Letter

Rhodium-Catalyzed Si–H Bond Insertion Reactions Using Functionalized Alkynes as Carbene Precursors

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Rhodium-Catalyzed Si–H Bond Insertion Reactions Using Functionalized Alkynes as Carbene Precursors

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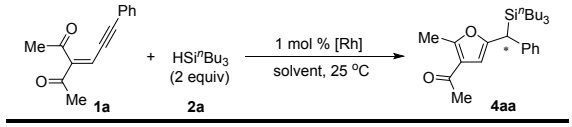
ABSTRACT: Enantioselective transition-metal-catalyzed carbene insertion into Si–H bonds is a promising method for preparing chiral organosilicons; however, all the carbene precursors used to date in this reaction have been diazo compounds, which significantly limits the structural diversity of the resulting chiral organosilicons. Herein, we report a protocol for rhodium-catalyzed asymmetric Si–H bond insertion reactions that use functionalized alkynes as carbene precursors. With chiral dirhodium tetracarboxylates as catalysts, the reactions of carbonyl-ene-ynes and silanes smoothly gave chiral organosilanes in high yields (up to 98%) with excellent enantioselectivity (up to 98% ee). Kinetic studies suggest that insertion of the in situ generated rhodium carbenes into the Si–H bonds of the silanes is probably the rate-determining step. This work represents the first enantioselective Si–H bond insertion reaction using alkynes as carbene precursors and opens the door for preparing chiral organosilicons with unprecedented structural diversity from readily available alkynes.
KEYWORDS: Asymmetric synthesis, chiral organosilicons, rhodium carbenes, Si–H bond insertion, alkynes

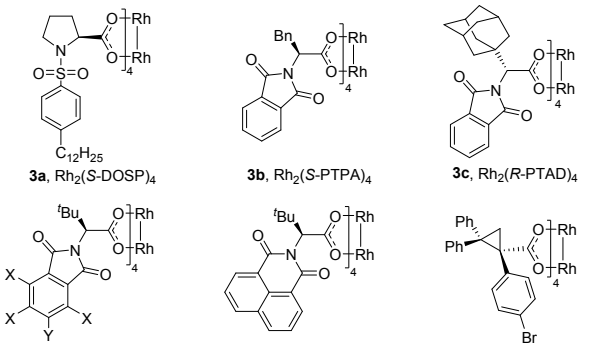
Organosilicon compounds have broad applications in the fields of materials science,[1a] agricultural chemistry,[1b] pharmaceutical chemistry,[1c] and organic synthesis.[1d–1f] The preparation of structurally diverse chiral organosilicon compounds can be expected to increase the utility of these compounds, and various asymmetric catalytic approaches have been developed for this purpose. Typical methods include desymmetrization of silanes,[2] asymmetric hydrosilylation,[3] and asymmetric silyl conjugated addition.[4] Enantioselective transition-metal-catalyzed insertion of carbenes into the Si–H bond of silanes is another straightforward route to organosilicon compounds with α-chiral centers.[5] Since Doyle and Moody's seminal work on rhodium-catalyzed asymmetric Si–H bond insertion reactions with diazo compounds as carbene precursors in 1996,[5b] extensive studies have revealed that chiral catalysts based on rhodium,[5b–5e] copper,[5f,5g] iridium,[5h,5i] ruthenium,[5j] iron,[5k] and even enzymes generated by directed evolution[5l] can afford good, high or excellent enantioselectivity in this reaction. However, despite significant progress, the carbene precursors used in asymmetric Si–H bond insertion reactions are strictly limited to stabilized diazo compounds, and therefore the structural diversity of the resulting chiral organosilicon compounds is poor. Recently, alkynes have emerged as promising carbene precursors when activated by π-acidic transition-metal catalysts, and alkynes have been successfully used for an increasing number of carbene-transfer reactions,[6] including some asymmetric versions.[7] Compared to diazo compounds,[8] alkynes are safe and readily accessible and can be used to generate carbenes with better structural diversity because there is no particular need for stabilization.

Although there have been several reports of Si–H bond insertion reactions using alkynes as carbene precursors,[9] the enantioselective version of this reaction remains unknown to the best of our knowledge. Herein, we report a highly enantioselective rhodium-catalyzed Si–H bond insertion reaction that uses alkynes as carbene precursors. In the presence of chiral dirhodium tetracarboxylate catalysts, asymmetric Si–H bond insertion reactions of carbenes generated *in situ* from carbonyl-ene-ynes smoothly gave furan-2-ylmethylsilanes in high yields with excellent enantioselectivities.

We began by exploring the reaction of carbonyl-ene-yne **1a** with tributylsilane **2a** in the presence of dirhodium tetracarboxylates **3** (1 mol %) in 1,2-dichloroethene (DCE) at 25 °C. (Table 1). All of the tested dirhodium tetracarboxylates promoted the reaction and gave high yields of desired product **4aa** (entries 1–8); however, the enantioselectivity depended strongly on the nature of the chiral ligand. Rh_2(*S*-DOSP)$_4$, which has *N*-sulfonylprolinate ligands,[10] gave a racemic product (entry 1); and Rh_2(*S*-PTPA)$_4$, Rh_2(*R*-PTAD)$_4$, Rh_2(*S*-PTTL)$_4$, Rh_2(*S*-*tert*PTTL)$_4$, Rh_2(*S*-TBPTTL)$_4$, and Rh_2(*S*-NTTL)$_4$, which have imide-type ligands,[11] gave low to moderate enantioselectivities (entries 2–7). Rh_2(*R*-BTPCP)$_4$, which has triarylcyclopropane carboxylate ligands,[12] exhibited the best enantioselectivity (90% ee), but the reaction was relatively slow (entry 8). In addition to DCE, CH_2Cl_2, $CHCl_3$, chlorobenzene, and toluene were suitable solvents (entries 9–12). In contrast, a reaction performed in THF, a coordinative solvent, failed to give the desired product (entry 13). The enantioselectivity could be improved to 96% ee by decreasing the reaction temperature to 0 °C (entry 14).

Table 1. Rhodium-catalyzed Asymmetric Si–H Bond Insertion Reaction of Alkynes with Silane HSi^nBu_3: Optimization of Reaction Conditions [a]





entry	[Rh]	solvent	t (h)	yield (%)[b]	ee[c]
1	**3a**	DCE	2	92	0
2	**3b**	DCE	2	90	12
3	**3c**	DCE	2	91	32
4	**3d**	DCE	4	94	13
5	**3e**	DCE	4	92	22
6	**3f**	DCE	4	83	12
7	**3g**	DCE	4	71	59
8	**3h**	DCE	10	92	90
9	**3h**	CH_2Cl_2	10	90	86
10	**3h**	$CHCl_3$	10	92	77
11	**3h**	PhCl	10	88	83
12	**3h**	toluene	10	89	84
13	**3h**	THF	10	N.D.[d]	--
14[e]	**3h**	DCE	20	92	96

[a] Reaction conditions: **3/1a/2a** = 0.002:0.2:0.4 (mmol), in 2 mL solvent. [b] Isolated yield. [c] The ee values were determined by HPLC. [d] N.D. = not detected. [e] Performed at 0 °C.

Various silanes were then evaluated in the Si–H bond insertion reaction with carbonyl-ene-yne **1a** to give insertion products **4** (Table 2). Less sterically hindered trialkylsilanes HSi^nBu_3, HSi^nPr_3, and $HSiEt_3$ afforded good results, although the enantioselectivity slightly decreased as the length of the alkyl chain decreased (entries 1–3). In contrast, the bulky trialkylsilane HSi^iPr_3 was essentially inactive (entry 4). The reaction with a phenyl silane $HSiMe_2Ph$ gave the desired product in high yield with good enantioselectivity (entry 5). As was the case for the trialkylsilane series, the bulkier phenyl silane $HSiPh_3$ showed a lower yield than the less bulky silane $HSiMe_2Ph$, but good enantioselectivity was retained (entry 6). Introduction of alkoxyl substituents to the silane substantially decreased its reactivity: the monoalkoxylsilane $HSiMe_2OEt$ gave a moderate yield and good enantioselectivity (entry 7), whereas the di- and trialkoxylsilanes $HSiMe(OEt)_2$ and $HSi(OEt)_3$ gave only complex mixtures containing none of the desired Si–H bond insertion product (entries 8 and 9). The disubstituted silane H_2SiPh_2 could be used as a Si–H donor, but the yield and ee value were only modest (entry 10). The monosubstituted silane H_3SiPh gave a messy result with only a trace of the desired product (entry 11). To sum up, the reactivity of the silanes was strongly related to their steric bulk as well as their electronic properties: less bulky silanes and silanes with electron-rich Si atoms generally exhibited better results.

Table 2. Rhodium-catalyzed Asymmetric Si–H Bond Insertion Reactions of Alkyne 1a and Various Silanes [a]

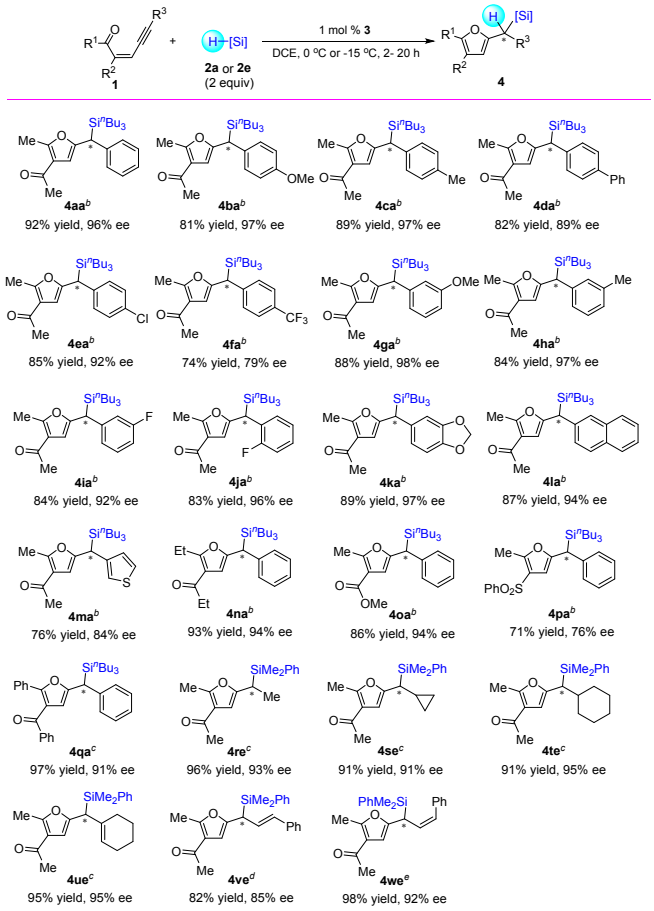
entry	H-[Si]	t (h)	yield (%)[b]	ee (%)[c]
1	HSi^nBu_3 (**2a**)	20	92	96
2	HSi^nPr_3 (**2b**)	20	87	95
3	$HSiEt_3$ (**2c**)	20	85	92
4	HSi^iPr_3 (**2d**)	24	trace	N.A. [d]
5	$HSiMe_2Ph$ (**2e**)	10	94	88
6	$HSiPh_3$ (**2f**)	24	7	92
7[e]	$HSiMe_2OEt$ (**2g**)	24	65	85 (*S*) [f]
8[e]	$HSiMe(OEt)_2$ (**2h**)	24	N.D. [g]	N.A.
9[e]	$HSi(OEt)_3$ (**2i**)	24	N.D.	N.A.
10[e]	H_2SiPh_2 (**2j**)	20	38	56
11[e]	H_3SiPh (**2k**)	20	trace	N.A.

[a] Reaction conditions: **3h/1a/2** = 0.002:0.2:0.4 (mmol), in 2 mL DCE at 0 °C. [b] Isolated yield. [c] The ee values were determined by HPLC. [d] N.A. = not analyzed. [e] Performed at 25 °C. [f] The absolute configuration was determined by oxidation of **4ag** to corresponding chiral alcohol and comparison of the specific rotation of the alcohol with the literature value.[7h] See supporting information (SI) for details. [g] N.D. = not detected.

The substrate scope of the reaction with respect to the carbonyl-ene-yne (**1**) was then investigated (Scheme 1). Generally, reactions of aryl-terminated carbonyl-ene-ynes (R^3 = aryl) performed well with catalysis by Rh_2(*R*-BTPCP)$_4$ whereas the alkyl- or alkenyl- terminated substrates (R^3 = alkyl or alkenyl) not (see SI for details). The aryl-terminated carbonyl-ene-ynes could bear a variety of substituents at different position of the aryl ring (**4ba**–**4ja**). Substrates with *para* electron-donating groups showed better enantioselectivity (**4ba**–**4ca**) than substrates with *para* electron-withdrawing groups or a *para* phenyl group (**4da**, **4ea**, **4fa**). In addition to a substituted phenyl ring, R^3 could also be a fused-ring moiety (**4ka**, **4la**) or a heteroaromatic ring (**4ma**). In addition to an acetyl group (**4aa**–**4ma**), R^2 could be a propionyl group (**4na**), an ester (**4oa**), a sulfonyl group (**4pa**), or a benzoyl group (**4qa**). However, reaction of the benzoyl substrate required the use of Rh_2(*S*-*tert*PTTL)$_4$ instead of Rh_2(*R*-BTPCP)$_4$ to achieve a satisfactory outcome. Similarly, when R^3 was changed from an aryl group to an alkyl group (**4re**, **4se**, **4te**) or a

cyclohexenyl group (**4ue**), good results could be obtained by using Rh_2(*S*-*tert*PTTL)$_4$ as a catalyst and $HSiMe_2Ph$ as the Si–H bond donor. The Si–H bond insertion reactions of two substrates with an *E*- or *Z*-cinnamnyl group at R^3 also afforded satisfactory results (**4ve** and **4we**) when Rh_2(*S*-NTTL)$_4$ and Rh_2(*S*-TBPTTL)$_4$, respectively, were used as catalysts.

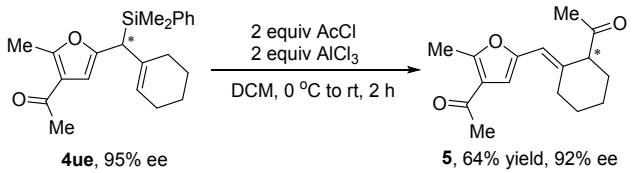
Scheme 1. Rhodium-catalyzed Asymmetric Si–H Bond Insertion Reactions of Carbonyl-ene-ynes 1 with Silanes 2a or 2e [a]



[a] Reaction conditions: **3**/**1**/**2** = 0.002:0.2:0.4 (mmol), in 2 mL of DCE. Isolated yield was given. The ee values were determined by HPLC. [b] Used Rh_2(*R*-BTPCP)$_4$ (**3h**) as catalyst and performed at 0 °C. [c] Used Rh_2(*S*-*tert*PTTL)$_4$ (**3e**) as catalyst and performed at -15 °C. [d] Used Rh_2(*S*-TBPTTL)$_4$ (**3f**) as catalyst and performed at -15 °C. [e] Used Rh_2(*S*-NTTL)$_4$ (**3g**) as catalyst and performed at -15 °C.

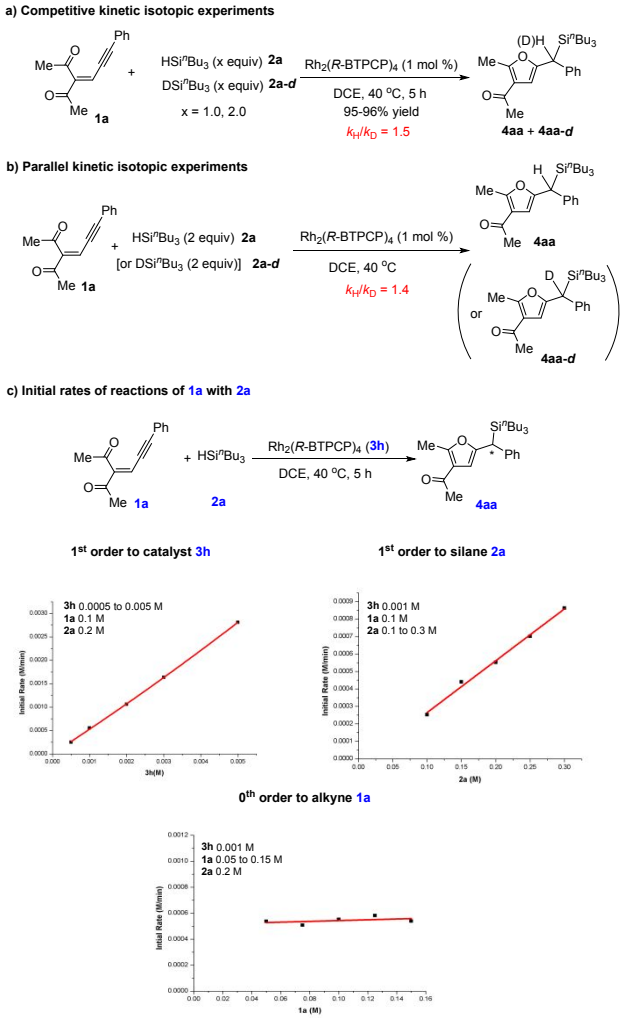
The allylic acylation[13] of Si–H bond insertion product **4ue** smoothly gave the corresponding ketone **5** with good retention of the ee value (Scheme 2). This transformation demonstrates the potential synthetic utility of the protocol described herein.

Scheme 2. Transformation of the Product 4ue



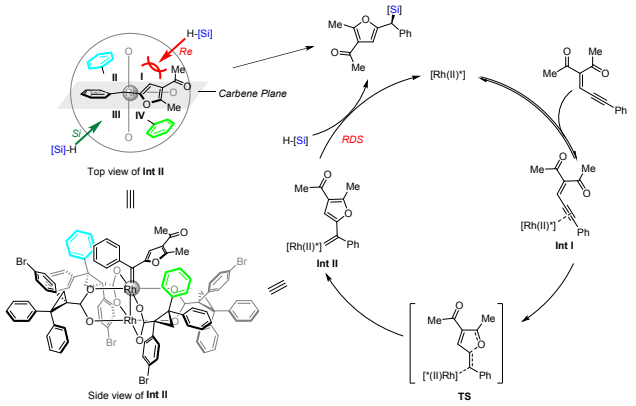
To shed light on the reaction mechanism, we carried out some *in situ* IR experiments using the Rh_2(*R*-BTPCP)$_4$-catalyzed reaction of **1a** with **2a** and deuterated **2a** as models (Scheme 3). In the name of efficiency, the reactions were performed at 40 °C so that they were complete within 5 h. Competitive experiments carried out with equimolar amounts of **2a** and **2a-*d***, either 1.0 or 2.0 equivalents each, in the same pot afforded identical k_H/k_D values (1.5, Scheme 3a); and parallel experiments with **2a** or **2a-*d*** afforded a similar value (1.4, Scheme 3b). By analogy with Si–H bond insertion reactions involving diazo compounds,[14] the small but significant kinetic isotope effect observed in these experiments imply that Si–H bond cleavage is slow. To verify this implication, we carried out some kinetics experiments at various initial concentrations of carbonyl-ene-yne substrate **1a**, silane **2a**, and catalyst **3h** (Scheme 3c). By tracking the time courses of the concentration of **1a** as the initial concentrations of the three components were varied independently, we could calculate the initial rates of reaction of the components and determine the reaction orders with respect to each of the components. These results revealed that the initial reaction was first order with respect to the dirhodium catalyst and the silane and zeroth order with respect to the substrate **1a**. These values result in a rate equation of $r = k[\mathbf{3h}][\mathbf{2a}]$, which confirms that Si–H bond insertion process was most likely the rate-determining step.

Scheme 3. Kinetic Studies



In analogy with the mechanisms of other carbene-transfer reactions of carbonyl-ene-ynes,[6] we propose that the rhodium-catalyzed Si–H bond insertion reactions described herein proceed via the mechanism shown in Scheme 4. The rhodium catalyst first activates the alkyne by acting as a Lewis π-acid (**Int I**) to trigger a *5-exo-dig* cyclization that forms carbene intermediate (**Int II**), which undergoes a Si–H bond insertion reaction to afford the desired product. Again, the above-described kinetics studies indicate that the Si–H bond insertion is probably the rate-determining step. We put forward a model to explain the enantioselectivity of the Si–H bond insertion reaction using Rh$_2$(*R*-BTPCP)$_4$ as a catalyst. According to the structural studies of Rh$_2$(*R*-BTPCP)$_4$ and its carbene intermediate by Davies et al.,[12] we propose a structure of **int II**, in which two opposite ligands stay in upward directions while the other two in equatorial positions to minimize steric repulsions between the ligands and carbene residue. The two upward phenyl rings of ligands block region **II** and **IV** in front of rhodium center. Because **int II** is a donor-donor diaryl carbene, the more steric congested and electron-deficient furyl ring (resulting from the methyl and the electron-withdrawing acetyl substituents on the furyl ring) adopts a nearly perpendicular orientation to the carbene plane and blocks region **I**, whereas the less sterically congested phenyl ring aligns coplanar to the carbene plane to stabilize the rhodium carbene.[15] As a result, the silane favors to approach carbene center from region **III** and gives the insertion product with *S*-configuration through a *Si-face* attack.

Scheme 4. Proposed Mechanism and Stereoselective Induction Model



In summary, we have realized the first highly enantioselective rhodium-catalyzed Si–H bond insertion reactions using functionalized alkynes as carbene precursors. Kinetics studies revealed that a Si–H bond insertion reaction of an in situ generated rhodium carbene is most likely the rate-determining step. Our findings reveal that organosilicons can be prepared with high enantioselectivity from readily accessible alkynes, and this reaction will undoubtedly facilitate the synthesis of structurally diverse chiral organosilicons.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectral data, specific rotation and details of *in situ* IR experiments. The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

§ M.-Y. Huang and J.-M. Yang contributed equally to this work.

Notes

The authors declare no competing financial interest.

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DEDICATION

This paper is dedicated to the 100th anniversary of Nankai University.

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