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Communication

C-H Amination

Catalytic Intramolecular C(sp³)–H Amination of Carbamimidates

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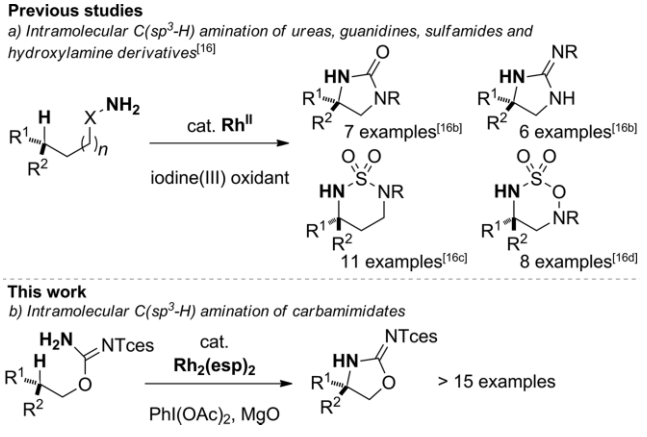
Abstract: The Rh^{II}-catalyzed intramolecular C(sp³)–H amination of carbamimidates allowed new nitrogen heterocycles to be isolated in yields up to 99 %. The reaction was best performed in the presence of the $Rh_2(esp)_2$ (esp = α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid) complex by using 2,2,2-trichloroethoxysulfonyl-protected compounds. The reaction could be applied to substrates possessing a benzylic, an allylic, a propargylic, or a tertiary C(sp³)–H bond.

Introduction

A recent study of the drugs approved by the US FDA has showcased the paramount importance of nitrogen in organic chemistry. More than 80 % of small-molecule drugs contain at least one nitrogen atom, and 59 % of them possess a nitrogen heterocycle.[1] Future drugs will also rely on the unique properties of nitrogen, as suggested by the new building blocks that are incorporated into final screening compounds.[2] The ubiquity of nitrogen in life sciences, accordingly, remains a driving force for organic chemists to design new amination methods.[3] Much attention has been paid to the development of improved catalytic methods for the synthesis of heterocycles that take into account the notions of step economy, selectivity, and molecular diversity.

The catalytic amination of C(sp³)–H bonds has emerged as a new powerful synthetic method for the preparation of nitrogen-containing compounds.[4] The direct conversion of a C–H bond into a C–N bond shortens synthetic schemes and gives access to molecular diversity likely to open a new space for intellectual property. In this context, much progress has been made with the application of catalytic nitrene C(sp³)–H insertions.[5] These C(sp³)–H amination reactions have been shown to be efficiently performed with Ru,[6] Cu,[7] Ag,[8] Co,[9] Fe,[10] Mn,[11] and Ir[12] complexes, but the most significant achievements have been reported with the use of dirhodium(II) complexes.[13] Several examples of the total syntheses of complex molecules demonstrate the unique capacity of these dinuclear species to mediate nitrene insertions with very high levels of efficiency and selectivity.[14]

Since Du Bois reported seminal studies with carbamates and sulfamates for the synthesis of 1,2- and 1,3-amino alcohols, respectively,[15] particular attention has been paid to the development of rhodium(II)-catalyzed intramolecular C(sp³)–H amination reactions. The design of the $Rh_2(esp)_2$ complex (esp = α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid) has allowed expansion of the scope to various substrates such as ureas, guanidines, *O*-sulfamoyl-hydroxylamine derivatives, and sulfamides, which thereby gives rapid access to various new nitrogen heterocycles (Scheme 1a).[16] In the context of molecular diversity, we decided to investigate the reactivity of carbamimidates as nitrene precursors (Scheme 1b). The use of carbamimidates in catalytic intramolecular C(sp³)–H amination has never been reported,[17,18] and it was hypothesized that the reaction would afford cyclic compounds that were recently described[19] and which are of potential value for medicinal chemistry.[20] In this communication, we therefore wish to report the rhodium(II)-catalyzed intramolecular C(sp³)–H amination of carbamimidates to provide new heterocyclic structures in very good yields.



Scheme 1. Extension of the scope of the intramolecular C(sp³)–H amination reaction.

Results and Discussion

The starting carbamimidates were prepared according to a protocol inspired by the method reported by Du Bois for the syn-

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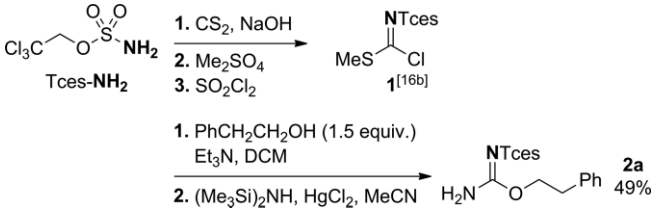
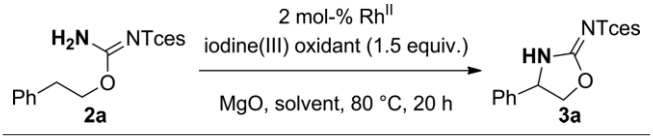
thesis of guanidines.[16b] On the basis of that study, we initially focused on the use of 2,2,2-trichloroethoxysulfonyl (Tces)-protected carbamimidates, which could be readily accessed from chloroimidothionate **1** obtained in two steps from trichloroethylsulfamate (Scheme 2). Reference substrate **2a**, which was used for our initial screening of the reaction conditions, was isolated in 49 % yield.



Scheme 2. Synthesis of Tces-protected carbamimidate **2a**.

The first experiment in the presence of $Rh_2(OAc)_4$ (2 mol-%), $PhI(OAc)_2$ (1.5 equiv.), and MgO (2.5 equiv.) in benzene allowed us to isolate the expected cyclic carbamimidate **3a** in 15 % yield (Table 1, entry 1). A rapid screening of rhodium(II) complexes then revealed the superior reactivity of $Rh_2(esp)_2$, as cyclic product **3a** was isolated in 80 % yield after 20 h at 80 °C (Table 1, entries 1–3).[21] With respect to the solvent, the best result was obtained if the reaction was performed in benzene, but toluene could provide a safer alternative, as its use allowed compound **3a** to be isolated in 74 % yield (Table 1, entries 3–6). Replacing $PhI(OAc)_2$ by $PhI(OPiv)_2$ (OPiv = OCO*t*Bu) proved detrimental to the yield (Table 1, entry 7), whereas lowering the amount of the iodine(III) oxidant significantly decreased the overall reactivity; in this case, the expected product **3a** was isolated in 72 % yield after 3 days (Table 1, entry 8). The presence of magnesium oxide was also required to ensure optimal conversion (Table 1, entry 9). Finally, though the intramolecular C(sp^3)–H amination could also be performed at room temperature with similar efficiency (Table 1, entry 10), we found that a very similar yield could be obtained after only 4 h of heating at 80 °C (Table 1, entry 11).

Table 1. Catalytic intramolecular C(sp^3)–H amination of **2a**.[a]

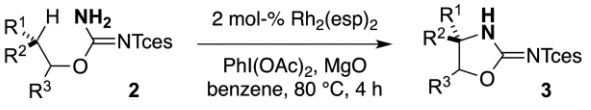


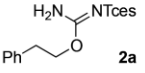
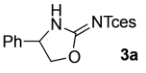
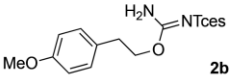
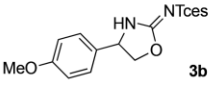
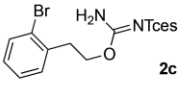
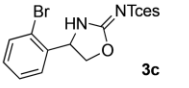
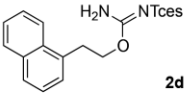
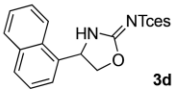
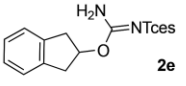
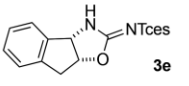
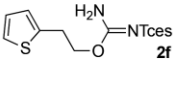
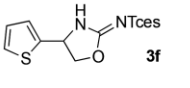
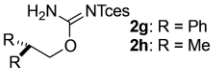
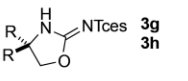
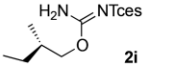
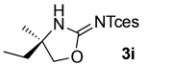
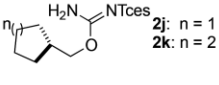
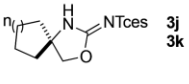
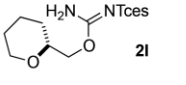
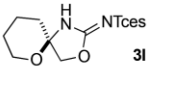
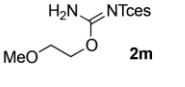
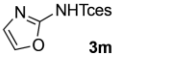
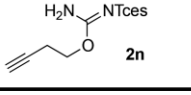
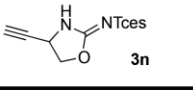
Entry	Catalyst	Solvent	Oxidant (equiv.)	Yield[b] [%]
1	$Rh_2(OAc)_4$	benzene	$PhI(OAc)_2$ (1.5)	15
2	$Rh_2(CF_3CONH)_4$	benzene	$PhI(OAc)_2$ (1.5)	48
3	$Rh_2(esp)_2$	benzene	$PhI(OAc)_2$ (1.5)	80
4	$Rh_2(esp)_2$	CH_2Cl_2	$PhI(OAc)_2$ (1.5)	48
5	$Rh_2(esp)_2$	$Cl_2CHCHCl_2$	$PhI(OAc)_2$ (1.5)	32
6	$Rh_2(esp)_2$	toluene	$PhI(OAc)_2$ (1.5)	74
7	$Rh_2(esp)_2$	benzene	$PhI(OPiv)_2$ (1.5)	61
8	$Rh_2(esp)_2$	benzene	$PhI(OAc)_2$ (1.2)	72[c]
9	$Rh_2(esp)_2$	benzene	$PhI(OAc)_2$ (1.5)	69[d]
10	$Rh_2(esp)_2$	benzene	$PhI(OAc)_2$ (1.5)	80[e]
11	$Rh_2(esp)_2$	benzene	$PhI(OAc)_2$ (1.5)	79[f]

[a] Reaction conditions, unless otherwise mentioned: **2a** (1.0 equiv.), iodine(III) oxidant (1.5 equiv.), Rh^{II} catalyst (2 mol-%), MgO (2.5 equiv.), solvent (0.12 M), 80 °C, 20 h. [b] Yield of isolated product. [c] After 3 days of reaction. [d] Without MgO. [e] After 18 h at r.t. [f] After 4 h at 80 °C.

We tested the reactivity of other *N*-protected carbamimidates, albeit unsuccessfully, as the *N*-sulfonyl- and *N*-alkoxycarbonyl derivatives proved either unstable or unreactive under the oxidizing conditions of the intramolecular reaction (Figure 1). The best conditions reported in Table 1 (entry 11) were then applied to study the scope of the reaction with respect to the alkyl side chain of *N*-Tces-carbamimidates **2** (Table 2).

Table 2. Catalytic intramolecular C(sp^3)–H amination of carbamimidates **2**.[a]



Entry	Substrate	Product	Yield[b]
1	 **2a**	 **3a**	80
2	 **2b**	 **3b**	55
3	 **2c**	 **3c**	58
4	 **2d**	 **3d**	68
5	 **2e**	 **3e**	68
6	 **2f**	 **3f**	32
7 8	 **2g**: R = Ph **2h**: R = Me	 **3g** **3h**	74 91
9	 **2i**	 **3i**	81
10 11	 **2j**: n = 1 **2k**: n = 2	 **3j** **3k**	85 99
12	 **2l**	 **3l**	84
13	 **2m**	 **3m**	63
14	 **2n**	 **3n**	41

[a] Reaction conditions: **2** (1.0 equiv.), $PhI(OAc)_2$ (1.5 equiv.), $Rh_2(esp)_2$ (2 mol-%), MgO (2.5 equiv.), benzene (0.12 M), 80 °C, 4 h. [b] Yield of isolated product.

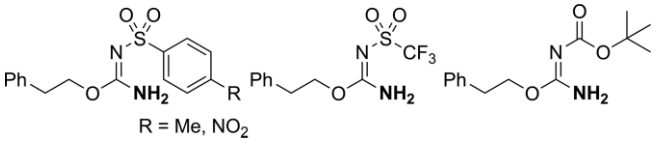
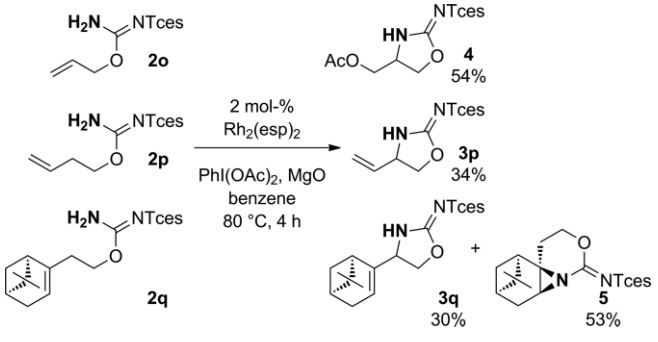


Figure 1. Other *N*-protected carbamimidates.

We found that the rhodium-catalyzed intramolecular C(sp^3)–H amination reaction could be applied to various classes of carbamimidates. Several aromatic substrates substituted by either an electron-donating or an electron-withdrawing group at the *ortho* or *para* position were converted into the corresponding cyclic carbamimidates **3** with yields ranging from 32 to 80 %, following reaction at the secondary benzylic position (Table 2, entries 1–6). In the case of substrates displaying a tertiary site, the reaction was even more efficient, and products **3g**–**i** were obtained in excellent yields (Table 2, entries 7–9). Worthy of note is the stereospecificity of the intramolecular C(sp^3)–H amination with optically pure substrate **2i** (see the Supporting Information for the X-ray structure), which is in line with that demonstrated for carbamates, sulfamates, and other nitrene precursors.[15,16,22] The high capacity of the carbamimidates to undergo reaction at tertiary centers was applied to the formation of azaspirocycles, which are currently receiving growing attention in medicinal chemistry.[23] Spirocyclic carbamimidates **3j**–**l** were thus isolated in 84–99 % yield (Table 2, entries 10–12). Compound **3l** highlights the propensity of carbamimidate-derived nitrenes to undergo C(sp^3)–H insertion α to a heteroatom. However, the analogous reaction from substrate **2m** only led to 2-aminooxazole **3m**, which was isolated in 63 % yield (Table 2, entry 13). This compound is believed to result from a first intramolecular C(sp^3)–H amination step α to the methoxy group followed by elimination of the methoxy group. Product **3n** demonstrates that carbamimidates can undergo propargylic C(sp^3)–H amination, though with moderate efficiency (Table 2, entry 14).[11,13j,13n]

We also investigated the reactivity of unsaturated substrates, as these raise the key issue of chemoselectivity, that is, the reactivity of the allylic C(sp^3)–H bond versus that of the π bond. However, as previously observed with various nitrene precursors in the presence of dirhodium(II) tetracarboxylates,[15,16b] low levels of chemoselectivity were observed (Scheme 3). We first checked that the alkene of allylic substrate **2o** could react under the optimized conditions. Not surprisingly, compound **4**, which is the product of alkene oxyamination, was isolated in 54 % yield.[24] We were pleased to notice that the homoallylic derivative **2p** gave the expected allylic amine **3p**, though only in 34 % yield.[25] By contrast, the nopol-derived carbamimidate **2p** afforded a ≈1:1.6 mixture of allylic amine **3q** and aziridine **5**.



Scheme 3. Intramolecular C(sp^3)–H amination of unsaturated carbamimidates.

Conclusions

In conclusion, this study demonstrated that carbamimidates are relevant nitrene precursors that allow the scope of the rhodium(II)-catalyzed intramolecular C(sp^3)–H amination reaction to be enhanced. Their reaction in the presence of $PhI(OAc)_2$ and the highly active $Rh_2(esp)_2$ (2 mol-%) complex afforded new heterocyclic structures in yields up to 99 %. Relative to the yields obtained with analogous carbamates, the slightly higher yields observed with carbamimidates suggest a beneficial effect of the imidoyl group on the reactivity of the nitrene, as previously shown with sulfonimidamides.[18] Work is in progress to increase the molecular diversity accessible through the application of catalytic C(sp^3)–H amination.

Experimental Section

General Procedure: An oven-dried sealable tube equipped with a stirring bar and flushed with argon was charged with acyclic carbamimidate **2** (1.0 equiv.), $Rh_2(esp)_2$ (2 mol-%), MgO (2.5 equiv.), benzene, and $PhI(OAc)_2$ (1.5 equiv.). The mixture was stirred at 80 °C for 4 h before it was filtered through a Celite pad (CH_2Cl_2). The filtrate was then concentrated under reduced pressure to afford the crude product, which was purified by flash chromatography (petroleum ether/EtOAc).

Acknowledgments

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Keywords: Amination · Nitrenes · Homogeneous catalysis · Rhodium · Nitrogen heterocycles

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