Enantioselective Hydrosilylation of Ketones with L*/[Rh(COD)Cl]2 and L*/[Ir(COD)Cl]2 Catalysts (L* = Ph2P(O)nCH2CH(NMe2)(CH2)mSMe (n = 0, 1; m = 1, 2))

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Enantioselective Hydrosilylation of Ketones with L*/[Rh(COD)Cl]$_2$ and L*/[Ir(COD)Cl]$_2$ Catalysts (L* = $Ph_2P(O)_nCH_2CH(NMe_2)(CH_2)_mSMe$ (n = 0, 1; m = 1, 2))

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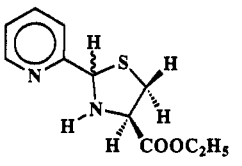
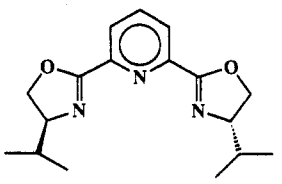
The enantioselective hydrosilylation of acetophenone with diphenylsilane in the presence of L*/[Rh(COD)Cl]$_2$ or L*/[Rh(NBD)Cl]$_2$ (L* = $Ph_2P(O)_nCH_2CH(NMe_2)(CH_2)_mSCH_3$ (n = 0, 1; m = 1, 2), COD = 1,5-cyclooctadiene, NBD = norbornadiene), followed by hydrolysis with *p*-toluenesulfonic acid in methanol, gave the expected *sec*-phenethyl alcohol in up to 62% enantiomeric excess (ee) with the (−)-(*S*) configuration predominating. Enantioselective hydrosilylation of acetophenone with the L*/[Ir(COD)Cl]$_2$ system gave up to 32% ee, but with the (+)-(*R*) configuration. The ee was very dependent upon the ligand L* used, but was found to be independent of the ligand to metal ratio. Enantioselective hydrosilylation of benzylacetone and α-tetralone followed by hydrolysis gave the (*S*)-alcohols in 57% and 51% ee, respectively.

Introduction

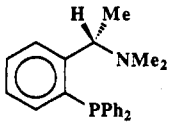
The asymmetric hydrosilylation of prochiral ketones to chiral siloxanes, followed by hydrolysis to chiral alcohols, has been a well-studied system over the past 20 years,[1] primarily owing to the importance of enantiomerically pure alcohols in organic synthesis.[2] Hydrosilylation is often preferred as a method of reduction over hydrogenation owing to the higher enantioselectivity of its products, and the milder conditions needed to carry out the reaction.[3] Bidentate phosphine ligands were used initially[4] but until recently the best results were obtained with the bidentate nitrogen ligands of Brunner,[5] such as 2-(2-pyridyl)-4-carbethoxy-1,3-thiazolidine. One disadvantage of these



2-(2-Pyridyl)-4-carbethoxy-1,3-thiazolidine

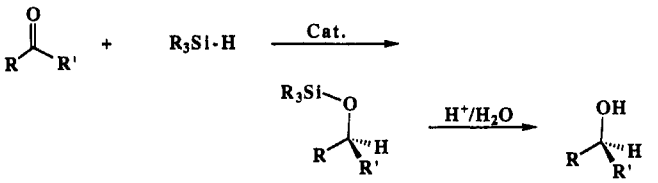


(*S,S*)-ip-Pybox

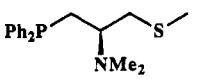


(*S*)-Amphos

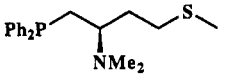
bidentate nitrogen ligands, however, is the large ligand to metal ratios necessary to achieve high enantioselectivity. Excellent results have also been observed with a catalyst obtained by Ag^+ removal of halide from the meridional tridentate complex [(*S,S*)-ip-pybox]$RhCl_3$ with three nitrogen donors. The pybox ligand is derived from pyridine-2,6-dicarboxylic acid and (*S*)-valinol.[6] In this case, no excess ligand was necessary to achieve high ee's, but it was proven that the (*S,S*)-ip-pybox ligand was labile from mixed ligand experiments.



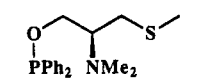
The recently prepared chiral tridentate ligands[7,8] **1** have shown promise in asymmetric catalysis reactions. Kellogg has shown that the complexes η^2-LNiCl_2 (L = **1a**, **1b**) can act as effective catalysts in asymmetric cross coupling



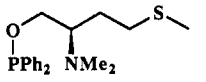
(*R*)-Cystphos, 1a



(*S*)-Methphos, 1b



(*R*)-Cystophos, 1c



(*S*)-Methophos, 1d

reactions of Grignards with vinyl halides, which gave

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Table 1. Results of Enantioselective Hydrosilylations of Acetophenone with Diphenylsilane Using Rh/L* Systems

run	ligand	metal complex	ligand/metal ratio	catalyst[a] concn, %	temp, % °C	time, h	conversion, %	% ee
1	**1a**	$[Rh(COD)Cl]_2$	1.1/1	0.5	0	48	100	61 (*S*)
2	**1a**	"	2.2/1	"	0	26	96	62 (*S*)
3	**1a**	"	4.4/1	"	"	16	62	62 (*S*)
	1a	"	"	"	"	84	92	62 (*S*)
4	**1a**	"	8.8/1	"	"	16	29	59 (*S*)
	1a	"	"	"	"	84	80	60 (*S*)
5	**1a**	"	2.2/1	5	"	18	100	62 (*S*)
6	**1a**	$[Rh(NBD)Cl]_2$	"	"	0→15	"	87	58 (*S*)
7	**1b**	$[Rh(COD)Cl]_2$	"	"	"	"	76	12 (*S*)
8	**1c**	$[Rh(NBD)Cl]_2$	"	"	0→25	"	80	9 (*S*)
9	**1d**	"	"	"	"	"	91	0
10	**1d**	$[Rh(COD)Cl]_2$	"	"	0	68	95	0
11		*b*		0.5	"	18	96	32 (*S*)
12		*c*		"	"	24	83	61 (*S*)
13	**1a**	$[Rh(COD)Cl]_2$	2.2/1, *d*	"	"	24	99	64 (*S*)

[a] Moles of Rh relative to moles of substrate. [b] Metal complex used, **2**, [(**1a**)Rh(COD)]SbF_6. [c] Metal complex used, **2**, [(**1a**)Rh(COD)]SbF_6, with 4 Me_4NCl/Rh added (in THF). [d] Added 4 Me_4NCl/Rh (in THF).

products in up to 65% ee in some cases.[7b] Evidence was also presented showing that the enantiomeric purity was not correlated with the steric effect of the ligand, but the presence and position of the sulfur atom. We have shown previously that **1d** can act as an effective chiral poison in the asymmetric hydrogenation of dimethyl itaconate.[9] The ligands **1** are readily prepared from the commercially available and inexpensive amino acids methionine and (*S*)-methyl-L-cysteine via a three step synthesis. We then decided to use the L*/$[M(COD)Cl]_2$ catalyst system in the hydrosilylation of ketones, mainly acetophenone, with diphenylsilane in order to investigate the potential of catalysts prepared *in situ* from these tridentate ligands and $[Rh(COD)Cl]_2$. Our expectation was that the high binding constants of a phosphorus donor combined with the high enantioselectivity of the nitrogen donor would give high enantioselectivity without the need of a large excess of ligand.

Results and Discussion

Hydrosilylation of Acetophenone with L*/[Rh(COD)Cl]$_2$ and L*/[Rh(NBD)Cl]$_2$ Systems. The catalysts were prepared *in situ* by stirring the metal complex with the ligand in acetophenone under N_2 for 1 h at room temperature, followed by cooling to 0 °C, and hydrosilylation was inititated with dropwise addition of diphenylsilane. The reaction was either kept at 0 °C or allowed to slowly warm after a period of 6 h at 0 °C.

The results in Table 1 show the clear superiority of **1a** in enantioselectivity, with products having enantiomeric purities as high as 62%. The other ligands **1b**, **1c**, and **1d** were found to give products in low to moderate ee. An interesting observation is that the ligand with the shortest chain lengths between the heteroatoms and the chiral carbon was found to give the highest enantiomeric purity. This contrasts with Kellogg's investigation of asymmetric cross coupling reactions where the highest ee's were attained when the chain length between the chiral carbon and the sulfur atom was the greatest.[7b] The results in Table 1 clearly show the opposite effect, the longer the chain length between the chiral carbon and the heteroatoms, the *lower* the ee. These correlations exist even though the sulfur may well not be coordinated in many intermediate complexes (*vide infra*). This better enantioselectivity for **1a** compared to **1b**, a ligand that only gives 12% ee (run 7), might be attributable to a conformational effect in the thioether arm of the ligand, rather than binding of the sulfur.

The enantioselectivity of the **1a**/$[Rh(COD)Cl]_2$ system compares favorably to phosphorus containing ligands previously tested by others. Ligands such as (+)-DIOP[1a] and (*S*)-amphos[10] have yielded products of as high as 58% ee. Our results still do not approach the optical purity of the catalyst systems with ligands containing two nitrogen donors; however, they are somewhat better than those reported for phosphorus containing ligands.

Another significant aspect of this system using **1a** is the consistency of the ee's, which are in the range 59–62%, with respect to variations in ligand concentration. The ligand/metal ratio was varied from 1.1/1 to 8.8/1 with very little difference in ee of the product. Addition of an excess of ligand merely impedes the rate of reaction. Contrary to the results found for most other ligand systems,[5e] this system is invariant to the ligand/metal ratio. Thus **1a** joins ip-pybox[6] and 6-substituted picolinyloxazolines[5e] as notable exceptions to the variations of product enantiomeric purity with ligand/metal ratio. One might be tempted to attribute this to the superior ligand to metal binding for a phosphorus ligand as opposed to most of the previously utilized nitrogen ligands of Brunner. But this may not be the case since the (*S*)-amphos/$[Rh(COD)Cl]_2$ system[10] also showed a variation in ee with respect to the ligand/metal ratio even though the presumed chelating portions of both **1a** and (*S*)-amphos are similar, with one nitrogen and one phosphorus donor bound to the rhodium.

Previous work with nickel and palladium complexes of **1a** and **1b**[7] would suggest that the thioether sulfur is probably not bound to the metal in the d^8 complexes. On the other hand, a sulfur bound intermediate, particularly in a Rh(III) intermediate may plan an important role in the catalysis. One might then consider whether the active species in the catalytic cycle contains a ligand coordinated in a tridentate fashion or one that is bidentate with a free arm, presumably the thioether portion of the ligand. In studies of asymmetric cross coupling reactions, it was found that analogues of **1a** with a hydrocarbon chain in place of the thioether portion were not effective in asymmetric synthesis. Furthermore, **1b** was more effective than **1a** in the asymmetric cross coupling. This may be related to the differing propensities for the potentially tridentate

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ligands to form or break the chelate involving binding of sulfur to a coordination site needed in the catalysis. In the hydrosilylations studied here, the "best" ligand, **1a** was the one with the shortest reach to the metal to give a tridentate ligand. In the d^8 complexes, the ligands are presumably bidentate, with the phosphorus and nitrogen bound to the metal, and the sulfur free. Ojima's proposed mechanism[11] for the hydrosilylation reaction suggested that the active catalyst, (L̂L)RhCl(solvent), contained a solvent molecule bound to the metal. Most of our reactions were performed without a coordinating solvent, so the "coordinated solvent" may well be the ketone itself. This solvent coordination site could be taken up by the third arm of the ligand at least some of the time, and this could affect the stereochemistry of the subsequent silyl hydride Rh(III) species.

L*/[Ir(COD)Cl]$_2$ System. In comparison with the Rh systems, Ir systems often give lower ee's and slower reaction rates. An exception is with **1b** in which the iridium complex gave a product of higher enantiomeric purity than rhodium. A particularly notable feature is that the (*R*) enantiomer predominates when using iridium, instead of the (*S*), as found with Rh. This is consistent with the report of Kreuzfeld,[10] using the (*S*)-amphos/[Rh(COD)Cl]$_2$ and (*S*)-amphos/[Ir(COD)Cl]$_2$ systems under very similar conditions. He reported opposite configurations of the products, i.e., (*S*) to (*R*) upon changing from Rh to Ir. Obviously, a change in the mechanism or catalyst geometry is occurring with respect to the rhodium system. An intriguing possibility is that the ligand may undergo intramolecular C–H activation of a methyl on the dimethylamino functionality in reactions with Ir(I), but not with Rh(I). This C–H activation has been observed by Graziani[12] in a similar system. When (COD)Ir[*o*-(Ph_2P)C_6H_4(NMe_2)]H was treated with excess ligand, [*o*-(Ph_2P)C_6H_4(NMe_2)]Ir[*o*-(Ph_2P)C_6H_4($NMeCH_2$–)]H_2 was formed. This inversion of configuration by using iridium may be a general phenomenon with these types of catalyst systems and could be used to give the opposite configuration of the alcohol if one wished to use naturally occurring amino acids to synthesize the ligands.

Effect of Chloride on Enantioselectivity of Catalytic Hydrosilylations. The cationic complexes **2** and **3** were prepared as in eq 1 in order to determine if the

$$[M(COD)Cl]_2 \xrightarrow[(2)\ \mathbf{21a}]{(1)\ 2AgSbF_6} 2[(\mathbf{1a})M(COD)]SbF_6 + 2AgCl \quad (1)$$

2 (M = Rh)
3 (M = Ir)

removal of chloride in the catalytic reaction would promote a closer association of the sulfur atom of **1a** with the metal and potentially improve the ee of the product. Unfortunately, the ee was found to be lower. In the hydrosilylation of acetophenone with **2**, the ee was only 32%, with the (*S*) configuration predominating. The hydrosilylation of acetophenone with **3** as a catalyst only gave an 11% ee, with the (*R*) configuration predominating. Addition of chloride in the form of NMe_4Cl to the reaction increased the ee to 61%, the same enantiomeric purity observed for catalysis by the **1a**/[Rh(COD)Cl]$_2$ system. Presumably, the same active species is formed in both cases, since the ee is identical.

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Table 2. Results of Hydrosilylations of Acetophenone with Diphenylsilane Using [Ir(COD)Cl]$_2$/L Systems

run	ligand	ligand/metal ratio	catalyst[a] concn, %	temp, °C	time, h	conversion, %	% ee
14	**1a**	2.2/1	0.5	0	22	69	27 (*R*)
15	**1b**	"	"	"	26	75	21 (*R*)
	"	"	"	"	72	85	22 (*R*)
16	**1a**	2.2/1	5	0→15	18	92	33 (*R*)
17	**1a**	4.4/1	"	"	18	67	26 (*R*)
18	**1d**	2.2/1	"	0	68	90	0
19	*b*		0.5	"	24	44	10 (*R*)
	b		"	"	48	65	11 (*R*)

[a] Moles of Rh relative to moles of substrate. [b] Metal complex used, **3**, [(**1a**)Ir(COD)]SbF_6.

The addition of excess chloride into the **1a**/[Rh(COD)Cl]$_2$ system did not improve the ee significantly. It was presumed that the chloride would be labile in the active catalyst and that the catalyst was in an equilibrium with a solvated species. Addition of excess chloride would have shifted the equilibrium to the chloride species with an increase in the ee. This was not the case. The chloride ligand is apparently required for high enantioselectivity in the active species.

Hydrosilylation of Other Ketones. Generally one expects lower enantioselectivity with dialkyl ketones than aryl alkyl ketones on the basis of steric arguments. The hydrosilylation of benzylacetone with **1a**/[Rh(COD)Cl]$_2$ (**1a**/Rh = 2.2/1) at 0 °C gave an ee of 57%, substantially higher than one might expect for this substrate. Nishiyama[6b] reported an ee of 66% for the [(*S*,*S*)-ip-pybox]-$RhCl_3/Ag^+$ catalyst system, whereas he found an ee of 94% with acetophenone as the substrate. Brunner's thiazolidine/[Rh(COD)Cl]$_2$ system[5b] only gave 55% ee for this hydrosilylation, whereas the same catalyst system gave 87% ee for the hydrosilylation of acetophenone under similar conditions. Though the ee is lower than Nishiyama's, it shows that there is a large variability in the ee with respect to substrate.

The asymmetric induction of α-tetralone with **1a**/[Rh(COD)Cl]$_2$ is moderate at 51% and does not approach the value of 99% reported for this reaction using [(*S*,*S*)-ip-pybox]$RhCl_3/Ag^+$ as the catalysts.[6b] Brunner also reports an 83% ee for the thiazolidine/Rh(COD)Cl]$_2$ system.[5c]

Experimental Section

All of the ketones and diphenylsilane were purchased from Aldrich Chemical Co. Ligands[7,8] **1a**, **1b**, **1c**, and **1d** as well as the complexes [Rh(COD)Cl]$_2$,[13] [Rh(NBD)Cl]$_2$, and [Ir(COD)Cl]$_2$[14] were prepared as in the literature. Enantiomeric excesses and percent conversions were found by gas chromatographic analysis using a J & W Scientific Cyclodex-B column. Most experiments were repeated at least once. Numbers reported are the averages of those runs. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Catalytic Reactions. The hydrosilylations of acetophenone were carried out by modification of Brunner's method[7] and the conditions and results are summarized in Tables 1 and 2. The metal complex, ligand, and 0.189 mL (1.62 mmol) of acetophenone were stirred at ambient temperature under N_2 for 1 h; then the reaction was cooled to 0 °C and 0.320 g (1.74 mmol) of diphenylsilane was added dropwise. The reaction was either kept at 0 °C or allowed to warm. Aliquots were sometimes removed and worked up to monitor the progress of the reaction.

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Hydrolysis was accomplished by adding 1 mL of a 1% solution of *p*-toluenesulfonic acid in methanol and stirring for 10 min, followed by rotary evaporation at room temperature and washing the residue through 1 cm of silica gel with diethyl ether. The filtrate was then concentrated by rotary evaporation at room temperature, and the residue was analyzed by GC.

Hydrosilylation of Benzylacetone. The hydrosilylation of benzylacetone basically followed the procedure above, except that 2 mL of toluene was used as a solvent. Benzyl acetone (0.224 g, 0.162 mmol) was added to a solution of $[Rh(COD)Cl]_2$ (0.0020 g, 0.004 mmol, 0.5 mol % Rh) and **1a** (0.0057 g, 0.018 mmol, 2.2 **1a**/Rh) in 2.0 mL of toluene, and the mixture was stirred for 1 h under N_2. The solution was cooled to 0 °C, and diphenylsilane (0.320 g, 1.74 mmol) was added dropwise. The reaction was kept at 0 °C for 48 h. Hydrolysis and workup were accomplished as above, to give by GC analysis a 57% ee of (+)-(*S*)-4-phenylbutan-2-ol with 95% conversion. The absolute configuration was determined by polarimetry and comparison with previously established relationships.[15]

Hydrosilylation of α-Tetralone. The hydrosilylation of α-tetralone followed the general hydrosilylation procedure. The amounts used were as follows: α-tetralone (0.244 g, 0.162 mmol, $[Rh(COD)Cl]_2$ 0.0020 g, 0.004 mmol, 0.5 mol % Rh; **1a** 0.0057 g, 0.018 mmol, 2.2 **1a**/Rh. After 5 h at 0 °C, the reaction was allowed to warm to 25 °C. After 18 h, hydrolysis and workup were accomplished as above, and analysis by GC gave (+)-(*S*)-1-tetralol in 51% ee with 90% conversion. The absolute configuration was determined by polarimetry and comparison with previously established relationships.[16]

Preparation of $[(Ph_2PCH_2CH(NMe_2)CH_2SMe)Rh(COD)]SbF_6$, 2. Into a 100-mL Schlenk flask containing a magnetic stirring bar and purged with N_2 was added 0.1221 g (0.284 mmol) of $[Rh(COD)Cl]_2$ and 10 mL of freshly distilled CH_2Cl_2. $AgSbF_6$ (0.171 g, 0.497 mmol) was then added slowly with stirring. The color of the solution immediately darkened, and a precipitate was observed. Stirring continued for 10 min, then 0.157 g (0.497 mmol) of **1a** was added and stirring was allowed to continue for 30 min. After that time, the mixture was filtered through Celite, the yellow filtrate was evaporated with a N_2 purge, and the residue was washed with *n*-heptane (3 × 15 mL). The residue was dried by high vacuum to give 0.333 g (0.436 mmol, 88%) of $[(Ph_2PCH_2CH(NMe_2)CH_2SMe)Rh(COD)]SbF_6$, **2**. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 7.81 (m, 2H, C_6H_5), 7.61 (m, 3H, C_6H_5), 7.48 (m, 3H, C_6H_5), 7.35 (m, 2H, C_6H_5), 4.50 (m (br), 2H, CH=CH), 4.25 (m (br), 2H, CH=CH), 3.00 (m, 2H), 2.75–2.50 (m, 5H), 2.42–2.25 (m, 4H), 2.35 (s, 6H, NCH_3), 2.33 (s, 3H, SCH_3), 2.10 (m, 2H). ^{31}P NMR (121 MHz, CD_2Cl_2, 25 °C): δ 25.57 (d, J = 143 Hz). Anal. Calcd for $C_{24}H_{36}NSPRhSbF_6$: C, 40.86; H, 4.75; N, 1.83; S, 4.19. Found: C, 40.94; H, 4.79; N, 1.77; S, 4.26.

Preparation of $[(Ph_2PCH_2CH(NMe_2)CH_2SMe)Ir(COD)]SbF_6$, 3. Basically the same method was used in the preparation of **3** as in **2**. The quantities used were 0.1198 g of $[Ir(COD)Cl]_2$ (0.179 mol), 0.123 g of $AgSbF_6$ (0.357 mmol), and 0.113 g of **1a** (0.357 mmol), which yielded 0.160 g (0.188 mmol, 52%) of **3**. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 7.89 (m, 2H, C_6H_5), 7.59 (m, 3 H, C_6H_5), 7.43 (m, 3H, C_6H_5), 7.14 (m, 2H, C_6H_5), 3.40–2.90 (multiplets, 7H), 2.89 (s, 3H, SMe), 2.68 (s, 6H, NMe), 2.59–2.17 (multiplets, 8H), 1.51 (m, 2H). ^{31}P NMR (121 MHz, CD_2Cl_2, 25 °C): δ 23.43 (s). Anal. Calcd for $C_{24}H_{36}NSPIrSbF_6$: C, 36.59; H, 4.25; N, 1.64; S, 3.76. Found: C, 36.65; H, 4.28; N, 1.58; S, 3.69.

Hydrosilylations Using 2 and 3. Into a Schlenk flask purged with N_2 was added 0.5 mol % of the catalyst and 0.189 mL of acetophenone. The mixture was stirred until all of the catalyst dissolved and then cooled to 0 °C. Diphenylsilane (0.320 g) was added dropwise with stirring. Hydrolysis and workup were accomplished as above.

Hydrosilylations with NMe_4Cl as the Chloride Source. Into a Schlenk flask purged with N_2 was added 0.5 mol % of the catalyst, along with 0.189 mL of acetophenone, 3.5 mg of NMe_4Cl, and 1.0 mL of freshly distilled tetrahydrofuran. After stirring until all of the catalyst and NMe_4Cl was dissolved the mixture was then cooled to 0 °C and 0.320 g of diphenylsilane was added dropwise with stirring. Hydrolysis and workup were accomplished as above.

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