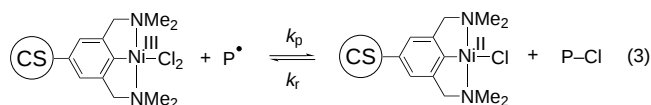
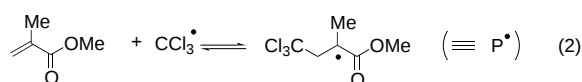
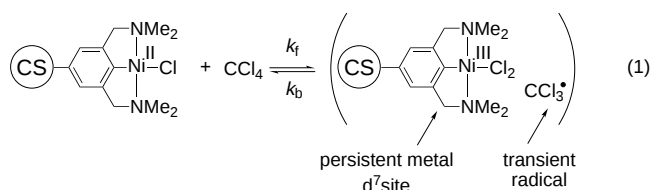


The “Dendritic Effect” in Homogeneous Catalysis with Carbosilane-Supported Arylnickel(II) Catalysts: Observation of Active-Site Proximity Effects in Atom-Transfer Radical Addition**

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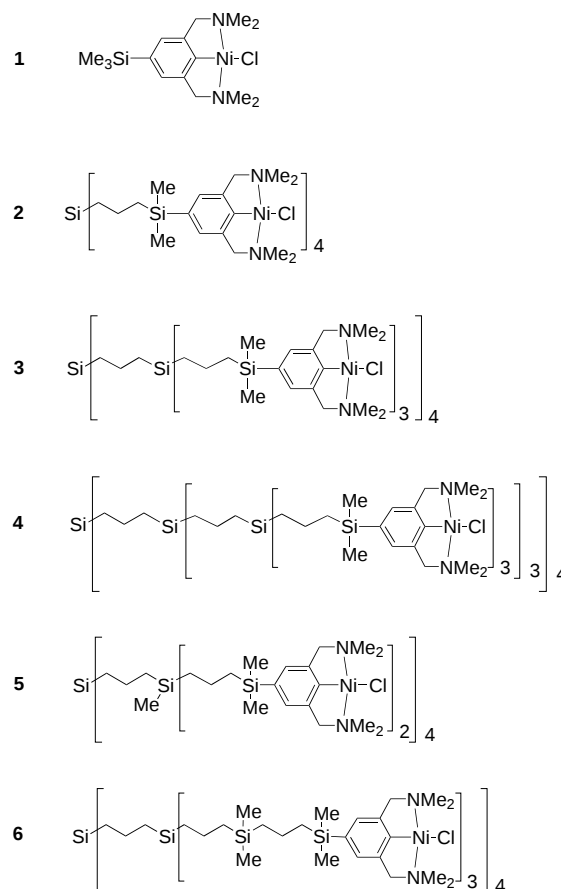
A promising application of (metallo)dendritic macromolecules^[1] is their use in homogeneous catalysis.^[2] Because of their size and well-defined molecular architecture, they may easily be recovered from reaction mixtures and so combine the advantages of homogeneous and heterogeneous catalysis. We have obtained such multimetallic catalytic materials,^[2a, 3, 4] by attaching potentially N,C,N-chelating aryldiamine ligands [2,6-{CH₂NMe₂}₂C₆H₃][−] (“NCN”),^[5] coordinated to a variety of transition metals, to the exterior of carbosilane dendrimers. The nickel-containing catalysts are active in atom-transfer radical addition (ATRA) reactions,^[6] for example the Kharasch addition reaction.^[7] In our original design,^[2a] the d⁸ [Ni^{II}(NCN)] catalytic sites were connected to the carbosilane (CS) support by long-chain carbamate linkers, and each nickel center acted as a single-site catalyst (Scheme 1).^[8]

To study the effect of the nature and length of the carbamate linkers on the catalytic activity, we connected the



Scheme 1. Postulated key intermediate steps in the Kharasch addition reaction catalyzed by the [Ni^{II}(NCN)] complexes. Abbreviations: k_f = forward reaction, k_b = back reaction, k_p = forward product-forming reaction, k_r = back “radical-reforming” reaction.

[Ni^{II}(NCN)] complexes directly to the silicon atoms of the CS support and varied the structure of the support (Scheme 2). We here present the first direct evidence for the existence of a “dendritic effect” in redox catalysis^[9] with CS-supported metal catalysts.



Scheme 2. Schematic structures of the mononuclear reference compound **1** and the different generations of catalytically active, nickel-centered carbosilane dendrimers **2–6**.

The nickel dendrimers^[10] (Scheme 2) were prepared by polyolithiation of the CS-ligand precursors and subsequent transmetalation with [NiCl₂(PEt₃)₂]. This gave the orange, oxidation-sensitive nickel derivatives **1–6** (with molecular weights up to ≈ 15 kD) in moderate to good yields (32–86 %). A disadvantage of this procedure is that not all NCN groups become metalated.^[11]

We have used materials **1–4** as catalysts in the Kharasch addition of CCl₄ to methyl methacrylate (MMA) under standard reaction conditions (see Table 1 and Experimental Section). The data show a marked decrease in catalytic activity with increasing generation number (Figure 1). During the catalytic runs with G1-Ni₁₂ (**3**) and G2-Ni₃₆ (**4**), purple to brown precipitates formed which had lost catalytic activity.^[12] We believe that in these precipitates the Ni^{II} sites are (partly) irreversibly oxidized to Ni^{III} sites (the [Ni^{III}X₂(NCN)] complexes are purple/brown and much less soluble than their Ni^{II} analogues). The formation of these precipitates indicates that the back reaction of the Ni^{III} site with the product radical P[•] (Equation (3) in Scheme 1) or with the initial radical •CCl₃ (Equation (1) in Scheme 1) becomes less efficient with time.

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Table 1. Catalytic and kinetic data for **1** and the CS–nickel(II) dendritic catalysts **2–6** in the Kharasch addition of CCl₄ to MMA.^[a]

Compound	t [h]	Conversion [%] ^[b]	TOF ^[c]	TTN (per Ni)
1	0.25	15	163	277 ^[d]
	2	91		
G0-Ni ₄ 2	0.25	9	98	272 ^[d]
	2	79		
G1-Ni ₁₂ 3	0.25	3	39	56 ^[d]
	2	17		
G2-Ni ₃₆ 4	0.25	0.2	2	9 ^[d]
	2	1.0		
G1'-Ni ₈ 5	0.25	5	47	253 ^[e]
	2	27		
G1''-Ni ₁₂ 6	0.25	8	85	257 ^[e]
	2	54		

[a] In all catalytic runs the concentration of nickel was kept constant. [b] Selectivity for the formation of the 1:1 adduct of methyl methacrylate and CCl₄ is >99%. Conversion calculated from the formation of the 1:1 addition product as determined with GC analysis using dodecane as an internal standard. [c] Per nickel center per hour; during the first 15 min. [d] After 4 h. [e] After ca. 22 h.

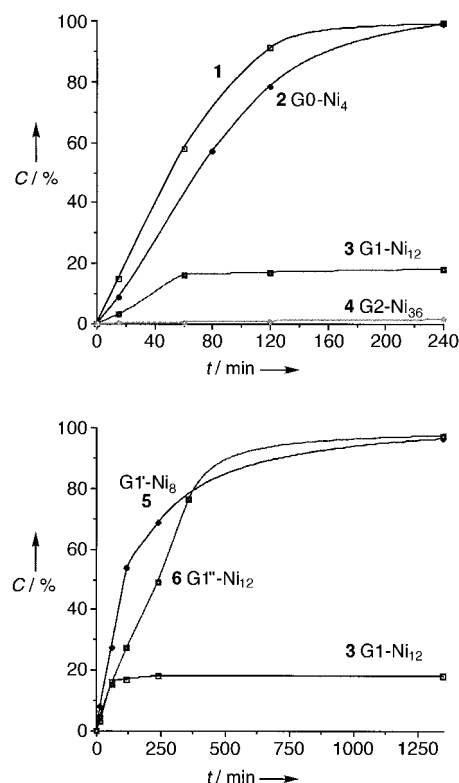


Figure 1. Catalytic activity of the nickel compounds **1–6** in the Kharasch addition of CCl₄ to MMA. C = conversion.

This inhibitive effect could be mimicked by treatment of model compound **1** with CCl₄ in the absence of MMA and (co-)solvent. This leads to the formation of a paramagnetic, brown compound which was identified by X-ray crystal structure analysis as [Ni^{III}Cl₂{C₆H₂-2,6-(CH₂NMe₂)₂-4-SiMe₃}].^[13] The only organic product formed was C₂Cl₆, probably by coupling of two CCl₃ radicals. For each C₂Cl₆ molecule formed in this way, two equivalents of the Ni^{III} site remain which in this case cannot be recycled into the Ni^{II} complex.

Molecular modeling (MM2) shows that in **3** the nickel sites are much closer (closest distances about 8–11 Å) than in **2**

(average distance about 19 Å). The Ni–Ni distance in the [G2] dendrimer **4** will certainly be even smaller.^[14] This suggests that the catalyst deactivation observed in **3** and **4** is caused by proximity effects in which the Ni^{III} sites interact with neighboring Ni^{II} sites (forming mixed-valence complexes) rather than with the transient radicals in solution. A related “dendritic effect” has recently been reported by Enomoto and Aida.^[15]

In order to test this hypothesis, two further [G1] dendrimers were synthesized: one G1'-Ni₈ species which contains fewer branches than **3** (**5**, Scheme 2) and one with an extra (CH₂)₃SiMe₂ tether, G1''-Ni₁₂ (**6**). In both dendrimers there is less congestion at the CS surface, and the proximity effect between the Ni^{II} sites should be smaller. When **5** and **6** were tested under the same standard conditions as given for **1–4** (see Table 1), both catalysts indeed showed a marked return of activity per metal atom. In fact, the total turnover numbers per nickel site were comparable to those of **1** and **2** (see Figure 1). These results support the view that the effectiveness of the reaction between the Ni^{III} site and the product radical P[•] in the series **2** (G0) > **3** (G1) > **4** (G2) is lowered by the increasing proximity of the Ni centers. What might happen is that in **3** and **4** a competing inner-sphere electron transfer occurs along the surface of the CS support between adjacent Ni^{II} and Ni^{III} centers (see Figure 2). Fabbrizzi et al. reported on a related redox-driven intramolecular anion translocation between a nickel and a copper metal center.^[16] In materials with high density of nickel, this would result in the formation of mixed-valence nickel sites which have a lower catalytic activity than single Ni^{II} sites.

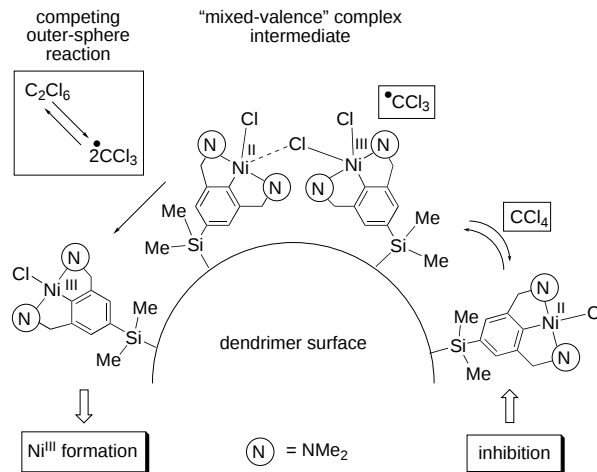


Figure 2. Schematic representation of the deactivation processes on the CS surface of the dendrimers **3** and **4**.

In summary, the catalytic activity of the nickelated dendrimers **2–6** is greatly affected by “surface congestion”, and thus the carbosilane support plays a pivotal role in active-site accessibility. The decrease in the catalytic activity observed with **3** or **4** is ascribed to formation of a mixed-valence Ni^{II}/Ni^{III} complex on the dendrimer periphery that competes for reaction with substrate radicals. These results support earlier work on metal-center accessibility as a key to metallodendrimer reactivity.^[15]

Experimental Section

Standard catalytic system: Prior to use, a mixture of MMA (28 mmol), CCl₄ (104 mmol), and dodecane (internal standard, 8.9 mmol) was degassed thoroughly using the freeze-pump-thaw method. The catalyst (ca. 9.1×10^{-5} mol) in CH₂Cl₂ (ca. 10 mL) was then added at room temperature under an inert atmosphere. The reaction was monitored by withdrawing samples for GC analysis at regular time intervals.

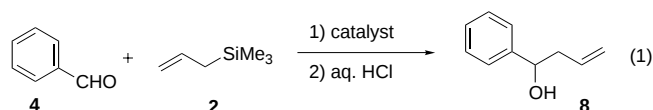
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- [10] Similar protocols have been used for the synthesis of related multiplatinated systems.^[3] The nickelated dendrimers **2–6**, as well as their ligand precursors, have been characterized by NMR techniques (¹H, ¹³C, ²⁹Si), mass spectrometry (FAB, MALDI-TOF), and microanalyses. Full experimental data will be reported elsewhere.
- [11] Nickel incorporation was found to be in the range of 80–89%. This incomplete nickel incorporation (estimated by ¹H and ¹³C NMR spectroscopy, elemental analyses, as well as mass spectrometry) can be ascribed to partial hydrolysis of the C–Li bond(s) during workup. However, this aspect does not hamper the use of these metallodendrimers in catalytic applications. Further details will be reported in a full paper.
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Aluminum Bis(trifluoromethylsulfonyl)amides: New Highly Efficient and Remarkably Versatile Catalysts for C–C Bond Formation Reactions**

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Lewis acids are powerful tools in many different reactions such as Diels–Alder reactions, aldol synthesis, and the Sakurai reaction. The aim is now to develop more-reactive Lewis acidic species that catalytically promote these synthetically valuable transformations.^[1] Metal triflates (triflate = OTf) are employed as Lewis acids to promote important carbon–carbon bond formation reactions since the trifluoromethylsulfonyl (Tf) group is one of the strongest neutral electron-withdrawing groups.^[1, 2] However, a major limitation of the known metal triflates is the synthesis of highly valuable homoallyl alcohols (for example, **8**) by the Lewis acid promoted reaction of aldehydes with inexpensive and non-toxic allyl trimethylsilane [Eq. (1)]. The formation of such homoallyl alcohols necessitates the use of allyl tin reagents instead.^[3, 4]



Attempts to develop more reactive Lewis acidic species for this transformation by modification of the triflate ion with more electron-withdrawing counterions have failed.^[5] Herein we report the first successful development of new versatile catalysts derived from the superacid bis(trifluoromethylsulfonyl)amine (Tf₂NH)^[6] that promote allylation and other important reactions with unprecedented efficiency.

Recently, ytterbium triflate (Yb(OTf)₃) was shown to promote the reaction between aldehydes and allyl tributyltin reagents but that allyl silanes were unaffected by this reagent.^[7] Attempts to develop a more-reactive Lewis acid by modification of the triflate ions with the more electron-withdrawing counterion bis(trifluoromethylsulfonyl)amide (bistriflylamide) failed.^[5] The desired homoallyl alcohol **8** was only formed in trace amounts and generated TMSNTf₂ (TMS = trimethylsilyl) as a side product, which is believed to be the actual promoter for this reaction. This proposal is supported by our finding that catalytic amounts of TMSNTf₂^[8] or Tf₂NH (**1**), which generates TMSNTf₂ in situ through reaction with **2**, form **8** in moderate yield along with substantial amounts of undesired products (Table 1, entries 1 and 2).

Similar results were obtained when (iPrO)₂Ti(NTf₂)₂^[9] and Al(NTf₂)₃^[9] were employed (Table 1, entries 3 and 4). These

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