Noncovalent Synthesis of Water-Soluble SCS Pd^{II} Pincer Assemblies

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Keywords: Palladium / Tridentate ligands / Noncovalent interactions / Dendrimers / Coordination chemistry

This article describes the noncovalent synthesis of water-soluble coordination assemblies based on SCS Pd^{II} pincer moieties. Two neutral solubilizing moieties, one based on a linear carbohydrate chain and the other on tetraethylene glycol residues, have been functionalized with pyridine and phosphane ligands. The coordination of the resulting molecules to various hydrophobic, cationic mono- and multimeric SCS Pd^{II} pincer systems has been investigated by ^1H and ^{31}P NMR spectroscopy, and by MALDI-TOF mass spectrometry. In general, the assemblies with tetraethylene glycol chains display a higher solubility in water than the ones containing linear sugar moieties. A hexapincer core decorated with six linear carbohydrates forms a hydrogel. Finally, a noncovalent water-soluble *metallodendrimer* having 18 peripheral tetraethylene glycol groups was constructed in a convergent manner.

Introduction

Dendrimers are highly branched globular macromolecules of low polydispersity.[1−8] They may lead to materials with new properties (e.g. catalytic, optical, magnetic, electro- and photochemical, and biomedical). The combination of dendrimer chemistry with the specific properties of (transition) metals is particularly appealing.[9−13] Metals can be incorporated either in the core,[14−19] the periphery,[20−25] or at each branching point[26] of dendrimers. They can also serve as the "glue" between dendritic building blocks.[27−29] Finally, metals may serve as structural auxiliaries (site-specific or random inclusion) in the dendritic framework, as shown by recent reports on the formation and stabilization of metal nanoclusters inside dendrimers,[30−33] which in some cases has led to new catalytic systems.[34,35]

In general, the solubility properties of dendrimers can be tailored by judicious choice of the peripheral groups. In this regard, dendrimers resemble globular proteins. The periphery of water-soluble, globular proteins (e.g., hemoglobin) is decorated with amino acids that have polar side chains such as glutamate, aspartate, lysine, and arginine.[36] Likewise, hydrophobic dendrimers have been solubilized in water by functionalization with carboxylates,[37−40] ammonium,[41,42] tris(hydroxymethyl)aminomethane ("tris"),[43,44] carbohydrate,[45−50] and oligoethylene glycol units.[51−53] The introduction of peripheral groups that render dendrimers water-soluble may prove a prerequisite for a number of (biochemical and pharmaceutical) applications. It has been shown that poly(amidoamine) (PAMAM) dendrimers and DNA form stable supramolecular complexes at physiological pH due to charge neutralization between the cationic ammonium groups of the dendrimer and the anionic phosphate groups of DNA.[54] Based on this phenomenon, the use of PAMAM dendrimers as efficient gene transfection vectors has been reported.[55,56]

Only a few groups have exploited *noncovalent* interactions between dendrimer peripheral guests and water-soluble hosts. Based on the well-known complexes between hydrophobic molecules and *cyclodextrins*,[57,58] Cuadrado, Kaifer and their co-workers solubilized dendrimers containing up to 64 peripheral ferrocene[59] and 32 cobaltocene[60] moieties in water. We have solubilized adamantyl-functionalized poly(propyleneimine) dendrimers of generations 1 to 5 in water at pH = 2 with β-cyclodextrin.[61]

The water solubility of metallodendrimers has hardly been investigated. Vögtle, Balzani, and their co-workers reported dendrimers based on a photo- and redoxactive $[Ru^{II}(bpy)_3]^{2+}$ core and peripheral "tris" or carboxylic acid moieties.[62] Constable et al. prepared multinuclear Ru^{II}−terpyridine assemblies by grafting linear oligonuclear complexes onto different cores.[63] The solubility of these complexes is dictated by the counterions. Whereas the chloride salts were soluble in methanol and water, the corresponding PF_6^- salts were soluble in acetonitrile and acetone.[64]

We have exploited the coordination chemistry of Pd^{II} in the noncovalent assembly of metallodendrimers using

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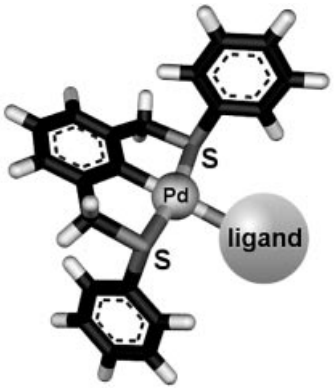


Figure 1. The SCS Pd^{II} pincer system; the fourth coordination site shown on the right (represented by the sphere labeled "ligand") is the anchoring position for dendritic building blocks

building blocks incorporating SCS Pd^{II} pincer moieties (Figure 1).[65]

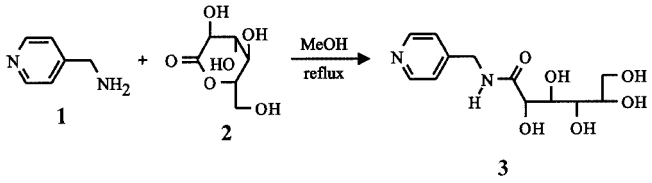
The coordination of cyano groups to Pd^{II} was first used in the *divergent* assembly of metallodendrimers up to generation five.[66] For convergent synthesis we combined nitrile, pyridine, and phosphane coordination.[67,68] Many of these polycationic metallodendrimers suffer from a low solubility in apolar organic solvents due to the presence of SCS Pd^{II} pincers at the periphery of the metallodendrimers. Therefore, we recently introduced a hydrophobic layer of covalently synthesized poly(aryl ether) dendrons at the metallodendrimer periphery, and found that the solubility of the assemblies in apolar solvents increased dramatically.[68]

In this article, the noncovalent synthesis of water-soluble coordination assemblies based on SCS Pd^{II} pincer moieties is described. Both carbohydrate and tetraethylene glycol chains, functionalized with pyridine and phosphane groups, have been employed as peripheral ligands for mono- and multinuclear SCS Pd^{II} pincer systems, resulting in water-soluble polyelectrolytes. Since SCS Pd^{II} pincers have recently been shown to be catalytically active,[69–73] the water-soluble multinuclear Pd^{II} pincers reported in this article might be useful as recyclable catalysts in aqueous systems. Because of their size, the assemblies should be separable from reaction mixtures by nanofiltration methods.[74–76]

Results and Discussion

Synthesis of Water-Solubilizing Ligands

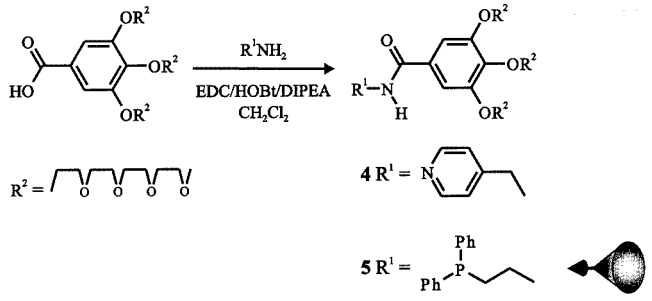
We have previously investigated the coordination strength of a variety of ligands towards the SCS Pd^{II} pincer system.[77] From this study and work by the group of Fujita,[78] we anticipated that water-solubilizing ligands based on pyridines or phosphanes should be suitable for preparing water-soluble coordination assemblies. A pyridine derivative with a polyhydroxylated tail (**3**) was synthesized by ring-opening of gluconolactone (**2**) with 4-aminomethylpyridine (**1**) (Scheme 1). A similar reaction was used by Aoyama et al. for the ring-opening of lactonolactone by a calix[4]resorcinareneoctaamine.[79]



Scheme 1. Ring-opening of gluconolactone **2** by 4-(aminomethyl)-pyridine (**1**)

Pyridine **3** precipitated from the reaction mixture upon refluxing stoichiometric amounts of **1** and **2** in methanol. It was characterized by ^1H and ^{13}C NMR spectroscopy, and FAB mass spectrometry. The CH framework of the linear carbohydrate chain could be assigned with the aid of ^1H-^1H COSY NMR spectroscopy in D_2O, whereas the COSY spectrum of **3** in [D_6]DMSO is more complex due to additional couplings with OH protons. Furthermore, the four CH carbon atoms of the carbohydrate chain display diagnostic signals between δ = 70 and 66 ppm in the ^{13}C NMR spectrum (see Exp. Sect.). The hydroxy groups of pyridine **3** provide a high solubility in water and DMSO, whereas the solubility in apolar solvents such as chloroform is negligible.

As another type of water-solubilizing ligand, the 3,4,5-tris(tetraethyleneoxy)benzoyl moiety, also used by Baars et al., was chosen.[80] Ligands **4** and **5** were prepared from 3,4,5-tris(tetraethyleneoxy)benzoic acid[80] by reaction with 4-(aminomethyl)pyridine and 2-(diphenylphosphanyl)ethylamine, respectively, using EDC/HOBt/DIPEA as the coupling reagents, both in 78% yield (Scheme 2).



Scheme 2. Synthesis of water-solubilizing ligands **4** and **5**; the schematic representation depicted next to **5** is used in Scheme 4

They were obtained as colorless oils and characterized by ^1H, ^{13}C, and ^{31}P (ligand **5**)[81] NMR spectroscopy, and FAB mass spectrometry. The ^1H NMR spectrum of **4** in CD_3CN is displayed in Figure 2 (top).

Both **4** and **5** display a high solubility in both water and apolar solvents such as chloroform and dichloromethane, which is an advantage compared to polyhydroxylated ligand **3** with respect to handling, characterization, and dendrimer construction (vide infra).

Coordination of Water-Solubilizing Ligands to SCS Pd^{II} Pincers

Having available water-solubilizing ligands **3**, **4**, and **5**, their coordination to a variety of SCS Pd^{II} pincer systems

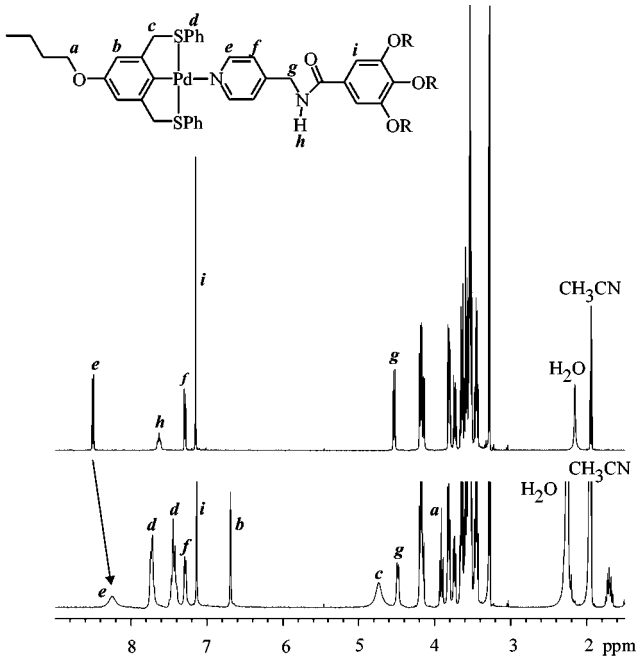


Figure 2. ^{1}H NMR spectra (CD_3CN, 298 K) of ligand **4** (top) and complex $[M\cdot\mathbf{4}]^+(BF_4^-)$

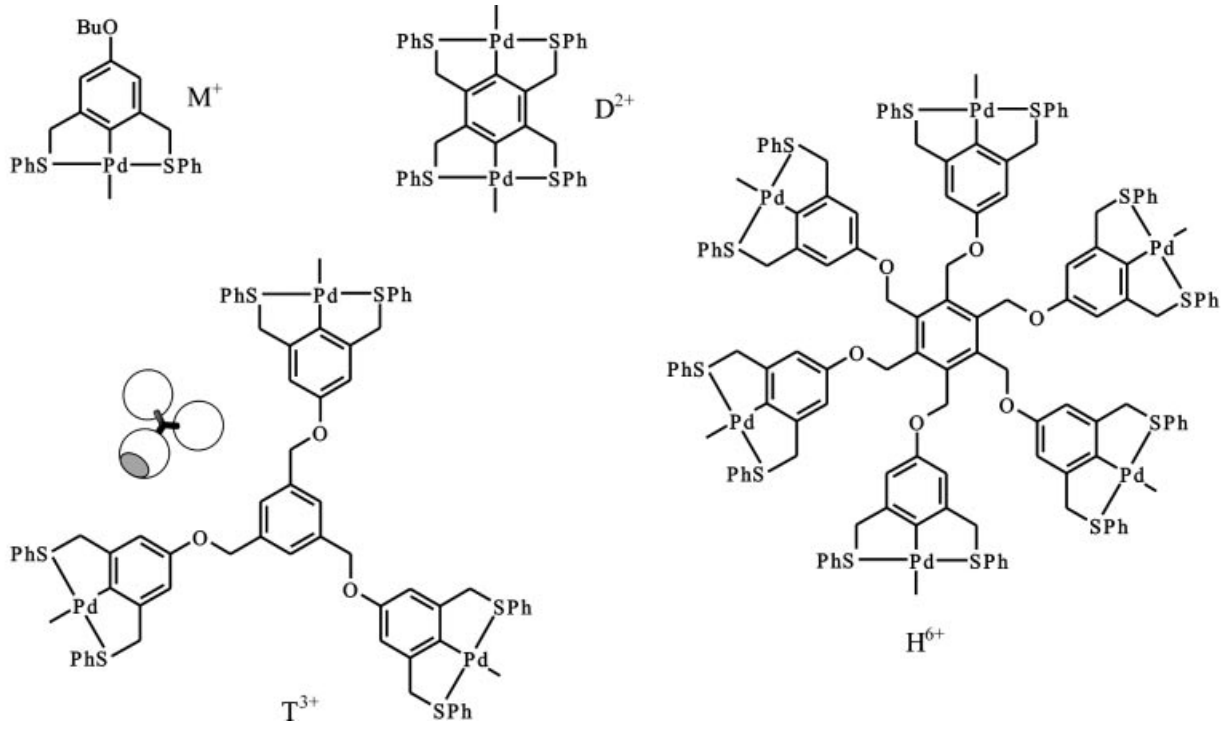
(monopincer M^+,[77] dipincer D^{2+},[82] tripincer T^{3+},[66] and hexapincer H^{6+}, Scheme 3) was investigated.

Hexapincer H^{6+} was synthesized by sixfold alkylation of hexakis(bromomethyl)benzene with 3,5-bis(phenylthiamethyl)phenol,[83] followed by cyclopalladation of the resulting hexapincer ligand with $Pd[MeCN]_4(BF_4)_2$. All cationic pincer systems were isolated as the corresponding tetrafluoroborate salts, which might affect their water solubility after coordination of **3**, **4**, or **5**. As mentioned before, the nature of the anions can be a determining factor in the solubility of metallodendrimers.[64]

Complexes with Ligand 3

The coordination of polyhydroxylated pyridine ligand **3** to SCS Pd^{II} pincers was investigated with T^{3+} and H^{6+}. $[T\cdot 3MeCN]^{3+}(BF_4^-)_3$, having three acetonitrile molecules as temporary ligands for Pd^{II}, was dissolved in CH_3CN and mixed with 3 equiv. of **3** in H_2O. After evaporation of the solvents, the resulting assembly was found to be insoluble in D_2O, and its ^{1}H NMR spectrum was therefore taken in [D_6]DMSO. The signal of the α-pyridyl protons of **3** is broad and shifted upfield compared to uncoordinated **3**, and the broad signal of the CH_2S protons of T^{3+} is shifted downfield with respect to $[T\cdot 3MeCN]^{3+}(BF_4^-)_3$. Both these features are in accordance with previous observations,[67,77] proving the coordination of pyridine ligand **3** to the pincer moieties of T^{3+}. Changing the deprotecting agent from $AgBF_4$ to $AgNO_3$, thereby introducing hydrophilic nitrate anions instead of hydrophobic tetrafluoroborate anions, resulted in a better water solubility of the trinuclear assembly. However, the ^{1}H NMR spectrum of this complex in D_2O has very broad signals which prevents definite assignment.

Hexanuclear $[H\cdot 6MeCN]^{6+}(BF_4^-)_6$ was mixed in CD_3CN with 6 equiv. of **3** dissolved in hot [D_4]MeOH. The clear solution thus obtained was analyzed by ^{1}H NMR spectroscopy. Coordination of **3** was again evident from the broadening and upfield shift of the signal from the α-pyridyl protons. After evaporation of the solvents, the assembly



Scheme 3. Structure of SCS Pd^{II} pincer systems M^+, D^{2+}, T^{3+}, and H^{6+}; the schematic representation depicted near T^{3+} is used in Scheme 4

could be dissolved in hot D_2O. Upon cooling of this solution, a gel was formed, and the ^1H NMR spectrum of the very viscous D_2O solution only shows signals that can be assigned to protons of ligand **3**. Gel formation from other polyhydroxylated dendrimers, e.g., the arborols having peripheral "tris" moieties reported by Newkome and others,[43,44] is a well-known phenomenon. The addition of [D_6]DMSO to the aqueous gel resulted in the appearance of signals that could be ascribed to the hexanuclear pincer moiety, although at 50% DMSO these signals were still very broad. In order to verify that H^{6+} was indeed present in the aqueous gel, an excess of [D_5]pyridine was added, which resulted in the precipitation of a yellow solid. This material was extracted with CH_2Cl_2, and subsequently identified as $[H{\cdot}6([D_5]pyr)]^{6+}(BF_4^-)_6$ by ^1H NMR spectroscopy.

Complexes with Ligand 4

Since M^+, D^{2+}, and H^{6+} were all synthesized as acetonitrile complexes, they are all highly soluble in acetonitrile. Therefore, they were mixed with 1, 2, and 6 equiv. of pyridine ligand **4** in CD_3CN, respectively, and the resulting clear solutions were analyzed by ^1H NMR spectroscopy. The following features are shared by the NMR spectra of $[M{\cdot}\mathbf{4}]^+(BF_4^-)$, $[D{\cdot}\mathbf{4}_2]^{2+}(BF_4^-)_2$, and $[H{\cdot}\mathbf{4}_6]^{6+}(BF_4^-)_6$ in CD_3CN:

a) An upfield shift from $\delta = 8.50$ (in free **4**) to $\delta = 8.25-8.15$ ppm of the α-pyridyl protons of ligand **4** upon coordination, as exemplified by the ^1H NMR spectra of **4** and $[M{\cdot}\mathbf{4}]^+(BF_4^-)$ displayed in Figure 2. Moreover, a significant broadening of the α-pyridyl proton signal (signal ***e*** in Figure 2) occurs upon coordination. This may be caused by slow rotation of the pyridine ligands with respect to the plane of coordination and/or a ligand exchange rate that is similar to the NMR time scale. Upon adding an excess of **4** (1.4 equiv.) the α-pyridyl proton signal remains broad and shifts downfield. No α-pyridyl proton doublet from uncoordinated **4** at $\delta = 8.5$ ppm is observed (as in the top spectrum of Figure 2), indicating that the signals are averaged due to ligand exchange in this solvent; however, the exchange is not fast enough to produce a sharp signal. In order to further probe which of the two above effects is dominant, the NMR spectrum of $[M{\cdot}\mathbf{4}]^+(BF_4^-)$ was also recorded in $CDCl_3$. The sharp doublet for the coordinated α-pyridyl protons at $\delta = 7.73$ ppm (shifted 0.77 ppm upfield compared to uncoordinated **4** in $CDCl_3$) indicates fast rotation of the pyridine ligand with respect to the plane of coordination. Moreover, the coordination shift of the α-pyridyl protons is much larger than in CD_3CN. Upon the addition of CD_3CN to the $CDCl_3$ solution the doublet at $\delta = 7.73$ ppm becomes broad and shifts downfield. In another experiment, the addition of excess pyridine ligand **4** to $[M{\cdot}\mathbf{4}]^+(BF_4^-)$ in $CDCl_3$ resulted in two separate signals for free and coordinated ligand, indicating slow ligand exchange on the NMR time scale. The influence of [D_6]DMSO on the pyridine exchange rate in $CDCl_3$ was discussed in a previous article,[77] and the rate increase upon adding [D_6]DMSO was rationalized by assuming that DMSO facilitates an associative solvolysis pathway. The ^1H NMR signals for uncoordinated and coordinated pyridine merge into one broad signal upon increasing the percentage of DMSO. A similar experiment with CD_3CN instead of [D_6]DMSO indicates that acetonitrile also increases the rate of ligand exchange. However, acetonitrile differs from DMSO in the sense that it also competes with **4** for ligation to the fourth coordination site of the pincer. Upon increasing the concentration of CD_3CN, the amount of ligand **4** that is expelled from the pincer by acetonitrile also increases. The fast ligand exchange then results in a downfield shift of the broad α-pyridyl proton signal toward the position of uncoordinated **4**. For $[M{\cdot}\mathbf{4}]^+(BF_4^-)$ in $CDCl_3$/CD_3CN, 90:10 (v/v), the α-pyridyl proton signal is found at $\delta = 7.78$ ppm (close to $\delta = 7.73$ ppm for neat $CDCl_3$), whereas in neat CD_3CN this signal is observed at $\delta = 8.23$ ppm (Figure 2 bottom). In summary, the above NMR observations indicate the following: 1. slow exchange of pyridine ligand **4** in $CDCl_3$, and no competition from the solvent for coordination to the SCS Pd^{II} pincer; 2. a ligand exchange rate that is similar to the NMR time scale in CD_3CN, and competition from the solvent for coordination.

b) A broad signal at $\delta = 4.62-4.74$ ppm of the CH_2S protons of the pincer moiety. This also indicates coordination of **4** to Pd^{II}, since the CH_2S protons give a signal at $\delta = 4.5-4.6$ ppm in the acetonitrile complexes.

c) Sharp signals of all other resonances.

After evaporation of CD_3CN, enough material of complexes $[D{\cdot}\mathbf{4}_2]^{2+}(BF_4^-)_2$ and $[H{\cdot}\mathbf{4}_6]^{6+}(BF_4^-)_6$ could be taken up in D_2O in order to obtain meaningful ^1H NMR spectra. Complex $[M{\cdot}\mathbf{4}]^+(BF_4^-)$ was less soluble in D_2O, and a satisfactory ^1H NMR spectrum could not be obtained. However, $[M{\cdot}\mathbf{4}]^+(BF_4^-)$ was successfully characterized by MALDI-TOF mass spectrometry (vide infra). In contrast to CD_3CN, $[D{\cdot}\mathbf{4}_2]^{2+}(BF_4^-)_2$ and $[H{\cdot}\mathbf{4}_6]^{6+}(BF_4^-)_6$ display very broad signals in their ^1H NMR spectra in D_2O. Moreover, the signals of the SCS pincer parts are very hard to distinguish. A representative spectrum of $[H{\cdot}\mathbf{4}_6]^{6+}(BF_4^-)_6$ in D_2O is shown in Figure 3.

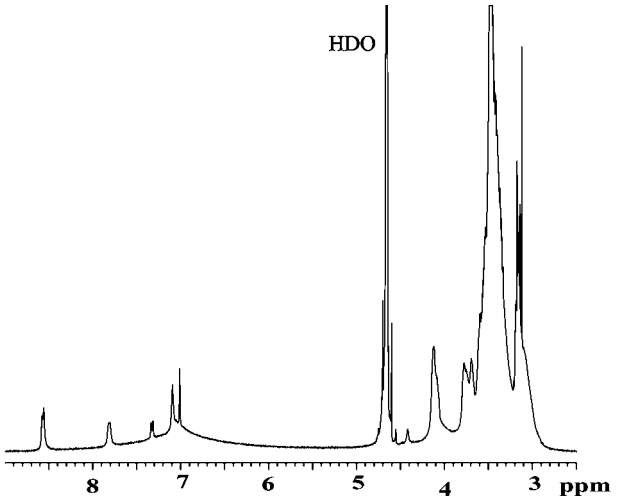


Figure 3. ^1H NMR spectrum (D_2O, 298 K) of $[H{\cdot}\mathbf{4}_6]^{6+}(BF_4^-)_6$

The sharp signals between δ = 6 and 9 ppm in this spectrum originate from coordinated ligand **4**, whereas the very broad signal centered at δ ≈ 7 ppm probably arises from protons of the hexanuclear core. It is probable that the hydrophobic parts of these assemblies are very restricted in their motion because they are shielded from the solvent by the more hydrophilic parts, and that this causes their very broad signals.

Trinuclear complex $[T{\cdot}\mathbf{4}_3]^{3+}(NO_3^-)_3$ was synthesized from T·3Cl by deprotection of the chloride ligands with $AgNO_3$ in CH_2Cl_2, followed by addition of 3 equiv. of pyridine ligand **4**. The resulting assembly was first investigated by ^{1}H NMR spectroscopy in D_2O. As in the case of the assemblies described in the previous paragraph, signals of the trinuclear core could not be distinguished, and the spectrum is nearly identical to that of **4** alone in D_2O. However, addition of CD_3CN resulted in a significant increase in the intensity of the signals of the core, although the integrals are still too low to fit a 1:3 ratio of T/**4**. Unfortunately, MALDI-TOF mass spectrometry of $[T{\cdot}\mathbf{4}_3]^{3+}(NO_3^-)_3$ gave poor results, and signals that could be assigned to $[M - n(NO_3)]^+$ (n = 1−3) were not found.

Complexes with Ligand 5

Hexanuclear complex H^{6+} was mixed in CD_3CN with 6 equiv. of phosphane ligand **5**. Coordination of all phosphane ligand to the pincers was evident from both ^{1}H and ^{31}P NMR spectroscopy. In the ^{1}H NMR spectrum of the assembly the doublet at δ = 6.72 ppm indicates the splitting of the Ar_{Pd} protons by ^{1}H-^{31}P coupling (as observed before for phosphane coordination to Pd^{II}),[77] whereas the ^{31}P NMR spectrum shows a shift from δ = −20.4 (free **5**) to 2.0 ppm upon coordination.

Assembly $[H{\cdot}\mathbf{5}_6]^{6+}(BF_4)_6$ is highly water-soluble; however, its ^{1}H NMR spectrum in D_2O again reveals very broad, unassignable signals. Moreover, the signal at δ = 2.0 ppm in the ^{31}P NMR spectrum has almost disappeared in D_2O. Again this is assigned to the restricted mobility of the hexanuclear core. The formation of assembly $[H{\cdot}\mathbf{5}_6]^{6+}(BF_4^-)_6$ was further evidenced by a very intense signal at m/z = 8959.2 in its MALDI-TOF mass spectrum, corresponding to $[M - BF_4]^+$ (calcd. 8960.2).

Convergent Metallodendrimer Synthesis Starting from Ligand 5

The convergent synthesis of metallodendrimers starting from phosphane dendritic wedges has recently been reported.[68] It was anticipated that replacing the phosphane dendrons by phosphane ligand **5** in this growth scheme would lead to water-soluble metallodendrimers. There are three advantages of using phosphane **5** for this purpose over pyridine **3**. First, ligand **5** is a better water-solubilizing ligand than **3**, due to its three tetraethylene glycol chains compared to one polyhydroxylated chain in **3**. Second, convergent growth starting from phosphanes enables higher dendritic generations to be constructed than growth commencing from pyridines.[68] Third, both ligand **5** and assemblies built from it are also soluble in apolar solvents such as CH_2Cl_2 and $CHCl_3$, which is advantageous in both synthesis and characterization.

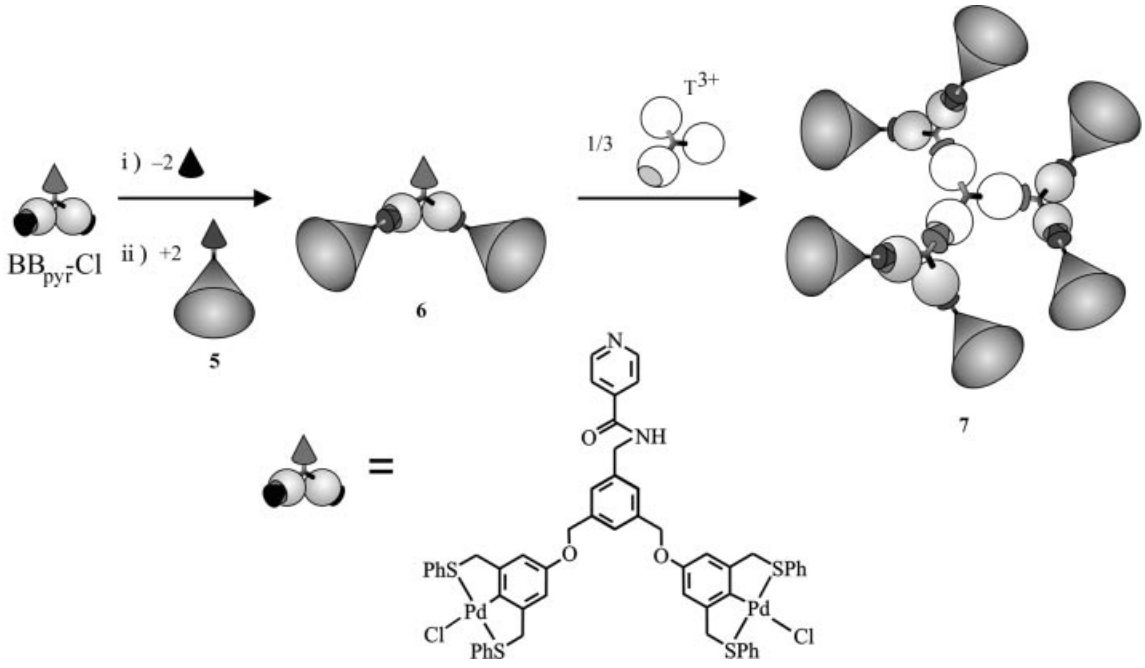
Two phosphane ligands **5** were coordinated to the SCS Pd^{II} pincer moieties of deprotected pyridine building block BB_{pyr}−Cl (Scheme 4) to give dendritic wedge **6** containing a focal pyridine moiety, which was immediately used for further coordination; 3 equiv. of **6** were complexed around T^{3+} to produce metallodendrimer **7** in 89% overall yield.

The integrity of the metallodendritic structure in $CDCl_3$ was confirmed by ^{1}H and ^{31}P NMR spectroscopy, and MALDI-TOF mass spectrometry. The coordination of the phosphane moieties to Pd^{II} was evident from the ^{31}P NMR spectrum of **7**, in which a diagnostic signal at δ = 2.2 ppm was observed. The very broad signal at δ ≈ 8.2 ppm in the ^{1}H NMR spectrum of **7** indicated the coordination of the pyridine groups of **6** to the Pd^{II} centers of T^{3+}. As for other metallodendrimers[67,68] and due to its size, broad signals for nearly all protons were observed in the ^{1}H NMR spectrum of metallodendrimer **7**. The intense signal at m/z = 11.2 kDa in the MALDI-TOF mass spectrum of **7**, originating from the $[M - BF_4]^+$ ion, confirms its successful assembly.

MALDI-TOF Mass Spectrometry of Water-Soluble Assemblies

Matrix-Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF) and Electrospray Ionization (ESI) mass spectrometry have emerged as powerful analytical techniques in supramolecular chemistry,[84] notably in the characterization of assemblies based on noncovalent metal−ligand coordination, and recently even in the mass determination of hydrogen-bonded assemblies.[84][85] Both ESI-MS and MALDI-TOF MS have been employed in the characterization of metallodendrimers constructed in our group.[66−68] Most of the water-soluble coordination assemblies reported herein were also characterized by MALDI-TOF mass spectrometry, and the results are compiled in Table 1. The spectrum of $[H{\cdot}\mathbf{5}_6]^{6+}(BF_4^-)_6$ shown in Figure 4 is representative.

The spot wells of the MALDI-TOF sample plate containing millimolar solutions of the assemblies in water or acetonitrile were covered with a thin poly(ethylene glycol) film.[86][87] In this way most of the original constitution of the sample solutions is preserved, and evaporation is kept to a minimum. Using this method, the $[M - BF_4]^+$ signals in the MALDI-TOF spectra confirm the stability of the assemblies in the original solutions. It can therefore be concluded from Table 1 that the noncovalent coordination assemblies based on pyridine and phosphane coordination are stable enough both in acetonitrile and in water in order to be characterized successfully by MALDI-TOF mass spectrometry, even though there is competition from acetonitrile for coordination to the pincer in the case of pyridine ligand **4**, as discussed above. The presence of $[M{\cdot}MeCN]^+(BF_4^-)$ in the acetonitrile solution of $[M{\cdot}\mathbf{4}]^+(BF_4^-)$ (the first entry in Table 1) was indicated by a signal at m/z = 500.8 in the MALDI-TOF spectrum of $[M{\cdot}\mathbf{5}]^+(BF_4^-)$, corresponding to



Scheme 4. Convergent synthesis of metallodendrimer **7** containing 18 peripheral tetraethylene glycol chains

Table 1. Characterization of coordination assemblies by MALDI-TOF mass spectrometry

Compound	Solvent	Fragment	Obsd. mass (Da)	Calcd. mass (Da)
$[M\cdot\mathbf{4}]^+(BF_4^-)$	CH_3CN	$[M - BF_4]^+$	1329.3	1329.5
$[D\cdot\mathbf{4}_2]^{2+}(BF_4^-)_2$	CD_3CN	$[M - BF_4]^+$	2534.6[a]	2526.4
$[D\cdot\mathbf{4}_2]^{2+}(BF_4^-)_2$	D_2O	$[M - BF_4]^+$	2530.1[a]	2526.4
$[H\cdot\mathbf{4}_6]^{6+}(BF_4^-)_6$	CH_3CN	$[M - BF_4]^+$	8224.7	8225.6
$[H\cdot\mathbf{4}_6]^{6+}(BF_4^-)_6$	H_2O	$[M - BF_4]^+$	8224.7	8225.6
$[H\cdot\mathbf{5}_6]^{6+}(BF_4^-)_6$	CH_3CN	$[M - BF_4]^+$	8959.2	8960.2
7	$CDCl_3$	$[M - BF_4]^+$	11227	11225.1

[a] Difference between experimentally observed and calculated mass might be due to some deuterium exchange of the solvent used and/or the accuracy of the mass assignment of the unresolved peak in the mass spectrum.

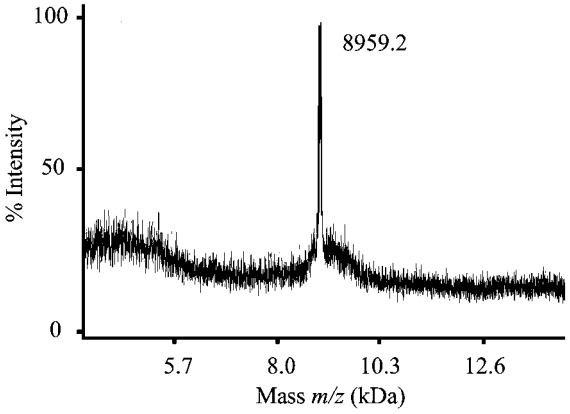


Figure 4. MALDI-TOF mass spectrum of $[H\cdot\mathbf{5}_6]^{6+}(BF_4^-)_6$

$[M - MeCN - BF_4]^+$. However, this signal might also originate from fragmentation during the ionization process of $[M\cdot\mathbf{4}]^+(BF_4^-)$ inside the mass spectrometer.

Conclusions

In this article the synthesis and characterization of water-soluble assemblies based on metal−ligand coordination have been described. Carbohydrate and oligoethylene glycol moieties have been functionalized with pyridine and phosphane groups, and the resulting molecules have been employed as water-solubilizing ligands for mono-, di-, tri-, and hexanuclear SCS Pd^{II} pincer systems. The majority of these assemblies are soluble in water, and most complexes could be characterized by NMR spectroscopy and MALDI-TOF mass spectrometry. An aqueous gel has been obtained for a hexanuclear SCS Pd^{II} pincer system decorated with six linear carbohydrate ligands. Finally, a water-soluble metallodendrimer has been obtained by convergent dendritic growth starting from a phosphane ligand containing three tetraethylene glycol residues.

The water-soluble multinuclear Pd^{II} pincers reported herein might be useful as recyclable catalysts in aqueous

systems. Because of their size, the assemblies should be separable from reaction mixtures by nanofiltration methods.

Experimental Section

General Remarks: CH_2Cl_2 was freshly distilled from $CaCl_2$. CH_3CN (p.a. from Merck) was stored over molecular sieves (4 Å). Other solvents (MeOH, acetone) were used as received (p.a. from Merck). All reagents were purchased from Aldrich and used without further purification. All solution manipulations with phosphanes were performed in degassed solvents. NMR spectra were recorded in $CDCl_3$ (unless stated otherwise) at 298 K with a Varian Unity 300 locked to the deuterated solvent at 300.1 (^{1}H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz, respectively. Chemical shifts are given relative to tetramethylsilane (TMS). FAB mass spectra were recorded with a Finnigan MAT 90 mass spectrometer with *m*-nitrobenzyl alcohol (NBA) as the matrix. Matrix-Assisted Laser Desorption Ionisation (MALDI) Time-of-Flight (TOF) mass spectra[88] were recorded using a Voyager-DE-RP MALDI-TOF mass spectrometer (Applied Biosystems/PerSeptive Biosystems, Inc., Framingham, MA, USA) equipped with delayed extraction.[89] A 337-nm UV nitrogen laser producing 3-ns pulses was used and the mass spectra were obtained in the linear and reflectron mode. Column chromatography was performed using silica gel (SiO_2, 0.040−0.063 mm, 230−240 mesh). 3,4,5-Tris(tetraethyleneoxy)benzoic acid,[80] T·3Cl,[66] BB_{pyr}−Cl,[67] $[M{\cdot}MeCN]^+(BF_4^-)$,[77] $[D{\cdot}2MeCN]^{2+}(BF_4^-)_2$,[82] and 3,5-bis(phenylthiamethyl)phenol[83] were synthesized according to literature procedures.

Pyridine Ligand 3: To a solution of gluconolactone (2.55 g, 14.3 mmol) in MeOH (50 mL) was slowly added 4-(aminomethyl)-pyridine (1.5 mL, 14.8 mmol). The mixture was refluxed overnight under argon, and subsequently the white precipitate was filtered and thoroughly dried. Pure product was obtained in this manner, as determined by TLC [R_f = 0.22 in 2-propanol/EtOAc/H_2O, 3:6:2 (v/v/v)]. Yield 2.98 g (73%). M.p. 169−171 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 3.40 (s, 1 H, CH), 3.51 (s, 1 H, CH), 3.59 (d, *J* = 9.9 Hz, CH_2OH), 3.98 (s, 1 H, CH), 4.10 (s, 1 H, CH), 4.29−4.41 (m, 4 H, CH_2N + OH), 4.54 (s, 1 H, OH), 4.59 (s, 1 H, OH), 5.53 (s, 1 H, OH), 7.27 (d, *J* = 5.9 Hz, 2 H, β-pyr H), 8.33 (t, *J* = 5.9 Hz, 1 H, NH), 8.44 (d, *J* = 5.9 Hz, 2 H, α-pyr H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 36.8, 59.3, 66.1, 67.5, 68.5, 69.9, 118.0, 144.7, 145.2, 169.0 ppm. FAB-MS: *m*/*z* = 287.1 ([M + H]$^+$, calcd. for $C_{12}H_{18}N_2O_6$: 287.1). A satisfactory elemental composition could not be obtained.

Pyridine Ligand 4: To a solution of 3,4,5-tris(tetraethyleneoxy)benzoic acid (1.08 g, 1.46 mmol), 1-hydroxybenzotriazole hydrate (0.22 g, 1.63 mmol), 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (0.31 g, 1.62 mmol), and *N*,*N*-diisopropylethylamine (0.63 mL, 3.62 mmol) in CH_2Cl_2 (100 mL) was added dropwise a solution of 4-(aminomethyl)pyridine (0.16 g, 1.48 mmol) in CH_2Cl_2 (20 mL). After the reaction mixture was stirred at room temp. overnight, the solution was washed with $NaHCO_3$ (satd.) and brine. After drying with Na_2SO_4, the organic phase was concentrated under reduced pressure. The crude product was purified by column chromatography using CH_2Cl_2/CH_3OH/NH_3 (25% aq.), 95:5:1 (v/v/v) as the eluent, affording a transparent viscous oil. Yield 0.95 g (78%). ^{1}H NMR: δ = 3.31 (s, 6 H, CH_3), 3.34 (s, 3 H, CH_3), 3.47−3.52 (m, 6 H, CH_2), 3.57−3.62 (m, 24 H, CH_2), 3.65−3.68 (m, 6 H, CH_2), 3.75−3.81 (m, 6 H, CH_2), 4.17−4.21 (m, 6 H, CH_2), 4.60 (d, *J* = 6.2 Hz, 2 H, CH_2N), 7.20 (s, 2 H, Ar H), 7.26 (d, *J* = 5.9 Hz, 2 H, β-pyr H), 7.37 (t, *J* = 6.2 Hz, 1 H, NH), 8.52 (d, *J* = 5.9 Hz, 2 H, α-pyr H) ppm. ^{13}C NMR: δ = 42.3, 58.4, 68.7, 69.2, 69.8, 70.0, 71.4, 71.8, 107.4, 122.0, 128.4, 141.4, 148.0, 149.0, 152.0, 166.6 ppm. FAB-MS: *m*/*z* = 831.5 ([M + H]$^+$, calcd. for $C_{40}H_{67}N_2O_{16}$: 831.4), 853.5 ([M + Na]$^+$), 869.5 ([M + K]$^+$).

Phosphane Ligand 5: To a solution of 3,4,5-tris(tetraethyleneoxy)-benzoic acid (0.55 g, 0.74 mmol), 1-hydroxybenzotriazole hydrate (0.11 g, 0.81 mmol), 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (0.16 g, 0.83 mmol), and *N*,*N*-diisopropylethylamine (0.26 mL, 1.49 mmol) in CH_2Cl_2 (50 mL) was added dropwise a solution of 2-(diphenylphosphanyl)ethylamine (0.17 g, 0.74 mmol) in CH_2Cl_2 (10 mL). After the reaction mixture was stirred at room temp. overnight under argon, the solution was washed with $NaHCO_3$ (satd.) and brine. After drying with Na_2SO_4, the organic phase was concentrated under reduced pressure. The crude product was purified by column chromatography using CH_2Cl_2/CH_3OH, 96:4 (v/v) as the eluent, affording a transparent viscous oil. Yield 0.55 g (78%). ^{1}H NMR: δ = 2.38−2.43 (m, 2 H, PCH_2), 3.33 (s, 6 H, CH_3), 3.35 (s, 3 H, CH_3), 3.48−3.56 (m, 8 H, CH_2), 3.59−3.70 (m, 30 H, CH_2), 3.75−3.83 (m, 6 H, CH_2), 4.15−4.18 (m, 6 H, CH_2), 6.55 (t, *J* = 5.7 Hz, 1 H, NH), 6.99 (s, 2 H, Ar H), 7.30−7.35 (m, 6 H, Ar H), 7.42−7.48 (m, 4 H, Ar H) ppm. ^{13}C NMR: δ = 27.9 (d, *J* = 13.1 Hz, PCH_2CH_2), 37.0 (d, *J* = 20.8 Hz, PCH_2), 58.5, 68.6, 69.2, 70.0−70.1, 71.4, 71.8, 106.8, 128.0, 128.3, 128.4, 130.1, 132.2, 137.2, 151.9, 166.3 ppm. FAB-MS: *m*/*z* = 952.6 ([M + H]$^+$, calcd. for $C_{48}H_{75}NO_{16}P$: 952.5), 968.6 ([MO + H]$^+$).

Hexapincer Ligand: A mixture of hexakis(bromomethyl)benzene (0.16 g, 0.25 mmol), 3,5-bis(phenylthiamethyl)phenol (0.60 g, 1.77 mol), K_2CO_3 (0.49 g, 3.55 mmol), and 18-crown-6 (0.07 g, 0.26 mmol) in acetone (100 mL) was refluxed overnight under argon. After evaporation of the solvent under reduced pressure, the resulting paste was taken up in CH_2Cl_2 (100 mL) and washed with brine. The organic phase was dried with Na_2SO_4, and subsequently concentrated to dryness. The crude product was purified by column chromatography using CH_2Cl_2/hexane, 60:40 (v/v) as the eluent, affording a colorless viscous oil. Yield 0.45 g (82%). ^{1}H NMR: δ = 3.91 (s, 24 H, CH_2S), 4.97 (s, 12 H, CH_2O), 6.63 (s, 12 H, Ar H), 6.82 (s, 6 H, Ar H), 7.07−7.22 (m, 30 H, SPh H) ppm. ^{13}C NMR: δ = 38.3, 63.2, 113.6, 122.0, 125.9, 128.3, 129.3, 135.7, 137.2, 138.8, 158.1 ppm. FAB-MS: *m*/*z* = 2179.6 ([M + H]$^+$, calcd. for $C_{132}H_{115}O_6S_{12}$: 2179.5).

$[H{\cdot}6MeCN]^{6+}(BF_4^-)_6$: To a solution of the hexapincer ligand (60 mg, 0.028 mmol) in a mixture of CH_3CN (40 mL) and CH_2Cl_2 (10 mL) was added $Pd(MeCN)_4(BF_4)_2$ (77 mg, 0.173 mmol) in one portion. The solution was stirred at room temp. under argon for 1 h, followed by evaporation of the solvents in vacuo. The crude product was purified by size exclusion chromatography using Sephadex LH-20 as the column material and CH_3CN as the eluent, affording a yellow/brown solid. Yield 53 mg (54%). ^{1}H NMR (CD_3CN): δ = 4.51 (br. s, 24 H, CH_2S), 5.14 (s, 12 H, CH_2O), 6.56 (s, 12 H, Ar_{Pd} H), 7.47−7.53 (m, 18 H, SPh H), 7.77−7.80 (m, 12 H, SPh H).

Metallodendrimer 7: To a solution of BB_{pyr}−Cl (5.6 mg, 4.7 μmol) in CH_2Cl_2 (2 mL) was added $AgBF_4$ (92 μL of a 0.1019 M solution, 9.4 μmol), and the mixture was stirred vigorously for 10 min, followed by addition of phosphane ligand **5** (8.9 mg, 9.4 μmol) in CH_2Cl_2 (1 mL). After stirring at room temp. for 10 min, the mixture was filtered through Hyflo and the solvents were evaporated to dryness. The resulting dendritic wedge **6** was dissolved in CH_2Cl_2 (1 mL) and added to T·3Cl (2.4 mg, 1.6 μmol) which had been de-

protected with $AgBF_4$ (46 μL of a 0.1019 M solution, 4.7 μmol). After stirring for 10 min, the mixture was filtered through Hyflo and the solvents were evaporated to dryness, affording a yellow film. Yield 15.6 mg (89%). ^1H NMR: δ = 2.55−2.65 (m, 12 H, CH_2), 3.30−3.36 (m, 54 H, OCH_3), 3.50−3.54 (m, 48 H, CH_2), 3.55−3.70 (m, 180 H, CH_2), 3.74−3.87 (m, 36 H, CH_2), 4.18 (br. s, 36 H, CH_2), 4.59 (m, 18 H, CH_2S + CH_2N), 4.69 (br. s, 24 H, CH_2S), 4.96−5.05 (m, 18 H, CH_2O), 6.67−6.79 (m, 18 H, Ar_{Pd} H), 7.00 (s, 12 H, Ar H) 7.05−7.22 (m, 66 H, SPh H + Ar H), 7.28−7.35 (m, 72 H, SPh H + PPh_2 H), 7.40−7.50 (m, 24 H, PPh_2 H), 7.58 (d, *J* = 5.7 Hz, 6 H, β-pyr H), 8.2 (br. s, 6 H, α-pyr H) ppm. ^{31}P NMR: δ = 2.2 ppm. MALDI-TOF MS: *m/z* = 11227.0 ($[M - BF_4]^+$, calcd. for $C_{522}H_{639}B_8F_{32}N_{12}O_{108}P_6Pd_9S_{18}$: 11225.1).

Supporting Information Available: Supporting information for this article is available on the WWW (see footnote on the first page of this article): ^1H NMR spectra of ligands **3**, **4**, **5**, metallodendrimer **7**, hexapincer ligand, and $[H{\cdot}6MeCN]^{6+}(BF_4^-)_6$.

Acknowledgments

Financial support of this research by the Council for the Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO) is gratefully acknowledged.

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Received April 25, 2002
[O02233]