1,4-Rhodium–Silicon Shift in an Enantioselective Synthesis of Indanols

Mechanistic proposal:

Significance: The tendency of rhodium and palladium catalysts to undergo 1,4-shifts from alkyl or vinyl to aryl positions is a well-documented phenomenon (see Review). In contrast to their earlier work (Angew. Chem. Int. Ed. **2009**, 48, 6320), the authors describe a 1,4-rhodium–silicon shift. This strategy is superior to the rhodium–hydrogen shift in the sense that functionality is introduced at the alkyl position, which can be easily further modified.

Review: F. Shi, R. C. Larock *Top. Curr. Chem.* **2010**, 292, 123–164.

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 Synfacts 2011, 3, 0277-0277 Published online: 16.02.2011
 DOI: 10.1055/s-0030-1259478; Reg-No.: L01011SF

Comment: Several selectivity issues were addressed by this work. High enantioselectivity in β -carbon cleavage could be achieved for the *trans* products using Difuorophos or Dolefin ligands. The *trans/cis* selectivity of the ketone addition could be modulated by the solvent and the ligand used. Olefin ligands were selective for silicon versus hydrogen migrations, with phosphine ligands favoring hydrogen shifts. Tricyclic products could also be formed, possibly from a rhodium-catalyzed Si–alkyl insertion. The silicon group could easily be converted into an alcohol, and vinyl or allyl silyl groups could also participate in the migration.

Category

**Metal-Catalyzed
Asymmetric
Synthesis and
Stereoselective
Reactions**

Key words

**1,4-silicon shift
indanols
rhodium**

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of the month