



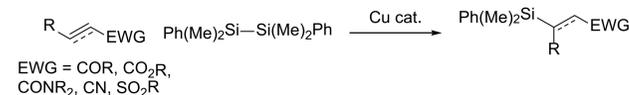
Copper-Catalyzed Silylation of C—C π -bonds

Ian Sherer, Cade Peratt, Jarett Posz, and Ryan Van Hoveln*

Department of Chemistry and Physics, Indiana State University, Terre Haute, IN 47809

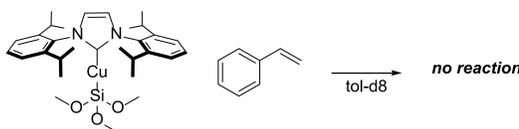
Introduction

Silylations that use readily available silicon sources generally require an expensive metal catalyst such as platinum or palladium.¹ At present, the silicone industry consumes 5-6 metric tons of platinum per year performing hydrosilylations.² Since platinum is a non-renewable and extremely valuable resource, an alternative is necessary for hydrosilylation to be sustainable. Our work is to incorporate a copper catalyst which will be economical and sustainable for hydrosilylation. Very little work has been done with copper and these transformations typically rely on silylboranes, which are difficult to synthesize and handle because of their air and water sensitivity.⁴ At present, there is a lack of inexpensive methods that use readily available silicon sources.



Alkenes bearing electron-withdrawing groups (EWGs) should silylate readily. The reason for this is due to their reactive π -bonds. Likely, different EWGs will require a different catalyst.

Previous Work



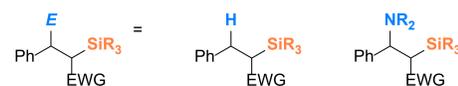
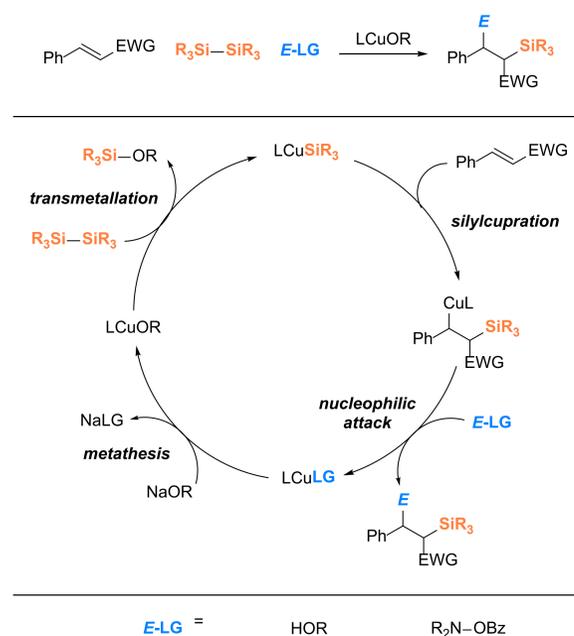
Hypotheses

1. A different electron deficient alkene will promote the silylcupration reaction.
2. An organocopper intermediate can react with a benzoyl amine to produce an aminosilylation product and regenerate the catalyst.
3. An alcohol can protonate the organocopper intermediate to make the hydrosilylation product and make a copper alkoxide. The alkoxide can then react with the disilane to regenerate the catalyst.

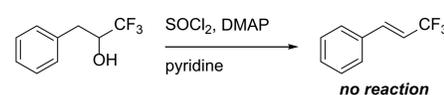
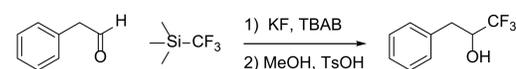
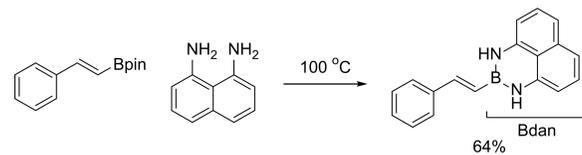
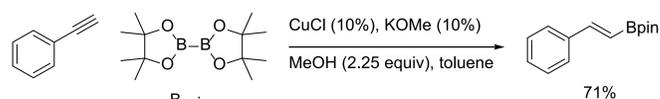
Objectives

1. Identify a variety of substrates and reagents that can form highly functionalized silane products.
2. Develop catalytic silylations involving activation of a disilane which incorporates silanes and amines into activated alkenes.

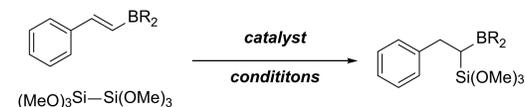
Proposed Mechanism for the Silylation of C—C π -bonds



Synthesis of Substrates

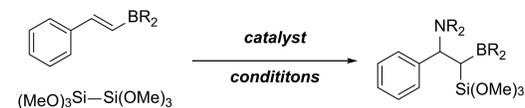


Optimization of Reaction Conditions

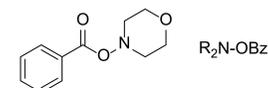


entry	catalyst	BR ₂	conditions	SM	styrene	product
1	IPrCuCl	Bpin	KOtBu (20%) MeOH (2 equiv) toluene	87%	0%	0%
2	IPrCuCl	Bpin	KOtBu (20%) tBuOH (2 equiv) toluene	77%	10%	7%
3	Cy ₃ P/CuCl	Bpin	KOMe (20%) MeOH (2 equiv) toluene	0%	74%	0%
4	IPrCuCl	Bdan	NaOtBu (20%) MeOH (2 equiv) toluene	83%	0%	0%

While other ligands, bases, solvents, and alcohols were tried, the results were generally the same with only a small amount of product forming and a large amount of protodeboration or no reaction at all.



entry	catalyst	BR ₂	conditions	SM	styrene	product
1	IPrCuCl	Bpin	NaOtBu (1.5 equiv) R ₂ N-OBz (1.2 equiv) toluene	0%	5%	0%
2	IPrCuCl	Bpin	KOMe (1.5 equiv) R ₂ N-OBz (1.2 equiv) toluene	0%	8%	4%
3	IPrCuCl	Bdan	NaOtBu (1.5 equiv) R ₂ N-OBz (1.2 equiv) THF	0%	1%	6%



While other conditions were attempted, the results were generally the same with mostly decomposition of the starting material. This is likely due to the excess base attacking the boron rather than the disilane.

Future Directions

1. Continue to optimize the hydrosilylation and aminosilylation of different activated alkenes.
2. Explore the substrate scope and the mechanism of hydrosilylation and aminosilylation reactions.
3. Continue developing other catalytic silylations of π -bonds including.

Conclusions

In conclusion, we have shown that a variety of copper catalysts do not seem to add to activated alkenes, but rather prefer protodeboration. It seems that substrates have a unique problem when it comes to silylation insofar that the copper silyl complex does not seem to add to the π -bond. Instead, the copper silyl complex seems to be protonated by the alcohol, which produces a hydrosilane which then reacts with an alcohol to produce hydrogen gas. Future work will focus on optimizing the silylations of activated alkenes and investigating the mechanism.

Acknowledgements

We would like to thank Prof. Rick Fitch for many helpful conversations and the Department of Chemistry and Physics for their generous support.

Funding

NSF grant CHE-0521075 (MRI 400 MHz NMR)
Start-up funds provided Indiana State University
Center for Student Research and Creativity at ISU

References

1. Roy, A. K. *Adv. Organomet. Chem.* **2007**, *55*, 1-59.
2. Sun, J.; Deng, L. *ACS Catal.* **2016**, *6*, 290-300.
3. Huang, Z.; Du, X. *ACS Catal.* **2017**, *7*, 1227-1243.
4. Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics* **2000**, *19*, 4647-4649.
5. Iannazzo, L.; Molander, G. A. *Eur. J. Org. Chem.* **2012**, 4923-4926.