Determination of Absolute Configuration of (π-Allyl)Palladium Complexes by NMR Spectroscopy and Stereoselective Complexation

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Abstract: The chiral chelating ligand *N*,*N*′-bis(phenylethyl)bispidine (**1**) forms a rigid cavity which accommodates (π-allyl)palladium species with high selectivity. In the resulting complex, the absolute configuration of the π-allyl ligand can be determined by the detection in NMR spectra of a few unambiguous interligand NOEs. Dynamic processes involving the π-allyl ligand can be investigated. Depending on the analytical target, ligand (*S*,*S*)-**1** or (*R*,*R*)-**1** may be used.

Keywords: absolute configuration · allyl ligands · chelates · chiral resolution · NMR spectroscopy · palladium

Introduction

(π-Allyl)palladium complexes are important intermediates in organometallic synthesis. They have attracted a great deal of interest because they allow the enantioselective formation of C–C bonds through allylic alkylation.[1] Therefore, the structural characterization of these compounds is of general interest, in particular when a chiral auxiliary ligand is present. Although the occurrence of enantiomeric π-allyl ligands, and their effects on NMR spectra, was recognized in the earliest investigations, their absolute configuration was not determined at that time.[2] Current investigations focused on their synthetic use mostly employ *meso*-π-allyl ligands together with chiral auxiliary ligands.[1] On the other hand, the absolute configuration of a few π-palladium complexes has been determined.[3] Because of their dynamic behavior, (π-allyl)Pd complexes are more challenging, even if their static structure is simple.

The chloro dimers of chiral π-allyl ligands show a broadening, and sometimes a splitting, of ^{13}C NMR signals, since several diastereomeric species are present (Scheme 1).[4] This effect disappears when the dimers are converted into monomers by the addition of achiral, chelating nitrogen ligands such as bipyridyl.

Here we present a method for determining the absolute configuration of chiral π-allyl ligands by using an auxiliary ligand in a straightforward NMR investigation and relying on the presence of a few key NOEs. In particular, assumptions about conformer equilibria, quantitative comparisons of NOE sizes, or time consuming computations are not involved.

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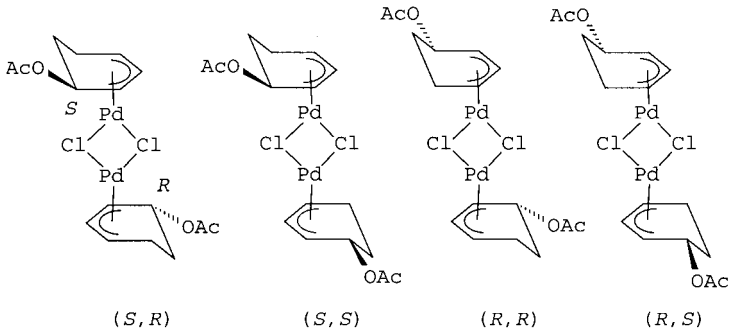

Scheme 1. Species present in a sample of racemic [4-acetoxy-(1,2,3-η^3)-cyclohexenyl]palladium (**4**).

Results

Auxiliary ligand: 3,7-(1′-Phenylethyl)-3,7-diazabicyclo[3.3.1]-nonane (**1**) was used as auxiliary ligand. Based on our previous structural work with bispidine derivatives,[5] we expected this ligand to form complexes with a tight chiral cavity for the (π-allyl)palladium unit. As can be shown by simple model building, in these complexes, steric interactions between the ligands should allow only one particular orientation of the phenylethyl groups (Figure 1). We have previously observed similar conformational restrictions with 1,5-dimethyl-3,7-(diphenyl)-3,7-diazabicyclo[3.3.1]nonan-9-one as a "molecular brake" ligand that could hinder rotation about a C–C single bond.[5b]

Ligand **1** was obtained by an improved literature synthesis that avoids the use of hydrazine (Scheme 2),[6] to yield (*S*,*S*)-**1** or its enantiomer (*R*,*R*)-**1** in 38% yield from (*S*)- or (*R*)-1-phenylethyl amine, respectively.

Complete signal assignment and conformational analysis of the free ligand was achieved by NMR spectroscopy as described previously.[7–9] The results are summarized in Figure 2 and indicate that the phenyl group is oriented toward the unoccupied space at the "bottom" of the molecule.

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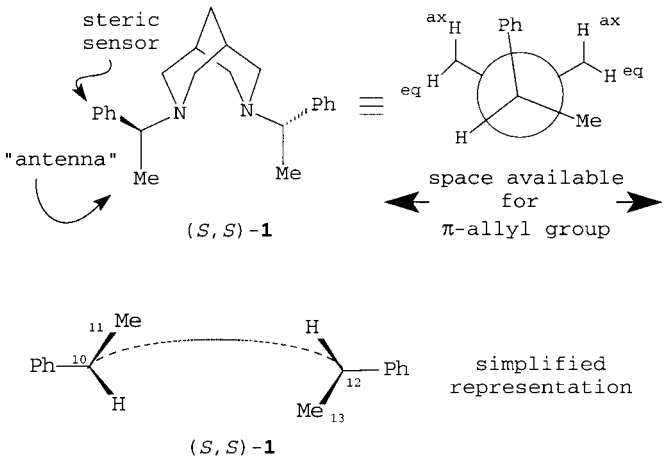
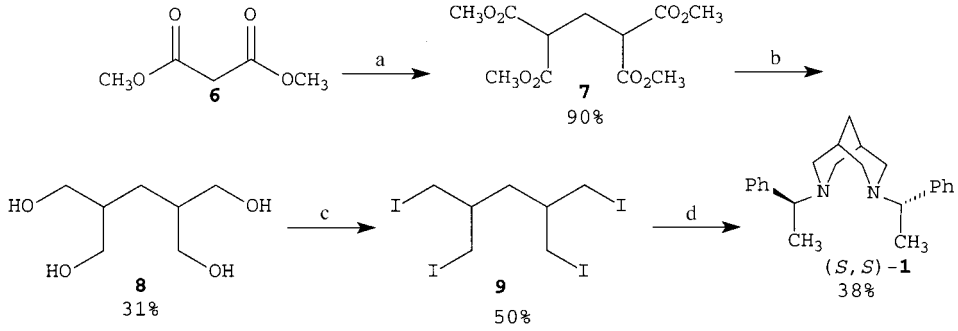


Figure 1. Steric characteristics of ligand **1**.



Scheme 2. Synthesis of **1**. a) $(CH_2O)_n$, KOH, EtOH. b) $LiAlH_4$, THF. c) I_2, P_{red}, 120 °C, $PhCH(NH_2)CH_3$, toluene.

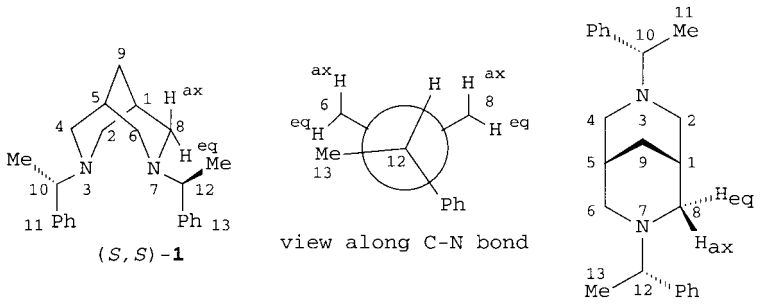


Figure 2. Solution conformation and numbering scheme for **1**.

Complexation studies: The suitability with auxiliary ligand **1** was tested in complexes with (π-allyl)Pd units of increasing steric demands; these contained nonchiral, acyclic chiral, conformationally flexible cyclic chiral, and rigid cyclic chiral π-allyl ligands.

Complex with (1,3-η^3-propenyl)palladium (2), [2·(*S*,*S*)-1]: This small ligand allows quick mapping of the chiral cavity, because only one conformation of the π-allyl ligand can exist. As expected, only one complex, with five nonequivalent π-allyl protons, is observed. The protons in the two halves of the auxiliary ligand **1** are nonequivalent with respect to the orientation of the π-allyl ligand when dynamic processes are slow on the NMR timescale (below −10 °C with a 400 MHz instrument). The presence of the π-allyl ligand forces the phenylethyl moieties of the bispidine ligand **1** into a conformation in which the phenyl groups point to the "sides" (Figure 3), thus providing a maximum space for the (π-allyl)Pd unit. This is confirmed by interligand NOEs with the aliphatic phenylethyl protons.

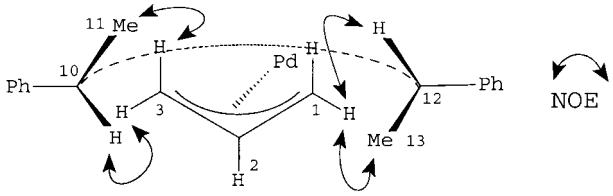


Figure 3. Interligand NOEs observed in [**2**·(*S*,*S*)-**1**].

Dynamic processes: Of the several dynamic processes that occur in (π-allyl)Pd complexes,[1a] apparent π-allyl rotation (Figure 4) often has the most pronounced effect on the appearance of the spectra. In the complex [**2**·(*S*,*S*)-**1**], the π-allyl proton signals are not affected owing to the C_2 symmetry of **1**. Protons in the two halves of the auxiliary ligand **1** that face either the base or the top (position H2, see Figure 3) of the π-allyl group, exchange between two positions. The free energy of activation for apparent π-allyl rotation is $\Delta G_c^{\ddagger} = 58\ kJ\,mol^{-1}$.

Exchange of *syn*- and *anti* protons on C1/C3 through a π–σ–π rearrangement is too slow at room temperature to affect the spectra, but can be detected by saturation transfer. Exchange of the coordination faces would result in pairwise exchange between the two *trans* and the two *cis* protons,[1a] but is not observed. Addition of Pd^0, which should increase the rate of this process, has no effect.

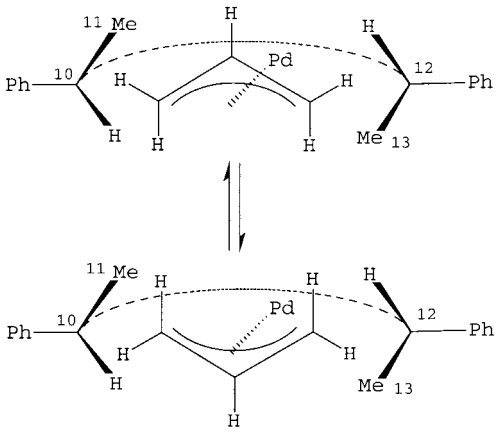
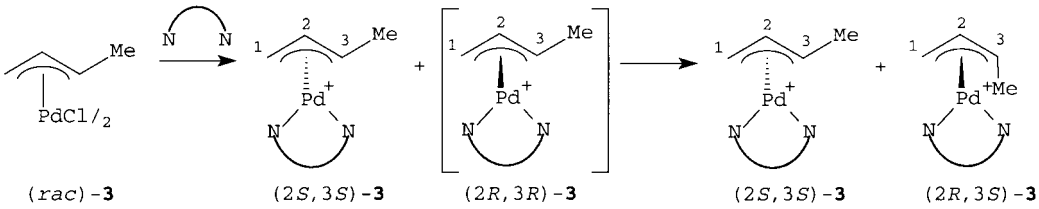


Figure 4. Apparent π-allyl rotation in complex [**2**·(*S*,*S*)-**1**].



(1)

Complex with (1,3-η^3-butenyl)palladium (3), [3·(*S*,*S*)-1]: This is the simplest possible model of a chiral (π-allyl)palladium unit, in which the chirality of the auxiliary ligand **1** is put into use.

Addition of the auxiliary ligand (*S*,*S*)-**1** to the racemic chloro dimer results in the formation of a mixture of diastereomeric complexes [Eq. (1)]: [(2*S*,3*S*)-**3**·(*S*,*S*)-**1**] and [(2*R*,3*R*)-**3**·(*S*,*S*)-**1**]. The latter undergoes a *syn*–*anti* isomerization at C3 of the π-allyl ligand within hours, presumably because of the strong steric interaction between the ligands. This results in a mixture of two diastereomeric complexes, that is {(*S*,*S*)-**1**·[(2*S*,3*S*)-(3-*syn*)(1,3-η^3-butenyl)palladium]}, [(2*S*,3*S*)-**3**·(*S*,*S*)-**1**], and {(*S*,*S*)-**1**·[(2*R*,3*S*)-(3-*anti*)(1,3-η^3-butenyl)palladium]}, [(2*R*,3*S*)-**3**·(*S*,*S*)-**1**]. Structural assignment was achieved by analysis of multiplet structure and NOEs. The *syn* and *anti* isomers were distinguished by the coupling constants between H2 and H3 (*syn* isomer: 11.2 Hz, *anti* isomer: 7.6 Hz), and by the NOE between H2 and either Me3 (*syn* isomer) or H3 (*anti* isomer). Orientation of the (1,3-η^3-butenyl) ligand towards (*S*,*S*)-**1** was indicated by interligand NOEs. The following observations are summarized in Figures 5 and 6, which also show the relative orientation of the ligands. In the complex with the *syn* isomer, NOEs were observed between $H1_{syn}$ and both Me13 and H12 in the phenylethyl group, and between H3 of the π-allyl group and Me11. In the complex with the *anti* isomer, the π-allyl $H1_{syn}$ showed an NOE with the methine proton H10, whereas the $H1_{anti}$ showed an NOE with the methyl group Me11. In this complex, NOE peaks are observed between the H3 of the π-allyl group and both Me13 and H12.

Evidently, the *syn*–*anti* isomerization is triggered by the very restricted cavity provided by the auxiliary ligand and which has to accommodate the π-allyl ligand. Whereas *syn*-(2*S*,3*S*)-**3** fits nicely, the methyl group of its enantiomer *syn*-(2*R*,3*R*)-**3** would bump into the phenylethyl methyl group, which is avoided by conversion to the *anti* isomer (Scheme 3).

Ligand-induced *syn*–*anti* isomerizations of (π-allyl)palladium species have been used for preparative purposes with bipyridyl and related heteroaromatic ligands and with varying success.[10] The *anti* effect of these auxiliary ligands was, however, usually less pronounced. Presumably these flat ligands cannot provide an equally well-defined cavity, and, therefore, ligand interaction is reduced by a distortion of the complex in which one ligand is bending out of the metal coordination plane. In other complexes, steric interaction between ligands has resulted in rotation of the π-allyl ligand about the ligand–metal axis.[11] This is not possible with bispidine derivatives. The present results also relate to recent work by Osborn in which steric interactions were used to explain the stereoselectivity of allylic alkylations.[12]

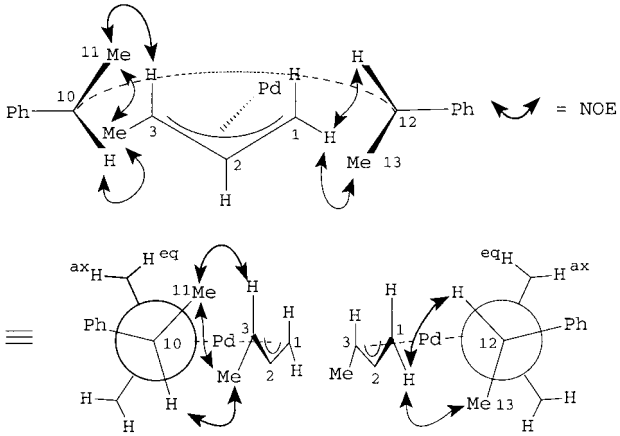


Figure 5. Interligand NOEs observed in [(2*S*,3*S*)-**3**·(*S*,*S*)-**1**].

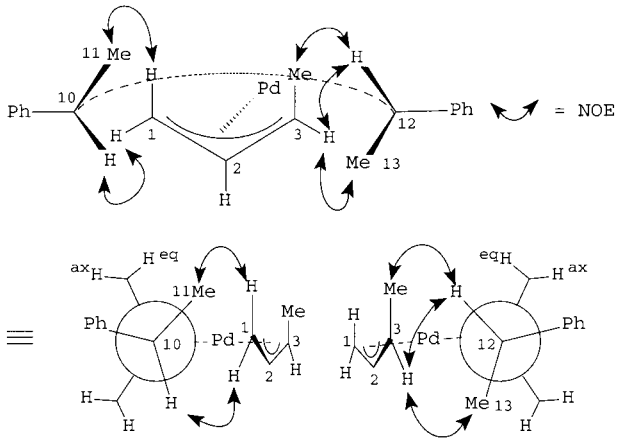
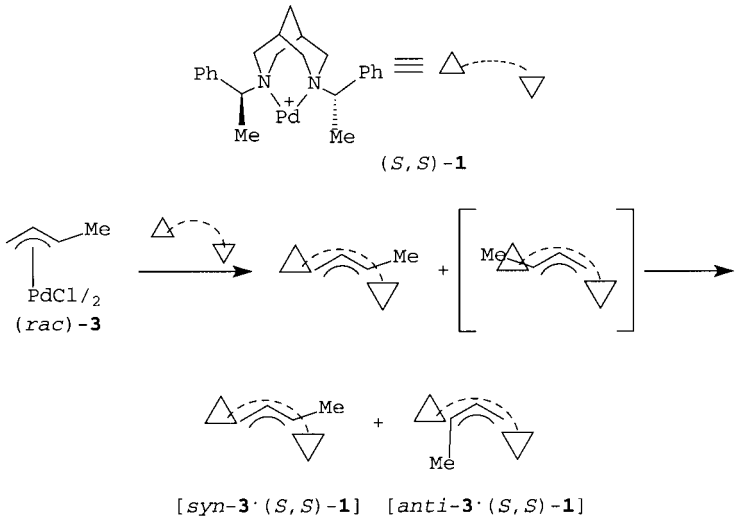


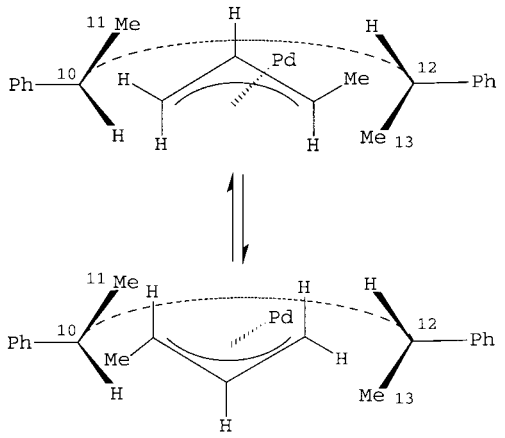
Figure 6. Interligand NOEs observed in [(2*R*,3*S*)-**3**·(*S*,*S*)-**1**].



Scheme 3. Formation of the *anti* isomer of **3** due to steric interaction with **1**.

0947-6539/01/0702-0398 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 2

Dynamic processes: In a static mixture, both diastereomers should show one set of signals for the π-allyl ligand and one set of signals for the auxiliary ligand. This is observed at low temperatures (ca. −30°C). At higher temperatures, the spectra are affected by the apparent π-allyl rotation (Figure 7),[13] in a way that corresponds to the observations with



[(2*S*,3*S*)-**3**·(*S*,*S*)-**1**]

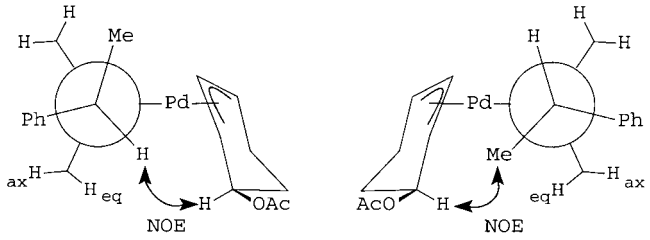
Figure 7. Apparent π-allyl rotation in complex [*syn*-**3**·(*S*,*S*)-**1**].

the propenyl ligand, **2**. For each diastereomer, this process reduces the number of signals from the auxiliary ligand, but has no effect on the π-allyl proton signals, owing to the C_2 symmetry of the auxiliary ligand. This is also observed for the two diastereomeric complexes. For example, the two methine-proton quartets of each diastereomer exchange with each other, but with different activation energies. For the *syn* isomer, $\Delta G^{\ddagger} = 64.6\ \mathrm{kJ\,mol^{-1}}$, whereas for the *anti* isomer a slightly higher value $\Delta G^{\ddagger} = 67.2\ \mathrm{kJ\,mol^{-1}}$ was observed. This is much higher than the value for the propenyl complex of $58\ \mathrm{kJ\,mol^{-1}}$, but might be due, in part, to the different counterions which had to be used (**2**: $CF_3SO_3^-$, **3**: BF_4^-).

Exchange of coordination face of the π-allyl ligand[1a] would result in an exchange between the *syn* and the *anti* forms of the (1,3-η^3-butenyl) ligand in the complex **3**·**1**. This was not observed. Exchange of *syn* and *anti* protons on C1 through a π−σ−π rearrangement is likely to occur at higher temperatures, but does not affect the chirality of the ligand, and was not investigated.

(4-Acetoxy-1,2,3-η^3-cyclohexenyl)palladium (4): The ^{1}H NMR spectra of the racemate **4** (cf. Scheme 1), prepared from 1,3-cyclohexadiene,[14] revealed the presence of two separate complexes [(*R*)-**4**·(*S*,*S*)-**1**] and [(*S*)-**4**·(*S*,*S*)-**1**], which have well-resolved signals (Figure 8). From this diastereomeric mixture, the former component with *R* configuration at C4 could be separated by crystallization.

Following a complete signal assignment by routine NMR methods (see Experimental Section), absolute configurations were assigned by using interligand NOEs between protons in the chiral phenylethyl groups of (*S*,*S*)-**1** and H4 at the chiral center C4 of the π-allyl ligand. The cyclohexenyl ring is most likely to occupy a chairlike conformation (Figure 9) with the acetoxy substituent in a pseudoequatorial position.[15]



[(*R*)-**4**·(*S*,*S*)-**1**] [(*S*)-**4**·(*S*,*S*)-**1**]

view along C-1'-N bond

Figure 9. Structurally significant interligand NOEs in the complexes formed from (*S*,*S*)-**1** and the two enantiomers of **4**.

In [(*R*)-**4**·(*S*,*S*)-1], for which the isomerically pure material could be isolated, an NOE is observed between a methine proton of the phenylethyl group and H4. This is possible only if the configuration at C4 is *R*. In the case of [(*S*)-**4**·(*S*,*S*)-1], an NOE is observed between one methyl group of (*S*,*S*)-**1** and

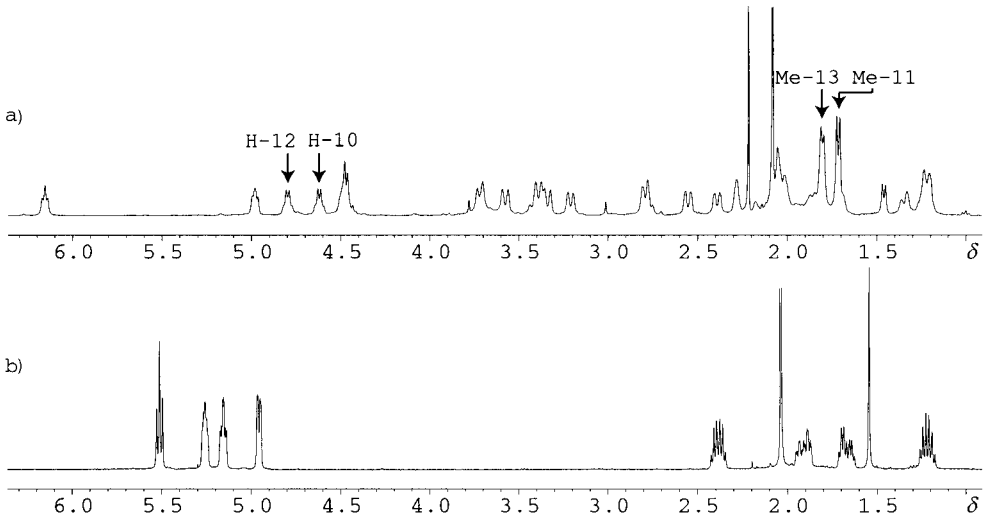


Figure 8. ^{1}H NMR spectra (400 MHz, $CDCl_3$, −50°C, phenyl region not shown) for (**4**): a) [(*R*)-**4**·(*S*,*S*)-1] isomer and b) chlorodimer of **4**.

H4 in the π-allyl ligand instead. Inspection of a molecular model reveals that these groups are only in the vicinity of each other if the configuration at C4 in the π-allyl ligand is *S* (Figure 9). Hence, one single NOE is sufficient to deduce the stereochemistry of **4**. Note that the orientation of the phenylethyl groups is the same as in the propenyl and butenyl complexes, that is, ligand **1** provides the same cavity for this larger π-allyl ligand.

1-(*S*)-2-methylene-6,6-dimethyl-bicyclo-[3.1.1]hept-2,3,10-η^3-enyl)palladium [(*S*)-5]: Complexes were formed between (*S*)-**5** (prepared from (1*S*)-*β*-pinene)[16] and the two ligands (*S*,*S*)-**1** and (*R*,*R*)-**1**. This seemed to be a good test of the method because the absolute stereochemistry of the π-allyl ligand is known. Interestingly, only (*S*,*S*)-**1** formed a stable complex, while (*R*,*R*)-**1** only showed a very weak complexation.

All proton signals in the complex [(*S*)-**5**·(*S*,*S*)-**1**] were assigned by standard procedures (see Experimental Section). Complexation is indicated by the appearance of two sets of aliphatic phenylethyl proton signals, that is, Me11 + H10 and Me13 + H12 (Figure 10). In this situation, for the complex

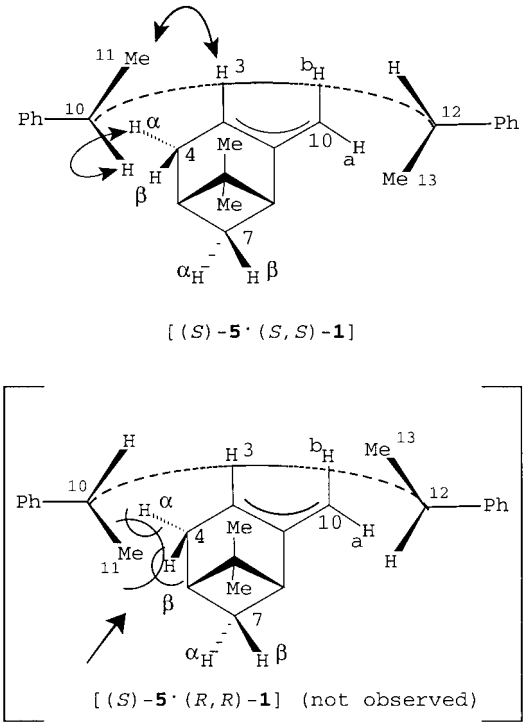


Figure 10. Structurally significant interligand NOEs in the complex formed from (*S*)-**5** and (*S*,*S*)-**1**. The structure of the unstable complex formed from (*R*,*R*)-**1** is also shown.

with the (*S*,*S*)-ligand, a geometry is obtained in which NOE peaks are observed between H10a and both the H12 proton and the Me13 group, but not for H10b. On the other side, an NOE peak is seen between H10 and H4*α* and between Me11 and H3. This latter effect would not be possible in the complex formed with the (*R*,*R*)-ligand.

Formation of the complex with (*R*,*R*)-**1** is disfavored because of the strong steric interactions that would be required to accommodate the methyl group on the C4 side (indicated by an arrow in Figure 10). In contrast to the complex of (1,3-η^3-butenyl)palladium (**2**), (*S*)-**5** can not avoid this steric interaction by *syn*–*anti* isomerization. This shows the enantioselectivity of ligand **1**.

Comparing the complexes between **1** and the (π-allyl)palladium species **5** or **4**, it should be noted that apparent π-allyl rotation is slow for [(*S*)-**5**·(*S*,*S*)-**1**]; this is indicated by the observation of separate signals for both sides of the bispidine ligands at room temperature. Corresponding behavior has previously been observed in complexes with *N*,*N*′-dibenzyl bispidine derivatives.[5a] On the other hand, for the complexes with **4**, this movement of the two ligands relative to each other had to be frozen out, indicating a stronger steric interaction for **5** than for **4**.

Discussion

The chiral bispidine derivative **1** allows straightforward determination of the absolute configuration of (π-allyl)Pd complexes. Another property of general interest is the strong steric interaction between the two organic ligands in its complexes, which may enforce isomerization of the π-allyl ligand (e.g. **3**) or facilitate isolation of the diastereomeric complexes (e.g. **4**). Investigation of the complexes by NMR spectroscopy provides structural information in a straightforward way. Only NOEs of easily located ligand signals, and the methyl and methine "antennae" (Figure 11), are required. A full assignment of the bispidine backbone protons is not necessary, although it has been provided here. The rigidity of **1** also makes computations of complex geometries unnecessary, and simple model building is sufficient.[17] For the present purpose, this ligand therefore has advantages compared with other types of chiral ligands used with (π-allyl)Pd complexes. In early investigations of simple (π-allyl)palladium complexes with the chiral ligand phenylethyl amine, no interligand NOEs were observed.[2c] Ligands such as 2,2′bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) and bis(diphenylphosphino)butane (Chiraphos)[1d–f] have been used for synthetic purposes, but in these, the chiral centers are further away from the metal than in **1** (Scheme 4). Moreover, these ligands direct two equal groups (e.g. phenyl) toward the π-allyl unit, as compared with the methyl and methine antennae of **1**. In addition, **1** possesses the rigid bispidine skeleton, whereas a more flexible backbone is present in chiraphos or other acyclic diphenylethane derivatives. Recently, ligands with C_1 symmetry have become increasingly popular for synthetic applications,[1e, f] but they result in more complicated NMR spectra than those observed for the complexes of **1**, which have C_2 symmetry.[18]

Complexes with the chiral ligand sparteine (Scheme 4), which is structurally related to **1** by having the same backbone, have been investigated.[1h] The disadvantages of sparteine for analytical purposes are its low symmetry, which results in complicated spectra, and its lack of large substituents that would protrude toward the π-allyl ligand. It should be noted that complexes of **1** are unreactive in, for example, allylic alkylations; this may also be attributed to the strong steric interactions between the organic ligands.

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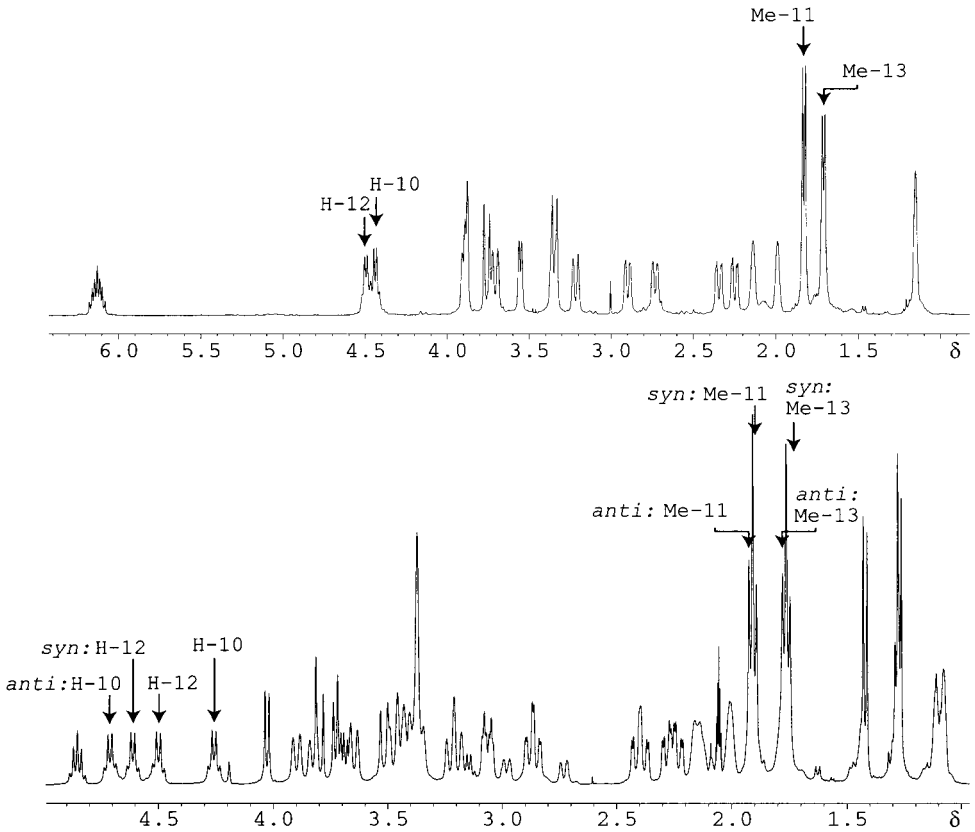
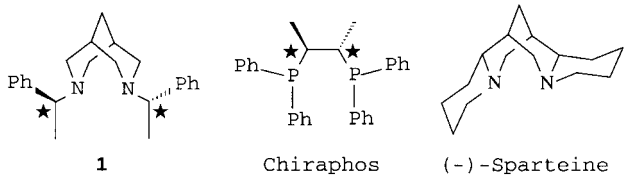


Figure 11. ^{1}H NMR spectra (400 MHz) of complexes [**2**·(*S*,*S*)-**1**] ($CDCl_3$, −40 °C; top) and [**3**·(*S*,*S*)-**1**] ([D_6]acetone, −30 °C; bottom).



Scheme 4. Chiral chelating ligands.

Conclusion

The (*S*,*S*)- and (*R*,*R*)-enantiomers of the chiral bispidine derivative **1** form complexes with (π-allyl)palladium species with high stereoselectivity. In the ^{1}H NMR spectra of the resulting complexes, signals of "antenna" protons are easily identified. Interligand NOEs involving these protons allow the absolute stereochemistry of the (π-allyl)palladium complex to be quickly and unambiguously determined. Computations of the complex geometry are not required. It should be possible to extend this application to other substrates, where alternative methods do not always produce reliable results.[19]

Experimental Section

General experimental details: ^{1}H and ^{13}C NMR spectra were recorded for $CDCl_3$ solutions at 400 and 100.6 MHz, respectively. Chemical shifts are reported in ppm referenced to TMS through the solvent signal (^{1}H: $CHCl_3$ at $\delta = 7.26$, CHD_2OD at $\delta = 3.30$, ^{13}C: $CDCl_3$ at $\delta = 77.0$, CD_3OD at $\delta = 49.0$). NMR signals were assigned from P.E.COSY,[20] HSQC,[21] HSBC,[22] NOESY[23], ROESY[24] and NOE difference spectra.[25] For NOESY and ROESY experiments, mixing times between 0.5 s and 1.2 s were used. Mass spectra were recorded on a Thermoquest GCQ instrument in EI mode at 70 eV. Infrared spectra were recorded on a Perkin–Elmer 1600 FTIR spectrometer. Progress of the reactions was followed by TLC on Merck precoated silica gel 60-F_{254} plates. For column chromatography, Merck Kieselgel 60 (230–400 mesh) was used. All melting points reported are uncorrected. Commercially available chemicals were used as purchased. Unless stated otherwise, complexes were formed by adding the chloro dimer of the (π-allyl)palladium complex and silver trifluoromethane sulfonate to chloroform (2 mL). The mixture was stirred under a nitrogen atmosphere for 1 min and then an equimolar amount, relative to palladium, of ligand **1** was added. After 10 min of stirring the mixture was filtered or centrifuged. Diethyl ether or cyclohexane was added to the clear solution to initiate precipitation, followed by storage of the mixture at −20 °C. The precipitate was collected and dried in vacuo. Because of the straightforward method of the preparation, elemental analyses were not performed. Free energies of activation were calculated from signal coalescence in NMR spectra ($\Delta G_c^{\ddagger}$), or by full line-shape analysis ($\Delta G^{\ddagger}$) by using gNMR v. 4.1.0 (Cherwell Scientific).

Propane-1,1,3,3-tetracarboxylic acid tetramethylester (7):[26] The literature procedure was used with modifications. Paraformaldehyde (1.1 g, 36 mmol) and dimethylmalonate (**6**; 19.1 g, 144 mmol) were heated to 70 °C and KOH in ethanol (10%, ten drops) was added. The temperature was increased to 95 °C and the heating was continued for 15 h. After cooling, the product was extracted with benzene/water (200 mL, 1:1; then benzene 2 × 50 mL) that was acidified to pH 3 with aq. HCl. The water phase was re-extracted with benzene and the combined organic phases were concentrated in vacuo. Excess dimethyl malonate was distilled off through a short column under reduced pressure (130 °C, 5 mm Hg). Cooling yielded white crystals, (8.93 g, 90%). M.p. 40–42 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 3.70$ (s, 12 H; CH_3), 3.49 (t, J(H,H) = 7.5 Hz, 2 H; CH), 2.46 (t, J(H,H) = 7.5 Hz, 2 H; CH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta = 168.8$, 52.7, 48.9, 27.3; IR (KBr) $\tilde{\nu} = 2990$, 1750, 1450, 1320 cm^{-1}.

1,5-Dihydroxy-2,4-di(hydroxymethyl)pentane (8):[26] $LiAlH_4$ (2.66 g, 70 mmol) was dissolved in dry THF (50 mL) and cooled in an ice bath. Compound **7** (8.28 g, 30 mmol) dissolved in dry THF (50 mL) was added drop by drop to the stirred $LiAlH_4$ solution, by means of a dropping funnel. After completion of the addition (ca. 30 min), stirring was continued for 30 min while keeping the temperature at 0 °C, followed by 5 h of heating under reflux. The reaction mixture was cooled in ice, and water (5 mL) was added, followed by aq. NaOH (15%, 5 mL) and water (10 mL). Stirring was continued for 30 min at 0 °C, and the reaction mixture was then filtered. The solid was collected and extracted for 24 h in a Soxhlet apparatus with THF (300 mL) as solvent. The THF was removed under reduced pressure yielding off-white crystals, (1.82 g, 28%). M.p. 130 °C (Lit: 129–130 °C); ^{1}H NMR (400 MHz, CD_3OD, 25 °C): $\delta = 3.54$ (m, 8 H; CH_2O), 1.71 (m, 2 H; CH) 1.25 (t, J(H,H) = 7.0 Hz, 2 H; CH_2); ^{13}C NMR (100.6 MHz, CD_3OD, 25 °C): $\delta = 62.9$, 40.7, 26.3; IR (KBr) $\tilde{\nu} = 3317$, 2934, 1560, 1507, 1474 cm^{-1}.

1,5-Diiodo-2,4-(diiodomethyl)pentane (9):[27] Red phosphorus (1.55 g, 50 mmol) and iodine (19.03 g, 150 mmol) were mixed and stirred at 100 °C for 1 h. Compound **8** (1.3 g, 6.13 mmol) was added in small portions, and the mixture was stirred at 120 °C for 4 h. The reaction mixture was cooled in an ice bath, and water (20 mL) was added and the mixture was

stirred at 0 °C for 1 h. The mixture was filtered and the solid was washed with water followed by acetone. The resulting crystals were recrystallized from carbon tetrachloride giving slightly yellow crystals that were dried under vacuum, (1.84 g, 50 %). M.p. 103 °C (Lit: 103 – 103.5 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 3.67$ (dd, J(H,H) = 10.1, 4.1 Hz, 4H; CH_2I), 3.18 (dd, J(H,H) = 10.1, 6.2 Hz, 4H; CH_2I), 1.51 (t, J(H,H) = 6.7 Hz, 2H; CH_2), 1.38 (m, 2H; CH); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta = 39.2$, 37.8, 13.0; IR(KBr) $\tilde{\nu} = 1560$, 1381, 916, 722 cm^{-1}.

(*S*,*S*)-3,7-Bis(1′-phenylethyl)-3,7-diazabicyclo[3.3.1]nonane ([(*S*,*S*)-1]): Compound **9** (1.8 g, 3 mmol) and (*S*)-1-phenylethyl amine [(*S*)-**10**] were mixed in toluene (25 mL) and refluxed for 60 h under a nitrogen atmosphere. After cooling, the reaction mixture was extracted with aq. NaOH (10 %). The aqueous phase was re-extracted with toluene, and the solvent of the combined organic phases was removed under reduced pressure. The resulting oil was purified by bulb-to-bulb distillation followed by column chromatography (pentane/diethyl ether/triethyl amine 9:9:2). Removal of solvents under reduced pressure yielded **1** as a clear oil (0.38 g, 38 %).[6a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.50$ (m, 4H; Ph_{ortho}), 7.32 (m, 4H; Ph_{meta}), 7.23 (tt, J(H,H) = 7.3, 1.4 Hz, 2H; Ph_{para}), 3.25 (q, J(H,H) = 6.7 Hz, 2H; H10), 2.93 (dd, J(H,H) = 10.5, 2.7 Hz, 2H; H2,6$_{eq}$), 2.72 (dd, J(H,H) = 10.5, 2.7 Hz, 2H; CH4,8$_{eq}$), 2.32 (dd, J(H,H) = 10.5, 3.9 Hz, 2H; H2,6$_{ax}$), 2.22 (dd, J(H,H) = 10.5, 3.9 Hz, 2H; H4,8$_{ax}$), 1.84 (m, 2H; H1, H5), 1.48 (t, J(H,H) = 3.3 Hz, 2H; H9), 1.34 (d, J(H,H) = 6.7 Hz, $CH_3$11); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta = 146.5$, 128.0, 127.6, 126.3, 65.4, 56.4, 54.2, 31.2, 30.1, 20.8; IR ($CDCl_3$ solution) $\tilde{\nu} = 3010$, 2748, 2248, 1600, 1490, 1450 cm^{-1}.

(*R*,*R*)-3,7-Bis(1′-phenylethyl)-3,7-diazabicyclo[3.3.1]nonane ([(*R*,*R*)-1]): This compound was prepared according to the procedure for the preparation of (*S*,*S*)-**1**, but with (*R*)-1-phenylethyl amine [(*R*)-**10**].

Bis[(1,2,3-η^3-propenyl)palladium chloride]—chlorodimer of 2: This compound was prepared according to literature procedures.[28]

[(*S*,*S*)-3,7-Bis(1′-phenylethyl)-3,7-diazabicyclo[3.3.1]nonane)-[(1,2,3-η^3-propenyl)palladium] trifluoromethanesulfonate] ([2·(*S*,*S*)-1]): This compound was prepared from the chlorodimer of **2** and (*S*,*S*)-**1**. ^{1}H NMR (400 MHz, $CDCl_3$, −40 °C): $\delta = 7.37 - 7.31$ (m, 10H; Ph), 6.13 (m, 1H; H2), 4.50 (q, J(H,H) = 6.4 Hz, 1H; H12), 4.43 (q, J(H,H) = 6.7 Hz, 1H; H10), 3.90 (m, 1H; H4$_{eq}$), 3.89 (m, 1H; H1′$_{syn}$), 3.77 (d, J(H,H) = 13.3 Hz, 1H; H1′$_{anti}$), 3.73 (m, 1H; H6$_{eq}$), 3.55 (d, J(H,H) = 6.6 Hz, 1H; H1$_{syn}$), 3.35 (d, J(H,H) = 11.6 Hz, 1H; H1$_{anti}$), 3.34 (m, 1H; H8$_{eq}$), 3.21 (m, 1H; H2$_{eq}$), 2.89 (m, 1H; H4$_{ax}$), 2.73 (m, 1H; H8$_{ax}$), 2.33 (m, 1H; H6$_{ax}$), 2.24 (m, 1H; H2$_{ax}$), 2.14 (m, 1H; H5,1), 2.00 (m, 1H; H5,1), 1.84 (d, J(H,H) = 6.7 Hz, 3H; $CH_3$11), 1.71 (d, J(H,H) = 6.4 Hz, 3H; $CH_3$13), 1.16 (m, 2H; $CH_2$9).

Bis[(1,2,3-η^3-butenyl)palladium chloride]—chlorodimer of 3:[29] $PdCl_2$ (1.45 g, 8.2 mmol) and NaCl (1.0 g, 17.1 mmol) were suspended in a mixture of methanol (25 mL) and water (3 mL). The suspension was heated until the solution became dark red and all the salts were dissolved. 3-Chlorobut-1-ene (5.0 mL, 50 mmol) was added in one portion. Carbon monoxide was passed through the solution, and a yellow solid started to precipitate. After 10 min, water (100 mL) was added until the salts were dissolved. The solution was extracted with chloroform (3 × 100 mL). The organic phase was dried over Na_2SO_4 and evaporated. The crude product was recrystallized from acetone/pentane (1:1) yielding a yellow solid (**3**·Cl)$_2$ (1.29 g, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 5.29$ (dddd, J(H,H) = 0.7, 6.8, 11.2, 11.9 Hz, 1H; H2), 3.91 (mqd, J(H,H) = 0.9, 6.3, 11.2 Hz, 1H; H3), 3.89 (dd, J(H,H) = 0.9, 6.8 Hz, 1H; H1$_{syn}$), 2.82 (ddd, J(H,H) = 0.9, 0.9, 11.9 Hz, 1H; H1$_{anti}$), 1.34 (dd, J(H,H) = 0.7, 6.3 Hz, 3H; CH_3).

[(*S*,*S*)-3,7-Bis(1′-phenylethyl)-3,7-diazabicyclo[3.3.1]nonane)(1,2,3-η^3)-butenyl palladium tetrafluoroborate] ([3·(*S*,*S*)-1]): The chlorodimer of **3** (19.6 mg, 100 μmol of monomer) and $AgBF_4$ (19.5 mg, 100 μmol) were dissolved in [D_6]acetone. After 10 min of stirring at room temperature under argon, silver chloride was removed by centrifugation. This solution was then added to ligand (*S*,*S*)-**1** (33.5 mg, 100 μmol), stirred for 10 min under argon, and subjected to NMR investigation. Equimolar mixture of two isomers: [(2*S*,3*S*)-**3**·(*S*,*S*)-**1**]: ^{1}H NMR (400 MHz, [D_6]acetone, −30 °C): $\delta = 7.2 - 7.6$ (m, 10H; Ph), 5.8 – 6.0 (m, 1H; H2$_{butenyl}$), 4.61 (q, J(H,H) = 6.9 Hz, 3H; H12), 4.26 (q, J(H,H) = 6.9 Hz, 3H; H10), 4.03 (m, 1H; H1$_{syn}$), 3.90 (m, 1H; H4$_{eq}$), 3.80 (m, 1H; H1$_{anti}$), 3.69 (m, 1H; H3$_{butenyl}$), 3.65 (m, 1H; H6$_{eq}$), 3.41 (m, 1H; H8$_{eq}$), 3.19 (m, 1H; H2$_{eq}$), 3.08 (m, 1H; H4$_{ax}$), 2.85 (m, 1H; H8$_{ax}$), 2.38 (m, 1H; H6$_{ax}$), 2.28 (m, 1H; H2$_{ax}$) 2.14 (m, 1H; H5), 2.01 (m, 1H; H1), 1.90 (d, J(H,H) = 6.9 Hz, 3H; $CH_3$11), 1.75 (d, J(H,H) = 6.9 Hz, 3H; $CH_3$13), 1.27 (d, J(H,H) = 6.8 Hz, 3H; $CH_{3\,butenyl}$), 1.08(m, 2H; $CH_2$9); [(2*R*,3*S*)-**3**·(*S*,*S*)-**1**], ^{1}H NMR (400 MHz, [D_6]acetone, −30 °C): $\delta = 7.2 - 7.6$ (m, 10H; Ph), 5.9 – 6.0 (m, 1H; H2$_{butenyl}$), 4.85 (m, 1H; H3$_{butenyl}$), 4.71 (q, J(H,H) = 6.9 Hz, 1H; H10), 4.50 (q, J(H,H) = 6.9 Hz, 1H; H12), 3.83 (m, 1H; H4$_{eq}$), 3.73 (m, 1H; H1$_{syn}$), 3.52 (m, 1H; H1$_{anti}$), 3.47 (m, 1H; H6$_{eq}$), 3.45 (m, 1H; H8$_{eq}$), 3.23 (m, 1H; H2$_{eq}$), 3.05 (m, 1H; H4$_{ax}$), 2.88 (m, 1H; H8$_{ax}$), 2.42 (m, 1H; H6$_{ax}$), 2.23 (m, 1H; H2$_{ax}$), 2.16 (m, 1H; H5), 2.00 (m, 1H; H1), 1.92 (d, J(H,H) = 6.9 Hz, 3H; $CH_3$11), 1.77 (d, J(H,H) = 6.9 Hz, 3H; $CH_3$13), 1.42 (d, J(H,H) = 6.8 Hz, 3H; $CH_{3\,butenyl}$), 1.11 (m, 2H; $CH_2$9).

***trans*-Bis[(4-acetoxy-(1,2,3-η^3)-cyclohexenyl)palladium chloride]—chlorodimer of 4**: This compound was prepared from cyclohexadiene.[14]

[(*S*,*S*)-3,7-Bis(1′-phenylethyl)-3,7-diazabicyclo[3.3.1]nonane]{*trans*-[(4-acetoxy-(1,2,3-η^3)-cyclohexenyl]palladium} trifluoromethanesulfonate} ([4·(*S*,*S*)-1]): The chlorodimer of **4**; 14.1 mg, 25 μmol) and silver trifluoromethanesulfonate (14.2 mg, 55 μmol) were added to chloroform (3 mL). After 10 min of stirring at room temperature, the solution was centrifuged until all the silver chloride was removed from the solution. This solution was then mixed with (*S*,*S*)-**1** (16.7 mg, 50 μmol) dissolved in chloroform (1 mL). After 5 min of stirring, the solvent amount was reduced to approximately 1 mL. Diethyl ether was added to initiate precipitation of the complex, followed by storage of the mixture at −20 °C over night. (20 mg, 54 %). Further crystallizations of this mixture of diastereomeric complexes yielded [(*R*)-**4**·(*S*,*S*)-1] in its pure form, (8 mg, 22 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.50 - 7.35$ (m, 10H; Ph), 6.21 (dd, J(H,H) = 6.1 Hz, 6.1, 1H; H2$_{allyl}$), 5.01 (dd, J(H,H) = 6.6, 2.1 Hz, 1H; H4$_{allyl}$), 4.79 (q, J(H,H) = 6.6 Hz, 1H; H12), 4.66 (q, J(H,H) = 6.6 Hz, 1H; H10) 4.55 (m, 1H; H1$_{allyl}$), 4.55 (m, 1H; H3$_{allyl}$), 3.74 (d, J(H,H) = 12.8 Hz, 1H; H8$_{eq}$), 3.60 (d, J(H,H) = 12.8 Hz, 1H; H2$_{eq}$), 3.47 (d, J(H,H) = 12.8 Hz, 1H; H4$_{eq}$), 3.43 (d, J(H,H) = 12.8 Hz, 1H; H6$_{eq}$), 3.23 (d, J(H,H) = 12.8 Hz, 1H; H8$_{ax}$), 2.84 (d, J(H,H) = 12.8 Hz, 1H; H4$_{ax}$), 2.59 (d, J(H,H) = 12.8 Hz, 1H; H2$_{ax}$), 2.44 (d, J(H,H) = 12.8 Hz, 1H; H6$_{ax}$), 2.26 (s, 1H; H1 in **1**), 2.17 (s, 1H; H5 in **1**), 2.07 (s, 3H; OAc), 2.02 (m, 1H; H5$_{eq\,allyl}$), 2.06 (m, 1H; H6$_{ax\,allyl}$), 1.87 (m, 1H; H6$_{eq\,allyl}$), 1.81 (d, J(H,H) = 6.6 Hz, 3H; $CH_3$13), 1.74 (d, J(H,H) = 6.6 Hz, 3H; $CH_3$11), 1.34 (d, J(H,H) = 13.8 Hz, 1H; H9), 1.26 (d, J(H,H) = 13.8 Hz, 1H; H9), 1.28 (m, 1H, H5$_{ax\,allyl}$); IR (KBr) $\tilde{\nu} = 3031$, 1726, 1602, 1555 cm^{-1}.

[(*S*)-**4**·(*S*,*S*)-**1**] (in a 1:1 mixture with [(*R*)-**4**·(*S*,*S*)-1]): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.50 - 7.30$ (m, 10H; Ph), 6.17 (dd, J(H,H) = 6.6, 6.6 Hz, 1H; H2$_{allyl}$), 5.13 (dd, J(H,H) = 6.6, 2.1 Hz, 1H; H4$_{allyl}$), 4.78 (m, 1H; H1$_{allyl}$), 4.77 (q, J(H,H) = 6.6 Hz, 1H; H10), 4.38 (q, J(H,H) = 6.6 Hz, 1H; H12), 4.05 (dd, J(H,H) = 6.6, 2.1, 1H; H3$_{allyl}$), 3.78 (d, J(H,H) = 12.8 Hz, 1H; H8$_{eq}$), 3.61 (d, J(H,H) = 12.8 Hz, 1H; H2$_{eq}$), 3.48 (d, J(H,H) = 12.8 Hz, 1H; H6$_{eq}$), 3.44 (d, J(H,H) = 12.8 Hz, 1H; H4$_{eq}$), 3.24 (d, J(H,H) = 12.8 Hz, 1H; H8$_{ax}$), 2.76 (d, J(H,H) = 12.8 Hz, 1H; H4$_{ax}$), 3.60 (d, J(H,H) = 12.8 Hz, 1H; H2$_{ax}$), 2.46 (d, J(H,H) = 12.8 Hz, 1H; H6$_{ax}$), 2.22 (s, 1H; H1 in **1**), 2.22 (m, 1H; H5$_{eq\,allyl}$), 2.03 (s, 3H; OAc), 1.73 (d, J(H,H) = 6.6 Hz, 3H; $CH_3$11), 1.50 (d, J(H,H) = 6.6 Hz, 3H; $CH_3$13), 1.40 (m, 1H; H5$_{ax\,allyl}$), 1.34 (d, J(H,H) = 13.8 Hz, 1H; H9), 1.22 (d, J(H,H) = 13.8 Hz, 1H; H9) (protons on C6 and H5 in **1** obscured); IR (KBr) $\tilde{\nu} = 3031$, 1726, 1602, 1555 cm^{-1}.

Bis[2-methylene-6,6-dimethylbicyclo[3.1.1]hept-(2,3,10-η^3)-enyl)palladium chloride]—chlorodimer of (*S*)-5: This compound was prepared from β-pinene.[16]

[(*S*,*S*)-3,7-Bis(1′-phenylethyl)-3,7-diazabicyclo[3.1.1]nonane]{[2-methylene-6,6-dimethylbicyclo[3.1.1]hept-(2,3,10-η^3)-enyl]palladium trifluoromethanesulfonate} ([(*S*)-5·(*S*,*S*)-1]): The chlorodimer of (*S*)-**5** (13.9 mg, 25 μmol) and silver trifluoromethane sulfonate (14.2 mg, 55 μmol) were added to chloroform (3 mL). After 10 min of stirring at room temperature, the solution was centrifuged until all the silver chloride was removed from the solution. This solution was then mixed with (*S*,*S*)-**1** (16.7 mg, 50 μmol) dissolved in chloroform (1 mL). After 5 min of stirring, the solvent amount was reduced to approximately 1 mL. Diethyl ether was added to initiate precipitation of the complex, followed by storage of the mixture at −20 °C over night; this yielded a colorless oil (17 mg, 59 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.40 - 7.30$ (m,10H; Ph), 4.46 (q, J(H,H) = 6.6 Hz, 1H; H10), 4.20 (s, 1H; H10b), 4.19 (d, J(H,H) = 11.8 Hz, 1H; H4$_{eq}$), 4.14 (q, J(H,H) = 6.6 Hz, 1H; H12), 3.92 (d, J(H,H) = 11.8 Hz, 1H; H6$_{eq}$), 3.90 (br s, 1H, H3), 3.65 (s, 1H; H10a), 3.23 (d, J(H,H) = 11.8 Hz, H8$_{eq}$), 2.98 (dd J(H,H) = 11.8, 3.5 Hz, 1H; H4$_{ax}$), 2.86 (d, J(H,H) = 11.8 Hz, 1H; H2$_{eq}$), 2.85 (m, 1H; H7β), 2.82 (d, J(H,H) = 11.8 Hz, 1H; H8$_{ax}$), 2.51 (m, 1H;

0947-6539/01/0702-0402 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 2

H1), 2.43 (dd, J(H,H) = 11.8, 3.5 Hz, 1H; $H2_{ax}$), 2.39 (dd, J(H,H) = 11.8, 3.5 Hz, 1H; $H6_{ax}$), 2.26 (m, 1H; H5), 2.16 (br s, 1H; H5 in **1**), 1.99 (br s, 1H; H1 in **1**), 1.90 (d, J(H,H) = 6.6 Hz, 3H; $CH_3$13), 1.85 (m, 1H; H7α), 1.80 (m, 1H; H4β), 1.65 (d, J(H,H) = 6.6 Hz, 3H; $CH_3$11), 1.43 (m, 1H; H4α), 1.42 (s, 3H; $CH_3$8), 1.15 (s, 2H; $CH_2$9 in **1**), 1.06 (s, 3H; $CH_3$9); IR (KBr) $\tilde{\nu}$ = 3010, 1569, 1494, 1425 cm^{-1}

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