*Polyolefins*

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# Efficient Mono- and Bifunctionalization of Polyolefin Dendrimers by Olefin Metathesis**

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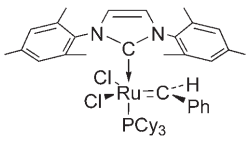
Olefin metathesis has recently transformed the way molecular chemists think about synthetic strategies.[1] Remarkable examples can be found in transition-metal architectures, such as ring-closing metathesis (RCM) of olefin-terminated ligands.[2,3] van Koten and Newkome have used stars for the nanofabrication of giant ring structures by using RCM,[4] and Zimmerman and co-workers have shown that RCM successfully allows molecular imprinting inside dendrimers and can be applied to the fabrication of nanotubes.[5] Indeed, RCM and ring-opening-metathesis polymerization (ROMP) are probably the most popular facets of olefin metathesis because of their considerable impact on the synthesis of biologically important cyclic compounds and polymers, respectively.[1] At first sight, cross metathesis (CM) is marred by the thermodynamic equilibrium that produces a mixture of compounds, but Blechert and co-workers showed that the excess of one olefin together with the Schrock Mo catalyst[1b] favors the formation of the cross product, whereas steric factors favor *E* stereoselectivity.[6] Grubbs and co-workers have shown that when a terminal olefin is metathesized with the second-generation Ru catalyst **A** (Cy = cyclohexyl) in the presence of another olefin bearing a strongly electron-withdrawing substituent, the stereoselectivity leads to high yields of the *E*-functionalized cross olefin.[7]




**A**

Despite the usefulness of this property in organic synthesis,[7] it has not been used in dendrimer chemistry.[8] Dendrimer functionalization is considerably more challenging than that of mono-olefin molecules, because it requires a clean and quantitative reaction to avoid the formation of mixtures among the branch termini.[8]

The $CpFe^+$-induced (Cp = cyclopentadienyl) activation of polymethylbenzenes under ambient or near-ambient conditions is known to efficiently produce polyolefin star and dendritic cores by reaction of such arene complexes with excess KOH and alkenyl halides in THF.[9] The reaction was extended to aryl ether complexes to yield to the phenol dendron $p$-$HOC_6H_4C(allyl)_3$ (**1**),[10a] which served as a brick for further dendrimer construction; for example, hydrosilylation of the polyolefin core with $HSiMe_2CH_2Cl$ followed by reaction of **1** yielded dendrimers with $3^n$ allyl branches ($n = 2$–10) starting from mesitylene.[10b] We now report that these star- and dendritic-shaped polyolefin dendrimers can be cleanly and stereospecifically mono- or bifunctionalized by CM or a combination of RCM + CM, respectively, using catalyst **A**. A quick, overall synthesis of water-soluble dendrimers from simple polymethylbenzenes, such as mesitylene and hexamethylbenzene, is therefore provided.

The reaction of $[CpFe(C_6Me_6)][PF_6]$ (**2**) with KOH + allyl bromide or 1-undecenyl iodide in THF, followed by visible-light irradiation in MeCN gives nearly quantitative yields of the known hexaolefin stars **4**[11a] and **5**,[11b] which give high yields of the new hexafunctionalized *trans* olefins **7** and **8** as the only reaction products upon reaction with $CH_2{=}CHCO_2R$ (R = H or Me) in the presence of 5 mol% of **A** (Scheme 1). The iron complex $[CpFe\{C_6(CH_2CH_2CH{=}CH_2)_6\}][PF_6]$ (**3**), the precursor of **4**, also gives hexafunctionalized iron complex **6a** upon metathesis with $CH_2{=}CHCO_2H$ using **A**, although partial decomplexation leads to reduced yields of the complexes.

In the case of mesitylene, complexation by the $CpFe^+$ species, reaction with KOH and allyl bromide in THF under ambient conditions, and decomplexation gives the known dendritic core $C_6H_3[C(CH_2CH{=}CH_2)_3]_3$ (**10**; generation 0 (G0)),[11c] whose metathetic reaction with $CH_2{=}CHCO_2R$ using **A** gives the new hetero-bifunctional compound **11**. This RCM + CM series of reactions inhibits the formation of the known capsule **12** formed from **10** in the absence of $CH_2{=}CHCO_2R$ with the same catalyst **A** (Scheme 2).[11d] As the tris-homofunctionalization of the triallylmethyl tripod is much less favored than RCM as an approach to form the cyclopentenyl group, we lengthened the dendritic tethers to prevent RCM. This lengthening of the tether was achieved by hydrosilylation of **10** with $HSiMe_2CH_2Cl$ followed by reaction with $p$-$OHC_6H_4O(CH_2)_9CH{=}CH_2$, thus giving the nonaolefin **13**. Contrary to **10**, the metathesis reaction of **13** with $CH_2{=}CHCO_2R$ only gives the CM product **14** (only *trans* isomers) which results from terminal-olefin functionalization (Scheme 2). Likewise, the tethers of the known 27- and 81-allyl dendrimers **15** and **18** (G1 and G2), which result from sequential hydrosilylation of **10** with $HSiMe_2CH_2Cl$,

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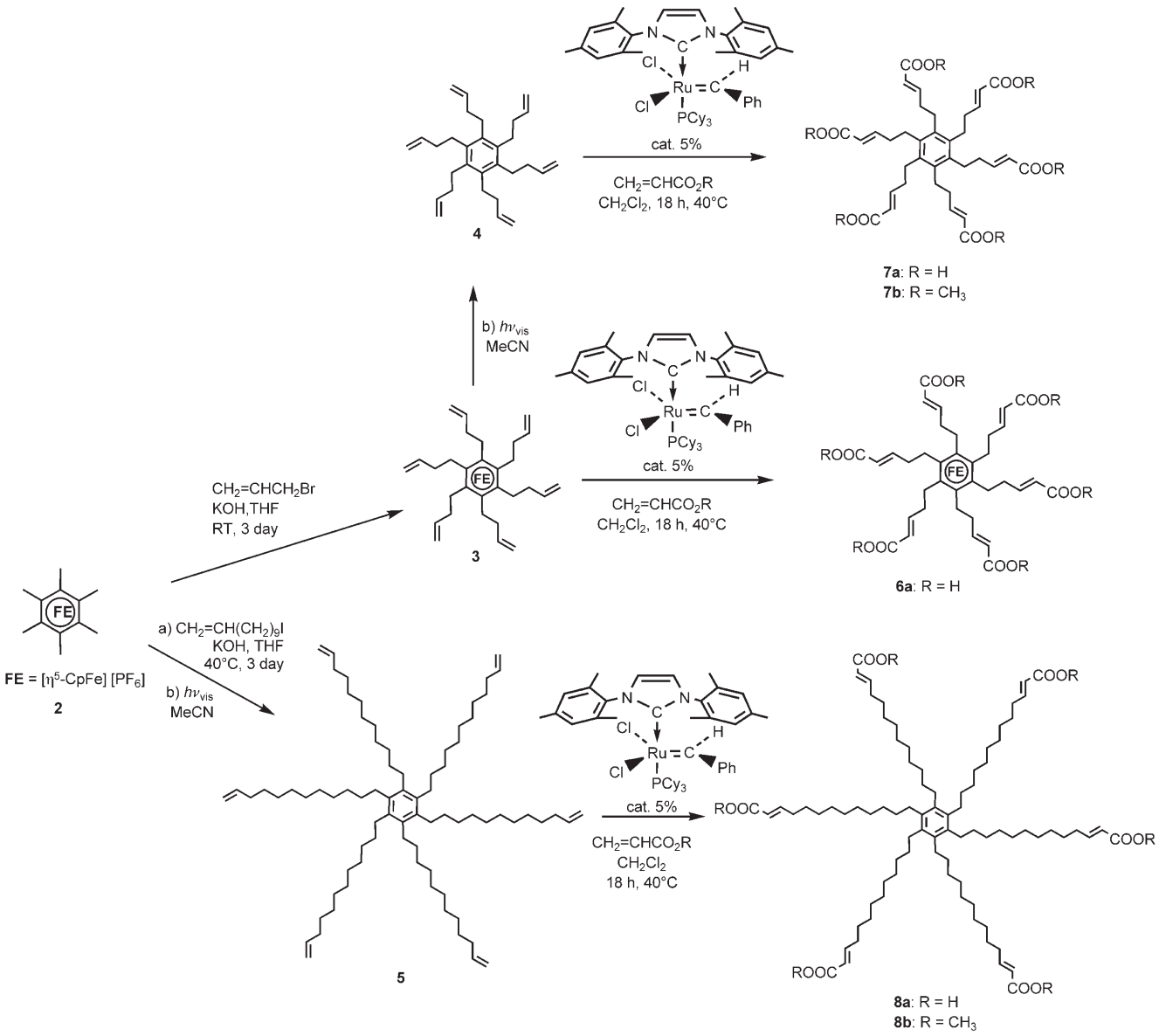
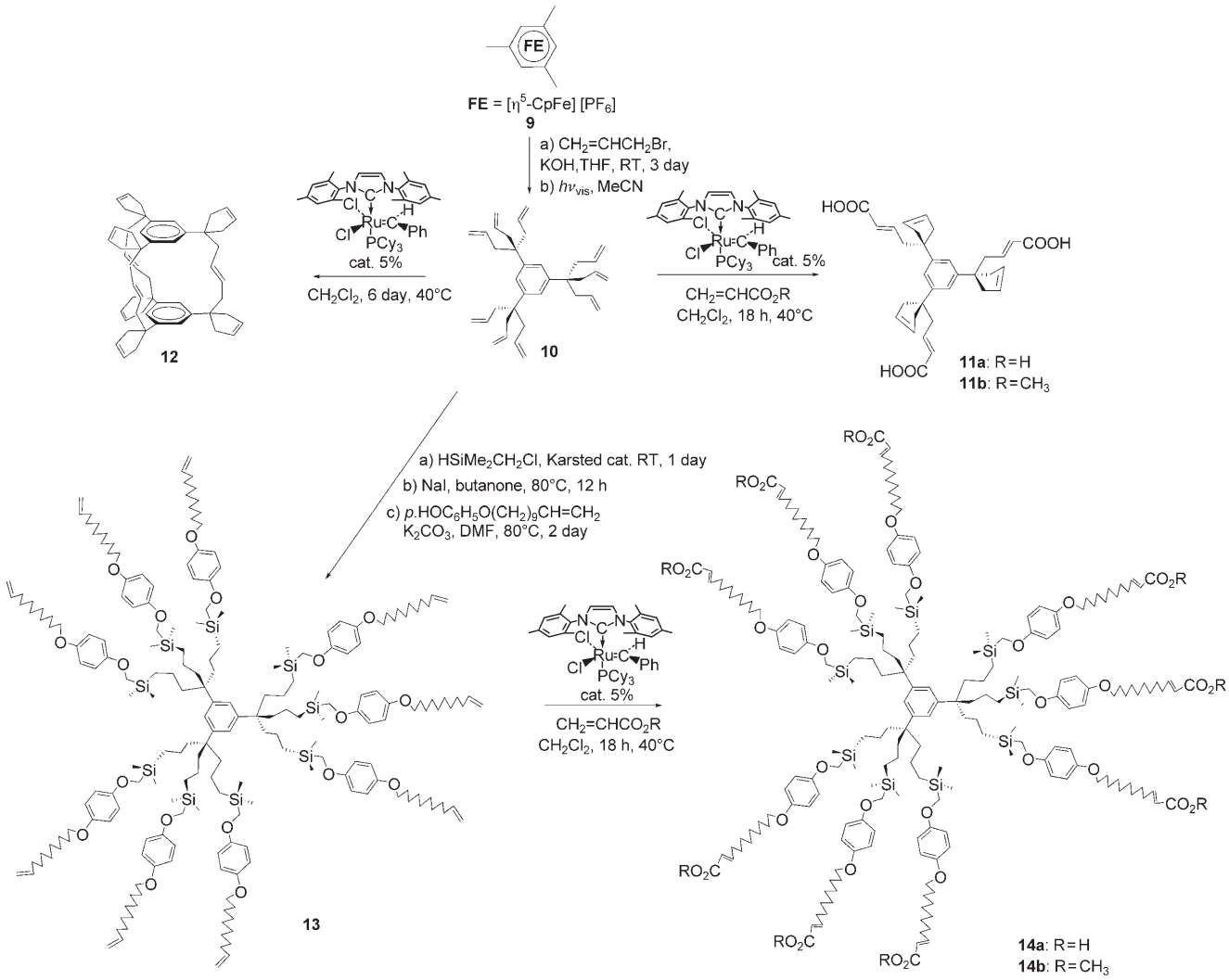



***Scheme 1.*** Synthesis of hexafunctionalized *trans* olefins **7** and **8**.

reaction with NaI, and treatment with $p$-$HOC_6H_4C(allyl)_3$, were lengthened in the same way to give the new 27- and 81-olefin dendrimers **16** and **19**; their metathesis with $CH_2$=$CHCO_2R$ proceeded analogously with **A** to give the polyfunctional dendrimers **17** and **20** (Schemes 3 and 4). All the polyfunctionalized dendrimers were characterized by $^1H$, $^{13}C$, and $^{29}Si$ NMR spectroscopy and elemental analysis. In addition, the MALDI-TOF mass spectra of **8a**, **8b**, **14a**, and **14b** only show the molecular peaks (see the Supporting Information), and size-exclusion chromatography (SEC) showing Gaussian-type distributions (Figure 1) confirm the monodispersities of the three generations of polyallyl and polyester dendrimers.

The poly(carboxylic acid) dendrimers give water- or methanol-soluble sodium carboxylate salts upon contact with aqueous NaOH or NaOH in methanol. Water-soluble dendrimers are used for applications such as molecular micelles and cation binding and transport.[12] The poly(carboxylic acid) dendrimers are also very useful for their reactions with various amines, a further functionalization procedure. For example, reaction of the new amine dendron $N[(CH_2)_4Fc]_3$ (Fc = ferrocenyl; **21**) with **20a** quantitatively yields the 243-ferrocenyl dendrimer **22** (Scheme 4) that shows a single wave in cyclic-voltammetric studies (see the Supporting Information), which is a key feature for redox sensing—the large dendrimer size also being favorable for electrode modification.[13] The formation of the 81 ammonium carboxylate linkages is shown by the change in solubility, from **20a** that is insoluble in $CH_2Cl_2$ (but soluble in acetone) to **22** that becomes soluble in $CH_2Cl_2$. Moreover, the $^1H$ and $^{13}C$ NMR signals of the methylene groups attached to the carboxylate and amine groups, respectively, are strongly shifted as expected in **22** relative to the precursors **20a** and **21** (see the Supporting Information).




***Scheme 2.*** Synthesis of the CM product **14**.

In conclusion, the finding of this remarkable quantitative chemio-, regio-, and stereoselective cross olefin metathesis with dendrimers using catalyst **A** provides a unique way to functionalize polyolefin-terminated dendrimers and to solubilize them in water and methanol. This reaction makes such useful dendrimers readily accessible on large scales from simple polymethylbenzenes in a few steps.[14]

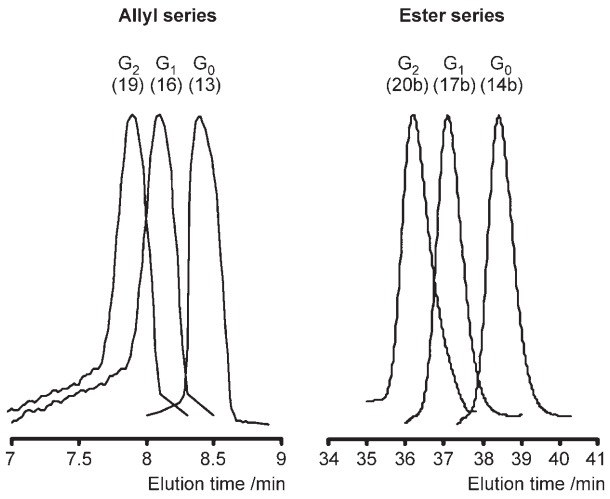
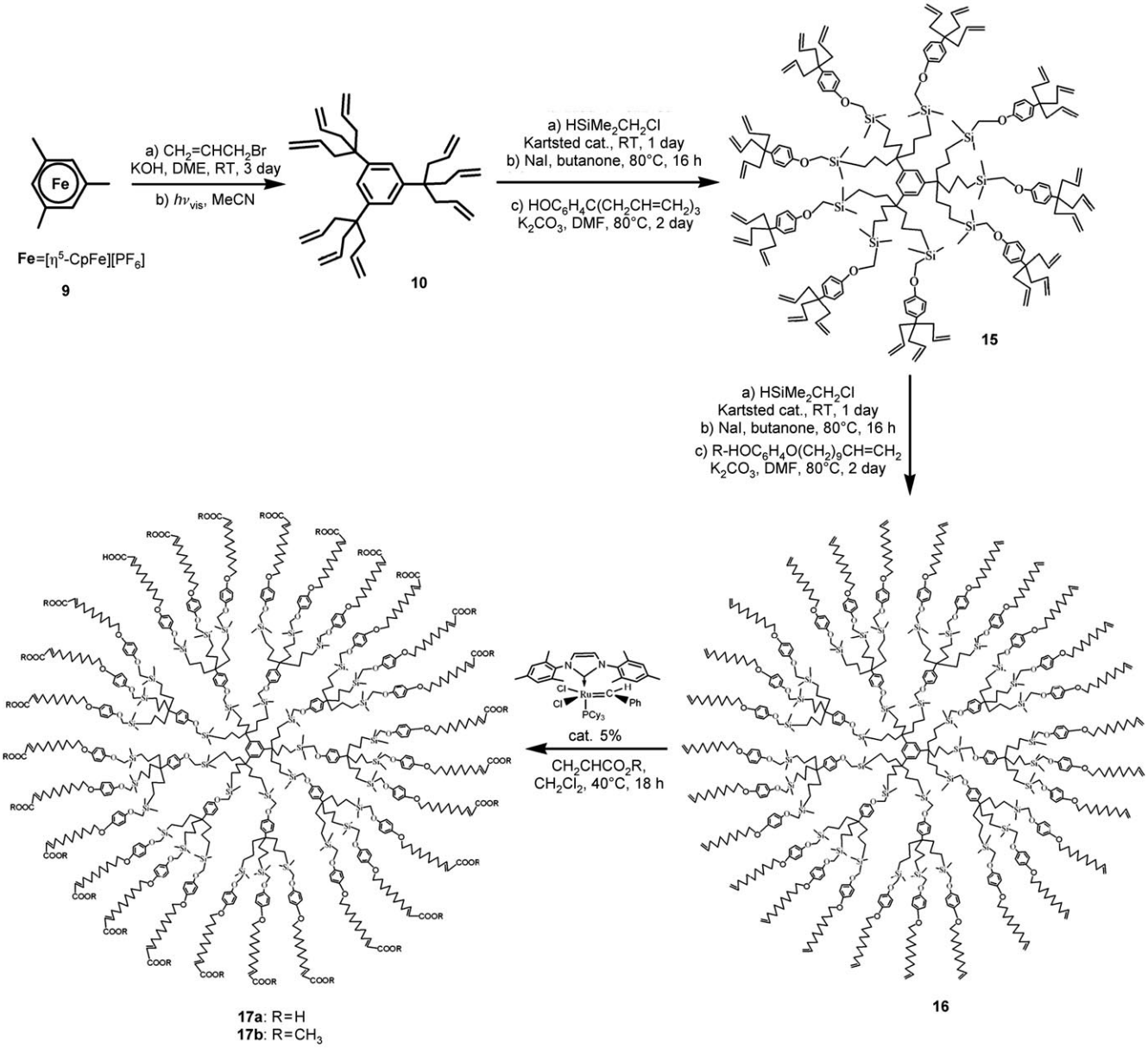



***Figure 1.*** Size-exclusion chromatograms of the three generations of dendrimers (9, 27, and 81 tethers, respectively) before (left) and after (right) functionalization by cross metathesis with methylacrylate. The polydispersity indices obtained from these chromatograms have values between 1.00 and 1.02. Apparent molar masses of the dendrimers were determined by using two different size-exclusion chromatographic apparatus, both equipped with a refractive index (RI; Jasco) and UV/Vis (Varian 2550, $l = 254$ nm) detectors. The columns used were four TSK-gel columns (7.8×300 mm, G 2000, G 3000, G 4000, G 5000 with particle sizes of 5, 6, 6, and 9 mm, respectively) and one PL Poly Pore column (7.5×300 mm, particle size = 5 mm). The eluent was THF (0.7 mL min$^{-1}$) at 25 °C and calibration was carried out using linear polystyrene standards.




***Scheme 3.*** Synthesis of the polyfunctional dendrimer **17**.

## *Experimental Section*

General metathesis experiments: the polyolefin dendrimer (0.0418 mmol/n dendritic tethers), dry $CH_2Cl_2$ (10–50 mL), methyl acrylate or acrylic acid (0.221 mmol), and catalyst **A** (5 mol% equivalents per dendritic branch, 0.0114 g, 0.0134 mmol) were successively introduced into a Schlenk flask in an inert atmosphere. The reaction solution was warmed to 40 °C for 18 h. After removal of the solvent under vacuum, the product was washed with methanol and precipitated by addition of a tenfold excess of methanol to a solution of the polyester dendrimers in $CH_2Cl_2$ or to a solution of the polycarboxylic acid dendrimers in THF. The colorless waxy organic dendrimers were usually obtained in 95–99% yield and were characterized by $^1H$, $^{13}C$, and $^{29}Si$ NMR spectroscopy; MALDI-TOF-MS of **8a**, **8b**, **14a**, **14b**, **16**, **17a**, **17b**, and **21** (observation of the molecular peak and absence of other peaks); elemental analysis; and size-exclusion chromatography (SEC, Figure 1).

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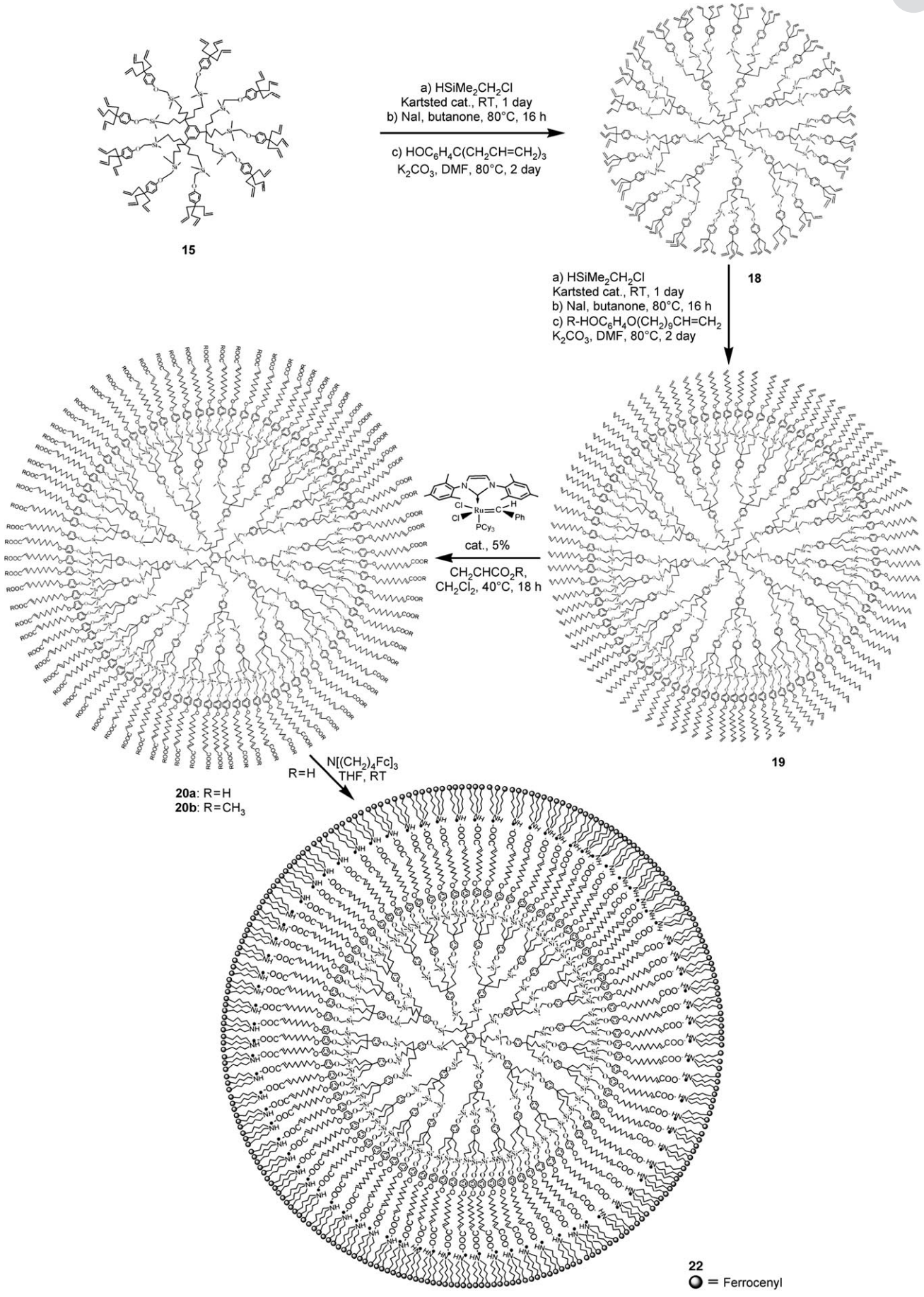


***Scheme 4.*** Synthesis of the polyfunctional dendrimer **22**.

  

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