Dalton Transactions

Cite this: *Dalton Trans.*, 2012, **41**, 2354

www.rsc.org/dalton

PAPER

Synthesis of multimetallic dendrimers through non-covalent interactions†

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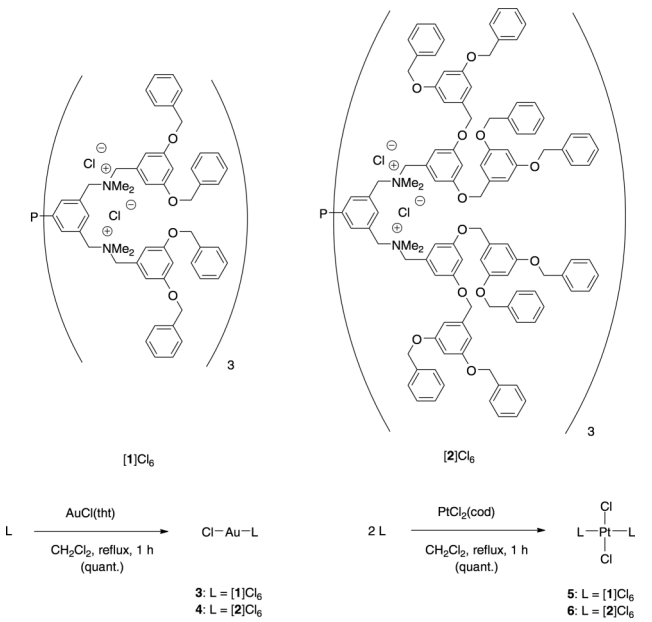
Received 9th August 2011, Accepted 17th November 2011
DOI: 10.1039/c1dt11505g

Hexa-ammonium functionalized *Dendriphos* ligands and mono-sulfonate functionalized metal complexes have been used as building blocks for the preparation of multimetallic dendritic assemblies. These metallodendrimers consist of a single metal centre surrounded by an oligocationic shell formed by the coordinated *Dendriphos* ligands and multiple associated anionic organometallic complexes.

Introduction

Metallodendrimers are usually classified as structures that either contain metal complexes at the periphery, at the core, or throughout the dendritic structure.[1] Dendritic structures that contain more than one type of organometallic fragment, especially when either the ligand moieties or the metal ions are different, are less common.[2] This is perhaps due to synthetic difficulties and the limited stability associated with these kind of structures. Such heterometallic dendrimers are nevertheless highly interesting, for example in the field of homogeneous catalysis. When both types of metal–ligand fragments are catalytically active, applications such as one-pot sequential or tandem catalysis[3] become possible.

A very powerful method to synthesize metallodendritic structures is the use of building blocks which self-assemble through non-covalent, for example ionic, interactions.[4] We have recently reported on octacationic dendrimers containing Fréchet-type dendrons[5] and have applied these as non-covalent supports for homogeneous catalysts.[6a,b] In analogy to these structures, hexacationic *Dendriphos* ligands[7] ([**1**]Cl_6 and [**2**]Cl_6, Scheme 1) were designed. In addition to six permanent cationic charges, these structures contain a single phosphine functionality located at the core of the dendrimer. The use of phosphines as building blocks in coordination-based self-assembly has recently been reviewed.[8] In view of the bifunctional character of the *Dendriphos* ligands, we envisaged the use of $[\mathbf{1}]^{6+}$ and $[\mathbf{2}]^{6+}$ as building blocks for the construction of metallodendritic assemblies.



Scheme 1 *Dendriphos* ligands [**1**]Cl_6 and [**2**]Cl_6 and their use in the synthesis of Au- and Pt- based metallodendrimers **3–6**.

Results and discussion

The synthesis of multimetallic dendritic assemblies was performed according to a stepwise procedure. First, [**1**]Cl_6 and [**2**]Cl_6 were reacted with either one equivalent of AuCl(tht) or 0.5 equivalents of $PtCl_2$(cod) in CH_2Cl_2 and stirred for 1 h at reflux temperature (Scheme 1). After evaporation of the solvent and removal of residual tht or cod, respectively, the products were isolated and fully characterized. Analysis of the products by ^{31}P-NMR showed one singlet resonance in all cases, indicating quantitative formation of the corresponding phosphine coordination complexes AuCl(L) (**3** and **4**) and $PtCl_2(L)_2$ (**5** and **6**; L = [**1**]Cl_6, [**2**]Cl_6). In the latter case, $^1J_{P,Pt}$ coupling constants of 2655 and 2661 Hz, respectively, were observed by ^{31}P-NMR. The magnitudes of these coupling constants are consistent with the simultaneous coordination of

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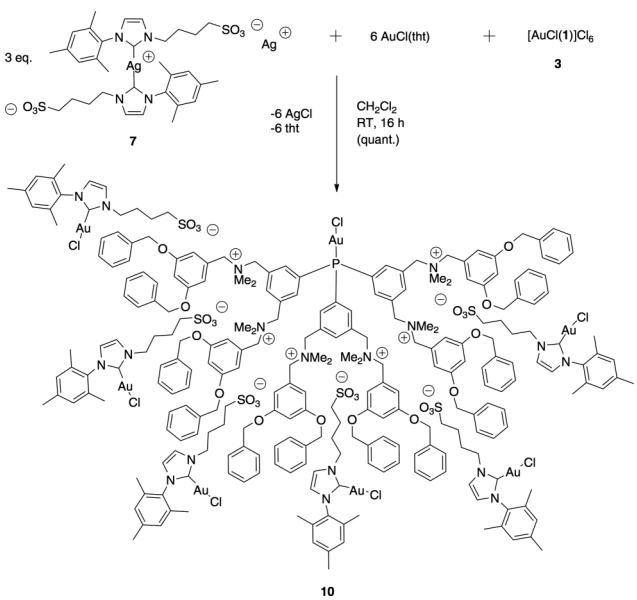
† Electronic supplementary information (ESI) available: ESI-MS spectra and selected ^{1}H-NMR spectra. See DOI: 10.1039/c1dt11505g

Table 1 Major ions observed by ESI-MS analysis of *Dendriphos* metal complexes and multimetallic assemblies

Entry	Structure	Major ions observed	Calcd (m/z)	Found (m/z)
1	[AuCl(**1**)]Cl_6 (**3**)	[Au(**1**)]Cl_5^{2+}	1399.5	1399.5
		[Au(**1**)]Cl_4^{3+}	921.04	921.01
2	[$PtCl_2$(**1**)$_2$]Cl_{12} (**5**)	[Pt(**1**)$_2$]Cl_{11}^{3+}	1811.8	1811.6
		[Pt(**1**)$_2$]Cl_{10}^{4+}	1350.0	1349.9
		[Pt(**1**)$_2$]Cl_9^{5+}	1072.9	1072.9
		[Pt(**1**)$_2$]Cl_8^{6+}	888.17	888.22
3	[AuCl(**1**)][**8**]$_6$ (**10**)	[AuCl(**1**)][**8**]$_4^{2+}$	2436.5	2436.7
		[AuCl(**1**)][**8**]$_3^{3+}$	1439.7	1439.8
4	[$PtCl_2$(**1**)$_2$][**8**]$_{12}$ (**11**)	[$PtCl_2$(**1**)$_2$][**8**]$_9^{3+}$	3366.9	3367.5
		[$PtCl_2$(**1**)$_2$][**8**]$_8^{4+}$	2386.7	2387.2
5	[$PtCl_2$(**1**)$_2$][**9**]$_{12}$ (**12**)	[$PtCl_2$(**1**)$_2$][**9**]$_9^{3+}$	3426.7	3427.2
		[$PtCl_2$(**1**)$_2$][**9**]$_8^{4+}$	2426.6	2427.1

two equivalents of [**1**]$^{6+}$ and [**2**]$^{6+}$, respectively, to the Pt(II) centre, with a *trans* configuration.[9] Analysis by ESI-MS of complexes **3** and **5** showed signals corresponding to the ions [Au(**1**)]$Cl_{(7-n)}^{n+}$ (n = 2, 3) and [Pt(**1**)$_2$]$Cl_{(14-n)}^{n+}$ (n = 3–6) (Table 1, entries 1 and 2; Fig. S2 and S3, ESI†) and confirm the assigned structures. These compounds can be classified as metallodendrimers consisting of a single metal centre surrounded by a dendritic shell formed by the coordinated *Dendriphos* ligands.

In a second step, the metallodendrimers [AuCl(**1**)]Cl_6 (**3**) and [$PtCl_2$(**1**)$_2$]Cl_{12} (**5**) were used as hosts for respectively six or twelve equivalents of an organometallic guest molecule containing a single sulfonate functionality. Homo-multimetallic assembly [AuCl(**1**)][**8**]$_6$ (**10**, Scheme 2) was synthesized according to a one-pot transmetalation/immobilization procedure which was previously developed in our group.[10] In this one-pot procedure, the ionic dendrimer serves both as a supporting agent and as a halide source for N-heterocyclic carbene (NHC) metal halide complexes. Starting from the Ag-bis-carbene zwitterion **7**, reaction with both a stoichiometric amount of AuCl(tht) as well as one sixth of an equivalent of **3** in CH_2Cl_2, led to the



Scheme 2 One pot transmetalation/immobilization procedure leading to homo-multimetallic assembly [AuCl(**1**)][**8**]$_6$ (**10**).

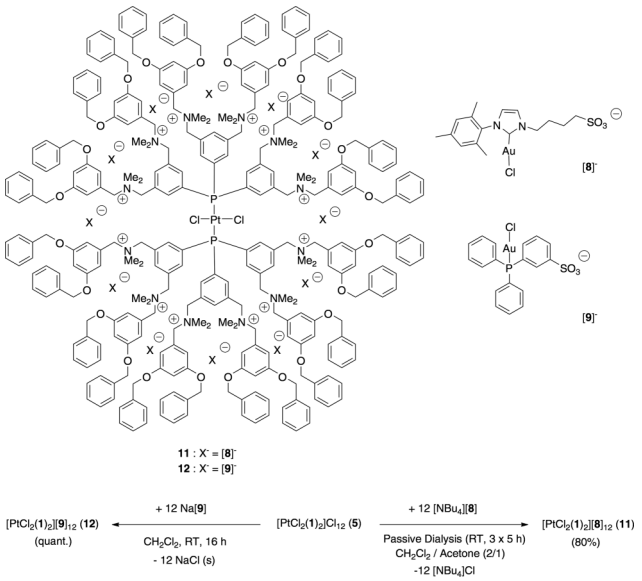
quantitative formation of the anionic NHC–Au complex [**8**]$^-$ and its concomitant immobilization on [AuCl(**1**)]$^{6+}$, along with precipitation of AgCl. After filtration, the resulting clear solution contained [AuCl(**1**)][**8**]$_6$ (**10**) in quantitative yield.

Analysis by ESI-MS led to the detection of ions corresponding to **10** minus two or three equivalents of **8**, *i.e.* [AuCl(**1**)][**8**]$_{6-n}^{n+}$ (n = 2, 3) (Table 1, entry 3 and Fig. S4, ESI†) and confirms the association of multiple guest molecules to the dendritic framework. The dissociation of n equivalents of the guest is assumed to occur during the ESI-MS measurement, which is generally observed for this type of non-covalent assemblies.[5,6,10]

The ^{1}H-NMR spectrum of **10**, measured in CD_2Cl_2, shows signals of both the hexacationic dendritic phosphine gold halide and the assembled gold–carbene sulfonate anions (Fig. S1, ESI†). A calculation of the number of [**8**]$^-$ molecules per dendritic host, using specific peak integration values, yields a ratio of 6 : 1 guest molecules per host. Significant changes in the chemical shifts were observed for several of the protons of the dendritic backbone. The spectrum furthermore shows a considerable sharpening of the signals attributed to the dendritic framework of the assembly [AuCl(**1**)][**8**]$_6$ (**10**) in comparison with [AuCl(**1**)]Cl_6 (**3**). In the ^{13}C-NMR spectrum of **10**, a characteristic signal at 170.9 ppm was observed, which is attributed to the carbenic carbon coordinated to Au.[10] The signal of the carbenic carbon in **7** had disappeared, indicating that complete transmetalation from Ag to Au had occurred. The ^{31}P-NMR spectrum of **10** showed a single peak at 36.8 ppm and confirms the integrity of the *Dendriphos*-Au-Cl moiety. These observations indicate that six equivalents of the anionic guest have been incorporated into the cationic dendrimer and that the guest molecules stay associated with the host in dichloromethane solution.

In a first attempt to prepare a hetero-multimetallic assembly, the procedure outlined in Scheme 2 was carried out using [RhCl(cod)]$_2$ instead of AuCl(tht) as the metal precursor for reaction with transmetalation agent **7**. Unfortunately, ^{31}P-NMR of the product indicated that the *Dendriphos*-Au-Cl moiety had not stayed intact during this procedure and instead had completely transformed into a *Dendriphos*-Rh complex. When the dendritic host was changed from [AuCl(**1**)]Cl_6 (**3**) to [$PtCl_2$(**1**)$_2$]Cl_{12} (**5**) while keeping AuCl(tht) as the metal precursor, ^{13}C-NMR indicated that transmetalation from Ag to Au was not complete. A different strategy was thus required for the synthesis of hetero-multimetallic assemblies. Therefore, twelve equivalents of pre-synthesized Au-carbene complex [NBu_4][**8**] were combined with one equivalent of **5** (Scheme 3). Removal of [NBu_4]Cl was achieved by passive dialysis, leading to hetero-multimetallic assembly [$PtCl_2$(**1**)$_2$][**8**]$_{12}$ (**11**) in 80% isolated yield. In addition, employing a slightly different immobilization strategy, twelve equivalents of TPPMS-Au complex Na[**9**] (TPPMS = monosulfonated triphenylphosphine) were combined with host **5** in dry CH_2Cl_2, which led to precipitation of NaCl, affording the assembly [$PtCl_2$(**1**)$_2$][**9**]$_{12}$ (**12**) in quantitative yield, without the need for dialysis (Scheme 3).

For both these hetero-multimetallic assemblies, ^{31}P-NMR exclusively showed *Dendriphos*-Pt(II) coordination. The observed chemical shifts as well as the $^1J_{P,Pt}$ coupling constants were very similar and did not change significantly compared to [$PtCl_2$(**1**)$_2$]Cl_{12} (**5**). The *Dendriphos*-platinum cores had thus in each case remained intact during the synthetic procedure, despite the presence of a twelve-fold excess of respectively Au-carbene or Au-phosphine



Scheme 3 Synthesis of Pt/Au heterometallic assemblies **11** and **12**.

complexes. Analysis by ESI-MS led to the detection of signals corresponding to the ions $[PtCl_2(\mathbf{1})_2]X_{12-n}^{n+}$ (X = **8**, **9**; n = 3, 4, see Table 1, entries 4 and 5 and Fig. 1 and S6, ESI†) and is consistent with the association of the guests $[\mathbf{8}]^-$ and $[\mathbf{9}]^-$, respectively, to the dendritic host $[PtCl_2(\mathbf{1})_2]^{12+}$. In the ^{1}H-NMR spectra, a sharpening of the signals, similar to that observed for **10** (Fig. S1, ESI†), was observed for **11**. This effect was less pronounced for **12**. A calculation of the guest/host ratios by specific peak integration in ^{1}H-NMR yielded a ratio of 10 : 6 for **11**. The deviation from the expected ratio of 12 suggests that a slightly lower number of guests have been incorporated into the dendritic host. Most likely this is a consequence of the employed passive dialysis step, in which a small quantity of $[NBu_4][\mathbf{8}]$ might pass through the membrane, resulting in a lower guest/host ratio in **11**. The integrity of the carbene-Au fragments in **11** was confirmed by the presence of a single peak in the carbenic carbon region of the ^{13}C-NMR spectrum, at 170.8 ppm.

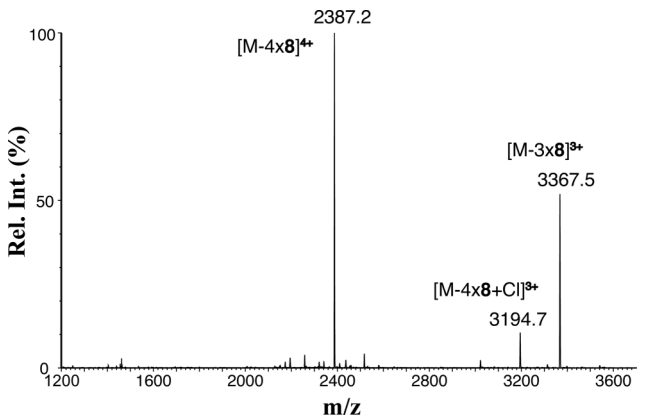


Fig. 1 ESI-MS spectrum of **11**.

For **12**, a reliable calculation of the guest/host ratio based upon integration of signals in ^{1}H-NMR was impossible due to overlap of signals. However, elemental analysis was consistent with quantitative functionalization for **12**, *i.e.* a guest/host ratio of 12. The ^{31}P-NMR spectrum of **12** shows a second signal, corresponding to the TPPMS phosphine functionality coordinated to gold. No additional signals were observed. The *Dendriphos* phosphorus signal appears as a broad singlet, while the TPPMS phosphorus signal appears as a sharp, very intense singlet. Therefore the two different phosphorus nuclei can be easily distinguished, confirming discrete *Dendriphos*-Pt and TPPMS-Au coordination after the synthetic procedure.

After the hetero-multimetallic assemblies had been allowed to stand in solution in CD_2Cl_2 for one week at room temperature, ^{31}P-NMR showed that considerable metal–ligand exchange had occurred during this period. In both cases, approximately 20% of *Dendriphos*-Au coordination was observed (indicated by a singlet at 37 ppm). This indicates the limited kinetic stability of these assemblies, which most likely are dynamic systems in solution. A metal–ligand exchange equilibrium, in which *Dendriphos*-Pt species undergo transmetalation to *Dendriphos*-Au species, most likely exists and may slowly shift to the thermodynamically most stable state. The kinetics of this exchange are expected to depend on the nature of the metal ions, the ligand fragments and the solvent.

Conclusions

In conclusion, hexa-ammonium functionalized *Dendriphos* ligands $[\mathbf{1}]^{6+}$ and $[\mathbf{2}]^{6+}$ and mono-sulfonate functionalized NHC-Au and phosphine-Au complexes $[\mathbf{8}]^-$ and $[\mathbf{9}]^-$ have been used as building blocks to construct multimetallic dendritic assemblies through non-covalent interactions. The employed stepwise synthetic strategy allows facile preparation of metallodendrimers containing discrete metal–ligand fragments, in very high yields. This strategy may be extended towards a range of combinations of transition metal complexes. Of particular interest is the incorporation of two discrete catalytically active transition metal complexes within the same metallodendrimer. Such assemblies could potentially find applications in tandem or sequential catalysis and given their very large molecular weight, may furthermore be easily recycled through nanofiltration.

Experimental

General remarks

Experiments involving free phosphines were performed under an inert N_2 atmosphere using standard Schlenk techniques and deoxygenated solvents. CH_2Cl_2 was dried over CaH_2 and distilled before use. Passive dialysis was performed using benzoylated cellulose membrane tubing (Aldrich) with a molecular weight cut-off of 1200.[6a] $[\mathbf{1}]Br_6$,[7a] $[\mathbf{2}]Br_6$,[7a] **7**,[10] $[NBu_4][\mathbf{8}]$[10] and $Na[\mathbf{9}]$[11] were synthesized according to previously reported procedures. NMR spectra were recorded on a Varian Inova 300 or a Varian AS 400 spectrometer at 25 °C. ^{1}H and ^{13}C {^{1}H} spectra were referenced to residual solvent signals. Elemental analyses were carried out by Dornis & Kolbe, Mikroanalytisches Laboratorium, Müllheim a/d Ruhr, Germany. Time-of-flight electrospray ionization mass spectra (ESI-MS) were measured by the Biomolecular Mass Spectrometry and Proteomics Group, Utrecht University, on a Micromass LC-T mass spectrometer (Waters, Manchester, UK), operating in positive ion mode. Samples were introduced at

concentrations of 20–50 μM. The nanospray needle potential was typically set to 1300 V and the cone voltage to 20–60 V. The source block temperature was set to 80 °C.

Dendriphos ligands [1]Cl_6 and [2]Cl_6

Exchange of the bromide counterions of [**1**]Br_6 and [**2**]Br_6 to chloride was performed using a biphasic mixture of DCM (300 mL) and a solution of LiCl in demineralized water (1 M, 3 × 150 mL), under a N_2 atmosphere. After separation of the layers, the organic layer was washed twice with demineralized water (150 mL) and evaporated to dryness, affording the products in 80–85% yield on a 2-gram scale.

[1]Cl_6

^{1}H-NMR (400 MHz, $CDCl_3$/CD_3OD, 9 : 1 (v/v)): δ (ppm) = 8.17 (d, $^3J_{P,H}$ = 6.8 Hz, 6H, *o*-Ar), 8.00 (s, 3H, *p*-Ar), 7.24–7.10 (m, 60H, Ph), 6.84 (s, 12H, *o*-Ar′), 6.57 (s, 6H, *p*-Ar′), 4.88 (s, 24H, OCH_2), 4.61 (s, 12H, den-CH_2N), 4.47 (s, 12H, den-NCH_2), 2.85 (s, 36H, $N(CH_3)_2$). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$/CD_3OD, 9 : 1 (v/v)): δ (ppm) = 159.9 (s, *m*-Ar′), 140.8 (m, overlapping *i*- and *o*-Ar), 139.0 (s, *p*-Ar), 136.1 (s, *o*-Ar′), 129.2 (d, $^3J_{P,C}$ = 7.0 Hz, *m*-Ar), 129.0 (s, Ph), 128.3 (s, Ph), 127.9 (s, Ph), 127.5 (s, Ph), 112.2 (s, *p*-Ar′), 104.0 (s, *i*-Ar′), 70.0 (s, OCH_2), 67.5 (s, NCH_2), 67.0 (s, NCH_2), 48.4 (s, $N(CH_3)_2$). ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$): δ (ppm) = −3.2. HR-ESI MS: (*m*/*z*) 623.307 {[M-4Cl]$^{4+}$, calc. 623.302}.

[2]Cl_6

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) = 8.25 (br. s, 6H, *o*-Ar), 7.8–7.0 (m, 123H, Ph and *p*-Ar), 6.91, 6.58, 6.41 (br. m, 54H, overlapping Ar′) 5.0–4.5 (br. m, 96H, overlapping CH_2), 2.97 (br. s, 36H, $N(CH_3)_2$). ^{13}C{^{1}H}-NMR (50 MHz, $CDCl_3$): δ (ppm) = 160.2, 160.0, 138.9, 136.8, 128.7, 128.1, 127.8, 112.5, 106.8, 101.8, 70.2, 67.7, 49.2. ^{31}P{^{1}H}-NMR (81 MHz, $CDCl_3$): δ (ppm) = −3.5. ESI MS: (*m*/*z*) 1699.4 {[M+O-3Cl]$^{3+}$, calc. 1698.2}, 1265.3 {[M+O-4Cl]$^{4+}$, calc. 1264.8}. Elem. anal. for $C_{330}H_{315}Cl_6N_6O_{36}P$ (5184.84): calc. (%) C 76.45, H 6.12, Cl 4.10, N 1.62, P 0.60; found C 76.37, H 6.18, Cl 3.96, N 1.57, P 0.58.

[AuCl(1)]Cl_6 (3)

To a solution of [**1**]Cl_6 (246 mg, 0.0930 mmol) in CH_2Cl_2 (5 mL) was added AuCl(tht) (30 mg, 0.094 mmol). The solution was heated at reflux temperature for 1 h, and subsequently dried *in vacuo*. The product was precipitated twice from CH_2Cl_2 by addition of Et_2O, yielding the product as a white powder (260 mg, quant.). ^{1}H-NMR (300 MHz, $CDCl_3$/CD_3OD, 3 : 1 (v/v)): δ (ppm) = 8.62 (d, $^3J_{P,H}$ = 12.0 Hz, 6H, *o*-Ar), 8.44 (s, 3H, *p*-Ar), 7.4-7.1 (m, 60H, Ph), 6.87 (s, 12H, *o*-Ar′), 6.65 (s, 6H, *p*-Ar′), 4.98 (s, 24H, OCH_2), 4.83 (s, 12H, den-CH_2N), 4.64 (s, 12H, den-NCH_2), 2.99 (br. s, 36H, $N(CH_3)_2$). ^{13}C{^{1}H}-NMR (100 MHz, CD_2Cl_2): δ (ppm) = 159.9 (s, *m*-Ar′), 142.9 (br. s, overlapping Ar), 141.2 (br. s, Ar), 136.6 (s, *o*-Ar′), 131.3 (br. s, Ar), 129.8 (s, Ph), 128.5 (s, Ph), 128.1 (s, Ph), 127.9 (s, Ph), 112.8 (s, *p*-Ar′), 104.0 (s, *i*-Ar′), 70.2 (s, OCH_2), 67.0 (br. s, NCH_2), 66.0 (br. s, NCH_2), 48.9 (s, $N(CH_3)_2$). ^{31}P{^{1}H}-NMR (121 MHz, $CDCl_3$/CD_3OD, 3 : 1 (v/v)): δ (ppm) = 37.6. ESI MS: (*m*/*z*) 1399.5 {[M-2Cl]$^{2+}$, calc. 1399.5}, 921.01 {[M-3Cl]$^{3+}$, calc. 921.04}. Elem. anal. for $C_{162}H_{171}AuCl_7N_6O_{12}P$ (2865.01): calc. (%) C 67.69, H 6.01, Cl 8.65, N 2.93, P 1.08; found C 67.65, H 5.94, Cl 8.43, N 2.79, P 1.11.

[AuCl(2)]Cl_6 (4)

Starting from [**2**]Cl_6 and AuCl(tht), an analogous procedure as described for [AuCl(**1**)]Cl_6 was followed, affording the product in quantitative yield. ^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) = 8.86 (br. s, 6H, *o*-Ar), 7.8–7.0 (m, 123H, Ph and *p*-Ar), 6.86, 6.59, (br. m, 54H, overlapping Ar′) 5.2–4.4 (br. m, 96H, overlapping CH_2), 2.96 (br. s, 36H, $N(CH_3)_2$). ^{13}C{^{1}H}-NMR (50 MHz, $CDCl_3$): δ (ppm) = 160.2, 138.8, 136.9, 128.8, 128.2, 127.8, 112.5, 106.7, 104.4, 101.8, 70.2, 49.3. ^{31}P{^{1}H}-NMR (81 MHz, $CDCl_3$): δ (ppm) = 36.7. Elem. anal. for $C_{330}H_{315}AuCl_7N_6O_{36}P$ (5381.81): calc. (%) C 73.17, H 5.86, Cl 4.58, N 1.55, P 0.57; found C 73.05, H 5.92, Cl 4.47, N 1.53, P 0.59.

[$PtCl_2$(1)$_2$]Cl_{12} (5)

To a solution of [**1**]Cl_6 (530 mg, 0.201 mmol) in CH_2Cl_2 (5 mL) was added $PtCl_2$(cod) (37 mg, 0.099 mmol). The solution was heated at reflux temperature for 1 h, and subsequently dried *in vacuo*. The product was precipitated twice from CH_2Cl_2 by addition of Et_2O, yielding the product as a light yellow powder (550 mg, quant.). ^{1}H-NMR (400 MHz, $CDCl_3$/CD_3OD, 3 : 1 (v/v)): δ (ppm) = 8.1 (br. s, 9H, Ar), 7.4–7.1 (m, 120H, Ph), 6.77 (br. s, 24H, *o*-Ar′), 6.59 (br. s, 12H, *p*-Ar′), 4.89 (s, 48H, OCH_2), 4.62 (br. s, 48H, NCH_2), 2.78 (br. s, 72H, $N(CH_3)_2$). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$/CD_3OD, 3 : 1 (v/v)): δ (ppm) = 159.8 (s, *m*-Ar′), 140.8 (br. s, Ar), 136.0 (s, *o*-Ar′), 128.8 (br. s, Ar), 128.2 (s, Ph), 127.9 (s, Ph), 127.8 (s, Ph), 127.4 (s, Ph), 112.3 (s, *p*-Ar′), 103.2 (s, *i*-Ar′), 69.9 (s, OCH_2), 66.9 (br. s, NCH_2), 49.1 (s, $N(CH_3)_2$). ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$/CD_3OD, 3 : 1 (v/v)): δ (ppm) = 25.4 (br. s, $^1J_{P,Pt}$ = 2655 Hz). ESI MS: (*m*/*z*) 1811.6 {[M-3Cl]$^{3+}$, calc. 1811.8}, 1349.9 {[M-4Cl]$^{4+}$, calc. 1350.0}, 1072.9 {[M-5Cl]$^{5+}$, calc. 1072.9}, 888.22 {[M-6Cl]$^{6+}$, calc. 888.17}. Elem. anal. for $C_{324}H_{342}Cl_{14}N_{12}O_{24}P_2Pt$ (5541.71): calc. (%) C 70.22, H 6.22, Cl 8.96, N 3.03, P 1.12; found C 69.85, H 6.20, Cl 8.87, N 2.94, P 1.15.

[$PtCl_2$(2)$_2$]Cl_{12} (6)

Starting from [**2**]Cl_6 and $PtCl_2$(cod), an analogous procedure as described for [$PtCl_2$(**1**)$_2$]Cl_{12} was followed, affording the product in quantitative yield. ^{1}H-NMR (400 MHz, $CDCl_3$/CD_3OD, 3 : 1 (v/v)): δ (ppm) = 8.1 (br. s, Ar), 7.4–7.1 (br. m, 240H, Ph), 7.0–6.6 (br. m, 108H, Ar′) 4.8–5.2 (br. s, 192H, CH_2), 3.2–2.6 (br. s, 72H, $N(CH_3)_2$). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$/CD_3OD, 3 : 1 (v/v)): δ (ppm) = 159.8, 142–138 (br. overlapping signals), 136.1, 136.0, 128.3, 127.9, 127.4, 112.3, 104.2, 104–102 (br. overlapping signals), 70.0, 66.9, 49.4. ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$/CD_3OD, 3 : 1 (v/v)): δ (ppm) = 27.0 (br. s, $^1J_{P,Pt}$ = 2661 Hz). Elem. anal. for $C_{660}H_{630}Cl_{14}N_{12}O_{72}P_2Pt$ (10635.67): calc. (%) C 74.53, H 5.97, Cl 4.67, N 1.58, P 0.58; found C 74.44, H 6.05, Cl 4.73, N 1.54, P 0.55.

[AuCl(1)][8]$_6$ (10)

To a solution of **7** (77.0 mg, 0.0895 mmol, *i.e.* 0.179 mmol Ag) in CH_2Cl_2 (5 mL) were subsequently added AuCl(tht) (58.3 mg,

0.182 mmol) and **3** (85.7 mg, 0.0299 mmol), both as solids and in one portion. The mixture was stirred at room temperature for 16 h under an inert atmosphere, filtered over Celite and subsequently dried *in vacuo*, yielding the product as a white powder (0.188 g, quant.). The product was precipitated twice from CH_2Cl_2 by addition of Et_2O, in order to remove residual tetrahydrothiophene. Yield: 0.156 g (87%). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ (ppm) = 8.54 (s, 6H, *o*-Ar), 8.50 (s, 3H, *p*-Ar), 7.4–7.2 (m, 60H, Ph), 7.12 (s, 6H, NCH), 6.90 (br. s, 24H, overlapping *o*-Ar′ and Mes-ArH), 6.76 (s, 6H, CHN), 6.66 (s, 6H, *p*-Ar′), 5.02 (s, 24H, OCH_2), 4.86 (s, 12H, den-CH_2N), 4.65 (s, 12H, den-NCH_2), 4.09 (t, $^3J_{H,H}$ = 6.2 Hz, 12H, NCH_2CH_2), 3.01 (s, 36H, N$(CH_3)_2$), 2.70 (br. s, 12H, $CH_2CH_2SO_3$), 2.27 (s, 18H, Mes-*p*-CH_3), 1.88 (br. s, 48H, overlapping Mes-*o*-CH_3 and NCH_2CH_2), 1.72 (m, 12H, $CH_2CH_2SO_3$). ^{13}C{^{1}H}-NMR (100 MHz, CD_2Cl_2): δ (ppm) = 170.9 (s, NHC-Au), 160.2 (s, *m*-Ar′), 142.4 (s, Ar), 140.7 (br. s, overlapping Ar), 139.7 (s, Mes), 136.7 (s, *o*-Ar′), 135.0 (s, Mes) 135.0 (s, Mes), 130.6 (d, $^3J_{C,P}$ = 12.1 Hz, *m*-Ar), 129.6 (s, Ph), 129.2 (s, Mes), 128.6 (s, Ph), 128.1 (s, Ph), 127.9 (s, Ph), 122.3 (s, NCH), 121.0 (s, NCH), 112.5 (s, *p*-Ar′), 104.2 (s, *i*-Ar′), 70.3 (s, OCH_2), 67.5 (NCH_2), 51.2 and 50.9 (s, NCH_2CH_3 and $CH_2CH_3SO_3$), 49.0 (s, N$(CH_3)_2$), 30.1 (s, NCH_2CH_3), 22.5 (s, $CH_2CH_3SO_3$), 20.9 (s, Mes-*p*-CH_3), 17.2 (s, Mes-*o*-CH_3). ^{31}P{^{1}H}-NMR (121 MHz, CD_2Cl_2): δ (ppm) = 36.8. ESI MS: (*m*/*z*) 2436.7 {[M-2[**8**]]$^{2+}$, calc. 2436.5}, 1439.8 {[M-3[**8**]]$^{3+}$, calc. 1439.7}.

[PtCl$_2$(1)$_2$][8]$_{12}$ (11)

To a solution of [NBu_4][**8**] (84 mg, 0.11 mmol) and **5** (48 mg, 8.7 μmol) in CH_2Cl_2 (30 mL) was added demineralized water (20 mL). The mixture was stirred at room temperature for 16 h, the organic layer was separated, concentrated and purified by dialysis, using CH_2Cl_2/acetone (2 : 1 (v/v)) as solvent (3 × 5 h). The product was precipitated twice from CH_2Cl_2 by addition of Et_2O. Yield: 65 mg (80%). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ (ppm) = 8.4 (br. s, 18H, Ar), 7.4–7.2 (m, 120H, Ph), 7.07 (s, 12H, NCH), 6.87 (s, 24H, Mes-ArH), 6.9 (br. m, 24H, *o*-Ar′) 6.69 (s, 12H, CHN), 6.7 (br. m, 12H, *p*-Ar′) 5.1–4.6 (br. m, 96H, OCH_2 and NCH_2), 3.97 (br. s, 24H, NCH_2CH_2), 2.95 (br. s, 72H, N$(CH_3)_2$), 2.68 (br. s, 12H, $CH_2CH_2SO_3$), 2.25 (s, 36H, Mes-*p*-CH_3), 1.84 (s, 96H, overlapping Mes-*o*-CH_3 and NCH_2CH_2), 1.67 (m, 12H, $CH_2CH_2SO_3$). ^{13}C{^{1}H}-NMR (100 MHz, CD_2Cl_2): δ (ppm) = 170.8 (s, NHC–Au), 160.2 (s, *m*-Ar′), 139.7 (s, Mes), 136.7 (s, *o*-Ar′), 135.0 (s, Mes) and 134.9 (s, Mes), 129.8 (s, Ph), 129.2 (s, Mes), 128.6 (s, Ph), 127.9 (s, Ph), 127.8 (s, Ph), 122.1 (s, NCH), 121.2 (s, NCH), 112.5 (s, *p*-Ar′), 103.6 (br. s, *i*-Ar′), 70.3 (s, OCH_2), 67.6 (br., overlapping NCH_2), 51.2 and 50.9 (s, NCH_2CH_3 and $CH_2CH_3SO_3$), 49.1 (s, N$(CH_3)_2$), 30.2 (s, NCH_2CH_3), 22.5 (s, $CH_2CH_3SO_3$), 20.9 (s, Mes-*p*-CH_3), 17.6 (s, Mes-*o*-CH_3) (signals for Ar not resolved). ^{31}P{^{1}H}-NMR (121 MHz, CD_2Cl_2): δ (ppm) = 25.1 ($^1J_{P,Pt}$ = 2680 Hz). ESI MS: (*m*/*z*) 3367.5 {[M-3[**8**]]$^{3+}$, calc. 3366.9}, 2387.2 {[M-4[**8**]]$^{4+}$, calc. 2386.7}.

[PtCl$_2$(1)$_2$][9]$_{12}$ (12)

To a solution of **5** (43.2 mg, 7.80 μmol), in dry CH_2Cl_2 (5 mL) was added Na[**9**] (56.0 mg, 0.0938 mmol) as a solid, in one portion. The mixture was stirred at room temperature for 16 h, filtered over Celite and subsequently dried *in vacuo*, yielding the product as a white powder (92 mg, quant.). ^{1}H-NMR (300 MHz, CD_2Cl_2): δ (ppm) = 9.3 (br. s, Ar), 8.3 (br. s, Ar), 8.01 (d, $J_{H,P}$ = 13.5 Hz, 12H, tppms-AuCl), 7.93 (br. s, 12H, tppms-AuCl) 7.4–6.9 (br. m, 264H, overlapping Ph and tppms-AuCl), 6.8–6.4 (br. m, 36H, Ar′), 4.9–4.3 (br. m, 96H, OCH_2 and NCH_2), 3.0–2.4 (br. s, 72H, N$(CH_3)_2$). ^{13}C{^{1}H}-NMR (100 MHz, CD_2Cl_2): δ (ppm) = 160.0 (s, *m*-Ar′), 148.2 (d, $J_{C,P}$ = 12.1 Hz, tppmsAuCl), 136.6 (s, *o*-Ar′), 134.4 (d, $J_{C,P}$ = 11.1 Hz, tppmsAuCl), 134.0 (d, $J_{C,P}$ = 13.7 Hz, tppmsAuCl), 132.1 (s, tppmsAuCl), 131.6 (d, $J_{C,P}$ = 16.6 Hz, tppmsAuCl), 129.7 (br. s, overlapping tppmsAuCl and Ph), 129.3 (d, $J_{C,P}$ = 12.1 Hz, tppmsAuCl), 128.5 (s, Ph) 127.9 (s, Ph), 127.8 (s, Ph), 112.4 (br. s, *p*-Ar′), 104.2 (br. s, *i*-Ar′), 70.1 (s, OCH_2), 67.6 (br., NCH_2), 49.1 (s, N$(CH_3)_2$). ^{31}P{^{1}H}-NMR (121 MHz, CD_2Cl_2): δ (ppm) = 34.4 (tppmsAuCl), 25.1 (*Dendriphos*, $^1J_{P,Pt}$ = 2700 Hz). ESI MS: (*m*/*z*) 3427.2 {[M-3[**9**]]$^{3+}$, calc. 3426.7}, 2427.1 {[M-4[**9**]]$^{4+}$, calc. 2426.6}. Elem. anal. for $C_{540}H_{510}Au_{12}Cl_{14}N_{12}O_{60}P_{14}PtS_{12}$ (12001.30): calc. (%) C 54.04, H 4.28, N 1.40, P 3.61; found C 54.00, H 4.34, N 1.37, P 3.52.

Acknowledgements

The authors thank Utrecht University for financial support and acknowledge the Dutch Council for Scientific research (CW-NWO) for a VIDI-grant to R. J. M. K. G.

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