

## Communications

### Multiple Tandem Catalysis: Facile Cycling between Hydrogenation and Metathesis Chemistry

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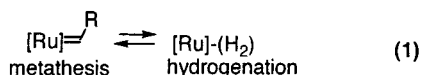
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**Summary:** Tandem ROMP–hydrogenation via a single Ru precursor permits catalytic reduction of ROMP polymers under exceptionally mild, homogeneous conditions (1 atm of H<sub>2</sub>, 60 °C). Repeated catalyst cycling between metathesis and hydrogenation chemistry is effected in a one-pot procedure.

Interest in rapid-throughput chemical synthesis has spurred development of technologies in which one catalyst supports several functions.<sup>1</sup> Particularly attractive in this context is the ability to simply, controllably, and reversibly “turn on” different modes of catalysis. Here we describe facile cycling of a single catalyst precursor between metathesis and hydrogenation activity (eq 1). Use of methanol in the hydrogenation

step permits complete polymer hydrogenation under extraordinarily mild conditions, at 1 atm of H<sub>2</sub>. This approach is equally relevant to reduction of unsaturated molecular species derived from ring-closing metathesis (RCM) or cross-metathesis.

Industrial demand continues to increase for lightweight, moldable optical-grade materials. Ring-opening metathesis polymerization (ROMP) of cycloolefins, followed by hydrogenation, enables synthesis of high-molecular-weight, narrow-polydispersity polyolefins with desirable optical characteristics.<sup>2</sup> Hydrogenation expands the range of applications open to ROMP materials by eliminating the inherent susceptibility of olefinic linkages to oxidative and thermal degradation.<sup>3,4</sup> Hydrogenation of all unsaturated polymers typically requires forcing conditions, as local steric effects are exacerbated by diffusion constraints associated with the random coil.<sup>3</sup> Steric problems are particularly acute in ROMP polymers, in which the olefinic groups are part of the polymer backbone;<sup>5</sup> in ROMP via **1**, they are also of predominantly trans geometry.<sup>6</sup> Nickel and rhodium



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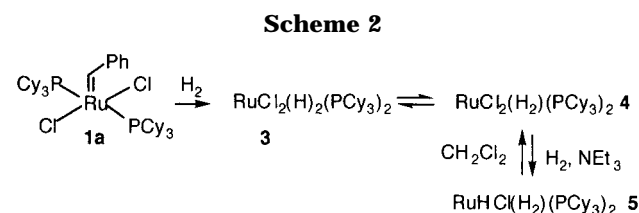
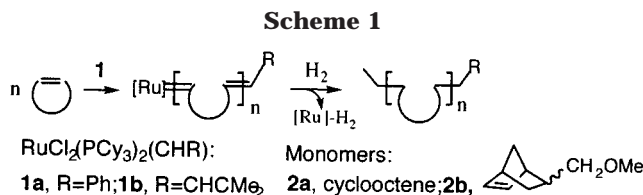
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(5) 1,2-Olefins in polybutadiene are reduced faster than 1,4-olefins and cis-1,4 units faster than trans-1,4 units.<sup>3a</sup>

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**Table 1. ROMP–Hydrogenation of Cyclooctene **2a** in CH<sub>2</sub>Cl<sub>2</sub><sup>a</sup>**

cosolvent	additive <sup>b</sup>	pH <sub>2</sub> (psi)	time (h)	conversion (%)
		1000	24	32
75% THF		1000	24	>99
75% THF		100	24	9
	NEt <sub>3</sub>	100	24	85
75% THF	NEt <sub>3</sub>	100	24	55
10% MeOH		100	4	51
20% MeOH		100	4	83
20% MeOH		50	24	97 <sup>c</sup>
20% MeOH	NEt <sub>3</sub>	15	24	>99 <sup>d</sup>
20% PrOH		100	4	54

<sup>a</sup> General conditions: ROMP at room temperature under N<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> (2 mL); 1.5 h, 1.2 mM **1a**, 204 equiv of **2a**, diluted as indicated for hydrogenation (total volume 10 mL). Conversions were determined by <sup>1</sup>H NMR; average of 3 trials (±3%). <sup>b</sup> NEt<sub>3</sub> (12 μmol) added immediately prior to hydrogenation. <sup>c</sup> Hydrogenation at 50 °C. <sup>d</sup> Hydrogenation at 60 °C.

complexes catalyze reduction of ROMP polymers at 100–135 °C and 300 psi.<sup>7</sup> Ru-catalyzed reduction typically requires even more drastic conditions<sup>2</sup> but is attractive for the possibility of tandem ROMP–hydrogenation (Scheme 1).<sup>8,9</sup>

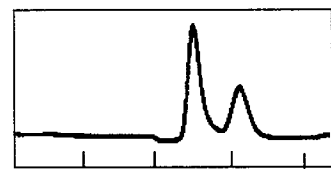
We recently reported H<sub>2</sub> hydrogenolysis of **1a** to liberate toluene and Ru tautomers **3** and **4** (Scheme 2).<sup>8a</sup> We find that, in CH<sub>2</sub>Cl<sub>2</sub>, reaction of Ru-terminated poly(octene) under 1 atm of H<sub>2</sub> is selective for hydrogenolysis. Low hydrogenation activity, even at 1000 psi (Table 1), we attribute to the predominance of octahedral complex **3**, the sole spectroscopically observable species in CD<sub>2</sub>Cl<sub>2</sub>. Reduction is faster in neat THF, in which both **3** and five-coordinate **4** are present. As ROMP is inefficient in THF,<sup>10</sup> however, we carried out the polymerization step in CH<sub>2</sub>Cl<sub>2</sub>, diluting with THF (3:1) for subsequent hydrogenation. Complete reduction of poly(octene) is then effected within 24 h at 1000 psi H<sub>2</sub>, though conversions drop sharply at lower pressures.

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**Figure 1.** GPC trace for polymer blend obtained by tandem ROMP–hydrogenation–ROMP of **2b**.

Transformation of **3/4** into **5** by addition of NEt<sub>3</sub> dramatically increases catalytic activity, giving 85% reduction at 100 psi.<sup>11</sup> When NEt<sub>3</sub> is used, THF cosolvent is no longer beneficial but is actually detrimental to overall hydrogenation activity. The role of THF in promoting tautomerism to **4** is clearly redundant under these conditions; its lower dielectric constant vs CH<sub>2</sub>Cl<sub>2</sub>, or its coordination to the metal center, may also hinder this catalysis.<sup>12</sup> The hydrogenation activity exhibits a nonstoichiometric dependence on [NEt<sub>3</sub>],<sup>13</sup> owing to chlorination of **5** by CH<sub>2</sub>Cl<sub>2</sub>, which regenerates **3/4** over the time scale of hydrogenation.<sup>14</sup> Further base is then required to restore **5**.<sup>15</sup>

No evidence of chain scission<sup>16</sup> is apparent within poly(octene) under these conditions. As hydrogenation of living polymers permits more rigorous examination of such effects, we undertook the synthesis and hydrogenation of living poly(**2b**). Near-monodisperse polyolefin ( $M_n = 29\,500$ , PDI = 1.04) was obtained with no detectable change in molecular weight following reduction under the reaction conditions described above. In view of the apparent molecular integrity of both polymer and catalyst, we were interested in the possibility of preparing polymer blends in which the molecular weight and structure of each component could be specified. Such materials offer precise models for investigation of the rheological properties of narrow-polydispersity polyolefin blends. Use of polymer blends to modulate melt and flow properties has emerged as a key solution to processing problems in metallocene-derived polyolefins.<sup>17</sup>

We established the feasibility of multiple cycles of ROMP and hydrogenolysis and/or hydrogenation by carrying out model studies in which the alkylidene

(11) Base is known to accelerate reduction via transition-metal dichlorides, promoting heterolytic activation of H<sub>2</sub> by abstraction of HCl and formation of catalytically active hydrido-chloro species. Chaloner, P. A.; Esteruelas, M. A.; Joo, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer: Boston, 1994.

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(13) At least 5 equiv required; see the Supporting Information.

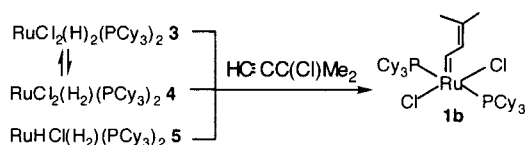
(14) Exchange of hydride for chloride is common in CHCl<sub>3</sub> or CH<sub>2</sub>Cl<sub>2</sub>, and such solvents are often avoided in small-molecule reduction. However, their use in polymer hydrogenation—as in the present case—can be dictated by solubility and reactivity considerations. Of the common solvents, only CH<sub>2</sub>Cl<sub>2</sub> and THF fully dissolve these polymer substrates. The limitations of THF are discussed above.

(15) While nucleophilic attack on CH<sub>2</sub>Cl<sub>2</sub> is, in principle, also possible, NEt<sub>3</sub> is rather unreactive toward methylene chloride (Nevstad, G. O.; Sonstad, J. *Acta Chem. Scand.* **1984**, *B38*, 469), though Pt complexes can promote amine chloromethylation: Mas, M.; Sola, J.; Solans, X.; Aguiló, M. *Inorg. Chim. Acta* **1987**, *133*, 217. If a CH<sub>2</sub>Cl<sub>2</sub>–NEt<sub>3</sub> reaction does occur, however, it clearly does not compete with initial abstraction of HCl from **3/4** to yield **5**. The latter reaction is immediate and quantitative.

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Scheme 3



functionality was reinstalled in **3**–**5**. All three species are cleanly converted into ROMP-active **1b** on reaction with 3-chloro-3-methyl-1-butyne<sup>18</sup> (Scheme 3).

On the basis of these results, we prepared a blend of unsaturated polymers via ROMP of **2b** (400 equiv), hydrogenolysis (1 atm  $\text{H}_2$ ;  $\text{NEt}_3$  added), conversion to **1b**, and addition of a further 100 equiv of **2b**. Gel permeation chromatography (GPC) confirmed the presence of a bimodal molecular weight distribution, in which the molecular weights of the two fractions were in good agreement with predicted values (calcd  $M_n = 55\,200$ ,  $14\,000$ ; found  $M_n = 54\,000$ ,  $19\,000$ ). ROMP–hydrogenation–ROMP was carried out likewise, using  $\text{H}_2$  pressures of 250 psi in the second step. A representative GPC trace is shown in Figure 1.

Solvents employed in catalytic reactions can have dramatic and unpredictable effects on reactivity.<sup>19</sup> We have discovered that methanol functions as a powerful accelerating agent in the hydrogenation chemistry. Rates increase with increased MeOH concentration, with an upper limit of  $\sim 20\%$  being imposed by the solubility of polyethylene: at higher MeOH concentrations, incompletely reduced polymer precipitates from solution. Such insolubility is usual for hydrocarbon polymers, and MeOH is in fact normally used for

isolation of such materials. The unorthodox expedient of using it as the reaction medium permits 97% reduction at 50 psi on warming to 50 °C. Quantitative polymer reduction is achieved at the unprecedentedly low pressure of 1 atm if  $\text{NEt}_3$  is also used.

Stoichiometric hydrogenolysis of **1a** in  $\text{CD}_2\text{Cl}_2$ –MeOH in the presence of  $\text{NEt}_3$  shows, in addition to **3** and **5**,  $^1\text{H}$  and  $^{31}\text{P}$  signals characteristic of the known<sup>20</sup> hydrogenation catalyst  $\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$ , presumably generated by decarbonylation of methanol. However, observation of an accelerating effect for 2-propanol, which is not subject to decarbonylation, may point toward an additional role for alcohol in coordination to the metal center.

In summary, we have demonstrated tandem ROMP–hydrogenation under unprecedentedly mild conditions and the use of simple chemical switches to “toggle” between metathesis and hydrogenation catalysis. Remarkably, addition of base as well as methanol permits *quantitative reduction at 1 atm of  $\text{H}_2$* . The ability to carry out this hitherto demanding transformation at atmospheric pressures, without specialized equipment, has important implications not only for hydrogenation of unsaturated polymers but also for the broader field of metathesis chemistry, in which tandem transformations may likewise be carried out on small molecules with great simplicity.

**Acknowledgment.** This work was supported by grants from the Natural Science and Engineering Research Council of Canada, the Canada Foundation for Innovation, and the Ontario Research and Development Corporation.

**Supporting Information Available:** Text and figures giving full experimental details, including a plot of base dependence and  $^1\text{H}$  NMR spectra showing progression from monomer to saturated polymer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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