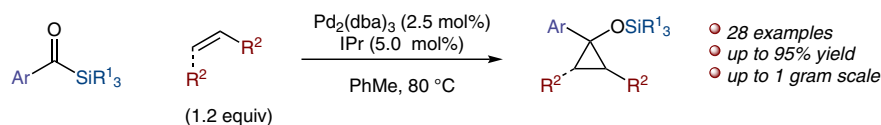


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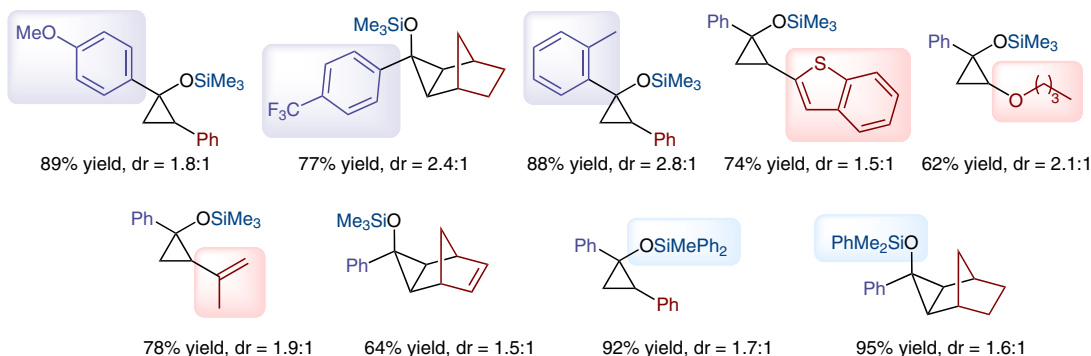
Palladium-Catalyzed Siloxycyclopropanation of Alkenes Using Acylsilanes

J. Am. Chem. Soc. **2022**, *144*, 1099–1105, DOI: 10.1021/jacs.1c11497.

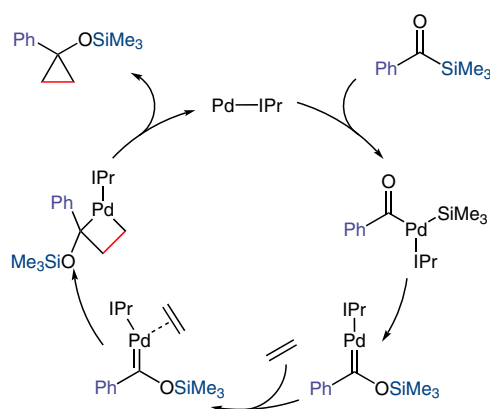
Cyclopropanation of Alkenes via a Siloxycarbene–Palladium Complex



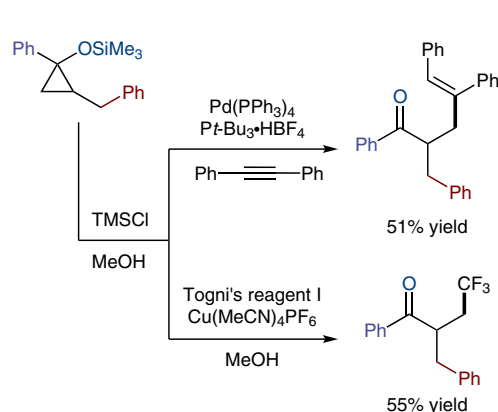
Selected examples:



Proposed mechanism:



Derivatizations:



Significance: The authors reveal that, under palladium catalysis, an acylsilane can serve as a source of an electron-rich carbene to undergo cyclopropanation with an alkene. The corresponding siloxy cyclopropanes serve as valuable homoenolates, as demonstrated through various derivatizations.

Comment: Both electron-neutral and electron-rich alkenes were compatible substrates in the cyclopropanation; however, electron-rich alkenes were more reactive, suggesting an electrophilic metal carbene species is involved in the catalytic pathway. DFT studies indicate that the mechanism of the cyclopropanation proceeds through a [2+2] cycloaddition to form a palladocyclobutane intermediate.

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Category

Metals in Synthesis

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