Iridium(I)-catalysed asymmetric hydrosilylation of ketones using a chiral oxazolylferrocene-phosphine hybrid ligand

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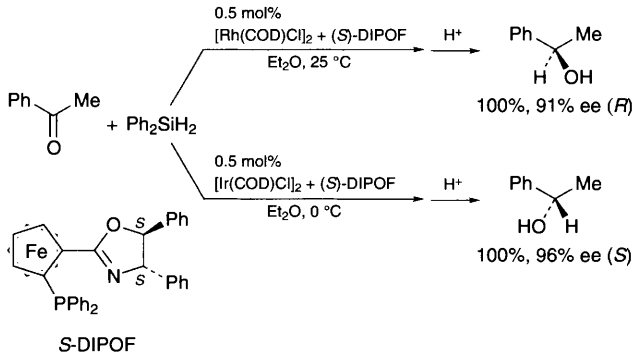
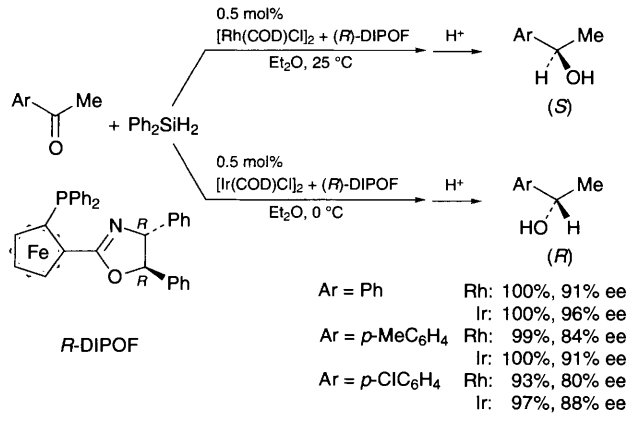
The chiral oxazolylferrocene-phosphine hybrid ligand (DIPOF) is a very effective ligand for Ir^{I}-catalysed asymmetric hydrosilylation of simple ketones to give the corresponding *sec*-alcohols (up to 96% ee) after acid hydrolysis.

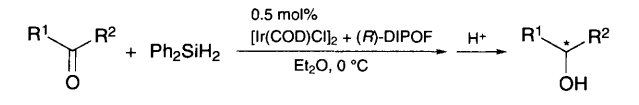
In sharp contrast to the rhodium(I)-catalysed asymmetric hydrosilylation of ketones using various chiral ligands,[1] iridium-catalysed highly enantioselective asymmetric hydrosilylation has not yet been developed.[2] Quite recently, we disclosed that the (*S*,*S*,*S*)-[2-(4,5-diphenyl-4,5-dihydro-1,3-oxazol-2-yl)ferrocenyl]diphenylphosphine [abbreviated as (*S*)-DIPOF] is a very effective chiral ligand for the Rh^{I}-catalysed hydrosilylation of a variety of simple ketones lacking a secondary coordinating functional group (up to 91% ee).[3] It was also observed that 1-phenylethanol of the opposite configura-



Scheme 1

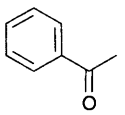
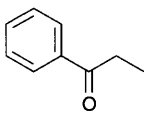
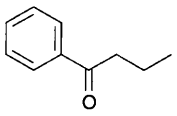
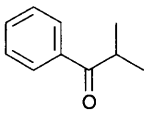
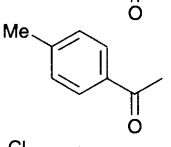
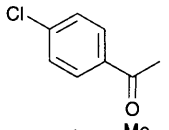
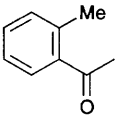
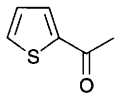
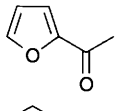
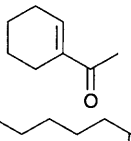
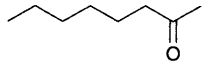


Scheme 2



Scheme 3

Table 1 Asymmetric hydrosilylation of various ketones catalysed by Ir^{I}-(*R*)-DIPOF[a]

Run	Ketones	Reaction time/h	Alcohols yield (%)[b]	ee (%)[c]	config.[d]
1		15	100	96	*R*
2		15	100	92	*R*
3		20	100	91	*R*
4		120	78	9	—
5		15	100	91	*R*
6		15	97	88	*R*
7		15	98	88	*R*
8		25	100	83	*R*
9		20	100	81	*R*
10		15	100	84	—
11		25	100	19	*S*

[a] All the reactions were carried out in the presence of [Ir(COD)Cl]$_2$ (0.25 mol%) and (*R*)-DIPOF (0.5 mol%) with diphenylsilane (1.5 mmol) and ketone (1.0 mmol) in Et$_2$O (4 cm^3) at 0 °C. [b] GLC yield. [c] Determined by HPLC and GLC. [d] By optical rotation.

tion was produced from acetophenone by changing Rh^I to Ir^I (Scheme 1).[3] This result prompted us to examine Ir^I-catalysed asymmetric hydrosilylation of other simple ketones in more detail. The preliminary results are reported here.

A mixture of a ketone, diphenylsilane, $[Ir(COD)Cl]_2$ (0.25 mol%) and (*R*)-DIPOF (0.5 mol%)† was stirred in diethyl ether at 0 °C for an appropriate time. Normal work-up procedure afforded the corresponding chiral alcohol in highly enantiomeric excess (ee) and in high yield.‡ For comparison we also carried out the Rh-catalysed hydrosilylation under similar conditions.§ The typical results using substituted acetophenones are shown in Scheme 2. It is worth noting that the corresponding *sec*-alcohols of the opposite configuration can be prepared highly selectively simply by changing Rh^I to Ir^I.

Hydrosilylation of a variety of ketones with diphenylsilane was then investigated in the presence of a catalytic amount of $[Ir(COD)Cl]_2$ and (*R*)-DIPOF (Scheme 3). The results are shown in Table 1 including the results shown in Scheme 2. Alkyl aryl ketones were hydrosilylated highly enantioselectively and almost quantitatively (runs 1–3), while a branched-alkyl aryl ketone reacted very slowly and its enantioselectivity was quite low (run 4). The chiral DIPOF ligand worked effectively for aryl methyl ketones (runs 5–7), heterocyclic methyl ketones[4] (runs 8 and 9) and α,β-unsaturated ketones (run 10), but in the case of simple dialkyl ketone octan-2-one the enantioselectivity was low (run 10).

Although the exact nature of the reaction is not certain, the first step seems to be the ligand exchange of cycloocta-1,5-diene of the iridium(I) complex with DIPOF followed by oxidative addition of Si and H of diphenylsilane to Ir and the subsequent coordination of carbonyl oxygen to Ir. To the best of our knowledge, this is the first example of the Ir-catalysed, highly enantioselective hydrosilylation of ketones. Further studies to clarify the reason why the absolute configuration of the product is different between Rh and Ir are now in progress.

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Footnotes

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† The preparation of (*R*)-DIPOF is as follows; Treatment of ferrocene carbonyl chloride with (1*S*, 2*R*)-(+)-2-amino-1,2-diphenylethanol and triethylamine in CH_2Cl_2 at room temperature produced the amide as a yellow solid (81% yield based on the amino alcohol). Treatment of the amide with thionyl chloride in CH_2Cl_2 at −78 °C to room temperature followed by the addition of 20% aqueous K_2CO_3 gave [(4*R*,5*R*)-diphenyl-4,5-dihydro-1,3-oxazol-2-yl]ferrocene as a yellow solid (54% yield based on the amide). After lithiation with *sec*-BuLi in diethyl ether at −78 °C, chlorodiphenylphosphine was added at −78 °C. The mixture was warmed to room temperature and then heated at reflux temperature for 12 h to afford a yellow solid which was purified by column chromatography on SiO_2 with hexane and ethyl acetate as eluents. The first fraction gave (*R*,*R*,*S*)-[2-(4,5-diphenyl-4,5-dihydro-1,3-oxazol-2-yl)ferrocenyl]diphenylphosphine (28% yield) and the second gave (*R*,*R*,*R*)-[2-(4,5-diphenyl-4,5-dihydro-1,3-oxazol-2-yl)ferrocenyl]diphenylphosphine (abbreviated as (*R*)-DIPOF) (mp 78–79 °C; 40% yield), both as yellow solids. *Selected spectroscopic data* for (*R*)-DIPOF: ^1H NMR (270 MHz, $CDCl_3$) δ 3.71 (m, 1 H), 4.29 (s, 5 H), 4.43 (t, 1 H, *J* 2.7 Hz), 4.93 (d, 1 H, *J* 7.70 Hz), 4.97 (d, 1 H, *J* 7.70 Hz), 5.08 (m, 1 H) and 7.0–7.5 (m, 20 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 70.9, 72.4, 74.1, 77.2, 88.6, 125.7, 126.9, 127.5, 128.0, 128.1, 128.3, 128.6, 128.8, 129.0, 132.9, 134.7, 140.8, 142.2 and 165.0.

‡ A typical reaction procedure is as follows; after stirring the $[Ir(COD)Cl]_2$ (0.0025 mmol) and the ligand (*R*)-DIPOF (0.005 mmol) in Et_2O (3 cm^3) at 25 °C for 1 h, acetophenone (1 mmol) and then diphenylsilane (1.5 mmol) were slowly added to the mixture, while keeping the temperature at 0 °C. The resulting mixture was stirred at 0 °C for 15 h and then quenched with methanol (2.5 cm^3). After hydrolysis with 1 mol dm^{-3} aqueous HCl (2.5 cm^3) the general work-up procedure afforded 1-phenylethanol quantitatively with 96% ee. The optical purity was determined by GLC or HPLC with a chiral phase. The absolute configuration was determined by an optical rotation.

§ The Rh-catalysed asymmetric hydrosilylation was carried out at 25 °C instead of 0 °C.

References

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3 Y. Nishibayashi, K. Segawa, K. Ohe and S. Uemura, *Organometallics*, 1995, **14**, 5486.

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