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Stereospecific Palladium-Catalyzed Reactions of Siliranes with Alkynes

Wylie S. Palmer and K. A. Woerpel*

Department of Chemistry, University of California, Irvine, California 92697-2025

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Summary: Palladium-catalyzed insertion of alkynes into siliranes and silylene extrusion reactions proceed with stereospecific retention of configuration at the carbon center.

Metal-mediated reactions of silirenes[1−4] and alkylidenesiliranes[5,6] with alkynes result in either transfer of the silylene unit or insertion of the alkyne into a C−Si bond. The mechanisms of these reactions are believed to involve oxidative addition and migratory insertion, although little experimental information has been provided about either of these steps. If metal-catalyzed reactions could be observed for siliranes bearing stereochemical markers, then the stereochemistry of both steps could be evaluated. We have used the dimethylsiliranes of Boudjouk[7] to address related stereochemistry issues regarding insertion reactions of aldehydes.[8] We report here that siliranes undergo stereospecific palladium-catalyzed silylene extrusion reactions and that the accompanying alkyne insertion reaction occurs stereospecifically with retention of configuration at the carbon atom. These experiments demonstrate that oxidative addition reactions of palladium into the C−Si bonds of siliranes proceed with retention of configuration at carbon.[9] This stereochemical outcome is not always observed for siliranes: insertion reactions without metal catalysts in some cases proceed with inversion of configuration[8] and in others the stereochemistry is scrambled.[8,10,11]

The siliranes *cis*-**1** and *trans*-**1** react with a variety of terminal acetylenes in the presence of <3 mol % of $(Ph_3P)_2PdCl_2$ to provide siloles **2** (eq 1, Table 1).[12,13] Minor quantities of alkyne insertion products, silacyclopentenes **3**, were also observed; more of these products

[⊗] Abstract published in *Advance ACS Abstracts*, February 15, 1997.

(1) Seyferth, D.; Vick, S. C.; Shannon, M. L. *J. Organomet. Chem.* **1977**, *135*, C37−C44.
(2) Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. *Organometallics* **1985**, *4*, 57−62.
(3) Ishikawa, M.; Ohshita, J.; Ito, Y.; Iyoda, J. *J. Am. Chem. Soc.* **1986**, *108*, 7417−7419 and references cited therein.
(4) Ohshita, J.; Ishikawa, M. *J. Organomet. Chem.* **1991**, *407*, 157−165.
(5) Similar reactions have been observed for alkylidenesiliranes, see: Saso, H.; Ando, W.; Ueno, K. *Tetrahedron* **1989**, *45*, 1929−1940.
(6) Saso, H.; Ando, W. *Chem. Lett.* **1988**, 1567−1570.
(7) Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrusciel, J.; Anderson, K. R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1355−1356.
(8) Bodnar, P. M.; Palmer, W. S.; Shaw, J. T.; Smitrovich, J. H.; Sonnenberg, J. D.; Presley, A. L.; Woerpel, K. A. *J. Am. Chem. Soc.* **1995**, *117*, 10575−10576.
(9) Although the stereochemistry of the oxidative addition into the C−Si bonds of alkylsilanes is not known, transmetalation to palladium has been observed to proceed with retention or inversion of configuration depending upon the conditions: Hatanaka, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1990**, *112*, 7793−7794.
(10) Boudjouk, P.; Black, E.; Kumarathasan, R.; Samaraweera, U.; Castellino, S.; Oliver, J. P.; Kampf, J. W. *Organometallics* **1994**, *13*, 3715−3727.
(11) In fact, insertion of conjugated acetylenes into siliranes and silirenes without catalysts are believed to involve diradical intermediates, which would be expected to lose stereochemical integrity: (a) Seyferth, D.; Duncan, D. P.; Shannon, M. L.; Goldman, E. W. *Organometallics* **1984**, *3*, 574−578. (b) Seyferth, D.; Vick, S. C.; Shannon, M. L. *Organometallics* **1984**, *3*, 1897−1905.
(12) For a review of group 14 metalloles, see: Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215−263.

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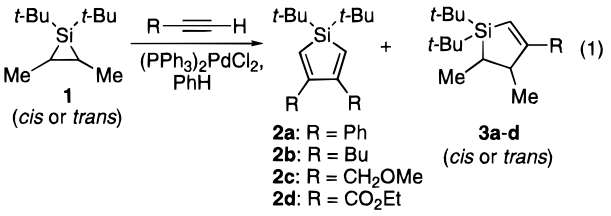
Table 1. Palladium-Catalyzed Reactions of Siliranes 1 with Terminal Acetylenes (eq 1)[a]

			isolated yields, %		
entry	acetylene (R)	silirane	**2**	*cis*-**3**	*trans*-**3**
1	Ph	*cis*-**1**	55	31	0
2	Ph	*trans*-**1**	83	0	1
3	Bu	*trans*-**1**	73	0	0
4	CH_2OMe	*trans*-**1**	67	0	0
5	CO_2Et	*cis*-**1**	57	14	0

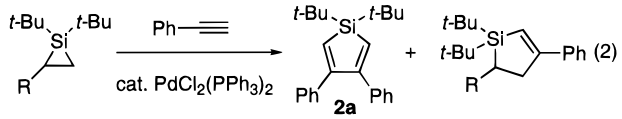
[a] Conditions: 2.0−3.5 equiv of acetylene, 0.2−3.0 mol % $PdCl_2(PPh_3)_2$, PhH as solvent (0.1 M), 23 °C.



were observed with *cis*-**1** than with *trans*-**1** (cf. entries 1 and 2, Table 1). In all cases, the silylene transfer products **2** were formed as single regioisomers with the substituents positioned away from the *tert*-butyl groups.[14] The insertion products were also formed with high regioselectivity: GC/MS indicates 99% regioselectivity for the formation of *cis*-**3a** from *cis*-**1**.[15] Control experiments indicate that the palladium catalyst was necessary for all of these reactions, excess phosphine slows the reaction, and the product distributions are kinetically controlled.[16] Although the formation of siloles from *trans*-**1** is a general reaction for terminal alkynes (Table 1), internal alkynes failed to react under these conditions.

The most striking aspect of these reactions is that both insertion and silylene transfer occur stereospecifically. Sealed NMR tube experiments in C_6D_6 revealed that when silirane *trans*-**1** was treated with phenylacetylene and the palladium catalyst (eq 1), silole formation was accompanied by the production of isomerically pure *trans*-2-butene. Similarly, *cis*-2-butene was formed from *cis*-**1**.[17] Therefore, the palladium-catalyzed extrusion of silylene from siliranes **1** proceeds stereospecifically with retention of configuration of the alkene component.[18] Similar stereospecificity has been observed for thermal silylene extrusion from siliranes.[7,19] The insertion process, although a minor reaction manifold, also proceeds stereospecifically: the cis-substituted silacyclopentene *cis*-**3a** was formed from *cis*-**1**, and *trans*-**3a** was formed predominately from *trans*-**1**. The small quantities of insertion products observed in the latter case do not permit a more quantitative analysis.[20] Whatever pathway or pathways produce both siloles **2** and silacyclopentenes **3** must occur with retention of stereochemistry at the carbon atoms.

The regioselectivity of the palladium-catalyzed transformations with respect to the silirane fragment were evaluated by treating the unsymmetrical siliranes **4a**−**c**[21] with phenylacetylene (eq 2). The major silylene



transfer products **2a** were accompanied by small amounts of insertion products **5a**−**c**. The regiochemistry in all cases results from an insertion at the less substituted position of the three-membered ring. This is not a general preference of siliranes: the insertion of benzaldehyde into silirane **4b** occurs at the more hindered bond.[8,22] Ando has reported that the regioselectivity of the palladium-catalyzed insertion of dimethyl acetylenedicarboxylate into an unsymmetrical alkylidenesilirane varied with the reaction conditions.[6]

A control experiment provided additional insight into the mechanism of these reactions. When the silirane

(13) General Procedure: A mixture of silirane *cis*-**1** (0.38 g, 1.9 mmol), phenylacetylene (0.43 g, 4.2 mmol), $PdCl_2(PPh_3)_2$ (6 mg, 0.4 mol %), and benzene (5.0 mL) was stirred under N_2 for 48 h at ambient temperature, then concentrated *in vacuo*. Purification by column chromatography (hexanes) yielded **2a** as a white crystalline solid (0.36 g, 55%) and *cis*-**3a** as a clear liquid (0.18 g, 31%). **2a:** mp 108.0−109.0 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.23−7.12 (m, 6H), 7.02 (m, 4H), 6.15 (s, $^2J_{Si-H}$ = 11.0 Hz, 2H), 1.14 (s, 18H); ^{29}Si NMR ($CDCl_3$, 99.3 MHz) δ 18.8; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.4, 141.3, 131.0, 127.9, 127.4, 126.7, 28.9, 19.5; IR (KBr) 3061, 2926, 2854, 1469, 1190, 839, 750, 698 cm^{-1}. HRMS (EI) *m*/z calcd for $C_{24}H_{30}Si$ (M^+): 346.2117. Found: 346.2123. Anal. Calcd for $C_{24}H_{30}Si$: C, 83.17; H, 8.72. Found: C, 83.04; H, 8.70. ***cis*-3a:** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.45 (d, *J* = 7.0 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.24 (m, 1H), 6.10 (s, 1H), 3.46 (m, 1H), 1.75 (m, 1H), 1.25 (d, *J* = 8.1 Hz, 3H), 1.09 (s, 9H), 1.02 (s, 9H), 0.98 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.2, 140.8, 128.2, 127.3, 126.5, 123.2, 43.9, 29.7, 29.4, 20.1, 19.9, 19.7, 16.4, 12.7; IR (thin film) 3057, 2932, 2855, 1472, 821, 756 cm^{-1}. HRMS (CI) *m*/z calcd for $C_{20}H_{33}Si$ ($M + H)^+$: 301.2351. Found: 301.2344. Anal. Calcd for $C_{20}H_{32}Si$: C, 79.92; H, 10.73. Found: C, 79.78; H, 10.79.

(14) The regiochemistry of the siloles was determined from analysis of Si−H and Si−C coupling constants; this data is provided as supporting information. In contrast, the unsymmetrical silole 1,1-di-*tert*-butyl-3,5-diphenyl-1-sila-2,4-cyclopentadiene was isolated (49% yield) from the reaction of hexa-*tert*-butyl-cyclotrisilane with $PdCl_2(PPh_3)_2$ and phenylacetylene: Schäfer, A.; Weidenbruch, M.; Pohl, S. *J. Organomet. Chem.* **1985**, *282*, 305−313.

(15) Analysis of the isolated silacyclopentene *cis*-**3a** by GC/MS indicated the regioisomer 1,1-di-*tert*-butyl-2-phenyl-4,5-dimethylsilacyclopent-2-ene was present in 1%. The regiochemistries of this and all major silacyclopentenes were determined by ^{1}H NMR homonuclear decoupling and NOE experiments.

(16) The reaction conditions were examined to determine whether the insertion reaction of silirane cis-**1** could be optimized. Although both reaction manifolds were found to be catalyzed by a wide variety of Pd(II) and Pd(0) sources, including $PdCl_2$(dppf), $PdCl_2(P[o\text{-tol}]_3)_2$, $PdCl_2(PPh_3)_2$, $PdCl_2(PhCN)_2$, $Pd(TFA)_2$, $Pd(OAc)_2$, $Pd(acac)_2$, $Pd_2(DBA)_3$, $Pd(PPh_3)_4$, and $Pd(P[OEt]_3)_4$, only moderate variations in product ratios were observed. Nickel complexes such as $Ni(P[OEt]_3)_4$, $NiCl_2$(dppe) and $Ni(OAc)_2$ led only to decomposition of silirane. Variation of solvents from polar (such as *N*,*N*-dimethylacetamide) to non-polar (such as hexane) also resulted in only minor differences in product ratios. Product ratios were unaffected by stoichiometry.

(17) A sealed NMR tube experiment with *cis*-**1** (an 89:11 mixture of cis and trans isomers as determined by ^{1}H NMR integration), the palladium-catalyzed reaction with phenylacetylene produced **2a** and *cis*-**3a** in a 73:27 ratio, and *cis*- and *trans*-2-butene in an 87:13 ratio. When the different propensities for insertion and silylene transfer of the two isomers are taken into account, one can demonstrate that the extrusion process is at least 98% stereoselective.

(18) Metal-mediated, stereospecific heteroatom (O, S) and group (NR) transfer reactions from three-membered rings are known. See, for example: Proulx, G.; Bergman, R. G. *Organometallics* **1996**, *15*, 133−141.

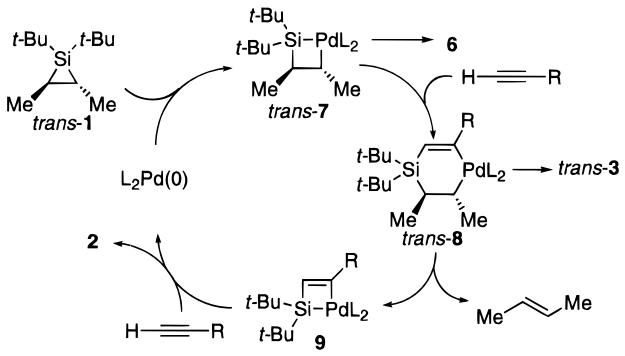
(19) Pae, D. H.; Xiao, M.; Chiang, M. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 1281−1288.

(20) Starting from *trans*-**1**, silacyclopentene **3a** (1%) was isolated as a mixture of trans and cis isomers in a 90:10 ratio; the production of *cis*-**3a** is believed to arise from contamination of the starting silirane *trans*-**1** by *cis*-**1**. This conclusion is reasonable, considering the propensity for *cis*-**1**, rather than *trans*-**1**, to undergo insertion. We have no reliable method for detecting such minute quantities of isomeric silirane impurities.

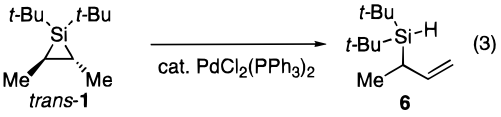
(21) Silirane **4a** was previously reported by Boudjouk, and **4b**,**c** were prepared by the same method. See: Boudjouk, P.; Black, E.; Kumarathasan, R. *Organometallics* **1991**, *10*, 2095−2096.

(22) For a recent example of isocyanide insertion into symmetrical and unsymmetrical siliranes, see: Kroke, E.; Willms, S.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Tetrahedron Lett.* **1996**, *37*, 3675−3678.

Scheme 1



trans-**1** was treated with the palladium catalyst without alkyne in C_6D_6, it slowly rearranged to form the silane **6** over the course of days (eq 3). This transformation



was attended by decomposition of the silirane to unidentified materials. This rearrangement product was not observed if an alkyne was present, indicating that the pathway leading to **6** is slower than those leading to other products.

The catalytic cycle shown in Scheme 1, adapted from the one originally proposed by Seyferth for silirenes,[2] is supported by the stereochemical data obtained for siliranes **1**. Oxidative addition of *in-situ*-generated Pd(0)[23−25] into the C−Si bond of *trans*-**1** occurs with stereospecific retention of configuration at the carbon atom to provide palladacyclobutane *trans*-**9**.[26,27] Similar stereospecificity must pertain to *cis*-**1** as well.[28] The palladasilacyclobutane intermediate *trans*-**7**, in the absence of alkyne, undergoes β-hydride elimination and reductive elimination to provide allylsilane **6**. In the presence of an alkyne, association and migratory insertion[29] leads to the palladasilacyclohexene *trans*-**8**.[27] Reductive elimination from *trans*-**8** would provide the silacyclopentene *trans*-**3** with retention of configuration at the carbon stereocenter.[30] Alternatively, *trans*-**8** may undergo migratory deinsertion to liberate *trans*-2-butene and palladasilacyclobutene **9**. This intermediate would lead to silole **2** after alkyne association, migratory insertion, and reductive elimination.[3]

In conclusion, the palladium-catalyzed extrusion of silylene from silirane occurs with retention of configuration, as does the insertion of alkyne. These results indicate that oxidative addition into the C−Si bond occurs with retention. The stereochemical aspects of these transformations, as well as the observation of allylsilane byproducts, are consistent with a common reaction mechanism.

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Supporting Information Available: A listing of full spectral, analytical, and experimental details for all new compounds (13 pages). Ordering information is given on any current masthead page.

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(23) Seyferth reported the reduction of $PdCl_2(PPh_3)_2$ to $Pd(PPh_3)_2$ by a silirane (ref. 2).

(24) Oxidative addition of platinum(0) complexes into the C−Si bond of silacyclobutanes has been reported: Yamashita, H.; Tanaka, M.; Honda, K. *J. Am. Chem. Soc.* **1995**, *117*, 8873−8874.

(25) Added phosphine slows these reactions, suggesting the presence of a coordinatively unsaturated palladium intermediate.

(26) Ando has suggested a palladasilacyclobutane intermediate was operative in neopentylidenesilirane chemistry (ref. 6).

(27) A related example in which a palladastannete has been characterized in the synthesis of stannoles was recently reported: Krause, J.; Haack, K.-J.; Pörschke, K.-R.; Gabor, B.; Goddard, R.; Pluta, C.; Seevogel, K. *J. Am. Chem. Soc.* **1996**, *118*, 804−821.

(28) In the case of unsymmetrical siliranes, the regiochemistry of insertion products **5** (eq 2) suggests that oxidative addition occurs at the less substituted carbon atom. Since only the regiochemistry of the minor reaction manifold could be assayed, the proposal of regioselective oxidative addition cannot be further supported.

(29) Tilley, T. D. In *The Silicon-Heteroatom Bond*; S. Patai and Z. Rappoport, Eds.; Wiley: New York, 1991; pp 245−364.

(30) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4981−4991.