

Rhodium(III)-catalyzed oxidative olefination of *N*-allyl sulfonamides†Cite this: *Org. Biomol. Chem.*, 2013, **11**, 2761Received 6th February 2013,
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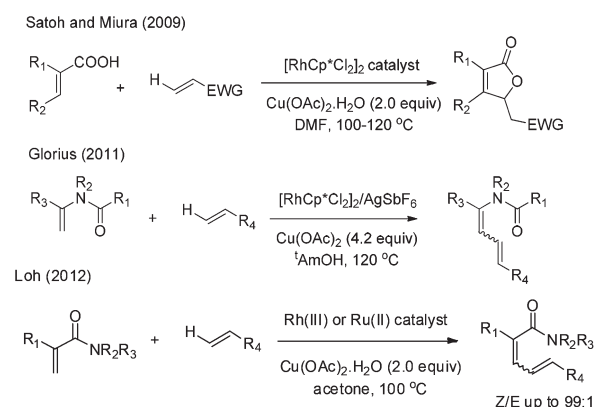
Rhodium(III)-catalyzed oxidative couplings between *N*-sulfonyl allyl amines and activated olefins have been achieved. Only olefination occurred for acrylates, and the butadiene product can be further cyclized under palladium-catalyzed aerobic conditions. The coupling with *N,N*-dimethylacrylamide followed a cyclization pathway.

Ever since the report of the pioneering work by Fujiwara and Moritani in 1967,¹ oxidative olefination of C–H bonds has attracted increasing attention. This synthetically important reaction represents a step-economic and waste-reducing process because unreactive C–H bonds are ubiquitous and no prior functionalization is necessary.² This strategy has been applied to the synthesis of many useful complex structures. Amongst the transition metal catalysts used, palladium complexes have been predominant. While early examples have shown that ruthenium(II)³ and rhodium(III)⁴ complexes can be active catalysts in this transformation, studies using these metals lag behind. It is only in recent years that rhodium(III)⁵ and ruthenium(II)⁶ species came to be realized as highly active catalysts for this purpose. In particular, rhodium(III) catalysts readily effect the olefination of a large scope of arenes with high selectivity and functional group compatibility. Thus simple arenes⁷ and arenes with heteroatom directing groups such as hydroxyl,⁸ amide,⁹ pyridyl,¹⁰ carbamate,¹¹ imine¹² and carboxyl¹³ have been olefinated under operationally simple conditions.¹⁴

While oxidative olefination of arenes has been extensively explored, the oxidative C–H/C–H couplings of two olefins have gained less attention.¹⁵ Pioneered by Gusevskaya,¹⁶ Ishii,¹⁷ and Loh,¹⁸ palladium catalysis still dominates in olefin–olefin oxidative couplings. Rh(III)-catalyzed such couplings have been reported, but the substrates are limited to acrylic acids,¹⁹

enamides,²⁰ and acrylamides²¹ (Scheme 1). Besides the limited scope, the *Z/E* selectivity of these couplings can be low in some cases. When an activated olefin was applied, the initial olefination product may be further complicated by *in situ* Michael cyclization (Scheme 1). Thus it is necessary to expand the scope of the olefins. We have recently reported rhodium(III)-catalyzed diversified couplings of *N*-allyl sulfonamides with internal alkynes under oxidative conditions, leading to the synthesis of pyridines, dihydropyridines, and cyclopentenones.²² These reactions occurred *via* a C–H activation pathway, suggesting that sulfonamide is a viable directing group in the activation of olefinic C–H bonds.²³ We now report rhodium(III)-catalyzed oxidative coupling of *N*-allyl sulfonamides with activated olefins.

We initiated our studies with the screening of the conditions for the coupling of *N*-tosyl allylamine (**1a**) and methyl acrylate (Table 1). On the basis of our outcomes in the coupling of **1a** with alkynes, acetone was designated as the solvent (100 °C). It was found that while oxidants such as Cu(OAc)₂, Ag₂O, and Ag₂CO₃ all effected this coupling reaction when [RhCp*Cl₂]₂ was used in 5 mol% (Table 1, entries 1–3), AgOAc proved to be a superior oxidant (entry 4), and product **3a** was isolated in 76% yield. The structure of **3a** was elucidated on



Scheme 1 Rh(III)-catalyzed olefin–olefin coupling.

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Table 1 Optimization studies

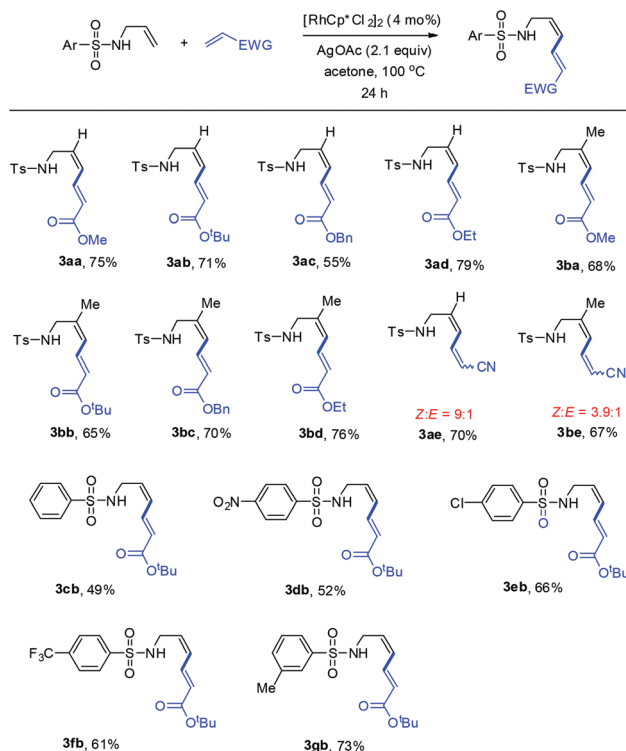
Entry	Catalyst	Loading (mol%)	Oxidant	Yield ^a (%)
1	[RhCp*Cl ₂] ₂	5	Cu(OAc) ₂	42
2	[RhCp*Cl ₂] ₂	5	Ag ₂ CO ₃	53
3	[RhCp*Cl ₂] ₂	5	Ag ₂ O	nd
4	[RhCp*Cl ₂] ₂	5	AgOAc	76
5	[RhCp*Cl ₂] ₂	4	AgOAc	75
6	[RhCp*Cl ₂] ₂	3	AgOAc	60
7 ^b	[RhCp*Cl ₂] ₂	4	AgOAc	72
8 ^c	[RhCp*Cl ₂] ₂	4	AgOAc	78

Conditions: *N*-tosyl allylamine (0.3 mmol), methyl acrylate (0.45 mmol), [RhCp*Cl₂]₂ (3–5 mol%), oxidant (2.1 equiv.), acetone (3 mL), 100 °C, 24 h, sealed tube under argon. ^a Isolated yield. ^b 4.5 equiv. of AgOAc was used. ^c 36 h.

the basis of ¹H and ¹³C NMR analyses. The isolated yield of **3a** stayed essentially the same when the catalyst loading was lowered to 4 mol% (entry 5). However, further decrease of the loading to 3 mol% caused an appreciable decrease of the catalytic efficiency (entry 6). Using a prolonged reaction time or an excess of AgOAc all failed to significantly improve the yield of **3a** (entries 7–8). Thus the conditions given in entry 5 were deemed optimal.

The scope and limitations of this reaction were next explored by following the optimized conditions (Scheme 2). A series of acrylates coupled with sulfonamide **1a** in moderate to good yield and the product was obtained as essentially a single stereoisomer (>95 : 5) on the basis of ¹H NMR analysis (**3aa**–**3ad**). Introduction of a methyl to the 2-position of the allyl group is well-tolerated, and coupling products **3ba**–**3bd** were isolated in comparable yield. In contrast to the high stereoselectivity for acrylates, the coupling between **1a** and acrylonitrile afforded a mixture of two isomeric (*Z,Z*) and (*Z,E*) dienes in 70% isolated yield and in 9 : 1 ratio, where the acrylonitrile moiety prefers to adopt a (*Z*) geometry. This selectivity dropped to 3.9 : 1 when an *N*-methallyl sulfonamide substrate was used, although the total yield of the product stayed essentially the same. The sulfonamide directing group is not limited to NHTs; both electron-donating (**3gb**) and -withdrawing groups (**3db**, **3eb** and **3fb**) in the phenyl ring of the sulfonamide can be tolerated, although the isolated yields of these products are generally lower than those obtained from **1a**. In contrast, when an *Ms* directing group was applied, no desired coupling reaction occurred, indicative of the limitation of this reaction. In addition, the olefin coupling partner is limited to an activated olefin because no reaction occurred for styrene even under more harsh conditions.

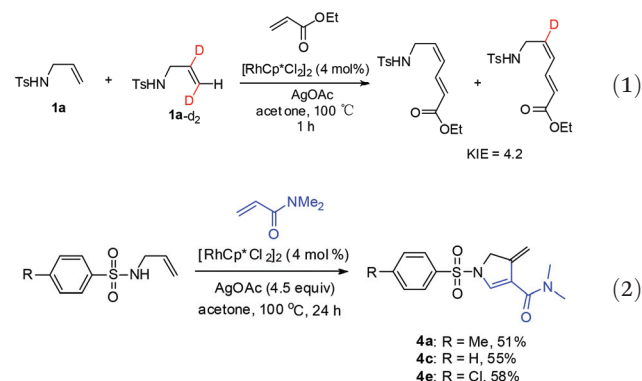
To probe the mechanism of this reaction, the kinetic isotope effect was studied for the cleavage of the C–H bond of **1a** in the competitive coupling of ethyl acrylate with an equimolar mixture of **1a** and **1a**-d₂ (eqn (1)). A value of *k*_H/*k*_D = 4.2



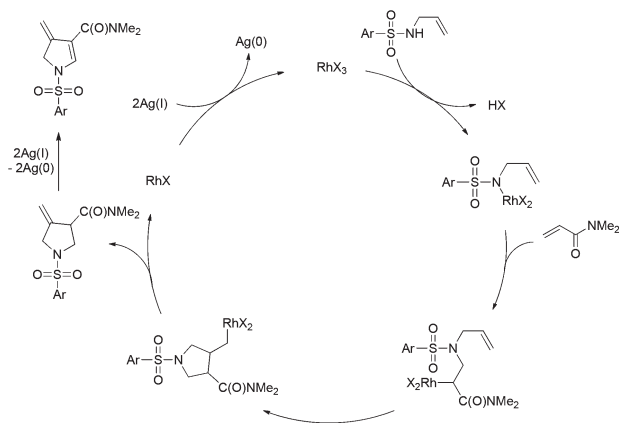
^a Conditions: *N*-Ts allylamine (0.3 mmol), olefin (0.45 mmol), [RhCp*Cl₂]₂ (4 mol%), AgOAc (0.63 equiv.), acetone (3 mL), 100 °C, 24 h, sealed tube under argon. ^b isolated yield.

Scheme 2 Oxidative olefination of *N*-sulfonyl allyl amines.^{a,b}

was obtained, indicating that C–H activation (cyclometalation) is involved in the turnover-limiting step. This KIE value is also consistent with that obtained in the Rh(III)-catalyzed oxidative coupling of **1a** and diphenylacetylene.²⁴



To better define the substrate scope, *N,N*-dimethylacrylamide was allowed to couple with **1a** under the standard conditions. To our surprise, no analogous butadiene could be isolated, and the major product obtained (28%) was a 2,3-dihydropyrrole with an exo-cyclized C=C bond (**4a**), as a result of twofold oxidation. Under these catalytic conditions, no isomerization of the exo-cyclic C=C was detected. Optimization by simply using an excess of AgOAc (4.2 equiv.) increased the yield of **4a** to 51%. Thus other direct analogues such as **4c** and



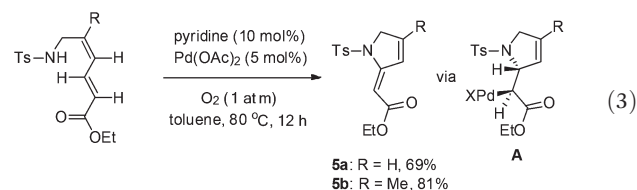
Scheme 3 Proposed catalytic cycle.

4e were obtained in similar yields (eqn (2)). Shifts of reaction selectivity when moving from acrylate to acrylamide substrates have been reported in previous systems,²⁵ and this is undoubtedly caused by the electronic effects of the olefin. In addition, the relatively high donating capacity of arylamides can also make a difference. Notably, palladium-catalyzed aerobic oxidative coupling of *N*-sulfonyl allylamine with olefins has been reported by Stahl,²⁶ but onefold oxidation products were obtained.

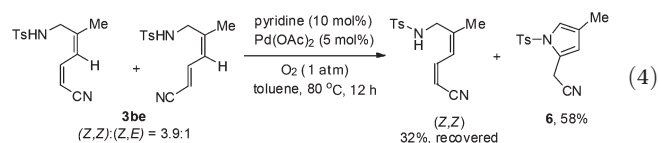
While no solid mechanistic studies have been performed, a plausible mechanism to account for the formation of **4a–e** has been proposed on the basis of previous reports (Scheme 3). A rhodium(III) amide was proposed to be an active intermediate. In line with Stahl's proposal,²⁶ this rhodium amide species rather undergoes a Rh–N bond insertion into an incoming acrylamide to give a rhodium(III) alkyl intermediate.²⁷ Subsequent insertion of the Rh–C bond into the terminal olefin yields a rhodium(III) primary alkyl intermediate. β -Hydrogen elimination affords an exo-cyclized pyridine intermediate and further oxidation by Ag(I) furnishes the final product.

To better demonstrate the synthetic utility of these butadiene products, further transformations of **3** have been performed. Clearly, the current conditions failed to allow any (oxidative) cyclization of these butadienes. In contrast, palladium catalysis has been well studied for aerobic oxidation reactions leading to C–N couplings.²⁸ Therefore palladium-catalyzed intramolecular oxidative C–N coupling for **3** was performed. Gratifyingly, smooth cyclization of **3ad** and **3bd** to **5a** and **5b**, respectively, was achieved using a Pd(OAc)₂ (5 mol%)-pyridine (10 mol%) catalyst under O₂ (balloon pressure) (eqn (3)). On the basis of ¹H and ¹³C NMR analyses, **5a** and **5b** were identified as a 2,5-dihydropyrrole bearing an exocyclic C=C bond. In particular, in the ¹³C NMR spectrum (CDCl₃) of **5a** the CHC(O)OEt resonates at a rather high field (δ = 91.2). The (*E*) geometry of the double bond follows from NOESY spectroscopic studies of **5b**. The exclusive *E* configuration of the product suggests a *cis* amidopalladation process, leading to the intermediacy of palladium alkyl **A** (eqn (3)).²⁹ We also

attempted but failed to prepare **5a** *via* palladium-catalyzed one pot aerobic oxidation starting from **1a** and ethyl acrylate, indicating that palladium catalysis failed at the oxidative olefination stage. It is noteworthy that although **5a,b** and **4a,c,e** are at the same oxidation level, they differ in connectivity. Achieving molecular diversity and complementary selectivities *via* substrate control and condition control constitutes an important task in synthesis.



Interestingly, when we applied these aerobic oxidative conditions to a mixture ((*Z,Z*) : (*Z,E*) = 3.9 : 1) of **3be**, a thermodynamically stable pyrrole **6** was obtained in 58% yield (eqn (4)), where the (*Z,E*) isomer seems to give a higher reactivity because only the (*Z,Z*) isomer remained after the reaction, which was recovered in 32% yield.



In summary, we have demonstrated the oxidative olefination of *N*-sulfonyl allylamines using activated olefins. Simple olefination occurred for acrylates to give a butadiene derivative. This butadiene can further undergo palladium catalyzed aerobic oxidative cyclization, leading to a 2,5-dihydropyrrole with an exo-cyclic double bond. *N,N*-Dimethylacrylamide followed a twofold oxidation pathway. These observed selectivities complement that reported in palladium-catalyzed aerobic oxidative coupling reactions between these two substrates, and the different selectivities in olefination reactions and in subsequent transformations likely render this method useful in the synthesis of complex structures. Exploration of other novel directing groups for C–H activation is underway in our laboratory.

Acknowledgements

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