Rhodium(I)-catalysed Asymmetric Hydrosilylation of Ketones using New Diferrocenyl Dichalcogenides (R,S)-$\{[EC_5H_3CHMe(NMe_2)]Fe(C_5H_5)\}_2$ (E = S, Se, Te), as Chiral Ligands

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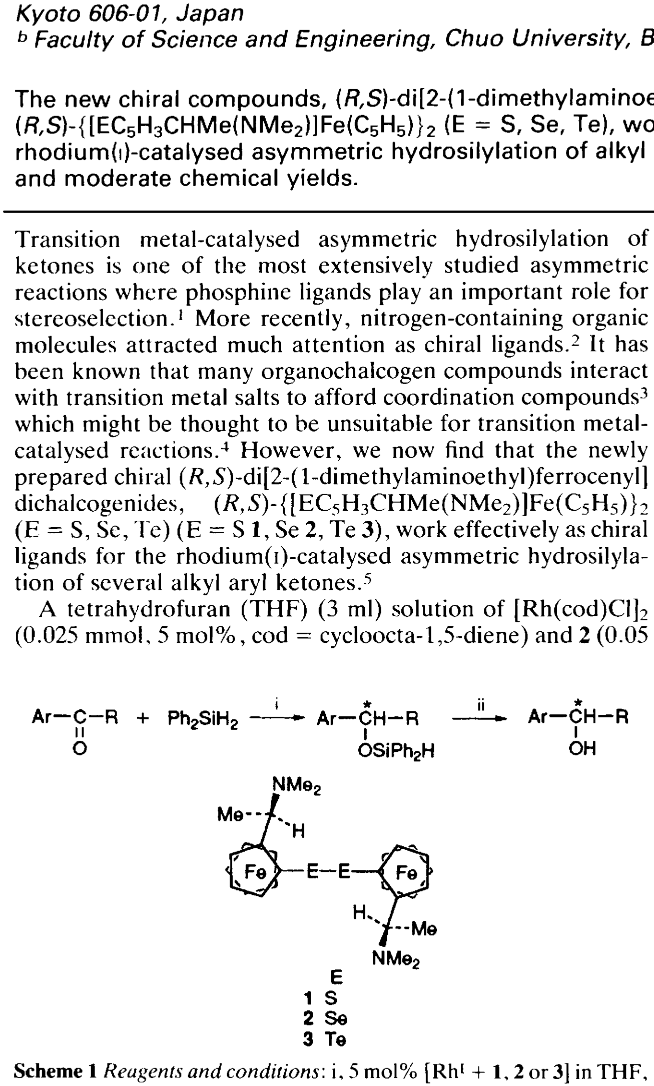
The new chiral compounds, (R,S)-di[2-(1-dimethylaminoethyl)ferrocenyl] dichalcogenides (R,S)-$\{[EC_5H_3CHMe(NMe_2)]Fe(C_5H_5)\}_2$ (E = S, Se, Te), work effectively as chiral ligands for the rhodium(I)-catalysed asymmetric hydrosilylation of alkyl aryl ketones resulting in high enantiomeric excess and moderate chemical yields.

Transition metal-catalysed asymmetric hydrosilylation of ketones is one of the most extensively studied asymmetric reactions where phosphine ligands play an important role for stereoselection.[1] More recently, nitrogen-containing organic molecules attracted much attention as chiral ligands.[2] It has been known that many organochalcogen compounds interact with transition metal salts to afford coordination compounds[3] which might be thought to be unsuitable for transition metal-catalysed reactions.[4] However, we now find that the newly prepared chiral (R,S)-di[2-(1-dimethylaminoethyl)ferrocenyl] dichalcogenides, (R,S)-$\{[EC_5H_3CHMe(NMe_2)]Fe(C_5H_5)\}_2$ (E = S, Se, Te) (E = S **1**, Se **2**, Te **3**), work effectively as chiral ligands for the rhodium(I)-catalysed asymmetric hydrosilylation of several alkyl aryl ketones.[5]

A tetrahydrofuran (THF) (3 ml) solution of $[Rh(cod)Cl]_2$ (0.025 mmol, 5 mol%, cod = cycloocta-1,5-diene) and **2** (0.05 mmol) was stirred at room temperature for 1 h under nitrogen and then a ketone (1.0 mmol) in THF (1 ml) was added. The solution was cooled to 0 °C to which diphenylsilane (1.5 mmol) was added and the mixture was stirred for an appropriate time. Quenching with dilute methanolic HCl afforded the corresponding chiral alcohol in high enantiomeric excess (ee) and in moderate chemical yield (Scheme 1). Similarly chiral **1** or **3** could be used as effective ligands. Typical results and reaction conditions are summarized in Table 1. The ee values were determined by HPLC using Daicel Chiralcel OB, OD and OJ columns.



Scheme 1 *Reagents and conditions*: i, 5 mol% [Rh^I + **1**, **2** or **3**] in THF, 0 °C; ii, 0.5 mol dm^{-3} HCl (MeOH), room temp.

Table 1 Asymmetric hydrosilylation of alkyl aryl ketones catalysed by Rh^I–$\{[EC_5H_3CHMe(NMe_2)]Fe(C_5H_5)\}_2$ **1–3**[a]

	Ketone					
Run	Ar	R	t/d	GLC yield (%)	Ee (%)[b]	Config.[c]
1	Ph	Me	1.5	31	85	*R*
2[d]	Ph	Me	3	46	31	*R*
3[e]	Ph	Me	3	67	50	*R*
4	Ph	Et	3	14	58	*R*
5	Ph	CH_2Cl	5	85	88	*S*
6	Ph	CO_2Me	1	31	60	*R*
7	Ph	Bu^t	10	5	85	*R*
8	Indanone		10	5	42	*R*
9	p-$NO_2C_6H_4$	Me	3	45	76	—
10	p-ClC_6H_4	Me	3	41	74	*S*
11	2-Thienyl	Me	4	100	78	*R*

[a] At 0 °C in THF. **2** was employed unless otherwise noted. [b] Enantiomeric excess was determined by HPLC using chiral columns. [c] Absolute configuration was determined by optical rotation. [d] **1** used. [e] **3** used.

The product yield or the reaction rate was much affected by the nature of alkyl and aryl groups of the ketone. As expected this decreased as the bulkiness of the alkyl group increased: Me > Et > Bu^t (runs 1, 4 and 7). For aryl groups the introduction of an electron-withdrawing group such as NO_2 and Cl (runs 9 and 10) or the use of thienyl group (run 11) increased the product yield, while the introduction of an electron-releasing group such as p-Me or p-OMe inhibited the reaction completely. Reasonably high ee values were obtained in many cases. However, it should be worth noting that the ee for the α-ketoester (run 6, 60% ee) was lower than that from acetophenone (run 1, 85% ee), because ee for α-ketosester is much higher than for acetophenone in the Rh^I-catalysed hydrosilylation using chiral phosphine ligands.[1] Although the exact nature of the reaction is not certain, the first step seems to be ligand exchange of the cyclooctadiene on the rhodium(I) complex with the dichalcogenide followed by oxidative addition of diphenylsilane on Rh and subsequent coordination of the carbonyl oxygen to Rh. Similar reactions also proceeded with the irridium(I) complex, $[Ir(cod)Cl]_2$, but the ee values were much lower; *i.e.* 13–22% in the case of acetophenone using **1–3** as ligands.

To our knowledge, this is the first example of a transition metal-catalysed asymmetric reaction using organic dichalcogenides as chiral ligands and may open a new field of coordination chemistry as well as organochalcogen chemistry.

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5 Compound **2** was prepared from (*R*)-(+)-*N,N*-dimethyl 1-ferrocenylethylamine, $Bu^{s}Li$ and selenium powder as reported (mp 98–100 °C, orange); Y. Nishibayashi, J. D. Singh, S. Fukuzawa and S. Uemura, *Tetrahedron Lett.*, 1994, **35**, 3115 and unpublished work. Compounds **1** (mp 169–170 °C, yellow, purified by Al_2O_3 column chromatography) and **3** (mp 55–56 °C, black, purified by Al_2O_3 column chromatography) were prepared by a similar method. Detailed preparative method as well as X-ray crystallographic data will be published in due course.