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Sterically-Directed Consecutive and Size-Selective Self-Assembly of Palladium Diphosphane Complexes with an Ar-BIAN Ligand: Unexpected Formation of Pentameric and Hexameric Aggregates**

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Abstract: The coordination properties of *N*,*N*′-bis[4-(4-pyridyl)phenyl]acenaphthenequinonediimine (L^1) and *N*,*N*′-bis[4-(2-pyridyl)phenyl]acenaphthenequinonediimine (L^2) were investigated in self-assembly with palladium diphosphane complexes [Pd(P^P)(H_2O)$_2$](OTf)$_2$ (OTf = triflate) by using various analytical techniques, including multinuclear (^{1}H, ^{15}N, and ^{31}P) NMR spectroscopy and mass spectrometry (P^P = dppp, dppf, dppe; dppp = bis(diphenylphosphanyl)propane, dppf = bis(diphenylphosphanyl)ferrocene, and dppe = bis(diphenylphosphanyl)ethane). Beside the expected trimeric and tetrameric species, the interaction of an equimolar mixture of $[Pd(dppp)]^{2+}$ ions and L^1 also generates pentameric aggregates. Due to the *E*/*Z* isomerism of L^1, a dimeric product was also observed. In all of these species, which correspond to the general formula $[Pd(dppp)L^1]_n(OTf)_{2n}$ ($n = 2$–5), the L^1 ligand is coordinated to the Pd center only through the terminal pyridyl groups. Introduction of a second equivalent of the $[Pd(dppp)]^{2+}$ tecton results in coordination to the internal, sterically more encumbered chelating site and induces enhancement of the higher nuclearity components. The presence of higher-order aggregates ($n = 5$, 6), which were unexpected for the interaction of *cis*-protected palladium corners with linear ditopic bridging ligands, has been demonstrated both by mass-spectrometric and DOSY NMR spectroscopic analysis. The sequential coordination of the $[Pd(dppp)]^{2+}$ ion is attributed to the dissimilar steric properties of the two coordination sites. In the self-assembled species formed in a 1:1:1 mixture of $[Pd(dppp)]^{2+}$/$[Pd(dppe)]^{2+}$/L^1, the sterically more demanding $[Pd(dppp)]^{2+}$ tectons are attached selectively to the pyridyl groups, whereas the more hindered imino nitrogen atoms coordinate the less bulky dppe complexes, thus resulting in a sterically directed, size-selective sorting of the metal tectons. The propensity of the new ligands to incorporate hydrogen-bonded solvent molecules at the chelating site was confirmed by X-ray diffraction studies.

Keywords: aggregation · bridging ligands · phosphane ligands · self-assembly · steric hindrance

Introduction

Steric interactions appear in many different forms in coordination chemistry. They affect the structural, physical, and chemical properties of coordination compounds, and, in the case of homogeneous catalytic transformations, they influence rates and selectivities.[1] Steric effects manifest themselves in a variety of ways in self-assembled metallamacro-

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[**] Ar-BIAN = bis(aryl)acenaphthenequinonediimine.

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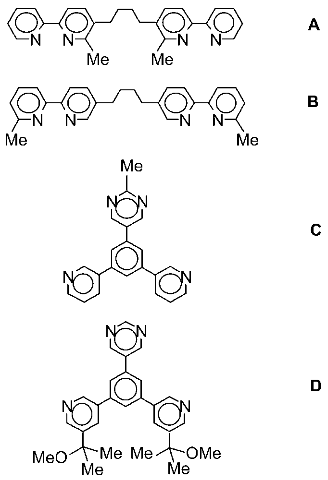
cycles. A group of systematic studies that focused on the potential effects of noncovalent interactions in self-assembly exploited the complementary arrangements of ligands that possess dissimilar steric demands. It has been shown that ditopic ligands in which two 6-methyl-2,2′-bipyridine units are connected by a $(CH_2)_4$ linker through C5 or C5′ (**A** and **B**, respectively; Scheme 1) form heterotopic dinuclear palladium complexes, whereas homo-complexation gives a mixture of oligomeric products.[2] The enhanced steric demands of 2,2′,6,6′-tetramethyl-4,4′-bipyridine (4,4′-bpy*) relative to unsubstituted 4,4′-bipyridine (4,4′-bpy) resulted in an alternate arrangement of the bridging ligands in the tetrameric ion $[Pd_2(en)_2(4,4'\text{-bpy})(4,4'\text{-bpy*})]_2^{8+}$ (bpy = bipyridine, en = ethylenediamine).[3] Similarly, the steric difference between 4,4′-bpy* and 4,4′-bis(4-pyridyl)biphenyl (4,4′-bpyPh) resulted in a spontaneous formation of the rectangular $[Pd_2(en)_2(4,4'\text{-bpyPh})(4,4'\text{-bpy*})]_2^{8+}$ ion. Without steric direction, homotopic complexes would have formed, as shown by the size-selective reactions of ditopic organoplatinum complexes with dipyridyl linkers of different lengths.[4] The complementary arrangement of building blocks of dissimilar steric demands has been employed as a successful strategy for the construction of coordination cages as well.[3,5,6]

Abstract in Hungarian: *Tanulmányoztuk az N,N′-bisz(4-(4-piridil)-fenil)-acenafténkinondiimin, L^1, és az N,N′-bisz(4-(2-piridil)-fenil)-acenafténkinondiimin, L^2, $[Pd(P^\wedge P)(H_2O)_2](OTf)_2$ palládium difoszfinkomplexekkel mutatott kölcsönhatását ($P^\wedge P$ = dppp, dppf, dppe). Az önszerveződéssel előálló elegyek jellemzésére multinukleáris (^1H, ^{15}N és ^{31}P) NMR-spektroszkópiai, DOSY-, és tömegspektrometriai vizsgálatokat végeztünk. A $[Pd(dppp)]^{2+}$ komplex kation és L^1 1:1 mólarányú elegyében főtermékként trimer, tetramer és pentamer komplexeket figyeltünk meg, melyek képződését a ligandum E/Z izomerizációja következtében dimer melléktermék keletkezése kíséri. E termékek esetében kizárólag a terminális piridilcsoportok koordinációját tapasztaltuk. Egy újabb ekvivalensnyi Pd-tekton a keláthelyzetű, sztérikusan gátoltabb iminonitrogének koordinációját eredményezi, mely a nagyobb aggregációjú komponensek relatív súlyának növekedéséhez vezet. Tömegspektrometriai és DOSY-vizsgálatainkkal a cisz-helyzetben védett síknégyzetes palládiumkomplexek és lineáris, kétfogú ligandumok kölcsönhatásában nem várt 5- és 6-tagú makrociklusok létét igazoltuk. A palládiumtekton konszekutív koordinációját a két koordinációs hely eltérő sztérikus sajátságával értelmeztük. A $[Pd(dppp)]^{2+}$:$[Pd(dppe)]^{2+}$:L^1 = 1:1:1 arányú elegyben olyan aggregátumok állnak elő, melyekben a terjedelmesebb dppp-komplex szelektíven a piridilcsoportokhoz, míg a kisebb térigényű dppe-komplex a sztérikusan árnyékoltabb iminonitrogénekhez kapcsolódik, megvalósítva ezáltal a palládiumtektonok sztérikusan irányított, méret szerinti szétválogatását. Az új ligandumok hidrogénkötés kialakítására mutatott fokozott hajlamát oldószeradduktumok röntgendiffrakciós szerkezetvizsgálatával igazoltuk.*



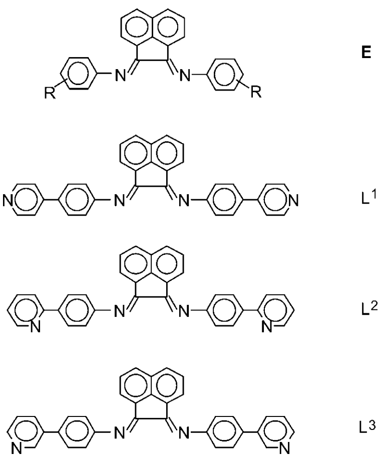
Scheme 1. Studied ligands with various steric demands.

The assembly pathways of the building blocks can also be regulated by the position and steric requirements of the substituents, which has been exemplified by the reaction of the $[Pd(en)]^{2+}$ ion with the triangular tetradentate ligands **C** and **D**. The product of the former ligand mimics a tetrahedron, whereas the latter is assembled into an open-cone structure due to the steric restrictions of the side chains.[7]

Several studies have demonstrated that intramolecular repulsions that emerge in self-assembled metallamacrocycles may affect the nuclearity of the aggregates. Although there are numerous reports on the formation of equilibrium mixtures that involve constituents with different numbers of metal centers, we have strived to present examples in which changing the nuclearity can be ascribed with certainty to steric effects rather than to the flexibility of the bridging ligand or the incorporation of guest molecules. In this respect, a notable study with *N*,*N*′-diphenylamidinates has clearly demonstrated that ligands without *ortho* substituents on the aryl moieties establish a dimer/tetramer equilibrium in solution with copper(I) ions, whereas replacement of the *ortho*-hydrogen atoms by methyl groups produces only a dimeric assembly.[8] The size of the metallamacrocycle has been shown to depend on the substituent (R) of the pyrazolonate ligand in the pyrazolonate rhenium(I) complexes that appeared as tetramers (R = H) or trimers (R = Me, Ph).[9] Interestingly, the phenoxy groups attached to the diazadibenzoperylene ligands (L) in $[Pd(dppp)(L)]_n^{2n+}$ (n = 3, 4; dppp = bis(diphenylphosphanyl)propane) complexes induce steric congestion between L on the edges rather than increasing repulsion with the chelating dppp units. Consequently, a preferential formation of the tetrameric assembly could be achieved by increasing the size of the phenoxy group.[10] However, predicting nuclearity is not always possible, as demonstrated by the unforeseen generation of trimeric species $[Rh_2(darf)_2(ox)]_3$,[11] $[Pt(PMe_3)_2(pyr)]_3^{6+}$,[12a] and $[Ru(dmso)_2(pyr)Cl_2]_3$[12b] (darf = *N*,*N*′-diarylformamidinate, dmso = dimethyl sulfoxide, ox = oxalate, pyr = pyrazine) in which the rigid bridging units (i.e., ox and pyr) were expected to construct tetrameric assemblies. Deviations from the sterically predicted behavior were also reported in studies with $[M(P^\wedge P)]^{2+}$ complexes (M = Pd, Pt; P^P = dppp, dppf, and depe; dppf = bis(diphenylphosphanyl)ferrocene; depe = bis(diethylphosphanyl)ethane).[13] On the contrary, we have shown with a series of sterically characterized $[Pd(N^\wedge N)]^{2+}$ complexes that the distribution of the tectons between the $[Pd(N^\wedge N)(4,4'\text{-bpy})]_n^{2n+}$ trimeric and tetrameric products ($n = 3$, 4) follows a trend concluded from crystallographic data (N^N = chelating diamine).[14]

Interested in how these steric effects are manifested, we planned and synthesized new bis(arylimino)acenaphthenes (Ar-BIANs). These compounds have been known for more than four decades, mostly involving their application in homogeneous catalysis,[15] structural and physicochemical studies,[16] and preparation and structural characterization of complexes with main-group elements.[17] To our knowledge, they have not been utilized for the self-assembly of metallamacrocycles.

Depending on the size and position of the R substituents, the aryl groups of bis(arylimino)acenaphthenes **E** exert steric hindrance on the chelating imino nitrogen atoms to a varying extent (Scheme 2).[16a,d] Our attempts to observe self-assembled macrocycles in the reaction of 4,4′-bpy with the palladium complexes of bis(2,4,6-trimethylphenyl)BIAN and bis(4-methoxyphenyl)BIAN (BIAN = 1,2-bis(imino)acenaphthene) failed, presumably due to the steric congestion around the coordinating nitrogen atoms of these ligands. Therefore, we introduced terminal pyridyl groups, thus generating the extended bipyridyls L^1 and L^3 (see Scheme 2) as bridging tectons and leaving the internal bis(imino) functionality to anchor the smaller constituents.



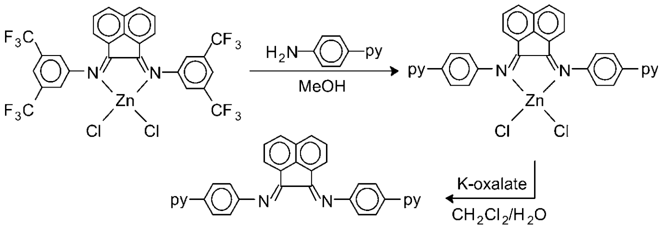
Scheme 2. Bis(arylimino)acenaphthenes **E**, L^1, L^2, and L^3.

Herein, we will discuss the coordination properties of L^1 and L^2. The steric features of the former ligand can control 1) the sequence of coordination of large metal centers in complexes to its sterically different donor groups and 2) can sort the interacting complexes by size between donor sites. The emergence of unexpected pentameric and hexameric complexes formed with this ligand will also be documented.

The coordination properties of the new ligands were probed by using palladium diphosphane complexes $[Pd(P^\wedge P)(H_2O)_2](OTf)_2$ (**1**; P^P = dppp (**1a**), dppf (**1b**), dppe (**1c**); OTf = triflate).

Results and Discussion

Synthesis and structural characterization of ligands L^1 and L^2: Ligands L^1 and L^2 were prepared by using a modified procedure of Ragaini and co-workers (Scheme 3).[16b,c] The treatment of the zinc complex of *N,N′*-bis[bis(3,5-trifluoromethyl)phenyl]acenaphthenequinonediimine in methanol with an amine results in exchange of the imine moieties. The free ligands L^1 and L^2 can then be isolated from their zinc complexes by suspending them in CH_2Cl_2 and shaking them with a solution of potassium oxalate in water. A standard workup of the organic phase yields the target compounds, from which minor contaminations can be effectively removed by precipitation from $CHCl_3$ with ethanol or diethyl ether.



Scheme 3. Preparation of L^1 and L^2. py = 2- or 4-pyridyl.

The protons of L^1 and L^2 show up separately in a narrow region between $\delta = 6.8$ and 9.0 ppm in the ^1H NMR spectra, but the ^1H NMR spectra of the metal complexes are much more complicated due to overlapping peaks. The 2D NMR spectra (COSY) of the free ligands reveal three isolated spin systems, which makes the assignment of the phenyl, pyridyl, and naphthyl protons straightforward. Beside the resonances attributable to the structures shown in Scheme 2, we observed peaks of low intensity in the aromatic region (Figure 1). These peaks did not change upon repeated recrystallization of the compounds, thus suggesting that the second set of resonances of low intensity may be due to structural (*E*/*Z*) isomerism around one of the C=N double bonds rather than contamination. We confirmed this conclusion by collecting the NMR spectroscopic data in several solvents ($CDCl_3$ and CD_2Cl_2). Figure 1 a,b shows that the ratio of the major and minor constituents depends on the solvent. Further, the enhanced proportion of the minor component in CD_2Cl_2 relative to that in $CDCl_3$ could be controlled by adding 2,2,2-trifluoroethanol to the sample, which suggests that the structural properties of L^1 in solution can be influenced by the presence of hydrogen-bond donors. We note that earlier studies on free aryl-BIAN ligands did not report the presence of *E*/*Z* isomers except for those carrying

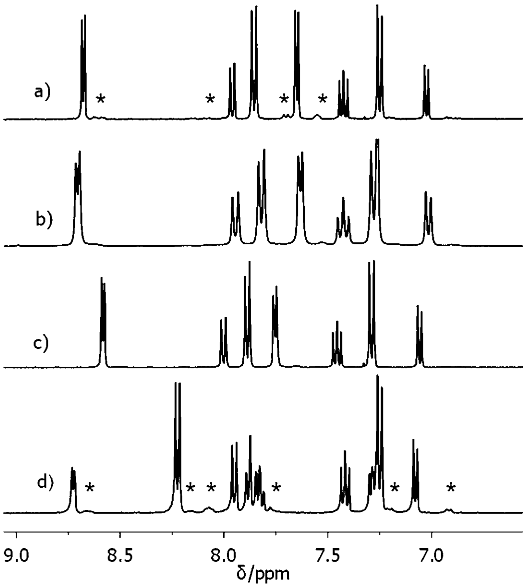


Figure 1. ^1H NMR spectra of L^1 in a) CD_2Cl_2, b) $CDCl_3$, and c) CD_2Cl_2/CF_3CH_2OH (50:3; 530 μL). d) ^1H NMR spectrum of L^2 in CD_2Cl_2 (asterisks indicate the resonances of the minor isomer).

a bis(3,5-trifluoromethyl)phenyl group at least at one of the imino nitrogen atoms.[15e,16a–c]

The remarkable affinity of the ligands to acidic hydrogen atoms (even very weak acids) has been demonstrated by X-ray diffraction studies on L^2. The molecular structure in Figure 2a shows that the product isolated from a CH_2Cl_2/EtOH mixture is a 1:1 adduct of L^2 and ethanol. The H(O) hydrogen atom is located 2.32 and 2.26 Å from the N8 and N8a imino nitrogen atoms, respectively, which supports the existence of weak hydrogen bonds between the chelating coordination site and the solvate molecule. No interaction was observed between the pyridyl nitrogen atoms and the ethanol solvent.

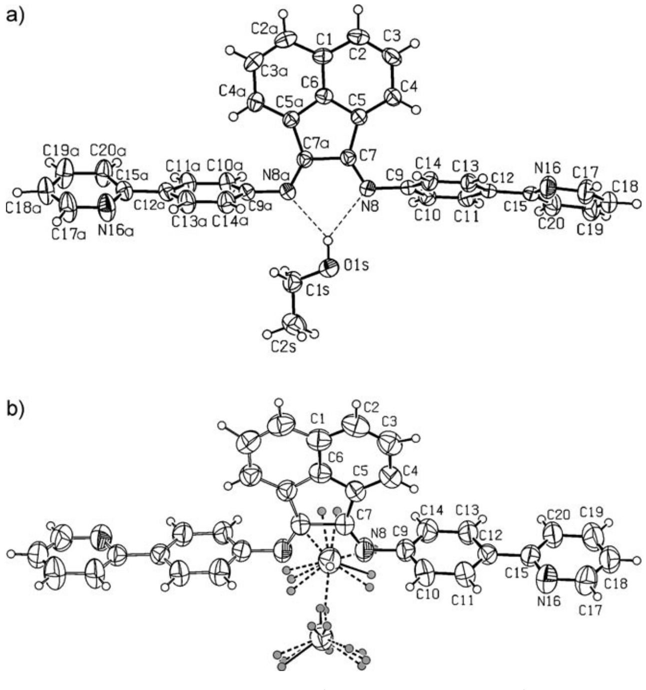


Figure 2. Molecular diagrams of a) $L^2{\cdot}CH_3CH_2OH$ and b) $L^2{\cdot}2\,CHCl_3$.

More importantly, crystallographic analysis of a single crystal isolated from $CHCl_3$ revealed two $CHCl_3$ molecules with hydrogen atoms pointed toward the chelating position (Figure 2b). Although the $H_{solvate}\cdots N8$ distances (i.e., 2.61 and 2.47 Å) are at the upper limit of the $D{-}H\cdots A$ distances that may be considered as hydrogen bonds, structures (a) and (b) show the proneness of the chelating imino nitrogen atoms to interact with positively charged or polarized particles. In line with the less acidic nature of dichloromethane, no hydrogen bonds were detected if the crystals were grown in CH_2Cl_2, even though one CH_2Cl_2 molecule for each L^2 ligand was observed in the crystal structure. This observation coincides well with the solution behavior of the ligands, namely, larger amounts of the minor constituent are detected in samples dissolved in less acidic CD_2Cl_2. It seems worth mentioning that a search of the Cambridge Crystallographic Database (CCDB)[18] for Ar-BIAN-type ligands has not yielded structures involving hydrogen-bonded solvent molecules at the chelating coordination site. However, the structural data, such as bond distances, bond angles, and tilting of the phenyl groups with respect to the acenaphthene moieties, do not show any unusual values (see the material deposited at the CCDC).

In summary, the major resonances in the ^1H NMR spectra of L^1 and L^2 have been attributed to the *E*/*E* isomers of the ligands as shown by the diagrams in Scheme 2, whereas the peaks of low intensity have been ascribed to molecules in which one of the C=N double bonds is isomerized. Both the coexistence of *E*/*E* and *E*/*Z* isomers in solution and the pronounced tendency of the chelating coordination sites to interact with hydrogen-bond donors, even with $CHCl_3$, are significant in the self-assembly reactions.

Self-assembly of L^1 with palladium diphosphane complexes 1a–c: Ligand L^1 possesses two types of coordination site: terminal pyridyl nitrogen atoms and chelating imino nitrogen atoms. One may speculate that these coordination sites are both energetically and sterically different. The position of the imino nitrogen atoms enables them to bind simultaneously to form chelate complexes, thus stabilizing the metal–nitrogen coordinate bond. As shown by a survey of CCDB, Ar-BIANs are coordinated as chelates in the majority of their complexes. However, one can expect considerable steric congestion for L^1 in the vicinity of the imino nitrogen atoms due to the relatively bulky phenyl groups attached to these atoms.[16d] On the contrary, the terminal pyridyl groups are not sterically constrained but their coordination is not enhanced by the chelate effect either. Therefore, L^1 may support a structurally induced selectivity in the spontaneous assembly of metallamacrocycles.

Self-assembly of a 1:1 molar ratio of Pd/L^1: The self-assembly of $[Pd(dppp)(H_2O)_2](OTf)_2$ with L^1 was studied in

CD_2Cl_2 and $CDCl_3$ in the concentration range 4–48 mM. The ^{1}H NMR spectrum of a 1:1 mixture of L^1 and $[Pd(dppp)(H_2O)_2](OTf)_2$ is shown in Figure 3b. A comparison with the ^{1}H NMR spectrum of L^1 (Figure 3a) shows characteristic shifts of the resonances attributed to protons at positions 3 and 7 (see the numbering scheme; Figure 3). The multiplets assignable to the *ortho*-hydrogen atoms of the pyridyl groups at $\delta \approx 9$ ppm indicate that the terminal donor atoms, rather than the internal imino nitrogen atoms, are involved in the interaction. The preferential coordination of the pyridyl groups over the chelating imino nitrogen atoms was further confirmed by ^{15}N NMR spectroscopic investigations. The data presented in Table 1 show that coordination of the $[Pd(dppp)]^{2+}$ ion to L^1 only induces a negligible decrease in the chemical shift attributed to the imino nitrogen atoms. On the other hand, the sign and magnitude of the observed coordination shift (a difference of $\Delta\delta \approx -62$ ppm was detected for the pyridyl nitrogen atoms) is indicative of the involvement of the terminal pyridyl groups in coordination and is in full agreement with the general trends.[19]

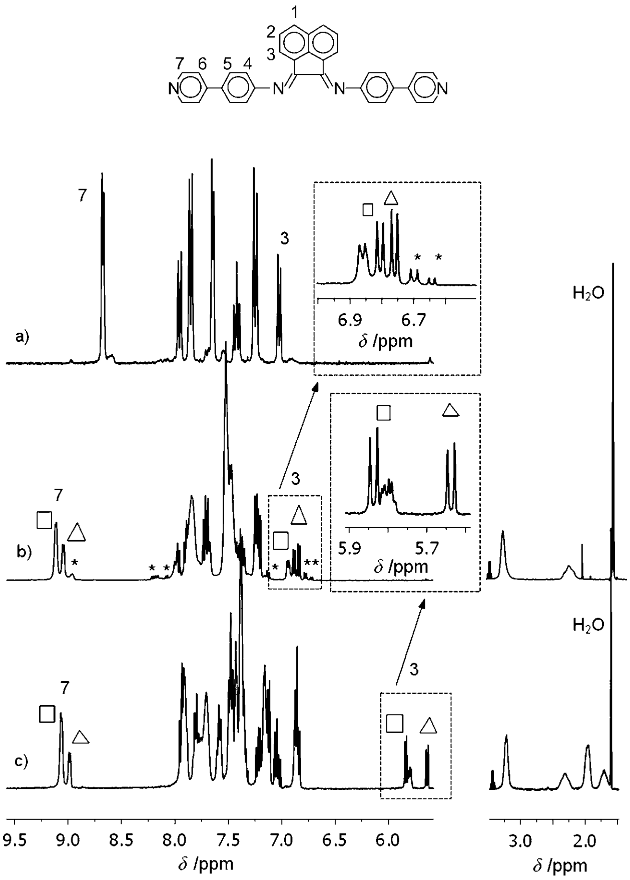


Figure 3. ^{1}H NMR spectra of L^1 (a) and mixtures of $[Pd(dppp)(H_2O)_2](OTf)_2/L^1$ in molar ratios of 1:1 (b) and 2:1 (c) in CD_2Cl_2 ($[L^1] = 16$ mM). The triangles and squares label peaks assigned to trimeric and tetrameric aggregates, respectively.

Table 1. ^{15}N NMR data of ligands L^1 and L^2 and their complexes with $[Pd(dppp)](OTf)_2$.

	δ (^{15}N) [ppm]		
	N(py)	N(C=N)	solvent
L1	304.5	336.7	$CDCl_3$
L^1 + $[Pd(dppp)](OTf)_2$	241.3,[a] 242.5[b]	335.0	$CDCl_3$
L^1 + $[Pd(dppp)](OTf)_2$	239.6,[a] 241.5[b]	340.6	CD_2Cl_2
L^1 + 2 $[Pd(dppp)](OTf)_2$	243.3,[a] 236.5[b]	260.0	CD_2Cl_2
L^2	306.6	339.1	CD_2Cl_2
L^2 + $[Pd(dppp)](OTf)_2$	303.0	260.3	CD_2Cl_2

[a] Tetrameric and higher aggregates. [b] Trimeric species.

The pyridine *ortho*-hydrogen signals occur in an area of the ^{1}H NMR spectra that is free of other overlapping peaks and provide information on the number of components formed in the self-assembly process. The two multiplets of comparable intensity around $\delta = 9.0$ ppm in the ^{1}H NMR spectrum suggest the presence of two major, highly symmetric constituents in the reaction mixture and can be tentatively assigned to tetrameric (square) and trimeric (triangular) species, on the basis of the abundant structural data accumulated on the reaction of *cis*-protected $[Pd(P\^{}P)(H_2O)_2](OTf)_2$ complexes with linear ditopic ligands.[10,13,20,21] The coexistence of two major constituents is strongly supported by Figure 3b and the concentration dependence of the equilibrium composition in CD_2Cl_2 studied by ^{1}H NMR spectroscopic analysis (see Figure S1 in the Supporting Information). As shown by a series of spectra recorded at various concentrations, the intensity ratios of the two major peaks around $\delta = 9$ ppm are inverted when the tecton concentration goes from 4 to 48 mM. This feature reflects a pronounced entropic control over the equilibrium and suggests that the ^{1}H NMR resonances at $\delta = 9.02$ and 8.95 ppm are due to the larger and smaller species, respectively.

Although the formation of two major constituents seems to be a reasonable interpretation of the NMR spectra, close inspection of Figure 3b and Figure S1 (see the Supporting Information) reveals that an attempt to describe these reaction mixtures as two-component systems is an undue simplification. A series of resonances of low intensity (labeled by asterisks) clearly indicate the formation of a third constituent, although it is present in a much smaller proportion than the major components at concentrations of ≥ 8 mM. Furthermore, the *ortho*-hydrogen atoms of the acenaphthene moiety could be expected to reflect the formation of the assumed trimeric and tetrameric aggregates, as do the pyridine *ortho* protons. Both the number and the relative intensities of the resonances between $\delta = 6.72$ and 6.86 ppm suggest that the formation of species other than trimers and tetramers should be considered (see the inset of Figure 3b and Figure S1 in the Supporting Information). All these observations will be discussed in an ongoing section.

Interaction of L^2 with $[Pd(dppp)(H_2O)_2](OTf)_2$ at Pd/L^2 = 1:1: Before we turned our attention to the self-assembly of L^1 with palladium diphosphane complexes at Pd/L^1 = 2:1, we studied the interaction of *N*,*N′*-bis[4-(2-pyridyl)phenyl]acenaphthenequinonediimine (L^2) with **1a**. It was anticipated that the position of the pyridyl nitrogen atoms in L^2 was not favorable for the formation of stable complexes with the bulky $[Pd(dppp)]^{2+}$ ions. Consequently, the interaction of L^2 with diphosphane complexes may offer insight into the structural changes induced by selective coordination at the chelating imino nitrogen atoms, thus facilitating the assignment of the spectra recorded at $Pd/L^1=2{:}1$ molar ratio.

A comparison of the ^1H NMR spectra in Figure 4 shows that the interaction of L^2 with **1a** leads to the formation of monomeric $[Pd(dppp)(L^2)](OTf)_2$ (**7a**), in which the palladium center coordinates to the imino rather than to the pyridyl nitrogen atoms. This outcome is well illustrated by the following observations: 1) the position of the pyridine *ortho*-hydrogen atoms is not affected by the coordination and 2) the *ortho*-hydrogen atoms of the acenaphthene moiety is shifted upfield by almost $\Delta\delta=1$ ppm. This latter feature can be ascribed to the more pronounced shielding by the neighboring phenyl groups and is certainly attributable to the enhanced steric congestion around the imino nitrogen atoms upon coordination of L^2 to the bulky palladium diphosphane complex.

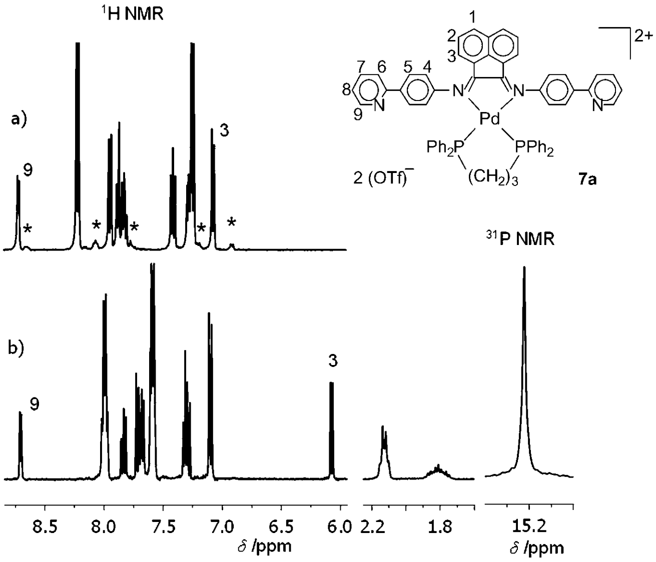


Figure 4. a) ^1H NMR spectrum of L^2 and b) ^1H and ^{31}P NMR spectra of the $[Pd(dppp)(L^2)](OTf)_2$ (**7a**) in CD_2Cl_2.

Thus, the remarkable shift of H3 (see the numbering scheme) provides evidence that the imino nitrogen atoms are involved in the coordination. A comparison of the resonances attributable to the dppp propylene chains in Figures 3b and 4b reveals further differences associated with the coordination mode of the $[Pd(dppp)]^{2+}$ tecton. Although the $CH_2(PPh_2)$ and $CH_2(CH_2)$ protons of the $[Pd(dppp)L^1]_n^{2n+}$ aggregates resonate at $\delta=3.26$ and 2.32 ppm in the former spectrum, the same hydrogen atoms show up at lower frequencies (i.e., $\delta=2.13$ and 1.81 ppm) in the ^1H NMR spectrum of the $[Pd(dppp)(L^2)]^{2+}$ complex. Therefore, ligand L^2 is an excellent model compound to identify the spectral changes associated with the incorporation of a palladium tecton at the chelating site.

Further, the ^{15}N NMR data in Table 1 confirm the utilization of the imino nitrogen atoms as donor atoms in the interaction of the $[Pd(dppp)]^{2+}$ ion with L^2. Finally, the sharp singlet in the ^{31}P NMR spectrum at $\delta=15.2$ ppm indicates a plane of symmetry in the complex and suggests that both dppp and L^2 act as bidentate ligands (Figure 4b).

Self-assembly at $Pd/L^1=2{:}1$: The ^1H NMR spectrum that proceeded the self-assembly of the $[Pd(dppp)]^{2+}$ ion with L^1 in a 2:1 molar ratio ($[L^1]=16$ mM) is presented in Figure 3c. Several apparent differencies are exhibited compared to the spectrum of a solution of a 1:1 molar ratio at the same concentration of L^1 (Figure 3b). The most striking feature of this spectrum is that new multiplets emerge in the region $\delta=5.6$–5.9 ppm, which was free of signals in samples of equimolar tectons. These resonances are attributed to the *ortho* protons of the acenaphthene moiety and are a consequence of binding a second palladium complex at the chelating site of L^1. This chelating coordination is further confirmed by looking at the ^1H NMR resonances attributed to the aliphatic protons (Figure 3b,c). Furthermore, the introduction of a second equivalent of the palladium tecton induces a significant shift of the resonances attributed to the chelating nitrogen atoms, whereas the pyridine nitrogen atoms are only moderately affected (Table 1). Finally, the ratio of the resonances at around $\delta=9$ ppm indicates the accumulation of the larger aggregate upon addition of a second palladium complex. Thus, anchoring the palladium complexes at the internal coordination sites has the same effect on the nuclearity as the inclusion of guest molecules in self-assembled species.[22]

Comparing the spectral portions between $\delta=1.5$–3.5 and 5.5–7.0 ppm in Figure 3b,c, we can draw the conclusion that the complexation of the first and second $[Pd(dppp)]^{2+}$ tectons takes place in a strictly consecutive manner. No 2:1 complex is formed until all the terminal pyridyl groups are consumed. However, a survey of the sections at $\delta=8.8$–9.1 and 5.5–6.0 ppm in Figure 3c leaves us in uncertainty regarding the number of species of different nuclearity, a case that has been observed before with 1:1 mixtures. Thus, two major issues have been left unanswered regarding the 1:1 and 2:1 reaction mixtures: 1) why is seemingly contradictory information inferred from the pyridine *ortho* hydrogen atoms and the acenaphthene *ortho* protons regarding the number of species and 2) how many tectons are involved in the observable species. To make an unambiguous assignment of the major resonances in the NMR spectra of the 1:1 and 2:1 reaction mixtures, mass-spectrometric studies were carried out with electrospray ionization (ESI). As demonstrated previously, mass-spectrometric analysis has been fruitfully utilized for characterizing self-assembled systems.[23–26] However, it is often hard to ionize weakly bound complexes without completely fragmenting them, even with soft ionization techniques, such as ESI. Mass-spectrometric parameters were carefully adjusted for detection of intact complexes. In the ESI-MS spectrum of the Pd/L^1 = 1:1 complex, the base peak is $[L^1+H]^+$, whereas the most intense peaks belong to the following ions: $[Pd(dppp)L^1]^{2+}$, $[Pd(dppp)Cl]^+$, $[Pd(dppp)(OTf)]^+$, $[Pd(dppp)L^1(OTf)]^+$, and $[Pd(dppp)L^1Cl]^+$.

The region *m/z* 1500–2500 of the ESI-MS spectrum recorded of a Pd/L^1 = 1:1 reaction mixture is presented in Figure 5. In the spectrum, the expected trimeric and tetrameric species can be readily identified. The isotope cluster centered at *m/z* 1588.82 (see the inset of Figure 5) corresponds to the intact square that carries five triflate anions, that is, $[Pd_4(dppp)_4L^1_4(OTf)_5]^{3+}$. The isotope distribution of the doubly charged $[Pd_4(dppp)_4L^1_4(OTf)_6]^{2+}$ ion (*m/z* 2457.66) overlaps with a less intense peak of the $[Pd_2(dppp)_2L^1_2(OTf)_3]^+$ ion (note that the instrument resolution permits separation of the two species). The tetrameric species can also be observed as a minor constituent at *m/z* 2401.13 as the $[Pd_4(dppp)_4L^1_4(OTf)_5Cl]^{2+}$ ion. This outcome shows that the triflate anion can be exchanged in part with chloride. Trimeric species have been detected as $[Pd_3(dppp)_3L^1_3(OTf)_4]^{2+}$ and $[Pd_3(dppp)_3L^1_3(OTf)_3Cl]^{2+}$ ions (*m/z* 1806.50 and 1749.52, respectively).

An important observation is that a pentameric complex can also be identified beside the expected trimeric and tetrameric species. The molecular masses and isotopic distributions at *m/z* 1986.23 and 2023.57 (i.e., ($[Pd_5(dppp)_5L^1_5(OTf)_6Cl]^{3+}$ and $[Pd_5(dppp)_5L^1_5(OTf)_7]^{3+}$ ions, respectively) clearly show the presence of these species, although at a relatively small intensity.

A combination of these observations with the concentration dependence of the ^1H and ^{31}P NMR spectra (see Figures S1 and S2 in the Supporting Information) allows us to assign the resonances to species of various nuclearity. The interaction of linear ditopic ligands with *cis*-protected palladium tectons preferentially leads to the formation of trimeric and tetrameric species (with the predominance of the former at low concentrations). The results of our mass-spectrometric and DOSY NMR spectroscopic experiments (see below) confirm that the resonances at $\delta = 6.74$ and 8.95 ppm belong to H3 and H7 (see Figure 3) of the macrocyclic trimeric aggregate **3a**, whereas the same hydrogen atoms of the tetrameric species **4a** were identified as doublets at $\delta = 6.78$ and 9.02 ppm. The intensity of the resonance at $\delta = 6.83$ ppm increases monotonously as the tecton concentration varies from 4 to 48 mM and was attributed to a pentameric product **5a**. Comparison of the integral values of the two major doublets at $\delta = 8.95$ and 9.02 ppm with those of the relevant acenaphthane *ortho* protons shows that the signals of the pyridine *ortho*-hydrogen atoms of the tetrameric and pentameric assemblies overlap.

To complete the interpretation of the ^1H NMR spectrum of the 1:1 adducts, the presence of a minor product labeled with asterisk in Figure 3b needs to be addressed. A summary of otherwise irrelevant observations sheds light on the nature of this species. The coordination of the second $[Pd(dppp)]^{2+}$ tecton to L^1 results in the fading of resonances, which is attributed to the unknown component (Figure 3). Furthermore, the concentration of the minor product was noticeably greater in CD_2Cl_2 than in $CDCl_3$, thus suggesting that its formation can be influenced by the nature of the solvent. This feature is similar to the behavior of the free ligand, for which the concentrations of the *E*/*E* and *E*/*Z* isomers depended on the solvent. The elimination of a series of

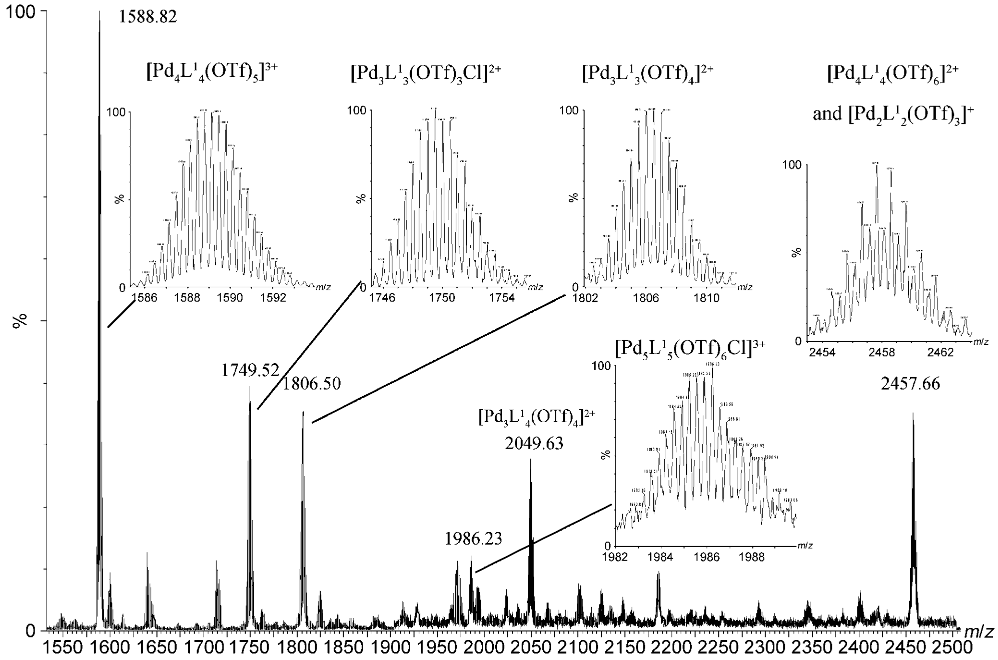


Figure 5. ESI-MS spectrum of a 1:1 mixture of $[Pd(dppp)(H_2O)_2](OTf)_2/L^1$ in acetone (c = 0.1 mM). The range at *m/z* 1900–2500 is magnified threefold. (Pd = $[Pd(dppp)]^{2+}$ ion).

resonances of low intensities in the ^{1}H NMR spectrum of L^2 upon coordinating a palladium complex to the chelating nitrogen atoms seems to be a related phenomenon (Figure 4). All these observations suggest that the formation of the minor product at $Pd/L^1 = 1{:}1$ is attributable to the *E*/*Z* isomeric form of ligand L^1. We may reasonably assume that two molecules of the bent isomer with two $[Pd(dppp)]^{2+}$ tectons can be combined into a dimeric complex, **2a**.

Spectroscopic evidence for the formation of dimeric species **2a** is observed in the ^{31}P NMR spectra of 1:1 mixtures in which resonances at $\delta = 6.73$, 6.51, 6.14, and 5.92 ppm can be clearly recognized as an AB doublet ($\delta_A = 6.05$ ppm, $\delta_B = 6.60$ ppm, $^2J_{PP} = 35$ Hz; see Figure S3 in the Supporting Information). The splitting pattern is in line with the nonequivalence of the phosphorus nuclei in the dimeric species.

Further evidence for the relative sizes of the self-assembled species of 1:1 mixtures has been extracted from ^{1}H DOSY NMR spectroscopic experiments. As the proportions of the components vary strongly with concentration (see Figure S1 in the Supporting Information), a spectrum recorded at [tecton] = 4 mM allowed us to identify the tetrameric ($0.29 \times 10^{-9}\,m^2 s^{-1}$), trimeric ($0.34 \times 10^{-9}\,m^2 s^{-1}$), and minor dimeric ($0.40 \times 10^{-9}\,m^2 s^{-1}$) components (Figure 6a). The calculated hydrodynamic radii ($r_{tetramer} = 18.3$ Å, $r_{trimer} = 15.7$ Å, $r_{dimer} = 13.3$ Å) support the conclusion that the $[Pd(dppp)L^1]_n^{2n+}$ complexes ($n = 2$, 3, 4) are all large molecular assemblies. On the other hand, a DOSY NMR spectrum obtained of a sample at [tecton] = 32 mM clearly shows that the species that prevail at high concentrations certainly has a nuclearity of $n > 4$ and has been identified as a pentameric complex (Figure 6b).

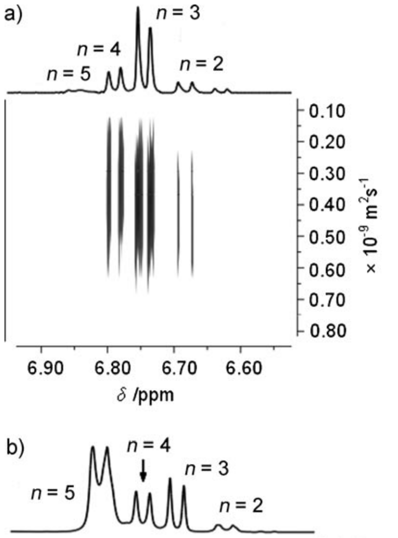


Figure 6. Sections of ^{1}H DOSY NMR spectra of a 1:1 mixture of Pd/L^1 recorded at tecton concentrations of a) 4 and b) 32 mM (CD_2Cl_2, 298 K).

Interestingly, the reaction of *cis*-$[Pt(Et_3P)_2](OTf)_2$ with structurally related dipyridyl ligands that have an embedded *N*,*N'*-ethylenebis(salicylimine) (salen) backbone followed a different pathway in constructing self-assembled products.[27] The exclusive formation of dimeric complexes was reported when the reaction was carried out with free bases, which could be rearranged to form squares by introducing a metal cation into the chelating site. It is assumed that a similar process occurs with the dimeric species reported herein, in which the equilibrium of the *E*/*E* and *E*/*Z* isomers is influenced by the incorporation of the second palladium tecton.

Multiple assemblies were also observed in the reaction mixtures of $[Pd(dppp)(H_2O)_2](OTf)_2$ and L^1 at a 2:1 molar ratio by using ESI-MS (Figure 7). A compilation of signals identified as $[Pd(dppp)L^1]_n$ backbones ($n = 3$–6) with varying amounts of additional $[Pd(dppp)]^{2+}$ tectons and triflate ions is given in Table S1 (see the Supporting Information). As the $[Pd(dppp)]^{2+}$ tecton preferentially coordinates to the terminal pyridyl group, deviations from the ideal $[\{Pd(dppp)\}_{2n}L^1{}_n(OTf)_m]^{(4n-m)+}$ formulae for 2:1 complexes ($n = 3$–6, $m < 4n$) can be attributed to the less advantageous energetics to bind palladium complexes at the sterically more congested chelating site. In the ^{1}H NMR spectra, however, the integrals of the $[Pd(dppp)]^{2+}$ complex ions anchored at the corners and on the edges are equal (see the aliphatic region of the spectrum in Figure 3c), thus indicating that both the terminal and central coordination sites of L^1 are fully occupied in solution. The presence of these intact species has been confirmed by ESI-MS. The spectra show ions that correspond, for example, to the following structures: $[Pd_6(dppp)_6L^1{}_3(OTf)_{10}]^{2+}$, $[Pd_8(dppp)_8L^1{}_4(OTf)_{13}]^{3+}$, $[Pd_{10}(dppp)_{10}L^1{}_5(OTf)_{16}]^{4+}$, and $[Pd_{12}(dppp)_{12}L^1{}_6(OTf)_{19}]^{5+}$ (*m*/*z* 3032.08, 2678.53, 2502.02, and 2395.69, respectively).

At a $Pd/L^1 = 2{:}1$ molar ratio, no dimeric species can be formed and the constituents present at low concentrations can be attributed to the trimeric and tetrameric species. Therefore, resonances at $\delta = 5.64$ and 9.00 ppm have been ascribed to H3 and 7 (see Figure 3c and Figure S4 in the Supporting Information) of the macrocyclic trimeric aggregate **3aa**, whereas hydrogen atoms of the tetrameric species **4aa** in the same positions have been detected as doublets at $\delta = 5.84$ and 9.06 ppm. Increasing the concentration does not generate new resonances in the ^{1}H NMR spectrum at around $\delta = 9$ ppm, but results in only a slight broadening of the outermost doublet. The relative intensities of two overlapping doublets at $\delta = 5.82$ and 5.80 ppm changes with increasing concentration (see the insets of Figure S4 in the Supporting Information). The resonance at $\delta = 5.82$ ppm has been ascribed to pentamers **5aa**, whereas the latter dominates at high concentration (24 mM) and has been attributed to a hexameric product **6aa**. Assignment of the ^{31}P NMR resonances (see Figure S5 in the Supporting Information)

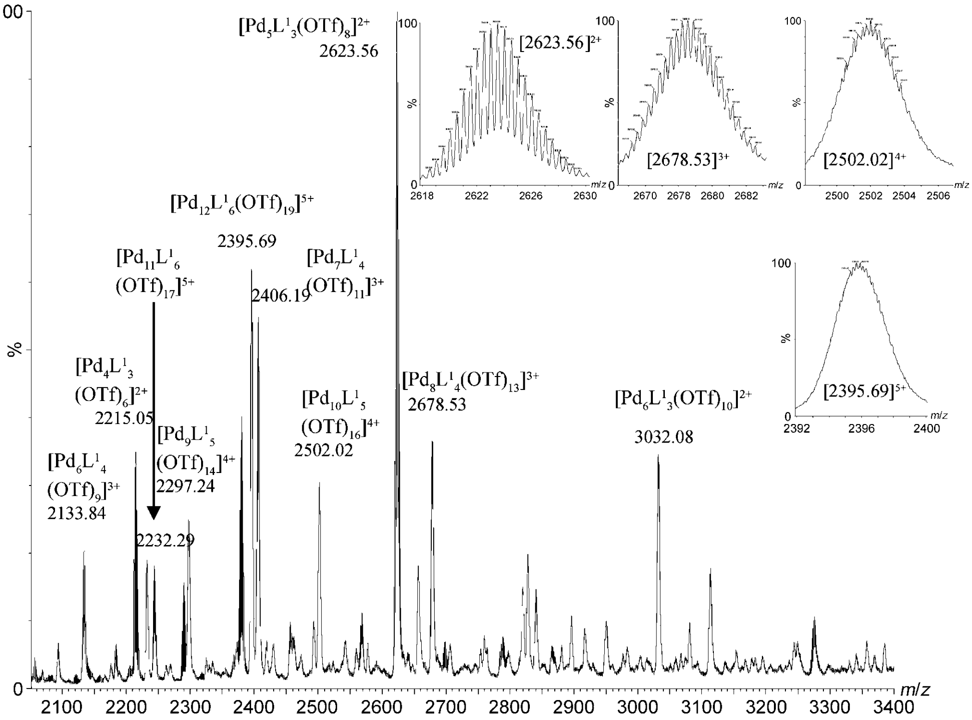


Figure 7. ESI-MS spectrum of a 2:1 mixture of [Pd(dppp)(H$_2$O)$_2$](OTf)$_2$/L^1 in acetone ([L^1] = 1 mM; Pd = [Pd(dppp)]$^{2+}$ ion).

has been accomplished accordingly. It is important to emphasize that compounds **5aa** and **6aa** also possess pyridine *ortho*-hydrogen atoms, although the resonances do not separate from those of the tetrameric species. To obtain the same ratio of integrals that was calculated for the resonances of the pyridine *ortho*-hydrogen atoms, it was necessary to compare the integral of the well-separated resonance at $\delta = 5.64$ (trimer **3aa**) with the sum of the signals between $\delta = 5.77$ and 5.89 ppm (**4aa**–**6aa**).

An identical assignment can be made on the basis of the ^{1}H DOSY NMR spectra recorded at L^1 concentrations of 4 and 24 mM (see Figure 8a,b). The resonances at $\delta = 5.64$ and 5.84 ppm, separated by the diffusion coefficient, were attributed to **3aa** and **4aa**, respectively, whereas the species that emerge at high concentration can be characterized by larger hydrodynamic radii; although the separation of the pentameric and hexameric species in the ^{1}H DOSY NMR spectrum could not be achieved due to their overlapping signals at 9.38 T.

In a detailed mass-spectrometric study on related palladium bispyridyl systems, Schalley et al. observed hexameric and octameric species that were ascribed to the formation of sandwich-like aggregations of trimers or tetramers in the ESI process.[23] This conclusion is in agreement with all spectroscopic observations as there are no NMR spectroscopic indications that self-assembled species other than trimers and tetramers exist in those systems. For the system presented herein, the emergence of a pentameric product in the 2:1 mixture cannot be explained by layered aggregation of a dimeric and trimeric species because at this molar ratio macrocyclic dimers (which would require the bent L^1 ligand) do

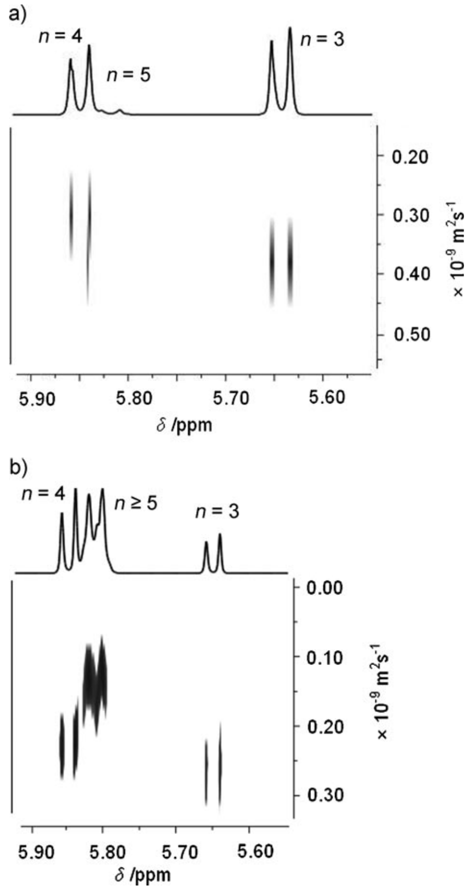
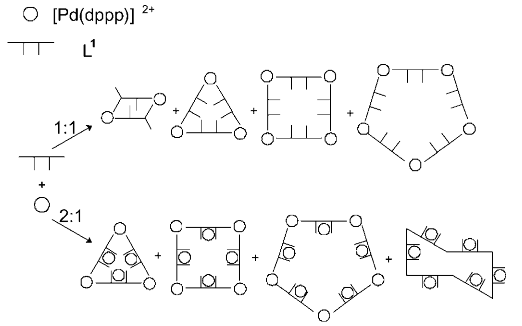


Figure 8. Sections of the ^{1}H NMR DOSY spectra of a 2:1 mixture of Pd/L^1 recorded at L^1 concentrations of a) 4 and b) 24 mM (CD$_2$Cl$_2$, 298 K).

not exist. It is also important that hexamers could be detected but higher-order assemblies were not observed, although they may also be formed by this mechanism. Most importantly, increasing the concentration not only changes the trimer/tetramer ratio but also results in the emergence of new resonances of slowly diffusing constituents, as demonstrated by the 1D NMR and DOSY spectra. Therefore, the aggregates with nuclearities higher than four are considered to be existing components of the [Pd(dppp)]/L^1 system in the solution phase. Although pentameric and hexameric complexes have been constructed from appropriately choosen linear and angular tectons[28] and the intermediacy of a pentameric aggregate with the sterically less demanding [Pd(en)]$^{2+}$ tecton has also been noted,[29] we are not aware of any reports on the formation of high-nuclearity species ($n=5$, 6) from *cis*-protected square planar diphosphane complexes and linear ditopic donor building blocks. It seems reasonable to attribute the unique ability of L^1 to form unusually large metallacycles to its size (ca. 20 Å) and flexibility, although a firm structure/reactivity relationship cannot be described at the current time. Further accumulation of data on the coordination properties of L^1 and similar ligands (e.g., L^3) are needed to provide a more definite answer to this question. The observations presented herein suggest that species of high nuclearity ($n=5$, 6) may be present in other related systems, although their concentration may be too low to be detected. However, their involvement in the interconversion of the observable constituents may be important; therefore, the direct observation of these aggregates in the present study may be of use in mechanistic considerations related to self-assembled systems.

To summarize the steric properties of L^1, we have shown that a 1:1 molar mixture of [Pd(dppp)(H$_2$O)$_2$](OTf)$_2$ and L^1 generates trimeric, tetrameric, and pentameric aggregates, depending on the concentration, as major constituents with the simultaneous formation of a minor amount of dimeric species. Whereas the former three products are constructed from the linear *E*/*E* isomer of L^1, the dinuclear constituent is attributed to the presence of traces of the *E*/*Z* form. The experimental data show that only the terminal pyridyl groups are coordinated in all these species. In other words, the primary coordination site of L^1 toward the sterically demanding [Pd(dppp)]$^{2+}$ complex is the terminal pyridyl group, despite the beneficial effect that the chelating position of donor atoms could exert in the stabilization of coordinate bonds. The internal, more-hindered imino nitrogen atoms interact with the palladium tecton only when the sterically less-hindered positions are occupied. Therefore, due to the sterically different environments of its donor atoms, ligand L^1 establishes a sterically induced sequence of coordination. No dimeric species can be detected at a 2:1 molar ratio of Pd/L^1, at which the coordination of a palladium complex at the chelating donor atoms hampers the formation of the bent isomer. Scheme 4 summarizes our experimental observations and gives a pictorial description of the interaction of the [Pd(dppp)]$^{2+}$ complex ion with L^1.



Scheme 4. Notes: 1) Charges and anions are not shown; 2) the drawings illustrate the connectivity and not the true spatial orientation of the tectons.

Self-assembly of L^1 with [Pd(dppf)]$^{2+}$ and [Pd(dppe)]$^{2+}$ complex ions: The interaction of L^1 with the more bulky [Pd(dppf)]$^{2+}$ cation ($\phi=96°$) leads to the same type of complexes that were observed with dppp as the ancillary ligand; therefore, only representative spectra are presented and discussed. At an equimolar ratio, the multiplets of the pyridyl *ortho*-hydrogen atoms indicate the presence of two major constituents that have been identified as trimer **3b** and tetramer **4b** on the basis of ^{1}H DOSY NMR spectra and the characteristic changes of the spectra upon increased tecton concentration (Figure 9a). A trace amount of species that presumably possess a nuclearity larger than four appears as a shoulder at $\delta=6.80$ ppm. The cyclopentadienyl protons of the trimeric and tetrameric species overlap.

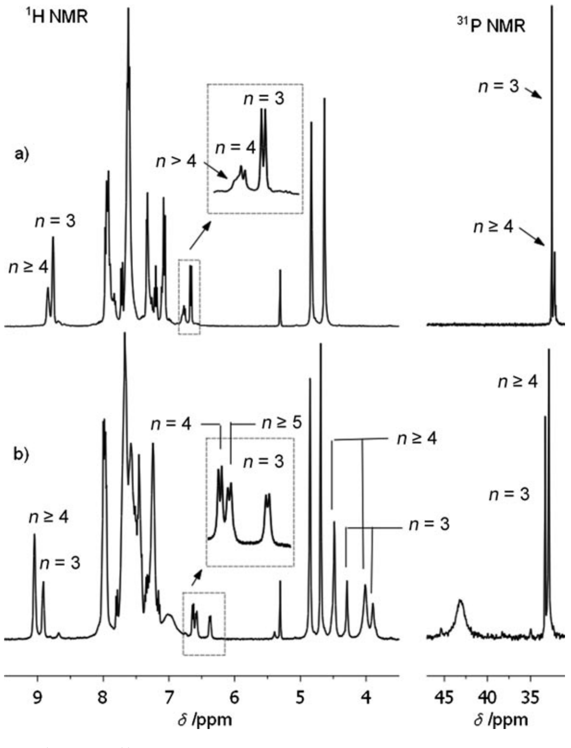


Figure 9. ^{1}H and ^{31}P NMR spectra of self-assembled species formed in the interaction of [Pd(dppf)(H$_2$O)$_2$](OTf)$_2$ with L^1 in molar ratios of a) 1:1 and b) 2:1 (CD$_2$Cl$_2$, 25 °C, [L^1] = 30 mM).

The introduction of a second $[Pd(dppf)]^{2+}$ tecton results is the enhancement of higher-order assemblies, which is demonstrated by the reversed ratio of peak intensities at $\delta = 9$ ppm in the ^{1}H NMR spectrum and around $\delta = 33$ ppm in the ^{31}P NMR spectrum. Although the $[Pd(dppf)]^{2+}/L^1$ system produced much less intensive peaks attributable to self-assembled species in the ESI-MS spectra, the signals at *m*/*z* 1616.06 ($[Pd_4L_3(OTf)_5]^{3+}$), 1935.76 ($[Pd_5L_3(OTf)_7]^{3+}$), 2417.53 ($[Pd_6L_4(OTf)_9]^{3+}$), 2736.86 ($[Pd_7L_4(OTf)_{11}]^{3+}$), and 2899.28 ($[Pd_7L_5(OTf)_{11}]^{3+}$) strongly indicate that trimeric, tetrameric, and pentameric aggregates are present in the equilibrium mixture. Based on the spectral changes observed in the NMR spectra upon increasing the tecton concentration or switching the Pd/L^1 ratio from 1:1 to 2:1, resonances at $\delta = 6.38$ and 6.64 ppm have been ascribed to the trimeric **3bb** and tetrameric **4bb** species. The formation of a third component was evidenced by a growing signal at $\delta = 6.58$ ppm as the L^1 concentration increased. This species has the largest hydrodynamic radius, as shown by the ^{1}H DOSY NMR spectroscopic experiment (Figure 10) and has been identified as pentameric species. As in the [Pd(dppp)]/L^1 system, the resonances of the pyridyl *ortho*-hydrogen atoms of the tetramers and pentamers overlap. Unlike the cyclopentadienyl protons (H(Cp)) of the [Pd(dppf)] tectons, which reside at the corners, the edge-bound [Pd(dppf)] moieties embedded in the trimeric and the $n \geq 4$ adducts of the 2:1 mixtures are clearly distinguishable (^{1}H DOSY NMR spectroscopy). The broad resonance in the ^{31}P NMR spectrum at $\delta = 43.2$ ppm is attributed to the edge-bound phosphane complexes.

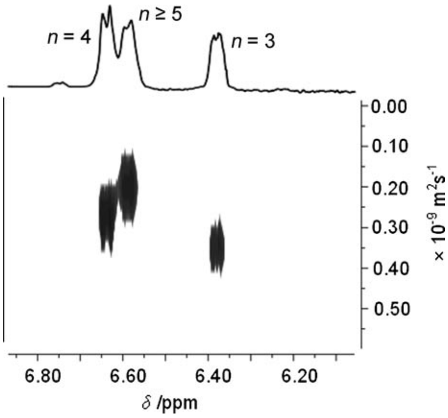


Figure 10. Section of the ^{1}H DOSY spectrum of a 2:1 mixture of **1b**/L^1 recorded at [L^1] = 30 mM (CD$_2$Cl$_2$, 298 K).

These observations support the previous conclusion that the preferred coordination sites of L^1 are the terminal pyridyl groups when the partners are bulky complexes. The formation of self-assembled aggregates with a nuclearity higher than four has also been confirmed.

It is not surprising that the reaction of L^1 with the sterically less demanding $[Pd(dppe)]^{2+}$ complex is less selective. The ^{31}P NMR spectrum of a 2:1 reaction mixture is similar to that of the [Pd(dppp)]/L^1 system (Figure 11 b). Resonances at $\delta = 64.68$ and 65.47 ppm have been ascribed to palladium tectons located on the tips of the squares (**4cc**) and triangles (**3cc**), respectively, whereas those at $\delta = 68.95$ and 68.51 ppm have been attributed to phosphorus atoms of edge-bound palladium complexes. At a 1:1 molar ratio, however, the $[Pd(dppe)]^{2+}$ tecton coordinates not only to the terminal pyridyl groups but to the internal imino nitrogen atoms as well, as shown by in Figure 11 a.

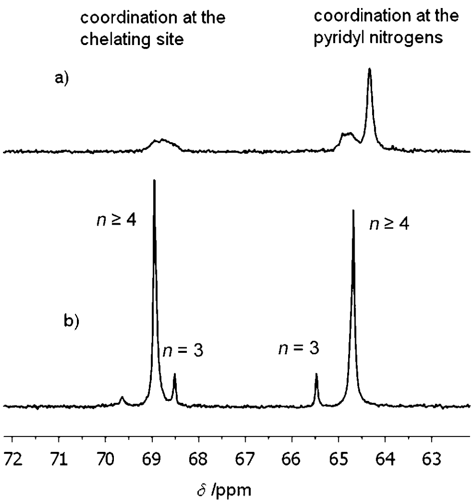


Figure 11. ^{31}P NMR spectra of the self-assembled complexes formed in the interaction of the $[Pd(dppe)]^{2+}$ ion with L^1 at molar ratios of a) 1:1 and b) 2:1 (CD$_2$Cl$_2$, 303 K, [L^1] = 15 mM).

Self-assembly becomes fully controlled sterically, however, when a metal/ligand ratio of 2:1 was established by using a 1:1:1 mixture of $[Pd(dppp)]^{2+}/[Pd(dppe)]^{2+}/L^1$. The ^{31}P NMR resonances of the dppp and dppe complexes appear in significantly different regions of the NMR spectra. A comparison of the data collected in Table 2 with the ^{31}P NMR spectrum in Figure 12 reveals that the resonances of **3ac** and **4ac** can be assigned to corner-bound dppp complexes and edge-positioned $[Pd(dppe)]^{2+}$ tectons, whereas those ascribable to the opposite cases are missing from the spectrum. In other words, the sterically more encumbered $[Pd(dppp)]^{2+}$ tectons selectively coordinate to the less-hindered pyridyl nitrogen atoms, whereas the sterically less-demanding dppe complexes occupy the more-hindered chelating positions. Thus, the steric properties of L^1 arrange the **1a** and **1c** tectons in a complementary manner to achieve the energetically most favorable conditions.

Table 2. ^{31}P NMR chemical shifts of complexes formed at Pd/L^1 = 2:1.

	δ (^{31}P) [ppm]			
	tetrameric and higher aggregates		trimeric species	
P^P	corner	edge	corner	edge
dppp	6.35	15.34,[a] 15.59	6.85	13.82
dppe	64.68	68.95	65.47	68.51
dppp + dppe	6.33, 6.37[a]	67.87	6.94	67.23

[a] Overlapping resonances.

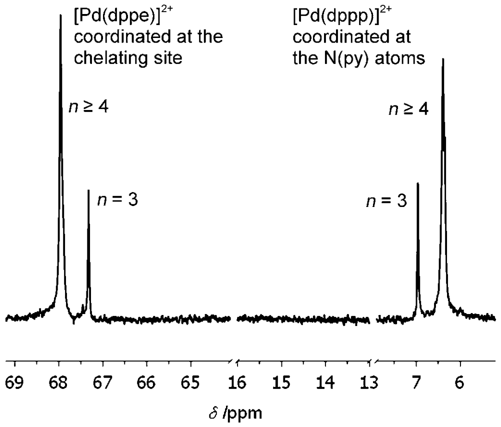


Figure 12. ^{31}P NMR spectra of the self-assembled complexes formed at a 1:1:1 mixture of $[Pd(dppp)]^{2+}/[Pd(dppe)]^{2+}/L^1$ (CD_2Cl_2, 298 K, $[L^1]$ = 32 mM).

Conclusions

The coordination properties of a novel Ar-BIAN ligand have been studied in the formation of self-assembled aggregates with *cis*-coordinated palladium complexes. We have shown that the dissimilar steric properties of the coordination sites, terminal pyridyl groups, and internal chelating imino nitrogen atoms can be exploited in two different ways to direct self-assemblies. With complexes of bulky diphosphanes, such as dppp and dppf, the steric differences can induce consecutive coordination of the metal complexes when the sterically more-hindered, chelating imino nitrogen atoms are utilized as donor sites only after the terminal pyridyl groups have been complexed. On the other hand, with an equimolar mixture of two metal complexes of dissimilar steric demands, a sterically-induced, size-selective coordination takes place and the components are arranged in a complementary manner. It should be possible to utilize this information to construct multinuclear, self-assembled catalysts with a frame that is held together by appropriately bulky corner tectons, whereas sterically less demanding metal complexes can act as catalytic centers at the more protected internal coordination positions. Furthermore, the observed proneness of the imino nitrogen atoms to establish hydrogen bonds may be a good starting point to design aggregates that are able to form host/guest complexes with multiple hydrogen-bond donors.

In the course of our studies to identify the self-assembled species, mass-spectrometric and DOSY NMR spectroscopic investigations have led to the unexpected observation of pentameric and hexameric aggregates. A joint evaluation of the results of our NMR and MS studies has shown that these high-nuclearity species should be considered as constituents of the reaction mixtures rather than artifacts of the ESI process. Structural studies on self-assembled aggregates of related Ar-BIAN ligands are in progress.

Experimental Section

Instrumentation: NMR spectra were recorded in CD_2Cl_2 or $CDCl_3$ on a Bruker Avance 400 spectrometer (^1H = 400 MHz, ^{31}P = 161.97 MHz, ^{15}N = 40.55 MHz (gradient-promoted, proton-detected HMBC experiments), ^{19}F = 376.498 MHz). A 5-mm *z*-gradient broadband observe (BBO) probe was used in all the experiments. Chemical shifts are referenced in ppm to trimethylsilane (TMS; Ξ = 100.000000 MHz) for ^1H or to external standards (^{31}P: 85% H_3PO_4, Ξ = 40.480742 MHz; ^{15}N: liquid NH_3, Ξ = 10.132912 MHz; ^{19}F: CCl_3F, Ξ = 94.094011 MHz). The software used was TOPSPIN 2.1.3. For ^{15}N NMR spectroscopy, HMQC spectra were recorded with ^{15}N–^1H coupling values between 3 and 8 Hz. Diffusion-ordered spectroscopy (DOSY)[30] used a standard BPP-LED sequence, a diffusion time of Δ = 50 ms, a gradient ramp adjusted to between 2 and 95% over 16 equidistant steps, and a gradient strength calibrated for the $CDHCl_2$ signal ($D_t = 3.17 \times 10^{-9}\,m^2 s^{-1}$). The DOSY spectra were processed using a monoexponential fitting procedure, and the experiments were carried out in standard 5-mm sample tubes without temperature regulation and heat-convection compensation. Abbreviations used in the description of the NMR spectra are s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, o = overlapping, sh = shoulder. The IR spectra were measured on a Thermo-Nicolet 320 FTIR spectrometer in KBr pellets. The ESI mass spectra of organic compounds were obtained on a Perkin–Elmer Sciex API 2000 triple quadrupole mass spectrometer fitted with an ESI source. The samples were dissolved in acetonitrile and introduced by flow-injection analysis. The mass-spectrometric experiments on the self-assembled complexes were performed on a high-resolution Q-TOF Premier mass spectrometer (Waters, Manchester) equipped with an electrospray ion source. The complexes were dissolved in acetone at different concentrations (i.e., 10 μM, 0.1 mM, 1 mM). These solutions were directly transferred into the ion source with a syringe pump at a flow rate of 5 $\mu L\,min^{-1}$. A positive ionization mode was applied using the following parameters: capillary voltage: 3 kV, cone: 0 eV, source temperature: 30 °C, desolvation temperature: 50 °C, desolvation gas: 800 $L\,h^{-1}$, cone gas: 20 $L\,h^{-1}$, collision energy: 0–10 eV. MassLynx 4.1 software was used for data acquisition and evaluation.

X-ray diffraction studies: Intensity data were collected on a Rigaku R-axis Rapid diffractometer with $Mo_{K\alpha}$ radiation (λ = 0.7107 Å). The data were corrected for absorption. The structures were solved by direct methods and refined by anisotropic least-squares against F^2 for the non-hydrogen atoms. Experimental temperature, final R and wR^2 values, number of reflections are as follows: 295 K, 0.0511, 0.1267, 6355 ($L^2{\cdot}CH_2Cl_2$); 151 K, 0.0428, 0.1020, 4843 ($L^2{\cdot}EtOH$); 295 K, 0.0622, 0.1100, 2960 ($L^2{\cdot}2\,CHCl_3$). CCDC-711119 ($L^2{\cdot}EtOH$), CCDC-711120 ($L^2{\cdot}2\,CHCl_3$), and CCDC-711350 ($L^2{\cdot}CH_2Cl_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Syntheses: All moisture-sensitive experiments were carried out under nitrogen using standard Schlenk techniques. Dichloromethane was freshly distilled from calcium hydride, methanol from magnesium methylate, and diethyl ether from sodium benzophenone ketyl. The starting materials for the ligand syntheses were purchased from commercial sources and used without purification. Palladium diphosphane complexes **1a**,[31] **1b**,[32] and **1c**;[33] 4-(4-pyridyl)aniline;[34] 4-(2-pyridyl)nitrobenzene;[35] and 4-(2-pyridyl)aniline[36] were prepared by using previously reported methods. The intermediate [(*N,N'*-bis{3,5-bis(trifluoromethyl)phenyl}bian)$ZnCl_2$] complex was synthesized by a modified procedure of Ragaini et al.[16b,c] Details of the preparations to yield L^1 and L^2 are described in the Supporting Information.[37]

Synthesis of metallacycles: The self-assembly of molecular aggregates from L^1 and the diphosphane complexes was accomplished both "in situ" in NMR tubes and on a preparative scale. To minimize the risk of hydrolysis of the imino functionality, which may be catalyzed by traces of acids, the NMR solvents were stored over CaH_2 and transferred into the NMR tubes by bulb-to-bulb distillation. The NMR spectroscopic data of species observable in solution are collected in Tables 1, S2, S3, and S4 (see the Supporting Information). Representative procedures are desribed below.

Preparation of assemblies 3a–5a: $[Pd(dppp)(H_2O)_2](OTf)_2$ (179.1 mg, 0.210 mmol) and L^1 (102.0 mg, 0.210 mmol) were stirred in dry CH_2Cl_2 (18 mL) in a Schlenk tube under N_2 for 90 min. The solvent was reduced to 5 mL under vacuum and freshly distilled diethyl ether (15 mL) was added slowly. The orange–yellow precipitate was collected on a Schlenk filter, washed with diethyl ether, and dried (252 mg, 92 %).

Preparation of assemblies 3aa–6aa: $[Pd(dppp)(H_2O)_2](OTf)_2$ (**1a**) (170.6 mg, 0.200 mmol) and L^1 (48.7 mg, 0.100 mmol) were placed in a Schlenk tube and dry CH_2Cl_2 (20 mL) was added. The solution was stirred at room temperature for 1.5 h under N_2. The yellow solution was concentrated to approximately 1/3 of the original volume and the product was precipitated by adding dry diethyl ether (10 mL). The lemon-yellow compound was isolated by filtration and dried (180 mg, 85 %). Reactions carried out analogously with **1b** resulted in a light-brown complex in nearly quantitative yield.

The reagents were weighed on a semimicro balance for the "in situ", NMR-scale experiments. A representative experiment was performed as follows: **1b** (16.42 mg, 0.0165 mmol) was charged into an NMR tube and placed in a Schlenk tube. The metal complex was evacuated and heated at 100 °C for 1.5 h. L^1 (8.03 mg, 0.0165 mmol) was placed into an oven-dried NMR tube and CD_2Cl_2 (0.55 mL) was added by bulb-to-bulb distillation. The suspension of the ligand was added to the metal complex to give a mixture of self-assembled complexes **3b**–**5b**. The ^1H NMR spectra indicates the presence of approximately 1/4 molecules of water for each $[Pd(dppf)L^1]$ building block. Self-assemblies with **1a** and **1c** tectons were carried out in a similar way to prepare $Pd/L^1 = 1{:}1$ and 2:1 complexes for NMR spectroscopic studies.

Preparation of the monomer 7a: $[Pd(dppp)(H_2O)_2](OTf)_2$ (12.4 mg, 0.0144 mmol) was dried in an NMR tube as described above. CD_2Cl_2 (0.6 mL) was distilled from a vial containing a suspension of CD_2Cl_2/CaH_2 into an NMR tube charged with L^2 (7.1 mg, 0.0144 mmol). The ligand was added to the metal complex under nitrogen to quantitatively yield **7a** (as shown by ^1H and ^{31}P NMR spectroscopic analysis).

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[37] Selected NMR spectra, mass-spectrometric data, detailed assignment of the ^{1}H and ^{31}P NMR spectra for all the major components, and the synthetic procedure for the preparation of ligands L^{1} and L^{2} are given in the Supporting Information.

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