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C–H Activation

Rh^{III}-Catalyzed Hydroacylation Reactions between *N*-Sulfonyl 2-Aminobenzaldehydes and Olefins

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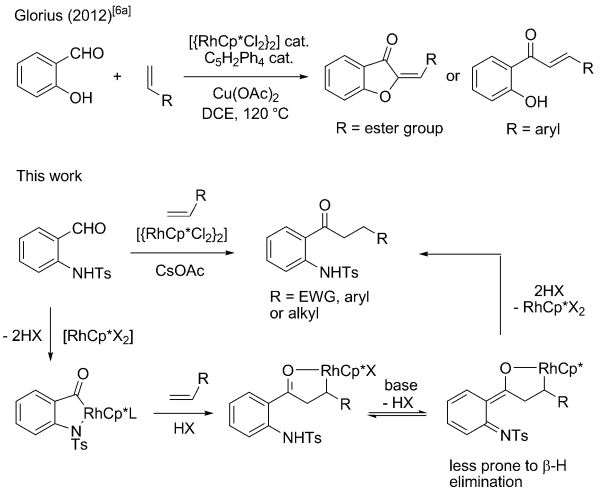
Abstract: Metal-catalyzed hydroacylation of olefins represents an important atom-economic synthetic process in C–H activation. For the first time highly efficient $Rh^{III}Cp^*$-catalyzed hydroacylation was realized in the coupling of *N*-sulfonyl 2-aminobenzaldehydes with both conjugated and aliphatic olefins, leading to the synthesis of various aryl ketones. Occasionally, oxidative coupling occurred when a silver(I) oxidant was used.

Activation and functionalization of C–H bonds with unsaturated molecules is a particularly attractive strategy in C–C bond formation.[1] This process is advantageous in terms of step- and atom-economy in that no pre-activation of the C–H bond is necessary. Hence it represents an attractive goal in synthetic chemistry, especially at low catalyst loading and low temperature. The hydroacylation[2] reaction of alkenes and alkynes is highly important and fulfills these criteria with 100% atom-economy. Two categories of hydroacylation methods have been realized for alkenes, namely organocatalysis (the Stetter reaction)[3] and metal catalysis, whereby the latter category is dominated by Rh^{I} catalysis by means of a C–H oxidative addition pathway.[4]

Recently rhodium(III)-catalyzed C–H activation has been extensively explored.[5] $Rh^{III}Cp^*$ (Cp^* = pentamethylcyclopentadienyl) complexes have stood out as active catalysts for C–H activation, leading to C–C, C–N, and C–O coupling with broad substrate scope and high activity. A large number of new coupling patterns have been developed that can complement those using Rh^{I}, Pd^{0}, and Pd^{II} catalysts. In contrast to the various reports on Rh^{I}-catalyzed hydroacylation reactions, no such reaction has been realized using Rh^{III} catalysis. This is because the C–H substrates in Rh^{III} catalysis are mostly limited to arenes and alkenes. While a few examples of Rh^{III}-catalyzed activation of formyl C–H bonds for C–C coupling have been reported (Scheme 1),[6] these systems are limited to oxidative couplings. On the other hand, Rh^{III}-catalyzed couplings using olefins mostly lead to oxidative Heck-type reactions.[7] Therefore, it is necessary to design olefin hydroacylation systems to expand the synthetic applicability of rhodium(III)-catalyzed C–H activation.



Scheme 1. Rh^{III}-catalyzed C–H activation of formyl groups.

We reasoned that *N*-sulfonyl 2-aminobenzaldehyde may undergo cyclometalation, and subsequent olefin insertion into the Rh–acyl bond could give a Rh^{III}–alkyl species (Scheme 1). However, when compared with the reported salicylaldehyde substrate (Scheme 1), the resulting carbonyl-chelated rhodacycle should be better stabilized and is conformationally more rigid owing to the higher donating ability of the amidate group. Therefore, this rhodacycle is less prone to β-hydride elimination and consequently protonolysis leading to a hydroacylation product is favored. In addition, the presence of a pendant sulfonyl group often allows further useful transformations.[8] We now report rhodium(III)-catalyzed coupling of *N*-sulfonyl 2-aminobenzaldehyde with olefins.

N-*p*-Toluenesulfonyl (Ts) 2-aminobenzaldehyde (**1a**) was readily prepared starting from 2-aminobenzylalcohol in two steps. The reaction conditions for the coupling of **1a** with ethyl acrylate were then screened. Using $[\{RhCp^*Cl_2\}_2]$ as a catalyst, coupling occurred in the presence of Ag_2CO_3 in dichloroethane (DCE, Table 1). Indeed, NMR analyses of the major product pointed to a hydroacylation product **3aa**, even though Ag_2CO_3 is a typical oxidant in oxidative C–H activation reactions.[5,9] Thus the Ag_2CO_3 only functions as a base, so a stoi-

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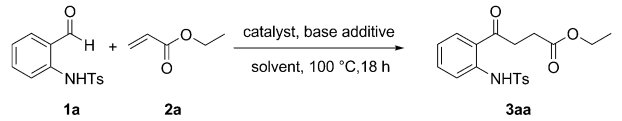
Table 1. Optimization studies.[a]



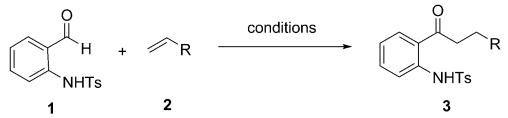
1a 2a 3aa

Entry	Catalyst (mol%)	Additive (equiv)	Solvent	Yield[b] [%]
1	$[\{RhCp^*Cl_2\}_2]$ (2.5)	Ag_2CO_3 (2)	DCE	68
2	$[\{RhCp^*Cl_2\}_2]$ (2.5)	Ag_2CO_3 (0.5)	DCE	87
3	$[RhCp^*(MeCN)_3][SbF_6]_2$ (5)	Ag_2CO_3 (0.5)	DCE	n.d.[d]
4	$[\{RhCp^*Cl_2\}_2]$ (4)	Ag_2CO_3 (0.5)	DCM	47
5	$[\{RhCp^*Cl_2\}_2]$ (2.5)	Ag_2CO_3 (0.5)	acetone	66
6	$[\{RhCp^*Cl_2\}_2]$ (2.5)	Ag_2CO_3 (0.5)	*t*AmOH	n.d.
7	$[\{RhCp^*Cl_2\}_2]$ (2.5)	Ag_2CO_3 (0.5)	CH_3CN	n.d.
8	$[\{RhCp^*Cl_2\}_2]$ (2.5)	Ag_2CO_3 (0.5)	dioxane	84
9	$[\{RhCp^*Cl_2\}_2]$ (2.5)	Ag_2CO_3 (0.2)	DCE	67
10	$[\{RhCp^*Cl_2\}_2]$ (2.5)	K_3PO_4 (1)	DCE	32
11	$[\{RhCp^*Cl_2\}_2]$ (2.5)	CsOAc (1)	DCE	88
12[c]	$[\{Rh(cod)Cl\}_2]/PPh_3$ (2.5/5)	K_3PO_4 (0.05)	DCE	82

[a] Reactions were carried out by using a catalyst, base additive, *N*-Ts 2-aminobenzaldehyde (0.2 mmol), and ethyl acrylate (4 equiv) in a solvent (2 mL) at 100 °C for 18 h. [b] Isolated yield after column chromatography. [c] Performed at 70 °C; cod = cyclooctadiene. For limitations of these conditions, see Supporting Information. [d] n.d. = not detected. [e] *t*AmOH = 2-methyl-2-butyl alcohol.

chiometric amount of Ag_2CO_3 seems unnecessary. Indeed, lowering the stoichiometry of Ag_2CO_3 to 0.5 equivalents did give rise to an improved efficiency (entries 1,2) and **3aa** was isolated in 87% yield (conditions **A**, entry 2). Further lowering the amount of Ag_2CO_3 gave inferior results (entry 9). DCE turned out to be the optimal solvent. Both a base additive and the $[\{RhCp^*Cl_2\}_2]$ catalyst are necessary and screening of other bases revealed CsOAc as the most efficient one (conditions **B**, entry 11). In comparison, although a typical Rh^I catalyst system[4b] also exhibited high activity in this reaction (entry 12), these Rh^I conditions gave poor results for unactivated olefins (Table 2).[10] It is not our objective to exhaust Rh^I conditions to obtained optimal results and given our continued interest in Rh^{III}-catalyzed C–H activation, the Rh^{III} conditions **B** were retained for further studies.

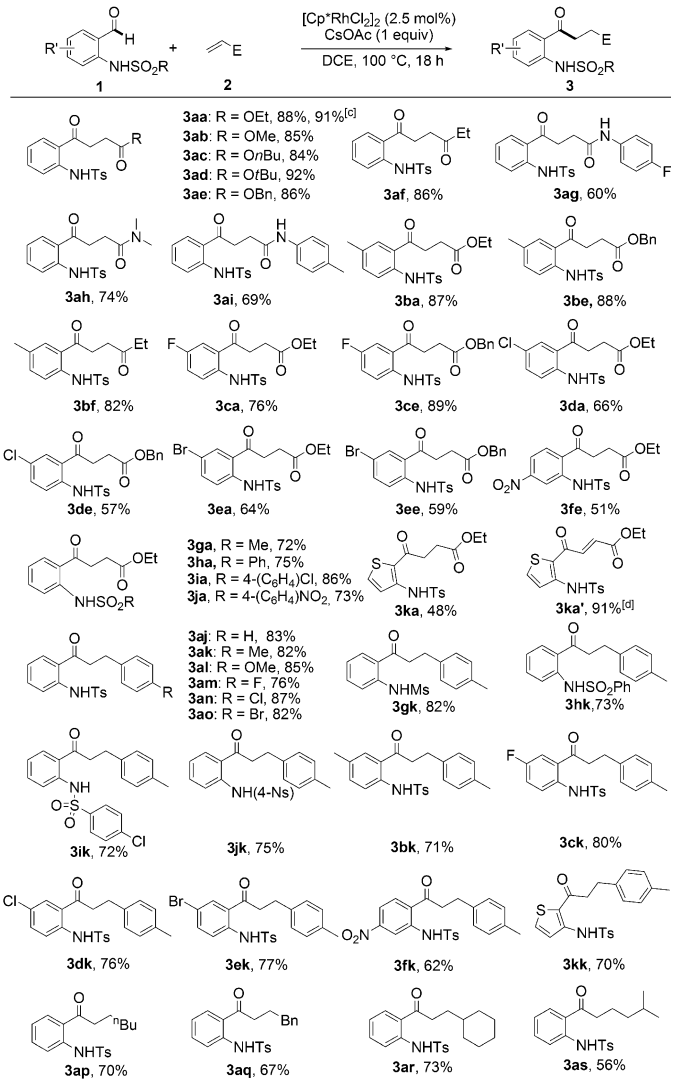
Table 2. Comparisons of yields [%] of three representative coupling reactions under different conditions.



1 2 3

R	Rh^I conditions[a,e]	Conditions **A**[b,e]	Conditions **B**[c,e]	Conditions **C**[d,e]
CO_2Et	82	87	88	87
Ph	71	< 5	83	81
*n*Bu	37	0	70	0

[a] Rh^I conditions: $[\{Rh(cod)Cl\}_2]$ (2.5 mol%), PPh_3 (5 mol%), K_3PO_4 (5 mol%), DCE, 70 °C, 18 h. [b] Conditions **A**: $[\{RhCp^*Cl_2\}_2]$, (2.5 mol%), Ag_2CO_3 (50 mol%), DCE, 100 °C, 18 h. [c] Conditions **B**: $[\{RhCp^*Cl_2\}_2]$, (2.5 mol%), CsOAc (1 equiv), DCE, 100 °C, 18 h. [d] Conditions **C**: $[\{RhCp^*Cl_2\}_2]$, (2.5 mol%), Ag_2CO_3 (2 equiv), KPF_6 (2 equiv), DCE, 110 °C, 18 h. [e] Isolated yield after column chromatography.



Scheme 2. Hydroacylation of different olefins.[a,b] [a] Reaction conditions: *N*-sulfonyl 2-aminobenzaldehyde (0.2 mmol), olefin (4 equiv), CsOAc (0.2 mmol), $[RhCp^*Cl_2]_2$ (0.005 mmol), DCE (2 mL), 100 °C, 18 h, sealed tube under nitrogen. [b] Isolated yield after column chromatography. [c] Reaction was performed in a 6.6 mmol scale. [d] Ag_2CO_3 (0.2 mmol) was used instead of CsOAc.

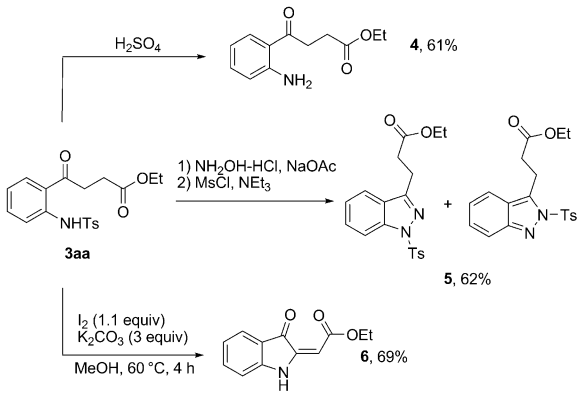
The scope and limitations of this coupling reaction were explored under conditions **B** (Scheme 2). Aldehyde **1a** coupled with different acrylates and an enone to give **3aa**–**3af** in 84–92% yields. Moreover, this reaction is scalable to multigram-scale synthesis as in the isolation of 2.24 g of **3aa** (91% yield). In addition, moderate-to-high yields were isolated when the olefin substrate was extended to acrylamides (**3ag**–**3ai**). Different ring-substituted (methyl, nitro, and halogens) benzaldehydes are also applicable, although somewhat lower yield tends to be isolated for a Cl- or Br-substituted benzaldehyde (**3da**–**3ee**). Variation of the sulfonyl group to methyl and aryl substituents is tolerated as shown by the isolation of (**3ga**–**3ja**) in good-to-high yields. Furthermore, the benzaldehyde ring can be extended to a 2-thiophenaldehyde (**3ka**), albeit with a lower yield. In contrast, only the C–H oxidative olefina-

tion product (**3 ka**′) was isolated in high yield when this reaction was conducted under conditions **A** with one equivalent of Ag_2CO_3, indicating that these two conditions might give complementary results.

The conditions **B** are equally viable for the coupling with styrenes. In line with the hydroacylation of acrylates, benzaldehyde **1 a** coupled with different styrenes with consistently high efficiency (**3 aj**–**3 ao**). Consistent with the scope of benzaldehydes in the coupling with activated olefins, variation of the sulfonyl group is well-tolerated (**3 gk**–**3 jk**). Variation of the substituent in the benzaldehyde ring (**3 bk**–**3 fk**), including introducing nitro and halogens groups, has no significant effect on the isolated yield. These functional groups should readily provide handles for further functionalization of these ketone products. The high yield obtained here for the halogen-substituted benzaldehydes stands in contrast to those in the coupling with acrylates. The same observation also applies to the coupling of a 2-thiophenaldehyde substrate (**3 kk**).

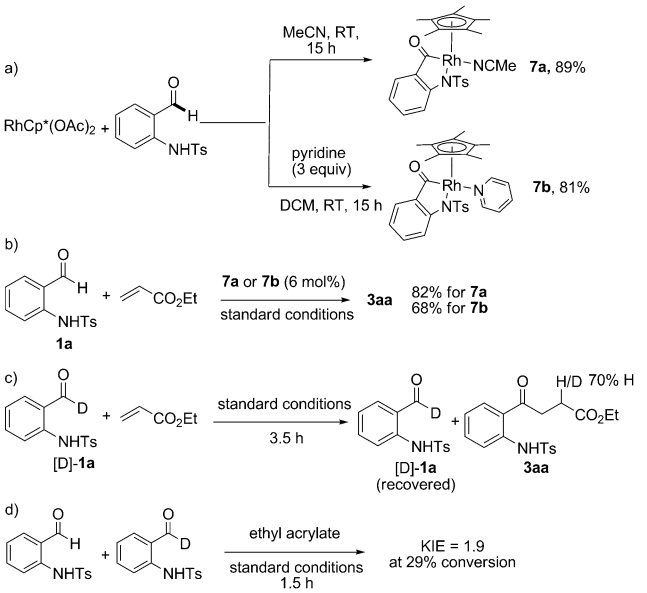
Gratifyingly, the current conditions are also applicable to the coupling for aliphatic olefins. Of note, these olefins are usually much less reactive in C–H activation reactions. Indeed, only a few systems of rhodium(III)-catalyzed olefination reactions for aliphatic olefins have been reported.[11] We found that this transformation is compatible with aliphatic alkenes such as 1-hexene, vinylcyclohexane, 4-methyl-1-pentene, and allylbenzene, and the coupled product was isolated in 56–73 % yield. In contrast, no desired reaction occurred when conditions **A** were applied.

To demonstrate the synthetic applicability of the hydroacylation product, derivatization of **3 aa** has been performed (Scheme 3). Desulfonylation by using H_2SO_4 afforded aniline **4**



Scheme 3. Derivatization of a hydroacylation product.

in 61 % yield. Oxime formation followed by nucleophilic cyclization afforded a mixture of *N*-Ts indazone and its tautomer (**5**). Significantly, I_2 oxidation readily gave a 3-oxoindolinylidene (**6**),[12] a synthetically useful exocyclized olefin, which is the aza analogue of the product obtained in the rhodium(III)-catalyzed oxidative coupling of salicylaldehyde with acrylates (Scheme 1).[6a] Furthermore, Chang and Cheng have independently documented additional functionalization reactions of closely related 2-aminoacetophenones.[13]

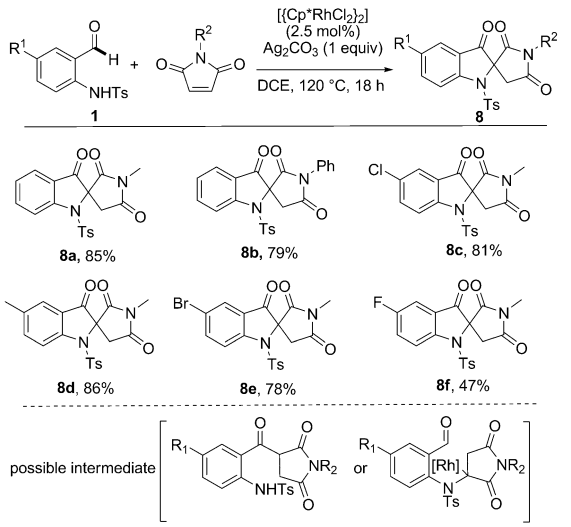


Scheme 4. Mechanistic studies.

Several experiments have been performed to explore the mechanism of this hydroacylation reaction (Scheme 4). To demonstrate the relevancy of C–H activation, two rhodacyclic complexes **7 a** and **7 b** have been readily prepared from the reaction of **1 a** and [RhCp*$(OAc)_2$] in different solvents (Scheme 4a), in which a concerted metalation–deprotonation mechanism is likely operational with the assistance of an acetate ligand,[1c,14] and which differs from the C–H oxidative addition mechanism in Rh^I-catalysis. Both complexes were fully characterized by NMR and IR spectroscopy, and HRMS. In particular, the Rh–*C*(O) resonates characteristically at $\delta = 249.8$ ppm (d, $J_{Rh-C} = 27.3$ Hz) for **7 b** in the ^{13}C NMR spectrum.[15] Both **7 a** and **7 b** (6 mol %) proved active for the coupling of **1 a** and **2 a**, as shown by the isolation of **3 aa** in 82 and 68 % yield, respectively (Scheme 4b). The lower catalytic efficiency observed for **7 b** is likely caused by stronger pyridine inhibition. To further probe this C–H activation process, the coupling between [D]-**1 a** and **2 a** was stopped at about 45 % conversion. ^1H NMR analysis of the recovered [D]-**1 a** revealed no H/D exchange at the acyl position, indicating that this C–H activation process is irreversible (Scheme 4c). H/D scrambling (30 % D) was observed at the α-position of the product, which agrees with proposed protonolysis of the Rh–alkyl bond in the catalytic cycle. The kinetic isotope effect (KIE) has been estimated for the competitive coupling of an equimolar mixture of **1 a** and [D]-**1 a** with ethyl acrylate. ^1H NMR analysis of the level of deuteration of the recovered aldehyde mixture at 29 % conversion (HPLC) gave $k_H/k_D = 1.9$ (see Scheme 4d and Supporting Information). This moderate value of KIE suggests that cleavage of the C–H bond might be involved in the rate-limiting step. Thus in a proposed mechanism following cyclometalation, migratory insertion of the acyl group into the olefin affords a rhodium(III) alkyl species (Scheme 1). Protonolysis of the Rh–C(alkyl) bond furnishes the final coupled product. The observation of hydroacylation as the exclusive pathway suggests that the protonolysis is

a lower energy pathway than the alternative β-hydride elimination process.

To better define the scope of activated olefins, *N*-substituted maleimides were examined. However, no desired hydroacylation product was generated under conditions **B**. We then turned to oxidative conditions using Ag_2CO_3 (1 equiv) as an oxidant (Scheme 5). Interestingly, a series of spiroketones (**8a**–**8f**) was isolated in good-to-high yield, possibly by following a sequence of hydroacylation/oxidative C–H amidation. Alternatively, a Rh^{III} tertiary alkyl complex is possible, as has been proposed by us in related Rh^{III}-catalyzed spiroamide formation (see Supporting information).[16] An asymmetric version of this reaction has been attempted for the synthesis of **8a** using [RhCp*{(*R*)-BINOLate}] (BINOL = 1,1′-bi-2-naphthol) as a catalyst.[17] Although good yield was isolated (78%), very poor enantioselectivity (3% *ee*) was obtained, indicating that design of chiral variants of the Cp* ring, instead of using a chiral auxiliary ligand (which dissociates to generate necessary vacant sites), should be the right choice.



Scheme 5. Oxidative cyclization with maleimides. See Supporting Information for detailed conditions.

In summary, we have achieved different coupling reactions of *N*-sulfonyl 2-aminobenzaldehydes with olefins. In most cases, hydroacylation has been realized for conjugated olefins as well as aliphatic olefins under operationally simple conditions. This hydroacylation process occurs by means of a C–H activation pathway, and cyclometalated Rh^{III}–acyl complexes have been prepared as a close analogue of the real active catalyst. Oxidative functionalization of the formyl C–H bond with activated olefins can occasionally occur depending on the nature of the olefin substrate when using Ag_2CO_3 as an oxidant. A broad scope of both coupling partners has been defined, and further transformations of the coupled products have been demonstrated. These coupling systems serve to broaden the scope of rhodium(III)-catalyzed C–H activation reactions, especially in redox-neutral reactions, and may find important applications.

Experimental Section

General procedure for the synthesis of 3: *N*-Sulfonyl 2-aminobenzaldehyde (0.2 mmol), olefin (0.8 mmol), [{Cp*$RhCl_2$}$_2$] (2.5 mol%), and CsOAc (0.2 mmol) were charged into a pressure tube, to which DCE (2 mL) was added under argon. The reaction mixture was stirred at 100 °C for 18 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography to afford the hydroacylation product.

General procedure for oxidative cyclization with maleimides—synthesis of 8: *N*-Sulfonyl 2-Aminobenzaldehyde (0.2 mmol), *N*-substituted maleimides (0.4 mmol), [{RhCp*Cl_2}$_2$] (2.5 mol%), and Ag_2CO_3 (0.2 mmol) were charged into a pressure tube, to which DCE (2 mL) was added under argon. The reaction mixture was stirred at 120 °C for 18 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using ethyl acetate/petroleum ether to afford the final product.

Acknowledgements

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Keywords: C–H activation · cyclization · hydroacylation · olefins · rhodium

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[10] Poor results were obtained for less reactive olefins such as 1-hexene under the Rh^{I} conditions, while our Rh^{III} conditions are equally optimal. Although further optimization of the Rh^{I} conditions may give improved results, this work focused on Rh^{III}-catalyzed C–H activation.

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