Transition Metal Catalysis Using Core-Functionalized Carbosilane Dendrimers.
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A series of carbosilane dendrimeric wedges up to the second generation functionalized with NCN pincer ligands at the focal point was prepared using a Suzuki coupling scheme. The nickel complexes of these ligands are catalytically active in the Kharasch addition reaction and the initial activities are comparable to those of the parent complex. This shows that the reagents can easily reach the catalytic center, which means that under these conditions the dendrimeric wedges are not sufficiently large to create site isolation of the metal site at the focal point. Retention measurements of the non-functionalized wedges shows that the size of the obtained systems is sufficiently large (retention up to 99.8 %) for the application of these systems in a continuous process using nanofiltration techniques.
5.1 Introduction

Dendrimer research is advancing at an enormous pace and the chemistry has advanced from mere curiosity-driven macromolecular structures to functional systems and applications. The design of (transition) metal-functionalized dendrimers for catalytic applications has received much attention. Our groups have reported early examples of catalytically active transition metal containing dendrimers and have shown their application in several catalytic reactions. We have studied aspects of dendrimeric catalysis such as recycling, “proximity effects” of the peripheral functionalities and the effect of the backbone on the catalyst performance. Furthermore, the synthesis and application of various core-functionalized dendrimers revealed that dendrimeric encapsulation has a considerable effect on non-covalent guest complexion and catalysis.

![Figure 1. Nickel complexes of the NCN pincer ligand.](image)

Monomeric, polymer-supported and dendrimer-supported nickel complexes based on the monoanionic “pincer” ligand \( \left[C_6H_3\{CH_2NMe_2\}-2,6\right]^- \) (NCN, see Figure 1) have been used extensively in atom-transfer radical addition (ATRA) catalysis, such as the Kharasch addition reaction of polyhalogenated alkanes to alkenes (Scheme 4). It has been observed that catalytically active complexes exhibit a proximity effect at the surface of dendrimers leading to a short catalyst lifetime. The decrease in catalytic activity might be explained by the higher local concentration of \( \text{CCl}_3^- \) radicals at the dendrimer surface, leading to a high proportion of combination of the \( \text{CCl}_3^- \) radicals. This results in the formation of insoluble Ni\( \text{III} \) metal species that are catalytically inactive.

Encapsulation of the NCN aryldiamine nickel complexes within a dendrimer shell might lead to site isolation and thus could possibly prevent radical combination and subsequent deactivation of the catalyst complexes. Furthermore, application of these ligands in a continuous process would allow high space-time yields with relatively low catalyst concentrations, also reducing radical combination. The nanosized metalloendrimers can be removed from the homogeneous reaction mixtures by nanofiltration techniques.

Here we report the synthesis of NCN pincer nickel complexes at the focal point of carbosilane dendrons and their application as catalysts in batchwise Kharasch reactions.
5.2 Results and discussion

5.2.1 Preparation of the ligands and the corresponding nickel complexes

Carbosilane dendrimeric wedges such as 4[4b, 8a] having allyl end groups were prepared divergently starting from p-bromostyrene using repetitive hydrosilylation and Grignard alkenylation reactions.[3b, 13] The unsaturated allyl groups can potentially interfere with catalytic reactions, which can be circumvented by using their saturated analogues. For all generations wedges, in the last step methylmagnesium chloride was employed as alkylating reagent, giving the methyl-terminated wedges 1 to 3. Generation-two allyl-terminated dendrimeric wedge 4 was hydrosilylated with chlorodimethylsilane, and subsequently made to react with methylmagnesium chloride to yield the third-generation dendrimeric wedge 5 (Scheme 1).

Scheme 1. Generation 0 to 2 wedges 1, 2, and 3, and synthesis of third-generation dendron 5 via hydrosilylation and Grignard alkylation of 4. Reagents and conditions: a) HSiMe₂Cl, (n-Bu₄N)₂PtCl₆, rt, 4h; b) MeMgCl, Et₂O, rt.

These wedges were converted into the corresponding boronic acid-functionalized wedges 6 to 9 via reaction with t-butyllithium and subsequent quenching of the reaction mixture with B(O-i-Pr)₃, followed by acidic workup (Scheme 2).[14] Palladium-catalyzed Suzuki coupling of 6-8 with 3,5-bis(dimethylamino)methyl]-1-iodobenzene[15] (10) afforded the corresponding dendrimeric NCN pincer ligands 11, 12, and 13 in 47-58 % yield after column
chromatography. Several attempts to couple boronic acid 9 with the iodopincer 10 were unsuccessful, presumably because the steric demands of the carbosilane branches inhibit the Suzuki reaction.\textsuperscript{[16]} The conversion of the aryl bromide to the boronic acid and the subsequent Suzuki coupling, which is a commonly used coupling reaction, widens the potential scope of this type of wedges.

\begin{equation}
\begin{array}{c}
\text{Br} \\
\text{1, 2, 3, 5} \\
\text{SiR}_3 \\
\end{array}
\xrightarrow{\text{a, b, c}}
\begin{array}{c}
\text{HO}_2B \\
\text{6, 7, 8, 9} \\
\text{SiR}_3 \\
\end{array}
\xrightarrow{\text{d}}
\begin{array}{c}
\text{Me}_2N \\
\text{10} \\
\text{Me}_2N \\
\text{SiR}_3 \\
\end{array}
\xrightarrow{\text{Me}_2N}
\begin{array}{c}
\text{11, 12, 13} \\
\text{Me}_2N \\
\text{SiR}_3 \\
\end{array}
\end{equation}

**Scheme 2.** Preparation of the boronic acid-functionalized dendrons 6-9 and subsequent Suzuki coupling reaction to yield ligands 11-13. Reagents and conditions: a) t-BuLi, THF, -70 °C; b) B(OMe)_3, -70 °C to rt; c) HCl, H_2O; d) Pd(PPh)_3, Na_2CO_3, H_2O, DME, Δ.

\begin{equation}
\begin{array}{c}
\text{Me}_2N \\
\text{11, 12, 13} \\
\text{SiR}_3 \\
\end{array}
\xrightarrow{\text{a, b}}
\begin{array}{c}
\text{Me}_2N \\
\text{14} \\
\text{Cl-Ni} \\
\text{Me}_2N \\
\text{15, 16} \\
\text{SiR}_3 \\
\end{array}
\end{equation}

**Scheme 3.** Nickel complexation of the dendrimeric ligands 14-16. Reagents and conditions: a) n-BuLi, pentane, rt; b) [NiCl_2(PEt_3)_2], Et_2O.

As depicted in Scheme 3, nickel complexes 14, 15, 16, and 17 were prepared by lithiation of the corresponding NCN-ligands and subsequent transmetalation with substoichiometric (0.95 equiv.) amounts of [NiCl_2(PEt_3)_2]. According to \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy transmetalation was complete, and after the reaction only free PEt\textsubscript{3} in the \textsuperscript{31}P NMR spectra was observed.\textsuperscript{[17]} The orange complexes could not be separated from the small excess of ligand (5%) due to similar solubility properties and the sensitivity of the complexes towards oxidation.
Scheme 4. The nickel-catalyzed Kharasch addition reaction of CCl₄ to ethyl methacrylate (MMA).

5.2.2 Application in the Kharasch addition reaction

From previous work, however, we know that the presence of free ligand does not affect the catalytic performance of the nickel complexes.[6a, 12] Preliminary experiments were performed to investigate the activity of the complexes in the Kharasch addition reaction of CCl₄ to methyl methacrylate (Scheme 4).[6a, 7a, 10a] Table 1 shows that all complexes exhibit similar initial turnover frequencies after 15 minutes (60-80 mol mol Ni⁻¹ h⁻¹). The relatively small dendrimeric wedges attached to the ligands clearly do not affect the activity of the catalyst as compared to the monomeric complex 17. Molecular modelling studies (Figure 2) show that the dendrimeric shell is still rather open and points away from the ligating site. The catalytic site is significantly exposed to bulk solution and thereby enables catalysis without any steric inhibition or site isolation effects. After 2 hours the conversions show some differences, which might be attributed to partial catalyst deactivation. Increasing the catalyst concentrations gave similar initial turnover numbers (after 15 minutes) and increased conversions after two hours. In particular 16 (compare entries 6 and 7, Table 1) exhibits an unexpectedly large increase from 7 % to 56 % conversion when the catalyst concentration is raised. The difference is presumably due to relatively high catalyst deactivation in the ‘low concentration’ experiment. This is in agreement with the better catalytic performance which is obtained when the reaction is performed at a larger scale.[6a]

5.2.3 Retention of the wedges in a continuous-flow membrane reactor

To evaluate the potential use of these systems in continuous processes the retention of carbosilane dendrimeric wedges 1, 2, 3, and 5 was determined. A dichloromethane solution of the wedges was injected in a continuous-flow membrane reactor, and the flow coming from the reactor was collected in small fractions. Size exclusion chromatography (SEC) analysis of these fractions and the remaining contents of the reactor was used to calculate the retention for the different generations (Table 2).

The nanofiltration membranes commonly used in a continuous-flow membrane reactor have a molecular weight (MW) cut-off as low as 400 Da,[4a, 4c-e, 5, 12, 18] which means that molecules with a MW of 400 Da exhibit an average retention of 99 %. The low retention of 1 in the membrane reactor shows that the retention drops dramatically for molecules with a MW
Table 1. Catalytic results using the nickel complexes 17, 14, 15, and 16 in the Kharasch addition reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>[Ni] (mmol)</th>
<th>Conversion[^b] (%)</th>
<th>TOF[^c] mol (mol Ni)^{-1} h^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17</td>
<td>0.0091</td>
<td>34[^d]</td>
<td>68[^d]</td>
</tr>
<tr>
<td>2</td>
<td>17</td>
<td>0.0273</td>
<td>85</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td>14</td>
<td>0.0091</td>
<td>25</td>
<td>58</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>0.0091</td>
<td>27</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>0.0273</td>
<td>67</td>
<td>68</td>
</tr>
<tr>
<td>6</td>
<td>16</td>
<td>0.0091</td>
<td>7</td>
<td>60</td>
</tr>
<tr>
<td>7</td>
<td>16</td>
<td>0.0273</td>
<td>56</td>
<td>55</td>
</tr>
</tbody>
</table>

[^a] Conditions: 1.00 mL CCl₄, 1.20 mL CH₂Cl₂, 0.20 mL decane, 0.30 mL MMA, room temperature; [^b] conversion after 120 minutes; [^c] TOF after 15 minutes; [^d] Compared to reactions performed at larger scale (ref [6a]), the catalyst performance was systematically lower, presumably due to catalyst deactivation.

Figure 2. Modelled structures of NCN pincer dendrons of generation two (a) and three (b) (hydrogens omitted for clarity).

below 400 Da. The MW of wedge 2 is above the cut-off, and the retention is indeed slightly above 99 %. When the generation number of dendrimers increases, generally a transition from a flat to a globular shape is observed (compare the two structures in Figure 2; G2 is planar,
whereas G3 is mainly spherical), which favors the retention of dendrimers compared to linear polymers. The observed retention of the largest wedges 3 and 5 is sufficiently high to use ligands based on this wedge in continuous processes (e.g. for 5, after 100 reactor volumes flushed, still 90.5 % would be retained in the reactor).

Table 2. Retention of carbosilane dendrons in a continuous membrane reactor (determined after 37 reactor volumes flushed)

<table>
<thead>
<tr>
<th>Dendron</th>
<th>MW</th>
<th>Retained (%)&lt;sup&gt;[a]&lt;/sup&gt;</th>
<th>Retention&lt;sup&gt;[b]&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>257</td>
<td>10.14</td>
<td>0.938</td>
</tr>
<tr>
<td>2</td>
<td>556</td>
<td>74.20</td>
<td>0.992</td>
</tr>
<tr>
<td>3</td>
<td>1460</td>
<td>89.08</td>
<td>0.997</td>
</tr>
<tr>
<td>5</td>
<td>4167</td>
<td>92.09</td>
<td>0.998</td>
</tr>
</tbody>
</table>

[a] Absolute quantities were measured by SEC analysis of solutions in CH2Cl2 (1.00 mL); [b] see experimental for the formula used.

5.3 Conclusions

Carbosilane dendrimeric wedges up to generation three have been functionalized at their focal point with boronic acid groups, which gives access to a range of new focal point-functionalized dendrimers via commonly used Suzuki coupling reactions.<sup>[19]</sup> The boronic acid groups were used to functionalize these dendrimeric wedges up to generation two with NCN pincer ligands. After nickel complexation of the ligands the obtained complexes showed activities in the Kharasch addition reaction comparable to the parent complex, showing that the obtained dendrimers are too small for site isolation of the catalyst located at the core.

The dendrimeric wedges were shown to be large enough for application in a continuous-flow membrane reactor, which means that the dendrimeric nickel complexes could serve as recoverable catalysts for the Kharasch addition reaction. In this respect the unaffected activity with increased dendron-size is desirable. Future work will concentrate on more efficient encapsulation of NCN pincer ligands in a dendrimeric shell (i.e. attachment of dendrimeric wedges at the ligand nitrogen atoms) to further investigate site isolation effects in (Kharasch) catalysis.
5.4 Experimental Section

Chemicals were purchased from Aldrich Chemical Co. and Acros Chimica and used as received. All manipulations involving air- or water-sensitive compounds were performed using standard Schlenk techniques. Compound 10 was described previously. Solvents were dried and distilled under N\textsubscript{2} prior to use. Silica 60 (SDS Chromagel, 70-200 \textmu m) was used for column chromatography. Analyses of the catalysis samples were run on a Perkin Elmer Autosystem GC (column PE-17 phase; 30 m x 0.320 mm; \textit{d} = 0.50 \textmu m) with FID detector. Size Exclusion Chromatography was run on a Shimadzu LC10-AT system with Waters Styragel HR1, HR2, and HR4 columns in series with a Shimadzu RID-10A refractive index detector and a SPD-10A-VP UV-Vis detector at 250 nm using CH\textsubscript{2}Cl\textsubscript{2} as eluent. 

\textsuperscript{1}H and \textsuperscript{13}C{\textsuperscript{'H}} NMR spectra were recorded using Bruker AMX 300 and Varian Mercury 300 spectrometers (both: \textsuperscript{1}H 300 MHz; \textsuperscript{13}C 75 MHz). The spectra were recorded in CDC\textsubscript{13}, acetone-d\textsubscript{6}, and C\textsubscript{6}D\textsubscript{6}, and chemical shifts are given in ppm versus TMS. Elemental analyses were carried out on an Elementar Vario EL apparatus. Infrared spectra were recorded on a Nicolet 510 FT-IR spectrophotometer. FAB mass spectra were measured on a JEOL JMS-SX/SX102A four sector mass spectrometer. MALDI-TOF mass spectra were acquired on a Voyager-DE Biospectrometry Workstation (PerSeptive Biosystems Inc., Framingham, MA, USA) mass spectrometer equipped with a nitrogen laser emitting at 337 nm (3 ns pulses).

Zeroth to third generation methyl-terminated carbosilane dendrons (1-3, and 5)

The synthesis and characterization of compounds 1 to 3 will be reported elsewhere. Compound 5 was prepared via a similar procedure starting from 4. Second generation allyl terminated wedge 4 (1.25 g, 0.58 mmol) was reacted with HSiMe\textsubscript{2}Cl (23.2 mL, 31.2 mmol) using (n-Bu\textsubscript{4}N)\textsubscript{2}PtCl\textsubscript{6} (16 mg, 25 \textmu mole). After removal of all volatiles, a 350 mL Et\textsubscript{2}O solution of the hydrosilylated product was dropped to a MeMgCl solution (25 mL of a 3 M solution in THF, 75 mmol) under vigorous stirring in an ice bath. After 4 hours of stirring at room temperature the reaction mixture Subsequent quenching with aqueous NH\textsubscript{4}Cl solution, followed by extraction with Et\textsubscript{2}O (3 x 150 mL), drying of the combined organic layers with MgSO\textsubscript{4}, and removal of the solvents. Filtration over silica using hexane as the eluent and subsequent concentration in \textit{vacuo} yielded 5 as a colorless oil: 1.41 g (58 {}). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \textit{\delta} = 7.36 (d, \textsuperscript{3}J(H,H) = 8.1 Hz, H\textsubscript{Ar}, 2H), 7.04 (d, \textsuperscript{3}J(H,H) = 8.1 Hz, H\textsubscript{Ar}, 2H), 2.55 (m, Ar-CH\textsubscript{2}, 2H), 1.32 (m, Si-CH\textsubscript{2}-CH\textsubscript{2}-CH\textsubscript{2}, 78H), 0.88 (m, Ar-CH\textsubscript{2}-CH\textsubscript{2}, 2H), 0.57 (t, \textsuperscript{3}J(H,H) = 8.1 Hz, Si-CH\textsubscript{2}-CH\textsubscript{2}, 156H), -0.01 (s, Si-CH\textsubscript{3}, 243H); \textsuperscript{13}C{\textsuperscript{'H}} NMR (CDCl\textsubscript{3}): \textit{\delta} = 144.3 (C\textsubscript{q}, 2C\textsubscript{Ar}), 131.3 (CH, 2C\textsubscript{Ar}), 129.5 (CH, 2C\textsubscript{Ar}), 118.6 (Br-C\textsubscript{q}, 1C\textsubscript{Ar}), 29.8 (C\textsubscript{Ar}-CH\textsubscript{2}-CH\textsubscript{2}, 1C), 21.7 (Si-CH\textsubscript{2}-CH\textsubscript{2}-CH\textsubscript{2}, 39C), 18.57 - 17.66 (multiple signals, Si-CH\textsubscript{2}-CH\textsubscript{2}-CH\textsubscript{2}, 78C), 14.9 (C\textsubscript{Ar}-CH\textsubscript{2}-CH\textsubscript{2}, 1C), -1.4 (Si-CH\textsubscript{3}, 81C); Elemental analysis calcd for C\textsubscript{206}H\textsubscript{485}BrSi\textsubscript{40}: H, 11.73; C, 59.39; Found: H, 11.69; C, 58.65; MS (MALDI-TOF) m/z = 4274.9 (M\textsuperscript{+}Ag, calculated 4274.7); IR/cm\textsuperscript{-1} (CH\textsubscript{2}Cl\textsubscript{2} solution) 3056w, 2955m, 2913s, 2874m, 1417w, 1250s (SiMe), 1142m, 901m, 866s, 839s.
Typical preparation of boronic acid-functionalized carbosilane dendrons

Compound 6 Two equivalents of t-butyllithium (9.5 mL of a 1.5 M solution in pentane, 14.3 mmol) were added to a THF solution of 1 (1.83 g, 7.15 mmol) at -70 °C. The reaction was monitored by GC-MS or 1H-NMR spectroscopy, and after complete lithiation (usually within 15 minutes) B(Ot-Pr), (2.15 g, 11.44 mmol) was added. The mixture was slowly warmed to room temperature and stirred overnight. Quenching of the reaction with 1 M HCl, followed by extraction with CH₂Cl₂ and drying with MgSO₄ yielded product 6 as a colorless oil in 1.43 g (91%) yield. 1H NMR (CDCl₃): δ= 8.16 (d, 3J(H,H) = 8.1 Hz, HAr, 2H), 7.36 (d, 3J(H,H) = 8.1 Hz, HAr, 2H), 5.35 (bs, O-H, 2H), 2.73 (m, Ar-CH₂-CH₂, 2H), 0.93 (m, Ar-CH₂-CH₂, 2H), 0.07 (s, Si-CH₃, 9H), the signal of the boronic acid B(OH)₂ was not observed; 13C{¹H} NMR (CDCl₃): δ= 150.5 (Cq, 1Cₐr), 136.0 (CH, 2Cₐr), 128.5 (B-Cq, 1Cₐr), 127.8 (CH, 2Cₐr), 30.7 (Cₐr-CH₂, 1C), 18.9 (Cₐr-CH₂-CH₂, 1C), -1.5 (Si-CH₃, 3C); MS (FAB) m/z= 222.08 (M⁺), calculated 222.1), 178.07 (IVT - B(OH)₂).

Compound 7 was prepared following the procedure described for 6, starting from 2 (3.19 g, 5.72 mmol). A white solid was obtained: 1.38 g (95%). 1H NMR (acetone-d₆): δ= 8.17 (d, 3J(H,H) = 7.8 Hz, HAr, 2H), 7.39 (d, 3J(H,H) = 8.1 Hz, HAr, 2H), 2.73 (m, Ar-CH₂-CH₂, 2H), 1.49 (m, Si-CH₂-CH₂-CH₂, 6H), 1.01 (m, Ar-CH₂-CH₂, 2H), 0.69 (m, Si-CH₂-CH₂-CH₂, 2H), 0.04 (s, Si-CH₃, 27H), the signal of the boronic acid B(OH)₂ was not observed; 13C{¹H} NMR (acetone-d₆): δ= 150.6 (Cq, 1Cₐr), 136.0 (CH, 2Cₐr), 127.7 (B-Cq, 1Cₐr), 127.1 (CH, 2Cₐr), 30.7 (Cₐr-CH₂, 1C), 21.6 (Si-CH₂-CH₂-CH₂, 3C), 18.8 and 17.4 (Si-CH₂-CH₂-CH₂, 6C), 15.0 (Cₐr-CH₂-CH₂, 1C), -1.9 (Si-CH₃, 9C).

Compound 8 was prepared following the procedure described for 6, starting from 3 (1.58 g, 1.08 mmol). A white solid was obtained: 1.50 g (97%). 1H NMR (CDCl₃): δ= 8.18 (d, 3J(H,H) = 8.1 Hz, HAr, 2H), 7.36 (d, 3J(H,H) = 7.8 Hz, HAr, 2H), 2.72 (m, Ar-CH₂-CH₂, 2H), 1.41 (m, Si-CH₂-CH₂-CH₂, 24H), 0.96 (m, Ar-CH₂-CH₂, 2H), 0.64 (t, Si-CH₂-CH₂-CH₂, 48H), 0.02 (s, Si-CH₃, 81H), the signal of the boronic acid B(OH)₂ was not observed; 13C{¹H} NMR (CDCl₃): δ= 150.6 (Cq, 1Cₐr), 135.9 (CH, 2Cₐr), 127.5 (B-Cq, 1Cₐr), 127.5 (CH, 2Cₐr), 30.8 (Cₐr-CH₂, 1C), 25.6 and 21.7 (Si-CH₂-CH₂-CH₂, 12C), 18.7 to 17.5 (Si-CH₂-CH₂-CH₂, 24C), 15.1 (Cₐr-CH₂-CH₂, 1C), -1.4 (Si-CH₃, 27C).

Compound 9 was prepared following the procedure described for 6, starting from 5 (1.46 g, 0.32 mmol). A white oil was obtained: 1.38 g (95%). 1H NMR (CDCl₃): δ= 7.62 (d, 3J(H,H) = 7.6 Hz, HAr, 2H), 7.21 (d, 3J(H,H) = 7.8 Hz, HAr, 2H), 2.61 (m, Ar-CH₂, 2H), 1.30 (m, Si-CH₂-CH₂-CH₂, 78H), 0.87 (m, Ar-CH₂-CH₂, 2H), 0.55 (t, Si-CH₂-CH₂-CH₂, 156H), -0.03 (s, Si-CH₃, 243H), the signal of the boronic acid B(OH)₂ was not observed; 13C{¹H} NMR (CDCl₃): δ= 149.4 (Cq, 1Cₐr), 133.9 (CH, 2Cₐr), 128.5 (B-Cq, 1Cₐr), 127.8 (CH, 2Cₐr), 30.0 (Cₐr-CH₂, 1C), 22.0 (Si-CH₂-CH₂-CH₂, 39C), 19.0 to 17.7 (Si-CH₂-CH₂-CH₂, 78C), 15.3 (Cₐr-CH₂-CH₂, 1C), -1.2 (Si-CH₃, 81C).

Typical preparation of NCN-pincer cored carbosilane dendrimers (11-13)

Compound 10 To an oxygen-free solution of 6 (0.78 g, 3.53 mmol) and 10 (1.02 g, 3.21 mmol) in DME (30 mL) was first added an aqueous solution of Na₂CO₃ (3.21 mL, 2 M, 6.41 mmol) and then Pd(PPh₃)₄ (110 mg, 0.096 mmol). The mixture was refluxed for 17 h. After cooling to room...
temperature 30 mL of Et₂O and 20 mL of brine were added, the aqueous layer was separated and extracted with Et₂O (3 x 10 mL). The combined organic fractions were dried over MgSO₄ and concentrated to give an orange oil. Column chromatography (eluent hexane, then CH₂Cl₂) gave pure **11**. Yield: 0.75 g (58 %). ¹H NMR (CDCl₃): δ = 7.54 (d, ³J(H,H) = 12.0 Hz, Hₘₐₜ, 2H), 7.44 (s, Hₘₐₜ, 2H), 7.24 (d, ³J(H,H) = 12.6 Hz, Hₘₐₜ, 2H), 7.21 (s, Hₘₐₜ, 1H), 3.48 (s, N-CH₂, 4H), 2.65 (m, Ar-CH₂CH₂, 2H), 2.26 (s, N-CH₃, 12H), 0.89 (m, Ar-CH₂CH₂, 2H), 0.02 (s, Si-CH₃, 9H); ¹³C {¹H} NMR (CDCl₃): δ = 144.3 (Cₚ, 1Cₚ), 139.0 (Cₚ, 1Cₚ), 138.1 (Cₚ, 1Cₚ), 136.5 (CH, 1Cₚ), 128.9 (Cₚ, 2Cₚ), 128.4 (CH, 2Cₚ), 127.0 (CH, 2Cₚ), 126.4 (CH, 2Cₚ), 64.3 (N-CH₂, 2C), 45.3 (N-CH₃, 4C), 29.6 (Cₚ-CH₂CH₂, 2C), 18.6 (Cₚ-CH₂CH₂, 1C), -1.7 (Si-CH₃, 3C); Elemental analysis calcd for C₃₀H₈₈N₄Si₄: H, 9.84; C, 74.94; Found: H, 9.79; C, 75.02.

**Compound 12** was prepared following to procedure described for **11**, starting from 7 (2.64 g, 4.98 mmol) yielding a colorless oil: 1.42 g (47%). ¹H NMR (CDCl₃): δ = 7.65 (d, ³J(H,H) = 8.2 Hz, Hₘₐₜ, 2H), 7.44 (s, Hₘₐₜ, 2H), 7.25 (d, ³J(H,H) = 8.0 Hz, Hₘₐₜ, 2H), 7.23 (s, Hₘₐₜ, 1H), 3.48 (s, N-CH₂, 4H), 2.65 (m, Ar-CH₂CH₂, 2H), 2.27 (s, N-CH₃, 12H), 1.36 (m, Si-CH₂CH₂CH₂, 6H), 0.90 (m, Ar-CH₂CH₂, 2H), 0.77 (m, Si-CH₂CH₂CH₂, 12H), 0.00 (s, Si₃Si, 27H); ¹³C {¹H} NMR (CDCl₃): δ = 144.7 (Cₚ, 1Cₚ), 141.0 (Cₚ, 1Cₚ), 139.2 (Cₚ, 1Cₚ), 138.2 (Cₚ, 1Cₚ), 128.4 (Cₚ, 2Cₚ), 128.0 (Cₚ, 2C), 127.1 (Cₚ, 2C), 126.4 (Cₚ, 2C), 64.4 (N-CH₂, 2C), 45.4 (N-CH₃, 4C), 29.9 (Ar-CH₂CH₂, 1C), 21.7 (Si-CH₂CH₂CH₂, 3C), 18.6 and 17.3 (Si-CH₂CH₂CH₂, 6C), 15.1 (Ar-CH₂CH₂, 1C), -1.5 (CH₃Si, 9C); MS (MALDI-TOF) m/z = 670.2 (M⁺, calculated 669.3); MS (FAB) m/z = 669.5 (M⁺, calculated 669.3, 100), 654, 639, 625 (M⁺ - NMe₃), 553, 293, 73; HRMS (FAB) m/z calcd for C₃₉H₇₈N₂S₄: 669.4851. Found: 669.4840.

**Compound 13** was prepared following to procedure described for **11**, starting from 8 (1.57 g, 1.10 mmol) yielding a colorless oil: 0.82 g (47%). ¹H NMR (CDCl₃): δ = 7.53 (d, ³J(H,H) = 8.2 Hz, Hₘₐₜ, 2H), 7.43 (s, Hₘₐₜ, 2H), 7.24 (d, ³J(H,H) = 8.0 Hz, Hₘₐₜ, 2H), 7.23 (s, Hₘₐₜ, 1H), 3.48 (s, N-CH₂, 4H), 2.63 (m, Ar-CH₂CH₂, 2H), 2.27 (s, N-CH₃, 12H), 1.35 (m, Si-CH₂CH₂CH₂, 24H), 0.90 (m, Ar-CH₂CH₂, 2H), 0.57 (m, Si-CH₂CH₂CH₂, 48H), -0.02 (s, CH₃Si, 81H); ¹³C {¹H} NMR (CDCl₃): δ = 144.7 (Cₚ, 1Cₚ), 141.0 (Cₚ, 1Cₚ), 139.2 (Cₚ, 1Cₚ), 138.2 (Cₚ, 1Cₚ), 128.4 (Cₚ, 2Cₚ), 128.0 (Cₚ, 2C), 127.1 (Cₚ, 2C), 126.5 (Cₚ, 2C), 64.4 (N-CH₂, 2C), 45.4 (N-CH₃, 4C), 30.0 (Ar-CH₂CH₂, 1C), 21.7 (Si-CH₂CH₂CH₂, 12C), 18.6, 18.0, 17.7 and 17.5 (Si-CH₂CH₂CH₂, 24C), 15.3 (Ar-CH₂CH₂, 1C), -1.4 (CH₃Si, 27C); MS (MALDI-TOF) m/z = 1572.8 (M⁺, calculated 1571.4);

**Preparation of the dendrimeric NCN-pincer nickel complexes 14, 15, and 16 and monomeric complex 17.**

Complexes **14** and **17** were prepared according to a literature procedure.[12] A solution of **11** (0.453 g, 1.23 mmol) in pentane (30 mL) was reacted with n-butyllithium (0.87 mL, 1.56 M, 1.35 mmol) at room temperature for 16 hours. The pentane was removed under reduced pressure, the oily product was dissolved in Et₂O (40 mL), and subsequently reacted with NiCl₂(Pent₃)₂ (0.517 g, 1.41 mmol). After washing with hexane (3 x 15 mL), benzene extraction (3 x 20 mL), and evaporation of all volatiles an
orange solid was obtained. 14: 0.47 g (83%). \({}^1\)H NMR (CD\(_2\)Cl\(_2\)): \(\delta = 7.58\) (d, \(^3\)J(H,H) = 7.8 Hz, H\(_{Ar}\), 2H), 7.23 (d, \(^3\)J(H,H) = 7.2 Hz, H\(_{Ar}\), 2H), 7.21 (s, H\(_{Ar}\), 2H), 3.08 (s, N-CH\(_3\), 4H), 2.61 (m, Ar-CH\(_2\)-CH\(_2\), 2H), 2.44 (s, N-CH\(_3\), 12H), 0.86 (m, Ar-CH\(_2\)-CH\(_2\), 2H), 0.00 (s, Si-CH\(_3\), 9H); \(^{13}\)C\({}^1\)H NMR (CD\(_2\)Cl\(_2\)): \(\delta = 148.3\) (C\(_{Ar}\), 2C\(_q\)), 140.2 (C\(_{Ar}\), 1C\(_q\)), 138.6 (C\(_{Ar}\), 1C), 129 (2C\(_{Ar}\) and 4 C\(_{Ar}\) underneath the C\(_6\)D\(_6\) signals), 129.7 (C\(_{Ar}\), 2C), 128.1 (C\(_{Ar}\), 2C), 117.7 (C\(_{Ar}\), 2C), 73.7 (CH\(_2\)-N, 2C), 51.0 (CH\(_3\)-N, 4C), 30.1 (Ar-CH\(_2\)-CH\(_2\), 1C), 19.2 (Ar-CH\(_2\)-CH\(_2\), 1C), -1.8 (Si-CH\(_3\), 3C); MS (FAB) \(m/z = 460.2\) (M\(^+\)), 425.2 (M\(^+\) - Cl), 367.3 (M\(^+\) - NiCl), 147, 73 (SiMe\(_3\), 100); HRMS (FAB) \(m/z\) calcd for C\(_{23}\)H\(_{35}\)C\(_{2}\)N\(_2\)NiSi: 460.616; Found 460.613.

Compound 15 was prepared starting from 12 (0.40 g, 0.60 mmol) following the procedure described for 14. Complex 15 was obtained as an orange oil: 0.21 g (47%).

\(^1\)H NMR (acetone-d\(_6\)): \(\delta = 7.45\) (d, \(^3\)J(H,H) = 8.0 Hz, H\(_{Ar}\), 2H), 7.25 (d, \(^3\)J(H,H) = 8.0 Hz, H\(_{Ar}\), 2H), 6.88 (s, H\(_{Ar}\), 2H), 3.77 (s, CH\(_2\)-N, 4H), 2.71 (m, Ar-CH\(_2\)-CH\(_2\), 2H), 2.63 (s, CH\(_3\)-N, 12H), 1.41 (m, Si-CH\(_2\)-CH\(_2\), 6H), 0.96 (m, Ar-CH\(_2\)-CH\(_2\), 2H), 0.66 (m, Si-CH\(_2\)-CH\(_2\)-CH\(_2\), 12H), 0.00 (s, Si-CH\(_3\)-N, 27H); \(^{13}\)C\({}^1\)H NMR (acetone-d\(_6\)): \(\delta = 149.3\) (C\(_{Ar}\), 1C\(_q\)), 145.1 (C\(_{Ar}\), 1C\(_q\)), 141.0 (C\(_{Ar}\), 1C\(_q\)), 139.5 (C\(_{Ar}\), 1C), 129.9 (C\(_{Ar}\), 2C\(_q\)), 129.7 (C\(_{Ar}\), 2C), 128.1 (C\(_{Ar}\), 2C), 118.5264 (C\(_{Ar}\), 2C), 75.1 (CH\(_2\)-N, 2C), 52.2 (CH\(_3\)-N, 4C), 29 (underneath aceton signals), 23.0 (Si-CH\(_2\)-CH\(_2\)-CH\(_2\), 3C), 20.2 and 18.8 (Si-CH\(_2\)-CH\(_2\)-CH\(_2\), 6C), 15.8 (Ar-CH\(_2\)-CH\(_2\), 1C), -0.6 (CH\(_3\)-Si, 9C); MS (FAB) 785.6 (M\(^+\) + Na), 762.4 (M\(^+\)), 725.4 (M\(^+\) - Cl), 667.5 (M\(^+\) - NiCl), 620, 351, 73 (SiMe\(_3\), 100); HRMS (FAB) \(m/z\) calcd for C\(_{28}\)H\(_{35}\)C\(_{2}\)N\(_2\)NiSi: 762.379; Found 762.379.

Compound 16 was prepared starting from 13 (385 mg, 0.245 mmol) following the procedure described for 14. Complex 16 was obtained as an orange oil: 133 mg (32%). \(^1\)H NMR (CD\(_2\)Cl\(_2\)): \(\delta = 7.62\) (d, \(^3\)J(H,H) = 8.1 Hz, H\(_{Ar}\), 2H), 7.35 (d, \(^3\)J(H,H) = 7.8 Hz, H\(_{Ar}\), 2H), 6.82 (s, H\(_{Ar}\), 2H), 3.08 (s, CH\(_2\)-N, 4H), 2.88 (m, Ar-CH\(_2\)-CH\(_2\), 2H), 2.42 (s, CH\(_3\)-N, 12H), 1.60 (m, Si-CH\(_2\)-CH\(_2\)-CH\(_2\), 24H), 0.95 (m, Ar-CH\(_2\)-CH\(_2\), 2H), 0.81 (m, Si-CH\(_2\)-CH\(_2\)-CH\(_2\), 48H), 0.08 (s, CH\(_3\)-Si, 81H).

**Nickel-catalyzed Kharasch addition reaction**

Prior to use CCl\(_4\), CH\(_2\)Cl\(_2\), dodecane and MMA were degassed. In a schlenk, 1.00 mL CCl\(_4\) (0.4 mol), 1.20 mL CH\(_2\)Cl\(_2\), 0.20 mL dodecane (internal standard), and 9.1 \(\mu\)mol Nickel complex were mixed at room temperature. The reaction was started upon addition of methyl methacrylate (0.30 mL). Samples were withdrawn after 15, 30, 60, 120, 240, and 1200 minutes, filtered over alumina, and analyzed by GC.

**Retention measurements**

The membrane (MPF-60 NF, Koch Membrane Systems, Düsseldorf Germany; MW cut-off 400 Da) was stored in ethanol, and pretreated with acetone and methanol. The membrane was carefully installed in a home-made continuous-flow autoclave[20] (volume 5 mL) and flushed with dichoromethane at 100 \(\mu\)L min\(^{-1}\) overnight using an HPLC pump. A solution of circa 20 mg of the carbosilane wedge was injected in the membrane reactor, after which it was flushed with
dichloromethane at a rate of 500 µL min⁻¹. The flow out of the reactor was collected for 370 minutes (37 reactor volumes). This fraction as well as the remaining contents of the reactor were concentrated under reduced pressure, dissolved in 1.50 mL of dichloromethane, and both analyzed with SEC. The retention was calculated using the following formula: \( Q_{ret} = Q_0 e^{(-(1-R)t/	ext{t}_\text{res})} \), in which \( Q_{ret} \) equals the quantity of the retentate at time \( t \) [mol l⁻¹], \( Q_0 \) the quantity of the retentate at time \( t=0 \) [mol l⁻¹], \( t \) the time [h], \( t_{\text{res}} \) the residence time, \( t_{\text{res}} = V_R/F \) [h], \( V_R \) the reactor volume [mL], \( F \) the flow [mL h⁻¹], and \( R \) the retention.[18]

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**5.5 References**


[14] During the course of this work, Casado and Stobart reported a modular approach towards higher generation carbosilane dendrimers based on the Suzuki coupling of similar boronic acid wedges (M. A. Casado, S. R. Stobart, Organic Letters 2000, 2, 1549).


Small orange crystals of 14 were obtained, but these were not suitable for X-ray structure determination.

