMe), the ortho protons of the phenyl ligand (H_o), and the α- and β-protons of the cyclohexyl ligand (H1, H2). The final assignment of the sets to either **1a** or **1b** is obtained by analyzing the steric interactions between protons of the phosphine ligand and protons of the C_8H_{12} chain by 2D-NOESY (vide infra). Using this information, the doubled ^{13}C NMR resonances can be assigned via HSQC.

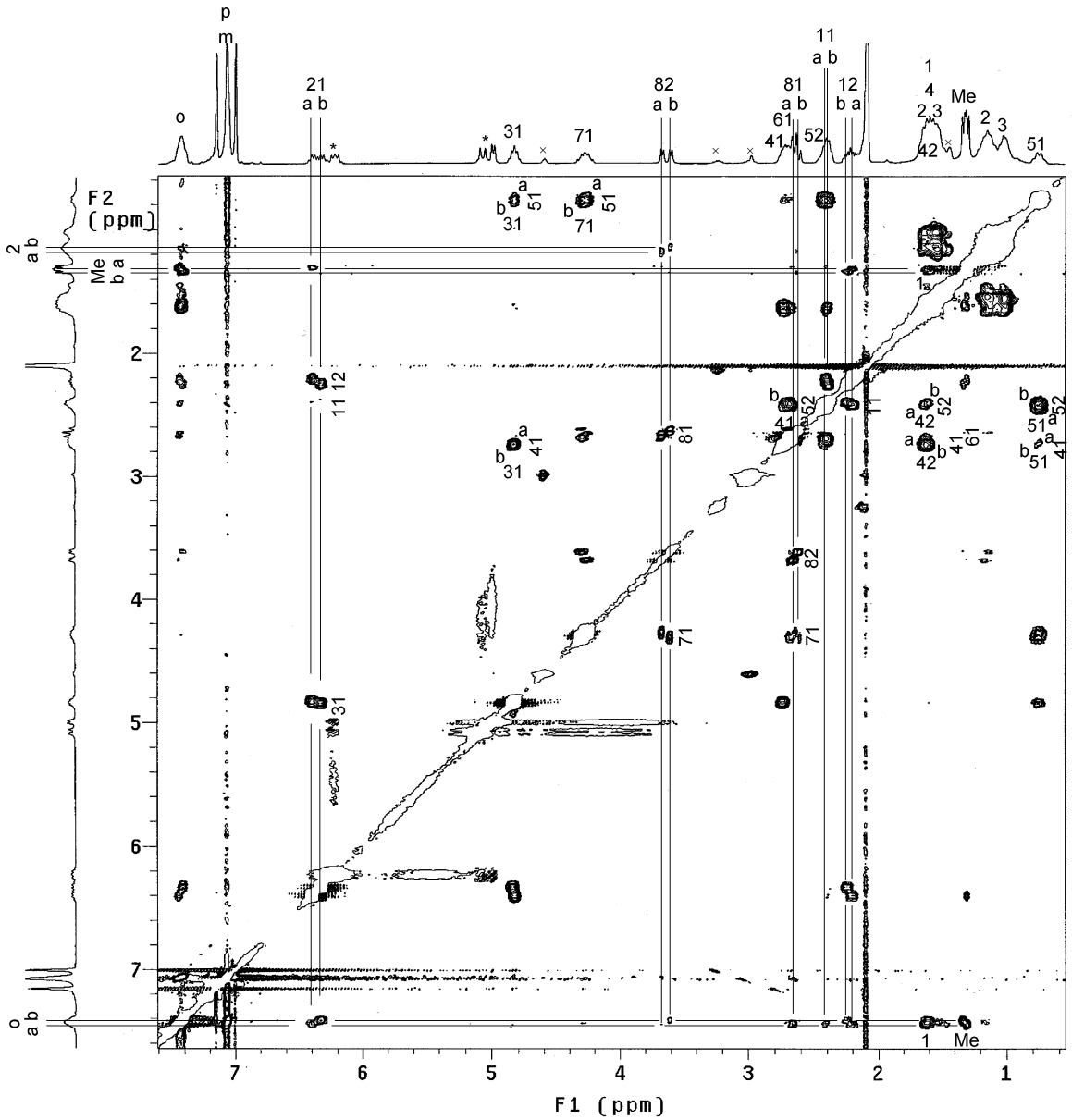
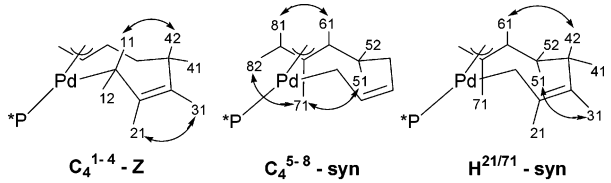


Figure 3. NOESY spectrum of a mixture of **1a** and **1b** in toluene-d_8 at −50 °C: (×) decomposition products not determinedp; (*) 1,3-butadiene. The NOE contacts due to steric interactions between the phosphine ligand and the C_8H_{12} chain in each diastereomer are outlined. For the numbering of the H atoms see Figure 2 and the NMR numbering scheme in the Experimental Section.

(b) C_8H_{12} Chain Part. The ^3J coupling constants between the olefinic protons H21 and H31 of the η^1-coordinating part of the C_8H_{12} chain amount to 10.8 Hz for **1a** and 10.9 Hz for **1b**. These values are in the range typical of cis protons and consistent with the configuration $C_4{}^{1-4}$-Z. The ^3J coupling constants between the η^3-allylic protons H61 and H71 are 12.9 Hz for **1a** and 12.1 Hz for **1b**. Both values are consistent with a $C_4{}^{5-8}$-syn configuration. The vicinal sp^3 protons H42 and H51 are each located at different C_4 subunits. Their ^3J coupling constant of 12.4 Hz for both diastereomers is in the range for positions anti to each other. The analysis of the steric interactions between the protons along the C_8H_{12} chain (Chart 1) by 2D-NOESY (Figure 2) confirms these results: for **1a** as well as for **1b,** two cross resonances for the protons H11/H42 and H21/H31 are observable, which is only consistent with $C_4{}^{1-4}$-Z. Three cross-peaks for the protons H51/H71, H61/H81, and H71/H82 are present for **1a**,**b**, corresponding to $C_4{}^{5-8}$-syn. Furthermore, each diastereomer shows two cross resonances between protons which are attached to different C_4 subunits (H42/H61, H31/H51) (right-hand side of Chart 1). In addition, both pairs of these interacting protons are located at opposite sides with respect to cp. Consequently, a conformation change of the C_8H_{12} chain, due to simultaneous rotation of the Pd−C1 and C4−C5 bonds, cannot occur and the position

Chart 1. Characteristic NOE Contacts for the Configuration of the C_8H_{12} Chain of 1a,b



P* = (+/-) P(Cy)(Me)(Ph)

Chart 2. Interresidue NOE Contacts between the Phosphine Ligand and the C_8H_{12} Chain Characteristic of Each Configuration of Diastereomer 1a (Left) and 1b (Right)

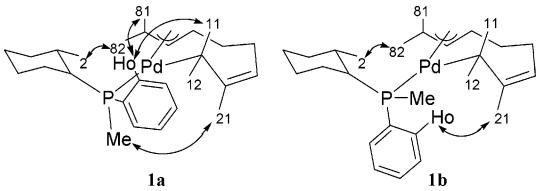


Table 3. Observed NOESY Cross-Peak Intensities for the Interresidue NOE Contacts[a]

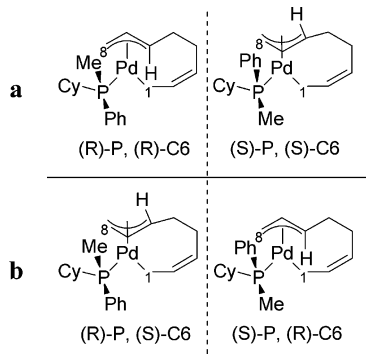
	1a			1b		
	H_o	H2	HMe	H_o	H2	HMe
H21	m		m	s		
H12	m		m	m		m
H82	w	m	-	w	m	
H11	m					
H81	m					

[a] Legend: w, weak; m, medium; s, strong.

of the two C_4 subunits relative to each other is $H^{21/71}$-syn, even in solution. In summary, the configuration of the C_8H_{12} chain for **1a** as well as for **1b** in solution corresponds to that found for **1b** in the X-ray molecular structure.

(c) P-ligand Part. Due to the steric demand of the bulky phosphine ligand, NOE contacts are observed between protons of the substituents (the ortho protons of the phenyl substituent H_o, the protons in positions β with respect to phosphorus of the cyclohexyl substituent H2, and the protons of the methyl substituent HMe) and the protons at both termini of the C_8H_{12} chain along with the meso proton of the η^1-allyic part (H11, H12, H81, H82, and H21) (Chart 2). Because of the rigid arrangement of the C_8H_{12} chain these protons adopt definite positions at that side of the C_1-symmetric $(\eta^1{:}\eta^3\text{-}C_8H_{12})Pd^{II}$ complex fragment which points toward the phosphine ligand. Therefore, these protons can be used in terms of probes to determine the topology of the phosphine ligand with respect to the coordination plane cp in **1a**,**b**: H82 and H12 adopt positions located close to cp, while H81 and H11 are both located on the opposite side of cp with respect to H21 (Table 1). H11, H12, and H21 on one hand and H81 and H82 on the other are, moreover, located at different termini of the C_8H_{12} chain (Chart 2). For each diastereomer the number and intensities of the cross-peaks between these protons differ greatly (Table 3), indicating specific rotameric arrangements of the phosphine ligand and thus a hindered rotation around the Pd−P bond. The presence of a corresponding cross resonance between H2 and H82, together with the absence of cross resonances between H2 and other protons of the C_8H_{12} chain, indicate that the cyclohexyl residue adopts in both diastereomers a position approximately in cp. The NOE contacts of the methyl substituent (HMe) vary for both diastereomers in the cross resonance between HMe and H21, which is only observable for **1a**. Also only for **1a** are cross resonances between the ortho protons of the phenyl substituent (H_o) and H11 as well as between H_o and H81 observed. H11 and H81 are both located on the same side with respect to cp. For **1b** the intensity of the cross resonance between H_o and H21, which is located at the opposite side of cp, is at a maximum. We conclude that two diastereomers having the same configuration of the $(\eta^1{:}\eta^3\text{-}C_8H_{12})Pd^{II}$ complex fragment only differ in the positional exchange of those substituents of the phosphine ligand which are not located in cp: the methyl and the phenyl substituents.

Chart 3. All Stereoisomers of 1a,b Occurring, with Their Stereochemical Descriptors



Conclusion

The NMR investigation reveals that in solution **1a**,**b** display an unexpected rigid topology of the C_8H_{12} chain. The $(\eta^1{:}\eta^3\text{-}C_8H_{12})Pd^{II}$ complex fragment exists only in the configurations C_4^{1-4}-Z, C_4^{5-8}-syn, and $H^{21/71}$-syn and the phosphine ligand only in two discrete rotameric arrangements. Hence, the stereochemistry of all stereoisomers can be described adequately by the use of only two stereochemical descriptors: first, the descriptor of local symmetry at the phosphine ligand,[10] and second, the descriptor of local symmetry at carbon atom C6, representative of the whole C_8H_{12} chain (Chart 3).

In the case of PCyMePh, stereoselectivity upon formation of **1a** or **1b** cannot be observed. According to our observations, this lack of stereoselectivity is not caused by racemization via configurational rearrangement of the C_8H_{12} chain. This leads to speculations as to whether the rigid configuration of the C_8H_{12} chain can be utilized to influence the formation of the enantiomeric $(\eta^1,\eta^3\text{-}C_8H_{12})Pd^{II}$ fragments in a catalytic reaction. It appears that the use of enantiopure phosphine ligands, analogous to that in **1a**,**b**, in which those substituents not belonging to the coordination plane are chosen in such a way that their steric interactions with the C_8H_{12} chain are maximized, could give rise to an asymmetric formation of the resulting diastereomeric phosphine($\eta^1{:}\eta^3$-octadienediyl)palladium(II) complexes. As this represents a crucial prerequisite for a potential enantioselective catalysis, it is the subject of our current research efforts.

Experimental Section

All manipulations were carried out with standard Schlenk techniques under an inert-gas atmosphere (argon 6.0 Air Liquide or Linde) using glass flasks that had been well heated in advance with reduced internal pressure. IR spectra were measured by a Bio-Rad 175 FT-IR spectrometer, and ESI mass spectroscopic data were collected by a HP series 100 MSD

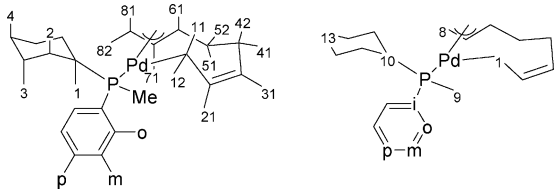
(10) We chose to use the stereochemical descriptor for the uncomplexed phosphine, because the descriptor would formally change upon complexation or decomplexation.

(eluent 5 mmol of NH_4OAc in MeOH, fragmentor voltage 10−200 V). Elemental analyses were carried out by *Kolbe Mikroanalytisches Labor*, Mühlheim (Ruhr), Germany. All NMR spectra were recorded by a Varian Unity INOVA (400 MHz) spectrometer. ^{1}H NMR chemical shifts for the toluene-d_8 solution are relative to those of residual protonated toluene (δ 2.09, 6.98, 7.00, 7.09), the ^{13}C NMR chemical shifts are relative to the septet of the solvent toluene-d_8 (δ 20.4), and the ^{31}P NMR chemical shifts are referenced to external 85% H_3PO_4 (δ 0 ppm). The NOESY spectra were recorded at 223.15 K with a mixing time of τ = 1000 ms, d1 = 1.6 s, 32 repetitions, and 512 increments.

Crystallographic data were collected by a Siemens Smart 1000 CCD diffractometer with a Mo Kα graphite monochromator. Intensities were corrected for Lorentzian and polarization effects. An empirical absorption correction was applied using the SADABS program.[11] The whole Ewald sphere was measured with 10/s by a ω scan ($\Delta\omega$ = 0.45°). Data were evaluated with the programs SHELX-97[12] and XPMA and ZORTEP.[13]

[(PCyMePh)((1-η^1:6−8-η^3)-C_8H_{12})Pd^{II}] (1a,b). [(η^3-C_3H_5)$_2$-Pd^{II}] (225.6 mg, 1.2 mmol) and PCyMePh (249.8 mg, 1.2 mmol) were suspended in a mixture of liquid 1,3-butadiene (45 mL) and THF (5 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred over a period of 192 h. After the mixture was cooled to −78 °C and subsequently filtered and half of the solvent was evaporated, the raw reaction product precipitated after 3 days as a pale yellow powder. Two washings with 5 mL of a butadiene/pentane mixture (1:1) at −78 °C and drying for 72 h at −50 °C in vacuo yielded 299.7 mg of the analytically pure compound (0.71 mmol, ∼59.36%).

The NMR numbering scheme is as follows:



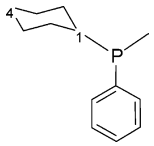
1a: [(*S*)-P,(*S*)-C6] and [(*R*)-P,(*R*)-C6] (50%). ^{1}H NMR (399.99 MHz, toluene-d_8, 223.15 K): δ 7.41 (m, $^3J_{o,m}$ = 7, $^4J_{o,p}$ = 2, $^3J_{o,P}$ = 10.3 Hz, 2H; H_oa), 7.04 (superimposed by solvent, 3H; H_ma, H_pa), 6.36 (ddd, superimposed by H21b, $^3J_{21,11}$ = 10.1, $^3J_{21,12}$ = 7.4, $^3J_{21,31}$ = 10.9 Hz, 1H; H21a), 4.79 (m, superimposed by H31b, $^3J_{31,21}$ = 10.8, $^3J_{31,41}$ = 5.5, $^3J_{31,42}$ = 8.0 Hz, 1H; H31a), 4.27 (dt, superimposed by H71b, $^3J_{71,61}$ = 12.1, $^3J_{71,81}$ = 13.0, $^3J_{71,82}$ = 7.4 Hz, 1H; H71a), 3.58 (d, 1H; H82a), 2.71 (m, superimposed by H41b, H61a, H61b, 1H; H41a), 2.68 (superimposed by H61b, H81a, H41a, H41b, $^2J_{61,P} \approx$ 8 Hz, 1H; H61a), 2.62 (d, 1H; H81a), 2.38 (m, superimposed by H52b; H11a, H11b, $^2J_{52,51}$ = 10 Hz, 1H; H52a), 2.38 (dd, $^2J_{11,12}$ = 6.9 Hz, 1H; H11a), 2.14 (dt, $^3J_{12,P}$ = 15.9 Hz, 1H; H12a), 1.67−1.42 (4H; H2, H3), 1.62 (2H; H4), 1.58 (m, superimposed by H2, H3, H4, $^3J_{42,31}$ = 8, $^2J_{42,41}$ = 10 Hz, 1H; H42a), 1.52 (1H; H1a), 1.26 (d, $^2J_{Me,P}$ = 7.4 Hz, 3H; HMe), 1.22−1.07 (2H; H2), 1.12−0.85 (2H; H3), 0.71 (m, br, $^3J_{51,42}$ = 12.4, $^2J_{51,52}$ = 10, $^3J_{51,61}$ = 11 Hz, 1H; H51a). ^{13}C{^{1}H} NMR (100.63 MHz, toluene-d_8, 243.1 K): δ 134.65 ($^1J_{i,P}$ = 30.9 Hz; Cia or Cib), 133.18 (C2a), 133.22 ($^2J_{o,P}$ = 7.2 Hz, Coa), 129.8 (Cma, Cpa, Cmb, Cpb), 115.00 ($^2J_{7,P}$ = 2.75 Hz; C7a), 106.91 (C3a), 69.18 ($^2J_{6,P}$ = 28.7 Hz; C6a), 56.83 (C8a), 39.45 ($^1J_{10,P}$ = 24.3 Hz; C10a), 27.72−27.51 and 26.71−26.47 (C11, C12), 26.26 (C13a,b), 24.62 (C4a), 23.8 (C5a), 12.03 ($^2J_{1,P}$ = 10.5 Hz; C1a), 10.12 ($^1J_{Me,P}$ = 23.75 Hz; CMe). ^{31}P{^{1}H} NMR (161.916 MHz, toluene-d_8, 223.1 K): δ 29.47 (s).

1b: [(*S*)-P,(*R*)-C6] and [(*R*)-P,(*S*)-C6] (50%). ^{1}H NMR (399.99 MHz, toluene-d_8, 223.1 K): δ 7.40 (m, $^3J_{o,m}$ = 7, $^5J_{o,p}$ = 2, $^3J_{o,P}$ = 10.3 Hz, 2H; H_ob), 7.03 (superimposed by solvent, 3H; H_mb and H_pb), 6.29 (ddd, superimposed by H21a, $^3J_{21,11}$ = 10.3, $^3J_{21,12}$ = 7.3, $^3J_{21,31}$ = 10.8 Hz, 1H; H21b), 4.82 (m, superimposed by H31a, $^3J_{31,21}$ = 10.9, $^3J_{31,41}$ = 5.5, $^3J_{31,42}$ = 8.0 Hz, 1H; H31b), 4.23 (dt, superimposed by H71a, $^3J_{71,61}$ = 12.9, $^3J_{71,81}$ = 13.0, $^3J_{71,82}$ = 7.4 Hz, 1H; H71b), 3.65 (d, 1H; H82b), 2.72 (m, superimposed by H41a, H61a, H61b, 1H; H41b), 2.69 (superimposed by H81a, H41a, H41b, $^3J_{61,P} \approx$ 8 Hz, 1H; H61b), 2.59 (d, 1H; H81b), 2.37 (m, superimposed by H52a, H11a, H11b, $^2J_{52,51}$ = 10 Hz, 1H; H52b), 2.37 (dd, $^2J_{11,12}$ = 6.9 Hz, 1H; H11b), 2.16 (dt, $^3J_{12,P}$ = 16.1 Hz, 1H; H12b), 1.67−1.42 (4H; H2, H3), 1.62 (2H; H4), 1.59 (1H; H1b), 1.52 (m, superimposed by H2, H3, H4, $^3J_{42,31}$ = 8 Hz, $^2J_{42,41}$ = 10 Hz, 1H; H42b), 1.29 (d, $^2J_{Me,P}$ = 7.0 Hz, 3H; HMe), 1.22−1.07 (2H; H2), 1.12−0.85 (2H; H3), 0.72 (m, br, $^3J_{51,42}$ = 12.4, $^2J_{51,52}$ = 10, $^3J_{51,61}$ = 11 Hz, 1H; H51b). ^{13}C{^{1}H} NMR (100.63 MHz, toluene-d_8, 243.1 K): δ 134.29 ($^1J_{i,P}$ = 12.2 Hz; C_ib or C_ia), 133.57 (C2b), 132.22 ($^2J_{o,P}$ = 7.2 Hz, C_ob), 129.8 (C_ma, C_pa, C_mb, C_pb), 114.90 ($^2J_{7,P}$ = 2.75 Hz; C7b), 107.17 (C3b), 69.18 ($^2J_{6,P}$ = 28.7 Hz; C6b), 56.43 (C8b), 39.75 ($^1J_{10,P}$ = 23.75 Hz; C10b), 27.72−27.51 and 26.71−26.47 (C11, C12), 26.26 (C13a,b), 25.10 (C4b), 24.43 (C5b), 11.47 ($^2J_{1,P}$ = 9.95 Hz; C1b), 10.13 ($^1J_{Me,P}$ = 23.75 Hz; CMeb). ^{31}P{^{1}H} NMR (161.916 MHz, toluene-d_8, 223.1 K): δ 27.05 (s).

All Stereoisomers. IR (KBr; ν, cm^{-1}): 3072 (w), 3048 (w), 2992 (m), 2918 (br), 2850 (m), 1655 (m), 1637 (m), 1602 (s), 1571 (m), 1485 (w), 1448 (m), 1434 (s), 1385 (m), 1344 (w), 1309 (w), 1289 (w), 1270 (w), 1174 (m), 1114 (m), 1102 (m), 1074 (w), 1027 (w), 1001 (s), 937 (w), 917 (m), 895 (s), 878 (s), 848 (m), 820 (w), 794 (w), 747 (s), 733 (s), 718 (s), 697 (vs), 581 (w), 515 (s), 486 (m), 462 (m), 408 (w). MS (ESI, fragmentor voltage 100 V; *m/z*): 437 (MHO^{2+}), 421 (MH^+, 100%), 223 ($CyMePhPOH^+$). Anal. Calcd for $C_{21}H_{31}PPd$: C, 59.93; H, 7.42; P, 7.36; Pd, 25.27. Found: C, 59.81; H, 7.54; P, 7.43; Pd, 25.16.

(+)-PCyMePh (2). To a solution of 7.16 g (0.04 mol) of $C_6H_5PCl_2$ in 40 mL of Et_2O at 0 °C was added slowly 40 mL of cyclohexyl Grignard reagent (0.1 N in diethyl ether) over a period of 4 h. For completion of the reaction the mixture was stirred at room temperature for 20 h more. After filtration of $MgCl_2$, the remaining liquid was cooled to −20 °C and poured slowly into 50 mL of MeLi (0.1 N in Et_2O) at −20 °C. Subsequent refluxing for 48 h, filtration of LiCl, and evaporation of the solvent under reduced pressure afforded the raw reaction product as a pale yellow oil, which was distilled (3×10^{-4} bar at 75 °C) to yield 5.101 g (61.3%) of analytically pure **2** in the form of a colorless oil.

The NMR numbering scheme is as follows:



^{1}H NMR (399.99 MHz, $CDCl_3$; 302.1 K): δ 7.39 (m, $^3J_{o,P}$ = 7.35 Hz, 2H, H_o,) 7.26 (m, 1H; H_p), 7.23 (m, 2H; H_m), 1.71−1.39 (5H; H1, H3), 1.15−0.88 (6H; H2, H4), 1.28 (d, $^2J_{Me,P}$ = 3.2 Hz, 3H; HMe). ^{13}C{^{1}H} NMR (100.63 MHz, $CDCl_3$; 302.1 K): δ 138.7 (d, $^1J_{i,P}$ = 14.6 Hz; C_i), 132.4 (d, $^2J_{o,P}$ = 17.8 Hz; C_o), 128.2 (d, $^3J_{m,P}$) = 34.0 Hz), 128.0 (C_p), 39.0 (d, $^1J_{1,P}$ = 9.7 Hz; C1), 29.4 and 28.8 (d, $^2J_{2,P}$ = 12.9 Hz; C2, C2′), 27.0 and 26.9 (d, $^3J_{3,P}$ = 9.7; C3, C3′), 26.4 (C4), 8.3 (d, $^1J_{Me,P}$ = 14.6 Hz; CMe). ^{31}P{^{1}H} NMR (161.916 MHz, $CDCl_3$, 302.1 K): δ −23.01 (s). IR (KBr−Nujol; ν, cm^{-1}): 3071 (w), 3055 (w), 1588 (w), 1282 (w), 1268 (w), 1174 (w), 1607 (w), 1207 (w), 1000 (w), 917 (w), 744 (m), 731 (m), 696 (m), 509 (w), 485 (w). MS (ESI, fragmentor voltage 10 V, eluent MeOH; *m/z*): 209 (M^+ + H).

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(12) Sheldrick, G. SHELXL-97; Universität Göttingen, Göttingen, Germany, 1997.
(13) Zsolnai, L. XPMA, ZORTEP; Universität Heidelberg, Heidelberg, Germany, 1997.

Anal. Calcd for $C_{13}H_{19}P$: C, 74.97; H, 10.16; P, 14.87. Found: C, 75.06; H, 9.68; P, 14.83.

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Supporting Information Available: Figures giving ^{1}H, ^{13}C, and HSQC spectra and extensions of the H,H-NOESY spectra. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data of the structure has been deposited at the Cambridge Crystallographic Database Centre as Supplementary Publication No. CCDC-240715 (**1b**). Copies of the data may be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44-1223-336033; email, deposit@ccdc.cam.ac.uk;web, http://www.ccdc.cam.ac.uk).

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