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Ruthenium-Catalyzed C–H Bond Activation of Michael Acceptors: An Unusual Reactivity Leading to Allylsilanes

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Abstract: We report here an improved catalyst for the functionalization of Michael acceptors, involving C–C bond formation *via* C–H bond activation, using an *in situ* generated ruthenium active species. Moreover, on some particular substrates, the C–H functionalization resulted unexpectedly in the formation of allylsilanes rather than in the expected conjugated adducts, affording a new straightforward methodology to access useful stereodefined trisubstituted allylsilanes *via* C–H bond activation. Preliminary results have shown that they were reactive in the allylation of aldehydes, providing an access to alcohols bearing a quaternary carbon center.

Keywords: allylsilanes; C–C bond formation; C–H activation; ruthenium; silanes

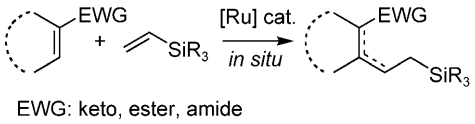
Catalytic processes involving C–H bond activation[1] are highly desirable, not only because they allow the functionalization of more easily available starting materials (atom economy concept[2]) but also because they produce clean reactions (reduced salts amounts). In the field of C–C bond formation *via* C–H activation, several catalytic reactions have been developed recently involving mainly low valent transition metals like palladium, rhodium and particularly ruthenium complexes which have been extensively developed in that field.[1,3]

Among the catalytic processes for C–C bond formation *via* C–H bond activation, hydroarylation processes, catalyzed by transition metal, allow the functionalization of alkenes with a total atom economy.[1,4] We recently reported a highly efficient catalytic system, generated in situ from easily available Ru(II) sources, allowing either the hydroarylation of vinylsilane (Murai reaction)[5,6] or the anti-Markovnikov arylation of styrenes.[7] The catalytically active ruthenium species was generated *in situ* from the reaction of inexpensive $[RuCl_2(p\text{-cym})]_2$ (*p*-cym = *p*-cymene) and sodium formate, in association with a phosphane ligand.

Even if intermolecular alkylation processes involving chelation-assisted aromatic C–H bond activation have been largely explored,[6] the activation of vinylic C–H bond of alkenes, and particularly Michael acceptors, has been scarcely explored.[8] Indeed, Murai and Trost have shown that some cyclic α,β-unsaturated esters,[8b] and a limited number of particular α,β-unsaturated ketones[8b,c] and aldehydes[8d] could be alkylated in the β-position in the presence of vinylsilanes and a catalytic amounts of $RuH_2(CO)(PPh_3)_3$. In all the reactions examined, conjugated alkylation products were obtained in moderate yields.

We want to report here an improved catalyst for the functionalization of Michael acceptors, using an *in situ* generated ruthenium active species (Scheme 1). Moreover, on some particular substrates, the C–H bond functionalization resulted unexpectedly in the formation of allylsilanes rather than in the expected conjugated adducts, affording a straightforward methodology to access useful trisubstituted allylsilanes[9] *via* C–H bond activation. Preliminary results have shown that they were reactive in the allylation of aldehydes, providing an access to alcohols bearing a quaternary carbon center.

The feasibility of the activation of α,β-unsaturated substrates was evaluated in the reaction of methyl cy-



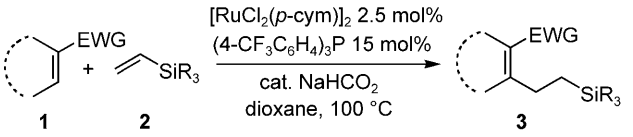
Scheme 1. Ruthenium-catalyzed functionalization of Michael acceptors.

clopent-1-enecarboxylate (**1a**) with triethoxyvinylsilane (**2a**), using an *in situ* generated ruthenium catalyst.[6,7] Several conditions were examined for the reaction of these model substrates and the previously reported conditions were found to be suitable, i.e., conducting the reaction at lower temperature: 120 °C compared to 140 °C for aromatic C–H bond activation (Table 1).[5] We also found that the use of (4-$CF_3C_6H_4)_3P$ as ligand of the ruthenium afforded higher yields, even allowing us to run the reaction in dioxane at 100 °C.[7] Under these conditions, good yields were achieved for the functionalization of cyclic substrates with triethoxyvinylsilane (Table 1, entries 1–4). Indeed, α,β-unsaturated esters (C_5 or C_6 rings), ketones or amides were alkylated in the β-position with yields ranging from 63 to 99%. Trisubstituted or phenyl-substituted linear α,β-unsaturated amide **1e** or **1f** (entries 5 and 6), and the useful Weinreb[10] amide **1h** (entry 8) reacted equally well, even if, in the later case, the yield was moderate. In the same way, a phenyl-substituted α,β-unsaturated ester was also alkylated with good yield (entry 10). However, linear alkyl-substituted α,β-unsaturated substrates reacted more sluggishly, and the formation of the expected adduct was hampered by the formation of isomers (entries 7 and 9). Among those isomers, β,γ-unsaturated species (allylsilanes) were the major by-products observed. The observation of the formation of such isomers is in contrast with Trost's results[8b] where, under quite similar conditions but using PPh_3 as ligand, it was found that, on some linear substrates, the use of dioxane as solvent inhibited the isomerization.

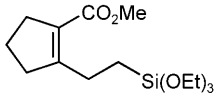
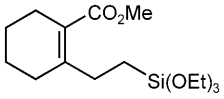
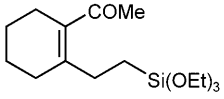
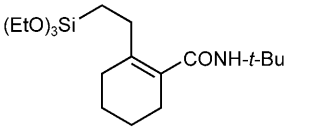
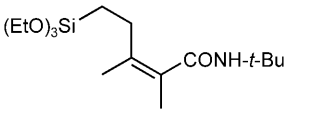
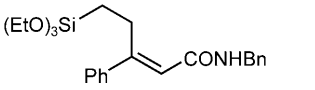
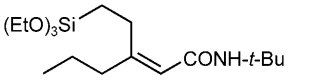
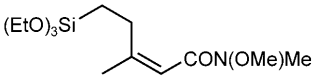
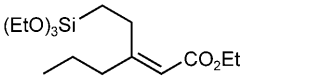
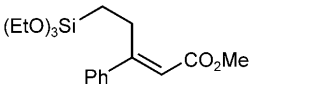
All tentative optimization studies (solvent, temperature, ligand), in order to achieve the exclusive formation of only one isomer at the expense of the other, failed. However, with these substrates (entries 7 and 9), the conjugated adducts **3ga** and **3ia** could be isolated in moderate yields (45 and 50%, respectively).

We were pleased to find that the reaction conducted on crotyl derivatives, under otherwise identical conditions, afforded nearly exclusively trisubstituted allylsilanes at the expense of the conjugated adducts (Table 2). We previously reported an example of the reaction of crotylamide affording allylsilane.[5] However, even if a good yield of allylsilane was achieved, the isomeric *E*/*Z* ratio was only 85:15, and we also faced reproducibility problems. During the course of our studies, we found that higher isomeric ratios were observed using (4-$CF_3C_6H_4)_3P$ as ligand and conducting the reaction in dioxane at lower temperature.[11] Indeed, the reaction of *tert*-butylcrotylamide (**1k**) with vinylsilane **1a**, in the presence of 2.5 mol% [$RuCl_2$(*p*-cym)]$_2$, 30 mol% of sodium formate and 15 mol% of (4-$CF_3C_6H_4)_3P$ as ligand, in dioxane at 100 °C, allowed the formation of allylsilane **4ka** in 69% yield and an *E*/*Z* ratio >97:3 (entry 1). Other allylsilanes, derived from **1k**, could be prepared by reacting amide **1k** with different vinylsilanes (entries 1–4), still with high stereoselectivities. In the same way, other crotylamides reacted equally well allowing the formation of allylsi-

Table 1. Ruthenium-catalyzed β-alkylation of Michael acceptors.[a]



1 2 3

Entry	Product		Yield[b] [%]
1		**3aa**	94 (87)
2		**3ba**	>99 (>99)
3		**3ca**	(63)[c]
4		**3da**	83 (50)
5		**3ea**	99[f] (76)
6		**3fa**	64 (30)
7		**3ga**	50[d]
8		**3ha**	32 (30)
9		**3ia**	45[e] (19)
10		**3ja**	80[f] (50)

[a] Reactions conducted with 1 mmol of **1**, 2 equiv. of **2**, 2.5 mol% of [$RuCl_2$(*p*-cym)]$_2$, 30 mol% $NaHCO_2$ and 15 mol% of (4-$CF_3C_6H_4)_3P$, at 100 °C in 1 mL 1,4-dioxane for 20 h.

[b] Isolated yields. Between parenthesis yields obtained using PPh_3 as ligand, conducting the reaction in toluene at 120 °C.

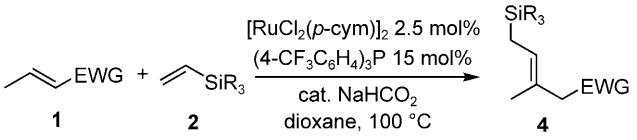
[c] Reaction conducted in toluene at 140 °C.

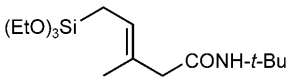
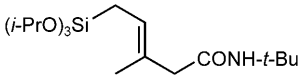
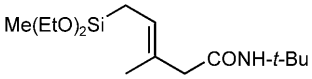
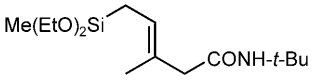
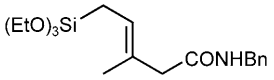
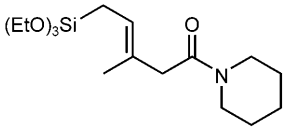
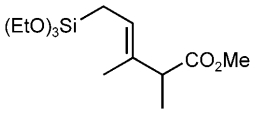
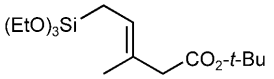
[d] Formation of 4% of allylsilane.

[e] Formation of 18% of allylsilane.

[f] Reaction time of 7 h.

Table 2. Ruthenium-catalyzed formation of allylsilanes *via* C–H activation.[a]

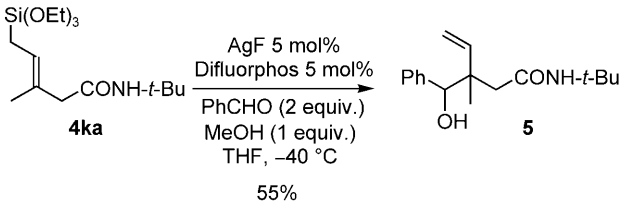


Entry	Product		Yield[b] [%]
1		**4ka**	69 (66)
2		**4kb**	61
3		**4kc**	70
4		**4kd**	58 (66)
5		**4la**	58 (68)
6		**4ma**	60
7		**4na**	50 (35)
8		**4oa**	50

[a] Reactions conducted with 1 mmol of **1**, 2 equiv. of **2**, 2.5 mol% of $[RuCl_2(p\text{-cym})]_2$, 30 mol% $NaHCO_2$ and 15 mol% of $(4\text{-}CF_3C_6H_4)_3P$, at 100 °C in 1 mL 1,4-dioxane for 20 h.

[b] Isolated yields. *E*/*Z* ratio for isolated allylsilanes were above 97:3. Between parenthesis yields obtained using PPh_3 as ligand, conducting the reaction in toluene at 120 °C, isomeric ratio *E*/*Z* being lower than 90:10.

lanes **4la** and **4ma** bearing benzyl- and piperidine-crotylamide substituents in 58 and 60% yields, respectively (entries 5 and 6). It also appeared that crotonic esters were also amenable to this reaction (entries 7 and 8) allowing a straightforward access to trisubstituted allylsilanes with an ester substituent. All the allylsilanes thus obtained have the (*E*) stereochemistry (*E*/*Z* > 97:3), which was confirmed by NOE NMR experiments. In all of the reactions conducted with those crotyl substrates, formation of the normal conjugated adduct was also observed, in yields ranging from 5 to 20%. The later were produced as a mixture of *Z*/*E* isomers, as judged by GC/MS and ^{1}H NMR analysis.



Scheme 2. Allylation of aldehydes with tri-substituted allylsilanes.

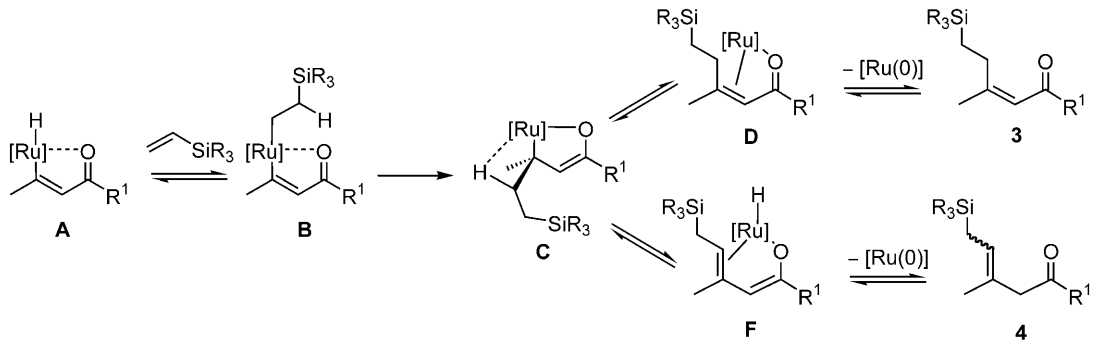
Indeed, these preliminary results show the possibility to generate directly, from the C–H bond activation of readily available substrates, functionalized trisubstituted allylsilanes, whose synthesis is not generally straightforward.[9]

The usefulness of such trisubstituted allylsilanes, was evaluated in the allylation of aldehydes. Indeed, reaction of the previously prepared allylsilane **4ka** with benzaldehyde using Yamamoto's conditions,[12] i.e., under Ag/Difluorphos catalysis, afforded alcohol **5**, bearing a quaternary carbon center, in a 55% unoptimized yield (Scheme 2). The latter was obtained as a 70/30 mixture of diastereoisomers.

To the best of our knowledge this example constitutes one of the rare examples of catalytic allylation of aldehydes with a trisubstituted allylsilane.[13] Indeed, starting from readily available substrates, α,β-unsaturated substrates, vinylsilanes and aldehydes, it was possible to access highly functionalized structures *via* two catalytic sequences involving intermediate ruthenium-catalyzed generation of allylsilane and its subsequent silver-catalyzed reaction with aldehyde.

Although the reaction mechanism is still under study, the reaction course of this ruthenium-catalyzed formation of either conjugated adduct or allylsilane can be rationalized (Scheme 3) on the basis of previously reported studies on the proposed reaction mechanism of the ruthenium-catalyzed functionalization of acetophenones, which is occurring under similar conditions.[6b,14] Intermediate **A**, resulting from oxidative addition of low-valent ruthenium(0) species into the β C–H bond of the Michael acceptor, reacts with vinylsilane to produce the alkenyl-alkyl-ruthenium species **B**. At this stage, reductive elimination can occur, affording the intermediate **D**. However, it has been demonstrated that, in this reaction, a particular two-step reductive elimination process is operating, involving the intermediate formation of a five-coordinated metallacycle with agostic interactions **C**.[14] From this intermediate, reductive elimination can occur, affording conjugated adducts **3**.

However, starting from metallacycle **C**, and depending on the steric and electronic nature of the activated substrate, a β-hydride elimination can occur giving the intermediate **F**. Then, reductive elimination allows the regeneration of the active ruthenium(0) species and results in the formation of the allylsilane **4**. Further stud-



Scheme 3. Proposed mechanistic interpretation for the allylsilanes formation.

ies are underway to understand the origin of the formation of the non-conjugated products.

In conclusion, we have described a quite general catalytic system for the selective alkylation of Michael acceptors in the β position. High yields were generally achieved using an *in situ* generated ruthenium catalyst in association with the electron-deficient (4-$CF_3C_6H_4)_3P$ ligand. Moreover, on some particular substrates, mainly crotonic acid derivatives, an unusual reactivity was observed, allowing the direct formation of stereodefined trisubstituted allylsilanes *via* C–H bond activation. The formation of such compounds is believed to be the result of β-hydride elimination followed by reductive elimination. Further studies are underway in order to extend the scope of the reaction, and particularly the direct formation of allylsilanes from Michael acceptors.

Experimental Section

Typical Procedure

A septum-capped vial equipped with a magnetic stirring bar was charged with $[RuCl_2(p\text{-cym})]_2$ complex (15,3 mg, 0.025 mmol), sodium formate (20.4 mg, 0.3 mmol) and tris(*p*-trifluoromethylphenyl)phosphane (69.9 mg, 0.15 mmol). The vial was closed and evacuated under vacuum during 10 min and placed under an argon atmosphere. Degassed 1,4-dioxane (1 mL) was added and the mixture was degassed by two vacuum/argon cycles. To this solution were added the Michael acceptor (1 mmol) and the vinylsilane (2 mmol) and the mixture was stirred for 10 min at room temperature and then placed into a preheated bath at 100 °C for 20 h (the completion of the reaction was checked by GC). After cooling the vessel to room temperature, the reaction mixture was purified by column chromatography.

Acknowledgements

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