M. SCHOLL, S. DING, C. W. LEE, R. H. GRUBBS* (CALIFORNIA INSTITUTE OF TECHNOLOGY, USA)

Synthesis and Activity of a New Generation of Ruthenium-Based Olefin Metathesis Catalysts Coordinated with 1,3-Dimesityl-4,5-dihydroimidazol-2-ylidene Ligands


**Grubbs Catalyst 2nd Generation: Synthesis and Activity of Ruthenium-Based Olefin Metathesis Catalysts**

**Preparation of catalysts:**

1. R¹-NH₂, acetone–H₂O
2. H₂, Pd/C, EtOH, or Na₂C₂B₆H₁₀, HCl, MeOH
3. HC(OE)₂, NH₄BF₄, 120 °C
4. R²-Br, PtC₂b₉₃, (-)-BINAP, t-BuONa, PhH, 100 °C

**Selected examples of RCM products:**

- **yield (X) = quant.**
  - (A) = quant.
  - (B) = quant.
- **yield (X) = 20%**
  - (A) = quant.
  - (B) = quant.
- **yield (X) = 0%**
  - (A) = 90%
  - (B) = 87%

**Significance:** Grubbs and co-workers reported a direct approach towards the preparation of the 4,5-dihydroimidazol-2-ylidene-substituted ruthenium-based catalysts. Compared to their predecessor, these 2nd generation catalysts display higher reactivity, better stability, and improved functional group tolerance.

**Comment:** Conveniently, these 2nd generation catalysts are air- and water-tolerant and can be handled without great loss in activity. Given the increased RCM activities observed with (A) and (B), the authors studied RCM at lower catalyst loadings and found 0.05 mol% to be an optimal lower limit in both cases.