

Supplementary Information

Selective and Unexpected Transformations of 2-Methylpropane to 2,3-Dimethylbutane and 2-Methylpropene to 2,3-Dimethylbutene Catalyzed by an Alumina-Supported Tungsten Hydride**

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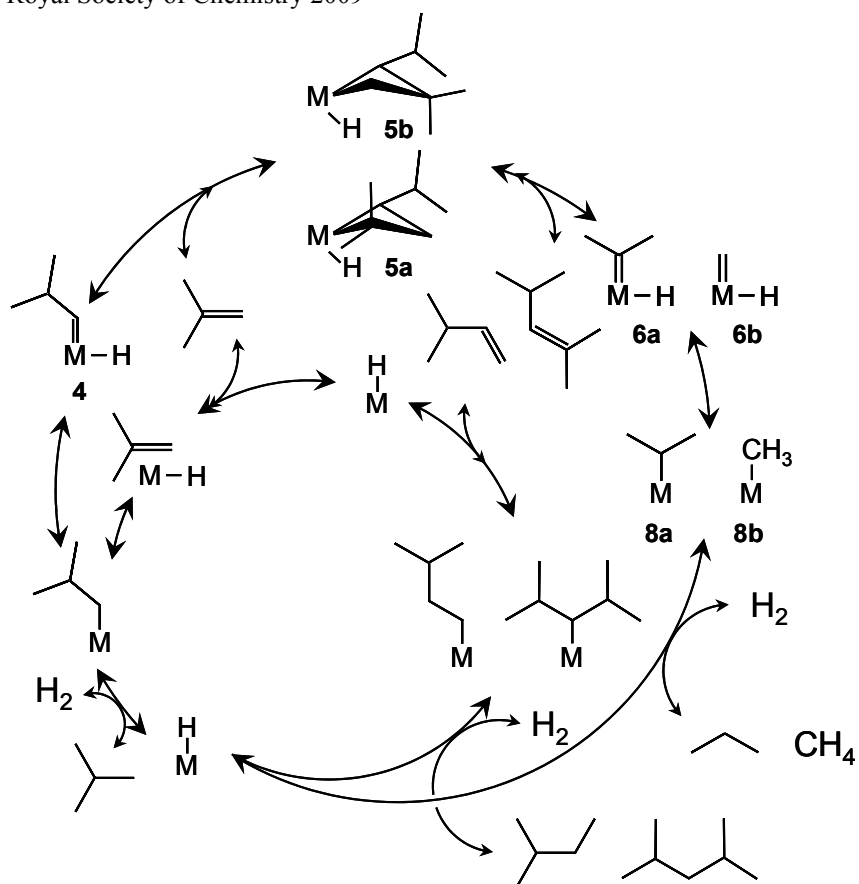
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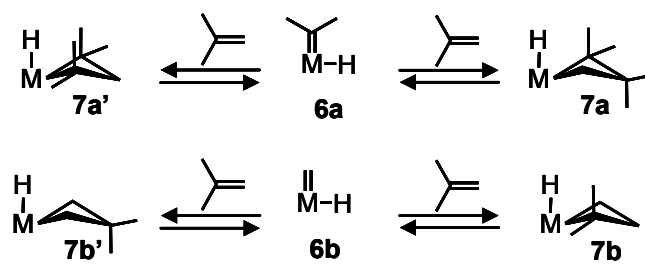
General procedure: all operations were performed with rigorous exclusion of air and water; standard Schlenk, high-vacuum and glovebox techniques were used for the preparation or handling of organometallic compounds and alumina supported materials.

The silica supported tantalum hydride **1a** and the alumina supported tungsten hydride **1b** were prepared as already reported.¹ Elemental analyses were performed at the Service Central d'Analyses of CNRS in Solaize (France).

Reaction of isobutane and isobutene metathesis in a continuous flow reactor: the metal hydride was charged using a glove box, into a stainless steel ½' cylinder reactor which can be isolated from atmosphere. After connection to the gas lines and purge of tubes, a flow of isobutane (or isobutene) controlled by a Brooks® mass flow-meter was sent onto the catalyst bed which was heated at 150°C. Hydrocarbon products and hydrogen were analyzed on line by GC (HP 8890 chromatograph fitted with an Al₂O₃/KCl 50m × 0.32mm capillary column, FID detector for hydrocarbons and a 3Å molecular sieve column, TCD detector for hydrogen).



Scheme S1. Classical mechanism of alkane metathesis applied to isobutane (M = Ta, W).



Scheme S2

¹ V. Vidal, A. Theolier, J. Thivolle-Cazat, J. M. Basset, *Science* 1997, 276, 99. J. M. Basset, C. Coperet, L. Lefort, B. M. Maunders, O. Maury, E. Le Roux, G. Saggio, S. Soignier, D. Soulivong, G. J. Sunley, M. Taoufik, J. Thivolle-Cazat, *J. Am. Chem. Soc.* **2005**, 127, 8604. E. Le Roux, M. Taoufik, A. Baudouin, C. Coperet, J. Thivolle-Cazat, J. M. Basset, B. M. Maunders, G. J. Sunley, *Adv. Synth. Catal.* **2007**, 349, 231. M. Taoufik, E. Le Roux, J. Thivolle-Cazat, J. M. Basset, *Angew. Chem., Int. Ed.* **2007**, 46, 7202.