gest that 9^- and 10^- are best thought of as complexes of "$[W(PhC{\equiv}CPh)_3]$" with R_3Sn^- anions and are therefore analogous to stibine complexes.

In addition to their implications for the evaluation of steric factors in the chemistry of these polyalkyne complexes of zero-valent group 6 metals, our results have shown that the reaction of $[W(CO)_3(NC_2H_5)_3]$ with alkynes can provide a more general route to $[W(alkyne)_3(CO)]$ complexes than was previously established—the key to preparing complexes of polymerization-prone terminal alkynes by this route has been to carry out the reaction in neat alkyne and to minimize product thermolysis by conducting the reaction at reflux under reduced pressure.

Acknowledgment. We thank the NSF for giving financial support to N.J.C.

Highly Enantioselective Hydrosilylation of Ketones with Chiral and C_2-Symmetrical Bis(oxazolinyl)pyridine–Rhodium Catalysts

Hisao Nishiyama,* Manabu Kondo, Takashi Nakamura, and Kenji Itoh

School of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441, Japan

Received July 31, 1990

Chiral and C_2-symmetrical 2,6-bis(4′-R-oxazolin-2′-yl)pyridines (pybox, **1a–e**, R = *i*-Pr, *sec*-Bu, *t*-Bu, Et, and Ph) have been newly designed and synthesized from the corresponding optically active β-amino alcohols and pyridine-2,6-dicarboxylic acid as auxiliaries for metal-catalyzed reactions. We have found that the trivalent rhodium–pybox complexes **2a–e** can act as catalysts for asymmetric reduction of ketones with diphenylsilane. The (*S*,*S*)-ip-pybox–rhodium complex **2a** (1 mol % with respect to the ketone) with the aid of $AgBF_4$ has exhibited an extremely high level of enantioselectivity for the reduction of acetophenone derivatives, above 90% ee on the average. Under the same reaction conditions, we have attained complete selection of the prochiral face of 1-tetralone in 99% ee. Several other ketones also have relatively higher results e.g. 95% ee for ethyl levulinate, 94% ee for 1-acetylnaphthalene, and 63% ee for 2-octanone. We have examined α,β-unsaturated ketones, resulting in an exclusive 1,2-reduction for benzalacetone, β-ionone, and chalcone but in lower enantioselection. We have also examined the effect of the substituents on the pybox ligands in the reduction of acetophenone and ethyl levulinate. In the mixed-ligand experiments a facile ligand-exchange reaction between the coordinating pybox and the free pybox ligand in the reaction media was observed, resulting in complete linearity of the enantiomeric excess between the product and the catalytic system.

Chiral organic molecules for metal-catalyzed reactions have been newly designed and synthesized as auxiliaries for enantiotopic-differentiative reactions and molecular recognition.[1] Especially, nitrogen-containing organic molecules have recently attracted much attention in asymmetric reduction, alkylation, and oxidation, including biomimetic reactions.[2]

In the reduction of ketones, chiral catalysts have currently been required to attain an extremely high level of enantioselectivity.[3] Although the reported highly enantioselective reduction of ketones by hydrogenation with chiral phoshine–metal catalysts is a very attractive method, giving optically active secondary alcohols, the reduction is accessible for hetero-substituted ketones, not for simle aliphatic and aromatic ketones.

It is noteworthy that some chiral nitrogen-containing ligands and their rhodium complexes can attain excellent enantioselection in the hydrosilylative reduction of ketones,[4] in which no chiral phosphine ligand could achieve optical yields higher than 90%.[5] In terms of enantioface recognition for simple ketones, we have been interested in the design and synthesis of new chiral and C_2-symmetrical terdentate pyridine ligands and their rhodium complexes as catalysts in the asymmetric hydrosilylation of ketones.

We report here the synthesis of new chiral pyridine ligands having two chiral oxazoline rings and their trivalent rhodium complexes, which exhibit extremely high enantioselectivity in the reduction of several aromatic and aliphatic ketones.[6] From a mechanistic viewpoint, we also disclose the effects of extra addition of the ligands and the linearity in asymmetric induction with the mixed-ligand system.

Results and Discussion

Design and Synthesis of the Chiral Bis(oxazolinyl)pyridine Ligand and Its Rhodium(III) Complex. Our design for the terdentate ligand includes two chiral oxazoline rings introduced at the 2,6-positions of a pyridine skeleton: 2,6-*bis*(*ox*azolinyl)*py*ridine (*pybox*). The chi-

(1) Brunner, H. *Topics in Stereochemistry*; Interscience: New York, 1988; Vol. 18, pp 129–247. Kagan, H. B. *Asymmetric Synthesis*; Academic Press: New York, 1985; Vol. 5, pp 1–39.

(2) Fritschi, H.; Leutenegger, U.; Pfaltz, A. *Helv. Chim. Acta* **1988**, *71*, 1533. Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1989**, *111*, 789. Oguni, N.; Matsuda, Y.; Kaneko, T. *Ibid.* **1988**, *110*, 7877. Soai, K.; Ookawa, A.; Kaba, T.; Ogawa, K. *Ibid* **1987**, *109*, 7111. Groves, J. T.; Viski, P. *Ibid.* **1989**, *111*, 8537. O'Malley, S.; Kodadek, T. *Ibid.* **1989**, *111*, 9116. Corey, E. J.; Jardine, P. D.; Virgil, S.; Yuen, P.-W.; Connell, R. D. *Ibid.* **1989**, *111*, 9243.

(3) Noyori, R.; Ohkuma, T.; Kitamura, M.; Takaya, H.; Sayo, N.; Kumobayashi, H.; Akutagawa, S. *J. Am. Chem. Soc.* **1987**, *109*, 5856. Kitamura, M.; Ohkuma, T.; Inoue, S.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Ohta, T.; Takaya, H.; Noyori, R. *Ibid.* **1988**, *110*, 629. Corey, E. J.; Bakshi, R. K.; Shibata, S.; Chen, C.-P.; Singh, V. K. *Ibid.* **1987**, *109*, 7925.

(4) Brunner, H.; Becker, R.; Riepl, G. *Organometallics* **1984**, *3*, 1354. Brunner, H.; Kürzinger, A. *J. Organomet. Chem.* **1988**, *346*, 413. Brunner, H.; Obermann, Uwe. *Chem. Ber.* **1989**, *122*, 499.

(5) For review: Ojima, I.; Hirai, K. *Asymmetric Synthesis*; Academic Press: New York, 1985; Vol. 5, pp 103–145. Ojima, I.; Kogure, T.; Kumagai, M. *J. Org. Chem.* **1977**, *42*, 1671.

(6) Preliminary communication: Nishiyama, H.; Sakaguchi, H.; Nakamura, T.; Horihata, M.; Kondo, M.; Itoh, K. *Organometallics* **1989**, *8*, 846.

0276-7333/91/2310-0500$02.50/0

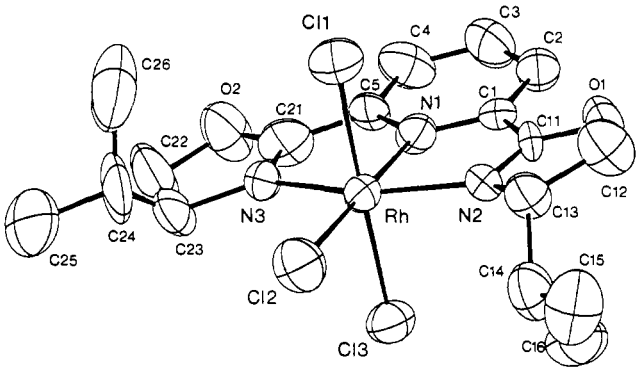
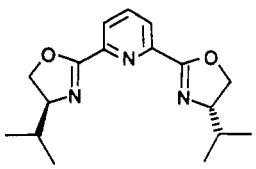
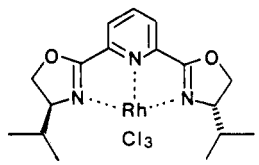


Figure 1. Molecular structure of [(*S*,*S*)-ip-pybox]$RhCl_3$ (**2a**).

rality of the oxazoline rings is derived from readily available optically active β-amino alcohols e.g. 2,6-bis-[4′-(*S*)-isopropyloxazolin-2′-yl]pyridine (**1a**; (*S*,*S*)-ip-pybox)



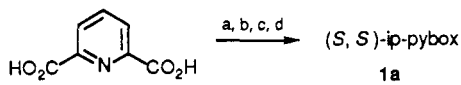
1a



2a

from (*S*)-valinol. The two chiral centers can afford the pybox molecule C_2-axis chirality. Therefore, the corresponding rhodium complex of the chiral pybox ligand is distinctive in that the two bulky alkyl group on the chiral oxazoline rings make a reasonable chiral and C_2-symmetrical concave to recognize one of the prochiral faces of unsymmetrical ketones selectively in hydrosilylation reactions. The trivalent rhodium complex of (*S*,*S*)-ip-pybox **2a** has the two isopropyl groups placed as close as possible to the reaction site as "chiral fences".

Starting from pyridine-2,6-dicarboxylic acid with (*S*)-valinol that was readily derived from L-valine by reduction with $LiAlH_4$, we can synthesize (*S*,*S*)-ip-pybox (**1a**) as white crystals in ca. 60% total yield in the four steps



(a) $SOCl_2$, reflux, 10 h; (b) (*S*)-valinol, Et_3N, room temperature, 1 day; (c) $SOCl_2$, reflux, 3 h; (d) NaOH, MeOH–H_2O, room temperature, 3 days

Treatment of **1a** with $RhCl_3(H_2O)_3$ in ethanol at 80 °C for 3 h gave [(*S*,*S*)-ip-pybox]$RhCl_3$ (**2a**) in 70% yield. The complex **2a** can be purified by column chromatography as a stable orange solid. The structural analysis of **2a** was performed by a single-crystal X-ray study, showing that the rhodium coordination geometry is slightly distorted octahedral. The N(2)–Rh–N(3) angle is 158.7° (Figure 1). In the terdentate system the oxazoline rings at the rhodium center make a C_2-symmetrical chiral environment with the two isopropyl groups spreading over the reaction site.

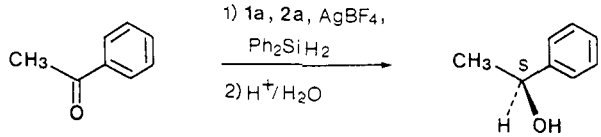
Hydrosilylation of Ketones with 1a and 2a. We first examined the asymmetric hydrosilylation of acetophenone by a combination of (*S*,*S*)-ip-pybox (**1a**) and $[Rh(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) as a catalyst. However, complete complexation of **1a** with $[Rh(COD)Cl]_2$ is so slow that the mixture in methanol–dichloromethane must be stirred for 1 day. After the solvent was removed, the reaction was started by addition of the ketone and a silane. In the presence of $[Rh(COD)Cl]_2$ (0.5 mol %) and **1a** (3 equiv), the reduction of acetophenone with diphenylsilane proceeded smoothly at −5 to 0 °C to give 76–78% ee of (*S*)-1-phenylethanol as the relatively high results. Other silanes were also examined but gave lower results.[7]

Table I. Hydrosilylation of Acetophenone with (ip-pybox)$RhCl_3$ (2a) and Diphenylsilane[a]

run no.	additive (amt, mol %)	amt of **1a**, mol %	temp, °C; time, h	(*S*)-1-phenylethanol yield, %	ee, %
1	none	1.7	room temp	no reacn	
2	$AgBF_4$ (2.0)	0	0; 6	86	83
3	$AgBF_4$ (2.0)	4.0	0; 2	91	94
4	$AgBF_4$ (2.0)	4.0	0; 3	94[b]	95[b]
5	$AgBF_4$ (1.0)	4.0	−5; 4.5	90	93
6	$AgPF_6$ (2.0)	4.0	−3; 5	80	87
7	AgOTf (1.3)	0	0; 26[c]	61	56
8	AgOTf (1.0)	3.0	0; 17[c]	84	83
9	AgOTf (1.0)	7.0	−5; 27[c]	96	89
10	$BF_3{\cdot}Et_2O$[d] (1.5)	3.5	0; 14[e]	90	82
11	$EtAlCl_2$[d] (1.5)	3.5	0; 18[e]	89	67

[a] Conditions: PhCOMe (8.0 mmol), Ph_2SiH_2 (12.8 mmol), **2a** (0.08 mmol), additive (0.08–0.16 mmol). After consumption of ketone was checked by TLC examination followed by hydrolysis, the yields were determined by GLPC (PEG 20 M). Small amounts of acetophenone (<5%) derived from the silyl enol ether were detected. The % ee was determined on the basis of ^1H NMR studies of the MTPA ester in accord with the optical rotation. [b] Ethyl levulinate (1.0 mmol) was initially added. After the mixture was stirred for 1 h, PhCOMe (8.0 mmol) was then added. [c] THF (6.0 mL). [d] At first **2a** was treated in dichloromethane with the acid at room temperature for 1 h. Then **1a**, the ketone, and the silane were added below 0 °C. [e] CH_2Cl_2 (1.0 mL).

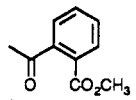
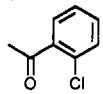
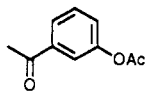
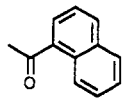
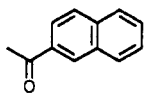
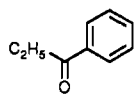
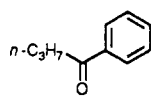
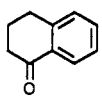
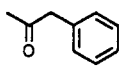
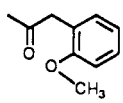
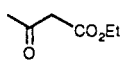
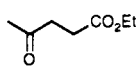
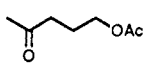
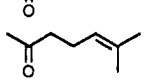
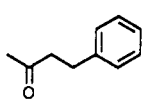
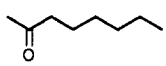
We then examined the rhodium trichloride complex **2a** as a catalyst for the asymmetric hydrosilylation of acetophenone (Table I). However, the complex **2a** showed no catalytic activity for the reduction even at 30 °C, because there was no reaction between **2a** itself and diphenylsilane. Therefore, we added some silver salts and Lewis acids to be able to make the complex active as a cationic species and thus react with the silane smoothly. When we added $AgBF_4$ (2 mol %), the complex **2a** (1 mol %) with diphenylsilane (1.6 equiv) could act as the catalyst, giving (*S*)-1-phenylethanol in 86% yield and 83% ee without extra addition of the ligand **1a** (run 2).[8] In general, in the catalytic hydrosilylation with nitrogen-containing chiral ligands previously reported, higher enantioselectivities could be obtained only when a large excess of ligand was employed.[4,6] Then we tried extra addition of the pybox compound **1a** (4 equiv), leading to a dramatic increase of the percent enantiomeric excess to 94% (run 3). Addition of the ligand with silver trifluoromethanesulfonate (AgOTf) and the ligand also improved the percent enantiomeric excess from 56 to 89% (runs 7–9). Moreover, boron trifluoride etherate and ethylaluminum dichloride also could collaborate with the rhodium complex (runs 10 and 11). These observations indicate that counteranions can play an important role in enantioselection.



(7) $PhMeSiH_2$, 32% product yield and 14% ee (*S*), 0 °C, 26 h; 1-$NpPhSiH_2$, 62% product yield and 62% ee (*S*), 0 °C, 4 days.

(8) Before addition of the ketone and the silane, the complex **2a** was treated in THF for 1 h with $AgBF_4$, giving a mixture of the corresponding cationic species (ip-pybox)$RhCl_n(BF_4)_{3-n}$. By filtration through a Celite (545) column, the cationic complexes are isolated and also show catalytic activity for hydrosilylation. We have also found that the naked silver cation itself shows catalytic activity: for acetophenone, 20 °C, 1 day, 20% yield with $AgBF_4$ and 60% yield with AgOTf. However, in the presence of the pybox ligand (>1 equiv) the silver salt does not act as a catalyst. Cu(I)-catalyzed hydrosilylation of ketones has already been reported; see: Brunner, H.; Miehling, W. *J. Organomet. Chem.* **1984**, *275*, C17.

Table II. Hydrosilylation of Ketones with (ip-pybox)$RhCl_3$ (2a), $AgBF_4$, and Diphenylsilane[a]

run no.	ketone	amt of **1a**, mol %	temp, °C; time, h	product *sec*-alcohol yield, %	ee, %	abs confign
1		6.0	0; 14	95	96	*S*
2		4.0	0; 4	74	94	
3		6.0	0; 24	81	92	
4		4.0	−5; 5	87	94	*S*
5		4.0	−5; 6	93	93	*S*
6		4.0	5; 4	73	91[b]	*S*
7		4.0	0–5; 5	82	82[b]	*S*
8		4.0	0; 2	92	99	*S*
9		6.0	0; 5	95	71[b]	*S*
10		6.0	−5; 4	95	82[c]	*S*
11		6.0	−5; 24	60	27[b]	*S*
12		6.0	0; 7	91	95	*S*
13		6.0	20; 24	85	68[d]	*S*
14		6.0	20; 20	94	70[b]	*S*
15		6.0	0; 5	92	66[b]	*S*
16		4.0	0; 2	85[e]	63	*S*

[a] Conditions: ketone (8.0 mmol), Ph_2SiH_2 (12.8 mmol), **2a** (0.08 mmol), $AgBF_4$ (0.16 mmol), THF (1.0 mL). After consumption of the ketone was checked by TLC examination, hydrolysis followed by Kugelrohr distillation or column chromatography gave the corresponding alcohol (isolated yields). Small amounts of the ketone (<7%) were recovered via the silyl enol ether. The % ee values were determined on the basis of ^1H NMR studies of their MTPA esters in accord with their optical rotations. [b] Determined by the optical rotation. [c] Compared to the authentic alcohol synthesized by alkylation of (*S*)-(−)-propylene oxide with (*o*-methoxyphenyl)lithium. [d] The product was subjected to alkaline hydrolysis, giving 1,4-pentanediol, to determine the optical rotation. [e] Ethyl levulinate (1.0 mmol) was initially added. After the mixture was stirred for 1 h, the ketone was added.

We have thus attained a highly enantioselective reduction of acetophenone in the catalytic system with the pybox ligand and the rhodium complex with the assistance of some additives.

Other ketones were subjected to the hydrosilylation with **2a** (1 mol %) under the following standard conditions: ketone (8.0 mmol), $AgBF_4$ (2 mol %), **1a** (4–6 mol %), Ph_2SiH_2 (12.8 mmol), THF (1.0 mL), −5 to +5 °C (Table II). For each run, the reaction temperatures were constantly controlled by a thermoregulator until the starting ketones disappeared by TLC examination. Below ca. 5–10 °C lower than the temperature described in the table, the hydrosilylation of ketones did not proceed, although the rhodium cationic complex reacted with the silane. Tetrahydrofuran was preferable as the solvent, especially for solid ketones.

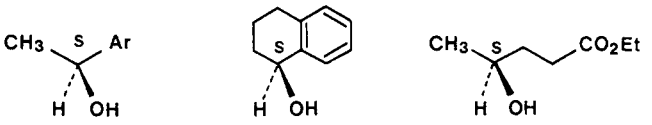
The derivatives of acetophenone were reduced below or at 0 °C for several hours to give extremely high enantiomeric excesses, 92–96% (runs 1–5, Table II). Compared to that for acetophenone (run 3, Table I), the enantiomeric excess decreased for the ethyl and the *n*-propyl phenyl ketones (runs 6 and 7, Table II, 91% and 82% ee, respectively).

It is quite noteworthy that the reduction of 1-tetralone resulted in the highest enantioselection, 99% (run 8). We assume that the planarity of 1-tetralone can preferably collaborate to match the pybox plane of the rhodium catalyst by stacking.

It is also quite interesting in that the levulinate, a γ-keto ester, was reduced in 95% ee (run 12). Some chelate effect of the hetero substituent on the substrate toward the rhodium center was previously postulated for the phosphine–rhodium catalyst by Ojima.[5] Similarly, in the case of runs 1 and 2 (Table II) for acetophenone, runs 9 and 10, and runs 13–16, respectively, slight increases of the enantiomeric excess were observed and accounted for the chelation.

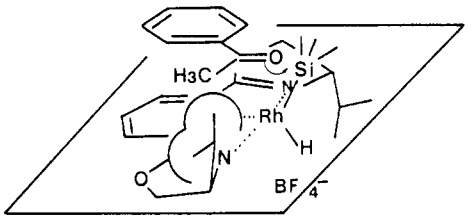
Linear aliphatic ketones also gave considerably high results as those from a catalytic system (runs 13–16), comparing to other catalytic and even stoichiometric systems.[9]

Our catalytic system with **1a** and **2a** can give the *S* absolute configuration for all secondary alcohol products, e.g. phenethyl alcohol derivatives **3**, (*S*)-1-tetralol (**4**), and ethyl (*S*)-4-hydroxypentanoate (**5**), derived from specific

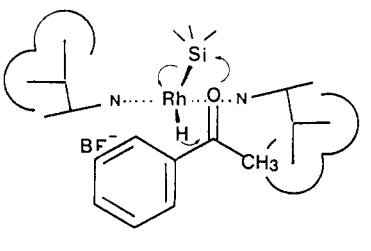


3 4 5

recognition of the *re* prochiral face. According to the reported mechanism for the hydrosilylation of ketones, we have assumed two hypothetical transition states: (1) an enantio-differentiative insertion of the ketone at the Rh–Si bond (A)[5] and (2) a five-membered concerted transition state (B).[10]



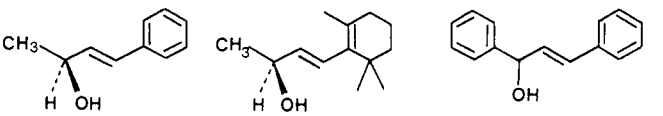
A



B

Then we examined any decrease of the enantioselectivity in the initial stage, generating a real rhodium catalyst. Under the standard conditions, ethyl levulinate (1.0 mmol) was added as a dummy ketone in the initial reaction mixture. After the reduction of the levulinate started (for ca. 0.5–1 h), acetophenone (8.0 mmol) was then added. The reduction of acetophenone proceeded very smoothly at 0 °C for 3 h to give 94% product yield and 95% ee (run 2, in Table I). Vice versa, with use of acetophenone (1.0 mmol) as a dummy, the reduction of ethyl levulinate resulted in 82% yield and 92% ee, almost the same as run 12 in Table II. Therefore, we consider that the same pybox–rhodium species initially generated by the activation with $AgBF_4$ and diphenylsilane can act as a catalyst during the whole reaction period, unaffected by the species of ketones.

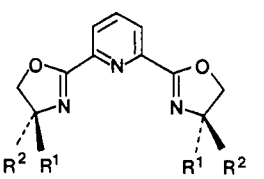
We have also investigated α,β-unsaturated ketones. Under the standard conditions described above, benzalacetone and β-ionone were reduced to give the 1,2-reduction products **6** in 91% yield and 22% ee (*S*) at 0 °C for 7 h and **7** in 91% yield and 44% ee (*S*) at 10 °C for 5 h, respectively, along with trace amounts of 1,4-reduction products (<2%). A similar high selectivity of 1,2-reduc-



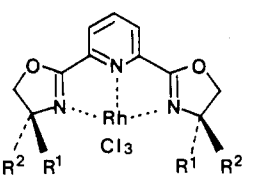
6 7 8

tion was also reported by using diphenylsilane and phosphine–rhodium catalyst.[11] A phenyl substituent on the unsaturated skeleton gives an increase in 1,4-reduction. In our system, chalcone also gave 1,2-reduction selectively, resulting in chalcol 8 in 87% yield and 71% ee at 0 °C for 45 h.[12]

Substituent Effect on the Oxazoline Rings. The isopropyl group on the oxazoline ring of (*S,S*)-ip-pybox (**1a**) can create an extremely good chiral environment around the reaction site of the rhodium metal to recognize the *re* prochiral face of the methyl ketone derivatives. We have also used ligands **1b–e**, having other subtituents on the oxazoline rings, in the reduction of acetophenone and ethyl levulinate.



1



2

R^1	R^2	pybox	(pybox)$RhCl_3$
i-Pro	H	**1a**, (*S,S*)-ip-pybox	**2a**
sec-Bu	H	**1b**, (*S,S*)-sb-pybox	**2b**
t-Bu	H	**1c**, (*S,S*)-tb-pybox	**2c**
H	Et	**1d**, (*R,R*)-et-pybox	**2d**
H	Ph	**1e**, (*R,R*)-ph-pybox	**2e**
Me	Me	**1f**, dm-pybox	**2f**

2,6-Bis(4′-R-oxazolin-2′-yl)pyridines (R = *sec*-Bu (**1b**), *t*-Bu (**1c**), Et (**1d**), Ph (**1e**)) were synthesized by the same method as for **1a** by using (*S*)-*sec*-leucinol, (*S*)-*tert*-leucinol, (*R*)-2-amino-1-butanol, and (*R*)-phenylglycinol, respectively. Treatment of **1b–e** with $RhCl_3(H_2O)_3$ in

(9) Itsuno, S.; Itoh, K.; Hirao, K.; Nakahama, S. *J. Org. Chem.* **1984**, *49*, 555 and references therein.
(10) Akita, M.; Mitani, O.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 527.
(11) Ojima, I.; Kogure, T. *Organometallics* **1982**, *1*, 1390.
(12) Kogure, T.; Ojima, I. *J. Organomet. Chem.* **1982**, *234*, 249. Hayashi, T.; Yamamoto, K.; Kumada, M. *Tetrahedron Lett.* **1972**, 5053. Hayashi, T.; Yamamoto, K.; Kumada, M. *Ibid.* **1975**, 3. For palladium catalyst: Keinan, E.; Greenspoon, N. *Ibid.* **1985**, *26*, 1353.

Table III. Hydrosilylation of Acetophenone and Ethyl Levulinate with (pybox)$RhCl_3$ (2a–f)[a]

Rh complex	product alcohol ee, % (abs config) [temp, °C; time, h; yield, %]			
	run no.	acetophenone	run no.	ethyl levulinate
2a	1	94 (*S*) [0; 2; 91][b]	2	95 (*S*) [0; 7; 91][c,d]
2b	3	91 (*S*) [−5; 10; 91][d]	4	94 (*S*) [0; 7; 82]
2c	5	83 (*S*) [0; 18; 92][e]	6	79 (*S*) [10; 18; 79][e,f]
2d	7	54 (*R*) [10; 2; 88][d]	8	75 (*R*) [10; 4; 80]
2e	9	19 (*R*) [20; 18; 82][g,h]	10	[<30°; no reaction]
2f	11	[20; 20; 66][h,i]		

[a] The same reaction scale as described in footnote *a* in Table II was used. The same ligand (4 equiv) to corresponding complex ratio was employed. [b] The same data as in Table I, run 2. [c] The same data as in Table II, run 12. [d] 6 equiv of the ligand. [e] AgOTf (2.0 mmol) was employed in place of $AgBF_4$. [f] Conversion was 48%. [g] Conversion was 58%. [h] No reaction below 10 °C. [i] PhCOMe (28%) was recovered via the silyl enol ether.

ethanol gave the corresponding pybox–rhodium(III) trichloride complexes **2b–e**, respectively. The nonchiral ligand **1f** and its rhodium complex **2f** were also prepared.

The results of hydrosilylation for acetophenone and ethyl levulinate with **2a–f** are summarized in Table III.

The *sec*-butyl derivative **2b** showed almost the same activity as the isopropyl catalyst **2a**, giving relatively high enantioselectivity. In the case of the *tert*-butyl catalyst **2c**, $AgBF_4$ gave considerably low enantiomeric excess, less than 10%. However, use of AgOTf increased the enantiomeric excess to 79–83% but gave a longer reaction time compared to those for **2a,b** (runs 5 and 6). The *tert*-butyl group might be too large to accept the methyl ketones around the chiral reaction site and might be strongly affected by the counteranion. However, this is interesting in that the smaller ethyl substituent can give a good to excellent enantiomeric excess, 75%, for the levulinate (run 8). In contrast, the phenyl catalyst **2e** did not act as a good catalyst for the reduction (runs 9 and 10).

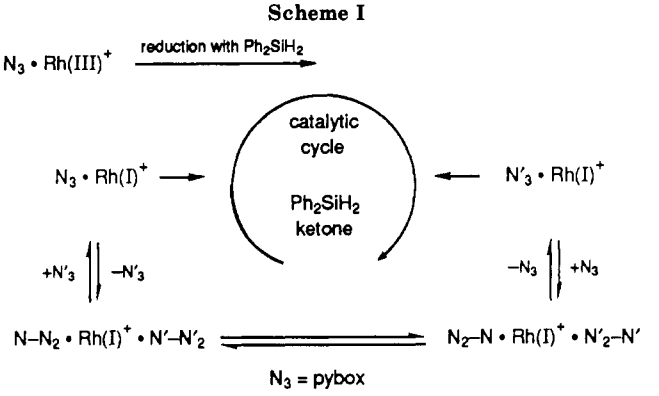
The nonchiral derivative **2f** with diphenylsilane could not reduce acetophenone below 10 °C but did reduce slowly at 20 °C, giving 66% product yield (run 11).

Thus, the reduction rates are strongly affected by the bulkiness of the substituents on the oxazoline rings.

Behavior of Excess Pybox Ligands. We have already mentioned that extra addition of the ligands is inevitable to attain higher enantioselectivity.[3] In order to study the behavior of the extra free ligands, we have carried out some mixed-ligand experiments (Table IV).

Addition of the (*R,R*)-et-pybox ligand **1d** (4 equiv) and the (*S,S*)-ip-pybox complex **2a** (1 mol %) to acetophenone

Scheme I



resulted in the reverse absolute configuration (*R*) of 1-phenylethanol in 22% ee (run 1). Vice versa, addition of **1a** (4 equiv) to the ethyl catalyst **2d** also gave the reverse configuration (*S*) in 31% ee (run 2). These phenomena could be accounted for by facile and fast ligand displacement between the coordinating ligand and the free ligand during the reduction.

We have confirmed *linearity* of the enantiomeric excess between the chiral catalysts and the product by using (*R,R*)-ip-pybox (**1a′**; R^1 = H, R^2 = *i*-Pr) and its rhodium complex **2a′**. Mixed systems of the ligands **1a** and **1a′** and the rhodium complexes **2a** and **2a′** gave enantioselectivities in accord with the calculated values: for run 3, 34% ee, calcd 40 × 0.94 = 37.6% ee; for run 4, 18% ee, calcd 20 × 0.94 = 18.8% ee. Interestingly, use of only **2a** as a catalyst with mixed ligands **1a** and **1a′** gave a higher enantiomeric excess than the calculated values of the total excess (runs 5–7). These facts indicate that the ligand-exchange reaction between the isopropyl derivatives is a little slower than the reduction process.

Addition of nonchiral pybox **1f** did not affect the reduction, giving almost the same result (84% ee, run 8) as run 2 in Table I (without extra addition), because the reduction with **2f** does not proceed below 10 °C. In contrast, addition of **1a** to **2f** made the reduction proceed smoothly at 0 °C for 7 h, giving a higher enantiomeric excess 86% (run 9).

We can assume that the active catalyst has only one pybox ligand on the rhodium atom during the reaction and can reduce the ketone enantioselectivity, but we cannot define whether or not the pybox ligand maintains terdentate coordination on the rhodium in the transition state. We think that in general nitrogen ligands may be relatively so labile, compared to phosphine ligands, that the extra pybox ligand may act as a supplement to protect the catalyst from decomposition, giving pybox-free rhodium species, which decrease the enantiomeric excess. We cannot define the real mechanism at this stage, but we

Table IV. Hydrosilylation of Acetophenone with the Mixed System of Ligands 1a,d,f[a]

run no.	Rh complex, (amt, mol %)	ligand (amt, mol %)	temp, °C	time, h	yield, %	ee, %	abs confign
1	**2a** (1.0)	**1d** (4.0)	0	3	94	22	*R*
2	**2d** (1.0)	**1a** (4.0)	0	2	94	31	*S*
3	**2a–2a′** (0.7:0.3)	**1a–1a′** (2.8:1.2)[b]	0	1	87	34	*S*
4	**2a–2a′** (0.6:0.4)	**1a–1a′** (2.4:1.6)[b]	0	2	90	18	*S*
5	**2a** (1.0)	**1a–1a′** (3.0:1.0)[b]	0	2	88	62	*S*
6	**2a** (1.0)	**1a–1a′** (2.0:2.0)[b]	0	2	91	39	*S*
7	**2a** (1.0)	**1a–1a′** (1.5:2.5)[b]	0	2	92	28	*S*
8	**2a** (1.0)	**1f** (4.0)	0	3	94	84	*S*
9	**2f** (1.0)	**1a** (4.0)	0	7	87	87	*S*

[a] Conditions: PhCOMe (8.0 mmol), Ph_2SiH_2 (12.8 mmol), rhodium complex (0.08 mmol), $AgBF_4$ (0.16 mmol), THF (1.0 mL). The procedure, the workup, and the determination of yields and the % ee are the same as described in footnote *a* Table I. [b] Calculated values of the total enantiomeric purity: for run 3, 40%; for run 4, 20%; for run 5, 60%; for run 6, for run 7, 0%.

postulate a possible outline of this hydrosilylation as shown in Scheme I.

Conclusion

We have attained the enantioselective hydrosilylation of methyl ketone derivatives such as substituted acetophenones, 1-tetralone, and ethyl levulinate with the newly designed chiral pybox ligands and their trivalent rhodium complexes with the aid of silver salts. We discovered the facile displacement behavior of the extra ligands in the reaction media, and we could observe the effects of substituents on the oxazoline rings affecting the enantioselectivity and the reaction rates. The role of the extra ligand in the reaction mechanism was also discussed.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of nitrogen. Tetrahydrofuran was distilled from sodium. Chloroform was dried by distillation under nitrogen with $CaCl_2$ after being washed with water. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-GX 270 spectrometer with tetramethylsilane as the internal reference. Infrared spectra were recorded on a JASCO A-3 spectrometer. Mass spectra were determined with a Hitachi M-80B mass spectrometer. GLPC analyses were performed with a Shimadzu CG-8A instrument using a 2 m × 3 mm column (PEG 20 M, 10%) and helium as carrier gas. Microanalyses were performed with a Yanagimoto MT-3 CHN corder. Optical rotation was measured on a JASCO DIP-140 polarimeter. 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 and 9385).

All optically active amino alcohols used were prepared by reduction of the corresponding commercially available amino acids with $LiAlH_4$ in THF.[13] (*S*)-*tert*-leucinol: bp 117–120 °C (57 mmHg), $[\alpha]^{25}_D$ = +37.24° (*c* = 1.02, EtOH); ^1H NMR (270 MHz, $CDCl_3$) δ 0.90 (s, 9 H), 1.80 (broad, 3 H), 2.50 (dd, *J* = 3.9, 10.3 Hz, 1 H), 3.21 (t, *J* = 10.3 Hz (×2), 1 H), 3.71 (dd, *J* = 3.9, 10.3 Hz, 1 H).

2,6-Bis[4′-(*S*)-isopropyloxazolin-2′-yl]pyridine, (*S*,*S*)-ip-pybox (1a). Pyridine-2,6-dicarboxylic acid (8.4 g, 50 mmol) was treated with $SOCl_2$ (54 mL) at reflux temperature for 10 h. Excess $SOCl_2$ was then removed under reduced pressure to give the acid chloride as a white solid. To a solution of (*S*)-valinol (11.3 g, 0.11 mol) and triethylamine (42 mL, 0.30 mol) in chloroform (200 mL) was slowly added a solution of the acid chloride in chloroform (100 mL) at 0 °C. The mixture was stirred for 1 day at room temperature. Then $SOCl_2$ (37 mL, 0.50 mol) was added, and the mixture was heated at reflux temperature for 2 h and was slowly poured into ice water. The organic layer was collected, washed with brine (50 mL) and aqueous K_2CO_3 (0.1 M, 50 mL), and dried over anhydrous Na_2SO_4. After concentration a white solid was obtained, which was passed through a silica gel column (dichloromethane and ether as eluents) to give mainly the 2 HCl salt of **1a** (16.4 g, ca. 44 mmol, ca. 88%) as a white solid, TLC R_f 0.6 (CH_2Cl_2:ether = 3:2). The solid (16.4 g) was treated with a solution of NaOH (12 g) in water (160 mL) and MeOH (340 mL) at room temperature for 3 days. The mixture was extracted with CH_2Cl_2 (550 mL). The extract was washed with brine and concentrated to give the white solid, which was purified by recrystallization with hexane–EtOAc to give **1a** as white needles in 61% total yield (9.1 g, 30 mmol). The product **1a** could be detected by TLC examination (R_f 0.35, CH_2Cl_2:ether = 3:2) but slightly decomposed on silica gel: mp 152–153 °C; $[\alpha]^{26}_D$ = −116.8° (*c* = 1.0, CH_2Cl_2); IR (KBr disk) 1630, 1465 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), 1.88 (m, 2 H), 4.18 (ddd, *J* = 6.6, 8.3, 9.5 Hz, 2 H, N–CH), 4.23 (t, *J* = 8.3 (×2) Hz, 2 H, O–CH), 4.54 (dd, *J* = 8.3, 9.5 Hz, 2 H, O–CH), 7.86 (t, *J* = 7.8 (×2) Hz, 1 H), 8.21 (d, 7.8 Hz, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) 18.33 (q), 19.01 (q), 32.87 (d), 70.98 (t), 72.94 (d), 125.73 (d), 137.14 (d), 146.96 (s), 162.24 (s); MS *m*/*e* (relative intensity) 302 (52, M + 1), 287 (19), 259 (base), 230 (95), 214 (48), 145 (95), 117 (95). Anal. Calcd for $C_{17}H_{23}N_3O_2$: C, 67.75; H, 7.69; N, 13.94. Found: C, 67.88; H, 7.72; N, 13.84.

2,6-Bis[4′-(*R*)-isopropyloxazolin-2′-yl]pyridine, (*R*,*R*)-ip-pybox (1a′). Pyridine-2,6-dicarboxylic acid (3.34 g, 20 mmol), $SOCl_2$ (36 mL), (*R*)-valinol (4.54 g, 44 mmol), triethylamine (17 mL), and $SOCl_2$ (15 mL) gave **1a′** as white needles in 63% yield (3.76 g, 12.5 mmol): mp 152–153 °C; $[\alpha]^{23}_D$ = +118.4° (*c* = 1.00, CH_2Cl_2). Anal. Calcd for $C_{17}H_{23}N_3O_2$: C, 67.75; H, 7.69; N, 13.94. Found: C, 67.59; H, 7.80; N, 14.06.

2,6-Bis[4′-(*S*)-(1-(*S*)-methylpropyl)oxazolin-2′-yl]pyridine, (*S*,*S*)-sb-pybox (1b). Pyridine-2,6-dicarboxylic acid (10 g, 60 mmol), $SOCl_2$ (66 mL), (*S*)-isoleucinol (15.5 g, 132 mmol), triethylamine (50 mL), and $SOCl_2$ (48 mL) gave the intermediate salts (ca. 23 g, 57 mmol). The salts (ca. 11 g) was treated with aqueous NaOH to give **1b** (6.4 g, 19.5 mmol) in 70% yield as white needles: mp 143–144 °C; $[\alpha]^{26}_D$ = −105.5° (*c* = 1.24, CH_2Cl_2); IR (KBr disk) 1636, 1465, 1380, 1130 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.88 (d, 3 H), 0.96 (t, 3 H), 1.26 (m, 4 H), 1.68 (m, 2 H), 1.82 (m, 2 H), 4.23 (m, 4 H), 4.50 (m, 2 H), 7.85 (t, *J* = 7.8 Hz, 1 H), 8.18 (d, *J* = 7.8 Hz, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 11.49 (q), 14.51 (q), 26.13 (t), 39.14 (d), 70.52 (t), 71.46 (d), 125.46 (d), 137.20 (d), 146.87 (s), 162.14 (s); MS *m*/*e* (relative intensity) 329 (53, M), 272 (base), 244 (97), 217 (48), 145 (75), 117 (52). Anal. Calcd for $C_{19}H_{27}N_3O_2$: C, 69.27; H, 8.26; N, 12.76. Found: C, 69.33; H, 8.20; N, 12.76.

2,6-Bis[4′-(*S*)-*tert*-butyloxazolin-2′-yl]pyridine, (*S*,*S*)-tb-pybox (1c). Pyridine-2,6-dicarboxylic acid (1.67 g, 10 mmol), $SOCl_2$ (11 mL), (*S*)-*tert*-leucinol (2.58 g, 22 mmol), triethylamine (8.4 mL), and $SOCl_2$ (7.3 mL) gave **1c** as white needles in 42% yield (1.39 g, 4.22 mmol): mp 242–243 °C; $[\alpha]^{26}_D$ = −114.8° (*c* = 1.07, CH_2Cl_2); IR (KBr disk) 1640, 1475, 1375, 1361, 1105 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.97 (s, 18 H), 4.33 (t, *J* = 8.8 (×2) Hz, 2 H), 4.12 (dd, *J* = 8.8, 10.3 Hz, 2 H), 4.48 (dd, *J* = 8.8, 10.3 Hz, 2 H), 7.86 (t, *J* = 7.8 (×2) Hz, 1 H), 8.27 (d, *J* = 7.8 Hz, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 25.76 (q), 33.75 (s), 69.26 (t), 76.18 (d), 125.56 (d), 136.84 (d), 146.69 (s), 161.94 (s). Anal. Calcd for $C_{19}H_{27}N_3O_2$: C, 69.27; H, 8.26; N, 12.76. Found: C, 69.14; H, 8.37; N, 12.51.

2,6-Bis[4′-(*R*)-ethoxyoxazolin-2′-yl]pyridine, (*R*,*R*)-et-pybox (1d). Pyridine-2,6-dicarboxylic acid (8.5 g, 51 mmol), $SOCl_2$ (57 mL), (*R*)-2-amino-1-butanol (10 g, 112 mmol), triethylamine (43 mL, 0.3 mol), and $SOCl_2$ (42 mL) gave **1d** as white solids in 62% yield (8.6 g, 32 mmol): mp 86–88 °C; $[\alpha]^{19}_D$ = +130.7° (*c* = 1.24, CH_2Cl_2); IR (KBr disk) 1620, 1360, 1050 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.02 (t, *J* = 7.5 Hz, 6 H), 1.62 (dq, *J* = 7.5 (×3), 6.8 Hz, 2 H), 1.77 (dq, *J* = 7.5 (×3), 6.4 Hz, 2 H), 4.16 (t, *J* = 7.8 (×2) Hz, 2 H, O–CH), 4.27 (m, *J* = 6.4, 6.8, 7.8 (×3) Hz, 2 H, N–CH), 4.59 (dd, *J* = 7.8 (×2) Hz, 2 H, O–CH), 7.86 (t, *J* = 7.8 (×2) Hz, 2 H), 8.19 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR (67.8 MHz $CDCl_3$) δ 10.09 (q), 28.55 (t), 68.24 (d), 72.85 (t), 125.58 (d), 137.15 (d), 146.86 (s), 162.22 (s); MS *m*/*e* (relative intensity) 274 (57, M + 1), 273 (54, M), 244 (95), 243 (base), 217 (95), 145 (95), 117 (95). Anal. Calcd for $C_{15}H_{19}N_3O_2$: C, 65.91; H, 7.01; N, 15.37. Found: C, 65.75; H, 6.88; N, 15.37.

2,6-Bis[4′-(*R*)-phenyloxazolin-2′-yl]pyridine, (*R*,*R*)-pybox (1e). Pyridine-2,6-dicarboxylic acid (3.34 g, 20 mmol), $SOCl_2$ (25 mL), (*R*)-phenylglycinol (11.0 g, 80 mmol), and $SOCl_2$ (15 mL) gave the intermediate salt (6.9 g, ca. 78% yield). The salt (230 mg, 0.52 mmol) was treated with aqueous NaOH (5%, 2 mL) in methanol (6 mL) at room temperature to give **1e** as a white solid in 88% yield (171 mg, 0.46 mmol): TLC R_f 0.4 (EtOAc); mp 170–172 °C; $[\alpha]^{26}_D$ = +183.5° (*c*, = 1.03, CH_2Cl_2); IR (KBr disk) 1645, 1565, 1160, 980, 750, 700 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.43 (t, *J* = 8.3 (×2) Hz, 2 H), 4.93 (dd, *J* = 8.3, 10.3 Hz, 2 H), 5.47 (dd, *J* = 8.3, 10.3 Hz, 2 H), 7.30–7.40 (m, 10 H), 7.92 (t, *J* = 7.8 (×2) Hz, 1 H), 8.35 (d, *J* = 7.8 Hz, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 70.3 (d), 75.5 (t), 126.3 (d), 126.8 (s), 127.8 (d), 128.8 (s), 137.4 (d), 141.7 (s), 146.8 (s), 163.4 (s). Anal. Calcd for $C_{23}H_{19}N_3O_3$: C, 74.78; H, 5.18; N, 11.37. Found: C, 74.81; H, 5.31; N, 11.25.

2,6-Bis[4′,4′-dimethyloxazolin-2′-yl]pyridine, dm-pybox (1f). Pyridine-2,6-dicarboxylic acid (5.0 g, 30 mmol), $SOCl_2$ (23 mL), 2,2-dimethyl-2-aminoethanol (14.0 g, 15.7 mmol), and $SOCl_2$ (13 mL) gave **1f** as a white solid in 66% yield (5.5 g, 20 mmol):

(13) Itsuno, S.; Hirao, A.; Nakahama, S.; Yamazaki, N. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1673.

mp 140–141 °C; IR (KBr disk) 1615, 1590, 1568, 1460, 1372, 1338, 1250, 1182, 1102, 1078 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.41 (s, 12 H), 4.22 (s, 4 H), 7.86 (t, J = 7.8 (×2) Hz, 1 H), 8.19 (d, J = 7.8 Hz, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 28.35 (q), 67.94 (s), 79.68 (t), 125.58 (d), 137.12 (d), 146.93 (s), 160.76 (s); MS m/e (relative intensity) 273 (M^+, 51), 258 (base peak), 230 (27), 202 (40), 130 (40). Anal. Calcd for $C_{15}H_{19}N_3O_2$: C, 65.91; H, 7.01; N, 15.37. Found: C, 65.81; H, 7.07; N, 15.24.

[(*S*,*S*)-ip-pybox]RhCl$_3$ (2a). A solution of rhodium(III) chloride trihydrate (410 mg, 1.56 mmol) and ip-pybox (**1a**; 469 mg, 1.56 mmol) in ethanol (5 mL) was heated at reflux temperature under a nitrogen atmosphere for 3 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography with ethyl acetate and methanol as eluents to give **2a** as an orange solid in 70% yield (604 mg, 1.09 mmol); mp 279 °C dec; $[\alpha]^{20}_D$ = +543° (c = 1.09, CH_2Cl_2); IR (KBr disk) 1608, 1495, 1408, 1280, 920 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$), δ 0.97 (d, J = 6.5 Hz, 6 H), 0.99 (d, J = 6.5 Hz, 6 H), 3.04 (m, J = 6.5 (×6), 3.0 Hz, 2 H), 4.62 (ddd, J = 10.4, 7.4, 3.0 Hz, 2 H), 4.94 (dd, J = 7.4, 19.8 Hz, 2 H), 4.98 (dd, J = 10.4, 19.8 Hz, 2 H), 8.09 (d, J = 8.3 Hz, 2 H), 8.43 (t, J = 7.9 Hz, 1 H); ^{13}C NMR (67.8 Hz, $CDCl_3$) δ 15.12 (q), 19.57 (q), 28.44 (d), 68.71 (d), 73.27 (t), 126.42 (d), 139.97 (d), 147.27 (s), 166.13 (s). Anal. Calcd for $C_{17}H_{23}N_3O_2RhCl_3 \cdot 0.5CH_2Cl_2$: C, 38.00; H, 4.37; N, 7.60. Found: C, 38.14; H, 4.40; N, 7.48.

[(*R*,*R*)-ip-pybox]RhCl$_3$ (2a′). Rhodium(III) chloride trihydrate (526 mg, 2.0 mmol), **1a′** (603 mg, 2.0 mmol), and ethanol (6 mL) were refluxed for 1 h. **2a′** was obtained as an orange solid in 51% yield (523 mg, 1.02 mmol): mp >300 °C; $[\alpha]^{24}_D$ = −545° (c = 0.99, CH_2Cl_2). Anal. Calcd for $C_{17}H_{23}N_3O_2RhCl_3$: C, 39.99; H, 4.54; N, 8.23. Found: C, 39.46; H, 4.65; N, 8.10.

[(*S*,*S*)-sb-pybox]RhCl$_3$ (2b). Rhodium(III) chloride trihydrate (263 mg, 1.0 mmol), sb-pybox (**1b**; 345 mg, 1.05 mmol), and ethanol (3 mL) were refluxed for 3 h. **2b** was obtained as an orange solid in 69% yield (414 mg, 0.69 mmol): mp >300 °C; $[\alpha]^{26}_D$ = +536° (c = 0.99, CH_2Cl_2); IR (KBr disk) 1605, 1575, 1483, 1380 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.98 (d, J = 6.8 Hz, 6 H), 1.00 (t, J = 7.32 Hz, 6 H), 1.30 (m, 4 H), 2.91 (m, 2 H), 4.72 (m, 2 H), 4.92 (m, 4 H), 8.03 (d, J = 8.3 Hz, 2 H), 8.33 (t, J = 7.9 (×2) Hz, 1 H); ^{13}C NMR (67.8 Hz, $CDCl_3$) 11.72 (q), 12.81 (q), 27.07 (t), 34.83 (d), 73.24 (t), 126.45 (d), 140.24 (d), 147.22 (s), 166.10 (s). Anal. Calcd for $C_{19}H_{27}N_3O_2RhCl_3$: C, 42.36; H, 5.05; N, 7.80. Found: C, 42.02; H, 5.14; N, 8.00.

[(*S*,*S*)-tb-pybox]RhCl$_3$ (2c). Rhodium(III) chloride trihydrate (105 mg, 0.40 mmol), tb-pybox (**1c**; 132 mg, 0.40 mmol), and ethanol (4 mL) were refluxed for 1 h. **2c** was obtained as an orange solid in 70% yield (151 mg, 0.28 mmol): mp >300 °C; $[\alpha]^{25}_D$ = +994° (c = 0.99, CH_2Cl_2); IR (KBr disk) 1600, 1570, 1490, 1474, 1410, 1370, 1255, 965, 925 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.15 (s, 18 H), 4.27 (dd, J = 3.9, 9.8 Hz, 2 H), 4.92 (t, J = 9.8 (×2) Hz, 2 H), 5.08 (dd, J = 3.9, 9.8 Hz, 2 H), 8.08 (d, J = 7.8 Hz, 2 H), 8.37 (t, J = 7.8 (×2) Hz, 1 H); ^{13}C NMR (67.8 Hz, $CDCl_3$) δ 26.51 (q), 35.42 (s), 72.41 (d), 76.01 (t), 126.65 (d), 140.03 (d), 147.19 (s), 167.71 (s). Anal. Calcd for $C_{19}H_{27}N_3O_2RhCl_3$: C, 42.36; H, 5.05; N, 7.80. Found: C, 42.30; H, 5.02; N, 7.79.

[(*R*,*R*)-et-pybox]RhCl$_3$ (2d). Rhodium(III) chloride trihydrate (526 mg, 2.0 mmol), et-pybox (**1d**; 547 mg, 2.0 mmol) and ethanol (8 mL) were refluxed for 1 h. **2d** was obtained as an orange solid in 62% yield (599 mg, 1.24 mmol): mp 194 °C dec; $[\alpha]^{26}_D$ = −325° (c = 1.04, CH_2Cl_2); IR (KBr disk) 1620, 1520, 1445, 1345, 1325, 1295, 1045, 955, 925 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.01 (t, J = 7.3 (×2) Hz, 6 H), 1.91 (m, 2 H), 2.61 (m, 2 H), 4.63 (m, 2 H), 4.81 (dd, J = 8.3, 8.9 Hz, 2 H), 5.14 (dd, J = 8.3, 8.8 Hz, 2 H), 8.03 (d, J = 7.8 Hz, 2 H), 8.31 (t, J = 7.8 (×2) Hz, 1 H); ^{13}C NMR (67.8 Hz, $CDCl_3$) δ 9.30 (q), 26.29 (t), 65.13 (d), 77.16 (t), 126.40 (d), 140.00 (d), 147.24 (s), 165.96 (s). Anal. Calcd for $C_{15}H_{19}N_3O_2RhCl_3 \cdot 0.5CH_2Cl_2$: C, 35.46; H, 3.84; N, 8.00. Found: C, 35.67; H, 3.93; N, 8.24.

[(*R*,*R*)-ph-pybox]RhCl$_3$ (2e). Rhodium(III) chloride trihydate (26.3 mg, 0.10 mmol), ph-pybox (**1e**; 36.9 mg, 0.11 mmol), and ethanol (3.0 mL) were refluxed for 2 h. **2e** was obtained as an orange solid in 75% yield (43.3 mg, 0.75 mmol): IR (KBr disk) 1605, 1570, 1492, 1408, 755, 695 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.95 (t, J = 9.3 (×2) Hz, 2 H), 5.40 (dd, J = 9.3, 10.3 Hz, 2 H), 5.56 (dd, J = 9.3, 10.3 Hz, 2 H), 7.33 (m, 6 H), 7.48 (m, 4 H), 8.11 (d, J = 7.8 Hz, 2 H), 8.32 (t, J = 7.8 (×2) Hz, 1 H); ^{13}C NMR (67.8 Hz, $CDCl_3$) δ 67.37, 80.27, 126.90, 128.51, 128.61, 129.01, 135.87, 147.20, 167.03.

(dm-pybox)RhCl$_3$ (2f). Rhodium(III) chloride trihydrate (263 mg, 1.0 mmol), dm-pybox (**1f**; 273 mg, 1.0 mmol), and ethanol (15 mL) were refluxed for 2 h. **2f** was obtained as an orange solid in 54% yield (260 mg, 0.538 mmol): mp >300 °C; IR (KBr disk) cm^{-1}; 1605, 1580, 1496, 1465, 1408, 1290, 1210, 990, 938, 740, 678 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.82 (s, 12 H), 4.73 (s, 4 H), 8.00 (d, J = 8.3 Hz, 2 H), 8.26 (t, J = 8.3 (×2) Hz, 1 H); ^{13}C NMR (67.8 Hz, $CDCl_3$) δ 27.37 (q), 69.54 (s), 84.43 (t), 126.22 (d), 139.74 (d), 147.63 (s), 164.26 (s). Anal. Calcd for $C_{15}H_{19}N_3O_2RhCl_3$: C, 37.33; H, 3.97; N, 8.71. Found: C, 37.10; H, 4.01; N, 8.72.

General Procedure for Hydrosilylation with the Rhodium Complexes 2 and Diphenylsilane. In a 20-mL flask was placed **1** (0.32 mmol, 4 mol %), **2** (0.08 mmol, 1 mol %), and silver salt (0.16 mmol) under a nitrogen atmosphere. Anhydrous THF (1.0 mL) was added, and then the mixture was magnetically stirred at room temperature for 1 h. After addition of ketone (8.0 mmol), the reaction flask was dipped in a thermoregulated bath of methanol–water at −10 °C. Diphenylsilane (2.36 g, 12.8 mmol) was slowly added by a syringe. The temperature was gradually raised to −5 and then to +5 °C. The reaction was monitored by TLC examination; e.g. acetophenone (R_f 0.2), the corresponding silyl ether (R_f 0.6), diphenylsilane (R_f 0.7), and 1-phenylethanol (R_f 0.1), with hexane–ether (5:1) as an eluent. For the workup, to the reaction mixture was slowly added methanol (5 mL) at 0 °C. After gas evolution ceased, the reaction mixture was poured into a solution of hydrochloric acid (1 N, 14 mL) at 0 °C. The reaction flask was washed with small amounts of methanol and ether, and the washings were also added into the acid solution. The mixture was stirred at 0 °C for 1 h and extracted with ether (15 mL × 4). The extract was washed with brine (6 mL) and dried over anhydrous $MgSO_4$. The product yield was determined by GLPC analysis with addition of 1-methylnaphthalene (0.50 mL, 3.52 mmol) as an internal standard.

The extract was concentrated under reduced pressure by an aspirator, and the residue was passed through a short column of silica gel (20 g, hexane–ether as an eluent). After Kugelrohr distillation of the product obtained, the optical rotation was measured. The product (ca. 0.1 mmol) was converted to the corresponding MTPA ester with (*R*)-(+)-MTPA (35 mg, 0.15 mmol) and $SOCl_2$ for determination of the optical yield by ^1H NMR spectroscopy.[14]

Hydrosilylation of Acetophenone with 1a, 2a, AgBF$_4$, and Diphenylsilane. Run 3, Table I. In a 20-mL flask were added $AgBF_4$ (31 mg, 0.16 mmol), **2a** (42 mg, 0.08 mmol), **1a** (97 mg, 0.32 mmol), and acetophenone (960 mg, 8.0 mmol) under a nitrogen atmosphere. After the mixture was stirred for 1 h at room temperature and cooled to −10 °C, diphenylsilane (2.36 g, 12.8 mmol) was added. The mixture was then stirred at 0 °C for 2 h. After the workup and GLPC analysis (91% yield) as described above, Kugelrohr distillation gave (*S*)-1-phenylethanol in 87% yield (849 mg, 7.0 mmol); 94% ee by ^1H NMR of the MTPA ester (CH_3O) δ 3.56 for *S* and 3.47 for *R*, the ratio 97:3; $[\alpha]^{25}_D$ = −48° (CH_2Cl_2).

Run 4, Table I. $AgBF_4$ (31 mg, 0.16 mmol), **2a** (42 mg, 0.08 mmol), **1a** (97 mg, 0.32 mmol), and THF (1.0 mL) were placed in a 20-mL flask. At 0 °C ethyl levulinate (0.14 mL, 1.0 mmol) was placed in the flask, and diphenylsilane (2.36 g, 12.8 mmol) was added at −5 °C. After 1 h at 0 °C, acetophenone (960 mg, 8.0 mmol) was added. The workup and the distillation gave (*S*)-1-phenylethanol in 85% yield (833 mg, 6.8 mmol, 94% yield), and acetophenone (6%) was detected by GLPC: 95% ee by ^1H NMR spectroscopy of the MTPA ester.

Hydrosilylation of Methyl 2-Acetylbenzoate with 1a, 2a, AgBF$_4$, and Diphenylsilane. Run 1, Table II. $AgBF_4$ (31 mg, 0.16 mmol), **2a** (42 mg, 0.08 mmol), **1a** (144 mg, 0.48 mmol), methyl 2-acetylbenzoate (1.42 g, 8.0 mmol), and THF (1.0 mL) were placed in a 20-mL flask. At −10 °C, diphenylsilane (2.36 g, 12.8 mmol) was added. The mixture was stirred at 0 °C for 14 h. Then a solution of *p*-toluenesulfonic acid (91 mg, 0.48 mmol) in methanol (14 mL) was added, and the mixture was stirred for 3 h at room temperature. After extraction and column chromatography,

(14) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

(*S*)-3-methylphthalide was obtained in 95% yield (^{1}H NMR, trichloroethylene as an internal standard). Small amounts of the starting ketone (<3%) were removed by oximation with NaOAc and NH_2OH·HCl in methanol and by chromatography to give the pure (*S*)-3-methylphthalide: 96% ee, $[\alpha]^{17}_D = -47.6°$ (*c* = 0.33, MeOH); lit.[15] $[\alpha]_D = -49.5°$ calcd for −30.7° (62.0% optical purity). Treatment of the methylphthalide with MeLi gave the corresponding diol 2-[*o*-(1′-hydroxyethyl)phenyl]-2-propanol, whose optical purity was also checked by ^{1}H NMR spectroscopy in the presence of $Eu(tfc)_3$[16] (ca. 30% to the diol in $CDCl_3$): 96% ee, ratio 98:2 from the $(CH_3)_2C$ signals.

Hydrosilylation of 1-Acetylnaphthalene with 1a, 2a, $AgBF_4$, and Diphenylsilane. Run 4, Table II. $AgBF_4$ (31 mg, 0.16 mmol), **2a** (42 mg, 0.08 mmol), **1a** (97 mg, 0.32 mmol), 1-acetylnaphthalene (1.36 g, 8.0 mmol), and THF (1.0 mL) were placed in a 20-mL flask. At −5 °C diphenylsilane (2.36 g, 12.8 mmol) was added. Kugelrohr distillation gave (*S*)-1-(1′-naphthyl)ethanol in 87% yield (1.20 g, 6.97 mmol): 94% ee by ^{1}H NMR of the MTPA ester (CH_3O) δ 3.58 for *S* and 3.46 for *R*, ratio 97:3.

Hydrosilylation of 1-Tetralone with 1a, 2a, $AgBF_4$, and Diphenylsilane. Run 8, Table II. $AgBF_4$ (31 mg, 0.16 mmol), **2a** (42 mg, 0.08 mmol), **1a** (97 mg, 0.32 mmol), 1-tetralone (1.17 g, 8.0 mmol), and THF (1.0 mL) were placed in a 20-mL flask. At −5 °C diphenylsilane (2.36 g, 12.8 mmol) was added. Kugelrohr distillation gave (*S*)-1-tetralol in 92% yield (1.09 g, 7.4 mmol; 93%, GLPC): 99% ee, $[\alpha]^{27}_D = +32.2°$ (*c* = 2.51, $CHCl_3$); lit.[17] $[\alpha]^{17}_D = +32.65°$ (*c* = 2.5, $CHCl_3$).

Hydrosilylation of Ethyl Levulinate with 1a, 2a, $AgBF_4$, and Diphenylsilane. Run 12, Table II. $AgBF_4$ (31 mg, 0.16 mmol), **2a** (42 mg, 0.08 mmol), **1a** (144 mg, 0.48 mmol), ethyl levulinate (1.15 g, 8.0 mmol), and THF (1.0 mL) were placed in a 20-mL flask. At −5 °C diphenylsilane (2.36 g, 12.8 mmol) was added. The mixture was stirred at 0 °C for 6 h. Then methanol (14 mL) was slowly added to the solution at 0 °C, and this mixture was stirred for 1 day. After extraction, the extract was concentrated to give the residual oil, which was purified by silica gel column chromatography (hexane–ether as the eluent). Kugelrohr distillation gave ethyl (*S*)-4-hydroxypentanoate in 91% yield (1.06 g, 7.3 mmol): 95% ee by ^{1}H NMR of the MTPA ester (CH_3O) δ 3.56 for *S* and 3.54 for *R*, ratio 97.5:2.5. The product alcohol was converted to (−)-(*S*)-γ-valerolactone by treatment with *p*-toluenesulfonic acid (1 mol %) in methanol: $[\alpha]^{20}_D = -31.6°$ (*c* = 0.86, CH_2Cl_2) and −31.7° (neat); lit.[18] for (*R*)-γ-valerolactone $[\alpha]^{23}_D = +30.1°$ (*c* = 0.85, CH_2Cl_2).

Hydrosilylation of 6-Methyl-5-hepten-2-one with 1a, 2a, $AgBF_4$, and Diphenylsilane. Run 14, Table II. $AgBF_4$ (31 mg, 0.16 mmol), **2a** (42 mg, 0.08 mmol), **1a** (144 mg, 0.48 mmol), and 6-methyl-5-hepten-2-one (1.03 g, 8.0 mmol) were placed in a 20-mL flask. At −5 °C diphenylsilane (2.36 g, 12.8 mmol) was added. Kugelrohr distillation gave (*S*)-6-methyl-5-hepten-2-ol (sulcatol) in 94% yield (0.96 g, 7.5 mmol): 70% ee, $[\alpha]^{25}_D = +12.2°$ (neat); lit.[17] $[\alpha]^{23}_D = +17.4°$ (neat).

Hydrosilylation of 2-Octanone with 1a, 2a, $AgBF_4$, and Diphenylsilane. Run 16, Table II. $AgBF_4$ (31 mg, 0.16 mmol), **2a** (42 mg, 0.08 mmol), **1a** (97 mg, 0.32 mmol), and THF (1.0 mL), were placed in a 20-mL flask. At 0 °C, ethyl levulinate (0.14 mL, 1.0 mmol) and diphenylsilane (2.36 g, 12.8 mmol) were added. After 1 h at 0 °C, 2-octanone (1.02 g, 8.0 mmol) was added. Kugelrohr distillation gave (*S*)-2-octanol in 85% yield (0.89 g, 6.8 mmol): 63% ee, $[\alpha]^{22}_D = +6.23°$ (neat); lit.[19] $[\alpha]^{16}_D = +9.87°$ (neat).

Determination of Optical Purity for Other Products. Optical rotations of the products and ^{1}H NMR data (270 MHz, $CDCl_3$) of the corresponding (+)-MTPA esters are as follows (δ for CH_3O signals): (*S*)-1-(*o*-chlorophenyl)ethanol, 96% ee, δ 3.58 and 3.52, ratio 98:2; (*S*)-1-(*m*-acetoxyphenyl)ethanol, 92% ee, δ 3.55 and 3.47, ratio 96:4; (*S*)-1-(2′-naphthyl)ethanol, 92% ee, δ 3.59 and 3.47, ratio 96:4; (*S*)-1-phenylpropanol, 91% ee, $[\alpha]^{21}_D = -41.5°$ (*c* = 5.13, $CHCl_3$), lit.[20] $[\alpha]^{20}_D = -45.45°$ (*c* = 5.15, $CHCl_3$); (*S*)-1-phenylbutanol, 82% ee, $[\alpha]^{21}_D = -37.17°$ (*c* = 4.78, C_6H_6), lit.[21] $[\alpha]_D = -45.2°$ (*c* = 4.81, C_6H_6); (*S*)-1-phenylpropan-2-ol, 71% ee, $[\alpha]^{28}_D = +20.2°$ (neat), lit.[22] $[\alpha]^{30}_D = +28.3°$ (neat); (*S*)-1-(*o*-methoxyphenyl)propan-2-ol, 82% ee, δ 3.44 and 3.39, ratio 91:9; (*S*)-1-(*o*-methoxyphenyl)propan-2-ol, 85% ee, $[\alpha]^{25}_D = +30.6°$ (*c* = 1.08, CH_2Cl_2) (the authentic sample was synthesized with (*S*)-propylene oxide (>99% ee) and (*o*-methoxyphenyl)lithium; >99% ee, $[\alpha]^{25}_D = +35.7°$ (*c* = 0.98, CH_2Cl_2)); ethyl 3-hydroxybutanoate, 27% ee, $[\alpha]^{20}_D = +5.20°$ (neat), lit.[5] $[\alpha]^{20}_D = +5.03°$ (neat); (*S*)-1,4-pentanediol, 68% ee, $[\alpha]^{25}_D = +9.2°$ (*c* = 1.08, MeOH), lit.[23] for the *R* isomer, $[\alpha]^{20}_D = -13.4°$ (*c* = 1.05, MeOH); (*S*)-4-phenyl-2-butanol, 66% ee, $[\alpha]^{21}_D = +9.1°$ (neat), lit.[24] $[\alpha]^{18.5}_D = +13.74°$ (neat); **6**, 22% ee, δ 3.56 and 3.59, ratio 61:39, $[\alpha]^{24} = -5.40°$ (*c* = 5.3, $CHCl_3$); **7**, 44% ee, δ 6.20 and 6.26 (d, C=C*H*Ph), ratio 72:28, $[\alpha]^{21}_D = -3.74°$ (*c* = 3.3, $CHCl_3$), lit.[25] $[\alpha]_D = -8.22°$ (*c* = 1.01, $CHCl_3$); **8**, 71% ee, δ 3.55 and 3.46, ratio 85.5:14.5, $[\alpha]^{21}_D = -24.8°$ (*c* = 2.48, $CHCl_3$).

Table V. Bond Distances and Selected Bond Angles for [(*S*,*S*)-ip-pybox]$RhCl_3$ (2a)

Bond Distances (Å)			
Rh–N(1)	2.003 (17)	C(1)–C(2)	1.374 (32)
Rh–N(2)	2.069 (19)	C(1)–C(11)	1.439 (38)
Rh–N(3)	2.083 (17)	C(2)–C(3)	1.381 (41)
Rh–Cl(1)	2.334 (6)	C(3)–C(4)	1.391 (36)
Rh–Cl(2)	2.352 (7)	C(4)–C(5)	1.366 (31)
Rh–Cl(3)	2.342 (8)	C(5)–C(21)	1.479 (31)
N(1)–C(1)	1.305 (29)	C(12)–C(13)	1.505 (40)
N(1)–C(5)	1.349 (30)	C(13)–C(14)	1.541 (37)
N(2)–C(11)	1.285 (33)	C(14)–C(15)	1.492 (41)
N(2)–C(13)	1.507 (30)	C(14)–C(16)	1.583 (60)
N(3)–C(21)	1.292 (29)	C(22)–C(23)	1.484 (35)
N(3)–C(23)	1.443 (30)	C(23)–C(24)	1.549 (35)
O(1)–C(11)	1.333 (34)	C(24)–C(25)	1.584 (41)
O(1)–C(12)	1.456 (34)	C(24)–C(26)	1.565 (42)
O(2)–C(21)	1.271 (28)		
O(2)–C(22)	1.480 (32)		
Bond Angles (deg)			
N(1)–Rh–N(2)	78.5 (8)	C(11)–N(2)–Rh	110.1 (17)
N(1)–Rh–N(3)	80.2 (8)	C(13)–N(2)–Rh	127.7 (15)
N(1)–Rh–Cl(1)	88.7 (5)	C(1)–N(1)–C(5)	124.3 (18)
N(1)–Rh–Cl(3)	89.6 (5)	C(1)–N(1)–Rh	118.9 (16)
N(1)–Rh–Cl(2)	178.3 (6)	C(5)–N(1)–Rh	116.7 (13)
N(2)–Rh–Cl(2)	101.5 (6)	C(21)–N(3)–C(23)	109.8 (18)
N(2)–Rh–N(3)	158.7 (7)	C(21)–N(3)–Rh	110.9 (14)
N(2)–Rh–Cl(1)	86.8 (6)	C(23)–N(3)–Rh	138.3 (14)
N(2)–Rh–Cl(3)	93.1 (6)	N(1)–C(1)–C(2)	118.5 (23)
N(3)–Rh–Cl(1)	92.8 (5)	N(1)–C(1)–C(11)	109.6 (19)
N(3)–Rh–Cl(3)	86.7 (5)	C(2)–C(1)–C(11)	131.9 (23)
N(3)–Rh–Cl(2)	99.7 (5)	N(1)–C(5)–C(4)	119.6 (19)
Cl(1)–Rh–Cl(3)	178.2 (2)	N(1)–C(5)–C(21)	111.3 (18)
Cl(1)–Rh–Cl(2)	90.2 (2)	C(4)–C(5)–C(21)	129.0 (20)
Cl(2)–Rh–Cl(3)	91.6 (3)	N(2)–C(11)–O(1)	115.3 (24)
C(11)–N(2)–C(13)	111.6 (21)	N(3)–C(21)–O(2)	116.2 (20)

X-ray Crystallography of 2a. Crystals suitable for X-ray diffraction were grown in a solution of ethanol–water at room temperature: $C_{17}H_{23}N_3O_2RhCl_3·H_2O$; fw 528.65 (orange prism); space group $P2_12_12_1$; a = 12.597 Å, b = 16.694 Å, c = 11.821 Å, V = 2485 (7) Å^3; Z = 4, D(calcd) = 1.387 g/cm^3. The data ($2 < 2\theta < 40°$) were collected on a Rigaku AFC-5 diffractometer by using Mo Kα radiation (0.710 68 Å): total observations, 2620; criteria for selecting data used in refinement $|F_o| > 3\sigma(|F_o|)$; number of data used in refinement, 1337; final R = 0.064 and R_w = 0.066 ($\sum w(|F_o| - |F_c|)/\sum w|F_o|$). The crystal decomposed during the data collection. The absolute configuration was assigned on the basis of that of the starting amino acid (*S*)-valinol. The bond distances

(15) Nagai, U.; Shishido, T.; Chiba, R.; Mitsuhashi, H. *Tetrahedron* **1965**, *21*, 1701.
(16) Jakovac, I. J.; Jones, J. B. *J. Org. Chem.* **1979**, *44*, 2165.
(17) Davies, A. G.; White, A. M. *J. Chem. Soc.* **1952**, 3300.
(18) Mori, K. *Tetrahedron* **1975**, *31*, 3011.
(19) Pickard, R. H.; Kenyon, J. *J. Chem. Soc.* **1913**, *103*, 1957.
(20) Kwart, H.; Hoster, D. P. *J. Org. Chem.* **1967**, *32*, 1867.
(21) Noyori, R.; Tomino, I.; Tanimoto, Y. *J. Am. Chem. Soc.* **1979**, *101*, 3129.
(22) Levene, P. A.; Stevens, P. G. *J. Biol. Chem.* **1930**, *89*, 471.
(23) Bolton, C. H.; Toster, A. B.; Stacey, M.; Webber, J. M. *J. Chem. Soc.* **1961**, 4831.
(24) Pickard, R. H.; Kenyon, J. *J. Chem. Soc.* **1914**, *105*, 1115.
(25) Noyori, Y.; Tomino, I.; Yamada, M.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6717.

and selected bond angles are summarized in Table V.

Acknowledgment. We thank Dr. M. Akita, Prof. H. Suzuki, and Prof. Y. Moro-oka (Tokyo Institute of Technology) for assistance with the X-ray analysis and Prof. H. Brunner for many helpful discussions. We acknowledge the financial support of Mitsui-Toatsu Co. Ltd. We thank Mr. H. Sakaguchi, Miss M. Horihata, and Mr. Y. Tenya for experimental assistance in the initial work.

Supplementary Material Available: Tables of atomic coordinates and anisotropic thermal parameters for **2a** (2 pages); a listing of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

Cobalt-Catalyzed Cyclocarbonylation of Acetylenes under Water Gas Shift Conditions: Selective Synthesis of Indan-1-ones

Takashi Joh,[†] Kazuo Doyama,[†] Keisuke Fujiwara,[†] Kazuo Maeshima,[‡] and Shigetoshi Takahashi*,[†]

The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567, Japan, and Central Research Laboratory, Sekisui Chemical Co., Ltd., Mishima-gun, Osaka 618, Japan

Received May 15, 1990

Carbonylation of phenylacetylene derivatives by a cobalt catalyst under water gas shift conditions afforded 2-substituted indan-1-ones in satisfactory yields. Addition of phosphines enhanced both the activity and the selectivity of the catalyst. The deuterium-labeling studies showed that the migration of the ortho hydrogen of the phenyl group to the acetylenic carbon adjacent to the phenyl group took place in the cyclocarbonylation.

It is well-known that acetylenes undergo carbonylation to give various carbonylated products such as acrylic acid, acrylates, aldehydes, lactones, and cyclic ketones depending on the reaction conditions, including catalysts, additives, and hydrogen sources.[1] The C-H bond activation of aromatic compounds by transition metals is one of the current interests in organometallic chemistry and has been successfully applied to unique carbonylation reactions in organic syntheses.[2] The reaction of diphenylacetylene derivatives with $Fe_3(CO)_{12}$ has been reported to afford (1,1,1-tricarbonylferraindene)-π-tricarbonyliron complexes and tricarbonyl(2-phenylindenone)iron complexes.[3] Recently the stoichiometric reaction of diphenylacetylene with $(\eta^5\text{-}C_5H_5)Fe(CO)_2Ar$ has been reported to give cyclocarbonylated products, indenones, in good yields.[4]

The water gas shift reaction has recently been applied to unique organic syntheses such as selective hydrogenation and specific carbonylation.[5] We have previously reported a new method for the synthesis of furan-2(5*H*)-ones by carbonylation of acetylenes under water gas shift conditions.[6] This reaction was effectively catalyzed by rhodium carbonyl clusters such as $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$, but $Co_2(CO)_8$ was almost inactive for the formation of furan-2(5*H*)-ones. An addition of phosphines to the cobalt catalyst led to a different type of carbonylation, i.e., cyclocarbonylation of acetylenes, and we have reported the preliminary results in a previous paper.[7] We report herein in detail the cyclocarbonylation of phenylacetylene derivatives affording 2-substituted 1-indanones.

Results and Discussion

Reaction of Diphenylacetylene. Diphenylacetylene (**1a**) was reacted with water and carbon monoxide (100 atm) in the presence of a catalytic amount of $Co_2(CO)_8$ and triphenylphosphine in tetrahydrofuran at 220 °C. The

Table I. Effect of the Amount of Water for the Formation of Indanone 2a[a]

entry	amt of H_2O, mL (mmol)	convsn, %	selectivity,[b] %
1	4.0 (222)	100	69
2	1.0 (56)	100	73
3	0.5 (28)	99	69
4	0.2 (11)	100	75
5	0.1 (5.6)	91	55
6	0 (0)	42	5

[a] Diphenylacetylene, 5.0 mmol; $Co_2(CO)_8$, 0.125 mmol; Ph_3P, 0.25 mmol; THF, 40 mL; CO, 100 atm; reaction temperature, 220 °C; reaction time, 4 h. [b] Based on diphenylacetylene consumed (determined by GLC).

Table II. Effect of Phosphines Added[a]

entry	phosphine	P/Co	convsn, %	selectivity,[b] %
1			66	56
2	PPh_3	1/1	100	73
3	PPh_3	2/1	100	73
4	PPh_3	5/1	100	77
5	PPh_2Me	2/1	100	85
6	$PPhMe_2$	2/1	100	85
7	PBu_3	2/1	100	88

[a] Diphenylacetylene, 5.0 mmol; $Co_2(CO)_8$, 0.125 mmol; THF, 40 mL; H_2O, 56 mmol; CO, 100 atm; reaction temperature, 220 °C; reaction time, 4 h. [b] Based on diphenylacetylene consumed.

[†] Osaka University.
[‡] Sekisui Chemical Co.

(1) Pino, P.; Braca, G. In *Organic Synthesis via Metal Carbonyl*, Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, p 419.
(2) Kim, P. J.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 2022. Hong, P.; Cho, B.; Yamazaki, H. *Chem. Lett.* **1979**, 339. Koyasu, Y.; Matsuzaka, H.; Hiroe, Y.; Uchida, Y.; Hidai, H. *J. Chem. Soc., Chem. Commun.* **1987**, 575. Sakakura, T.; Tanaka, M. *Chem. Lett.* **1987**, 249.
(3) Brayne, E. H.; Huebel, W. *J. Organomet. Chem.* **1965**, *3*, 38.
(4) Butler, I. R.; Cullen, W. R.; Lindsell, W. E.; Preston, P. N.; Rettig, S. T. *J. Chem. Soc., Chem. Commun.* **1987**, 439.

0276-7333/91/2310-0508$02.50/0