An efficient synthesis combining phosphorus dendrimers and 15-membered triolefinic azamacrocycles: towards the stabilization of platinum nanoparticles†

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The synthesis of a new series of phosphorus-containing dendrimers bearing as terminal groups triazatriolefinic macrocycles is reported, from generation 1 (6 macrocycles) to generation 4 (48 macrocycles). These macrocycles are linked to the dendrimers through diazaphospholane moieties (5-membered rings). The complexation ability of these dendrimers and of a compound possessing a single macrocycle was tested towards $Pt_2(dba)_3$. A discrete complex could be isolated only in the case of the model compound, whereas the dendrimers afford highly branched networks of Pt(0) nanoparticles interweaved with the dendrimers.

Introduction

Macromolecules with special three-dimensional architectures such as macrocycles[1] and dendrimers[2] have attracted the attention of researchers for several decades due to their properties in numerous fields such as complexation, catalysis, medicine, *etc*. Combination of both types of macromolecules can increase the level of pre-organization and induce cooperative effects affording specific properties different from those produced by the separated parts.[3] The association of dendrimers and macrocycles started to develop approximately fifteen years ago, by the use of azacrown ether macrocycles as constituents of the branches of a dendrimer.[4] However, in most cases, macrocycles are used as core of dendrimers: porphyrins,[5] phthalocyanines,[6] cyclam,[7] crown ethers,[8] or phosphorus macrocycles[9] among other macrocycles were used for this purpose. On the contrary and surprisingly, dendrimers bearing macrocycles at the periphery are still relatively rare, despite the fact that increasing the number of macrocyclic units could enhance the properties of such assemblies. Examples with porphyrins,[10] phthalocyanines,[11] and crown ethers[12] as peripheral substituents are known. More particular substituents such as tetraazamacrocycles[13] and TTF-semicrown ethers[14] were also grafted as end groups of phosphorus-containing dendrimers.[15]

In the present study, the macrocycles used are 15-membered triazamacrocycles containing 3 olefins obtained through a synthesis based on a multistep process with 3 different available routes.[16] These macrocycles are known to complex different metals such as Pd(0), Pt(0) or more moderately Ag(I).[17] In order to graft them onto dendrimers, they must be selectively functionalized. The possibility to have one, two or three different types of aryl substituents to confer specific properties has been recently largely reviewed.[18] The aim of this article is to demonstrate the ability, through an efficient method, to combine phosphorus dendrimers and 15-membered azamacrocycles on the outer shell, and to demonstrate the interest of these dendrimers functionalized with macrocycles in the field of organometallic chemistry.

Results and discussion

Synthesis of the macrocycles and their grafting to phosphorus dendrimers

The macrocycle that we used contains three nitrogen atoms linked to aromatic rings, two of them are 2,4,6-triisopropylaryl group chosen to increase the solubility, and the last one is a fluoroaryl group, to be used later for the grafting to dendrimers through a linker. During the course of the known synthesis (Scheme 1),[16] we could isolate a single crystal of **1** (crystallization from hexane–AcOEt) and obtain an X-ray structure, showing that both bromine atoms are in *anti*-position as depicted on Fig. 1.

After cyclisation of compound **1** affording the azamacrocycle **2**,[19] the latter could be easily functionalized with diamine chains *via* an aromatic nucleophilic substitution of the fluoride atom. In presence of ethylene diamine or 1,3-diaminopropane as a solvent (T = 95 °C) compounds **3**[19] and **4** were obtained in excellent yield (91 and 92% after work-up, respectively). ^{19}F NMR allowed us to determine if reaction had gone to completion by disappearance of the initial signal at $\delta = -105$ ppm.

We have already reported the condensation of compound **3** on aldehyde terminal groups of dendrimers;[20] the reduction of

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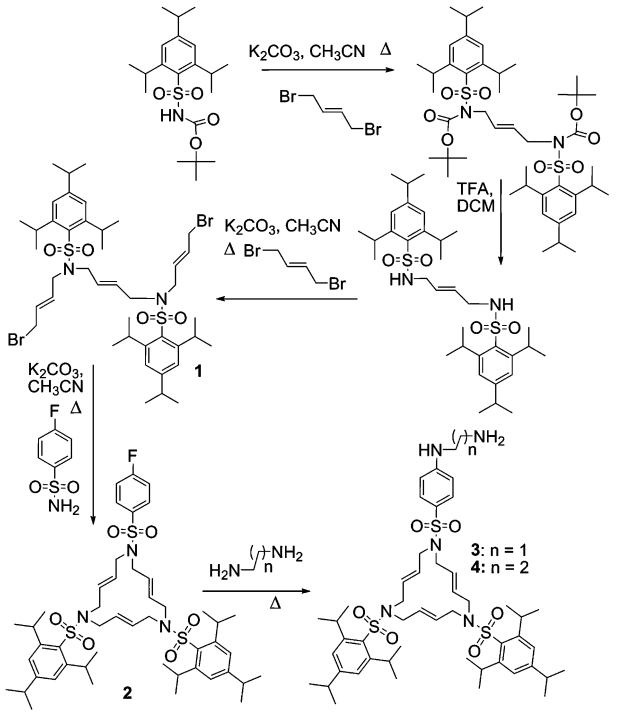


Scheme 1 Synthesis of 15-membered azamacrocycles functionalized with two different diamine chains (compounds **3** and **4**).

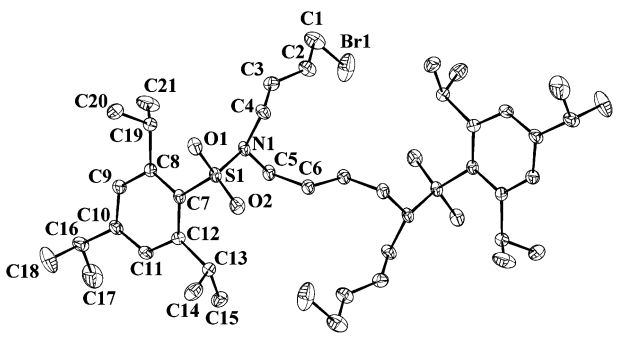
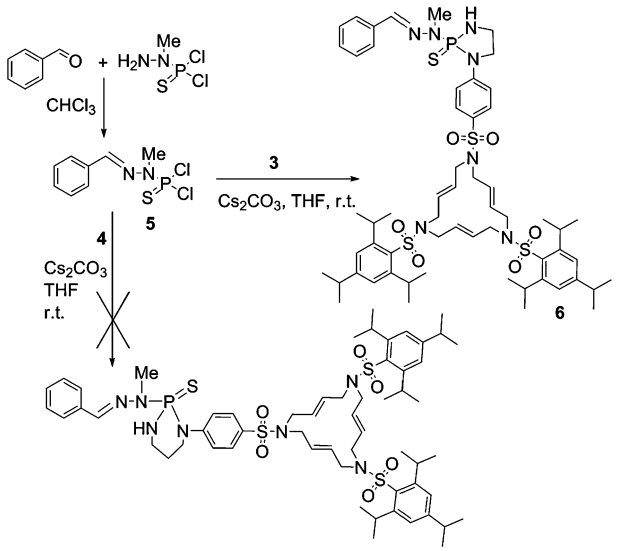


Fig. 1 ORTEP view of **1** after crystallization in a mixture AcOEt–hexane (H atoms are omitted for clarity).

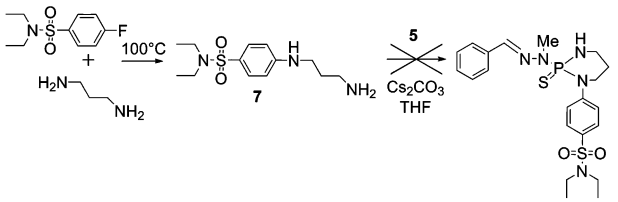
the imine linkages was required to stabilize these compounds. In the present paper, we report a more straightforward way to graft these macrocycles to phosphorus dendrimers, by using the diamine chain for a cyclization reaction with $P(S)Cl_2$ terminal groups; formation of a 5-membered (diazaphospholane) ring with macrocycle **3** or 6-membered (diazaphosphorinane) ring with macrocycle **4** is expected to occur. However, before starting the peripheral modification of phosphorus dendrimers, we decided to synthesize a model compound to determine the feasibility of our concept (Scheme 2). The phosphorhydrazone **5** (easily obtained by condensation of N-methyldichlorothiophosphorhydrazone on benzaldehyde) was elected as it mimicks one arm of a dendrimer. By reacting one equivalent of compounds **3** and **5** in presence of a base (Cs_2CO_3), we could form the expected 5-membered ring adduct. The reaction went fast and while the signal corresponding to starting material at δ = 62.5 ppm disappeared in ^{31}P NMR, we could distinguish the formation of the desired



Scheme 2 Attempts to synthesise the model compounds.

final compound **6** at δ = 68.57 ppm. This shift was in good agreement with previous surface modification of phosphorus dendrimers with two amine substituents;[13,21] a monosubstitution with a single amine on $P(S)Cl_2$ would lead to a signal at δ *ca.* 73 ppm,[22] which is never observed here. Both nucleophilic substitutions took place simultaneously; the stability of the newly formed 5-membered adduct allowed isolation of compound **6** in excellent yield (91%). The phosphorus atom was a stereogenic center and diastereotopic protons could be identified through a 2D experiment. In fact, two signals for each proton of the methylene of the newly formed heterocycle were clearly visible: signals of the protons attached to the carbon C_a (see Fig. 7 for numbering) appeared as two multiplets at δ = 3.65 and 3.85 ppm, while signals for the ones attached to C_b appeared equally as two multiplets at δ = 3.94 and 3.99 ppm. Another proof of the appropriate achievement of the reaction was the chemical shift of C_1 at δ = 145.74 ppm (d, $^2J_{CP}$ = 7.3 Hz) compared to the initial value of 151.8 ppm. Mass spectrometry (FAB, m/z: 1132 $[M]^+$) also gave a positive result.

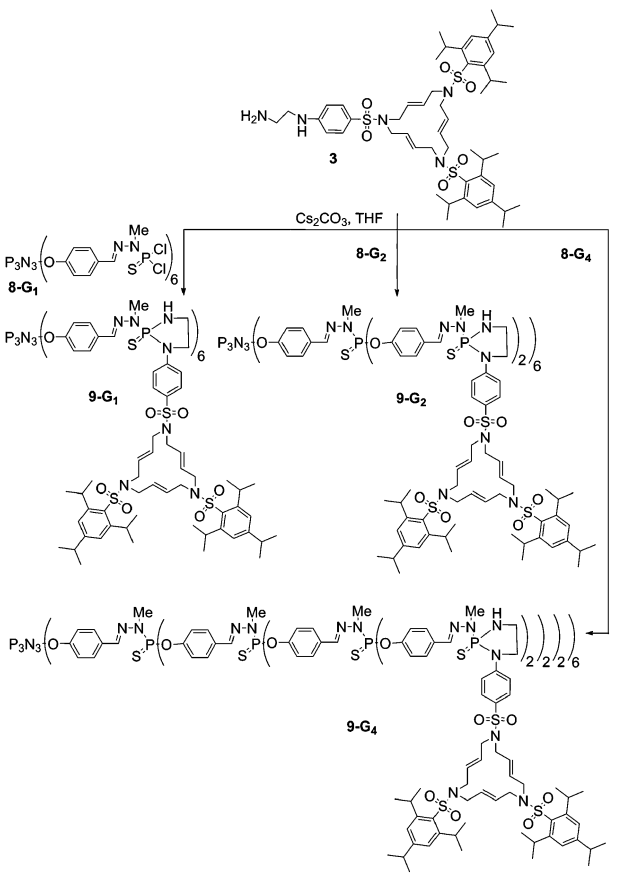
With the first attempt of our model compound to form a 5-membered ring being successful, we followed the same methodology to try to obtain the 6-membered ring adduct from compounds **4** and **5**. By using the same conditions (Cs_2CO_3 and THF), we unfortunately could not obtain the desired compound: in fact, the presence of an additional carbon between the two amines seemed to give more flexibility to the system. For this reason, we suspected that a non-aromatic amine coming from another macrocycle could react before the cyclization took place and hampered the formation of our desired target. To determine if this undesired effect could be due to the hindrance of the macrocycle, we easily synthesized compound **7** (yield 89%) following a previously published procedure[23] in order to perform the expected reaction. The result of the reaction of **7** with **5** was unfortunately analogous to the reaction of **4** with **5** with a major peak at δ = 58 ppm in the ^{31}P NMR. Attempted purification by silica gel chromatography afforded multiple new peaks in the



Scheme 3 Failure to obtain a diazaphosphorinane heterocycle even in the absence of the macrocycle.

^{31}P NMR, demonstrating the dead-end of this route to obtain such a 6-membered ring heterocycle (Scheme 3). We may presume that the difference in the reactivity of the alkylamine compared to the aromatic amine was compensated for by the close proximity between this aromatic amine and the P–Cl bond after reaction of the alkylamine in the case of the 5-membered ring, but not in the case of the 6-membered ring. In the latter case, the second H of the alkylamine may react with another P–Cl function, to afford presumably a kind of dimer possessing a diazadiphosphetidine 4-membered ring.[24]

Our model compound demonstrated the viability of a 5-membered ring adduct by reacting a $P(S)Cl_2$ extremity and a diamine, the amino groups being linked through a CH_2–CH_2 spacer; we could then move on to the first generation dendrimer, built from a cyclotriphosphazene core[25] (Scheme 4). We hoped to conserve the same reactivity (no intra- or intermolecular side reactions) between the two



Scheme 4 Synthesis of **9-G$_1$**, **9-G$_2$** and **9-G$_4$** with 6, 12 and 48 macrocycles, respectively, at the periphery.

starting materials even if a major modification of the topology is induced by the presence of the dendrimer. Reaction between one equivalent of the first generation phosphorus dendrimers **8-G$_1$** and 6 equivalents of macrocycle **3** in presence of a base (Cs_2CO_3, 24 eq) led to the desired compound **9-G$_1$** in good yield after classical purification by precipitation with pentane (81% yield). In fact, as shown by the presence of only one signal (singlet at δ = 68.44 ppm) for the phosphorus attached to the macrocycle, no side reactions occurred. The presence of a stereogenic center for each phosphorus at the periphery induced the appearance of a multiplet for the phosphorus located at the core (δ = 7.70 ppm). Such a phenomenon was previously observed at the (n − 1) generation for dendrimers bearing uncontrolled chiral entities as end groups of the n generation.[26] The presence of signals at similar shifts for C_a (m, δ = 40.39 ppm) and C_b (s, δ = 47.56 ppm) compared to **6** strongly supported the achievement of the reaction on all reactive sites.

Following the same procedure, we carried out the reaction at the periphery of the second generation dendrimer (**8-G$_2$**), which possesses 12 $P(S)Cl_2$ end-groups. The reaction proceeded readily and could be monitored by ^{31}P NMR: signal of the P(S) groups of the second generation shifted to δ = 67.99 ppm (singlet) as expected, while signal of the first generation appeared as a multiplet between δ = 61.90–63.00, confirming the assumption made for **9-G$_1$**; signal of the core (δ = 8.37 ppm) remained a singlet (see Fig. 2 for the ^{31}P NMR spectrum). After a similar purification process to the one used with the first generation, final compound **9-G$_2$** (see Fig. 3 for an extended structure) was isolated with a yield of 83%.

In order to confirm the ability of our dendrimers to be functionalized with this macrocycle even for a high generation, we decided to test directly on the fourth generation **8-G$_4$**. We proceeded as before: no side reaction took place and **9-G$_4$** was isolated with a yield of 74%. ^{31}P NMR could allow us to discern a singlet for the P(S) of the fourth generation (δ = 67.92 ppm), a large singlet containing the signals of generations one to three (δ = 62.27 ppm) and a singlet for the signal

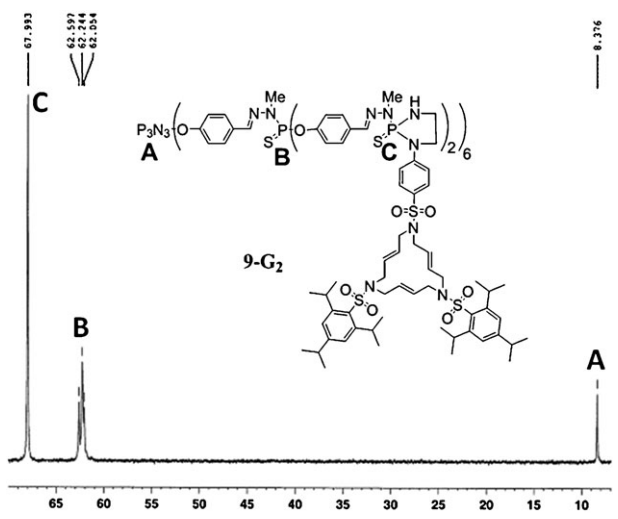


Fig. 2 ^{31}P-{^{1}H} NMR spectrum of dendrimers **9-G$_2$** bearing 12 macrocycles on the periphery. Effect of chirality is clearly visible on the phosphorus of the first generation (B).

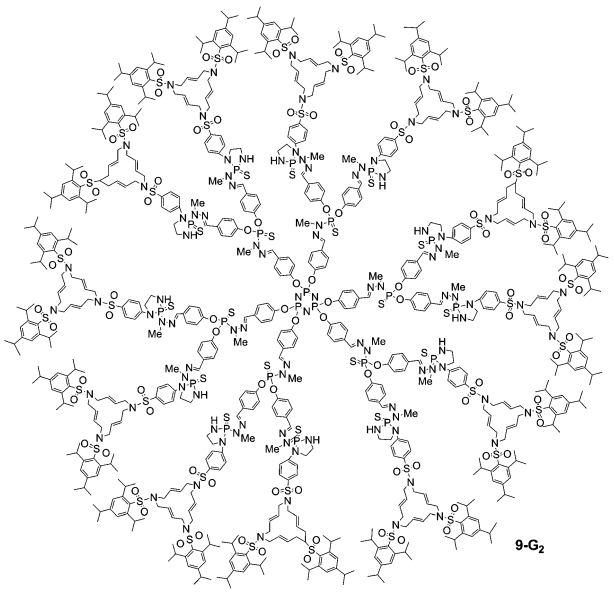
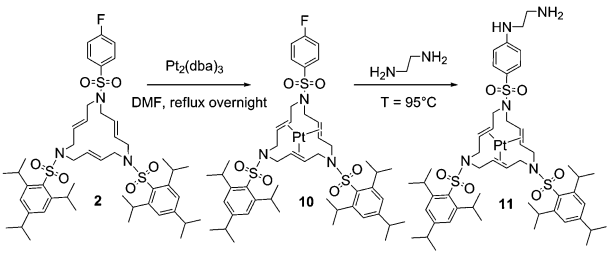


Fig. 3 Extended structure of **9-G$_2$**.

of the core (δ = 8.03 ppm). A suitably integrated ^{31}P NMR spectrum corresponded to expected theoretical values indicating the complete modification of the periphery. The pattern of ^{1}H NMR spectrum demonstrated that no degradation had occurred. In addition, integrations of all signals suited well with theoretical values. ^{13}C NMR also displayed all the expected signals, in particular those corresponding to C_a (40.43 ppm) and C_b (47.69 ppm) (see Fig. 7 for numbering).

Complexation of platinum and obtaining of Pt nanoparticle networks

Regarding our initial goal of using these compounds in organometallic chemistry, we intended to complex a metal inside the triolefinic macrocycle to obtain nanoassemblies combining dendrimers, macrocycles and metals. We have previously reported in the case of the macrocycles grafted to the dendrimers by condensation/reduction and having twice the number of macrocycles at the same generation compared to **9-G$_n$**, that these compounds were able to complex Pd(0), $Pd(dba)_2$ being the best precursor for such a purpose.[20] On the other hand, a previous report mentioned the possibility to complex Pt(0) with $Pt(PPh_3)_4$ as a precursor, but reaction time was long (4 days) and the yield quite moderate (52%).[27] For this reason, and by analogy with the reaction of $Pd(dba)_2$ with this azamacrocycle (reaction overnight with high yield), we decided to move on to $Pt_2(dba)_3$ as a new precursor (Scheme 5). The latter was synthesized according to a previously reported procedure.[28] First, complexation experiments were carried out with the macrocycle **2**. Indeed, this simple compound would allow us to determine all the characteristic data of the complexation, and help us later to determine if the same reaction would occur with dendrimers. After only one night in refluxing DMF complexation of macrocycle **2** was fully accomplished. Disappearance of the olefin signals at δ = 5.7–5.8 ppm on the ^{1}H NMR spectrum was the key element to assert total complexation. However, a black precipitate was also observed; thus, column



Scheme 5 Preparation of the Pt(0)-metallated macrocycles **10** and **11**.

chromatography was needed to afford the desired compound **10**, with a yield of 67%. A splitting of the signals of the three CH_2–CH=CH–CH_2 linkages of the macrocycle was observed, both by ^{1}H and ^{13}C NMR, as previously described.[29] This is due to the fact that the 3 olefins are not involved in the same manner in the complexation with Pt, and this is complicated by the presence of two different aryl substituents on the macrocycle.

Having this metallated macrocycle in hand, we thought that an alternative route to the direct complexation of Pt by the dendrimers **9-G$_n$** could be the grafting of complexed macrocycles to dendrimers **8-G$_n$**. For this purpose, we tried to functionalize compound **10** for further grafting on $P(S)Cl_2$ extremities. Addition of ethylene diamine had to be handled with care to avoid decomplexation, Pt being really sensitive to the presence of nitrogen atoms. Indeed, the direct complexation of macrocycle **3** failed to afford the expected macrocyclic complex. Following previous methodology with free macrocycle **2**, ethylenediamine was reacted with the complex **10** at 95 °C but only for 3 h and the reaction was monitored with ^{19}F NMR. We obtained pure compound **11** in excellent yield (97%). It must be emphasized that no decomplexation occurred at this step. Indeed, uncomplexed CH=CH as in compound **3** should give a singlet at 5.7–5.8 ppm in ^{1}H NMR, which is not detected in the spectrum of compound **11**.

At this step, we decided to perform a complete characterization of the metallated macrocycle **11** by NMR, to be able to later compare its behaviour before and after grafting at the periphery of dendrimers. Firstly, two signals appeared in the ^{195}Pt NMR at δ = −6165 and −6163 ppm; a previous report demonstrated that all three olefins were not involved in the same manner in the complexation process, two of them binding more strongly to the metal than the third.[17b] Thus, due to the wide scale of platinum in NMR and the fact that **11** has two types of aryl substituents, it easily explains the presence of two peaks, which should correspond to structures **11′** and **11″**, approximately in a 1 : 2 ratio as expected for a statistical reaction. Secondly, original HMQC experiments ^{195}Pt-^{1}H NMR (Fig. 4) allowed us as well to clearly distinguish the signals coming from both adducts in ^{1}H NMR; both CH=CH and CH_2 groups inside the macrocycle correlate with Pt. With the help of COSY ^{1}H–^{1}H and HSQC ^{1}H–^{13}C NMR experiments, we could detect a very different chemical shift for each H of the CH_2 groups inside the macrocycle, for instance 1.45 and 4.62 ppm (see the experimental section for the other couples of chemical shifts for CH_2 in ^{1}H NMR).

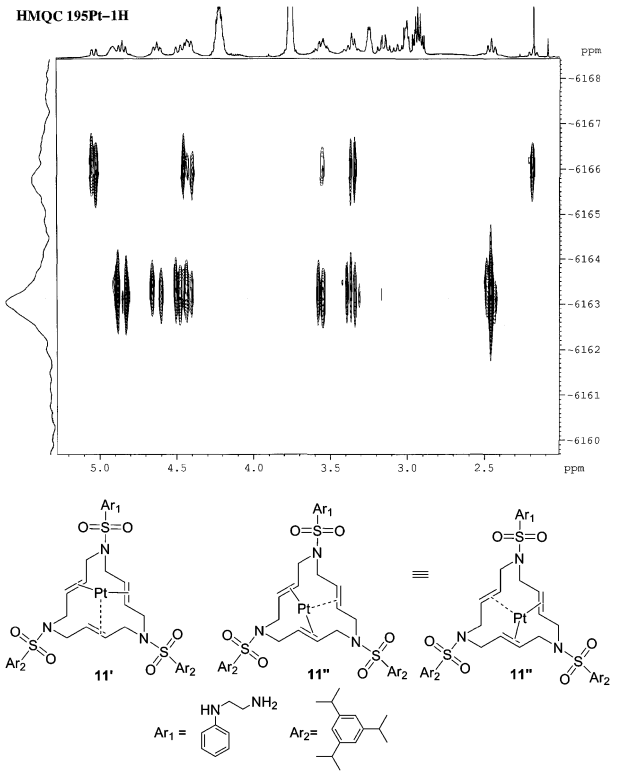


Fig. 4 Two dimensional HMQC ^{195}Pt–^{1}H experiments display the presence of two different forms for complex **11** (**11**′ minor, **11**′′ major).

Following the same procedure as before, we intended to graft **11** at the periphery of **8-G$_1$**: in the same conditions decomplexation unfortunately took place after 2 days, as we could distinguish easily in ^{1}H NMR the presence of the signals corresponding to the free olefins (δ = 5.7 ppm). A second attempt with a more concentrated solution was carried out but the same result was obtained. We have to point out that the stability of the complex **11** in solution was not excellent, the solution moving from slightly to strongly yellow after 2 days in the NMR tube.

To circumvent the problem of the instability of compound **11**, we tried to implement complexation directly at the periphery of the dendrimers. For this purpose, we reacted $Pt_2(dba)_3$ with dendrimers **9-G$_1$**, **9-G$_2$** and **9-G$_4$** overnight in refluxing THF and under air, using a stoichiometry of 1.2 Pt atoms per macrocycle. With this stoichiometry, we expected to obtain discrete complexes, as in the case of the reaction with macrocycle **2**, and also when using palladium previously. However, deep black solutions were obtained in all cases, which afforded only very broad signals in NMR. In order to understand what happened, a drop of the crude solutions of the reaction of dendrimers **9-G$_n$** with $Pt_2(dba)_3$, and also of the black precipitate obtained in the synthesis of **10**, was diluted in THF then analyzed by transmission electron microscopy (TEM). Totally unexpected results were obtained: despite the low amount of Pt used and the very mild conditions applied, oriented dendritic superstructures of Pt were observed in all cases, as shown by low resolution TEM. We recently reported detailed investigations about these ''dendritic structures within dendritic structures'', in which the branches of the network are

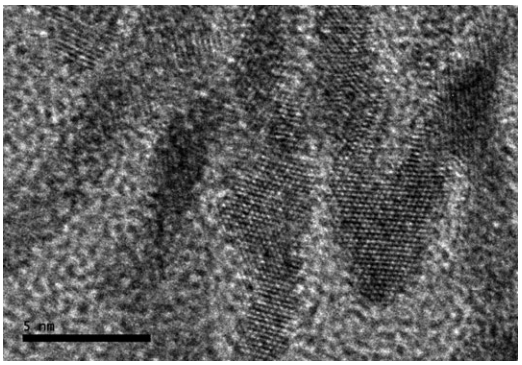


Fig. 5 High resolution TEM image of the result of the reaction of **9-G$_1$** with $Pt_2(dba)_3$, showing the Pt network.

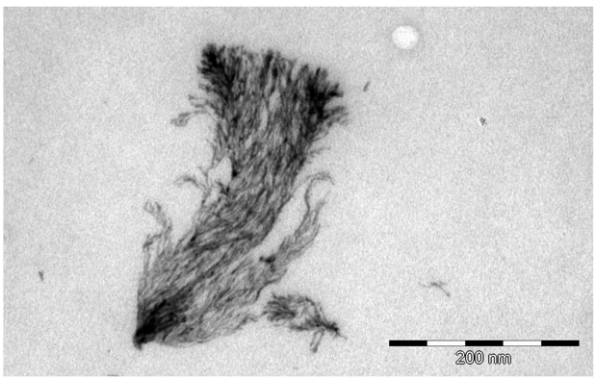


Fig. 6 TEM image of the result of the reaction of **9-G$_4$** with $Pt_2(dba)_3$.

not only composed of Pt but also of dendrimers.[30] High resolution TEM images display a continuous network of Pt nanoparticles (Fig. 5); thus, we deduced that the dendrimers wrap the ribbons of nanoparticles to ensure their cohesion, and can also probably connect the ribbons to induce either an almost linear continuation of the network, or the branching points.

Fig. 6 displays one of the TEM images obtained for the reaction of **9-G$_4$** with $Pt_2(dba)_3$. An astonishing observation could be made for these experiments: when the generation (the size) of the dendrimer increases, the branches of the Pt networks lengthen, while the monomer does not create any network. The ability of dendrimers to create large dendritic-like assemblies (more precisely dendron-like assemblies) with nanoparticles is unprecedented, but in the very first paper by Tomalia *et al.*, PAMAM dendrimers reacted with sodium hydroxide self-assembled in dendritic ''snow-flakes'',[31] illustrating the potential of dendrimers for supramolecular superstructures.

Conclusion

The reaction of a $P(S)Cl_2$ extremities of dendrimers with 15-membered azamacrocycle functionalized with a 1,2-diamine led to the formation of one 5-membered ring (diazaphospholane) on each phosphorus terminal group. Such reaction was carried out with a monomeric model compound and with first, second

and fourth generations of phosphorus dendrimers (1, 6, 12, 48 macrocycles as terminal groups, respectively). Such reaction generates stereogenic centers on the external layer, which induce the splitting of the signal of the previous generation on ^{31}P NMR spectra, demonstrating the sensitivity of ^{31}P NMR to subtle structural changes. The monomeric species of these macrocycles is able to complex one Pt(0) atom obtained from $Pt_2(dba)_3$. A ^{195}Pt NMR study displays the presence of two different forms due to the different complexation of Pt by essentially two of the three olefinic bonds of the macrocycle. This phenomenon has no consequence when the macrocycle has 3 identical aryl groups, but in our case the presence of two different aryl substituents in a 1 : 2 ratio induces two different forms for the Pt complexes. This discrete complexation could not been obtained when the macrocycles are connected to the dendrimers whatever the generation. Instead, unprecedented organic/inorganic hyperbranched superstructures, in which the dendrimers wrap and organize ribbons of Pt nanoparticules, creating "dendritic structures (the dendrimers) within dendritic structures (the inorganic network of Pt)" were obtained.[30]

Experimental section

General

Macrocycles **2** and **3**,[19] dendrimers **8-G$_n$**[25] and $Pt_2(dba)_3$[28] were synthesized using published procedures. All manipulations were carried out with standard high-vacuum techniques under a dry argon atmosphere. The solvents were freshly dried and distilled (THF over sodium/benzophenone, pentane and CH_2Cl_2 over phosphorus pentoxide). Melting points were uncorrected and obtained with an Electrothermal melting point apparatus. Mass spectrometry was carried out with Finniganmat TSQ 7000. ^1H, ^{13}C, ^{31}P, ^{19}F and ^{195}Pt NMR spectra were recorded on Bruker ARX250, DPX300, AV300 and AV500 spectrometers.

References for NMR chemical shifts are 85% H_3PO_4 for ^{31}P NMR, $SiMe_4$ for ^1H and ^{13}C NMR, Na_2PtCl_6 in D_2O for ^{195}Pt NMR and trifluoroacetic acid for ^{19}F NMR. The attribution of ^1H and ^{13}C NMR signals has been done using J_{mod}, two-dimensional COSY, HMBC and HMQC, broad band or CW ^{31}P decoupling experiments when necessary. The numbering used for NMR is shown on Fig. 7.

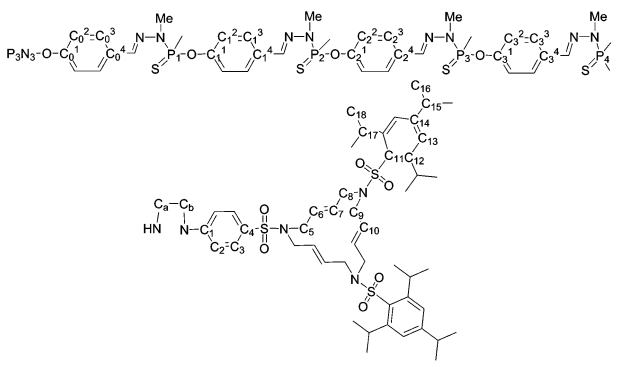


Fig. 7 Numbering scheme used for NMR assignments.

Syntheses

Compound 4. compound **2** (263 mg, 0.292 mmol) was dissolved in 1,3-diaminopropane (3.15 mL, 37.73 mmol) in presence of catalytic amount of Cs_2CO_3 at 95 °C overnight. When reaction was over, water was added to the reaction mixture, followed by a filtration on a Büchner. The solution was evaporated to dryness under reduced pressure, and final compound **4** was obtained as a white powder with a yield of 92%. ^1H NMR ($CDCl_3$, 500.33 MHz): δ = 1.24–1.29 (m, 36H, $CH(CH_3)_2$), 1.82 (q, $^3J_{HH}$ = 6.5 Hz, 2H, NH_2–CH_2–CH_2), 2.92 (m, 4H, $CH(CH_3)_2$, NH–CH_2), 3.28 (t, $^3J_{HH}$ = 6.5 Hz, 2H, NH_2–CH_2), 3.77 (m, 12H, CH_2–CH), 4.10 (sept, $^3J_{HH}$ = 7.5 Hz, 4H, $CH(CH_3)_2$), 5.73–5.77 (m, 6H, CH_2–CH═), 6.58 (d, $^3J_{HH}$ = 8.9 Hz, 2H, HC_2), 7.17 (s, 4H, HC_{13}), 7.57 (d, $^3J_{HH}$ = 8.9 Hz, 2H, HC_3); ^{13}C-{^1H} NMR ($CDCl_3$, 125.80 MHz): δ = 23.59 (s, C_{16}), 24.84 (s, C_{18}), 29.25 (s, C_{17}), 31.59 (s, NH_2–CH_2–CH_2), 34.17 (s, C_{15}), 40.33 (s, NH–CH_2), 41.98 (s, NH_2–CH_2), 48.78, 48.79 (2 s, C_8, C_9), 51.28 (s, C_5), 111.64 (s, C_2), 123.95 (s, C_{13}), 125.06 (s, C_4), 128.96, 129.87 (2 s, C_7, C_{10}), 129.23 (s, C_3), 130.77 (s, C_{11}), 131.02 (s, C_6), 151.49 (s, C_1), 151.85 (s, C_{12}), 153.18 (s, C_{14}) ppm. IR (neat): 3389 (N–H), 2958 (C–H), 2928 (C–H), 2868 (═C–H), 1600 (C═C), 1462 (SO_2), 1150 (SO_2) cm^{-1}. MS (DCI): m/z = 952.4 $[M]^+$. MP: 90–92 °C.

Compound 5. At 0 °C (ice bath) a solution of *N*-methyldichlorothiophosphorhydrazide (c = 0.19 mol L^{-1} in $CHCl_3$, 37 mL) was added slowly on benzaldehyde (0.478 mL, 4.71 mmol) under good stirring, then the reaction mixture was left to react for 3 h at room temperature (r.t.). When the reaction was over, a filtration on a pad of silica (DCM–pentane 1 : 9) was accomplished to remove the excess of phosphorhydrazide. Final compound **5** was obtained as a white powder with a yield of 95%. ^{31}P–{^1H} NMR ($CDCl_3$, 81.0 MHz): δ = 62.5 (s, P═S); ^1H NMR ($CDCl_3$, 200.13 MHz): 3.50 (d, $^3J_{HH}$ = 13.5 Hz, 3H, N–Me), 7.39–7.77 (m, 6H, CH═N, H_{ar}); ^{13}C–{^1H} NMR ($CDCl_3$, 50.32 MHz): δ = 31.77 (d, $^2J_{CP}$ = 13.7 Hz, N–Me), 127.41 (s, C_0^2). 128.84 (s, C_0^3), 130.20 (s, C_0^1), 134.06 (s, C_0^4), 141.82 (d, $^3J_{CP}$ = 18.6 Hz, CH═N) ppm. IR (neat): 2963 (═C–H), 1571 (C═N) cm^{-1}. MP: 61–62 °C.

Compound 6. Compound **5** (13.6 mg, 0.05 mmol) was dissolved in THF, then caesium carbonate (68.4 mg, 0.209 mmol) and compound **3** (47.8 mg, 0.05 mmol) were added to the reaction mixture and left to react at r.t. overnight. After centrifugation for removal of the salts, residual solvents were removed under low pressure. Final compound **6** was obtained as a white powder with a yield of 91%. ^{31}P–{^1H} NMR ($CDCl_3$, 202.53 MHz): δ = 68.57 (s, P═S); ^1H NMR ($CDCl_3$, 500.33 MHz): δ = 1.25 (d, $^3J_{HH}$ = 7.2 Hz, 12H, $CH(CH_3)_2$), 1.27 (d, $^3J_{HH}$ = 7.1 Hz, 24H, $CH(CH_3)_2$), 2.84 (m, 2H, $CH_{15}H(CH_3)_2$), 3.07 (d, $^2J_{HP}$ = 14.5 Hz, 1H, NH), 3.51 (d, $^3J_{HP}$ = 10.1 Hz, 3H, N–Me), 3.65–3.85 (m, 14H, CH_2–CH, C_a–H), 3.94, 3.99 (2 m, 2H, C_b–H), 4.11 (m, 4H, $CH_{17}H(CH_3)_2$), 5.67–5.80 (m, 6H, CH═CH), 7.17 (s, 4H, HC_{13}), 7.23–7.70 (m, 10H, CH═N, H_{Ar}); ^{13}C–{^1H} NMR ($CDCl_3$, 125.80 MHz): δ = 23.57 (s, C_{16}), 24.83 (s, C_{18}), 29.24 (s, C_{17}), 32.44 (d, $^2J_{CP}$ = 13.8 Hz, N–Me), 34.15 (s, C_{15}), 40.44 (s, C_a), 47.79 (d, $^2J_{CP}$ = 12.6 Hz, C_b); 48.72, 48.79

(2 s, C_8, C_9), 51.32 (s, C_5), 116.00 (d, $^3J_{CP}$ = 6.3 Hz, C_2), 123.94 (s, C_{13}), 126.60 (s, C_4, $C_0{}^2$), 128.39 (s, $C_0{}^3$), 129.16, 129.24 (2 s, C_7, C_{10}), 129.86 (s, C_6), 130.46 (s, $C_0{}^1$), 130.69, 130.86 (2 s, C_3, C_{11}), 135.06 (s, $C_0{}^4$), 138.87 (d, $^3J_{CP}$ = 13.4 Hz, CH═N), 145.74 (d, $^2J_{CP}$ = 7.3 Hz, C_1), 151.50 (s, C_{12}), 153.16 (s, C_{14}) ppm. MS (FAB) *m*/*z*: 1132 $[M]^+$.

Compound 7. 4-Fluorodiethylsulfonamide (500 mg, 2.16 mmol) was dissolved in 1,3-diaminopropane (3.6 mL, 42.73 mmol) at 100 °C overnight. When reaction was over, water (20 mL) was added to the reaction mixture, followed by two extractions with DCM (2 × 80 mL). Organic phase was then dried over $MgSO_4$ and after removal of the residual solvents final compound **7** was obtained as a white powder with a yield of 89%. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.10 (t, $^3J_{HH}$ = 7.0 Hz, 6H, CH_3), 1.31 (s, 2H, NH_2), 1.76 (q, $^3J_{HH}$ = 6.5 Hz, 2H, NH_2–CH_2–*CH_2*), 2.86 (t, $^3J_{HH}$ = 6.5 Hz, 2H, NH–*CH_2*), 3.18 (pseudo q, $^3J_{HH}$ = 7 Hz, 6H, NH_2–*CH_2*, CH_2), 5.28 (s, 1H, NH), 6.55 (d, $^3J_{HH}$ = 8.8 Hz, 2H, HC_2), 7.55 (d, $^3J_{HH}$ = 8.8 Hz, 2H, HC_3); ^{13}C–{^{1}H} NMR ($CDCl_3$, 75.45 MHz): δ = 14.12 (s, CH_3), 31.96 (s, NH_2–CH_2–CH_2), 40.36 (s, NH_2–CH_2), 41.87 (s, *CH_2*CH_3), 41.95 (s, NH–*CH_2*), 111.46 (s, C_2), 126.42 (s, C_4), 128.99 (s, C_3), 151.52 (s, C_1) ppm. MS (DCI): *m*/*z* = 286.2 $[M + H]^+$. Anal Calcd (%): C 54.71, H 8.12, N, 14.72. Found: C 54.38, H 7.98, N 14.52.

Compound 9-G$_1$. Dendrimer **8-G$_1$** (22.5 mg, 0.0123 mmol) was dissolved in THF, then caesium carbonate (104.13 mg, 0.319 mmol) and compound **3** (75 mg, 0.08 mmol) were added to the reaction mixture and left overnight under good stirring. After reaction completion, salts were removed by centrifugation and the clear solution was evaporated under reduced pressure. The residue was then dissolved in the minimum amount of THF (*ca.* 0.5 mL) and precipitated with pentane. The resulting powder was filtered off and the procedure was repeated once to afford **9-G$_1$** as a brownish powder in 81% yield. ^{31}P–{^{1}H} NMR ($CDCl_3$, 121.49 MHz): δ = 7.70 (m, P═N), 68.44 (s, P_1═S); ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.22–1.28 (m, 216H, CH(*CH_3*)$_2$), 2.84 (m, 12H, *$CH_{15}H$*(CH_3)$_2$), 3.25 (br s, 6H, NH), 3.45 (br m, 18H, N–Me), 3.55–3.98 (m, 96H, *CH_2*–CH, C_a–H, C_b–H), 4.09 (m, 24H, *$CH_{17}H$*(CH_3)$_2$), 5.60–5.78 (m, 36H, CH═CH), 6.90–7.78 (m, 78H, CH═N, H_{Ar}); ^{13}C–{^{1}H} NMR ($CDCl_3$, 75.46 MHz): δ = 23.57 (s, C_{16}), 24.83 (s, C_{18}), 29.23 (s, C_{17}), 32.53 (d, $^2J_{CP}$ = 12.7 Hz, N–Me), 34.14 (s, C_{15}), 40.33 (s, C_a), 47.73 (m, C_b), 48.72, 48.84 (2 s, C_8, C_9), 51.30 (s, C_5), 115.96 (br s, C_2), 121.01 (br s, $C_0{}^2$), 123.94 (s, C_{13}), 127.69 (s, C_4), 128.37 (s, $C_0{}^3$), 129.36, 129.85 (2 s, C_7, C_{10}), 130.34 (s, C_6), 130.57, 130.83 (2 s, C_3, C_{11}), 132.30 (s, $C_0{}^3$), 137.62 (d, $^3J_{CP}$ = 13.6 Hz, CH═N), 145.74 (d, $^2J_{CP}$ = 6.0 Hz, C_1), 150.88 (br s, $C_0{}^1$), 151.47 (s, C_{12}), 153.18 (s, C_{14}) ppm. IR (neat): 3356 (N–H), 2955 (C–H), 2867 (═C–H), 1596 (C═C), 1461 (SO_2), 1149 (SO_2) cm^{-1}.

Compound 9-G$_2$. Dendrimer **8-G$_2$** (31 mg, 6.62 × 10^{-3} mmol) was dissolved in THF, then caesium carbonate (104.17 mg, 0.319 mol) and compound **3** (75 mg, 0.08 mmol) were added to the reaction mixture and left overnight under good stirring. After reaction completion, salts were removed by centrifugation and the clear solution was evaporated under reduced pressure. The residue was then dissolved in the minimum amount of THF (*ca.* 1 mL) and precipitated with pentane. The resulting powder was filtered off and the procedure was repeated once to afford **9-G$_2$** as a brownish powder with a yield of 83%. ^{31}P–{^{1}H} NMR ($CDCl_3$, 121.49 MHz): δ = 8.37 (s, P═N), 61.90–63.00 (m, P_1═S), 67.99 (s, P_2═S); ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.18–1.30 (m, 432H, CH(*CH_3*)$_2$), 2.90 (m, 24H, *$CH_{15}H$*(CH_3)$_2$), 3.22 (m, 12H, NH), 3.30 (m, 18H, N(Me)–P_1), 3.45 (m, 36H, N(Me)-P_2), 3.55–3.95 (m, 192H, *CH_2*–CH, C_a–H, C_b–H), 4.06 (m, 48H, $C_{17}H(CH_3)_2$), 5.55–5.75 (m, 72H, CH═CH), 6.90–7.70 (m, 192H, CH═N, H_{Ar}) ppm. ^{13}C–{^{1}H} NMR ($CDCl_3$, 75.46 MHz): δ = 23.57 (s, C_{16}), 24.84 (s, C_{18}), 29.23 (s, C_{17}), 32.49 (d, $^2J_{CP}$ = 13.2 Hz, N(Me)-P_2), 32.53 (d, $^2J_{CP}$ = 11.2 Hz, N(Me)-P_1), 34.14 (s, C_{15}), 40.39 (s, C_a), 47.56 (m, C_b), 48.69, 48.83 (2 s, C_8, C_9), 51.35 (s, C_5), 115.97 (br s, C_2), 121.30 (br s, $C_0{}^2$), 121.69 (br s, $C_1{}^2$), 123.95 (s, C_{13}), 127.80 (s, C_4, $C_0{}^3$), 128.35 (s, $C_1{}^3$), 129.30, 129.82 (2 s, C_7, C_{10}), 130.63 (s, C_6), 130.82, 131.60 (2 s, C_3, C_{11}), 132.28 (s, $C_0{}^4$) 132.68 (s, $C_1{}^4$), 137.46 (m, CH═N–N–P_2) 139.00 (br d, CH═N–N–P_1), 145.54 (d, $^2J_{CP}$ = 7.0 Hz, C_1), 150.88 (br s, $C_1{}^1$), 151.14 (s, $C_0{}^1$), 151.46 (s, C_{12}), 153.19 (s, C_{14}) ppm. IR (neat): 3369 (N–H), 2956 (C–H), 2867 (═ C–H), 1596 (C═C), 1461 (SO_2), 1148 (SO_2) cm^{-1}.

Compound 9-G$_4$. Dendrimer **8-G$_4$** (36 mg, 1.60 10^{-3} mmol) was dissolved in THF, then caesium carbonate (104.17 mg, 0.319 mol) and compound **3** (75 mg, 0.08 mmol) were added to the reaction mixture and left overnight under good stirring. After reaction completion, salts were removed by centrifugation and the clear solution was evaporated under reduced pressure. The residue was then dissolved in the minimum amount of THF (*ca.* 1 mL) and precipitated with pentane. The resulting powder was filtered off and the procedure was repeated once to afford **9-G$_4$** as a brownish powder in 74% yield. ^{31}P–{^{1}H} NMR ($CDCl_3$, 202.53 MHz): δ = 8.03 (br s, P═N), 62.27 (br s, P_1═S, P_2═S, P_3═S), 67.92 (s, P_4═S); ^{1}H NMR ($CDCl_3$, 500.33 MHz): δ = 1.28 (m, 1728H, CH(*CH_3*)$_2$), 2.89 (m, 96H, *$CH_{15}H$*(CH_3)$_2$), 3.15 (br s, 48H, NH), 3.27 (br s, 126H, N(Me)-$P_{1,2,3}$), 3.38 (br s, 144H, N(Me)-P_4), 3.60–3.95 (m, 768H, *CH_2*–CH, C_a–H_2, C_b–H_2), 4.09 (m, 192H, *$CH_{17}H$*(CH_3)$_2$), 5.55–5.75 (m, 288H, CH═CH), 7.10–7.80 (m, 834H, CH═N, H_{Ar}) ppm. ^{13}C–{^{1}H} NMR ($CDCl_3$, 125.80 MHz): δ = 23.58 (s, C_{16}), 24.85 (s, C_{18}), 29.23 (s, C_{17}), 32.49 (d, $^2J_{CP}$ = 12.9 Hz, N(Me)-P_4), 33.01 (br s, N(Me)–$P_{1,2,3}$), 34.12 (s, C_{15}), 40.43 (s, C_a), 47.69 (br s, C_b), 48.67, 48.82 (2 s, C_8, C_9), 51.34 (s, C_5), 115.99 (br s, C_2), 121.76 (br s, $C_{0,1,2,3}{}^2$), 123.94 (s, C_{13}), 127.81 (s, C_4), 128.37 (s, $C_{0,1,2,3}{}^3$), 129.25, 129.80 (2 s, C_7, C_{10}), 130.69 (s, C_6), 130.85 (s, C_3, C_{11}), 132.41 (s, $C_{0,1,2}{}^4$) 132.64 (s, $C_3{}^4$), 137.66 (m, CH═N–N–P_4) 139.15 (br m, CH═N–N–$P_{1,2,3}$), 145.65 (br s, C_1), 150.88 (br s, $C_{0,1,2,3}{}^1$), 151.44 (s, C_{12}), 153.18 (s, C_{14}) ppm. IR (neat): 3369 (N–H), 2956 (C–H), 2867 (═C–H), 1596 (C═C), 1461 (SO_2), 1148 (SO_2) cm^{-1}.

Compound 10. Compound **2** (100 mg, 0.111 mmol) was dissolved in DMF, then $Pt_2(dba_3)$[28] (106 mg, 0.133 mmol) was added to the reaction mixture and left to react at 130 °C overnight. When reaction was over (TLC monitoring), after

removal of the solvents, the residue was subjected to flash chromatography (pentane–AcOEt: 1 : 0 → 9 : 1) to afford the desired compound **10** as a brownish powder in 67% yield. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.27 (m, 36H, $CH(CH_3)_2$), 1.39–1.90 (m, 4H, CH_2), 2.12–2.60 (m, 2H, *CH*), 2.9 (sept, $^{3}J_{HH}$ = 7.0 Hz, 2H, $CH(CH_3)_2$), 3.00–3.25 (q, $^{3}J_{HH}$ = 7.1 Hz, 4H, CH_2), 3.30–3.70 (m, 4H, CH), 4.21 (sept, $^{3}J_{HH}$ = 7.0 Hz, 2H, $CH(CH_3)_2$), 4.35–5.20 (m, 6H, CH_2), 7.16 (m, 2H, H_{ar}), 7.20 (s, 4H, H_{ar}), 7.75–7.95 (m, 2H, H_{ar}) ppm. ^{13}C–{^{1}H} NMR ($CDCl_3$, 62.5 MHz): δ = 24.0 (s, C_{16}), 25.2 (s, C_{18}), 25.3 (s, C_{18}), 29.6 (s, C_{17}), 29.7 (s, C_{17}), 34.6 (s, C_{15}), 43.4, 45.0, 45.8, 45.9, 47.2, 47.3, 47.9, 49.3 (s, CH_2–CH), 62.8, 63.1, 63.3, 63.6, 63.7, 64.2, 69.0, 70.2, 70.5 (s, CH═CH), 116.9 (d, $^{2}J_{CF}$ = 21.7 Hz, C_2), 117.0 (d, $^{2}J_{CF}$ = 21.7 Hz, C_2), 124.4 (s, C_{13}), 129.5–130.5 (m, C_3, C_{11}), 131.5–131.9 (m, C_{11}), 134.6 (d, $^{4}J_{CF}$ = 4.0 Hz, C_4), 135.5 (d, $^{4}J_{CF}$ = 4.0 Hz, C_4), 151.70 (m, C_{12}), 153.72 (s, C_{14}), 165.46 (d, $^{1}J_{CF}$ = 251.87 Hz, C_1) ppm. IR (neat): 2956 (C–H), 2867 (═C–H), 1593 (C═C), 1148 (SO_2) cm^{-1}. MP: 135–137 °C. Anal Calcd (%): C 52.73, H 6.27, N 3.84. Found: C 52.51, H 6.44, N 3.94.

Compound 11. Compound **10** (52 mg, 0.047 mmol) was dissolved in ethylenediamine (100 μL, 1.49 mmol) at 95 °C for 3 h. When reaction was over, 10 mL of water were added to the reaction mixture, followed by two extractions with DCM (80 mL). Organic phase was then dried over Na_2SO_4 and after removal of the residual solvents, final compound **11** was obtained as a brownish powder with a yield of 97%. ^{1}H NMR ($CDCl_3$, 500.33 MHz): δ = 1.26 (m, 36H, $CH(CH_3)_2$), 1.45 and 4.62 (2 m, $C_{5,8,9}H_2$-**11**″), 1.85 and 4.38–4.53 (2 m, $C_{5,8,9}H_2$), 2.18 (br t, $^{3}J_{HH}$ = 12 Hz, $C_{6,7,10}$H-**11**′), 2.45 (br t, $^{3}J_{HH}$ = 12 Hz, $C_{6,7,10}$H-**11**″), 2.93 (m, 2H, C_{15}H), 3.00 (m, 2H, C_aH_2), 3.06 and 5.03 (2 m, $C_{5,8,9}H_2$-**11**′), 3.14 and 4.85 (2 m, $C_{5,8,9}H_2$-**11**″), 3.25 (m, 2H, C_bH_2), 3.36 (m, $C_{6,7,10}$H), 3.57 (m, $C_{6,7,10}$H), 4.21 (m, 4H, C_{17}H), 4.91 (br s, NH, NH_2), 6.60 (d, $^{3}J_{HH}$ = 8.7 Hz, C_2H-**11**″), 6.61 (d, $^{3}J_{HH}$ = 8.7 Hz, C_2H-**11**′), 7.20 (s, 4H, C_{13}H), 7.53 (d, $^{3}J_{HH}$ = 8.7 Hz, C_3H-**11**″), 7.61 (d, $^{3}J_{HH}$ = 8.7 Hz, C_2H-**11**′) ppm. ^{13}C-{^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ = 23.52 (s, C_{16}), 24.79, 24.86 (2 s, C_{18}), 29.21, 29.26 (2 s, C_{17}), 34.15 (s, C_{15}), 40.39 (s, C_a), 43.04 (s, $C_{5,8,9}$-**11**″), 44.46 (s, $C_{5,8,9}$-**11**′), 44.66 (s, C_b), 45.60, 46.87, 47.03 (3 s, $C_{5,8,9}$), 47.45, 48.88 (2 s, $C_{5,8,9}$-**11**′), 62.69, 63.08, 63.13, 63.23, 63.47 (5 s, $C_{6,7,10}$), 69.45 (s, $C_{6,7,10}$-**11**″), 69.67 (s, $C_{6,7,10}$-**11**′), 111.91 (s, C_2-**11**″), 112.01 (s, C_2-**11**′), 123.94 (s, C_{13}), 129.07 (s, C_3-**11**′), 129.29 (s, C_3-**11**″), 131.19, 131.38, 131.44 (3 s, $C_{4,11}$), 151.30, 151.38 (2 s, C_{12}), 151.71 (s, C_1), 153.24 (s, C_{14}) ppm. ^{195}Pt-{^{1}H} NMR ($CDCl_3$, 107.55 MHz): δ = −6163.08 (s, **11**″), −6165.77 (s, **11**′) ppm. IR (neat): 3375 (N–H), 2956 (C–H), 2867 (═C–H), 1597 (C═C), 1147 (SO_2) cm^{-1}. MP: 123–126 °C.

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