Efficient and Recyclable Monomeric and Dendritic Ru-Based Metathesis Catalysts

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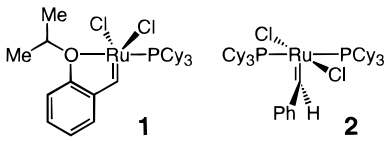
Abstract: Several highly active, recoverable and recyclable Ru-based metathesis catalysts are presented. The crystal structure of Ru complex **5**, bearing a 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene and styrenyl ether ligand is disclosed. The heterocyclic ligand significantly enhances the catalytic activity, and the styrenyl ether allows for the easy recovery of the Ru complex. Catalyst **5** promotes ring-closing metathesis (RCM) and the efficient formation of various trisubstituted olefins at ambient temperature in high yield within 2 h; the catalyst is obtained in >95% yield after silica gel chromatography and can be used directly in subsequent reactions. Tetrasubstituted olefins can also be synthesized by RCM reactions catalyzed by **5**. In addition, the synthesis and catalytic activities of two dendritic and recyclable Ru-based complexes are disclosed (**32** and **33**). Examples involving catalytic ring-closing, ring-opening, and cross metatheses are presented where, unlike monomer **5**, dendritic **33** can be readily recovered.

Introduction

We recently reported the synthesis and catalytic activity of Ru-based complex **1**,[1] which can efficiently catalyze the ring-closing metathesis (RCM) of dienes that contain terminal olefins.[2] We demonstrated that **1** can be recovered from the reaction mixture by silica gel chromatography in high yield and reused in subsequent C−C bond forming reactions. Despite the above unique attributes, several shortcomings remained to be addressed: (1) Similar to benzylidene catalyst **2**,[3] complex **1** is efficient mostly for substrates that contain terminal alkenes (synthesis of disubstituted alkenes). (2) In certain cases, because of adventitious coelution, isolation of **1** from the substrate is problematic. We therefore decided to turn our attention to alternative transition metal ligands that would enhance catalytic activity so that, upon release from 2-isopropoxystyrene, the propagating Ru-carbene is substantially more reactive. To address the issue of ease of recovery, we set out to design, synthesize, and examine Ru-based dendritic complexes.[4,5]

Organometallic dendrimers offer an attractive avenue for catalyst development because of their ease of characterization, their solubility in common organic solvents, and the facility and high level of certainty with which metal-containing sites can



1 **2**

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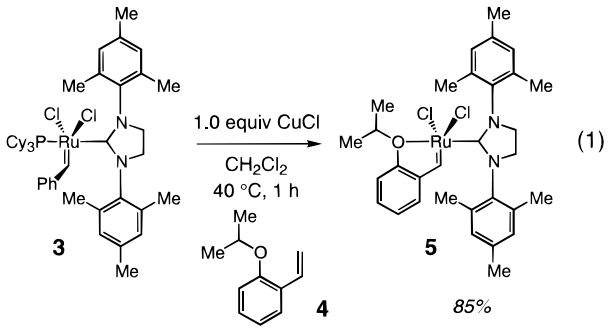
be incorporated within the macromolecular ensemble.[6] We suspected that Ru release and return (cf. Scheme 3) in the present systems would be more efficient than those in related polymer-bound analogues, largely because of the exposed binding sites at the dendrimer periphery. In general, catalyst efficiency is expected to be superior with a dendritic complex, since the more densely coiled backbone of a linear polymer in a heterogeneous solid support may hinder the availability and subsequent retrieval of the transition metal.[6]

Herein, we report the results of our studies designed to address the above issues. We disclose the synthesis of a new recyclable Ru-based catalyst[7] that is substantially more active than **1**. The first generation of dendritic and recyclable metathesis catalysts are presented here as well. Our studies demonstrate that Ru-based dendrimers are readily characterized and serve as homogeneous metathesis catalysts that are highly active and allow for significantly more facile catalyst recovery when compared to their corresponding monomers.

Results and Discussion

Synthesis and Structure of Ru Complex 5. To address the question of reactivity and maintain the structural features of the catalyst that allow it to be easily recyclable (by preserving the styrenyl alkoxide bidentate ligation), we set out to synthesize, characterize, and examine the catalytic activity of **5**. This strategy was based on the recently reported accelerating effect of a variety of saturated imidazolin-2-ylidene[8] and unsaturated[9] imidazol-2-ylidene carbene ligands[10] on the metathetic activity of Ru-based complexes. Thus, we established that, as depicted in eq 1, treatment of **3**[8a] with 1.0 equiv of CuCl and 0.97 equiv of **4** in CH_2Cl_2 at 40 °C delivers **5** within 1 h; styrenyl complex **5** can be isolated in air as a bright green solid in 85% yield after silica gel chromatography (mp = 178−181 °C dec).[11]



(1)

Single-crystal X-ray structure analysis of **5** (Figure 1; IMES = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) confirms the structural assignment.[12] Selected bond lengths and angles are provided in Table 1. The overall geometry around the transition metal center and most of the bond angles and bond lengths in **5** are analogous to their related values in complex **6** (see Scheme 1).[1a]

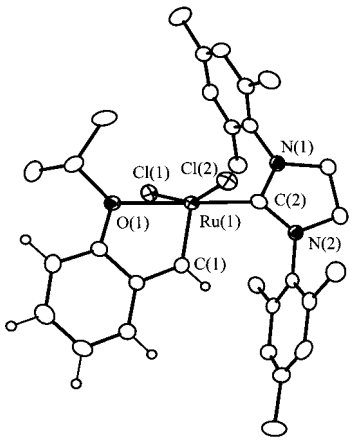


Figure 1. ORTEP diagram of $Cl_2Ru(=CH\text{-}o\text{-}OiPrC_6H_4)$(4,5-dihydroIMES) (**5**). Thermal ellipsoids are drawn at the 30% probability level. For selected bond distances and angles, see Table 1.

Comparison of the ^{1}H NMR spectra of **1** and **5** sheds light on some of the subtle structural attributes of these complexes. As illustrated in Scheme 1, there are two distinct chemical shift changes in the 400 MHz ^{1}H NMR spectra of **1** and **5**; one variation is observed at the *iso*-Pr methine proton and another at the carbene CH (H_α). In both instances, the protons for the imidazolin-2-ylidene system **5** are more shielded. These differences may be attributed to higher electron density at the transition metal center of **5**, caused by the stronger electron

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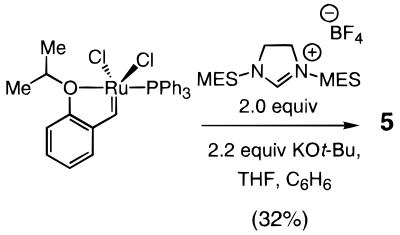
(11) The route shown below was also examined but proved to be less efficient (32% isolated yield is unoptimized; MES = 2,4,6-trimethylphenyl). See the Experimental Section for details of the synthesis of the imidazolinium salt.

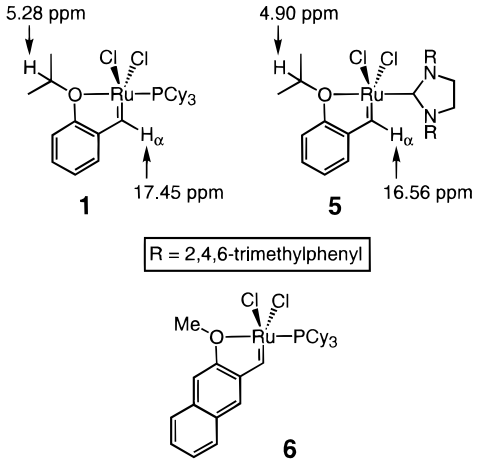


(12) A single crystal of **5** was obtained by slow diffusion of hexanes into a concentrated methylene chloride solution (−20 °C); crystal size 0.5 × 0.25 × 0.25 mm^3; monoclinic; space group $P2_1/n$; a = 13.7075(1) Å, b = 10.4555(8) Å, c = 22.846(2) Å; β = 95.3170(1)°; V = 3274.4(4) Å^3, D_{calcd} = 1.443 g/cm^3 for Z = 4; T = 293(2) K. The crystal lattice contained methylene chloride. Further details, including tables of crystallographic data, are available in the Supporting Information.

Table 1. Selected Bond Lengths and Angles for $Cl_2Ru(=CH\text{-}o\text{-}OiPrC_6H_4)$(4,5-dihydroIMES) (**5**)

Bond Lengths (Å)			
Ru(1)−C(1)	1.828(5)	Ru(1)−Cl(1)	2.328(12)
Ru(1)−C(2)	1.981(5)	Ru(1)−Cl(2)	2.340(12)
Ru(1)−O(1)	2.261(3)	C(2)−N(1)	1.351(6)
		C(2)−N(2)	1.350(6)
Bond Angles (deg)			
C(1)−Ru(1)−O(1)	79.3(17)	O(1)−Ru(1)−Cl(1)	86.9(9)
C(1)−Ru(1)−C(2)	101.5(14)	O(1)−Ru(1)−Cl(2)	85.3(9)
C(2)−Ru(1)−O(1)	176.2(14)	C(2)−Ru(1)−Cl(1)	96.6(12)
C(1)−Ru(1)−Cl(1)	100.2(15)	C(2)−Ru(1)−Cl(2)	90.9(12)
C(1)−Ru(1)−Cl(2)	100.1(15)	Cl(1)−Ru(1)−Cl(2)	156.5(5)
		N(1)−C(2)−N(2)	106.9(4)

Scheme 1

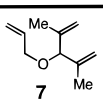
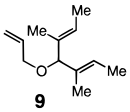
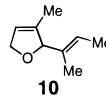
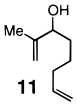
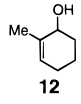
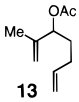
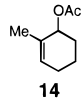
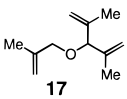
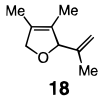
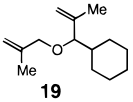
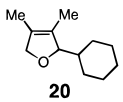


donation by the heterocyclic ligand (relative to PCy_3).[8] Thus, the weaker electron donation by the oxygen ligand to the Ru center in **5** may be manifested by the more upfield appearance of the isopropyl methine proton (4.90 versus 5.28 ppm). These comparisons must be tempered however, because the difference in the chemical shifts of H_α may be partially due to an anisotropic effect caused by the aryl units of the ligand in **5**.

Catalytic Activity and Recovery of Complex 5. As illustrated in Table 2, the Ru complex **5** serves as an effective catalyst for the RCM of dienes; hetero- and carbocyclics bearing trisubstituted alkenes are obtained from the corresponding precursor dienes in the presence of 5 mol % catalyst at ambient temperature within 10 min to 4 h. As shown in entries 1 and 2 of Table 2, both 1,1-disubstituted (**7**) and trisubstituted olefins (**9**) may be utilized in the synthesis of trisubstituted cyclic alkenes.[13] The catalytic RCM in entries 3 and 4 indicates that trisubstituted allylic alcohols (**12**)[14] and acetates (**14**) can be accessed in the presence of 5 mol % **5** within 2 h. As before, the Ru catalyst is recovered with high efficiency (95% and >98% yield, respectively). It must be noted that the recyclable catalyst **1** would be significantly less efficient in promoting the above transformations. As an example, treatment of **11** with 5 mol % **1** (22 °C, CH_2Cl_2) leads to only 15% conversion after 2 h (as judged by 400 MHz ^1H NMR analysis).

Two important points in connection to the above data merit mention: (1) In all instances, the catalyst is recovered along with the desired cyclic product in high yield after simple silica gel chromatography. Moreover, *addition of 2 equiv of styrene ether* **4** *(relative to the catalyst) to a solution of a transformation promoted by* **3** *at the end of the reaction time leads to the isolation of the recyclable catalyst* **5**. As an example, treatment of diene carbinol **11** with 5 mol % **3** (CH_2Cl_2, 22 °C, 1 h), followed by the addition of 10 mol % **4** and additional stirring for 1 h, leads to the formation of **12** and **5** in 98% and 82% yields, respectively (after silica gel chromatography). (2) Catalyst loadings lower than 5 mol % are sufficient. As exemplified by the reaction in entry 2, catalytic RCM can readily proceed to completion with only 1 mol % **5**. As another example, catalytic RCM of **7** occurs within 10 min at 22 °C in the presence of 1 mol % **5** to afford **8** in 73% isolated yield (>98% conversion); recovered **5** is obtained in 92% yield after chromatography.

Table 2. Ring-Closing Metathesis of Acyclic Dienes by Ru Complex **5**[a]

entry	substrate	product	time	conv (%)	product yield (%)[b]	catalyst recovery (%)[b]
1	 **7**	 **8**	10 min	>98	82	98
2	 **9**	 **10**	20 min	>98	87	98
3	 **11**	 **12**	2 h	>98	75	95
4	 **13**	 **14**	1.5 h	>98	82	>98
5	 **15**	 **16**	4 h	>98	98	95
6	 **17**	 **18**	44 h	42	38	81
7	 **19**	 **20**	30 min	70	65	60

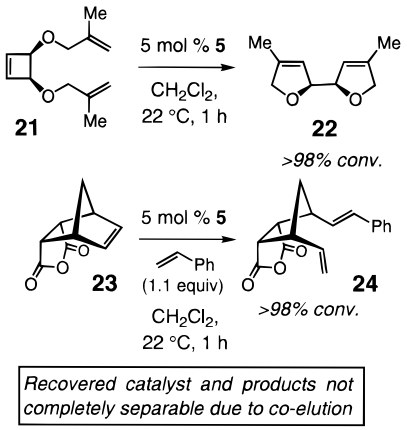
[a] Conditions: 5 mol % **5** for entries 1 and 3−7, 1 mol % **5** for entry 2, 22 °C, CH_2Cl_2 (entries 1−5); 24 h at 22 °C and 20 h at 40 °C, CH_2Cl_2 for entry 6; toluene, 80 °C for entry 7. [b] Isolated yields after silica gel chromatography.

As the reaction in entry 5 of Table 2 indicates, catalytic RCM involving 1,1-disubstituted alkenes of α,β-unsaturated carbonyls[9f] are also efficiently promoted by **5**. Tetrasubstituted olefins can even be obtained through catalytic RCM promoted by **5**, but less efficiently (entry 6). Nonetheless, even in this instance, the Ru catalyst is recovered in >80% yield. When toluene[9f] (80 °C) is used as the solvent in the catalytic RCM of **19** (entry 7), tetrasubstituted alkene **20** is formed in 65% isolated yield within 30 min (70% conversion); the catalyst recovery, however, suffers under these conditions (60%). Prolonged reaction times (1 h at 80 °C in toluene) lead to similar or lower yields of product and <10% catalyst recovery. The lower levels of efficiency observed in the synthesis of tetrasubstituted alkenes may be partly due to the fact that the styrenyl ligand effectively competes with the 1,1-disubstituted olefins, thus preventing the efficient

(13) Ru complex **3** is equally efficient in effecting the RCM reactions in Table 2. For example, catalytic RCM of **7**, **11**, and **13** proceeds in the presence of 5 mol % **3** and in a similar length of time as that for **5** (22 °C) to afford the desired products **8**, **12**, and **14** in 93%, 64%, and 72% yield, respectively. It is worth noting that all previously reported reactions promoted by **3** were carried out at 45 °C (see ref 8).

(14) For a recent report on the accelerating effect of an α-hydroxyl group on Ru-catalyzed RCM reactions, see Hoye, T. R.; Zhao, H. *Org. Lett.* **1999**, *1*, 1123−1125.

Scheme 2



formation of the requisite Ru-carbene derived from the triene substrate. In addition, the catalyst (or the released Ru-methylene) may not be stable under metathesis conditions at 80 °C for more than a few minutes.[15,16]

The catalyst retrieved from the above transformations after silica gel chromatography (recrystallization not needed) may be used in subsequent metathesis reactions with equal efficiency. For example, the catalyst recovered from the reaction in entry 1 of Table 2 was reused in the same reaction to afford the desired product **8** in 71% isolated yield (10 min, 22 °C). Complex **5** was again recovered in 98% yield after chromatography.

As the representative transformations in Scheme 2 indicate, **5** is an efficient catalyst in ROM/RCM[17] and ROM/CM[18] processes as well. Both transformations are completed within 1 h (>98% conversion). However, due to coelution, repeated and extensive attempts to accomplish a complete separation of the desired products from the recovered catalyst proved unsuccessful (>90% mass balance in both cases). At this point, we turned our attention to the preparation of active Ru-based catalysts that are more easily recoverable.

Dendritic Ru Complexes. We judged that macromolecular Ru complexes, because of their different polarities compared to the monomeric species, could be more easily separated from reaction products, and that one reasonable first step would be to prepare and examine dendritic rather than polymer-bound systems. This decision was also largely based on the relative ease with which dendrimers can be spectroscopically analyzed, allowing us to design and construct the molecular environment within which the Ru complex resides. With Ru-containing dendrimers, it would be possible to gauge rigorously the efficiency with which the active Ru-carbene leaves the ligation site and returns to the macromolecule (see below for details). Such mechanistic information would be invaluable, pointing the way to the design and synthesis of other more efficient dendritic or polymer-supported Ru-based catalysts.

In addition to the above considerations, we elected to pursue dendritic ensembles based on the proposed mechanism through which this class of Ru complexes likely serve as metathesis catalysts. As summarized in Scheme 3,[1a] a diene substrate probably first reacts with the initial Ru complex to remove the transition metal from the styrene ligand and release the styrene ether **4**. Upon consumption of the diene, the active Ru-carbene reacts with the previously occupied styrenyl ether to cause reformation of the initial complex (return). We argued that both the release of the Ru center from the styrenyl ligand (initiation) and the return of the active Ru to the initial site (recovery) would be more efficient with the more accessible and exposed terminal sites within a soluble dendrimer structure. Complications regarding the rate of diffusion of diene substrates to the active metal center have been previously noted in connection with heterogeneous polymer-bound Ru-based metathesis catalysts (processes promoted by Ru attached to solid support).[7a] Consequently, the bound catalysts proved to be significantly less efficient than related monomeric species. In a more recent example,[7b] involving a polymer-bound Ru complex that, similar to **1** and **5**, operates through a release/return mechanism, catalyst activity is reduced significantly after the first round of recycling. This complication may be partly because styrenes are less effective than bidentate alkoxy styrenyl systems in retrieval of the active metal through olefin metathesis with the propagating Ru-carbene. We speculate that the released and highly active Ru-methylene undergoes competitive decomposition prior to its return to the polymer-supported ligand. Entropy may thus play a prominent role in the efficient recovery of Ru by bidentate ligand **4**.

Synthesis of Ru-Containing Dendrimers. Initially, we set out to prepare a dendrimer bearing *siloxane*-containing side chains, based on the pioneering work of Van Koten.[4b] However, this system proved susceptible to decomposition upon purification, presumably because of hydrolysis of alkyl(Me_2)Si−O bonds. Accordingly, we opted to prepare the more robust tetra*alkyl*silyl systems. The route for the synthesis of dendrimer **32** is illustrated in Scheme 4. The key features of the synthesis include the attachment of the requisite vinyl group through a Pd-catalyzed Stille coupling (→**28**)[19] and preparation of the dendrimer backbone by a Pt-catalyzed hydrosilation/alkylation[20]/

(15) To assess the thermal stability of complexes **3** and **5** in the absence of substrate, 0.05 M toluene solutions of these catalysts (containing ferrocene as an internal standard) were heated to 80 °C for 12 h in a temperature-controlled oil bath. Resulting solutions were then analyzed by 400 MHz ^{1}H NMR spectroscopy. Catalyst **5** gave a clean spectrum, indicating <2% each of free 2-isopropoxybenzaldehyde and 2-isopropoxystyrene (or its derived homodimer). In contrast, no carbene proton signal could be detected for benzylidene **3**. It should be stressed, however, that the results in Table 2 are a more appropriate measure of catalyst integrity, since propagating, electron-deficient intermediates are involved. In addition, any direct comparison of complexes **3** and **5** is complicated by the unique kinetic profiles which govern catalysis in each system. This experiment is therefore simply an indication of the relative facility with which initiation occurs in **3** (dissociative loss of the labile PCy_3). For other studies on Ru catalyst decomposition and longevity, see: (a) Ulman, M.; Grubbs, R. H. *J. Org. Chem.* **1999**, *64*, 7202−7207. (b) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5375−5380.

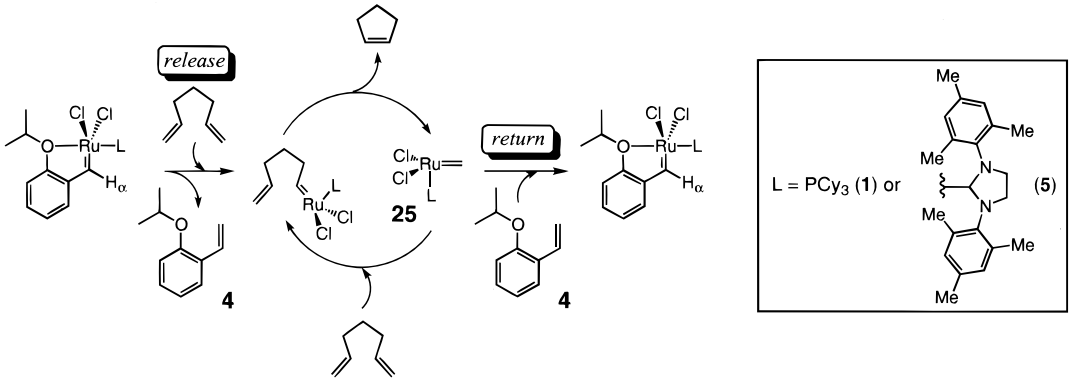
(16) To ensure that initiation is facilitated, 10 mol % of diallyl ether was added to react with **5** and release the transition metal from the styrene alkoxide ligand. This strategy, however, did not improve reaction efficiency probably because the resulting $L_nRu{=}CH_2$ returns to its original styrene ligand faster than reacting with a substrate-disubstituted olefin (i.e., initiation is not the problem). For the application of diallyl ether or ethylene to metal-catalyzed metathesis, see: (a) Reference 1b. (b) Reference 1c. (c) Johannes, C. W.; Visser, M. S.; Weatherhead G. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1998**, *120*, 8340−8347. (d) Mori, M.; Sakakibara, N.; Kinoshita, A. *J. Org. Chem.* **1998**, *63*, 6082−6083. (e) Lautens, M.; Hughes, G. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 129−131. (f) Weatherhead, G. S.; Ford, J. G.; Alexanian, E. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 1828−1829.

(17) For studies on Ru-catalyzed ROM/RCM processes, see: (a) ref 16a−b. (b) Zuercher, W. J.; Hashimoto, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 6634−6640. (c) Burke, S. D.; Quinn, K. J.; Chen, V. J. *J. Org. Chem.* **1998**, *63*, 8626−8627.

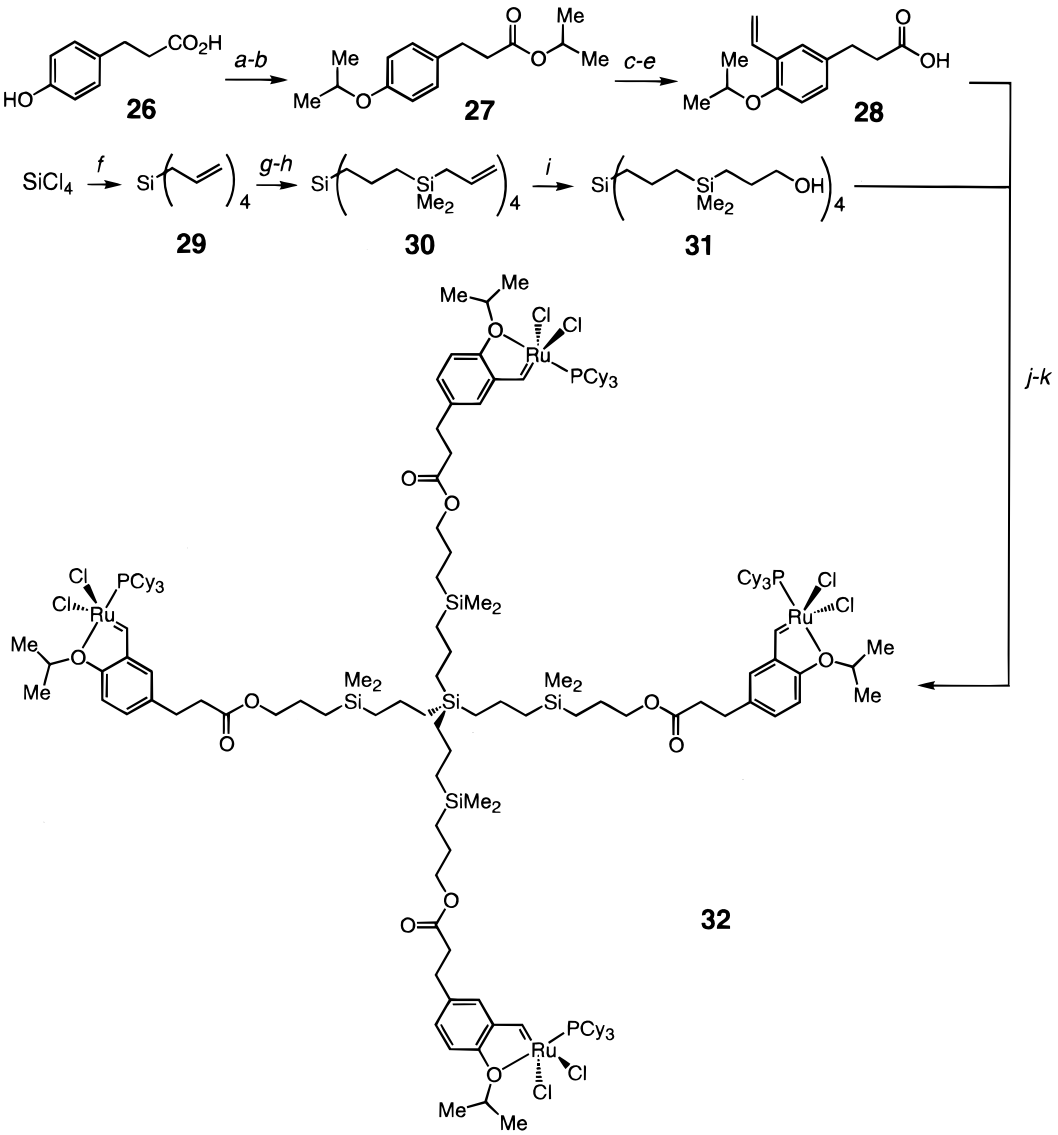
(18) For studies on Ru-catalyzed ROM/CM processes, see: (a) Randall, M. L.; Tallarico, J. A.; Snapper, M. L. *J. Am. Chem. Soc.* **1995**, *117*, 9610−9611. (b) Snapper, M. L.; Tallarico, J. A.; Randall, M. L. *J. Am. Chem. Soc.* **1997**, *119*, 1478−1479. (c) Schneider, M. F.; Lucas, N.; Velder, J.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 257−259. (d) Cuny, G. D.; Cao, J.; Hauske, J. R. *Tetrahedron Lett.* **1997**, *38*, 5237−5240. (e) Cao, J.; Cuny, G. D.; Hauske, J. R. *Mol. Diversity* **1998**, *3*, 173−179.

(19) (a) McKean, D. R.; Parrinello, G.; Renaldo, A. F.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 422−424. For a related review, see: (b) Farina, V.; Krishnamurthy, V.; Scott, W. J. *Org. React.* **1998**, *50*, 1−652.

Scheme 3



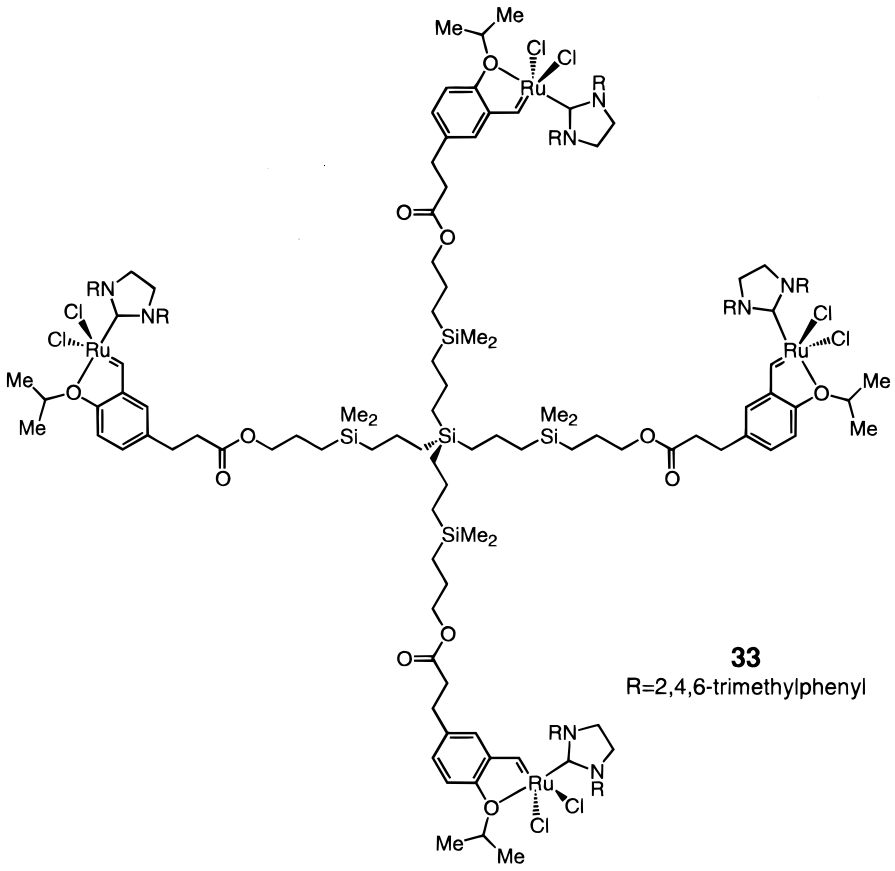
Scheme 4



[a] Anhydrous HCl, *i*-PrOH, 98%. [b] 2 equiv NaH, 2 equiv *i*-PrI, DMF, THF, 82%. [c] 1.1 equiv Br_2, HOAc, CH_2Cl_2, 98%. [d] 1.1 equiv $Bu_3SnCHCH_2$, 3 mol % $Pd(PPh_3)_4$, <1 mol % BHT, tol, 110 °C, 67%. [e] 1 M KOH (40 equiv), 100 °C, 91%. [f] 4.1 equiv CH_2CHCH_2MgBr, Et_2O, 35 °C, 88%. [g] 4.6 equiv HMe_2SiCl, 0.25 mol % H_2PtCl_6, THF, 65 °C. [h] 4.2 equiv CH_2CHCH_2MgBr, Et_2O, 90% overall for two steps. [i] 4.7 equiv 9-BBN, THF; NaOH, H_2O_2, EtOH, THF. [j] 4.8 equiv EDC·HCl, 4.4 equiv **28**, 0.5 equiv DMAP, 5.0 equiv Et_3N, CH_2Cl_2, 63% overall for two steps. [k] 4.3 equiv **2**, 4.8 equiv CuCl, CH_2Cl_2, 87%.

hydroboration[21] sequence (**29** → **30** → **31**). Coupling of **31** with 4 equiv of **28**, followed by incorporation of the Ru center through treatment with **2** in the presence of CuCl, affords the desired **32** as an air-stable brown solid (mp = 92−98 °C dec).[22]

The related Ru dendrimer **33** is prepared as an air-stable dark green solid by the same sequence of reactions as shown in

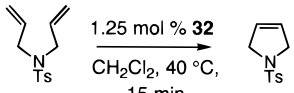


33
R=2,4,6-trimethylphenyl

Scheme 4, except that the last step involves treatment of the vacant dendritic structure with 4.8 equiv of **3** and 4.9 equiv of CuCl in CH_2Cl_2 for 2 h (55% yield; mp = 114−117 °C dec).[23]

Catalytic RCM, ROM, and CM Promoted by Dendritic Ru Complexes 32 and 33. As illustrated in Table 3, treatment of diene **34** with 1.25 mol % **32** (5 mol % Ru) leads to efficient and catalytic RCM. The desired product (**35**) is first isolated in 99% yield by silica gel chromatography through elution with CH_2Cl_2. Subsequent washing of the silica with Et_2O leads to the isolation of the dendritic catalyst (>98% mass balance). Recovered **32** was analyzed by 400 MHz ^{1}H NMR spectroscopy; the resulting spectrum indicated that 13% of the styrenyl ligands were vacant (13% Ru loss, 93% isolated yield of **32**).[24]

Table 3. Utility of Dendritic **30** in Catalytic RCM



34 **35**

cycle	product yield[a] (%)	Ru content[b] (%)
1	99	87
2	91	76
3	96	72
4	89	64
5	92	48
6	87	41

[a] Isolated yields after silica gel chromatography. [b] Determined by analysis of the 400 MHz ^{1}H NMR of the purified reaction mixture of dendrimer after silica gel purification (devoid of other Ru-containing impurities).

As illustrated in Table 3, repeated use of **32** as a catalyst, despite steady loss of Ru per reaction, results in complete conversion of **34** to **35** and isolation of the desired product in >86% isolated yield. These data thus illustrate that dendrimer **32** is effective in promoting the catalytic RCM of terminal dienes in an efficient manner and can be easily recovered by simple silica gel filtration and reused repeatedly in subsequent reactions. Several additional points in connection with the data in Table 3 deserve comment: (1) After repeated use, the partially depleted dendrimer complex can be easily remetalated upon treatment with the appropriate equivalents of **2** and CuCl in CH_2Cl_2. (2) The dendritic complex remains active even after nearly 50% of the Ru content has been depleted (see cycle 6 in Table 3). This level of reactivity may be attributed, at least partially, to the fact that **32** (similar to **1** and **5**) releases a highly active monophosphine Ru complex (cf. **25**, Scheme 3) into the solution. In the absence of a second equivalent of PCy_3 that can recoordinate to Ru and retard its catalytic activity (which

(20) For carbosilane dendimer structures based on a repetitive alkenylation/hydrosilation sequence, see: (a) van der Made, A. W.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1400−1401. (b) van der Made, A. W.; van Leeuwen, P. W. N. M.; de Wilde, J. C.; Brandes, R. A. C. *Adv. Mater.* **1993**, *5*, 466−468. (c) Roovers, J.; Toporowski, P. M.; Zhou, L.-L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*, 182. (d) Zhou, L.-L.; Roovers, J. *Macromolecules* **1993**, *26*, 963. (e) Roovers, J.; Zhou, L.-L.; Toporowski, P. M.; van der Zwan, M.; Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1993**, *26*, 4324. (f) Seyferth, D.; Son, D. Y.; Rheingold, A. L.; Ostrander, R. L. *Organometallics* **1994**, *13*, 2682−2690.

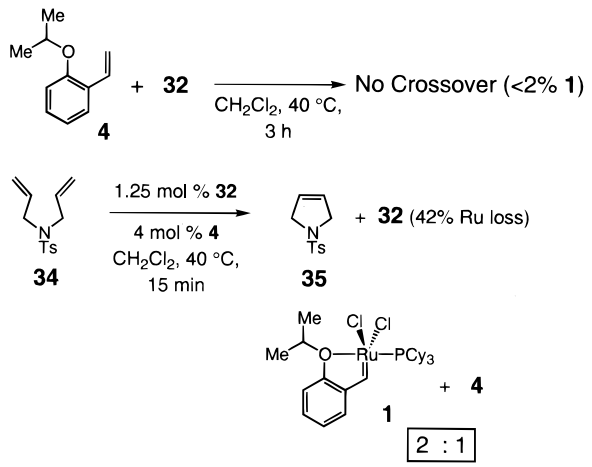
(21) For carbosilane dendimers based on a repetitive alkenylation/hydroboration/oxidation sequence, see: Kim, C.; Son, S.; Kim, B. *J. Organomet. Chem.* **1999**, *588*, 1−8.

(22) An attractive attribute of this route is that it is amenable to modification so that related and more highly branched dendrimers can be prepared. For example, catalytic hydrosilation of **30** with $HSiCl_3$ followed by alkylation of the 12 Si−Cl bonds with allylmagnesium bromide should lead to a 12-branch dendritic core structure. Synthesis and study of these and related dendrimers are in progress.

(23) Dendritic complexes **32** and **33** and their corresponding precursors were fully characterized by IR, ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and mass spectrometry. See the Experimental Section for details.

(24) 13% loss of Ru constitutes a 7% loss of the total mass of the fully metalated dendrimer. The reported quantitative (>98%) mass balance for the purified macromolecule is based on a theoretical yield which has been corrected for the minor loss of the metal and its associated ligands.

Scheme 5



is the case when **2** or **3** is used as a catalyst),[25] and since styrene ethers probably do not kinetically reassociate with Ru as efficiently as PCy_3 during propagation,[26] even a small amount of Ru release can lead to substantial amounts of metathesis activity.

The data in Table 3 and the above mechanistic considerations raise the possibility that **32** and **33** may simply be releasing small but sufficient amounts of highly active monophosphine Ru complexes (e.g., **25**, Scheme 3) into solution that effect complete conversion, and that little or none of the released metal complexes return to the dendritic complex.

To address this possibility, the metal crossover experiments depicted in Scheme 5 were carried out. These studies were facilitated by a minor chemical shift difference for the carbene proton signals of dendritic (**32**) and monomeric (**1**) Ru-carbenes. Thus, the amount of Ru bound to the dendritic versus monomeric ligands is readily determined by integration of the appropriate downfield signals in the ^{1}H NMR spectrum of the mixture. Treatment of **4** with dendritic Ru complex **32** (1.0 equiv) results in no metal crossover (<2% **1** is formed by 400 MHz ^{1}H NMR analysis).[27] When diene substrate **34** is treated with 1.25 mol % of fully loaded **32** and 4 mol % of **4**, RCM product **35** is obtained within 15 min. The amount of recovered **32**, however, bears 42% less Ru compared to 13% metal reduction when the reaction is carried out in the absence of **4** (see Table 3, cycle 1). In addition, ~30% of uncomplexed **4** is isolated after the reaction; the remainder of the monomeric styrenyl isopropyl ether is recovered as Ru complex **1**. These observations indicate that the Ru metal, after reacting with the diene substrate and leaving the dendrimer, can be trapped again by a styrenyl ether. Thus, in the absence of **4**, the catalytically active Ru-monophosphine would likely return to a styrene unit within the dendritic structure. Moreover, these data suggest that indeed a significant portion of the active Ru-carbene is released into the reaction mixture.

Dendrimer **33** exhibits catalytic activity higher than that observed for **32**. Unlike **1** or **32**, but similar to **5**, dendritic **33** efficiently promotes the formation of trisubstituted allylic alcohol **12** (eq 2); in addition to the desired product (78%), the dendrimer is recovered in 90% yield after silica gel chromatography, with 8% loss in Ru loading (judged by analysis of 400 MHz ^{1}H NMR spectrum). Moreover, as shown in eq 3, similar to **5**, dendrimer **33** effectively catalyzes tandem ROM/RCM of **21** and the formation of **22** (94%). However, in contrast to the corresponding monomer **5**, dendrimer **33** can be easily separated from **22** and recovered in 90% yield (8% Ru loss).[28] The transformation in eq 4 indicates that **33** effectively promotes catalytic ROM/CM reactions as well and, as before, it can be recovered readily and in good yield (>98% *trans*-olefins in **24** and **36**, as judged by 400 MHz ^{1}H NMR analysis).[29] In each case (eqs 2−4), owing to its high polarity, isolation of the dendrimer is a straightforward operation. Reaction mixtures are loaded onto a small plug of silica gel, and products are eluted with CH_2Cl_2. The column is then washed with Et_2O to retrieve **33**. Thus, *dendritic catalyst* **33** *retains the high activity of monomeric* **5** *and provides the valuable practical advantage of being readily separable from metathesis products (compare eqs 3 and 4 with reactions in Scheme 2).*

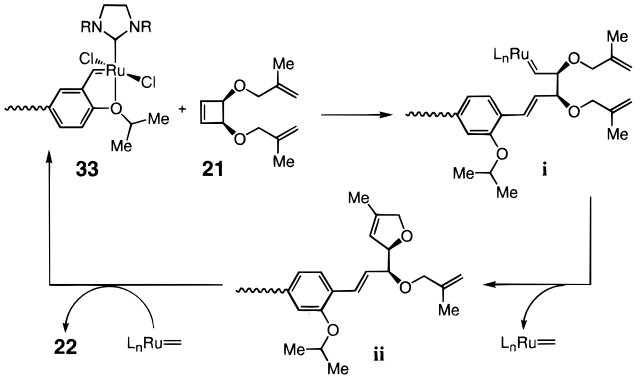
Similar to monomeric **5**, lower loadings of **33** are sufficient for efficient catalytic metathesis. As an example, when triene **7** (cf. Table 2, entry 1) is treated with 0.25 mol % **33** (CH_2Cl_2, 22 °C) for 10 min, RCM adduct **8** is formed with >98% conversion. In addition to dihydrofuran **8**, isolated in 84% yield,

(25) (a) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887−3897. (b) Reference 1a. For a report on a related monophosphine and catalytically active Ru complex, see: (c) Tallarico, J. A.; Bonitatebus, P. J.; Snapper, M. L. *J. Am. Chem. Soc.* **1997**, *119*, 7157−7158.

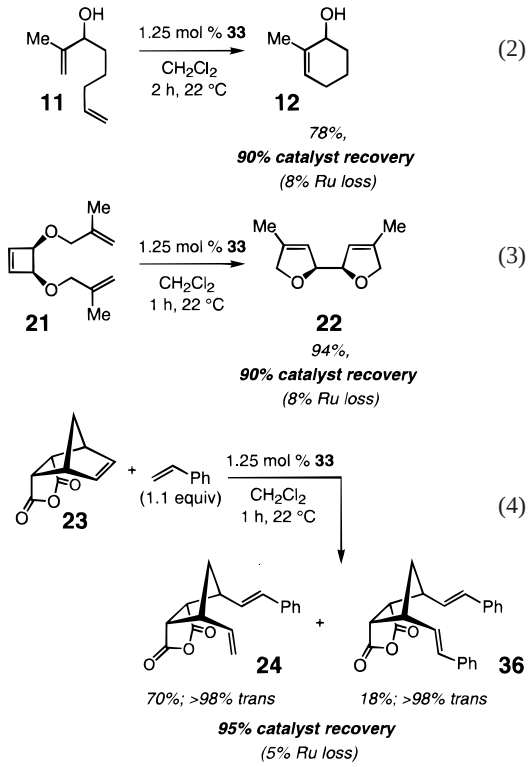
(26) Recoordination to Ru by styrene ether probably requires olefin metathesis, and the styrenyl C=C and the neighboring isopropyl ether are inferior Lewis bases in comparison to PCy_3. Our previous studies (ref 1a) indicate that **1** initiates approximately 30 times slower than and propagates four times faster than the bis(phosphine)Ru complex **2**. The slower rate of initiation of **1** is likely due to the less facile dissociation of the bidentate ligand from the metal center; the higher rate of propagation of **1** is caused by the absence of the competing PCy_3 ligand. The unusual stability of **1** is a result of steric congestion at the transition metal center (the corresponding methyl ether complex is significantly less stable) and thermodynamic stability provided by a styrene ether ligand.

(27) The relative inability of **4** to remove Ru from the dendritic structure, in contrast to **34**, is noteworthy and may be due to steric factors; electronic issues may also play a role in this reactivity difference, where electronically mismatched systems undergo cross metathesis more effectively. See: Blackwell, H. E.; O'Leary, D. J.; Chatterjee, A. K.; Washenfelder, R. A.; Bussmann, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 58−71 and references therein.

(28) Analysis of the unpurified reaction mixture indicates that approximately 3% of the Ru loss (3% loss of the total Ru sites) may be due to the isolation of the cross-metathesis product **ii**, which is presumably formed upon release of the transition metal from the dendrimer (**33**). The formation of compounds such as **ii** only occurs with substrates that do not contain terminal alkenes. Otherwise, as shown in Scheme 2, the terminal styrenyl alkoxide is formed upon Ru departure. Presumably, most of **ii** is reverted back to dendritic **33** through reaction with the Ru-methylene complex. Ru return may occur via **ii** through formation of the 1,1-disubstituted Ru-carbene followed by intramolecular RCM. Alternatively, cross-metathesis at the conjugated alkene can either afford **33** and the diene precursor to **22** or give the terminal styrene olefin and the Ru-carbene precursor to **22**. Regardless, all of the above possibilities eventually afford **22** and recover **33**. The recovery of 3% **ii** may be due to competitive Ru-methylene decomposition.



(29) It is not clear whether diene **36** is formed in the reaction of monomeric catalyst **5** (see Scheme 2); analysis of the outcome of the reaction promoted by monomeric **5** was complicated by the presence of the inseparable Ru complex (**5**).



recovered **33** is obtained in 88% yield after silica gel chromatography (22% Ru loss).[30]

Conclusions

We present a new class of highly active and recyclable Ru-based metathesis catalysts. These complexes, both monomeric (**5**) and dendritic (**33**), promote RCM, ROM, and CM reactions in a highly efficient manner. Unlike the first generation recoverable Ru-based complexes (**1** and **32**), **5** and **33** effect the efficient formation of trisubstituted alkenes through catalytic RCM. Tetrasubstituted olefins can be catalytically accessed too, but less efficiently than trisubstituted olefins. The related dendritic systems are recyclable and as active as their corresponding monomers but offer the added advantage of being more readily isolable (cf. eqs 3 and 4 and Scheme 2).

The appreciable levels of efficiency observed with Ru dendrimers is due to the fact that the active Ru species are readily released and recaptured. The fact that dendritic structures can be readily characterized by various spectroscopic methods and serve as useful mechanistic probes renders these macromolecular systems excellent starting points for the ultimate design and synthesis of more efficient recyclable catalysts. Such positive attributes have already provided us with important information. For example, comparison of our previously published data[1a] and those in Tables 2 and 3 and Scheme 5 suggests that dendritic systems **32** and **33** might be less efficient in Ru retrieval than the corresponding monomers; whereas 5−13% Ru loss is observed with dendritic structures (cf. Table 3 and eqs 2−4), 5% or less metal loss is detected with monomeric units (cf. Table 2 and Scheme 5). Coiling of the relatively flexible arms of **32** and **33**, leading to slower capture of the free Ru-carbene by the styrenyl ether ligand, may be responsible for this difference. The above studies thus imply that more efficient dendritic or other macromolecular complexes may be designed that bear rigid side chains; as such, coiling may be minimized and less Ru loss may occur per transformation.

Accordingly, the design, synthesis, and reactivity of various other dendritic and subsequent polymer-supported recyclable Ru-based metathesis catalysts are underway in these laboratories. It is hoped that the studies described above will lead to the development of even more active and more readily recoverable and recyclable catalysts. In addition, synthesis of various chiral versions of the above monomeric, dendritic, and related polymer-bound complexes and their application to asymmetric catalytic metathesis[31] are being actively pursued.

Experimental Section

General. Infrared (IR) spectra were recorded on a Perkin-Elmer 781 spectrophotometer, with ν_{max} in inverse centimeters. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded on a Varian Unity 300 (300 MHz), a Gemini 2000 (400 MHz), or an INOVA 500 (500 MHz) spectrometer. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm. CD_3CN: δ 1.94 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, br = broad, m = multiplet), coupling constants (Hz), integration, and assignment. ^{13}C NMR spectra were recorded on a Varian Unity 300 (75 MHz), a Gemini 2000 (100 MHz), or an INOVA 500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent as the internal reference ($CDCl_3$: δ 77.00 ppm. CD_3CN: δ 1.19 ppm). ^{31}P NMR spectra were recorded on a Varian Gemini 2000 (162 MHz) spectrometer with complete proton decoupling. The chemical shifts of the phosphorus resonances were determined relative to phosphoric acid as an external standard (H_3PO_4: δ 0.0 ppm). Mass spectra were recorded at the University of Illinois (Urbana-Champaign, IL) and Harvard University (Cambridge, MA). Combustion analyses were performed by Robertson Microlit Laboratories (Madison, NJ).

All reactions were carried out under an atmosphere of dry Ar in oven- (135 °C) and flame-dried glassware with standard Schlenk or vacuum-line techniques. In most instances, solid organometallic compounds were purified and recovered in air and later stored in a drybox under an atmosphere of argon. $(PCy_3)_2Cl_2Ru{=}CHPh$ (**2**)[3] and tetraallylsilane (**29**)[32] were prepared according to literature procedures. (4,5-DihydroIMES)$(PCy_3)Cl_2Ru{=}CHPh$ (**3**) and its requisite starting materials were prepared by a modification of the published method[8a] (see below for further details). 2-Isopropoxystyrene (**4**) was prepared from salicylaldehyde (Aldrich) by alkylation and Wittig olefination. All other materials were obtained from commercial sources and typically purified before use. Tetrahydrofuran, diethyl ether, benzene, and toluene were distilled from sodium metal/benzophenone ketyl. Dichloromethane, pentane, hexanes, 2-propanol, triethylamine, and ethanol were distilled from calcium hydride under Ar. Methanol was distilled over Mg under Ar. 2,4,6-Trimethylaniline (Aldrich) was vacuum distilled. Triethylorthoformate (Aldrich) was distilled from $MgSO_4$ under reduced pressure. 3-(4-Hydroxyphenyl)propionic acid (Aldrich) was recrystallized from water. 2-Iodopropane (Aldrich) was distilled from $MgSO_4$ under argon. Dimethylformamide (Fisher) was stored over 4 Å molecular sieves prior to use. Tributyl(vinyl)tin (Aldrich) was vacuum distilled from $MgSO_4$. Allylmagnesium bromide was freshly

(30) Although the recovered dendrimer is relatively less loaded with lower catalyst loading (78% return for 0.25 mol % **33** versus 90−95% for 1.25 mol % **33**), the amount of recovered Ru per mmole of product formed is nearly identical for both conditions.

(31) For Mo-catalyzed asymmetric RCM reactions, see: (a) Alexander, J. B.; La, D. S.; Cefalo, D. R.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 4041−4042. (b) La, D. S.; Alexander, J. B.; Cefalo, D. R.; Graf, D. D.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 9720−9721. (c) Zhu, S. S.; Cefalo, D. R.; La, D. S.; Jamieson, J. Y.; Davis, W. M.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 8251−8259. (d) Fujimura, O.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 2499−2500. (e) Fujimura, O.; Grubbs, R. H. *J. Org. Chem.* **1998**, *63*, 824−832. For application of catalytic asymmetric RCM in target-oriented synthesis see: (f) Burke, S. D.; Muller, N.; Beudry, C. M. *Org. Lett.* **1999**, *1*, 1827−1829. For Mo-catalyzed asymmetric ROM reactions see: (g) La, D. S.; Ford, J. G.; Sattely, E. S.; Bonitatebus, P. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 11603−11604. (h) Reference 16f.

(32) Abel, E. W.; Rowley, R. J. *J. Organomet. Chem.* **1975**, *84*, 199−229.

prepared from distilled allyl bromide (Aldrich) and Mg turnings (Strem) and titrated before use. Silicon tetrachloride (Strem) and chlorodimethylsilane (Aldrich) were distilled under argon. 9-Borabicyclo[3.3.1]nonane (9-BBN) was freshly prepared from distilled 1,5-cyclooctadiene (Aldrich), borane−dimethyl sulfide complex (Aldrich), and anhydrous dimethoxyethane (Aldrich, distilled from sodium metal/benzophenone ketyl).[33] 4-(Dimethylamino)pyridine (DMAP) (Aldrich) was recrystallized from anhydrous toluene. The following materials were purchased from commercial sources and used as received: glyoxal (40 wt % solution in water) (Aldrich), sodium cyanoborohydride (Aldrich), bromocresol green (Fisher), ammonium tetrafluoroborate (Aldrich), potassium *tert*-butoxide (Strem), copper(I) chloride (Strem), anhydrous HCl (Aldrich), sodium hydride (Aldrich), bromine (Aldrich), acetic acid (Fisher), sodium thiosulfate (Aldrich), 2,6-di-*tert*-butyl-4-methylphenol (Aldrich), tetrakis(triphenylphosphine)palladium(0) (Strem), activated carbon (Aldrich), chloroplatinic acid hexahydrate (Speier's catalyst) (Strem), platinum−divinyltetramethylsiloxane complex in xylene (Karstedt's catalyst) (Gelest), hydrogen peroxide (30 wt % solution in water) (Aldrich), citric acid (Aldrich), and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC) (Advanced Chemtech).

All silica gel column chromatography was driven with compressed air and performed with silica gel 60 (230−400 mesh; pH (10% suspension) 6.5−7; surface area 500 m^2/g; pore volume 0.75 mL/g) obtained from TSI Chemical Co. (Cambridge, MA). The use of other commercially available silica gels repeatedly gave unsatisfactory results in the purification of the Ru complexes reported herein.

Similar to the original monomer (**1**), dendritic catalyst **32** forms a dark brown solution in organic solvents. In contrast, the more active catalysts bearing the 4,5-dihydroIMES ligand form bright green-colored organic solutions. The purification of the above complexes can be easily monitored visually, since they appear as dark brown or green bands on the column. Denritic complexes **32** and **33** are significantly more polar than the corresponding monomers. Following a metathesis reaction mediated by **32** or **33**, isolation of both product and catalyst typically involved simply a filtration of the crude mixture through a silica gel plug in 100% CH_2Cl_2 followed by a column "flush" in 100% Et_2O (TLC R_f of **32** and **33** < 1.0 in CH_2Cl_2). See below for further details.

((2,4,6-Trimethylphenyl)NCH)$_2$.[34] Glyoxal (3.73 mL of a 40% weight solution in water, 32.5 mmol) was dissolved in 325 mL of reagent-grade methanol in a 500 mL flask. 2,4,6-Trimethylaniline (8.25 mL, 58.8 mmol, 1.81 equiv) was added dropwise to this solution by syringe. The mixture was stirred for 12 h at 22 °C as a bright yellow precipitate slowly formed. The mixture was diluted with CH_2Cl_2, dissolving the solid. The resulting yellow solution was dried over $MgSO_4$, filtered, and concentrated to a yellow-orange solid residue. The unpurified product was recrystallized from anhydrous methanol (for every 10 g, 850−900 mL of MeOH was required for complete dissolution at reflux). After slow cooling to 22 °C followed by subsequent storage of the sample at −20 °C for 12 h, long canary yellow crystals formed. The product was recovered by vacuum filtration, washed with pentane, and dried under high vacuum (7.40 g, 25.3 mmol, 86%). IR (NaCl): 3005 (m), 2946 (s), 2916 (s), 2854 (m), 2725 (w), 1617 (s), 1595 (w), 1476 (m), 1438 (w), 1374 (m), 1265 (m), 1202 (s), 1141 (m), 1031 (w), 850 (s), 780 (m), 739 (s), 705 (w), 609 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 2H, NCH), 6.93 (s, 4H, aromatic CH), 2.31 (s, 6H, mesityl *p*-CH_3), 2.18 (s, 12H, mesityl *o*-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.31, 147.29, 134.13, 128.86, 126.44, 20.83, 18.28. HRMS Calcd for $C_{20}H_{23}N_2$: 292.1861 $(M-H)^+$. Found: 291.1862. Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.15; H, 8.27. Found: C, 81.99; H, 8.12.

((2,4,6-Trimethylphenyl)NHCH$_2$)$_2$. The bis(imine) ((2,4,6-trimethylphenyl)NCH)$_2$ (7.30 g, 25.0 mmol) was suspended in 250 mL of MeOH in a 500 mL round-bottom flask. Several crystals of bromocresol green were added as a pH indicator, and the mixture was cooled to 0 °C. $NaCNBH_3$ (10.0 g, 159 mmol, 6.4 equiv) was added to the reaction mixture in one portion as a solid. Vigorous bubbling was observed, and the reaction mixture turned a deep blue-green color (alkaline pH). After 10 min, concentrated HCl was added dropwise to the mixture, restoring its original yellow color. Additional reduction slowly occurred, causing the mixture to again become basic. The acidification process was repeated (typically two more times) until the yellow color persisted. The reaction mixture was warmed to 22 °C and stirred for 1 h. A solution of 2 M KOH was added dropwise until the mixture was weakly alkaline (pH = 8−9). The mixture was then diluted with water (300 mL), transferred to a separatory funnel, and washed three times with Et_2O (500 mL). The combined organic layers were washed with 800 mL of a saturated solution of sodium chloride, dried over $MgSO_4$, filtered, and concentrated to a yellow oil. Silica gel chromatography (TLC R_f = 0.32 in 4:1 pentane/Et_2O) afforded the product as a colorless oil (7.13 g, 24.1 mmol, 96%). IR (NaCl): 3367 (br), 2996 (s), 2916 (s), 2854 (s), 2729 (w), 1612 (w), 1485 (s), 1446 (s), 1373 (m), 1344 (w), 1228 (s), 1207 (m), 1154 (m), 1110 (m), 1062 (w), 1030 (m), 1012 (m), 853 (s), 822 (w), 801 (w), 738 (m), 563 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (s, 4H, aromatic CH), 3.30 (br, 2H, NH), 3.17 (s, 4H, NCH_2CH_2N), 2.30 (s, 12H, mesityl *o*-CH_3), 2.25 (s, 6H, mesityl *p*-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.24, 131.35, 129.65, 129.38, 49.19, 20.60, 18.50. HRMS Calcd for $C_{20}H_{28}N_2$: 296.2252. Found: 296.2258. Anal. Calcd for $C_{20}H_{28}N_2$: C, 81.03; H, 9.52. Found: C, 81.28; H, 9.41.

1,3-Dimesitylimidazolinium tetrafluoroborate.[35] A 25 mL round-bottom flask was charged with ((2,4,6-trimethylphenyl)$NHCH_2)_2$ (7.81 g, 26.4 mmol) and ammonium tetrafluoroborate (2.77 g, 26.4 mmol, 1.0 equiv). Triethylorthoformate (4.39 mL, 26.4 mmol, 1.0 equiv) was added by syringe. The flask was equipped with a reflux condenser and submerged into a preheated oil bath at 120 °C. The mixture was refluxed for 3 h and cooled to 22 °C. A tan-colored solid precipitated, leaving a cloudy suspension. This mixture was recrystallized from hot anhydrous ethanol. The resulting bright white crystals of product were recovered by vacuum filtration, washed with pentane, and dried under high vacuum (5.62 g, 14.3 mmol, 54%). Additional product could be obtained by further recrystallization of the mother liquor. IR (NaCl): 3091 (w), 2979 (br), 2941 (br), 1633 (s), 1487 (w), 1459 (w), 1393 (w), 1313 (w), 1269 (m), 1214 (w), 1092 (m), 1054 (s), 1036 (s), 965 (w), 880 (w), 852 (m). ^{1}H NMR (400 MHz, CD_3CN): δ 8.14 (s, 1H, NCHN), 7.08 (s, 4H, aromatic CH), 4.43 (s, 4H, NCH_2CH_2N), 2.37 (s, 12H, mesityl *o*-CH_3), 2.32 (s, 6H, mesityl *p*-CH_3). ^{13}C NMR (100 MHz, CD_3CN): δ 160.41 (d, J_{NC} = 10.3 Hz), 141.54, 136.50, 131.36, 130.61, 52.21, 21.16, 17.92. HRMS Calcd for $C_{21}H_{27}N_2$: 307.2174 (cation only). Found: 307.2175. Anal. Calcd for $C_{21}H_{27}BF_4N_2$: C, 63.97; H, 6.90. Found: C, 63.79; H, 6.85.

(4,5-DihydroIMES)(PCy$_3$)Cl$_2$Ru=CHPh (3). The ligand salt 1,3-dimesitylimidazolinium tetrafluoroborate (2.94 g, 7.46 mmol, 1.2 equiv) was suspended in 50 mL of THF in a 250 mL round-bottom flask. This mixture was then treated with a solution of potassium *tert*-butoxide (840 mg, 7.49 mmol, 1.2 equiv) in 50 mL of THF via cannula at 22 °C. This mixture was immediately transferred by cannula (20 mL of THF used as rinse) to a second vessel containing a solution of $(PCy_3)_2Cl_2Ru$=CHPh (**2**) (5.01 g, 6.09 mmol, 1.0 equiv) in 100 mL of benzene (additional stirring of the ligand salt mixture at 22 °C prior to exposure to the Ru-carbene often resulted in incomplete conversion to the desired product). The resulting mixture was refluxed at 80 °C for 30 min and then cooled to 22 °C. All manipulations from this point forward were carried out in air with reagent-grade solvents. The solvents were removed at reduced pressure, leaving a red-brown solid residue. The unpurified residue was dissolved in 8:1 hexanes/Et_2O and loaded onto a wide plug of silica gel. Elution with the same solvent system slowly removed a pink-red band of the desired product from the column. Concentration of the product fractions in vacuo removed the more polar and volatile Et_2O and resulted in spontaneous precipitation of the catalyst from hexanes as a cranberry red, microcrystalline solid (3.78 g, 4.45 mmol, 73%). These crystals were dried under high vacuum. IR

(33) Soderquist, J. A.; Alvin, N. *Org. Synth.* **1991**, *70*, 169−176.

(34) Grubbs and co-workers recently reported (see ref 8a) the syntheses of the first four compounds described in this Experimental Section. However, experimental details and complete characterization for all of these materials were not provided. A recent disclosure (Arduengo, A. J., III; Goerlich, J. R.; Marshall, W. J. *J. Am. Chem. Soc.* **1995**, *117*, 11027−11028) also describes 1,3-dimesitylimidazolinium chloride, but characterization is only mentioned for the corresponding 1,3-dimesitylimidazolin-2-ylidene. We have found the procedures described above satisfactory for the efficient synthesis of these materials in multigram quantities.

(35) Saba, S.; Brescia, A.-M.; Kaloustain, M. K. *Tetrahedron Lett.* **1991**, *32*, 5031−5034.

(NaCl): 3057 (m), 3039 (m), 3015 (m), 2927 (s), 2850 (s), 1608 (w), 1479 (s), 1446 (s), 1421 (s), 1380 (m), 1328 (w), 1266 (s), 1243 (m), 1205 (w), 1174 (m), 1129 (w), 1036 (w), 1005 (m), 909 (m), 849 (m), 737 (s), 703 (m), 687 (m), 624 (w), 578 (w). ^{1}H and ^{31}P NMR data were in agreement with those reported by Scholl et al.[8a] Anal. Calcd for $C_{46}H_{65}Cl_2N_2PRu$: C, 65.08; H, 7.72. Found: C, 65.18; H, 7.71.

(4,5-DihydroIMES)Cl_2Ru=CH-*o*-O*i*PrC_6H_4 (5). (4,5-DihydroIMES)-(PCy_3)Cl_2Ru=CHPh (**3**) (895 mg, 1.05 mmol, 1.03 equiv) and CuCl (104 mg, 1.05 mmol, 1.00 equiv) were weighed into a 100 mL round-bottom flask in a glovebox and dissolved in 20 mL of CH_2Cl_2. 2-Isopropoxystyrene (**4**) (166 mg, 1.02 mmol, 0.97 equiv) was cannulated into the resulting deep red solution in 20 mL of CH_2Cl_2 at 22 °C. The flask was equipped with a condenser, and the solution was stirred at 40 °C for 1 h. From this point forth, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated in vacuo to a dark brown solid residue. The unpurified material was dissolved in a minimal volume of 1:1 pentane/CH_2Cl_2 and loaded onto a plug of silica gel. Insoluble copper−phosphine precipitates can complicate chromatography and must be removed during loading of the sample. This was readily accomplished by passing the solution through a second Pasteur pipette containing a plug of cotton as the column was loaded. Elution with 1:1 pentane/CH_2Cl_2 removed a bright green band from the column. Removal of solvent and drying under high vacuum afforded 543 mg (0.87 mmol, 85%) of a bright green crystalline solid. The addition of hexanes just prior to complete removal of the chromatography solvent will result in spontaneous precipitation of the product. Alternatively, crystallization can be effected by layering concentrated CH_2Cl_2 solutions with pentane or hexanes. IR (NaCl): 2922 (br), 2853 (m), 1730 (w), 1606 (w), 1589 (m), 1575 (w), 1478 (s), 1452 (s), 1420 (s), 1397 (m), 1384 (m), 1295 (m), 1263 (s), 1217 (m), 1160 (w), 1113 (s), 1098 (w), 1035 (w), 938 (m), 852 (w), 801 (w), 746 (m), 737 (m), 580 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 16.56 (s, 1H, Ru=CHAr), 7.48 (m, 1H, aromatic CH), 7.07 (s, 4H, mesityl aromatic CH), 6.93 (dd, J = 7.4, 1.6 Hz, 1H, aromatic CH), 6.85 (dd, J = 7.4, 7.0 Hz, 1H, aromatic CH), 6.79 (d, J = 8.6 Hz, 1H, aromatic CH), 4.90 (septet, J = 6.3 Hz, 1H, $(CH_3)_2CHOAr$), 4.18 (s, 4H, $N(CH_2)_2N$), 2.48 (s, 12H, mesityl *o*-CH_3), 2.40 (s, 6H, mesityl *p*-CH_3), 1.27 (d, J = 5.9 Hz, 6H, $(CH_3)_2CHOAr$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 296.83 (q, J = 61.5 Hz), 211.13, 152.04, 145.13 (d, J_{OC} = 3.9 Hz), 145.09, 138.61, 129.39 (d, J_{NC} = 3.9 Hz), 129.35, 129.17, 122.56, 122.11, 112.75, 74.86 (d, J_{OC} = 10.7 Hz), 51.42, 30.86, 25.93, 21.08. HRMS Calcd for $C_{31}H_{38}Cl_2N_2O^{99}Ru$: 623.1421. Found: 623.1411. Anal. Calcd for $C_{31}H_{38}Cl_2N_2ORu$: C, 59.42; H, 6.11; Cl, 11.32; N, 4.47. Found: C, 59.28; H, 6.35; Cl, 11.36; N, 4.12.

Isopropyl-1-(*p*-hydroxyphenyl)propionate. Through a stirring solution of 3-(4-hydroxyphenyl)propionic acid (**26**) (5.00 g, 30.1 mmol) in 2-propanol (167 mL, 72.0 equiv) was bubbled anhydrous HCl for 50 min. The flask was sealed under Ar, and the solution was stirred for 12 h at 22 °C. The solvent was removed under reduced pressure with gentle heating, leaving a thick, colorless oil. Removal of residual 2-propanol under high vacuum at 22 °C resulted in spontaneous precipitation of the desired product as a bright white crystalline solid (6.12 g, 29.4 mmol, 98%). IR (NaCl): 3412 (br), 3024 (w), 2981 (m), 2930 (w), 2873 (w), 1712 (m), 1613 (s), 1595 (m), 1519 (s), 1449 (m), 1377 (s), 1298 (m), 1266 (s), 1225 (s), 1149 (m), 1108 (s), 904 (m), 837 (m), 820 (m), 609 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (d, J = 8.4 Hz, 2H, aromatic CH), 6.74 (d, J = 8.4 Hz, 2H, aromatic CH), 5.80 (s, 1H, ArOH), 5.00 (septet, J = 6.3 Hz, 1H, $(CH_3)_2CHO$), 2.87 (t, J = 7.6 Hz, 2H, CH_2CO_2iPr), 2.57 (t, J = 7.6 Hz, 2H, $ArCH_2$), 1.20 (d, J = 6.3 Hz, 6H, $(CH_3)_2CHO$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.97, 154.04, 132.19, 129.28, 115.19, 68.07 (d, J_{OC} = 9.8 Hz), 36.64, 30.23, 21.85. HRMS Calcd for $C_{12}H_{16}O_3$: 208.1099. Found: 208.1099. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.43; H, 7.88.

Isopropyl-1-(*p*-isopropoxyphenyl)propionate (27). A solution of isopropyl-1-(*p*-hydroxyphenyl)propionate (0.822 g, 3.95 mmol) in THF (10 mL) was treated via cannula with a suspension of sodium hydride (104 mg, 5.92 mmol, 1.1 equiv) in THF (10 mL) at 0 °C. After gas evolution subsided, DMF (20 mL) and 2-iodopropane (0.40 mL, 4.0 mmol, 1.0 equiv) were syringed into the reaction mixture. The resulting suspension was stirred at 22 °C for 6 h, at which time additional sodium hydride (71.0 mg, 2.96 mmol. 0.75 equiv) in THF (5 mL) and 2-iodopropane (0.30 mL, 3.0 mmol, 0.75 equiv) were added. This procedure was repeated if necessary until no starting material could be detected by TLC analysis (we suspect that competing elimination of the electrophile is reponsible for incomplete product conversions, requiring us to resubject the reaction mixture). The mixture was then diluted with Et_2O (150 mL) and water (200 mL) and transferred to a separatory funnel. The organic layer was removed, and the aqueous layer was washed twice with Et_2O (100 mL). The combined organic layers were washed with three volumes of water to remove residual DMF. The organic solution was then dried over $MgSO_4$, filtered, and concentrated in vacuo to a pale yellow oil. The product was passed through a short column of silica gel in 7:1 hexanes/Et_2O, affording 811 mg (3.24 mmol, 82%) of a colorless oil (TLC R_f = 0.30 in 7:1 hexanes/Et_2O). IR (NaCl): 2978 (m), 2934 (w), 1731 (s), 1612 (w), 1510 (s), 1452 (w), 1383 (m), 1295 (w), 1242 (s), 1182 (m), 1109 (s), 957 (w), 829 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, J = 8.6 Hz, 2H, aromatic CH), 6.80 (d, J = 8.6 Hz, 2H, aromatic CH), 5.00 (septet, J = 6.3 Hz, 1H, $(CH_3)_2CHO_2C$), 4.50 (septet, J = 6.3 Hz, 1H, $(CH_3)_2CHOAr$), 2.87 (t, J = 7.8 Hz, 2H, CH_2CO_2iPr), 2.55 (t, J = 7.8 Hz, 2H, $ArCH_2$), 1.32 (d, J = 6.3 Hz, 6H, $(CH_3)_2CHOAr$), 1.20 (d, J = 6.3 Hz, 6H, $(CH_3)_2CHO_2C$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.39, 156.12, 132.43, 129.15, 115.81, 69.86 (d, J_{OC} = 3.4 Hz), 67.59 (d, J_{OC} = 9.8 Hz), 36.59, 30.26, 22.14, 21.88. HRMS Calcd for $C_{15}H_{22}O_3$: 250.1569. Found: 250.1566. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 72.26; H, 9.04.

Isopropyl-1-(*m*-bromo-*p*-isopropoxyphenyl)propionate. A 50 mL round-bottom flask was charged with isopropyl-1-(*p*-isopropoxyphenyl)-propionate (**27**) (1.09 g, 4.34 mmol) and CH_2Cl_2 (20 mL, 0.20 M). Acetic acid (10 μL, 0.18 mmol) was added to the solution. Bromine (0.235 mL, 4.56 mmol, 1.05 equiv) was then slowly added dropwise via syringe, forming a red solution. Over the course of 0.5 h the solution gradually turned pale yellow as the bromine was consumed. After 1 h, the reaction was quenched with 5 mL of saturated sodium thiosulfate. The mixture was diluted with water (200 mL) and Et_2O (200 mL) and partitioned in a separatory funnel. The aqueous layer was washed with 2 × 150 mL of Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated to a yellow oil. This material could be purified by vacuum distillation or silica gel chromatography (TLC R_f = 0.23 in 10:1 hexanes/Et_2O) to deliver the product as a colorless oil (1.40 g, 4.25 mmol, 98%). Crucial to the success of this reaction is the use of *exactly* 1.0−1.1 equiv of bromine; an excess of the reagent leads to dibrominated adducts. If these impurities are generated, a CH_2Cl_2/pentane solvent system must be used as eluant to effect purification of the desired product on silica gel (TLC R_f = 0.30 in 3:2 CH_2Cl_2/pentane). The halogenated solvent mix also promotes a facile separation of the product and the starting material (**27**) in the event that the reaction does not proceed to completion (<1.0 equiv of Br_2). IR (NaCl): 2979 (m), 2936 (w), 1729 (s), 1604 (w), 1493 (s), 1384 (m), 1373 (m), 1281 (m), 1253 (s), 1240 (m), 1180 (m), 1140 (m), 1109 (s), 1046 (w), 954 (m), 812 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 2.2 Hz, 1H, aromatic CH), 7.06 (dd, J = 8.4, 2.2 Hz, 1H, aromatic CH), 6.83 (d, J = 8.4 Hz, 1H, aromatic CH), 4.96 (septet, J = 6.2 Hz, 1H, $(CH_3)_2CHO_2C$), 4.50 (septet, J = 6.2 Hz, 1H, $(CH_3)_2CHOAr$), 2.85 (dd, J = 7.7, 7.3 Hz, 2H, CH_2CO_2iPr), 2.55 (dd, J = 7.7, 7.3 Hz, 2H, $ArCH_2$), 1.36 (d, J = 5.9 Hz, 6H, $(CH_3)_2CHOAr$), 1.20 (d, J = 6.6 Hz, 6H, $(CH_3)_2CHO_2C$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.06, 152.84, 134.36, 133.09 (d, J_{OC} = 7.3 Hz), 128.03, 115.98, 113.63, 72.34 (d, J_{OC} = 3.9 Hz), 67.80 (d, J_{OC} = 12.2 Hz), 36.29, 29.90, 22.15 (d, J_{OC} = 2.4 Hz), 21.89 (d, J_{OC} = 3.4 Hz). HRMS Calcd for $C_{15}H_{21}BrO_3$: 328.0674. Found: 328.0671. Anal. Calcd for $C_{15}H_{21}BrO_3$: C, 54.72; H, 6.43. Found: C, 54.84; H, 6.43.

Isopropyl-1-(*p*-isopropoxy-*m*-vinylphenyl)propionate. $Pd(PPh_3)_4$ (166 mg, 0.144 mmol, 3 mol %) and 2,6-di-*tert*-butyl-4-methylphenol (1 mg, 0.005 mmol) were weighed into a 50 mL pear-shaped flask in a glovebox and dissolved in 25 mL of dry toluene. This solution was transferred through a cannula into a neat sample of isopropyl-1-(*m*-bromo-*p*-isopropoxyphenyl)propionate (1.58 g, 4.79 mmol) in a 50 mL round-bottom flask. The resulting pale yellow solution was stirred for 15 min at 22 °C. Tributyl(vinyl)tin (1.54 mL, 5.27 mmol, 1.1 equiv) was then added dropwise to the reaction mixture through a syringe.

The flask was equipped with a condenser and heated at 110 °C for 12 h. As the reaction progressed, a shiny mirrorlike film of Bu_3SnBr salts was gradually deposited onto the walls of the flask. After cooling to 22 °C, the reaction mixture was passed through a small plug of Celite and activated carbon using Et_2O as the eluant and concentrated in vacuo to give a yellow oil. Purification by silica gel chromatography (TLC $R_f = 0.27$ in 8:1 hexanes/Et_2O) afforded 888 mg of a colorless oil (3.22 mmol, 67%). IR (NaCl): 2978 (s), 2936 (m), 2873 (w), 1731 (s), 1627 (w), 1491 (s), 1373 (m), 1246 (s), 1180 (m), 1109 (s), 996 (w), 957 (m), 904 (w), 814 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 2.3 Hz, 1H, aromatic CH), 7.07−6.99 (m, 2H, aromatic CH and ArC*H*CH_2), 6.80 (d, J = 8.2 Hz, 1H, aromatic CH), 5.71 (dd, J = 17.8, 1.6 Hz, 1H, ArCHC*H*$_2$), 5.22 (dd, J = 11.3, 1.6 Hz, 1H, ArCHC*H*$_2$), 5.00 (septet, J = 6.3 Hz, 1H, $(CH_3)_2CHO_2C$), 4.49 (septet, J = 6.3 Hz, 1H, $(CH_3)_2CHOAr$), 2.88 (dd, J = 7.8, 7.4 Hz, 2H, CH_2CO_2iPr), 2.57 (dd, J = 8.2, 7.4 Hz, 2H, $ArCH_2$), 1.33 (d, J = 6.3 Hz, 6H, $(CH_3)_2CHOAr$), 1.21 (d, J = 6.3 Hz, 6H, $(CH_3)_2CHO_2C$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.37, 153.50, 132.52, 131.81, 128.38, 127.67, 126.21 (d, J_{OC} = 5.4 Hz), 114.42, 113.76 (d, J_{OC} = 8.3 Hz), 70.01 (d, J_{OC} = 3.4 Hz), 67.64 (d, J_{OC}= 11.2 Hz), 36.58, 30.40, 22.28, 21.93. HRMS Calcd for $C_{17}H_{24}O_3$: 276.1725. Found: 276.1716. Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 73.71; H, 8.73.

1-(*p*-Isopropoxy-*m*-vinylphenyl)propionic Acid (28). A 100 mL round-bottom flask was charged with isopropyl-1-(*p*-isopropoxy-*m*-vinylphenyl)propionate (462 mg, 1.67 mmol) and 66.8 mL of 1 M KOH (66.8 mmol, 40 equiv). The reaction vessel was equipped with a condenser and heated at 100 °C for 12 h. The mixture was then cooled to 0 °C and neutralized by the dropwise addition of concentrated HCl. At a pH of ∼7−8, a white cloudy precipitate began to form in the reaction mixture. At this point, the mixture was transferred to a separatory funnel and washed with 150 mL of Et_2O (an emulsion may form, requiring extended time for phase separation). The aqueous layer was acidified further with HCl, inducing additional precipitation. The aqueous layer was washed with additional Et_2O. This process was repeated until no further precipitation was observed upon addition of the acid (pH 3−4). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford 355 mg (1.52 mmol, 91%) of a light yellow solid which proved to be >98% pure as judged by ^{1}H NMR spectroscopy (400 MHz). If necessary, the acid could be further purified by silica gel chromatography (TLC $R_f = 0.31$ in 3:2 hexanes/Et_2O). It is recommended that the above procedure be followed with care, since the product is quite prone to acid-catalyzed polymerization of the styrene moiety. IR (NaCl): 2979 (m), 2935 (w), 2860 (w), 2760 (w), 1686 (s), 1600 (s), 1243 (s). ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.26 (br, 1H, CO_2H), 7.32 (d, J = 2.3 Hz, 1H, aromatic CH), 7.06−7.00 (m, 2H, aromatic CH and ArC*H*CH_2), 6.81 (d, J = 8.5 Hz, 1H, aromatic CH), 5.72 (dd, J = 17.8, 1.5 Hz, 1H, ArCHC*H*$_2$), 5.23 (dd, J = 11.0, 1.5 Hz, 1H, ArCHC*H*$_2$), 4.50 (septet, J = 6.1 Hz, 1H, $(CH_3)_2CHOAr$), 2.90 (dd, J = 8.0, 7.6 Hz, 2H, CH_2CO_2iPr), 2.67 (dd, J = 8.0, 7.6 Hz, 2H, $ArCH_2$), 1.34 (d, J = 6.2 Hz, 6H, $(CH_3)_2CHOAr$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.78, 153.77, 132.13, 131.88, 128.40, 127.87, 126.29, 114.48, 113.99, 70.99, 35.80, 29.88, 22.19. HRMS Calcd for $C_{14}H_{18}O_3$: 234.1256. Found: 234.1257. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.71; H, 7.68.

Si[(CH$_2$)$_3$Si(Me)$_2$CH=CH$_2$]$_4$ (30). A 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ (Speier's catalyst)[36] was freshly prepared in anhydrous 2-propanol. The hydrosilation could also be effected with Karstedt's catalyst.[37] A 25 mL round-bottom flask was charged with the tetraene (**29**) (762 mg, 3.96 mmol), HMe_2SiCl (2.00 mL, 18.0 mmol, 4.6 equiv), and THF (0.5 M, 8.0 mL). The platinum catalyst (10.0 μL, 0.010 mmol, 0.0025 equiv) was added dropwise by syringe, and the colorless solution was heated at reflux (65 °C) for 12 h. After 20 min, the mixture had turned dark green. Reaction progress was monitored readily by TLC;the starting material (TLC $R_f = 0.9$ in hexanes) stains bright yellow with $KMnO_4$. Following the removal of solvent and excess silane in vacuo, ^{1}H NMR analysis (400 MHz) of the unpurified mixture indicated that <5% of the α-substituted product was present and that the material was sufficiently pure for the subsequent alkylation step. Thus, the product was dissolved in 20 mL of Et_2O and transferred by cannula into a solution of freshly prepared allylmagnesium bromide (0.936 M, 17.8 mL, 16.7 mmol, 4.2 equiv). The reaction was stirred for 12 h at 22 °C and quenched with 10 mL of a saturated solution of ammonium chloride. The mixture was diluted with water (200 mL) and Et_2O (150 mL) and partitioned in a separatory funnel. The aqueous layer was washed with 2 × 100 mL of Et_2O. The combined organic layers were washed with a volume of saturated sodium chloride, dried over $MgSO_4$, and vacuum filtered through a coarse frit funnel containing Celite. Removal of volatiles gave a light orange oil which was purified by silica gel chromatography (TLC $R_f = 0.63$ in hexanes). The product was recovered as a colorless oil (2.11 g, 3.56 mmol, 90%). IR (NaCl): 3077 (w), 2954 (m), 2913 (s), 2876 (m), 1630 (m), 1418 (w), 1250 (s), 1153 (m), 1034 (w), 990 (w), 932 (w), 893 (s), 844 (s), 698 (w), 629 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.78 (ddt, J = 16.8, 10.2, 8.2 Hz, 4H, C*H*=CH_2), 4.87−4.79 (m, 8H, CH=C*H*$_2$), 1.51 (d, J = 8.2 Hz, 8H, SiC*H*$_2$CH=CH_2), 1.32 (m, 8H, $SiCH_2CH_2CH_2CH_2Si$), 0.62−0.53 (m, 16H, $SiCH_2CH_2CH_2Si$), −0.02 (s, 24H, $Si(CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.21, 112.47, 23.49, 19.93, 18.55, 17.54, −3.52. HRMS Calcd for $C_{32}H_{67}Si_5$: 591.4089 $(M-H)^+$. Found: 591.4072. Anal. Calcd for $C_{32}H_{68}Si_5$: C, 64.78; H, 11.55. Found: C, 64.98; H, 11.55.

[(*p*-Isopropoxy-*m*-vinylphenyl)(CH$_2$)$_2$CO$_2$(CH$_2$)$_3$Si(Me)$_2$-(CH$_2$)$_3$Si]$_4$. Si[$(CH_2)_3Si(Me)_2CH=CH_2]_4$ (**30**) (587 mg, 0.989 mmol) was weighed into a 50 mL round-bottom flask and dissolved in 10 mL of THF. This solution was treated by cannula with freshly prepared 9-BBN (527 mg, 4.69 mmol, 4.74 equiv) in 10 mL of THF. After 12 h at 22 °C, 10 mL each of H_2O_2 (30 wt % solution in water), 2 M NaOH, and ethanol were added. The mixture was then allowed to stir an additional 12 h at 22 °C. Water (100 mL) and Et_2O (100 mL) were added, and the organic layer was removed. The aqueous layer was washed with 2 × 100 mL of Et_2O. The combined organic layers were dried over $MgSO_4$ and filtered. Removal of volatiles gave a crude oil that was purified by silica gel chromatography (TLC $R_f = 0.36$ in EtOAc). ^{1}H NMR analysis (400 MHz) indicated that the product contained minor impurities (including cyclooctadiol) which made characterization of the material difficult. Thus, the crude product was carried directly into the next step. The tetraol was transferred to a 25 mL round-bottom flask, dissolved in 15 mL of CH_2Cl_2, and cooled to 0 °C. 1-(*p*-Isopropoxy-*m*-vinylphenyl)propionic acid (**28**) (1.02 g, 4.35 mmol, 4.4 equiv), 1-(3-dimethylaminopropyl)-3-ethyl carbodiimide (EDC) (912 mg, 4.76 mmol, 4.8 equiv), and DMAP (61 mg, 0.50 mmol, 0.50 equiv) were then directly added in succession to the mixture as solids. Et_3N (0.69 mL, 4.95 mmol, 5.0 equiv) was added through a syringe. The resulting mixture was stirred for 4 h and quenched with 2 mL of a 10% citric acid solution. Additional water was added (200 mL), and the aqueous layer was washed with 3 × 100 mL of Et_2O. The combined organic layers were washed with 1 volume each of a saturated solution of sodium chloride and water. Drying over $MgSO_4$, filtration, and concentration gave a yellow oil which was purified by silica gel chromatography (TLC $R_f = 0.36$ in 4:1 hexanes/EtOAc). The desired tetra(ester) was recovered as a colorless oil (954 mg, 0.623 mmol, 63%). IR (NaCl): 2974 (m), 2951 (m), 2919 (s), 2873 (m), 2855 (m), 1735 (s), 1627 (w), 1491 (m), 1451 (w), 1384 (w), 1372 (w), 1293 (w), 1247 (s), 1139 (m), 1119 (m), 958 (w), 906 (w), 837 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 2.4 Hz, 4H, aromatic CH), 7.02 (d, J = 6.4 Hz, 4H, aromatic CH), 7.02 (dd, J = 19.8, 9.4 Hz, 4H, ArC*H*CH_2), 6.79 (d, J = 8.8 Hz, 4H, aromatic CH), 5.71 (dd, J = 17.8, 1.6 Hz, 4H, ArCHC*H*$_2$), 5.21 (dd, J = 11.4, 1.6 Hz, 4H, ArCHC*H*$_2$), 4.48 (septet, J = 6.2 Hz, 4H, $(CH_3)_2CHOAr$), 4.01 (t, J = 7.0 Hz, 8H, CO_2CH_2), 2.88 (t, J = 7.8 Hz, 8H, $ArCH_2CH_2CO_2$), 2.59 (t, J = 7.8 Hz, 8H, $ArCH_2CH_2CO_2$), 1.58 (m, 8H, $CO_2CH_2CH_2CH_2Si(Me)_2$), 1.36−1.25 (m, 8H, $SiCH_2CH_2CH_2Si(Me)_2$), 1.33 (d, J = 5.6 Hz, 24H, $(CH_3)_2CHOAr$), 0.58−0.52 (m, 16H, $CH_2Si(Me)_2CH_2$), 0.47−0.42 (m, 8H, $Si(CH_2)_4$), −0.04 (s, 24H, $Si(Me)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.77, 153.44, 132.40, 131.76, 128.30, 127.61, 126.14, 114.30, 113.78, 70.96, 67.16, 36.30, 30.38, 23.33, 22.33, 20.20, 18.65, 17.63, 11.30, −3.26. LRMS Calcd for $C_{88}H_{140}O_{12}Si_5K$ $(M+K)^+$: 1569.9. Found: 1569.5. Anal. Calcd for $C_{88}H_{140}O_{12}Si_5$: C, 69.06; H, 9.22. Found: C, 69.31; H, 9.36.

(36) (a) Speier, J. L.; Webster, J. A.; Barnes, G. H.; *J. Am. Chem. Soc.* **1957**, *79*, 974−979. (b) Musolf, M. C.; Speier, J. L. *J. Org. Chem.* **1964**, *29*, 2519.

(37) Karstedt, B. D. U.S. Patent 3,775,452, 1973.

[(PCy$_3$)Cl$_2$Ru═CH-*o*-O*i*PrC$_6$H$_3$(CH$_2$)$_2$COO(CH$_2$)$_3$Si(Me)$_2$-(CH$_2$)$_3$Si]$_4$ (32). (PCy$_3$)$_2$Cl$_2$Ru═CHPh (**2**) (792 mg, 0.962 mmol, 4.3 equiv) and CuCl (106 mg, 1.07 mmol, 4.8 equiv) were added to a 25 mL round-bottom flask and suspended in 12 mL of CH_2Cl_2. [(*p*-Isopropoxy-*m*-vinylphenyl)(CH$_2$)$_2$CO$_2$(CH$_2$)$_3$Si(Me)$_2$(CH$_2$)$_3$Si]$_4$ (341 mg, 0.223 mmol, 1.0 equiv) was added to this mixture through a cannula in 10 mL of CH_2Cl_2. The mixture was stirred for a period of 3 h at 22 °C, during which time the original purple solution turned dark brown. The following workup procedures were conducted in air with reagent-grade solvents. The mixture was concentrated at reduced pressure and passed through a short plug of silica gel in 3:2 hexanes/Et_2O (brown band rapidly elutes). Product fractions were pooled and concentrated. This material was passed through a second column of silica gel, this time with a gradient elution (1:1 hexanes/CH_2Cl_2 to 2:3 hexanes/CH_2Cl_2 to 1:3 hexanes/CH_2Cl_2 to 100% CH_2Cl_2). Finally, the column was flushed with Et_2O, at which point the product elutes (brown band). Solvent removal afforded a dark brown crystalline solid (637 mg, 0.194 mmol, 87%). IR (NaCl): 2927 (s), 2852 (s), 1955 (w), 1733 (s), 1684 (w), 1610 (w), 1582 (w), 1488 (m), 1447 (m), 1417 (w), 1385 (m), 1296 (w), 1247 (m), 1222 (m), 1204 (m), 1134 (m), 1104 (m), 913 (w), 891 (w), 849 (m), 774 (w), 735 (m), 702 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 17.38 (d, J = 4.0 Hz, 4H, Ru═CHAr), 7.52 (s, 4H, aromatic CH), 7.46 (d, J = 8.8 Hz, 4H, aromatic CH), 6.98 (d, J = 8.8 Hz, 4H, aromatic CH), 5.23 (septet, J = 6.2 Hz, 4H, (CH$_3$)$_2$C*H*OAr), 4.03 (t, J = 7.1 Hz, 8H, CO$_2$CH$_2$), 3.03 (t, J = 7.7 Hz, 8H, ArCH$_2$C*H*$_2$CO$_2$), 2.64 (t, J = 7.7 Hz, 8H, ArC*H*$_2$CH$_2$CO$_2$), 2.32 (m, 12H, PCH), 2.20−1.20 (m, 136H, CO$_2$CH$_2$C*H*$_2$CH$_2$Si(Me)$_2$, SiCH$_2$C*H*$_2$CH$_2$Si(Me)$_2$, and P(CH(C*H*$_2$)$_5$)$_3$), 1.79 (d, J = 6.2 Hz, 24H, (C*H*$_3$)$_2$CHOAr), 0.60−0.52 (m, 16H, C*H*$_2$Si(Me)$_2$C*H*$_2$), 0.50−0.45 (m, 8H, Si(CH$_2$)$_4$), −0.03 (s, 24H, Si(Me)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 279.24, 172.60, 151.29, 143.79, 134.69, 129.42, 122.51 (d, J_{OC} = 5.9 Hz), 113.19, 75.50 (d, J_{OC} = 7.8 Hz), 67.27, 36.36, 35.67 (d, J_{PH} = 24.4 Hz), 30.14, 29.73, 27.80 (d, J_{PH} = 10.7 Hz), 26.33, 23.26, 22.14, 20.14, 18.58, 17.56, 11.26, −3.33. ^{31}P NMR (162 MHz, $CDCl_3$): δ 59.17 (s, PCy$_3$). LRMS Calcd for C$_{156}$H$_{264}$Cl$_8$O$_{12}$P$_4$Ru$_4$Si$_5$Na$_2$ (M + 2Na)$^+$: 3331.2. Found: 3331.8. Anal. Calcd for C$_{156}$H$_{264}$Cl$_8$O$_{12}$P$_4$Ru$_4$Si$_5$: C, 57.05; H, 8.10. Found: C, 56.80; H, 8.00.

[(4,5-DihydroIMES)Cl$_2$Ru═CH-*o*-O*i*PrC$_6$H$_3$(CH$_2$)$_2$COO(CH$_2$)$_3$Si-(Me)$_2$(CH$_2$)$_3$Si]$_4$ (33). The unmetalated dendrimer (227 mg, 0.148 mmol, 1.0 equiv) was weighed into a 25 mL round-bottom flask and dissolved in 15 mL of CH_2Cl_2. (4,5-DihydroIMES)(PCy$_3$)Cl$_2$Ru═CHPh (**3**) (606 mg, 0.714 mmol, 4.8 equiv) and CuCl (72.0 mg, 0.731 mmol, 4.9 equiv) were added directly to this solution as solids. The mixture was stirred for 2 h at 22 °C, during which time the original purple solution turned a dark green/brown color. The following workup procedures were conducted in air with reagent-grade solvents. The mixture was concentrated at reduced pressure and passed through a short column of silica gel (gradient elution: 100% CH_2Cl_2 to 4:1 hexanes/Et_2O to 1:1 hexanes/Et_2O to 100% Et_2O). The green band was collected and concentrated, affording a green microcrystalline solid (277 mg, 0.0816 mmol, 55%). IR (NaCl): 3432 (b), 2915 (m), 1732 (s), 1632 (w), 1607 (w), 1595 (w), 1487 (s), 1418 (m), 1259 (s), 1221 (m), 1132 (m), 1104 (m), 1034 (w), 912 (w), 849 (w), 579 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 16.51 (s, 4H, Ru═CHAr), 7.33 (d, J = 7.0 Hz, 4H, aromatic CH), 7.07 (s, 16H, mesityl aromatic CH), 6.74−6.66 (m, 8H, aromatic CH), 4.85 (septet, J = 6.3 Hz, 4H, (CH$_3$)$_2$C*H*OAr), 4.17 (s, 16H, N(CH$_2$)$_2$N), 4.02 (t, J = 7.0 Hz, 8H, CO$_2$CH$_2$), 2.91 (t, J = 7.8 Hz, 8H, ArCH$_2$C*H*$_2$CO$_2$), 2.53 (t, J = 7.8 Hz, 8H, ArC*H*$_2$CH$_2$-CO$_2$), 2.47 (s, 48H, mesityl *o*-CH$_3$), 2.41 (s, 24H, mesityl *p*-CH$_3$), 1.61 (m, 8H, CO$_2$CH$_2$C*H*$_2$CH$_2$Si(Me)$_2$), 1.40−1.25 (m, 8H, SiCH$_2$C*H*$_2$CH$_2$-Si(Me)$_2$), 1.24 (d, J = 6.3 Hz, 24H, (C*H*$_3$)$_2$CHOAr), 0.61−0.45 (m, 24H, C*H*$_2$Si(Me)$_2$C*H*$_2$ and Si(CH$_2$)$_4$), −0.02 (s, 24H, Si(Me)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 297.07 (d, J = 166.0 Hz), 211.32, 172.81, 150.80, 145.16, 138.76, 134.28, 130.42, 130.29, 129.80, 129.39, 128.74, 128.22, 74.41, 67.19, 51.44, 36.03, 29.54, 23.14, 21.53, 20.96, 20.60, 20.03, 18.48, 17.47, 11.12, −4.13. LRMS Calcd for C$_{168}$H$_{240}$Cl$_8$N$_8$O$_{12}$Ru$_4$Si$_5$ (M + 4H)$^+$: 3393.1. Found: 3393.1. Anal. Calcd for C$_{168}$H$_{236}$Cl$_8$N$_8$O$_{12}$-Ru$_4$Si$_5$: C, 59.56; H, 7.02. Found: C, 59.55; H, 6.96.

Representative Experimental Procedure for RCM Catalyzed by Monomeric (4,5-DihydroIMES)Cl$_2$Ru═CH-*o*-O*i*PrC$_6$H$_4$ (5). Triene (**7**) (50.1 mg, 0.329 mmol, 1.0 equiv) was weighed out in a 25 mL round-bottom flask and dissolved in 3 mL of CH_2Cl_2 (0.1 M). (4,5-DihydroIMES)Cl$_2$Ru═CH-*o*-O*i*PrC$_6$H$_4$ (**5**) (9.80 mg, 0.0156 mmol, 0.0474 equiv) was added as a solid, and the resulting deep green solution was stirred at 22 °C. TLC analysis after 10 min indicated completion of the reaction. As usual, workup procedures were conducted in air using reagent-grade solvents. The mixture was concentrated at reduced pressure and passed through a short column of silica gel in 2:1 hexanes/CH_2Cl_2, affording diene (**8**) (33.4 mg, 0.269 mmol, 82%) as a colorless oil (TLC R_f = 0.46 in 9:1 hexanes/Et_2O). The catalyst was then retrieved as a green solid by flushing the silica column with 100% CH_2Cl_2 (9.60 mg, 0.0153 mmol, 98%).

Representative Experimental Procedure for RCM Catalyzed by Dendritic [(PCy$_3$)Cl$_2$Ru═CH-*o*-O*i*PrC$_6$H$_3$(CH$_2$)$_2$COO(CH$_2$)$_3$Si(Me)$_2$-(CH$_2$)$_3$Si]$_4$ (32). Tosyl amide (**34**) (250 mg, 0.995 mmol, 1.0 equiv) and dendritic catalyst **32** (43.9 mg, 0.0140 mmol, 0.014 equiv) were weighed into a 50 mL round-bottom flask. The flask was equipped with a reflux condenser, evacuated, and filled with an atmosphere of argon. The vessel was charged with CH_2Cl_2 (20 mL, 0.05 M) and submerged into an oil bath preheated to 40 °C. The reaction was stirred for 15 min, at which point TLC analysis indicated completion of the reaction. Removal of the solvent in vacuo afforded a dark brown oil that was purified by silica gel chromatography (100% CH_2Cl_2), affording **35** as a white solid (219 mg, 0.983 mmol, 99%). The column was then flushed with 100% Et_2O to recover the dendritic catalyst as a brown solid residue (42.7 mg, 0.0130 mmol, 93%). The recovered catalyst was transferred directly into a new flask for a subsequent reaction. As discussed above, Ru recovery on the dendrimer can be analyzed upon inspection of the ^{1}H NMR (400 MHz) spectrum. Integration of the benzylic methylene protons at 3.03 ppm (metal-occupied sites) and 2.88 ppm (metal-vacant sites) provided a ratio of 87:13, respectively.

Representative Experimental Procedure for RCM Catalyzed by Dendritic [(4,5-DihydroIMES)Cl$_2$Ru═CH-*o*-O*i*PrC$_6$H$_3$(CH$_2$)$_2$COO-(CH$_2$)$_3$Si(Me)$_2$(CH$_2$)$_3$Si]$_4$ (31). Diene (**11**) (32.7 mg, 0.233 mmol, 1.0 equiv) was weighed into a 25 mL round-bottom flask and dissolved in 5 mL of CH_2Cl_2 (0.05 M). Dendritic catalyst **33** (12.4 mg, 0.00366 mmol, 0.016 equiv) was added as a solid, and the solution was allowed to stir at 22 °C. TLC analysis after 2 h indicated completion of the reaction. Workup procedures proceeded in air with reagent-grade solvents. The mixture was concentrated at reduced pressure and passed through a short plug of silica gel in 100% CH_2Cl_2, affording **12** (20.4 mg, 0.1819 mmol, 78%) as a colorless oil (TLC R_f = 0.25 in 4:1 hexanes/Et_2O). The catalyst was then flushed off of the column with 100% Et_2O, affording 11.2 mg (0.00329 mmol, 90%) of a green solid. Ru recovery on the dendrimer was assessed using ^{1}H NMR spectroscopy (400 MHz). Integration of the isopropoxy methine proton for both metal-occupied (4.90 ppm) and metal-vacant (5.71 ppm) sites gave a ratio of 92:8 respectively, indicative of 8% metal loss.

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Supporting Information Available: Crystallographic details for **5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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