Simply Assembled and Recyclable Polymer-Supported Olefin Metathesis Catalysts.

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Supporting Information

Experimental

General Considerations: All reactions were carried out under an atmosphere of dry argon with standard Schlenk tube techniques or in a MBraun glovebox containing less than 1 ppm of oxygen and water. Anhydrous solvents were purchased from Aldrich and used as received. Divinylbenzene (tech. 55%) was purchased from Aldrich and degassed prior to use. Diethyldiallylmalonate was purchased from Aldrich, dried over P_2O_5, and vacuum distilled prior to use. Diallytosylamine[1], diethyldi(2-methylallyl)malonate[2], $PCy_3Ru(IMes)(=CHPh)Cl$ and $PCy_3Ru(IMes^*)(=CHPh)Cl_2$) (see text) were prepared according to literature procedures. The yields of the catalytic reactions were analyzed using a HP 5890 GC with a FID detector and HP-5 column. NMR spectra were recorded on a Varian 400 MHz spectrometer. Elemental analyses and atomic absorption spectroscopy were performed by Desert Analysis, Tucson AZ. Experimental synthetic procedures, leading to the isolation of previously unreported complexes, are described below.

Synthesis of Poly-DVB: In the glovebox, AIBN (1.5 wt.% of divinylbenzene, 0.066 g), divinylbenzene (tech., 55%, 4.44 g, 5 mL) and toluene (5 mL) were added to a 20 mL scintillation vial sealed with a teflon-covered screw cap. The vial was then heated to 80 ˚C for 24 hours to give a white insoluble polymer. The vial was opened in the air, the polymer was scraped off the vial and ground to a powder. The solvent was removed in *vacuo*.

Synthesis of Polymer-Supported Ruthenium Catalysts 4, 5 and 6: In the glovebox, poly-DVB (1.0 g) and the ruthenium catalyst **1**, **2** or **3** (10 wt.%, 0.1 g) and toluene (10 mL) were added to a Schlenk flask. The reaction mixtures was heated to 50 ˚C for 5 hours and stirred at room temperature for 12 hours. The slurry were then filtered on a Schlenk frit, washed with toluene (3 X 10 mL) and dried in *vacuo* to yield a pale pink solid. Elemental analyses, Ru%: **4**, 0.6; **5**, 0.38 and **6**, 1.2%.

General Procedure for Ring Closing Metathesis: In the glovebox, poly-DVB/Ru catalyst (100 mg (**4** and **5**) and 50 mg (**6**)), solvent (2 mL) and the substrate (1 M solution, 118 μL) were loaded in a Schlenk flask. The reaction mixture was heated under argon to temperatures shown in Tables 1-3. Extent of reaction was monitored by GC.

Experiments on the recycling and re-use of catalysts 4, 5 and 6: After the allotted times mentioned in the Tables 1-3 for each reaction, the polymer-supported catalyst precursors were filtered, washed with the same solvent used in the reactions and dried in *vacuo*. The catalysts were loaded into fresh Schlenk flasks and a fresh sample of the solvent (2 mL) was then added to each catalyst followed by another aliquot of the substrate (1M, 118 μL). The extent of reaction was then monitored by GC after the allotted times mentioned in Tables 1-3. The percentage of the leached ruthenium for each supported catalyst after 4 cycles was determined by atomic absorption spectroscopy. Ru%: **4**, 0.033; **5**, 0.009; **6**, 0.020.

(1) Fürstner, A.; Ackerman, L. *Chem. Commun.* **1999**, 95-96.
(2) Kirkland, T. A.; Grubbs, R. H. *J. Org. Chem.* **1997**, *62*, 1310-1318.