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Atropoisomerism in Phosphepines and Azepines

Ester Fjellander, Zoltán Szabó, and Christina Moberg*

KTH School of Chemical Science and Engineering, Department of Chemistry, SE 100 44 Stockholm, Sweden

kimo@kth.se

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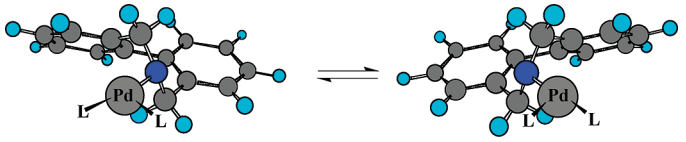

Free energy barriers to biaryl tropoinversion in metal complexes with tropos phosphepine and azepine ligands were determined by temperature-dependent ^{31}P NMR inversion-transfer experiments and line shape analysis of the temperature-dependent ^{1}H NMR spectra, respectively. The barrier in the $PdCl_2$ complex of the azepine ligand was found to be slightly higher than that of the corresponding free ligand. Studies of a tridentate azepine ligand suggested that configurational change takes place without prior decoordination from the metal.

Introduction

Configurationally flexible ligands with their stereochemistry controlled by a neighboring chiral group have been the subject of extensive recent studies.[1] Among the available flexible structural motifs, tropos biaryl ligands, which can rapidly interconvert due to a low energy barrier for rotation around the biaryl axis, have been particularly well studied.[2] The topic was pioneered by Mikami and co-workers, who in complexes obtained by replacement of the binaphthyl moiety in BINAP for the analogous conformationally flexible bis(phosphanyl)biphenyl (BIPHEP, A, Figure 1) were able to control the configuration of the flexible element by virtue of a second coordinating chiral ligand.[3,4] This allowed the tropos phosphanes to be successfully applied in asymmetric catalysis in the presence of the chiral activator.[5,6] Other chirally flexible systems based on benzophenone and diphenylmethane have been shown to function in an analogous way.[7]

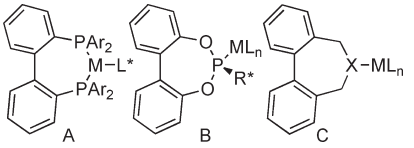

FIGURE 1. Metal complexes with tropos ligands: (A) BIPHEP; (B) 2,2-biphenol; (C) dibenzoazepine (X = NR) or dibenzophosphepine (X = PR).

Stereochemical control in atropisomeric ligands can also be achieved via chirality transfer from a stereogenic center incorporated in the same ligand as the biphenyl group. This has been realized for a variety of structures containing 2,2′-biphenol residues (B). Early examples include phosphites used in catalytic hydrogenations[8] and conjugate additions,[9] as well as phosphoramidites, where binaphthyl groups could be replaced by suitably substituted biphenyls without any observed loss in enantioselectivity.[10] More recently this concept has been further exploited in a number of cases.[11]

*To whom correspondence should be addressed. Fax: (+46) 8 791 2333.

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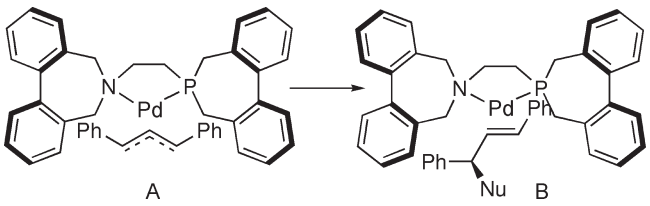

FIGURE 2. η^3-Allyl complex with C_s conformation and olefin complex with C_2 conformation of ligand.

Dibenzoazepines (C, X = NR)[12] and dibenzophosphepines (C, X = PR)[13] are nonplanar tropos analogues of the more extensively studied stereochemically rigid dinaphthoazepines[14] and dinaphthophosphepines.[15] The flexible dibenzoazepine[16] and dibenzophosphepine[17] structures have recently been used in catalytic reactions, and the former has also been used for determination of the absolute configuration of carboxylic acids.[18]

We have taken advantage of the tropos nature of the dibenzo derivatives in the design of electronically dissymmetric ligands with the ability to convert between *pseudo*-C_2 and *pseudo*-C_s symmetry,[19] and thereby to adapt their structure to a reacting substrate.[20] In model complexes containing dibenzoazepines it was shown that the C_s conformation is favored in the presence of η^3-allyl ligands, whereas the ligand adopts C_2 conformation in the presence of trans olefins (Figure 2). In reactions where promotion of high enantioselectivities relies on the ability of the tropos ligand to adopt both tropoisomeric conformations within the catalytic cycle, conformational change needs to be rapid in relation to the catalytic reaction.[21] For this reason knowledge about the rate of configurational change may be essential for successful ligand design.

Energy barriers have been determined for several types of tropos structures, in the free ligands as well as in their metal complexes. Lower free energy barriers are generally found for the free ligands than for their metal complexes. The activation barrier to tropoisomerization for bis(diphenylphosphino)biphenyl (BIPHEP) was determined to be 22 kcal mol^{-1}, and the ligand racemizes readily above 25 °C.[22] In contrast, tropoinversion in a Pd(II) complex of the same ligand containing (*R*)-2,2-diamino-1,1-binaphthyl was observed only by heating at 80 °C.[23] Slightly lower free energy barriers were found for 2-(diphenylphosphino)-2′-(dimethylamino)biphenyl and 2-(dicyclohexylphosphino)-2′-(dimethylamino)biphenyl, 17.5 and 18.8 kcal mol^{-1}, respectively, whereas the barrier to tropoisomerization for Pd(II) complexes was found to be around 22 kcal^{-1}.[24] The barriers found for 2,2′-biphenol-containing phosphites are even lower, as expected due to a lower degree of sterical crowding. For a bis(3,5-*tert*-butylphenol) incorporated in a sterically congested phosphite the free energy barrier to biphenyl rotation was found to be 10.2−10.8 kcal mol^{-1},[25] and that in a less crowded phosphite was 8.5 kcal mol^{-1},[11c] whereas that of a Rh complex containing a phosporamidite with biphenol was determined to be 13−14.5 kcal mol^{-1} depending on the solvent;[26] single phosphorus signals were observed in the ^{31}P NMR spectrum of the free ligand as well as of the metal complex at room temperature.

TABLE 1. Free Energy Barriers to Conformational Inversion in 2,2′-Bridged Biaryls

X	$\Delta G^{\ddagger}$ (kcal mol^{-1})
CH_2	12.3[a,27]
$C(CO_2Et)_2$	14.0 at 282 K[28]
$C(OR)_2$	14.0−14.8 at 258−278 K[29]
O	9.2 ± 1.0 at 189 K[30]
S	16.1 ± 0.3 at 315 K[30]
SO_2	18.2 at 360 K[28]
NMe_2Br	13.4 at 272 K[28]
POMe	19.3 at 298 K[17a]

[a]No temperature given.

Values for interconversion of the two enantiomeric forms of several 2,2′-bridged biphenyls (C, Figure 1) have also been determined, by experimental as well as theoretical methods. For both electronic and steric reasons, the values vary with the type of X atom or group (C, Figure 1). Some examples are shown in Table 1.

From these values it is obvious that not only the heteroatom incorporated in the seven-membered ring is important for the size of the inversion barrier, but also the groups

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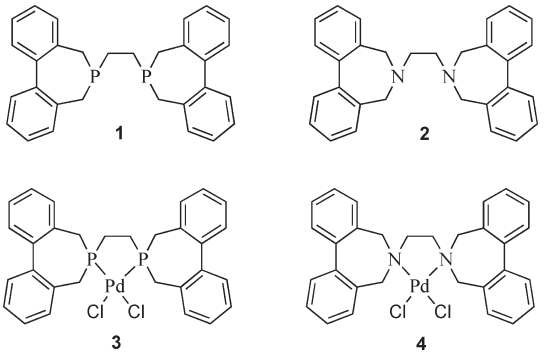
attached to that atom (compare CH_2 and $C(CO_2Et)_2$, and S and SO_2).

Information about the behavior of azepines and phosphepines is, however, scarce; in addition to the computed value for a *N*,*N*-dimethylammonium derivative,[28] to our knowledge rotation barriers only for *N*-methylazepines with substituents in the 6- and 6′-positions (NO_2: 30 kcal mol^{-1}; and F: 28 kcal mol^{-1}) are known,[31] and the only reported values for phosphepine-containing ligands are those determined for phosphinites (see later).[17a] Due to our interest in self-adaptable ligands,[20] we needed information about the barriers to tropoisomerization of metal complexes of the two types of ligands and therefore decided to study their dynamic behavior.

Results and Discussion

Preparation of Ligands and Metal Complexes. Phosphorus and nitrogen ligands **1** and **2** were selected as suitable structures for studies of inversion barriers. The $PdCl_2$ complex **3** was prepared by reaction of bis(acetonitrile)-dichloropalladium(II) with **1** prepared from bis(dichlorophosphino)ethane and bis(lithiomethyl)biphenyl. We have only been able to isolate this type of ligand as their complexes with BH_3,[19b] and rapid decomposition precluded studies of the free ligand **1**. Complex **4** was obtained in an analogous way from **2**, prepared as previously described[16a] by reaction of 2,2′-bis(bromomethyl)biphenyl[32] with 1,2-diaminoethane.



Variable-Temperature NMR Measurements. To determine the energy barrier to configurational inversion, model complexes **3** and **4** were studied with variable-temperature dynamic NMR spectroscopy. The nitrogen (phosphorus) atoms are not stereogenic, and therefore the only stereogenic elements are the two biphenyl axes. *Like* configuration of the biphenyls gives rise to a pair of enantiomeric complexes with C_2 symmetry, while an *unlike* configuration results in a single C_s-symmetric complex.

The ^1H and proton decoupled ^{31}P NMR spectra (Figure 3 and Supporting Information) of complex **3** recorded at room temperature in $CDCl_3$ show the two diastereomeric complexes, present in a 4:1 ratio. The appearance of separated signals in both spectra indicates that the isomers are in slow exchange on the NMR time scale determined by their ^1H and ^{31}P chemical shift differences. While the proton signals in the lower field region are well separated, the integrals indicate that a doublet from the minor conformer is partly hidden by the doublet at 2.07 ppm, and that another minor doublet is completely hidden by the doublet at 2.42 ppm. These observations are confirmed by the $^1H-^1H$-COSY spectrum, since the signal at 2.42 ppm shows cross-peaks with both the major doublet at 4.15 ppm and the minor doublet at 5.01 ppm. Likewise, the major doublet at 2.07 ppm couples to the signal at 3.65 ppm, while the minor doublet at 2.04 ppm, which appears as a shoulder at the major signal at 2.07 ppm, couples to the one at 3.52 ppm. These eight doublets originate from the benzylic methylene protons of the diphosphine ligand. The protons of the ethylene bridge between the phosphorus atoms give rise to relatively broad signals, especially for the major isomer, probably as a result of the flexibility of the five-membered chelate ring. The COSY spectrum also shows cross-peaks between these pairs of methylene protons (2.52 and 1.33 ppm for the major complex and at 1.80 and 1.62 ppm for the minor complex). Surprisingly, no couplings to phosphorus were observed.

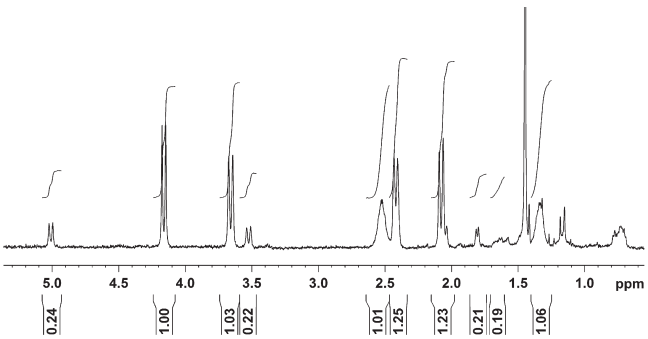


FIGURE 3. The nonaromatic region of the ^1H NMR spectrum for complex **3** recorded in $CDCl_3$ at 298 K.

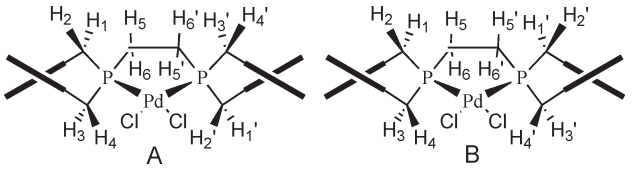


FIGURE 4. C_2- (A) and C_s-symmetric (B) $PdCl_2$ complexes.

Assignment of the proton signals to the two conformational isomers and mapping of their exchange pattern were made with the help of a two-dimensional NOESY (EXSY)[33] spectrum (the spectrum, recorded in $CDCl_3$ at 298 K, is given in the Supporting Information). This allowed the major complex to be identified as the C_2-symmetric conformer and the minor complex as that having C_s symmetry. Both conformers possess only one symmetry element, making the protons equivalent two by two (H_1 and H_1', H_2 and H_2', etc., Figure 4). Upon flipping one of the biphenyl units, the symmetry element changes from a C_2 axis to a mirror plane or vice versa. Therefore, a proton in the nonflipping part of the complex and its previously symmetry-equivalent proton in the flipping part of the complex are exchanged with a pair of nonequivalent protons in the new isomer (for example, symmetry-equivalent H_1 and H_1' exchange with

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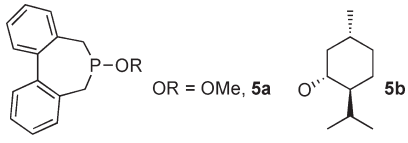
(33) Exchange Spectroscopy. The same pulse sequence is used in these two experiments. A compound with both exchange and NOE effects will therefore show both in the same spectrum.

nonequivalent H_1 and H_3', and symmetry-equivalent bridge protons H_5 and H_5' exchange with H_5 and H_6' in the new isomer). In this way, all four different bridge proton signals (two signals for the C_s complex and two for the C_2 complex) are in chemical exchange with each other. The eight different benzylic signals (four from each isomer) become divided into two groups of four signals each (two from each isomer), where all signals within a group are connected by exchange.

To determine the barrier to tropoisomerization, the temperature dependence of the ^{1}H and ^{31}P spectra was studied. Only a relatively narrow temperature range (between 293 and 328 K) could be used in order to avoid thermal decomposition of the complex. In this temperature range the exchange rate was not fast enough to affect the line width of the NMR signals significantly; approximately only a 5 Hz difference in the line widths was observed between the ^{1}H and ^{31}P spectra measured at the lowest and the highest temperatures. Therefore, to increase the accuracy of the determination of the kinetic parameters, the rate constants were determined at different temperatures by one-dimensional inversion-transfer experiments,[34] as detailed in the Supporting Information. Because of the multisite exchange pattern observed in the proton spectrum, proton decoupled ^{31}P NMR inversion-transfer experiments were performed. Since only two signals can be observed in the ^{31}P spectrum, from the dynamic NMR point of view the exchange can be treated as a two-site system. The large chemical shift difference (almost 1000 Hz) between the two phosphorus signals from the two isomers served as an excellent possibility to their selective excitation. Five experiments were carried out at every 5 deg in the temperature range between 293 and 313 K by inverting the signal for the major isomer at 73.8 ppm. The rate constants at each temperature were calculated by a nonlinear fitting procedure. The experimental and the fitted curve showing the time dependence of the signal intensities are given as Supporting Information. Linear regression of the data using the Eyring equation resulted in the following activation parameters for the conformational change: $\Delta H^{\ddagger} = 19.8 \pm 1.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = 5.1 \pm 5.3$ cal mol^{-1} K^{-1}, where the errors are from the least-squares fit (the plot is shown in the Supporting Information). The activation enthalpy and entropy are close to those previously determined by us for the two phosphinite ligands **5a** and **5b** (shown below) ($\Delta G^{\ddagger} = 19.3$ and 18.5 kcal mol^{-1} at 298 K, respectively) containing the same phosphepine unit.[17a] It thus seems that coordination of the phosphorus lone pair to palladium chloride does not impair the flipping process of the biphenyl unit to any larger extent.



In contrast to complex **3**, the nitrogen analogue **4** is in fast exchange at room temperature. Only three nonaromatic proton resonances were observed in dichloromethane-d_2, two doublets for the benzylic protons at 4.92 and 3.44 ppm, and a singlet for the bridge protons at 2.97 ppm (see the Supporting Information). However, at 180 K the exchange between the conformational isomers was slow enough to observe their separate NMR signals. The isomers were present in a ratio of approximately 3:1. With help of a COSY spectrum, all peaks for the major complex and benzylic signals for the minor complex could be assigned.

To determine the barriers to conformational inversion, line shape simulations were performed separately for the two benzylic signals in $CDCl_3$, every 10 deg in the temperature range from 238 to 298 K (see the Supporting Information). Linear regression of the rate data using the Eyring equation gave two values for the activation parameters, which were identical within experimental error. For the low field signal we obtained $\Delta H^{\ddagger} = 14.7 \pm 0.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = 15.9 \pm 3.0$ cal mol^{-1} K^{-1}, while the high field signal yielded $\Delta H^{\ddagger} = 14.7 \pm 1.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = 15.7 \pm 3.6$ cal mol^{-1} K^{-1} (errors are from the least-squares fit).

For comparison, a similar study was performed on free ligand **2** (see the Supporting Information). The line shape was simulated every 20 deg from 238 to 298 K. Linear regression of the rate constants in an Eyring plot gave the following activation parameters: $\Delta H^{\ddagger} = 11.3 \pm 1.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = 0.8 \pm 6.2$ cal mol^{-1} K^{-1}.

Mechanism for Conformational Change. Inversion of configuration in BIPHEP complexed to Ru(II) was suggested by Mikami to proceed either via rupture of a Ru−P bond followed by rotation around the biphenyl axis, or directly within the seven-membered metallacycle through a planar seven-membered transition state.[3] Experimental studies by Gagné did not allow a definite distinction between the two possibilities to be determined,[35] but later theoretical studies by Mikami demonstrated that isomerization is preceded by one-arm decomplexation.[4,36]

The situation in complexes **3** and **4** is different since the metal does not form part of the seven-membered ring, and therefore decomplexation should not be required for steric reasons. The slightly different barriers for the metal complex **4** and the free ligand **2** indeed suggest that inversion in **3** and **4** is not preceded by decoordination. In addition, the modest ΔS values found serve as an indication that no bond breaking takes place in the transition state; these values are, however, somewhat uncertain and cannot be used to unambiguously distinguish between the two mechanisms. To gain the required insight into the inversion process, tropoinversion of the palladium(II) chloride complex of ligand **6**, prepared from 1,1,1-tris(aminomethyl)ethane and 2,2′-bis(bromomethyl)biphenyl, was studied. The chelate rings formed from **6** and **4** differ in size by one atom, but they are assumed to have similar stability[37] and the likelihood for decoordination should therefore be comparable in the two cases. In a situation where decoordination does not occur, the size of the chelate ring is expected to have a negligible effect on the process since the conformation of that ring is affected only to a minor extent by the flipping process. The dynamic behavior of the Pd(II) complex of **6**, as revealed by NMR spectroscopic investigations, was therefore envisaged to serve as a

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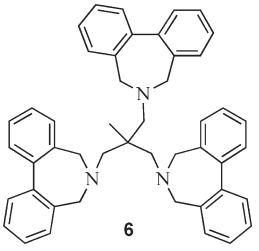
suitable probe for studies of the mechanism for biaryl tropoinversion.



6

This ligand contains three nitrogen atoms and is potentially tridentate, although with Pd(II) bidentate coordination and square-planar geometry are expected, leaving one ligand arm free. Several dynamic processes are possible. Inversion at the noncoordinated nitrogen atoms and conformational changes in the seven-membered chelate ring are assumed to be rapid on the NMR time scale at room temperature. This leaves two basic processes to consider: the decoordination−recoordination of nitrogen to palladium, and the inversion of axial chirality ("flip") of the biphenyl systems. Moreover, the rate of tropoisomerization might be different for coordinated and free ligand arms (as indeed observed for **2** and its metal complex **4**), and recoordination to the same nitrogen atom might be more facile than coordination to the previously free arm, allowing inversion of nitrogen in the "coordinated" arm.

Eight different situations can be identified,[38] each giving rise to one or more complexes. Each situation is expected to give rise to characteristic ^{1}H NMR patterns (see the Supporting Information for an analysis of all possible situations). The experimental ^{1}H NMR spectrum of the $PdCl_2$ complex of **6** (**7**) at room temperature exhibited four doublets of equal intensity and one singlet with twice the intensity of each doublet. This pattern is compatible only with a situation where all biaryls undergo rapid inversion and where both metal decoordination−recoordination and ligand exchange are slow, thus demonstrating that tropoisomerization takes place while the ligand is coordinated to palladium. This conclusion is in accordance with the slightly lower energy barrier to tropoisomerization observed for dibenzoazepine ligand **2** than for its complex with palladium chloride, **4**. The instability of the corresponding phosphorus ligand did not allow any conclusion regarding the mechanism for configurational inversion in its complex with palladium(II).

Conclusion

Energy barriers for inversion of configuration were determined for palladium chloride complexes of dibenzophosphepine and dibenzoazepines ligands as well as for the free nitrogen ligand. The observation of a higher barrier for the palladium complex than for the free ligand suggests that decoordination does not take place prior to configurational change. This conclusion was corroborated by a ^{1}H NMR study of the palladium chloride complex of a tridentate dibenzoazepine ligand. As a consequence, tropoisomerization observed upon nucleophilic attack on a Pd(II) η^3-allyl complex containing a dibenzoazepine ligand, to yield a Pd(0) olefin complex, does not require decoordination of the metal (see Figure 2).

Experimental Section

[1,2-Bis(4,5-dihydro-*3H*-dibenzo[*c*-*e*]phoshepino)ethane]dichloropalladium (3). All manipulations were performed under N_2. *n*-BuLi in Et_2O (4.5 mL, 2.1 M, 9.45 mmol) was added dropwise to a solution of 2,2′-dimethylbiphenyl (720 mg, 3.95 mmol) and freshly distilled TMEDA (1.43 mL, 9.48 mmol) in Et_2O (10 mL) at 0 °C. The mixture was stirred at room temperature for 25 h, then the lithium salt formed was filtered off and dried under vacuum (yellow powder, 825 mg, 1.93 mmol, 49%). 1,2-Bis(dichlorophosphino)ethane (146 μL, 0.96 mmol) dissolved in hexane (5 mL) was added dropwise to a slurry of the lithium salt in hexane (25 mL) at −78 °C, and the reaction mixture was allowed to reach room temperature over a period of 4 h. After 20 h of reaction time, the supernatant was decanted. Evaporation of hexane gave, according to ^{1}H and ^{31}P NMR, the crude ligand together with other compounds with unknown structures as a white milky oil (122 mg) that was dissolved in benzene (5 mL). Addition of a small amount of bis(acetonitrile)-dichloropalladium (14 mg, 54.0 μmol) gave, after stirring at room temperature for 21 h, a precipitate that was isolated by centrifugation and removal of the supernatant consisting of **3** (27 mg, white solid). Ligand **1**: ^{1}H NMR ($CDCl_3$): δ 2.67−2.58 (m), 2.40−2.28 (m), 2.18−2.09 (m); aromatic signals overlap with those from byproduct. ^{31}P NMR ($CDCl_3$): δ 4.4, 3.5. Complex **3**: ^{1}H NMR ($CDCl_3$; see Figure 4 for numbering) C_2 isomer: δ 7.94 (d, J = 6.4 Hz, 2H), 7.31−7.11 (m, 6H), 7.09−6.92 (m, 6H), 6.86 (br d, J = 5.6 Hz, 2H), 4.15 (d, J = 13.4 Hz, H_2 and $H_{2'}$), 3.65 (d, J = 13.4 Hz, H_3 and $H_{3'}$), 2.52 (br s, H_6 and $H_{6'}$), 2.42 (d, J = 13.4 Hz, H_1 and $H_{1'}$), 2.07 (d, J = 15.2 Hz, H_4 and $H_{4'}$), 1.33 (br s, H_5 and $H_{5'}$). C_s isomer: δ 8.00 (br s, 2H), 7.31−7.11 (m, 6H), 7.09−6.92 (m, 6H), 6.88 (br, 2H), 5.01 (d, J = 14.3 Hz, H_4 and $H_{4'}$), 3.6 (d, J = 14.8 Hz, H_1 and $H_{1'}$), 2.42 (hidden, H_3 and $H_{3'}$), 2.04 (partly hidden, H_2 and $H_{2'}$), 1.80 (br s, 2H), 1.62 (br s, 2H). The rate of exchange between the two isomers was in the intermediate range of the NMR time scale determined by the ^{13}C chemical shift differences of the corresponding carbon atoms, hence only very broad signals could be observed, which prevented us from assigning the individual carbon signals for the isomers. ^{31}P NMR ($CDCl_3$): δ 73.6 (C_2 isomer), 69.1 (C_s isomer). HRMS (m/z) $[M - Cl]^+$ calcd 591.038, found 591.037.

[1,2-Bis(4,5-dihydro-*3H*-dibenzo[*c*-*e*]azepino)ethane]dichloropalladium (4). 1,2-Bis[4,5-dihydro-*3H*-dibenzo[*c*-*e*]azepino]ethane[20] (28.1 mg, 67.5 μmol) and bis(acetonitrile)dichloropalladium (17.5 mg, 67.5 μmol) were dissolved in freshly distilled benzene (6 mL) and the solution was stirred at room temperature for 22 h. The mixture was centrifuged and the supernatant removed. The precipitate was washed twice with dry benzene and then dried under vacuum to give **4** as a yellow solid (35 mg, 87%). ^{1}H NMR (CD_2Cl_2): δ 7.63 (d, J = 8.0 Hz, 4H), 7.58−7.50 (m, 8H), 7.45−7.40 (m, 4H), 4.92 (d, J = 13.2 Hz, 4H), 3.44 (d, J = 13.1 Hz, 4H), 2.97 (br s, 4H). ^{13}C NMR ($CDCl_3$) δ 140.8 132.3 131.1 129.7 128.1 128.0 62.8 60.1. HRMS (m/z) $[M - Cl]^+$ calcd 557.097, found 557.096.

1,1,1-Tris[(4,5-dihydro-*3H*-dibenzo[*c*-*e*]azepino)methyl]ethane (6). 2,2′-Dibromomethyl-1,1′-biphenyl (827 mg, 2.43 mmol) and NEt_3 (0.7 mL, 5 mmol) were added to a solution of 1,1,1-tris(aminomethyl)ethane[39] (95 mg, 0.85 mmol) in acetonitrile (2 mL), and the mixture was stirred at 60 °C for 24 h. K_2CO_3 (0.5 M aqueous solution, 10 mL) was added and the mixture was extracted 3 times with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and concentrated in vacuo to give the crude product as a brown solid. Flash chromatography (silica gel, hexanes:EtOAc 10:1 with ca. 1% NEt_3 added) afforded the product as a white solid (95 mg, 145 μmol, 18%). Part of this

(38) Eight unlikely or irrelevant situations are not considered.

(39) Brown, E. C.; Johnson, B.; Palavicini, S.; Kucera, B. E.; Casella, L.; Tolman, W. B. *Dalton Trans.* **2007**, 3035–3042.

solid was recrystallized from toluene/EtOH for characterization. ^{1}H NMR ($CDCl_3$): δ 7.58−7.32 (m, 24H, aromatic), 3.53 (s, 12H, benzylic), 2.73 (s, 6H, methylene), 1.26 (s, 3H, methyl). ^{13}C NMR ($CDCl_3$): δ 141.3, 136.1, 129.6, 127.8, 127.7, 127.5 (aromatic), 62.3 (methylene), 58.3 (benzylic), 44.6 (quaternary), 21.9 (methyl). Upon standing in air compound **6** formed a complex with water with ^{1}H NMR signals separate from those of **6**: δ 8.00−7.25 (m, 24H, aromatic), 3.81 (br s, 12H, benzylic), 3.28 (s, 6H, methylene), 1.61 (s, 3H, methyl). NMR assignments are based on EXSY crosspeaks with the free compound. HRMS (*m*/*z*) $[M + H]^+$ calcd 652.369, found 652.369.

[1,1,1-Tris[(4,5-dihydro-*3H*-dibenzo[*c*-*e*]azepino)methyl]ethane]-dichloropalladium (7). 1,1,1-Tris[(4,5-dihydro-*3H*-dibenzo[*c*-*e*]-azepino)methyl]ethane (2.6 mg, 3.99 μmol) and bis(acetonitrile)-dichloropalladium (1.0 mg, 3.93 μmol) were placed in an NMR tube, which was then sealed. After the air was exchanged for N_2, $CDCl_3$ (0.5 mL) was added, and the mixture was stirred vigorously for 30 s, causing the solids to dissolve. ^{1}H NMR indicated complex formation. The complex was only moderately stable in solution at room temperature, and precipitation of Pd-black could be observed after ca. 10 h. ^{1}H NMR ($CDCl_3$): δ 7.93 (d, J = 7.2 Hz, 2H, aromatic), 7.72 (d, J = 7.6 Hz, 2H, aromatic), 7.62−7.33 (m, 18H, aromatic), 7.17 (d, J = 7.2 Hz, 2H, aromatic), 5.17 (d, J = 13.2 Hz, 2H, benzylic, coordinated arm), 5.08 (d, J = 12.5 Hz, 2H, benzylic, coordinated arm), 3.47 (d, J = 13.1 Hz, 2H, benzylic, coordinated arm), 3.42 (d, J = 12.8 Hz, 2H, benzylic, coordinated arm), 3.35 (s, 4H, free benzylic), 2.90 (s, 4H, methylene, coordinated arm), 2.70 (s, 2H, free methylene), 1.26 (s, 3H, methyl); assignments are based on an EXSY spectrum. In addition to these signals, signals from free triamine, its water complex, and free acetonitrile were observed. The ^{13}C NMR spectrum could not be recorded since some carbons are coupled to the quadrupolar ^{14}N atoms which resulted in broad signals, and therefore long experimental time was needed in order to obtain a satisfactory signal-to-noise ratio; during this time the complex decomposed.

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Supporting Information Available: ^{1}H NMR spectra of **3**, **4**, **6**, and **7**, temperature-dependent ^{1}H NMR spectra of **2** and **4**, ^{13}C NMR spectra of **4** and **6**, ^{31}P NMR spectra of **1** and **3**, EXSY/NOESY spectra for **3** and **7**, Eyring plots for **2**, **3**, and **4**, peak intensities from inversion transfer experiments for **3**, and analysis of stereodynamics of **7**. This material is available free of charge via the Internet at http://pubs.acs.org.