Table I. Silylformylation of Alkynes with Me_2PhSiH[a]

entry		alkyne 1 R^1	alkyne 1 R^2	product 2 yield[c] (%)	product 2 $Z:E$[d]
1	a	H	H	73	0:100
2	b	Me	H	99	80:20
3	c	C_2H_5	H	91	100:0
4	d	$^nC_3H_7$	H	93	95:5
5	d	$^nC_3H_7$	H	62[e]	90:10
6	e	Me_3Si	H	55	100:0
7	f	Ph	H	89	88:12
8	g	Me_3SiCH_2	H	93	91:9
9	h	CH_2=$CHCH_2$	H	90	48:52
10	i	$^cC_6H_{11}$	H	96	100:0
11	j	$HOCH_2$	H	83	37:63
12	j	$HOCH_2$	H	73[e]	77:23
13	k	Me	Me	93	100:0
14	l	$^nC_3H_7$	Me	85	(70:30)
15	m	Ph	Ph	90	95:5
16	n	Ph	Me	95	(89:11)
17	o	Ph	CO_2Et	43	100:0
18	p	Me	CO_2Me	67	100:0

[a] Reactions were conducted on a scale of 2-10 mmol in benzene solution including 1 mol % of $Rh_4(CO)_{12}$ and equimolar amounts of **1**, Me_2PhSiH, and Et_3N under CO pressure (10-30 kg/cm^2) for 2 h at 100 °C. [b] All products were identified by ^1H NMR, ^{13}C NMR, and IR spectra. All new compounds gave satisfactory combustion analyses. [c] Isolated yield. [d] The values in parentheses show the ratio of **2**:**3**. [e] The reaction was carried out in the absence of Et_3N.

for 2 h, a new compound **2** was obtained in excellent yield after purification of the reaction mixture by column chromatography. The most interesting feature of this result is the survival of the formyl group under the reaction conditions.[8] Analogous reactions proceeded smoothly with both of the terminal or internal alkynes. The results are summarized in Table I. The presence of an extremely small quantity of $Rh_4(CO)_{12}$ was sufficient for complete conversion; for example, a turnover number of catalyst greater than 12000 was observed in the case of **1d**. Catalysis by rhodium was demonstrated by control experiments for the case of **1f**, in which the incorporation of carbon monoxide was not observed either in the absence of catalyst or the presence of $Co_2(CO)_8$ or $Ru_3(CO)_{12}$ instead of $Rh_4(CO)_{12}$. Although the role of triethylamine is ambiguous at present, its inclusion improved yields of **2** and *Z*-selectivity in **2** as shown in entries 4 and 5. By contrast, the $Z:E$ ratio for **2j** was greater in the absence of Et_3N (entries 11 and 12). The isomerization of (*Z*)-**2** to (*E*)-**2** under the reaction conditions is a possible explanation for entries 1, 9, and 11.

It should be noted that the terminal carbon of 1-alkynes is silylated specifically to give **2** (R^2 = H, entries 1-12) and that the olefinic part of **1h** and the hydroxy group of **1j** remained intact under the reaction conditions (entries 9, 11, and 12). A bulky substituent on the acetylenic carbon seems to prevent such silylformylation. 3,3-Dimethyl-1-butyne, 1-phenyl-2-trimethylsilylethyne, and 1-trimethylsilylpropyne did not give any attractive products. Our results contrast those of a recent report on the reactions of alkynes in the presence of $Rh_4(CO)_{12}$.[5,9] We therefore carried out the reaction of **1d** with Me_2PhSiH under a pressure of both CO (25 kg/cm^2) and ethene (15 kg/cm^2) in the presence of $Rh_4(CO)_{12}$. Aldehyde **2d** (95%) was again the sole product, and ethene was not incorporated at all.

The regioselectivity toward internal alkynes seems to depend on the steric effect of the substituent (entries 14 and 16). However, an alkoxycarbonyl group consistently contributes to the formation of **2** (entries 17 and 18), although the yields of formylated products are rather low; this point is quite separate from the observation that a steric effect seems to be more important than electronic effects in determining the product distribution.[5]

Unfortunately, any clear information to rationalize the catalytic sequence has not been obtained from the results of control experiments and the spectroscopic observation of an equimolar mixture of $Rh_4(CO)_{12}$ and Me_2PhSiH in the presence of CO.[10] The oxidative addition of Me_2PhSiH to form $Me_2PhSiRh$ species may be an important step at the first stage as shown in hydrosilylations.[11] Mechanistic aspects aside, however, the present novel reaction composed of an alkyne, hydrosilane, and carbon monoxide should prove to be a simple and efficient approach to form **2**. The structure of **2** is of interest as a versatile building block for the synthesis of complex molecules via a Peterson olefination,[12] a Nazarov type cyclopentenone annelation,[13] or a Trost type cyclopentane annelation.[14]

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Asymmetric Synthesis with Chiral Ferrocenylamine Ligands: The Importance of Central Chirality

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The development of synthetic methodology for the diastereo- and enantioselective formation of C-C bonds derived through the use of catalytic quantities of chiral transition-metal catalysts is today a topic of fundamental importance.[1-6] In 1986 Ito and Hayashi reported an elegant synthesis of oxazolines utilizing a gold(I)-catalyzed aldol reaction in the presence of chiral ferrocenylamine ligands that possess both planar and central chirality.[7] For example, the reaction of **1** with **2** catalyzed by bis(cyclohexyl isocyanide)gold(I) tetrafluoroborate, **3**,[8] in the presence of the chiral ferrocenylamine ligand (*R*)-(*S*)-**4** gave a mixture of the *trans*- and *cis*-oxazolines **5** and **6**, respectively (Scheme I). The trans isomer **5** illustrated was the dominant isomer formed in 91% enantiomeric excess (ee).[9]

Kumada et al. investigated the effect of the central chirality of the stereogenic carbon atom of **4** on the diastereo- and enantioselectivity of transition-metal-catalyzed Grignard cross-coupling reactions.[10,11] Kumada came to the reasonable conclusion from the experimental data obtained that the planar chirality of **4** plays

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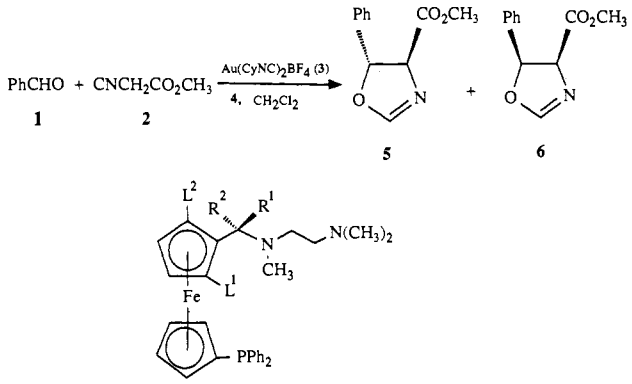
Scheme I



(*R*)-(*S*)-**4** $R^1 = CH_3$; $R^2 = H$; $L^1 = PPh_2$; $L^2 = H$
(*S*)-(*R*)-**4** $R^1 = H$; $R^2 = CH_3$; $L^1 = H$; $L^2 = PPh_2$
(*R*)-(*R*)-**4** $R^1 = CH_3$; $R^2 = H$; $L^1 = H$; $L^2 = PPh_2$
(*S*)-(*S*)-**4** $R^1 = H$; $R^2 = CH_3$; $L^1 = PPh_2$; $L^1 = H$

Table I. The Effect of Varying Ligand Chirality upon Product Enantio- and Diastereoselectivity

entry	ligand	% *trans*-**5** [ee]	% *cis*-**6** [ee][a,b]
1	(*R*)-(*S*)-**4**	89.6 [91 (4*S*,5*R*)]	10.4 [7 (4*S*,5*S*)]
2	(*S*)-(*S*)-**4**	83.5 [41 (4*R*,5*S*)]	16.5 [20 (4*S*,5*S*)]
3	(*S*)-(*R*)-**4**	89.6 [90 (4*R*,5*S*)]	10.4 [12 (4*R*,5*R*)]

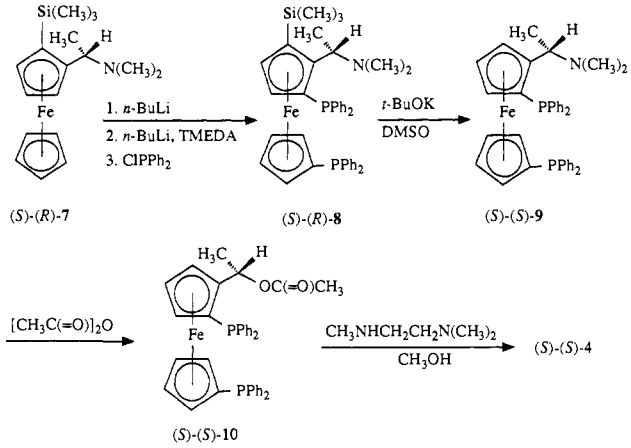
[a] The enantiomer in ee is given in parentheses. [b] Estimated ±3% error in ee.

the dominant role in determining product stereochemistry. Upon the basis of this work, subsequent studies on the gold(I)-catalyzed aldol reaction and other transition-metal-catalyzed reactions[12-21] have implicitly presumed that the planar chirality of **4** plays the major role in determining *product* stereochemistry. As part of an extensive effort in our laboratory directed toward ascertaining the nature of the stereoselective step in the gold(I)-catalyzed aldol reaction,[22] we have investigated this contention.

The chiral ferrocenylamine (*S*)-(*S*)-**4** was prepared by an improvement in the procedure reported by Kumada et al.,[23] the details of which will be reported at a later date (see Scheme II). The reaction of **1** with **2** was used as a model reaction to determine the effect of central chirality on product stereoselectivity because the absolute stereochemistry of all the isomeric products formed have previously been delineated by Hayashi.[7]

The results of this study clearly demonstrate that the central chirality of the stereogenic carbon atom in the ferrocenyl side chain strongly effects the resultant product stereochemistry (see Table I).[24,25] The examination of entry **1** and **2** of Table I reveals that

Scheme II



not only does a change of the central chirality of the stereogenic carbon atom from *R* to *S* result in both a reduction of the trans-to-cis product ratio and the ee of the trans isomer but also *the opposite trans-oxazoline enantiomer is formed in enantiomeric excess*. Furthermore, the ee of the cis isomer increased. Optimum diastereo- and enantioselectivity is obtained for the trans product **5** when the ferrocenylamine ligand **4** employed has opposite planar and central chirality. These results clearly indicate that the insensitivity of product stereoselectivity to the central chirality of the stereogenic carbon atom in the ferrocenylamine side chain observed for Grignard cross-coupling reactions cannot be generalized to other reaction types involving chiral ferrocenylamine ligands. The changes in product diastereo- and enantioselectivity appear to be due to conformational changes in the transition-state structure of the stereoselective step proposed by Ito and Hayashi. These conformational changes are the result of different steric interactions in the transition-state structure brought about by a change of chirality at the stereogenic carbon atom.

It is now clear that steric interactions due to the central chirality of the stereogenic carbon atom in the ferrocenylamine side chain play a more important role then previously supposed. Furthermore, the results of this study strongly suggest that the planar chirality and central chirality may act in either a cooperative or noncooperative sense. This constitutes the first example in a chiral transition-metal ligand containing both planar and central chirality of *internal cooperativity of chirality in the control of product diastereo- and enantioselectivity* similar in concept to the principle of matched and mismatched pairs (external cooperativity of chirality) advocated by Masamune.[26] Further studies in progress that support the concept of internal cooperativity will be reported at a later date.

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Supplementary Material Available: Experimental procedures and characterization of all new compounds (3 pages). Ordering information is given on any current masthead page.

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