In this paper, we wish to report the high-yield single-step formation of alkynylphosphonium triflates **2** via the reaction of readily available[3,4] alkynyl(phenyl)iodonium triflates **1** with Ph_3P.

$$\underset{\textbf{1a: R = CH}_3\ \textbf{b: R = t-Bu}\ \textbf{c: R = Me}_3\textbf{Si}\ \textbf{d: R = n-Bu}\ \textbf{e: R = Ph}}{RC{\equiv}CIPh(OTf)} + Ph_3P \xrightarrow[30\ min,\ -PhI]{CH_2Cl_2,\ -78\ to\ 25\ ^\circ C} \underset{\textbf{2a: R = CH}_3\ \textbf{b: R = t-Bu}\ \textbf{c: R = Me}_3\textbf{Si}\ \textbf{d: R = n-Bu}\ \textbf{e: R = Ph}}{RC{\equiv}CPPh_3(OTf)}$$

Reaction of **1** with a 5% excess of Ph_3P in CH_2Cl_2 at −78 to 25 °C for 30 min affords the appropriate crude alkynyl phosphonium triflates **2** in essentially quantitative yield. Recrystallization from CH_2Cl_2 and ether affords the pure final product in 88–98% isolated yield as colorless microcrystalline solids for **2a–d** and slight yellow for **2e**.

The product phosphonium salts are characterized by multinuclear NMR and IR spectroscopy and by elemental analysis. Specifically, the singlet between 5.2 and 7 ppm in the ^{31}P NMR spectrum is typical for the phosphorus signal in alkynylphosphonium salts.[5] The presence of the $^-OSO_2CF_3$ counter ion is indicated by the characteristic ^{19}F signal at −78 ppm as well as the typical absorptions[6] for ionic triflates in the IR spectrum. The IR spectrum shows signals for the C≡C bond between 2134 and 2212 cm^{-1}. Most characteristic are the C≡C signals in the ^{13}C NMR spectrum, where the C_α resonates between 60 and 79 ppm with a $^1J_{CP}$ = 162–192 Hz and the C_β is at much lower field between 118 and 133 ppm with a $^2J_{PC}$ = 12–33 Hz. The remainder of the ^{13}C spectra as well as the ^1H spectra are completely consistent with the proposed structures.

Finally, unlike the reaction of the analogous alkynyl(phenyl)iodonium tetrafluoroborate species,[7] the reaction of **1** with Ph_3P does not require light.[8] These reactions occur readily in the dark. Moreover, the reaction of **1** with Ph_3P is not inhibited by radical traps such as O_2 or 2,6-di-*tert*-butyl-4-methylphenol (BHT). Hence, we believe that, unlike the proposed radical cation-like reactions[7] of the $^-BF_4$ salts, the triflate salts **1** react by the standard[3] nucleophilic acetylenic substitution (S_N-A) process involving iodonium ylides and alkylidenecarbenes as intermediates.

Experimental Section

Melting points were obtained in capillary tubes and are uncorrected. Infrared (IR) spectra were recorded as CCl_4 thin films. NMR spectra were recorded on a Varian XL 300 spectrometer using $CDCl_3$ as solvent. Chemical shifts for ^{31}P are reported in parts per million downfield from 85% H_3PO_4, and ^{19}F NMR shifts are relative to $CFCl_3$. Commercially available Ph_3P was recrystallized from hexanes prior to use. CH_2Cl_2 was distilled from CaH_2. Alkynyl(phenyl)iodonium triflates **1** were prepared by standard methods.[3,4]

General Procedure for the Preparation of Alkynylphosphonium Triflates (2). Alkynyl(phenyl)iodonium triflate **1** (1.00 mmol) was dissolved in 30 mL of CH_2Cl_2 and then cooled to −78 °C. A solution of Ph_3P (1.05 mmol) in 10 mL of CH_2Cl_2 was added slowly over 2 min. The reaction mixture was then allowed to warm to room temperature over 30 min. Solvent was then removed by rotary evaporation, and the residue was washed several times with diethyl ether. The product was then recrystallized by dissolving the crude material in a small amount of CH_2Cl_2 followed by the addition of diethyl ether; the resulting crystals were washed again, filtered, and dried in vacuo.

Propynyl(triphenyl)phosphonium Triflate (2a). Yield: 446 mg (97%) as white crystals with mp 128–129 °C dec. IR: 2212 (C≡C), 1265, 1223, 1033 cm^{-1}. ^1H NMR: δ 7.76–7.74 (m, 3 H's), 7.74–7.60 (m, 12 H's), 5.20 ($^3J_{P,H}$ = 5 Hz). ^{13}C NMR: δ 135.65 ($^4J_{P,C}$ = 3 Hz), 132.97 ($^2J_{P,C}$ = 12 Hz), 130.52 ($^3J_{P,C}$ = 14 Hz), 121.41 (βC≡C, $^2J_{P,C}$ = 33 Hz), 120.83 ($^1J_{F,C}$ = 321 Hz), 118.16 ($^1J_{P,C}$ = 100 Hz), 60.14 (αC≡C, $^1J_{P,C}$ = 192 Hz), 6.32 ($^3J_{P,C}$ = 4 Hz). ^{31}P NMR: δ 5.99. ^{19}F NMR: δ −78.26. Anal. Calcd for $C_{22}H_{18}PSO_3F_3$: C, 58.67; H, 4.03. Found: C, 58.62; H, 3.99.

(3,3-Dimethylbutynyl)(triphenyl)phosphonium Triflate (2b). Yield: 484 mg (98%) as white crystals with mp 158–159 °C. IR: 2174 (C≡C), 1271, 1224, 1033 cm^{-1}. ^1H NMR: δ 7.85–7.81 (m, 3 H's), 7.76–7.61 (m, 12 H's), 1.45. ^{13}C NMR: δ 136.13 ($^4J_{P,C}$ = 3 Hz), 133.15 ($^2J_{P,C}$ = 12 Hz), 131.12 (βC≡C, $^2J_{P,C}$ = 28 Hz), 130.96 ($^3J_{P,C}$ = 14 Hz), 121.12 ($^1J_{F,C}$ = 321 Hz), 118.37 ($^1J_{P,C}$ = 100 Hz), 63.39 (αC≡C, $^1J_{P,C}$ = 187 Hz), 30.01 ($^3J_{P,C}$ = 3 Hz), 29.64. ^{31}P NMR: δ 6.02. ^{19}F NMR: δ −78.22. Anal. Calcd for $C_{25}H_{24}PSO_3F_3$: C, 60.97; H, 4.91. Found: C, 60.83; H, 4.95.

[(Trimethylsilyl)ethynyl](triphenyl)phosphonium Triflate (2c). Yield: 500 mg (98%) as white crystals with mp 134–136 °C dec. IR: 2212 (C≡C), 1272, 1225, 1033 cm^{-1}. ^1H NMR: δ 7.90–7.83 (m, 3 H's), 7.78–7.64 (m, 12 H's), 0.39. ^{13}C NMR: δ 136.07 ($^4J_{P,C}$ = 3 Hz), 133.06 ($^2J_{P,C}$ = 12 Hz), 132.94 (βC≡C, $^2J_{P,C}$ = 18 Hz), 130.80 ($^3J_{P,C}$ = 14 Hz), 120.87 ($^1J_{F,C}$ = 321 Hz), 117.45 ($^1J_{P,C}$ = 100 Hz), 83.97 (αC≡C, $^1J_{P,C}$ = 162 Hz), −1.22. ^{31}P NMR: δ 5.28. ^{19}F NMR: δ −78.22. Anal. Calcd for $C_{24}H_{24}PSiSO_3F_3$: C, 56.67; H, 4.76. Found: C, 56.45; H, 4.74.

Hexynyl(triphenyl)phosphonium Triflate (2d). Recrystallization from CH_2Cl_2 and hexanes gave 434 mg (88%) of white crystals with mp 97–98 °C dec. IR: 2208 (C≡C), 1262, 1224, 1029 cm^{-1}. ^1H NMR: δ 7.82–7.52 (m, 15 H's), 2.79–2.72, 1.76–1.65, 1.49–1.36, 0.93–0.85. ^{13}C NMR: δ 135.75 ($^4J_{P,C}$ = 3 Hz), 132.98 ($^2J_{P,C}$ = 12 Hz), 130.62 ($^3J_{P,C}$ = 14 Hz), 125.06 (βC≡C, $^2J_{P,C}$ = 31 Hz), 120.88 ($^1J_{F,C}$ = 321 Hz), 118.21 ($^1J_{P,C}$ = 108 Hz), 60.98 (αC≡C, $^1J_{P,C}$ = 190 Hz), 28.89, 22.01, 20.28 ($^3J_{P,C}$ = 3 Hz), 13.25. ^{31}P NMR: δ 5.97. ^{19}F NMR: δ −78.34. Anal. Calcd for $C_{25}H_{24}PSO_3F_3$: C, 60.97; H, 4.91. Found: C, 60.86; H, 4.90.

(Phenylethynyl)(triphenyl)phosphonium Triflate (2e). Recrystallization from THF and diethyl ether gave 441 mg (85%) of yellow crystals with mp 138–139 °C. IR: 2178 (C≡C), 1265, 1224, 1031 cm^{-1}. ^1H NMR: δ 7.89–7.72 (m, 17 H's), 7.64–7.57 (t, 1 H), 7.54–7.46 (t, 2 H's). ^{13}C NMR: δ 136.15 ($^4J_{P,C}$ = 3 Hz), 133.73 ($^4J_{P,C}$ = 2 Hz), 133.43, 133.26 ($^2J_{P,C}$ = 12 Hz), 130.98 ($^3J_{P,C}$ = 14 Hz), 129.34, 121.12 ($^1J_{F,C}$ = 321 Hz), 118.79 (βC≡C, $^2J_{P,C}$ = 31 Hz), 118.11 ($^1J_{P,C}$ = 100 Hz), 116.85 ($^3J_{P,C}$ = 5 Hz), 78.93 (αC≡C, $^1J_{P,C}$ = 187 Hz). ^{31}P NMR: δ 7.04. ^{19}F NMR: δ −78.16. Anal. Calcd for $C_{27}H_{20}PSO_3F_3$: C, 63.28; H, 3.93. Found: C, 63.12; H, 3.94.

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(7) Ochiai, M.; Kunishima, M.; Nagao, Y.; Fuji, K.; Fujita, E. *J. Chem. Soc., Chem. Commun.* **1987**, 1708.
(8) For a related reaction of RC≡CIPh(OTs) with $P(OR)_3$ to give $RC{\equiv}CP(O)(OR)_2$ see: Lodoya, J. S.; Koser, G. F. *J. Org. Chem.* **1990**, *55*, 1513. This reaction also does not require light to occur.

Electronic Substituent Effect of Nitrogen Ligands in Catalytic Asymmetric Hydrosilylation of Ketones: Chiral 4-Substituted Bis(oxazolinyl)pyridines

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Recent interest in transition-metal-catalyzed asymmetric reactions have focused attention on the development of chiral cyclic nitrogen ligands.[1] We have reported the chiral

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Table I. Asymmetric Hydrosilylation of Ketones with 4-Substituted-pybox/Rhodium Catalysts[a]

run	ketone	catalyst (mol %)	addition of pybox (mol %)	temp; time °C; h	turn over number	yield (%)	%ee
1[b]	A	7 (1.0)	0	0; 6	100	86	83
2	A	8 (1.0)	0	−5; 3	100	94	83
3	A	9 (1.0)	0	10; 3	100	89	89
4	A	10 (1.0)	0	20; 6	100	78	92
5	A	7 (0.5)[c]	0	20; 1	128	64	43
6	A	8 (0.5)[c]	0	20; 1	154	77	2
7	A	9 (0.5)[c]	0	20; 1	85	42	58
8	A	10 (0.5)[c]	0	20; 1	43	22	59
9[b]	A	7 (1.0)	4	0; 2	100	91	94
10	A	8 (1.0)	4	−5; 3	100	90	94
11	A	9 (1.0)	4	10; 18	100	86	93
12	A	10 (1.0)	4	20; 16	100	83	90
13[b]	B	7 (1.0)	4	0; 2	100	92	99
14	B	8 (1.0)	4	−5; 2	100	93	99
15	B	9 (1.0)	4	10; 18	100	93	99
16	B	10 (1.0)	4	20; 7	100	95	97
17[b]	C	7 (1.0)	4	0; 5	100	92	66
18	C	8 (1.0)	4	−5; 3	100	84	80
19	C	9 (1.0)	4	25; 6	100	88	51
20	C	10 (1.0)	4	30; 17	100	96	49

[a] Ketone (8.0 mmol); A, acetophenone; B, α-tetralone; C, 2-phenylethyl methyl ketone, Ph_2SiH_2 (12.8 mmol), $AgBF_4$ (0.16 mmol), THF (1 mL). The all-product alcohols have (*S*) absolute configuration. [b] See ref 2. [c] Acetophenone (16.0 mmol), Ph_2SiH_2 (25.6 mmol), $AgBF_4$ (0.16 mmol), THF (2 mL).

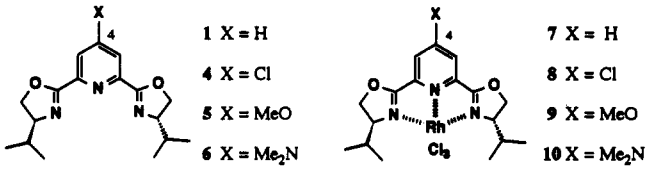
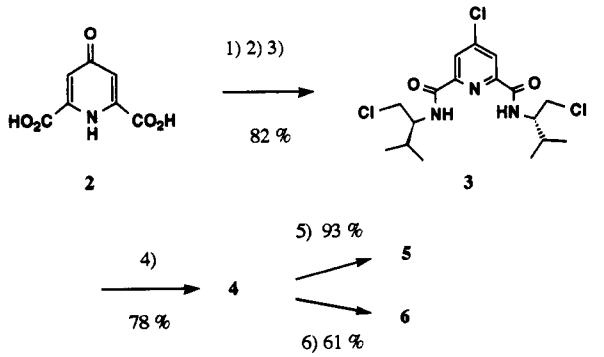


Figure 1.

terdentate nitrogen ligand, bis(oxazolinyl)pyridine (pybox) [X = H, (1)], for asymmetric hydrosilylation of ketones.[2] In general, the nitrogen ligands are easily available from optically active amine derivatives and their modification is relatively facile, compared to the chiral phosphine ligands. We have synthesized several pybox derivatives having certain alkyl groups in place of the isopropyl group in **1**, and we disclosed the steric effect for the asymmetric induction by the substituents situated near the catalytic center.[2] However, we have been interested in net electronic control by the remote substituents far from the catalytic center through π-bonds containing metal orbitals in the hydrosilylation reaction. We report here the synthesis of 4-substituted pybox derivatives (**4–6**) and their rhodium complexes (**8–10**) and disclose their effects in the asymmetric hydrosilylation of ketones.[3]

We synthesized the 4-substituted pybox (**4–6**) from commercially available chelidamic acid (**2**), which was initially converted to the corresponding bis(chloroamide)-pyridine (**3**) in 82% yield in three steps with thionyl chloride and (*S*)-valinol. Treatment of **3** with NaH in THF gave the 4-chloro-pybox (**4**) in 78% yield (Scheme I). We could obtain the corresponding 4-methoxy- and 4-(dimethylamino)-pybox, **5** and **6**, by displacement reactions of **4** with methanol–sodium hydroxide and dimethylamine, respectively. The corresponding pybox/rhodium(III) complexes (**8–10**) of the pybox ligands were obtained in

Scheme I[a]



[a] Key: (1) $SOCl_2$, reflux, 1 day; (2) (*S*)-valinol, Et_3N, $CHCl_3$; (3) $SOCl_2$, 60 °C, 10 h; (4) NaH, THF, rt; (5) NaOH, MeOH–H_2O, 40 °C, 1 day; (6) Me_2NH, H_2O–THF, 40 °C, 1 day.

63–72% by heating a solution of rhodium(III) chloride and the pybox (**4–6**) in ethanol.

We examined the reduction of acetophenone (A), often used as a standard ketone for the asymmetric hydrosilylation, with diphenylsilane in the presence of the rhodium complexes (**8–10**) (Table I).

The introduction of the substituents on the pyridine skeleton of pybox ligand influenced *the critical reaction temperature*, at which the rhodium catalyst and the silane proceed to reduce the ketone smoothly; ca. 5 °C below the temperature indicated in Table I, the reduction did not occur. The critical temperature for the reduction with the 4-methoxy- and 4-(dimethylamino)-pybox/rhodium complexes, **9** and **10**, proved to be higher (>20–10 °C) (run 3 and 4) than that for the reduction with 4-H-pybox/rhodium complex (**7**) (0 °C) (run 1). Nevertheless, the reduction with **9** and **10** resulted in an increase of the enantioselectivity (89% ee and 92% ee, respectively) (run 3 and 4) compared to 83% with **7** (run 1). In contrast, the reduction with 4-chloro-pybox/rhodium complex (**8**) proceeded very smoothly even at −5 °C giving 94% yield and 83% ee (run 2).

We compared the reaction rates by turn-over-number (ton) of the rhodium complexes (**7–10**) for 1 h at 20 °C to observe the same tendency; *the electron-withdrawing*

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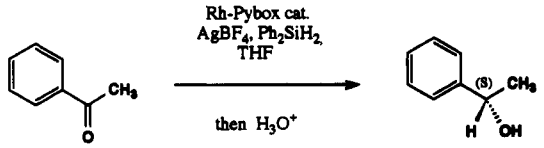
Scheme II



group increases the reaction rate ton >150) and the electron-donating group decreases it (ton = 40–90) (runs 5–8). However, the enantioselectivity with 4-chloro-pybox/rhodium complex (8) drastically decreased at 20 °C (run 6). We assume that the intermediary chiral catalyst derived from 8 is unstable at higher temperatures and decomposes to certain nonchiral catalysts during the reaction.

It is well-known that the addition of extra nitrogen ligands[4] normally improves the enantioselectivities in the asymmetric hydrosilylation. Addition of the 4-substituted pybox ligands proved to be also effective to improve the enantioselectivity up to 90–94% (runs 9–12).

For the reduction of other ketones, such as α-tetralone (B) and 2-phenylethyl methyl ketone (C), a similar electronic substituent effect was observed predominantly in the critical temperature (i.e., reaction rates) and moderately in the enantioselectivities (runs 13–20). An exception is 4-chloro-pybox/rhodium catalyst which gave a high enantioselectivity (80% ee) for 2-phenylethyl methyl ketone at −5 °C (run 18).

We think that the electronic control of the remote substituents can be rationalized by the catalytic cycle shown in Scheme III. Although the rate-determining step may be the product-developing path from the intermediary higher valent rhodium species (ii) as postulated befor,[5] the electron-donating group could stabilize these species or the corresponding transition states eliminating the product to decrease the reaction rate. In contrast, the electron-withdrawing group would increase the reaction rate by destabilization of the higher valent rhodium species of activating the transition states, but at higher reaction temperature the catalysts may decompose and decrease the enantioselectivity.

Similar modification of the electronic properties by remote substituents on chiral ligands has been recently reported as *electronic tuning* of asymmetric catalytic oxidation.[6]

We have confirmed the electronic effect of the remote substituents by extended Hückel molecular orbital calculations of the 4-substituted pybox ligands and their rhodium trichloride complexes to find that the substituents at 4-position of the pyridine skeleton can influence greatly not only the electron density on the nitrogen atom of the pyridine skeleton but the rhodium(III) atom of the complexes. However, there is no effect on the two nitrogen atoms of the oxazoline rings for both the ligands and the complexes.[7,8]

Thus, we have demonstrated interesting electronic effects of remote substituents on the pyridine skeleton of pybox ligands in the asymmetric induction of the catalytic hydrosilylation of ketones.

Experimental Section

All reactions were carried out under N_2. THF was distilled under nitrogen from sodium. ^1H and ^{13}C NMR spectra were recorded at 270 and 67.8 MHz, respectively. Analytical TLC was performed on Merck (Art 5715) precoated silica gel plates (0.25 mm). Column chromatography was performed with silica gel (Merck, Art 7734). The extended Hückel molecular orbital calculation of the pybox/rhodium complexes was performed with a NEC PC-9801 RX personal computer, and the program (MS-DOS version, 1989) edited by Nishimoto and Imamura was purchased from Kodansha Scientific, Tokyo. The cartesian coordinate of the pybox/rhodium skeleton is determined on the basis of the X-ray analysis for the related complex.[2]

4-Chloro-2,6-bis[4′(*S*)-isopropyloxazolin-2′-yl]pyridine (4). Chelidamic acid (2) (0.92 g, 5.0 mmol) was treated with $SOCl_2$ (27 mL) at reflux temperature for 2 days. Excess $SOCl_2$ was then removed under reduced pressure to give the acid chloride as a white solid. To a solution of (*S*)-valinol (1.24 g, 12.0 mmol) and triethylamine (5.0 mL, 36.0 mmol) in $CHCl_3$ (25 mL) was slowly added a solution of the acid chloride in $CHCl_3$ (25 mL) at 0 °C. The mixture was stirred for 1 day at rt. Then $SOCl_2$ (15 mL) was added, and the mixture was heated at reflux temperature for 9 h and was slowly poured into ice–water. The organic layer was collected, washed with brine, and dried (Na_2SO_4). After concentration, the white solid was purified by silica gel column chromatography with CH_2Cl_2–ether (20:1) as eluent to give 3 as a white solid in 82% (1.68 g, 4.11 mmol); TLC R_f = 0.8 (ethyl acetate); mp 140 °C; $[\alpha]^{23}_D$ = −61.9° (CH_2Cl_2, c = 1.03); IR (KBr disk) 1680, 1645, 1540, 750 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.03 (d, J = 6.6 Hz, 6 H), 1.06 (d, J = 6.6 Hz, 6 H), 2.12 (m, 2 H), 3.76 (dd, J = 3.4, 11.2 Hz, 2 H), 3.89 (dd, J = 3.4, 11.2 Hz, 2 H), 4.17 (m, 2 H), 7.92 (d, J = 9.8 Hz, 2 H), 8.34 (s, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) 18.78, 19.34, 29.67, 46.75, 55.02, 125.5, 148.1, 149.9, 161.9. Anal. Calcd for $C_{17}H_{24}N_3O_2Cl_3$: C, 49.95; H, 5.92; N, 10.28. Found: C, 49.97; H, 6.00; N, 10.24.

To a suspension of NaH (1.7 g, 50% oil, 34 mmol) in THF (25 mL) was added a solution of 3 (5.0 g, 12.2 mmol) in THF (50 mL). The mixture was stirred over night. After filtration and concentration, the residue was extracted with ether (300 mL). The extract gave a white solid, which was recrystallized with hexane–ethyl acetate to give 4 as white needles in 78% (3.2 g, 9.5 mmol): TLC R_f = 0.5 (ethyl acetate); mp 82–83 °C; $[\alpha]^{23}_D$ = −99.2° (CH_2Cl_2, c = 1.01); IR (KBr disk) 1640, 1560, 1380, 1275, 1120, 940, 785 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.94 (d, J = 6.6 Hz, 6 H), 1.05 (d, J = 6.6 Hz, 6 H), 1.87 (m, 2 H), 4.18 (m, 2 H), 4.23 (t, J = 8.3, 8.3 Hz, 2 H), 4.54 (dd, J = 8.3, 9.2 Hz, 2 H), 8.21 (s, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) 18.31, 18.98, 32.80, 71.23, 72.96, 125.8, 145.3, 148.1, 161.4; MS m/e (relative intensity) 336 (M, 32), 292 (100), 264 (30), 250 (20), 179 (30), 151 (40). Anal. Calcd for $C_{17}H_{22}N_3O_2Cl$: C, 60.80; H, 6.60; N, 12.51. Found: C, 60.89; H, 6.65; N, 12.37.

4-Methoxy-2,6-bis[4′(*S*)-isopropyloxazolin-2′-yl]pyridine (5). To a solution of 4 (300 mg, 0.89 mmol) in methanol (8.0 mL) was added aqueous NaOH (2.5 N, 5.0 mL). The mixture was stirred for 10 h at 40 °C. The mixture was extracted with CH_2Cl_2, dried over ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography with ethyl acetate to give 5 as a white solid in 93% yield (276 mg, 0.83); TLC R_f = 0.3 (ethyl acetate); mp 83–84 °C; $[\alpha]^{25}_D$ = −83.6° (CH_2Cl_2, c = 0.53); IR (KBr disk) 1590, 1475, 1390, 1090, 1020 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.94 (d, J = 6.6 Hz, 6 H), 1.05 (d, J = 6.6 Hz, 6 H), 1.87 (m, 2 H), 3.95 (s, 3 H), 4.15 (m, 2 H), 4.22 (t, J = 8.3, 8.3 Hz, 2 H), 4.52 (dd, J = 8.3, 9.3 Hz, 2 H), 7.71 (s, 2 H); ^{13}C NMR (67.8 Hz, $CDCl_3$) 18.24, 19.03, 32.82, 55.71, 70.97, 72.82, 111.7, 148.3, 162.3, 166.6; MS m/e (relative intensity) 332 (M + 1, 45), 288 (100), 260 (30), 147 (35). Anal. Calcd for $C_{18}H_{25}N_3O_3(0.5H_2O)$: C, 63.51; H, 7.70; N, 12.34. Found: C, 63.90; H, 7.60; N, 12.34.

4-(Dimethylamino)-2,6-bis[4′(*S*)-isopropyloxazolin-2′-yl]pyridine (6). To a solution of 4 (336 mg, 1.0 mmol) in THF

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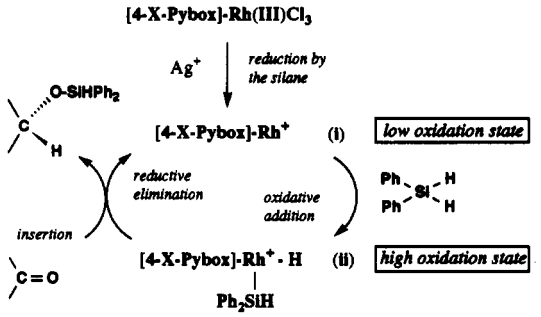
(8) For better comparison of the substituent-effect, we tried the preparation of pybox ligands with much stronger electron-withdrawing groups, such as cyano group. However, several attempts to effect substitution of 4-chloro-pybox (4) with cyanide were unsuccessful.

Scheme III



(10 mL) was added an aqueous solution of dimethylamine (50 wt %, 30 mL). The mixture was stirred for 3 days at 40 °C. The workup and purification were similar to those for **5** as described above to give **6** as a white solid in 61% (210 mg, 0.61 mmol) yield: TLC R_f = 0.2 (ethyl acetate); mp 81–82 °C; $[\alpha]^{24}_D$ = −42.5° (CH_2Cl_2, c = 0.52); IR (KBr disk) 1595, 1418, 1350, 1180 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.94 (d, J = 6.6 Hz, 6 H), 1.06 (d, J = 6.6 Hz, 6 H), 1.86 (m, 2 H), 3.11 (s, 6 H), 4.14 (m, 2 H), 4.19 (t, J = 8.3, 8.3 Hz, 2 H), 4.49 (dd, J = 8.3, 9.3 Hz, 2 H), 7.37 (s, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) 18.26, 19.18, 32.85, 39.48, 70.69, 72.79, 108.0, 147.0, 155.0, 163.3. Anal. Calcd for $C_{19}H_{28}N_4O_2(H_2O)$: C, 62.95; H, 8.34; N, 15.46. Found: C, 62.53; H, 8.35; N, 15.79.

(4-Chloro-pybox)$RhCl_3$ (8). A solution of $RhCl_3/(H_2O)_3$ (263 mg, 1.0 mmol) and 4-chloro-pybox (**4**) (336 mg, 1.0 mmol) in ethanol (8.0 mL) was heated at reflux for 2 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography with ethyl acetate–methanol as eluents to give **8** as an orange solid in 63% (346 mg, 0.63 mmol) yield: mp 207–208 °C dec; $[\alpha]^{25}_D$ = +551° (CH_2Cl_2, c = 0.54); IR (KBr disk) 1575, 1480, 1375, 1248, 1064, 960, 910 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.99 (d, J = 6.8 Hz, 6 H), 1.00 (d, J = 6.8 Hz, 6 H), 3.05 (m, 2 H), 4.66 (m, 2 H), 4.96 (dd, J = 7.8, 9.3 Hz, 2 H), 5.03 (dd, J = 9.3, 10.3 Hz, 2 H), 7.98 (s, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) 15.09, 19.49, 28.45, 68.87, 73.54, 126.8, 147.7, 148.7, 165.5. Anal. Calcd for $C_{17}H_{22}N_3O_2RhCl_4(0.5H_2O)$: C, 36.85; H, 4.18; N, 7.58. Found: C, 36.41; H, 4.06; N, 7.52.

(4-Methoxy-pybox)$RhCl_3$ (9). $RhCl_3/(H_2O)_3$ (263 mg, 1.0 mmol), 4-methoxy-pybox (**5**) (332 mg, 1.0 mmol), and ethanol (5.0 mL) were refluxed for 3 h. **9** was obtained as an orange solid in 71% yield (383 mg, 0.71 mmol): mp 210–211 °C dec; $[\alpha]^{25}_D$ = +468.7° (CH_2Cl_2, c = 0.53); IR (KBr disk) 1580, 1490, 1465, 1380, 1240, 1120, 1080 cm^{-1}; 1H NMR (270 MHz, $CDCl_3$) δ 0.98 (d, J = 6.8 Hz, 6 H), 1.00 (d, J = 6.8 Hz, 6 H), 3.06 (m, 2 H), 4.10 (s, 3 H), 4.64 (m, 2 H), 4.86–5.05 (m, 4 H), 7.47 (s, 2 H); ^{13}C NMR (67.8 Hz, $CDCl_3$) 15.06, 19.49, 28.36, 57.61, 68.67, 73.13, 113.0, 147.5, 166.0, 169.2. Anal. Calcd for $C_{18}C_{25}N_3O_3RhCl_3(0.5CH_2Cl_2)$: C, 38.10; H, 4.49. Found: C, 38.29; H, 4.55.

(4-(Dimethylamino)-pybox)$RhCl_3$ (10). $RhCl_3/(H_2O)_3$ (263 mg, 1.0 mmol), 4-(dimethylamino)-pybox (**6**) (334 mg, 1.0 mmol), and ethanol (6.0 mL) were refluxed for 1 h. **10** was obtained as an orange solid in 72% yield (396 mg, 0.72 mmol): mp >300 °C; $[\alpha]^{25}_D$ = +447.6° (CH_2Cl_2, c = 0.53); IR (KBr disk) 1580, 1530, 1420, 1380, 1240, 1080 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.96 (d, J = 6.8 Hz, 6 H), 1.00 (d, J = 6.8 Hz, 6 H), 3.05 (m, 2 H), 3.27 (s, 6 H), 4.61 (m, 2 H), 4.87 (dd, J = 8.8, 9.8 Hz, 2 H), 4.90 (dd, J = 8.8, 13.2 Hz, 2 H), 7.06 (s, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) 15.06, 19.49, 28.25, 40.57, 68.44, 72.67, 108.4, 145.2, 156.1, 166.5. Anal. Calcd for $C_{19}H_{28}N_4O_2RhCl_3$: C, 41.21; H, 5.10; N, 10.12. Found: C, 41.18; H, 5.05; N, 10.23.

Typical Procedure for Asymmetric Hydrosilylation: Reduction of Acetophenone with (4-Chloro-pybox)$RhCl_3$ (8) and Diphenylsilane. A suspension of **8** (43.6 mg, 0.08 mmol) and $AgBF_4$ (31 mg, 0.16 mmol) in THF (1.0 mL) was stirred at rt for 1 h. After addition of acetophenone (0.93 mL, 8.0 mmol), diphenylsilane (2.36 g, 12.8 mmol) was added at −5 °C. The mixture was stirred for 3 h and treated with methanol and then hydrochloric acid (1.0 N) at 0 °C. The product yield was determined by GLPC analysis. After Kugelrohr distillation of the product, the enantioselectivity was determined by the optical rotation and by ^1H NMR spectroscopy of the MTPA ester. See ref 2 for the values of optical rotation.

Ring Expansion of *tert*-Butyl 1-Vinylcyclopropane-1-carboxylates to α-Ethylidenebutyrolactones

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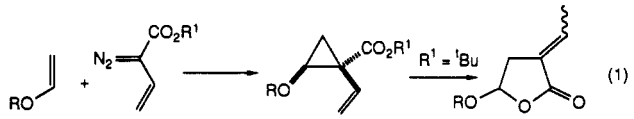
Significant advances have been made recently in the development of synthetic transformations based on cyclopropane ring-expansion reactions.[1,2] Cyclopropanes which contain both donor and acceptor functionalities are particularly effective in this regard because they react under mild conditions.[1,3] Several methods are available for the synthesis of donor–acceptor-substituted cyclopropanes but the most general approach has been cyclopropanation of electron-rich alkenes by metal-stabilized carbenoids.[1,4] Over the last few years we have shown that rhodium(II)-stabilized vinylcarbenoids are useful for the stereoselective synthesis of seven-membered carbocycles.[5] Furthermore, their reaction with electron-rich alkenes leads to an intriguing class of donor–acceptor substituted cyclopropanes **1**.[6] In principle, competing rearrangements are possible for **1** involving either the vinyl or the carbonyl group. In this paper we describe the rearrangements of the *tert*-butyl esters of **1**, which lead to the formation of α-ethylidenebutyrolactones **2** as illustrated in eq 1.[7]



(1)

1 **2**

The thermolysis of the methyl ester **3** at 230 °C resulted in the expected vinylcyclopropane rearrangement to generate the cyclopentene **4** in low yield (20%). Due to the presence of the donor–acceptor functionality in **3**, the reaction occurred under less vigorous conditions than are typically required.[8] The reaction could be carried out

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