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Reductive Cyclization of Dimethyl Diallylmalonate Catalyzed by Palladium−Bisoxazoline Complexes in the Presence of Silane and Water

Nicholas S. Perch, Philip Kisanga, and Ross A. Widenhoefer*

P. M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27708-0346

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Reaction of dimethyl diallylmalonate (**1**) with a stoichiometric amount of water and $HSiEt_3$ catalyzed by a 1:1 mixture of (N−N)Pd(Me)Cl [N−N = 4,4′-dibenzyl-4,5,4′,5′-tetrahydro-2,2′-bisoxazoline] (**4a**) and $NaBAr_4$ [Ar = 3,5-$C_6H_3(CF_3)_2$] at 50 °C in 1,2-dichloroethane led to the isolation of a 4.4:1 mixture of *trans*-dimethyl-3,4-dimethylcyclopentane-1,1-dicarboxylate (**5**) ($\geq$ 95% de, 38% ee) and dimethyl dipropylmalonate (**6**) in 88% combined yield. Reaction of **1** with a stoichiometric mixture of $D_2O/HSiEt_3$ or $H_2O/DSiEt_3$ catalyzed by **4a**/$NaBAr_4$ formed predominantly the **5**-d_1 isotopomer, which possessed a single deuterium atom at one of the exocyclic methyl groups. Reaction of **1** with a stoichiometric mixture of $D_2O/DSiEt_3$ catalyzed by **4a**/$NaBAr_4$ formed predominantly the **5**-d_2 isotopomer with a single deuterium atom at each of the exocyclic methyl groups.

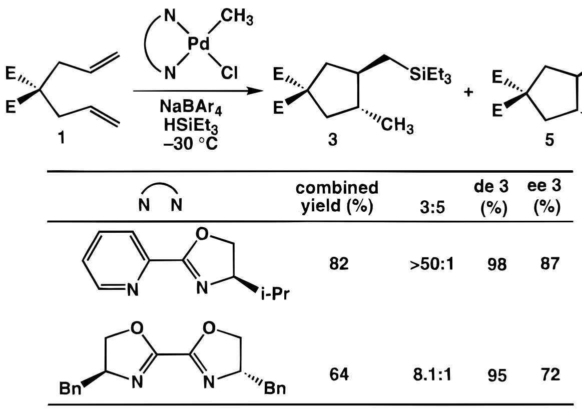
Introduction

As part of a program directed toward the cyclization of functionalized dienes,[1] we recently reported that optically active palladium pyridine−oxazoline complexes catalyzed the asymmetric cyclization/hydrosilylation of 1,6-dienes.[2] For example, reaction of dimethyl diallylmalonate (**1**) and $HSiEt_3$ catalyzed by a 1:1 mixture of (N−N)Pd(Me)Cl [N−N = (*R*)-(+)-4-isopropyl-2-(2-pyridinyl)-2-oxazoline] (**2**) and $NaBAr_4$ [Ar = 3,5-C_6H_3-$(CF_3)_2$] (5 mol %) led to the isolation of silylated cyclopentane **3** as the exclusive product with >95% de and 87% ee (Scheme 1). In comparison, reaction of **1** and triethylsilane catalyzed by a 1:1 mixture of the palladium bisoxazoline complex (N−N)Pd(Me)Cl [N−N = 4,4′-dibenzyl-4,5,4′,5′-tetrahydro-2,2′-bisoxazoline] (**4a**) and $NaBAr_4$ led to isolation of an 8.1:1 mixture of **3** (95% de, 72% ee) and an unexpected reductive cyclization product, *trans*-dimethyl 3,4-dimethylcyclopentane-1,1-dicarboxylate (**5**) in 64% combined yield (Scheme 1). The reductive cyclization product **5** had not previously been observed in our palladium chemistry, and we began to investigate the origins of its formation. Here we report that the formation of **5** from reaction of **1** and silane can be traced to the presence of water in the reaction mixture.

Results and Discussion

The transition metal-catalyzed reductive cyclization of dienes,[3] enynes,[4,5] and diynes[6] has been reported and employs a variety of hydrogen atom sources. For example, the highly electrophilic yttrocene methyl complex $(C_5Me_5)_2Y(Me)THF$ catalyzes the reductive cyclization of 1,5- and 1,6-dienes under a hydrogen atmosphere to form saturated five- and six-membered carbocycles, respectively.[3] Conversely, formic acid provides the hydrogen atoms required for the reductive cyclization of enynes catalyzed by a mixture of palladium acetate and PPh_3.[4] Alternatively, a combination of silane and acetic acid provides the reducing equivalents required for the reductive cyclization of enynes[5] and diynes[6] catalyzed by a mixture of $Pd(DBA)_2·CHCl_3$ [DBA = dibenzylideneacetone] and P(*o*-tolyl)$_3$ (eq 1). The palladium-catalyzed reductive cyclization of enynes has been

Scheme 1



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[1] (a) Widenhoefer, R. A.; Perch, N. S. *Org. Lett.* **1999**, *1*, 1103. (b) Widenhoefer, R. A.; DeCarli, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 3805. (c) Widenhoefer, R. A.; Vadehra, A. *Tetrahedron Lett.* **1999**, *40*, 8499. (d) Widenhoefer, R. A.; Stengone, C. N. *J. Org. Chem.* **1999**, *64*, 8681. (e) Stengone, C. N.; Widenhoefer, R. A. *Tetrahedron Lett.* **1999**, *40*, 1451. (f) Widenhoefer, R. A.; Vadehra, A.; Cheruvu, P. K. *Organometallics* **1999**, *18*, 4614. (g) Pei, T.; Widenhoefer, R. A. *Org. Lett.* **2000**, *2*, 1469.

[2] (a) Perch, N. S.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 6960. (b) Perch, N. S.; Pei, T.; Widenhoefer, R. A. *J. Org. Chem.*, in press.

[3] Molander, G. A.; Nichols, P. J. *J. Am. Chem. Soc.* **1995**, *117*, 4415.

[4] (a) Oh, C. H.; Jung, H. H.; Kim, J. S.; Cho, S. W. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 752. (b) Oh, C. H.; A. Kim, C. Y.; Rhim, C. Y.; Kang, J. H.; Park, B. S. *Bull. Korean Chem. Soc.* **1996**, *17*, 879. (c) Oh, C. H.; Rhim, C. Y.; Kang, J. H.; Kim, A.; Park, B. S.; Seo, Y. *Tetrahedron Lett.* **1996**, *37*, 8875. (d) Oh, C. H.; Jung, H. H. *Tetrahedron Lett.* **1999**, *40*, 1535. (e) Oh, C. H.; Rhim, C. Y.; Hwang, S. K. *Chem. Lett.* **1997**, 777.

[5] Trost, B. M.; Rise, F. *J. Am. Chem. Soc.* **1987**, *109*, 3161.

[6] Trost, B. M.; Lee, N. C. *J. Am. Chem. Soc.* **1988**, *110*, 7255.

10.1021/om000251g CCC: $19.00
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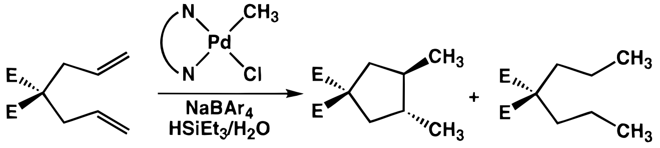
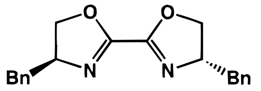
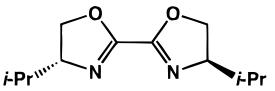
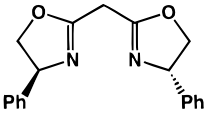
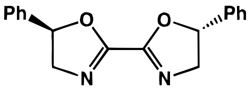
Table 1. Reaction of 1 with a Mixture of Water and $HSiEt_3$ Catalyzed by a 1:1 Mixture of Palladium Bisoxazoline Complexes 4a−d and $NaBAr_4$ in DCE

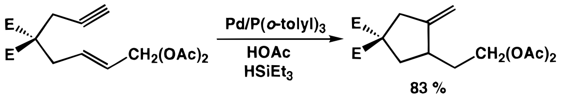


1 (E = CO_2Me) 5 6

entry	pre-catalyst		temp (°C)	total yield (%)[a]	selectivty for 5[b]	de of 5 (%)[b]	ee of 5 (%)[c]
1	4a		25	82	66 %[d]	≥95	18
2			50	88	81 %	≥95	38
3	4b		75	76	76 %	≥95	10
4	4c		50	51	≤ 5 %	—	—
5	4d		75	74	≤ 5 %[d]	—	—

[a] Refers to the combined yield of **5**, **6**, and **7**. [b] Determined by capillary GC analysis of the crude reaction mixture. [c] Determined by chiral GC. [d] Contained traces of **7**.

employed in the synthesis of several naturally occurring carbocycles.[7]



(1)

By analogy with the palladium-catalyzed reductive cyclization of enynes and diynes employing acetic acid and silane, we considered that adventitious water could be serving as a hydrogen atom source in the palladium-catalyzed conversion of **1** to **5**. In an effort to test this hypothesis, water (100 μL) was added to the reaction of diene **1** (0.50 mmol) and $HSiEt_3$ (1.0 mmol) catalyzed by **4a**/$NaBAr_4$ (5 mol %) in 1,2-dichloroethane (DCE) at room temperature for 2 h. Significantly, <1% of the silylated carbocycle **3** was formed and instead a 2.0:1 mixture of **5** (>95% de, 18% ee) and dimethyl dipropylmalonate (**6**) along with traces (<2%) of 4,4-dicarbomethoxy-1-heptene (**7**) was isolated in 82% combined yield (Table 1, entry 1).[8] The chemo- and enantioselectivity of the reaction improved with increasing temperature, and at 50 °C a 4.4:1 ratio of **5**:**6** was isolated in 88% yield (38% ee) (Table 1, entry 2). The isopropyl-substituted catalyst **4b** also catalyzed the conversion of **1** to **5** at 75 °C with low enantioselectivity (Table 1, entry 3). In contrast, the phenyl-substituted bisoxazoline catalysts **4c** and **4d** led to reduction without cyclization (Table 1, entries 4 and 5).

In an effort to probe the role of water and silane in the palladium-catalyzed reductive cyclization of **1**, several deuterium labeling studies were performed. In one experiment, **1** was treated with a stoichiometric amount of D_2O (98% D) and $HSiEt_3$ and a catalytic mixture of **4a**/$NaBAr_4$ to form a 4.1:1 mixture of **5**-*d* and **6**-*d*, from which a 19:1 mixture of **5**-*d*:**6**-*d* was isolated in 18% yield.[9] NMR and MS analyses of **5**-*d* obtained from this reaction were consistent with the incorporation of approximately one deuterium atom per molecule of **5** exclusively into the exocyclic methyl groups. For example, the ^{13}C NMR spectrum of **5**-*d* displayed a ∼1:1 ratio of peaks at δ 41.9 and 41.8 (isotopic shift = 57 ppb), corresponding to the tertiary carbon atoms bonded to an exocyclic CH_3 and CH_2D group, respectively (Figure 1, spectrum b). The ^{13}C NMR spectrum also displayed a singlet at δ 17.5 and a 1:1:1 triplet at δ 17.2 (J = 19 Hz, isotopic shift = 292 ppb) in a 1.6:1 ratio corresponding to the exocyclic CH_3 and CH_2D groups, respectively (Figure 1, spectrum b).[10] Cutting and weighing the carbomethoxy (δ 3.74) and exocyclic (δ 0.90) methyl resonances in the ^1H NMR spectrum of **5**-*d* indicated the incorporation of 0.9 ± 0.2 deuterium atoms per molecule of **5**-*d* (Table 2). The mass spectrum of **5**-*d* established an 18:74:8 ratio of **5**:**5**-d_1:**5**-d_2, which corresponds to 0.89 ± 0.05 deuterium per molecule of **5**-*d*, in good agreement with the value obtained from the ^1H NMR spectrum (Table 2).

In a second labeling experiment, reaction of **1** with a stoichiometric mixture of $DSiEt_3$ (≥95% D) and H_2O catalyzed by a mixture of **4a**/$NaBAr_4$ formed a 4.1:1

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[7] (a) Trost, B. M.; Kondo, Y. *Tetrahedron Lett.* **1991**, *32*, 1613. (b) Trost, B. M.; Edstrom, E. D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 520. (c) Trost, B. M.; Edstrom, E. D.; Carter-Petillo, M. B. *J. Org. Chem.* **1989**, *54*, 4489. (d) Wender, P. A.; McDonald, F. E. *J. Am. Chem. Soc.* **1990**, *112*, 4956.

[8] A control experiment established that silylated carbocycle **3** was not converted to **5** under reaction conditions.

[9] No effort was made to analyze the isotopic composition of **6**-*d*. The small quantities of **6**-*d* present in the samples of **5**-*d* affected neither the NMR nor MS analysis of **5**-*d*.

[10] The intensities of the resonances cannot be compared directly due to the more efficient relaxation and greater NOE enhancement of the CH_3 group relative to the CH_2D group.

Table 2. Cyclization of 1 Catalyzed by a 1:1 Mixture of 4a/NaBAr$_4$ in DCE at 50 °C

$$\mathbf{1} \xrightarrow[\text{additives}]{\text{4a/NaBAr}_4} \mathbf{5}\text{-}d$$

additives	5:5-d_1:5-d_2[a]	D/molecule of 5 ^{1}H NMR[b]	 MS
HSiEt$_3$/D$_2$O	18:74:8	0.9 ± 0.2	0.89 ± 0.05
DSiEt$_3$/H$_2$O	13:74:13	1.0 ± 0.2	0.97 ± 0.05
DSiEt$_3$/D$_2$O	4:14:81	1.8 ± 0.2	1.76 ± 0.05

[a] Determined by MS analysis. [b] Determined by comparison of the intensity of the carbomethoxy and exocyclic methyl resonances.

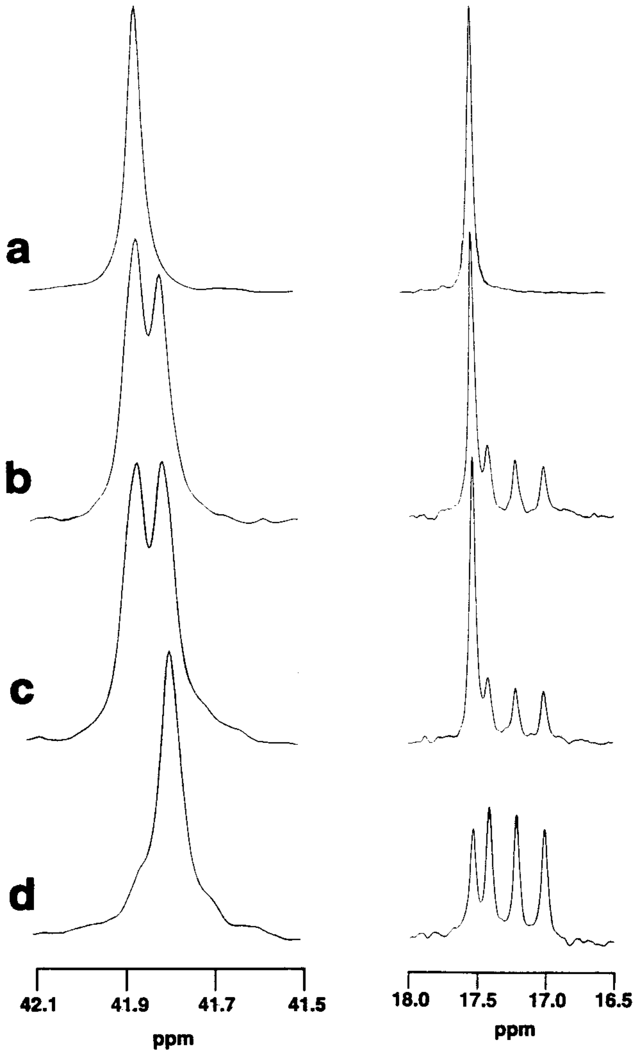

Figure 1. Partial ^{13}C{^{1}H} NMR spectra displaying the tertiary carbon resonances (δ 41.5−42.1, left column) and the exocyclic methyl resonances (δ 16.5−18.0, right column) for the isotopomers of **5** generated from cyclization of **1** in the presence of (a) H$_2$O/HSiEt$_3$, (b) D$_2$O/HSiEt$_3$, (c) H$_2$O/DSiEt$_3$, and (d) D$_2$O/DSiEt$_3$ catalyzed by **4a**/NaBAr$_4$ at 50 °C in DCE.

mixture of **5**-*d* and **6**-*d*, from which a 13:1 mixture of **5**-*d*:**6**-*d* was isolated in 23% yield.[9] The ^{13}C NMR spectrum of **5**-*d* obtained from this reaction displayed a ~1:1 ratio of peaks at δ 41.9 and 41.8 and a 1.7:1 ratio of peaks at δ 17.5 (s) and 17.2 (t, J = 19 Hz) (Figure 1, spectrum c), similar to the ^{13}C NMR spectrum of **5**-*d* obtained from reaction of **1** with D$_2$O/HSiEt$_3$ (Figure 1, spectrum b). Comparison of the intensity of the carbomethoxy and exocyclic methyl groups in the ^{1}H NMR spectrum of **5**-*d* obtained from reaction of **1** with H$_2$O/DSiEt$_3$ revealed the incorporation of 1.0 ± 0.2 deuterium per molecule of **5** (Table 2). The mass spectrum of **5**-*d* isolated from reaction of **1** with H$_2$O/DSiEt$_3$ established a 13:74:13 ratio of **5**:**5**-d_1:**5**-d_2, which corresponds to 0.97 ± 0.05 deuterium per molecule of **5**-*d* (Table 2).

In a third experiment, reaction of **1** with a stoichiometric mixture of D$_2$O and DSiEt$_3$ in the presence of a catalytic mixture of **4a**/NaBAr$_4$ formed a 4:1 mixture of **5**-*d* and **6**-*d*, from which a 16:1 mixture of **5**-*d*:**6**-*d* was isolated in 21% yield.[9] The ^{13}C NMR spectrum of **5**-*d* isolated from this reaction displayed a resonance at δ 41.8 with a small shoulder at δ ~41.9 along with a 1:3.5 ratio of peaks at δ 17.5 (s) and 17.2 (t, J = 19 Hz) (Figure 1, spectrum d), which is diminished significantly from the ~1.7:1 ratio of resonances observed for **5**-*d* isolated from either HSiEt$_3$/D$_2$O or DSiEt$_3$/H$_2$O (Figure 1, spectra b and c). Comparison of the intensity of the carbomethoxy and exocyclic methyl groups in the ^{1}H NMR spectrum of **5**-*d* obtained from reaction of **1** with D$_2$O/DSiEt$_3$ indicated the presence of 1.8 ± 0.2 deuterium per molecule of **5**-*d* (Table 2). Mass spectral analysis of **5**-*d* generated from D$_2$O/DSiEt$_3$ established a 4:14:81 ratio of **5**:**5**-d_1:**5**-d_2, which corresponds to 1.76 ± 0.05 deuterium atoms per molecule of **5**-*d* (Table 2).

The predominant formation of the **5**-d_1 isotopomer from reaction of **1** with either DSiEt$_3$/H$_2$O or HSiEt$_3$/D$_2$O and the predominant formation of the **5**-d_2 isotopomer from reaction of **1** with DSiEt$_3$/D$_2$O indicate that of the two hydrogen atoms that are incorporated into **5**, one originates from silane and the second originates from water. We propose a mechanism for reductive cyclization of **1** in the presence of water and silane in accord with this requirement. Brookhart has shown that chloride abstraction from palladium methyl chloride complexes such as **4a** with NaBAr$_4$ forms cationic palladium methyl complexes[11] which react rapidly with triethylsilane to form cationic palladium−silyl complexes.[12] In a similar manner, the palladium silyl complex **I** could react with water to form triethylsilanol and the palladium hydride intermediate **II** (Scheme 2).[8,13] Hydrometalation of one olefin of diene **1** could then form the palladium alkyl intermediate **III**, which could undergo intramolecular carbometalation via the palladium alkyl olefin intermediate **IV** to form the palladium methylcyclopentyl intermediate **V** (Scheme 2, path a). Metathesis of the Pd−C bond of **V** with the H−Si bond of free silane would then release carbocycle **5** and regenerate the palladium−silyl intermediate **I**. Alternatively, palladium alkyl intermediate **III** could react with silane prior to cyclization, leading to formation of **7**, which would ultimately be converted to **6** (Scheme 2, path b).

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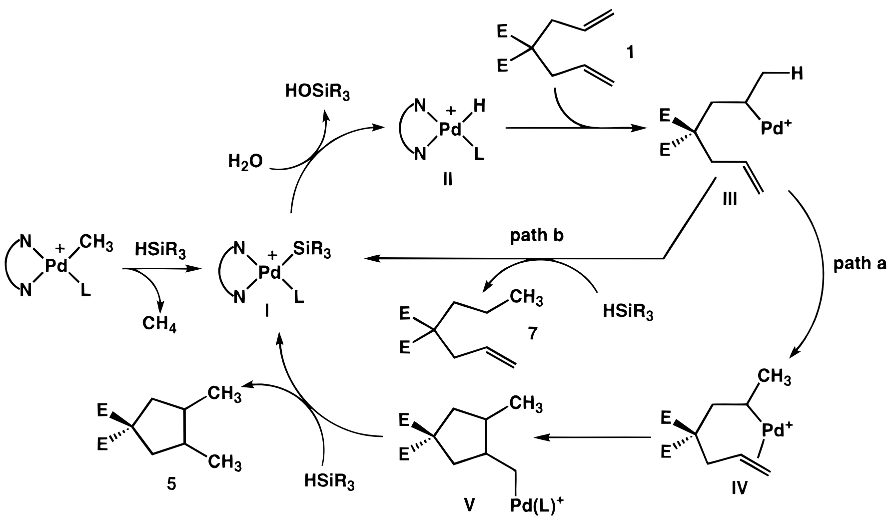
(11) (a) Brookhart, M.; Wagner, M. I.; Balavoine, G. G. A.; Haddou, H. A. *J. Am. Chem. Soc.* **1994**, *116*, 3641. (b) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267.

(12) LaPointe, A. M.; Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 906.

(13) Although the triethylsilanol was not observed in the reaction, considerable amounts of hexaethyldisiloxane (**8**) were formed. However, because **8** was also formed in the reaction of **1** and HSiEt$_3$ catalyzed by (phen)Pd(Me)Cl, in which **5** was not formed,[1] it is not clear whether the silanol also reacted with **I** to form **II** and **8**, or if **8** was formed from triethylsilanol in a separate reaction manifold.

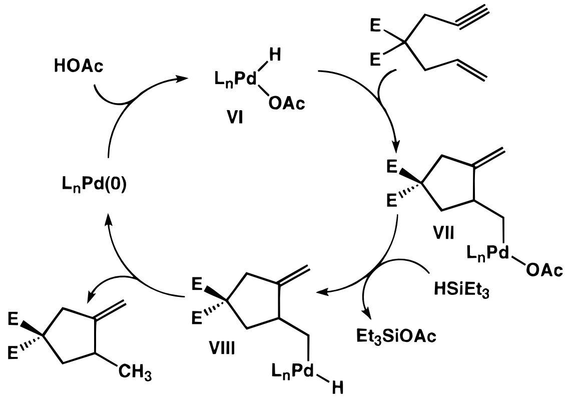
Scheme 2



The small amounts of **5** and **5**-d_2 formed in addition to **5**-d_1 in the reaction of **1** with either $DSiEt_3/H_2O$ or $HSiEt_3/D_2O$ point to the presence of a hydrogen/deuterium exchange pathway. A plausible mechanism for this hydrogen/deuterium exchange is via the degenerate metathesis of the Si−H bond of the silane with the Pd−H bond of intermediate **II**. For example, in the reaction of **1** with D_2O and $HSiEt_3$, initial reaction of D_2O with palladium silyl intermediate **I** would form palladium deuteride intermediate **II**-*d*. Metathesis of free silane with **II**-*d* could then form the corresponding palladium hydride complex **II** and $DSiEt_3$. Subsequent reaction of **II** with **1** would generate intermediate **V**, which could react with $HSiEt_3$ to form unlabeled **5**. Due to the relatively small pool of free silane employed in these reactions (2-fold excess relative to **1**), the $DSiEt_3$ released in the reaction of **II**-*d* and $HSiEt_3$ could eventually react with the deuterated intermediate **V**-*d*, leading to the observed formation of **5**-d_2.

The transfer of one hydrogen atom each from the silane and the water to the diene is similar to the transfer of one hydrogen atom each from acetic acid and silane in the palladium-catalyzed reductive cyclization of enynes.[5] However, the proposed mechanism for diene reductive cyclization catalyzed by **4a** differs markedly from the proposed mechanism for palladium-catalyzed reductive cyclization of enynes employing acetic acid and silane. Specifically, in the latter system, the Pd(0) catalyst is believed to oxidatively add acetic acid to form the Pd(II) acetoxy hydride species **VI**, which undergoes successive hydrometalation and carbometalation to form a palladium (acetoxy) methylcyclopentyl intermediate **VII** (Scheme 3). Metathesis of the H−Si bond of the silane with the Pd−OAc bond of **VII** then generates the palladium hydride intermediate **VIII**, which undergoes reductive elimination to form the carbocycle and regenerate Pd(0).[5]

Scheme 3



In summary, reaction of dimethyl diallylmalonate (**1**) with a stoichiometric amount of water and triethylsilane and a catalytic mixture of the palladium bisoxazoline catalyst **4a** and $NaBAr_4$ forms predominantly 1,1-dicarbomethoxy-3,4-dimethylcyclopentane (**5**) with excellent diastereoselectivity (>95%) and low enantioselectivity (<40%). Despite the presence of a hydrogen/deuterium exchange pathway, deuterium labeling experiment employing $D_2O/HSiEt_3$, $H_2O/DSiEt_3$, and $D_2O/DSiEt_3$ were consistent with the transfer of one hydrogen atom apiece from the silane and the water to the substrate in the conversion of **1** to **5**.

Experimental Section

General Methods. All reactions were performed under an atmosphere of nitrogen employing standard Schlenk techniques. Routine gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 25 m poly(dimethylsiloxane) capillary column. Chiral gas chromatography was performed on a 20 m × 0.25 mm Chiraldex G-TA column (Advanced Separation Technologies) at 15 psi column head pressure. Flash chromatography was performed employing 200−400 mesh silica gel (EM), and elemental analyses were performed by E+R Microanalytical Laboratories (Parsippany, NJ). Methylene chloride and DCE were distilled from CaH_2 under nitrogen. Triethylsilane (Aldrich), D_2O (Cambridge Isotopes), and dimethyl diallylmalonate (Lancaster) were used as received. Palladium precatalysts,[2] $NaB[3,5\text{-}C_6H_3(CF_3)_2]_4$,[14] and $DSiEt_3$ (>95% D by ^1H NMR analysis) were prepared by published procedures.[15]

***trans*-1,1-Dicarbomethoxy-3,4-dimethylcyclopentane (5).**[16,17] Triethylsilane (351 mg, 3.0 mmol) and water (600 μL, 33 mmol) were added via syringe to a solution of **1** (312 mg,

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[14] Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.

[15] Doyle, M. P.; McOsker, C. C.; West, C. T. *J. Org. Chem.* **1976**, *41*, 1393.

[16] Curran, D. P.; Shen, W. *J. Am. Chem. Soc.* **1993**, *115*, 6051.

[17] Kuehne, M. E.; Damon, R. E. *J. Org. Chem.* **1977**, *42*, 1825.

1.47 mmol), **4a** (23 mg, 7.2×10^{-2} mmol), and $NaBAr_4$ (73 mg, 7.2×10^{-2} mmol) in DCE (20 mL) at 0 °C and stirred at 50 °C for 1 h to form a dark solution. Evaporation of solvent and flash chromatography of the residue (hexanes/EtOAc = 35:1) gave a 4.4:1 mixture of **5**:**6** (275 mg, 88%) as a colorless oil. Repeated (2×) chromatography provided a 20:1 mixture of **5**:**6** (97 mg, 31%), which was used for NMR characterization of **5**. ^1H NMR (400 MHz, $CDCl_3$): δ 3.64 (s, 6 H), 2.45 (dd, $J = 6.7$, 13.5 Hz, 2 H), 1.66 (dd, $J = 10.7$, 13.6 Hz, 2 H), 1.41 (m, 2 H), 0.90 (d, $J = 6.1$ Hz, 6 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 173.6, 58.2, 52.7, 43.0, 41.9, 17.5.

Dimethyl Dipropylmalonate (6).[18] Reaction of $HSiEt_3$ (116 mg, 1.0 mmol), water (200 μL, 11 mmol), **1** (104 mg, 1.47 mmol), **4c** (8 mg, 7.2×10^{-2} mmol), and $NaBAr_4$ (26 mg, 7.2×10^{-2} mmol) in DCE (10 mL) at 50 °C for 1 h formed a dark solution. Evaporation of solvent and flash chromatography of the residue (hexanes/ether = 20:1 → 5:1) gave pure **6** (52 mg, 50%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 3.65 (s, 6 H), 1.80 (m, 4 H), 1.12 (m, 4 H), 0.87 (t, $J = 7.3$ Hz, 6 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.6, 57.9, 52.4, 35.0, 17.7, 14.5.

Synthesis of 5-*d*. Reaction of D_2O (600 μL, 33 mmol) and $HSiEt_3$ (330 mg, 2.8 mmol), **1** (300 mg, 1.4 mmol), **4a** (24 mg, 0.075 mmol), and $NaBAr_4$ (72 mg, 0.075 mmol) in DCE at 50 °C for 15 min formed a 4.1:1 mixture of **5**-*d* and **6**-*d*. Repeated chromatography (hexanes/EtOAc = 35:1) led to the isolation of a 5.6:1 ratio of **5**-*d*:**6**-*d* in 82% yield, and ultimately a 19:1 ratio of **5**-*d*:**6**-*d* in 18% yield, which was employed for spectroscopy. Reaction conditions, product isolation and analysis for the reaction of **1** with $DSiEt_3/H_2O$, and the reaction of **1** with $DSiEt_3/D_2O$ were performed analogously.

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