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Organometallic Zwitterions: Arylpalladium(II) (Pincer) Complexes with a Tethered Sulfato Group as *para*-Substituent

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Arylpalladium (NCN-pincer) complexes $[NBu_4][O_3SO(CH_2)_nSiMe_2NCNPdCl]$ (n = 3 (**1a**) and n = 6 (**1b**)) with a tethered sulfato group as *para*-substituent were synthesized. These novel complexes combine an anionic sulfato group and a neutral NCN−Pd−Cl group in one molecule. Furthermore, **1a**,**b** were converted into their corresponding cationic Pd-aqua complexes **9a**,**b**, which bear both separated anionic sites and Pd cationic sites stabilized by counterions. These mixed, zwitterionic salts can be isolated devoid of counterions to give the pure unimolecular zwitterions $[O_3SO(CH_2)_nSiMe_2NCNPd(OH_2)]$ (n = 3 (**2a**) and n = 6 (**2b**)) that aggregate in order to stabilize their ionic sites. The crystal structure of $HO(CH_2)_6$-$SiMe_2NCNPdCl$ (**8b**) was revealed and used to study the effect of the tether group on the type of aggregate that is formed. The crystal structure of **8b** comprises a dimeric structure, which is formed via noncovalent interactions, i.e., O−H···Cl−Pd hydrogen bonds.

Introduction

The synthesis and characterization of well-defined organometallics that are potentially zwitterionic species, i.e., have in the same molecule both potentially cationic and anionic sites, is still a challenge.[1] Various representative types are shown in Chart 1. Compounds **A** and **B**[2,3] combine an organometallic site with an ionizable M−X bond (M = transition metal; X = halide) and an ionic organic group such as $-C{\equiv}C^-$, $-SO_3^-$, or $-PO_3^-$ (counterion, e.g., Na^+, K^+). Metal complexes **C**−**F**[1,4] contain permanent cationic and anionic sites. These cationic and anionic groups can be interconnected by covalent linking as in **A**, **B**, **D**, and **E** or by the coordination of a ligand (**C** and **F** in Chart 1). The latter type of compounds have found use as homogeneous catalysts in water,[5] whereas we have proposed the use of compounds **B** as building blocks for the formation of one-dimensional polymers. These polymers could involve either covalent linking (Pt−C σ-bonding) or noncovalent linking, comprising H-bonding when coordinated water ligands are involved.

Recently, we have focused on the synthesis and characterization of the arylpalladium (NCN-Pd) complexes **1** that bear a C_3SiMe_2- or C_6SiMe_2-tethered sulfato group as *para*-substituent (Chart 2). The sulfato group in **1a**,**b** has been introduced to serve as an anionic binding site for the noncovalent attachment of the NCN aryl palladium entities to polycationic core−shell dendritic supports. The use of this design for the synthesis of assemblies of multimetallic, nanosize catalytic species has recently been reported.[6] The sulfato group can be connected to the arylpalladium moiety at varying distances through the Si-alkanediyl chain. The nature of the connecting group of the tether, either $SiMe_2$ or CH_2, to the *para*-position of the aryl NCN grouping can influence the conformation of the tether. The aim of the present study is to outline the synthesis and purification

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Chart 1. Various Types of (Potentially) Zwitterionic Metal Complexes

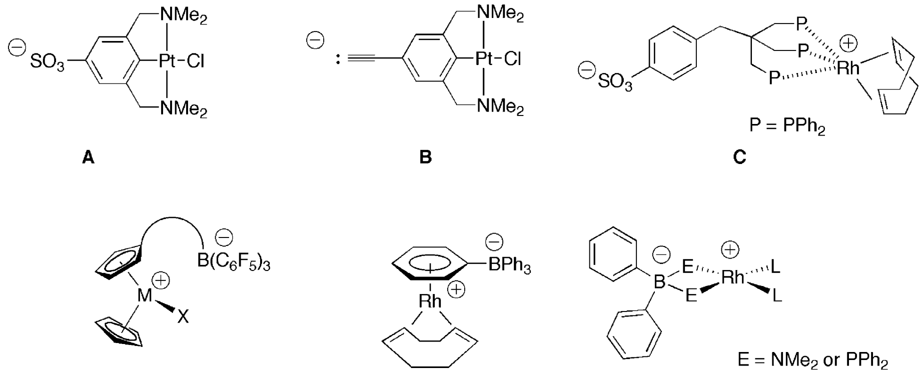
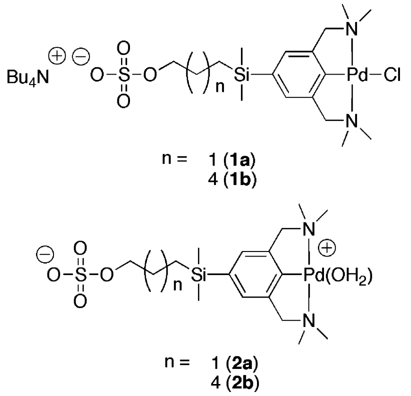
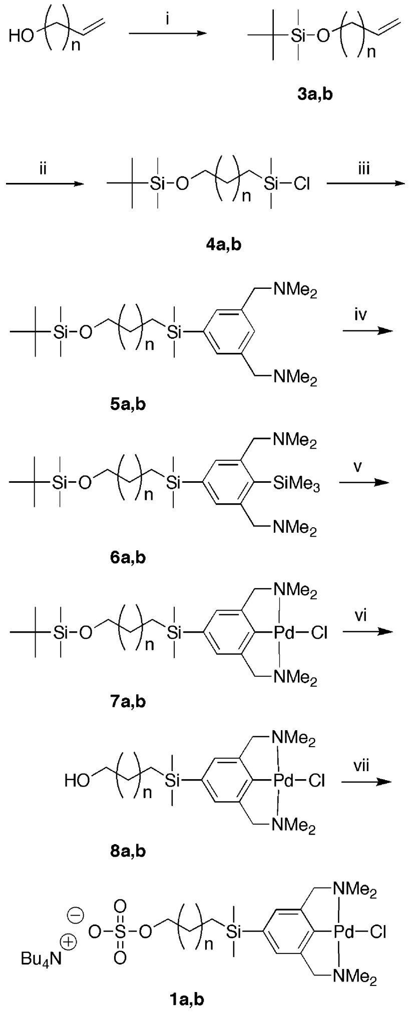


Chart 2. NCN-Pd(II) Complexes 1a,b and Their Corresponding Zwitterionic Palladium(II) Complexes 2a,b



Scheme 1. Synthesis of Pd(II) Complexes 1a,b[a]



[a] Reagents and conditions: (i) *t*-BuMe$_2$SiCl, imidazole, THF; (ii) excess HSiMe$_2$Cl, [(Bu$_4$N)$_2$PtCl$_6$]; (iii) [LiC$_6$H$_3$(CH$_2$NMe$_2$)$_2$-3,5], Et$_2$O, −78 °C; (iv) 1.2 equiv *n*-BuLi, hexane, 0 °C; 1.8 equiv Me$_3$SiOTf, 0 °C; (v) Pd(OAc)$_2$, MeOH; excess LiCl; (vi) Bu$_4$NF, H$_2$O, THF; (vii) 3 equiv py·SO$_3$, pyridine, CH$_2$Cl$_2$; excess (Bu$_4$N)Cl.

protocols for this type of compounds, to identify their nature in solution and in the solid state, and to isolate the zwitterionic species **2** derived from **1** by selective removal of their counterions (Chart 2).

Results

Synthesis of NCN-Pd(II) Complexes 1. A general synthetic procedure was developed for **1a**,**b**, which contain a tethered sulfato substituent at the *para*-position of the NCN ligand (Scheme 1). Complex **1a** was prepared starting from allyl alcohol, which was first protected with a *tert*-butyldimethylsilyl group via reaction with *tert*-butyldimethylsilyl chloride in the presence of imidazole, affording **3a** in 72% yield. Subsequently, **3a** was quantitatively hydrosilylated in pure dimethylchlorosilane using bis(tetrabutylammonium)hexachloroplatinate as catalyst to give chlorosilane **4a**, which was used without further purification.[7] Chlorosilane **4a** was reacted with [LiC$_6$H$_3$(CH$_2$NMe$_2$)$_2$-3,5] to afford **5a** in 63% yield.[8] Compound **5a** was selectively lithiated with a slight excess of *n*-butyllithium in hexane at 0 °C. The resulting lithium intermediate was converted to **6a** by reaction with an excess of trimethylsilyl trifluoromethanesulfonate (Me$_3$SiOTf) in 87% yield.[9] Selective palladation of the C−Si bond was achieved by reaction of **6a** with Pd(OAc)$_2$/LiCl in MeOH at room

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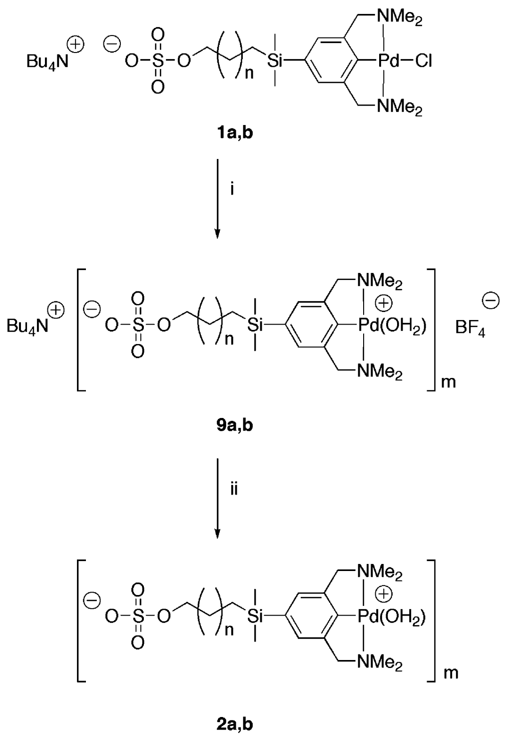
temperature. The palladated compound **7a** was obtained in 89% yield. Interestingly, both the *tert*-butyldimethylsilyl group and the C−Si bond at the *para*-position of the NCN moiety remained unaffected during this palladation reaction. In a subsequent reaction, the *tert*-butylsilyl group was quantitatively removed by treatment of **7a** with tetrabutylammonium fluoride in tetrahydrofuran to give alcohol **8a** as an off-white powder in 59% yield. The hydroxyl group of **8a** was then converted into a sulfato group with an excess of pyridine sulfur trioxide in the presence of pyridine as a base in dichloromethane.[10] Initially, this reaction was carried out with a large excess of pyridine sulfur trioxide. Further research revealed that smaller quantities could also be used. However, to achieve full conversion after several hours, at least 3 equiv of pyridine sulfur trioxide had to be used. The resulting pyridinium salt was treated with an excess of tetrabutylammonium chloride to quantitatively exchange the pyridinium cation for a tetrabutylammonium cation. The desired NCN-Pd(II) complex **1a** was obtained as a hygroscopic, white fluffy powder in 14% overall yield based on allyl alcohol. The NCN-Pd(II) complex **1b**, which bears a C_6SiMe_2 tether between the sulfate group and the NCN-palladium moiety, was prepared in a manner similar to that for **1a**. Starting from 5-hexen-1-ol instead of allyl alcohol, **1b** was isolated in 45% overall yield.

Synthesis of Zwitterionic Palladium(II) Complexes 2. Complexes **1a**,**b** were converted into their corresponding Pd(II) aqua complexes with $AgBF_4$ in wet acetone. The precipitated silver salts were filtered out with a plug of Celite, and the afforded filtrates were concentrated in vacuo. To ensure quantitative removal of silver salts,[11] the resulting off-white solids were dissolved in dichloromethane and filtered once more through a plug of Celite to give **9a**,**b** as white solids in quantitative yield (Scheme 2).

During the purification of a relatively concentrated solution of **9a** in acetone (15 mM), the zwitterionic C_3-NCN-Pd(II) moiety precipitated and was filtered from acetone and filtered off by a plug of Celite. The counterions, i.e., tetrabutylammonium and BF_4, remained in solution and ended up in the filtrate. Zwitterionic NCN-Pd(II) species **2a** was extracted from the Celite with MeOH, whereupon the colorlesss filtrate was concentrated in vacuo to give **3** as a white fluffy solid (33% yield). The zwitterionic moiety of NCN-Pd(II) **9b**, which bears a C_6SiMe_2 tether unit, did not precipitate from acetone or dichloromethane solution. Attempts to precipitate the zwitterionic species by addition of pentane to a solution of **9b** in dichloromethane were not effective, since in the precipitate small amounts of counterions remained present. An alternative approach involved quantitative extraction of the counterions in a two-phase water−dichloromethane system. After thirty-five (!) washing steps with water, the zwitterionic Pd(II) complex **2b** (soluble in dichloromethane) was quantitatively isolated free of counterions (soluble in water) as a white, foamy solid in 72% yield. Interestingly, the hygroscopic zwitterionic species **2a**,**b** are soluble in various organic solvents, such as acetone and dichloromethane, but are insoluble in water.

Scheme 2. Synthesis of Zwitterionic Palladium(II) Complexes 2a,b[a]



[a] Reagents and conditions: (i) 1.0 equiv $AgBF_4$, wet acetone; (ii) 35 washing steps with H_2O.

Characterization of the Novel NCN-Pd(II) Complexes. The $[Bu_4N][O_3SO(CH_2)_nSiMe_2NCN\text{-}PdCl]$ complexes **1a**,**b**, $[Bu_4N][O_3SO(CH_2)_nSiMe_2NCN\text{-}Pd(OH_2)][BF_4]$ complexes **9a**,**b**, and $[O_3SO(CH_2)_nSiMe_2NCN\text{-}Pd(OH_2)]$ complexes **2a**,**b** were identified and characterized with NMR spectroscopy, electrospray ionization mass spectroscopy, IR spectroscopy, and elemental analysis. The ESI mass spectra of **1a**,**b** show characteristic isotope patterns for (**1a** − Cl)$^+$ and (**1b** − $[NBu_4][Cl]$ + H)$^+$ at *m/z* = 734 and 535, respectively. Besides monomeric species also dimeric species were observed at *m/z* = 1228 and 1072, which were assigned to (2 × **1a** − 2 × Cl − $[NBu_4]$)$^+$ and (2 × **1b** − 2 × $[NBu_4][Cl]$ + H)$^+$. Interestingly, tetrabutylammonium tetrafluoroborate clusters were observed in the mass spectrum of **9a** at *m/z* = 901 and 571 corresponding to $[NBu_4]_3[BF_4]_2$ and $[NBu_4]_2[BF_4]$, respectively. Clustering of ammonium salts is a known phenomenon in mass spectrometry and has been reported in detail in the literature.[12]

Significant chemical shift differences were observed in ^1H NMR and $^{13}C\{^1H\}$ NMR between **1a**,**b** and their zwitterionic NCN-Pd(II) species **9a**,**b** with and **2a**,**b** without having NBu_4 and BF_4 as counterions (Table 1). In the ^1H NMR spectra of **9a**,**b** the proton resonance of the CH_2O group shifted upfield (0.1−0.2 ppm), as compared with **1a**,**b**, respectively, while in the corresponding $^{13}C\{^1H\}$ NMR spectra upfield shifts were observed for the *ipso*-carbon from 160 (**1a**) and 158 ppm (**1b**) to 152 (**9a**) and 153 ppm (**9b**). The $^{19}F\{^1H\}$ NMR

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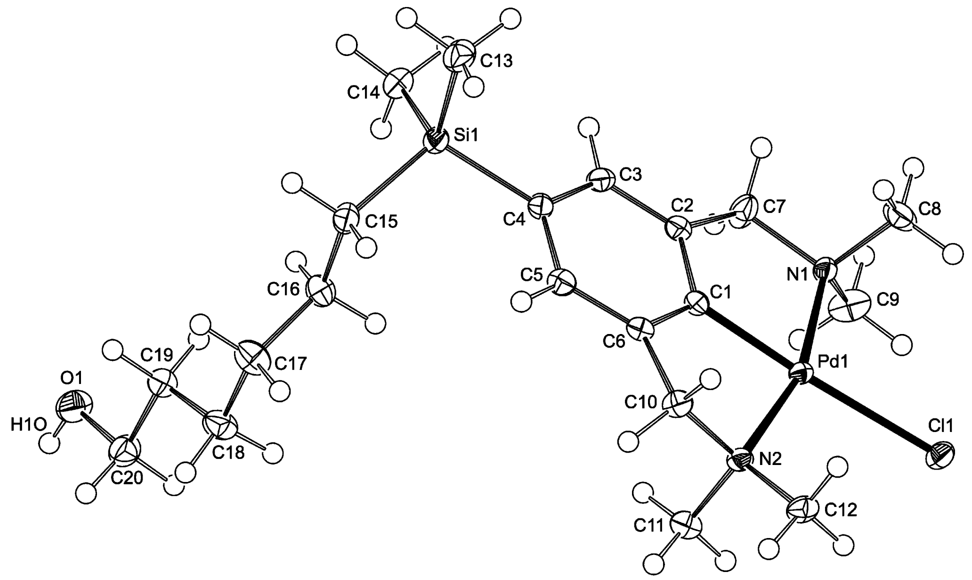

Figure 1. Displacement ellipsoid plot of **8b** (50% probability level) in the solid state, together with the adopted atom-numbering scheme.

Table 1. Selected ^1H NMR and $^{13}C\{^1H\}$ NMR Data of Pd(II) Complexes 1a,b, 9a,b, and 2a,b[a]

	^1H NMR (δ in ppm)		$^{13}C\{^1H\}$ NMR (δ in ppm)					
complex	CH_2O	NMe_2	CH_2O	NMe_2	C_{ipso}	C_{ortho}	C_{meta}	C_{para}
1a	3.83	2.88	75.0	53.4	159.7	145.4	135.3	125.3
1b[b]	3.86	2.85	74.5	52.8	157.7	144.5	135.1	124.4
9a[c]	4.02	2.78	73.7	52.1	152.2	144.6	135.3	125.2
9b	3.99	2.89	74.2	52.5	152.6	145.2	136.3	125.5
2a	3.94	2.86	74.2	52.5	152.8	145.4	135.8	125.8
2b	3.99	2.85	74.2	52.7	152.7	145.3	136.5	125.6

[a] 24 mM solutions in CD_2Cl_2 unless stated otherwise. [b] $^{13}C\{^1H\}$ NMR in $CDCl_3$. [c] In $CDCl_3$.

spectra of **9a**,**b** showed a singlet resonance at −164.7 and −163.3 ppm, respectively, which is attributed to the BF_4 counterions. The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra of these NCN-Pd(II) aqua complexes are similar to those of their corresponding zwitterionic species **2a**,**b**. In the $^{19}F\{^1H\}$ NMR spectra of the latter two complexes no sign of BF_4 was found. Furthermore, their ^1H NMR spectra showed the absence of proton signals related to NBu_4 cations, pointing to the successful removal of both counterions.

Further evidence for the successful isolation of zwitterionic complexes **2a**,**b** was provided by IR analysis. The IR spectra of **1a**,**b** showed a number of strong bands in the region 1100−1280 cm^{-1}, which are characteristic for S−O stretching vibrations of sulfato groups.[13] The IR spectra of **9a**,**b** showed broad bands in the region of 900−1200 cm^{-1}, which is characteristic for the B−F stetching vibrations of the BF_4 anion.[13,14] After the removal of the counterions of **9a**,**b**, the IR spectra of the afforded **2a**,**b** showed the absence of the strong BF_4^- band. The strong bands that remained present in the region 1100−1280 cm^{-1} correspond to ν_{S-O} bands of the sulfato group. The halide abstraction and subsequent introduction of a water ligand resulted in a shift to lower wavenumbers of the broad $\nu_{O-H}(H_2O)$ bands in the IR sprecta from $\nu_{O-H}(H_2O) = 3513$ cm^{-1} (**1a**) and 3530 cm^{-1} (**1b**) to $\nu_{O-H}(H_2O) = 3245$ cm^{-1} (**9a**) and 3433 cm^{-1} (**9b**). Additional changes were observed for the $\nu_{O-H}(H_2O)$ bands after the removal of the NBu_4 and BF_4 ions of **9a**,**b**, which afforded the pure zwitterionic Pd(II) complexes **2a** ($\nu_{O-H}(H_2O) = 3283$ cm^{-1}) and **2b** ($\nu_{O-H}(H_2O) = 3300$ cm^{-1}).

Conductivity Measurements. The molar conductivities of solutions of **1a**,**b**, **9a**,**b**, and **2a**,**b** were measured in dichloromethane and were compared with those of simple NBu_4 and BF_4 salts. The conductivity of the NCN-Pd complexes was plotted against the sample concentration, which gives typical curves for weak electrolytes.[15] The molar conductivities of 1 mM sample solutions were taken for comparison. The molar conductivities of **9a**,**b**, amounting to 17.8 and 17.1 S cm^2 mol^{-1}, respectively, are significantly higher than those measured for **1a**,**b** (12.6 and 11.8 S cm^2 mol^{-1}, respectively) but are comparable to the molar conductivities of tetrabutylammonium bromide (17.9 S cm^2 mol^{-1}) and tetrabutylammonium tetrafluoroborate (19.6 S cm^2 mol^{-1}). The molar conductivities of zwitterionic complexes **2a**,**b** (0.2 and 0.3 S cm^2 mol^{-1}, respectively) are well below the characteristic range for mono-ionic salts in dichloromethane ($19 < \Lambda_M < 22$ S cm^2 mol^{-1}).[16] As the conductivity of a compound is proportional to its net charge,[15] which is zero for zwitterions containing equimolar, separated cationic and anionic sites, the molar conductivities of **2a**,**b** are indeed expected to be close to zero.

Molecular Structure of $HO(CH_2)_6SiMe_2NCNPdCl$ (8b) in the Solid State and in Solution. Colorless, needle-shaped single crystals, which were suitable for X-ray structure determination, were obtained by adding pentane to a saturated solution of **8b** in dichloromethane. The structure of **8b** comprises a centrosymmetric, hydrogen-bonded dimeric motif (Figure 1 and

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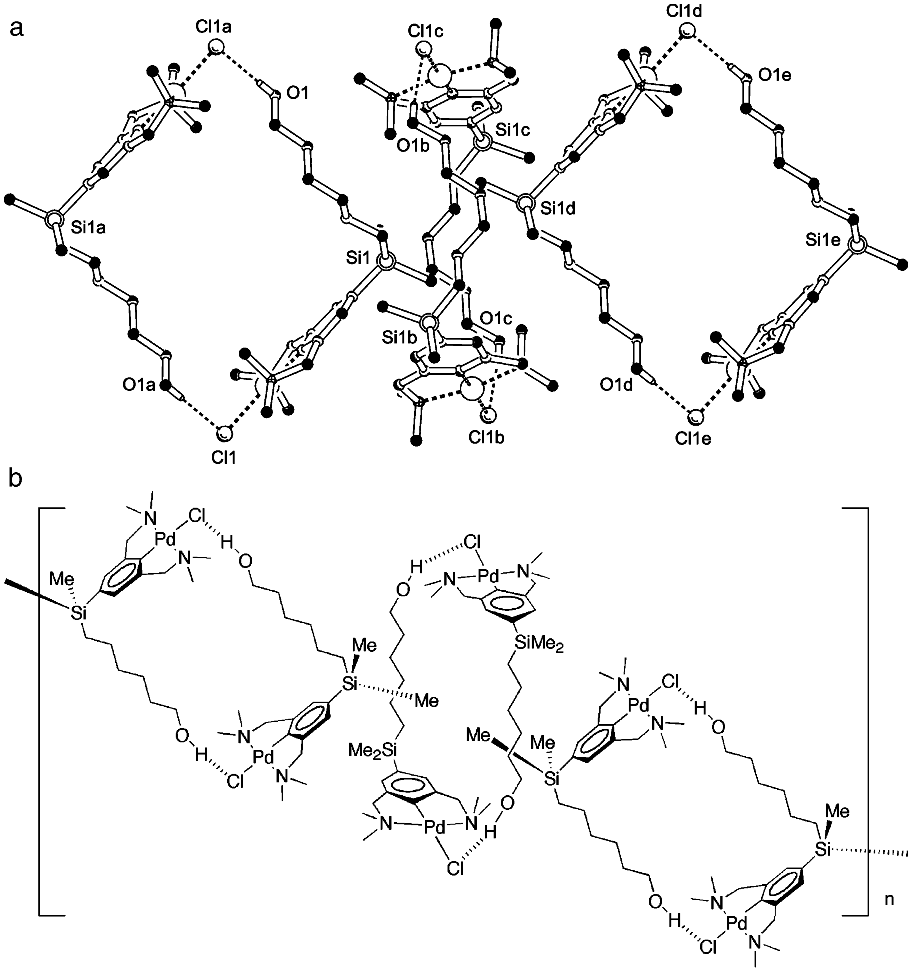

Figure 2. (a) Centrosymmetric, hydrogen-bonded dimers of **8b** in rectangular shape (symmetry operations a: 1−*x*, 1−*y*, −*z*; b: *x*, 1.5−*y*, 0.5+*z*; c: 1−*x*, 0.5+*y*, 0.5−*z*; d: 1−*x*, 2−*y*, 1−*z*; e: *x*, 1+*y*, 1+*z*). (b) Schematic representation of the packing of the dimers of **8b** in the crystal.

Table 2. Selected Bond Lengths (Å) and Angles and Torsion Angles (deg) of Palladium(II) Complex 8b with SDs in Parentheses (R1 = 0.0298, space group $P2_1/c$ (no. 14))

	Bond Distances		
Pd(1)−C(1)	1.912(2)	Pd(1)−N(1)	2.096(2)
Pd(1)−N(2)	2.109(2)	Pd(1)−Cl(1)	2.4469(6)
C(4)−Si(1)	1.880(2)	C(13)−Si(1)	1.872(3)
C(14)−Si(1)	1.871(3)	C(15)−Si(1)	1.872(3)
C(20)−O(1)	1.418(3)		
	Bond Angles		
Cl(1)−Pd(1)−C(1)	176.26(7)	Cl(1)−Pd(1)−N(1)	96.87(6)
Cl(1)−Pd(1)−N(2)	99.34(6)	C(1)−Pd(1)−N(1)	82.26(9)
C(1)−Pd(1)−N(2)	81.73(9)	N(1)−Pd(1)−N(2)	163.54(8)
	Torsion Angles		
Pd(1)−C(1)−C(2)−C(7)	1.8(3)	C(1)−C(6)−C(10)−N(2)	−27.4(3)
C(1)−C(2)−C(7)−N(1)	−11.4(3)	C(2)−C(3)−C(4)−Si(1)	179.97(18)
C(6)−C(5)−C(4)−Si(1)	−177.11(18)	C(5)−C(4)−Si(1)−C(15)	−33.8(2)
C(3)−C(4)−C(5)−C(6)	0.5(3)	C(4)−Si(1)−C(15)−C(16)	−60.6(2)
C(5)−C(4)−Si(1)−C(13)	85.8(2)	C(15)−C(16)−C(17)−C(18)	174.5(2)
Si(1)−C(15)−C(16)−C(17)	175.67(19)	C(16)−C(17)−C(18)−C(19)	−69.1(3)
C(17)−C(18)−C(19)−C(20)	−175.0(2)	C(18)−C(19)−C(20)−O(1)	−178.1(2)
Pd(1)−C(1)−C(6)−C(10)	8.1(3)		

Figure 2). The unit cell contains two of these dimeric units. The coordination plane around each of the palladium centers in the dimer is distorted square planar with *cis*-angles between 81.73(9)° and 99.34(6)° (angle sum 360.2°) and interatomic distances to carbon, nitrogen, and chloride that are comparable to those found for similar NCN-Pd(II) complexes (Table 2).[2]

A remarkable twist in the torsion angles in the aliphatic tether unit was observed. All torsion angles along the alkanediyl chain point to a *trans* conformation, whereas the torsion angle of −69.1(3)° created by C(16)−C(17)−C(18)−C(19) points to a *gauche* conformation. Finally, the torsion angle of C(5)−C(4)−Si(1)−C(15) has a value (−33.8(2)°) intermediate between a *gauche* and *trans* conformation.

The dimeric structure is formed by intermolecular hydrogen bonding between the OH group as donor and the Cl ligand as acceptor. The interatomic distance between H(1O) and Cl(1)a is 2.36(3) Å, and the contact angle of O(1)−H(1O)···Cl(1)a is 173(3)° (symmetry operation a: 1−*x*, 1−*y*, −*z*). The angle Pd(1)−Cl(1)−H(1O)a is close to rectangular at chloride (90.9(7)°). Interestingly, the dimer has a rectangular shape with an intramolecular Si(1)−Cl(1) distance of 9.0237(10) Å and an intermolecular Si(1)−Cl(1)a distance of 10.8400(10) Å (see Figure 2a). The cavity in this rectangle is filled with methyl groups C(13)b and C(13)c from dimers above and below (symmetry operations **b**: 1−*x*, *y*−0.5, 0.5−*z*; **c**: *x*, 1.5−*y*, *z*−0.5) (Figure 2b). The rectangles are arranged perpendicular to each other, thus forming a two-dimensional network parallel to the crystallographic *b*,*c*-plane.

The observed hydrogen bonding was studied in the solid state as well as in solution at room temperature with infrared spectroscopy. The spectrum of **8b** in KBr is identical to that in NaCl, which indicates that the nature of the halide and the metal ion of the matrix do not affect the hydrogen bonding. Both spectra showed a relatively narrow absorption band at $\nu = 3377$ cm^{-1}, which is characteristic for the stretching vibration of a hydrogen-bonded OH group.[13] The absorption band is slightly asymmetric most likely because of lattice vibration in the solid. In solutions of **8b** in CCl_4, two absorption bands are visible: one broad band at $\nu = 3428$ cm^{-1} assigned to a dimeric or oligomeric hydrogen-bonded species and a sharper band at $\nu = 3638$ cm^{-1} corresponding to a monomeric species.[17] Upon concentrating the solution from 5.5×10^{-5} M to 6.2×10^{-3} M, an increased ratio of the hydrogen-bonded species versus monomer from 0.25 to 4 was estimated from the IR spectra.[18]

The IR spectrum of $HO(CH_2)_3SiMe_2NCNPdCl$ (**8a**) in NaCl showed a relatively sharp band at $\nu = 3399$ cm^{-1}, while a saturated solution in CCl_4 showed two absorption bands at $\nu = 3637$ and 3434 cm^{-1}, indicating that **8a**,**b** have similar structural features in the solid state and in solution. In addition, the asymmetric absorption band of the monomeric species in solution indicates the presence of different rotamers for primary alcohols **8a**,**b**.[17]

The difference between the ν_{O-H} of the monomeric and dimeric species in solution is directly related to the binding enthalpy of the hydrogen bond in the O−H···Cl unit. The binding enthalpies of the hydrogen bonds in **8a**,**b** can be calculated using the equation of Poliakoff[19] and amount to $\Delta H° = -18.6$ kJ/mol (**8b**), which is slightly higher than that calculated for **8a**, $\Delta H° = -18.2$ kJ/mol. Indirect evidence for the existence of a dimeric species rather than oligomeric species of these organometallic alcohols in solution was provided by electrospray ionization mass spectra, which showed molecular mass peaks at 413.2 [**8a** − Cl]$^+$ and 455.1 [**8b** − Cl]$^+$ as well as peaks pointing to dimeric species at 863.4 [2 × **8a** − Cl]$^+$ and 947.0 [2 × **8b** − Cl]$^+$. In ^{1}H NMR spectra, however, for both **8a** and **8b** in $CDCl_3$ an average set of signals for monomer and H-bonded species were observed, which points to a dynamic equilibrium on the NMR time scale between monomer and the hydrogen-bonded di- or oligomeric species independent of the temperature (25 to −90 °C).

Stability of Pd(II) Complex 1b Bearing a Sulfate-Terminated Substituent. Various groups have reported on the acid- or base-catalyzed hydrolysis of organosulfate salts in aqueous solutions.[20] Only a few of these were devoted to a study of decomposition reactions of organosulfates in organic media.[21] Although the NCN-pincer type palladium complexes are known for their thermal stability,[2b] nothing is known concerning the stability of organosulfato groups in combination with an arylpalladium unit. For this reason, a study on the chemical and thermal stability of NCN-Pd(II) complex **1b**, as a representative of the complexes, in organic solutions was conducted.

Acid-catalyzed hydrolysis was studied by treating a 7.6 mM solution of **1b** in $CDCl_3$ with 5 equiv of triflic acid. After two weeks the resulting brown-colored solution contained a small amount of brown precipitate, pointing to the formation of Pd(0). However, the NMR spectra of the reaction solution showed no indication for decomposition of the sulfato moiety. Base-catalyzed hydrolysis was studied by leaving **1b** (1.7 mM) in a 1 M methanol solution of tetrabutylammonium hydroxide for several days. The reaction mixture was analyzed at regular intervals with ^{1}H NMR; after 3 days no significant changes were observed. In addition, no decomposition occurred when **1b** was kept in wet acetone for 3 h at reflux temperature.

Discussion

The present study shows that true zwitterionic species of the type **A** (Chart 1), having free cationic and anionic sites, are accessible. The precursor arylpalladium complexes **1a**,**b**, bearing a tethered sulfato group and a potentially cationic NCN-Pd site, were synthesized and characterized in solution and in the solid state. The species with the free sulfato group (**1a**,**b**) are monomeric, whereas the species with a cationic metal site in addition to the anionic sulfato group (**9a**,**b**) are in solution in equilibrium with the species **2a**,**b**, respectively, devoid of the counterions. The solubility of the zwitterionic species **2a**,**b** in organic solvents can be explained by self-assembly through Coulombic forces, which leads to the formation of oligomers or polymers. Whether the self-assembly of **2a**,**b** leads to linear or

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[17] Lutz, B. T. G.; van der Maas, J. H. *J. Mol. Struct.* **1997**, *436−437*, 213−231.

[18] The ratio between dimer and monomer was estimated by calculating the ratio between the areas of the corresponding bands.

[19] The equation employed is $\Delta H° = -1.28(\Delta\nu)^{1/2}$; see for example: Kazarian, S. G.; Hamley, P. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1993**, *115*, 9069−9079.

[20] For literature on the base, acid, or enzymatic hydrolysis of sulfate esters in aqueous media see for example: (a) Benkovic, S. J.; Benkovic, P. A. *J. Am. Chem. Soc.* **1966**, *88*, 5504−5511. (b) Burwell, R. L., Jr. *J. Am. Chem. Soc.* **1952**, *74*, 1462−1466. (c) Benkovic, S. J. *J. Am. Chem. Soc.* **1966**, *88*, 5511−5515. (d) Spencer, B. *Biochem. J.* **1958**, *69*, 155−159.

[21] For literature on acid-catalyzed hydrolysis of sulfate esters in organic media see for example: Batts, B. D. *J. Chem. Soc. Sect. B* **1966**, 547−551.

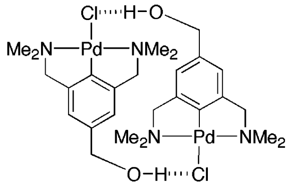

Figure 3. Molecular square type of structure of dimeric [PdCl(NCN-CH_2OH)].[2b]

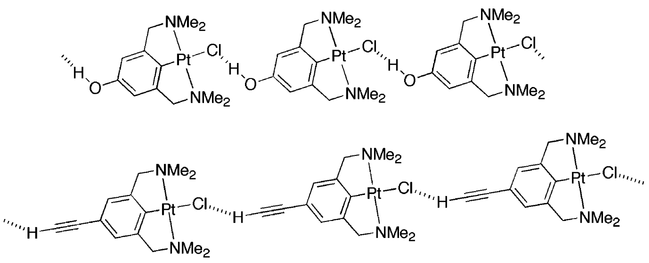

Figure 4. Noncovalent linear polymers built up from organometallic monomers, i.e., arylplatinum complexes bearing hydroxyl[22] or ethynyl[3] groups as hydrogen bond donor connected by Pt−Cl···H−R hydrogen bonds.

cyclic oligo- or polymers is dependent on the conformation of the chain interlinking the sulfato anionic site and the Pd(OH_2) cationic site. In this respect, the molecular structure of $HO(CH_2)_6SiMe_2NCNPdCl$ (**8b**) provides a structural model (Figure 1). This compound shows a self-assembly process via hydrogen bonding leading to the formation of dimers. Molecular structures of other aryl-M complexes[2,22] already showed the importance of M−Cl···H−O binding for the formation of self-assembled structures. When a hydrogen bond donor, i.e., an OH group (see Figure 4), is connected directly to the aryl group, a linear arrangement of H-acceptor and -donor sites and, thus, one-dimensional polymers (zigzag chains) can be obtained.[22] In the present case, the conformation about the Si−C aryl bond is dictated by the three substituents at silicon, i.e., the two smaller Me groups and the larger alkanediyl chain containing the sulfato anion, and leads to the antiplanar orientation of this chain. Consequently, the arylmetal pincer group and the Si-alkanediyl chain define one corner of a molecular rectangle (Figure 2). The size of this square is clearly dependent on the tether unit. In an earlier study, a smaller square was obtained with a NCN-Pd-Cl complex functionalized at the *para*-position with a CH_2-tethered hydroxy group (Figure 3).[2b]

Whereas most of the torsion angles in the chain of **8b** are predominately *trans*, one angle (C(16)−C(17)−C(18)−C(19)) adopts a *gauche* conformation due to the hydrogen bonding. The short distance between the OH donor and Pd-Cl acceptor (H(10)···Cl(1)a = 2.36(3) Å) and the large contact angle O(1)−H(1O)···Cl(1)a (173(3)°) in the solid state are indicative of a medium-strong hydrogen bond.[23] In general, hydrogen bonds between X-H donors and M-Cl acceptors comprise H···Cl distances between 2.1 and 2.3 Å and H···Cl−M angles of 100−120°.[24] The angle Pd(1)−Cl(1)−H(1O)a is, however, rectangular at chloride (91°), which is probably due to the directional forces of the more basic *p*-type lone pair of the chloride ligand.[25]

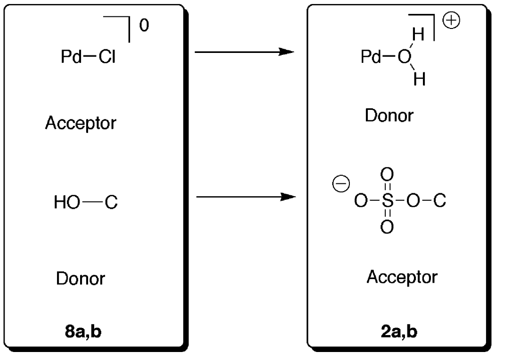

Figure 5. Inversion of hydrogen bond donor and acceptor sites in the arylpalladium complexes.

It is interesting to compare the crystal structure of **8b** with the structures of earlier reported NCN-Pt-Cl complexes, which bear a hydroxyl group[22] or ethynyl group[3] as the *para*-substituent (Figure 4). The latter two complexes form related molecular arrays in the solid state, i.e., zigzag chains linked by R−H···Cl−Pt hydrogen bonds. The binding enthalpy of the hydrogen bonds in polymers formed by the hydroxyl complex is $\Delta H° = -22$ kJ/mol, which is slightly higher than the binding enthalpies of **8a**,**b** (−18.2 and −18.6 kJ/mol, respectively). While **8a**,**b** contain OH groups as hydrogen bond donors, in the zwitterionic Pd(II) complexes **2a**,**b** these groups are converted into sulfato groups, which are hydrogen bond acceptors. Compared to complexes **8a**,**b**, the hydrogen bond donor and acceptor sites of **2a**,**b** are, therefore, inverted with respect to the Si-alkanediyl chain (Figure 5). Consequently, zwitterionic complexes **2a**,**b** cannot aggregate through hydrogen bonds based on the M−X···H−O binding motif.

Crystal structures reported for other Pd(II) aqua complexes show hydrogen bond acceptors, such as BF_4,[26] PF_6,[27] and O_3SCF_3,[28] in close proximity to the water ligand. In the solid-state structure of [Pd{$C_6H_3(CH_2NMe_2)_2$-2,6}(OH_2)]BF_4[26b] intermolecular hydrogen-bonding networks are formed, with infinite chains of cations and anions. Each BF_4 anion is connected to two water ligands via hydrogen bonds. In the molecular structure of [Pt{$C_6H_3(CH_2NMe_2)_2$-2,6}(OH_2)][O_3SCF_3] two cationic Pt(II)-aqua complexes ions are linked by hydrogen bonds from the coordinated water molecules to two bridging CF_3SO_3 anions to form dimeric clusters around the inversion center.[28a] Zwitterionic **2a**,**b** bear both a Pd(II)-aqua moiety and a hydrogen bond acceptor group, i.e., a sulfato group, in the same molecule. The IR

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[28] (a) Schmülling, M.; Grove, D.; van Koten, G.; van Eldik, R.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 1384−1391 (including a discussion on the acidity of the H_2O ligand in cationic NCN-pincer metal(OH_2) complexes). (b) Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127−2138. (c) Maassarani, F.; Pfeffer, M.; Le Borgno, G. *Organometallics* **1987**, *6*, 2043−2053.

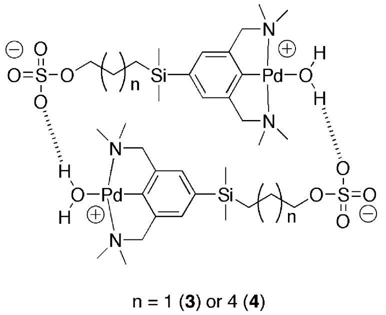

Figure 6. Proposed molecular dimeric structure, based on IR spectra, of zwitterionic Pd(II) complexes **2a**,**b**.

spectra of **1a**,**b** show $\nu_{O-H}(H_2O)$ bands in the upper region of 3550−3200 cm^{-1}, which is characteristic for lattice water. The hygroscopic character of these organometallic salts was also observed on a macroscopic level. When exposed to air, **1a**,**b** (as well as **2a**,**b**), which are white fluffy solids, turn rapidly into sticky wet solids. Upon conversion of the NCN-Pd-Cl sites of **1a**,**b** to cationic Pd(II)-aqua sites (**9a**,**b**), the $\nu_{O-H}(H_2O)$ bands shift to lower wavenumbers. The broad band is most probably composed of the stretching vibrations of two types of water molecules, i.e., water molecules that hydrate the ammonium sulfato end groups of **9a**,**b** and the water ligand at palladium which is hydrogen-bonded to the weakly coordinated BF_4 anion. In the IR spectra of pure zwitterionic Pd(II) complexes **2a**,**b**, which are devoid of BF_4 and Bu_4N counterions, the ν_{O-H} bands correspond to the water ligands coordinated to the cationic Pd(II) sites. In this case, a weakly coordinated sulfato group of an adjacent zwitterionic Pd(II) complex is probably hydrogen-bonded to the coordinated water ligands. The hydrogen bond donor and acceptor sites in **2a**,**b** are interconnected by Si-alkanediyl chains that favor the formation of a dimeric aggregate. Much like the structure of **8b**, related dimer structures are proposed for pure **2a**,**b**, i.e., the zwitterionic Pd(II) complexes free from counterions (Figure 6).

Conclusions

Complexes **1a**,**b** with a C_3SiMe_2- or C_6SiMe_2-tethered sulfato group as *para*-substituent were synthesized and characterized in solution and in the solid state. These novel complexes combine an anionic sulfato group and a NCN-Pd-Cl group. In the present study, **1a**,**b** were converted into their corresponding cationic Pd-aqua complexes **9a**,**b**, which bear both separated anionic sites and cationic sites stabilized by counterions. These mixed, zwitterionic salts can be isolated devoid of counterions to give the pure unimolecular zwitterions **2a**,**b** that aggregate in order to stabilize their ionic sites. The crystal structure of $HO(CH_2)_6SiMe_2NCNPdCl$ (**8b**) is useful to study the effect of the tether group on the type of aggregate that is formed; it comprises a dimeric structure, which is formed via noncovalent interactions, i.e., O−H···Cl−Pd hydrogen bonds.

Organometallic zwitterions such as **1a**,**b** are unique building blocks, as they allow the synthesis of metallodendritic assemblies, like the one shown in Figure 7, based on assembly using exclusively Coulombic forces from the Pd(II) complexes **1a**,**b** bearing an anionic sulfato group as *para*-substituent and polycationic core−shell dendrimers.[6] These can be applied as nanosize catalysts or as container molecules in phase transfer systems. An inert tether unit of variable length would be useful to tune the position of the palladium site with respect to the sulfato group and, ultimately, with respect to the periphery of the dendritic backbone.

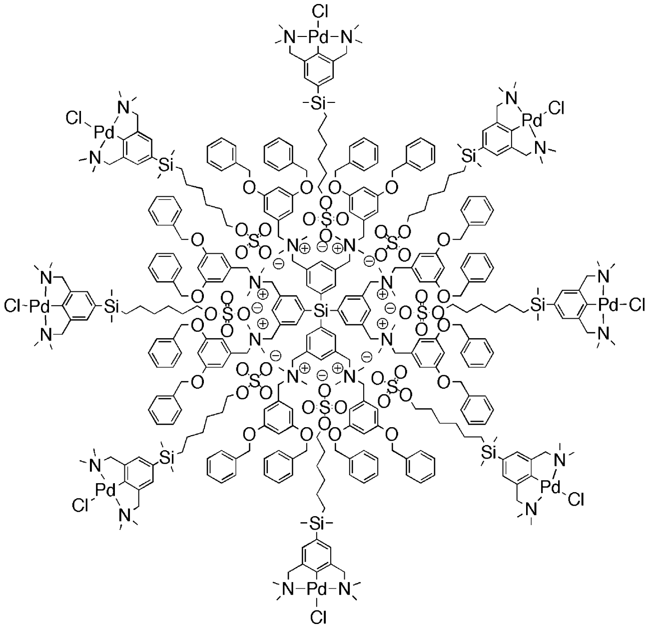

Figure 7. Example of a noncovalent metallo-dendritic assembly derived from complex **1b**.

Experimental Section

Materials and Methods. All experiments were conducted under a dry nitrogen atmosphere using standard Schlenk techniques unless differently stated. Diethyl ether, tetrahydrofuran, pentane, and hexane were dried over sodium using benzophenone as indicator. Dichloromethane was dried over CaH_2. All previous solvents were distilled prior to use. Methanol p.a. was used as solvent in the palladation reactions. Technical acetone was used for the conversion of the Pd(II) complexes into their corresponding Pd(II) aqua complexes. Chemicals that were purchased from Acros Chemicals or Aldrich were used without further purification. 1-Bromo-3,5-{bis(dimethylamino)benzene} was prepared according to a literature procedure.[29] ^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectroscopic measurements were carried out on a Varian Inova/Mercury 300 or 200 MHz spectrometer at 25 °C, and chemical shifts (δ) are given in ppm referenced to the residual solvent peak. The elemental analyses were performed by Dornis and Kolbe, Mikroanalytische Laboratorium, Mülheim a/d Ruhr, Germany.

(*tert*-Butyl)$(Me)_2SiOCH_2CHCH_2$ (3a). To a solution of 2-propene-1-ol (3.70 g, 63.7 mmol) in THF (100 mL) was added imidazole (10.30 g, 151 mmol) and *tert*-butyldimethylsilyl chloride (11.60 g, 77.0 mmol). The resulting white suspension was stirred for 48 h at room temperature. The reaction mixture was filtered through a plug of layered Celite and silica. The Celite/silica layer was extracted with pentane. The resulting colorless filtrate was concentrated in vacuo, and the residue was dissolved in pentane (75 mL). The organic solution was washed with H_2O (4 × 40 mL), washed with brine (2 × 40 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo to afford **5** (7.88 g, 45.7 mmol, 72%) as a colorless liquid. ^1H NMR (300 MHz, $CDCl_3$): δ 5.98−5.86 (m, 1H, $CH_2{=}CH$), 5.26

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(doublet of quartets, $^3J_{HH}$ = 17.1 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, *trans* $HCH{=}CHCH_2$), 5.08 (double quartets, $^3J_{HH}$ = 10.5 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, *cis* $HCH{=}CHCH_2$), 4.18 (d, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.8 Hz, 2H, OCH_2), 0.91 (s, 9H, $C(CH_3)_3$), 0.07 (s, 6H, $OSi(CH_3)_2$). ^1H NMR (300 MHz, C_6D_6): δ 5.89−5.77 (m, 1H, CH_2CH), 5.35−5.01 (m, $^4J_{HH}$ = 1.9 Hz, 2H, CH_2CH), 4.03−4.00 (m, 2H, OCH_2), 0.97 (s, 9H, $C(CH_3)_3$), 0.04 (s, 6H, $OSi(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 137.7 (CH_2CH), 114.1 (CH_2CH), 64.3 (OCH_2), 26.1 ($C(CH_3)_3$), 18.6 ($C(CH_3)_3$), −5.1 ($OSi(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 138.0 (CH_2CH), 113.7 (CH_2CH), 64.1 (OCH_2), 26.1 ($C(CH_3)_3$), 18.5 ($C(CH_3)_3$), −5.2 ($OSi(CH_3)_2$). Anal. Calcd for $C_9H_{20}OSi$: C 62.72; H 11.70; Si 16.30. Found: C 62.77; H 11.80; Si 16.27.

(*tert*-Butyl)(Me)$_2$SiO(CH$_2$)$_3$Si(Me)$_2$Cl (4a). To a mixture of **3a** (10.2 g, 59.1 mmol) in THF (5 mL) was added dimethylchlorosilane (24 mL, 215 mmol). After addition of a catalytic amount of $[(NBu_4)_2Pt(IV)Cl_6]$ solvated in EtOH the reaction mixture was refluxed for 24 h at 90 °C. The reaction mixture was concentrated in vacuo to obtain **4a** as a colorless liquid in 96% yield (15.5 g, 56.8 mmol). ^1H NMR (200 MHz, $CDCl_3$): δ 3.59 (t, $^3J_{HH}$ = 6.6 Hz, 2H, OCH_2), 1.75−1.55 (br m, 2H, OCH_2CH_2), 0.89 (s, 9H, $C(CH_3)_3$), 0.83−0.77 (br m, 2H, $ArSiCH_2$), 0.40 (s, 6H, $ArSi(CH_3)_2$), 0.05 (s, 6H, $OSi(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 65.4 (OCH_2), 26.5 (OCH_2CH_2), 26.1 ($C(CH_3)_3$), 18.5 ($C(CH_3)_3$), 15.1 ($ClSiCH_2$), 1.8 ($ClSi(CH_3)_2$), −5.2 ($OSi(CH_3)_2$).

1-(*tert*-Butyl)(Me)$_2$SiO(CH$_2$)$_3$Si(Me)$_2$C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-3,5 (5a). To a solution of 1-bromo-3,5-{bis(dimethylamino)benzene} (6.68 g, 25.1 mmol) in Et_2O (50 mL) was added *t*-BuLi (34 mL of a 1.5 M solution in pentane, 51 mmol) at −78 °C. After stirring the white-yellow suspension for 2 h, a solution of **4a** (6.7 g, 25.1 mmol) in Et_2O (10 mL) was dropwise added, whereupon the resulting suspension was allowed to reach room temperature. The reaction mixture was stirred for 24 h, whereupon an extra amount of *t*-BuLi (1 mL of a 1.5 M solution in pentane, 4.5 mmol) was added at −78 °C to react with the excess of 1-bromo-3,5-{bis(dimethylamino)benzene} to yield its corresponding organolithium species. After stirring for 10 min the reaction mixture was allowed to reach room temperature, after which H_2O (26 mL) was added to hydrolyze the excess of organolithium species. The organic layer was separated off, and the water layer was extracted with pentane (3 × 75 mL), washed with brine (2 × 75 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The product, a viscous yellow oil, was further purified by careful distillation using a Kugelrohr apparatus. After the low-boiling impurities (120−140 °C, 0.1−0.2 mbar) were distilled off, the product was isolated as a colorless oil (140−150 °C, 0.03 mbar). Yield: 6.63 g (15.7 mmol, 63%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.29 (s, 2H, ArH), 7.23 (s, 1H, ArH), 3.54 (t, $^3J_{HH}$ = 6.9 Hz, 2H, OCH_2), 3.41 (s, 4H, $ArCH_2$), 2.23 (s, 12H, $N(CH_3)_2$), 1.56−1.46 (br m, 2H, OCH_2CH_2), 0.87 (s, 9H, $C(CH_3)_3$), 0.71−0.66 (br m, 2H, $ArSiCH_2$), 0.26 (s, 6H, $ArSi(CH_3)_2$), 0.02 (s, 6H, $OSi(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 139.2, 138.1, 133.2, 130.8 (ArC), 66.3 (OCH_2), 64.6 ($ArCH_2$), 45.6 ($N(CH_3)_2$), 27.5 (OCH_2CH_2), 26.1 ($C(CH_3)_3$), 18.5 ($C(CH_3)_3$), 11.6 ($O(CH_2)_2CH_2$), −2.8 ($ArSi(CH_3)_2$), −5.1 ($OSi(CH_3)_2$). $^{29}Si\{^1H\}$ NMR (60 MHz, $CDCl_3$): δ 18.7 (OSi), −2.3 (ArSi). Anal. Calcd for $C_{23}H_{46}N_2OSi_2$: C, 65.34; H, 10.97; N, 6.63; Si, 13.29. Found: C, 65.26; H, 10.91; N, 6.74; Si, 13.36.

1-(*tert*-Butyl)(Me)$_2$SiO(CH$_2$)$_3$Si(Me)$_2$-4-Si(Me)$_3$C$_6$H$_2$-(CH$_2$NMe$_2$)$_2$-3,5 (6a). To a solution of **5a** (3.43 g, 8.1 mmol) in hexane (60 mL) was added *n*-BuLi (6.3 mL of a 1.6 M solution in hexane, 10.1 mmol) at 0 °C. After stirring the solution for 10 min the mixture was allowed to reach room temperature and was stirred for 3 h. To the resulting orange-yellow solution was added Me_3SiOTf (2.8 mL, 14.5 mmol) at 0 °C. After stirring the reaction mixture for 10 min, the suspension was allowed to reach room temperature and stirred for another 20 min. The hexane layer was separated from the precipitate by centrifugation. The residue was extracted with hexane (5 × 40 mL). The combined organic layers were washed with NaOH (1 M, 50 mL), water (2 × 50 mL), and brine (2 × 50 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo to obtain **6a** as a yellow oil in 87% yield (3.48 g, 7.0 mmol). An alternative procedure to purify the crude product that was obtained after centrifugation is column chromatography (neutral alumina), eluting with a hexane−Et_3N−EtAc mixture (v/v/v 94:5:1). The product was obtained as a slightly yellow oil. In this case the yield is lower (50%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.39 (s, 2H, ArH), 3.54 (t, $^3J_{HH}$ = 6.9 Hz, 2H, OCH_2), 3.54 (s, 4H, $ArCH_2$), 2.11 (s, 12H, $N(CH_3)_2$), 1.57−1.47 (br m, 2H, OCH_2CH_2), 0.88 (s, 9H, $C(CH_3)_3$), 0.75−0.68 (br m, 2H, $ArSiCH_2$), 0.36 (s, 9H, $ArSi(CH_3)_3$), 0.26 (s, 6H, $ArSi(CH_3)_2$), 0.02 (s, 6H, $OSi(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 145.3, 139.5, 139.3, 134.0 (ArC), 66.3 ($ArCH_2$), 65.6 (OCH_2), 45.1 ($N(CH_3)_2$), 27.5 (OCH_2CH_2), 26.2 ($C(CH_3)_3$), 18.5 ($C(CH_3)_3$), 11.5 ($O(CH_2)_2CH_2$), 3.4 ($ArSi(CH_3)_3$), −2.9 ($ArSi(CH_3)_2$), −5.1 ($OSi(CH_3)_2$). Anal. Calcd for $C_{26}H_{54}N_2OSi_3$: C, 63.09; H, 11.00; N, 5.66; Si, 17.02. Found: C, 62.92; H, 11.11; N, 5.51; Si, 17.08.

[PdCl(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6-{Si(Me)$_2$(CH$_2$)$_3$OSi(Me)$_2$(*tert*-butyl)}-4)] (7a). To a solution of **6a** (5.1 g, 10.3 mmol) in MeOH (40 mL) was added a solution of $Pd(OAc)_2$ (2.65 g, 11.8 mmol) in MeOH (20 mL). After stirring for 75 min LiCl (1.33 g, 31.7 mmol) was added to the dark red reaction solution. The reaction mixture was stirred for another 16 h, whereupon it was concentrated in vacuo. The resulting crude product was extracted with CH_2Cl_2 (25 mL) and separated from the excess LiCl by centrifugation. The supernatant was filtered, washed with H_2O (3 × 60 mL) and brine (1 × 60 mL), and dried over $MgSO_4$. After filtration through a plug of Celite the organic solution was concentrated in vacuo to give **7a** as an orange-brown solid in 89% yield (5.22 g, 9.2 mmol). ^1H NMR (300 MHz, $CDCl_3$): δ 6.84 (s, 2H, ArH), 3.95 (s, 4H, $ArCH_2$), 3.49 (t, $^3J_{HH}$ = 6.0 Hz, 2H, OCH_2), 2.89 (s, 12H, $N(CH_3)_2$), 1.46 (br signal, 2H, OCH_2CH_2), 0.83 (s, 9H, $C(CH_3)_3$), 0.62 (t, $^3J_{HH}$ = 8.1 Hz, 2H, $ArSiCH_2$), 0.16 (s, 6H, $ArSi(CH_3)_2$), −0.02 (s, 6H, $OSi(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 158.2, 144.7 134.9, 124.6 (ArC), 74.8 ($ArCH_2$), 66.0 (OCH_2), 53.1 ($N(CH_3)_2$), 27.3 (OCH_2CH_2), 26.0 ($C(CH_3)_3$), 18.4 ($C(CH_3)_3$), 11.4 ($O(CH_2)_2CH_2$), −2.9 ($ArSi(CH_3)_2$), −5.2 ($OSi(CH_3)_2$). Anal. Calcd for $C_{23}H_{45}ClN_2OPdSi_2$: C, 49.01; H, 8.05; N, 4.97; Si, 9.97. Found: C, 49.12; H, 8.02; N, 4.82; Si, 9.86.

[PdCl(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6-{Si(Me)$_2$(CH$_2$)$_3$OH}-4)] (8a). To a solution of **7a** (5.12 g, 9.0 mmol) in THF (100 mL) was added Bu_4NF (16.5 mL of a 1 M solution in THF). After stirring the dark brown solution for 1.5 h H_2O (41 mL) was added and the solution was stirred for 60 h. The reaction mixture was concentrated to dryness, and the residue was dissolved in CH_2Cl_2 (60 mL). The organic layer was washed with H_2O (3 × 100 mL) and brine (100 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The orange-brown residue was redissolved in CH_2Cl_2 (ca. 15 mL), and the product was precipitated with pentane (60 mL). The precipitate was isolated, washed with pentane (50 mL), and dried in vacuo to give **8a** as a off-white powder in 59% yield (2.39 g, 5.3 mmol). ^1H NMR (300 MHz, $CDCl_3$): δ 6.87 (s, 2H, ArH), 3.99 (s, 4H, $ArCH_2$), 3.57 (t, $^3J_{HH}$ = 6.8 Hz, 2H, OCH_2), 2.93 (s, 12H, $N(CH_3)_2$), 1.61−1.52 (br m, 2H, OCH_2CH_2), 0.71−0.65 (br m, 2H, $ArSiCH_2$), 0.22 (s, 6H, $ArSi(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 158.4, 144.9, 134.8, 124.7 (ArC), 74.9 ($ArCH_2$), 65.8 (OCH_2), 53.2 ($N(CH_3)_2$), 27.3 (OCH_2CH_2), 11.7 ($O(CH_2)_2CH_2$), −2.8 ($ArSi(CH_3)_2$). MS (ES+, THF): *m/z* 863.4 $[2M - Cl]^+$, 413.2 $[M - Cl]^+$. Anal. Calcd for $C_{17}H_{31}ClN_2OPdSi$: C, 45.43; H, 6.95; N, 6.23; Si, 6.25. Found: C, 45.28; H, 6.84; N, 6.15; Si, 6.28.

[PdCl(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6-{Si(Me)$_2$(CH$_2$)$_3$OSO$_3$}-4)]-[NBu$_4$] (1a). To a solution of **8a** (2.67 g, 5.96 mmol) in CH_2Cl_2 (50 mL) was added pyridine sulfur trioxide (7.98 g, 50.0 mmol). After addition of pyridine (100 mL, 1.24 mmol) the mixture was stirred for 4 h. The white-yellow suspension was purified by centrifugation to remove the undissolved pyridine sulfur trioxide. The pellet was extracted with CH_2Cl_2 (2 × 50 mL), whereupon the combinated organic layers were treated with $\mathrm{Bu_4NCl}$ (21.0 g, 75.6 mmol). After stirring for 16 h the yellow solution was washed with $\mathrm{H_2O}$ (3 × 100 mL) and concentrated in vacuo. The residue was dissolved in $\mathrm{CH_2Cl_2}$, precipitated with $\mathrm{Et_2O}$ (2 × 50 mL), and concentrated and dried in vacuo to obtain **1a** as a white foamy solid in 69% yield (3.17 g, 4.11 mmol).

The synthesis was also carried with a smaller excess of pyridine sulfur trioxide: To a solution of **8a** (130.4 mg, 0.29 mmol) in $\mathrm{CH_2Cl_2}$ (15 mL) were added $\mathrm{py{\cdot}SO_3}$ (138.6 mg, 0.87 mmol) and pyridine (23.4 μL, 0.29 mmol). The reaction mixture was stirred for 3 h, whereupon the undissolved pyridine sulfur trioxide was removed by centrifugation. The supernatant was treated with $\mathrm{Bu_4NCl}$ (aq) (3 × 20 mL of M solution 5 g in 100 mL), whereupon it was washed with deionized water (6 × 20 mL) and concentrated in vacuo. The resulting orange foamy solid was purified by precipitation from $\mathrm{CH_2Cl_2}$ (5 mL) with $\mathrm{Et_2O}$ (40 mL) to give **1** (129.1 mg; 0.17 mmol, 58%) as an off-white foamy solid. ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$, 24 mM): δ 6.90 (s, 2H, $\mathrm{Ar}H$), 3.99 (s, 4H, $\mathrm{ArC}H_2$), 3.83 (t, $^3J_{\mathrm{HH}}$ = 7.1 Hz, 2H, $\mathrm{OC}H_2$), 3.19 (m, 8H, $\mathrm{CH_3(CH_2)_2C}H_2\mathrm{N}$) 2.88 (s, 12H, $\mathrm{NMe_2}$), 1.68−1.56 (overlapping signals, 16H, $\mathrm{C}H_2\mathrm{CH_2N}$ and $\mathrm{C}H_2\mathrm{CH_2Si}$), 1.42 (sextet, $^3J_{\mathrm{HH}}$ = 8H, $\mathrm{C}H_2\mathrm{CH_2CH_2N}$), 1.00 (t, $^3J_{\mathrm{HH}}$ = 7.2 Hz, 12H, $\mathrm{C}H_3\mathrm{(CH_2)_3N]}$), 0.71 (m, 2H, $\mathrm{CH_2Si}$) 0.21 (s, 6H, SiMe). ^{13}C{^{1}H} NMR (75 MHz, $\mathrm{CD_2Cl_2}$): δ 159.7, 145.4, 135.3, 125.3 (Ar), 75.0 ($\mathrm{CH_2OS}$), 70.0 ($\mathrm{CH_2N}$), 59.4 ($\mathrm{[Bu_4N]}$), 53.4 (NMe), 24.7 ($\mathrm{CH_2}$), 24.5, 20.3, 13.9 ($\mathrm{[Bu_4N]}$), 12.2 ($\mathrm{CH_2}$), −2.7 (SiMe). ^{29}Si{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ −2.4. MS (ES+, THF): *m/z* 1228 $(2 \times \mathrm{M} - 2 \times \mathrm{Cl} - [\mathrm{NBu_4}])^+$, 1011 $(2 \times \mathrm{M} - 2 \times [\mathrm{NBu_4}][\mathrm{Cl}] + \mathrm{Na}])^+$, 734 $(\mathrm{M} - \mathrm{Cl})^+$, 493 $(\mathrm{M} - [\mathrm{NBu_4}][\mathrm{Cl}] + \mathrm{H})^+$, 242 $(\mathrm{NBu_4})^+$. IR: ν (cm^{-1}) 3530 (w, HO−H, stretch), 3451.18 (w, HO−H, stretch), 3050−2800 (m, C−H, stretch), 1466 (m, C═C(Ar), stretch), 1246−1180 (vs, S═O, stretch), 1221.3 (vs, S═O, stretch), 1046−1032 (s, S═O, stretch), 983 (s), 881 (s). Λ_{M} ($\mathrm{CH_2Cl_2}$, 1 mM): 12.6 S cm^2 mol^{-1}. Anal. Calcd for $\mathrm{C_{33}H_{66}ClN_3O_4PdSSi}$: C, 51.41; H, 5.45; N, 8.63; S, 4.16. Found: C, 51.28; H, 5.52; N, 8.54; S 4.12.

{[BF$_4$][(H$_2$O)Pd(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6-{Si(Me)$_2$(CH$_2$)$_3$-OSO$_3$}-4)][NBu$_4$]} (9a). To a solution of **1a** (93.1 mg, 121.4 μmol) in wet acetone (15 mL) was added $\mathrm{AgBF_4}$ (23.7 mg; 121.7 μmol), which resulted in instantaneous precipitation of AgCl. After 1 h the resultant reaction mixture was filtered through a plug of Celite and concentrated in vacuo. The white solid was dissolved in dichloromethane (10 mL), filtered through a plug of Celite, and concentrated in vacuo to give **9a** as a white solid in quantitative yield. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 24 mM): δ 6.87 (s, 2H, ArH), 4.02 (t, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 2H, $\mathrm{OCH_2}$), 3.97 (s, 4H, $\mathrm{CH_2N}$), 3.19 (m, 8H, $\mathrm{NC}H_2\mathrm{CH_2}$), 2.85 (s, 12H, $\mathrm{N(CH_3)_2}$), 1.70−1.57 (overlapping signals, 10H, $\mathrm{C}H_2\mathrm{CH_2N}$ and $\mathrm{C}H_2\mathrm{CH_2Si}$), 1.42 (sextet, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 8H, $\mathrm{NCH_2CH_2C}H_2$), 0.99 (t, $^3J_{\mathrm{HH}}$ = 7.2 Hz, 12H, $\mathrm{NCH_2CH_2CH_2C}H_3$), 0.71 (m, 2H, $\mathrm{CH_2Si}$), 0.22 (s, 6H, $\mathrm{Si(CH_3)_2}$). ^{13}C{^{1}H} NMR (75 MHz, $\mathrm{CDCl_3}$, 24 mM): δ 152.2, 144.6 135.3, 125.2 (Ar), 73.7 ($\mathrm{CH_2OS}$), 70.8 ($\mathrm{CH_2N}$), 58.6 ($\mathrm{[Bu_4N]}$), 52.1 (NMe), 24.0 ($\mathrm{CH_2}$), 23.8, 19.6, 13.6 ($\mathrm{[Bu_4N]}$), 11.7 ($\mathrm{CH_2}$), −3.0 (SiMe). ^{19}F{^{1}H} NMR (282.5 MHz, $\mathrm{CD_2Cl_2}$): δ −164.7. MS (ES+, THF): *m/z* 986 $(2 \times \mathrm{M} - 2 \times [\mathrm{Bu_4N}][\mathrm{BF_4}] - 2\ \mathrm{H_2O} + \mathrm{H})^+$, 901 $([\mathrm{Bu_4N}]_3[\mathrm{BF_4}]_2)^+$, 752 $(\mathrm{M} - \mathrm{BF_4})^+$, 734 $(\mathrm{M} - \mathrm{BF_4} - \mathrm{H_2O})^+$, 571 $([\mathrm{Bu_4N}]_2[\mathrm{BF_4}])^+$, 534 $(\mathrm{M} - [\mathrm{Bu_4N}][\mathrm{BF_4}] + \mathrm{Na})^+$, 511 $(\mathrm{M} - [\mathrm{Bu_4N}][\mathrm{BF_4}] + \mathrm{H})^+$, 493 $(\mathrm{M} - [\mathrm{Bu_4N}][\mathrm{BF_4}] - \mathrm{H_2O} + \mathrm{H})^+$, 242 $([\mathrm{Bu_4N}])^+$. IR: ν (cm^{-1}) 3500 (w, HO−H, stretch), 3246 (w, HO−H, stretch), 3050−2800 (m, C−H, stretch), 1464 (m, C═C(Ar), stretch), 1265−1182 (s, S═O, stretch), 1046.8−1032.3 (vs, B−F, stretch), 976.5 (s). Λ_{M} ($\mathrm{CH_2Cl_2}$, 1 mM): 17.8 S cm^2 mol^{-1}.

[Pd(H$_2$O)(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6-{Si(Me)$_2$(CH$_2$)$_3$OSO$_3$}-4)] (2a). To a solution of **9a** (177 mg, 231 μmol) in acetone (15 mL) was added $\mathrm{AgBF_4}$ (47 mg, 241 μmol). The solution was stirred for 90 min, whereupon the white suspension was filtered over a plug of Celite. The white precipitate on the Celite layer was extracted with MeOH (20 mL). The filtrate was concentrated in vacuo to obtain **2a** as a white foamy solid in a 33% yield (62 mg, 72 μmol). ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$, 24 mM): δ 6.93 (s, 2H, ArH), 4.00 (s, 4H, $\mathrm{CH_2N}$), 3.94 (t, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 2H, $\mathrm{OCH_2}$), 2.78 (s, 12H, $\mathrm{N(CH_3)_2}$), 1.64 (m, 2H, $\mathrm{C}H_2\mathrm{CH_2Si}$),0.71 (m, 2H, $\mathrm{CH_2Si}$), 0.23 (s, 6H, $\mathrm{Si(CH_3)_2}$). ^{13}C{^{1}H} NMR (300 MHz, $\mathrm{CD_2Cl_2}$, 24 mM): δ 152.8, 145.4, 135.8, 125.8 (Ar), 74.2 ($\mathrm{CH_2OS}$), 71.2 ($\mathrm{CH_2N}$), 52.5 (NMe), 24.6, 12.2 ($\mathrm{CH_2}$), −2.7 (SiMe). MS (ES+, THF): *m/z* 1995.2 $[4\ \mathrm{M} - 4\ \mathrm{H_2O} + \mathrm{Na}]^+$, 1973.2 $[4\ \mathrm{M} - 4\ \mathrm{H_2O} + \mathrm{H}]^+$, 1502.2 $[3\ \mathrm{M} - 3\ \mathrm{H_2O} + \mathrm{Na}]^+$, 1480.2 $[3\ \mathrm{M} - 3\ \mathrm{H_2O} + \mathrm{H}]^+$, 1009.1 $[2\ \mathrm{M} - 2\ \mathrm{H_2O} + \mathrm{Na}]^+$, 987.2 $[2\ \mathrm{M} - 2\ \mathrm{H_2O} + \mathrm{H}]^+$, 493.1 $[\mathrm{M} - \mathrm{H_2O} + \mathrm{H}]^+$. IR: ν (cm^{-1}) 3284 (br, HO−H, stretch), 3050−2800 (m, C−H, stretch), 1461 (m, C═C(Ar), stretch), 1268−1177 (s, S═O, stretch), 1046−1025 (s, S═O, stretch), 975.1 (s). Λ_{M} ($\mathrm{CH_2Cl_2}$, 1 mM): 0.2 S cm^2 mol^{-1}. Anal. Calcd for $\mathrm{C_{17}H_{32}N_2O_5PdSSi}$: C, 39.96; H, 6.31; N, 5.48. Found: C, 39.83; H, 6.34; N 5.56.

(*tert*-Butyl)(Me)$_2$SiO(CH$_2$)$_4$CHCH$_2$ (3b). To a solution of 5-hexene-1-ol (6.34 g, 63.3 mmol) and imidazole (10.81 g, 159 mmol) in THF (100 mL) was added dropwise a solution of *tert*-butyldimethylsilyl chloride (11.74 g, 77.9 mmol) in THF (50 mL). The resultant white suspension was stirred for 72 h at room temperature, whereupon it was filtered through a plug of layered silica and Celite, eluting with pentane. The resulting colorless solution was concentrated in vacuo and dissolved in pentane (150 mL). The organic solution was washed with $\mathrm{H_2O}$ (3 × 75 mL), washed with brine (2 × 75 mL), dried over $\mathrm{MgSO_4}$, filtered, and concentrated in vacuo to afford 12.88 g (60.07 mmol, 95%) of **3b** as a colorless liquid. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 5.88−5.74 (m, 1H, $\mathrm{CH_2C}H$), 5.03−4.92 (m, 2H, $\mathrm{C}H_2\mathrm{CH}$), 3.61 (t, $^3J_{\mathrm{HH}}$ = 6.2 Hz, 2H, $\mathrm{OC}H_2$), 2.05 (q, $^3J_{\mathrm{HH}}$ = 6.2 Hz, 2H, $\mathrm{O(CH_2)_3C}H_2$), 1.58−1.39 (m, 4H, $\mathrm{OCH_2(C}H_2\mathrm{)_2}$), 0.90 (s, 9H, $\mathrm{C(C}H_3\mathrm{)_3}$), 0.05 (s, 6H, $\mathrm{OSi(C}H_3\mathrm{)_2}$. ^{13}C{^{1}H} NMR (75 MHz, $\mathrm{CDCl_3}$): δ 139.1 ($\mathrm{CH_2CH}$), 114.5 ($C\mathrm{H_2CH}$), 63.2 ($\mathrm{O}C\mathrm{H_2}$), 33.7 ($\mathrm{OCH_2}C\mathrm{H_2}$), 32.5 ($\mathrm{O(CH_2)_2}C\mathrm{H_2}$), 26.1 ($\mathrm{C(}C\mathrm{H_3)_3}$), 25.3 ($\mathrm{O(CH_2)_3}C\mathrm{H_2}$), 18.5 ($C\mathrm{(CH_3)_3}$), −5.1 ($\mathrm{OSi(}C\mathrm{H_3)_2}$). ^{29}Si{^{1}H} NMR (60 MHz, $\mathrm{C_6D_6}$): δ 17.8. Anal. Calcd for $\mathrm{C_{12}H_{26}OSi}$: C, 67.22; H, 12.22; Si, 13.10. Found: C, 66.97; H, 12.16; Si, 13.08.

(*tert*-Butyl)(Me)$_2$SiO(CH$_2$)$_6$Si(Me)$_2$Cl (4b). To a mixture of **3b** (7.87 g, 37 mmol) in THF (10 mL) were added $\mathrm{HSiMe_2Cl}$ (24 mL, 216 mmol) and a catalytic amount of $\mathrm{[(NBu_4)_2PtCl_6]}$ solvated in EtOH. The reaction mixture was shortly heated to reflux, whereupon the mixture was stirred for 15 h at room temperature. The reaction mixture was concentrated in vacuo to obtain **4b** as a colorless liquid (11.15 g, 36 mmol, 98%). ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): δ 3.60 (t, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 2H, $\mathrm{OC}H_2$), 1.60−1.45 (br m, 2H, $\mathrm{OCH_2C}H_2$), 1.45−1.26 (br m, 6H, $\mathrm{O(CH_2)(C}H_2\mathrm{)_3}$), 0.89 (s, 9H, $\mathrm{C(C}H_3\mathrm{)_3}$), 0.84−0.76 (br m, 2H, $\mathrm{ClSi(C}H_3\mathrm{)_2}$), 0.40 (s, 6H, $\mathrm{ClSi(C}H_3\mathrm{)_2}$), 0.05 (s, 6H, $\mathrm{OSi(C}H_3\mathrm{)_2}$). ^{13}C{^{1}H} NMR (75 MHz, $\mathrm{CDCl_3}$): δ 63.6 ($\mathrm{O}C\mathrm{H_2}$), 33.5 ($\mathrm{OCH_2}C\mathrm{H_2}$), 32.9 ($\mathrm{O(CH_2)_2}C\mathrm{H_2}$), 26.2 ($\mathrm{C(}C\mathrm{H_3)_3}$), 25.8 ($\mathrm{O(CH_2)_3}C\mathrm{H_2}$), 23.4 ($\mathrm{O(CH_2)_4}C\mathrm{H_2}$), 18.6 ($C\mathrm{(CH_3)_3}$), 16.6 ($\mathrm{ClSi}C\mathrm{H_2}$), −1.9 ($\mathrm{ClSi(}C\mathrm{H_3)_2}$), −5.0 ($\mathrm{OSi(}C\mathrm{H_3)_2}$).

1-(*tert*-Butyl)(Me)$_2$SiO(CH$_2$)$_6$Si(Me)$_2$C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-3,5 (5b). To a solution of 1-bromo-3,5-{bis(dimethylamino)-benzene} (4.54 g, 16.8 mmol) in $\mathrm{Et_2O}$ (50 mL) was added *t*-BuLi (21.4 mL of a 1.5 M solution in pentane, 32 mmol) at −80 °C. After stirring the resulting yellow suspension for ca. 40 min, a solution of **4b** (4.73 g, 15.3 mmol) in $\mathrm{Et_2O}$ (20 mL) was added dropwise, whereupon the resulting suspension was allowed to reach room temperature and stirred for 20 h. Subsequently, an extra amount of *t*-BuLi (5.00 mL of a 1.5 M solution in pentane, 7.5 mmol) was added at −80 °C. The reaction mixture was stirred for 45 min, followed by addition of $\mathrm{H_2O}$ (75 mL) to hydrolyze the excess of organolithium species. The organic layer was separated off, and the water layer was extracted with pentane (4 × 75 mL). The combined organic layers were washed with $\mathrm{H_2O}$ (4 × 100 mL), washed with brine (2 × 100 mL), dried over $\mathrm{MgSO_4}$, filtered, and concentrated in vacuo. Excess of $\mathrm{[C_6H_4(CH_2NMe_2)_2\text{-}3,5]}$ was removed by Kugelrohr distillation (120 °C, 0.1−0.2 mmHg) to gain **5b** as a yellow oil. Yield: 5.64 g (12.1 mmol, 79%). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 7.29 (s, 2H, $\mathrm{Ar}H$), 7.22 (s, 1H, $\mathrm{Ar}H$), 3.57 (t, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 2H, $\mathrm{OC}H_2$), 3.41 (s, 4H, $\mathrm{ArC}H_2$), 2.23 (s, 12H, $\mathrm{N(C}H_3\mathrm{)_2}$), 1.51−1.42 (br m, 2H, OCH$_2$C*H*$_2$), 1.30 (br signal, 6H, O(CH$_2$)$_2$(C*H*$_2$)$_3$), 0.88 (s, 9H, C(C*H*$_3$)$_3$), 0.77−0.69 (br m, 2H, ArSiC*H*$_2$), 0.24 (s, 6H, ArSi(C*H*$_3$)$_2$), 0.03 (s, 6H, OSi(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 139.6, 137.9, 133.3, 130.8 (Ar*C*), 64.6 (Ar*C*H$_2$), 63.5 (O*C*H$_2$), 45.5 (N(*C*H$_3$)$_2$), 33.5 (OCH$_2$*C*H$_2$), 32.9 (O(CH$_2$)$_2$*C*H$_2$), 26.1 (C(*C*H$_3$)$_3$), 25.6 (O(CH$_2$)$_3$*C*H$_2$), 24.0 (O(CH$_2$)$_4$*C*H$_2$), 18.5 (*C*(CH$_3$)$_3$), 15.9 (O(CH$_2$)$_5$*C*H$_2$), −2.8 (ArSi(*C*H$_3$)$_2$), −5.1 (OSi(*C*H$_3$)$_2$). ^{29}Si{^{1}H} NMR (60 MHz, C$_6$D$_6$): δ 17.2 (O*Si*), −3.4 (Ar*Si*). Anal. Calcd for C$_{26}$H$_{52}$N$_2$OSi$_2$: C, 67.17; H, 11.27; N, 6.03; Si, 12.08. Found: C, 67.28; H, 11.36; N, 5.94; Si, 11.92.

1-(*tert*-Butyl)(Me)$_2$SiO(CH$_2$)$_6$Si(Me)$_2$-4-Si(Me)$_3$C$_6$H$_2$-(CH$_2$NMe$_2$)$_2$-3,5 (6b). To a solution of **5b** (3.15 g, 6.78 mmol) in hexane (40 mL) was added *n*-BuLi (4.6 mL of a 1.56 M solution in pentane, 7.2 mmol) at room temperature. The dark red solution was stirred for 16 h at room temperature. To the resultant yellow solution was added dropwise Me$_3$SiOTf (1.70 mL, 8.80 mmol) with a syringe in 5 min at 0 °C. After stirring the reaction mixture for 10 min at 0 °C, the suspension was allowed to reach room temperature and stirred for another 25 min. The hexane layer was separated from the precipitate by centrifugation. The residue was extracted with hexane (5 × 30 mL). The combined organic layers were then filtered through Celite, eluting with hexane. The filtrate was concentrated in vacuo, and **6b** was obtained as a slightly yellow oil. Yield: 2.60 g (4.84 mmol, 71%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.37 (s, 2H, Ar*H*), 3.58 (t, $^3J_{\mathrm{HH}} = 6.6$ Hz, 2H, OC*H*$_2$), 3.52 (s, 4H, ArC*H*$_2$), 2.10 (s, 12H, N(C*H*$_3$)$_2$), 1.51−1.43 (br m 2H, OCH$_2$C*H*$_2$), 1.31 (br signal, 6H, O(CH$_2$)$_2$(C*H*$_2$)$_3$), 0.89 (s, 9H, C(C*H*$_3$)$_3$), 0.78−0.69 (br m, 2H, ArSiC*H*$_2$), 0.36 (s, 9H, ArSi(C*H*$_3$)$_3$), 0.24 (s, 6H, ArSi(C*H*$_3$)$_2$), 0.03 (s, 6H, OSi(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 145.4, 139.4, 139.3, 133.9 (Ar*C*), 65.8 (Ar*C*H$_2$), 63.5 (O*C*H$_2$), 45.2 (N(*C*H$_3$)$_2$), 33.5 (OCH$_2$*C*H$_2$), 32.9 (O(CH$_2$)$_2$*C*H$_2$), 26.2 (C(*C*H$_3$)$_3$), 25.6 (O(CH$_2$)$_3$*C*H$_2$), 24.1 (O(CH$_2$)$_4$*C*H$_2$), 18.5 (*C*(CH$_3$)$_3$), 15.8 (O(CH$_2$)$_5$*C*H$_2$), 3.4 (ArSi(*C*H$_3$)$_3$), −2.9 (ArSi(*C*H$_3$)$_2$), −5.1 (OSi(*C*H$_3$)$_2$). ^{29}Si{^{1}H} NMR (60 MHz, C$_6$D$_6$): δ 17.7 (OSi), −3.4 (ArSi), −7.5 (ArSi(CH$_3$)$_3$). Anal. Calcd for C$_{29}$H$_{60}$N$_2$OSi$_3$: C, 64.86; H, 11.26; N, 5.22; Si, 15.69. Found: C, 64.97; H, 11.19; N, 5.12; Si, 15.48.

[PdCl(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6-{Si(Me)$_2$(CH$_2$)$_6$OSi(Me)$_2$(*tert*-butyl)}-4)] (7b). To a solution of **6b** (4.71 g, 8.77 mmol) in MeOH (150 mL) was added Pd(OAc)$_2$ (2 g, 8.91 mmol). After stirring the resulting, dark brown reaction mixture for 1 h, LiCl (1.12 g, 26.4 mmol) was added. The mixture was stirred for another 10 min at room temperature, whereupon it was filtered through a plug of Celite. The yellow filtrate was concentrated to dryness to afford a yellow solid, which was dissolved in pentane (200 mL), washed with H$_2$O (5 × 100 mL), washed with brine (100 mL), dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo to yield **7b** as a yellow solid (4.90 g, 8.09 mmol, 92%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.87 (s, 2H, ArH), 3.99 (s, 4H, ArCH$_2$), 3.58 (t, $^3J_{\mathrm{HH}} = 6.5$ Hz, 2H, OCH$_2$), 2.94 (s, 12H, N(CH$_3$)$_2$), 1.51−1.42 (br m, 2H, OCH$_2$C*H*$_2$), 1.30 (br signal, 6H, O(CH$_2$)$_2$(C*H*$_2$)$_3$), 0.88 (s, 9H, C(CH$_3$)$_3$), 0.72−0.64 (br m, 2H, ArSiCH$_2$), 0.19 (s, 6H, ArSi(CH$_3$)$_2$), 0.03 (s, 6H, OSi(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 160.1, 145.4, 134.5, 124.6 (Ar*C*), 74.9 (Ar*C*H$_2$), 63.4 (O*C*H$_2$), 52.9 (N(*C*H$_3$)$_2$), 33.9 (OCH$_2$*C*H$_2$), 33.3 (O(CH$_2$)$_2$*C*H$_2$), 26.2 (C(*C*H$_3$)$_3$), 26.0 (O(CH$_2$)$_3$*C*H$_2$), 24.5 (O(CH$_2$)$_4$*C*H$_2$), 18.5 (*C*(CH$_3$)$_3$), 16.4 (O(CH$_2$)$_5$*C*H$_2$), −2.5 (ArSi(*C*H$_3$)$_2$), −5.1 (OSi(*C*H$_3$)$_2$). ^{29}Si{^{1}H} NMR (60 MHz, C$_6$D$_6$): δ 17.9 (OSi), −2.9 (ArSi). Anal. Calcd for C$_{26}$H$_{51}$ClN$_2$OPdSi$_2$: C, 51.5; H, 8.49; N, 4.62. Found: C, 51.66; H, 8.53; N, 4.54.

[PdCl(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6-{Si(Me)$_2$(CH$_2$)$_6$OH}-4)] (8b). To a solution of **7b** (2.50 g, 4.13 mmol) in THF (125 mL) was added Bu$_4$NF (4.13 mL of a 1.0 M solution in THF, containing ca. 5% water, 4.13 mmol). After stirring the dark red solution for 2 h at room temperature, H$_2$O (3.5 mL) was added and the solution was stirred for 16 h at room temperature. Subsequently, the reaction mixture was concentrated in vacuo, and the yellow-brown residue was dissolved in CH$_2$Cl$_2$ (200 mL), washed with water (4 × 100 mL) and brine (100 mL), dried over MgSO$_4$, filtered, and concentrated in vacuo to give **8b** as a white crystalline solid (1.5 g, 3.05 mmol, 79%). Slightly yellow needle-shaped crystals suitable for X-ray diffraction readily crystallized from a solution of **8b** in CH$_2$Cl$_2$ and pentane at room temperature. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.84 (s, 2H, ArH), 3.97 (s, 4H, ArCH$_2$), 3.58 (t, $^3J_{\mathrm{HH}} = 6.6$ Hz, 2H, OC*H*$_2$), 2.90 (s, 12H, N(C*H*$_3$)$_2$), 1.55−1.46 (br m, 2H, OCH$_2$C*H*$_2$), 1.30 (br signal, 6H, O(CH$_2$)$_2$(C*H*$_2$)$_3$), 0.68−0.62 (br m, 2H, ArSiC*H*$_2$), 0.16 (s, 6H, ArSi(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 158.8, 145.3, 135.5, 125.1 (Ar), 75.2 (Ar*C*H$_2$), 63.2 (OCH$_2$), 53.4 (N(CH$_3$)$_2$), 33.9 (OCH$_2$*C*H$_2$), 33.3 (O(CH$_2$)$_2$*C*H$_2$), 25.9 (O(CH$_2$)$_3$*C*H$_2$), 24.4 (O(CH$_2$)$_4$*C*H$_2$), 16.3 (O(CH$_2$)$_5$*C*H$_2$), −2.6 (ArSi(*C*H$_3$)$_2$). ^{29}Si{^{1}H} NMR (60 MHz, CD$_2$Cl$_2$): δ −0.8. MS (ES+, THF): *m*/*z* 455.1 [M − Cl]$^+$, 526 [M + THF]$^+$, 947.0 [2 M − Cl]$^+$. Anal. Calcd for C$_{20}$H$_{37}$ClN$_2$OPdSi: C, 48.88; H, 7.59; N, 5.70; Si, 5.71. Found: C, 48.78; H, 7.48; N, 5.62; Si, 5.82.

{[PdCl(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6-{Si(Me)$_2$(CH$_2$)$_6$OSO$_3$}-4)]-[NBu$_4$]} (1b). To a solution of **8b** (2.05 g; 4.17 mmol) in CH$_2$Cl$_2$ (250 mL) under a nitrogen atmosphere were added pyridine sulfur trioxide (2.0 g; 12.51 mmol) and pyridine (0.34 mL; 4.17 mmol). The resultant reaction mixture was stirred at room temperature for 3 h, whereupon undissolved pyridine sulfur trioxide was removed by centrifugation. Subsequently, the supernatant was concentrated to a fifth of its original volume, treated with [Bu$_4$N]Cl(aq) (3 × 20 mL of a 0.3 M solution), and washed with deionized water (5 × 75 mL). After precipitation from the organic phase by diethyl ether, **1b** was obtained as an off-white foamy solid (3 g; 3.7 mmol; 88%). ^{1}H NMR (CD$_2$Cl$_2$, 24 mM): δ 6.89 (s, 2H, ArH), 3.99 (s, 4H, ArCH$_2$), 3.86 (t, $^3J_{\mathrm{HH}} = 6.9$ Hz, 2H, CH$_2$O), 3.22 (m, 8H, CH$_3$(CH$_2$)$_2$C*H*$_2$N), 2.89 (s, 12H, NMe$_2$), 1.8−1.2 (br m, 16H, CH$_3$(C*H*$_2$)$_2$CH$_2$N and (C*H*$_2$)$_4$CH$_2$Si), 1.01 (t, $^3J_{\mathrm{HH}} = 7.2$ Hz, 12H, C*H*$_3$(CH$_2$)$_3$N]), 0.69 (m, 2H, CH$_2$Si), 0.20 (s, 6H, SiMe). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 157.7, 144.4, 135.1, 124.4 (Ar), 74.5 (CH$_2$N), 67.1 (OCH$_2$), 58.5 (N*C*H$_2$CH$_2$) 52.8 (N(CH$_3$)$_2$), 33.1, 29.3, 25.3 (CH$_2$), 23.8 (NCH$_2$*C*H$_2$), 23.6 (CH$_2$), 19.5 (N(CH$_2$)$_2$CH), 15.6 (CH$_2$), 13.5 (N(CH$_2$)$_3$CH$_3$), −3.0 (ArSi(CH$_3$)$_2$). MS (ES+, THF): *m*/*z* 1626.9 [3 M − 3 Bu$_4$NCl + Na]$^+$, 1071.6 [2 M − 2 Bu$_4$NCl + H]$^+$, [M − Bu$_4$NCl + H + Na]$^+$, 535.0 [M − Bu$_4$NCl + H]$^+$. IR: ν (cm^{-1}) 3513 (w, HO−H, stretch), 3050−2800 (m, C−H, stretch), 1468 (m, C=C(Ar), stretch), 1263−1194 (vs, S=O, stretch), 1095−1055 (s, S=O, stretch), 802 (s). Λ_{M} (CH$_2$Cl$_2$, 1 mM): 11.8 mM S cm^2 mol^{-1}. Anal. Calcd for C$_{36}$H$_{72}$ClN$_3$O$_4$PdSSi: C, 53.18; H, 8.93; N, 5.17; Cl, 4.36. Found: C, 53.06; H, 8.81; N, 5.20; Cl, 4.32.

{[BF$_4$][(H$_2$O)Pd(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6-{Si(Me)$_2$(CH$_2$)$_6$-OSO$_3$}-4)][NBu$_4$]} (9b). To a solution of **1b** (53.1 mg; 65.3 μmol) in wet acetone (3 mL) was added AgBF$_4$ (13.4 mg; 69.5 μmol), which resulted in instantaneous precipitation of AgCl. After 30 min the resulting reaction mixture was filtered through a plug of Celite and concentrated to dryness. The off-white residue was dissolved in CH$_2$Cl$_2$ (5 mL), filtered through a plug of Celite, and concentrated in vacuo to obtain **9b** as a white solid (55.2 mg; 62.6 μmol; 96%). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 24 mM): δ 6.88 (s, 2H, ArH), 3.99 (t, $^3J_{\mathrm{HH}} = 6.6$ Hz, 2H, CH$_2$O), 3.95 (s, 4H, ArCH$_2$N), 3.14 (m, 8H, CH$_3$(CH$_2$)$_2$C*H*$_2$N) 2.86 (s, 12H, NMe$_2$), 1.8−1.2 (br m, 16H, CH$_3$(C*H*$_2$)$_2$CH$_2$N and (C*H*$_2$)$_4$CH$_2$Si), 1.01 (t, $^3J_{\mathrm{HH}} = 7.7$ Hz, 12H, C*H*$_3$(CH$_2$)$_3$N), 0.67 (m, 2H, CH$_2$Si) 0.19 (s, 6H, SiMe). ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$, 24 mM): δ 152.6, 145.2, 136.3, 125.5 (Ar), 74.2 (CH$_2$N), 66.7 (OCH$_2$), 59.3 (N*C*H$_2$CH$_2$), 52.5 (N(CH$_3$)$_2$), 33.5, 29.8, 26.0, 24.3 (CH$_2$), 20.2 (N(CH$_2$)$_2$CH$_3$), 16.2 (CH$_2$), 13.9 (N(CH$_2$)$_3$*C*H$_3$), −2.6 (ArSi(CH$_3$)$_2$). ^{19}F{^{1}H} NMR (75 MHz; CDCl$_3$): δ −163.3. MS (ES+, THF): *m*/*z* 2163.32 [4 M − 4 Bu$_4$N − 4 BF$_4$ − 4 H$_2$O + Na]$^+$, 1843.7 [3 M − 2 Bu$_4$N − 3 BF$_4$ − 3 H$_2$O]$^+$, 1627.4 [3 M − 3 Bu$_4$N − 3 BF$_4$ − 3 H$_2$O + Na]$^+$, 1312.5 [2 M − Bu$_4$N − 2 BF$_4$ − 2 H$_2$O]$^+$, 1093.2 [2 M − 2 Bu$_4$N − 2 BF$_4$ − 2 H$_2$O + Na]$^+$, 1069.2 [2 M − 2 Bu$_4$N − 2 BF$_4$ − 2 H$_2$O + H]$^+$, 571.5 [[Bu$_4$N]$_2$BF$_4$]$^+$, 557.1 [M − Bu$_4$N − BF$_4$ − H$_2$O + Na]$^+$, 242.4 [NBu$_4$]. IR: ν (cm^{-1}) 3433 (w, HO−H, stretch), 3050−2800 (m, C−H, stretch), 1469 (m, C=C(Ar), stretch), 1265−1195 (vs, S=O, stretch), 1097−1057 (vs, B−F, stretch), 802 (s). Λ_M (CH_2Cl_2, 1 mM): 17.1 S cm^2 mol^{-1}.

[Pd(H_2O)(C_6H_3{CH_2NMe_2}$_2$-2,6-{Si(Me)$_2$(CH_2)$_6$$OSO_3$}-4)] (2b). A solution of **9b** in CH_2Cl_2 (25 mL) was washed with deionized water (35 × 10 mL), whereupon it was concentrated and dried in vacuo to give **2b** (41.8 mg, 78.1 μmol, 72%) as a white solid. ^{1}H NMR(300 MHz, CD_2Cl_2, 24 mM): δ 6.88 (s, 2H, ArH), 3.99 (t, $^3J_{HH}$ = 6.6 Hz, 2H, CH_2O), 3.95 (s, 4H, ArCH_2), 2.85 (s, 12H, NMe_2), 1.8−1.5 (br m, 2H, OCH_2CH_2), 1.3−1.2 (br m, 3H, (CH_2)$_3$$CH_2$Si), 0.67 (m, 2H, CH_2Si) 0.18 (s, 6H, SiMe). ^{13}C{^{1}H} NMR (300 MHz, CD_2Cl_2, 24 mM): δ 152.7, 145.3, 136.5, 125.6 (Ar), 74.2 (CH_2N), 68.8 (OCH_2), 52.5 (N(CH_3)$_2$), 33.6, 29.8, 26.0, 24.3, 16.2 (CH_2), −2.6 (ArSi(CH_3)$_2$). MS (MALDI-TOF, 2,5-dihydroxybenzoic acid): *m/z* 1626.5 (3 × M + Na)$^+$, 1070.6 (2 × M)$^+$, 536.9 (M + H)$^+$. MS (ES+, THF): *m/z* 2060.5 [4 M − SO_3 − 4 H_2O + H]$^+$, 1628.3 [3 M − 3 H_2O + Na]$^+$, 1523.3 [3 M − SO_3 − 3 H_2O + H]$^+$, 1093.2 [2 M − 2 H_2O + Na]$^+$, 1071.2 [2 M − 2 H_2O + H]$^+$, 991.2 [2 M − SO_3 − 2 H_2O + H]$^+$, 557.1 [M − H_2O + Na]$^+$, 535.1 [M − SO_3 − 2 H_2O + H]$^+$. IR: ν (cm^{-1}) 3600−3100 (br, HO−H, stretch), 3050−2825 (m, C−H, stretch), 1462 (m, C=C(Ar), stretch), 1248−1180 (s, S=O, stretch), 1116−1145 (vs), 959 (vs), 878.8 (s), 834.1 (vs), 797.8 (vs), 724.0 (s). Λ_M (CH_2Cl_2, 1 mM): 0.3 S cm^2 mol^{-1}. Due to the highly hygroscopic nature of this material, no satisfactory elemental analysis could be obtained.

Conductivity Measurements. The conductivity measurements were performed using a Consort C832 multi-parameter analyzer (Consort nv., Turnhout, Belgium) at 20 °C. The conductometer was calibrated using aqueous solutions of potassium chloride. Sample solutions with a concentration of 1 mM in dichloromethane were prepared and analyzed. The sample solutions were stepwise diluted until a concentration of 0.03 mM was reached. After each dilution step the conductivity (κ in S cm^{-1}) was measured. The molar conductivities (Λ_M in S cm^2 mol^{-1}) of the sample solutions were calculated for each concentration (*c* in mol/L) using the following equation: $\Lambda_M = 1000 \times \kappa/c$.[15]

MALDI-TOF MS. The MALDI-TOF spectra were acquired using a Voyager-DE BioSPectrometry Workstation (Perseptive Biosystems Inc., Framingham, MA) mass spectrometer equipped with a nitrogen laser emitting at 337 nm. The instrument was operated at an accelerating voltage of 24 000 V. External calibration was performed using a mixture of C_{60} and C_{70}. Sample solutions with an approximate concentration of 5−10 mg/mL in THF were prepared. The matrix was 3,5-dihydroxybenzoic acid in THF (20−30 mg/mL). A 0.2 μL portion of the sample solution and 0.2 μL of the matrix solution were combined and placed on a gold MALDI target and analyzed after evaporization of the solvent.

Time-of-Flight Electrospray Ionization Mass Spectra. The time-of-flight electrospray ionization mass spectra were recorded on a Micromass LC-T mass spectrometer (Manchester, UK) operating in the positive ion mode. In all experiments dendrimer samples at a concentration of 10−20 μM were introduced into the electrospray needles. The nanospray needle potential was typically set to 1300 V and the cone voltage to 60 V. The source block temperature was set to 80 °C. The mass spectra were obtained at the Department of Biomolecular Mass Spectrometry, Utrecht University.

Infrared Spectroscopy. Infrared spectra were recorded on a Perkin-Elmer 2000 Fourier transform spectrometer equipped with a DTGS detector by accumulating 25 scans at a data point resolution of 2 cm^{-1}. Solid-state spectra were obtained by preparing 13 mm KBr/NaCl pellets of the powedered sample. Measurements of solutions were carried out in a 0.5 mm NaCl cell. The correspondig spectra were corrected for solvent absorptions by spectral subtraction using the solvent spectrum as the reference. The sample compartment was flushed with dry air to reduce interference of H_2O and CO_2.

X-ray Crystallographic Analysis of 8b. $C_{20}H_{37}ClN_2OPdSi$, fw = 491.46, yellow needle, 0.18 × 0.09 × 0.09 mm^3. Monoclinic crystal system, space group $P2_1/c$ (no. 14). Cell parameters: a = 14.9052(2) Å, b = 14.9631(1) Å, c = 10.4417(1) Å, β = 99.4680(3)°, V = 2297.07(4) Å^3. Z = 4, ρ = 1.421 g/cm^3, μ = 0.988 mm^{-1}; 44 137 reflections were measured on a Nonius KappaCCD diffractometer with rotating anode and Mo Kα radiation (graphite monochromator, λ = 0.71073 Å) at a temperature of 125(2) K. An absorption correction based on multiple measured reflections was applied (PLATON[30] routine MULABS, 0.81−0.92 correction angle); 5280 reflections were unique (R_{int} = 0.0582), of which 4308 were observed [$I > 2\sigma(I)$]. The structure was solved with direct methods using the program SIR97[31] and refined with the program SHELXL97[32] against F^2 of all reflections up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 Å^{-1}. Non hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. The OH hydrogen was refined freely with isotropic displacement parameters; all other hydrogen atoms were refined as rigid groups; 245 refined parameters, no restraints. R (obsd reflns): R1 = 0.0298, wR2 = 0.0611. R (all data): R1 = 0.0435, wR2 = 0.0646. Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0133P)^2 + 3.1057P]$, where $P = (F_o^2 + 2F_c^2)/3$. GoF = 1.073. Residual electron density between −0.58 and 0.69 e/Å^3. The drawings, geometry calculations, and checking for higher symmetry were performed with the program PLATON.[30]

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Supporting Information Available: Crystallographic data for compound **8b** in cif format is available free of charge via the Internet at http://pubs.acs.org.

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