Enantioselective Diene Cyclization/Hydrosilylation Catalyzed by Optically Active Palladium Bisoxazoline and Pyridine−Oxazoline Complexes

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A 1:1 mixture of (N−N)Pd(Me)Cl [N−N = (*S*,*S*)-4,4′-dibenzyl-4,5,4′,5′-tetrahydro-2,2′-bisoxazoline] (*S*,*S*-**4a**) and $NaBAr_4$ [Ar = 3,5-$C_6H_3(CF_3)_2$] (5 mol %) catalyzed the asymmetric cyclization/hydrosilylation of dimethyl diallylmalonate (**2**) and triethylsilane at −30 °C for 48 h to form an 8.1:1 mixture of the silylated carbocycle (*S*,*S*)-*trans*-1,1-dicarbomethoxy-4-methyl-3-[(triethylsilyl)-methyl]cyclopentane (*S*,*S*-**3**) (95% de, 72% ee) and dimethyl 3,4-dimethylcyclopentane-1,1-dicarboxylate (*S*,*S*-**6**) in 64% combined yield. In comparison, a 1:1 mixture of the palladium pyridine−oxazoline complex (N−N)Pd(Me)Cl [N−N = (*R*)-(+)-4-isopropyl-2-(2-pyridinyl)-2-oxazoline] (*R*-**5b**) and $NaBAr_4$ (5 mol %) catalyzed the asymmetric cyclization/hydrosilylation of **2** and triethylsilane at −32 °C for 24 h to form carbocycle *S*,*S*-**3** in 82% yield (>95% de, 87% ee) as the exclusive product. Asymmetric diene cyclization catalyzed by complex *R*-**5b** was compatible with a range of functional groups and produced carbocycles with up to 91% ee. The procedure also tolerated substitution at a terminal olefinic position and at the allylic position of the diene.

Introduction

Asymmetric C−C bond formation remains of central importance in organic synthesis due to the pronounced tendency of naturally occurring compounds to display optical activity and due to the increasingly stringent requirements concerning the optical purity of pharmaceuticals. A particularly appealing and successful approach toward asymmetric C−C bond formation is via catalysis employing optically active transition metal complexes.[1,2] For example, copper[3−5] and rhodium[6] complexes catalyze the cyclopropanation of olefins with high (98%) enantioselectivity. Optically active palladium complexes catalyze the asymmetric nucleophilic displacement of allylic acetates[7] and the asymmetric coupling of aryl triflates and cyclic enol ethers[8] with good enantioselectivity. Platinum[9] and rhodium[10] phosphine complexes catalyze the hydroformylation of olefins with up to 98% ee and 95% ee has been achieved in the nickel-catalyzed cross-coupling of aryl bromides and Grignard reagents.[11]

The application of asymmetric C−C bond formation to the synthesis of cyclic compounds is of particular importance due to the prevalence of carbocycles in biologically active and naturally occurring molecules.[12] However, examples of highly enantioselective transition metal-catalyzed annulation procedures remain limited. A notable example is the palladium-catalyzed asymmetric intramolecular Heck reaction which has been applied extensively to the synthesis of complex functionalized carbocycles.[13] In addition, rhodium[14] and cobalt[15] bisphosphine complexes catalyze the asymmetric [4 + 2] cycloisomerization of unactivated dienynes and trienes with excellent selectivity (98% ee). Cationic Rh(I) bisphosphine complexes catalyze the asymmetric intramolecular hydroacylation of 4-pentenals with 90−99% ee.[16] Titanium(II) metallocene complexes and palladium phosphine complexes catalyze the asymmetric cyclocarbonylation[17] and cycloisomerization,[18] respectively, of 1,6-enynes with 75−95% ee. Rhodium-catalyzed asymmetric intramolecular cyclopropanation[19] and C−H insertion[20] of diazoacetates also generate carbocycles with high enantioselectivity.

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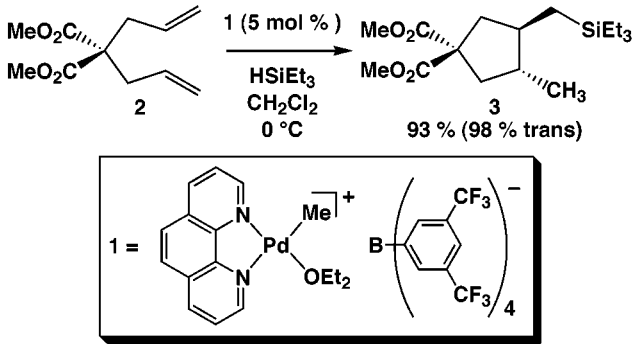
Cyclization/hydrosilylation is emerging as a potential route toward the synthesis of functionalized carbocycles. For example, nickel[21] and rhodium[22] complexes catalyze the cyclization/hydrosilylation of 1,7-diynes and 1,6-enynes, respectively. Similarly, lanthanide metallocene complexes catalyze the cyclization/hydrosilylation of both dienes and enynes.[23] We have recently reported the cyclization/hydrosilylation of functionalized 1,6- and 1,7-dienes catalyzed by cationic palladium complexes such as (phen)PdMe(OEt_2)$^+$ BAr_4^- [phen = 1,10-phenanthroline; Ar = 3,5-$C_6H_3(CF_3)_2$] (**1**).[24−27] For example, reaction of dimethyl diallylmalonate (**2**) and triethylsilane catalyzed by **1** at 0 °C for 5 min led to the isolation of the *trans*-silylated cyclopentane **3** in 93% yield (98% trans) (Scheme 1).[24]

Scheme 1



In contrast to the effective cyclization/hydrosilylation procedures described above, asymmetric cyclization/hydrosilylation has not been reported. However, the high activity and exceptional diastereoselectivity realized in palladium-catalyzed diene cyclization/hydrosilylation pointed to the potential of palladium-catalyzed asymmetric cyclization/hydrosilylation. Here we provide a detailed report on the employment of optically active palladium bisoxazoline and pyridine−oxazoline complexes as catalysts for the asymmetric cyclization/hydrosilylation of functionalized dienes.[28]

Results and Discussion

Synthesis of Palladium Precatalysts. In our previous studies, in situ generation of cationic complex **1** via halide abstraction from (phen)Pd(Me)Cl with $NaBAr_4$ [Ar = 3,5-$C_6H_3(CF_3)_2$] was found superior to the generation of **1** via protonation of (phen)$PdMe_2$ with $HBAr_4$.[25] Therefore, optically active palladium methyl chloride complexes were employed as precatalysts in this study. The requisite palladium bisoxazoline complexes **4a**−**d** (Table 1, entries 1−4) and palladium pyridine−oxazoline complexes **5a**−**l** (Table 1, entries 5−16) were prepared by reaction of the appropriate ligand with (COD)Pd(Me)Cl in CH_2Cl_2 at room temperature. Evaporation of solvent and trituration with ether gave the desired complexes as off-white or pale yellow solids which were characterized by spectroscopy and elemental analysis except *R*-**5d** and *S*-**5i**, which could not be isolated free from ligand and were characterized by spectroscopy (Table 1, entries 8 and 13). ^{1}H NMR spectroscopy of pyridine−oxazoline complexes **5** revealed the presence of a single stereoisomer in solution. Difference NOE spectroscopy of the isopropyl-substituted complex (N−N)Pd(Me)Cl [N−N = (*R*)-4-*i*-Pr-2-(2-pyridinyl)-2-oxazoline) (*R*-**5b**) established the cis relationship between the oxazoline ring and the palladium methyl group.

I. Cyclization/Hydrosilylation Catalyzed by Palladium Bisoxazoline Complexes. We initially targeted optically active palladium bisoxazoline complexes **4** as catalysts for asymmetric diene cyclization/hydrosilylation due to their availability[4,29] and due to the wealth of asymmetric transformations which utilize these ligands. For example, copper bisoxazoline complexes catalyze the asymmetric cyclopropanation of olefins[3,4] and the asym-

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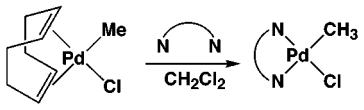
Table 1. Synthesis of Palladium Bisoxazoline and Pyridine−Oxazoline Precatalysts



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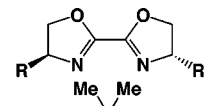
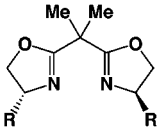
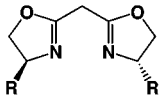
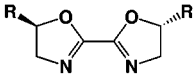
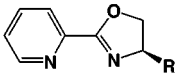
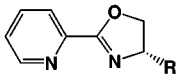
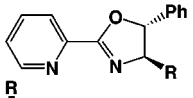
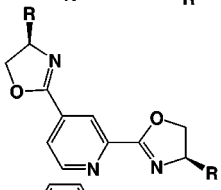
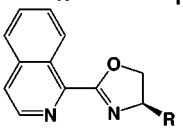
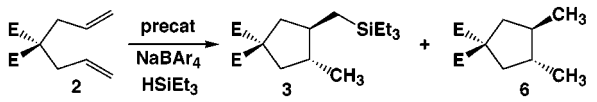
1		Bn	*S,S*-4a	80
2		Me	*R,R*-4b	98
3		Ph	*S,S*-4c	—[a]
4		Ph	*R,R*-4d	66
5		Me	*R*-5a	98
6		*i*-Pr	*R*-5b	85
7		Cy	*R*-5c	47
8		Ph	*R*-5d	—[b]
9		CH_2SMe	*S*-5e	88
10		*i*-Bu	*S*-5f	51
11		CH_2Cy	*S*-5g	76
12		(*S*)-*s*-Bu	*S,S*-5h	92
13		*t*-Bu	*S*-5i	—[b]
14		CH_2OMe	*R,R*-5j	99
15		*i*-Pr	*R,R*-5k	100
16		*i*-Pr	*R*-5l	43

[a] Previously reported in ref 34. [b] Not isolated free from ligand.

metric aziridination of olefins[30] and imines.[31] Iridium bisoxazoline complexes catalyze the asymmetric transfer hydrogenation of aryl ketones with up to 91% ee[4] while the corresponding rhodium complexes catalyze the hydrosilylation of acetophenone with moderate 84% ee.[32] Iron, copper, and magnesium bisoxazoline complexes

Table 2. Asymmetric Cyclization/Hydrosilylation of 2 Employing Palladium Bisoxazoline and Pyridine−Oxazoline Precatalysts 4 (5 mol %) and $HSiEt_3$ in CH_2Cl_2



entry	precat	temp (°C)	time (h)	**3**:**6**[a]	yield **3** + **6** (%)	de **3** (%)[a]	ee **3** (%)[b]
1	*S,S*-**4a**	25	0.2	4.5:1	70	92	53 (*S,S*)
2		0	1	5.5:1	65	94	68 (*S,S*)
3		−30	24	8.1:1	64	96	72 (*S,S*)
4	*R,R*-**4b**	25	2.5	8.0:1	69	>95	37 (*R,R*)
5	*S,S*-**4c**	25	24	1:4.4	31	>95	52 (*R,R*)
6	*R,R*-**4d**	25	0.2	35:1	89	>95	>5 (−)

[a] Product ratio and de determined by capillary GC. [b] ee determined by chiral GC.

catalyze the asymmetric Diels−Alder reaction.[33] Palladium−bisoxazoline complexes catalyze the nucleophilic substitution of allylic acetates with moderate enantioselectivity[4,34] and also catalyze the copolymerization of α-olefins and CO to form highly stereoregular polyketones.[35]

Reaction of diene **2** and $HSiEt_3$ catalyzed by a 1:1 mixture of the benzyl-substituted precatalyst (N−N)Pd(Me)Cl [N−N = (*S,S*)-4,4′-dibenzyl-4,5,4′,5′-tetrahydro-2,2′-bisoxazoline] (*S,S*-**4a**) and $NaBAr_4$ [Ar = 3,5-C_6H_3-$(CF_3)_2$] (5 mol %) at room temperature for 15 min led to isolation of a 4.5:1 mixture of silylated carbocycle (*S,S*-**3**) (92% de, 54% ee) and dimethyl 3,4-dimethylcyclopentane-1,1-dicarboxylate[36,37] (*S,S*-**6**) (77% de, 35% ee) in 70% combined yield (Table 2, entry 1).[38] Both the chemo- and stereoselectivity increased with decreasing reaction temperature and at −30 °C, an 8.1:1 mixture of **3**:**6** was isolated in 64% yield with 96% de and 72% ee for **3**. The methyl-substituted bisoxazoline precatalysts *R,R*-**4b** gave diminished levels of enantioselectivity relative to *S,S*-**4a** (Table 2, entry 4), while the phenyl-substituted bisoxazoline precatalyst *S,S*-**4c** was inefficient and formed only traces of carbocycle **3** (~6%) (Table 2, entry 5).

Relative to palladium phenanthroline catalyst **1**, employment of palladium bisoxazoline catalysts in the cyclization/hydrosilylation of **2** led to diminished product yield, sluggish reaction rates, and poor chemoselectivity. In an effort to probe the role of steric and electronic effects on the efficiency of bisoxazoline-catalyzed cyclization/hydrosilylation, the unhindered 5,5-diphenylbisoxazoline complex *R,R*-**4d** was employed as a cyclization precatalyst. Reaction of **2** and $HSiEt_3$ catalyzed by *R,R*-**4d** led to the isolation of a 35:1 ratio of **3**:**6** in 89% yield (>95% de) but with <5% ee (Table 2, entry 6). Comparison of this result with those obtained with precatalysts *S,S*-**4a** and *R,R*-**4b** indicated that excessive steric crowding of the coordination plane was detrimental to the

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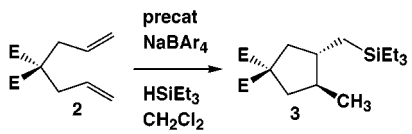
(32) Helmchen, G.; Krotz, A.; Ganz, K.-T.; Hansen, D. *Synlett*, **1991**, 257.
(33) (a) Corey, E. J.; Imai, N.; Zhang, H. Y. *J. Am. Chem. Soc.* **1991**, *113*, 728. (b) Corey, E. J.; Ishihara, K. *Tetrahedron Lett.* **1992**, *33*, 6807. (c) Evans, D. A.; Miller, S. J.; Leckta, T. *J. Am. Chem. Soc.* **1993**, *115*, 6460. (d) Evans, D. A.; Murry, J. A.; von Matt, P.; Norcross, R. D.; Miller, S. J. *J. Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 798.
(34) von Matt, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566.
(35) Brookhart, M.; Wagner, M. I.; Balavoine, G. G. A.; Haddou, H. A. *J. Am. Chem. Soc.* **1994**, *116*, 3641.
(36) Kuehne, M. E.; Damon, R. E. *J. Org. Chem.* **1977**, *42*, 1825.
(37) Curran, D. P.; Shen, W. *J. Am. Chem. Soc.* **1993**, *115*, 6051.
(38) The formation of **6** was traced, at least in part, to the presence of trace amounts of water in the solvent and/or borate salt.

Table 3. Asymmetric Cyclization/Hydrosilylation of 2 Employing Palladium Pyridine−Oxazoline Precatalysts 5 (5 mol %) and $HSiEt_3$ in CH_2Cl_2



entry	precat	temp (°C)	time (h)	yield (%)	de (%)[a]	ee (%)[b]
1	*R*-**5a**	25	0.2	81	>95	66 (*S*,*S*)
2	*R*-**5a**	−18	12	89	>95	76 (*S*,*S*)
3	*R*-**5a**	−43	48	85	>95	80 (*S*,*S*)
4	*R*-**5b**	−18	12	89	>95	84 (*S*,*S*)
5	*R*-**5b**	−32	24	82	>95	87 (*S*,*S*)
6	*R*-**5c**	−18	12	96[c]	>95	80 (*S*,*S*)
7	*R*-**5d**[d]	−18	12	82	>95	49 (*S*,*S*)
8	*S*-**5e**	−18	12	96	92	59 (*S*,*S*)
9	*S*-**5f**	−45	48	84	>95	77 (*R*,*R*)
10	*S*-**5g**	−18	12	74	>95	77 (*R*,*R*)
11	*S*,*S*-**5h**	−18	12	91	>95	79 (*R*,*R*)
12	*S*-**5i**[d]	−18	12	83[c]	83	73 (*R*,*R*)
13	*S*-**5i**[d]	−40	48	89[c]	91	91 (*R*,*R*)
14	*R*,*R*-**5j**	−18	12	76	>95	71 (*S*,*S*)
15	*R*,*R*-**5k**	−18	12	96	>95	81 (*S*,*S*)
16	*R*-**5l**	−18	12	88	>95	83 (*S*,*S*)

[a] Product ratio and de determined by GC. [b] ee Determined by chiral GC. [c] Product contained traces (∼5% of **6**). [d] Generated in situ from reaction of (COD)Pd(Me)Cl and ligand.

efficiency of cyclization. However, this comparison also revealed that a substituent adjacent to the oxazoline nitrogen atom was required for asymmetric induction.

II. Cyclization/Hydrosilylation Catalyzed by Palladium Pyridine−Oxazoline Complexes. Palladium pyridine−oxazoline complexes are both relatively uncrowded and possess a chiral center adjacent to the oxazoline nitrogen atom. As a result, these complexes were targeted as catalysts for asymmetric cyclization/hydrosilylation. However, a potential problem associated with the pyridine−oxazoline ligand is the formation of multiple diastereomeric transition states in the stereochemical determining step due to the low C_1-symmetry of the ligand. Perhaps because of this, examples of highly enantioselective catalytic transformations which employ pyridine−oxazoline ligands remain scarce. These examples are limited to the rhodium-catalyzed hydrosilylation of acetophenone which generated silylated alcohols with up to 94% ee[39] and to the copper-catalyzed asymmetric phenylation of 1,2-diols which formed phenols with low (≤50% ee) selectivity.[40]

Despite the low symmetry of the pyridine−oxazoline ligand, employment of palladium pyridine−oxazoline complexes as catalysts for asymmetric diene cyclization/hydrosilylation led to the formation of silylated carbocycles with higher yield and improved chemo-, diastereo-, and enantioselectivity relative to the bisoxazoline complexes (Table 3). For example, reaction of diene **2** and $HSiEt_3$ catalyzed by a 1:1 mixture of the methyl-substituted complex (N−N)Pd(Me)Cl [N−N = (*R*)-(+)-4-Me-2-(2-pyridinyl)-2-oxazoline] (*R*-**5a**) at room temperature for 10 min led to the isolation of *S*,*S*-**3** in 81% yield (>95% de, 66% ee) as the exclusive product (Table 3, entry 1). The enantioselectivity of the reaction increased with decreasing temperature and cyclization of **2** at −43 °C for 48 h gave *S*,*S*-**3** in 85% yield with 80% ee (Table 3, entries 2, 3). Noteworthy was that the pyridine−oxazoline catalysts led the opposite sense of asymmetric induction relative to the bisoxazoline catalysts.

Table 4. Effect of Solvent and Silane on the Cyclization/Hydrosilyation of 2 Catalyzed by a 1:1 Mixture of *R*-5b and $NaBAr_4$ (5 mol %) at −18 °C

entry	solvent	silane	carbocycle	yield (%)	ee (%)
1	DCE	$HSiEt_3$	**3**	86	74 (*S*,*S*)[a]
2	C_6H_5Cl	$HSiEt_3$	**3**	85	70 (*S*,*S*)[a]
3	1,1-DCE	$HSiEt_3$	**3**	83	75 (*S*,*S*)[a]
4	$CHCl_3$	$HSiEt_3$	**3**	96	74 (*S*,*S*)[a]
5	CH_2Cl_2	$HSiMe_2Et$	**7**	71	82 (*S*,*S*)[a]
6[b]	CH_2Cl_2	$HSiMe_2t$-Bu	**8**	87	89 (*S*,*S*)[d]
7[b]	CH_2Cl_2	$HSiMe_2Ph$	**9**	38	80 (*S*,*S*)[d]

[a] ee determined by chiral GC. [b] Reaction run at −40 °C. [c] 10 mol % catalyst employed. [d] ee determined by ^1H NMR spectroscopy.

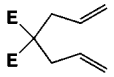
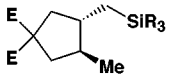
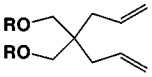
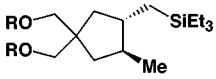
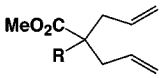
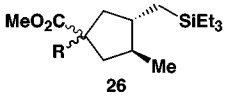
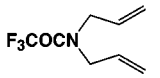
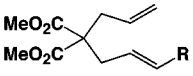
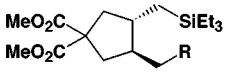
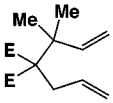
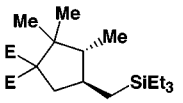
Effect of Catalyst Structure. The enantioselectivity of cyclization/hydrosilylation of **2** with $HSiEt_3$ was probed as a function of the substituent at the 4-position of the oxazoline ring. Precatalysts possessing a primary alkyl substituent such as an *i*-Bu (*S*-**5f**) or cyclohexylmethyl (*S*-**5g**) formed carbocycle **3** in good yield with 77−79% ee, comparable to precatalyst *R*-**5a** (Table 3, entries 9, 10). Precatalysts substituted with a secondary alkyl group such as *i*-Pr (*R*-**5b**), *s*-Bu (*S*,*S*-**5h**), or Cy (*R*-**5c**) led to improved enantioselectivity (82−87% ee) while maintaining good chemical yield (Table 3, entries 4−6, 11). The *tert*-butyl precatalyst (*S*-**5i**) provided even higher levels of enantioselectivity (91% ee), but suffered from diminished chemo- and diastereoselectivity (Table 3, entry 13). Precatalysts which possessed a 4-phenyl (*R*-**5d**), sulfide (*R*-**5e**), or a methoxymethyl group (*R*,*R*-**5j**) led to lower levels of enantioselectivity than did the precatalysts substituted with an alkyl group of comparable steric bulk (Table 3, entries 7, 8, 14). Substitution on the pyridine ring of the palladium pyridine−oxazoline complex had little effect on the efficiency or enantioselectivity of cyclization/hydrosilylation (Table 3, entries 15, 16).

Effect of Solvent and Silane. The efficiency and enantioselectivity of cyclization/hydrosilylation was then probed as a function of solvent and silane employing isopropyl-substituted precatalyst *R*-**5b**. In general, efficient cyclization/hydrosilylation required a chlorinated solvent such as $CHCl_3$, 1,1-dichloroethane, 1,2-dichloroethane, or chlorobenzene although employment of these solvents led to diminished enantioselectivity relative to CH_2Cl_2 (Table 4, entries 1−4). In addition, trialkylsilanes such as $HSiMe_2Et$ and $HSiMe_2CMe_3$ reacted with **2** to form carbocycles **7** and **8** with good yield and selectivity (Table 4, entries 5, 6). The enantioselectivity appeared to increase with the increasing steric bulk of the silane in the order $HSiMe_2Et$ (82% ee) < $HSiEt_3$ (84−87% ee) < $HSiMe_2CMe_3$ (89% ee). In contrast, reaction of **2** and $HSiMe_2Ph$ required 10% catalyst loading and formed carbocycle **9** in moderate yield (38%, 80% ee) (Table 4, entry 7). The concentration of the ligand or of the silane had no significant effect on the efficiency or enantioselectivity of cyclization/hydrosilylation.

(39) (a) Nishiyama, H.; Sakaguchi, H.; Nakamura, T.; Horihata, M.; Kondo, M.; Itoh, K. *Organometallics* **1989**, *8*, 846. (b) Brunner, H.; Oberman, U. *Chem. Ber.* **1989**, *122*, 499. (c) Brunner, H.; Brandl, P. *J. Organomet. Chem.* **1990**, *390*, C81. (d) Brunner, H.; Brandl, P. *Tetrahedron: Asymm.* **1991**, *2*, 919.

(40) Brunner, H.; Obermann, U.; Wimmer, P. *Organometallics* **1989**, *8*, 821.

Table 5. Asymmetric Cyclization/Hydrosilylation of 1,6-Dienes Employing a 1:1 Mixture of *R*-5b and $NaBAr_4$ (5 mol %) in CH_2Cl_2

Entry	Diene	Temp (° C)[a]	Carbocycle	Yield[b]	%de[c]	%ee
						
1	10 (E = CO_2CMe_3)	−18	19	85	≥95	87[e]
2		−40[f]		79[g]	≥98	90[d]
3	11 (E = CO_2Bn)	−40	20	83	95	86[d]
4	12 (E = CO_2i-Pr)	−40	21	75	98	85[d]
						
5	13 (R = Me)	−18	22	87	95	72[d]
6	14 (R = Bn)	−40	23	91	95	79[d]
7	15 (R = COMe)	−18	24	89	98	86[d]
8	16 (R = $COCMe_3$)	−18	25	89	97	91[d]
						
9	17 (R = SO_2Me)	−18	26	74	44	82[e,h]
10	18 (R = Ph)	−18	27	84	47	89[e,h]
11	 28	25	 29	76	95	33
						
12	30 (R = Me)	−40	32	79	92	85[e]
13	31 (R = Bu)	−40	33	75	93	87[e]
14	34 (R = Ph)	−18	34	62	96	73[e]
15	 36 (E = CO_2Me)	−18	 37	62	95	81[e]

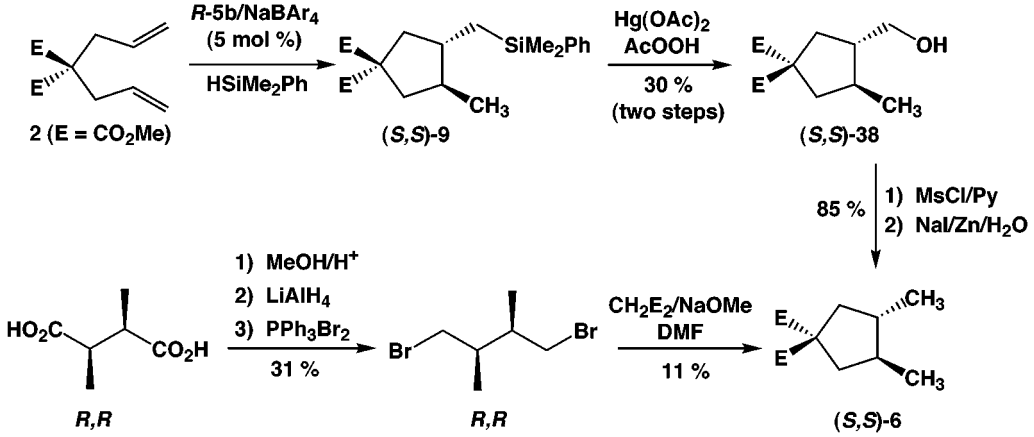
[a] Reaction times: −18 °C, 12 h; −40 °C, 48 h. [b] Yield refers to isolated material of >95% purity. [c] de determined by GC. [d] ee determined by chiral GC. [e] ee determined by ^1H NMR spectroscopy. [f] 10 mol % catalyst employed. [g] Product isolated as the corresponding dicarbomethoxy derivative. [h] ee of major diastereomer.

Scope of Asymmetric Cyclization/Hydrosilylation. The scope of asymmetric cyclization/hydrosilylation was probed with respect to the diene employing $HSiEt_3$ and *R*-**5b** (Table 5). Efficient asymmetric cyclization/hydrosilylation required a homoallylic ester, ether, ketone, or acetoxy group, similar to the requirements for cyclization with achiral catalyst **1**.[25] For example, diesters **10**−**12**, diethers **13** and **14**, protected diols **15** and **16**, and monoesters **17** and **18** reacted with $HSiEt_3$ to form carbocycles **19**−**27** in good yield and with good enantioselectivity (Table 5, entries 1−10). Although complex *R*-**5b** catalyzed the cyclization/hydrosilylation of diallyltrifluoroacetamide (**28**) to form the corresponding pyrrolidine **29** in good yield, enantioselectivity was low (Table 5, entry 11). The enantioselectivity of cyclization appeared to roughly parallel the steric bulk of the homoallylic substituents of the diene, which is presumably related to the ease of cyclization (Thorpe−Ingold).[41] For example, the enantioselectivity of cyclization/hydrosilylation increased in the order $COCF_3$ (33% ee) < $(CH_2OMe)_2$ (72% ee) < $(CO_2Me)_2$ (84−87% ee) < $(CH_2CO_2CMe_3)_2$ (91% ee).

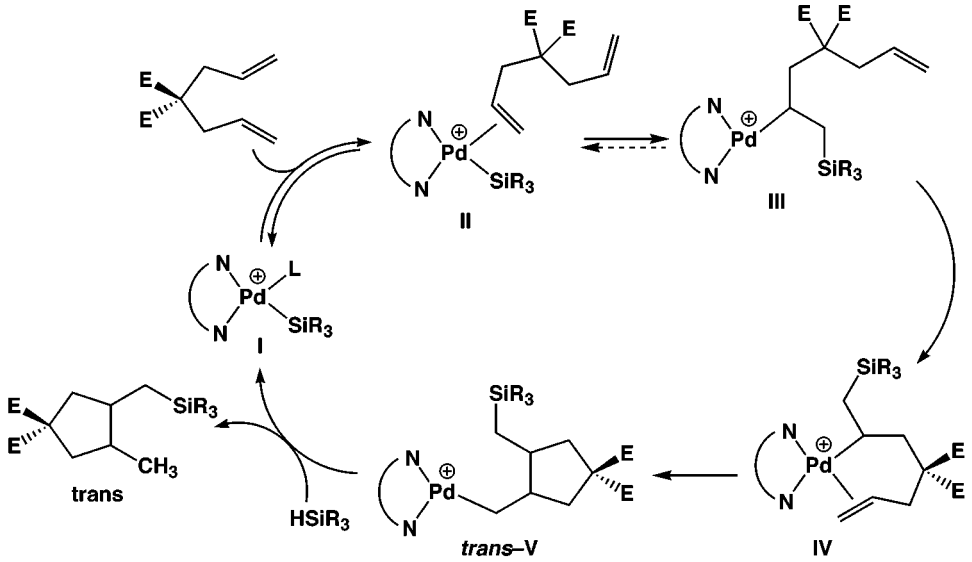
Asymmetric cyclization/hydrosilylation also tolerated limited substitution at the allylic and terminal olefinic positions. Cyclization/hydrosilylation of these substrates displayed excellent regioselectivity for delivery of the silane to the less-hindered olefin, as was observed with the achiral phenanthroline catalyst **1**.[25] For example, dienes substituted at a terminal olefinic carbon atom with a methyl (**30**) or butyl (**31**) group underwent asymmetric cyclization/hydrosilylation in high yield to form carbocycles **32** and **33** with ≥85% ee although diastereoselectivity was somewhat diminished relative to unsubstituted dienes (Table 5, entries 12 and 13). The procedure also tolerated a terminal phenyl group (**34**) to form carbocycle **35** although considerably lower enantioselectivity was achieved (Table 5, entry 14). In a similar manner, 4,4-dicarbomethoxy-3,3-dimethyl-1,6-heptadiene (**36**), which possesses *gem*-dimethyl substitution at a

(41) (a) DeTar, D. F.; Luthra, N. P. *J. Am. Chem. Soc.* **1980**, *102*, 4505. (b) Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 208. (c) Eliel, E. L. *Stereochemistry of Carbon Compounds*; McGraw-Hill: New York, 1962; pp 197−202. (d) Schore, N. E. in *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, p 1037.

Scheme 2



Scheme 3



single allylic carbon atom underwent cyclization/hydrosilylation to form **37** in high yield and with good stereoselectivity (Table 5, entry 15).

Determination of Absolute Configuration. Diene **2** was treated with dimethylphenylsilane in the presence of *R*-**5b**/$NaBAr_4$ (5 mol %) at room temperature for 2 h to form carbocycle *S*,*S*-**9**. Carbocycle *S*,*S*-**9** was then oxidized with mercuric acetate and peracetic acid[42] to form 1,1-dicarbomethoxy-3-methyl-4-(hydroxylmethyl)-cyclopentane (*S*,*S*-**38**) in 30% yield (92% de, 66% ee) from **2**. Alcohol **38** was mesylated (MsCl/py) and then reduced with sodium iodide, zinc, and water[43] to give *S*,*S*-**6** in 85% yield from **38** (Scheme 2). An authentic sample of *S*,*S*-**6** (57% de, 62% ee) was synthesized in four steps from (*R*,*R*)-2,3-dimethylsuccinic acid[44] employing a procedure similar to that developed by Kuehne (Scheme 2).[35] The absolute configuration of *S*,*S*-**6** obtained from precatalyst *R*-**5b** was identical to that of the authentic sample of *S*,*S*-**6** as determined by both optical rotation and chiral ^{1}H NMR spectroscopy employing $Eu(hfc)_3$. Carbocycles **3**, **7**, and **8** generated from precatalyst *R*-**5b** were also assigned the *S*,*S*-configuration due to the similar shifts of these carbocycles relative to *S*,*S*-**9** in the chiral ^{1}H NMR spectra.

Mechanistic Hypotheses. We propose a mechanism for palladium-catalyzed asymmetric diene cyclization/hydrosilylation analogous to that postulated for diene cyclization/hydrosilylation catalyzed by palladium phenanthroline complex **1** (Scheme 3).[25] Coordination of one olefin of the diene to the palladium silyl intermediate **I** would form the palladium silyl olefin complex **II**. Subsequent β-migratory insertion of the olefin into the Pd−Si bond could form the palladium−alkyl intermediate **III**. Coordination of the pendant olefin followed by β-migratory insertion of the olefin into the Pd−C bond of **IV** would form palladium cyclopentylmethyl intermediate **V**. The conversion of **IV** to **V** is significant as this step both forms the C−C bond and sets the trans stereochemistry of the carbocycle. Reaction of **V** with free triethylsilane could then release the carbocycle and regenerate the palladium−silyl intermediate **I** (Scheme 3).

In the palladium-catalyzed hydrosilylation of unfunctionalized olefins, both intermolecular olefin coordination

(42) (a) Fleming, I.; Henning, R.; Plaut, H. *J. Chem. Soc., Chem. Commun.* **1984**, 29. (b) Fleming, I.; Sanderson, P. E. J. *Tetrahedron Lett.* **1987**, *28*, 4229. (c) Jones, G. R.; Landais, Y. *Tetrahedron* **1996**, *52*, 7599.

(43) Kocovsky, P.; Cerny, V. *Coll. Czech. Chem. Commun.* **1979**, *44*, 246.

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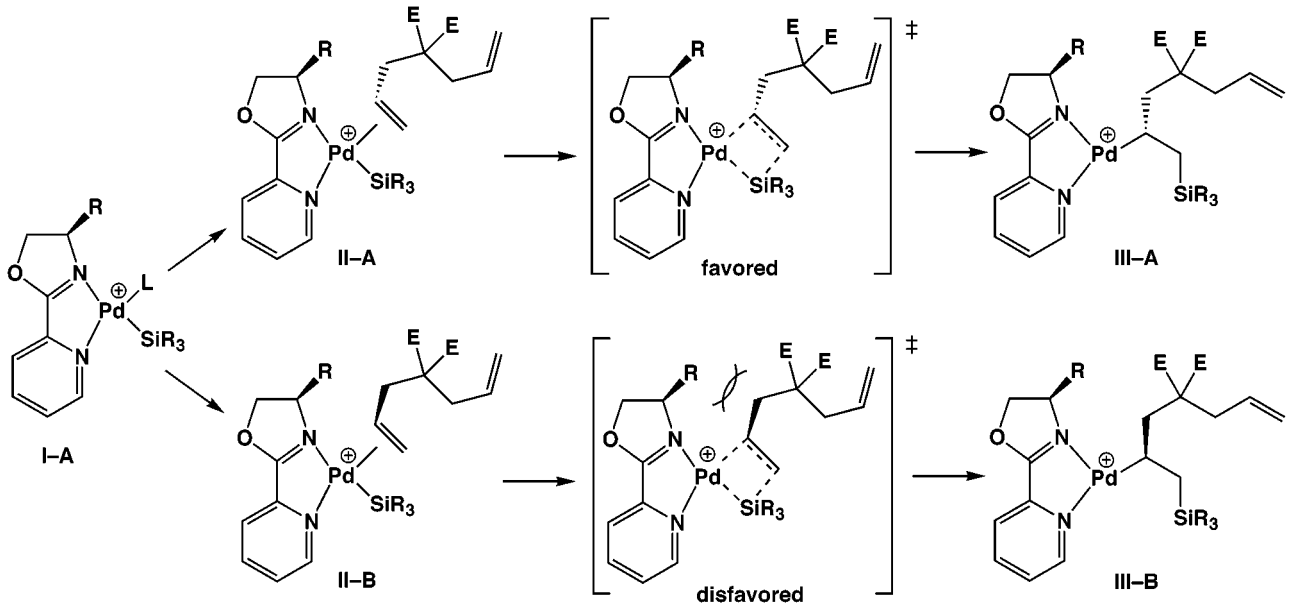
Scheme 4



to **I** and β-migratory insertion of the olefin into the Pd−Si bond is rapid and reversible.[45] However, in the case of cyclization/hydrosilylation catalyzed by palladium pyridine−oxazoline complexes, coordination of the pendant olefin of intermediate **III** to form **IV** would fill the coordination site required for β-silyl elimination and may therefore render C−Si bond formation irreversible. Under these conditions, enantioselectivity would be determined by the selectivity of olefin insertion into the Pd−Si bond of **II** to form **III** (Scheme 3). Olefin coordination to the *R*-pyridine−oxazoline palladium intermediate **I-A** could potentially form eight diastereomeric palladium silyl olefin complexes **II** (Scheme 4). However, a cis arrangement of the prochiral olefin and the oxazoline ring is presumably required to account for the high levels of asymmetric induction observed experimentally and the terminal end of the olefin must be directed toward the silane to account for the regioselectivity of insertion.[46] Of the two diastereomers which meet these requirements (**II-A** and **II-B**), intermediate **II-A** should undergo insertion at a higher rate than does **II-B** as the oxazoline and olefinic substituents are directed toward opposite faces of the coordination plane in the transition state for insertion (Scheme 4). Subsequent trans-cyclization of **III-A** followed by metathesis would then form the *S,S*-carbocycle, in accord with experimental observations.

Cyclization/hydrosilylation employing bisoxazoline precatalysts *S,S*-**4a** and *R,R*-**4b** led the opposite sense of asymmetric induction relative to the pyridine−oxazoline catalysts.[47] This reversal in enantioselectivity most likely results from a change in the stereochemical determining step. As one possibility, the distal oxazoline substituent of (*R,R*)-bisoxazoline alkyl intermediates **III-C** and **III-D** may hinder coordination of the pendant olefin and render C−Si bond formation reversible (Scheme 5). Under these conditions, enantioselectivity will be determined by the selectivity of either C−C bond formation (**IV** → **V**) (Scheme 5). Of the two possible diastereomeric alkyl olefin intermediates **IV-C** and **IV-D**, intermediate **IV-C** should be of higher energy due to steric interaction between the alkyl(trialkylsilyl) group and the proximal oxazoline substituent. Because the transition states for both formation and consumption of intermediates **IV-C** and **IV-D** should closely resemble the corresponding intermediate, **IV-D** should be both formed and consumed faster than **IV-C**, ultimately leading to preferential formation of the *R,R*-carbocycle, as was observed experimentally.

Conclusions

Optically active palladium bisoxazoline complexes **4** catalyze the cyclization/hydrosilylation of dimethyl diallylmalonate (**2**) and triethylsilane to form mixtures of silylated carbocycle **3** and carbocycle **6** in moderate yield and with up to 72% ee for **3**. Optically active, palladium pyridine−oxazoline complexes **5** catalyze the asymmetric cyclization/hydrosilylation of **2** and $HSiEt_3$ to form **3** as the exclusive product in good yield and with up to 87% ee. The latter procedure was applied to the asymmetric cyclization/hydrosilylation of a range of functionalized dienes including those with olefinic and allylic substitution. The enantioselectivity of cyclization/hydrosilylation roughly paralleled the steric bulk of the homoallylic substituents and ranged from 33% ee for cyclization of diallyltrifluoroacetamide (**28**) to 91% ee for the cyclization/hydrosilylation of 4,4-bis(trimethylacetoxymethyl)-1,6-heptadiene (**16**). A number of silanes were employed in the cyclization/hydrosilylation procedure although dimethylphenylsilane was not particularly efficient. Because of this latter limitation, further studies will be directed toward the identification of effective silanes for asymmetric cyclization/hydrosilylation which undergo oxidative cleavage under mild conditions.

Experimental Section

General Methods. All reactions were performed under an atmosphere of nitrogen employing standard Schlenk techniques. NMR spectra were obtained in $CDCl_3$ at 300 MHz for

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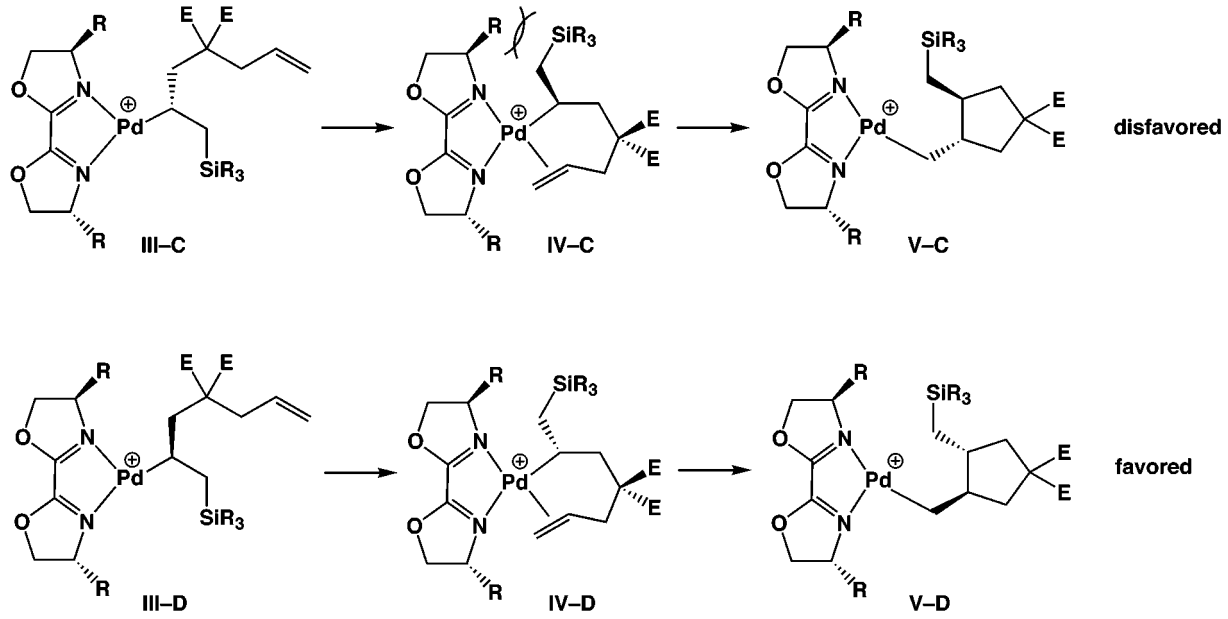
(46) The C−C bond of the olefin must lie in the coordination plane for β-migratory insertion to occur through a concerted four-centered transition state.

(47) Although bisoxazoline catalyst *S,S*-**4c** led to the opposite sense of asymmetric induction relative to bisoxazoline catalysts *S,S*-**4a** and *R,R*-**4b**, use of catalyst *S,S*-**4c** led to formation of only traces (~6%) of silylated carbocycle.

Scheme 5



^{1}H and 75 MHz for ^{13}C unless otherwise noted. 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). Flash chromatography was performed employing 200−400 mesh silica gel (EM). Elemental analyses were performed by E+R Microanalytical Laboratories (Parsippany, NJ). Methylene chloride, dichloroethane, chloroform, and chlorobenzene were distilled from CaH_2 under nitrogen. Ether and THF were distilled from Na/benzophenone under nitrogen. *N*,*N*-Dimethylformamide (Aldrich, anhydrous) was used as received.

Silanes (Aldrich) were distilled from CaH_2 under nitrogen. Dimethyl diallylmalonate, (*S*,*S*)-4,4′-dibenzyl-2,2′-bis(2-oxazoline), (*S*,*S*)-2,2′-methylenebis(4-phenyl-2-oxazoline) (Fluka), dimethyl malonate, and (±)-2,3-dimethylsuccinic acid (Aldrich) were used as received. The remaining bisoxazoline ligands were prepared employing published procedures.[29] Pyridine−oxazoline ligands were prepared employing the method of Bolm (see Supporting Information).[48] Dienes **10**,[49] **13**,[50] **17**,[25] **18**,[51] **28**,[25] **34**,[25] and **36**[25] were prepared by known procedures; the syntheses of the remaining dienes is included in the Supporting Information. NaB[3,5-$C_6H_3(CF_3)_2$]$_4$ was prepared by known procedures.[52] (COD)PdMeCl was prepared by known procedures and stored under inert atmosphere at −30 °C.[53] Carbocycles **8**, **9**, **19**, **22**, **26**, **29**, **32**, and **37** have been previously characterized.[25]

Precatalysts. [(*S*,*S*)-4,4′-Dibenzyl-2,2′-bis(2-oxazoline)]-Pd(Me)Cl (*S*,*S*-4a). A solution of (COD)PdMeCl (200 mg, 0.75 mmol) and (*S*,*S*)-4,4′-dibenzyl-2,2′-bis(2-oxazoline) (260 mg, 0.82 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 15 min to form a bright yellow solution. Evaporation of solvent and trituration with ether gave a yellow solid which was dried under a flow of nitrogen to yield *S*,*S*-**4a** (284 mg, 80%). ^{1}H NMR (CD_2Cl_2): δ 7.29−7.36 (m, 10 H), 4.53−4.69 (m, 5 H), 4.45 (dd, J = 7.2, 8.8 Hz, 1 H), 3.47 (dd, J = 3.6, 14.0 Hz, 1 H), 3.15 (dd, J = 3.2, 14.0 Hz, 1 H), 3.02 (dd, J = 8.4, 14.0 Hz, 1 H), 2.79 (dd, J = 8.4, 13.6 Hz, 1 H), 1.07 (s, 3 H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 161.1, 158.5, 136.9, 135.8, 130.8, 130.6, 129.9, 129.7, 128.4, 128.0, 77.3, 77.2, 66.3, 64.9, 40.5, 40.0, −6.8. Anal. Calcd (found) for $C_{21}H_{23}N_2O_2PdCl$: H, 4.86 (4.71); C, 52.94 (52.88).

[(*S*,*S*)-2,2′-Methylenebis(4-phenyl-2-oxazoline)]Pd(Me)-Cl (*S*,*S*-4c). Off-white solid. ^{1}H NMR (400 MHz): δ 7.30 (m, 8 H), 7.12 (m, 2 H), 5.80 (m, 1 H), 5.29 (m, 1 H), 4.66 (dt, J = 3.7, 8.6 Hz, 2 H), 4.49 (dd, J = 4.6, 8.8 Hz, 1 H), 4.31 (dd, J = 4.0, 8.4 Hz, 1 H), 3.83, 3.70 (ABquartet, J = 20.7 Hz, 2 H), 0.22 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz): δ 167.7, 163.9, 142.3, 141.3, 130.0, 129.5, 129.3, 128.8, 127.9, 126.6, 77.9, 77.6, 70.3, 68.1, 28.4, −4.3. Anal. Calcd (found) for $C_{20}H_{21}N_2OPdCl$: H, 4.58 (4.48); C, 51.94 (52.01).

[(*R*,*R*)-5,5′-Diphenyl-2,2′-bis(oxazoline)]Pd(Me)Cl (*R*,*R*-4d). Yellow solid. ^{1}H NMR (400 MHz): δ 7.437 (m, 10 H), 6.07 (dt, J = 4.8, 9.98 Hz, 1 H), 5.96 (t, J = 9.8 Hz, 1 H), 4.43 (m, 2 H), 4.09 (dd, J = 9.1, 16.2 Hz, 2 H), 4.01 (dd, J = 9.2, 15.2 Hz, 1 H), 1.03 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz): δ 131.1, 130.8, 130.3, 130.2, 129.8, 129.6, 127.5, 127.5, 88.6, 88.5, 59.5, 59.0, −7.0. Anal. Calcd (found) for $C_{19}H_{19}N_2OPdCl$: H, 4.27 (4.32); C, 50.89 (51.12).

[(*R*)-(+)-4-Methyl-2-(2-pyridinyl)-2-oxazoline]Pd(Me)-Cl (*R*-5a). Yellow solid. ^{1}H NMR (400 MHz): δ 8.96 (m, 1 H), 7.93 (m, 1 H), 7.72 (m, 1 H), 7.61 (m, 1 H), 4.89 (t, J = 8.4 Hz, 1 H), 4.48 (t, J = 8.8 Hz, 2 H), 1.38 (d, J = 6.4 Hz, 3 H), 0.96 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz): δ 167.6, 148.8, 142.2, 137.8, 128.0, 122.86, 77.2, 58.3, 20.6, −10.0. Anal. Calcd (found) for $C_{10}H_{13}N_2OPdCl$: H, 4.11 (4.10); C, 37.64 (37.76).

[(*R*)-(+)-4-Isopropyl-2-(2-pyridinyl)-2-oxazoline]Pd(Me)-Cl (*R*-5b). Pale yellow solid. ^{1}H NMR: δ 8.97 (d, J = 5.5 Hz, 1 H), 7.94 (dt, J = 1.7, 7.8 Hz, 1 H), 7.70 (d, J = 7.7 Hz, 1 H), 7.60 (ddd, J = 1.2, 5.0, 7.6 Hz, 1 H), 4.71 (m, 2 H), 4.35 (m, 1 H), 2.27 (doublet of septets, J = 3.3, 7.0 Hz, 1 H), 0.95 (s, 3 H), 0.93 (d, J = 7.0 Hz, 3 H), 0.79 (d, J = 6.8 Hz, 3 H). ^{13}C-{^{1}H} NMR: δ 168.4, 149.6, 142.9, 138.8, 129.0, 123.9, 71.8, 68.0, 29.8, 19.1, 14.3, −9.0. Anal. Calcd (found) for $C_{12}H_{17}N_2$-OPdCl: H, 4.94 (4.72); C, 41.52 (41.45).

Structural Determination of *R*-5b by NOE. Irradiation of H_1 gave a 20.5% enhancement of the signal for H_2. Irradiation of H_5 gave an 8.8% enhancement for H_6, a 2.2% enhancement for H_4, and a 3.4% enhancement for H_3. Irradiation of H_3 gave a 9.1% enhancement for H_6 and a 15.9% enhancement for H_5.

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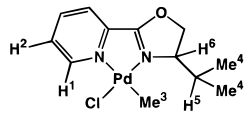

***R*-5b**

[(*R*)-4-Cyclohexyl-2-(2-pyridinyl)-2-oxazoline]Pd(Me)Cl (*R*-5c). Pale yellow solid. ^{1}H NMR (400 MHz): δ 9.03 (ddd, J = 0.9, 1.7, 5.0 Hz, 1 H), 7.93 (dt, J = 1.7, 7.7 Hz, 1 H), 7.71 (dt, J = 1.0, 7.7 Hz, 1 H), 7.63 (ddd, J = 1.3, 5.0, 7.7 Hz, 1 H), 4.76 (dd, J = 4.8, 9.2 Hz, 1 H), 4.63 (t, J = 9.4 Hz, 1 H), 4.26 (m, 1 H), 1.98−1.87 (m, 1 H), 1.81−0.83 (m, 10 H), 0.99 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz): δ 168.3, 149.7, 142.9, 138.7, 128.9, 123.8, 72.4, 67.6, 39.8, 29.6, 26.4, 26.3, 25.6, 24.7, −8.9. Anal. Calcd (found) for $C_{14}H_{21}N_2OPdCl$: H, 5.47 (5.42); C, 46.53 (46.44); N, 7.23 (7.13).

[(*R*)-4-Phenyl-2-(2-pyridinyl)-2-oxazoline]Pd(Me)Cl(*R*-5d). ^{1}H NMR (400 MHz): δ 8.99 (d, J = 4.7 Hz, 1 H), 7.96 (t, J = 7.7 Hz, 1 H), 7.81 (d, J = 7.7 Hz, 1 H), 7.64 (br t, J = 6.2 Hz, 1 H), 7.29 (m, 5 H), 5.48 (dd, J = 6.7, 10.8 Hz, 1 H), 5.21 (dd, J = 10.2, 10.8 Hz, 1 H), 4.64 (dd, J = 7.0, 9.7 Hz, 1 H), 0.63 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz): δ 169.7, 149.8, 142,8, 139.2, 138.7, 129.3, 129.2, 129.0, 126.8, 124.1, 79.4, 67.0, −7.9.

[(*S*)-4-Methylmercaptomethyl-2-(2-pyridinyl)-2-oxazoline]Pd(Me)Cl (*S*-5e). Yellow powder. ^{1}H NMR (400 MHz): δ 9.02 (br d, J = 4.1 Hz, 1 H), 7.96 (dt, J = 1.4, 7.9 Hz, 1 H), 7.78 (d, J = 7.7 Hz, 1 H), 7.66 (br s, 1 H), 4.87 (br s, 2 H), 4.59 (br s, 1 H), 2.98 (b, 1 H), 2.63 (br s, 1 H), 2.24 (br s, 3 H), 0.96 (s, 3 H). ^{13}C NMR was not obtained due to excessive broadening of the resonances which was also observed in the ^{1}H NMR spectrum. Anal. Calcd (found) for $C_{11}H_{15}N_2OSPdCl$: H, 4.14 (4.30); C, 36.18 (36.27).

[(*S*)-4-(2-Isobutyl)-2-(2-pyridinyl)-2-oxazoline]Pd(Me)Cl (*S*-5f). Yellow powder. ^{1}H NMR (400 MHz): δ 8.95 (m, 1 H), 7.93 (m, 1 H), 7.71 (m, 1 H), 7.61 (m, 1 H), 4.87 (m, 1 H), 4.60 (m, 1 H), 4.35 (m, 1 H), 1.81 (m, 1 H), 1.64 (m, 1 H), 1.41 (m, 1 H), 0.95 (d, J = 3.0 Hz, 6 H), 0.94 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz): δ 167.5, 148.8, 142.1, 137.8, 128.0, 122.8, 61.2, 43.0, 24.7, 22.9, 20.8, −9.6. Anal. Calcd (found) for $C_{13}H_{19}N_2OPdCl$: H, 5.30 (5.40); C, 43.23 (43.33).

[(*S*)-4-Cyclohexylmethyl-2-(2-pyridinyl)-2-oxazoline]-Pd(Me)Cl (*S*-5g). Yellow powder. ^{1}H NMR (400 MHz): δ 9.00 (dd, J = 0.3, 4.6 Hz, 1 H), 7.93 (dt, J 1.6, 7.7 Hz, 1 H), 7.71 (d, J = 7.3 Hz, 1 H), 7.61 (ddd, J = 1.2, 5.1, 7.7 Hz, 1 H), 4.81 (t, J = 8.9 Hz, 1 H), 4.59 (dd, J = 5.0, 8.7 Hz, 1 H), 4.34 (m, 1 H), 1.89 (m, 1 H), 1.77−1.58 (m, 5 H), 1.39−0.85 (m, 7 H), 0.96 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz): δ 168.3, 149.7, 143.1, 138.7, 128.9, 123.6, 61.6, 42.6, 35.0, 34.4, 32.5, 26.4, 26.1, −8.7. Anal. Calcd (found) for $C_{16}H_{23}N_2OPdCl$: H, 5.78 (5.83); C, 47.90 (48.14); N, 6.98 (6.91).

[(*S*,*S*)-4-*sec*-Butyl-2-(2-pyridinyl)-2-oxazoline]Pd(Me)Cl (*S*,*S*-5h). Yellow powder. ^{1}H NMR: δ 9.05 (dq, J = 5.1, 0.9 Hz, 1 H), 7.96 (dt, J = 7.5, 1.8 Hz, 1 H), 7.73 (d, J = 7.8 Hz, 1 H), 7.65 (ddd, J = 1.2, 5.1, 7.8 Hz, 1 H), 4.67 (m, 2 H), 4.44 (ddd, J = 3.0, 6.0, 9.0 Hz, 1 H), 2.08 (m, 1 H), 1.27 (m, 2 H), 0.99 (s, 3H), 0.97 (t, J = 7.5 Hz, 3 H), 0.79 (d, J = 6.9 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 168.5, 149.8, 143.0, 138.8, 129.0, 123.9, 71.8, 66.6, 36.6, 26.6, 12.2, 12.1, −8.9. Anal. Calcd (found) for $C_{13}H_{19}N_2OPdCl$: H, 5.30 (5.38), C, 43.23 (43.59); N, 7.76 (7.65).

[(*S*)-4-*tert*-Butyl-2-(2-pyridinyl)-2-oxazoline]Pd(Me)Cl (*S*-5i). ^{1}H NMR: δ 9.02 (d, J = 4.8 Hz, 1 H), 8.04 (dt, J = 1.3, 7.6 Hz, 1 H), 7.96 (d, J = 1.4 Hz, 1 H), 7.64 (ddd, J = 1.2, 3.8, 7.7 Hz, 1 H), 4.86 (dd, J = 2.9, 9.4 Hz, 1 H), 4.04 (dd, J = 2.9, 9.0 Hz, 1 H), 1.00 (s, 9 H); 0.97 (s, 3 H). ^{13}C{^{1}H} NMR: δ 149.7, 142.7, 138.5, 128.8, 123.7, 73.2, 70.5, 35.5, 25.7, −5.4.

[(*R*,*R*)-4-(Methoxymethyl)-5-phenyl-2-(2-pyridinyl)-2-oxazoline]Pd(Me)Cl (*R*,*R*-5j). Yellow powder. ^{1}H NMR (400 MHz): δ 9.07 (br d, J = 6.0 Hz, 1 H), 7.96 (dt, J = 1.5, 7.9 Hz, 1 H), 7.81 (br d, J = 7.7 Hz, 1 H), 7.67 (ddd, J = 1.4, 5.1, 8.3 Hz, 1 H), 7.40 (m, 3 H), 7.30 (m, 2 H), 5.97 (d, J = 5.3 Hz, 1 H), 4.35 (m, 1 H), 3.69 (m, 2 H), 3.43 (s, 3 H), 0.95 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz): δ 169.1, 149.9, 142.8 138.8, 137.8, 129.9, 129.5, 129.3, 126.1, 124.1, 87.9, 87.8, 72.2, 70.7, 70.6, 59.5, −9.2.

{2,4-Bis[2-((*R*)-4-isopropyl-2-oxazolinyl)]pyridine}Pd-(Me)Cl (*R*,*R*-5k). Yellow powder. ^{1}H NMR (400 MHz): δ 9.08 (d, J = 5.3 Hz, 1 H), 8.25 (t, J = 0.9 Hz, 1 H), 8.05 (dd, J = 1.5, 5.3 Hz, 1 H), 4.70 (m, 2 H), 4.47 (dd, J = 7.9, 9.1 Hz, 1 H), 4.33 (m, 1 H), 4.14 (m, 2 H), 2.29 (m, 1 H), 1.83 (m, 1 H), 1.01 (d, J = 6.8 Hz, 3 H), 1.00 (s, 3 H), 0.94 (d, J = 7.0 Hz, 3 H), 0.92 (d, J = 6.7 Hz, 3 H), 0.80 (d, J = 6.9 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz): δ 168.2, 160.1, 150.1, 143.1, 138.1, 127.1, 122.5, 73.5, 71.7, 71.5, 68.1, 33.0, 29.7, 19.1, 19.0, 18.5, 14.2, −8.6. Anal. Calcd (found) for $C_{18}H_{26}N_3O_2PdCl$: H, 5.72 (5.72); C, 47.18 (47.12); N, 9.17 (9.08).

[(*R*)-4-Isopropyl-2-isoquinolinyl-2-oxazoline]Pd(Me)Cl (*R*-5l). Bright yellow powder. ^{1}H NMR (400 MHz): δ 9.10 (d, J = 5.8 Hz, 1 H), 8.87 (d, J = 8.5 Hz, 1 H), 7.99 (d, J = 5.8 Hz, 1 H), 7.93 (d, J = 7.9 Hz, 1 H), 7.78 (m, 2 H), 4.87 (m, 2 H), 4.40 (ddd, J = 3.3, 5.2, 9.4 Hz, 1 H), 2.38 (m, 1 H), 1.05 (s,3 H), 1.00 (d, J = 7.1 Hz, 3 H), 0.84 (d, J = 6.9 Hz, 3). ^{13}C-{^{1}H} NMR (100 MHz): δ 170.1, 141.5, 141.4, 137.5, 131.9, 130.2, 127.9, 126.9, 125.6, 70.0, 67.0, 29.8, 19.0, 14.3, −8.1. Anal. Calcd (found) for $C_{16}H_{19}N_2OPdCl$: H, 4.82 (4.68); C, 48.38 (48.00); N, 7.05 (6.78).

General Procedure for Cyclization/Hydrosilylation. Methylene chloride (10 mL) was added via syringe to a mixture of the diene (0.60 mmol), (N−N)PdMeCl (7 mg, 2.2 × 10^{-3} mmol) and NaB[3,5-$C_6H_3(CF_3)_2$]$_4$ (24 mg, 2.3 × 10^{-3} mmol) at −20 °C. Silane (300 μL) was added via syringe and the resulting solution was stirred at −18 °C for 12 h. Solvent and excess silane were evaporated under vacuum, and the oily residue was chromatographed on silica gel to give the carbocycle as a colorless oil. Carbocycles which possessed carbo-*tert*-butoxy groups (Table 5, entries 1 and 2) were isolated as the corresponding carbomethoxy derivatives employing the following procedure: A solution of the crude di-*tert*-butoxy carbocycle (~0.40 mmol) and H_2SO_4 (10 drops) in MeOH (5 mL) was heated at 60 °C for 12 h. Ether (10 mL) and aqueous $NaHCO_3$ (10 mL) were added, the layers were separated, and the aqueous layer was extracted with ether (2 × 10 mL). The combined organic layers were dried and evaporated under vacuum, and the residue was chromatographed (hexane:EtOAc = 24:1) to give the pure dicarbomethoxy carbocycle.

Dimethyl *trans*-4-Methyl-3-[(dimethylethylsilyl)methyl]cyclopentane-1,1-dicarboxylate (7). ^{1}H NMR: δ 3.66 (s, 6 H), 2.52 (dd, 1 H, J = 6.6, 13.5), 2.46 (dd, 1 H, J = 6.6, 13.5), 1.61 (dd, 2 H, J = 10.8, 12.9), 1.39 (m, 2 H), 0.90 (d, J = 6.0, 3 H), 0.87 (t, J = 7.8 Hz, 3 H), 0.82 (dd, J = 2.1, 14.4, Hz, 1 H), 0.44 (q, J = 7.8 Hz, 2 H), 0.23 (dd, J = 10.8, 14.4 Hz, 1 H), −0.06 (s, 6 H). ^{13}C{^{1}H} NMR: δ 172.7, 57.4, 51.9, 51.8, 42.9, 42.8, 42.1, 41.4, 17.7, 16.5, 6.7, 6.6, −3.7, −3.9. IR (neat, cm^{-1}): 1738 (C=O). HRMS (CI) calcd (found) for $C_{15}H_{29}SiO_4$ (MH^+): 301.1835 (301.1848).

Dibenzyl *trans*-4-Methyl-3-(triethylsilylmethyl)cyclopentane-1,1-dicarboxylate (20). ^{1}H NMR: δ 7.30−7.22 (m, 10 H), 5.08 (m, 4 H), 2.58 (dd, J = 6.8, 13.4 Hz, 1 H), 2.50 (dd, J = 7.0, 13.6 Hz, 1 H), 1.69 (ddd, J = 6.6, 10.7, 13.4 Hz, 2 H), 1.45 (m 2 H), 0.93 (d, J = 6.2 Hz, 3 H), 0.89 (t, J = 7.8 Hz, 9 H), 0.47 (q, J = 7.8 Hz, 6 H), 0.24 (dd, J = 11.0 Hz, 14.6 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 172.8, 135.9, 128.7, 128.4, 128.2, 128.1, 67.2, 58.6, 44.0, 43.5, 43.1, 42.3, 17.5, 14.9, 7.7, 4.0. Anal. Calcd (found) for $C_{29}H_{40}SiO_4$: H, 8.39 (8.56); C, 72.46 (72.44).

Diisopropyl *trans*-4-Methyl-3-(triethylsilylmethyl)cyclopentane-1,1-dicarboxylate (21). ^{1}H NMR: δ 5.13 (septet, J = 6.2 Hz, 1 H), 5.12 (septet, J = 6.2 Hz, 1 H), 2.64 (dd, J = 6.7, 13.3 Hz, 1 H), 2.55 (dd, J = 6.7, 13.2 Hz, 1 H), 1.74 (ddd, J = 6.0, 10.7, 13.3 Hz, 2 H), 1.60−1.48 (m, 2 H), 1.32 (d, J = 6.2 Hz, 12 H), 1.07 (d, J = 5.1 Hz, 3 H), 1.04 (t, J = 7.9 Hz, 9 H), 0.97 (dd, J = 2.2, 11.4 Hz, 1 H), 0.63 (q, J = 7.9 Hz, 6 H), 0.39 (dd, J = 11.0, 14.6 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 172.7, 68.6, 58.5, 43.9, 43.4, 43.0, 42.1, 21.7, 17.5, 14.9, 7.6, 4.0. Anal. Calcd (found) for $C_{21}H_{40}SiO_4$: H, 10.48 (10.39); C, 66.58 (66.42).

1,1-Bis(benzyloxylmethyl)-4-methyl-3-(triethylsilylmethyl)cyclopentane (23). ^{1}H NMR: δ 7.30 (m, 10 H), 4.50 (m, 4 H), 3.30 (m, 4 H), 1.85 (dd, J = 6.5, 12.9 Hz, 1 H), 1.76 (dd, J = 6.7, 13.2 Hz, 1 H), 1.2−1.1 (m, 2 H), 0.91 (t, J = 8.0 Hz, 9 H), 0.90 (d, J = 5.4 Hz, 3 H), 0.45 (q, J = 8.0 Hz, 6 H), 0.18 (dd, J = 10.9, 14.5 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 139.3, 128.5, 127.6, 127.5, 75.7, 73.3, 45.6, 43.6, 43.1, 42.4, 41.6, 18.0, 15.3, 7.8, 4.2. HRMS (CI) calcd (found) for $C_{29}H_{44}SiO_2$ (M^+): 452.3111 (452.3127).

1,1-Bis(acetoxymethyl)-3-(triethylsilylmethyl)-4-methylcyclopentane (24). ^{1}H NMR: δ 3.90 (s, 4 H), 2.04 (s, 6 H), 1.74 (m, 2 H), 1.10 (m, 1 H), 1.05 (m, 2 H), 1.02 (m, 1 H), 0.90 (t, J = 8.1 Hz, 9 H), 0.49 (q, J = 7.8 Hz, 6 H), 0.20 (dd, J = 3.6, 10.8 Hz, 1 H). CH−CH_3 protons obscured. ^{13}C{^{1}H} NMR: δ 171.0, 105.6, 77.4, 77.0, 76.6, 68.2, 65.3, 43.1, 20.7, 20.6, 3.7. IR (neat, cm^{-1}): 1745 (C═O). HRMS (CI) calcd (found) for $C_{19}H_{36}SiO_4$ (MH^+): 357.2461 (357.2461). Anal. Calcd (found) for $C_{19}H_{36}SiO_4$: H, 10.18 (9.87); C, 64.00 (64.91).

1,1-Bis(trimethylacetoxymethyl)-4-methyl-3-(triethylsilylmethyl)cyclopentane (25). ^{1}H NMR: δ 3.89 (m, 4 H), 1.80 (dd, J = 6.7, 13.2 Hz, 1 H), 1.71 (dd, J = 6.5, 13.1 Hz, 1 H). 1.5−1.3 (m, 2 H), 1.18 (s, 18 H), 1.00 (m, 2 H), 0.93 (d, J = 6.0 Hz, 3 H), 0.90 (t, J = 7.8 Hz, 9 H), 0.47 (q, J = 7.9 Hz, 6 H), 0.20 (dd, J = 11.1, 14.6 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 178.5, 68.4, 43.9, 43.6, 41.8, 40.8, 39.0, 27.3, 17.8, 15.1, 7.6, 4.0. Anal. Calcd (found) for $C_{25}H_{48}SiO_4$: H, 10.98 (11.13); C, 68.13 (68.02).

1-Carbomethoxy-4-methyl-1-phenyl-3-(triethylsilylmethyl)cyclopentane (27). ^{1}H NMR: δ 7.17−6.98 (m, 5 H), 3.42 (s, 3 H), [2.74 (dd, J = 5.1, 11.7 Hz), 2.40 (d, J = 7.8 Hz), 2:3, 2 H], 2.24−2.05 (m, 2 H), 1.39−1.31 (m, 2 H), [0.83 (d, J = 6.6 Hz), 0.80 (d, J = 5.4 Hz), 2:3, 3 H], 0.75 (t, J = 8.1 Hz, 9 H), [0.36 (q, J = 7.8 Hz), 0.35 (q, J = 7.8 Hz), 6 H], 0.13 (dd, J = 10.8, 14.7 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 177.2, 144.9, [128.3, 126.3 (2:3)], 57.2, 52.1, [44.7, 44.0 (3:2)], [43.9, 43.8 (2:3)], [43.7, 43.2 (3:2)], [19.5, 18.9 (3:2)], [16.0, 15.0 (2:3)], 7.9, 3.9. IR (neat, cm^{-1}): 1731 (C═O). Anal. Calcd (found) for $C_{19}H_{36}O_4Si$: H, 9.89 (9.68); C, 72.78 (72.67).

Dimethyl *trans*-4-Pentyl-3-(triethylsilylmethyl)cyclopentane-1,1-dicarboxylate (33). ^{1}H NMR: δ 3.69 (s, 6 H), 2.53 (td, J = 5.9, 12.9 Hz, 2 H), 1.7−1.2 (m, 12 H), 0.91 (t, J = 7.9 Hz, 9 H), 0.86 (t, J = 7.0 Hz, 3 H), 0.51 (q, J = 8.0 Hz, 6 H), 0.27 (dd, J = 11.0 Hz, 14.6 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 173.6, 58.5, 52.8, 49.2, 43.0, 42.0, 40.2, 33.4, 32.4, 28.1, 22.9, 15.3, 14.3, 7.7, 4.1. Anal. Calcd (found) for $C_{21}H_{40}SiO_4$: H, 10.48 (10.66); C, 65.58 (65.60).

Preparation of *S,S*-6 from *S,S*-9. A solution of **2** (1.06 g, 5 mmol), $HSiMe_2Ph$ (2.05 g, 15 mmol), $NaBAr_4$ (444 mg, 0.5 mmol), and *R*-**5b** (174 mg, 0.5 mmol) in DCE (60 mL) was stirred at room temperature for 2 h. Volatile material was evaporated, and the residue was dissolved (hexane:EtOAc = 30:1), filtered through a plug of silica gel, and concentrated to give *S,S*-**9** (1.43 g, ∼75%) which was ∼90% pure by GC analysis. Crude *S,S*-**9** was then oxidized as previously described[25] to form pure 1,1-dicarbomethoxy-3-methyl-4-(hydroxylmethyl)cyclopentane (*S,S*-**38**) (340 mg, 30% from **2**). A solution of *S,S*-**38** (1.30 g, 5.65 mmol) in pyridine (12 mL) was treated with methanesulfonyl chloride (2.63 mL, 34.0 mmol) at 0 °C and stirred for 2.5 h. Workup and chromatography (hexane:EtOAc = 10:1) gave 1,1-dicarbomethoxy-3-methyl-4-(methanesulfonoxy)methylcyclopentane (*S,S*-**39**) (1.48 g, 85%) as a colorless oil. Sodium iodide (1.40 g, 9.4 mmol), zinc powder (1.40 g, 22 mmol), and water (0.5 mL, 28 mmol) were added sequentially to a solution of *S,S*-**39** (1.48 g, 4.8 mmol) in 1,2-dimethoxyethane (15 mL), and the mixture was refluxed overnight.[43] The resulting suspension was diluted with ether and filtered, and the filtrate was washed with 1 N HCl, saturated aqueous $NaHCO_3$, 10% aqueous sodium thiosulfate, and water, dried (Na_2SO_4), and concentrated under vacuum to give *S,S*-**6** (0.98 g, 100%) as a colorless oil.

For 39: ^{1}H NMR: δ 4.25 (dd, J = 4.8, 9.9 Hz, 1 H), 4.11 (dd, J = 6.9, 9.9 Hz, 1 H), 3.72 (d, J = 1.7 Hz, 6 H), 3.02 (s, 3 H), 2.53 (m, 2 H), 2.08 (dd, J = 9.4, 13.8 Hz, 1 H), 1.96 (m, 1 H), 1.83 (m, 2 H), 1.05 (d, J = 6.2 Hz, 3 H). ^{13}C{^{1}H}NMR: δ 173.0, 172.9, 71.4, 58.8, 53.2, 46.0, 42.8, 37.7, 36.8, 18.5. IR (neat, cm^{-1}): 1730 (C═O). HRMS (CI) calcd (found) for $C_{11}H_{17}SO_6$ (M^+-OCH_3): 277.0746 (277.0742).

For 6: ^{1}H NMR: δ 3.70 (s, 6 H), 2.51 (dd, J = 6.6, 13.6 Hz, 2 H), 1.72 (dd, J = 10.8, 13.6 Hz, 2 H), 1.47 (m, 2 H), 0.96 (d, J = 6.0 Hz, 6 H). ^{13}C{^{1}H}NMR: δ 173.8, 58.4, 52.9, 43.2, 42.0, 17.6.

Preparation of (*S,S*)-6 from (*R,R*)-2,3-Dimethylsuccinic Acid. An authentic sample of *S,S*-**6** was synthesized employing a procedure similar to that developed by Kuehne.[36] Resolution of a mixture of *rac*- and *meso*-2,3-dimethylsuccinic acid with L-Brucine according to the method of McCasland[44] gave a 4:1 mixture of (*R,R*)-2,3-dimethylsuccinic acid (62% ee) and *meso*-2,3-dimethylsuccinic acid which was used without further purification. The optically enriched 2,3-dimethylsuccinic was first esterified ($MeOH/H_2SO_4/Na_2SO_4$, reflux, 12 h) to give 2,3-dimethylsuccinic acid dimethyl ester in 91% yield as a pale yellow oil. The diester was reduced ($LiAlH_4$, ether, 25 °C, 12 h) to give 2,3-dimethylbutane-1,4-diol in 91% yield as a pale yellow oil. PPh_3Br_2 (23.6 g, 55.8 mmol) was added to a solution of the diol (2.20 g, 18.6 mmol) in DMF (60 mL), and the resulting mixture was stirred overnight at room temperature, quenched with water, and extracted with ether. Workup and chromatography (pentane:ether = 15:1) gave 2,3-dimethyl-1,4-dibromobutane as a colorless oil (1.73 g, 38%). Dimethyl malonate (0.40 mL, 3.5 mmol) and the dibromide (0.74 g, 3.0 mmol) were added sequentially to a solution of NaOMe (0.45 g, 8.0 mmol) in DMF (35 mL) at room temperature, and the mixture was heated at 115 °C for 36 h. Workup and chromatography (hexane:ether = 12:1) gave (*S,S*)-**6** (57% de, 62% ee) (70 mg, 11%) as a colorless oil.

Determination of Enantiomeric Excess. The enantiomeric excess of carbocycles **3**, **6**, **7**, **8**, **22**, and **29** was determined by chiral GC. The enantiomeric excess of **9**, **19**, **26**, **27**, **32**, **33**, **34**, and **37** was determined by ^{1}H NMR spectroscopy employing $Eu(hfc)_3$ as a chiral shift reagent. Carbocycle **20** was converted to **3** by transesterification (MeOH, H_2SO_4, reflux, 48 h) and analyzed by chiral GC. Carbocycle **21** was converted to **3** by saponification (NaOMe, MeOH, H_2O, reflux, 12 h) followed by esterification (MeOH, H_2SO_4, reflux, 12 h) and analyzed by chiral GC. Carbocycle **23** was hydrogenated (10% Pd/C, 1 atm H_2, 25 °C, 4 h)[54] to give 1,1-bis(hydroxymethyl)-4-methyl-3-[(triethylsilyl)methyl]-cyclopentane (**40**), converted to 1,1-bis(trifluoroacetoxymethyl)-3-[(triethylsilyl)methyl]-4-methylcyclopentane (**41**) [$(CF_3CO)_2O$, NEt_3, CH_2Cl_2, 25 °C, 30 min],[55] and analyzed by chiral GC. Carbocycle **24** was hydrolyzed (K_2CO_3, MeOH, 25 °C, 2 h) to form **40**,[56] converted to **41**, and analyzed by chiral GC. Carbocycle **25** was also hydrolyzed (KOH, $MeOH/H_2O$, reflux, 2 h)[57] to form **40**, converted to **41**, and analyzed by chiral GC.

For 40: ^{1}H NMR: δ 3.55 (m, 4 H), 2.62 (br s, 2 H), 1.76 (dd, J = 6.9, 12.9 Hz, 1 H), 1.71 (dd, J = 6.7, 12.4 Hz, 1 H), 1.4−1.2 (m, 4 H), 0.92 (d, J = 6.1 Hz, 3 H), 0.90 (t, J = 8.1 Hz, 9 H), 0.49 (q, J = 7.9 Hz, 6 H), 0.20 (dd, J = 11.1, 14.6 Hz, 1 H), one Et_3Si-CH_2 proton obscured. ^{13}C{^{1}H}NMR: δ 70.2, 70.0, 46.2, 43.2, 42.7, 41.4, 40.5, 17.8, 15.2, 7.6, 4.0. HRMS (CI) calcd (found) for $C_{15}H_{33}SiO_2$ (MH^+): 273.2250 (273.2241).

For 41: ^{1}H NMR: δ 4.21 (m, 4 H), 1.85 (dd, J = 6.8, 13.6 Hz, 1 H), 1.80 (dd, J = 6.8, 13.7 Hz, 1 H), 1.53−1.36 (m, 2 H), 1.07 (ddd, J = 8.4, 11.0, 13.6 Hz, 2 H), 0.96 (d, J = 6.1 Hz, 3 H), 0.91 (t, J = 8.0 Hz, 9 H), 0.48 (q, J = 8.0 Hz, 6 H), 0.23 (dd, J = 11.0, 14.7 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 157.7 (q, J = 43 Hz), 114.8 (q, J = 285 Hz), 71.4, 71.3, 43.9, 43.6, 43.2, 41.4, 40.5, 17.5, 15.2, 7.5, 4.1. Anal. Calcd (found) for $C_{19}H_{30}SiF_6O_4$: H, 6.51 (6.22); C, 49.13 (48.94).

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Supporting Information Available: Experimental procedures, spectroscopic and analytical data for the synthesis of new pyridine−oxazoline ligands and new dienes. This material is available free of charge via the Internet at http://pubs.acs.org.

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