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Self-Adaptable Catalysts: Substrate-Dependent Ligand Configuration

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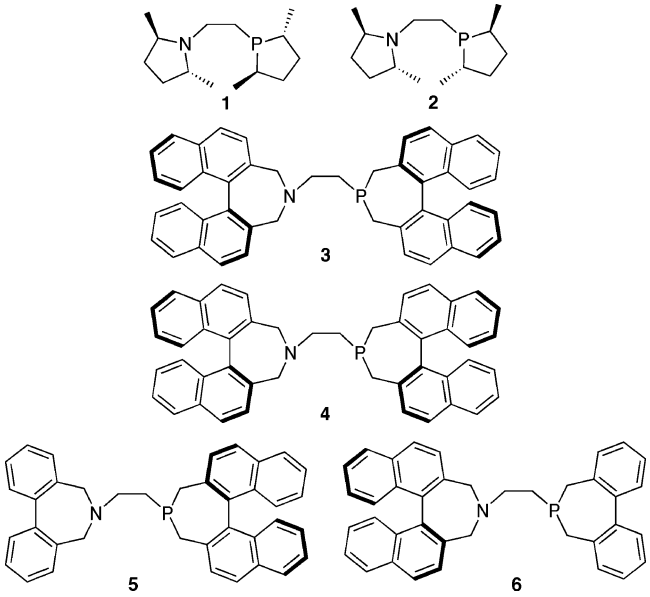
Abstract: Pd(II) allyl and Pd(0) olefin complexes containing the configurationally labile ligand 1,2-bis-[4,5-dihydro-3*H*-dibenzo[*c*−*e*]azepino]ethane were studied as models for intermediates in Pd-catalyzed allylic alkylations. According to NMR and DFT studies, the ligand prefers C_s conformation in both η^3-1,3-diphenylpropenyl and η^3-cyclohexenyl Pd(II) complexes, whereas in Pd(0) olefin complexes it adopts different conformations in complexes derived from the two types of allyl systems in both solution and, as verified by X-ray crystallography, in the solid state. These results demonstrate that the Pd complex is capable of adapting its structure to the reacting substrate. The different structural preferences also provide an explanation for the behavior of 1,3-diphenyl-2-propenyl acetate and 2-cyclohexenyl acetate in Pd-catalyzed allylic alkylations using *pseudo*-C_2 and *pseudo*-C_s symmetric ligands.

Introduction

Many of the most general and efficient methods for the preparation of enantioenriched chiral compounds rely on asymmetric metal catalysts. For this reason large efforts are devoted to the design of chiral ligands capable of efficient chirality transfer.[1] For optimal catalyst performance, structural modifications of the catalyst are usually needed for each substrate to be subjected to a particular reaction. In order to avoid time-consuming ligand synthesis, catalysts with a broad substrate spectrum are desirable. The ultimate goal would be to have access to catalysts being able to adapt their structures to the particular substrate undergoing reaction. Ligands containing structurally flexible units are likely to be suitable candidates for this purpose.

We have previously studied palladium-catalyzed allylic alkylations employing rigid phospholane-pyrrolidine ligands **1** and **2** and binaphthyl derivatives **3** and **4** as well as ligands containing a flexible unit which either adopts *R* or *S* configuration, **5** and **6**, in order to study the influence of both steric and electronic effects on the catalyst performance.[2] We then found that while the *pseudo*-C_2-symmetric ligands **1** and **3** provided the product from reaction of *rac*-1,3-diphenylpropenyl acetate (eq 1) with good to excellent enantioselectivities (81 and 98% ee, respectively), use of the *pseudo*-C_s-symmetric ligands **2** and **4** resulted in lower selectivities (67 and 37% ee, respectively) and, in the case of **4**, in lower reactivity (Table 1). The result using flexible ligand **6** (78% ee) was the same as that experimentally found using a 1:1 mixture of **3** and **4**, and that observed using **5** (87% ee) was the same as that expected using a 1:1 mixture of **3** and *ent*-**4** (as calculated from the ee



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(1) (a) Ojima, I., Ed. *Catalytic Asymmetric Synthesis*; Wiley; New York, 2000. (b) Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds. *Comprehensive Asymmetric Catalysis*; Springer: Berlin, 1999.
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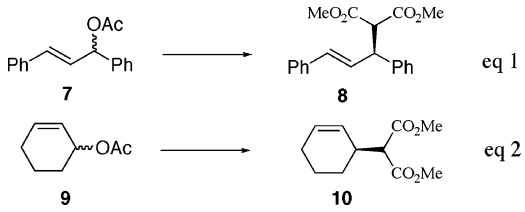
Table 1. Yields and Enantioselectivities in Allylic Alkylations[a] Using Pd Catalysts Containing Ligands **1**−**6**



ligand	7 → 8	9 → 10
1	81 (*S*) 7 h 100%	− 120 h 0%
2	67 (*R*) 7 h 100%	24 (*R*) 192 h 73%
3	98 (*S*) 6 h 100%	12 (*R*) 24 h 40%
4	37 (*R*) 72 h 95%	26 (*R*) 24 h 70%
5	87 (*S*) 4 h 60%	20 (*S*) 4 d 22%
6	78 (*S*) 5 h 55%	

[a] Conditions: dimethyl malonate, η^3-(C_3H_5)$PdCl_2$, ligand, *N*,*O*-bis(trimethylsilyl)acetamide (BSA), KOAc. Results are from ref 2.

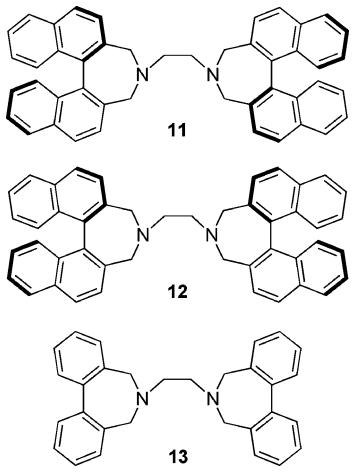
values observed and the different reactivities of **3** and **4**).[2] This demonstrates that **5** and **6** behave as 1:1 mixtures of their rigid analogues and thus that conformational change probably is slow in comparison with the catalytic reaction. Although the types of ligands studied were not well suited for small cyclic substrates, the reverse situation was true for alkylations of *rac*-3-cyclohexenyl acetate (eq 2), the *pseudo*-C_s type of ligands being those that afforded products with highest yields and selectivities (Table 1). Assuming equal reactivity of catalysts containing **3** and **4**, an ee of about 7% of the (*S*)-product is expected for a catalytic system containing a 1:1 mixture of **3** and *ent*-**4**. The value actually found for **5**, 20% ee in favor of the (*S*)-enantiomer, is close to that expected using only *ent*-**4**, consistent with the assumption that for cyclic substrates catalysts containing *pseudo-meso* type ligands are more reactive. As judged from the results using flexible ligands **5** and **6** and 1,3-diphenylpropenyl acetate, the actual catalysts contained about equal amounts of the two conformational diastereomers of the ligands. The stability of palladium complexes with the two types of ligands most probably differs, however, and the results of the catalytic reactions therefore suggest that tropoisomerization was slow compared to nucleophilic attack, i.e., that the reactions did not occur under Curtin-Hammett conditions.

In order to further study the conformational preferences of the ligands and to investigate whether the structure of the ligand indeed is affected by the nature of the η^3-allyl and η^2-olefin groups, a series of model Pd(II) and Pd(0) complexes containing allyl and olefin ligands, respectively, and a configurationally flexible ligand were prepared and their structures studied by means of NMR spectroscopy and X-ray crystallography. The structures of the allyl complexes and the olefin complexes resulting from their reaction with nucleophiles were also studied by DFT computations.

Results and Discussion

In palladium-catalyzed alkylations of symmetrically substituted allylic compounds, nucleophilic attack is the stereochemistry-determining step.[3] In order to relate the conformation of the ligand to the results of the catalytic reactions, the transition-state structures need to be considered. The stereochemistry-determining step is usually considered to have a late transition state, and the η^2-olefin complexes resulting from nucleophilic attack on the allyl complexes should therefore be closer in structure to the transition state than the starting allyl complexes.[4] In order to gain information about the entire process, both types of complexes need to be studied.

Bisnitrogen ligands **11**,[5] **12**,[2] and **13**[6] were selected as suitable model compounds since (1) they have the required stereochemical properties, (2) they are more stable than their *P*,*N*-analogues and therefore easier to handle, and (3) their higher symmetries facilitate interpretation of NMR spectra. η^3-Allyl palladium complexes containing the three ligands were first prepared using bis[(η^3-cyclohexenyl)palladium chloride][7] and bis[(η^3-1,3-diphenylpropenyl)palladium chloride].[8]



^{1}H NMR Studies of η^3-Allyl Complexes. First, the structures of η^3-allyl complexes derived from ligands **11** and **12** were studied. Due to the C_2 symmetry of **11**, a single complex, [**14**]-[PF_6], was obtained from this ligand and 3-cyclohexenyl acetate. As expected, the complex was devoid of symmetry and showed three separate signals, δ 5.63, 4.41, and 3.87, for the allylic protons. From ligand **12** and the same allylic acetate, two complexes (endo and exo) may form, although a single compound, most probably the exo isomer [**15**][PF_6], was observed by NMR. In accordance with the expected C_s symmetry, a symmetrical spectrum was observed at 298 K, with resonances at δ 5.52 for the central allylic proton and at δ 3.83 for the two terminal allylic protons. The small coupling constant (J = 6.4 Hz) is consistent with the anti allylic structure. Pairwise identity of the methylene protons confirmed the mirror symmetry of the complex. At lower temperature (193 K) separate signals were observed for the terminal allylic protons, probably as a

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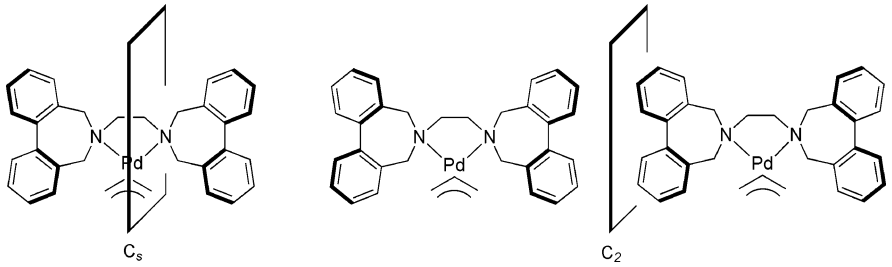
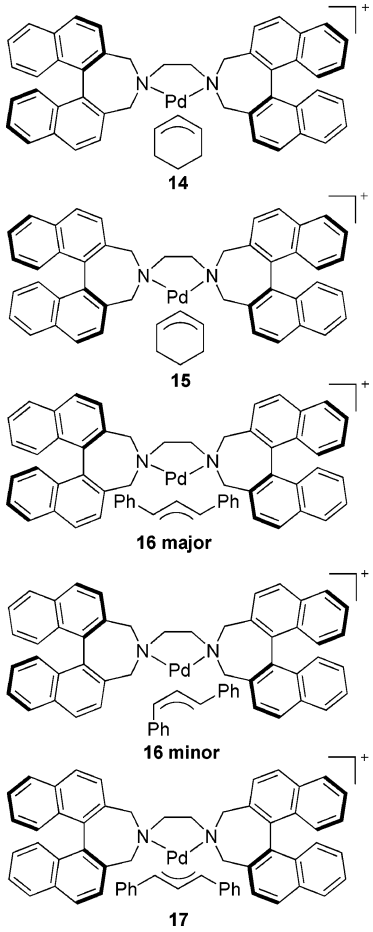


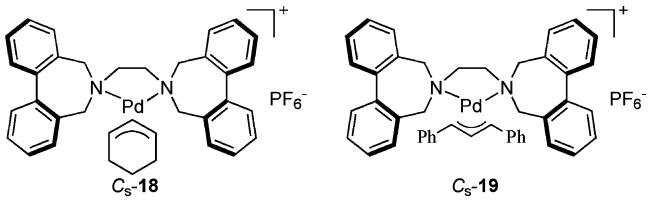
Figure 1. Mirror-image symmetry in C_s complexes and between enantiomers of complexes with C_2-symmetric ligands.

result of lower symmetry due to slow flipping of the five-membered chelate ring.



The ^{1}H NMR spectrum of the η^3-allyl complex prepared from the 1,3-diphenylallyl substrate and **12** suggested the presence of a single symmetric species. Sharp signals were observed at 223 K. Signals from the central allylic proton were found at 6.13 and the terminal allylic protons at 4.59, and again, the methylene protons were pairwise identical. The large coupling constant ($J = 11.7$ Hz) is strong indication of a syn,syn complex, probably the exo isomer [**17**][PF_6]. The spectrum of the complex containing the C_2-symmetric ligand **11** was more complex, indicating the presence of more than one isomer. The major complex, [**16**][PF_6], had signals from the allylic group at δ 6.01, 5.46, and 3.81. Again, the large coupling constants ($J = 13.2$ and 10.1 Hz) are strong indications of a syn,syn stereochemistry of the allylic group. The minor isomer showed signals for the allylic protons at δ 5.91 (dd, $J = 12.4$, 8.1 Hz), 4.50 (d, $J = 8.1$ Hz), and 4.42 (d, $J = 12.4$ Hz), indicative of a syn,anti allyl system.

The ^{1}H NMR spectra of complexes [**14**][PF_6] and [**15**][PF_6] were then compared to those obtained from the complexes containing **13**. The NMR spectrum of the PF_6 salt of the cyclohexenyl complex, [**18**][PF_6], exhibited high symmetry and resembled that of [**15**][PF_6], with signals at δ 5.60 for the internal allylic proton, 4.25 for the terminal allylic protons, four signals for the benzylic methylene protons and two for the bridge protons. This spectrum is not compatible with a chiral complex or with a mixture of two meso complexes but is characteristic of a single meso structure. At lower temperature the symmetry disappeared, in analogy to the situation with **15**. Most probably **13** therefore forms one meso complex, [C_s-**18**]-[PF_6], with a five-membered C−C−N−Pd−N ring flipping slowly at low temperature. The spectrum of [**19**][PF_6] was somewhat more complicated than that of [**18**][PF_6]. A major isomer with a quite symmetric spectrum, with two signals for the allylic protons at δ 6.18 and 4.85, was consistent with a meso structure, [C_s-**19**][PF_6]. In addition, a minor isomer (~3%) was present, with an ^{1}H NMR spectrum showing a dd at δ 5.94 with coupling constants $J = 12.6$ and 8.2, consistent with the presence of an allylic group with syn,anti configuration. We were not able to determine the configuration of the ligand in this complex.



Complexes with Chiral Anions. In order to verify that the complexes obtained from ligand **13** were C_s-symmetric, spectra of salts containing chiral TRISPHAT (**20**)[9] and BINPHAT (**21**)[10] anions were studied. These hexacoordinated phosphorus anions exist as Δ or Λ enantiomers and are effective NMR chiral solvating agents for cationic (and neutral) organic and organometallic species and coordination compounds.[11]

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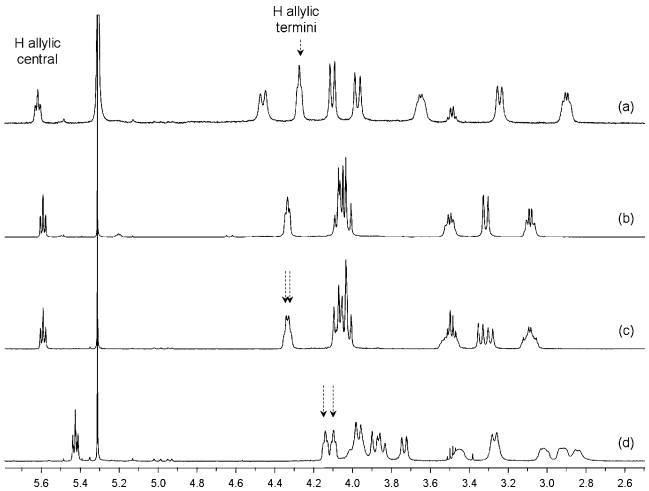
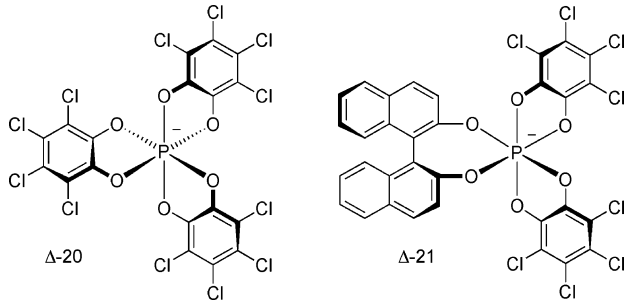


Figure 2. ^{1}H NMR spectra (parts, 500 MHz, $CDCl_3$) of salts (a) [**18**][PF_6], (b) [**18**][*rac*-**20**], (c) [**18**][Δ-**20**], and (d) [**18**][Δ-**21**].

In this context, they are particularly useful for the enantiodifferentiation of structures containing biphenylazepine moieties.[12]



By replacing the PF_6 counterion with these nonracemic anions, we reasoned that structures with C_s and C_2 symmetry could be distinguished. In the C_s structure, enantiotopic nuclei would become diastereotopic and thus ought to give rise to separate signals, whereas atoms residing in the mirror plane, in the present case only the central allylic proton and carbon atoms (and a methylene group in the cyclohexenyl ring), are achirotopic and would not split (Figure 1). For a chiral complex with the ligand in C_2-symmetric conformation, all atoms are chirotopic, and a doubling of all ^{1}H and ^{13}C NMR signals should result.[13]

Salts **[18]**[*rac*-**20**], [**18**][Δ-**20**], and [**18**][Δ-**21**] were prepared following previously reported conditions.[14] The racemic TRISPHAT salt displayed ^{1}H and ^{13}C spectra similar to that of [**18**][PF_6], ensuring a lack of conformational change of the complex upon association with the larger lipophilic counterion, this latter salt displaying furthermore a solubility in low polarity solvents useful for spectroscopic analysis. In ^{1}H NMR spectroscopy, whereas little change was observed in the case of the Δ-TRISPHAT salt (with the exception of a split of a doublet signal around 3.3 ppm), most signals of the ligands of **18** were effectively differentiated in the presence of the Δ-BINPHAT (see Figure 2, spectra c and d). Only the internal allylic proton remained unsplit in salt [**18**][Δ-**21**] with a slight drift toward lower frequencies (5.42 ppm). The signals of the methylene protons bridging the two nitrogen atoms split into four signals, and the terminal allyl protons became diastereotopic and nonequivalent (respectively ca. 4.14 and 4.10 ppm).

Confirmation of the NMR enantiodifferentiation efficiency of the BINPHAT anion was obtained in ^{13}C NMR spectroscopy as most signals of complex **18** were split in the presence of the anion. In Figure 3 are represented the most informative signals that are those of the η^3-cyclohexenyl ligand.[15] As shown, the signals of the internal allylic and the C4 methylene atoms are unaffected, while those of the terminal allylic and C3 atoms are clearly split in salt [**18**][Δ-**21**] ($\Delta\delta$ 48 and 2.6 Hz respectively, 125 MHz). All this information is consistent with a C_s-symmetric nature of compound **18**.

An analogous study was made for the complexes obtained from 1,3-diphenylpropenyl acetate and ligand **13**. Also in this case, the spectrum of the complex containing flexible ligand **13** resembled that of the complex containing the meso ligand. This was essentially confirmed by studies of the salts containing the chiral nonracemic anions. Compounds [**19**][*rac*-**20**], [**19**]-[Δ-**20**], and [**19**][Δ-**21**] were prepared in an analogous fashion to that of derivatives **18**. A splitting of ^{1}H signals was observed for both Δ-TRISPHAT and Δ-BINPHAT salts, except for the central allylic hydrogen atom that remained sharp (Figure 4).[16]

In ^{13}C NMR spectroscopy, an efficient split of the signals of the diamino ligand was observed, the signals of the methylene carbons (δ 57−61 ppm) being more particularly affected by the presence of the enantiopure anions (Figure 5). For the allylic ligand, the signal of the internal carbon remained unchanged, as expected (δ ca. 105 ppm). However, a bit to our surprise, it was also the case for terminal allylic carbons (δ ca. 77.2 ppm). The effective shielding of these carbon atoms by the phenyl substituents is possibly the reason for the lack of chiral discrimination.

Nevertheless, combined with the ^{1}H NMR study, all this information is consistent with a C_s-symmetric nature of compound **19** as well. In a chiral C_2-symmetric environment, the central allylic atoms would be diastereotopic in the presence of nonracemic anions and should therefore be split. Such an enantiodifferentiation is visible for the central signal of the minor syn,anti isomer of **19** (dd, J = 13 and 8 Hz) for which two sets of signals are clearly seen in the presence of Δ-TRISPHAT and Δ-BINPHAT ($\Delta\delta$ 25.5 Hz (Figure 6) and 36.7 Hz, respectively, 500 MHz instrument).

This study clearly demonstrates that for all types of η^3-allyl complexes, a C_s conformation of the ligand is favored, one

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(13) Only in the "improbable" case that would see the chiral anion fully control the configuration of the organometallic complex would the same number of signals occur.

(14) Prepared by ion-exchange metathesis of [**18**][PF_6] and [Et_2NH_2][*rac*-**20**], [cinchonidinium][Δ-**20**], and [Me_2NH_2][Δ-**21**], respectively, and isolated in chemically pure form by chromatography (Al_2O_3 or SiO_2, CH_2Cl_2). See ref 12 and Vachon, J.; Pérollier, C.; Monchaud, D.; Marsol, C.; Ditrich, K.; Lacour, J. *J. Org. Chem.* **2005**, *70*, 5903−5911.

(15) ^{13}C NMR distortionless enhancement by polarization transfer-135 (DEPT135) experiments produce usually positive signals for CH and CH_3 carbons and negative signals for CH_2 carbons, and exclude quaternary carbons and deuterated solvent signals. This latter characteristic was of importance for the clean observation of the signals of the termini allylic carbons (δ 76−77 ppm) in deuterated chloroform.

(16) In salt [**19**][Δ-**21**], the central allylic hydrogen atom remains sharp in the presence of the chiral anion; an induced lower frequency shift indicates, however, an influence of the counterion.

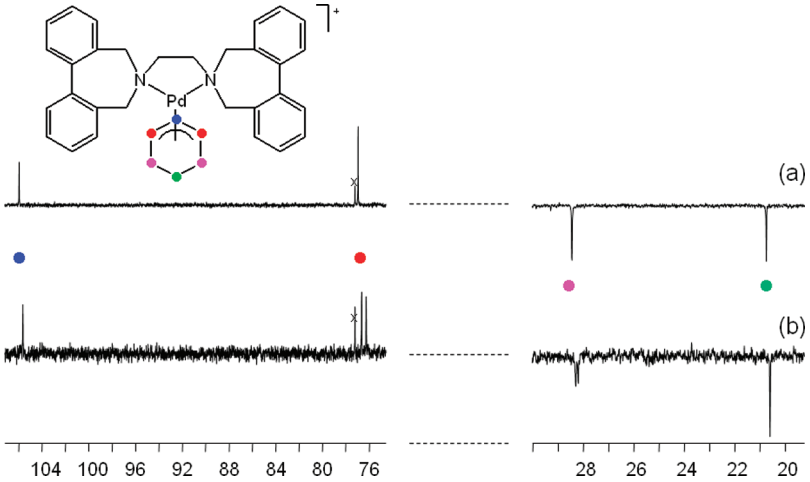


Figure 3. ^{13}C NMR spectra (DEPT135, parts, 125 MHz, $CDCl_3$) of (a) [**18**][*rac*-**20**] and (b) [**18**][Δ-**21**].

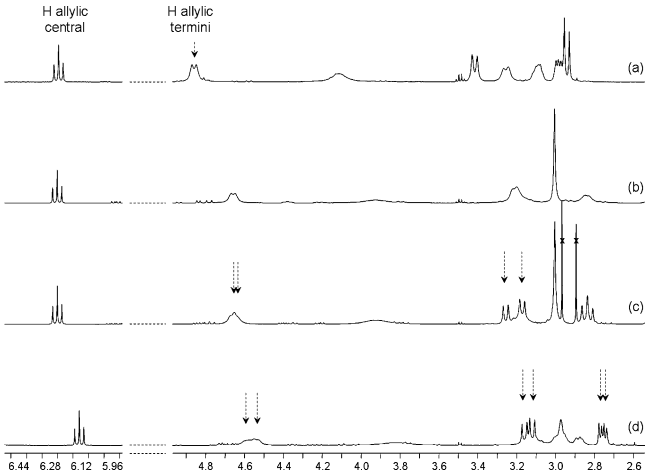
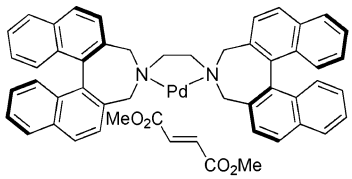


Figure 4. ^{1}H NMR spectra (parts, 500 MHz, $CDCl_3$) of salts (a) [**19**][PF_6], (b) [**19**][*rac*-**20**], (c) [**19**][Δ-**20**], and (d) [**19**][Δ-**21**].

exception possibly being the minor syn,anti diphenylallyl complex **19**. Since the transition state is assumed to be late and to resemble the olefin complex rather than the precursor allyl complex in Pd-catalyzed allylic alkylations, studies of the structures of the former type of complexes may be more relevant in order to gain knowledge about the stereochemistry-determining step. Therefore, in order to further explain the results of the catalytic reactions, structures of model olefin complexes were prepared and studied by ^{1}H NMR spectroscopy and X-ray crystallography.

Pd(0) Olefin Complexes. Since the olefin complexes of the present ligands were expected to be unstable,[17] model complexes containing stabilizing olefins carrying electron-withdrawing substituents were studied experimentally. Dimethyl fumarate and maleic anhydride were selected as model olefins since their complexes were considered to sterically resemble the structure of the complexes derived from syn,syn allyl and anti,anti allyl complexes, respectively, and since structural elucidations are facilitated by the symmetry properties of the complexes. Complexes with the two olefins were prepared from rigid ligands **11** and **12** and from flexible ligand **13** by mixing equimolar amounts of the ligand, olefin, and $Pd_2(dba)_3$·$CHCl_3$ in deuteriochloroform-d_1.

From ligand **11** and dimethyl fumarate two diastereomeric complexes may be obtained, although only one (**22**) was observed. The ^{1}H NMR spectrum of this complex was highly symmetric, showing a total of six different methylene protons, a single signal for the ester methyl protons, and a single signal for the olefinic protons, all in agreement with the expected C_2



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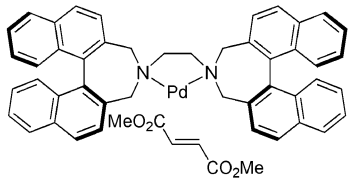

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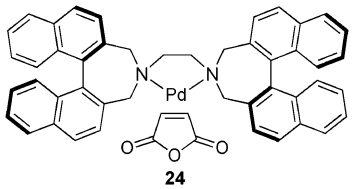

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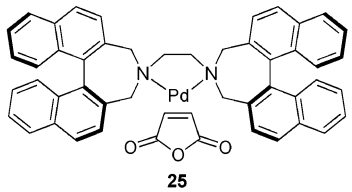

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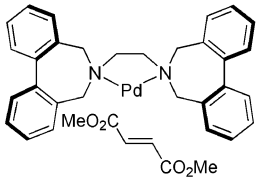

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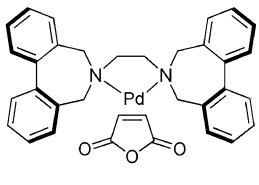

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(17) van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1994**, *33*, 1521−1531.

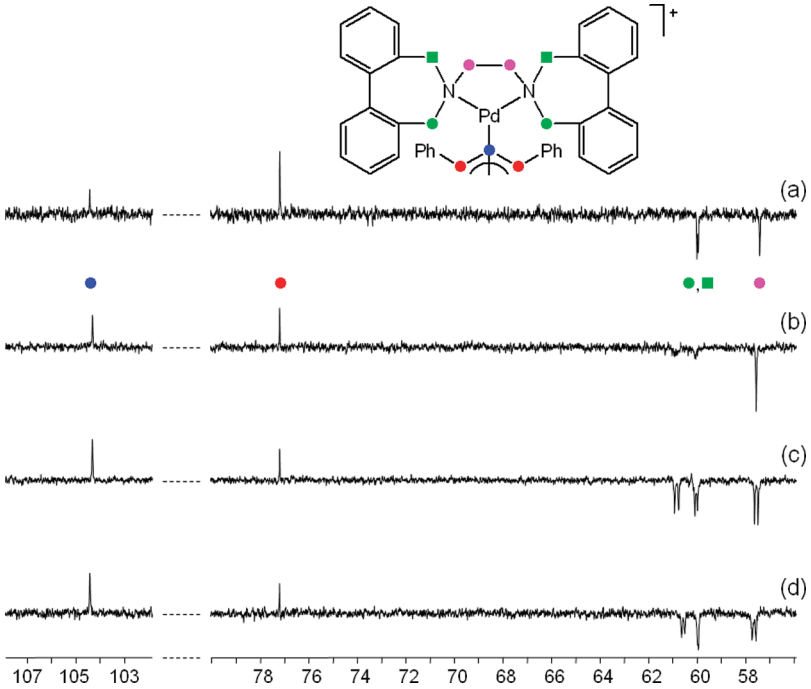


Figure 5. ^{13}C NMR spectra (DEPT135, parts, 125 MHz, $CDCl_3$) of (a) [**19**][PF_6], (b) [**19**][*rac*-**20**], (c) [**19**][Δ-**20**], and (d) [**19**][Δ-**21**].

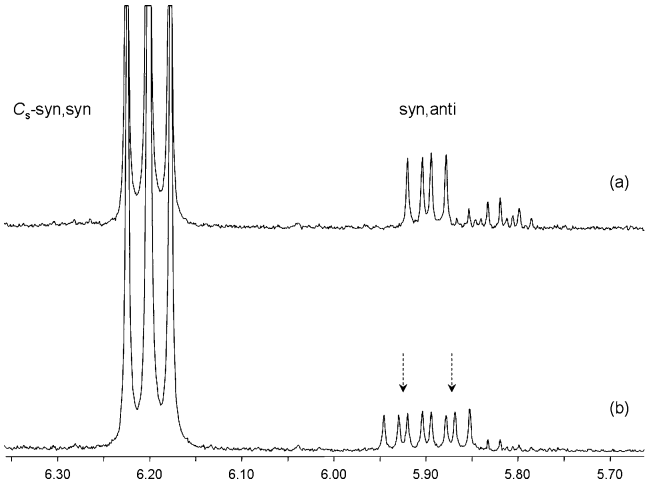


Figure 6. ^{1}H NMR spectra (parts, 500 MHz, $CDCl_3$) of salts (a) [**19**][*rac*-**20**] and (b) [**19**][Δ-**20**].

symmetry. Two enantiomers (**23** and *ent*-**23**) are expected from C_s-ligand **12** and dimethyl fumarate. Due to lack of symmetry, the ^{1}H NMR spectrum was considerably more complicated than that of **22**, with different signals for each proton. The only complex obtained from **11** and maleic anhydride (**24**) also showed separate signals for the methylene protons (albeit two of them (out of 12) overlapped, giving rise to a unique doublet). Two doublets (J = 3.8 Hz) for the olefinic protons showed that olefin rotation and exchange between uncoordinated and coordinated olefin are slow on the NMR time scale. The single complex observed from **12** and maleic anhydride (**25**, one out of two possible diastereomers) gave rise to a symmetric spectrum in accordance with the expected C_s structure.

Having the complexes with known configuration of the ligands in hand, we proceeded to studies of complexes containing flexible ligand **13**. The ^{1}H NMR spectra of both complexes were symmetric and resembled those of **22** and **25**, respectively, establishing the C_2 and C_s nature of the symmetry of the ligand backbone and thus structures **26** and **27** for the two complexes.

In all complexes the olefinic protons appeared at high field (3.2−3.4 ppm), indicative of rehybridization toward sp^3.

X-ray Crystallography. In order to verify the structures, single crystals of **26** and **27** were characterized using single-crystal X-ray diffraction. The structures were in agreement with those deduced from NMR (Figure 7).

Calculations. The structure of η^3-allyl complexes containing the ligand **13** were calculated and compared to those derived from the experimental studies. In Scheme 1 all possible Pd(II) allyl complexes are shown, together with selected product Pd(0) olefin complexes. For the diphenylpropenyl complexes with the ligand in C_2-symmetric configuration the syn,syn (A, Scheme 1) and one syn,anti structure (B) were considered, the second syn,anti structure (C) assumed to be less important for sterical reasons, and for those with C_s-symmetric ligand all complexes (D−G) were calculated. For complexes containing the cyclohexenyl group, which is forced to have anti,anti stereochemistry, all possible complexes (H, I, and J) were computed.

Calculations were performed on DFT/B3LYP level with *Jaguar 6.0*[18] quantum chemistry package. Preliminary gas-phase geometry optimization was carried out with LACVP* basis to assess possible configurations, in particular with respect of geometrical arrangement of an ion−anion pair. All stationary points were verified by vibrational analysis and found to be proper equilibrium structures. There has been a debate whether or not the B3LYP functional provides sufficient accuracy for reactions involving palladium. Recently, highly accurate ab initio benchmarks were computed,[19] and B3LYP

(18) *Jaguar 6.0*; Schrödinger, LLC: Portland, Oregon, 2005.
(19) de Jong, G. T.; Bickelhaupt, F. M. *J. Chem. Theory Comput.* **2006**, *2*, 322−335.

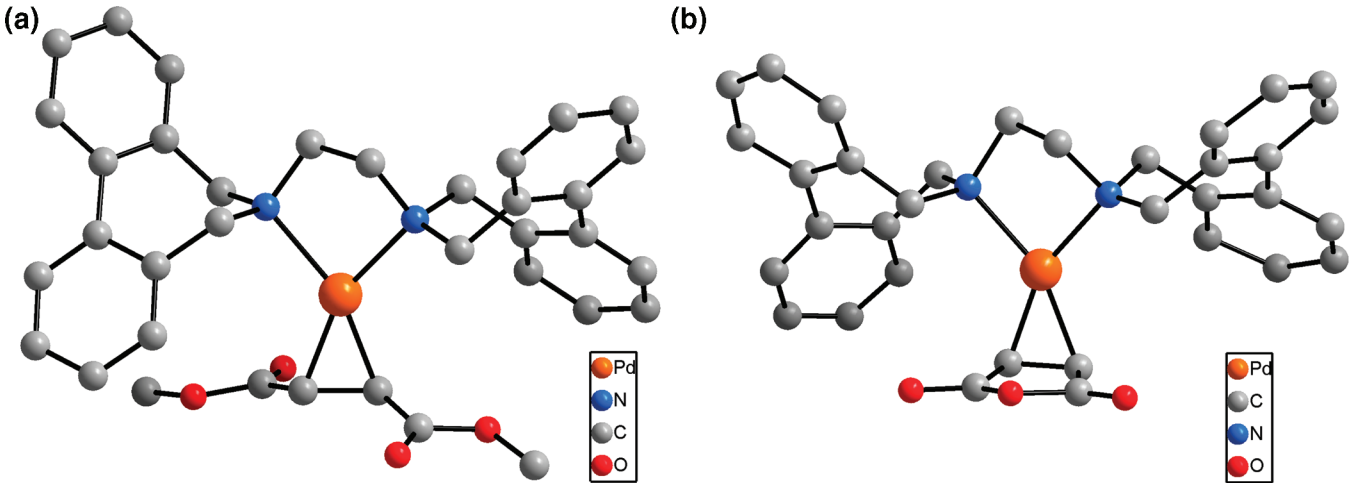
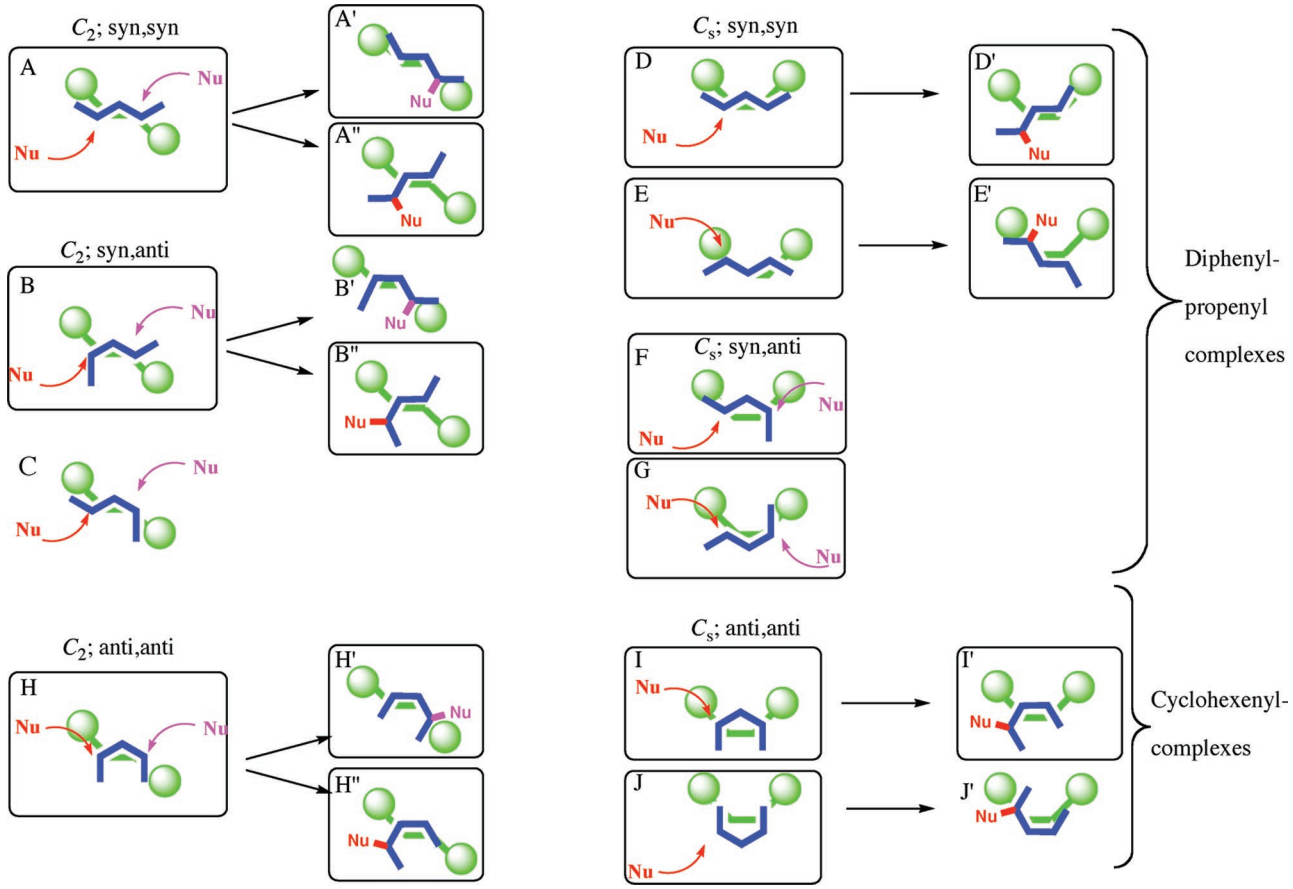


Figure 7. X-ray structures of complexes **26** (a) and **27** (b).

Scheme 1. Front View of *syn,syn-*, *syn,anti-*, and *anti,anti-*η^3-Allyl and -Olefin Pd Complexes with C_2- and C_s-Symmetric Ligands; Computed Structures in Frames

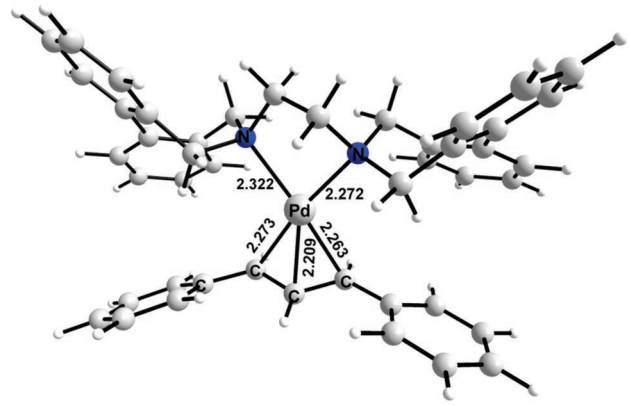


functional was validated to be accurate enough (within a reasonably small error) for studies of reactions and complexes involving palladium.

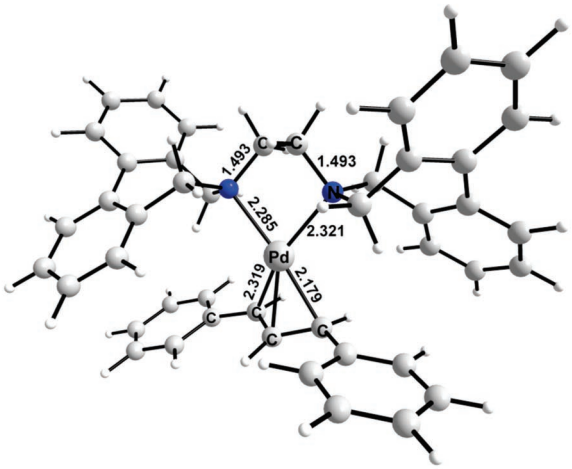
The best structures were selected for refinement with a larger basis set, LACVP*+.[20,21] Solvent effects (in dichloromethane) were evaluated both with respect to optimized gas-phase geometries and PCM-optimized[22] structures. The latter are expected to be more realistic with respect to typical experimental conditions.

(20) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299−310. (d) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257−2261. (e) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654−3665. (f) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213−222.

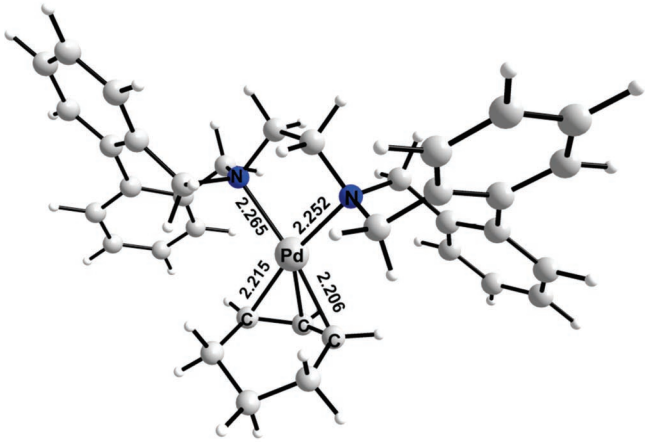
(21) LACVP* and LACVP*+ are fairly standard basis sets. The LACVP series of basis sets is a combination of the successful double-ζ 6-31G basis set with the LANL2DZ effective core basis set (the "*" option places polarization functions on all atoms except for transition metals, H, and He; the "+" option places diffuse functions on all atoms except H and He). Specifically, the atoms H−Ar are described with the 6-31G* and 6-31+G* basis sets while heavier atoms (Pd) are modeled using the LANL2DZ basis set (LACVP basis set family describes atoms beyond Ar in the periodic table using the standard Los Alamos effective core potential developed by Hay and Wadt, see details in ref 20c and references therein). Therefore, only the Pd atom is described using the effective core potential.



E

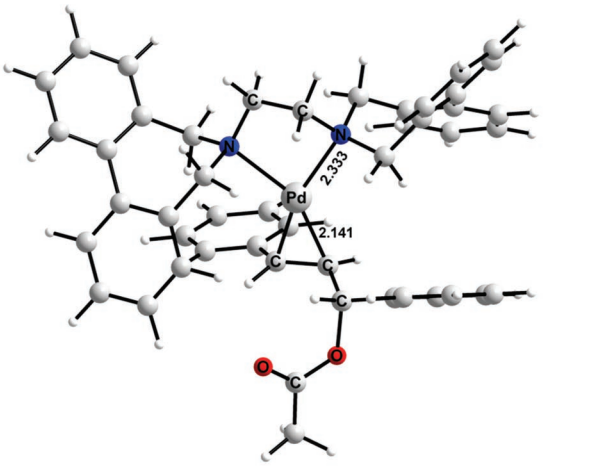


A

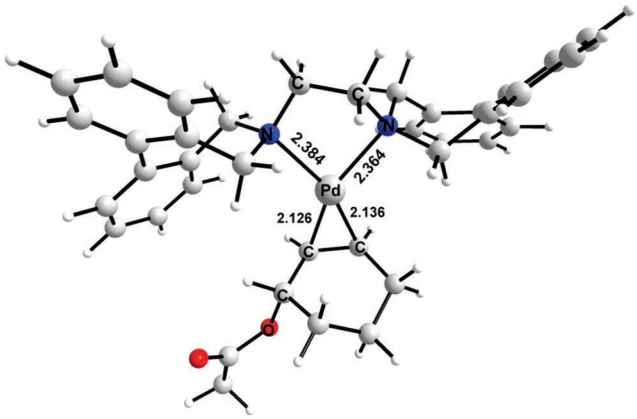


I

Figure 8. η^3-Allyl complexes. A: C_2; E and I: C_s. All complexes were optimized in solvent with PF_6^- ion (not shown).



A”



I’

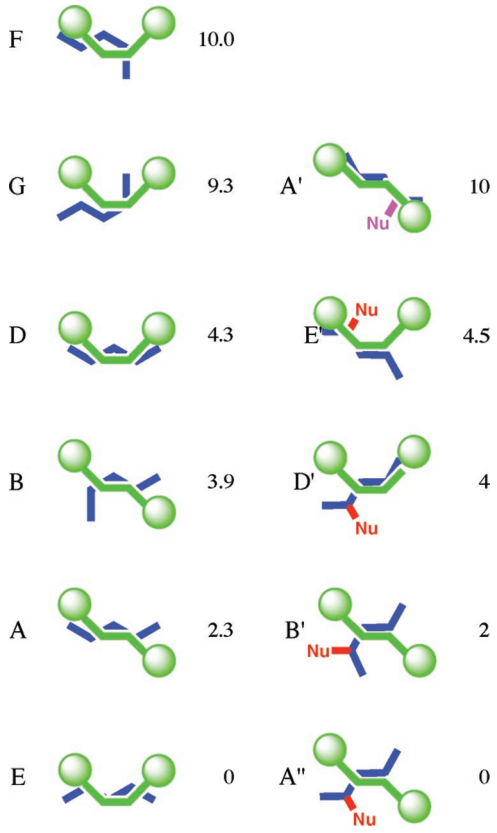
Figure 9. Olefin complexes. A″: C_2 and I′: C_s.

Several models were considered. The most simple model did not include the PF_6^- ion. This model was partially unable to provide agreement with our experimental data from NMR experiments, incorrectly predicting A to be more stable than E. Addition of the PF_6^- reduced the energy difference between A and E. To correct for limitations of gas-phase geometry optimizations, complete self-consistent geometry optimizations were carried out in PCM model representing polar dichloromethane. As a result, Pd−P distances typically increased in PCM-optimized geometries by 0.15 Å.

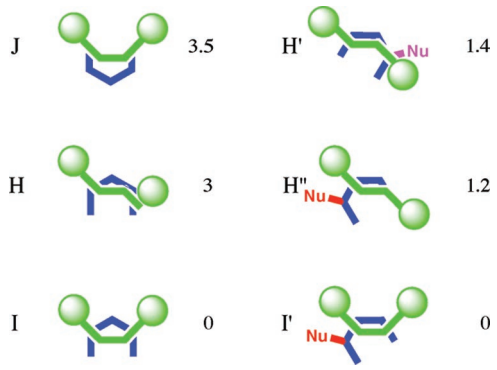
Among the η^3-allyl complexes with syn,syn and syn,anti geometry of the allyl moiety, the C_s-symmetric complex E (Scheme 1, Figure 8) was found to be of lowest energy, 2.3 kcal/mol more stable than complex A with C_2-symmetric ligand (Scheme 2). Complexes B and D were 3.9 and 4.3 kcal/mol, respectively, less stable than E, and complexes G and F considerably less stable (9.3 and 10 kcal/mol, respectively). Meso complex I was found to be the most stable cyclohexenyl complex, of about 3 and 3.5 kcal/mol lower energy than H and J, respectively (Scheme 3). This study thus confirms the experimental findings that structures with the ligand in C_s-configuration are of lowest energy for both types of allylic substrates. The large energy difference observed between the endo and exo anti,anti C_s complexes (I and J) is in accordance with the observation of a single complex by NMR. The energy difference between the lowest-energy diphe-

(22) The *Jaguar 6.0* package treats solvated molecular systems with the SCRF method, using its own Poisson−Boltzmann solver, which makes possible the computation of solvation energies and minimum-energy solvated structures of solvated transition states. For details see: (a) Tannor, D. J.; Marten, B.; Murphy, R.; Friesner, R. A.; Sitkoff, D.; Nicholls, A.; Ringnalda, M.; Goddard, W. A., III; Honig, B. *J. Am. Chem. Soc.* **1994**, *116*, 11875−11882. (b) Marten, B.; Kim, K.; Cortis, C.; Friesner, R. A.; Murphy, R. B.; Ringnalda, M. N.; Sitkoff, D.; Honig, B. *J. Phys. Chem.* **1996**, *100*, 11775−11788. (c) Cramer, C. J.; Truhlar, D. G. *Chem. Rev.* **1999**, *99*, 2161−2200.

Scheme 2. Computed Relative Energies (kcal/mol) of η^3-Allyl and η^2-Olefin Complexes Obtained from 1,3-Diphenyl-2-propenyl Acetate (only values within the same column can be compared)



Scheme 3. Computed Relative Energies (kcal/mol) of η^3-Allyl and η^2-Olefin Complexes Obtained from 2-Cyclohexenyl Acetate (only values within the same column can be compared)



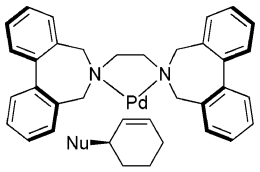
nylallyl complexes, E, and the next computed isomer, A, with the ligand in C_2-conformation, is somewhat smaller (2.3 kcal/mol). The observed minor isomer should, according to calculations, be A although the experimental results rather suggest it to be B.

In order to further study the different preferences of the two types of substrates, product Pd(0) olefin complexes were also calculated. Acetate was selected as nucleophile. The olefin complexes obtained from the calculated allyl complexes are shown in Scheme 1; for the complexes formed from the achiral meso complexes only one enantiomer is shown. For the complex containing the diphenylpropenyl group, five structures were computed, one of the structures obtained from the syn,anti allyl complex B (B′) and those obtained from the syn,anti complex C being omitted.

Among the cyclohexenyl complexes an olefin complex with a C_s-symmetric ligand (I′) was found to be of lowest energy, although only 1.2 and 1.4 kcal/mol more stable than structures with a C_2-symmetric ligand (H″ and H′, respectively). In contrast, a diphenylallyl complex with a C_2-symmetric ligand (A″) was found to be 4 kcal/mol more stable than the most stable complex with a C_s-symmetric ligand (D′).

The large energy difference observed between the two olefin complexes (A′ and A″) resulting from nucleophilic attack at the syn,syn C_2 complex (A) may provide an explanation for the high enantioselectivity in allylations using rigid binapthyl analogue **3** and its *N*,*N*-analogue since it is generally assumed that the enantiodiscriminating step has a late transition state, resembling the product olefin complex.[23] The low selectivity observed using **3** in reactions with 3-cyclohexenyl acetate is also in accordance with the low energy difference between H″ and H′.

From the computational studies it could thus be concluded that the most stable Pd−olefin complexes with the two types of olefins have the ligands in different conformations (**28** and **29**, respectively), in line with the experimental studies of the model *cis*- and *trans*-olefin complexes.



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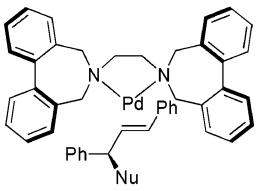
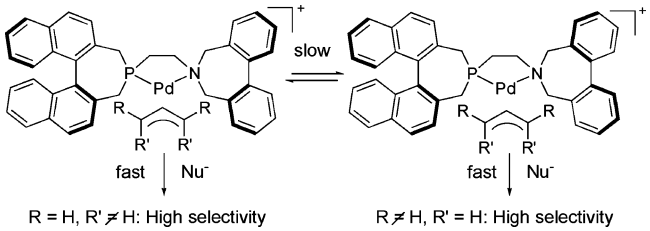


29

Although flexible ligands **5** and **6** were not able to undergo conformational change prior to nucleophilic attack in reactions with *rac*-1,3-diphenyl-3-propenyl acetate and *rac*-3-cyclohexenyl acetate, our experimental and computational studies provide clear examples of catalysts capable of adapting to the reacting substrate, since the flexible ligands evidently have the ability to change their configuration to that which is most suitable for a particular substrate. The fact that ligands **5** and **6** behave as 1:1 mixtures of configurational isomers is therefore most likely due to nucleophilic attack being fast compared to configurational change.



Conclusions

The flexible ligand 1,2-bis-[4,5-dihydro-3*H*-dibenzo[*c*−*e*]-azepino]ethane has been shown to change its configuration from *R*,*S* in its cationic η^3-1,3-diphenylallyl complex to *R**,*R** in the olefin complex resulting from nucleophilic attack at the allylic ligand. In contrast, the ligand retains its *R*,*S* configuration upon nucleophilic addition to an η^3-cyclohexenyl complex. The

(23) Saitoh, A.; Achiwa, K.; Tanaka, K.; Morimoto, T. *J. Org. Chem.* **2000**, *65*, 4227−4240.

different configurational preferences of the ligand provide an explanation for the contrasting behavior of different types of allylic substrates in Pd-catalyzed allylic alkylations employing *P*,*N*-ligands which are electronically dissymmetric and sterically exhibit C_2 or C_s-symmetry (*pseudo*-C_2- and *pseudo*-C_s-symmetric, respectively). The complexes containing the configurationally flexible ligand provide examples of a new class of self-adaptable catalytic systems.

Experimental Section

General. All air-sensitive reactions were performed in oven-dried glassware under nitrogen. CH_2Cl_2 was taken from a Glass-contour solvent-dispensing system. ^{1}H and ^{13}C NMR spectra were run at 500 and 125 MHz, respectively, and chemical shifts are reported relative to $CHCl_3$. Compounds **11**,[5] **12**,[2] bis[(η^3-cyclohexenyl)palladium chloride][7] and bis[(η^3-1,3-diphenylpropenyl)palladium chloride][8] were prepared according to published methods.

1,2-Bis-[(*R*)-4,5-dihydro-3*H*-dinaphtho[1,2-*c*:2′,1′-*e*]azepino]-ethane (13). A mixture of 2,2′-bis(bromomethyl)-1,1′-biphenyl (200 mg, 0.59 mmol), 1,2-diaminoethane (20.6 μL, 0.31 mmol), and triethylamine (2.25 mL) in PhMe (1.5 mL) was heated in SmithProcess Vial in a microwave cavity for 10 min at 160 °C. H_2O (10 mL) and saturated aqueous $NaHCO_3$ (3 mL) were added, and the mixture was extracted with CH_2Cl_2 (2 × 20 mL). The solvent was evaporated, and the crude product was purified by column chromatography on silica gel (column 2 cm × 12 cm) (CH_2Cl_2 (100 mL) and then CH_2Cl_2/MeOH 95:5) to give **13** (61 mg, 50%). ^{1}H NMR and ^{13}C NMR are in agreement with literature data.[6]

[1,2-Bis-[(*R*)-4,5-dihydro-3*H*-dinaphtho[1,2-*c*:2′,1′-*e*]azepino]-ethane] η^3-Cyclohexenyl Palladium Hexafluorophosphate (14). CH_2Cl_2 (15 mL) was added to a mixture of *R*a,*R*a-*N*,*N*-ligand **11** (66 mg, 107 μmol), bis[(η^3-cyclohexenyl)palladium chloride] (24.8 mg, 53 μmol), and $AgPF_6$ (27.1 mg, 107 μmol) in a sealed flask at −78 °C, and the mixture was degassed. The temperature was allowed to increase to 50 °C, and the mixture was stirred at that temperature under N_2 for 10 min. After rapid cooling to room temperature the mixture was filtered through a Celite plug and concentrated. After recrystallization of the crude product from CH_2Cl_2/hexane, complex **14** (72 mg, 71%) was obtained; mp 232−233 °C; $[\alpha]^{25}_D$ −440.0 (*c* 0.10, CH_2Cl_2); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.07−7.96 (m, 4H), 7.85−7.75 (m, 5H), 7.61 (d, J = 8.3 Hz, 1H), 7.54−7.47 (m, 3H), 7.42−7.33 (m, 4H), 7.31−7.19 (m, 3H), 7.17−7.09 (m, 2H), 7.03−6.98 (m, 2H), 5.63 (app t, J = 6.6 Hz, 1H), 4.41 (d, J = 12.3 Hz, 1H), 4.34 (d, J = 11.8 Hz, 1H), 4.29−4.24 (m, 2H), 4.09 (s, 2H), 4.00 (d, J = 13.5 Hz, 1H), 3.87 (m, 1H), 3.23−3.15 (m, 1H), 3.04−2.93 (m, 2H), 2.84 (d, J = 11.7 Hz, 1H), 2.30−2.23 (m, 2H), 1.74−1.64 (m, 2H), 1.55−1.45 (m, 2H), 1.27−1.18 (m, 1H), 0.96−0.86 (m, 1H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 137.4, 137.0, 136.3, 136.2, 135.6, 135.5, 134.7, 134.3, 134.2, 134.1, 132.3, 132.0, 131.9, 131.6, 131.5, 130.3, 129.9, 129.7, 129.6, 129.5, 129.3, 129.2, 129.0, 128.9, 128.8, 128.7, 128.4, 128.1, 128.0, 127.8, 127.6, 127.5, 127.4, 127.2, 127.1, 127.0, 126.9, 126.8, 107.0, 78.3, 78.2, 62.4, 61.6, 61.3, 58.7, 57.8, 55.8, 29.7, 28.1, 20.9.

[1-[(*R*)-4,5-Dihydro-3*H*-dinaphtho[1,2-*c*:2′,1′-*e*]azepino]-2-[(*S*)-4,5-dihydro-3*H*-dinaphtho[1,2-*c*:2′,1′-*e*]azepino]ethane] η^3-Cyclohexenyl Palladium Hexafluorophosphate (15). This complex was prepared from *R*a,*S*a-*N*,*N*-ligand **12** (57.6 mg, 93 μmol) by the same procedure as that used for the preparation of **14** (stirring at 50 °C for 30 min). Recrystallization from CH_2Cl_2/hexane gave **15** (64 mg, 72%); mp 217−218 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01−7.85 (m, 8H), 7.75 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 8.2 Hz, 2H), 7.49−7.36 (m, 6H), 7.33−7.15 (m, 6H), 5.52 (t, J = 6.4 Hz, 1H), 4.57 (d, J = 13.6 Hz, 2H), 4.05 (d, J = 11.7 Hz, 2H), 3.88 (d, J = 13.9 Hz, 2H), 3.83 (m, 2H), 3.56 (m, 2H), 3.10 (d, J = 11.5 Hz, 2H), 2.58 (m, 2H), 1.42−1.33 (m, 1H), 1.23−1.04 (m, 4H), 0.61−0.50 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.1, 135.1, 133.8, 133.6, 131.6, 131.5, 131.1, 130.2, 129.6, 128.7, 128.6, 128.5, 128.4, 127.9, 127.7, 127.3, 126.8, 126.7, 126.3, 105.4, 77.6, 61.4, 59.2, 55.3, 53.4, 27.6.

[1,2-Bis-[(*R*)-4,5-dihydro-3*H*-dinaphtho[1,2-*c*:2′,1′-*e*]azepino]-ethane] η^3-1,3-Diphenylpropenyl Palladium Hexafluorophosphate (16). This complex was prepared from *R*a,*R*a-*N*,*N*-ligand **11** (11.1 mg, 18 μmol) and bis[(η^3-1,3-diphenylpropenyl)palladium chloride] (6.0 mg, 9 μmol), by the same procedure as that used for the preparation of **14** (stirring at 50 °C for 20 min). Recrystallization from CH_2Cl_2/hexane gave **16** (12 mg, 62%); mp 227−229 °C; $[\alpha]^{25}_D$ −397.0 (*c* 0.125, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30−8.25 (m, 2H), 8.22−8.16 (m, 3H), 8.08−7.84 (m, 4H), 7.83−7.73 (m, 1H), 7.71−7.63 (m, 3H), 7.60−7.46 (m, 4H), 7.41−7.18 (m, 8H), 7.08−6.89 (m, 5H), 6.76−6.68 (m, 2H), 6.46−6.33 (m, 2H), 6.01 (dd, J = 13.2, 10.1 Hz, 1H), 5.46 (d, J = 13.2 Hz, 1H), 5.28 (d, J = 12.3 Hz, 1H), 4.20 (d, J = 11.9 Hz, 1H), 3.83 (d, J = 13.7 Hz, 1H), 3.81 (d, J = 10.1 Hz, 1H), 3.11−3.01 (m, 1H), 2.82 (d, J = 13.8 Hz, 1H), 2.58−2.36 (m, 4H), 2.17 (d, J = 11.9 Hz, 1H), 1.50 (d, J = 12.9 Hz, 1H), 1.37 (d, J = 13.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.6, 137.2, 136.5, 134.7, 134.2, 134.1, 133.9, 133.2, 133.1, 132.9, 132.3, 132.2, 131.7, 131.5, 130.9, 130.6, 130.0, 129.5, 129.2, 129.1, 129.0, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.4, 126.9, 126.8, 126.6, 126.5, 126.3, 126.1, 125.8, 125.7, 102.2, 92.2, 67.2, 60.1, 59.7, 59.6, 58.6, 57.8, 56.1.

[1-[(*R*)-4,5-Dihydro-3*H*-dinaphtho[1,2-*c*:2′,1′-*e*]azepino]-2-[(*S*)-4,5-dihydro-3*H*-dinaphtho[1,2-*c*:2′,1′-*e*]azepino]ethane] η^3-1,3-Diphenylpropenyl Palladium Hexafluorophosphate (17). This complex was prepared from *R*a,*S*a-*N*,*N*-ligand **12** (11.1 mg, 18 μmol) according to the procedure used for the preparation of **16** (stirring at 50 °C for 5 min). Recrystallization from CH_2Cl_2/hexane gave **17** (10 mg, 52%); mp 225−226 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, J = 8.0 Hz, 2H), 8.16 (d, J = 8.2 Hz, 2H), 8.00 (d, J = 8.2 Hz, 2H), 7.93−7.88 (m, 5H), 7.72−7.54 (m, 10H), 7.52−7.16 (m, 11H), 6.67−6.61 (m, 2H), 6.13 (t, J = 11.7 Hz, 1H), 4.59 (d, J = 11.8 Hz, 2H), 4.42 (d, J = 11.9 Hz, 2H), 3.69 (d, J = 14.3 Hz, 2H), 3.56−3.45 (m, 2H), 3.13 (d, J = 12.0 Hz, 2H), 2.56 (d, J = 14.0 Hz, 2H), 2.55−2.47 (m, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 137.1, 135.8, 135.1, 134.7, 134.0, 132.6, 131.8, 131.5, 130.5, 130.1, 129.4, 129.0, 128.9, 128.7, 128.6, 128.5, 128.3, 128.2, 128.0, 127.6, 127.1, 126.9, 126.7, 126.6, 109.5, 78.1, 78.0, 77.7, 77.5, 62.3, 58.7, 55.9.

[1,2-Bis-[4,5-dihydro-3*H*-dibenzo[*c*−*e*]azepino]ethane] η^3-Cyclohexenyl Palladium Hexafluorophosphate (18). This complex was prepared from ligand **13** (46.7 mg, 112 μmol) by the same procedure as that used for the preparation of **14** (stirring at 50 °C for 30 min). Recrystallization from CH_2Cl_2/hexane gave **18** (26 mg, 31%); mp 192−193 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 7.5 Hz, 2H), 7.63−7.44 (m, 14H), 5.60 (t, J = 6.6 Hz, 1H), 4.45 (d, J = 13.7 Hz, 2H), 4.25 (app t, J = 5.8 Hz, 2H), 4.08 (d, J = 11.9 Hz, 2H), 3.95 (d, J = 13.7 Hz, 2H), 3.63 (m, 2H), 3.22 (d, J = 11.9 Hz, 2H), 2.88 (m, 2H), 1.62−1.55 (m, 1H), 1.51−1.42 (m, 2H), 1.37−1.29 (m, 2H), 0.85−0.76 (m, 1H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 142.0, 141.3, 132.9, 131.2, 130.9, 130.3, 130.1, 129.0, 128.9, 128.6, 128.5, 106.3, 77.4, 61.5, 60.0, 56.0, 28.2, 20.4.

[1,2-Bis-[4,5-dihydro-3*H*-dibenzo[*c*−*e*]azepino]ethane] η^3-1,3-Diphenylpropenyl Palladium Hexafluorophosphate (19). This complex was prepared from ligand **13** (31.2 mg, 75 μmol) according to the procedure used for the preparation of **16** (stirring at 50 °C for 20 min). Recrystallization from CH_2Cl_2/hexane gave **19** (25 mg, 39%); mp 224−225 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 6.8 Hz, 2H), 7.58−7.46 (m, 7H), 7.45−7.33 (m, 8H), 7.09−6.88 (m, 9H), 6.18 (t, J = 11.8 Hz, 1H), 4.85 (d, J = 11.8 Hz, 2H), 4.19−4.02 (m, 2H), 3.40 (d, J = 13.0 Hz, 2H), 3.29−3.19 (m, 2H), 3.12−3.03 (m, 2H), 3.01−2.87 (m, 4H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 141.7, 141.3, 136.1, 132.8, 132.1, 131.5, 130.5, 130.1, 130.0, 129.7, 129.0, 128.9, 128.7, 128.6, 128.1, 105.1, 79.6, 60.7, 60.3, 57.9.

TRISPHAT and BINPHAT Complexes. Salts [**18**][*rac*-**20**], [**18**]-[Δ-**20**], [**18**][Δ-**21**], [**19**][*rac*-**20**], [**19**][Δ-**20**], and [**19**][Δ-**21**] were

prepared from the hexafluorophosphate precursors [**18**][BF_4] and [**19**]-[BF_4] by ion-exchange metathesis with salts [Et_2NH_2][*rac*-**20**], [cinchonidinium][Δ-**20**], and [Me_2NH_2][Δ-**21**] and were isolated by chromatography (SiO_2 or basic Al_2O_3, eluent CH_2Cl_2) as the most eluted compounds.[14]

General Procedure for the Preparation of Complexes 22−27. Ligand (**11**, **12**, or **13**, 1 μmol), olefin (dimethylfumarate or maleic anhydride, 1 μmol), and Pd_2dba_3·$CHCl_3$ (0.5 μmol) were stirred in $CDCl_3$ in the glove box. Complex formation was complete after 30 min when maleic anhydride was used and after 8 h when dimethylfumarate was used. All the aromatic protons in the ^{1}H NMR spectra were localized in the region between 7.20 and 8.00 ppm. Assignment of the signals was not possible due to the signals from dibenzylideneacetone and chloroform. **22**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20−8.00 (aromatic protons), 4.47 (d, J = 10.6 Hz, 2H), 3.98 (d, J = 13.8 Hz, 2H), 3.82 (d, J = 13.6 Hz, 2H), 3.19 (s, 2H), 3.10 (d, J = 8.8 Hz, 2H), 2.94 (d, J = 10.6 Hz, 2H), 2.55 (d, J = 9.0 Hz, 2H), 2.35 (s, 6H). **23**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20−8.00 (aromatic protons), 4.41 (d, J = 14.2 Hz, 1H), 4.21 (d, J = 10.7 Hz, 1H), 4.15 (d, J = 14.2 Hz, 1H), 4.11 (d, J = 11.0 Hz, 1H), 3.99 (d, J = 14.2 Hz, 1H), 3.66 (d, J = 13.9 Hz, 1H), 3.51 (m, 1H), 3.24 (d, J = 9.8 Hz, 1H), 3.21 (d, J = 10.7 Hz, 1H), 3.11 (d, J = 9.5 Hz, 1H), 2.83 (m, 2H), 2.57 (s, 3H), 2.47 (d, J = 12.3 Hz, 1H), 2.39 (m, 1H), 1.94 (s, 3H). **24**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20−8.00 (aromatic protons), 4.38 (d, J = 11.0 Hz, 1H), 4.18 (d, J = 11.0 Hz, 1H), 4.40 (m, 2H), 3.92 (m, 2H), 3.37 (d, J = 3.8 Hz, 1H), 3.24 (d, J = 3.8 Hz, 1H), 3.18 (d, J = 11.0 Hz, 1H), 3.07 (m, 1H), 2.80 (m, 2H), 2.70 (m, 2H). **25**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20−8.00 (aromatic protons), 4.19 (d, J = 11.0 Hz, 2H), 4.06 (s, 4H), 3.33 (s, 2H), 3.24 (m, 2H), 3.15 (d, J = 11.0 Hz, 2H), 2.60 (m, 2H). **26**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20−8.00 (aromatic protons), 4.43 (d, J = 11.0 Hz, 2H), 3.99 (d, J = 13.3 Hz, 2H), 3.64 (d, J = 13.5 Hz, 2H), 3.37 (s, 2H), 3.23 (d, J = 11.3 Hz, 2H), 3.05 (s, 6H), 3.04 (d, J = 10.1 Hz, 2H), 2.88 (d, J = 10.1 Hz, 2H). ^{13}C NMR (125 MHz, CDCl3) δ 174.5 (C═O, 141.5, 141.0, 133.6, 133.4, 132.3, 131.8, 130.0, 128.9, 128.8, 128.2, 127.4, 60.5, 60.0, 55.9, 50.2 (CH_3), 40.8 (olefinic). One aromatic carbon missing, the signal is probably hidden under the signals from dibenzylideneacetone. **27**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20−8.00 (aromatic protons), 4.11 (d, J = 11.7 Hz, 2H), 4.07 (d, J = 13.9 Hz, 2H), 3.81 (d, J = 13.6 Hz, 2H), 3.42 (s, 2H), 3.27 (d, J = 11.7 Hz, 2H), 3.23 (m, 2H), 2.82 (m, 2H). ^{13}C NMR (125 MHz, CDCl3) δ 171.5 (C═O), 141.4, 141.1, 133.0, 131.8, 130.8, 129.5, 129.1, 128.3, 128.2, 127.9, 127.8, 60.3, 59.4, 55.0, 40.6 (olefinic). One aromatic carbon missing, the signal is probably hidden under the signals of dibenzylideneacetone.

X-ray. Structure determination of **26**: $C_{36}H_{36}N_2O_7Pd$, M_r = 715.1, monoclinic, *I*2/*a*, brown needle, a = 23.10 (2) Å, b = 12.32 (1) Å, c = 12.78 (1) Å, β = 92.03 (1)°, 299 K, Z = 4, R = 0.076, GOF = 1.10. Data collected on a Bruker-Nonius KappaCCD diffractometer, solution with direct methods, refinement on F^2.

Structure determination of **27**: $C_{34}H_{30}N_2O_3Pd$, M_r = 621.0, orthorhombic, $P2_12_12_1$, pale-yellow plate, a = 8.3600 (14) Å, b = 12.466 (5) Å, c = 30.729 (12) Å, 299 K, Z = 4, R = 0.123, GOF = 1.18, Data collected on a Bruker-Nonius KappaCCD diffractometer, solution with direct methods, refinement as inversion twin on F^2.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of Pd allyl and olefin complexes, computational details, and Ortep plots of **27** and **28**. This material is available free of charge via the Internet at htpp://pubs.acs.org.

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