anisotropy, may be a result of the special asymmetry of this enantiopure molecular magnet. We are presently performing experiments to probe the origin of such results as well as investigating the magneto–optic properties of this intriguing material.

Experimental Section

1: *(R)*-Methyl[3-(4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy-3-oxide) phenoxy]-2-propionate ((*R*)-3MLNN (50 mg, 0.15 mmol), ref.[4]) in CH_2Cl_2 (20 mL) was added to a warm heptane (20 mL) solution of manganese(II) bis(hexafluoroacetylacetonate) (70 mg, 0.15 mmol) and the mixture was allowed to cool to room temperature. Upon standing green needles of **1** (55 mg, 45%) crystallized. The complex gave satisfactory elemental, mass spectrometry, and IR spectroscopic analysis. Crystal data for **1** $C_{27}H_{25}F_{12}MnN_2O_9$, $M = 804.43$, orthorhombic, space group $P2_12_12_1$, $a = 12.022(4)$, $b = 14.219(5)$, $c = 20.294(7)$ Å, $\alpha = \beta = \gamma = 90°$, $U = 3469.2(19)$ Å^3, $Z = 4$, $\rho = 1.540\ \mathrm{g\,cm^{-3}}$, $\mu = 0.495\ \mathrm{cm^{-1}}$, $F(000) = 1624$, 3994 measured reflections, 2981 unique reflections, collected on a Bruker P4 diffractometer with monochromatic $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.71073$ Å). Number of parameters 460 for 3994 independent reflections with $I > 2\sigma(I)$; solution SHELXS-97 (Sheldrick, 1990), refinement SHELXL-97 (Sheldrick, 1997), final R indices $[I > 2\sigma(I)]$: $R = 0.0801$, $R_w = 0.1941$. Weighted R-factors R_w and all goodness-of-fit S are based on F^2. CCDC-158455 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Magnetic measurements were performed on crystalline samples of the complex. The temperature dependence of the magnetic susceptibility in the range 2–350 K was measured in a field of 500 G using a Quantum Design SQUID magnetometer. The low-temperature measurements below 7 K were made using a high-field SQUID magnetometer developed at CRTBT/CNRS.

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[13] We note that fitting the data to the three-parameter Vogel–Fulcher law $\tau = \tau_0 \exp(E_o/k_B(T - T_f)$ or critical slowing down $\tau = \tau_0(T - T_c)^{-z\bar{\nu}}$ does not improve the fit and gives non-physical values for τ_0, E_o, T_f, and T_c and thus rule out that this behavior is that of a re-entrant spin-glass.

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The First Polymer-Supported and Recyclable Chiral Catalyst for Enantioselective Olefin Metathesis[**]

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The rise of catalytic olefin metathesis as a practical and reliable method for efficient C–C bond formation has had a remarkable impact on organic and polymer synthesis.[1] Ring-closing (RCM), ring-opening (ROM), and cross metathesis (CM) reactions have been developed in various laboratories

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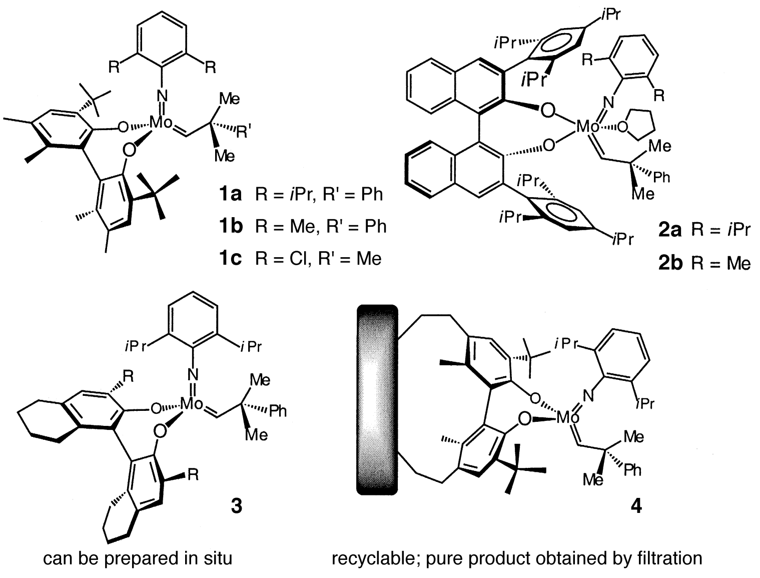
and provided access to organic molecules that would otherwise be difficult to prepare. In this context, research in our laboratories has recently involved the design, discovery, and development of chiral metathesis catalysts that exploit the power of catalytic metathesis and deliver a wide range of olefin enriched or pure materials (for example, **1**–**3**; Scheme 1).[2] Questions of efficiency and enantioselectivity have so far been the main focus of our programs.



can be prepared in situ

recyclable; pure product obtained by filtration

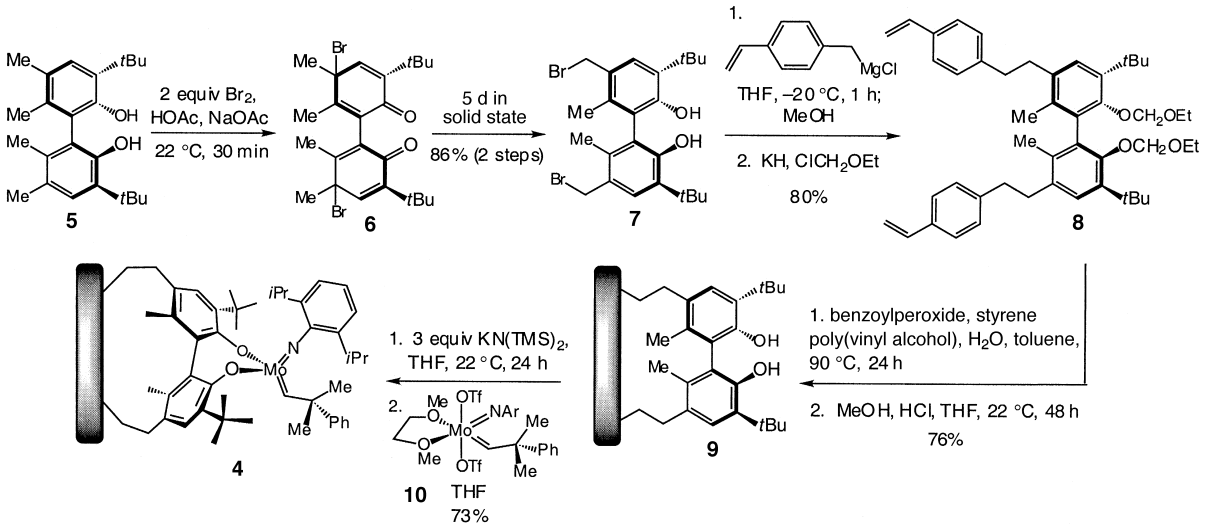
Scheme 1. Representative chiral Mo-based catalysts for olefin metathesis. TMS = $SiMe_3$, Tf = CF_3SO_2.

More recently, however, we have begun to address the important issue of practicality. As part of this initiative, we have reported a chiral catalyst (**3**, Scheme 1), prepared in situ from a commercially available metal complex and a chiral ligand, that can give rise to high levels of efficiency and enantioselectivity.[3] We have also been investigating the possibility of developing supported chiral catalysts.[4,5] Such complexes would be easily removable from the reaction mixture to allow access to products that are significantly less tainted by toxic metal impurities and would be of particular value in combinatorial synthesis and medicinal chemistry.[6] Herein, we disclose the preparation and utility of the first chiral polymer-bound metathesis catalyst (**4**, Scheme 1). The supported chiral complex delivers appreciable levels of reactivity and excellent enantioselectivity; it can be recycled and easily removed from unpurified mixtures to leave behind relatively small amounts of impurities.

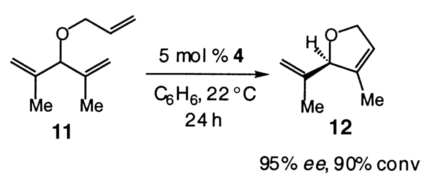
In designing a structurally robust and effective supported catalyst, we chose to prepare a system where the chiral ligand is attached to the polymer by a nonlabile tether that imposes little or no steric influence at the reactive Mo center. Accordingly, we set out to synthesize and examine chiral Mo complex **4** (Scheme 2).

The route to the solid-supported chiral ligand is illustrated in Scheme 2. Treatment of biphenol **5** with Br_2 and NaOAc in acetic acid afforded nonaromatic dibromide **6** as a yellow powder. After five days in the solid state, the initially formed **6** smoothly rearranged to give bis(bromide) **7** as a white powder in 86% overall yield (from **5**).[7] Subjection of **7** to four equivalents of *p*-vinylbenzyl magnesium chloride and subsequent protection of the phenol groups as the corresponding ethoxy methyl ethers led to the formation of **8** in 80% yield (pale yellow oil).[8] Bis(styrene) **8** was then co-polymerized in suspension in the presence of styrene[9] and the protecting groups were removed under acidic conditions to afford the supported chiral ligand **9** as a white powder in 76% overall yield.[10] After the polymer was allowed to dry in vacuo at 60 °C for 24 hours, it was deprotonated with 3 equivalents of $KN(TMS)_2$ in THF for 24 hours, then washed thoroughly with THF, and dried in vacuo. Treatment with bis(triflate) **10** in THF for 7 hours led to the formation of **4** as a dark brown powder in 73% yield (from **9**).[11–13]

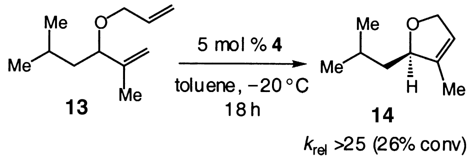
With the supported chiral catalyst **4** in hand, we examined its ability to promote asymmetric olefin metathesis reactions. We first investigated asymmetric RCM (ARCM) represented in Equations (1) and (2). These transformations indicated that



Scheme 2. Synthesis of supported chiral catalyst **4**.



(1)



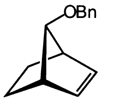
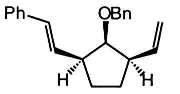
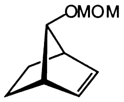
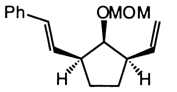
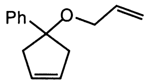
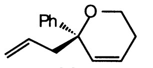
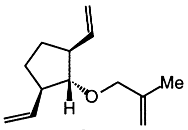
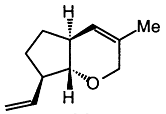
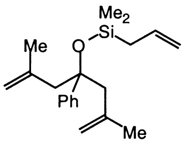
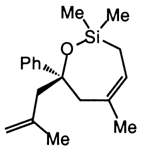
(2)

although **4** is less efficient than the parent homogeneous catalyst **1a** (>98% conversion to **12** in 6 h at 22 °C), excellent levels of enantioselectivity can be attained in desymmetrization (**11**→**12**) and kinetic resolution (**13**→**14**) processes.[14] Importantly, workup simply consists of removal of the catalyst resin through filtration and evaporation of solvent in vacuo. Moreover, in contrast to unpurified products from reactions of **1a**, which are often dark brown in color, those delivered through catalysis by **4** are faint yellow which indicates lower amounts of metal impurity (see Figure 1 and related discussion below).

A variety of additional catalytic asymmetric processes can be promoted by the supported catalyst. As illustrated in entries 1 and 2 of Table 1, asymmetric ring-opening/cross metathesis (AROM/CM) with 7-oxynorbornene substrates (for example, **15** and **17**) and styrene (2 equiv) proceed efficiently and enantioselectively.[2d, 2h] The asymmetric conversion of cyclopentenyl ether **19** to **20** was less facile with **4** than with **1a** (57% vs >93% conv; entry 3, Table 1),[2g] but the supported catalyst gave higher levels of asymmetric induction (33% vs 19% *ee*).[15] Desymmetrization of **21** to afford bicyclic compound **22** (entry 4) can be promoted by supported catalyst **4** with high asymmetric induction (93% *ee*) but again less efficiently than the homogeneous variant (**1a**).[2f] Mo-catalyzed synthesis of didehydro 1,2-silaoxepane **24** (entry 5, Table 1) is nearly as efficient with **4** as it is with **1a** (95% vs >98% conv after 2 h).[16] Although the reaction in the presence of **4** gave the desired product less selectively, the level of asymmetric induction (81% *ee*) is synthetically useful, particularly when the relative paucity of alternative methods for the preparation of tertiary ethers and alcohols (obtained by desilylation of **24**) is considered.[17]

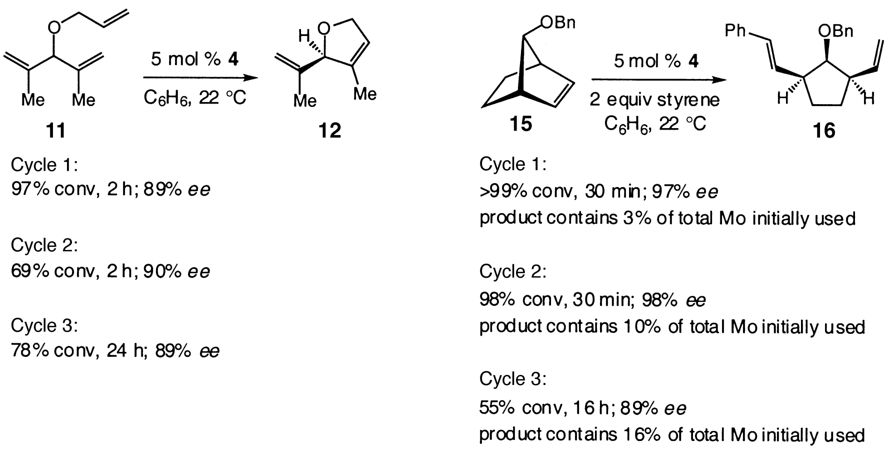
Several additional points regarding the transformations shown in Table 1 merit mention: 1) Higher substrate concentrations may be used to accelerate reactions. As an example, when Mo-catalyzed ARCM of **21** (see entry 4, Table 1) was performed on a 0.5 M solution, 82% conversion was attained within 80 minutes (<2% homodimeric or oligomeric adducts formed). 2) Initial attempts to carry out catalytic asymmetric

Table 1. Catalytic asymmetric olefin metathesis reactions promoted by supported chiral catalyst.[a]

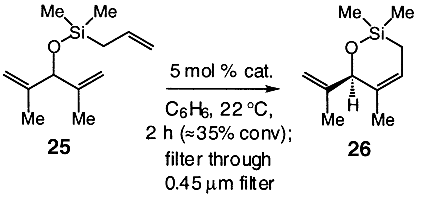
Entry	Substrate	Product	*t* [h]	Isolated catalyst conv [%][b]	Isolated catalyst yield [%][c]	Isolated catalyst *ee*[d]	Supported catalyst conv [%][b]	Supported catalyst yield [%][c]	Supported catalyst *ee*[d]
1[e, f]	 **15**	 **16**	0.5	>98	89	>98	>98	92	98
2[e, g]	 **17**	 **18**	0.5	>98	88	>98	>98	89	95
3	 **19**	 **20**	24	93	88	19	57	45	33
4	 **21**	 **22**	2	93	84	>98	57	41	93
5	 **23**	 **24**	2	>98	97	93	95	92	81

[a] Conditions: 5 mol% **4** (based on Mo), C_6H_6 (0.1 M), 22 °C. [b] Conversions determined by analysis of 400 MHz ^1H NMR spectra of unpurified mixtures. [c] Yields of isolated products after silica gel chromatography. [d] Determined by chiral HPLC (Chiralcel OD for entry 1, Chiralcel AD for entry 2 and Chiralcel OJ for entry 5) and chiral GLC (Betadex column for entries 3–4). [e] Reactions performed in the presence of 2 equiv styrene. [f] Bn = benzyl. [g] MOM = methoxy methyl.

metatheses with **4** in the absence of solvent were unsuccessful. Treatment of triene **23** with **4** (5 mol% Mo) resulted in <2% conv after 24 h (22 °C). However, addition of C_6H_6 (~100 µL for 0.63 mmol **23**) to the mixture led to the smooth formation of **24** (>98% conv, 94% yield, 71% *ee* after 24 h). This difference in reactivity and the requirement for the presence of solvent may be attributed to the more effective access of substrate molecules to the catalytic site in the Mo-bearing resin as a consequence of polymer-swelling by the solvent. 3) As alluded to earlier, a significant advantage of the polymer-supported chiral catalyst is that simple filtration of the reaction mixture delivers materials that contain noticeably lower amounts of Mo impurity than in cases when homogeneous catalysts are utilized. For example, as illustrated in Equation (3), with **1a** as the catalyst, 91% of the metal residue used is found as part of the product after filtration. In contrast, when **4** is employed, only 5% of the Mo residue contaminates the product mixture. As shown in Figure 1, this difference in purity of products directly obtained from reactions of unbound and polymer-supported catalysts is readily evident from the appearance of the respective unpurified product samples.



Scheme 3. Recycling of supported chiral metathesis catalyst **4**. Amount of Mo residue was determined by ICP-MS analysis of the unpurified product mixture.



(3)

Figure 1. Difference in the appearance of solutions of asymmetric olefin metathesis product **16** obtained from reaction with **1a** (left) and supported catalyst **4** (right).

The supported chiral catalyst may be recycled. The examples shown in Scheme 3, regarding catalytic asymmetric syntheses of **12** and **16**, are illustrative. Not only does the product contain minimal Mo impurity after the first round (3% of the total Mo used in cycle 1 for **15**→**16**), after filtration under inert atmosphere, the polymer may be utilized to effect a second round, where 98% conversion is attained within 30 min and **16** is obtained in 98% *ee*. Despite the observed Mo loss after the first cycle, there is little difference in reaction time and levels of enantioselectivity between the first and second cycles. In the third cycle, high enantioselection and conversion are still obtained but catalyst activity is notably diminished (see Scheme 3).

In brief, we have synthesized and demonstrated the utility of the first example of a polymer-supported chiral metathesis catalyst. In most cases, the polymer-bound catalyst provides similarly high levels of enantioselectivity as the corresponding homogeneous variant (**1a**); it can also be recycled with appreciable efficiency. This first generation of supported chiral Mo catalysts is, as should perhaps be expected, less active than the parent system (**1a**). The lower levels of activity exhibited by **4** may result from inefficient diffusion of substrate molecules into the polymer. The supported catalyst is expected to be less susceptible to bimolecular decomposition of highly reactive methylidene intermediates.[18] In this regard, synthesis of more rigid polymer supports or those that represent lower Mo loading should further minimize bimolecular decomposition pathways and lead to a more robust class of catalysts. Studies towards preparation of alternative systems that give rise to more effective supported catalysts for asymmetric olefin metathesis, as well as the related applications to combinatorial synthesis of optically pure compounds, are in progress.

Experimental Section

(*R*)-**9**: A vigorously stirred suspension of (*R*)-**8**[19] (412 mg, 0.586 mmol), styrene (4.20 g, 40.3 mmol), divinylbenzene (83 mg, 55% of 0.64 mmol, remainder are ethylbenzenes), benzoyl peroxide (48 mg, 0.14 mmol, containing 30% water), poly(vinyl alcohol) (46 mg), toluene (6 mL) and water (50 mL) was stirred at 22 °C for 1 h to homogenize the particle size. The suspension was heated to 90 °C for 24 h. The polymer was washed thoroughly with THF, methanol and pentane and dried in vacuo for 24 h to give white beads (4.4 g, 83% yield). The resulting bis(methoxy ethoxy ether) (4.4 g) was suspended in 30 mL of a mixture of conc. HCl, methanol and THF (1:10:50) for 48 h. The polymer was isolated by filtration, washed thoroughly with THF, methanol and pentane and dried in vacuo for 24 h at

60 °C to afford the desired product (*R*)-**9** as white beads (4.3 g, 91 % yield; 76 % yield from **8**). IR (KBr): $\tilde{\nu} = 3510$ (m), 2900 – 3060 (s), 2362 (m), 2344 (m), 1870 (w), 1719 (m), 1654 (w), 1602 (m), 1492 (s), 1452 (s), 1388 (w), 1270 (m), 1229 (w), 1157 (m), 1115 (w), 1028 (s), 960 (m), 823 (w), 758 (m), 699 (s) 543 (w) cm^{-1}.

(*R*)-**4**. Solid potassium hexamethyldisilazane (94 mg, 0.47 mmol) was added in portions to a suspension of (*R*)-**9** (1.00 g) in THF (10 mL). The resulting mixture was agitated for 24 h; the polymer was subsequently filtered and washed with THF (3 × 5 mL). The polymer was dried in vacuo and resuspended in THF (8 mL). At this point, solid **10** (108 mg, 0.136 mmol) was added and the mixture was agitated for 7 h. The polymer was washed with THF (4 × 5 mL) and pentane (2 × 5 mL). The resulting solid was dried in vacuo to give 1.04 g of (*R*)-**4** as a brown powder.

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[12] In contrast to the homogeneous complex **1a**, analysis of ^{1}H NMR spectra indicates that the supported catalyst retains approximately one equivalent of THF, despite prolonged vacuum treatment and washing with toluene or pentane. It is unclear at the present time whether THF is actually coordinated to molybdenum or if it is simply absorbed within the polymer matrix.

[13] Mo loading determined by ICP-MS analysis of the resin. Catalyst amount is thus calculated on the basis of loading of the supported catalyst sample (0.24 mmol g^{-1} of polymer).

[14] Catalytic resolution of **13** afforded lower levels of selectivity in C_6H_6 ($k_{rel} = 5$). Relative rates are calculated based on the equation reported by Kagan. See: a) K. B. Kagan, J. C. Fiaud, *Top. Stereochem.* **1988**, *18*, 249 – 331. For additional reviews on metal-catalyzed kinetic resolutions, see: b) A. H. Hoveyda, M. T. Didiuk, *Curr. Org. Chem.* **1998**, *2*, 537 – 574; c) G. R. Cook, *Curr. Org. Chem.* **2000**, *4*, 869 – 885; d) J. M. Keith, J. F. Larrow, E. N. Jacobsen, *Adv. Synth. Catal.* **2001**, *343*, 5 – 26.

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