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Enantioselective catalysis

LIII *. Enantioselective catalysis with Rh complexes containing optically active iron compounds as ligands. Crystal structure of $CpFe(CO)(COMe)PPh_2ORh(COD)$ **

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Abstract

Cleavage of the PN bond in $(+)_{436}$- and $(-)_{436}$-$CpFe(CO)(COMe)PPh_2NMe$-$CHMePh$ with aqueous HBF_4 gives $(+)_{436}$- and $(-)_{436}$-$CpFe(CO)(COMe)PPh_2OH$. The reactions of $(+)_{436}$- and $(-)_{436}$-$CpFe(CO)(COMe)PPh_2OH$ with $[Rh(COD)Cl]_2$/KOH give the binuclear complexes $(+)_{436}$- and $(-)_{436}$-$CpFe(CO)(COMe)$-$PPh_2ORh(COD)$. These complexes and the in situ catalysts, consisting of the procatalyst $[Rh(COD)Cl]_2$ and the cocatalysts (+)- and (−)-$CpFe(CO)(COMe)$-Diop, were used in the enantioselective hydrogenation of *Z*-α-*N*-acetamidocinnamic acid and in the enantioselective hydrosilylation of acetophenone with diphenylsilane. Optical inductions of up to 76% were obtained in the hydrogenation and 6.1% in the hydrosilylation reaction. The structure of $CpFe(CO)(COMe)PPh_2ORh$-(COD) was determined by X-ray diffraction.

Introduction

Progress in enantioselective catalysis with transition metal complexes depends on the development of new optically active ligands [2,3]. Most ligands used up to now contain the chiral information in the form of asymmetric carbon atoms or asymmetric phosphorus atoms, but axial and planar chirality have also been used in ligand systems. However, there have been only a few reports on ligands in which the optical activity centers at a chiral transition metal atom [4–6]. We describe here

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* Part LII. see Ref. 1.

** Dedicated to Professor F.G.A. Stone in recognition of his 65th birthday.

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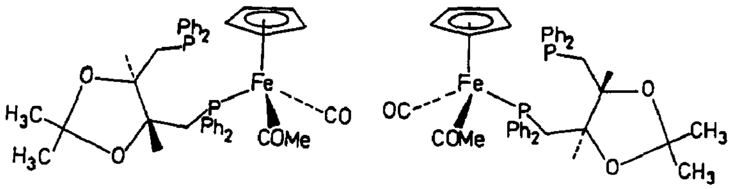
optically active ligands containing chiral Fe atoms. These ligands have been used in the Rh catalysed hydrogenation of *Z*-*α*-*N*-acetamidocinnamic acid and in the hydrosilylation of acetophenone with diphenylsilane. Compounds **1** and **2** (Scheme 1) serve as cocatalysts for in situ catalysts, whereas compound **4** is the ligand in the stable isolated catalyst **6** (Scheme 2).

Synthesis and characterisation of compounds 4–6

The synthesis and characterisation of compounds **1** and **2** (Scheme 1) were described previously [7]. **1** and **2** contain *R*,*R*-Diop as a unidentate ligand with one pendant PPh_2 group available for further coordination. The configurations at the asymmetric Fe atoms are *R* in **1** and *S* in **2**.

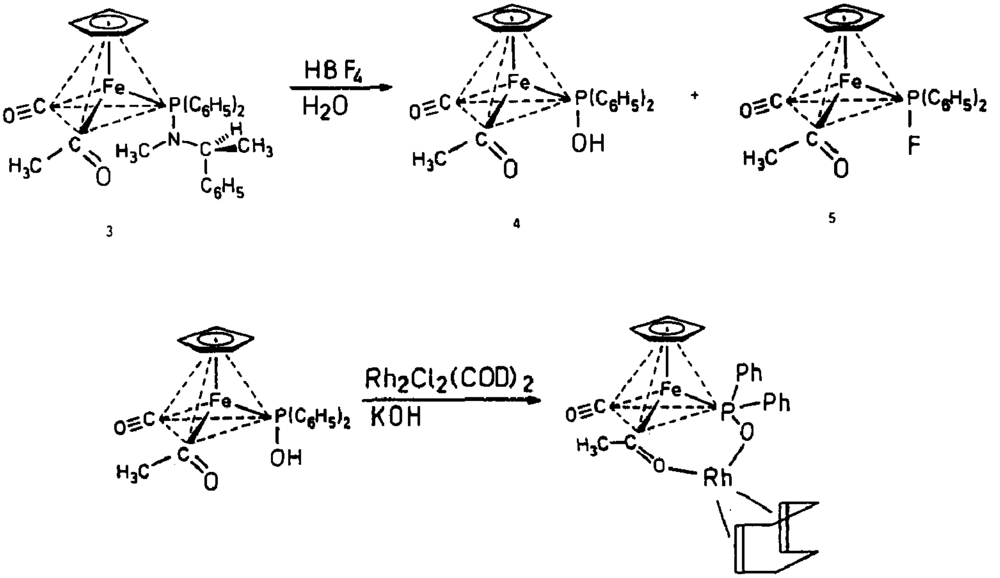
Complex **4** was prepared as shown in Scheme 2, starting from CpFe(CO)-(COMe)PPh_2NMeCHMePh (**3**), the synthesis of which was described previously [8].

Addition of 48% aqueous HBF_4 to a toluene solution of **3** gives **4** in 82% yield as a yellow oil. Owing to its instability, **4** must be characterised and used without prolonged storage.



1 2

Scheme 1



3 4 5

4 6

Scheme 2

Use of gaseous BF_3 instead of aqueous HBF_4 in the reaction with **3** produces complex **5** [8]. Phosphorus fluorides similar to **5** have been prepared previously by HF cleavage of the P–N bond in complexes of type **3** [9]. Reaction of **3** with $BF_3 \cdot OEt_2$ gives a mixture of **4** and **5** that is difficult to separate by chromatography.

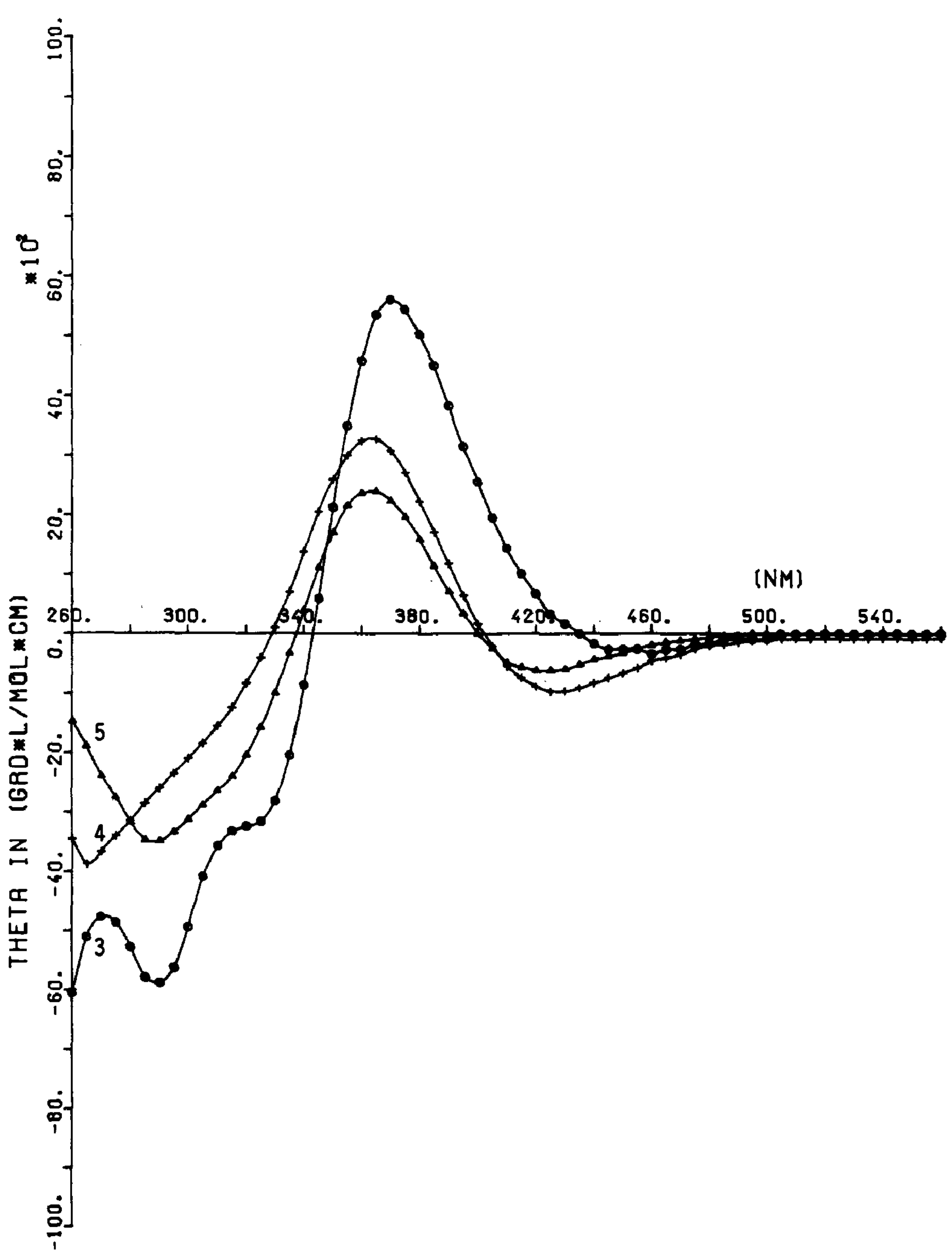


Fig. 1. CD spectra, $2\cdot10^{-3}$ *M* hexane solution of $(+)_{436}$-CpFe(CO)(COMe)PPh_2NMeCHMePh (3), $(+)_{436}$-CpFe(CO)(COMe)PPh_2F (5) and $(+)_{436}$-CpFe(CO)(COMe)PPh_2OH (4).

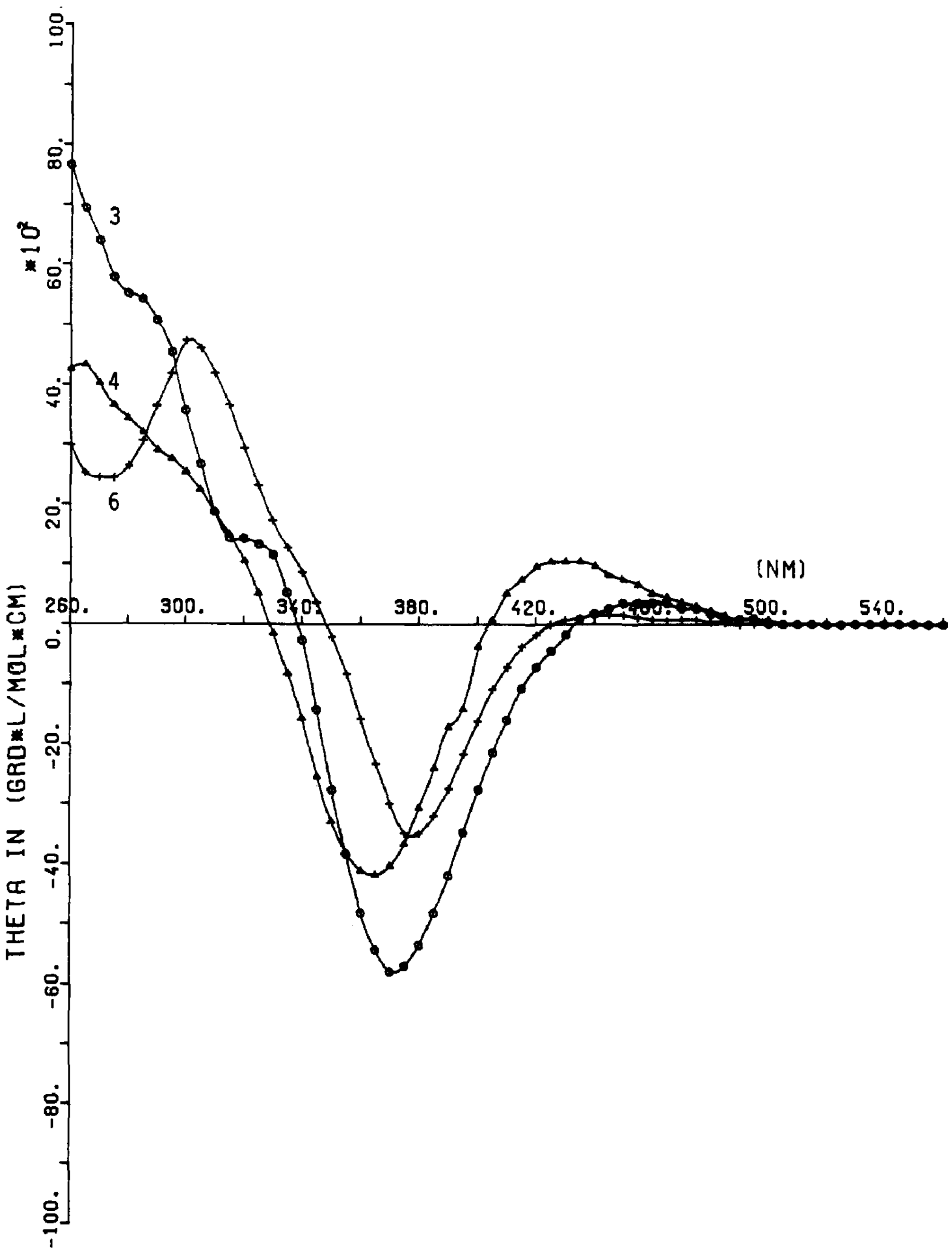


Fig. 2. CD spectra, $2 \cdot 10^{-3}$ *M* hexane solution of $(-)_{436}$-CpFe(CO)(COMe)PPh$_2$NMeCHMePh (3), $(-)_{436}$-CpFe(CO)(COMe)PPh$_2$OH (4) and $(-)_{436}$-CpFe(CO)(COMe)PPh$_2$ORh(COD) (6).

If the reaction with aqueous HBF$_4$ is carried out with optically active $(+)_{436}$-**3**, optically active $(+)_{436}$-**4** is formed. Similarly, $(-)_{436}$-**3** gives $(-)_{436}$-**4**. The enantiomeric purity could not be determined with the usual optishift reagents, but the agreement in shape and intensity between the CD spectra of the $(+)_{436}$-complexes **3**, **4**, and **5** (Fig. 1) and those of the $(-)_{436}$-complexes **3** and **4** (Fig. 2) indicate that the reactions occur with high or complete stereoselectivity and with retention of configuration at the Fe atom [8]. As the $(+)_{436}$- and $(-)_{436}$-compounds **3** have $R_{\mathrm{Fe}}S_{\mathrm{C}}$ and $S_{\mathrm{Fe}}S_{\mathrm{C}}$ configurations [8], the $(+)_{436}$-compounds **4** and **5** have the R_{Fe} configuration and the $(-)_{436}$-compound **4** has the S_{Fe} configuration.

Complex **4** is an analogue of the enol form of acetylacetone, and so it should be possible to use it as an anionic ligand for the synthesis of other complexes. In behaviour paralleling that involved in the synthesis of (acac)Rh(COD) (COD = 1.5-cyclooctadiene) treatment of **4** with KOH in toluene solution gives the corresponding anion, which is treated in situ with $[\mathrm{Rh(COD)Cl}]_2$. After chromatography the binuclear complex **6** is obtained as a yellow powder in 79% yield (Scheme 2), optically active $(-)_{436}$-**4** giving optically active $(-)_{436}$-**6**. The CD spectrum of

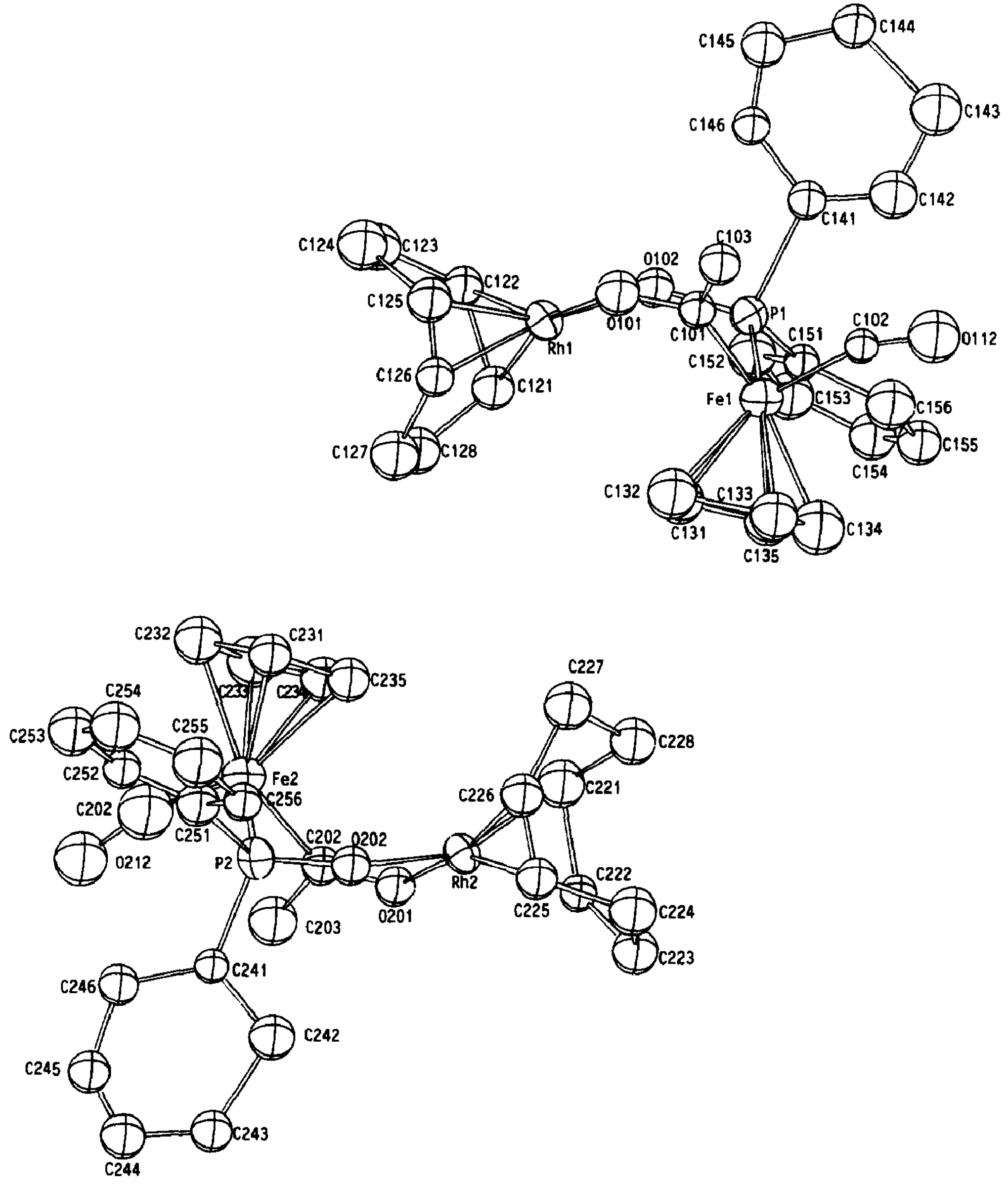


Fig. 3. Structure of $\mathrm{CpFe(CO)(COMe)PPh_2ORh(COD)}$ (**6**) in the crystal.

Table 1

Positional parameters and their estimated standard deviations for **6**

Atom	x	y	z	B(Å^2) [a]
Rh(1)	0.470	0.830	0.580	2.65(2)
Rh(2)	0.0338(1)	0.9655(1)	0.07064(8)	2.68(2)
Fe(1)	0.5359(2)	1.1571(2)	0.4524(1)	2.95(4)
Fe(2)	−0.0336(2)	0.6370(2)	0.1970(2)	3.01(5)
P(1)	0.4099(4)	1.0946(3)	0.6176(3)	2.66(8)
P(2)	0.0939(4)	0.6992(3)	0.0320(3)	2.66(7)
O(101)	0.667(1)	0.9220(8)	0.5242(7)	3.9(2) [b]
O(102)	0.3852(9)	0.9553(7)	0.6635(6)	2.8(2) [b]
O(112)	0.649(1)	1.360(1)	0.4841(8)	5.3(2) [b]
O(201)	−0.1751(9)	0.8838(7)	0.1167(6)	2.4(2) [b]
O(202)	0.1419(9)	0.8311(7)	0.0027(6)	2.9(2) [b]
O(212)	−0.183(1)	0.4565(9)	0.1521(8)	4.8(2) [b]
C(101)	0.681(1)	1.039(1)	0.4997(9)	2.7(2) [b]
C(102)	0.624(1)	1.266(1)	0.4837(8)	2.0(2) [b]
C(103)	0.856(1)	1.051(1)	0.4837(9)	2.6(2) [b]
C(121)	0.242(2)	0.793(1)	0.588(1)	4.0(3) [b]
C(122)	0.330(1)	0.700(1)	0.690(1)	3.3(3) [b]
C(123)	0.388(2)	0.571(1)	0.711(1)	3.3(3) [b]
C(124)	0.534(2)	0.557(1)	0.644(1)	4.6(3) [b]
C(125)	0.584(1)	0.672(1)	0.551(1)	3.0(3) [b]
C(126)	0.528(1)	0.718(1)	0.4753(9)	2.5(2) [b]
C(127)	0.387(2)	0.696(1)	0.432(1)	4.5(3) [b]
C(128)	0.237(2)	0.714(1)	0.509(1)	3.9(3) [b]
C(131)	0.398(2)	1.098(1)	0.375(1)	4.1(3) [b]
C(132)	0.545(2)	1.090(1)	0.318(1)	4.3(3) [b]
C(133)	0.566(2)	1.236(1)	0.280(1)	4.2(3) [b]
C(134)	0.464(2)	1.296(1)	0.315(1)	4.7(3) [b]
C(135)	0.345(2)	1.221(1)	0.375(1)	4.2(3) [b]
C(141)	0.495(1)	1.119(1)	0.7336(9)	2.2(2) [b]
C(142)	0.485(2)	1.227(1)	0.743(1)	3.6(3) [b]
C(143)	0.546(2)	1.245(1)	0.837(1)	4.8(4) [b]
C(144)	0.613(1)	1.103(1)	0.909(1)	3.2(3) [b]
C(145)	0.615(1)	0.989(1)	0.884(1)	3.3(3) [b]
C(146)	0.561(1)	1.010(1)	0.8010(8)	1.9(2) [b]
C(151)	0.227(1)	1.1779(9)	0.6406(8)	1.6(2) [b]
C(152)	0.108(2)	1.094(2)	0.708(1)	5.4(4) [b]
C(153)	−0.041(2)	1.169(1)	0.714(1)	3.9(3) [b]
C(154)	−0.060(2)	1.298(1)	0.671(1)	4.5(3) [b]
C(155)	0.046(2)	1.365(1)	0.616(1)	3.9(3) [b]
C(156)	0.223(2)	1.317(1)	0.588(1)	5.1(4) [b]
C(201)	−0.195(1)	0.776(1)	0.1519(9)	2.6(2) [b]
C(202)	−0.107(2)	0.520(2)	0.181(1)	5.9(4) [b]
C(203)	−0.343(2)	0.731(1)	0.145(1)	4.3(3) [b]
C(221)	−0.019(3)	1.059(1)	0.190(1)	4.4(3) [b]
C(222)	−0.104(1)	1.130(1)	0.0813(9)	2.7(2) [b]
C(223)	−0.051(2)	1.238(1)	−0.017(1)	3.6(3) [b]
C(224)	0.139(2)	1.224(1)	−0.046(1)	4.6(3) [b]
C(225)	0.198(1)	1.082(1)	−0.033(1)	2.8(2) [b]
C(226)	0.247(1)	1.026(1)	0.0527(9)	2.4(2) [b]
C(227)	0.266(2)	1.043(1)	0.163(1)	3.7(3) [b]
C(228)	0.116(2)	1.138(1)	0.184(1)	3.6(3) [b]
C(231)	0.170(1)	0.617(1)	0.266(1)	2.8(2) [b]

Table 1 (continued)

Atom	x	y	z	B(Å^2) [a]
C(232)	0.088(2)	0.514(1)	0.324(1)	4.4(3) [b]
C(233)	−0.086(2)	0.589(1)	0.371(1)	4.0(3) [b]
C(234)	−0.070(2)	0.693(1)	0.343(1)	3.4(3) [b]
C(235)	0.077(1)	0.731(1)	0.275(1)	3.0(3) [b]
C(241)	0.014(1)	0.692(1)	−0.0733(9)	2.0(2) [b]
C(242)	−0.045(2)	0.805(1)	−0.139(1)	4.5(3) [b]
C(234)	−0.113(1)	0.767(1)	−0.241(1)	3.1(3) [b]
C(244)	−0.098(2)	0.654(1)	−0.255(1)	3.8(3) [b]
C(245)	−0.045(1)	0.579(1)	−0.190(1)	3.1(3) [b]
C(246)	0.012(1)	0.576(1)	−0.104(1)	3.1(3) [b]
C(251)	0.282(2)	0.599(1)	0.020(1)	4.2(3) [b]
C(252)	0.305(1)	0.488(1)	0.0512(9)	2.1(2) [b]
C(253)	0.426(2)	0.412(1)	0.044(1)	3.4(3) [b]
C(254)	0.567(2)	0.476(1)	−0.014(1)	4.8(3) [b]
C(255)	0.551(2)	0.596(1)	−0.052(1)	5.0(4) [b]
C(256)	0.405(1)	0.6696(9)	−0.0367(8)	1.6(2) [b]

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) * [a^2 * B_{1,1} + b^2 * B_{2,2} + c^2 * B_{3,3} + ab(\cos \gamma) * B_{1,2} + ac(\cos \beta) * B_{1,3} + bc(\cos \alpha) * B_{2,3}]$. [b] Isotropically refined.

Table 2

Bond lengths (Å) for **6** in the crystal [a]

Rh(1)–O(101)	2.098(7)	P(2)–O(202)	1.546(5)	C(152)–C(153)	1.50(1)
Rh(1)–O(102)	2.045(4)	P(2)–C(241)	1.709(6)	C(153)–C(154)	1.41(1)
Rh(1)–C(121)	2.152(7)	P(2)–C(251)	1.921(9)	C(154)–C(155)	1.28(1)
Rh(1)–C(122)	2.096(7)	O(101)–C(101)	1.296(8)	C(155)–C(156)	1.63(2)
Rh(1)–C(125)	2.055(6)	O(112)–C(102)	1.138(8)	C(201)–C(203)	1.541(9)
Rh(1)–C(126)	2.103(7)	O(201)–C(201)	1.203(9)	C(221)–C(222)	1.67(1)
Rh(2)–O(201)	2.135(6)	O(212)–C(202)	1.25(2)	C(221)–C(228)	1.61(1)
Rh(2)–O(202)	2.049(4)	C(101)–C(103)	1.584(9)	C(222)–C(223)	1.533(8)
Rh(2)–C(221)	2.106(9)	C(121)–C(122)	1.69(2)	C(223)–C(224)	1.69(1)
Rh(2)–C(222)	2.132(6)	C(121)–C(128)	1.592(9)	C(224)–C(225)	1.60(2)
Rh(2)–C(225)	2.119(7)	C(122)–C(123)	1.460(9)	C(225)–C(226)	1.233(8)
Rh(2)–C(226)	2.099(6)	C(123)–C(124)	1.46(1)	C(226)–C(227)	1.555(8)
Fe(1)–P(1)	2.184(4)	C(124)–C(125)	1.536(9)	C(227)–C(228)	1.654(9)
Fe(1)–C(101)	1.802(7)	C(125)–C(126)	1.152(8)	C(231)–C(232)	1.410(9)
Fe(1)–C(102)	1.763(6)	C(126)–C(127)	1.58(1)	C(231)–C(235)	1.473(8)
Fe(1)–C(131)	2.059(6)	C(127)–C(128)	1.550(8)	C(232)–C(233)	1.775(9)
Fe(1)–C(132)	2.109(8)	C(131)–C(132)	1.403(9)	C(233)–C(234)	1.150(8)
Fe(1)–C(133)	2.122(7)	C(131)–C(135)	1.423(9)	C(234)–C(235)	1.491(9)
Fe(1)–C(134)	2.136(7)	C(132)–C(133)	1.62(2)	C(241)–C(242)	1.415(9)
Fe(1)–C(135)	2.108(6)	C(133)–C(134)	1.177(8)	C(241)–C(246)	1.51(1)
Fe(2)–P(2)	2.186(3)	C(133)–C(135)	2.140(9)	C(242)–C(243)	1.765(9)
Fe(2)–C(201)	2.030(6)	C(134)–C(135)	1.422(9)	C(243)–C(244)	1.349(9)
Fe(2)–C(202)	1.67(2)	C(141)–C(142)	1.27(2)	C(243)–C(245)	2.077(9)
Fe(2)–C(231)	2.169(5)	C(141)–C(146)	1.417(8)	C(244)–C(245)	1.126(8)
Fe(2)–C(232)	2.187(7)	C(142)–C(143)	1.53(1)	C(245)–C(246)	1.32(2)
Fe(2)–C(233)	2.135(7)	C(143)–C(144)	1.70(1)	C(251)–C(252)	1.209(9)
Fe(2)–C(234)	2.150(8)	C(144)–C(145)	1.433(8)	C(251)–C(256)	1.425(9)
Fe(2)–C(235)	2.156(6)	C(144)–C(146)	2.171(9)	C(252)–C(253)	1.306(9)
P(1)–O(102)	1.553(5)	C(145)–C(146)	1.228(7)	C(253)–C(254)	1.51(1)
P(1)–C(141)	1.943(6)	C(151)–C(152)	1.501(9)	C(154)–C(255)	1.32(1)
P(1)–C(151)	1.812(6)	C(151)–C(156)	1.53(2)	C(255)–C(256)	1.474(9)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3

Bond angles (°) for **6** in the crystal

O(101)–Rh(1)–O(102)	88.2(2)	C(221)–Rh(2)–C(225)	95.8(3)
O(101)–Rh(1)–C(121)	158.5(2)	C(221)–Rh(2)–C(226)	82.2(3)
O(101)–Rh(1)–C(122)	154.6(2)	C(222)–Rh(2)–C(225)	86.6(2)
O(101)–Rh(1)–C(125)	91.2(2)	C(222)–Rh(2)–C(226)	99.5(2)
O(101)–Rh(1)–C(126)	95.2(2)	C(225)–Rh(2)–C(226)	34.0(2)
O(102)–Rh(1)–C(121)	88.1(2)	P(1)–Fe(1)–C(101)	86.3(2)
O(102)–Rh(1)–C(122)	90.5(2)	P(1)–Fe(1)–C(102)	93.2(2)
O(102)–Rh(1)–C(125)	158.1(3)	P(1)–Fe(1)–C(131)	97.0(2)
O(102)–Rh(1)–C(126)	169.4(2)	P(1)–Fe(1)–C(132)	129.1(2)
C(121)–Rh(1)–C(122)	46.6(3)	P(1)–Fe(1)–C(133)	156.5(2)
C(121)–Rh(1)–C(125)	100.0(3)	P(1)–Fe(1)–C(134)	127.7(2)
C(121)–Rh(1)–C(126)	85.1(3)	P(1)–Fe(1)–C(135)	95.8(2)
C(122)–Rh(1)–C(125)	80.8(3)	C(101)–Fe(1)–C(102)	90.4(3)
C(122)–Rh(1)–C(126)	90.7(3)	C(101)–Fe(1)–C(131)	111.8(3)
C(125)–Rh(1)–C(126)	32.1(2)	C(101)–Fe(1)–C(132)	89.4(4)
O(201)–Rh(2)–O(202)	93.1(2)	C(101)–Fe(1)–C(133)	114.2(4)
O(201)–Rh(2)–C(221)	93.7(3)	C(101)–Fe(1)–C(134)	145.8(3)
O(201)–Rh(2)–C(222)	84.3(3)	C(101)–Fe(1)–C(135)	151.7(3)
O(201)–Rh(2)–C(225)	156.1(2)	C(102)–Fe(1)–C(131)	156.1(3)
O(201)–Rh(2)–C(226)	169.9(2)	C(102)–Fe(1)–C(132)	137.6(3)
O(202)–Rh(2)–C(221)	155.4(2)	C(102)–Fe(1)–C(133)	98.0(3)
O(202)–Rh(2)–C(222)	158.0(2)	C(102)–Fe(1)–C(134)	90.8(3)
O(202)–Rh(2)–C(225)	87.2(2)	C(102)–Fe(1)–C(135)	117.7(3)
O(202)–Rh(2)–C(226)	87.0(3)	C(131)–Fe(1)–C(132)	39.3(3)
C(221)–Rh(2)–C(222)	46.5(3)	C(131)–Fe(1)–C(133)	65.5(3)
C(131)–Fe(1)–C(134)	65.9(3)	C(202)–Fe(2)–C(235)	157.3(4)
C(131)–Fe(1)–C(135)	40.0(2)	C(231)–Fe(2)–C(232)	37.8(2)
C(132)–Fe(1)–C(133)	45.0(3)	C(231)–Fe(2)–C(233)	69.7(2)
C(132)–Fe(1)–C(134)	67.4(3)	C(231)–Fe(2)–C(234)	66.5(2)
C(132)–Fe(1)–C(135)	67.4(3)	C(231)–Fe(2)–C(235)	39.8(3)
C(133)–Fe(1)–C(134)	32.1(2)	C(232)–Fe(2)–C(233)	48.6(3)
C(133)–Fe(1)–C(135)	60.8(3)	C(232)–Fe(2)–C(234)	66.2(3)
C(134)–Fe(1)–C(135)	39.1(2)	C(232)–Fe(2)–C(235)	65.9(2)
P(2)–Fe(2)–C(201)	88.7(3)	C(233)–Fe(2)–C(234)	31.1(2)
P(2)–Fe(2)–C(202)	97.6(3)	C(233)–Fe(2)–C(235)	63.6(2)
P(2)–Fe(2)–C(231)	90.6(2)	C(234)–Fe(2)–C(235)	40.6(2)
P(2)–Fe(2)–C(232)	117.4(3)	Fe(1)–P(1)–O(102)	116.9(2)
P(2)–Fe(2)–C(233)	159.7(3)	Fe(1)–P(1)–C(141)	116.5(2)
P(2)–Fe(2)–C(234)	136.2(2)	Fe(1)–P(1)–C(151)	115.1(2)
P(2)–Fe(2)–C(235)	98.2(2)	O(102)–P(1)–C(141)	101.2(3)
C(201)–Fe(2)–C(202)	100.6(4)	O(102)–P(1)–C(151)	106.5(3)
C(201)–Fe(2)–C(231)	135.1(3)	C(141)–P(1)–C(151)	98.2(3)
C(201)–Fe(2)–C(232)	149.2(3)	Fe(2)–P(2)–O(202)	113.1(3)
C(201)–Fe(2)–C(234)	83.7(3)	Fe(2)–P(2)–C(251)	110.1(3)
C(201)–Fe(2)–C(235)	96.0(2)	O(202)–P(2)–C(241)	107.5(3)
C(202)–Fe(2)–C(231)	124.0(4)	O(202)–P(2)–C(251)	103.8(3)
C(202)–Fe(2)–C(232)	92.3(4)	C(241)–P(2)–C(251)	103.7(3)
C(202)–Fe(2)–C(233)	97.6(4)	Rh(1)–O(101)–C(101)	128.9(5)
C(202)–Fe(2)–C(234)	126.2(4)	Rh(1)–O(102)–P(1)	123.5(3)
Rh(2)–O(201)–C(201)	128.2(5)	Fe(1)–C(132)–C(131)	68.4(4)
Rh(2)–O(202)–P(2)	125.4(3)	Fe(1)–C(132)–C(133)	68.0(4)
Fe(1)–C(101)–O(101)	123.3(5)	C(131)–C(132)–C(133)	96.7(6)
Fe(1)–C(101)–C(103)	127.9(4)	Fe(1)–C(133)–C(132)	67.1(4)

Table 3 (continued)

O(101)–C(101)–C(103)	106.1(5)	Fe(1)–C(133)–C(134)	74.6(6)
Fe(1)–C(102)–O(112)	158.0(6)	Fe(1)–C(133)–C(135)	59.3(3)
Rh(1)–C(121)–C(122)	65.0(3)	C(132)–C(133)–C(134)	114.0(8)
Rh(1)–C(121)–C(128)	110.1(4)	C(132)–C(133)–C(135)	75.6(4)
C(122)–C(121)–C(128)	106.9(5)	C(134)–C(133)–C(135)	38.5(4)
Rh(1)–C(122)–C(121)	68.5(4)	Fe(1)–C(134)–C(133)	73.4(5)
Rh(1)–C(122)–C(123)	116.4(5)	Fe(1)–C(134)–C(135)	69.4(4)
C(121)–C(122)–C(123)	129.6(6)	C(133)–C(134)–C(135)	110.5(7)
C(122)–C(123)–C(124)	111.8(7)	Fe(1)–C(135)–C(131)	68.2(4)
C(123)–C(124)–C(125)	116.3(7)	Fe(1)–C(135)–C(133)	59.9(3)
Rh(1)–C(125)–C(124)	111.3(4)	Fe(1)–C(135)–C(134)	71.5(3)
Rh(1)–C(125)–C(126)	76.2(5)	C(131)–C(135)–C(133)	75.8(4)
C(124)–C(125)–C(126)	125.2(7)	C(131)–C(135)–C(134)	106.8(5)
Rh(1)–C(126)–C(125)	71.7(5)	C(133)–C(135)–C(134)	31.0(3)
Rh(1)–C(126)–C(127)	112.6(4)	P(1)–C(141)–C(142)	119.1(6)
C(125)–C(126)–C(127)	135.7(7)	P(1)–C(141)–C(146)	114.4(5)
C(126)–C(127)–C(128)	112.2(5)	C(142)–C(141)–C(146)	126.7(7)
C(121)–C(128)–C(127)	115.6(5)	C(141)–C(142)–C(143)	119.1(7)
Fe(1)–C(131)–C(132)	72.3(4)	C(142)–C(143)–C(144)	105.8(6)
Fe(1)–C(131)–C(135)	71.9(4)	C(143)–C(144)–C(145)	127.1(5)
C(132)–C(131)–C(135)	111.8(7)	C(143)–C(144)–C(146)	94.8(4)
C(145)–C(144)–C(146)	32.3(3)	C(222)–C(223)–C(224)	109.0(6)
C(144)–C(145)–C(146)	109.2(6)	C(223)–C(224)–C(225)	109.8(6)
C(141)–C(146)–C(144)	93.6(4)	Rh(2)–C(225)–C(224)	110.4(5)
C(141)–C(146)–C(145)	132.1(5)	Rh(2)–C(225)–C(226)	72.1(4)
C(144)–C(146)–C(145)	38.6(3)	C(224)–C(225)–C(226)	115.2(6)
P(1)–C(151)–C(152)	112.6(4)	Rh(2)–C(226)–C(225)	73.9(4)
P(1)–C(151)–C(156)	114.9(5)	Rh(2)–C(226)–C(227)	109.0(4)
C(152)–C(151)–C(156)	132.6(6)	C(225)–C(226)–C(227)	141.6(6)
C(151)–C(152)–C(153)	109.1(6)	C(226)–C(227)–C(228)	101.1(4)
C(152)–C(153)–C(154)	124.0(7)	C(221)–C(228)–C(227)	102.2(5)
C(153)–C(154)–C(155)	124.0(8)	Fe(2)–C(231)–C(232)	71.8(3)
C(154)–C(155)–C(156)	126.5(8)	Fe(2)–C(231)–C(235)	69.6(3)
C(151)–C(156)–C(155)	103.7(5)	C(232)–C(231)–C(235)	109.9(5)
Fe(2)–C(201)–O(201)	125.1(5)	Fe(2)–C(232)–C(231)	70.4(3)
Fe(2)–C(201)–C(203)	113.6(5)	Fe(2)–C(232)–C(233)	64.2(4)
O(201)–C(201)–C(203)	120.4(6)	C(231)–C(232)–C(233)	100.4(5)
Fe(2)–C(202)–O(212)	163.6(8)	Fe(2)–C(233)–C(232)	67.3(3)
Rh(2)–C(221)–C(222)	67.6(4)	Fe(2)–C(233)–C(234)	75.2(5)
Rh(2)–C(221)–C(228)	110.8(5)	C(232)–C(233)–C(234)	106.3(7)
C(222)–C(221)–C(228)	108.0(6)	Fe(2)–C(234)–C(233)	73.7(5)
Rh(2)–C(222)–C(221)	65.9(4)	Fe(2)–C(234)–C(235)	70.0(3)
Rh(2)–C(222)–C(223)	109.8(4)	C(233)–C(234)–C(235)	117.3(7)
C(221)–C(222)–C(223)	127.3(6)	Fe(2)–C(235)–C(231)	70.6(3)
Fe(2)–C(235)–C(234)	69.5(3)	C(243)–C(245)–C(246)	98.6(5)
C(231)–C(235)–C(234)	106.1(5)	C(244)–C(245)–C(246)	135.1(8)
P(2)–C(241)–C(242)	116.2(5)	C(241)–C(246)–C(245)	121.7(7)
P(2)–C(241)–C(246)	124.8(5)	P(2)–C(251)–C(252)	128.8(7)
C(242)–C(241)–C(246)	118.8(6)	P(2)–C(251)–C(256)	112.8(6)
C(241)–C(242)–C(243)	105.0(5)	C(252)–C(251)–C(256)	118.3(7)
C(242)–C(243)–C(244)	126.3(5)	C(251)–C(252)–C(253)	113.4(7)
C(242)–C(243)–C(245)	96.5(4)	C(252)–C(253)–C(254)	113.7(6)
C(244)–C(243)–C(245)	29.8(3)	C(253)–C(254)–C(255)	116.8(8)
C(243)–C(244)–C(245)	113.7(6)	C(254)–C(255)–C(256)	123.1(7)
C(243)–C(245)–C(244)	36.6(4)	C(251)–C(256)–C(255)	114.7(6)

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[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

$(-)_{436}$-**6** is shown in Fig. 2. In $(-)_{436}$-**6** the Fe atom has the *S* configuration.

CpFe(CO)(COMe)PPh$_2$ORh(COD) (**6**) was characterised by a single crystal X-ray structure analysis. There are two slightly different molecules in the unit cell. The ORTEP diagram is shown in Fig. 3. The atomic parameters are given in Table 1, and bond lengths and bond angles in Tables 2 and 3. The crystallographic data are summarized in the Experimental Section.

Hydrogenations

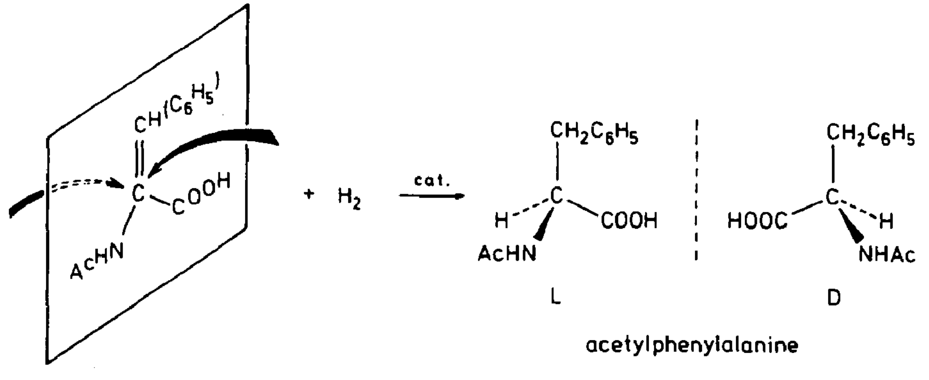
The hydrogenation of *Z*-α-*N*-acetamidocinnamic acid was carried out as indicated in Scheme 3.

The catalysts with complexes **1** and **2** as ligands were prepared in situ from [Rh(COD)Cl]$_2$ in methanol solution by stirring for 15 min at room temperature. The hydrogenation time was 20 h at a hydrogen pressure of 1.1 bar. Work up and determination of chemical and optical yields involved standard procedures [10,11].

The hydrogenations were carried out with Rh/ligand ratios of 1/0.96–1/1.12 and 1/1.95–1/2.13. The Rh/substrate ratios varied between 1/49 and 1/63. For Rh/ligand ratios of 1/1, $(-)_{436}$-**1**, the ligand with $R_{Fe}R_CR_C$ configuration, gave 68.9–70.7% ee, whereas $(+)_{436}$-**2**, the ligand with $S_{Fe}R_CR_C$ configuration, gave 69.7–76.0% ee. In both cases the product was (*R*)-(−)-*N*-acetylphenylalanine. For Rh/ligand ratios of 1/2, the optical yields with **2** were only 25.5–29.9% ee, the *R*-configuration again being preferred. The hydrogenation was quantitative or almost so in all cases [12].

In complexes **1** and **2**, one of the two PPh$_2$ groups in Diop is blocked by the CpFe(CO)(COMe) fragment and formation of PP chelate complexes with rhodium is no longer possible. In spite of this, high optical yields of 69–76% ee are obtained. Similar behaviour has been observed previously with CpMn(CO)$_2$Diop, which gives 78% ee [4]. In contrast to the Mn complex, the iron complexes **1** and **2** have additional chiral centers of *R* and *S* configuration at the metal atom which could influence the optical induction in enantioselective catalysis. Unfortunately, the in situ catalysts [Rh(COD)Cl]$_2$/**1** and **2** give optical inductions slightly lower than CpMn(CO)$_2$Diop and Diop, the epimers **1** and **2** showing only small differences.

For a Rh/ligand ratio of 1/1 the formation of the catalytically active species CpFe(CO)(COMe)DiopRhCl(COD) was to be expected, and in the reaction of CpFe(CO)(COMe)Diop with [Rh(COD)Cl]$_2$ in a H$_2$ atmosphere the product gave a



Scheme 3

molecular ion at m/z 936 in the field desorption mass spectrum consistent with this formulation.

Ligands **1** and **2** could even bind via the acetyl group as chelates to rhodium, as ligand **4** does in complex **6**. However, the formation of CpFe(CO)(COMe)DiopRhCl(COD) rules out an interaction between the acetyl group and the rhodium atom. As a consequence, in CpFe(CO)(COMe)DiopRhCl(COD) the chiral Fe atom is so far away from the rhodium atom that it does not appreciably influence product formation. However, it restricts the conformational freedom of the Diop unit, imposing a rigidity on the monodentate Diop that leads to much higher optical yields than expected for monodentate ligands of that type. Thus, Glyphos, a monodentate ligand which contains the same ketal ring as Diop, gives an optical yield of only 15% ee in the hydrogenation of *Z*-*α*-*N*-acetamidocinnamic acid [13]. Thus, the selectivity comes from the chiral centers in Diop, and the chiral centers at the Fe atoms have almost no influence on the enantioselectivity of the hydrogenation catalysts.

Degradation of the iron complexes **1** and **2** in methanol occurs only at higher temperatures. Furthermore, complexes $[CpFe(CO)(COMe)]_2Diop$ [7], in which both PPh_2 groups of Diop are blocked by coordination, do not catalyse the hydrogenation reaction of Scheme 3 within 4 d [12]. These findings seem to rule out participation of free Diop in the hydrogenation reactions discussed.

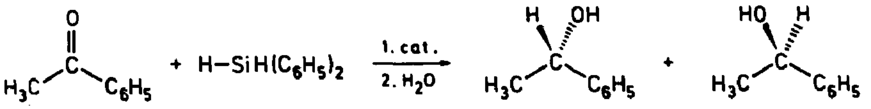
Complex **6** is not a catalyst for the hydrogenation of *Z*-*α*-*N*-acetamidocinnamic acid. After 3 h, elementary rhodium is deposited from **6**. At 50 bar hydrogen pressure there is no hydrogenation of *Z*-*α*-*N*-acetamidocinnamic acid with complex **6** as catalyst [14].

Hydrosilylations

As a standard reaction the hydrosilylation of acetophenone with diphenylsilane was used. Upon hydrolysis the product gives 1-phenylethanol (Scheme 4).

The hydrosilylation was carried out as previously described [15,16]. The chemical yields were between 88 and 97% and the optical inductions between 2 and 10% ee. As in the hydrosilylation with $CpMn(CO)_2Diop$ [4], these values are independent of the Rh/ligand ratio. The optical inductions are much lower than those for Diop and Glyphos [13]. The diastereomer 1a yields 1.8–4.1% ee and the diastereomer **2** 5.6–6.1% ee. In both cases the *R* enantiomer of 1-phenylethanol is predominantly formed. Thus, the stereoselectivity depends on the epimer used, demonstrating the effect of the asymmetric Fe atom. As in the hydrogenation, however, the selectivity is dominated by the Diop substructure.

In the reaction shown in Scheme 4, complex **6** gives a chemical yield of 75% in 40 h but with no optical induction. With an in situ catalyst consisting of $[Rh(COD)Cl]_2$ and ligand **4** the same chemical yield is obtained, but again no optical induction [14].



Scheme 4

Experimental

Synthesis of $(+)_{436}$- and $(-)_{436}$-$CpFe(CO)(COMe)PPh_2OH$ (4)

To the solution of 346 mg $(+)_{436}$-$CpFe(CO)(COMe)PPh_2NMeCHMePh$ (3) [17] in 5 ml of toluene at room temperature was added aqueous HBF_4 (48 weight %). After addition of one equivalent of HBF_4, the colour changed from red to yellow. Chromatography (SiO_2, column 15 × 2 cm) with ether as eluent gave the product **4** in a yellow band, from which a yellow green oil was obtained. Yield 220 mg (82%). **4** is soluble in all common organic solvents. In solution at $-20\,^\circ$C, it is stable for a short time. Found: C, 60.94; H, 4.86. $C_{20}H_{19}FeO_3P$ (394.2) calcd.: C, 60.98; H, 4.96%. IR (pentane): 1948 (s), 1558 (m) cm^{-1}. ^1H NMR (C_6D_6, i-TMS): δ 2.60 (s, 3H, COMe), 4.17 (s, 5H, Cp), 7.03–7.60 (m, 10H, Ph), 11.13 (br, 1H, OH). MS (field desorption, toluene): m/z 394 (M^+). Optical rotations (c 0.1, toluene): $[\alpha]_{578}$ -25, $[\alpha]_{546}$ -52, $[\alpha]_{436}$ $+1022°$.

$(-)_{436}$-$CpFe(CO)(COMe)PPh_2OH$ is analogously synthesised from $(-)_{436}$-$CpFe(CO)(COMe)PPh_2NMeCHMePh$ (3) [17].

Synthesis of $(-)_{436}$-$CpFe(CO)(COMe)PPh_2ORh(COD)$ (6)

To the solution of 100 mg (0.25 mmol) of $(-)_{436}$-$CpFe(CO)(COMe)PPh_2OH$ (4) in 4 ml of toluene, 63 mg (0.13 mmol) of $[Rh(COD)Cl]_2$ and a tenfold excess of pulverised KOH were added at $0\,^\circ$C. After 10 min the mixture was chromatographed (SiO_2, column 20 × 2 cm); toluene eluted a weak yellow band of unchanged $[Rh(COD)Cl]_2$, and ether eluted a yellow band of the product **6**. Evaporation of the ether yielded a yellow oil, which solidified on addition of petroleum ether to give a yellow-green powder. Yield 121 mg (79%), m.p. $142\,^\circ$C. Found: C, 55.54; H, 5.01. $C_{28}H_{30}FeO_3PRh$ (604.3) calcd.: C, 55.65; H, 5.00%. IR (toluene): 1929 cm^{-1}. ^1H NMR (C_6D_6, i-TMS): δ 1.52–1.59, 2.11–2.33, 3.68 (m, 12H, COD), 2.47 (d, J 1 Hz, 3H, COMe), 4.76 (d, J 1 Hz, 5H, Cp), 6.87–7.95 (m, 10H, Ph). MS (field desorption, toluene): m/z 604 (M^+). Optical rotations (c 0.1, toluene): $[\alpha]_{578}$ $+91$, $[\alpha]_{546}$ $+99$, $[\alpha]_{436}$ $-357°$.

Crystal data for $CpFe(CO)(COMe)PPh_2ORh(COD)$ (6)

Formula $C_{28}H_{30}FeO_3PRh$; M 604.27. Space group $P1$; a 9.096(3), b 11.475(2), c 13.076(2) Å; α 71.68(1), β 78.43(2), γ 81.55(2)°; $V = 1264.1$ Å^3. Two formula units in the elementary cell. D_C: 1.59 g/cm^3. Crystal size: 0.12 × 0.16 × 0.8 mm^3 (needle). Diffractometer: Enraf-Nonius CAD4; Mo-K_α radiation; μ 13.06 cm^{-1}. θ range $2 < \theta < 25°$. Reflections measured 4723, reflections used 3919. Patterson + MULTAN methods. Variables refined 300 (anisotropic). $R = 0.051$, $R_w = 0.056$; $w = 4I/\sigma^2(I)$. No attempt was made to determine the absolute configuration.

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