Conformational Restriction of Acyclic π-Allyl Ligands in (3,7-Diphenyl-1,5-dimethylbispidinone)(η^3-alkenyl)palladium Complexes

Adolf Gogoll,* Helena Grennberg, and Andreas Axén

Department of Organic Chemistry, University of Uppsala, Box 531, 751 21 Uppsala, Sweden

Received April 22, 1998

A chelating dinitrogen ligand based on the bispidine skeleton is shown to restrict the conformational freedom of small, acyclic π-allyl ligands in palladium complexes. The π-allyl ligand is locked into one single rotamer by entirely steric interactions. These interactions do not require the presence of bulky substituents on the π-allyl ligand. The geometry of these complexes has been investigated by NMR spectroscopy in combination with semiempirical calculations.

Introduction

The existence of rotamer equilibria is the main obstacle in structural characterization of small acyclic compounds by NMR spectroscopy.[1] In the equilibrium mixture, significant parameters such as vicinal coupling constants ($^3J_{HH}$ or $^3J_{CH}$), NOEs, or chemical shifts are weighted averages of several rotamers. A simplification would be possible if the flexible molecule could be locked into a single rotamer.

Single rotamers might be obtained if intramolecular interactions between substituents on an acyclic backbone are large.[2] In acyclic (π-allyl)palladium complexes such interactions are usually too weak.[3] Intermolecular interactions might here constitute an attractive possibility to construct a "conformational brake"[4] (Figure 1). In this context, a conformational brake is a molecular entity which forces the flexible π-allyl chain to adopt one single conformation. We recently have communicated a first approach[5] and report here a substantial improvement.

In the previous investigation, the diastereomeric complexes *R*,R**-**1** and *R*,S**-**1** (Scheme 1) could be assigned after introduction of chelating nitrogen ligands such as bipyridine (bpy). This resulted in changed rotamer equilibria for the diastereomers, indicated by a change of the coupling constant $^3J_{H4-H5}$.[6] This method required, however, the study of trends for parameters in a series of complexes. Due to the weak steric interaction between the π-allyl and dinitrogen ligands in these complexes, individual rotamers about the C4−C5 single bond could not be observed.

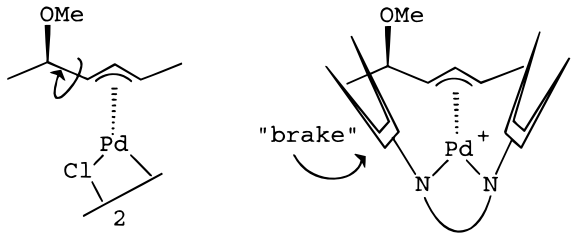
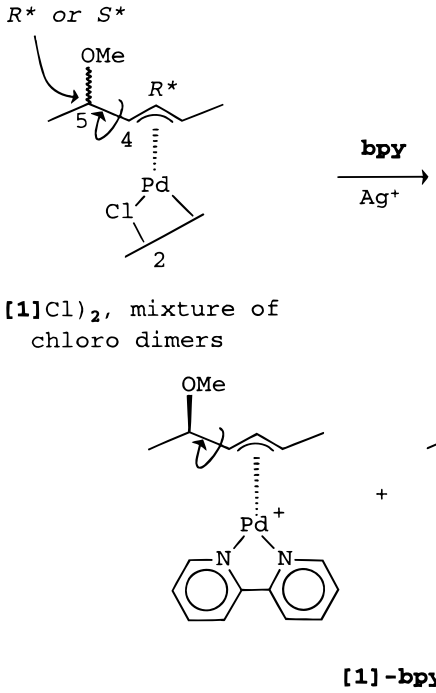


Figure 1.

Scheme 1



(1) This resembles the situation for structural work on small peptides: Williamson, M. P.; Waltho, J. P. C*hem. Soc. Rev.* **1992**, *21*, 227.

(2) (a) Göttlich, R.; Kahrs, B. C.; Krüger, J.; Hoffmann, R. W. *Chem. Commun.* **1997**, 247. (b) Hildebrandt, B.; Brinkmann, H.; Hoffmann, R. W. *Chem. Ber.* **1990**, *123*, 869. (c) Pettersson, H.; Gogoll, A.; Bäckvall, J. E. *J. Org. Chem.* **1992**, *57*, 6025.

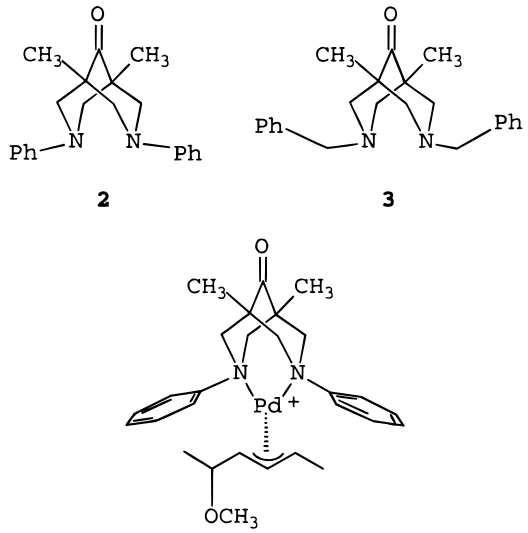
(3) Rotational barriers about C−C single bonds in ethane: 12 kJ/mol, lower in alkene derivatives, giving rise to rapidly exchanging rotamers also at low temperatures (ca. −60 °C). See: (a) Bothner-By, A. A.; Castellano, S.; Ebersole, S. J.; Günther, H. *J. Am. Chem. Soc.* **1966**, *88*, 2466. (b) Gung, B. W.; Wolf, M. A.; Zhu, Z. *J. Org. Chem.* **1993**, *58*, 3350. (c) Wiberg, K. B.; Martin, E. *J. Am. Chem. Soc.* **1985**, *107*, 5035. Higher values for sp^2-sp^3 bonds involving steric interactions: (d) Rubiralta, M.; Jaime, C.; Feliz, M.; Giralt, E. *J. Org. Chem.* **1990**, *55*, 2307. (e) Lomas, J. S.; Dubois, J.-E. *Tetrahedron* **1981**, *37*, 2273.

(4) (a) Kelly, T. R.; Bowyer, M. C.; Bhaskar, K. V.; Bebbington, D.; Garcia, A.; Lang, F.; Kim, M. H.; Jette, M. P. *J. Am. Chem. Soc.* **1994**, *116*, 3657. (b) Imashiro, F.; Takegoshi, K.; Terao, T.; Saika, A. *J. Am. Chem. Soc.* **1982**, *104*, 2247. (c) Fanizzi, F. P.; Lanfranchi, M.; Natile, G.; Tiripicchio, A. *Inorg. Chem.* **1994**, *33*, 3331.

(5) Gogoll, A.; Gomes, J.; Bergkvist, M.; Grennberg, H. *Organometallics* **1995**, *14*, 1354.

10.1021/om980309f CCC: $15.00
Publication on Web 10/30/1998

Chart 1



2 **3**

[**1**]-**2**

Table 1. Selected Experimental Data for the Complexes (Syn−Syn Isomers; Scheme 2)

complex[a]	Δδ(CH3-1)[b]	Δδ(CH3-6)[b]	Δδ(H-5)[b]	Δδ(H-2)[b]
[3R*,5R*-**1**]-**2**	−1.55	−0.48	−2.60	0.44
[3R*,5R*-**1**]-dmphen	0.05	0.01	0.01	0.78
[3R*,5S*-**1**]-**2**	−1.76	−0.55	−3.05	0.43
[3R*,5S*-**1**]-dmphen	−0.20	−0.39	−0.32	−0.07

[a] dmphen, dimethylphenanthroline.[5] [b] Chemical shift difference $\Delta\delta = \delta$(complex with **2** at −50 to −55 °C) − δ(chloro dimer, room temperature).

We have therefore designed ligand **2** (Chart 1), which should yield stronger steric interactions with the π-allyl ligand.[8] According to models, the π-allyl ligand cannot avoid steric interaction by positioning itself above the coordination plane defined by the metal and the nitrogen atoms, an essential difference from the situation in complexes with bpy-type ligands.[9]

Results and Discussion

Complexation. When ligand **2** binds to (π-allyl)-palladium complexes, tight steric interaction between the organic ligands is indicated by considerably lower chemical shifts of groups positioned above the plane of the aromatic rings, as compared with the chloro dimers.[8] For the acyclic (π-allyl)palladium complex **1** (Scheme 1), the largest chemical shift changes Δδ are observed for groups at the termini of the acyclic chain, namely CH_3-1, CH_3-6, and H-5 (Table 1 and Figure 2). Negative Δδ values indicate that these protons are located on top of the phenyl rings.[10] In contrast, chemical shift changes for complexes with 2,9-dimethyl-1,10-phenanthroline, which also is a large and rigid ligand, are smaller and sometimes positive.[11]

Molecular Geometry. More detailed structural information is obtained from the coupling constant $^3J_{H4-H5}$ and by quantifying the chemical shift changes Δδ with the Johnson−Bovey model.[12] This requires more accurate geometries, which were obtained by energy minimizations using a semiempirical method.[13] A possible arrangement of ligands in complex [*R**,*R**-**1**]-**2** is shown in Figure 3.

Three low-energy rotamers about the C4−C5 bond (**r1**−**r3**, Figure 4) are obtained by geometry optimization. Of these rotamers, only rotamer **r1** has an undistorted ligand arrangement around the metal (i.e., square planar coordination). In contrast, in rotamers **r2** and **r3** the π-allyl ligand is rotated in the metal coordination plane[14] (Figure 5). This results in a larger distance between the phenyl rings and the π-allyl ligand.

Solution Structure of Complexes. The actual rotamer distribution might now be deduced from the observed coupling constant $^3J_{H4-H5}$, using a suitable Karplus equation.[15] Independently, the chemical shift change Δδ observed for proton H-5 should also indicate its location.

Acyclic (π-allyl)palladium complexes can occur as mixtures of three syn−anti isomers (Chart 2)[16] which do not exchange on the NMR time scale.[17] For brevity, we discuss in the following reasoning only the syn−syn isomer of both (*3R**,*5R**)-[(5-methoxy-(2−4-η^3)-hexenyl)-palladium] (*R**,*R**-**1**) and (*3R**,*5S**)-[(5-methoxy-(2−4-η^3)-hexenyl)palladium] (*R**,*S**-**1**). However, the same reasoning has been applied to the syn−anti and the anti−syn isomers, and the results from these isomers have been used as controls for the conclusion drawn for the syn−syn isomer.

(6) The coupling constants J_{H4-H5} were more similar for the chloro dimers (*R**,*R**-isomer, 4.1 Hz; *R**,*S**-isomer, 3.5 Hz). With various bpy-type ligands, J_{H4-H5} was 2−3 Hz (R*,R*-isomer) and >4 Hz (R*,S*-isomer), respectively. Electrostatic interactions within the complex or orbital interactions may be responsible for this effect of the chelating ligands.[5,7]

(7) (a) Szabó, K. J. *Chem. Eur. J.* **1997**, *3*, 592. (b) Szábo, K. J. *J. Am. Chem. Soc.* **1996**, *118*, 7818.

(8) Gogoll, A.; Grennberg, H.; Axén, A. *Organometallics* **1997**, *16*, 1167.

(9) (a) Deeming, A. J.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.* **1979**, 670. (b) Fanizzi, F. P.; Intini, F. P.; Maresca, L.; Natile, G.; Lanfranchi, M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1991**, 1007.

(10) Chemical shift changes due to electronic effects are less likely for these peripheral protons, as can be seen by comparing chemical shift values for corresponding protons in the chloro dimers and in complexes with ligand **3**, which lacks the anisotropy effect on the π-allyl ligand protons due to the orientation of the phenyl rings.[8]

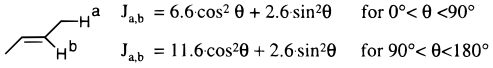
(11) The reason is the different orientation of the aromatic rings toward the π-allyl ligand. Steric interactions in complexes with bpy-type ligands are also small because the organic ligands avoid contact by distortion of the complex geometry: (a) Reference 9b. (b) Sjögren, M.; Hansson, S.; Norrby, P.-O.; Åkermark, B. *Organometallics* **1992**, *11*, 3954.

(12) (a) Johnson, C. E.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012. (b) Haigh, C. W.; Mallion, R. B. in *Progress in NMR Spectroscopy*; Emsley, J. W., Feeney, J., Sutcliffe, L. H., Eds.; Pergamon Press: Oxford, U.K., 1980. (c) Reference 8. (d) Corrections for ring current variations have not been made.

(13) Rotamer geometries were obtained from PM3(TM) calculations using Spartan 4.1.1 (Wavefunction Inc., Irvine, CA).

(14) Corresponding ligand tilting has been reported for complexes with steric repulsion between ligands: (a) Farrar, D. H.; Payne, N. C. *J. Am. Chem. Soc.* **1985**, *107*, 2054. (b) Togni, A.; Burckhardt, U.; Gramlich, V.; Pregosin, P. S.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031. (c) Togni, A.; Rihs, G.; Pregosin, P. S.; Ammann, C. *Helv. Chim. Acta* **1990**, *73*, 723. (d) Pfaltz, A. *Acta Chem. Scand.* **1996**, *50*, 189.

(15) Approximate values calculated according to: Garbisch, E. W. *J. Am. Chem. Soc.* **1964**, *86*, 5561.



(16) Anti−anti isomers are not observed. This isomerisation results primarily in more complicated spectra, containing one separate set of signals for each isomer (cf. Experimental Section).

(17) Equilibration times between 2 min and several days have been reported for comparable complexes.[5,11b]

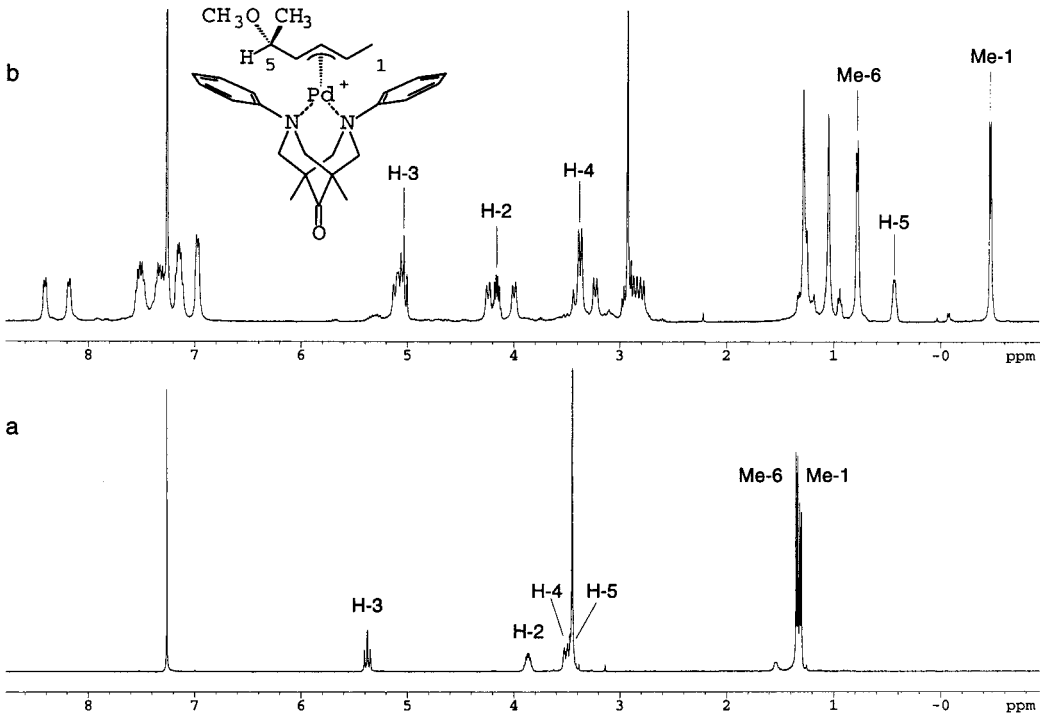


Figure 2. ^{1}H NMR spectra (400 MHz, $CDCl_3$ solution) of [*3R*,5R**-**1**]: (a) chloro dimer, 25 °C; (b) [*3R*,-R**-**1**]-**2**, −55 °C. Signals for the main (syn−syn) isomer are labeled.

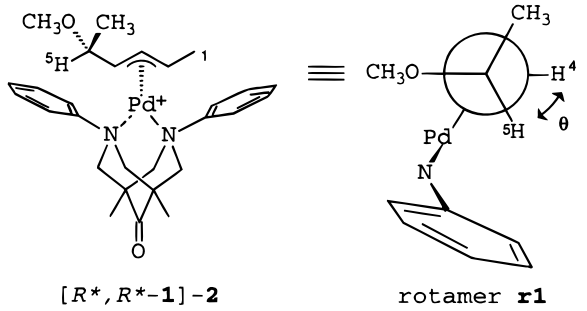


Figure 3. Arrangement of ligands in the main rotamer **r1**.

As can be seen from Table 2, both coupling constants and chemical shift changes indicate that rotamer **r1** dominates in both isomers, in agreement with the geometry calculations. The small observed coupling constants $^3J_{H4-H5} = 4.1$ Hz (*R*,S**-isomer) and 3.7 Hz (*R*,R**-isomer) exclude any substantial population of rotamer **r2**, which should result in a conciderable larger value ($^3J_{H4-H5}$ for this rotamer > 11 Hz). The observed chemical shift changes for proton H-5, $\Delta\delta = -3.05$ (*R*,S**-isomer) and −2.60 (*R*,R**-isomer), exclude significant populations of both rotamers **r2** and **r3**, for which considerably smaller $\Delta\delta$ values would be expected according to calculations (Table 2). Corresponding observations are made for the syn−anti and anti−syn isomers.[19]

The calculated and the observed $\Delta\delta$ values for **r1** do agree reasonably well. The main reason for the remaining deviations should be the choice of reference complex. For practical reasons, we use here the chloro dimers at room temperature, which provide reasonable reference chemical shift values for all but the π-allyl protons. Chemical shift values for the chloro dimers at low temperatures (−55 °C) are only slightly different. Complexes with ligand **3** should be more suitable reference compounds regarding charge distribution, but they have the disadvantage that all signals for the syn−syn isomer of [*3R*,5R**-**1**]-**3** could not be observed due to signal overlap. A further source of error, regardless of the chosen reference complex, are differences between calculated and actual geometries. It is known that small changes in position result in large changes of the calculated $\Delta\delta$ values when protons are very close to an aromatic ring.[12a,b] However, the data obtained are sufficient for our purpose. The remarkable similarity of the experimental parameters for both complexes *R*,R**-**1** and *R*,S**-**1** indicates a similar arrangement of the acyclic ligand by locking proton H-5 in a cavity on top of a phenyl ring (Figure 6).

A final confirmation of these structures is provided by NOE experiments. The predominance of rotamer **r1** results in NOEs between Me-6 and H-3 which are considerably lower in the complex of the *R*,R**-isomer than in the complex of the *R*,S**-isomer.[20] This is in accordance with the geometries shown in Figure 7.

Because of the inherent dynamic behavior of (π-allyl)-palladium complexes, the complexes with ligand **2** show single rotamers only at low temperatures.[21] At room temperature, apparent π-allyl rotation[22] "releases" the brake, resulting in averaging of NMR parameters. This

(18) Calculations of $\Delta\delta$ were done with QCPE program No. 536, using the Johnson−Bovey method; see also ref 8.

(19) The main isomer for the *R*,S**-series, anti−syn, has, according to the calculations, a dihedral angle between H-4 and H-5 of 72.1°, corresponding to J_{H4-H5} of 3.0 Hz. Observed: 2.6 Hz. Complex with bpy: 1.9 Hz.

(20) NOEs were determined from volume integrals of ROESY spectra (mixing time 800 ms) at −50 °C. Effects were normalized for the Me-1−H-3 interaction, yielding 0.3 for the *R*,R**-isomer and 1.1 for the *R*,S**-isomer.

(21) In addition to rotation about the C−C bond, apparent π-allyl rotation[22] is the main dynamic process in these systems. It is revealed by an exchange of nonequivalent protons of ligand **2** in the complex, with $\Delta G^{\ddagger}$ between 43 and 57 kJ/mol.[8]

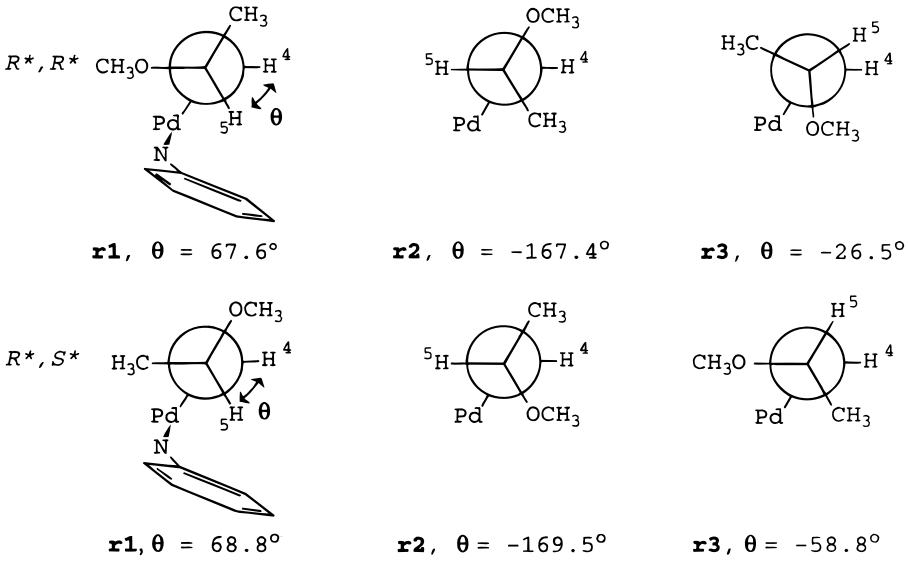


Figure 4. Low-energy rotamers about the C4−C5 bond in complexes [**1**]-**2**.

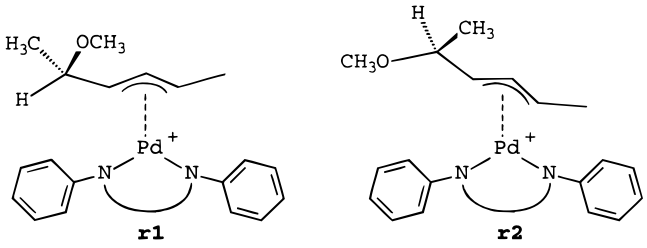
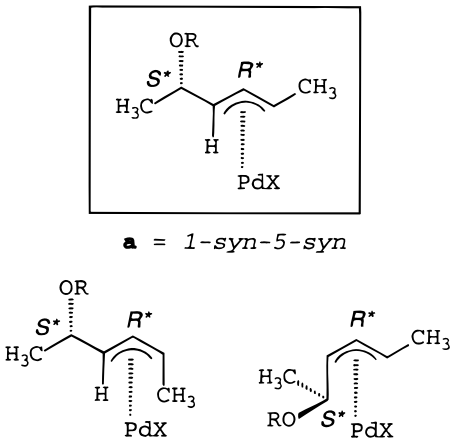


Figure 5. Relative orientation of ligands in two rotamers of [*3R**,*5S**-**1**]-**2**.

Chart 2



is indicated by an increased chemical shift of H-5, e.g., δ(25 °C) = 0.84 and δ(−55 °C) = 0.44 for [*R**,*R**-**1**]-**2**, which also shows that rotamer **r1** still dominates.[23] This process also results in an averaging of the phenyl proton chemical shifts and of the methylene protons of ligand **2**.

(22) Apparent π-allyl rotation: (a) Vrieze, K.; Volger, H. C.; van Leeuwen, P. W. N. M. *Inorg. Chim. Acta Rev.* **1969**, 109. (b) Vrieze, K. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975. (c) Gogoll, A.; Örnebro, J.; Grennberg, H.; Bäckvall, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 3631. (d) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395.

(23) A chemical shift change closer toward the value for the complex [*R**,*R**-**1**]-**3**, i.e., δ = 3.56, would be expected for complete averaging.

Table 2. Chemical Shift Changes $\Delta\delta$ and $^3J_{H4-H5}$ for the Syn Syn Isomers of [*3R,*5R**-1]-2 and [*3R**,*5S**-1]-2**

	calcd			
	r1	**r2**	**r3**	observed
	*R**,*S**-Isomer			
$\Delta\delta$ for H_5[a]	−2.84	−0.75	−0.31	−3.05
$^3J_{H4-H5}$ (Hz)[b]	3.0	11.3	3.7	4.1
	*R**,*R**-Isomer			
$\Delta\delta$ for H_5[a]	−2.34	−1.43	−0.30	−2.60
$^3J_{H4-H5}$ (Hz)[b]	3.2	11.2	5.8	3.7

[a] Chemical shift difference $\Delta\delta = \delta$(complex with **2** at −50 to −55 °C) − δ(chloro dimer, room temperature). Calculated values: ref 18. [b] Calculated values: ref 15.

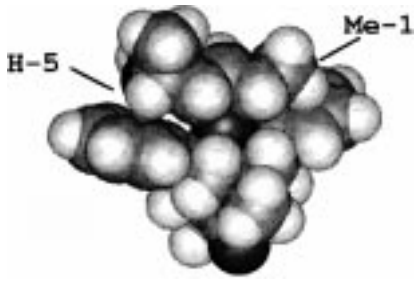


Figure 6. Space filling model of [*3R**,*5R**-**1**]-**2** (rotamer **r1**).

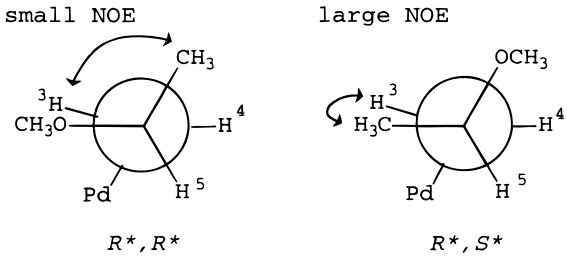


Figure 7. Structurally significant NOEs in main rotamers of [**1**]-**2**.

The observed preference for rotamer **r1**, in which H-5 faces the aromatic ring, can be explained as being the most efficient way of minimizing the steric interaction between the two organic ligands on palladium. In **r1**, this proton can be accommodated in the groove above

the center of the phenyl ring. All other rotamers would distort the ligand sphere around the metal (Figure 5), which is energetically unfavorable.

The current results are in contrast to the recently investigated complexes with bipyridyl-type ligands,[5] where complexes of *R*,R**-**1** and *R*,S**-**1** with various ligands showed significantly different coupling constants. Similarly, complexes with ligand **3** show considerably different values for J_{H4-H5}, i.e., 4.2 Hz for [*3R*,5R**-**1**]−**3**, and 9.6 Hz for [*3R*,5S**-**1**]−**3** (anti−syn isomers). Also, in the complexes with bipyridyl type ligands no unambiguous NOEs were possible to detect due to rotation about C−C single bonds, which gave rise to conformational averaged NOEs also at low temperature. These observations also support the conclusion that the interactions which determine the rotamer preference must be entirely steric and not, as in previously studied systems, electronic.[5,7]

Further Examples. The observed effect of ligand **2** is not limited to (π-allyl)palladium complex **1**. Complexes with larger acyclic π-allyl ligands which resemble the center part of **1** behaved similarly. Thus, the complex of (*3R*,5R**)-[(1,4-diphenyl-4-methoxy-(1,2,3-η^3)-butenyl)palladium] (**5**) with ligand **2** has a coupling constant of $^3J_{H3-H4} = 2.4$ Hz. The larger ligand (*6R*,-8R**)-[(8-methoxy-(5−7-η^3)-*n*-dodecenyl)palladium] (**4**) shows $^3J_{H7-H8} = 1.9$ Hz (corresponding to $^3J_{H4-H5}$ in **1**) and low chemical shifts for the protons which approach the face of the phenyl ring, assuming an undistorted metal coordination sphere and dominance of rotamer **r1**. In this latter case, not all protons in the terminal sections of the alkyl chain could be assigned due to unresolved multiplet patterns. In conclusion, also for these larger ligands a conformation which has the proton at the stereogenic center locked on top of the phenyl ring in the chelating ligand was preferred. This is quite remarkable in view of the considerable steric strain which must exist between these ligands and which might be expected to yield unstable or distorted complexes.[24]

Conclusions

We have shown the possibility to construct a molecular brake for a system without bulky substituents, i.e., an acyclic π-allyl ligand. Previous examples of molecular brakes have usually involved hindered rotation of larger, rigid substituents such as triptycenyl, anthryl, etc.[4,14b] Hindered rotation is of course a trivial phenomenon if sterically demanding substituents are involved. A well-known example would be hindered rotation of phenyl groups in various metal complexes,[25] which is also observed in the present complexes. It needs to be emphasized that the function of the brake in the present system does not require a bulky substituent on the π-allyl ligand but relies on the ability to accommodate a hydrogen atom.

Experimental Section

General Experimental Methods. NMR spectra were recorded for ^{1}H at 400 MHz and for ^{13}C at 100.6 MHz for solutions in $CDCl_3$ at 25 °C unless stated otherwise. Chemical shifts were indirectly referenced to TMS via the solvent signal (^{1}H, $CHCl_3$ at 7.26 ppm; ^{13}C, $CDCl_3$ at 77.0 ppm). NMR signals were assigned from PE COSY,[26] HSQC,[27] HSBC,[28] NOESY,[29] ROESY,[30] and NOE difference spectra.[31] For NOESY and ROESY experiments, mixing times between 0.5 and 1.2 s were used. Relative NOEs were determined by volume integration of cross-peaks. Relative amounts of syn−anti isomers (**a**:**b**:**c**, Chart 2) were determined by integration of corresponding signals of the respective isomers. For some minor isomers, signal overlap prevented complete signal assignment. IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer. Melting points are uncorrected. Commercially available chemicals were used as supplied.

General Method for the Preparation of Complexes. To chloroform (2 mL) was added the chloro dimer of the (π-allyl)-palladium complex and silver trifluoromethanesulfonate. The mixture was stirred under a nitrogen atmosphere for 1 min, and then an equimolar amount, relative to palladium, of the nitrogen ligand was added. After 10 min of stirring the mixture was filtered. Diethyl ether or cyclohexane was added to the filtrate to initiate precipitation, followed by storage at −20 °C. The precipitate was collected and dried in vacuo. Because of the straightforward method of the preparation, elemental analyses were not performed.

(3,7-Diphenyl-1,5-dimethylbispidinone)[(*3R*, 5R)-[(5-methoxy-(2−4-η^3)-hexenyl)palladium]] trifluoromethanesulfonate ([*3R*,5R**-1]-2)** was prepared from (*3R*,5R**)-bis[(5-methoxy-(2−4-η^3)-hexenyl)palladium chloride][32] (12.8 mg, 25 μmol), silver trifluoromethanesulfonate (12.8 mg, 50 μmol), and 3,7-diphenyl-1,5-dimethylbispidinone (**2**) (16.0 mg, 50 μmol). Yield: 22 mg (65%), oil.

^{1}H NMR of 1-syn−5-syn isomer (80%) (25 °C): δ 7.60−7.10 (m, 10H, Ar), 5.14 (dd, J = 11.0, 11.0 Hz, 1H, H-3), 4.59 (d, J = 12.4 Hz, 4H, eq), 4.31 (dq, J = 11.0, 6.1 Hz, 1H, H-2), 3.45 (m, 1H, H-4), 3.07 (d, J = 12.4 Hz, 4H, ax), 3.04 (s, 3H, MeO), 1.19 (s, 6H, Me), 0.86 (d, J = 6.1 Hz, 3H, Me-6), 0.84 (m, 1H, H-5), −0.24 (d, J = 6.1 Hz, 3H, Me-1). ^{1}H NMR (−55 °C): δ 8.40−7.00 (m, 10H, Ar), 5.12 (d, J = 12.4 Hz, 1H, eq), 5.07 (d, J = 12.4 Hz, 1H, eq), 5.03 (dd, J = 11.7, 11.7 Hz, 1H, H-3), 4.24 (d, J = 12.4 Hz, 1H, eq), 4.16 (dq, J = 11.7, 6.0 Hz, 1H, H-2), 4.00 (d, J = 12.4 Hz, 1H, eq), 3.42 (d, J = 12.4 Hz, 1H, ax), 3.37 (dd, J = 11.7, 3.7 Hz, 1H, H-4), 3.23 (d, J = 12.4 Hz, 1H, ax), 2.86 (d, J = 12.4 Hz, 1H, ax), 2.93 (s, 3H, MeO), 2.79 (d, J = 12.4 Hz, 1H, ax), 1.28 (s, 3H, Me), 1.05 (s, 3H, Me), 0.78 (d, J = 6.1 Hz, 3H, Me-6), 0.44 (m, 1H, H-5), −0.46 (d, J = 6.0 Hz, 3H, Me-1).

Isomer ratios from H-3 at 25 °C, δ isomers **b** and **c**: 5.47 (dd, J = 12.3, 7.5 Hz), 5.34 (dd, J = 12.3, 7.9 Hz).

IR ($CDCl_3$): 2979, 2853,1739, 1597,1399 cm^{-1}.

(3,7-Dibenzyl-1,5-dimethylbispidinone)[(*3R*,5R)-[(5-methoxy-(2−4-η^3)-hexenyl)palladium]] trifluoromethanesulfonate ([*3R*,5R**-1]-3)** was prepared from (*3R*,5R**)-bis[(5-methoxy-(2−4-η^3)-hexenyl) palladium chloride][32] (12.8 mg, 25 μmol), silver trifluoromethanesulfonate (14.1 mg, 55 μmol), and 3,7-dibenzyl-1,5-dimethylbispidinone (**3**) (17.4 mg, 50 μmol). Yield: 13 mg (36%), oil.

(24) A complex with *4R*,6R**-[6-methoxy-2,2,7,7-tetramethyl-(3−5-η^3)-octenyl)palladium[5] could not be prepared.

(25) Examples of hindered phenyl rotation are abundant in the literature, e.g.: Dale, J. *Stereochemistry and Conformational Analysis*; Universitetsforlaget: Oslo, 1978. For examples in related metal complexes, see refs 4c and 8.

(26) Mueller, L. *J. Magn. Reson.* **1987**, *72*, 191.

(27) (a) Bodenhausen, G.; Ruben, D. J. *Chem. Phys. Lett.* **1980**, *69*, 185. (b) Torres, A. M.; Nakashima, T. T.; McClung, R. E. D. *J. Magn. Reson.* **1993**, *A102*, 219.

(28) Kövér, K. E.; Prakash, O.; Hruby, V. J. *Magn. Reson. Chem.* **1993**, *31*, 231.

(29) (a) States, D. J.; Haberkorn, R. A.; Ruben, D. J. *J. Magn. Reson.* **1982**, *48*, 286. (b) Wider, G.; Macura, S.; Kumar, A.; Ernst, R. R.; Wüthrich, K. *J. Magn. Reson.* **1984**, *56*, 207.

(30) Bothner-By, A. A.; Stephens, R. L.; Lee, J. M., Warren, C. D.; Jeanloz, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 811.

(31) Sanders, J. K. M.; Mersh, J. D. In *Progress in Nuclear Magnetic Resonance Spectroscopy*; Emsley, J. W., Feeney, J., Sutcliffe, L. H., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 15, p 353.

(32) Bäckvall, J. E.; Nordberg, R. E.; Wilhelm, D. *J. Am. Chem. Soc.* **1985**, *107*, 6892.

^{1}H NMR for the 1-syn−5-syn isomer (76%) (25 °C): δ 7.39−7.22 (m, 10H, Ar), 5.55 (dd, J = 11.4, 11.4 Hz, 1H, H-3), 4.68 (dq, J = 11.4, 6.1 Hz, 1H, H-2), 4.47 (s, 4H, Bz), 3.88 (d, J = 12.2 Hz, 4H, eq), 3.41 (dd, J = 11.4, 3.4 Hz, 1H, H-4), 3.56 (dq, J = 6.1, 3.4 Hz, 1H, H-5), 3.35 (s, 3H, MeO), 2.76 (d, J = 12.2 Hz, 4H, ax), 1.37 (d, J = 6.1 Hz, 3H, Me-1), 1.22 (d, J = 6.1 Hz, 3H, Me-6), 0.88 (s, 6H, Me).

^{1}H NMR for the 1-anti−5-syn isomer (13%) (25 °C): δ 7.39−7.22 (m, 10H, Ar), 5.98 (dd, J = 12.4, 7.6 Hz, 1H, H-3), 4.55 (dq, J = 6.1, 7.6 Hz, 1H, H-2), 4.47 (s, 4H, Bz), 3.88 (d, J = 12.2 Hz, 4H, eq), 4.27 (dd, J = 12.4, 4.2 Hz, 1H, H-4), 3.85 (dq, J = 6.1, 4.2 Hz, 1H, H-5), 3.33 (s, 3H, MeO), 2.76 (d, J = 12.2 Hz, 4H, ax), 1.45 (d, J = 6.1 Hz, 3H, Me-6), 1.29 (d, J = 6.1 Hz, 3H, Me-1), 0.88 (s, 6H, Me).

^{1}H NMR for the 1-syn−5-anti isomer (11%) (25 °C): δ 7.39−7.22 (m, 10H, Ar), 5.98 (m, 1H, H-3), 4.47 (s, 4H, Bz), 4.29 (m, 1H, H-2), 3.88 (d, J = 12.2 Hz, 4H, eq), 3.86 (m, 1H, H-4), 3.56 (m, 1H, H-5), 3.13 (s, 3H, MeO), 2.76 (d, J = 12.2 Hz, 4H, ax), 1.52 (d, J = 6.1 Hz, 3H, Me-6), 1.40 (d, J = 6.1 Hz, 3H, Me-1), 0.88 (s, 6H, Me).

IR ($CDCl_3$): 2825, 1735, 1710, 1602, 1584 cm^{-1}.

(3,7-Diphenyl-1,5-dimethylbispidinone)[(*3R*,5S)-[(5-methoxy-(2−4-η^3)-hexenyl)palladium]] trifluoromethanesulfonate ([*3R*,5S**-1]-2)** was prepared from (*3R*,5S**)-bis[(5-methoxy-(2−4-η^3)-hexenyl) palladium chloride][32] (12.8 mg, 25 μmol), silver trifluoromethanesulfonate (12.8 mg, 50 μmol), and 3,7-diphenyl-1,5-dimethylbispidinone (**2**) (16.0 mg, 50 μmol). Yield: 12 mg (35%), oil.

^{1}H NMR for the 1-syn−5-syn isomer (20%) (−50 °C): δ 8.30−7.00 (m, 10H, Ar), 5.19 (dd, J = 11.8, 11.8 Hz, 1H, H-3), 5.27 (d, J = 12.2 Hz, 1H, eq), 5.24 (d, J = 12.2 Hz, 1H, eq), 4.63 (d, J = 12.2 Hz, 1H, eq), 3.85 (d, J = 12.2 Hz, 1H, eq), 3.61 (dd, J = 11.8, 4.1 Hz, 1H, H-4), 3.34 (d, J = 12.2 Hz, 1H, ax), 3.30 (d, J = 12.2 Hz, 1H, ax), 3.13 (d, J = 12.2 Hz, 1H, ax), 2.90 (s, 3H, MeO), 2.82 (d, J = 12.2 Hz, 1H, ax), 4.30 (m, 1H, H-2), 1.26 (s, 3H, Me), 1.19 (s, 3H, Me), 0.82 (d, J = 6.6 Hz, 3H, Me-6) 0.57 (m, 1H, H-5), −0.45 (d, J = 6.0 Hz, 3H, Me-1).

^{1}H NMR for the 1-anti−5-syn isomer (65%) (25 °C): δ 7.55−7.10 (m, 10H, Ar), 5.25 (dd, J = 11.9, 7.9 Hz, 1H, H-3), 4.62 (d, J = 12.2 Hz, 4H, eq), 3.42 (s, 3H, MeO), 3.37 (dd, J = 11.9, 2.6 Hz, 1H, H-4), 3.12 (d, J = 12.2 Hz, 4H, ax), 2.81 (dq, J = 7.9, 6.1 Hz, 1H, H-2), 1.22 (s, 6H, Me), 0.97 (m, 3H, Me-1), 0.82 (m, 1H, H-5), 0.81 (m, 3H, Me-6). ^{1}H NMR (−50 °C): δ 8.30−7.00 (m, 10H, Ar), 5.19 (dd, J = 11.9, 7.9 Hz, 1H, H-3), 5.27 (d, J = 12.2 Hz, 1H, eq), 5.24 (d, J = 12.2 Hz, 1H, eq), 4.63 (d, J = 12.2 Hz, 1H, eq), 3.85 (d, J = 12.2 Hz, 1H, eq), 3.34 (dd, J = 11.9, 2.6 Hz, 1H, H-4), (d, J = 12.2 Hz, 1H, ax), 3.30 (d, J = 12.2 Hz, 1H, ax), 3.13 (d, J = 12.2 Hz, 1H, ax), 2.99 (s, 3H, MeO), 2.82 (d, J = 12.2 Hz, 1H, ax), 2.68 (dq, J = 7.9, 6.1 Hz, 1H, H-2), 1.26 (s, 3H, Me), 1.19 (s, 3H, Me), 0.96 (d, J = 6.1 Hz, 3H, Me-1), 0.78 (m, 3H, Me-6) 0.76 (m, 1H, H-5).

Isomer ratios from Me-1 at −50 °C, δ isomer **c**: −0.10 (d, J = 6.1 Hz).

IR ($CDCl_3$): 2979, 1739, 1597, 1498, 1460 cm^{-1}.

(3,7-Dibenzyl-1,5-dimethylbispidinone)[(*3R*,5S)-[(5-methoxy-(2−4-η^3)-hexenyl)palladium]] trifluoromethanesulfonate ([*3R*,5S**-1]-3)** was prepared from (*3R*,5S**)-bis[(5-methoxy-(2−4-η^3)-hexenyl)palladium chloride][32] (12.8 mg, 25 μmol), silver trifluoromethanesulfonate (14.1 mg, 55 μmol), and 3,7-dibenzyl-1,5-dimethylbispidinone (**3**) (17.4 mg, 50 μmol). Yield: 17 mg (41%), oil.

^{1}H NMR for 1-anti−5-syn (57%) (25 °C): δ 7.41−7.23 (m, 10H, Ar), 5.72 (dd, J = 12.4, 7.9 Hz, 1H, H-3), 4.65 (s, 4H, Bz), 4.37 (dd, J = 9.6, 7.9 Hz, 1H, H-4), 4.34 (dq, J = 12.4, 6.1 Hz, 1H, H-2), 3.68 (d, J = 12.2 Hz, 4H, eq), 3.54 (s, 3H, MeO), 3.50 (dq, J = 9.6, 6.1 Hz, 1H, H-5), 2.76 (d, J = 12.2 Hz, 4H, ax), 1.40 (d, J = 6.1 Hz, 3H, Me-1), 1.20 (d, J = 6.1 Hz, 3H, Me-6), 0.88 (s, 6H, Me).

Isomer ratios from H-3 at 25 °C: δ isomer **a**, 5.55 (dd, J = 12.9, 12.9 Hz); δ isomer **c**, 5.75 (dd, J = 12.1, 8.0 Hz).

IR ($CDCl_3$): 2226, 2252, 1735, 1710, 1610 cm^{-1}.

(3,7-Diphenyl-1,5-dimethylbispidinone)[(*6R*,8R)-[(8-methoxy(5−7-η^3)-*n*-dodecenyl)palladium]] trifluoromethanesulfonate ([*6R*,8R**-4]-2)** was prepared from (*6R*,8R**)-bis[(8-methoxy-(5−7-η^3)-*n*-dodecenyl)palladium chloride][5] (17.0 mg, 25 μmol), silver trifluoromethanesulfonate (14.1 mg, 55 μmol), and 3,7-diphenyl-1,5-dimethylbispidinone (**2**) (16.0 mg, 50 μmol). Yield: 24 mg (62%), oil.

^{1}H NMR for mixture of syn−anti isomers, main isomer 4-syn−8-syn (25 °C): δ 7.45−7.00 (m, 10H, Ar), 5.01 (dd, J = 11.0, 11.0 Hz, 1H, H-6), 4.51 (d, J = 13.2 Hz, 4H, eq), 3.79 (s, 3H, MeO), 3.09 (d, J = 13.2 Hz, 4H, ax), 4.14 (m, 1H, H-5), 3.34 (m, 1H, H-7), 1.19 (s, 6H, Me).

^{1}H NMR (−50 °C): δ 8.40−7.00 (m, 10H, Ar), 4.99 (dd, J = 11, 11 Hz, 1H, H-6), 3.78 (s, 3H, MeO), 4.14 (m, 1H, H-5), 3.30 (dd, J = 11, 1.9, 1H, H-7), 0.88 (s, 6H, Me) 0.30 (m, 2H, H-8), 0.17 (m, 1H, H-4a), −0.99 (m, 1H, H-4b).

IR ($CDCl_3$): 3039, 1740, 1599, 1259 cm^{-1}.

(3,7-Diphenyl-1,5-dimethylbispidinone)[(1*R*,3R)[(1,4-diphenyl-1-methoxy-(2−4-η^3)-butenyl)palladium]] trifluoromethanesulfonate ([*1R*,3R**-5]-2)** was prepared from (*1R*,3R**)-bis-[(5-methoxy-(2−4-η^3)-butyl)palladium chloride][5] (19.0 mg, 25 μmol), silver trifluoromethanesulfonate (14.1 mg, 55 μmol), and 3,7-diphenyl-1,5-dimethylbispidinone (16.0 mg, 50 μmol). Yield: 30 mg (72%). Mp: 98−100 °C.

^{1}H NMR for 1-syn−*ipso*-syn (94%) (25 °C): δ 7.55−6.90 (m, 20H, Ar), 5.94 (dd, J = 11.7, 11.7 Hz, 1H, H-2),_4.61 (d, J = 12.4 Hz, 4H, eq), 4.61 (d, J = 11.7 Hz, 1H, H-1), 3.97 (dd, J = 11.7, 2.4 Hz, 1H, H-3), 3.01 (d, J = 12.4 Hz, 4H, ax), 3.01 (s, 3 H, MeO), 1.18 (d, J = 2.4 Hz, 1H, H-4), 1.18 (s, 6H, Me). ^{1}H NMR (−50 °C): δ 8.00−6.30 (m, 20H, Ar), 5.90 (dd, J = 11.7, 11.7 Hz, 1H, H-2), 3.72 (d, J = 12.4 Hz, 4H, eq), 4.43 (d, J = 11.7 Hz, 1H, H-1), 3.95 (dd, J = 11.7, 2.4 Hz, 1H, H-3), 2.97 (d, J = 12.4 Hz, 4H, ax), 2.79 (s, 3 H, MeO), 1.25 (d, J = 2.4 Hz, 1H, H-4), 1.18 (s, 6H, Me).

Isomer ratios from H-3 at 25 °C: δ isomer **c**, 5.86 (dd, J = 12.0, 8.0 Hz); isomer **b** not detected.[5]

IR (KBr): 2976, 1741, 1600, 1497, 1460 cm^{-1}.

Acknowledgment. The Swedish Natural Science Research Council and Magn. Bergvalls Stiftelse are acknowledged for financial support.

OM980309F