



Catalytic asymmetric hydrosilylation with (triazolinylidene)rhodium complexes containing an axis of chirality

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Abstract: (Triazolinylidene)rhodium(COD) complexes **1–3** containing an axis of chirality have been prepared with *de*=91–97%. The application of these complexes as catalysts in an asymmetric hydrosilylation reaction of methyl ketones **4–7** has been investigated, resulting in an *ee* of up to 44%. A non-linear temperature effect ('principle of isoinversion') has been examined. © 1997 Elsevier Science Ltd

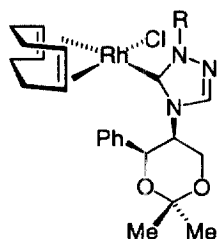
Introduction

Nucleophilic carbenes and their application as ligands in organometallic chemistry have already been broadly investigated.¹ Chiral complexes of these carbenes, firstly introduced by Lappert *et al.* in 1983,² were also reported by Herrmann *et al.*³ and our group⁴ during the past year. The hydrosilylation reaction with achiral (imidazolidinylidene)rhodium(COD) complexes by Lappert *et al.*⁵ was further developed by Herrmann *et al.* using chiral imidazolinylidene ligands which gave enantiomeric excesses of up to 32%.^{3a}

Results and discussion

We report the preparation of chiral (triazolinylidene)rhodium(COD) complexes, which, upon incorporation of a C₁-symmetrical carbene ligand, contain an axis of chirality because of its position perpendicular to the square-plane of the complex.^{4a} An epimerization of these complexes could be possible by a rotation about the carbene-carbon rhodium bond. The preparation of the complexes was carried out by reaction of a triazolium perchlorate, [(COD)RhCl]₂ and NEt₃ in THF. By using the 2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl group as chiral substituent of the triazolinylidene, the axially-chiral complexes **1–3** (Figure 1) could be prepared with a diastereomeric excess of *de*=91–97%.⁶

We investigated the potential of these complexes **1–3** as catalysts in an enantioselective hydrosilylation reaction, with several methyl ketones **4–7** as starting materials and diphenylsilane, using 1 mol% of **1–3**⁷ (Scheme 1).



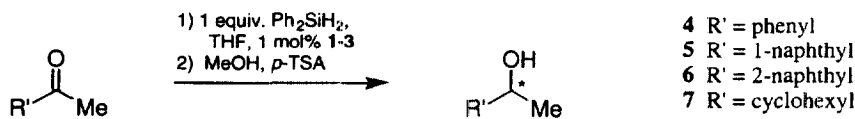
1 R = Me, *de* = 93%

2 R = Ph, *de* = 91%

3 R = ^tBu, *de* = 97%

Figure 1. Axially-chiral (triazolinylidene)rhodium(COD) complexes **1–3**.

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Scheme 1. Asymmetric hydrosilylation of methyl ketones 4–7.

Table 1. Reaction conditions, yields and enantiomeric excesses of the hydrosilylation reaction

entry	catalyst	ketone	temperature [°C]	time	yield [%]	ee [%]
1	1	4	22	4h	90	20 (<i>S</i>)
2	3	4	11	6d	60	40 (<i>R</i>)
3	1	5	-42	4h	80	37 (<i>R</i>)
4	2	5	2	10d	40	32 (<i>R</i>)
5	1	6	2	5d	90	19 (<i>S</i>)
6	3	6	22	16h	40	24 (<i>R</i>)
7	1	7	-10	6d	75	44 (<i>S</i>)
8	2	7	2	4d	80	43 (<i>S</i>)
9	3	7	22	3d	70	43 (<i>R</i>)

THF appeared to be the best solvent for this reaction, giving the highest yields and enantioselectivities. A dependence of the enantioselectivity on reaction time or amount of catalyst was not observed, whereas the yield increased with longer reaction times and an increased amount of catalyst. The reaction conditions giving the highest enantioselectivities for each system are summarized in Table 1.

Enantiomeric excesses of up to 44% were achieved with similar results being observed for aromatic and aliphatic ketones. The configuration of the resulting alcohol depends on the achiral group R at N1 of the triazolinylidene ligand, for example changing from *ee*=44% (*S*) (entry 7, Table 1) to *ee*=43% (*R*) (entry 9) with acetylcyclohexane 7 as starting material and no change of the chirality information within the catalyst. A similar effect concerning the exchange of an achiral substituent of the ligand has been observed by Brunner *et al.*⁸ in a hydrosilylation reaction using Pymox ligands.

In order to obtain the highest enantioselectivities, the optimum reaction temperature has to be varied from +42°C to -10°C for the different systems. While investigating the temperature effects, we found a decreasing enantioselectivity both with increasing or decreasing temperature with respect to the optimum conditions. Using the principle of isoinversion by Scharf *et al.*,⁹ the Eyring plots $\ln [R]/[S]$ against $1/T$ of several systems were found to show two linear regions intersecting at an inversion point T_{inv} (Figure 2). This non-linear temperature effect has also been observed by Scharf *et al.*¹⁰ for a hydrosilylation reaction with rhodium(NBD) complexes and chiral cyclic monophosphonite ligands.

The $\delta\Delta\Delta H^\ddagger$ against $\delta\Delta\Delta S^\ddagger$ plot (values calculated out of the Eyring plots) was found to be linear with a slope of 285 K ($T_{iso}=13^\circ\text{C}$), in spite of the broad variation of temperatures of inversion (+42°C to -10°C) with a correlation coefficient of 0.99. Because of this, the best enantioselectivities are to be expected at about 13°C (Figure 3).

The ratio of the two enantiomeric products is therefore highly dependent on the reaction temperature and the position of small and large substituents of the chiral ligand, showing the influence of steric hindrance on the enantiotopic face differentiation.

These results show the influence of C_1 -symmetrical chiral triazolinylidene ligands inducing axial chirality on the rhodium(COD) complexes, causing higher enantioselectivities and a non-linear temperature effect, compared to rhodium(COD) complexes of C_2 -symmetrical chiral imidazolinylidene ligands (higher enantioselectivities at lower temperatures).^{3a}

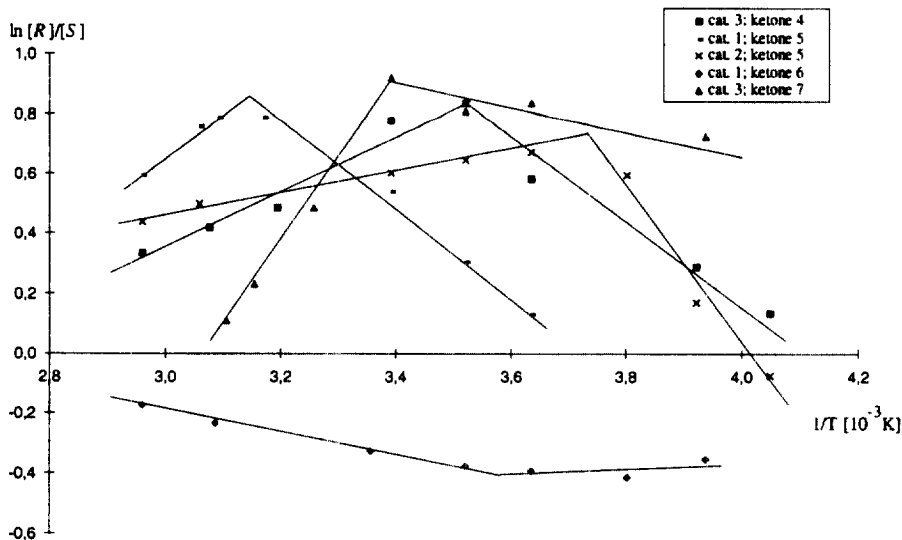


Figure 2. Eyring plots.

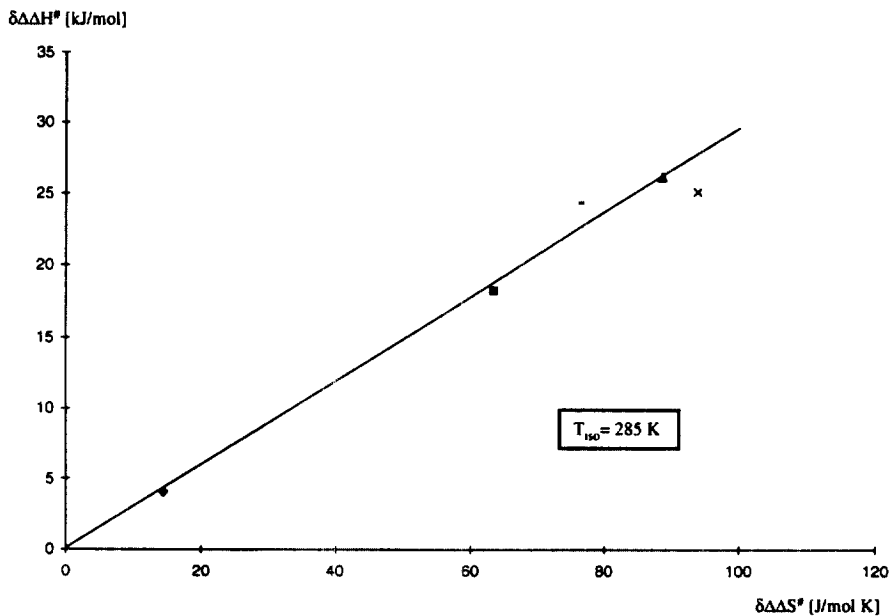


Figure 3. Temperature of isoinversion.

Acknowledgements

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6. The new complexes **1–3** gave appropriate spectroscopic data (IR, NMR, MS, HR-MS).
7. *General procedure*: Under a nitrogen atmosphere, the ketone **4–7** (1 mmol) and Ph₂SiH₂ (184 mg, 1 mmol) were added to a solution of the (triazolinylidene)rhodium(COD) complex **1–3** (1 mol%) in 2 ml of THF stirred at reaction temperature. The reaction was quenched by addition of methanol (0.5 ml) containing 1% of *p*-toluenesulfonic acid (*p*-TSA). After evaporation of the solvent *in vacuo* and purification of the product by column chromatography (silica gel, pentane:Et₂O=2:1), the enantiomeric excess of the product alcohol was determined by gas chromatography (LIPODEX E, CP-CHIRASIL-DEX CB, 7-CD PERME).
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