ACS Catalysis

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# Three-Component Ni-Catalyzed Silylacylation of Alkenes

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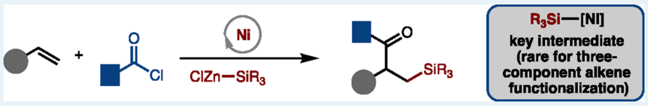
Cite This: *ACS Catal.* 2021, 11, 1858−1862 Read Online

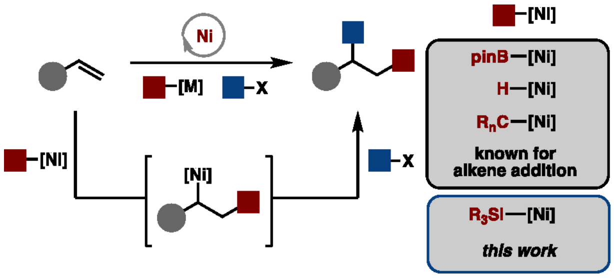
**ABSTRACT:** A Ni-catalyzed silylacylation of alkenes is presented. The reaction combines alkenes, $ClZnSiR_3$, and acid chlorides to provide rapid access to $\beta$-silyl ketones. Importantly, the method involves a [Ni]-$SiR_3$ complex as a catalytic intermediate, which is rarely described for three-component alkene functionalization. Finally, the synthetic utility of the products is demonstrated, and the mechanistic details are described.



**KEYWORDS:** *nickel, alkene, silylation, acylation, zinc*

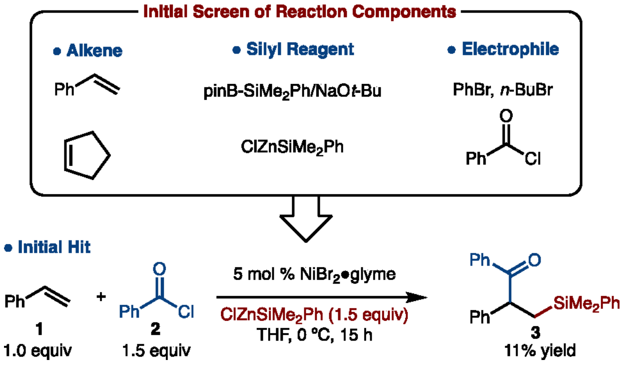
Nickel-catalyzed alkene functionalization is a powerful method for chemical synthesis.[1] In particular, three-component processes are particularly valuable as molecular complexity is rapidly generated. Of the many mechanistic paradigms that exist within this area, one involves the generation of nucleophilic [Ni]-R complexes, which can engage alkenes to generate secondary [Ni]-alkyl complexes capable of reacting with various electrophiles (Scheme 1).[2] To date, this chemistry has been advanced predominately with [Ni]-Bpin,[3] [Ni]-H,[4,5] and [Ni]-$CR_n$[6] in conjunction with several differing electrophiles. Development of variants that involve nucleophilic [Ni]-$SiR_3$ intermediates would aid in the synthesis of silicon-containing molecules.[7] While the involvement of [Ni]-$SiR_3$ complexes has been demonstrated in various contexts such as cross coupling,[8] dehydrogenative alkene silylation,[9,10] and two-component alkene functionalization,[11] the use in three-component alkene functionalization reactions as shown in Scheme 1 is rare. For example, Yin has very recently demonstrated a Ni-catalyzed alkene arylsilylation,[12] while Kamei has reported on a Ni-catalyzed alkene protosilylation process.[13]

**Scheme 1. Ni-Catalyzed Three-Component Alkene Functionalization**



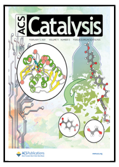
Initial efforts to develop a Ni-catalyzed silyl functionalization began with an evaluation of nucleophilic silyl reagents (pinB-$SiMe_2Ph$/NaO*t*-Bu, $ClZnSiMe_2Ph$), alkenes (styrene, cyclopentene) and electrophiles (PhBr, *n*-BuBr, PhC(O)Cl) (Scheme 2). From these attempts, we identified that the combination of $ClZnSiMe_2Ph$, styrene, and PhC(O)Cl led to formation of **3** in 11% yield, which represent an unprecedented silylacylation.[14−17]

**Scheme 2. Reaction Discovery**



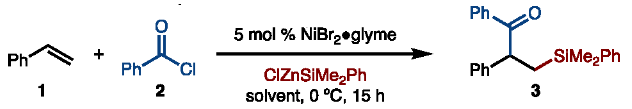
Following this initial result, standard reaction optimization was undertaken (Table 1). It was found that change of solvent from THF to THF/MeCN resulted in an improved yield (Table 1, entry 3). It should be noted that $ClZnSiMe_2Ph$ is prepared in THF, and thus, inclusion of this solvent is necessary. A major byproduct of the reaction is an acylsilane that forms from direct (uncatalyzed) addition of $ClZnSiMe_2Ph$ to benzoyl chloride. Therefore, to overcome this problem, increased equivalents and portion-wise addition of the reagents were used (Table 1, entries 6−8).

Received: December 11, 2020
Revised: January 22, 2021
Published: January 26, 2021



https://dx.doi.org/10.1021/acscatal.0c05449
*ACS Catal.* 2021, 11, 1858−1862

**Table 1. Reaction Optimization**



| entry | **2** (equiv) | zinc reagent (equiv) | solvent | yield[a] |
|---|---|---|---|---|
| 1 | 1.5 | 1.5 | THF | 11% |
| 2 | 1.5 | 1.5 | DMA/THF (1/1) | 33% |
| 3 | 1.5 | 1.5 | MeCN/THF (1/1) | 40% |
| 4 | 1.5 | 1.5 | MeCN/THF (3/1) | 52% |
| 5[b] | 1.5 | 1.5 | MeCN/THF (3/1) | 53% |
| 6 | 2 | 2 | MeCN/THF (3/1.3) | 57% |
| 7 | 3 | 3 | MeCN/THF (3/2) | 50% |
| 8 | 2 × 1.5 | 2 × 1.5 | MeCN/THF (3/2) | 65% |

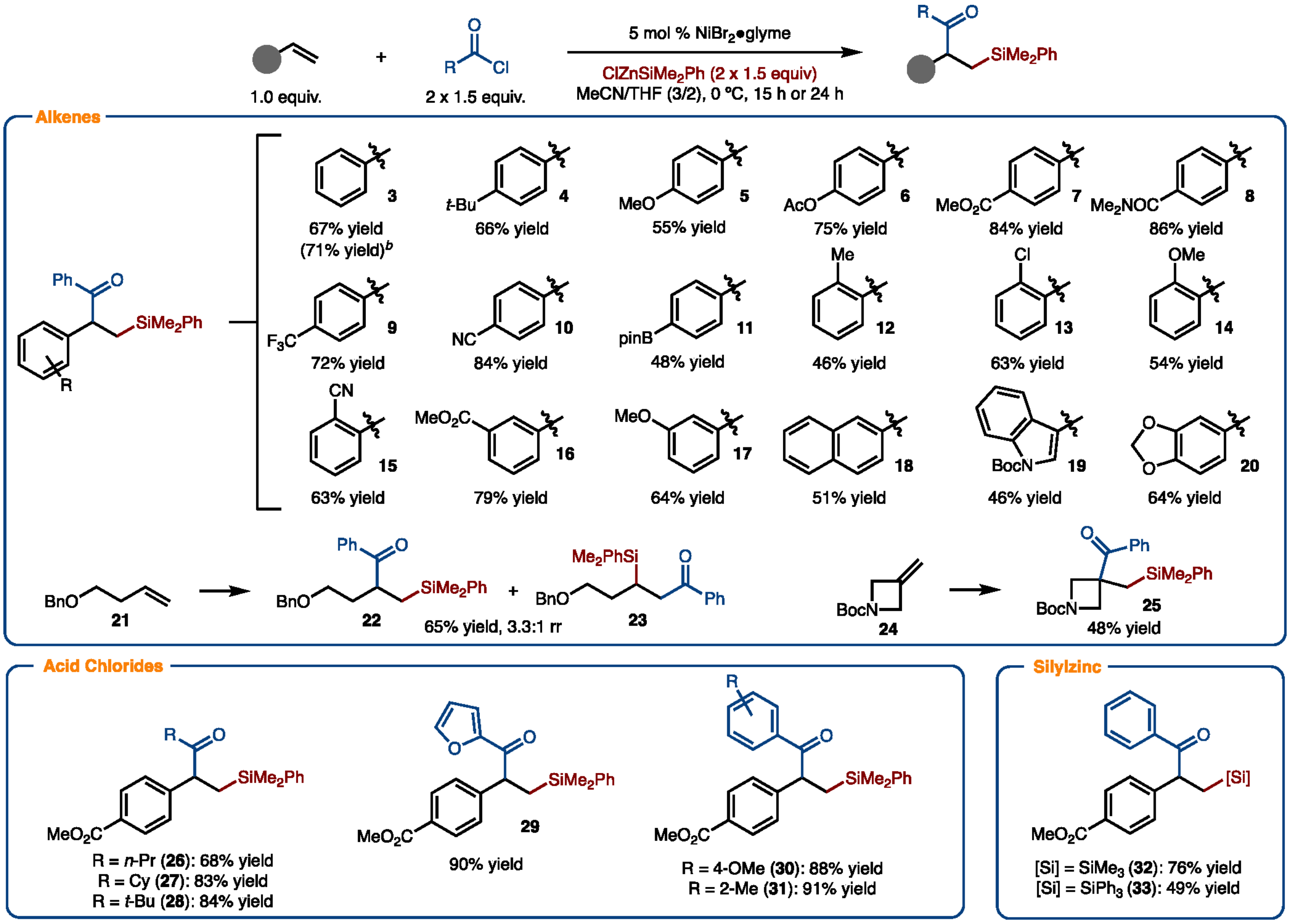
[a] Yield determined by GC with a calibrated internal standard. [b] Reaction run with 5 mol % Ni(COD)$_2$ instead of NiBr$_2$·glyme.

Under the optimized set of conditions (Table 1, entry 8), the substrate scope of the reaction was evaluated (Scheme 3). It was identified that a variety of styrene derivatives that bear electron-accepting (products **6**–**11**, **15**, **16**), electron-donating (product **5**, **14**, **17**, **20**), and sterically demanding groups (products **12**–**15**) were tolerated. In general, substrates that bear electron-withdrawing groups underwent reaction in the highest yield likely due to a more favorable addition of the nucleophilic [Ni]-SiMe$_2$Ph. Various functional groups such as ester (products **6**, **7**, **16**), amide (product **8**, **19**), chloride (**13**), and nitrile (products **10**, **15**) derivatives did not impede the reaction. Unactivated alkene **21** also reacted; however, the formation of both branched (**22**) and linear isomers (**23**) was observed. While more highly substituted alkenes (1,2-, 1,1-, or trisubstituted) were unreactive, strained alkene **24** underwent reaction to generate the quaternary carbon containing product **25** as a single observable regioisomer. In addition, various alkyl and aryl acid chlorides were tolerated to deliver the products **26**–**31** in uniformly good yields. Finally, ClZnSiMe$_3$ and ClZnSiPh$_3$ worked to deliver the products **32** and **33** in moderate yield.

The products of the silylacylation could be elaborated in various ways (Scheme 4); for example, Tamao-Fleming oxidation[18] allowed for synthesis of alcohol **34**. The ketone functionality was easily reduced with L-selectride to provide alcohol **35** in >20:1 dr. Furthermore, addition of PhMgBr occurred with high selectivity to generate **36** (X-ray). The selectivity for the reduction and addition reaction can be rationalized by the Felkin-Ahn model (**37**).[19]

With respect to the mechanism of the reaction, two general pathways were considered (Scheme 5A). Along Path A, direct

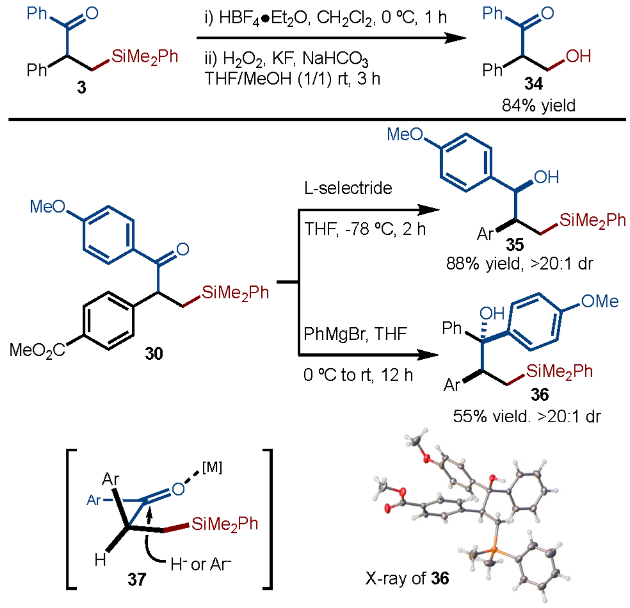
**Scheme 3. Ni-Catalyzed Silylacylation**[a]



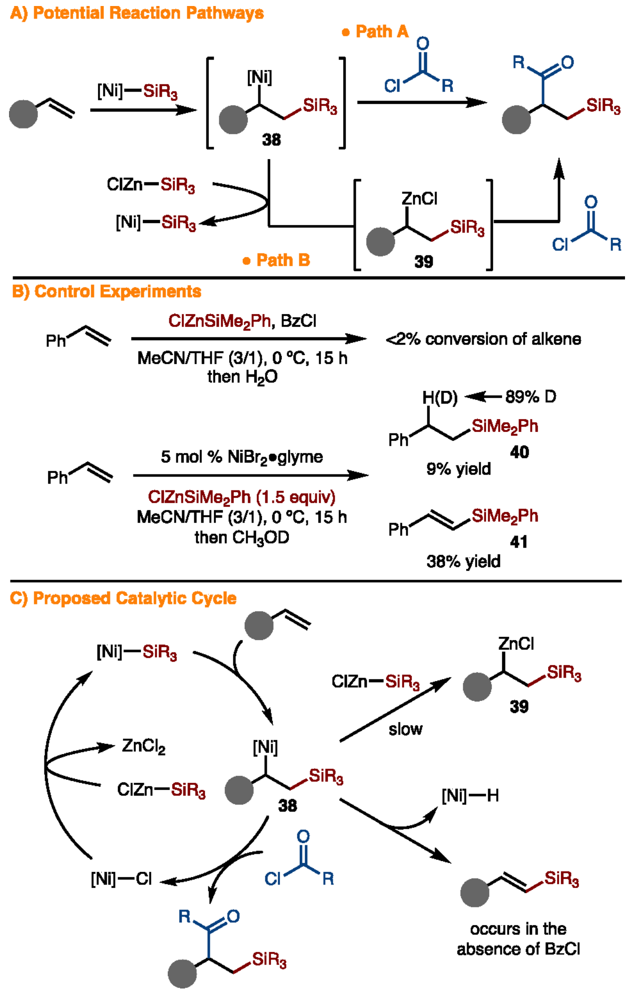
[a] Reactions run on 0.2 mmol. Yield of isolated product after silica gel column chromatography (average of 2 or more runs). [b] Reaction run on 2.0 mmol scale

https://dx.doi.org/10.1021/acscatal.0c05449
ACS Catal. 2021, 11, 1858–1862

### Scheme 4. Transformations of Products



### Scheme 5. Mechanistic Studies



capture of the alkyl-[Ni]-complex **38** generates product. Alternatively, alkyl-[Ni]-complex **38** could undergo transmetalation with ClZnSiR$_3$ forming alkyl-ZnCl intermediate **39**, which ultimately is trapped by the electrophile as shown in Path B (analogous to Cu-catalyzed processes).[17] Uncatalyzed addition of ClZnSiMe$_2$Ph to styrene is unlikely because <2% conversion of alkene was observed in the absence of Ni-catalyst (Scheme 5B), which is consistent with prior reports.[17] When Ni-catalyst was included in the reaction, but without the electrophile, a mixture of product **40** and **41** was formed, thus demonstrating that Ni catalyzes the addition of ClZnSiMe$_2$Ph. It is likely that **40** was formed via protonation of an in situ generated alkyl-Zn-intermediate, whereas **41** was generated by $\beta$-hydride elimination of an alkyl-[Ni]-complex. Comparing relative rates of intermediate steps based on product outcome, transmetalation to form alkyl-ZnCl intermediate **39** must be slower than $\beta$-hydride elimination to generate **41**. In addition, because the desired three-component coupling product is observed in preference to formation of **41** in the standard reaction conditions, direct electrophile capture of the alkyl-[Ni]-complex **38** must be faster than $\beta$-hydride elimination. Therefore, it is proposed that Path A is most likely, and it is fully illustrated in Scheme 5C. Upon generation of [Ni]-SiR$_3$, addition to the alkene occurs to form alkyl-[Ni]-complex **38**. This complex undergoes direct reaction with the acid chloride to generate the product and turnover the catalyst. The mechanism for reaction of the alkyl-[Ni]-complex with the acid chloride may either proceed via direct addition or by an oxidative addition/reductive elimination sequence.

In summary, described herein is an alkene functionalization that involves a [Ni]-SiR$_3$ complex as a catalytic intermediate. The acylsilylation reaction works well for several different classes of alkenes and acid chlorides to generate products that are amenable to further transformation. Finally, mechanistic studies have established the general catalytic cycle that an alkyl-[Ni]-complex is likely generated, which undergoes direct reaction with an electrophile. Development of additional reactions that utilize [Ni]-SiR$_3$ intermediates for alkene functionalization are in progress.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c05449.

Experimental procedures characterization data, X-ray crystal structure, and NMR spectra (PDF)

X-ray data for **36** (CIF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank Indiana University and the NIH (R35GM131755) for financial support. This project was partially funded by the Vice Provost for Research through the Research Equipment Fund and the NSF (CHE1726633).

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