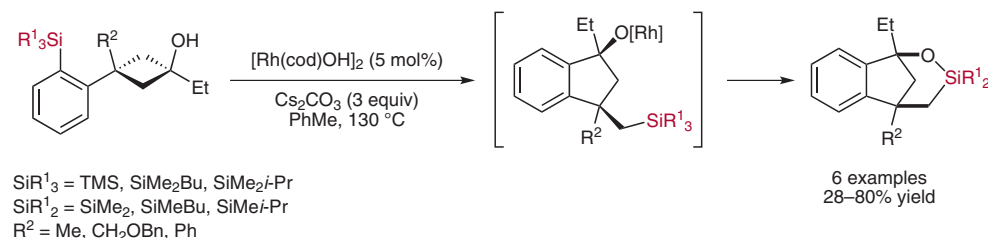
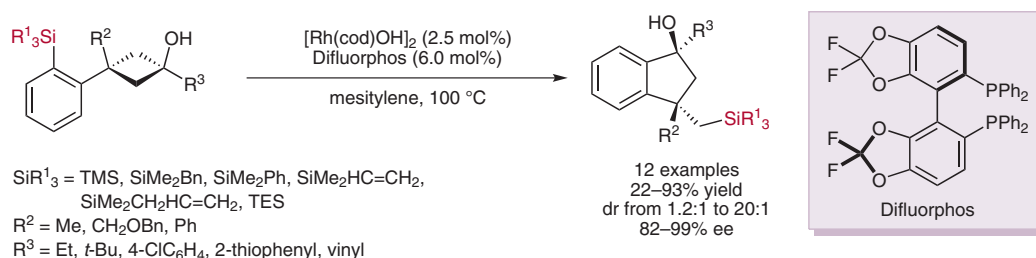


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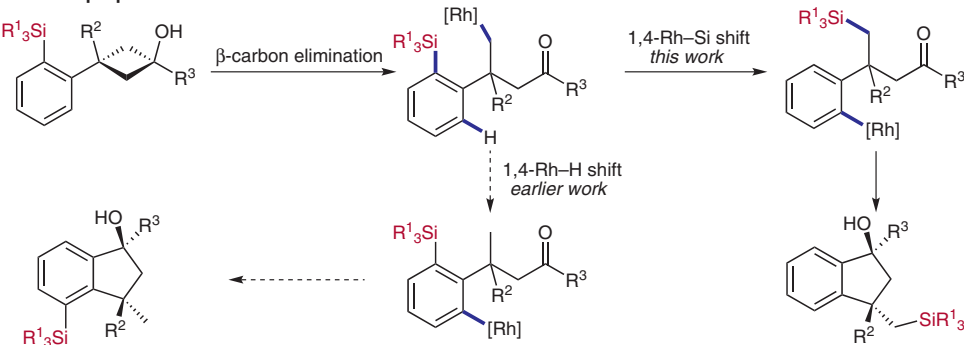
Rhodium(I)-Catalyzed 1,4-Silicon Shift of Unactivated Silanes from Aryl to Alkyl: Enantioselective Synthesis of Indanol Derivatives

Angew. Chem. Int. Ed. **2010**, *49*, 10163–10167.

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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Comment: Several selectivity issues were addressed by this work. High enantioselectivity in β -carbon cleavage could be achieved for the *trans* products using Difluorophos 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