

# A polycationic dendrimer as noncovalent support for anionic organometallic complexes†

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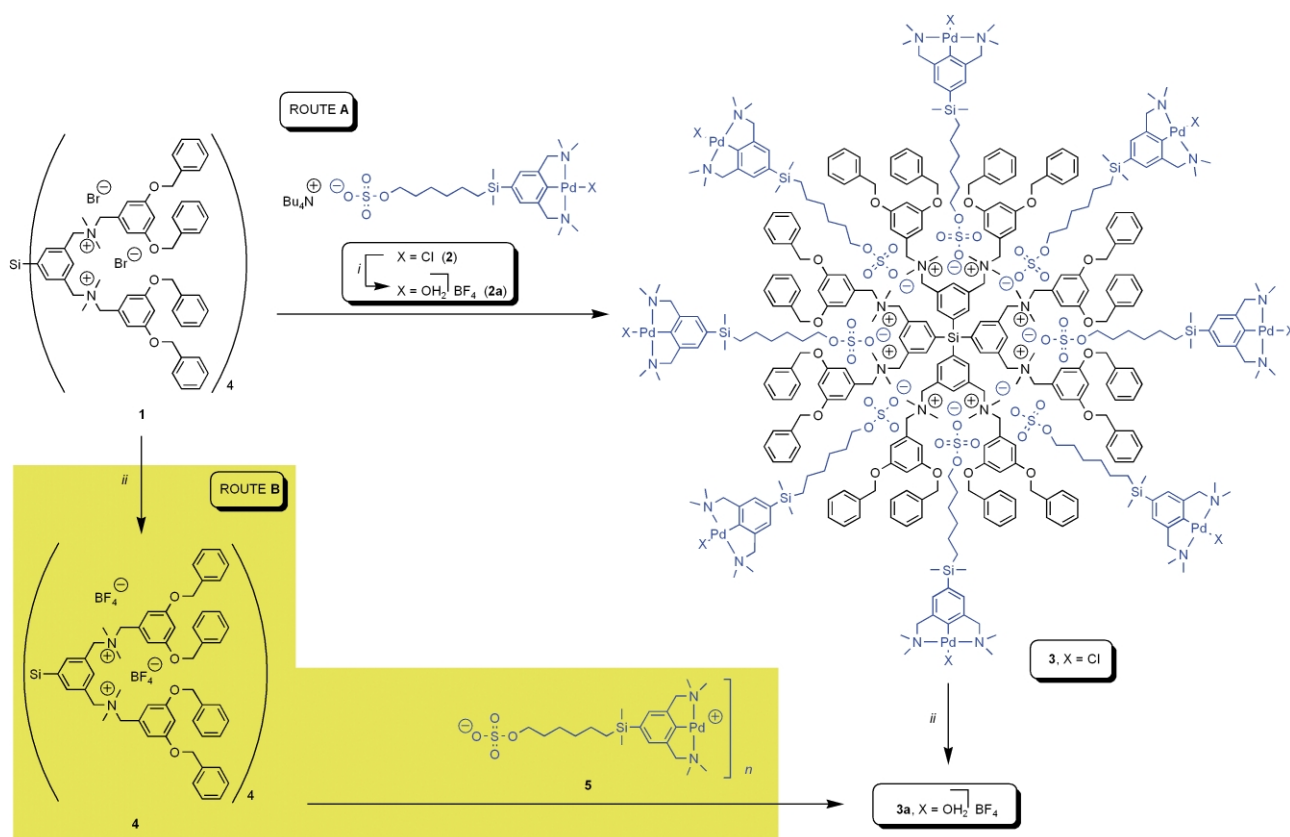
Polycationic dendrimer **1** forms a well-defined, stoichiometric assembly with eight anionic metal complexes; this assembly is successfully applied as a Lewis acidic catalyst which performs comparably to the unsupported metal complex.

Recycling and reuse of transition metal catalysts are key issues of homogeneous catalytic processes in terms of environmental impact and of both commercial viability and industrial applicability. These aspects highly benefit from an efficient retrieval of both precious metal streams and of (chiral) ligands and auxiliaries. A popular approach toward these aims is to covalently attach a known homogeneous catalyst to a macroscopic support, thereby facilitating recuperation by means of filtration or precipitation.<sup>1</sup> Several supports have been used for this approach including insoluble (silica, alumina, *etc.*) and soluble macromolecules (linear poly(olefines), dendrimers, hyperbranched polymers, *etc.*).

† Electronic supplementary information (ESI) available: <sup>1</sup>H NMR data (including *T*<sub>1</sub> and *T*<sub>2</sub> data) and IR data for **1**, **2**, **2a**, **3**, **3a**, **4** and **5**. ESI-MS and elemental analysis data for **3**. Space-filling model of the calculated molecular structure of **3**. See <http://www.rsc.org/suppdata/cc/b2/b201491b/>

Here, we present a new approach for the noncovalent attachment of transition metal complexes to a soluble, dendritic support.<sup>2,3</sup> A noncovalent manner of attachment could result in a reversible assembly from which both the support and the complex can be retained separately. Intrinsically, such a reversible binding mode would allow facile functionalization, defunctionalization and refunctionalization of the dendritic support. Recently, we described polycationic dendrimer **1** that can reversibly bind a predefined number of anionic (in)organic substrates (Scheme 1).<sup>4</sup> This dendrimer is composed of a rigid octacationic core, derived from tetraphenylsilane, which is decorated with a soft, hydrophobic shell of Fréchet-type dendritic wedges. We have now investigated the interaction of the anionic palladium complex **2** with dendrimer **1** (Scheme 1).

Palladium(II) complex **2** is derived from the mono-anionic pincer-type ligand [C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-2,6</sub>] (= NCN).‡ A sulfate-terminated aliphatic tail was connected to the NCN ligand *via* a silane linkage.<sup>5</sup> Binding of the stable tetrabutylammonium sulfate **2** to octacationic dendrimer **1** was performed *via* anion exchange in a biphasic system (H<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub>). Compounds **2** and **1** were dissolved in dichloromethane in an 8.1 : 1 molar ratio, respectively, after which this



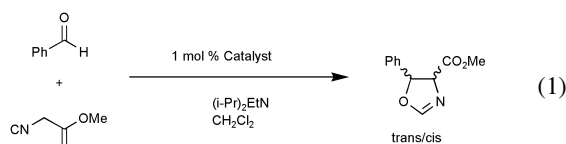
Scheme 1 Synthesis of metallodendritic assemblies **3** and **3a**. Reagents and conditions: i, 1 equiv. AgBF<sub>4</sub>, wet acetone; ii, 8 equiv. AgBF<sub>4</sub>, wet acetone.

phase was washed with deionized water to remove formed  $\text{NBu}_4\text{Br}$ . Excess of **2** was removed *via* dialysis of the organic phase using a commercially available dialysis membrane,<sup>6</sup> resulting in the isolation of the pure, metallodendritic assembly **3** in 99% yield (Scheme 1; route A).<sup>†</sup>

The  $^1\text{H}$  NMR spectrum of **3** in  $\text{CD}_2\text{Cl}_2$  shows the presence of the cationic dendritic host and the anionic  $\text{Pd}^{\text{II}}$  guests in a 1:8 molar ratio. In addition,  $^1\text{H}$  NMR titration of **1** with **2** confirms the binding of a maximum of eight equivalents of **2** in the formation of assembly **3**. Compared to the individual host **1** and guest **2**, the most pronounced changes in chemical shifts were observed for the protons at the core of the dendrimer **3** (see ESI<sup>†</sup>). Furthermore, the electrospray ionization mass spectrum of assembly **3** shows several peaks at  $m/z = 3991.2$ ,  $3455.7$  and  $2634.4$  corresponding to the fragment ions  $[\text{M} - 2\text{Cl}]^{2+}$ ,  $[\text{M} - 2[\text{O}_3\text{SO}(\text{CH}_2)_6\text{SiMe}_2\text{NCNPdCl}]^{2+}$  and  $[\text{M} - 3\text{Cl}]^{3+}$ , respectively. Although halide scrambling (Cl/Br) during the analysis was observed, isotope patterns and fragmentation patterns (loss of anionic guests) unequivocally point to the 1:8 stoichiometry of **3**. Molecular mechanics calculations (MMFF94)<sup>7</sup> on assembly **3** support the information on its molecular structure obtained from NMR analysis (see ESI<sup>†</sup>). The calculated three-dimensional structure of the metallodendritic assembly consists of a rather spherical dendritic backbone of the host in which the anionic tails of the organometallic fragments are buried close to the cationic sites. The palladium head groups are exposed near the periphery of the dendrimer. Changes in the molecular structure and chemical composition of dendrimer **1** upon binding guest **2** were observed experimentally, *e.g.* by the increased solubility of **3** compared to **1**.

In order to investigate the application of this novel metallodendritic assembly in homogeneous catalysis, **3** was converted into the corresponding Lewis acidic  $\text{Pd}^{\text{II}}$  aqua complex with  $\text{AgBF}_4$  yielding assembly **3a** (Scheme 1, route A). The  $^1\text{H}$  NMR spectrum of **3a** in  $\text{CD}_2\text{Cl}_2$  shows the presence of the cationic dendritic host and the  $\text{Pd}^{\text{II}}$  guests in a 1:8 molar ratio. However, assembly **3a** bears a zwitterionic  $\text{Pd}(\text{II})$  guest which can stabilize itself intra- or intermolecularly, *e.g.* by means of aggregation. Depending on the number of zwitterionic guest molecules that dissociate from the dendritic host, this can ultimately lead to an octacationic dendrimer with one or multiple incorporated  $\text{BF}_4^-$  anions. An alternative synthesis of **3a** was performed by combining an octacationic dendrimer with eight  $\text{BF}_4^-$  ions ( $\text{Si}(\text{NCN})_4 \cdot 8[\text{G}-1] \cdot 8\text{BF}_4$  **4**) with the zwitterionic  $\text{Pd}^{\text{II}}$  complex ( $[\text{O}_3\text{SO}(\text{CH}_2)_6\text{SiMe}_2\text{NCNPd}]_n$  **5**), devoid of halide and ammonium ions, in an 1:8 ratio, respectively (Scheme 1, route B).<sup>‡</sup> The  $^1\text{H}$  NMR spectrum of **3a** shows similar chemical shift values as observed for **4** and **5**, which indicates that either the zwitterions are not bound to the dendritic host or that there is fast exchange of cations and anions on the NMR timescale (see ESI<sup>†</sup>).

The catalytic performance of metallodendrimer assembly **3a** was tested in a model reaction<sup>8</sup> shown in eqn. (1) and compared



with those of unsupported  $\text{Pd}^{\text{II}}$  aqua complex **2a**, of zwitterionic complex **5**, and of  $\text{Pd}^{\text{II}}$  aqua complex **6** bearing a neutral *para*-substituent (Table 1). Both **3a** prepared *via* route A and **2a** show a higher initial turnover frequency (TOF) than **6**. These results show that the dendritic support does not influence the catalytic properties of **2a**, *i.e.* identical product distribution and TON are observed. The catalytic activity of **5**, however, is low compared to **2a**, which indicates that the presence of both ammonium and  $\text{BF}_4^-$  ions benefits the catalytic activity of the zwitterion. In addition, a low catalytic activity was observed for assembly **3a** formed after mixing **5** and dendrimer **4** (route B). Although this assembly is spectroscopically equivalent to the one prepared *via* route A, their catalytic performance differs remarkably.

In conclusion, we have presented a new approach for the noncovalent immobilization of a well-defined number of transition metal complexes to a soluble (molecular) supporting material. Two alternative routes were studied to synthesize the corresponding  $\text{Pd}$ -cation species which was applied as Lewis acidic catalyst. Currently, we are investigating the physical properties of these and related species to understand the role of ion pairing on both the physical and catalytic properties.

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## Notes and references

<sup>‡</sup> Details on the syntheses of **2**, **2a**, **4** and **5** will be published elsewhere.

**Table 1** Catalytic and kinetic data for the aldol condensation of benzaldehyde and methyl isocyanatoacetate in the absence and presence of metallodendrimer **3a**, unsupported **2a**, **5**, or reference compound **6a** [ $\text{Bu}^t\text{Me}_2\text{SiO}(\text{CH}_2)_6\text{NCNPd}(\text{OH})_2$ ] $\text{BF}_4$

Catalyst	TOF <sup>b</sup>	Conversion <sup>c</sup> (%)	<i>trans/cis</i> <sup>d</sup>
<b>3a</b>	51	100	58/42
<b>2a</b>	55	100	58/42
<b>6</b>	35	91	62/38
<b>5</b>	28	64	63/37
<b>3a</b> <sup>e</sup>	29	60	60/40

<sup>a</sup> Reaction carried out in  $\text{CH}_2\text{Cl}_2$  (5 mL) at RT in the presence of 10 mol%  $\text{Pr}_2\text{EtN}$  and 1 mol% of catalyst in terms of  $[\text{Pd}]$ . <sup>b</sup> Per hour, during the first hour. <sup>c</sup> Calculated after 5 h by specific  $^1\text{H}$  NMR spectroscopy signal integration using mesitylene as an internal standard. <sup>d</sup> Calculated after 24 h. <sup>e</sup> Assembly obtained *via* route B (Scheme 1).

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- A commercially available dialysis membrane (benzoylated cellulose, SIGMA) with a cut-off mass of  $1200 \text{ g mol}^{-1}$  was used. The molecular weights of **3** and **2** are 7783.5 and  $813.0 \text{ g mol}^{-1}$ , respectively.
- Geometry optimization using the MMFF94 mechanics force field. SPARTAN SGI Version 5.1.1, Wavefunction, Inc., 18401 Von Karman Ave., Ste. 370, Irvine, CA 92612 USA.
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