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Synthesis and characterization of platinum(II)-terminated dendritic carbosilanes: X-ray crystal structure of the model species $[PtCl(C_6H_3\{CH_2NMe_2\}\text{-}2\text{-}SiMe_3\text{-}5)(PPh_3)]$

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Dedicated to Professor H. Brunner on the occasion of his 65th birthday

Abstract

A series of cycloplatinated carbosilane dendrimers appended with the monoanionic C,N-bidentate ligand $[C_6H_4\{CH_2NMe_2\}\text{-}2]^-$ (CN) was prepared via a multiple C–H activation reaction. Ligand exchange in the parent model species $[PtCl(C_6H_3\{CH_2NMe_2\}\text{-}2\text{-}SiMe_3\text{-}5)(DMSO)]$ (**1**) in the presence of PPh_3 gave the phosphine complex $[PtCl(C_6H_3\{CH_2NMe_2\}\text{-}2\text{-}SiMe_3\text{-}5)(PPh_3)]$ (**2**). The crystal structure of **2** was also determined, showing a close proximity between one of the Ar–H of the phosphine ligand and the Ar–H_{ortho} of the CN ligand. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbosilanes; C–H activation; Dendrimers; Platinum

1. Introduction

Recently, the field of polymer science has advanced tremendously due to the introduction of new types of macromolecules known as dendrimers [1]. These highly branched, regularly structured materials are usually prepared in a step-wise manner, and this particular aspect allows the easy control over the molecular architecture. At present, a broad variety of dendrimers is known with different kinds of functional groups present on the periphery or throughout the dendritic structure [2]. We are currently interested in the use of dendrimers as soluble supports for organometallic groups [3]. Furthermore, we have shown that these metallodendrimers are active as catalysts in a number of organic transformations [3,4,5a] and, more importantly, that these nano-sized molecules could meet the requirements for an effective recovery from product/substrate streams by means of nanofiltration membrane techniques [5].

In our previous work, we demonstrated the selective synthesis of different generations of carbosilane dendrimers [6] functionalized with the monoanionic ligands $[C_6H_4\{CH_2NMe_2\}\text{-}2]^-$ (CN) and $[C_6H_3\{CH_2NMe_2\}_2\text{-}2,6]^-$. These peripheral ligands could be selectively lithiated and the resultant polylithiated reagents were used as starting materials for the preparation of Group 8 metallodendritic species. However, a major drawback of this lithiation/transmetallation sequence is the incomplete Group 8 metal introduction (i.e. 80–90%) [4a,7]. In this paper we will show that an alternative approach can be used for the incorporation of metal sites onto the periphery of carbosilane dendrimers. Platinum(II) centers could be conveniently and quantitatively introduced in a small series of carbosilane dendrimers containing CN ligands by a multiple, aromatic C–H activation reaction. The specific spectroscopic features of a parent, mononuclear model species will also be presented, including its structural motifs.

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2. Results and discussion

2.1. Synthesis and characterization of cycloplatinated carbosilanes

In the last decade, several reports have appeared in which the synthesis of cycloplatinated ferrocenylamine ligands was described [8]. These cycloplatinated derivatives were prepared by a direct (aromatic) C–H activation process using metal salts like $PtCl_2(DMSO)_2$ [9] in combination with an external base. Following this lead, we investigated whether this platinum reagent could also be used for the synthesis of cycloplatinated carbosilanes functionalized with the monoanionic, arylamine CN-ligand. Therefore, a simple model compound was first tested for its feasibility towards C–H activation by $PtCl_2(DMSO)_2$.

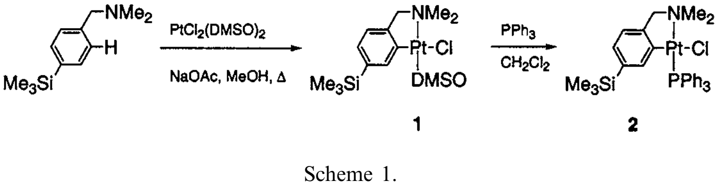
Mixing of 1-trimethylsilyl-4-[(dimethylamino)-methyl]benzene [10] with a slight excess of $PtCl_2(DMSO)_2$ [11] in the presence of NaOAc as an external base in refluxing MeOH resulted in the dissolution of the initially formed suspension into a clear, yellow solution. Most probably this increase in solubility observed for the metallating reagent can be ascribed to pre-coordination of the N-donor substituent of the CN ligand to the platinum center by substituting one DMSO ligand. After a few hours, the presence of a white precipitate was noted and after work-up, this was identified as the cycloplatinated derivative **1** (80% yield, Scheme 1).

Direct evidence for a cycloplatinated species was provided by the ^{1}H-NMR spectrum of **1**, which displayed a low-field shifted, aromatic ortho proton ($\delta = 8.2$ ppm) with diagnostic platinum satellites. Furthermore, characteristic shifts were observed for the CH_2N and $N(CH_3)_2$ groupings, together with the appearance of a singlet resonance at 3.54 ppm with platinum satellites, which was attributed to the methyl groupings of a coordinated dimethyl sulfoxide ligand. These results clearly showed that direct and selective cycloplatination of carbosilane molecules functionalized with CN-ligands was feasible. The relatively weakly bound DMSO ligand could be exchanged for a stronger Lewis base; upon addition of PPh_3 to a solution of **1** in CH_2Cl_2, phosphine complex **2** was formed instantaneously (Scheme 1). Evidence for this ligand exchange reaction was given by NMR spectroscopy (^{1}H, $^{13}C\{^1H\}$ and ^{31}P), elemental analyses and X-ray diffraction studies. It should be mentioned that in the ^{1}H-NMR spectrum of **2**, the $Ar–H_{ortho}$ of the ligand system underwent a significant high-field shift from 8.18 (in **1**) to 6.78 ppm (in **2**). Likewise, for the $SiMe_3$ group a high-field shift of 0.55 ppm was noted. This suggested a close proximity between the coordinated PPh_3 ligand and both the $Ar–H_{ortho}$ as well as the $SiMe_3$ group (vide infra). The ^{31}P-NMR spectrum of **2** showed the presence of a singlet resonance with the expected platinum satellites ($^1J(Pt–P) = 4316$ Hz). The coupling constant found corresponded well with those usually encountered for, for example, triphenylphosphine complexes of cycloplatinated ferrocenyl amine ligands [8].

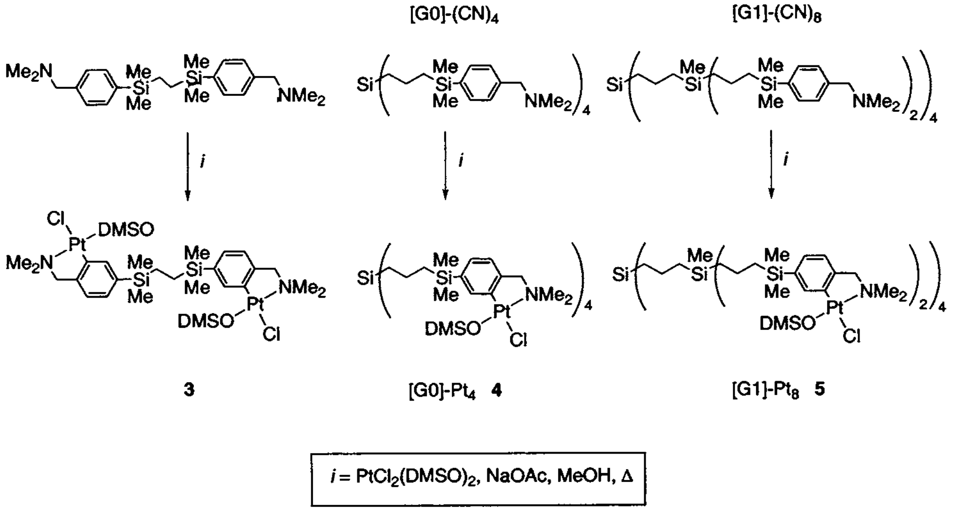
The diplatinated carbosilane derivative $[CH_2SiMe_2–(C_6H_3\{CH_2NMe_2\}\text{-}4\text{-}(PtCl\{DMSO\})\text{-}3]_2$ (**3**), the [G0] generation dendrimer [G0]-Pt_4 (**4**) and the [G1] generation dendrimer [G1]-Pt_8 (**5**) were prepared in a similar fashion to **1** starting from the CN-functionalized carbosilanes $[CH_2SiMe_2–(C_6H_4\{CH_2NMe_2\}\text{-}4]_2$ [7a], [G0]-$SiMe_2$–CN [7a] and [G1]-$(CN)_8$ [13] respectively and a slight excess of $PtCl_2(DMSO)_2$ [11] in refluxing methanol (Scheme 2). This typical procedure gave the multiplatinated species **3**–**5** as (off)white-colored solids in 70–74% yield (not optimized). These polyplatinated, dendritic carbosilanes were fully characterized by FT-IR and NMR spectroscopy (^{1}H, $^{13}C\{^1H\}$), mass spectrometry and elemental analyses, which confirmed in all cases the proposed stoichiometry. It should be noted that, in contrast to the incomplete transmetallation obtained in our earlier work using polylithiated precursors [4a], here the quantitative platination of the CN-functionalized carbosilane dendrimers was achieved in the isolated materials.

2.2. Mass spectrometric analysis of the dendritic species

The structures of $[CH_2SiMe_2–(C_6H_3\{CH_2NMe_2\}\text{-}4\text{-}(PtCl\{DMSO\})\text{-}3]_2$ (**3**), [G0]-Pt_4 (**4**) and [G1]-Pt_8 (**5**) were investigated with FAB- and MALDI-TOF-MS. The mass spectra of **3**–**5** proved to be very informative; in all the cases studied they showed several fragmented ions that had lost (multiple) chloride and/or DMSO ligands. As a result of this fragmentation behavior, no molecular ions were detected. An illustrative example was the MALDI-TOF mass spectrum obtained for dendrimer [G1]-Pt_8 (**5**) (Fig. 1). The fragment ion with the highest m/z was attributed to $[\mathbf{5} - Cl - DMSO]^+$ (m/z observed 4592.23, calc. 4592.16) and even the fragment ion $[\mathbf{5} - Cl - 7DMSO]^+$ (m/z observed 4123.32, calc. 4123.27) was detected.



Scheme 1.



Scheme 2.

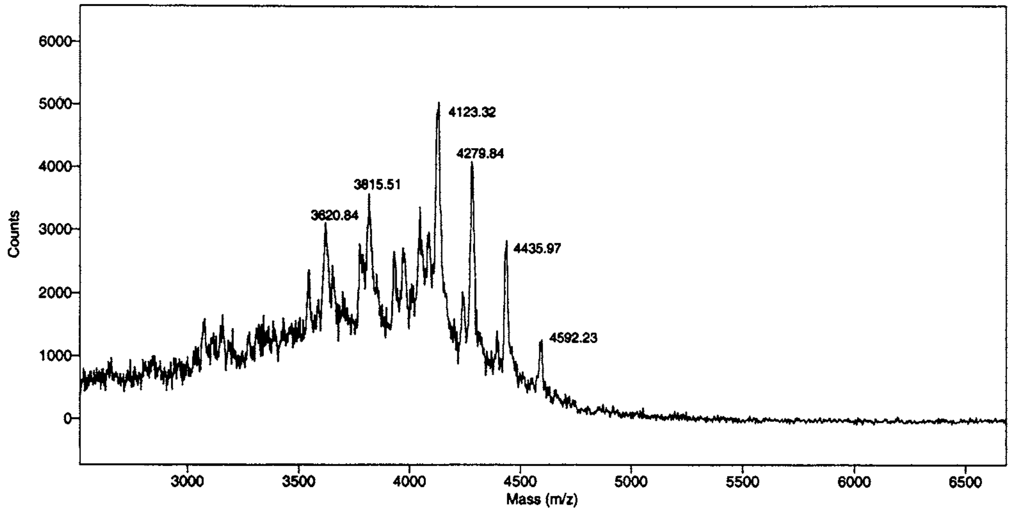


Fig. 1. MALDI-TOF spectrum of compound **5**.

2.3. X-ray crystal structure of complex 2

Crystals of **2** were obtained by diffusion of Et_2O into a concentrated solution of the isolated product in CH_2Cl_2. This batch of crystals of **2** was subjected to an X-ray crystal structure determination. The molecular structure of **2** in the crystal is presented in Fig. 2, and relevant bond distances and bond angles are collected in Table 1.

The platinum center in **2** has a planar coordination geometry, which, however, is significantly distorted by an acute CN-bite angle of 80.5(5)°. Two of the phenyl rings of the PPh_3 ligand are in a gauche conformation with respect to the Pt–C1 bond with C1–P–Pt–C19 and C1–P–Pt–C25 torsion angles of $-76.1(7)$ and 45.3(6)° respectively. This results in a short contact between one aromatic ring proton (H30) of the PPh_3 ligand, and the aromatic ortho proton attached to C2 (CN ligand) of 2.61 Å (H30···H2). This close proximity was also suggested by the ^1H-NMR spectroscopic features found for **2** (vide supra).

3. Conclusions

In summary, we have demonstrated the use of a simple synthetic methodology for the quantitative introduction of Pt(II) sites on the periphery of CN-derivatized carbosilane dendrimers. These preparations included a unique, multiple and selective C–H bond activation in the dendritic ligand systems. The present studies suggest a general applicability for the ready introduction of Pt(II) sites onto supported CN-type ligands, and studies toward this are currently under way. Because of their high loading of platinum metal and structural diversity, the dendritic multiplatinated carbosilane derivatives might have a great potential toward amplified anti-tumor activity by forming intra- or inter-strand linkages with DNA strands [12].

4. Experimental

4.1. General

All air-sensitive manupilations were carried out in an inert (nitrogen) atmosphere using standard Schlenk techniques. All solvents were carefully dried and distilled prior to use. Standard chemicals were purchased from Acros Chimica or Aldrich and used without further purification. The dendritic compounds [G0]-$(CN)_4$ [7a] and [G1]-$(CN)_8$ [13] were prepared according to previously reported procedures. ^1H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectroscopic measurements were carried out on a Varian Inova/Mercury 200 or 300 MHz spectrometer at room temperature (r.t.) and chemical shifts δ are given in ppm with Me_4Si as an external standard unless noted otherwise. The MALDI-TOF mass spectrum of **5** was acquired using a Voyager-DE BioSpectrometry Workstation (PerSeptive Biosystems Inc., Framingham, MA, USA) mass spectrometer. The matrix was 9-nitro-anthracene (9-NA). 0.2 μl of the sample solution and 0.2 μl of the matrix solution were combined and placed on a golden MALDI target and analyzed after evaporation of the solvents. Elemental analyses were performed by Dornis und Kolbe, Mülheim a/d Ruhr, Germany.

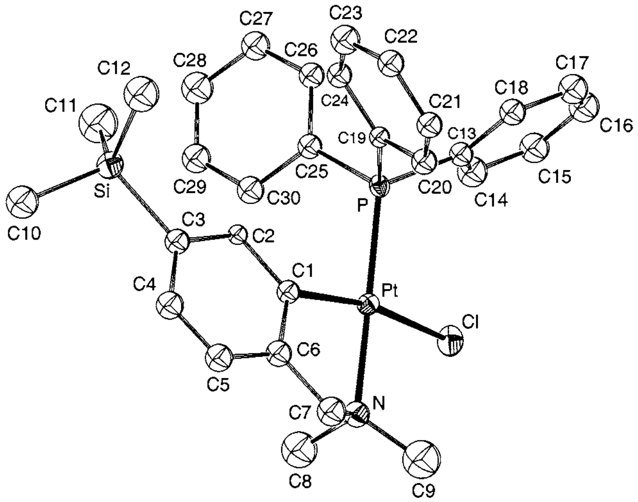


Fig. 2. Molecular structure of **2** in the crystal. H-atoms have been omitted for clarity.

Table 1
Selected bond distances (Å), bond angles (°) and torsion angles (°) for the cycloplatinated complex **2**

Bond distances			
Pt–C1	2.030(14)	Pt–Cl	2.391(4)
Pt–N	2.147(12)	Pt–P	2.222(3)
Bond angles			
Cl–Pt–C1	168.3(4)	P–Pt–N	172.6(3)
P–Pt–C1	94.2(4)	Cl–Pt–P	95.50(12)
N–Pt–C1	80.5(5)	Cl–Pt–N	90.4(4)
Torsion angles			
N–Pt–C1–C2	−158.1(12)	Pt–C1–C6–C5	−169.8(11)
C6–C1–Pt–P	−162.2(9)	Pt–C1–C2–C3	167.4(10)
C13–P–Pt–C1	163.0(6)	C19–P–Pt–C1	45.3(6)
C25–P–Pt–C1	−76.1(7)		

4.2. $[PtCl(C_6H_3\{CH_2NMe_2\}\text{-}2\text{-}SiMe_3\text{-}5)(DMSO)]$ (**1**)

General procedure: to a stirred solution of [1-(dimethylamino)methyl-4-trimethylsilyl]benzene (0.31 g, 1.50 mmol) in MeOH (25 ml) was added solid $PtCl_2(DMSO)_2$ (0.73 g, 1.73 mmol) and NaOAc (0.15 g, 1.83 mmol). The initially formed yellow solution was heated to reflux for 16 h, during which time a white precipitate was formed. The solvent was removed in vacuo and CH_2Cl_2 (30 ml) and H_2O (25 ml) were added to the solid residue. The organic layer was separated and subsequently washed with H_2O (2 × 25 ml), dried on anhydrous Na_2CO_3 and evaporated to dryness to yield a yellow solid (0.62 g, 1.20 mmol, 80%). Analytically pure **1** was obtained by crystallization from CH_2Cl_2–Et_2O. M.p. (dec.): 175–176°C. FT-IR (CH_2Cl_2, cm^{-1}): 1143 $\nu_{S=O}$. ^1H-NMR ($CDCl_3$): $\delta =$ 8.18 (s, 1H, ^3J(Pt–H) = 45.3 Hz, Ar–H_{ortho}), 7.23 (d, 1H, ^3J(H–H) = 7.4 Hz, Ar–H), 7.04 (d, 1H, ^3J(H–H) = 7.5 Hz, Ar–H), 3.97 (s, 2H, J(Pt–H) = 39.9 Hz, CH_2N), 3.53 (s, 6H, J(Pt–H) = 24.9 Hz, SMe), 2.93 (s, 6H, J(Pt–H) = 33.9 Hz, NMe_2), 0.25 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta = 146.6$ (Ar–C), 139.0 (^2J(Pt–C) = 55.8 Hz, Ar–C), 138.2 (Ar–C), 135.2 (Ar–C_{ipso}, J(Pt–C) not resolved), 129.8 (Ar–C), 121.0 (^3J(Pt–C) = 33.9 Hz, Ar–C), 74.8 (^2J(Pt–C) = 54.5 Hz, CH_2N), 52.2 ($N(CH_3)_2$), 46.7 (^2J(Pt–C) = 64.5, $S(CH_3)_2$), −1.1 ($Si(CH_3)_3$). Anal. Found: C, 32.78; H, 5.16; N, 2.77; Si, 5.53. Calc. for $C_{14}H_{26}ClNOPtSSi$: C, 32.65; H, 5.09; N, 2.72; Si, 5.45%.

4.3. $[PtCl(C_6H_3\{CH_2NMe_2\}\text{-}2\text{-}SiMe_3\text{-}5)(PPh_3)]$ (**2**)

A mixture of **1** (0.31 g, 0.60 mmol) and PPh_3 (0.19 g, 0.57 mmol) in CH_2Cl_2 (25 ml) was stirred for 16 h at room temperature. The solvent was removed under reduced pressure and the product was purified by slow diffusion of Et_2O into a concentrated solution of **2** in CH_2Cl_2 to afford large, off-white, block-shaped crystals that were suitable for an X-ray analysis (0.23 g, 0.33 mmol, 57%). M.p. (dec.): > 200°C. ^1H-NMR ($CDCl_3$): $\delta = 7.80$–7.76 (m, 6H, P–Ar–H_{ortho}), 7.43–7.33 (m, 9H, P–Ar–H), 7.05 (d, 1H, $^3J = 7.5$ Hz, Ar–H), 7.02 (d, 1H, $^3J = 7.5$ Hz, Ar–H), 6.78 (d, 1H,

^4J(P–H) = 3.0 Hz, ^3J(Pt–H) = 55.5 Hz, Ar–H$_{ortho}$), 4.08 (d, 2H, ^4J(P–H) = 2.7 Hz, ^3J(Pt–H) = 28.5 Hz, CH$_2$N), 3.02 (d, 6H, ^4J(P–H) = 2.7 Hz, ^3J(Pt–H) = 24.6 Hz, N(CH$_3$)$_2$), − 0.30 (d, 9H, ^2J(Si–H) = 6.3 Hz, Si(CH$_3$)$_3$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ = 147.83 (Ar–C), 143.33 (J(P–C) = 179.7 Hz, J(Pt–C) = 332.4 Hz, Ar–C), 136.46 (J(P–C) = 9.9 Hz, Ar–C), 136.25 ((J(P–C) = 26.7 Hz, Ar–C), 135.06 (J(P–C) = 43.8 Hz, ^1J(Si–C) = 162.6 Hz, Ar–C–Si), 130.84 (Ar–C), 130.30 (J(P–C) = 9.9 Hz, Ar–C), 130.02 (Ar–C), 127.58 (J(P–C) = 43.8 Hz, Ar–C), 120.79 (J(Pt–C) = 118.8 Hz, Ar–C), 74.13 (^3J(P–C) = 14.4 Hz, ^2J(Pt–C) = 204.0 Hz, CH$_2$N), 50.79 (^3J(P–C) = 12.0 Hz, ^2J(Pt–C) = 470.7 Hz, N(CH$_3$)$_2$), − 1.68 (^1J(Si–C) = 203.7 Hz). ^{31}P-NMR (CDCl$_3$, 81.03 MHz): δ = 22.3 (s, ^1J(Pt–P) = 4316 Hz). Anal. Found: C, 51.38; H, 5.01; N, 1.97; Si, 4.12. Calc. for C$_{30}$H$_{35}$ClNPPtSi: C, 51.53; H, 5.05; N, 2.00; Si, 4.02%.

*4.4. [CH$_2$SiMe$_2$–(C$_6$H$_3${CH$_2$NMe$_2$}-4-(PtCl{DMSO})-5)]$_2$ (**3**)*

To a solution of [CH$_2$SiMe$_2$–(C$_6$H$_4${CH$_2$NMe$_2$}-4)]$_2$ [7a] (0.24 g, 0.58 mmol) in MeOH (30 ml) was added PtCl$_2$(DMSO)$_2$ (0.54 g, 1.28 mmol) and NaOAc (0.10 g, 1.22 mmol). After the resulting mixture was brought to reflux temperature, the yellow solution turned into a white suspension after 1.5 h. Then the solid was isolated by centrifugation, washed with MeOH (50 ml) and Et$_2$O (50 ml) and finally dried in vacuo to give a white solid (0.42 g, 0.41 mmol, 70%). Analytically pure **3** was obtained by slow diffusion of Et$_2$O into a concentrated solution of the product in CH$_2$Cl$_2$. M.p. (dec.): 194–195°C. FT-IR (CH$_2$Cl$_2$, cm^{-1}): 1143 $\nu_{S=O}$. ^{1}H-NMR (CDCl$_3$): δ = 8.15 (s, 2H, ^3J(Pt–H) = 45.7 Hz, Ar–H$_{ortho}$), 7.20 (d, 2H, ^3J(H–H) = 7.2 Hz, Ar–H), 7.03 (d, 2H, ^3J(H–H) = 7.2 Hz, Ar–H), 3.97 (s, 4H, ^3J(Pt–H) = 39.9 Hz, CH$_2$N), 3.53 (s, 12H, ^3J(Pt–H) = 24.9 Hz, S(CH$_3$)$_2$), 2.93 (s, 12H, ^3J(Pt–H) = 33.9 Hz, N(CH$_3$)$_2$), 0.68 (s, 4H, –(CH$_2$)$_2$–), 0.23 (s, 12H, Si(CH$_3$)$_2$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ = 146.6 (J(Pt–C) not resolved, Ar–C), 139.5 (^2J(Pt–C) = 55.7 Hz, Ar–C), 137.5, 135.2 (Ar–C$_{ipso}$, J(Pt–C) not resolved), 130.3 (Ar–C), 121.0 (^3J(Pt–C) = 32.9 Hz, Ar–C), 74.9 (^2J(Pt–C) = 53.7 Hz, CH$_2$N), 52.3 (N(CH$_3$)$_2$), 46.8 (^2J(Pt–C) = 64.6 Hz, S(CH$_3$)$_2$), 8.04 (–(CH$_2$)$_2$–), − 3.5 (Si(CH$_3$)$_2$). FAB-MS: m/z 990.84 [M − Cl]$^+$, 948.82 [M − DMSO]$^+$, 912.87 [M − Cl − DMSO]$^+$, 870.84 [M − 2DMSO]$^+$, 834.86 [M − Cl − 2DMSO]$^+$. Anal. Found: C, 32.58; H, 4.87; N, 2.66. Calc. for C$_{28}$H$_{50}$Cl$_2$N$_2$O$_2$Pt$_2$S$_2$Si$_2$: C, 32.71; H, 4.90; N, 2.72%.

*4.5. [G0]-Pt$_4$ (**4**)*

A solution of [G0]-(CN)$_4$ (0.16 g, 0.17 mmol) in MeOH (15 ml) was treated with PtCl$_2$(DMSO)$_2$ (0.35 g, 0.83 mmol) at reflux temperature for 16 h, during which time a white solid precipitated. After decanting the solvent, this solid was washed with MeOH (10 ml) and Et$_2$O (10 ml) and evaporated to dryness (0.27 g, 0.12 mmol, 74%). M.p. (dec.): 181°C. FT-IR (CH$_2$Cl$_2$, cm^{-1}): 1141 $\nu_{S=O}$. ^{1}H-NMR (CDCl$_3$): δ = 8.14 (s, 4H, ^3J(Pt–H) = 45.7 Hz, Ar–H$_{ortho}$), 7.19 (d, 4H, ^3J(H–H) = 7.2 Hz, Ar–H), 7.03 (d, 4H, ^3J(H–H) = 7.2 Hz, Ar–H), 3.96 (s, 8H, ^3J(Pt–H) = 39.4 Hz, CH$_2$N), 3.52 (s, 24H, ^3J(Pt–H) = 24.6 Hz, S(CH$_3$)$_2$), 2.92 (s, 24H, ^3J(Pt–H) = 33.6 Hz, N(CH$_3$)$_2$), 1.35–1.25 (m, 8H, SiCH$_2$CH$_2$–), 0.81–0.73 (m, 8H, –CH$_2$Si(CH$_3$)$_2$), 0.55–0.48 (m, SiCH$_2$CH$_2$–), 0.22 (s, 24H, Si(CH$_3$)$_2$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ = 146.4 (4J(Pt–C) = 21.2 Hz, Ar–C), 139.3 (^2J(Pt–C) = 55.4 Hz, Ar–C), 137.7 (^2J(Pt–C) = 46.6 Hz, Ar–C), 135.3 (^1J(Pt–C) = 1065 Hz, Ar–C$_{ipso}$), 130.2 (Ar–C), 121.1 (^3J(Pt–C) = 33.8 Hz, Ar–C), 74.9 (^2J(Pt–C) = 53.5 Hz, CH$_2$N), 52.3 (N(CH$_3$)$_2$), 46.6 (^2J(Pt–C) = 64.5 Hz, S(CH$_3$)$_2$), 20.7, 18.6, 17.5 (3 × CH$_2$), − 2.7 (Si(CH$_3$)$_2$). FAB-MS: m/z 2116.0 [M − DMSO]$^+$, 2081.0 [M − Cl − DMSO]$^+$, 1924.8 [M − 2Cl − 2DMSO]$^+$, 1882.7 [M − 3Cl − 2DMSO]$^+$. Anal. Found: C, 35.11; H, 5.28; N, 2.46; Si, 6.41. Calc. for C$_{64}$H$_{116}$N$_4$O$_4$Pt$_4$S$_4$Si$_5$: C, 35.00; H, 5.32; N, 2.55; Si, 6.39%.

*4.6. [G1]-Pt$_8$ (**5**)*

A mixture of [G1]-(CN)$_8$ (0.19 g, 0.085 mmol), PtCl$_2$(DMSO)$_2$ (0.31 g, 0.73 mmol) and NaOAc (0.11 g, 1.34 mol) was refluxed in MeOH (40 ml) for 16 h, upon which a sticky solid precipitated. Then the solvent was removed in vacuo and the product extracted with CH$_2$Cl$_2$, washed with H$_2$O (2 × 100 ml) and dried on solid Na$_2$CO$_3$. After filtration and evaporation of the solvent under reduced pressure, a white solid was obtained which was washed with Et$_2$O and dried (0.28 g, 0.060 mmol, 70%). FT-IR (CH$_2$Cl$_2$, cm^{-1}): 1140 $\nu_{S=O}$. ^{1}H-NMR (CDCl$_3$): δ = 8.14 (s, ^3J(Pt–H) = 45.4 Hz, 8H, Ar–H$_{ortho}$), 7.18 (d, ^3J(H–H) = 7.0 Hz, 8H, Ar–H), 7.01 (d, ^3J(H–H) = 7.0 Hz, 8H, Ar–H), 3.94 (s, ^3J(Pt–H) = 39.6 Hz, 16H, CH$_2$N), 3.51 (s, ^3J(Pt–H) = 23.0 Hz, 48H, S(CH$_3$)$_2$), 2.91 (s, ^3J(Pt–H) = 33.2 Hz, 48H, N(CH$_3$)$_2$), 1.33 (m, CH$_2$, dendrimer backbone), 0.78 (m, CH$_2$, dendrimer backbone), 0.54 (m, CH$_2$, dendrimer backbone), 0.22 (s, 48H, Si(CH$_3$)$_2$), − 0.12 (s, 12H, SiCH$_3$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ = 146.82 (^4J(Pt–C) = 23.1 Hz), 139.45 (^2J(Pt–C) = 55.3 Hz), 137.58 (^2J(Pt–C) = 45.8 Hz), 135.46 (^1J(Pt–C) = 1100 Hz, Ar–C$_{ipso}$), 130.31, 121.21 (^3J(Pt–C) = 32.2 Hz), 75.04 (^2J(Pt–C) = 54.0 Hz, CH$_2$N), 52.50 (N(CH$_3$)$_2$), 47.01 (^2J(Pt–C) = 64.5 Hz, SCH$_3$), 20.79, 19.52, 19.03, 18.79, 17.98 (5 × CH$_2$, one signal coincident with another), − 2.43 (Si(CH$_3$)$_2$), –4.61 (SiCH$_3$). MALDI-TOF-MS: m/z 4592.23 [M − Cl − DMSO]$^+$, 4435.17 [M − Cl − 3DMSO]$^+$, 4281.19 [M − Cl −

5DMSO]$^+$, 4125.88 [M − Cl − 7DMSO]$^+$. Anal. Found: C, 36.66; H, 5.81; N, 2.27; Si, 7.65. Calc. for $C_{144}H_{268}Cl_8N_8O_8Pt_8S_8Si_{13}$: C, 36.75; H, 5.74; N, 2.38; Si, 7.76%.

4.7. Crystal structure determination of **2**

For **2**: $C_{30}H_{35}ClNPPtSi$, formula weight 699.19, yellowish plate, $0.70 \times 0.45 \times 0.10$ mm^3, orthorhombic, $Pna2_1$ (no. 33), $a = 17.661(3)$, $b = 15.8241(17)$, $c = 10.3071(9)$ Å, $V = 2880.5(6)$ Å^3, $Z = 4$, $\rho = 1.612$ g cm^{-3}. 3507 reflections were measured on an Enraf–Nonius CAD4T diffractometer with rotating anode ($\lambda = 0.710\ 73$ Å) at a temperature of 150(2) K. 3458 reflections were unique ($R_{int} = 0.066$). 2821 reflections were observed ($I > 2\sigma(I)$). Absorption correction with PLATON [14] (routine DELABS, $\mu = 5.08$ mm^{-1}, 0.11–0.57 transmission). Structure solved with Patterson methods (DIRDIF97 [15]) and refined with SHELXL97 [16] against F^2 of all reflections. Cl, P, Pt and Si atoms were refined freely with anisotropic displacement parameters. Owing to high absorption, the other atoms were only refined with isotropic displacement parameters. Hydrogen atoms were refined as rigid groups. 161 refined parameters. R-values [$I > 2\sigma(I)$]: $R_1 = 0.0519$, $wR_2 = 0.1185$. R-values (all reflections): $R_1 = 0.0702$, $wR_2 = 0.1292$. GoF = 1.030. Rest electron density between -1.19 and 1.48 e$^-$ Å^{-3}. Molecular illustration, structure checking and calculations were performed with the PLATON package [14].

5. Supplementary material

^{1}H-NMR (200 MHz) of compound **5**. The crystallographic data for the structure analysis of **2** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 145135. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax. +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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