Rhodium(I)-Catalyzed Highly Enantioselective Insertion of Carbenoid into Si−H: Efficient Access to Functional Chiral Silanes

Diao Chen, Dong-Xing Zhu, and Ming-Hua Xu*

State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, 555 Zuchongzhi Road, Shanghai 201203, China

S *Supporting Information*

ABSTRACT: The first rhodium(I)-catalyzed enantioselective Si−H insertion reaction of α-diazoesters and α-diazophosphonates has been developed. The use of a C_1-symmetric chiral diene ligand enabled the asymmetric reaction to proceed under exceptionally mild conditions and give versatile chiral α-silyl esters and phosphonates with excellent enantioselectivities (up to 99% ee). The mechanism and stereochemical pathway of this novel Rh(I)-carbene-directed Si−H insertion was investigated by deuterium kinetic isotope effect experiments and DFT calculations.

Organosilanes are frequently used in organic synthesis and medicinal chemistry.[1] Among them, α-chiral silanes are particularly valuable intermediates in stereoselective synthesis.[1d] Despite a growing focus toward synthetic efforts, access to chiral silanes in a highly enantioenriched form remains a great challenge and the development of new methods continues to be an active area of research. Recently, transition-metal-catalyzed enantioselective silyl addition to α,β-unsaturated carbonyl compounds,[2a−d] aldehydes,[2e] and aldimines[2f,g] using Suginome's $Me_2PhSiBPin$ as the silicon pro-nucleophile has emerged and been certified as a useful approach to obtain functional chiral silanes. Another direct and efficient approach that has been increasingly explored in recent decades is transition-metal-mediated asymmetric carbenoid insertion into the Si−H bond of silanes. Since the first report by Doyle and Moody in 1996,[3a] a series of rhodium(II),[3,4] copper(I)/(II),[5] and iridium(III) complexes[6] have been developed as suitable catalysts to promote asymmetric Si−H insertion. Notable advances have been achieved in this transformation with an α-diazoester at a relatively low temperature (−30 to −78 °C) by using unique copper(II)−spirodiimine[5c] and iridium(III)−salen complexes[6a] as catalysts. Surprisingly, although much attention has been given to the asymmetric Si−H insertion of rhodium(II) carbenoids relying in diverse chiral ligands such as carboxylates,[3a−f] carboxamidates,[3g] and phosphoric acids,[3h] excellent enantioselective control was only achieved in limited examples. In 1997, Davies and co-workers[3b] reported that rhodium(II) N-[p-(dodecylphenyl)sulfonyl]prolinate could catalyze the reaction of α-diazovinylacetate and dimethyl-phenylsilane with 77−95% ee. In 2006, Corey and Ge[3f] achieved the asymmetric Si−H insertion of α-diazocyclo-hexenone with 77−94% ee mediated by a rhodium(II) Nf-proline complex. In 2010, Ball and co-workers[3i] succeeded in

utilizing dirhodium(II) metallopeptide catalysts for asymmetric insertion of α-diazoarylacetates into Si−H bonds (up to 99% ee), but the selectivity was much lower for ortho-substituted aryl substrates (20−49% ee), leaving room for improvement. Given these facts, it is still very desirable to design and develop new effective catalysts for highly efficient and general asymmetric Si−H insertion, particularly under mild and user-friendly conditions.

In contrast to the widely studied rhodium(II) carbenoid transformations, the Rh(I)−carbene chemistry is far less studied and the known examples are mainly involved in nonasymmetric C−C bond-forming reactions. Only recently have promising rhodium(I) carbenoid complexes bearing suitable chiral ligands been demonstrated to exhibit powerful ability in the catalytic asymmetric construction of C−C bonds.[7] More recently, we discovered for the first time that a rhodium(I)−diene complex could direct the asymmetric B−H insertion of α-diazo carbonyl compounds with easily available amine−borane adducts, giving organoboranes with excellent enantioselectivity.[8] This success showcases the great versatility of rhodium(I) carbenoid intermediates in asymmetric carbon−heteroatom bond formation. Thus, we envisage that this new Rh(I)−carbene strategy might be effective in constructing chiral C−Si bonds. Herein, we communicate our success on the first Rh(I)-catalyzed Si−H insertion of α-diazoesters and α-diazophosphonates to access highly enantioenriched organo-silanes under mild conditions (up to 99% ee). The proposed chiral rhodium(I) carbenoid intermediate has been identified by DFT calculations.

Initial experiments began with the reaction of methyl α-diazophenylacetate (**1a**) and dimethylphenylsilane (**2a**) in dichloromethane in the presence of 2.5 mol % of [Rh(cod)Cl]$_2$ at rt. As expected, the Si−H insertion was successfully achieved in 86% yield (Table 1, entry 1), clearly indicating that the rhodium(I) complex could also serve as a suitable catalyst for Si−H insertion. Thus, investigation of a rhodium(I) complex with various chiral olefin ligands mainly developed by our group as a potential catalyst for this transformation was subsequently performed.[9] Unfortunately, almost no reaction proceeded with our sulfinamide-based branched olefin ligand **L1**,[9c] while the bicyclo[3.3.0]-diene **L2**[9d] exhibited poor catalytic activity and enantioselectivity (entries 2−3). Gratify-ingly, screening of Hayashi diene **L3**[10] revealed that the

Table 1. Ligand and Conditions Optimization for Rh(I)-Catalyzed Asymmetric Si–H Insertion of α-Diazophenylacetates[a–c]

| entry	R	ligand/catalyst	T (h)	3	yield (%)[b]	ee (%)[c]
1[d]	Me	–	6	3a	86	–
2	Me	L1	12	3a	trace	–
3	Me	L2	6	3a	18	−23
4	Me	L3	6	3a	82	85
5	Me	L4	12	3a	59	36
6	Me	L5	6	3a	82	88
7	Me	L6	4	3a	91	90
8	Me	L7	4	3a	91	93
9	Et	L7	6	3b	84	94
10	i-Pr	L7	6	3c	67	94
11	Ph	L7	12	3d	60	96
12[e]	Et	[RhCl(L7)]$_2$	6	3b	85	94
13[f]	Et	[Rh(OH)(L7)]$_2$	12	3b	55	93
14[g]	Et	L7	12	3b	63	31

[a]The reaction was performed with 1 (0.1 mmol), 2a (0.15 mmol), [Rh(C$_2$H$_4$)$_2$Cl]$_2$ (1.5 mol %), ligand (3.3 mol %) in 2 mL of CH$_2$Cl$_2$ at rt unless otherwise noted. [b]Isolated yield. [c]Determined by chiral HPLC. [d]2.5 mol % of [Rh(cod)Cl]$_2$ was used. [e]1.5 mol % of [RhCl(L7)]$_2$ complex was used as catalyst. [f]1.5 mol % of [Rh(OH)(L7)]$_2$ complex was used as catalyst. [g]5 mol % of NaBAr$^F_4$ was used as cocatalyst.

bicyclo[2.2.2]octadiene skeleton could induce promising results (82% yield, 85% ee, entry 4).

Following this observation, a series of analogous C$_1$-symmetric dienes[11] bearing a bicyclo[2.2.2]octadiene structure were synthesized and examined in the same Si–H insertion reaction (entries 5−8). Among them, ligands L6 and L7 that possess electron-withdrawing CF$_3$ substituents on the phenyl ring showed great results (entries 7, 8). Significantly improved enantioselectivity (93% ee) was attained by using L7 as a ligand (entry 8). With respect to the substituent at the substrate ester moiety (R), phenyl α-diazophenylacetate could afford the insertion product 3a with the highest enantioselectivity (96% ee), but it also led to a dramatic decrease of the reaction yield (entries 8−11).

To gain some insight into the characteristic feature of the catalyst, two preprepared rhodium(I)/diene complexes [RhCl-(L7)]$_2$ and [Rh(OH)(L7)]$_2$ were examined as the catalyst. In the case of [RhCl(L7)]$_2$, essentially the same catalytic activity and enantioselectivity as those generated in situ were observed (entry 12). While the use of [Rh(OH)(L7)]$_2$ as a catalyst had no obvious impact on the ee value, it led to a significant decrease in the yield (55% yield, 93% ee, entry 13). When 5 mol % of NaBAr$^F_4$ was employed as the cocatalyst, the reaction became much less efficient with poor selectivity (63% yield, 31% ee, entry 14), suggesting that a vacant coordination site at the square-planar rhodium(I) complex has an adverse effect on the reaction stereocontrol.[12] By comparing these results, we might envisage that the presence of an electron-withdrawing,

sterically appropriate group (Cl) adjacent to the carbenoid is helpful to enhance the carbenoid reactivity by increasing its electrophilicity, and essential for the high enantioselectivity of the Si–H insertion (Figure 1).
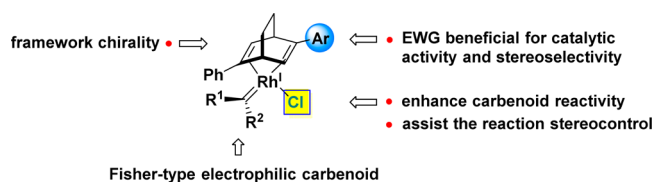
Figure 1. Controlling factors of rhodium(I) carbenoid.

Having optimized reaction conditions, we then focused on evaluation of the substrate scope of this asymmetric Si–H insertion. The results are summarized in Table 2. A variety of

Table 2. Substrate Scope for Asymmetric Si–H Insertion of α-Diazoesters[a–e]

3b Ar = C$_6$H$_5$, 84%, 94% ee
3e Ar = 3-FC$_6$H$_4$, 75%, 95% ee
3f Ar = 3-MeC$_6$H$_4$, 80%, 96% ee
3g Ar = 3-MeOC$_6$H$_4$, 75%, 96% ee
3h Ar = 3-ClC$_6$H$_4$, 90%, 96% ee
3i Ar = 4-CF$_3$C$_6$H$_4$, 72%, 93% ee
3j Ar = 4-FC$_6$H$_4$, 85%, 97% ee
3k Ar = 2-FC$_6$H$_4$, 68%, 91% ee
3l Ar = 2-ClC$_6$H$_4$, 68%, 93% ee
3m Ar = 2-MeC$_6$H$_4$, 70%, 94% ee
3n Ar = 2-Naphthyl, 90%, 93% ee

3o Ar = 2-MeC$_6$H$_4$, R = Et, 50%, 95% ee
3p Ar = 1-Naphthyl, R = Et, 60%, 96% ee
3q Ar = 4-BrC$_6$H$_4$, R = Ph, 82%, 95% ee
3r Ar = 4-MeOC$_6$H$_4$, R = Ph, 70%, 97% ee

3s R = Et, 82%, 95% ee
3t R = ^{n}Pr, 75%, 97% ee

3u 45%, 77% ee
3v 34%, 70% ee
3w 41%, 90% ee
3x Ar = 4-MeOC$_6$H$_4$, 36%, 89% ee
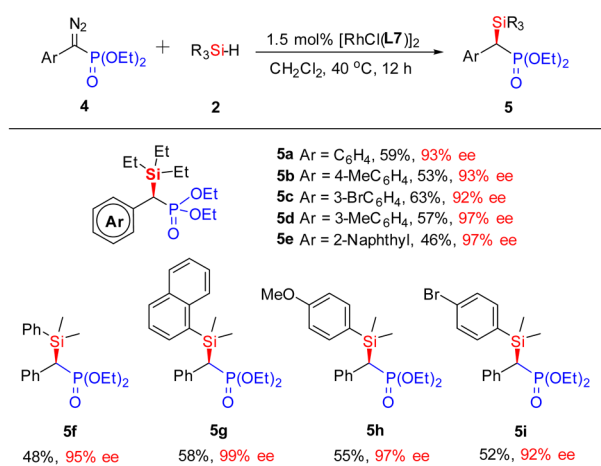3y Ar = 3,4,5-(MeO)$_3$C$_6$H$_2$, 28%, 94% ee

[a]The reaction was performed with 1 (0.1 mmol), 2 (0.15 mmol), [Rh(C$_2$H$_4$)$_2$Cl]$_2$ (1.5 mol %), L7 (3.3 mol %) in 2 mL of CH$_2$Cl$_2$ at rt. [b]The absolute configuration was determined by comparison with [α]$_D$ and the HPLC of 3b, 3u in literature. [c]Isolated yield. [d]Determined by chiral HPLC. [e]3m and 3w−y were obtained by the reaction performed at 40 °C for 12 h.

ethyl α-diazoarylacetates bearing either an electron-donating or -withdrawing substituent on each aromatic carbon were tested in the reaction with dimethylphenylsilane. In all cases, the reaction was accomplished within 6 h at rt and gave the corresponding insertion products 3 with good to excellent yields and enantioselectivities (3b−3n, 91−97% ee). Other silanes, such as substituted aryl silanes, triethylsilane, and tripropylsilane were also successfully applied in this transformation, affording the desired α-silylesters in moderate to good yields with excellent enantioselectivities (3o−3t, 95−97% ee). It might be interesting to note that the reaction of nonaromatic substrates could also take place to afford the insertion products (3u, 3v), albeit with moderate yield and ee. Compared to the previous results obtained by Cu(II)/spiro-diimine,[5c] and the Rh(II)/polypetide[3i] system at low temperature (−40 and −35 °C), our Rh(I)/diene complex could promote this reaction with better enantioselectivity. Gratifyingly, with vinyl substituted diazo substrates, the corresponding

allyl silanes (**3w**−**y**) could be attained with high enantiose-lectivities.[13]

Inspired by the above-mentioned success with α-diazoesters, we then turned our attention to the more challenging α-diazophosphonate substrates in an attempt to obtain a chiral α-silyl phosphonate.[14] In contrast to the commonly studied α-diazoesters, asymmetric X−H insertion with more stable α-diazophosphonates is far less investigated.[15] To our knowledge, asymmetric insertion of α-diazophosphonates into Si−H bonds has not yet been explored. After some careful experiments, we were delighted to find that the expected Si−H insertion could be achieved under the slightly modified conditions when using the preprepared rhodium(I)/diene complex as the catalyst. As revealed in Table 3, a series of α-diazoarylphosphonates having

Table 3. Substrate Scope for the Asymmetric Si−H Insertion of α-Diazophosphonates[a−c]

5a Ar = C_6H_4, 59%, 93% ee
5b Ar = 4-MeC_6H_4, 53%, 93% ee
5c Ar = 3-BrC_6H_4, 63%, 92% ee
5d Ar = 3-MeC_6H_4, 57%, 97% ee
5e Ar = 2-Naphthyl, 46%, 97% ee

5f 48%, 95% ee
5g 58%, 99% ee
5h 55%, 97% ee
5i 52%, 92% ee

[a]The reaction was performed with **4** (0.1 mmol), **2** (0.15 mmol), [Rh(**L7**)Cl]$_2$ (1.5 mol %) in 2 mL of CH$_2$Cl$_2$ at 40 °C. [b]Isolated yield. [c]Enantioselectivity was determined by chiral HPLC.

various substituents on the benzene ring were subjected to reaction with triethylsilane in the presence of [RhCl(**L7**)]$_2$ in CH$_2$Cl$_2$ at 40 °C. In general, the reactions proceeded well to give the corresponding Si−H insertion products in moderate yields with excellent enantioselectivities (**5a**−**5e**, 92−97% ee). Notably, various aryl-substituted silanes were also suitable for use in the reaction to afford highly enantioenriched α-silyl phosphonates (**5f**−**5i**). In the case of sterically bulky dimethyl(1-naphthalenyl)silane, a particularly high enantiose-lection (**5g**, 99% ee) was obtained. Assuming an analogous reaction mechanism, the absolute configuration at the newly created stereocenter of **5** was assigned to be S.

Rhodium(I) complexes with phosphorus-, nitrogen-, and N-heterocyclic carbene-based strong σ-donor ligands are effective catalysts for hydrosilylation[16] in which a rhodium(III) species is known to be readily formed in the first step via oxidative addition of the silane. In our case, NMR examination of the reaction of Rh(I)/diene complex ([RhCl(**L7**)]$_2$) and dimethyl-phenylsilane did not reveal any conversion after 6 h at rt, thus suggesting a rhodium(I)−carbeniod insertion mechanism in the presence of diazo compounds. For a better understanding, kinetic isotopic studies were carried out. In a competition experiment, the kinetic isotope effect (KIE) for the insertion reaction between dimethylphenylsilane and **1b** was determined to be 1.5 (Scheme 1). This K_H/K_D value is in accord with the

**Scheme 1. Competition Experiments for Kinetic Isotope Effect**
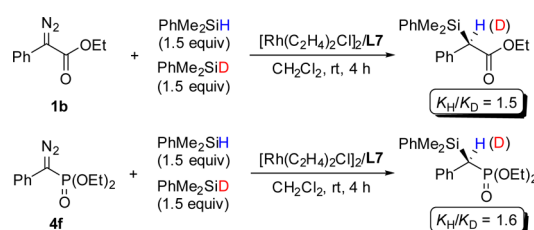
reported value of carbenoid Si−H insertion catalyzed by other transition metals such as Rh(II), Cu(I), and Ir(III).[17] On the other hand, asymmetric insertion of α-diazophosphonate **4f** showed a similar KIE (K_H/K_D = 1.6). These results suggest that the rhodium(I)-catalyzed insertion reaction also proceeds in a concerted mechanism in which the Si−H bond adds onto the electrophilic rhodium−carbenoid center through a three-center transition state.

We have also performed a structural X-ray investigation of the catalyst [RhCl(**L7**)]$_2$. It was found that the diene moiety of **L7** coordinates to the rhodium(I) center in a very similar way as the known complex [RhCl(**L3**)]$_2$.[10b] We believe that the better catalytic activity of **L7** is attributed to the strong electron-withdrawing property of trifluoromethyl groups. The more electron-deficient double bond is expected to accelerate the formation of rhodium(I) carbene and enhance the reactivity of the carbene *trans* to it.

To probe the origin of enantioselectivity, two key rhodium-(I) carbenoid intermediates that would likely be involved in the transition states for the stereochemical pathway of insertion of ethyl α-diazophenylacetate were investigated by computational analysis (Scheme 2). The Gibbs free energy of intermediate **B** is

Scheme 2. DFT Calculations and the Proposed Stereochemical Pathway
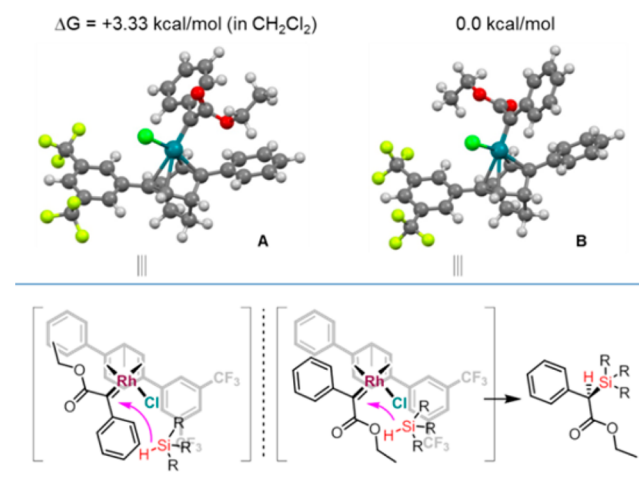
approximately 5.91 kcal/mol (vacuum) and 3.33 kcal/mol (in CH$_2$Cl$_2$) lower than that of intermediate **A**, calculated by Guassian09 at the B3LYP level of theory using the lanl2dz and 6-31+G** basis set for Rh and other atoms. This DFT calculation result suggests that the carbenoid intermediate **B** is energetically more favorable than the carbenoid intermediate **A**. Addition of the Si−H bond onto the electrophilic rhodium(I) carbenoid **B** takes place preferentially from the unblocked *Re*-

face at the site adjacent to Cl to give the R product, which agrees with the experimental stereochemical outcome.

In conclusion, the first rhodium(I)-catalyzed asymmetric Si−H insertion reaction has been developed. The reaction allows a broad range of substrates including α-diazophosphonates for the first time in Si−H insertion and enables the efficient synthesis of valuable chiral α-silyl esters and phosphonates with excellent enantioselectivities under exceptionally mild and user-friendly conditions. The easily prepared C_1-symmetric chiral bicyclo[2.2.2]octadiene ligands have exhibited extraordinary ability in this transformation. Preliminary mechanistic investigations, including deuterium-labeling kinetic isotopic studies and DFT calculations for stereochemical pathway, show that the reaction proceeds via a concerted, stereospecific rhodium-(I)-carbene mediated transition state. Further investigations to expand this promising rhodium(I)−carbene chemistry in constructing other chiral carbon−heteroatom bonds are currently in progress in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b12960.

> Experimental procedures, characterization data (PDF)
> Crystallographic data for [Rh(**L7**)Cl]$_2$ (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*xumh@simm.ac.cn

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) (a) Franz, A. K.; Wilson, S. O. J. Med. Chem. 2013, 56, 388. (b) Langkopf, E.; Schinzer, D. Chem. Rev. 1995, 95, 1375. (c) Showell, G. A.; Mills, J. S. Drug Discovery Today 2003, 8, 551. (d) Fleming, I.; Barbero, A.; Walter, D. Chem. Rev. 1997, 97, 2063. (e) Jones, G. R.; Landais, Y. Tetrahedron 1996, 52, 7599.

(2) For selected examples, see: (a) Walter, C.; Auer, G.; Oestreich, M. Angew. Chem., Int. Ed. 2006, 45, 5675. (b) Walter, C.; Oestreich, M. Angew. Chem., Int. Ed. 2008, 47, 3818. (c) Lee, K.-S.; Hoveyda, A. H. J. Am. Chem. Soc. 2010, 132, 2898. (d) Ibrahem, I.; Santoro, S.; Himo, F.; Córdova, A. Adv. Synth. Catal. 2011, 353, 245. (e) Cirriez, V.; Rasson, C.; Hermant, T.; Petrignet, J.; Diaz Alvarez, J.; Robeyns, K.; Riant, O. Angew. Chem., Int. Ed. 2013, 52, 1785. (f) Hensel, A.; Nagura, K.; Delvos, L. B.; Oestreich, M. Angew. Chem., Int. Ed. 2014, 53, 4964. (g) Mita, T.; Sugawara, M.; Saito, K.; Sato, Y. Org. Lett. 2014, 16, 3028.

(3) For asymmetric attempts of rhodium(II) carbenoid Si−H insertion, see: (a) Buck, R. T.; Doyle, M. P.; Drysdale, M. J.; Ferris, L.; Forbes, D. C.; Haigh, D.; Moody, C. J.; Pearson, N. D.; Zhou, Q.-L. Tetrahedron Lett. 1996, 37, 7631. (b) Davies, H. M. L.; Hansen, T.; Rutberg, J.; Bruzinski, P. R. Tetrahedron Lett. 1997, 38, 1741. (c) Buck, R. T.; Coe, D. M.; Drysdale, M. J.; Moody, C. J.; Pearson, N. D. Tetrahedron Lett. 1998, 39, 7181. (d) Kitagaki, S.; Kinoshita, M.; Takeba, M.; Anada, M.; Hashimoto, S. Tetrahedron: Asymmetry 2000, 11, 3855. (e) Buck, R. T.; Coe, D. M.; Drysdale, M. J.; Ferris, L.; Haigh, D.; Moody, C. J.; Pearson, N. D.; Sanghera, J. B. Tetrahedron:

Asymmetry 2003, 14, 791. (f) Ge, M.; Corey, E. J. Tetrahedron Lett. 2006, 47, 2319. (g) Doyle, M. P.; Hu, W.; Phillips, I. M.; Moody, C. J.; Pepper, A. G.; Slawin, A. M. Z. Adv. Synth. Catal. 2001, 343, 112. (h) Hrdina, R.; Guénée, L.; Moraleda, D.; Lacour, J. Organometallics 2013, 32, 473. (i) Sambasivan, R.; Ball, Z. T. J. Am. Chem. Soc. 2010, 132, 9289.

(4) For racemic attempts of rhodium(II) carbenoid Si−H insertion, see: (a) Bagheri, V.; Doyle, M. P.; Taunton, J.; Claxton, E. E. J. Org. Chem. 1988, 53, 6158. (b) Bulugahapitiya, P.; Landais, Y.; Parra-Rapado, L.; Planchenault, D.; Weber, V. J. Org. Chem. 1997, 62, 1630. (c) Landais, Y.; Parra-Rapado, L.; Planchenault, D.; Weber, V. Tetrahedron Lett. 1997, 38, 229. (d) Qu, A.; Shi, W.; Wang, J. J. Org. Chem. 2001, 66, 8139. (e) Wong, F. M.; Wang, J.; Hengge, A. C.; Wu, W. Org. Lett. 2007, 9, 1663.

(5) For copper carbenoid Si−H insertion examples, see: (a) Dakin, L. A.; Ong, P. C.; Panek, J. S.; Staples, R. J.; Stavropoulos, P. Organometallics 2000, 19, 2896. (b) Dakin, L. A.; Schaus, S. E.; Jacobsen, E. N.; Panek, J. S. Tetrahedron Lett. 1998, 39, 8947. (c) Zhang, Y.-Z.; Zhu, S.-F.; Wang, L.-X.; Zhou, Q.-L. Angew. Chem., Int. Ed. 2008, 47, 8496.

(6) For iridium(III) carbenoid Si−H insertion examples, see: (a) Yasutomi, Y.; Suematsu, H.; Katsuki, T. J. Am. Chem. Soc. 2010, 132, 4510. (b) Wang, J.-C.; Xu, Z.-J.; Guo, Z.; Deng, Q.-H.; Zhou, C.-Y.; Wan, X.-L.; Che, C.-M. Chem. Commun. 2012, 48, 4299.

(7) (a) Nishimura, T.; Kawamoto, T.; Nagaosa, M.; Kumamoto, H.; Hayashi, T. Angew. Chem., Int. Ed. 2010, 49, 1638. (b) Nishimura, T.; Maeda, Y.; Hayashi, T. Angew. Chem., Int. Ed. 2010, 49, 7324. (c) Ma, X.; Jiang, J.; Lv, S.; Yao, W.; Yang, Y.; Liu, S.; Xia, F.; Hu, W. Angew. Chem., Int. Ed. 2014, 53, 13136. (d) Yada, A.; Fujita, S.; Murakami, M. J. Am. Chem. Soc. 2014, 136, 7217.

(8) Chen, D.; Zhang, X.; Qi, W.-Y.; Xu, B.; Xu, M.-H. J. Am. Chem. Soc. 2015, 137, 5268.

(9) (a) Li, Y.; Xu, M.-H. Chem. Commun. 2014, 50, 3771. (b) Zhu, T.-S.; Jin, S.-S.; Xu, M.-H. Angew. Chem., Int. Ed. 2012, 51, 780. (c) Wang, H.; Jiang, T.; Xu, M.-H. J. Am. Chem. Soc. 2013, 135, 971. (d) Wang, Z.-Q.; Feng, C.-G.; Xu, M.-H.; Lin, G.-Q. J. Am. Chem. Soc. 2007, 129, 5336. For a review on chiral olefins, see: (e) Defieber, C.; Grützmacher, H.; Carreira, E. M. Angew. Chem., Int. Ed. 2008, 47, 4482.

(10) (a) Tokunaga, N.; Otomaru, Y.; Okamoto, K.; Ueyama, K.; Shintani, R.; Hayashi, T. J. Am. Chem. Soc. 2004, 126, 13584. (b) Otomaru, Y.; Okamoto, K.; Shintani, R.; Hayashi, T. J. Org. Chem. 2005, 70, 2503.

(11) A series of C_1-symmetric dienes were synthesized by taking advantage of the creative work of Abele and co-workers. See: Abele, S.; Inauen, R.; Spielvogel, D.; Moessner, C. J. Org. Chem. 2012, 77, 4765.

(12) A single vacant site at the square-planer rhodium center is necessary in Hayashi's work; see ref 7a and 7b.

(13) The low yield of the reaction is mainly due to the decomposition of less stable vinyldiazoacetates.

(14) For the use of a chiral α-functional phosphonate, see: (a) Kafarski, P.; Lejczak, B. Phosphorus, Sulfur Silicon Relat. Elem. 1991, 63, 193. (b) Patel, D. V.; Rielly-Gauvin, K.; Ryono, D. E.; Free, C. A.; Rogers, W. L.; Smith, S. A.; DeForrest, J. M.; Oehl, R. S.; Petrillo, E. W. J. Med. Chem. 1995, 38, 4557.

(15) Zhou, Q.-L.; Zhu, S.-F.; Chen, W.-Q.; Zhang, Q.-Q.; Mao, H.-X. Synlett 2011, 2011, 919.

(16) Riener, K.; Högerl, M. P.; Gigler, P.; Kühn, F. ACS Catal. 2012, 2, 613.

(17) (a) Landais proposed the rhodium(II) carbenoid Si−H insertion proceeds through a concerted pathway based on kinetic studies, $K_H/K_D = 1.5$. See ref 4c. (b) The copper(I) carbenoid Si−H insertion gave a similar value ($K_H/K_D = 1.3$, at 0 °C). See ref 5a. (c) The iridium(III) carbenoid Si−H insertion also gave a similar value ($K_H/K_D = 1.6$, at −30 °C). See ref 6a for details.