(π-Allyl)palladium Complexes with *N,N′*-Diphenylbispidinone Derivatives as a New Type of Chelating Nitrogen Ligand: Complexation Studies, Spectroscopic Properties, and an X-ray Structure of (3,7-Diphenyl-1,5-dimethylbispidinone)[(1,3-η^3-propenyl)-palladium] Trifluoromethanesulfonate†

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A series of 3,7-diazabicyclo[3.3.1]nonane (bispidine) derivatives have been synthesized, and their properties as bidentate nitrogen ligands for (π-allyl)palladium complexes have been investigated. Complexes of these ligands and of *N,N′*-diphenylpiperazine (**7**) and *N,N′*-diphenyl-1,5-diazacyclooctane (**8**) with (1,3-η^3-propenyl)palladium are described, in particular their effects on the proton chemical shifts of the π-allyl ligand. Ligand dynamics of the complexes is discussed. The structure of [(3,7-diphenyl-1,5-dimethylbispidinone)(1,3-η^3-propenyl)Pd]CF_3SO_3 (**15**) has been determined by X-ray crystallography. *N,N′*-Diphenylbispidine derivatives show an unusually large steric interaction with the π-allyl ligand, indicated by a tilt of the π-allyl plane toward the N−Pd−N plane by 122.8(8)°. Chemical shift changes of the π-allyl protons due to the aromatic ring current are related to the geometry of the complexes. The ligands are tested on the larger 2-methylene-6,6-dimethylbicyclo[3.1.1]hept-2,3,10-η^3-enyl ligand, demonstrating their potential as chemical shift reagents.

Introduction

Palladium-catalyzed reactions are among the most important tools of current preparative organic chemistry,[1] and various types of ligands have been developed to increase their versatility and selectivity.[2] More recently, the importance of interligand steric interactions for the stereoselectivity of these reactions have been addressed,[2e,3] in particular regarding enantioselective palladium-catalyzed reactions. Such steric interactions have also been utilized for structure analysis of (π-allyl)palladium complexes. The method is based on measurement of interligand NOEs in complexes with chelating nitrogen ligands based on 2,2′-bipyridyl (bpy) (**1**) and its congeners.[4] For both synthetic work and analytical applications it is important to identify the dynamic processes in these complexes.[5]

Recently we have investigated the suitability of bpy-type nitrogen ligands for structural analysis of palladium complexes with acyclic π-allyl ligands.[6] Here, interligand contacts are not sufficiently strong to restrict the conformational flexibility of the π-allyl ligand, making the method less powerful. It is therefore of great interest to find new types of ligands that give stronger interligand contacts.

However, increased steric interaction is not necessarily obtained by increasing the ligand size. A larger bpy-type ligand tends to minimize steric contacts by sliding beneath the π-allyl ligand plane.[7] We therefore need a ligand which (i) is very rigid in order to prevent conformational changes, (ii) has substituents which occupy space both above and below the metal coordination plane, thus minimizing decrease of steric interaction by distortion of the square planar metal coordination, and (iii) has a high binding constant for the metal, thus preventing release of sterical strain by dissociation. To be useful as an analytical tool, the ligand would also need to have a high degree of symmetry to produce reasonably simple ^{1}H NMR spectra. As promising

† Dedicated to Prof. Hans-J. Schäfer on the occasion of his 60th birthday.

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(1) (a) Tsuji, J. *Palladium Reagents and Catalysts: Innovations in Organic Chemistry*; Wiley: Chichester, U.K., 1995. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) Examples for ligand types: (a) Trost, B. M.; Van Vranken, D. L.; Bingel, C. *J. Am. Chem. Soc.* **1992**, *114*, 9327. (b) Trost, B. M.; van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (c) Albinati, A.; Pregosin, P. S.; Wick, K. *Organometallics* **1996**, *15*, 2419. (d) Trost, B. M.; Bunt, R. C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 99. (e) Togni, A.; Burckhardt, U.; Gramlich, V.; Pregosin, P. S.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031. (f) Frost, C. G.; Williams, J. M. J. *Tetrahedron Lett.* **1993**, *34*, 2015. (g) Sprinz, J.; Helmchen, G. *Tetrahedron Lett.* **1993**, *34*, 1769. (h) Knühl, G.; Sennhenn, P.; Helmchen, G. *J. Chem. Soc., Chem. Commun.* **1995**, 1845. (i) Leutenegger, U.; Umbricht, G,; Fahrni, C.; von Matt, P.; Pfaltz, A. *Tetrahedron* **1992**, *48*, 2143. (j) van Asselt, R.; Elsevier, C. J. *Organometallics* **1994**, *13*, 1972.

(3) (a) Sjögren, M.; Hansson, S.; Norrby, P.-O.; Åkermark, B. *Organometallics* **1992**, *11*, 3954. (b) Brown, J. M.; Hulmes, D. I.; Guiry, P. J. *Tetrahedron* **1994**, *50*, 4493. (c) Pfaltz, A. *Acta Chem. Scand.* **1996**, *50*, 189.

(4) (a) Albinati, A.; Ammann, C. J.; Pregosin, P. S.; Rüegger, H. *Organometallics* **1990**, *9*, 1826. (b) Albinati, A.; Kunz, R. W.; Ammann, C. W.; Pregosin, P. S. *Organometallics* **1991**, *10*, 1800. (c) Bäckvall, J. E.; Granberg, K. L.; Andersson, P. G.; Gatti, R.; Gogoll, A. *J. Org. Chem.* **1993**, *58*, 5445. (d) Bookham, J. L.; McFarlane, W. *J. Chem. Soc., Chem. Commun.* **1993**, 1352.

(5) (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) Ref 2b.

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

(7) (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.

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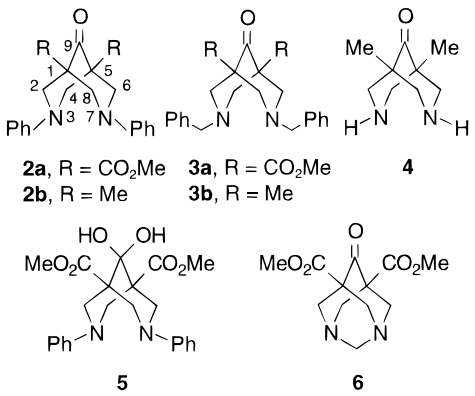
Chart 1



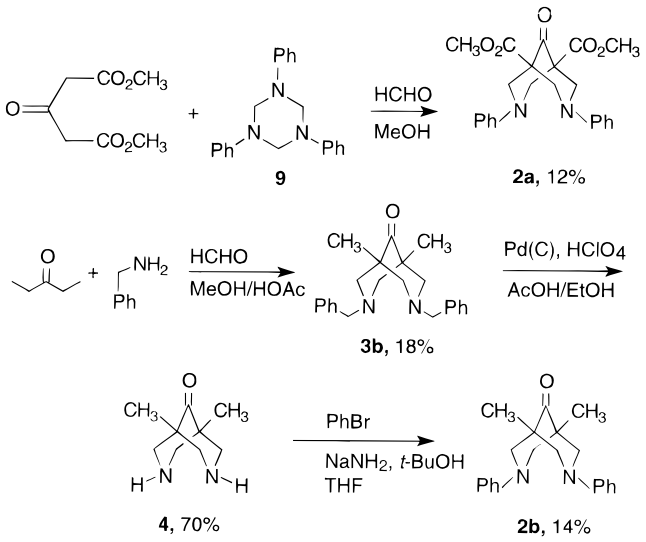
candidates emerged bispidine (bpd) derivatives (Chart 1). Related ligands have recently been used as strong complexing agents for a variety of metal cations.[8]

In the present paper we report on the synthesis and properties of a series of *N*,*N*′-diphenylbispidinone derivatives and their interaction with (1,3-η^3-propenyl)-palladium complexes. The analytical potential of these ligands is shown on the [2-methylene-6,6-dimethylbicyclo-[3.1.1]hept-2,3,10-η^3-enyl]Pd complex derived from β-pinene.

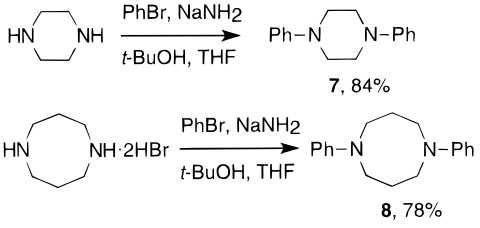
Results and Discussion.

Syntheses. The most commonly used synthetic route to bispidine derivatives involves Mannich condensation between a ketone or a piperidone, an amine and formaldehyde.[9] *N*,*N*′-diphenylbispidinone derivatives cannot be obtained directly from aniline in this way.[10] However, 1,5-dicarbomethoxybispidinone derivative **2a** could be prepared by a modified procedure (Scheme 1), representing the first direct synthesis of a bispidine derivative from an aromatic amine. An alternative although longer pathway *via* the *N*,*N*′-dibenzyl derivative **3b** was found to be more suitable for the 1,5-dimethylbispidinone derivative **2b** (Scheme 1). The synthesis of **3b** by Mannich reaction from pentane-3-one was improved to 18% as compared to previously reported 5%.[8c] Two reference ligands, *N*,*N*′-diphenylpiperazine (**7**) and *N*,*N*′-diphenyl-1,5-diazacyclooctane (**8**), were prepared by phenylation of the corresponding amines (Scheme 2). Recently introduced methods for phenylation of monoamines[11] all failed with the diamines described here, probably due to interference of the strongly chelating starting materials or small amounts of products with the catalytic amounts of

Scheme 1



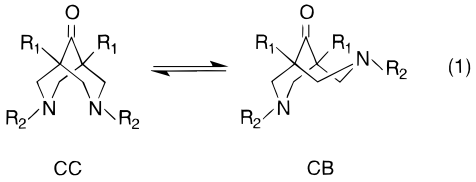
Scheme 2



metals. Complexes with (1,3-η^3-propenyl)palladium were prepared by known procedures.[4,6]

Upon debenzylation of **3a** the diazaadamantane derivative **6** was obtained, rendering this route impractical for the synthesis of **2a**. Obviously under the acidic reaction conditions part of the starting material undergoes a retro-Mannich reaction, generating free formaldehyde which traps the debenzylation product to produce **6**.

Characterization of Ligands. Bispidine derivatives are known to undergo conformational equilibria in solution which are shifted far to the side of the chair, chair conformer (CC, eq 1) even with large substituents



(1)

on the nitrogen.[12,13] For the present derivatives **2** and **3**, the presence of CB conformers, which might be indicated by the appearance of additional signals in the

(8) (a) Hosken, G. D.; Hancock, R. D. *J. Chem. Soc., Chem. Commun.* **1994**, 1363. (b) Black, D. St. C.; Horsham, M. A.; Rose, M. *Tetrahedron* **1995**, *51*, 4819. (c) Black, D. St. C.; Deacon, G. B.; Rose, M. *Tetrahedron* **1995**, *51*, 2055. (d) Hancock, R. D.; Pattrick, G.; Wade, P. W.; Hosken, G. D. *Pure Appl. Chem.* **1993**, *65*, 473. (e) Black, D. St. C.; Craig, D. C.; Horsham, M. A.; Rose, M. *J. Chem. Soc., Chem. Commun.* **1996**, 2093.

(9) (a) Jeyaraman, R.; Avila, S. *Chem. Rev.* **1981**, *81*, 149. (b) Zefirov, N. S.; Palyulin, V. A. In *Topics in Stereochemistry*; Eliel, E. L., Wilen, S. H., Eds.; Wiley: Chichester, 1991; Vol. 20, p 171.

(10) The only *N*,*N*′-diphenylbispidine derivative which could be located in the literature was reported in an X-ray crystallography investigation without any synthetic data: Levina, O. I.; Potekhin, K. A.; Kurkutova, E. N.; Struchkov, Y. T.; Palyulin, V. A.; Zefirov, N. S. *Dokl. Akad. Nauk SSSR* **1984**, *277*, 367.

(11) (a) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217. (b) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609. (c) Wolfe, J. P.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 1133. (d) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Eng.* **1995**, *34*, 1348.

(12) (a) Douglass, J. E.; Ratliff, T. B. *J. Org. Chem.* **1968**, 33, 355. (b) Zefirov, N. S. *Russ. Chem. Rev.* **1975**, *44*, 196.

(13) CB conformers might be present if the nitrogens have endo substituents: (a) McCabe, P. H.; Milne, N. J.; Sim, G. A. *J. Chem. Soc., Chem. Commun.* **1985**, 625. (b) References 8b and 9b. (c) Quast, H.; Müller, B.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1982**, *115*, 3631. (d) Jackman, L. M.; Dunne, T. S.; Müller, B.; Quast, H. *Chem. Ber.* **1982**, *115*, 2872. (e) Zefirov, N.; Palyulin, V. A.; Chemodanova, S. V.; Samoshin, V. V. *Mendeleew Commun.* **1992**, 162. (f) the $\Delta G^{\ddagger}$ for the exchange CB $\rightleftharpoons$ BC was 40.6 kJ/mol at −63 °C (observed by ^{13}C NMR): Takeuchi, Y.; Scheiber, P.; Takada, K. *J. Chem. Soc., Chem. Commun.* **1980**, 403. (g) $\Delta G^{\ddagger}$ = 38.1 kJ/mol was reported for a macrocyclic derivative, where the CB isomer had lower energy than CC.[8e]

Table 1. pK_a Values for Various Amines and Nitrogen Chelating Ligands[a]

compd	pK_a
triethylamine	9.2
1	4.2
pyridine	5.2[b]
2a	4.4
2b	4.5
3a	5.3
3b	7.7
4	7.0
N,*N*′-dimethyl-1,5-diphenylbispidinone	8.1[c]
N,*N*′-dimethylbispidine	11.88[12a]

[a] Dimethyl sulfoxide solution, $c = 0.02$ M, 25 °C, titrated with 0.1 M *p*-TosOH, referring to the first protonation step. [b] Solvent H_2O. [c] Solvent 2-methoxyethanol/H_2O.[18b]

low-temperature ^{13}C NMR spectra,[13a,f,8e] could not be detected. This is favorable for complex formation.[14]

Compounds **2** and **3** have reasonably simple ^1H NMR spectra in the aliphatic chemical shift region, namely a singlet for the methoxy or carbomethoxy protons and the benzyl protons for **3** and a pair of doublets for the methylene protons. The doublet at higher chemical shift belongs to the equatorial protons in the 1,5-dimethyl derivatives **3** but to the axial protons in the 1,5-dicarbomethoxy derivatives **2**.[15]

Binding capabilities, i.e. donor properties of nitrogen ligands may be correlated to their pK_a, but few data are available in the literature.[16] Binding behavior may also be discussed in view of σ-donor and π-acceptor properties of the ligands, but these parameters are not directly available.[17] In the present investigation, the pK_a values were determined for solutions in dimethyl sulfoxide[18] by titration with *p*-toluenesulfonic acid and are summarized in Table 1. The *N*,*N*′-dibenzyl derivative **3b** shows a pK_a comparable to aliphatic amines, whereas the corresponding *N*,*N*′-diphenyl derivative **2b** has a value close to heteroaromatic compounds. We notice also that the keto function has a strong lowering effect on the pK_a, which changes by ca. 4 orders of magnitude from *N*,*N*′-dimethylbispidine (pK_a = 11.88)[12a] to **3b** (pK_a = 7.7) and **4** (pK_a = 7.0). Such an effect has been related to interactions between the nitrogen lone pairs and the keto function through σ bonds.[18c,19] An approximately equally large further decrease by 3.2 pK_a units is observed upon introduction of a phenyl substituent, i.e. comparing **3b** with **2b**. A smaller decrease by only 0.9 units is observed for **3a** and **2a**, since the pK_a of **3a** is already low. In a similar way, the carbomethoxy substituent lowers the pK_a, i.e. comparing **2a** with **2b** and **3a** with **3b**. In conclusion, due to similar pK_a values, the *N*-phenyl-substituted bispidinone derivatives are expected to have σ-donor properties comparable to the bipyridyl type ligands but might bind weaker since they are not π-accepors.

Table 2. Chemical Shifts of the π-Allyl Protons in Various (1,3-η^3-Propenyl)palladium Complexes[a]

		H_{syn}		H_{anti}		H-2	
complex	ligand	δ	$\Delta\delta_{ar}$	δ	$\Delta\delta_{ar}$	δ	$\Delta\delta_{ar}$
10	*b*	4.11		3.04		5.46	
13	**1**	4.29		3.56		6.01	
14	**2a**	2.21	−1.67	2.98	−0.77	5.67	−0.54
18	**5**	2.11	−1.77	2.96	−0.79	5.52	−0.69
15	**2b**	2.22	−1.65	3.07	−0.71	5.60	−0.61
16	**3a**	3.88		3.75		6.21	
17	**3b**	3.87		3.78		6.21	
19	**7**	3.98	0.11	3.05	−0.73	5.58	−0.63
20	**8**	2.28	−1.59	2.86	−0.92	5.57	−0.64

[a] $CDCl_3$ solutions, counterion $CF_3SO_3^-$. Chemical shift differences $\Delta\delta_{ar}$ refer to the the corresponding complex with **3b** or with **3a** (for **2a** and **5**). [b] Chloro dimer **10**.

Complexation. All bispidinone ligands **2** and **3** form stable complexes with (1,3-η^3-propenyl)Pd. Complex formation is indicated by interligand NOEs, which for the N-phenylated ligands are observed between the ortho and meta protons and the terminal π-allyl protons. In addition, substantial chemical shift changes of the terminal π-allyl protons are observed for complexes involving ligands **2a**,**b** (Table 2). These result from electronic effects and from the magnetic anisotropy of the aromatic ring (*vide infra*).

X-ray Crystallography. Because of the considerable difference between the *N*,*N*′-diphenylbispidinone ligands and previously applied chelating ligands, it was important to obtain accurate structural information for their (π-allyl)palladium complexes. Thus, we have investigated the structure of complex **15** by X-ray crystallography (Tables 3 and 4). An ORTEP presentation of the structure is shown in Figure 1.[20] The geometry of the complex shows considerable deviation from other (π-allyl)palladium complexes with chelating nitrogen ligands. The main difference is the unusually large inclination of the π-allyl plane relative to the N−Pd−N plane, which is 122.8(8)°. For comparison, this angle is 111.5° in the chloro dimer, i.e. bis[(1,3-η^3-propenyl)palladium chloride],[21] and 109.4° in (2,2′-bipyridyl)(2-methyl-1,3-η^3-propenyl)palladium trifluoromethanesulfonate.[4b] We find the trifluoromethanesulfonate counterion in the apical position above the metal facing C-2 of the π-allyl ligand, which is less obscured due to the tilt of the π-allyl group. Furthermore, the distances between the palladium and the nitrogen atoms are larger (2.169(4) and 2.184(4) Å) than in the (2,2′-bipyridyl)(2-methyl-1,3-η^3-propenyl)palladium complex (2.089(2) and 2.085(3) Å)[4b] and also slightly larger than in a reported (spartein)(1,3-η^3-

(14) Stronger complexation can be expected if the conformations of free and complexed ligand are similar (i.e., close to CC), which can be achieved by preorganizing the ligand through rigid structural features: Hancock, R. D.; Ngwenya, M. P.; Wade, P. W.; Boeyens, J. C. A.; Dobson, S. M. *Inorg. Chem.* **1990**, *29*, 264; see also ref 8a,d.

(15) Gogoll, A.; Axén, A.; Grennberg, H. *Magn. Reson. Chem.* **1997**, *35*, 13. This order is reversed to $\delta_{H,ax} < \delta_{H,eq}$ in the palladium complexes.

(16) (a) For various chelating nitrogen ligands it was shown that ligand preorganization affects ligand basicity, i.e. pK_a, and the equilibrium constant for binding of Cu(II) in the same way. Incorporation of the rigid bispidine skeleton into the ligand structure resulted in a further increase of both the pK_a and the equilibrium constant for Cu(II) binding.[8a] (b) Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497.

(17) Moberg, C.; Adolfsson, H.; Wärnmark, K. *Acta Chem. Scand.* **1996**, *50*, 195.

(18) (a) Meurling, L. *Chem. Scr.* **1975**, *7*, 23. The pK_a values in water and dimethyl sulfoxide for various amines were different by ca. ±1.5 units. (b) Settimj, G.; del Guidice, M. R.; D'Angelo, S.; di Simone, L. *Ann. Chim. (Rome)* **1974**, *64*, 281. (c) Settimj, G.; del Guidice, M. R.; D'Angelo, S.; di Simone, L. *Gazz. Chim. Ital.* **1979**, *109*, 345.

(19) Sasaki, T.; Eguchi, S.; Kiriyama, T.; Sakito, Y. *J. Org. Chem.* **1973**, *38*, 1648.

(20) The structure determination was complicated by the presence of an equimolar amount of solvent in the crystals. These solvent molecules are oriented randomly at room temperature; i.e., they are not complexed to the metal. An example of a palladium complex with coordinated solvent as well as intercalated solvent molecules has been reported: Hansson, S.; Norrby, P.-O.; Sjögren, M. P. T.; Åkermark, B.; Cucciolito, M. E.; Giordano, F.; Vitagliano, A. *Organometallics* **1993**, *12*, 4940.

(21) Smith, A. E. *Acta Crystallogr.* **1965**, *18*, 331.

Table 3. Crystal Data and Structure Refinement for 15

empirical formula	$C_{24}H_{29}N_2OPd^+CF_3SO_3^-\cdot CDCl_3$
fw	701.93
temp	296(1) K
m	8.7 cm^{-1}
radiation (λ, Å)	Mo Kα (0.710 73)
cryst system	monoclinic
space group	$P2_1$
unit cell dimens	a = 10.1746(3) Å, α = 90°
	b = 17.5309(3) Å, β = 95.0950(10)°
	c = 17.8717(4) Å, γ = 90°
V	3175.18(13) $Å^3$
Z	4
D(calcd)	1.4684(1) Mg/m^3
abs coeff	0.87 mm^{-1}
F(000)	1420
cryst size	0.4 × 0.12 × 0.08 mm
θ range for data collcn	1.63−23.24°
index ranges	$-5 \le h \le 11$, $-19 \le k \le 19$, $-19 \le l \le 19$
reflcns collcd	11 843
indepdt reflcns	4478 [R(int) = 0.0673]
abs corr	none
refinement method	full-matrix least-squares on F^2
data/restraints/param	4478/0/332
goodness-of-fit on F^2	1.079
final R indices ($I > 2\sigma_I$)	$R1$ = 0.0459, w$R2$ = 0.1243
R indices (all data)	$R1$ = 0.0526, w$R2$ = 0.1292
extinction coeff	0.0017(4)
largest diff peak and hole	0.362 and −0.641 e·$Å^{-3}$

cyclohexenyl)palladium complex (2.14(1) and 2.16(1) Å).[22] On the other hand, the distances between the palladium atom and the π-allyl carbons are with 2.125-(6) Å (terminal) to 2.128(5) Å (central) in the usual range, i.e. slightly larger than in the mentioned bpy complex and the chloro dimer but somewhat shorter than in the spartein complex (2.14(2) Å and 2.09(2) Å).[22] Finally, we note that the terminal π-allyl carbons are positioned below the plane defined by Pd and the nitrogen atoms (C-1′, −0.225(7) Å; C-3′, −0.233(7) Å; Figure 2), and that the central carbon is above this plane (C-2′, 0.319(9) Å). Again, this shows a somewhat distorted geometry when compared to e.g. the (2,2′-bipyridyl)(2-methyl-1,3-η^3-propenyl)palladium complex, where the corresponding values were ca. −0.2 and −0.1 Å for the terminal carbons and +0.5 Å for the central carbon.[4b]

In conclusion, the arrangement of the 1,3-η^3-propenyl ligand in **15** is distorted as compared to other (π-allyl)-palladium complexes. A likely source of this distortion is the large steric interaction between the phenyl rings and even such a small π-allyl ligand.

Chemical Shift Effects. In complexes between 1,3-η^3-propenyl and the N-phenylated ligands **2a**,**b** and **8** the chemical shift of the syn protons changes to lower frequencies, as compared to chloro dimer **10**. A much smaller effect is observed for the N-benzylated ligands **3a**,**b**, and for the N-phenylated ligand **7**. This observation can be rationalized by the aromatic ring current effect, i.e. the chemical shift anisotropy of the phenyl rings, which are located close to the π-allyl ligand in complexes with **2a**,**b** and **8**. Expectedly, the more distant anti protons and the central proton H-2 are less affected. It would be of practical value if this effect could be quantified and then be utilized to map the geometry of the π-allyl ligand. Several empirical models have been developed for this purpose,[23] but practical applications to small molecules are not common,[24] with the exception of cyclophanes[25] and porphyrins.[26] The reason is probably that the conformational mobility of the molecule under investigation must be low, a condition not often met in nonrigid small molecules. We estimate the contribution of the phenyl ring current to the chemical shift changes of the π-allyl protons, i.e. $\Delta\delta_{ar} = \delta - \delta_{ref}$ by using complex **17** as a reference (Table 2).[27] Complex **16** is a more suitable reference for complexes of ligands **2a** and **5**. The ligands **2a**,**b** and **8** give $\Delta\delta_{ar,syn} \approx -1.6$ to -1.8 ppm, $\Delta\delta_{ar,anti} \approx -0.7$ to -0.9 ppm, and $\Delta\delta_{ar,H-2} \approx -0.6$ ppm. This is in fact in excellent agreement with $\Delta\delta_{ar}$ calculated using the Johnson−Bovey model,[28] based on the geometry determined for **15** by X-ray crystallography (Chart 2). It is important to note that (i) corrections to the ring current[23c] are not necessary and (ii) the coordinates for the static crystallographic structure are applicable to the solution structure although dynamic phenomena exist (vide infra).

A larger distance between the phenyl rings of the chelating ligand and the π-allyl ligand protons is suggested by the small value $\Delta\delta_{arom,syn} = -0.20$ measured for **19**, in agreement with its different geometry.[29] Another explanation would be low complex stability. Weak binding of **7**, which was also indicated by easy decomposition of the complex, could be due to the "wrong" bite angle of this ligand,[8d] which is 39° as opposed to 89.3° for the bispidine ligands.

Further Effects. Ligand **8** as well as ligands **2a**,**b** exhibited the unexpected tendency to form stable complexes with the silver ions used to precipitate the chloride of the starting (π-allyl)palladium chloride dimers.[30] The synthetically most readily accessible bispidinone derivative **2a** showed an unexpected reactivity upon complexation, i.e. conversion of the carbonyl group into the hydrate. Hydrate formation is revealed by the disappearance of the keto carbonyl signal from the ^{13}C NMR spectrum and the appearance of a new signal at δ 92.5, assigned to $R_2C(OH)_2$. In addition, a NOE is detected between the OH protons and the axial CH_2 protons of the bispidine ligand. Finally, the

(22) Togni, A.; Rihs, G.; Ammann, C. *Helv. Chim. Acta* **1990**, *73*, 723.

(23) (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; Vol. 13, p 303. See also: (c) Agarwal, A.; Barnes, J. A.; Fletcher, J. L.; McGlinchey, M. *J. Can. J. Chem.* **1977**, *55*, 2575.

(24) Applications for proteins are more common. For a comparison of different models, see: Williamson, M. P.; Asakura, T. *J. Magn. Reson., Ser. B* **1993**, *101*, 63.

(25) (a) Fukazawa, Y.; Usui, S.; Tanimoto, K.; Hirai, Y. *J. Am. Chem. Soc.* **1994**, *116*, 8169. (b) Schneider, H.-J.; Rüdiger, V.; Cuber, U. *J. Org. Chem.* **1995**, 60, 996. (c) Fukazawa, Y.; Ogata, K.; Usui, S. *J. Am. Chem. Soc.* **1988**, *110*, 8692. (d) Estimation of the ring current in various cyclic π-systems *via* the chemical shift changes imposed on protons situated above or below these rings: De Jong, H. A. P.; Wynberg, H. *Tetrahedron* **1965**, *21*, 515.

(26) (a) Cross, K. J.; Wright, P. E. *J. Magn. Reson.* **1985**, *64*, 220. (b) Abraham, R. J.; Medforth, C. J. *Magn. Reson. Chem.* **1987**, *25*, 432.

(27) Assuming that ligand **3b** in **17** causes similar electronic effects but no ring current effects because of the long distance between its phenyl rings and the π-allyl ligand.

(28) Calculations of $\Delta\delta_{ar}$ were done with QCPE program no. 536, using the Johnson−Bovey method.

(29) In **19**, bidentate ligand **7** and metal form a five-membered ring in contrast to the six-membered rings formed by the bispidine derivatives and **8**, which puts the phenyl rings further away from the π-allyl ligand.

(30) No such complexes are formed with **7**. Formation of silver complexes can be avoided by first adding the silver salt to the chloro dimer, waiting until all silver is precipitated as chloride, and then adding the nitrogen ligand.

Table 4. Selected Geometry Parameters for Complex 15 and Related Bispidine Derivatives

	15				*N,N′*-diphenylbispidine	
	X-ray cryst[a]	MM+[b]	PM3(TM)[c]	(L)$CuCl_2$ X-ray cryst[d]	X-ray cryst[e]	MM+[b]
Pd−N(7), Pd−N(3) (Å)	2.169(4), 2.184(4)	2.154	2.103	2.004, 1.965[f]		
N(3)−N(7) (Å)	2.966	2.915	2.840	2.71	3.07	3.006
Pd−C(1′), Pd−C(3′) (Å)	2.126(6), 2.125(6)	2.240, 2.240	2.122			
Pd−C(2′) (Å)	2.128(5)	2.203	2.142			
N−C_{ipso} (Å)	1.463, 1.471	1.488	1.492		1.39	1.358
N−CH_2 (Å)	1.487−1.506	1.528	1.546−1.526	1.500	1.47	1.47
N−Pd−N (deg)	85.93	85.2	85.0	86.3 (N−Cu−N)		
C(9)−N−C_{ipso}−C_{ortho}[g] (deg)	92.1, 88.0	60.9	68.7		81.2, 87.4	0.0
C(1′)−Pd−C(3′) (deg)	67.7	64.9	69.1			
allyl vs N−Pd−N[h] (deg)	122.8(8)	129	104.0			
dihedral between Ph planes (deg)	127.8	120.8	121.8	125.0[i]	102.0	104.0
C(1′), C(3′) vs N−Pd−N plane[j] (Å)	−0.225(7), −0.233(7)	−0.77	+0.12			
C(2′) vs N−Pd−N plane[j] (Å)	0.319(9)	−0.24	+0.92			

[a] This investigation, X-ray crystallography. [b] Hyperchem 4.0, MM+ parameter set[37] with additional parameters for (π-allyl)Pd.[38] [c] Spartan 4.1.1.[39] [d] L = *N,N′*-dimethyl-1,5-diphenylbispidin-9-one.[41] Ionic radii: Pd^{2+} = 0.80 Å, Cu^{2+} = 0.72 Å. [e] X-ray crystallography.[10] [f] Cu−N. [g] C_{ortho} oriented toward the π-allyl base. [h] Angle between plane of π-allyl system and plane containing both nitrogen atoms and Pd. [i] Angle between $N-CH_3$ bonds. [j] Negative value = below plane.

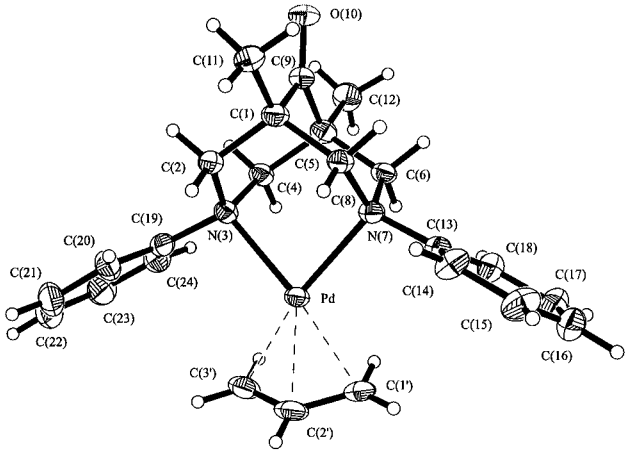


Figure 1. Molecular structure (ORTEP view) of the cation of **15**, showing 50% probability thermal ellipsoids.

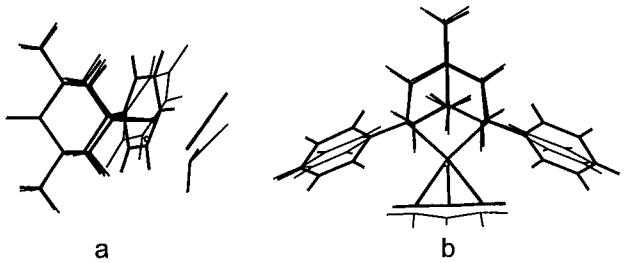


Figure 2. Overlay of structures of **15** from X-ray crystallography (bold lines) and geometry optimized with PM3-(TM) (narrow lines). One set of phenyl rings has been removed from (a) for better visibility.

required change of its elemental composition could be confirmed when this conversion had gone to completion after a few days.[31] Unfortunately, the carbonyl group of the free ligand could not be protected,[32] although reduction with sodium borohydride yielded the corresponding alcohols.[15] Thus, 3,7-diphenyl-1,5-dimethylbispidinone (**2b**) emerged as the candidate of choice for an analytically applicable ligand.

Dynamic Behavior. All complexes showed the expected dynamic behavior, namely the so-called ap-

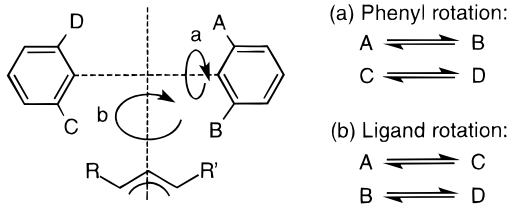
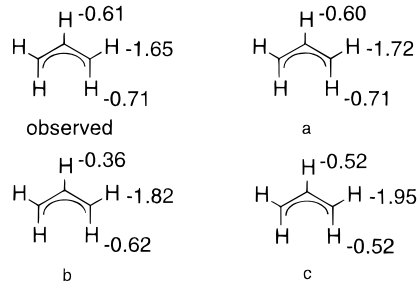


Figure 3. Exchange pattern of phenyl protons as a result of phenyl rotation and ligand rotation.

Chart 2

$\Delta\delta_{ar}$ (ppm) of π-allyl ligand protons in **15**:



[a] Geometry based on X-ray crystallography.
[b] Geometry based on molecular modeling.
[c] Geometry based on PM3(TM).

parent ligand rotation (Figure 3).[5b,33] As a result, signals of bispidinone protons situated above or below the metal coordination plane are averaged. Free energies of activation $\Delta G^{\ddagger}$ for this and additional processes (*vide infra*) were obtained from signal coalescence (Table 5) and correlated nicely with the pK_a values, i.e., the base strength of the ligands. Of the bispidinone derivatives **2** and **3**, the one with higher pK_a also has the

(31) The free ligand behaves similarly in the presence of acid, e.g. addition of *p*-toluenesulfonic acid hydrate to a dimethyl sulfoxide solution of **2a**. For related observations, see: (a) Gonikberg, E. M.; le Noble, W. J. *J. Org. Chem.* **1995**, *60*, 7751. (b) Halm, J. M.; le Noble, W. J. *J. Am. Chem. Soc.* **1992**, *114*, 1916.

(32) The reason was the low reactivity of 1,5-dicarboalkoxybispidinone derivatives, which has already been reported by Mannich upon their first preparation: Mannich, C.; Veit, F. *Ber. Dtsch. Chem. Ges.* **1935**, *68*, 506. Commonly applied derivatization reactions such as ketalization, reduction, and reaction with hydrazine and its derivatives all failed. It has been suggested that the keto group in bispidinones should behave more like an amide carbonyl group due to interaction with the nitrogen lone pair.[19] For transformations of related compounds, see: (a) Ferris, J. P.; Miller, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 1325. (b) House, H. O.; Müller, H. C. *J. Org. Chem.* **1962**, *27*, 4436.

(33) (a) Albinati, A.; Kunz, R. W.; Ammann, C. J.; Pregosin, P. S. *Organometallics* **1991**, *10*, 1800. (b) Gogoll, A.; Örnebro, J.; Grennberg, H.; Bäckvall, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 3631. (c) Elguero, J.; Fruchier, A.; de la Hoz, A.; Jalón, F. A.; Manzano, B. R.; Otero, A.; Gómez-de la Torre, F. *Chem. Ber.* **1996**, *129*, 589. (d) For a summary, see ref 2b.

Table 5. Free Energies of Activation $\Delta G^{\ddagger}$ for Dynamic Processes in Complexes [(L)(π-allyl)Pd]CF_3SO_3[a]

		apparent ligand rotation		phenyl rotation[b]	
complex	ligand L	$\Delta G^{\ddagger}$ (kJ/mol)	T_c (K)[c]	$\Delta G^{\ddagger}$ (kJ/mol)	T_c (K)[c]
13[d]	**1**	63.8	323		
14	**2a**	40	188		
18	**5**	42	188		
15	**2b**	42.9	223	42.5	216
16	**3a**	52.7	298		
17	**3b**	57.5	296		
19	**7**[e]	41.9	223	53[g]	278
20	**8**[f]	54	273	54, 60[g]	293, 313[g]
21	**2b**	57	263	56	263
22	**3b**	72[h]			

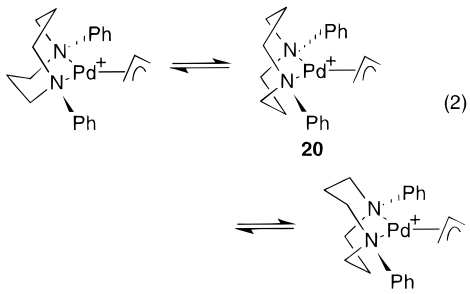
[a] All measurements were performed for acetone-d_6 solutions except for the 1,5-dicarboxymethyl derivatives **2a** and **3a** (1:1 mixture of CBr_2F_2/CH_2Cl_2). $\Delta G^{\ddagger}$ values obtained from coalescence of the equatorial methylene proton signals. For **7**, the ring methylene signals were used. [b] Coalescence of ortho proton signals. [c] Coalescence temperature. [d] Complex with (*2S*,3R**-2-methoxy-3,4,5-η^3-hexenyl)Pd, coalescence of bipyridyl protons H-6 and H-6′.[6] [e] Solvent CD_2Cl_2. [f] Solvent $CDCl_3$. [g] Complete ligand dissociation. [h] From line shape analysis at 313 K.

higher $\Delta G^{\ddagger}$ value for its complex. This fits well with our recent observation that the apparent ligand rotation involves breaking of a metal−nitrogen bond.[33b] The complexes of carbomethoxy derivatives **2a** and **3a** have lower $\Delta G^{\ddagger}$ values than those of their methyl analogs **2b** and **3b**. A likely reason is a reduced nitrogen electron density for the β-keto dicarboxylic acid esters **2a** and **3a**, with a resulting weaker metal−nitrogen bond. The difference is less pronounced for the *N*-phenyl derivatives **2a**,**b**, since here the electron density is low already. The complex with ligand **5**, i.e. the hydrate of **2a**, has a higher $\Delta G^{\ddagger}$ than the one with **2a** itself, slightly lower than the value measured for **2b**. This seems reasonable since the number of carbonyl groups decreases in the sequence **2a** > **5** > **2b**. For the complex with **8**, a $\Delta G^{\ddagger}$ value in the region of the *N*-benzyl derivatives **3** is not surprising, since this ligand is lacking the electron-withdrawing carbonyl substituents but has the *N*-phenyl substituents instead. The ligands **7** and bpy do not fit into this picture because their complexes have a different geometry (**7**, *vide infra*) or different nitrogen hybridization (bpy).

For the complexes with **2b** and **3b**, addition of excess chelating ligand (ca. 0.2 equiv), chloride ions, or a trace of hydrochloric acid did not significantly change the observed $\Delta G^{\ddagger}$ values. However, exchange between free and complexed chelating ligand was detected for **2b** by NOESY and saturation transfer experiments but not for **3b**. This is in accordance with the higher pK_a of **3b** as compared to **2b** (Table 1); i.e., the nitrogen−metal bond is stronger for **3b**. Addition of chloride ions (0.5−2 equiv of LiCl) induces dissociation of the chelating nitrogen ligand. Addition of an excess of hydrochloric acid triggers decomposition of the complexes. For the bpy complex **12**, addition of free ligand does decrease the $\Delta G^{\ddagger}$ value, in accordance with previous observations.[33b] The observed dynamic behavior of the complexes thus supports a mechanism of apparent ligand rotation *via* dissociation of one side of the chelating ligand.

A second dynamic process which can be observed in complexes of N-phenylated ligands **2a**,**b**, **7**, and **8** is restricted phenyl rotation (Figure 3), resulting in *ortho* and *meta* proton signals being split into two separate multiplets. Typical free energies of activation for the rotation of an unsubstituted phenyl ring in aromatic amines are around 46 kJ/mol, higher upon protonation.[34] In the present complexes, the energies are virtually the same as those for the apparent ligand rotation of the respective complex.[35] Molecular models of the complexes show that a phenyl rotation is sterically impossible as long as both nitrogen atoms of the chelating ligand are bound to the metal. This leaves two explanations: Either the same process, i.e. dissociation of one nitrogen atom from the metal, facilitates both processes or, as an alternative, the phenyl rings might not rotate at all, and the positions of two ortho protons relative to the π-allyl ligand are interchanged by the apparent ligand rotation. Because of the π-allyl ligand symmetry, these two possibilities cannot be distinguished (Figure 3). Such a distinction would be possible with a π-allyl ligand without a plane of symmetry through its center (*vide infra*).

The complexes with **7** and **8** showed a further dynamic process with higher free energy of activation (**7**, 53 kJ/mol; **8**, 60 kJ/mol). This process has to be complete dissociation of the chelating ligand, since it exchanges protons on different faces of the piperazine or diazacyclooctane rings. As an example, the ^{1}H NMR spectrum of **20** at 25 °C shows two signals for the N−CH_2 protons (δ 4.02 and 3.48). At 50 °C, only one signal is observed, as is in the spectrum of the free ligand. In complex **19**, the rates associated with the dynamic processes are ca. 710 s^{-1} (apparent ligand rotation, $T_c = -50$ °C) and 650 s^{-1} (ligand dissociation, $T_c = +5$ °C); i.e., apparent ligand rotation does not require complete dissociation. Complex **20** shows broad signals for ligand **8** at all accessible temperatures. This is due to the high conformational flexibility of **8**, which is lacking the bridge of the bispidine skeleton, resulting in additional equilibria between conformers with the C_3-chains of the 1,5-diazacyclooctane ring folded either toward or away from the metal (eq 2).[36]



(2)

Calculated Geometries. As a complementary source of information, the complex geometries were investigated by molecular modeling[37,38] and by the semiempirical method PM3(TM).[39] Such a comparison of

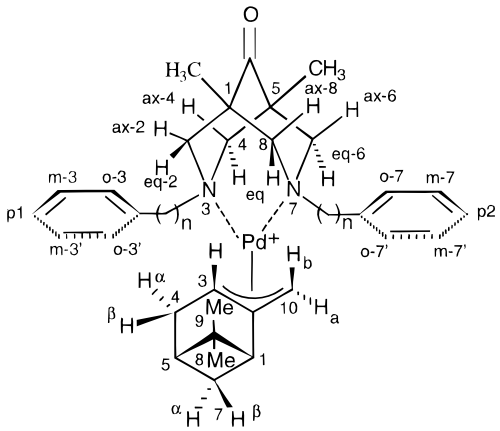
(34) Sternhell, S. in *Dynamic NMR Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: San Diego,CA, 1975; p 163.
(35) For the complex of **7**, $\Delta G^{\ddagger}$ for phenyl rotation could not be determined due to signal overlap.
(36) Musker, W. K. *Coord. Chem. Rev.* **1992**, *117*, 133.
(37) Using the MM+ force field in Hyperchem 4.0 (Hypercube Inc., Waterloo, Canada) with some additional parameters for (π-allyl)Pd from ref 38.
(38) Norrby, P.-O.; Åkermark, B.; Hæffner, F.; Hansson, S.; Blomberg, M. *J. Am. Chem. Soc.* **1994**, *115*, 4859.
(39) Using PM3(TM) as present in Spartan 4.1.1 (Wavefunction Inc., Irvine, CA).

observed and calculated geometries is also of a more general interest. More recently calculated geometries have been exploited to obtain detailed structural information on palladium complexes when crystallographic data were not available.[40] Such information has then been used to explain the chemical behavior of these complexes. Key structural parameters thus obtained for **15** are compared with the corresponding crystallographic data in Table 4 and in Figure 2. Both calculated structures show significant deviations from the crystal structure, with the semiempirical method performing better. In particular, the π-allyl ligand is situated too far away from the metal, and its position with respect to the N−Pd−N plane is too high (Figure 2a). Furthermore, the tilt of the phenyl rings against a plane through the nitrogen atoms and C-9 of the bispidine skeleton is smaller (68.7° compared to ca. 90°). Another striking difference is the tilt of the π-allyl ligand with respect to the N−Pd−N plane, which is 104° (PM3) as compared to 122.8(8)° in the crystal. Furthermore, the angles of the phenyl rings toward each other are smaller than in the crystal (121.8° for PM3, 127.8° from the crystallographic structure). In conclusion, the steric interactions between the two organic ligands on the palladium are stronger in reality than the theoretical calculations suggest, illustrating the potential danger in conclusions based on such data for new types of ligands. The observed deviations reemphasize also the difference between this new type of ligand and previously used ligands, including e.g. sparteine,[22] which has the same backbone as the bispidine skeleton but lacks the N-phenyl substituents. In fact, calculated geometries for complexes of (1,3-η^3-propenyl)palladium with the *N*-benzyl ligands (i.e. **3**) have the propenyl ligand in a position closer to the one found in the crystal structure of **15**. Because of the structural deviations, calculated ring current effects on the π-allyl protons diverge from the observed values more than those based on the crystallographic structure (Chart 2).[42] As is apparent from Figure 2, the larger distance of the π-allyl ligand from the phenyl rings is in part compensated by their tilt toward this ligand. Therefore, the calculated values are sufficiently good to probe the stereochemistry of the π-allyl ligand.[43]

For the free ligands, there is also a difference between the lowest energy conformer according to molecular modeling[37] and the conformer found in a previously reported crystal structure.[10] Molecular modeling has the phenyl rings aligned in a plane with the two nitrogen atoms and C-9 (dihedral angle C(9)−N−C_{ipso}−C_{ortho} ≈ 90°). In the crystal, they are aligned almost perpendicular to this plane (Table 4).

Further Complexes. With the characteristic features of ligand **2b** and its congeners established, it was important to prove its complexation to palladium complexes with sterically more demanding π-allyl ligands.

Chart 3



21, n = 0 **22**, n = 1

Table 6. Chemical Shifts of the π-Allyl Ligand Protons in (6-Dimethyl-2-methylenebicyclo[3.1.1]-1,3-η^3-heptenyl)palladium Complexes[a]

proton	**11**	**21**	**22**	$\Delta\delta_{ar}$, obsd	$\Delta\delta_{ar}$, calcd[b,c]	$\Delta\delta_{ar}$, calcd[b,d]
1	2.32	1.95	2.45	−0.50	−0.52	−0.24
3	4.08	3.67	4.48	−0.81	−0.82	−0.46
4α	1.79	−1.15	1.68	−2.83	−1.15	−3.47
4β	1.79	0.63	1.77	−1.14	−1.20	−0.87
5	2.08	1.66	2.21	−0.55	−0.26	−0.41
7α	2.38	1.32	1.78	−0.46	0.08	−0.09
7β	2.64	2.58	2.85	−0.27	0.05	−0.09
10a	3.68	1.86	3.50	−1.64	−1.95	−1.78
10b	2.96	3.54	4.07	−0.53	−0.44	−0.89
Me-8	1.35	1.17	1.39	−0.22	−0.02	−0.23
Me-9	0.97	0.66	1.02	−0.36	−0.09	−0.24

[a] $CDCl_3$ solution, 25 °C. [b] Johnson−Bovey model.[28] [c] Structure derived using modified MM+ parameter set.[37] [d] Structure derived from PM3(TM) parameter set in Spartan 4.1.1.[39]

We therefore prepared the complexes **21** and **22**, derived from β-pinene (Chart 3). Both bispidine derivatives **2b** and **3b** formed stable complexes, and as expected, large chemical shift changes were observed for those protons in complex **21** which were close to the phenyl rings (Table 6). In particular, the proton signals are dispersed over a larger chemical shift range than in both complex **22** and the chloro dimer **11** (4.8 ppm as compared to 3.5 and 3.1 ppm, respectively). The signals of H-4α and H-4β, which overlap in **11**, are well separated in **21**, and coupling constants can be measured for several protons because of the simpler multiplet patterns (Figure 4). The methylene protons on C-7, C-4, and C-10 can easily be distinguished due to the very different extent of their chemical shift changes. To obtain a more quantitative picture, we again relate the chemical shift changes to the complex geometry, using complex **22** as a reference. From the geometries obtained with PM3(TM),[44] chemical shift changes due to the aromatic ring currents were calculated as for **15** (Table 6). Observed and calculated changes agree reasonably well, with the exception of those protons located very close to the aromatic rings. The proton with the largest ring current effect $\Delta\delta_{ar}$ = −2.83 (at 25°C), H-4α, is embedded in a cavity on top of one phenyl ring (Figure 5). Ring current effects for most protons are slightly larger at −55 °C (see Experi-

(40) (a) Peña-Cabrera, E.; Norrby, P.-O.; Sjögren, M.; Vitagliano, A.; De Felice, V.; Oslob, J.; Ishii, S.; O'Neill, D.; Åkermark, B.; Helquist, P. *J. Am. Chem. Soc.* **1996**, *118*, 4299. (b) Andersson, P. G.; Harden, A.; Tanner, D.; Norrby, P.-O. *Chem. Eur. J.* **1995**, *1*, 12.

(41) Levina, O. I.; Potekhin, K. A.; Kurkutova, E. N.; Struchkov, Y. T.; Zefirova, O. N.; Palyulin, V. A.; Zefirov, N. S. *Dokl. Akad. Nauk SSSR* **1986**, *289*, 876.

(42) Some deviations are also to be expected because the protons were placed at standard positions in the crystallographic structure, i.e., assuming idealized geometry.

(43) Deviations between observed and measured ring current effect of ca. 0.1−0.2 ppm are common.[23,25]

(44) To obtain a better geometry, the π-allyl carbons were fixed during geometry optimization at positions corresponding to those found in the crystals of **15**.

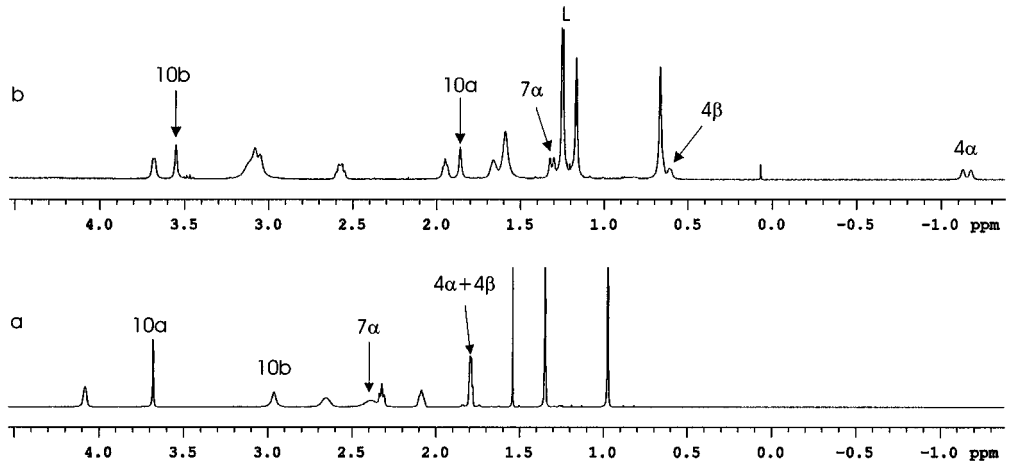


Figure 4. ^{1}H NMR spectra of (a) (2-methylene-6,6-dimethylbicyclo[3.1.1]hept-2,3,10-η^3-enyl)palladium chloride dimer (**11**) and (b) the corresponding complex **21** with ligand **2b** (400 MHz, $CDCl_3$ solution, 25 °C).

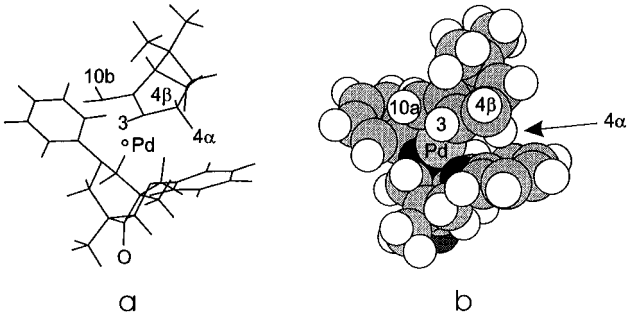


Figure 5. Space-filling presentation (right) of complex **21**, showing the close interaction between the phenyl ring and proton H-4α (geometry optimized with PM3(TM)). Left: Stick structure.

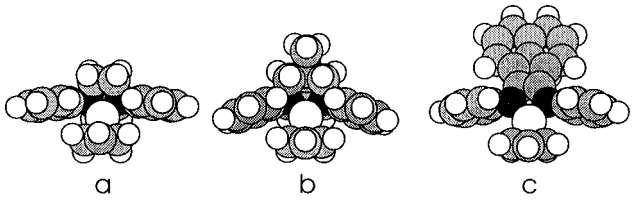


Figure 6. Phenyl ring positions relative to 1,3-η^3-propenyl ligands in complexes (a) **19**, (b) **15**, and (c) complex with bis(arylimino)acenafthen (BIAN). Geometries shown are from X-ray crystallography for **15** and from PM3(TM) for **15** and the bis(arylimino)acenafthen complex.

mental Section), indicating the impact of ligand and phenyl ring rotation at higer temperatures.

In comparison of **21** with **22**, $\Delta G^{\ddagger}$ of apparent ligand rotation again was higher for the complex with the N-benzylated ligand (**3b**, complex **22**, $\Delta G^{\ddagger} = 72$ kJ/mol) than for the one with the N-phenylated ligand (**2b**, complex **21**, $\Delta G^{\ddagger} = 57$ kJ/mol). Interestingly, the difference of $\Delta G^{\ddagger}$ between the two complexes, 15 kJ/mol, is approximately the same as the one found between **17** and **15**, 14.6 kJ/mol. This supports the previous assumption that $\Delta G^{\ddagger}$ is related to ligand basicity, i.e. pK_a, but clearly steric factors are involved as well. Because of the difference in $\Delta G^{\ddagger}$, at room temperature all methylene protons of **22** are nonisochronous, whereas only two averaged signals of 4 protons each for the equatorial and the axial bispidinone protons are observed for **21**. These signals are separated into individual signals at −55 °C.

The lack of symmetry of the π-allyl ligand in **21** makes it possible to determine whether phenyl rotation is involved in the exchange of the phenyl protons or if they exchange only via ligand rotation. If the π-allyl ligand has the symmetry of 1,3-η^3-propenyl (C_s, Figure 3, R = R′), the exchange pattern of e.g. the *ortho* protons resulting from phenyl rotation would be indistinguishable of the one observed if only ligand rotation took place (*vide supra*), because protons in locations B and C have the same chemical shift. This is not so for complex **21**, where all four *ortho* protons have different chemical shifts. Hence, the observed direct exchange of e.g. *o*-Ph-3 with *o*-Ph-3′ as well as *o*-Ph-7′ proves that phenyl rotation as well as apparent ligand rotation do occur simultaneously. The NOESY and ROESY experiments run to detect this exchange were done with sufficiently short mixing times as to avoid complete scrambling of the information due to stepwise, indirect exchange such as *o*-Ph-3 → *o*-Ph-7′ → *o*-Ph-7; i.e., a cross-peak between *o*-Ph-3 and *o*-Ph-7 was not observed. It is reasonable to assume that the 1,3-η^3-propenyl ligand has the same dynamic behavior. In those cases where $\Delta G^{\ddagger}$ could be determined for both dynamic processes, the values are the same within experimental error (Table 5). One may therefore assume that they depend upon a similar rate-determining step. This could be the breaking of one Pd−N bond, in accordance with previous observations.[33b]

Conclusions. *N*,*N*′-Diphenylbispidinone derivatives form stable complexes with even bulky (π-allyl)palladium. Close steric interactions between the phenyl rings and the π-allyl ligands on the palladium result in large anisotropic chemical shift effects. This results from two structural features: (i) the double chair conformation of the *N*,*N*′-diphenyldiazacyclooctane motif, which forms a six-membered ring upon complexation, i.e. counting the metal, the two nitrogen atoms, and the C_3 chain linking them; (ii) the one-carbon bridge between C-1 and C-5 adding further rigidity to the complex, which now resembles an adamantane-like substructure. In contrast, *N*,*N*′-diphenylpiperazine (**7**) is a less efficient ligand, because it forms a five-membered ring upon complexation. This causes the phenyl rings to bend away from the π-allyl ligand (Figure 6).[45] At first glance, these ligands might remind one of the bis(arylimino)acenafthen (BIAN) ligands

(45) The angle between the two phenyl ring planes is ca. 127.8° for **15** and 155° for **19**.

introduced by Elsevier et al.,[2j,46] but these have the phenyl rings farther apart and at a much larger angle.[47]

Ligand **2b** is therefore a promising new analytical tool for the NMR spectroscopic characterization of (π-allyl)-palladium complexes and as a chemical shift reagent for ligands with complicated proton NMR spectra.

Experimental Section

General Experimental Details. NMR spectra were recorded for ^{1}H at 300 and 400 MHz and for ^{13}C at 75.4 and 100.6 MHz, at 25 °C unless stated otherwise. Chemical shifts are indirectly referenced to TMS via the solvent signal ($CDCl_3$, 7.26 and 77.00; acetone-d_6, 2.04 and 206.0; CD_2Cl_2, 5.32 and 53.80). Mass spectra were recorded on a Finnigan MAT INCOS 50 instrument at 70 eV (EI mode). IR spectra were recorded on a Perkin-Elmer 1600 FTIR. Elemental analyses were performed by Analytische Laboratorien, Engelskirchen, Germany. The X-ray crystallographic analysis was done by Dr. V. Langer, Dept. of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, Göteborg, Sweden. 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 are uncorrected. Commercially available chemicals were used as supplied.

The pK_a values were determined by titration of a solution of the compound in dimethyl sulfoxide (dried with molecular sieves and distilled, $c = 0.02-0.01$ M, 25 °C) with a solution of *p*-toluenesulfonic acid in the same solvent ($c = 0.1$ M).[18a] A glass electrode (Schott pH-meter CG825) was used. The reported values are estimated to be accurate within ±0.2 units. NMR signals were assigned from PECOSY,[48] HSQC,[49] HSBC,[50] NOESY,[51] ROESY,[52] and NOE difference spectra.[53] For NOESY and ROESY experiments, mixing times between 0.5 and 1.2 s were used. Free energies of activation $\Delta G^{\ddagger}$ were estimated from the coalescence behavior of the proton NMR signals[54] or by line shape analysis.[55] Their accuracy is estimated as ±1 kJ/mol (±2 kJ/mol for **22**).

Crystallographic Analysis. Crystals of **15** were obtained from a $CDCl_3$ solution and are of needle shape. The largest available crystal was selected for data collection and mounted on a glass fiber. Measurements were made on a CCD-detector-based SMART diffractometer (Siemens) using Mo Kα radiation ($\lambda = 0.710\ 73$ Å) (sealed tube at 50 kV and 45 mA). Cell parameters were obtained by least-squares refinement on 8188 reflections with $I/\sigma(I) > 10$. Crystal data, data collection parameters, and results are listed in Tables 3 and 4. The structure solution and full-matrix least-squares refinement were performed with the programs SHELXS-86[56a] and SHELXL-93[56b] on F^2. During the solution, the presence of $CDCl_3$ molecules became evident, the position of which could not be refined due to its disordered orientation. Therefore, the procedure SQUEEZE[57] was applied. The positions of the hydrogen atoms were calculated by assuming idealized geometry (C−H = 0.95 Å), methyl groups were located on circular Fourier maps using local 3-fold symmetry, and then all hydrogen atom positions were riding on the respective pivot atoms. The final *R* indices are as follows: on observed data $I > 2\sigma(I)$, $R1 = 0.0459$, w$R2 = 0.1243$; on all data, $R1 = 0.0526$, w$R2 = 0.1292$. Maximum and minimum peaks in the final difference map were 0.362 and −0.641 e·Å^{-3}, respectively.

3,7-Dibenzyl-1,5-dicarbomethoxybispidinone (3a). To methanol (400 mL) cooled on ice, were added dimethyl acetonedicarboxylate (5.85 mL, 40 mmol), formaldehyde (14.8 mL 30% solution in water, 164 mmol), and benzylamine (9.0 mL, 82 mmol). The solution was stirred at 0 °C during 15 h. Thereafter, the temperature was allowed to rise to room temperature and the stirring continued for an additional 10 h. The solvent was evaporated under reduced pressure to approximately half its volume, the precipitate was filtered off, and the residue was washed with two portions (25 mL) of cold methanol. The product was dried *in vacuo* overnight: White powder (7.5 g, 17.2 mmol, 43%), mp 117 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (m, 10H, aromatic), 3.96 (s, 4H, benzylic), 3.86 (s, 6H, CH_3), 3.28 (d, $J = 11.1$ Hz, 4H, H_{ax}), 3.15 (d, $J = 11.1$ Hz, 4H, H_{eq}); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 203.4 (C-9), 170.2 (COO), 137.1 (C_{ipso}), 128.7 (C_{ortho}), 128.1 (C_{meta}), 127.1 (C_{para}), 60.7 $PhCH_2$), 59.7 (CH_2), 58.9 (C), 52.1 (CH_3); IR (KBr) 1743, 1716 cm^{-1}; MS *m/e* 436 (M^+, 1.3%), 313, 218, 167, 91. Anal. Calcd for $C_{25}H_{28}N_2O_5$: C, 68.79; H, 6.47; N, 6.42. Found: C, 68.64; H, 6.41; N, 6.46.

Methyleneaniline (Trimeric) (9). To ethanol (200 mL) were added aniline (9.0 mL, 0.1 mol) and formaldehyde (18.0 mL 30% solution in water, 0.2 mol). The solution was stirred during 20 h at room temperature. Thereafter water (100 mL) was added and the precipitate was immediately filtered off and discarded. The filtrate was left until a new precipitate formed. This precipitate was collected, and the solution was left until a new precipitate was formed. The procedure was repeated until no new precipitate was formed. The combined solids were dried *in vacuo* over night: Colorless solid (3.0 g, 9.52 mmol, 29%), mp = 136 °C (lit.[58] mp 139.5 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (m, 6H, *m*-Ph), 7.02 (m, 6H, *o*-Ph), 6.87 (m, 3H, *p*-Ph), 4.89 (s, 6H, CH_2); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 148.2, 129.1, 120.9, 117.7, 68.6; IR (KBr) 1596, 1498 cm^{-1}; MS *m/e* 315 (M^+, 0.8%), 105, 77.

3,7-Diphenyl-1,5-dicarbomethoxybispidinone (2a). To methanol (100 mL) were added dimethyl acetonedicarboxylate (0.88 mL, 6 mmol), formaldehyde (6.0 mL 30% solution in water, 13 mmol), and methyleneaniline (trimeric) (1.4 g, 4.4 mmol). The solution was stirred for 20 h at room temperature. The solvent was removed under reduced pressure. The remaining oil was dissolved in chloroform (3 mL) and purified by column chromatography (1:1 diethyl ether/n-pentane). The first eluted fractions, containing mainly a mixture of the desired product and methyleneaniline, were combined, and the solvent was removed. The remaining solid was dissolved in methanol (20 mL). When the sample was cooled to −20 °C, precipitation of methyleneaniline and the desired product was initiated. The solid was collected and dissolved in methanol/chloroform (9:1, 10 mL). When the sample was cooled to −20 °C, the desired product crystallized as colorless needles which

(46) van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1994**, *33*, 1521.
(47) This angle is determined from the geometry obtained with PM3(TM) as 170.8° in the (1,3-η^3-propenyl)Pd complex; X-ray crystallography of a corresponding Pd(0)−olefin complex[46] found ca. 190°. In the PM3(TM)-optimized structures of (L)[(1,3-η^3-propenyl)palladium complexes, the distance between the aromatic ring centers is ca. 8.26 Å for L = BIAN, as compared to 8.06 Å for L = **2b** and 8.32 Å for L = **7**.
(48) Mueller, L. *J. Magn. Reson.* **1987**, *72*, 191.
(49) (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.
(50) Kövér, K. E.; Prakash, O.; Hruby, V. J. *Magn. Reson. Chem.* **1993**, *31*, 231.
(51) (a) States, D. J.; Haberkorn, R. A.; Ruben, D. J. *J. Magn. Reson.* **1983**, *48*, 286. (b) Wider, G.; Macura, S.; Kumar, A.; Ernst, R. R.; Wüthrich, K. *J. Magn. Reson.* **1984**, *56*, 207.
(52) Bothner-By, A. A.; Stephens, R. L.; Lee, J. M.; Warren, C. D.; Jeanloz, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 811.
(53) 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.
(54) Anderson, J. E.; Lehn, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 81.
(55) Günther, H. *NMR Spectroscopy*, 2nd ed.; Wiley: Chichester, U.K., 1995; p 335. Spectra were simulated with: *gNMR*, v. 3.6.5; Cherwell Scientific Publ.: Oxford, U.K., 1996.
(56) (a) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. (b) Sheldrick, G. M. *J. Appl. Crystallogr.*, Manuscript in preparation.
(57) SQEEZE[57b] is part of the the software PLATON[57a] which was used for geometry calculation: (a) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34. (b) Spek, A. L. Abstracts of Papers; American Crystallographic Association, Atlanta Meeting; American Crystallographic Association: New York, 1994; Paper M05.
(58) Miller, J. G.; Wagner, E. C. *J. Am. Chem. Soc.* **1932**, *54*, 3698.

were collected and recrystallized under the same conditions. The crystals were dried *in vacuo* (285 mg, 0.7 mmol, 12%): mp 96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (m, 4H, *m*-Ph), 7.01 (m, 4H, *o*-Ph), 6.94 (m, 2H, *p*-Ph), 4.13 (d, J = 12.0 Hz, 4H, H_{ax}), 3.91 (d, J = 12.0 Hz, 4H, H_{eq}), 3.73 (s, 6H, CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 201.7 (C-9), 169.6 (COO), 149.6 (C_{ipso}), 129.0 (C_{meta}), 120.9 (C_{para}), 117.4 (C_{ortho}), 59.0 (C), 57.8 (CH_2), 52.6 (CH_3); IR (KBr) 1747, 1733 cm^{-1}; MS *m/e* 408 (M^+, 21.8%), 288, 120, 105, 77. Anal. Calcd for $C_{23}H_{24}N_2O_5$: C, 67.62; H, 5.93; N, 6.86. Found: C, 67.68; H, 5.92; N, 6.85.

1,5-Dicarbomethoxy-3,7-diazaadamantan-9-one (6). 3,7-Dibenzyl-1,5-dicarbomethoxybispidinone (**3a**) (1.96 g, 4 mmol) was dissolved in acetic acid (20 mL) and ethanol (4 mL). Palladium on activated carbon (10%, 0.2 g) was added. The mixture was shaken under hydrogen pressure (3 atm) during 20 h. Thereafter, the mixture was filtered and the solid was washed with acetic acid (10 mL) and ethanol (10 mL). The solvent was evaporated, and the remaining oil was dissolved in chloroform (15 mL) and washed with water (2 × 50 mL). The chloroform phase was dried over $MgSO_4$, and the solvent was evaporated. The remaining product was dissolved in chloroform/diethyl ether (1:1) and recrystallized at −20 °C. The solid was collected and dried *in vacuo* (0.5 g, 1.9 mmol, 47%): mp 167 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.05 (s, 2H, CH_2), 3.76 (s, 6H, CH_3), 3.70 (d, J = 12.8 Hz, 2H, H_{eq}), 3.60 (d, J = 12.8 Hz, 2H, H_{ax}); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 200.3 (C-9), 168.8 (COO), 72.4 (N−CH_2−N), 60.7 (CH_2), 55.9 (C), 52.3 (CH_3O); IR (KBr) 2958, 1732, 1699, 1443 cm^{-1}; MS *m/e* 268 (M^+, 2.7%), 240, 113, 59. Anal. Calcd for $C_{12}H_{16}N_2O_5$: C, 53.71; H, 6.01; N, 10.45. Found: C, 53.81; H, 6.15; N, 10.31.

3,7-Dibenzyl-1,5-dimethylbispidinone (3b). A slight modification of a literature procedure was employed.[8c] Benzylamine (28.4 mL, 260 mmol) was added to 50 mL of ethanol in a round-bottomed flask equipped with a reflux condenser. The mixture was cooled on ice, and acetic acid (15 mL) was added. Paraformaldehyde (15.0 g, 0.5 mol) and diethyl ketone (13.2 mL, 125 mmol) were added, and the mixture was refluxed for 15 h. The reaction mixture was then cooled on ice, and 300 mL of diethyl ether was added. Perchloric acid was added until the pH was 3 or lower. After 12 h at −20 °C the solid was collected and suspended in methylene chloride (200 mL). The suspension was treated with 20% aqueous NaOH (500 mL). In the case of the remaining solid, more sodium hydroxide (solid) was added until all precipitate was dissolved. The aqueous phase was separated and extracted with methylene chloride (50 mL). The combined organic phases were washed with water (2 × 300 mL). The methylene chloride was removed under reduced pressure, and the resulting oil was purified by column chromatography (diethyl ether/n-pentane, 1:1). The appropriate fractions were combined, and the solvent was removed. Repeated crystallization from 95% ethanol at −20 °C gave white crystals which were dried *in vacuo* (7.86 g, 45.2 mmol, 18%) (lit. 5.0%): mp 83−84 °C (lit.[8c] mp 84−86 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 10H, aromatic), 3.53 (s, 4H, benzylic), 3.04 (d, J = 11.0 Hz, 4H, H_{eq}), 2.38 (d, J = 11.0 Hz, 4H, H_{ax}), 0.96 (s, 6H, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 215.0 (C-9), 138.4 (C_{ipso}), 128.7 (C_{ortho}), 128.2 (C_{meta}), 127.0 (C_{para}), 65.5 (CH_2), 61.3 ($PhCH_2$), 46.7 (C), 20.0 (CH_3); IR (KBr) 3024, 1720, 1653, 1601 cm^{-1}; MS *m/e* 348 (M^+, 0.8%), 214, 134, 91.

1,5-Dimethylbispidinone (4). A general procedure[8b] was employed. 3,7-Dibenzyl-1,5-dimethylbispidinone (**3b**) (3.0 g, 8.6 mmol) was dissolved in a mixture of acetic acid (25 mL), ethanol (5 mL), and perchloric acid (2 drops), and palladium on activated carbon (10%, 0.3 g) was added. The mixture was shaken under hydrogen pressure (3 atm) at room temperature for 60 h. The reaction mixture was filtered, and the solid was washed with ethanol (20 mL) and acetic acid (10 mL). The filtrate was concentrated under reduced pressure and dissolved in chloroform (10 mL). The solution was washed with 10% aqueous NaOH (10 mL). The chloroform was removed under reduced pressure, and the remaining oil was recrystallized from diethyl ether, yielding colorless crystals which were collected and dried *in vacuo* (1.0 g, 6.0 mmol, 69%): mp 61−62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36 (d, J = 12.2 Hz, 4H, H_{eq}), 2.95 (d, J = 12.2 Hz, 4H, H_{ax}), 2.67 (s, 2H, NH), 0.88 (s, 6H, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 215.4 (C-9), 61.8 (CH_2), 49.4 (C), 17.2 (CH_3); IR (KBr) 3353, 1700, 1209 cm^{-1}; MS *m/e* 168 (M^+, 9.6%), 138, 124, 69. Anal. Calcd for $C_9H_{16}N_2O$: C, 64.25; H, 9.59; N, 16.65. Found: C, 64.01; H, 9.42; N, 16.49.

3,7-Diphenyl-1,5-dimethylbispidinone (2b). Following a general procedure for phenylation of amines,[59] freshly prepared sodium amide[60] (3.9 g, 100 mmol) was suspended in dry THF (10 mL) in a round-bottomed flask equipped with a reflux condenser and a gas lock. The suspension was cooled on ice and magnetically stirred. *tert*-Butanol (1.2 mL, 12 mmol) was added dropwise. 1,5-Dimetylbispidinone (0.9 g, 5 mmol) was added followed by phenyl bromide (1.26 mL, 12 mmol) that was added dropwise under 5 min. The temperature was raised and kept at 45 °C during 12 h under a nitrogen atmosphere. The reaction mixture was cooled on ice, and water (10 mL) was added in small portions. The reaction mixture was poured into a separation funnel containing water (100 mL), and the funnel was left for 30 min. The mixture was then extracted with methylene chloride (2 × 50 mL). The methylene chloride phases were combined, and the solvent was removed under reduced pressure. The remaining oil was purified by column chromatography (*n*-pentane/diethyl ether, 95:5). The appropriate fractions were combined, and the solvent was removed under reduced pressure. The remaining solid was recrystallized from ethanol, and repeated crystallization gave the pure product as white needle-shaped crystals (0.23 g, 0.72 mmol, 14%): mp 126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (m, 4H, *m*-Ph), 6.81 (m, 4H, *o*-Ph), 6.77 (m, 2H, *p*-Ph), 3.93 (d, J = 12.2 Hz, 4H, H_{eq}), 3.18 (d, J = 12.2 Hz, 4H, H_{ax}), 1.16 (s, 6H, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 214.0 (C-9), 149.5 (C_{ipso}), 129.0 (C_{meta}), 118.9 (C_{para}), 115.4 (C_{ortho}), 62.3 (CH_2), 47.0 (C), 18.3 (CH_3); IR (KBr) 1717, 1684, 1647, 1364 cm^{-1}; MS *m/e* 320 (M^+, 0.5%), 200, 130, 120, 77. Anal. Calcd for $C_{21}H_{24}N_2O$: C, 78.70; H, 7.55; N, 8.75. Found: C, 78.59; H, 7.46; N, 8.84.

***N,N′*-Diphenylpiperazine (7)** was prepared according to the literature:[59] Yellowish crystals, mp 169−170 °C (lit.[59] mp 166 °C); yield 7.55 g, 31.7 mmol, 84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 4H, *m*-Ph), 7.00 (m, 4H, *o*-Ph), 6.90 (m, 2H, *p*-Ph), 3.35 (s, 8H, CH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 151.2 (C_{ipso}), 129.2 (C_{meta}), 120.1 (C_{para}), 116.3 (C_{ortho}), 49.4 (CH_2); IR (KBr) 2831, 1598, 1496, 1447, 940 cm^{-1}; MS *m/e* 238 (M^+, 56%), 132, 105, 77.

***N,N′*-Diphenyl-1,5-diazacyclooctane (8).** The dihydrobromide of 1,5-diazacyclooctane was obtained by condensation of the disodium salt of *N,N′*-ditosyl-1,3-propanediamine with 1,3-ditosyloxypropane according to reported procedures[61] (yield 60%), followed by detosylation with HBr/glacial acetic acid[61a] (80 °C, 67 h, 89%).[61c] To a solution of *tert*-butanol (2.0 g, 27 mmol) in dry THF (22 mL) was added sodium amide (10.0 g, 256 mmol) with vigorous stirring (gas lock). 1,5-Diazacyclooctane dihydrobromide (3.84 g, 13.9 mmol) was added, and after the initial gas evolution had ceased, the mixture was kept at 45 °C. Bromobenzene (4.6 g, 29.3 mmol) was added in portions during 30 min. The initially gray and then brown suspension was stirred for another 5 h. Water (30 mL) was added to the dark brown solution. The mixture was poured into water (150 mL) and left for 2 h at room temperature, after which time a dark brown solid had formed on the surface of a yellow solution. The solid was filtered off on a Büchner funnel and dissolved in diethyl ether/ethanol (1:1). The remaining solution was extracted with diethyl ether (50 mL) and the

(59) Cambére, P.; Derozier, N. *Bull. Soc. Chim. Fr.* **1969**, 1737.
(60) Vogel, A. I. *Textbook of Practical Organic Chemistry*, 5th ed.; Longman: Harlow, U.K., 1989; p 462.
(61) (a) Börjesson, L.; Welch, C. J. *Acta Chem. Scand.* **1991**, *45*, 621. (b) Rickman, J. E.; Atkins, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 2269.

ether phase combined with the ether/ethanol solution. Filtration followed by evaporation yielded a yellowish-brown solid, contaminated with a dark brown oil. The crude product (3.7 g) was dissolved in cyclohexane, the solution dried over sodium sulfate, and recrystallized from diethyl ether: yield 2.77 g (10.8 mmol, 78%); mp 116 −117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (m, 4H, *m*-Ph), 6.72 (m, 5H, *o*-Ph, *p*-Ph), 3.48 (m, 8H, NCH_2), 2.02 (m, 4H, CH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 147.5 (C_{ipso}), 129.3 (C_{meta}), 115.5 (C_{para}), 111.3 (C_{ortho}), 48.7 (NCH_2), 25.2 (CH_2); IR (KBr) 2872, 1471, 1360, 692 cm^{-1}; MS *m/e* 266 (M^+, 5%), 237, 146, 104, 77. Anal. Calcd for $C_{18}H_{22}N_2$: C, 81.16; H, 8.32; N, 10.52. Found: C, 81.00; H, 8.18; N, 10.56.

Bis[(1,3-η^3-propenyl)palladium chloride] (10) was prepared according to a literature procedure:[62] mp 159 °C (lit.[62] mp 160 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.46 (tt, J = 12.1 Hz, 6.7, 1H, H-2$_{\pi-allyl}$), 4.11 (d, J = 6.7 Hz, 2H, H_{syn}), 3.04 (d, J = 12.1 Hz, 2H, H_{anti}); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 111.2 (CH), 63.0 (CH_2); IR (KBr) 1457, 1382, 1022 cm^{-1}.

Bis[(2-methylene-6,6-dimethylbicyclo[3.1.1]hept-2,3,-10-η^3-enyl)palladium chloride] (11) was prepared from β-pinene.[63] ^{1}H NMR: Table 6.

General Method for Preparation of Complexes [(L)-(1,3-η^3-propenyl)Pd] CF_3SO_3. To chloroform (3 mL) was added chlorodimer **10** and a 10% excess of silver trifluoromethanesulfonate. The mixture was stirred during 1 min at room temperature under a nitrogen atmosphere, and then an equimolar amount of nitrogen ligand was added. After a further 10 min the mixture was filtered. To the filtrate was added diethyl ether to initiate crystallization, followed by storage at −20 °C overnight. The obtained solids were collected and dried *in vacuo*. Because of the straightforward method of preparation, elemental analyses were performed only for selected complexes.

(Bipyridyl)(1,3-η^3-propenyl)palladium trifluoromethanesulfonate (12) was prepared from **10** (36.6 mg, 100 μmol), bipyridine (**1**) (31.2 mg, 200 μmol), and silver trifluoromethanesulfonate (56.6 mg, 220 μmol) according to the general procedure but with methanol as solvent (80 mg, 76%): mp 288 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (ddd, J = 0.8, 1.7, 5.4 Hz, 2H, H-6$_{bpy}$), 8.59 (ddd, J = 0.8, 1.3, 8.1 Hz, 2H, H-3$_{bpy}$), 8.25 (ddd, J = 1.7, 7.7, 8.1 Hz, 2H, H-4$_{bpy}$), 7.77 (ddd, J = 1.3, 5.4, 7.7 Hz, 2H, H-5$_{bpy}$), 6.01 (tt, J = 7.1 Hz, 12.7 Hz 1H, H-2$_{\pi-allyl}$) 4.29 (d, J = 7.1 Hz, 2H, H_{syn}), 3.56 (d, J = 12.7, 2H, H_{anti}); ^{1}H NMR (400 MHz, acetone-d_6) δ 9.05 (ddd, J = 0.8, 1.6, 5.3 Hz, 2 H, H-6$_{bpy}$), 8.68 (ddd, J = 0.8, 1.2, 8.1 Hz, 2H, H-3$_{bpy}$), 8.40 (ddd, J = 1.6, 7.7, 8.1 Hz, 2H, H-4$_{bpy}$), 7.83 (ddd, J = 1.2, 5.3, 7.7 Hz, 2H, H-5$_{bpy}$), 6.16 (tt, J = 7.0 Hz, 12.7 Hz 1H, H-2$_{\pi-allyl}$), 4.48 (d, J = 7.0, 2H, H_{syn}), 3.56 (d, J = 12.7, 2H, H_{anti}); IR (KBr) 3082, 1599, 1493, 1471, 1445 cm^{-1}.

(Bipyridyl)[(2S*,3R*)-(2-methoxy-3,4,5-η^3-hexenyl)]palladium]trifluoromethane sulfonate (13) was prepared as described previously.[6]

(3,7-Diphenyl-1,5-dicarbomethoxybispidinone)(1,3-η^3-propenyl)palladium trifluoromethanesulfonate (14) was prepared from **10** (18.3 mg, 50 μmol), 3,7-diphenyl-1,5-dicarbomethoxybispidinone (**2a**) (40.8 mg, 100 μmol), and silver trifluoromethanesulfonate (28.3 mg, 110 μmol) (50 mg, 70%): mp 137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (m, 4H, *o*-Ph), 7.39 (m, 4H, *m*-Ph), 7.13 (m, 2H, *p*-Ph), 5.67 (tt, J = 12.5, 6.9 Hz, 1H, H-2$_{\pi-allyl}$), 5.03 (br, 4H, H_{eq}), 3.88 (br s, 4H, H_{ax}), 3.85 (s, 6H, CH_3), 2.98 (d, J = 12.5 Hz, 2H, H_{anti}), 2.21 (d, J = 6.9 Hz, 2H, H_{syn}); ^{1}H NMR (400 MHz, 1:1 CBr_2F_2/CD_2Cl_2): δ 7.63 (m, 4H, *o*-Ph), 7.47 (m, 4H, *m*-Ph), 7.19 (m, 2H, *p*-Ph), 5.67 (tt, J = 12.5, 6.9 Hz, 1H, H-2$_{\pi-allyl}$), 5.18 (br, 4H, H_{eq}), 3.97 (s, 6H, CH_3), 3.70 (d, J = 12.2, 4H, H_{ax}), 3.03 (d, J = 12.5, 2H, H_{anti}), 2.27 (br, 2H, H_{syn}); ^{13}C NMR (100.6 MHz, $CDCl_3$, −25 °C) δ 200.2 (C-9), 165.6 (COO), 154.1 (C_{ipso}), 129.3 (C_{meta}), 125.6 (C_{para}), 120.7 (C-2$_{\pi-allyl}$), 117.5 (C_{ortho}), 120.5 (CF_3, J_{CF} = 321 Hz), 68.1 (C-1, C-3$_{\pi-allyl}$), 61.5 (CH_2), 57.0 (C), 53.7 (CH_3); IR (KBr) 2957, 1743, 1721, 1598, 1498 cm^{-1}.

(3,7-Diphenyl-1,5-dimethylbispidinone)(1,3-η^3-propenyl)palladium trifluoromethanesulfonate (15) was prepared from **10** (18.3 mg, 50 μmol), 3,7-diphenyl-1,5-dimethylbispidinone (**2b**) (40.8 mg, 100 μmol), and silver trifluoromethanesulfonate (28.3 mg, 110 μmol) (50 mg, 70%): mp 109 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (m, 4H, *o*-Ph), 7.41 (m, 4H, *m*-Ph), 7.14 (m, 2H, *p*-Ph), 5.60 (tt, J = 12.4, 6.8 Hz, 1H, H-2$_{\pi-allyl}$), 4.88 (d, J = 12.6 Hz, 4H, H_{eq}), 3.07 (d, J = 12.4 Hz, 2H, H_{anti}), 3.05 (d, J = 12.6 Hz, 4H, H_{ax}), 2.22 (d, J = 6.8 Hz, 2H, H_{syn}), 1.27 (s, 6H, CH_3); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.68 (m, 4H, *o*-Ph), 7.42 (m, 4H, *m*-Ph), 7.16 (m, 2H, *p*-Ph), 5.72 (tt, 12.4, 6.6 Hz, 1H, H-2$_{\pi-allyl}$), 4.98 (d, J = 12.4 Hz, 4H, H_{eq}), 3.26 (d, J = 12.4 Hz, 4H, H_{ax}), 2.95 (d, J = 12.4 Hz, 2H, H_{anti}), 2.17 (d, J = 6.6 Hz, 2H, H_{syn}), 1.27 (s, 6H, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 210.1 (C-9), 154.6 (C_{ipso}), 129.3 (C_{meta}), 125.3 (C_{para}), 120.7 C-2$_{\pi-allyl}$), 117.4 (C_{ortho}), 68.3 (C-1, C-3$_{\pi-allyl}$), 66.5 (CH_2), 46.4 (C), 17.7 (CH_3); IR ($CDCl_3$) 2348, 1740, 1594, 1460 cm^{-1}. Anal. Calcd for $C_{25}H_{29}N_2O_4SF_3Pd\cdot CDCl_3$: C, 42.35; H, 4.24; N, 3.80. Found: C, 43.33; H, 4.09; N, 3.69. Deviations are due to solvent inclusion; see the X-ray crystallographic data.

(3,7-Dibenzyl-1,5-dicarbomethoxybispidinone(1,3-η^3-propenyl)palladium trifluoromethanesulfonate (16) was prepared from **10** (18.3 mg, 50 μmol), 3,7-dibenzyl-1,5-dicarbomethoxybispidinone (**3a**) (43.6 mg, 100 μmol), and silver trifluoromethanesulfonate (28.3 mg, 110 μmol) (30 mg, 50%): mp 156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.40 (m, 10H, aromatic), 6.21 (tt, J = 12.5 Hz, 7.1 Hz, 1H, H-2$_{\pi-allyl}$), 4.69 (s, 4H, benzyl), 4.17 (d, J = 13.0 Hz, 4H, H_{eq}), 3.88 (d, J = 7.1 Hz, 2H, H_{syn}), 3.75 (d, J = 12.5 Hz, 2H, H_{anti}), 3.67 (s, 6H, CH_3), 3.56 (d, J = 13.0 Hz, 4H, H_{ax}); ^{13}C NMR (100.6 MHz, $CDCl_3$, −55 °C) δ 199.9 (C-9), 165.8 (COO), 132.1 (C_{ortho}), 129.4 (C_{ipso}), 128.7 (C_{para}), 128.3 (C_{meta}), 121.7 (C-2$_{\pi-allyl}$), 120.3 (CF_3, J_{CF} = 320 Hz), 70.9 ($PhCH_2$), 65.0 (C-1$_{\pi-allyl}$, C-3$_{\pi-allyl}$), 58.1 (CH_2), 57.8 (CH_2), 56.9 (C), 56.8 (C), 53.6 (CH_3); IR (KBr) 2360, 1746, 1724, 1497, 1255 cm^{-1}. Anal. Calcd for $C_{29}H_{33}N_2O_8SF_3Pd\cdot H_2O$: C, 46.38; H, 4.70; N, 3.73. Found: C, 46.51; H, 4.68; N, 3.66.

(3,7-Dibenzyl-1,5-dimethylbispidinone)(1,3-η^3-propenyl)-palladium trifluoromethanesulfonate (17) was prepared from **10** (36.6 mg, 100 μmol), 3,7-dibenzyl-1,5-dimethylbispidinone (**3b**) (69.6 mg, 200 μmol), and silver trifluoromethanesulfonate (56.6 mg, 220 μmol) (43 mg, 41%): mp 132 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.37 (m, 10H, aromatic) 6.21 (tt, J = 12.4, 6.8 Hz, 1H, H-2$_{\pi-allyl}$), 4.61 (s, 4H, benzylic), 3.90 (br, 4H, H_{eq}), 3.87 (d, J = 6.8 Hz, 2H, H_{syn}), 3.78 (d, 12.4 Hz, 2H, H_{anti}), 2.74 (d, J = 12.4, 4H, H_{ax}), 0.90 (s, 6H, CH_3); ^{1}H NMR (100.6 MHz, acetone-d_6): δ 7.37−7.47 (m, 10H, aromatic) 6.20 (tt, J = 12.5, 7.1, 1H, H-2$_{\pi-allyl}$), 4.81 (s, 4H, benzylic), 4.09 (d, J = 7.1, 2H, H_{syn}), 4.00 (br s, 4H, H_{eq}), 3.69 (d, J = 12.5 Hz, 2H, H_{anti}), 2.86 (d, J = 12.5, 4H, H_{ax}), 0.86 (s, 6H, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 210.1 (C-9), 132.2, 129.4, 129.2, 128.7, 121.8 (C-2$_{\pi-allyl}$), 71.1 (benzylic), 65.1 (C-1,C-3$_{\pi-allyl}$), 63.4 (CH_2), 46.5 (C), 17.5 (CH_3); IR ($CDCl_3$) 2869, 1735, 1542, 1261 cm^{-1}. Anal. Calcd for $C_{27}H_{33}N_2O_4SF_3Pd$: C, 50.30; H, 5.16; N, 4.35. Found: C, 48.93; H, 4.92; N, 4.24.

(3,7-Diphenyl-1,5-dicarbomethoxybispidin-9-diol)(1,3-η^3-propenyl)palladium trifluoromethanesulfonate (18) was obtained in solution by storing **14** in chloroform at room temperature during 48 h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (m, *o*-Ph), 7.41 (m, 4H, *m*-Ph), 7.13 (m, *p*-Ph), 5.52 (tt, J = 12.4, 6.6 Hz, 1H, H-2$_{\pi-allyl}$), 5.26 (s, 2H, OH), 4.80 (d, J = 12.2 Hz, 4H, H_{eq}), 3.94 (s, 6H, CH_3), 3.65 (d, J = 12.2 Hz, 4H, H_{ax}), 2.96 (d, J = 12.4 Hz, 2H, H_{anti}), 2.11 (d, J = 6.6 Hz, 2H, H_{syn}); ^{13}C NMR (100.6 MHz, $CDCl_3$) 171.1 (COO), 155.3 (C_{ipso}), 129.3 (C_{meta}), 125.3 (C_{para}), 117.4 (C_{ortho}), 113.2 (C-2$_{\pi-allyl}$), 92.6 ($C(OH)_2$), 68.0 (C-1,C-3$_{\pi-allyl}$), 57.5 (CH_2), 53.9 (CH_3), 50.6 (C). Anal. Calcd for $C_{27}H_{29}N_2O_8SF_3Pd\cdot H_2O$; C, 44.85; H, 4.32; N, 3.87. Found: C, 45.12; H, 4.10; N, 3.94.

(62) Hüttel, R.; Kratzer, J.; Bechter, M. *Chem. Ber.* **1961**, *94*, 766.
(63) Trost, B. M.; Strege, P. E. *Tetrahedron* **1974**, *30*, 2603.

(*N*,*N*′-Diphenylpiperazine)(1,3-η^3-propenyl)palladium trifluoromethane sulfonate (19) was prepared from **10** (36.6 mg, 100 μmol), *N*,*N*′-diphenylpiperazine (**7**) (48.0 mg, 200 μmol), and silver trifluoromethanesulfonate (56.6 mg, 220 μmol): yield 50 mg (70%); mp 118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (m, 8H, *o*-Ph, *m*-Ph), 7.19 (m, 2H, *p*-Ph), 5.58 (tt, J = 12.1, 6.7 Hz, 1H, H-2$_{\pi-allyl}$), 3.98 (d, J = 6.7 Hz, 2H, H_{syn}), 3.74 (br, 8H, CH_2), 3.05 (d, J = 12.1 Hz, 2H, H_{anti}); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.35 (m, 8H, *o*-Ph, *m*-Ph), 7.05 (m, 2H, *p*-Ph), 5.91 (tt, J = 12.1, 6.8 Hz, 1H, H-2$_{\pi-allyl}$), 4.12 (d, J = 6.8 Hz, 2H, H_{syn}), 3.28 (d, J = 12.1 Hz, 2H, H_{anti}), 3.67 (br s, 8H, CH_2); IR ($CDCl_3$) 1732, 1598, 1495, 1214 cm^{-1}. Low stability prevented elemental analysis.

(*N*,*N*′-Diphenyldiazacyclooctane)(1,3-η^3-propenyl)palladium Trifluoromethanesulfonate (20). To 2 mL of chloroform was added **10** (18.3 mg, 50 μmol) and silver trifluoromethanesulfonate (56.6 mg, 100 μmol). The mixture was magnetically stirred during 10 min at room temperature under a nitrogen atmosphere and was thereafter filtered. To the filtrate was added *N*,*N*′-diphenyl-diazacyclooctane (**8**) (26.6 mg, 100 μmol). This mixture was stirred for an additional 10 min under a nitrogen atmosphere. Diethyl ether was added drop by drop to induce crystallization, and the solution was stored at −20 °C overnight. The light yellow crystals were collected and dried *in vacuo* (18 mg, 44%): mp 138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00−7.32 (m, 10 H, aromatic), 5.57 (tt, J = 12.3, 6.7 Hz, 1H, H-2$_{\pi-allyl}$), 4.02 (br, 4H, CH_2), 3.48 (br, 4H, CH_2), 2.86 (d, J = 12.3 Hz, 2 H, H_{anti}), 2.46 (br, 4 H, CH_2), 2.28 (br, 2H, H_{syn}); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.20−6.60 (m, broad, 10 H, aromatic), 5.90 (m, 1H, H-2$_{\pi-allyl}$), 4.02 (br, 4H, CH_2), 3.48 (br, 4H, CH_2), 2.92 (d, J = 11.7 Hz, 2H, H_{anti}) 2.46 (br, 4H, CH_2), 1.98 (br, 4H, H_{syn}); IR (KBr) 1595, 1504, 1267, 1160 cm^{-1}. Anal. Calcd for $C_{22}H_{27}N_2F_3PdSO_3$: C, 46.94; H, 4.83; N, 4.98. Found: C, 46.80; H, 4.98; N, 5.08.

(3,7-Diphenyl-1,5-dimethylbispidinone)(2-methylene-6,6-dimethylbicyclo[3.1.1]hept-2,3,10-η^3-enyl)palladium trifluoromethanesulfonate (21) was prepared from **11** (13.9 mg, 50 μmol), **2b** (16 mg, 50 μmol), and silver trifluoromethanesulfonate (14.1 mg, 55 μmol) according to the general procedure (25 mg, 70%): mp 130−132 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.57 (m, 4H, *o*-Ph$_L$), 7.40 (m, 4H, *m*-Ph$_L$), 7.12 (m, 2H, *p*-Ph$_L$), 4.90 (br, 4H, H_{eqL}), 3.67 (d, 5.2, 1H, H-3), 3.54 (br s, 1H, H-10b), 3.08 (br, 4H, H_{axL}), 2.58 (ddd, 5.5, 6.2, 9.5, 1H, H-7β), 1.95 (dd, 5.2, 5.5, 1H, H-1), 1.86 (s, 1H, H-10a), 1.66 (br s, 1H, H-5), 1.32 (d, 9.5, 1H, H-7α), 1.25 (s, 6H, Me$_L$), 1.17 (s, 3H, Me-8), 0.66 (s, 3H, Me-9), 0.63 (dd, 5.4, 18.8, 1H, H-4β), −1.15 (dd, 1.6, 18.8, 1H, H-4α); (400 MHz, $CDCl_3$ −55°): δ 8.21 (1H, *o*-Ph-3), 7.86 (1H, *o*-Ph-7), 7.49 (1H, *m*-Ph-3), 7.45 (1H, *m*-Ph-7), 7.30 (1H, *m*-Ph-7′), 7.27 (1H, *m*-Ph-3′), 7.12 (1H, *p*-Ph-3), 7.08 (1H, *p*-Ph-7), 7.05 (1H, *o*-Ph-7′), 7.00 (1H, *o*-Ph-3′), 5.48 (d, J = 12.7 Hz, 1H, H-2$_{eqL}$), 5.39 (d, 12.4, 1H, H-8$_{eqL}$), 4.30 (d, 12.2, 1H, H-6$_{eqL}$), 3.86 (d, 12.1, 1H, H-4$_{eqL}$), 3.58 (d, 5.1 Hz, 1H, H-3), 3.42 (s, 1H, H-10b), 3.29 (d, 12.1, 1H, H-4$_{axL}$), 3.17 (d, 12.2, 1H, H-6$_{axL}$), 3.00 (d, 12.7, 1H, H-2$_{axL}$), 2.97 (d, 12.4, 1H, H-8$_{axL}$), 2.54 (ddd, 4.9, 6.5, 9.0 Hz, 1H, H-7β), 1.94 (dd, 4.9, 4.9, 1H, H-1), 1.77 (s, 1H, H-10a), 1.62 (m, 1H, H-5), 1.26 (s, 3H, Me-1$_L$/Me-5$_L$), 1.20 (s, 3H, Me-1$_L$/Me-5$_L$), 1.18 (d, 9.2 Hz, 1H, H-7α), 1.11 (s, 3H, Me-8), 0.60 (s, 3H, Me-9), 0.56 (dd, 5.1, 18.4 Hz, 1H, H-4β), −1.31 (dd, 3.8, 18.4 Hz, 1H, H-4α). ^{13}C NMR ($CDCl_3$, −55 °C) δ 210.9, 154.6, 152.0, 145.2, 130.5, 129.9, 128.5, 127.9, 125.4, 124.8, 122.8, 122.0, 119.4, 114.5, 73.6, 69.0, 68.4, 66.6, 66.0, 65.5, 46.4, 45.8, 45.0, 38.7, 37.3, 35.1, 25.9, 25.4, 21.4, 18.6, 17.2; IR ($CDCl_3$) 2977, 1792, 1739, 1496, 1461 cm^{-1}.

(3,7-Dibenzyl-1,5-dimethylbispidinone)(2-methylene-6,6-dimethylbicyclo[3.1.1]hept-2,3,10-η^3-enyl)palladium trifluoromethanesulfonate (22) was prepared from **11** (27.8 mg, 100 μmol), **3b** (34.8 mg, 100 μmol), and silver trifluoromethanesulfonate (28.3 mg, 110 μmol) according to the general procedure (36 mg, 49%): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.26−7.39 (m, 10H, Ph$_L$), 4.66 (d, 13.4, 1H, Bz-7$_L$), 4.48 (m, 2H, Bz-3$_L$), 4.48 (m, 1H, H-3), 4.46 (m, 1H, H-8$_{eqL}$), 4.41 (dd, 2.3, 12.4, 1H, H-2$_{eqL}$), 4.32 (d, 13.4, 1H, Bz-7$_L$), 4.07 (s, 1H, H-10b), 3.50 (s, 1H, H-10a), 3.43 (dd, 2.3, 12.5, 1H, H-4$_{eqL}$), 3.19 (dd, 2.4, 12.4, 1H, H-6$_{eqL}$), 2.87 (d, 12.4, 1H, H-6$_{axL}$), 2.85 (m, 1H, H-7β), 2.77 (d, 12.6, 1H, H-8$_{axL}$), 2.76 (d, 12.4, 1H, H-2$_{axL}$), 2.68 (d, 12.5, 1H, H-4$_{axL}$), 2.45 (dd, 5.4, 5.4, 1H, H-1), 2.21 (m, 1H, H-5), 1.78 (d, 9.7, 1H, H-7α), 1.77 (m, 1H, H-4β), 1.68 (dd, 4.0, 18.3, 1H, H-4α), 1.39 (s, 3H, Me-8), 1.02 (s, 3H, Me-9), 0.96 (s, 3H, Me-5$_L$), 0.84 (s, 3H, Me-1$_L$); (400 MHz, $CDCl_3$ −50 °C) δ 7.44−7.23 (m, 10H, Ph$_L$), 4.62 (d, 13.4, 1H, Bz-3$_L$), 4.54 (d, 13.6, 1H, Bz-7$_L$), 4.44 (m, 1H, H-3), 4.44 (m, 1H, H-2$_{eqL}$), 4.43 (m, 1H, Bz-7$_L$), 4.41 (m, 1H, H-8$_{eqL}$), 4.29 (d, 13.4, 1H, Bz-3$_L$), 4.02 (s, 1H, H-10b), 3.46 (s, 1H, H-10a), 3.40 (d, 12.7, 1H, H-6$_{eqL}$), 3.15 (d, 12.2, 1H, H-4$_{eqL}$), 2.88 (d, 12.2, 1H, H-4$_{axL}$), 2.80 (m, 1H, H-7β), 2.76 (two d, 12.7, 2H, H-2$_{axL}$, H-2$_{axL}$), 2.73 (d, 12.7, 1H, H-6$_{axL}$), 2.43 (dd, 5.3, 5.3, 1H, H-1), 2.18 (br, 1H, H-5), 1.76 (m, 1H, H-4β), 1.68 (m, 2H, H-4α, H-7α), 1.37 (s, 3H, Me-8), 1.00 (s, 3H, Me-9), 0.95 (s, 3H, Me-5$_L$), 0.84 (s, 3H, Me-1$_L$); ^{13}C NMR ($CDCl_3$, −55 °C) δ 210.2, 145.8, 132.5 (2C), 131.7 (2C), 129.8, 129.4, 129.3, 129.1, 128.7 (2C). 128.6 (2C), 71.2, 70.5, 69.2, 64.7, 64.4, 64.1, 64.0, 62.2, 46.7, 46.3, 46.2, 39.8, 38.4, 34.4, 29.6, 25.9, 21.9, 17.9, 17.1; IR ($CDCl_3$) 2935, 1736, 1584, 1260 cm^{-1}.

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Supporting Information Available: Tables of positonal and thermal parameters and bond distances and angles (4 pages). Ordering information is given on any current masthead page.

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