[5] E. A. Permyakov, L. J. Berliner, *FEBS Lett.* **2000**, *473*, 369–374.
[6] D. A. Dolgikh, R. I. Gilmanshin, E. V. Brazhnikov, V. E. Bychkova, G. V. Semisotnov, S. Venyaminov, O. B. Ptitsyn, *FEBS Lett.* **1981**, *136*, 311–315.
[7] V. Forge, R. T. Wijesinha, J. Balbach, K. Brew, C. V. Robinson, C. Redfield, C. M. Dobson, *J. Mol. Biol.* **1999**, *288*, 673–688.
[8] T. Kühn, H. Schwalbe, *J. Am. Chem. Soc.* **2000**, *122*, 6169–6174.
[9] a) C. Frieden, S. D. Hoeltzli, I. J. Ropson, *Protein Sci.* **1993**, *2*, 2007–2014; b) J. Balbach, V. Forge, N. A. van Nuland, S. L. Winder, P. J. Hore, C. M. Dobson, *Nat. Struct. Biol.* **1995**, *2*, 865–870; c) S. D. Hoeltzli, C. Frieden, *Proc. Natl. Acad. Sci. USA* **1995**, *92*, 9318–9322; d) J. Balbach, V. Forge, W. S. Lau, N. A. van Nuland, K. Brew, C. M. Dobson, *Science* **1996**, *274*, 1161–1163; e) M. Spraul, M. Hoffmann, H. Schwalbe, DE 19548977 C 1 [*Chem. Abstr.* **1997**, *126*: *232572*].
[10] a) J. Bargon, H. Fischer, U. Johnson, *Z. Naturforsch. A* **1967**, *22*, 1551–1555; b) P. J. Hore, R. W. Broadhurst, *Prog. Nucl. Magn. Reson. Spectrosc.* **1993**, *25*, 345–402; c) R. Kaptein, *Biol. Magn. Reson.* **1982**, *4*, 145–191.
[11] K. Maeda, C. E. Lyon, J. J. Lopez, M. Cemazar, C. M. Dobson, P. J. Hore, *J. Biomol. NMR* **2000**, *16*, 235–44.
[12] R. Wijesinha-Bettoni, C. M. Dobson, C. Redfield, *J. Mol. Biol.* **2001**, *307*, 885–898.
[13] G. C. R. Ellis-Davies, J. H. Kaplan, *J. Org. Chem.* **1988**, *53*, 1966–1969.
[14] a) F. M. Richards, *Ann. Rev. Biophys. Bioeng.* **1977**, *6*, 151–176; b) B. Lee, F. M. Richards, *J. Mol. Biol.* **1971**, *55*, 379–400.
[15] C. Tanford, *Adv. Protein Chem.* **1968**, *23*, 218–282.
[16] A. T. Alexandrescu, R. W. Broadhurst, C. Wormald, C. L. Chyan, J. Baum, C. M. Dobson, *Eur. J. Biochem.* **1992**, *210*, 699–709.
[17] A. C. Pike, K. Brew, K. R. Acharya, *Structure* **1996**, *4*, 691–703.
[18] R. Koradi, M. Billeter, K. Wüthrich, *J. Mol. Graphics* **1996**, *14*, 51–55.

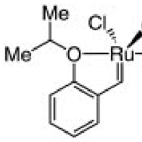
Immobilization of Olefin Metathesis Catalysts on Monolithic Sol–Gel: Practical, Efficient, and Easily Recyclable Catalysts for Organic and Combinatorial Synthesis[**]

Jason S. Kingsbury, Steven B. Garber,
Jonathan M. Giftos, Brian L. Gray,
Mariko M. Okamoto, Richard A. Farrer,
John T. Fourkas,* and Amir H. Hoveyda*

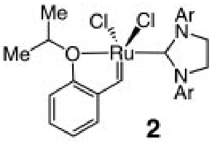
Environmental issues and recent developments in chemistry and biology have introduced a number of compelling requirements that must be met in the development of practical catalysts. Recyclability is one important attribute. Retrievable catalysts that are recovered inexpensively and without significant waste generation efficiently deliver products of higher purity and lower toxicity. The emerging significance of combinatorial chemistry demands that a catalyst promote reactions efficiently and selectively while being easily adaptable to 96-well and higher density formats; repeated weighing of catalysts or substrates for a library synthesis and subsequent purification of each mixture is costly and time-consuming.

Herein we disclose the synthesis and activity of Ru complexes supported by monolithic (smallest dimension = 1 mm) samples of porous sol–gel glass that effectively promote various olefin metathesis reactions.[1] These catalysts can be easily employed in a library synthesis format without multiple weighings, in air and with undistilled commercial reagent-grade solvents. Catalyst recovery is simply carried out with a pair of tweezers; it does not require filtration and generates minimal solvent waste. The catalyst retains its activity after multiple cycles (>15), affording products that are of high (often analytical) purity without recourse to any purification steps.

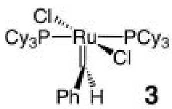
Recent reports from our laboratories relate to the chemistry of recyclable monomeric metathesis catalysts (**1** and **2**).[2] A key feature of these systems is the isopropyl styrenyl ether; this bidentate ligand favors efficient metal recovery for entropic reasons, allowing the promotion of olefin metathesis by a release/return mechanism.[2] These Ru complexes can also offer reactivity and chemo- and stereoselectivity profiles[3] which differ from the alternative catalysts **3**,[4] **4**,[5] and **5**.[6]



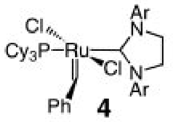
1



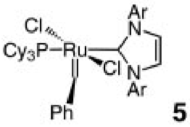
2



3



4



5

Ar = 2,4,6-trimethylphenyl

Although **1** and **2** are robust and recyclable, catalyst retrieval generates substantial amounts of silica gel and solvent waste. Based on the release/return mechanism, Ru–carbenes **1**,[7] **3**,[8] and **5**[9] were subsequently attached to insoluble cross-linked and monoporous polystyrene polymers as well as to a soluble polyethylene glycol (PEG) resin. However, these supported catalysts typically suffer from one or more of the following shortcomings: 1) There are no reports of catalyst utility in the synthesis of trisubstituted olefins; efficient processes involve only ring-closing metathesis (RCM) reactions with terminal olefin substrates or those that benefit from entropic factors.[7–9a] 2) Diminished

---

[*] Prof. J. T. Fourkas, Prof. A. H. Hoveyda, J. S. Kingsbury, S. B. Garber, J. M. Giftos, B. L. Gray, M. M. Okamoto, R. A. Farrer
Department of Chemistry
Merkert Chemistry Center
Boston College, Chestnut Hill, MA 02467 (USA)
Fax: (+1) 617-552-1442
E-mail: amir.hoveyda@bc.edu

[**] This research was supported by the NSF (CHE-9905806 to A.H.H., CHE-0073228 to J.T.F., and a predoctoral fellowship to J.S.K.) and Boehringer-Ingelheim. J.M.G. and B.L.G. acknowledge Pfizer for fellowships.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

activity upon reuse.[7a, 8, 9] 3) Requirement for the addition of solvent during precipitation of the soluble resin[7b] or filtration of nonsoluble ones.[7a, 8, 9] 4) Requirement for alkene additives to ensure reasonable catalyst activity upon reuse.[8, 9a] 5) The need for silica gel chromatography[10] or other purification methods[11] to obtain products with acceptable levels of purity (largely to minimize Ru content). In addition to the above approaches, two systems have been developed which involve permanent attachment to a resin.[12] These variants are either significantly less active than free complexes[12a] or lose substantial reactivity upon recovery.[12b] In all of the above cases, use in a library synthesis would require numerous and deliberate weighing measurements of the catalysts and substrates. If a stock solution of a homogeneous catalyst is used to introduce equal loadings per transformation, the amount of substrate in each well must then be carefully measured. This ultimately leads to higher levels of metal contamination in the products and is equally tedious and time-consuming, since libraries usually contain substrates of varying molecular weights.

In search of an appropriate support, we were attracted to inorganic sol–gels[13] since they offer several advantages: 1) These porous glasses retain a rigid and exposed surface area (300–1000 m^2g^{-1}), whereas conventional polymer beads typically swell and shrink variably in different media, often resulting in unpredictable effects on catalyst activity. 2) Surface functionalization of a monolithic gel results in a bulk catalyst sample; this obviates the filtration step usually needed for catalyst isolation and minimizes solvent waste. 3) Gelation occurs after a sol is cast into a mold; the gel samples may thus be tailored to a desired size or shape.

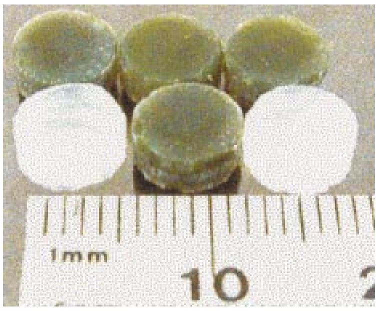
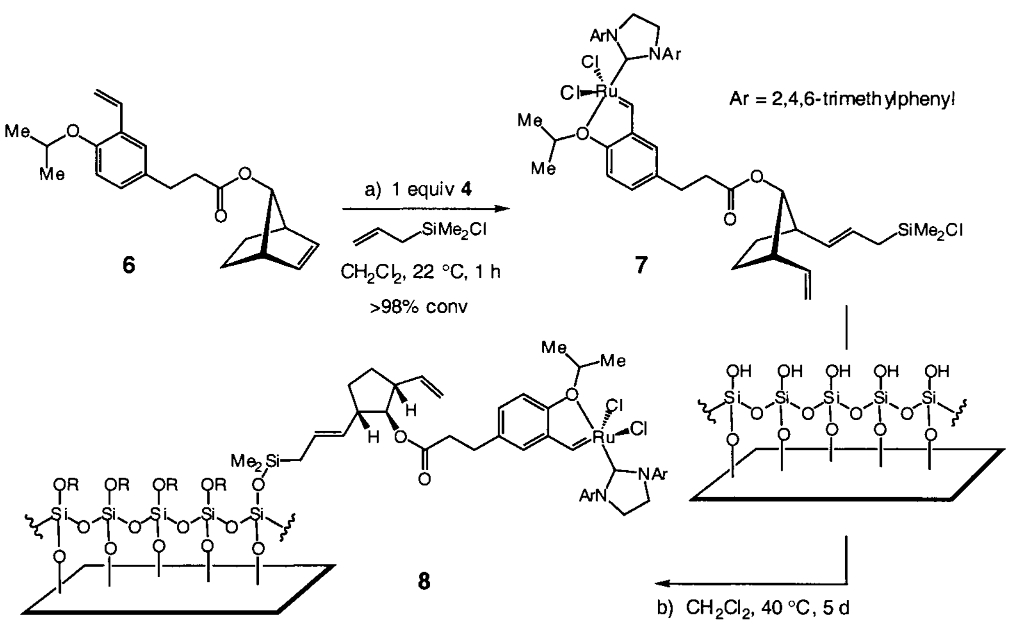


Figure 1. Unfunctionalized (white) and Ru-containing (green) sol–gel monoliths.

For this study, we selected a commercially available (Geltech) glass monolith with an average pore size of 200 Å (Figure 1).[14] Installation of the Ru center on sol–gel and synthesis of an appropriate linker are carried out efficiently in a single vessel (Scheme 1). Treatment of styrene ether **6** with one equivalent of Ru complex **4** and allylchlorodimethylsilane (CH_2Cl_2, 22 °C) leads to facile tandem ring-opening metathesis (ROM)/cross metathesis (CM) and subsequent deposition of the Ru center at the bidentate site. Preweighed monolithic sol–gels are added to the solution, and the mixture is allowed to stand at 40 °C for five days[15] to afford loaded dark green glass samples which are washed with CH_2Cl_2 and dried in vacuo (Figure 1). These samples may be stored in air without significant loss of activity.[16] Sol–gel systems **9** and **10** were also prepared by an identical procedure with the corresponding norbornene precursors,[17] and possess similar physical appearance to **8**.

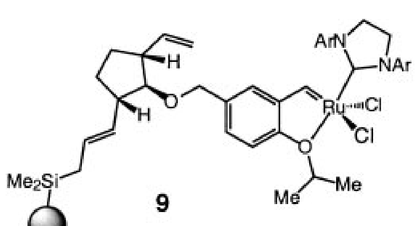
Sol–gel-supported Ru catalysts **8**–**10** provide excellent levels of reactivity for the formation of trisubstituted olefin **12** (see Table 1). There is minimal diminution in reactivity after four cycles (>98 % yield in all cases).[18] With purified solvent and under N_2 atmosphere, catalyst **10** was used in the synthesis of **12** for eleven additional rounds (total of fifteen cycles). Although extended times were required for complete conversion,[19] all transformations proceeded to completion (>98 % yield). With reagent-grade solvent (used directly from a bottle of Mallinkrodt, AR grade) and under air, the catalyst was employed efficiently three times (>98 % conv); however, the reaction did not proceed to completion during the fourth cycle under these conditions.[17]



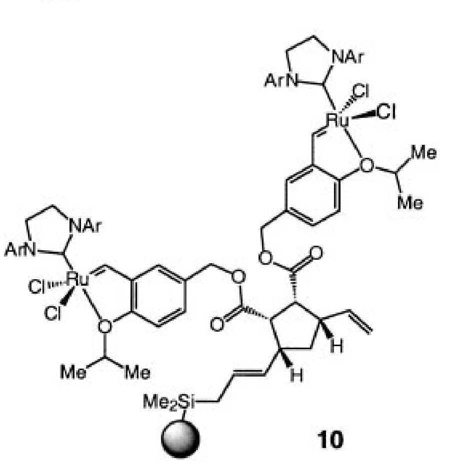
Scheme 1. Attachment of Ru complex and linker to glass support in a single vessel.

Glass samples recovered from the fourth cycle (N_2 and purified solvent) were used with different substrates in the ROM/CM process cycle 5 (**13**→**14**). The reaction proceeds to completion, and careful analysis (400 MHz ^1H NMR analysis) of the unpurified product shows <2 % contamination from the product of the previous RCM (**12**). The same is true for transformations in cycles 6–8: no products or by-products from the previous transformation were detected in any of the unpurified product samples (<2 % by 400 MHz ^1H NMR spectroscopy).

Several additional issues regarding the data in Table 1 merit mention: 1) In contrast to

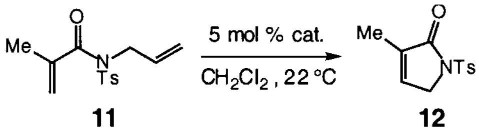


9

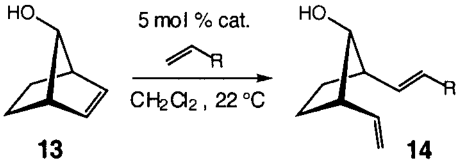


10

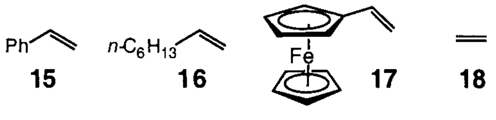
Table 1. Recycling studies with glass-bound metathesis catalysts **8**–**10**.



Cycle (t)	**8** as catalyst (conv [%]; yield [%])	**9** as catalyst (conv [%]; yield [%])	**10** as catalyst (conv [%]; yield [%])
cycle 1 (3 h)	> 98; > 98	> 98; > 98	> 98; > 98
cycle 2 (3 h)	> 98; > 98	> 98; > 98	> 98; > 98
cycle 3 (3 h)	> 98; > 98	> 98; > 98	> 98; > 98
cycle 4 (3 h)	> 98; > 98	> 98; > 98	> 98; > 98



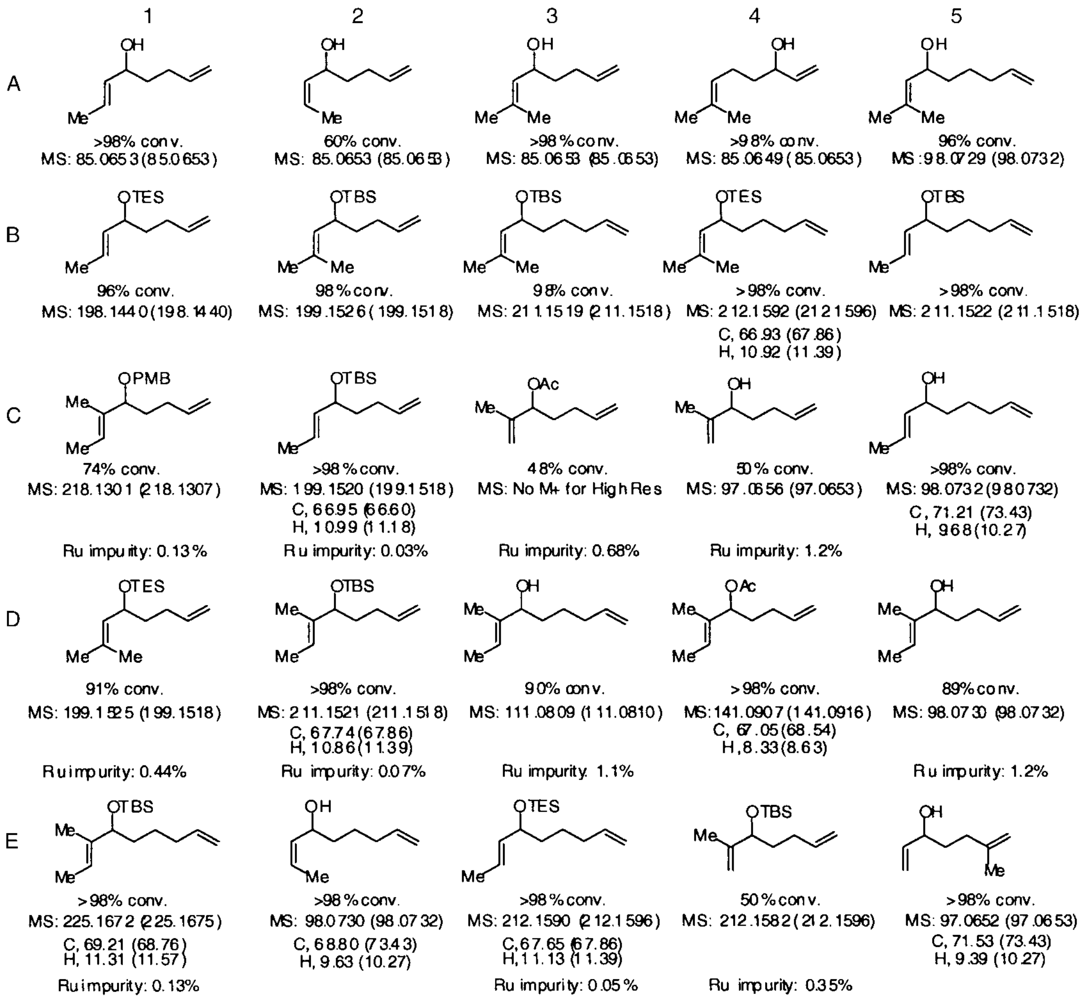
	(alkene; conv [%])	(alkene; conv [%])	(alkene; conv [%])
cycle 5 (1 h)	15; > 98	15; > 98	15; > 98
cycle 6 (1 h)	16; > 98	16; > 98	16; > 98
cycle 7 (1 h)	17; > 98	17; > 98	17; > 98
cycle 8 (1 h)	18; > 98	18; > 98	18; > 98



processes run with 5 mol % monomer **2** or **4**, the unpurified reaction mixture (cycles 1–4) in every case consisted of > 98 % pure cycloolefin, where no catalyst or by-product thereof could be detected (400 MHz ^{1}H NMR spectroscopy). Removal of CH_2Cl_2 in vacuo delivered pure cycloolefin as an off-white solid in > 98 % yield; silica gel chromatography or distillation was not required. The resulting unpurified materials were determined to be analytically pure (C,H analysis) for all twelve of the experiments in cycles 1–4 of Table 1.[20] Inductively coupled plasma mass spectrometry (ICP-MS) analysis of product samples indicates only 0.04–0.06 % (by mass) Ru contamination in the unpurified products, values that are substantially lower than those obtained with homogeneous monomeric catalysts, where all of the catalyst remains in the product mixture which must be purified by silica gel chromatography or distillation. 2) Filtration is not needed for product isolation. The reaction mixture is simply removed with a Pasteur pipette, and the glass sample is rinsed with minimal amounts of CH_2Cl_2. 3) After four rounds of RCM for each supported catalyst, the gel pellets were dried in vacuo and weighed. Highly reproducible mass differences indicated a net 20–25 % Ru loss over the four cycles. 4) The functionalized monoliths are physically robust and do not chip or fragment in the presence of small stir bars. Catalytic olefin metathesis can be carried out with supported complexes **8**–**10** without stirring. However, the shortest reaction times are observed with either rotary agitation or magnetic stirring.

Despite the diminution in Ru loading, the catalytic activities of the recycled pellets are still high, as demonstrated by the levels of conversion in the additional cycles. This minor, but steady, loss of active metal content detected after each round of catalysis accounts for the low, but detectable (ICP-MS), levels of Ru in products and the increase in reaction times required for complete conversion during the later rounds.[19] Since the isopropyl styrene ether remains bound to the glass surface during catalysis, it is unavailable to serve as a stabilizing Lewis base for electron-deficient and highly active metal complexes in solution, leading to some Ru–carbene decomposition. It is therefore plausible that small amounts of Ru are released into solution, where the extremely high propagation rate for the metal–carbene gives rise to substantial levels of conversion. The glass-bound catalysts may not be recycled as efficiently when metathesis is performed in the presence of air due to sensitivity of this unstabilized and highly reactive unbound Ru–carbene. Detailed mechanistic studies are underway to rigorously establish whether and to what extent, as observed with monomeric and dendritic variants,[2] any of the released Ru returns to the isopropoxy ligand at the surface of the glass (release/return mechanism).

The practicality of glass-bound Ru complexes in high-throughput synthesis was demonstrated by synthesis of olefin metathesis libraries shown in Schemes 2 and 3 and promoted by glass-supported catalysts **8**–**10**. The first 25-member library (Scheme 2) involved catalytic RCM reactions of a range of dienes with varying levels of alkene substitution. Reactions were carried out for six hours at 22 °C in air with reagent-grade solvent in the presence of one small catalyst pellet within each well. Since the functionalized glass-bound catalyst samples are of uniform size and loading, individual and repetitive weighings of catalyst samples are not needed. An appropriate number of pellets of a given size may be added to a well, depending on the substrate amount. Because the Ru–carbene is released by the available substrate

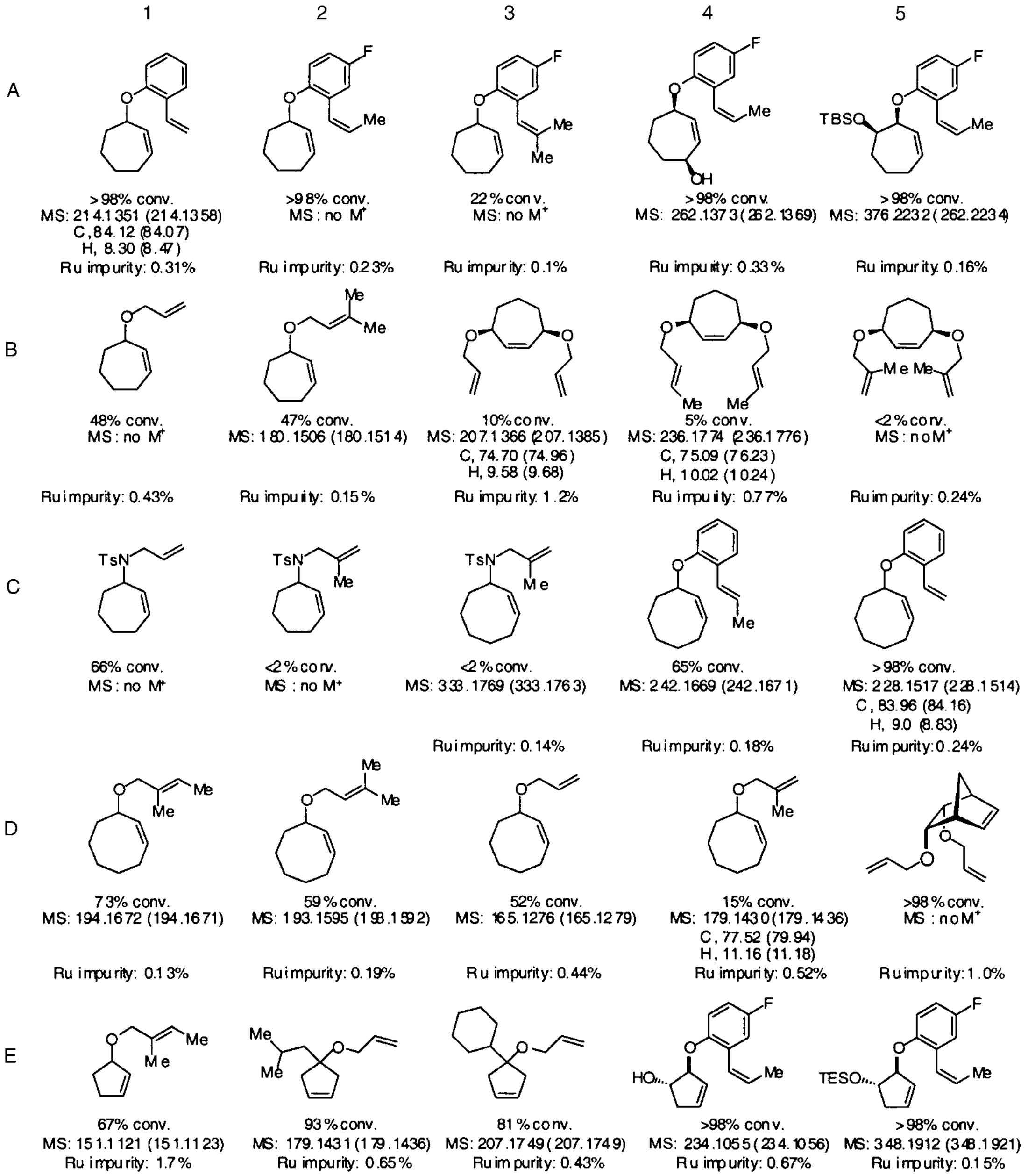


Scheme 2. Library of ring-closing metathesis reactions catalyzed by **8**–**10** (substrates shown only). Conditions: One pellet per well (~5 mol% catalyst available on glass), 0.2 M in CH_2Cl_2, 22 °C, 6 h. Conversions determined by analysis of 400 MHz ^1H NMR spectrum of the reaction mixture. Analysis data obtained from unpurified reaction products after removal of solvent in vacuo. Representative found and calculated values for C, H elemental analyses and high resolution mass spectroscopy are shown below each substrate; calculated values are in parantheses. Level of Ru impurity determined by ICP-MS and shown as percent by mass.

molecules[2] and only small amounts of highly active free Ru–carbene lead to appreciable conversion, larger glass samples or those carrying an excess of catalyst might be used. Most of the Ru remains attached and can simply be recovered by taking away the loaded glass upon completion of the reaction. Workup involves removal of the solutions (pipette), washing of each container and its bound catalysts with CH_2Cl_2 ($3 \times \sim 0.5$ mL) and evaporation of volatiles in vacuo. As the data in Scheme 2 indicate, all reactions, including those involving trisubstituted olefins, proceeded efficiently. In all but one case (C3), the formation of the desired cyclic adduct was confirmed by high-resolution mass spectrometry. Representative C,H, and ICP-MS analyses show that the products—without any purification—are of high purity and the level of Ru contamination is typically below 1%.

The glass-bound catalysts recovered from the library in Scheme 2 were used to carry out the synthesis of a second library of tandem catalytic ROM/RCM products (Scheme 3). These reactions were allowed to stir in commercial CH_2Cl_2 at 22 °C in air (0.10 mmol substrate as in the first library) and represent a more challenging class of substrates;[1] reactivity is diminished since olefins of higher substitution are involved (e.g., C3 or D2 in Scheme 3). Nevertheless, similar levels of reactivity, as observed with monomeric **2**, were detected in reactions of the second library. Mass spectrometric analysis confirmed the presence of the desired compound in 18 out of 25 cases. Selected elemental analyses indicate products of high purity prior to any purification (e.g., A1 and C5, Scheme 3).

We have thus designed an efficient new strategy for one-pot surface functionalization of monolithic sol–gels that can be effected catalytically or stoichiometrically under mild conditions. Importantly, the strategy for modification of glass surfaces may be readily adapted for immobilization of other catalyst systems. The Ru-based catalysts described herein represent a new class of convenient and practical olefin metathesis catalysts that exhibit high reactivity and can be easily recycled without significant loss of activity or the need for additives or solvents. These catalysts provide products that are of excellent purity before silica gel chromatography or



Scheme 3. Library of tandem ring-opening/cross metathesis reactions catalyzed by **8**–**10** (substrates shown only). Conditions: One pellet per well (~5 mol% catalyst available on glass), 0.2 M in CH_2Cl_2, 22 °C, 24 h. See legend for Scheme 2 for details on conversion determination and analytical data.

distillation, and can be employed readily in combinatorial synthesis in air and with reagent-grade commercial solvents. The generality and significance of olefin metathesis, together with the chemically and environmentally attractive attributes of the catalysts discussed above, should render these glass-supported Ru-based catalysts of extensive utility in chemistry and all of its related applications.

Receved: August 10, 2001 [Z17703]

---

[1] a) R. H. Grubbs, S. Chang, *Tetrahedron* **1998**, *54*, 4413–4450; b) A. Furstner, *Angew. Chem.* **2000**, *112*, 3140–3172; *Angew. Chem. Int. Ed.* **2000**, *39*, 3012–3043; c) A. H. Hoveyda, R. R. Schrock, *Chem. Eur. J.* **2001**, *7*, 945–950.

[2] a) J. S. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus, A. H. Hoveyda, *J. Am. Chem. Soc.* **1999**, *121*, 791–799; b) S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168–8179.

[3] a) See the Supporting Information in: J. Limanto, M. L. Snapper, *J. Am. Chem. Soc.* **2000**, *122*, 8071–8072; b) S. Gessler, S. Randl, S. Blechert, *Tetrahedron Lett.* **2000**, *41*, 9973–9976; c) S. Randl, S. Gessler, H. Wakamatsu, S. Blechert, *Synlett* **2001**, 430–432; d) J. Cossy, S. BouzBouz, A. H. Hoveyda, *J. Organomet. Chem.* **2001**, *624*, 327–332; for an application of **2** in target-oriented synthesis, see: e) S. BouzBouz, J. Cossy, *Org. Lett.* **2001**, *3*, 1451–1454.

[4] a) P. Schwab, M. B. France, J. W. Ziller, R. H. Grubbs, *Angew. Chem.* **1995**, *107*, 2179–2181; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2039–2041; b) P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100–110.

[5] M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953–956.

[6] a) M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, *Tetrahedron Lett.* **1999**, *40*, 2247–2250; b) J. Huang, E. D. Stevens, S. P. Nolan, J. L. Petersen, *J. Am. Chem. Soc.* **1999**, *121*, 2647–2678; c) L. Ackermann,

A. Furstner, T. Weskamp, F. J. Kohl, W. A. Hermann, *Tetrahedron Lett.* **1999**, *40*, 4787–4790.

[7] a) J. Dowden, J. Savovic, *Chem. Commun.* **2001**, 37–38; b) Q. Yao, *Angew. Chem.* **2000**, *112*, 4060–4062; *Angew. Chem. Int. Ed.* **2000**, *39*, 3896–3898.

[8] M. Ahmed, A. G. M. Barrett, D. C. Braddock, S. M. Cramp, P. A. Procopiou, *Tetrahedron Lett.* **1999**, *40*, 8657–8662.

[9] a) M. Ahmed, T. Arnauld, A. G. M. Barrett, D. C. Braddock, P. A. Procopiou, *Synlett* **2000**, 1007–1009; b) L. Jafarpour, S. P. Nolan, *Org. Lett.* **2000**, *2*, 4075–4078.

[10] D. D. Long, A. P. Termin, *Tetrahedron Lett.* **2000**, *41*, 6743–6747.

[11] For approaches where Ru impurities are removed by addition of a phosphane, $Pb(OAc)_4$ and a phosphine oxide, respectively, see: a) H. D. Maynard, R. H. Grubbs, *Tetrahedron Lett.* **2000**, *40*, 4137–4140; b) L. A. Paquette, J. D. Schloss, I. Efremov, F. Fabris, F. Gallou, J. Mendez-Andino, J. Yang, *Org. Lett.* **2000**, *2*, 1259–1261; c) Y. M. Ahn, K. Yang, G. I. Georg, *Org. Lett.* **2001**, *3*, 1411–1413.

[12] a) S. T. Nguyen, R. H. Grubbs, *J. Organomet. Chem.* **1995**, 195–200; b) S. C. Schürer, S. Gessler, N. Buschman, S. Blechert, *Angew. Chem.* **2000**, *112*, 4062–4065; *Angew. Chem. Int. Ed.* **2000**, *39*, 3898–3901.

[13] C. J. Brinkler, G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing.* Academic Press, San Diego, CA, **1990**.

[14] Each pellet weighs about 50 mg and is about 6 mm in diameter and 3 mm thick.

[15] Extensive optimization studies regarding glass derivatization revealed that shorter reaction times lead to lower loadings of Ru per unit surface area of support. These results suggest that addition of free hydroxy groups on the glass surface to the Si–Cl bond is slow.

[16] Ru loading is calculated from the mass increase which accompanies functionalization of the glass surface. ICP-MS analysis for Ru was also carried out for the supported catalyst. However, the former is more reproducible and reliable.

[17] See the Supporting Information for all experimental details.

[18] Analysis of the 400 MHz ^{1}H NMR spectrum of the unpurified reaction mixtures indicated no difference in reaction efficiency among the three catalysts.

[19] Five hours for cycle 5, six hours for cycles 6 and 7, seven hours for cycle 8, eight hours for cycles 9 and 10, nine hours for cycle 11, ten hours for cycle 12, twelve hours for cycle 13 and fourteen hours for cycles 14 and 15.

[20] Elemental analyses were not obtained for product samples in cycles 5–8, since multiple ROCM products are produced in these reactions along with substantial amounts of uncharacterized oligomers (derived from ROMP of **13**). Similar product distributions are obtained by the monomeric **2**.

Host–Guest Chemistry Aids and Abets a Stereospecific Photodimerization in the Solid State[**]

Dafni G. Amirsakis, Miguel A. Garcia-Garibay,[*]
Stuart J. Rowan, J. Fraser Stoddart,[*]
Andrew J. P. White, and David J. Williams[*]

In memory of Donald J. Cram

The ability to preorganize olefins for their solid-state photochemical dimerization[1] within a crystalline lattice is a challenging problem.[2] It has been ascertained[3] that, in order for such reactions to occur, the olefinic functions need to be aligned in a parallel manner and to have centroid–centroid separations of about 3.5–4.2 Å. The utilization of supramolecular assistance toward the alignment of stilbenes[4] in the solid state offers a potential solution to this problem of preorganization. To date, examples of this methodology include 1) double-stranded complexes of stilbenes bound within the torus of γ-cyclodextrin,[5, 6, 7] 2) the functionalization of the aromatic units of stilbenes to encourage donor–acceptor π–π stacking interactions,[8, 9] and 3) the incorporation of hydrogen-bond acceptors into a stilbene derivative that are capable of forming a noncovalent macrocycle upon cocrystallization with a hydrogen-bond donor.[10] Herein we demonstrate that cocrystallization of a crown ether with a bis(dialkylammonium) salt—which contains a central *trans*-stilbenoid unit—generates a 2:2 complex within which the two (*E*)-olefinic bonds are aligned in an appropriate geometry that facilitates subsequent stereospecific solid-state photochemical dimerization.

Supramolecular complexes with pseudorotaxane-like architectures that are formed spontaneously from dialkylammonium ions and crown ethers have been studied extensively.[11] It has been demonstrated[12] that the bis(dialkylammonium ion)-containing threadlike dication **1**-$H_2 \cdot 2PF_6$ and the crown ether bis-*p*-phenylene[34]crown-10 (BPP34C10) form a doubly encircled and doubly threaded 2:2 complex $[(BPP34C10)_2 \cdot (\mathbf{1}\text{-}H_2)_2][PF_6]_4$ (Scheme 1) upon cocrystallization in the solid state. This result suggested to us a method for aligning stilbene derivatives in the solid state. By replacing the *p*-phenylene unit of $\mathbf{1}^{2+}$ with a *trans*-stilbenoid unit (namely, producing *trans*-**2**-$H_2 \cdot 2PF_6$) we anticipated that a 2:2 complex $[(BPP34C10)_2 \cdot (\mathbf{2}\text{-}H_2)_2][PF_6]_4$ would form upon cocrystallization in which adjacent *trans*-stilbene olefinic bonds

---

[*] Prof. M. A. Garcia-Garibay, Prof. J. F. Stoddart, D. G. Amirsakis, S. J. Rowan
Department of Chemistry and Biochemistry
University of California, Los Angeles
405 Hilgard Avenue, Los Angeles, CA 90095-1569 (USA)
Fax: (+1) 310-206-1843
E-mail: mgg@chem.ucla.edu, stoddart@chem.ucla.edu

Prof. D. J. Williams, Dr. A. J. P. White
Chemical Crystallography Laboratory
Department of Chemistry, Imperial College
South Kensington, London, SW7 2AY (UK)
Fax: (+44) 207-594-5835

[**] We thank the National Science Foundation for funding this research.