Click Co Sandwich-Terminated Dendrimers as Polyhydride Reservoirs and Micellar Templates

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Electronic Supplementary Information (ESI)

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ABBREVIATIONS:

DHR: Dendritic hydride reservoir
DER: Dendritic electron reservoir
IR: Infrared spectroscopy
CV: Cyclic voltammogram
TEM: Transmission electron microscopy
AFM: Atomic force microscopy
Trz: 1,2,3-Triazolyl group
MS: Mass spectrum
DCM: Dichloromethane
UV-vis.: UV-visible
AuNPs: Gold nanoparticles
AgNPs: Silver nanoparticles
PdNPs: Palladium nanoparticles
General data
Reagent-grade tetrahydrofuran (THF) was predried over Na foil and distilled from sodium-benzophenone anion under argon immediately prior to use. All other solvents and chemicals were used as received.

The $^1$H NMR spectra were recorded at 25°C with a Bruker AVANCE II 400 MHz spectrometer. The $^{13}$C NMR spectra were obtained in the pulsed FT mode at 100 MHz with a Bruker AVANCE 400 spectrometer. All chemical shifts are reported in parts per million (δ, ppm) with reference to Me$_4$Si (TMS). The infrared (IR) spectra were recorded on an ATI Mattson Genesis series FT-IR spectrophotometer.

The mass spectra were performed at the CESAMO (University of Bordeaux, France) on a QStar Elite mass spectrometer (Applied Biosystems). The instrument is equipped with an ESI source, and spectra were recorded in the positive mode. The electrospray needle was maintained at 5000V and operated at room temperature. Samples were introduced by injection through a 20μL sample loop into a 4500 μL/min flow of methanol from the LC pump. The mass spectrum of benzylmethyl-(trz-$\eta^4$-C$_5$H$_5$CoCp) was recorded by the CESAMO on a AccuTOF- GcV (JEOL) that is a GC-TOF. The instrument is equipped with a sample introduction system named FD (Field Desorption). The MALDI-TOF mass spectra were performed on a PerSeptive Biosystems Voyager Elite (Framingham, MA) time of flight mass spectrometer.

All electrochemical measurements (CV) were recorded under the following conditions. Solvent: dry DMF; temperature: 20°C; supporting electrolyte: [nBu$_4$N][PF$_6$] 0.1M; working and counter electrodes: Pt; reference electrode: Ag; internal reference: FeCp*$_2$ (Cp* = $\eta^5$-C$_5$Me$_5$); scan rate: 0.200 V.s$^{-1}$.

UV-visible: UV-visible absorption spectra were measured with a Perkin–Elmer Lambda 19 UV visible spectrometer.

AFM of filled DHR 4, 5 and 6: All measurements were made using tapping mode operation with an Agilent Technologies 5500 microscope and a Nanosensor ‘PPP-NCL®’ TIP.

AFM of AuNPs-8: Dimension ICON (BRUKER), mode PEAK FORCE TAPPING (exclusivity BRUKER): every interaction between tip and sample is analyzed, allowing the benefits of Peak Force Tapping. Modulus, adhesion, dissipation, deformation are mapped simultaneously with topography. Individual curves can be examined and analyzed offline (SpeakForce Capture). Nanosensor tip used: ‘PFQNE-Al’.
**Preliminary studies:**

A triazolyl-cobalticinium (Co\textsuperscript{III}) model (benzyl-methyl-triazolycobalticinium hexafluorophosphate) proved to be an efficient hydride reservoir (±H\textsuperscript{−}). The stability of the reduction product (Co\textsuperscript{I}) and the reversibility of the system (Co\textsuperscript{I}/Co\textsuperscript{III}) is of utmost importance when similar procedures are envisaged for large nanosystems.

**Scheme S1:** Reaction of benzyl-methyl-triazolyl(\(\eta^5\)-C\textsubscript{5}H\textsubscript{4}Co\textsuperscript{III}Cp) with NaBH\textsubscript{4} giving the neutral benzylmethyl-(trz-\(\eta^4\)-C\textsubscript{5}H\textsubscript{5}Co\textsuperscript{I}Cp) product by addition of an hydride on the Cp ring, which then in the presence of a protonic source will react with H\textsuperscript{+} giving back the cationic product benzyl-methyl-triazolyl(\(\eta^5\)-C\textsubscript{5}H\textsubscript{4}Co\textsuperscript{III}Cp)\textsuperscript{+} (X\textsuperscript{−}) by production of molecular hydrogen. (Cp = \(\eta^5\)-C\textsubscript{5}H\textsubscript{5})

X\textsuperscript{−} = PF\textsubscript{6}\textsuperscript{−} or Cl\textsuperscript{−}. A single Co\textsuperscript{I} isomer is represented. For the structures of the four isomers, see Figure S1.

**Synthesis of benzylmethyl-(trz-\(\eta^4\)-C\textsubscript{5}H\textsubscript{5}Co\textsuperscript{I}Cp)**

The reduction of this ‘model’ monomer benzyl-triazolyl-cobalticenium hexafluorophosphate compound was studied in order to test if the triazole ligand is stable under these conditions. The orange cationic compound reacted in THF with NaBH\textsubscript{4} to produce the wine-red neutral triazolyl \(\eta^4\)-cyclopentadiene-cobalt(I)- \(\eta^5\)-cyclopentadienyl complex according to equation (S1).

\[
\text{Benzylmethyl-(trz-}\eta^5\text{-C}_5\text{H}_4\text{Co}^{\text{III}}\text{Cp})^\text{+}(\text{PF}_6)^\text{−} + \text{NaBH}_4\ (s) \rightarrow \text{benzylmethyl-(trz-}\eta^4\text{-C}_5\text{H}_5\text{Co}^{\text{I}}\text{Cp}) + \text{NaPF}_6\quad (\text{S1})
\]

The color of the orange solution changed to wine-red and the neutral product benzylmethyl-(trz-\(\eta^4\)-C\textsubscript{5}H\textsubscript{5}Co\textsuperscript{I}Cp) was extracted in distilled diethyl ether under N\textsubscript{2} in which NaPF\textsubscript{6} salt –also formed- was not soluble. The addition of the hydride anion is added onto four different carbons of the Cp ring, providing isomers (figure S1).
**Figure S1:** Addition of a hydride anion occurs onto four different positions: i) ipso, ii) 1,2 or iii) 1,3 position of the cyclopentadienyl ligand attached to the triazole or iv) onto the free cyclopentadienyl ligand.

**Experimental procedure**: 
A mixture of 1 equiv. of benzylmethyl(triazolyl)-\(\eta^5\)-C\(_5\)H\(_4\)Co\(\text{III}\)Cp(PF\(_6\)) (150 mg, 0.31mmol) with 1.1 equiv. of NaBH\(_4\) (12.71 mg, 0.34mmol) indistilled THF (20 mL) was stirred for 20 min at 0°C under N\(_2\). Then, the solvent was evaporated under vacuum, and distilled diethyl ether was added to solubilize the neutral product. After filtration under N\(_2\) and evaporation of the solvent, the product was obtained as a deep red powder; yield 95%. \(^1\)H NMR (1D, 1H) CDCl\(_3\), 400 MHz: \(\delta = 7.41–7.31\) (5H, CH of Ph), 7.13 and 6.66 (1H of trz), 5.51–5.34 (2H of Ph-CH\(_2\) and 2H of diene), 4.88–4.52 (5H of free Cp and 4H of substituted Cp when H\(^-\) is added to free Cp), 2.93–2.88 (2H of diene), 2.09–2.04 (2H free) ppm.
UV-Vis. studies

The UV-vis spectroscopic technique proved to be an excellent way to differentiate the cationic benzylmethyl(triazolyl)-η⁵-C₅H₄Co⁺Cp(PF₆) compound from the benzylmethyl-(trz-η⁴-C₅H₅Co⁺C₅) neutral compound. The hydride addition on the Cp ring of the cobalticenium complex leading to the neutral CpCo⁺η⁴-cyclopentadiene causes a push-pull electronic effect between the electron-withdrawing triazolyl group and the electron-donor CpCo⁺cyclopentadiene group. This results in a bathochromic shift (red shift) of the two absorption bands of the cationic compound at 350 nm and 420 nm in the UV-vis. spectrum that moved to 410 nm and 520 nm respectively. The absorption band at 410 nm is assigned to the d-d* transitions of the cobalt complex, whereas the band appearing at 530 nm is assigned to the d−d* transitions mixed with charge transfer from the ligand to the metal (L→MCT).

Figure S2: UV-vis. spectra of a) benzylmethyl(triazolyl)-η⁵-C₅H₄Co⁺Cp(PF₆) and b) the benzylmethyl-(trz-η⁴-C₅H₅Co⁺C₅) compounds (a single isomer is represented, for the isomer structures, see Figure S1.)
Mass spectrometry studies

The mass spectrum of benzylmethyl-(trz-η⁴-C₅H₅CoC₆H₄) was performed at the CESAMO on a AccuTOF- GcV (JEOL) that is a GC-TOF. The instrument is equipped with a sample introduction system named FD (Field Desorption).

Figure S3: FD MS of neutral benzylmethyl-(trz-η⁴-C₅H₅CoC₆H₄) (M = 347 Da), showing the successful addition of the hydride onto the complex benzylmethyl(triazolyl)- η⁵-C₅H₅CoIII Cp (PF₆) for which the calculated mass is 346 Da[1].
$^1$H NMR of benzylmethyl-(trz-$^\eta^4$-C$_5$H$_5$Co$^4$Cp)

NMR spectroscopy indicates the mixture of isomers.

**Figure S4:** $^1$H NMR (1D 1H), (CDCl$_3$ 400 MHz): δppm: 7.41-7.31 (5H, CH of Ph), 7.13 and 6.66 (1H of triazole), 5.51-5.34 (2H of Ph-CH$_2$ and 2H of diene), 4.88-4.52 (5H of Cp free and 4H of Cp sub. when H$^-$ is added to Cp free), 2.93-2.88 (2H of diene), 2.09-2.04 (2H free).
Oxidation of benzylmethyl-(trz-η⁴-C₅H₅Co) giving back the cationic compound benzylmethyl(triazolyl)-η⁵-C₅H₄Co³⁺Cp (PF₆).

a) ESI-MS

Interestingly, upon recording the ESI-MS of benzylmethyl-(trz-η⁴-C₅H₅Co), the molecular peak of the cationic compound was observed. This method used a flow of methanol that reacted with the neutral compound (-trz η⁴-C₅H₅Co) to give back the starting material (-trz η⁵-C₅H₄Co³⁺Cp). It is believed that the hydride of benzylmethyl-(trz-η⁴-C₅H₅Co), is protonated by minute water amount in methanol to give molecular hydrogen⁵ and cobalticenium hydroxide.

ESI MS Spectrum:

![ESI MS Spectrum](image)

**Figure S5: ESI MS(m/z):** Calcd for C19H17N3Co: 346.2916, Found: 346.0748.

The instrument is equipped with an ESI source, and spectra were recorded in the positive mode. The electrospray needle was maintained at 5000V and operated at room temperature. Samples were introduced by injection through a 20µL sample loop into a 4500 µL/min flow of methanol from the LC pump.
b) CV after one night under air

Cyclic voltammetry also confirmed the oxidation of benzylmethyl-(trz-η^4-C_5H_5Co^I(Cp)), back to benzylmethyl(triazolyl)- η^5-C_5H_4Co^{III}Cp(PF_6). The CV of benzylmethyl-(trz-η^4-C_5H_5Co^I(Cp)), was recorded in CH_2Cl_2 where two irreversible oxidation waves were found at 0.3 V and 0.65 V vs. [FeCp_2^*]^{+0} (corresponding to the oxidation of triazolycyclopentadiene-cobalt-Cp due to the preferential hydride reduction of the electron-poorer substituted ring and triazolycyclopentadienyl-cobalt-cyclopentadiene respectively). After evaporating the solvent overnight under air, THF was added, and the CV was recorded again in which the two distinct reduction waves of cationic cobalticenium (PF_6) appeared. However, scanning towards the positive potentials the two oxidation waves of benzylmethyl-(trz-η^4-C_5H_5Co^I(Cp)), were not found indicating again the reoxidation of the neutral product to cationic benzylmethyl(triazolyl)- η^5-C_5H_4Co^{III}Cp(PF_6) one and the reversibility of the system.

Figure S6: (a) CV in distilled CH_2Cl_2, (b) CV in THF after one night in air. Reference electrode: Ag; working and counter electrodes: Pt; scan rate: 0.2 V/s; supporting electrolyte: [n-Bu_4N][PF_6].

Oxidation of benzylmethyl-(trz-η^4-C_5H_5Co^I(Cp)) with HCl
After these observations the oxidation experiment was conducted. benzylmethyl-(trz-η⁴-C₅H₅Co¹Cp), in THF reacted with a diluted aqueous solution of 1.5 equiv. of HCl (aq.), and the color of the solution changed immediately from wine-red to light yellow (figure 1). The solvents were evaporated and the yellow sticky solid was all dissolved in H₂O showing that benzylmethyl(triazolyl)-η⁵-C₅H₅Co¹³Cp(Cl) was formed, and that the reaction was quantitative (equation S2). ¹H NMR in D₂O showed all the corresponding proton peaks of benzylmethyl(triazolyl)-η⁵-C₅H₅Co¹³Cp(Cl), whereas the UV-vis. spectrum showed the disappearance of the absorption bands at 410 nm and 530 nm and the appearance of the absorption bands of cationic triazolyl-cobalticenium.

\[
\text{benzylmethyl-trz-η⁴-C₅H₅Co¹Cp + HCl (aq.)} \rightarrow \text{benzylmethyl-trz-η⁵-C₅H₅Co¹³Cp(Cl) + H}_2 \quad (S2)
\]

![Figure S7: Photographs of a) benzylmethyl-(trz-η⁴-C₅H₅Co¹Cp) and b) benzylmethyl(triazolyl)-η⁵-C₅H₅Co¹³Cp(Cl) after addition of an aqueous HCl solution.

Experimental procedure for the synthesis of benzylmethyl(triazolyl)-η⁵-C₅H₅Co¹³Cp(Cl)

Benzylmethyl-(trz-η⁴-C₅H₅Co¹Cp) (15 mg, 0.04 mmol, 1 equiv.) was solubilized in 60 mL of THF. Then a 10 mL aqueous solution of HCl (0.05 mmol, 1.2 equiv.) was added dropwise, and the color gradually changed from deep red to light yellow giving back the cationic product benzylmethyl(triazolyl)-η⁵-C₅H₅Co¹³Cp(Cl) and molecular hydrogen. After stirring for 10 min. the mixture of solvents was evaporated. Solubilization in water, filtration and evaporation of the solvent gave benzylmethyl(triazolyl)-η⁵-C₅H₅Co¹³Cp(Cl) as a yellow waxy product in quantitative yield (14 mg). ¹H NMR (1D 1H), (D₂O, 400 MHz): δppm: 8.45 (1H, C of triazole), 7.47 (5H, C of Ar), 6.25 (2H, C of Cp sub.), 5.88 (2H, CH of Cp sub.), 5.70 (2H, Ar-CH2), 5.60 (5H, Cp free). UV-vis.: λ_max₁ = 350 nm, λ_max₂ = 410 nm.
$^1$H NMR of benzylmethyl(triazolyl)-$\eta^5$-$C_5H_4Co^{III}$Cp(Cl)

Figure S8: $^1$H NMR (1D 1H), (D$_2$O, 400 MHz): $\delta$ppm: 8.45 (1H, CH of triazole), 7.47 (5H, CH of Ar), 6.25 (2H, CH of Cp sub.), 5.88 (2H, CH of Cp sub.), 5.70 (2H, Ar-CH2), 5.60 (5H, Cp free).
Figure S9: Observation of an absorption band at $\lambda_{\text{max}}^1 = 350$ nm and an absorption shoulder at $\lambda_{\text{max}}^2 = 410$ nm corresponding to benzylmethyl(triazolyl)-$\eta^5$-C$_5$H$_4$Co$^{III}$Cp(Cl) product.
Formation of molecular hydrogen during oxidation of benzylmethyl-(trz-\(\eta^4\)-C\(_5\)H\(_5\)Co\(^{III}\)Cp).

The oxidation reaction was repeated in a sealed NMR tube in which benzylmethyl-(trz-\(\eta^4\)-C\(_5\)H\(_5\)Co\(^{III}\)Cp) was solubilized in deuterated THF; 1.1 equiv. of HPF\(_6\) (aq.) was added into the tube (equation S3). The color changed from red to orange instantaneously and the \(^1\)H NMR spectrum was recorded. Except of the typical proton peaks of benzylmethyl(triazolyl)- \(\eta^5\)-C\(_3\)H\(_4\)Co\(^{III}\)Cp(PF\(_6\)) formed and the disappearance of the proton peaks of the product benzylmethyl-(trz-\(\eta^4\)-C\(_5\)H\(_5\)Co\(^{III}\)Cp), a new proton peak at 4.6 ppm was observed and assigned to H\(_2\).

benzylmethyl-trz-\(\eta^4\)-C\(_5\)H\(_5\)Co\(^{III}\)Cp + HPF\(_6\) (aq.) \(\rightarrow\) benzylmethyl-trz-\(\eta^5\)-C\(_3\)H\(_4\)Co\(^{III}\)Cp(PF\(_6\))+ H\(_2\) \hspace{1cm} (S3)

**Figure S10:** \(^1\)H NMR (1D 1H), (THF, 300 MHz): In situ oxidation of benzylmethyl(triazolyl)- \(\eta^5\)-C\(_3\)H\(_4\)Co\(^{III}\)C\(_5\)H\(_6\) in a sealed NMR tube by addition of HPF\(_6\). The proton peak at 4.66 ppm corresponds to the hydrogen produced.

In the zoom is shown a) the area 5.0-4.0 ppm before the addition of HPF\(_6\) and b) after the addition of HPF\(_6\).

**Dendrimer filled DHR 4 (G\(_0\))**
Figure S11: Structure of filled DHR 4. A single isomer is represented for each branch; for the structures of the four isomer structures, see Figure S1. For 9 branches, there are 36 possible isomers.
Experimental procedure for DHR 4

The empty DHR 1 (PF$_6$)$^2$ (solid, 20 mg, 0.004 mmol, 1 equiv.) reacted with solid NaBH$_4$ (2 mg, 0.06 mmol, 13.5 equiv.) in distilled THF (30 mL) for 20 min at 0°C under N$_2$. The color of the solution changed from light yellow to deep red. Then, the solution was filtered under nitrogen. The solvent was evaporated in vacuo. The deep red solid was washed three times with 15 mL of distilled H$_2$O. The filled DHR 4 was obtained as a deep red powder in quantitative yield (13 mg). $^1$H NMR (1D, 1H), (CD$_3$CN, 400 MHz) of 4: $\delta_{ppm}$: 7.00, 6.83 and 6.51 (9H, CH of trz and 3H, CH of arom.core), 5.93-5.15 (18H of diene), 4.69-4.48 (45H of free Cp and 36H of substituted Cp when H$^-$ is added to free Cp), 4.34 (18H, SiCH$_2$-trz), 3.18-2.91 (18H of diene), 2.33-2.04 (18H free), 1.61 (18H, CH$_2$CH$_2$CH$_2$Si), 1.23 (18H, CH$_2$CH$_2$CH$_2$Si), 0.54 (18H, 18H, CH$_2$CH$_2$CH$_2$Si), -0.05 (54H, Si(CH$_3$)$_2$). $^{13}$C NMR (1D, 1H), (CD$_3$COCD$_3$, 100 MHz) of 4: $\delta_{ppm}$: 150.62 (Cq of arom.core), 148.41 and 147.82 (Cq of trz), 127.57 and 121.83 (CH of trz), 124.28 (CH of arom.core), 80.02-72.96 (CH of Cp free, CH of Cp sub., Cq of Cp sub. and CH of diene), 48.48-39.81 (CqCH$_2$CH$_2$CH$_2$Si, CqCH$_2$CH$_2$CH$_2$Si, trz-CH$_2$Si, CH of diene and CH$_2$ of Cp), 19.51-15.53 (CqCH$_2$CH$_2$CH$_2$Si and CqCH$_2$CH$_2$CH$_2$Si), -3.62 (Si(CH$_3$)$_2$). UV-vis.: $\lambda_{max1}$ = 410 nm, $\lambda_{max2}$ = 537 nm. ESI MS of 4 (C$_{171}$H$_{222}$Si$_9$N$_{27}$Co$_9$(OH)$_3$): calc. 3490.0 Da; found. 3491.0 Da.
Figure S12: An absorption band is observed at $\lambda_{\text{max}}_1 = 410$ nm and an absorption shoulder appears at $\lambda_{\text{max}}_2 = 537$ nm corresponding to the product 4.
Figure S13: IR(KBr) of DHR 4: 3110, 2928, 2869, 2741, 1694, 1251, 1153, 1050 (cm^{-1}).
The method has a limit of 2000 m/z Da for the molar mass, m being the mass and z the charge. When the mass is large, the product is found within this limit, in a form of ‘monocharged’ fragments (z = 1) or ‘dicharged’ entities (z = 2). The actual mass m is calculated as: M = m/z., i.e. the double of the m/z peak. For the molecular peak, the calculated M value is 3490.0 Da that is observed below as major peaks at 1745.0 and 1745.5 as expected corresponding to 3490.0 Da and 3491.0 Da respectively, fully conforming the DHR structure of 4.

Figure S14: ESI MS of 4 (C_{171}H_{223}Si_{9}N_{27}Co_{9}(OH)_{3}): calc. 3490.0 Da; found. 3491.0 Da
AFM of DHR 4

AFM microscopy of 4 (packages of several dendrimers together) shows the average height on the mica surface of $h = 0.45$ nm (presenting another bilayer at $h' = 1.2$ nm due to the small size of dendrimer 4). The following generations ($G_1$ and $G_2$) present this phenomenon to a much lesser extent.

Figure S15: AFM topography image of 4 on a mica surface.
Figure S16: Statistical height distribution of 4.

Figure S17: 3D AFM topography image
**1H NMR of DHR 4**

**Figure S18:** \(^1H\) NMR (1D, 1H), (CD\(_3\)CN, 400 MHz) of 4: \(\delta_{ppm}: 7.00, 6.83\) and 6.51 (9H, CH of trz and 3H, CH of arom.core), 5.93-5.15 (18H of diene), 4.69-4.48 (45H of free Cp and 36H of substituted Cp when H is added to free Cp), 4.34 (18H, Si\(CH_2\)-trz), 3.18-2.91 (18H of diene), 2.33-2.04 (18H free), 1.61 (18H, \(CH_2CH_2CH_2Si\)), 1.23 (18H, \(CH_2CH(CH_2)Si\)), 0.54 (18H, 18H, \(CH_2CHCHSi\)), -0.05 (54H, Si(\(CH_3\))\(_2\)).
$^{13}$C NMR of DHR 4

Figure S19: $^{13}$C NMR (1D, 1H), (CD$_3$COCD$_3$, 100 MHz) of 4: $\delta_{ppm}$: 150.62 (Cq of arom.core), 148.41 and 147.82 (Cq of trz), 127.57 and 121.83 (CH of trz), 124.28 (CH of arom.core), 80.02-72.96 (CH of Cp free, CH of Cp sub., Cq of Cp sub. and CH of diene), 48.48-39.81 (CqCH$_2$CH$_2$Si, CqCH$_2$CH$_2$Si, trz-CH$_2$Si, CH of diene and CH$_2$ of Cp), 19.51-15.53 (CqCH$_2$CH$_2$Si and CqCH$_2$CH$_2$Si), -3.62 (Si(CH$_3$)$_2$).

HSQC 2D NMR spectroscopy of DHR 4
Figure S20: HSQC 2D NMR spectrum of 4.

Dendrimer filled DHR 5 (G₁)
Figure S21: Structure of filled DHR 5. A single isomer is represented on each branch. For the 4 possible isomers on each branch, see Figure S1. With 27 branches, there are 108 possible isomers.

Experimental procedure for 5
The empty DHR 2(PF₆) solid (25 mg, 0.002 mmol, 1 equiv.) reacted with NaBH₄ (3 mg, 0.08 mmol, 40.5 equiv.) in distilled THF (20 mL) for 20 min at 0°C under N₂. The color of the solution changed from colorless to deep red. Then, the solution was filtered under nitrogen. The solvent was evaporated in vacuo. The deep red solid was washed three times with 10 mL of distilled H₂O. The filled DHR 5 was obtained as a deep red powder in quantitative yield (21 mg). ¹H NMR (1D, 1H), (CD₃COCD₃, 400 MHz) of 5: δ ppm: 7.20, 7.05 6.92 and 6.63 (27H, CH of trz and 39H, CH of arom.core), 5.84-5.31 (54H of diene), 4.94-4.72 (135H of free Cp and 108H of substituted Cp when H⁻ is added to free Cp), 4.53 (54H, SiCH₂-trz), 3.38 (18H, SiCH₂O) 3.25-2.84 (54H of diene), 2.50-2.02 (54H free), 1.69 (72H, CH₂CH₂CH₂Si), 1.22 (72H, CH₂CH₂CH₂Si), 0.65 (72H, 18H, CH₂CH₂CH₂Si), 0.06 (216H, Si(CH₃)₂). ¹³C NMR (1D, 1H), (CD₃COCD₃, 75 MHz) of 5: δ ppm: 160.05 (arom. OCq), 139.95 and 134.83 (Cq of trz and Cq of aromatic core), 129.48-125.32 (CH of trz and CH aromatic), 81.96-78.30 (CH of Cp free, CH of Cp sub., Cq of Cp sub. and CH of diene), 68.10 (CH₂OAr), 49.87-41.73 (CqCH₂CH₂CH₂Si, CqCH₂CH₂CH₂Si, trz-CH₂Si, CH of diene and CH₂ of Cp), 24.34-15.21 (CqCH₂CH₂CH₂Si and CqCH₂CH₂CH₂Si), -5.88 (Si(CH₃)₂). UV-vis.: λ max1 = 415 nm, λ max2 = 527 nm.

UV-visible spectrum of DHR 5
Figure S22: An absorption shoulder is observed at $\lambda_{\text{max}}_1 = 415$ nm and an absorption shoulder appears at $\lambda_{\text{max}}_2 = 527$ nm corresponding to the product 5.
Figure S23: IR (KBr) of 5: 3100, 2956, 2924, 2872, 1651, 1249, 1152, 1050 (cm$^{-1}$).

AFM studies of DHR 5
Figure S24: AFM topography image of 5 on a mica surface.

Figure S25: Statistical height distribution of 5.

$^1$H NMR of DHR 5
Figure S26: $^1$H NMR (1D, 1H), (CD$_3$COCD$_3$, 400 MHz) of 5: $\delta$ ppm: 7.20, 7.05 6.92 and 6.63 (27H, CH of trz and 39H, CH of arom.core), 5.84-5.31 (54H of diene), 4.94-4.72 (135H of free Cp and 108H of substituted Cp when H is added to free Cp), 4.53 (54H, SiCH$_2$-trz), 3.38 (18H, SiCH$_2$O ) 3.25-2.84 (54H of diene), 2.50-2.02 (54H free), 1.69 (72H, CH$_2$CH$_2$CH$_2$Si), 1.22 (72H, CH$_2$CH$_2$CH$_2$Si), 0.65 (72H, 18H, CH$_2$CH$_2$CH$_2$Si), 0.06 (216H, Si(CH$_3$)$_2$).

$^{13}$C NMR of DHR 5
Figure S27: $^{13}$C NMR (1D, 1H), (CD$_3$COCD$_3$, 100 MHz) of 5: $\delta_{ppm}$: 160.05 (arom. OCq), 139.95 and 134.83 (Cq of trz and Cq of aromatic core), 129.48-125.32 (CH of trz and CH aromatic), 81.96-78.30 (CH of Cp free, CH of Cp sub., Cq of Cp sub. and CH of diene), 68.10 (CH$_2$OAr), 49.87-41.73 (CqCH$_2$CH$_2$CH$_2$Si, CqCH$_2$CH$_2$CH$_2$Si, trz-CH$_2$Si, CH of diene and CH$_2$ of Cp), 24.34-15.21 (CqCH$_2$CH$_2$CH$_2$Si and CqCH$_2$CH$_2$CH$_2$Si), -5.88 (Si(CH$_3$)$_2$).

HSQC 2D NMR spectroscopy of DHR 5
Figure S28: HSQC 2D NMR spectrum of 5.

Dendrimer filled DHR 6

Experimental procedure for 6
The empty DHR 3\((\text{PF}_6)\) solid (20 mg, \(0.4 \times 10^{-3}\) mmol, 1 equiv.) reacted with NaBH\(_4\) (1.9 mg, 0.05 mmol, 121.5 equiv.) in distilled THF (20 mL) for 20 min at 0°C under \(\text{N}_2\). The color of the solution changed from colorless to deep red. Then, the solution was filtered under nitrogen. The solvent was evaporated \textit{in vacuo}. The deep red solid was washed three times with 10 mL of distilled H\(_2\)O. The filled DHR 6 was obtained as a deep red powder in quantitative yield (14 mg). UV-vis.: \(\lambda_{\text{max}1} = 408\) nm, \(\lambda_{\text{max}2} = 524\) nm.

**AFM studies of DHR 6**

![AFM topography image of 6 on a mica surface.](image)

**Figure S29:** AFM topography image of 6 on a mica surface.

![Statistical height distribution of 6.](image)

**Figure S30:** Statistical height distribution of 6.

**UV-visible spectrum of DHR 6**
Figure S31: An absorption shoulder is observed at $\lambda_{\text{max}_1} = 408$ nm, and another absorption shoulder appears at $\lambda_{\text{max}_2} = 524$ nm, both corresponding to the product 6. 

IR (KBr) of DHR 6
Figure S32: IR (KBr) of 6: 3150, 2960, 2919, 2855, 2264, 1641, 1460, 1106, 1050 (cm$^{-1}$).

Dendrimer empty DHR 1 (Cl$^-$)
Figure S33: Structure of empty DHR 1(Cl−)
Experimental procedure for DHR 1(Cl)

The filled DHR 4 (10 mg, 0.003 mmol, 1 equiv.) was solubilized in 10 mL of THF. Then a 10 mL aqueous solution of HCl (0.03 mmol, 11 equiv.) was added dropwise, and the color gradually changed from deep red to light yellow giving back the empty DHR 1(Cl) and molecular hydrogen. After stirring for 10 min. the mixture of solvents was evaporated. Solubilization in water, filtration and evaporation of the solvent gave DHR 1(Cl) as a yellow waxy product in quantitative yield (11 mg). The empty DHR 1(Cl) is now water-soluble. $^1$H NMR (1D 1H), (D$_2$O, 400 MHz) : $\delta$ppm: 8.39 (9H, CH of trz), 6.28 (18H, CH of Cp sub.), 5.91 (18H, CH of Cp sub.), 5.61 (45H, CH of Cp), 4.10 (18H, SiCH$_2$-trz), 1.34 (18H, CH$_2$CH$_2$CH$_2$Si), 0.88 (18H, CH$_2$CH$_2$CH$_2$Si), 0.47 (18H, 18H, CH$_2$CH$_2$CH$_2$Si), -0.04 (54H, Si(CH$_3$)$_2$). UV-vis.: $\lambda_{max1}$ = 356 nm, $\lambda_{max2}$ = 412 nm (shoulder).
$^1$H NMR spectroscopy of DHR 1(Cl)

Figure S34: $^1$H NMR spectrum of 1(Cl) (1D 1H), (D$_2$O, 400 MHz) : $\delta_{ppm}$: 8.39 (9H, CH of trz), 6.28 (18H, CH of Cp sub.), 5.91 (18H, CH of Cp sub.), 5.61 (45H, CH of Cp), 4.10 (18H, SiCH$_2$-trz), 1.34 (18H, CH$_2$CH$_2$CH$_2$Si), 0.88 (18H, CH$_2$CH$_2$CH$_2$Si), 0.47 (18H, 18H, CH$_2$CH$_2$CH$_2$Si), -0.04 (54H, Si(CH$_3$)$_2$).

UV-visible spectrum of DHR 1(Cl)
Figure S35: An absorption band is observed at $\lambda_{\text{max}_1} = 356$ nm and an absorption shoulder appears at $\lambda_{\text{max}_2} = 412$ nm corresponding to the product $\text{I}$(Cl).

IR (KBr) of DHR $\text{I}$(Cl)
Figure S36: IR (KBr) of 1(Cl): 3102, 2923, 2855, 2337, 1649, 1447, 1260 (cm$^{-1}$).

Dendrimer empty 2(Cl)
Figure S37: Structure of 2(Cl).

Experimental procedure for 2(Cl)
The filled DHR 5 (20 mg, 0.002 mmol, 1 equiv.) was solubilized in 10 mL of THF. Then a 10 mL aqueous solution of HCl (0.06 mmol, 33 equiv.) was added dropwise, and the color gradually changed from deep red to light yellow giving back the empty DHR 2(Cl) and molecular hydrogen. After stirring for 10 min. the mixture of solvents was evaporated. Solubilization in water, filtration and evaporation of the solvent gave DHR 2(Cl) as a yellow waxy product in quantitative yield (25 mg). The empty DHR 2(Cl) is now water-soluble. 1H NMR (1D 1H), (D2O, 400 MHz): δ ppm: 8.28 (27H, CH of trz), 7.00, 6.66 (39H, CH of arom.core), 6.09 (54H, CH of Cp sub.), 5.72 (54H, CH of Cp sub.), 5.39 (135H, CH of Cp), 3.90 (54H, SiCH2-trz), 3.43 (18H, SiCH2O), 1.44 (72H, CH2CH2CH2Si), 0.94 (72H, CH2CH2CH2Si), 0.39 (72H, 18H, CH2CH2CH2Si), -0.14 (216H, Si(CH3)2). UV-vis.: λmax1 = 357 nm, λmax2 = 410 nm (shoulder).

UV-visible spectrum of DHR 2(Cl)
Figure S38: An absorption band is observed at $\lambda_{\text{max}}_1 = 357$ nm, and an absorption shoulder appears at $\lambda_{\text{max}}_2 = 410$ nm corresponding to the product 2(Cl).

$^1$H NMR of DHR 2(Cl)
Figure S39: $^1$H NMR spectrum of 2(Cl) (1D 1H), (D$_2$O, 400 MHz): 8.28 (27H, CH of trz), 7.00, 6.66 (39H, CH of arom.core), 6.09 (54H, CH of Cp sub.), 5.72 (54H, CH of Cp sub.), 5.39 (135H, CH of Cp), 3.90 (54H, SiCH$_2$-trz), 3.43 (18H, SiCH$_2$O), 1.44 (72H, CH$_2$CH$_2$CH$_2$Si), 0.94 (72H, CH$_2$CH$_2$CH$_2$Si), 0.39 (72H, 18H, CH$_2$CH$_2$CH$_2$Si), -0.14 (216H, Si(CH$_3$)$_2$).

Dendrimer empty DHR 3(Cl)
Experimental procedure for DHR 3 (Cl)

The filled DHR 6 (15 mg, 0.4 x 10^{-3} mmol, 1 equiv.) was solubilized in 5 mL of THF. Then a 10 mL aqueous solution of HCl (0.04 mmol, 97 equiv.) was added dropwise, and the color gradually changed from deep red to light yellow giving back the empty DHR 3(Cl) and molecular hydrogen. After stirring for 10 min. the mixture of solvents was evaporated. Solubilization in water, filtration and evaporation of the solvent gave DHR 3(Cl) as a yellow waxy product in quantitative yield (15 mg). The empty DHR 3(Cl) is now water-soluble. \(^1\)H NMR (1D 1H), (D\(_2\)O, 400 MHz): \(\delta_{\text{ppm}}\) : 8.35 (81H, CH of trz), 7.09, 6.76 (147H, CH arom.), 6.18 (162H, CH of Cp sub.), 5.80 (162H, CH of Cp sub.), 5.49 (405H, CH of Cp), 4.02 (162H, SiCH\(_2\)-trz), 3.51 (72H, SiCH\(_2\)O), 1.51 (234H, CH\(_2\)CH\(_2\)CH\(_2\)Si), 1.00 (234H, CH\(_2\)CH\(_2\)CH\(_2\)Si), 0.51 (234H, 18H, CH\(_2\)CH\(_2\)CH\(_2\)Si), -0.13 (702H, Si(CH\(_3\))\(_2\)). UV-vis.: \(\lambda_{\text{max1}} = 355 \text{ nm}, \lambda_{\text{max2}} = 412 \text{ nm (shoulder)}\).
**1H NMR of DHR 3(Cl)**

Figure S41: 1H NMR spectrum of 3 (Cl) (1D 1H), (D$_2$O, 400 MHz); $\delta_{ppm}$: 8.35 (81H, CH of trz), 7.09, 6.76 (147H, CH arom.), 6.18 (162H, CH of Cp sub.), 5.80 (162H, CH of Cp sub.), 5.49 (405H, CH of Cp), 4.02 (162H, SiCH$_2$-trz), 3.51 (72H, SiCH$_2$O), 1.51 (234H, CH$_2$CH$_2$CH$_2$Si), 1.00 (234H, CH$_2$CH$_2$CH$_2$Si), 0.51 (234H, 18H, CH$_2$CH$_2$CH$_2$Si), -0.13 (702H, Si(CH$_3$)$_2$).
Figure S42: An absorption band observed at $\lambda_{\text{max}_1} = 355$ nm and an absorption shoulder at $\lambda_{\text{max}_2} = 412$ nm corresponding to product 3 (Cl).
AuNPs-7 and AuNPs-8

General information:

1) The **AuNPs-7** and **AuNPs-8** were synthesized according to the following equation:

\[
\text{Den-(Trz-Co}^1\text{H)}_n + \frac{2n}{3} \text{HAuCl}_4 \rightarrow \text{Den-(Trz-Co}^{\text{III}}\text{Cl)}_n, 2\frac{n}{3}\text{Au}^0 + \frac{5n}{3} \text{HCl (aq)}
\]

2) After the reaction the pH was found to be acidic: **pH = 5-6**

![Figure S43](image)

**Figure S43:** Schematic representation of capsules containing AuNPs-7 or AuNPs-8.

3) Upon synthesis, the color immediately became **pink-red**:

![Figure S45](image)

**Figure S45:** Photograph of AuNPs-8.

4) A test has been performed using a flux of hydrogen gas into a solution of HAuCl₄, and reduction of Au(III) to Au(0) started to occur after 15 minutes, proving that the hydride transfer from filled DHRs 4 and 5 to Au(III) is responsible for the Au(III) reduction to AuNPs. The consumption of both starting materials stoichiometrically as well as the remaining acidic pH confirm the above statement.
**Experimental procedure of AuNPs-7**

The filled DHR 4 (8 mg, 0.002 mmol, 1 equiv.) was dissolved in 1.5 mL THF and was added dropwise at 0°C into a solution of HAuCl₄ (4.7 mg, 0.012 mmol, 18 equiv.) in 35 mL of H₂O/THF 3:1, under vigorous stirring. The color instantaneously changed from yellow to pink red, and stirring was continued for another 10 min. The mixture was concentrated *in vacuo* to 25 mL. UV-vis.: \( \lambda_{\text{max}} = 351 \text{ nm} \), SPR: \( \lambda_{\text{max}} = 534 \text{ nm} \). TEM: \( d_{\text{AuNPs}} = 4.5 \pm 0.5 \text{ nm} \), \( d_{\text{Capsules}} = 45 \pm 7 \text{ nm} \).

**Experimental procedure of AuNPs-8**

The filled DHR 5 (10 mg, \( 0.8 \times 10^{-3} \text{ mmol} \), 1 equiv.) was dissolved in 1 mL THF and was added dropwise at 0°C in a solution of HAuCl₄ (5.7 mg, 0.014 mmol, 18 equiv.) in 40 mL of H₂O/THF 3:1, under vigorous stirring. The color instantaneously changed from yellow to pink red, and stirring was continued for another 10 min. The mixture was concentrated *in vacuo* to 30 mL. UV-vis.: \( \lambda_{\text{max}} = 348 \text{ nm} \), SPR: \( \lambda_{\text{max}} = 527 \text{ nm} \). TEM: \( d_{\text{AuNPs}} = 3 \pm 0.5 \text{ nm} \), \( d_{\text{Capsules}} = 85 \pm 20 \text{ nm} \).
Figure S46: UV-vis. spectrum of AuNPs-7.

$\lambda_{\text{max}} = 347$ nm, SPR: $\lambda_{\text{max}} = 534$ nm
TEM of AuNPs-7

Figure S47: TEM image of AuNPs-7. The diameter of the AuNPs is: $d_{\text{AuNPs}} = 4.5 \pm 0.5 \text{ nm}$, and that of the capsules is: $d_{\text{Capsules}} = 45 \pm 7 \text{ nm}$. 
Size distribution of AuNPs-7

Figure S48.
S49: UV-vis. spectrum of AuNPs-8.

$\lambda_{\text{max}} = 348$ nm, SPR: $\lambda_{\text{max}} = 527$ nm
Size distribution of AuNPs-8

Figure S50.
AFM studies of AuNPs-8

Figure S51: AFM image (height sensor) of AuNPs-8 at a larger scale (10 µm) where packages of capsules are also observed.
Figure S52: Calculation of distinct capsules’ diameter and height containing AuNPs-8 by AFM topography image ($d_{\text{Capsules}} = 103 \pm 14 \text{ nm}$, $h_{\text{Capsules}} = 33 \pm 3 \text{ nm}$) which is in agreement with TEM measurements ($d_{\text{Capsules}} = 85 \pm 20 \text{ nm}$).

AuNPs-9
General information:

1) The AuNPs-9 were synthesized according to the following equation:

\[
\text{Den-(Trz-Co}^I\text{H)}_n + 2n/3 \text{AuCl}_3 \rightarrow \text{Den-(Trz-Co}^{III}\text{Cl)}_n, 2n/3\text{Au}^0 + n \text{HCl (THF)}
\]

![Schematic representation of capsules containing AuNPs-9.](image)

**Figure S53:** Schematic representation of capsules containing AuNPs-9.

2) The color changed immediately from yellow to **purple**:

![Photo of AuNPs-9.](image)

**Figure S54:** Photo of AuNPs-9.

3) The fact that the reaction happens instantaneously confirms that the hydride transfer reduces Au(III) (in this case there is no acidic protons).
Experimental procedure for AuNPs-9

The filled DHR 5 (10 mg, 0.8 x 10^{-3} mmol, 1 equiv.) was dissolved in 1 mL THF and added dropwise at 0°C into a solution of AuCl₃ (4.4 mg, 0.014 mmol, 18 equiv.) in 35 mL of THF, under vigorous stirring. The color instantaneously changed from yellow to violet, and stirring was continued for another 10 min. The mixture was kept in a closed flask. UV-vis.: λ_{max} = 350 nm, SPR: λ_{max} = 571 nm. TEM: d_{AuNPs} = 33 ± 3 nm, d_{Capsules} = 220 ± 40 nm.
Size distribution of AuNPs-9

![Size distribution of AuNPs-9](image)

Figure S55
**AuNPs-10**

**General information**

For comparison a common reductant NaBH₄ was used to reduce HAuCl₄ to give **AuNPs-10** that were stabilized by the empty DHR 2 (Cl⁻).

The reaction happened instataneously and the color changed immediately from yellow to grey-purple.

![Figure S56: Photo of AuNPs-10](image)

From TEM analysis capsules were not observed, whereas comparative stability tests were performed.

The same concentration was used as in case of **AuNPs-8**, but under these conditions **AuNPs-10** flocculated. They could be reversibly re-dissolved, however.

The pH after the reaction becomes pH = 7.
Experimental procedure for AuNPs-10

The empty DHR 2(Cl) (10 mg, 0.8 x 10⁻³ mmol, 1 equiv.) was dissolved in 4 mL H₂O and was added in a solution of HAuCl₄ (5.7 mg, 0.014 mmol, 18 equiv.) in 25 mL of H₂O, under vigorous stirring. Then a solution of NaBH₄ (1.7 mg, 0.04 mmol, 54 equiv.) in 1 mL H₂O was added dropwise under vigorous stirring. The color instantaneously changed from yellow to grey-purple and stirring was continued for another 10 min. UV-vis.: λ_max = 348 nm, SPR: λ_max = 535 nm. TEM: d_{AuNPs} = 5 ± 1 nm.
TEM of AuNPs-10

Figure S57: TEM image of AuNPs-10. The calculated diameter was found: $d = 5 \pm 1$ nm.
Size distribution of AuNPs-10

![Size distribution of AuNPs-10](image)

Figure S58

UV-vis. of AuNPs-10

![UV-vis. spectrum of AuNPs-10](image)

Figure S59: UV-vis. spectrum of AuNPs-10.

$\lambda_{\text{max}} = 348 \text{ nm}$, SPR: $\lambda_{\text{max}} = 535 \text{ nm}.$
Stability comparison of AuNPs-8 and AuNPs-10

1) Time

The **AuNPs-8** were stable for several months. Precipitation did not occur, and the UV-vis. spectrum after several months showed the same plasmon band as when they were freshly prepared.

**UV-vis of AuNPs-8 after 6 months**

![Figure S60: UV-vis. spectrum of AuNPs-8.](image)

$\lambda_{\text{max}} = 350 \text{ nm}$, SPR: $\lambda_{\text{max}} = 529 \text{ nm}$.

On the other hand, **AuNPs-10** could not be re-dissolved after one month time, showing that their stability is weaker comparing to capsules containing **AuNPs-8**.
2) Temperature

Both AuNPs-8 and AuNPs-10 were heated at 100° C during one hour. After 30 min, AuNPs-10 were irreversibly precipitated, whereas in the case of AuNPs-8 nothing changed (color or solubility). The UV-vis. spectrum was recorded after heating AuNPs-8 giving the same plasmon band as before heating.

Figure S61: Photograph of AuNPs-8 and AuNPs-10 after heating at 100°C for 1h.
UV-vis. spectrum of AuNPs-8 after heating at 100°C during 1h

\[ \lambda_{\text{max}} = 348 \text{ nm}, \quad \text{SPR: } \lambda_{\text{max}} = 526 \text{ nm}. \]
AuNPs-11

A mixture of empty DHR 2 (PF₆⁻) and AuCl₃ was reduced by NaBH₄ resulting in the simultaneous reduction of dendrimer 2 (PF₆⁻) to the filled DHR 5 and Au(III) to Au(0). The color changed from yellow to purple (instantaneous reduction of Au(III)) and subsequently to red when the empty DHR was reduced to filled DHR (AuNPs-11). After 5 min, the AuNPs-11 flocculated which is taken into account by the absence of electrostatic stabilization and could be reversibly dissolved by stirring the reaction medium. These nanoparticles were kept under nitrogen.

Figure S63: Synthesis of AuNPs-11.

Figure S64: Photo of AuNPs-11.
Experimental procedure for AuNPs-11

The empty DHR $2\text{PF}_6$ (8 mg, $0.5 \times 10^{-3}$ mmol, 1 equiv.) and AuCl$_3$ (2.8 mg, 0.009 mmol, 18 equiv.) were put in a flask, and 10 mL of distilled THF was added under nitrogen. Then NaBH$_4$ (2 mg, 0.05 mmol, 100 equiv.) was added, and the solution was left stirring vigorously for 10 min. The color instantaneously changed from yellow to purple and then gradually became red suggesting first the reduction of Au$^{III}$ and then gradually the reduction of cobalticenium. The solution was quickly filtered. The flocculation of AuNPs-11 was observed after 5 min. UV-vis.: $\lambda_{\text{max}} = 408$ nm (shoulder), SPR: $\lambda_{\text{max}} = 519$ nm. TEM: $d_{\text{AuNPs}} = 4 \pm 0.5$ nm.
**Figure S65:** UV-vis. spectrum of AuNPs-11. Absorption shoulder: $\lambda_{\text{max}} = 408$ nm. SPB: $\lambda_{\text{max}} = 519$ nm.
Figure S66: TEM image of flocculated AuNPs-11.

Size distribution of AuNPs-11
Figure S67
Oxidation of AuNPs-11 by HCl (AuNPs-12)

Experimental procedure for AuNPs-12

To the solution of AuNPs-11 (S66) another 20mL of THF was added. Then a solution of HCl (0.02 mmol, 33 equiv.) in 10 mL of H₂O was added dropwise at 0°C under vigorous stirring and stirring continued for 10 min. AuNPs-12 were obtained in light orange/purple color. UV-vis.: $\lambda_{\text{max}} = 356$ nm (shoulder), SPR: $\lambda_{\text{max}} = 513$ nm. TEM: $d_{\text{AuNPs}} = 4 \pm 0.5$ nm.
TEM of AuNPs-12

**Figure S68:** TEM image of AuNPs-12 stabilized by the cationic empty DHR 2 (Cl\(^-\)). It is clearly seen that the re-arrangement of the AuNPs into capsules occurred when the filled DHR 5 changed back to empty DHR 2 (Cl\(^-\)).
Size distribution of AuNPs-12

Figure S69
Figure S70: UV-vis. spectrum of AuNPs-12. Absorption: $\lambda_{\text{max}} = 357$ nm. SPB: $\lambda_{\text{max}} = 513$ nm.

References


