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Rhodium(II)-Alkynyl Carbenoids Insertion into Si−H bonds: An Entry to Propargylic Geminal Bis(silanes)

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Supporting Information

ABSTRACT: α-Alkynyl-α'-trimethylsilylhydrazones are used as novel Rh(II)-carbenoids precursors. These new carbenoids have shown very good reactivity in Si−H insertion reactions, leading to original propargylic geminal-bis(silanes) in a two-step sequential process.

Transition metal carbenoids are very versatile intermediates in organic synthesis.[1] Among them, rhodium carbenes derived from diazocompounds and rhodium(II) catalysts have been reported to participate in multiple transformations.[2] According to the well-established classification popularized by Davies, the reactivity of these species strongly relies on the nature of the substituents adjacent to the carbene center (Figure 1).[3]

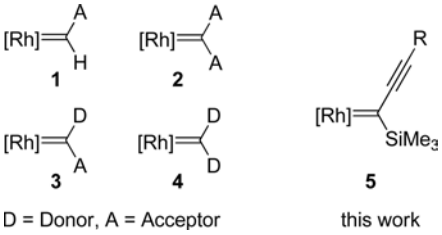
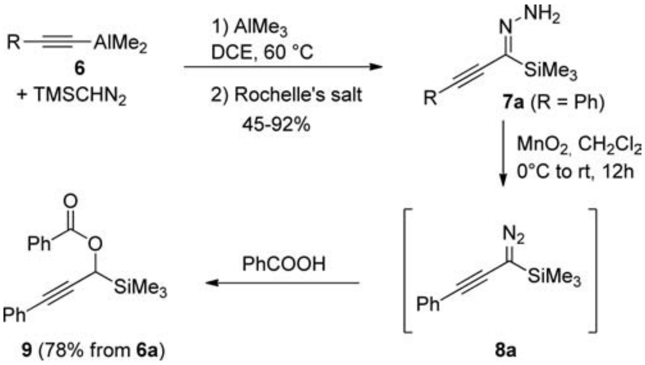


Figure 1. Classes of rhodium carbenoid intermediates and carbenes investigated in this study.

"Donor" groups (vinyl, aryl, alkynyl, heteroaryl) are expected to make the carbenoid more stable and chemoselective, whereas "acceptor" groups (carbonyl, sulfonyl, cyano, etc.) increase the reactivity of these species by enhancing their electrophilic character. A wide range of reactions starting from diazocompounds bearing a combination of these substituents have been reported, with a recent emphasis on the use of donor−acceptor carbenes for selective intermolecular insertion reactions.[4] Surprisingly, although the alkynyl group is described in reviews to behave as a donor substituent for carbenoid intermediates, the use of alkynyldiazo compounds in Rh(II) catalyzed insertion reactions has never been described and only a single example of cyclopropanation based on such a reagent has been reported.[5] Similarly, despite the stability provided to diazocompounds by a trimethylsilyl group, the reactivity studies of Rh(II) α-silylated carbenoids generated from this class of reagents are rare.[6] We recently described a general access to α-silylated alkynylhydrazones from mixed dimethylalkynylaluminum reagents and trimethylsilyl (TMS) diazomethane (Scheme 1).[7] We report herein that these derivatives can lead to the corresponding diazo compounds and serve as new precursors for Rh(II)-catalyzed Si−H insertion reactions,[8] leading to propargylic bis(silanes). Although the reactivity of allylic bis(silanes) has been described,[9] the reactivity of their propargylic analogues has received little attention to date.[10]

Scheme 1. Previous Report on the Synthesis of α-Silylated Alkynyl Hydrazones and First Example of Diazo Preparation (ref 7)



Our initial report on the preparation of diazo **8a** from hydrazone **7a** using manganese dioxide (MnO_2) showed that the purification of compound **8** could be difficult. We therefore envisaged carrying out the insertion reaction immediately after the oxidation step, in a one pot procedure as reported by Shaw,[11] or in a sequential manner, with or without filtration between the two steps. For this purpose we first investigated the oxidation step in various solvents and found that this reaction proceeds smoothly at −15 °C within 2 h in solvents such as dichloroethane (DCE), toluene, and pentane (Table 1). A slow degradation of the starting material could be noticed

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when the oxidation was conducted at lower temperature, and the use of acetonitrile only led to degradation.

Table 1. Optimization of Metal-Catalyzed Carbene Si–H Insertion[a]

entry	solvent	catalyst	temp (°C)	time (h)	yield[b] (%)
1[c]	DCE	$Rh_2(OAc)_4$	rt	16	11
2[d]	DCE	$Rh_2(OAc)_4$	rt	16	16
3[e]	DCE	$Rh_2(OAc)_4$	rt	16	36
4[e]	DCE	Rh_2DOSP_4	rt	16	traces
5[e]	DCE	CuCl	rt	16	18
6[e]	DCE	$Cu(OTf)_2$	rt	16	21
7[f]	DCE	$Cu(OTf)_2$	rt	16	23
8[f]	DCE	$Pd(OAc)_2$	rt	16	25[g]
9[f]	DCE	$Rh_2(OAc)_4$	−30	3	45
10[f]	toluene	$Rh_2(OAc)_4$	−30	3	45
11[f]	toluene	$Rh_2(OAc)_4$	−30	3	42[h]
12[f]	toluene	$Rh_2(OAc)_4$	−78 to rt	3 + 16	54[i]
13[f]	toluene	$Rh_2(esp)_2$	−78 to rt	3 + 16	61[i]
14[f]	toluene	$Rh_2(TFA)_2$	−78 to rt	3 + 16	n.d.[i]
15[f]	pentane	$Rh_2(esp)_2$	−78 to rt	3 + 16	25[i]

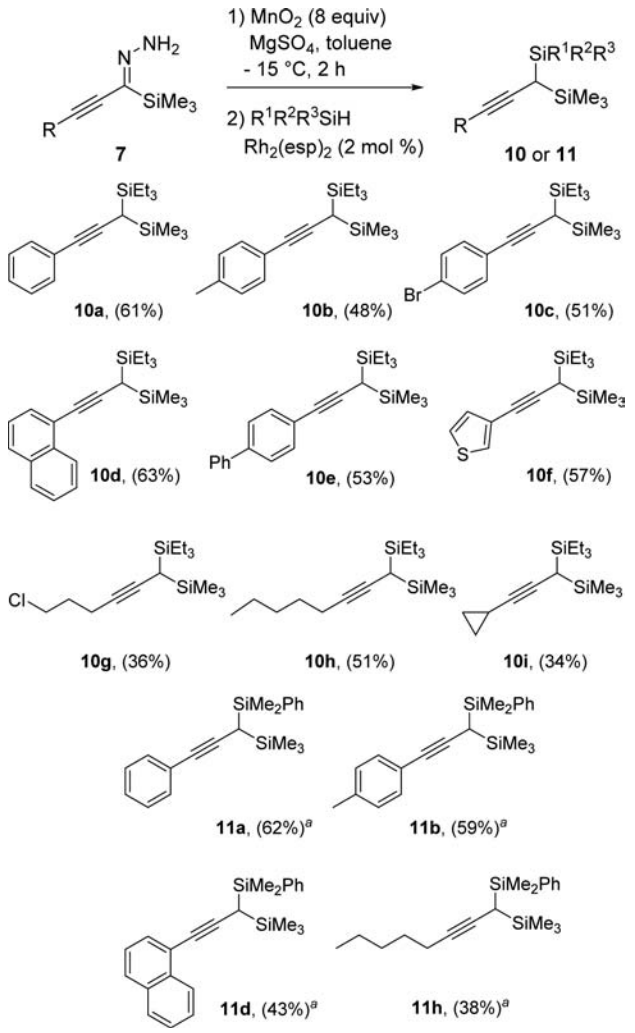
[a] The reaction was carried out with **7a** (0.2 mmol). [b] Isolated yield from **7a**. [c] The two steps were carried out in one pot, at 0.025 M, with 1 equiv of Et_3SiH. [d] The two steps were carried out in one pot, at 0.01 M, with 1 equiv of Et_3SiH. [e] The two steps were carried out in one pot, at 0.01 M, with 10 equiv of Et_3SiH. [f] The two steps were carried out in the same pot, but in a sequential manner with removal of the Mn salts by filtration, at 0.01 M, with 10 equiv of Et_3SiH. [g] A mixture of Si–H insertion regioisomeric products was isolated resulting from a [1,3]-metallotropic shift of the alkynyl palladium carbenoid. [h] Slow addition of the diazo compound for 3 h. [i] 3 h at −78 °C and then 16 h at rt.

The optimization of the reaction sequence was first investigated on hydrazine **7a** using $Rh_2(OAc)_4$ as a catalyst. The reaction proceeded in a one-pot fashion at 0.025 M (entry 1) or 0.01 M concentration (entry 2), with 1 equiv of triethylsilane. The yield could be improved if an excess (10 equiv) of silane was used (entry 3). Only traces of insertion product could be detected using the chiral catalyst Rh_2DOSP_4 (entry 4).[12] The use of copper (entries 5–7) or palladium (entry 8) salts proved to be less efficient. The best results were obtained when removing solid residues by filtration between the oxidation and the insertion steps (entry 9) and by conducting the second step at lower temperature. Finally, better results were obtained using $Rh_2(esp)_2$ as a catalyst and conducting the insertion step at −78 °C in toluene (entry 14).

Interestingly, no sign of isomeric insertion product arising from a possible [1,3]-metallotropic shift of the alkynyl metal carbenoid was observed.[13] This high selectivity might be explained by a stabilizing effect of the carbon–metal bond by the vicinal TMS group.

The scope of the reaction was then investigated (Scheme 2)

Scheme 2. Scope of Rh(II)-Catalyzed Insertion into Si–H Bonds



[a] The reaction was carried out with 1 equiv of $PhMe_2SiH$ (0.2 mmol).

In all the cases, hydrazones **7a–i** were prepared according to our previously reported method[7] and were converted smoothly to the corresponding disilanes **10** or **11** in a sequential two-step fashion in yields over two steps from 34% to 63%. The optimized reaction conditions were found to be suitable for various aromatic derivatives including substrates bearing an electron-donating (**7b**) or electron-withdrawing group (**7c**) giving desired disilanes **10b** and **10c** in 48% and 51% yields, respectively. The introduction of 1-naphthyl- (**10d**), 1,1′-biphenyl (**10e**), or 3-thiophenyl (**10f**) groups on the alkylnyl moiety did not change the outcome of the reaction, and these disilanes were obtained in 63%, 53%, and 57% yields, showing tolerance of the reaction against aromatic group modifications. Interestingly, this two-step process was found to be very chemoselective, as no Büchner-type reaction byproduct could be observed while using aromatic substrates.[14] Alkyl-substituted α-alkynylhydrazone reactivities were also investigated, and substrates containing linear chains **7g** and **7h** led to the desired disilanes **10g** and **10h** in 36% and 51% yields, respectively. However, α-alkynylcyclopropyl-α-TMS-hydrazone **7i** was found to be a difficult substrate in our hands and only 34% of the volatile disilane **10i** could be obtained. We next examined the possibility of extending our method to the insertion of Rh-carbenoid into various Si–H bonds.[8] We were pleased to find that phenyldimethylsilane reacted smoothly with various aromatic and aliphatic α-alkynyl-α-TMS-hydrazones **7a**,**b**, **7d**, and **7h** and gave the corresponding disilanes in good yields. In these cases, optimal results were obtained using only 1 equiv of the silane. A complex mixture was obtained when Chatgilialoglu reagent (tris(trimethylsilyl)silane)[15] was used.

Since "donor–donor" carbenoids are seldom used in intermolecular reactions, we investigated the reactivity of carbenoids **5** in other insertion reactions (Scheme 3). As expected, the stabilizing effects of the alkynyl and silyl substituents lower the reactivity of the rhodium carbenoid in O–H, N–H, and C–H insertion reactions. Rhodium- or copper-catalyzed cyclopropanation of alkenes or alkynes also proved to be unsuccessful. All these results outline the low electrophilicity of the carbenoids of type **5** that selectively react with Si–H bonds and suggest that stronger electron-withdrawing ligands are required to expand the reactivity scope of carbenoids derived from alkynyl silylated diazo compounds.

Scheme 3. Scope of Rh(II)-Catalyzed Intermoleculer Insertion Reactions

In conclusion, we have shown that Rh(II) α-silylated alkynyl carbenoids, prepared from the corresponding diazo, can insert in a selective manner into Si–H bonds. This unprecedented reaction provides a simple and general access to propargylic geminal bis(silanes) bearing two different silicon moieties at the propargylic carbon.[16] The reactivity of these new reagents is currently under investigation in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02264.

General experimental procedures and analytical data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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