Carbenes

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Versatile Reactivity of Rhodium–Iminocarbenes Derived from *N*-Sulfonyl Triazoles**

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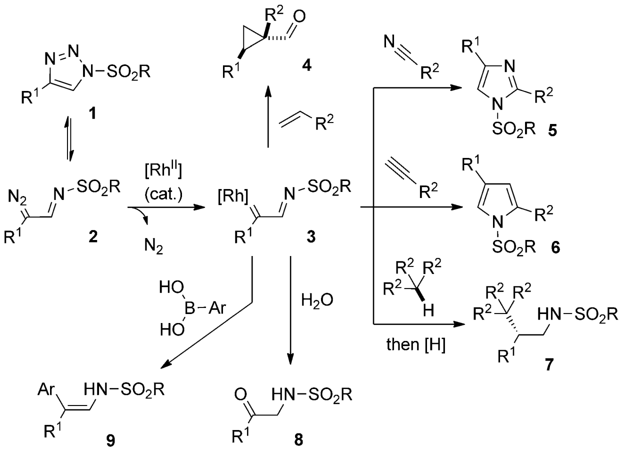
Rhodium-stabilized carbenes possess diverse reactivity in a variety of organic transformations, such as addition to C=C and C=heteroatom multiple bonds, insertion into C–H and C–heteroatom bonds, as well as ylide formation.[1] However, this powerful chemistry is mostly limited to rhodium carbenes derived from the corresponding diazo compounds. Obviously, development of new and efficient methods to access Rh carbenoids from alternative and stable precursors could expand the scope of this chemistry.

It is known that the stability of the 1,2,3-triazole ring is affected by the substituents at the N1, C4, and C5 atoms of the heterocycle.[2] For example, triazoles **1** that bear a sulfonyl group at the N1 atom exist in equilibrium with diazoimine tautomer **2**.[3] Gevorgyan and Fokin took advantage of this process by trapping diazoimine **2** with a Rh^{II} catalyst to produce the putative Rh^{II}–iminocarbene **3** (Scheme 1).[4] This intermediate possessed reactivity inherent for Rh^{II} carbenoids. For example, it reacted with alkenes to form cyclopropane derivatives **4**.[4] Later, this process was performed by Fokin and co-workers in a highly enantioselective manner.[5] On the other hand, the presence of the imino group at the α-position of **3** opens opportunities for novel heterocyclizations. Thus, the transannulation[6] reaction of *N*-sulfonyl triazoles with nitriles produced imidazoles **5**,[4] whereas the reaction with alkynes[7a] led to pyrroles **6**.[7b] As shown by Fokin and co-workers, Rh–iminocarbene **3** could also undergo insertion into a secondary or tertiary C–H bond of alkanes (as a solvent) to produce valuable β-chiral amines **7** in high yields and enantioselectivities.[8a] In 2012, Murakami reported an efficient Rh^{II}-catalyzed hydration of triazoles **1** to form α-aminoketones **8**, proceeding through insertion of the Rh^{II}–iminocarbene intermediate into the O–H bond of water.[8b] Shortly after, Fokin and co-workers disclosed the Rh^{II}-catalyzed reaction of *N*-sulfonyl triazoles **1** with arylboronic acids, thus stereoselectively furnishing enamines **9**.[8c] Noteworthy, the *N*-sulfonyl triazole precursors are easily available by Cu-catalyzed alkyne–azide cycloaddition (CuAAc) reaction,[9] which makes this approach to Rh-stabilized carbenes attractive for the synthesis of valuable carbo- and heterocyclic molecules (Scheme 1).



Scheme 1. Use of *N*-sulfonyl triazole to form Rh–iminocarbene.

Very recently, the groups of Murakami[10] and Fokin[11] independently reported the Rh^{II}-catalyzed denitrogenative rearrangement of 1-(*N*-sulfonyl-triazol-4-yl)alkanols **10**, proceeding through migration of different groups to the Rh–carbene center of **12**. The subsequent elimination of rhodium from the **12** produces iminoenol **14**, which is converted to *Z*-substituted enaminone **11** upon facile proton transfer (Scheme 2).

In general, the migratory aptitude of different groups to the Rh–carbene center derived from a diazo compound follows the common tendency: hydride > phenyl > primary alkyl > secondary alkyl groups.[12] Likewise, in the transformation **12**→**13**, the 1,2-migration of hydride is favored over the 1,2-shift of alkyl and phenyl groups (Table 1, entries 1 and 2, respectively). The phenyl group, in turn, migrates more easily than the methyl group (entry 3), whereas the methyl group migrates more easily than the isopropyl group (entry 4). Furthermore, cyclic 1-triazolylalkanols **10f** underwent efficient ring expansion to produce the corresponding cyclic enaminones **11f** (entries 7 and 8). The reaction of fluorenol derivative **10g** led almost quantitatively to the corresponding hydroxyphenanthrene derivative **11g** (entries 9 and 10). In most cases, a predominant formation of the *Z*-stereoisomer was observed, which can be attributed to the concerted transformation **14**→**11** (kinetic control), and to the higher

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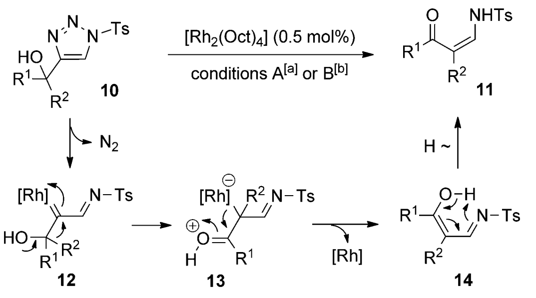
stability of the *Z*-stereoisomer as a result of an additional stabilization through intramolecular hydrogen bonding (thermodynamic control).

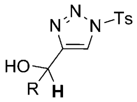
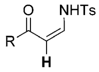
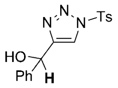
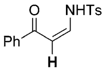
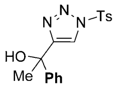
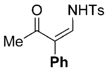
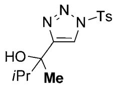
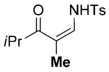
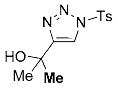
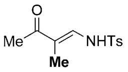
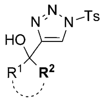
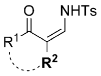
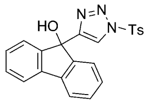
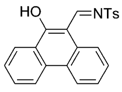
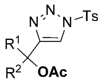
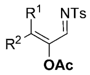
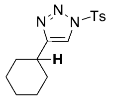
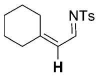
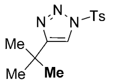
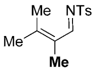
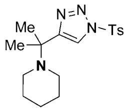
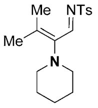
Interestingly, protection of the hydroxy group as acetate enabled its selective migration to the carbene center to form products **16** (entry 11). It was also shown that 4-cyclohexyl and 4-*tert*-butyl triazoles gave the products of hydride and methyl group migration (**18a** and **18b**, respectively) under these reaction conditions (entries 12 and 13). Moreover, Fokin and co-workers reported the first example of amine migration to the Rh^{II} carbenoid center. Thus, the reaction of 4-alkylamino triazole **17c** produced the corresponding enamine **18c** in good yields (entry 14).[11]

In conclusion, the Rh^{II}–iminocarbenes, derived from the corresponding *N*-sulfonyl 1,2,3-triazoles, could be used in several transformations inherent for metal carbenoids. Thus, cyclopropanation of alkenes, reactions with alkynes, nitriles, and boronic acids, as well as insertion into C–H and O–H bonds were impressively developed. In addition, the recent reports also disclosed migrations of different groups to the Rh^{II}–carbene center of imino carbenoids. The *N*-sulfonyl 1,2,3-triazole precursors are easily available by CuAAc reaction of alkynes with azides, which makes this approach very useful for straightforward generation of Rh^{II} carbenoids. Some transformations could even be efficiently performed in a one-pot manner starting from alkynes and sulfonyl azides. Therefore, the reactivity of Rh^{II}–iminocarbenes can be tuned easily by variation of substituents in the parent triazole through the simple CuAAc approach. Moreover, a natural low concentration of diazoimine, which exists in equilibrium with triazoles, maintains a low concentration of the reactive Rh^{II} carbenoid, which obviates the necessity of slow-addition techniques that are often required in the reactions of diazo compounds.



Scheme 2. The Rh^{II}-catalyzed rearrangement of triazolyl alcohols. Conditions A (Miura and Murakami[10]): $CHCl_3$, 140 °C, microwave, 15 min. Conditions B (Fokin[11]): $CHCl_3$, 70 °C, 5–60 min. Oct = octanoate, Ts = 4-toluenesulfonyl.

Table 1: Migrations of different groups to the metal–carbene center of Rh^{II}–iminocarbenes (see Scheme 2).

Entry	Triazole		Product		Results
1[a,c]		**10a**		**11a**	79–94 %
2[a]		**10b**		**11b**	58 % (25 % 1,2-Ph migration)
3[a]		**10c**		**11c**	86 %, $E/Z = 12{:}88$ (5 % 1,2-Me migration)
4[a]		**10d**		**11d**	47 %, $E/Z = 24{:}76$ (19 % 1,2-*i*Pr migration)
5[a] 6[b]		**10e**		**11e**	90 %, $E/Z = 88{:}12$ 92 %, $E/Z = 75{:}25$
7[a,d] 8[b,d]		**10f**		**11f**	74–98 % 71–95 %
9[a] 10[b]		**10g**		**11g**	96 % 95 %
11[b,e]		**15**		**16**	92–96 %
12[b]		**17a**		**18a**	96 %
13[b]		**17b**		**18b**	91 %
14[b]		**17c**		**18c**	71 %

[a] Conditions A (Miura and Murakami, Ref. [10]): $CHCl_3$, 140 °C, microwave, 15 min. [b] Conditions B (Fokin, Ref. [11]): $CHCl_3$, 70 °C, 5–60 min. [c] R = Me, *n*Pr, *i*Pr, *t*Bu. [d] R^1,R^2 = alkyl. [e] R^1,R^2 = Me, $-C_5H_{10}-$.

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[11] N. Selander, B. T. Worrell, V. V. Fokin, *Angew. Chem.* **2012**, *124*, 13231 – 13234; *Angew. Chem. Int. Ed.* **2012**, *51*, 13054 – 13057.

[12] For migration of different groups to Rh–carbene centers, see Ref. [10] and references therein.