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Enantioselective catalysis Part 129. A new rhodium(I) complex with a μ_2-H bridged Cp_2WH_2 ligand☆

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Abstract

The optically active complex $\{[(-)\text{-diop}]Rh(\mu_2\text{-}H)_2WCp_2\}PF_6$ was prepared and characterized. In four different models of enantioselective catalysis the complex gave the same enantioselectivity as the catalysts $[Rh(cod)Cl]_2/(-)$-diop and $[Rh(cod)Cl]_2/(-)$-diop/Cp_2WH_2.

Keywords: Enantioselectivity; Catalysis; Optical activity

1. Introduction

The square planar rhodium(I) complex $[(Ph_3P)_2Rh(\mu_2\text{-}H)_2WCp_2]PF_6$ was prepared by Alcock and Moore [2] from $[Rh(cod)Cl]_2$ (**1**), PPh_3 and Cp_2WH_2 (**5**). With the optically active bidentate ligand $(-)$-diop (**2**) [3,4] instead of the triphenylphosphine ligands the new complex $\{[(-)\text{-diop}]Rh(\mu_2\text{-}H)_2WCp_2\}PF_6$ (**6**) would arise, a candidate for enantioselective catalysis. We wanted to investigate whether the μ_2-H bridged Cp_2WH_2 ligand would change the optical induction compared to the Cp_2WH_2-free system.

The present paper deals with the preparation and characterization of **6**. The results of four different asymmetric catalyses with **6** are presented and compared with the in situ catalysts **1**/**2** and **1**/**2**/**5**. The catalytic systems were the hydrogenation of (*Z*)-α-*N*-acetamidocinnamic acid [5], the hydrogenation of ketopantolactone [1], the hydrosilylation of acetophenone [6] and the isomerization of 2-*n*-butyl-4,7-dihydro-1,3-dioxepin [7].

2. Synthesis and spectra of $\{[(-)\text{-diop}]Rh(\mu_2\text{-}H)_2WCp_2\}PF_6$ (6)

Complex **6** could be synthesized in two steps according to the preparation of $[(Ph_3P)_2Rh(\mu_2\text{-}H)_2WCp_2]PF_6$ [2]. Complex **1** reacted with **2** in the presence of NH_4PF_6 in CH_2Cl_2/water at room temperature (r.t.). The separated organic phase was filtered and **3** could be recrystallized as orange crystals in a 71% yield. Then **3** was dissolved in acetone. At a static pressure of 1.1 bar of hydrogen the 1,5-cyclooctadiene ligand of **3** was removed by hydrogenation. Without isolation the octahedral solvent complex **4** was treated with a small excess of **5**. Immediately the solution turned from orange to deep green. Complex **6** could be obtained in an analytically pure form after chromatography on silica and recrystallization in a 55% yield (Scheme 1). In solution compound **6** is readily decomposed by oxygen, but in the solid state it is moderately stable.

The IR spectrum of **6** exhibits the bands of aromatic and aliphatic ν(C–H) as well as aromatic ν(C=C) vibrations owing to the presence of both ligands $(-)$-diop (**2**) and Cp_2WH_2 (**5**) in the complex. Compared to the stretching absorption of the terminally bound W–H of free **5** at 1910 cm^{-1} the μ_2-H bridge (Rh–H–W)

☆ For Part 128 see Ref. [1].

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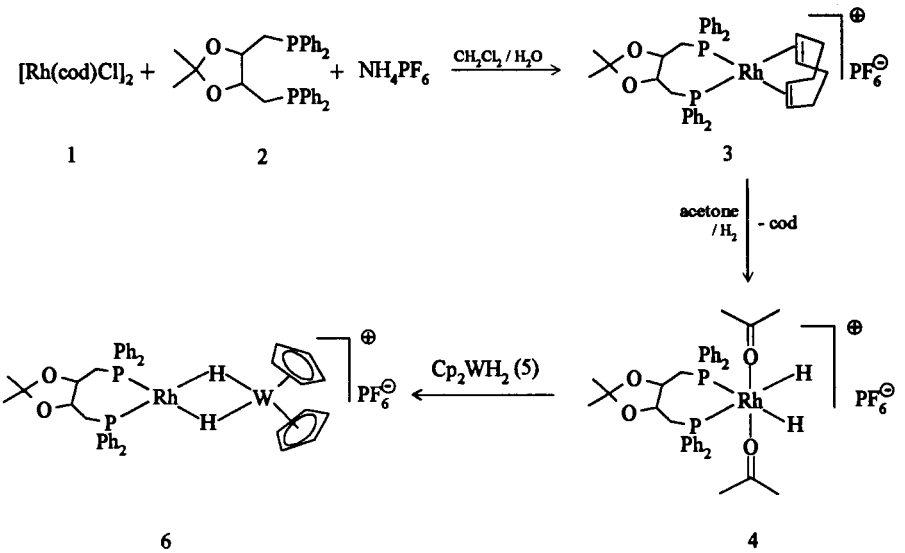

Scheme 1. Preparation of {[(−)-diop]Rh(μ_2-H)$_2$WCp$_2$}PF$_6$ (**6**).

stretching absorption of **6** is shifted to 1625 cm^{-1} and broadened ($\Delta\nu_{1/2}$ ca. 95 cm^{-1}). This phenomenon is characteristic of complexes in which hydrogen is in a position bridging two (or more) metals [8]. The PF_6 anion shows a strong absorption at 810 cm^{-1}.

Due to the C_2-symmetry of the complex cation the ^{1}H-NMR spectrum of **6** in acetone-d$_6$ at r.t. is relatively simple. The spectrum consists of various peaks in the phenyl region in the range of 7.08–8.07 ppm as a result of different orientations of the phenyl rings bound to phosphorus. The ten protons of the Cp rings show a singlet at 5.20 ppm. The two methine protons in the dioxolane system exhibit a multiplet at 3.65 ppm. This pattern results from coupling to the methylene protons and vicinal coupling with the phosphorus nuclei. For the methylene protons two multiplets at 2.86 and 2.69 ppm are found due to their different chemical environment being either in the *cis* or *trans* position to the methine protons [9,10]. In addition, they couple with the geminal phosphorus atoms, the vicinal rhodium atoms and the methine protons. The methyl groups show a singlet at 1.14 ppm. The hydride signal appears at −17.99 ppm. Direct coupling with rhodium ($^1J(^{103}Rh,^1H) = 29.1$ Hz) and geminal coupling with phosphorus ($^2J(^{31}P,^1H) = 10.0$ Hz) leads to a doublet of triplets. Furthermore, there are tungsten satellite peaks. The coupling constant ($^1J(^{183}W,^1H) = 107.3$ Hz) is only accessible with the help of the $^1H\{^{31}P\}$-NMR spectrum. The metal–H coupling constants are comparable to those of the terminal hydrides in [(Ph$_3$P)$_2$-RhH$_2$(OCMe$_2$)$_2$]PF$_6$ ($^1J(^{103}Rh,^1H) = 26$ Hz) and Cp$_2$WH$_2$ ($^1J(^{183}W,^1H) = 74$ Hz) [2], consistent with a (μ_2-H)$_2$ bridge between rhodium and tungsten in **6**. The hydride signals of the ^{1}H- and $^1H\{^{31}P\}$-NMR are shown in Fig. 1.

The $^{31}P\{^1H\}$-NMR spectrum of **6** in acetone-d$_6$ at r.t. consists of a doublet at 32.4 ppm as a result of the coupling of the magnetically equivalent phosphorus nuclei of diop with the rhodium center ($^1J(^{103}Rh,^{31}P) = 158.6$ Hz). The PF_6^- signal is split into a septet at −142.6 ppm ($^1J(^{19}F,^{31}P) = 707.8$ Hz).

3. Discussion of the results of the catalyses

To test the catalytic activity and the enantioselectivity of compound **6** it was used in four different model systems of enantioselective catalysis. To obtain information about the influence of the μ_2-H bridged ligand **5** in complex **6** a comparison between the isolated catalyst **6** and the in situ systems **1**/**2** and **1**/**2**/**5** was made for some catalytic systems. Compound **1** can be regarded as the procatalyst, **2** as the ligand with the chiral information in the backbone and **5** as an achiral coligand. The values of the enantiomeric excess obtained with the catalytic system **1**/**2** were used to control whether the values published in the literature could be reproduced.

3.1. Hydrogenation of (*Z*)-α-*N*-acetamidocinnamic acid

The enantioselective hydrogenation of the standard substrate (*Z*)-α-*N*-acetamidocinnamic acid to give *N*-acetylphenylalanine with rhodium(I) complexes is es-

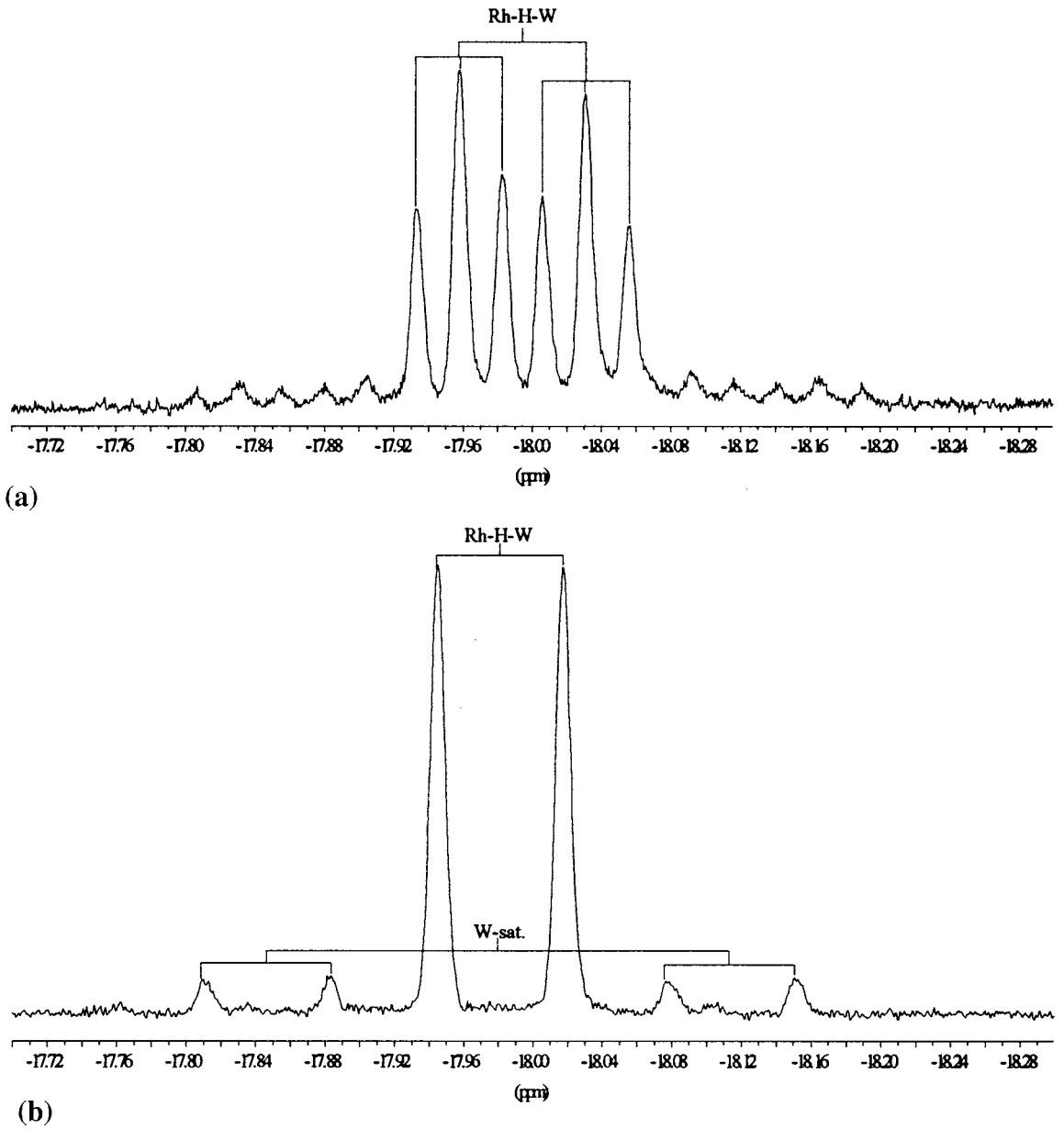

Fig. 1. Hydride region of (a) 400 MHz ^{1}H-NMR spectrum of **6** in acetone-d_6 at r.t.; (b) 400 MHz ^{1}H{^{31}P}-NMR spectrum of **6** in acetone-d_6 at r.t.

tablished to test new ligands or catalysts [5,11–13]. The catalysis as well as the determination of the chemical and optical yield was carried out as described [5]. Table 1 summarizes the reaction conditions and results.

With an optical induction of 82.0% ee (no. 1) the literature value of 80.9% ee (no. 4) [5] was reproduced for the in situ catalyst system **1**/**2**. The colour of the in situ system **1**/**2**/**5** with the metallocenedihydride **5** as a coligand was orange under nitrogen (similar to the system **1**/**2**) but turned green after an hour under working conditions in hydrogen atmosphere. Thus, the formation of **6** in solution must be assumed. However, the ee of 82.5% (no. 2) was within the limits of error of no. 1. The hydrogenation with the isolated complex **6** (no. 3) gave a slightly higher optical yield (average 83.9%). The short reaction time in the hydrogenation with **6** could be attributed to the missing induction period required to remove the 1,5-cyclooctadiene ligand from the procatalyst **1**. The hydrogenations were stopped when there was no further change in the level of the gas burette (a relative unprecise measure).

3.2. Hydrogenation of ketopantolactone

The hydrogenation of ketopantolactone to pantolactone was carried out as described [1,14,15]. The enan-

Table 1
Enantioselective hydrogenation of (*Z*)-α-*N*-acetamidocinnamic acid to *N*-acetylphenylalanine at room temperature and 1.1 bar of hydrogen pressure in methanol[a]

No.	Procatalyst or catalyst	Ligand/coligand	Reaction time (h)	Conversion (%)	ee (Configuration) (%)	Runs
1	**1**	**2**	19	>99	82.0 (*R*)-(−)	1
2	**1**	**2**/**5**	19	>99	82.5 (*R*)-(−)	1
3	**6**	–	0.75	>99	83.9 (*R*)-(−)	4
4[5]	**1**	**2**	24	>99	80.9 (*R*)-(−)	6

[a] Ratio catalyst:substrate 1:200, ratio [Rh]:ligand:substrate 1:1.1:200, ratio [Rh]:ligand:coligand:substrate 1:1.1:1.1:200.

Table 2
Enantioselective hydrogenation of ketopantolactone to pantolactone at 50°C and 50 bar of hydrogen pressure in toluene[a]

No.	Catalyst	Reaction time (h)	Conversion (%)	ee (Configuration) (%)	Runs
5	**6**	96	>99	55.4/54.7 (*R*)-(−)	2
6[1]	**1**/**2**	44	>99	53.2 ± 0.2 (*R*)-(−)	2

[a] Ratio catalyst:substrate 1:200.

tioselectivity of **6** is about 3% higher (Table 2) than that of the procatalyst/ligand system **1**/**2** given in the literature [1].

3.3. Hydrosilylation of acetophenone

The hydrosilylation system rhodium(I)-acetophenone-diphenylsilane is well established [6,16–18]. It involves the oxidative addition of a Si–H bond to the carbonyl function of acetophenone yielding the optically active silylalkyl ether, the acidic hydrolysis of which leads to the chiral alcohol 1-phenylethanol. Work-up and analysis was carried out as published [16]. The enantioselectivity obtained with compound **6** (no. 9) was 28.9% ee. The values for the in situ catalysts (no. 7, 8) were about 2% lower but they were in the same range as a similar literature system (no. 10) [19] for which details on temperature, solvent and catalyst/substrate ratio have not been given. In all of these reactions no silylenol ether was formed which is a frequent by-product in the hydrosilylation of enolizable ketones [18] (Table 3).

3.4. Isomerization of 2-n-butyl-4,7-dihydro-1,3-dioxepin

In the asymmetric double-bond isomerization of 2-*n*-butyl-4,7-dihydro-1,3-dioxepin the double bond is shifted from the allyl to the vinyl position [7,20]. The in situ system **1**/**2** gave 12% ee [20] as can be seen in Table 4 (no. 12). The enantioselectivity of the catalyst **6** was comparable (no. 11).

Summarizing the results obtained with the isolated catalyst **6** in the four different catalytic systems it must be stated that **6** gave almost the same enantioselectivity as the in situ catalysts **1**/**2** and **1**/**2**/**5**. Thus, it must be assumed that during the catalysis with **6** the $(\mu_2\text{-H})_2$ bridged metallocenehydride ligand **5** dissociates [2,21–23], leaving the fragment Rh(−)-diop as the actual catalyst [2,23].

4. Experimental

All complexes were prepared under an atmosphere of dried nitrogen using standard Schlenk techniques. Solvents were dried and distilled prior to use according to standard procedures. IR spectra were recorded on a Beckman IR 4240 spectrometer. ^{1}H-, ^{1}H{^{31}P}- and ^{31}P{^{1}H}-NMR spectra were obtained on a Bruker ARX 400 spectrometer (400.13 MHz (^{1}H) and 161.98 MHz (^{31}P)). Chemical shifts are in ppm downfield from TMS or 85% H_3PO_4, respectively. FD mass spectra were determined on a Finnigan MAT 95 instrument. Literature methods were used to prepare (−)-diop (**2**) [3,4], $[Rh(cod)Cl]_2$ (**1**) [24], Cp_2WH_2 (**5**) [25] and {Rh(cod)[(−)-diop]}PF_6 (**3**) [26,27].

4.1. {[(−)-diop]Rh(μ_2-H)$_2$WCp$_2$}PF$_6$ (6)

The complex {Rh(cod)[(−)-diop]}PF_6 (**3**) (0.86 g, 1.00 mmol) was dissolved in 10 ml of acetone. The dinitrogen atmosphere was replaced by dihydrogen (1.1 bar). After 4 h of stirring the orange colour of the solution had deepened due to the formation of the solvent complex **4**. Then, a suspension of Cp_2WH_2 (**5**) (0.35 g, 1.10 mmol) in 20 ml of acetone was added. Immediately, the solution turned green. It was stirred for 1 h and subsequently concentrated to 5 ml and purified by chromatography on silica with toluene/acetone 4:1. An excess of **5** was eluted as a yellow band

Table 3
Enantioselective hydrosilylation of acetophenone with diphenylsilane in the temperature range from 0°C to room temperature without solvent in an argon atmosphere[b]

No.	Procatalyst or catalyst	Ligand/coligand	Reaction time (h)	Conversion[a] (%)	Amount of silylenol ether[a] (%)	ee (Configuration) (%)	Runs
7	**1**	**2**	22	89/94	0/0	26.4/26.9 *R*-(+)	2
8	**1**	**2**/**5**	22	97/97	0/0	25.1/26.6 *R*-(+)	2
9	**6**	–	20	94/96	0/0	28.2/29.4 *R*-(+)	2
10[19]	**1**	**2**	–	–	–	30 *R*-(+)	–

[a] Complete conversion of diphenylsilane. Conversion, yield of acetophenone. No silylenol ether was formed.
[b] Ratio catalyst:substrate 1:200, ratio [Rh]:ligand:substrate 1:1.1:200, ratio [Rh]:ligand:coligand:substrate 1:1.1:1.1:200.

Table 4
Enantioselective isomerization of 2-*n*-butyl-4,7-dihydro-1,3-dioxepin with $NaBH_4$ at room temperature in THF/methanol 2:1[a]

No.	Catalyst or procatalyst	Ligand	Reaction time (h)	Conversion (%)	Degree of isomerizaton (%)	e.e. (Optical rotation) (%)	Runs
11	**6**	–	24	>99	>99	10.2/11.5 (+)	2
12[20]	**1**	**2**	24	>99	>85	12 (+)	–

[a] Ratio catalyst:$NaBH_4$:substrate 1:26:200, ratio [Rh]:ligand:$NaBH_4$:substrate 1:4:26:200.

followed by the main product **6** as a green band and a by-product as a red band. Deep green crystals were obtained from acetone. Yield 0.59 g (55%), m.p. 150°C (dec.). Anal. Found: C, 46.83; H, 4.21. $C_{41}H_{44}F_6O_2P_3RhW$ (1062.5). Calc.: C, 46.35; H, 4.17. IR (KBr, cm^{-1}): 3090w (arom. C–H, Cp), 3020w (arom. C–H, Ph), 2950, 2890w (aliph. C–H), 1625m (vbr) (bridging Rh–H–W), 1410w (arom. C=C, Cp), 810vs (P–F). ^{1}H-NMR (acetone-d_6): δ 7.08–8.07 (m, 20H, Ph–H), 5.20 (brs, 10H, cp–H), 3.65 (m, 2H, CH^{diop}), 2.86 (m, 2H, CH_2^{diop}), 2.69 (m, 2H, CH_2^{diop}), 1.14 (s, 6H, CH_3^{diop}), −17.99 (dt, $^1J(^{103}Rh,^1H) = 29.1$ Hz, $^2J(^{31}P,^1H) = 10.0$ Hz, $^1J(^{183}W,^1H) = 107.3$ Hz, 2H, Rh–H–W). $^{31}P\{^1H\}$-NMR (acetone-d_6): δ 32.4 (d, $^1J(^{103}Rh,^{31}P) = 158.6$ Hz, 2P, Rh–P), −142.6 (m, $^1J(^{19}F,^{31}P) = 707.8$ Hz, 1P, PF_6).

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