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[17] All new compounds were fully characterized by spectroscopic methods (^{1}H NMR, ^{13}C NMR, MS), elemental analyses and crystal structure analyses. **6**: Colorless solid, m.p. 245–246 °C (decomp); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.57-0.66$ (m, 8H), 0.73–0.90 (m, 24H); ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): $\delta = 4.63$ ($8\,CH_2$), 7.25 ($8\,CH_2$), 21.44 (8C), 26.57 (4C), 114.17 (2C); elemental analysis (%) calcd for $C_{30}H_{32}$ (392.6): C 91.78, H 8.22; found: C 91.64, H 8.09. **7**: Colorless solid, m.p. 212 °C (decomp); ^{1}H NMR: $\delta = 0.61-0.94$ (m, 28H), 1.15–1.25 (m, 4H); ^{13}C NMR: $\delta = 4.99$, 6.78, 7.01, 7.67 ($4\,CH_2$), 19.04 (8C), 17.85 (4C), 32.45 (2C), 37.69 (C); elemental analysis (%) calcd for $C_{31}H_{32}Cl_2$ (475.5): C 78.31, H 6.78, Cl 14.91; found: C 78.20, H 6.75, Cl 14.68. **8**: Colorless solid, m.p. 223–225 °C (decomp); ^{1}H NMR: $\delta = 0.61-1.00$ (m, 30H), 1.34–1.42 (m, 2H); ^{13}C NMR: $\delta = 4.87$, 4.98, 6.63, 6.80, 6.86, 6.98, 7.54 ($2\,CH_2$), 6.51 (d, $^{5}J_{C,F} = 3.8$ Hz, $2\,CH_2$), 17.55, 18.08, 18.96, 32.46 (2C), 18.63 (d, $^{4}J_{C,F} = 3.1$ Hz, 2C), 31.88 (d, $^{3}J_{C,F} = 1.8$ Hz, 2C), 34.08 (d, $^{2}J_{C,F} = 10.6$ Hz, 2C), 90.60 (d, $^{1}J_{C,F} = 320.7$ Hz, C); elemental analysis (%) calcd for $C_{31}H_{32}BrF$ (503.5): C 73.95, H 6.41, Br 15.87; found: C 73.84, H 6.38, Br 15.64. **9**: Colorless solid, m.p. 191–193 °C; ^{1}H NMR: $\delta = 0.47-0.60$ (m, 8H), 0.63–0.86 (m, 24H), 0.94 (s, 2H); ^{13}C NMR: $\delta = 3.02$, 4.64, 5.99, 6.49 ($4\,CH_2$), 5.83 (CH_2), 18.00, 18.49, 27.64, 22.55 (2C); elemental analysis (%) calcd for $C_{31}H_{34}$ (406.6): C 91.57, H 8.43; found: C 91.81, H 8.56.

[18] Systematic names: 24-dichloro- (**7**), 24-bromo-24-fluoro- (**8**), tetradecaspiro[2.0.2.0.0.0.0.0.2.0.2.0.0.0.2.0.2.0.0.1.0.0.2.0.2.0.0.0]untriacontane (**9**).

[19] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-142835 (**6**), -142836 (**7**), -142041 (**8**), and -142837 (**9**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[21] For comparison, in spiropentane itself the angles Ψ and Φ are 90.2 and 179.6°, respectively, while in ethano-bridged spiropentane Ψ and Φ are 80.0 and 154.0°, respectively. See for example R. Boese, D. Bläser, K. Gomann, U. H. Brinker, *J. Am. Chem. Soc.* **1989**, *111*, 1501–1503.

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Cross-Linked Scandium-Containing Dendrimers: A New Class of Heterogeneous Catalysts

Manfred T. Reetz* and Dirk Giebel

Dedicated to Professor José Barluenga
on the occasion of his 60th birthday

Interest in metal-containing dendrimers as catalysts[1] is increasing because in principle they combine the advantages of homogeneous and heterogeneous catalysis in one system.[1c] Nevertheless, recyclization and reuse of such catalysts is not always demonstrated, which raises the question of whether in such cases the synthetic effort necessary in their preparation is actually meaningful.[1d] Here we report on scandium-containing dendrimers, which have useful catalytic properties as Lewis acids and which can also be easily recycled and reused without any appreciable loss in activity. In contrast to soluble dendritic catalysts previously described, our materials are heterogeneous catalysts that are insoluble due to a Sc-promoted cross-linking of individual dendrimer units.[2–4] Application in catalysis is based on previous reports by Kobayashi according to which scandium salts having electron-withdrawing ligands as in $Sc(OTf)_3$ (Tf = triflate = F_3CSO_2), $ScCl_3$, $Sc(NTf_2)_3$, $Sc(PF_6)_3$, or polyallyl scandium trifylamido ditriflate (PA-Sc-TAD) are effective catalysts in Mukaiyama aldol additions to aldehydes and aldimines, Diels–Alder and Michael additions as well as Friedel–Crafts acylations.[5]

The commercially available dendrimer DAB-dendr-$(NH_2)_{32}$ **1**[6] with 32 outer primary amino groups was first subjected to sulfonylation using Tf_2O/Et_3N. The reaction afforded a solid compound **2** which turned out to be only slightly soluble in conventional solvents. The IR spectrum does not show any bands near 3359 cm^{-1} typical of primary amino groups; rather, absorption at 3489 cm^{-1} characteristic of $(R)HNSO_2CF_3$ functions is clearly visible. Thus, most of the outer amino groups appear to have been sulfonylated. We then envisioned that these functional groups can bind to scandium with concomitant cross-linking of the dendritic units **2**. For this purpose a suspension **2** in THF was treated with different amounts of the cross-linking agent $Sc(OTf)_3$ in the presence of KH as base. As a typical result the completely insoluble solid material **3** was formed, which according to elemental analysis has a Sc/N ratio of 0.2 corresponding to about 40 % Sc-loading (see Experimental Section). Although a large proportion of the outer amino groups are likely to exist as $N(Tf)[Sc(OTf)_2]$ units, some of them serve as cross-linking points with two (or three) sulfonamido ligands at scandium (symbolized by **3**). The X-ray powder diffractogram points to a completely amorphous solid. Thus, the possible presence of nonreacted $Sc(OTf)_3$ trapped in the solid matrix can be excluded.

In order to obtain some information concerning the surface morphology and the actual cross-linking, a scanning electron

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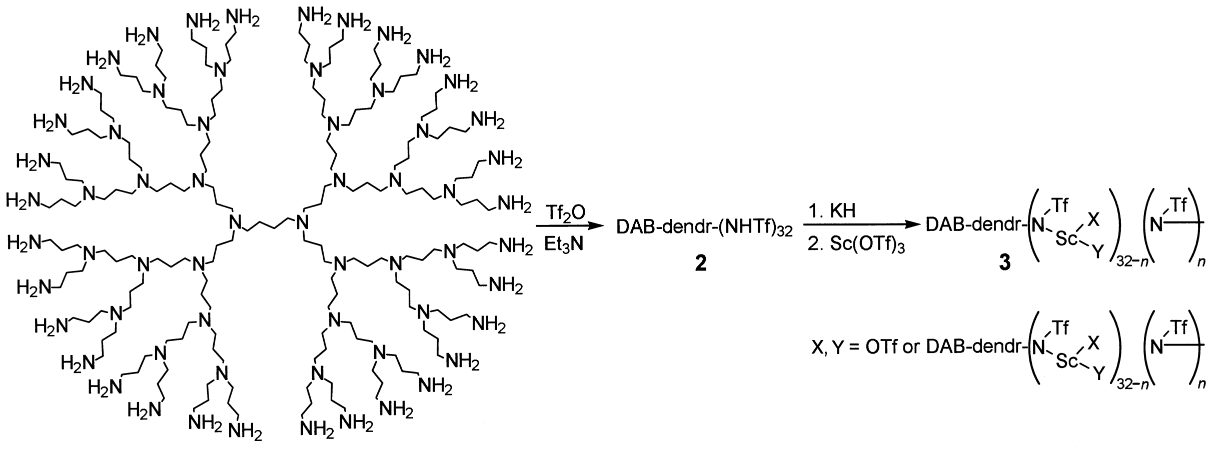
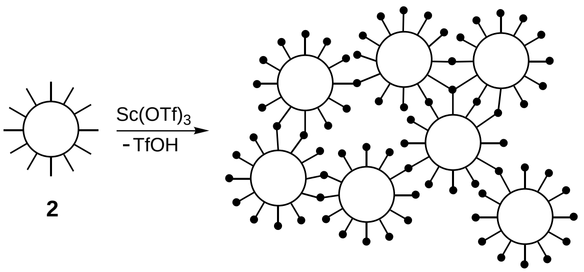


1 (DAB-dendr-$(NH_2)_{32}$)

microscopic (SEM) study was undertaken. Compound **3** was first attached to an aluminum surface using conductive carbon adhesive tabs and then treated with some gold vapor in order to prevent charge buildup on the surface. The SEM pictures show the presence of a wide-meshed scalelike morphology, the individual scales being about 10–20 μm large (Figure 1a). Upon further magnification threads become visible which probably result from outer shearing forces during preparation and which speak for the polymeric nature of the material (Figure 1b). Even at maximum magnification no dendritic structures are visible on the scales, because under the conditions used maximum resolution of the instrument has been reached.



3 (• = Sc)

Scheme 1. Schematic representation of **3** (Sc units bear two sulfonamido groups; cross-linking Sc units bear one or no such groups).

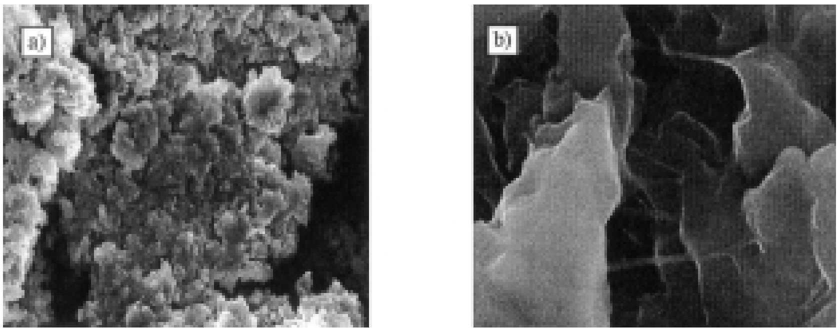
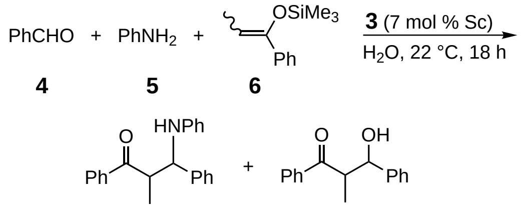


Figure 1. SEM visualization of samples of **3** at different magnification: a) ×500; b) ×10000.

The cross-linking can be represented schematically as in Scheme 1. At this point of our investigation it remained unclear whether the catalytically active Sc centers in the inner part of the solid material **3** are actually accessible for potential reaction partners.

Additional studies pertaining to the nature of the surface and the porosity of the solid **3** were performed with argon adsorption measurements. The adsorption isotherms indicate Ar adsorption only at saturation pressure. Thus, the material is not porous. The Brunauer–Emmet–Teller (BET) evaluation resulted in a value of only 9 $m^2 g^{-1}$.[7]

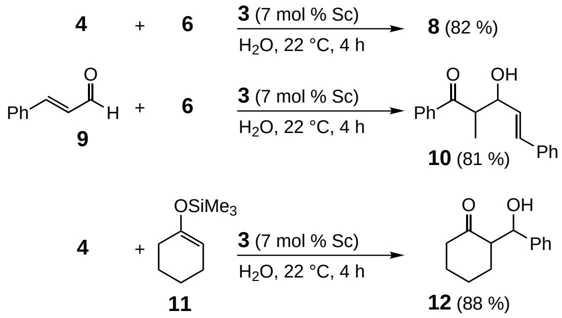
Although appreciable catalytic activity seemed unlikely in view of these results, experiments directed towards testing **3** in catalytic reactions were nevertheless performed. The three-component reaction of benzaldehyde (**4**), aniline (**5**), and enolsilane **6** with formation of the β-amino ketone **7** was tested first.[5] Accordingly, the catalyst **3** (7 mol% Sc) was added to the two-phase system composed of water and the three reaction components **4**, **5**, and **6**, and the mixture was vigorously stirred at 22 °C (see Experimental Section). During this process a swelling of the solid material **3** was observed. Following separation of the solid, the aldimine adduct **7** was isolated as the only product (89%). Thus, the catalyst is highly active and completely chemoselective. It is likely that the swelling allows for efficient transport of the reaction partners and therefore enables access to the catalytically active Sc centers in the interior of the material. Moreover, the recycled catalyst showed identical performance (88–89% yield; **7**:**8** >99:1), which remained constant even after three runs.



7 (88-89 %) >99:1 **8**

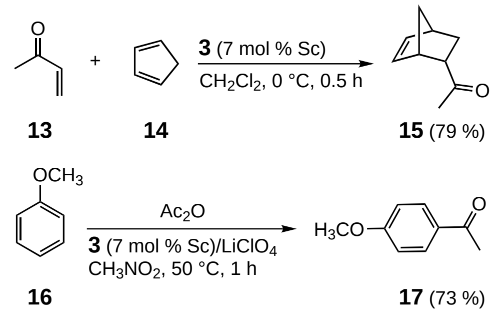
For comparison the use of $Sc(OTf)_3$ (10 mol %) in CH_2Cl_2/CH_3CN (2/1) as solvent, this time in the presence of the usual molecular sieves (4 Å), afforded an 86:14 product mixture of **7** and **8** (90 % total yield), whereas under identical conditions the polymeric catalyst PA-Sc-TAD resulted in the exclusive formation of the β-amino ketone **7**.[5] Thus, the dendritic catalyst **3** and the polymeric catalyst PA-Sc-TAD[5] have similar catalytic properties which are quite different from the "monomeric" Sc catalyst $Sc(OTf)_3$. The reason is probably not so much the so-called polymer effect,[5] but rather the influence of the ligands. On the practical side, recyclization of the solid material **3** is simpler than that of the rubberlike PA-Sc-TAD. In no case did the aqueous filtrate of the suspension of catalyst **3** turn out to be catalytically active, thereby proving that Sc leaching followed by homogeneous catalysis does not occur. Indeed, the ICP analysis of the aqueous filtrate showed essentially no scandium (< 1 ppm Sc). Hydrolysis with formation of catalytically active CF_3SO_3H, although conceivable, is also excluded.

In a further test reaction the Mukaiyama aldol addition of **6** to **4** was performed in water at 22 °C (4 h) using **3** (7 mol % Sc) as the catalyst, resulting in an 82 % yield of **8** as a 1:1 diastereomer mixture. Here again the multiply recycled catalyst showed no decrease in activity. Similar results were observed in the addition of **6** to cinnamaldehyde (**9**) and of **11** to benzaldehyde (**4**). In all cases the usual swelling of the catalyst was observed, a prerequisite for the efficient transport of reaction components into the inner part of the solid catalyst. Thus, not only the outer, but also the inner Sc centers are involved in catalysis.



It is also possible to use the heterogeneous dendritic catalyst **3** in organic solvents, as in the Diels–Alder reaction of methyl vinyl ketone (**13**) with cyclopentadiene (**14**) with formation of adduct **15** (*endo*/*exo* = 85:15). Finally, the **3**-catalyzed acylation of anisol (**16**) with acetic acid anhydride and $LiClO_4$ as an additive[5] afforded *p*-methoxyacetophenone (**17**) in 73 % yield. This is the first example of a Friedel–Crafts reaction induced by a dendritic catalyst.

In summary, we have shown that cross-linked Sc-containing dendrimers of the type **3** are stable, effective, and environmentally benign heterogeneous catalysts with Lewis acidic properties. They can be handled in air, used in aqueous or organic medium, and are easily recycled and reused without any appreciable loss of catalytic activity.[8] The concept of metal-induced cross-linking of appropriate dendrimers may well lead to new and efficient heterogeneous catalysts in other cases as well, for example in Al analogues of **3**.



Experimental Section

Preparation of **3**: To the solution of dendrimer **1**[6] (233 mg, 2.12 mmol) in dry 1,2-dichloroethane (5 mL) was added dropwise trifluoromethane sulfonic acid anhydride (370 µL, 2.20 mmol). Triethylamine (310 µL, 2.2 mmol) was then added dropwise and the mixture was stirred for 30 min at −20 °C. Thereafter the mixture was stirred at 60 °C for 15 h, the solvent was removed and the residue was washed three times with H_2O, 5 % NaOH, dioxane, and diethyl ether, respectively, providing **2** (476 mg; > 90 %) as a light brown solid. To the stirred suspension of **2** (432 mg, 1.8 mmol) in THF (10 mL) was added carefully potassium hydride (72 mg, 1.8 mmol). The mixture was stirred at 22 °C for 10 min, and the highly viscous solution was treated with scandium(III) trifluoromethane sulfonate ($Sc(OTf)_3$) (886 mg, 1.8 mmol). After the mixture had been stirred for 24 h, a brown gel had formed which was freed from the solvent in vacuo. The residue was washed three times with H_2O, diethyl ether, and H_2O/diethyl ether, respectively, to yield a light brown solid material which was dried in vacuo (0.9 g; ca. 80 %).

Procedure for the three-component reaction of **4**, **5**, and **6** with **3**: To the two-phase system composed of benzaldehyde (**4**) (53 mg, 0.5 mmol), aniline (**5**) (46.6 mg, 0.5 mmol), enolsilane **6** (155 mg, 0.75 mmol), and H_2O (3 mL) was added the catalyst **3** (30 mg, 7 mol % Sc), and the mixture was vigorously stirred for 18 h at 22 °C. The catalyst was filtered off and washed with H_2O (10 mL) and twice with dichloromethane (10 mL). The aqueous phase was washed with dichlormethane (10 mL), the combined organic phases were dried over $MgSO_4$ and the residue following removal of the solvent was subjected to flash chromatography using petoleum ether/ethyl ester (9/1) on silica gel: 140 mg (89 %) **7** as a 1:1 diastereomer mixture.

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[5] a) S. Kobayashi, *Eur. J. Org. Chem.* **1999**, 15–27; b) S. Kobayashi, S. Nagayama, *J. Am. Chem. Soc.* **1996**, *118*, 8977–8978; c) S. Kobayashi, S. Nagayama, *Synlett* **1997**, 653–654; d) D. Longbottom, *Synlett* **1999**, 2023.

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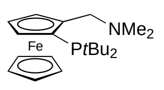
A New Palladium-Catalyzed Intramolecular Cyclization: Synthesis of 1-Aminoindole Derivatives and Functionalization of their Carbocylic Rings

Makoto Watanabe,* Toshihide Yamamoto, and Masakazu Nishiyama

Palladium-catalyzed cyclization reactions are a versatile and efficient method for the synthesis of a large number of heterocycles.[1] The formation of the indole ring system is of interest and has been carried out by many methods[2] because indole derivatives exhibit pharmacological[3] and physiological activity.[4] The palladium-catalyzed synthesis of indoles from *o*-haloaniline precursors is one of the most useful methods for the preparation of this class of compounds.[5]

Palladium-catalyzed C–N bond formation of amines with aryl halides recently proved to be a versatile method for the synthesis of a wide range of arylamines.[6] Transformation of the amination products into indole derivatives was examined. First, palladium-catalyzed cyclization of *o*-bromo-*β*-phenethylamines followed by dehydrogenation of the resulting indolines with Pd/C gave indoles with substituents in the 7-position.[7] Second, palladium-catalyzed coupling of benzophenone hydrazone with aryl bromides was also reported to give *N*-arylhydrazones, which were used as substrates for Fischer indole synthesis.[8] However, palladium-catalyzed direct formation of the indole ring by N-arylation of aryl halides has not been reported.

However, palladium catalyst systems employing $PtBu_3$ and mono- and bidentate phosphanes bearing P–*t*Bu bonds were reported for amination,[9] aryl ether formation,[10] Suzuki coupling,[9b, 11] the Heck reaction,[12] and ketone arylation,[13] after we disclosed that bulky electron-rich $PtBu_3$ afforded much higher catalytic activity than other phosphanes in the palladium-catalyzed amination of aryl halides with both aliphatic and aromatic amines.[14] One of the advantages of such phosphanes is the possibility of using unreactive aryl chlorides as substrates. Here we report a new method for the direct conversion of *o*-chloroarylacetaldehyde *N*,*N*-disubstituted hydrazones (**1**) into 1-aminoindole derivatives **2** and **4** by palladium-catalyzed intramolecular ring closure of **1** in the presence of $PtBu_3$, 1,1′-bis(di-*tert*-butylphosphanyl)ferrocene (DB^{t}PF), and 2-(dimethylaminomethyl)-1-(di-*tert*-butylphosphanyl)ferrocene (**3**) as ligands [see Eqs. (1) and (2)].



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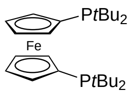

DB^{t}PF

o-Chloroarylacetaldehydes can be synthesized from commercially available *o*-chloroarylmethyl chlorides.[10c] Hydrazone derivatives **1** were prepared from the above aldehydes and *N*,*N*-disubstituted hydrazines, and isolated in 90–93% yield by distillation.[15] The palladium-catalyzed cyclization of **1** gave a 1-aminoindole ring system. The results of the indolization of **1** are summarized in Table 1. The reaction with sodium *tert*-butoxide in *o*-xylene at 120 °C in the presence of $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) and a bulky electron-rich phosphane gave a moderate yield of 1-(dimethylamino)indole (entry 1). A low yield was obtained in dioxane (entry 2). Whereas the yield of the reaction with the bidentate bis-phosphane DB^{t}PF[16] was lower than with $PtBu_3$ (entry 3), the reaction in the presence of the P,N ligand **3** gave 78% yield (entry 4).[17] Although many P,N ligands bearing *t*Bu–P bonds are available, we chose **3** because it can be readily synthesized in one step from commercially available dimethylaminomethylferrocene.[18] Cs_2CO_3 and Rb_2CO_3 could also be used as bases (entries 5 and 6). Synthesis of indoles with substituents on the carbocyclic rings was also possible (entries 7–9). Since indole derivatives bearing a Cl substituent on the carbocyclic ring can be utilized as substrates for more elaborate indoles in palladium-catalyzed reactions such as

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