ELSEVIER

Journal of Organometallic Chemistry 532 (1997) 243–249

Journal of Organometallic Chemistry

IX. [1]Mono- and biphasic asymmetric hydroformylation with rhodium catalysts of the diphosphine ligand NAPHOS and its sulfonated derivatives [2]

Robert W. Eckl, Thomas Priermeier, Wolfgang A. Herrmann *

Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Received 22 August 1996

Abstract

Both enantiomers of the diphosphine 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthyl NAPHOS were prepared by resolution of the racemic *P,P'*-dioxide and subsequently applied in the rhodium-catalyzed, asymmetric hydroformylation of styrene. Optically active, highly water-soluble derivatives BINAS were prepared by direct sulfonation of the enantiopure diphosphine NAPHOS and applied in aqueous/organic, two-phase hydroformylation of styrene. The catalytically active rhodium complexes $HRh(CO)_2(P-P)$ of both NAPHOS and BINAS were prepared and characterized by infrared and NMR spectroscopy. Optical yields are lower in two-phase hydroformylation compared with the conventional single-phase (organic solvent) technique.

Keywords: Water-soluble phosphines; Rhodium; Biphasic catalysis; Hydroformylation; Asymmetric catalysis

1. Introduction

Rhodium-catalyzed asymmetric hydroformylation, as one of the most practical approaches to enantioselective carbon–carbon coupling, continues to be a major challenge in catalysis [1]. Academic interest in this topic was re-invigorated after Takaya's breakthrough in 1993 [2]. Using biaryl-based phosphine–phosphite ligands such as BINAPHOS **A**, various substrates were converted into the desired aldehydes with enantioselectivities up to 95% *ee* and decent regioselectivity [3]. Similar chiral diphosphite ligands were successfully employed in styrene hydroformylation by van Leeuwen and coworkers [4] after DuPont had disclosed comparable bisphosphite-type ligands based on (2*R*,4*R*)-pentane-2,4-diol **B** [5].

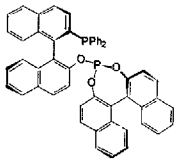
By way of contrast, all chiral diphosphine ligands tested so far in asymmetric hydroformylation as rhodium catalysts gave disappointing enantioselectivities. For styrene as the most thoroughly investigated substrate, enantiomeric excesses remained below 30% [1], with the best value resulting from an Rh/DBP–DIOP catalyst [6]. As a matter of fact, almost all bisphosphines applied up to now form five- to seven-membered chelate rings with rhodium, while the diphosphites and phosphine–phosphite ligands mentioned above give rise to eight- or nine-membered interchelate rings. To this day only one bidentate phosphine capable of forming nine-membered rings was examined in asymmetric hydroformylation of styrene and vinylacetate: in situ rhodium-catalysts of the ligand (2*S*,5*S*)-NORBORNYL **C**, for which a natural bite angle of 123° was calculated, converted styrene in 97% selectivity into the branched aldehyde; however 'no significant asymmetry' was reported for the product obtained at 30 °C [7].

* Corresponding author.

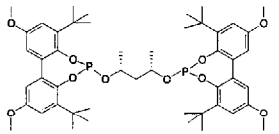
[1] Water-Soluble Metal Complexes and Catalysts, Part 9. Part 8: W.A. Herrmann, G.P. Albanese, R.B. Manetsberger, H. Bahrmann and P. Lappe, *Angew. Chem., 107* (1995) 893; *Angew. Chem., Int. Ed. Engl., 34* (1995) 811.

[2] Dedicated to the memory of the late Professor Hidemasa Takaya.

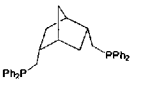
PII S0022-328X(96)06745-9



A
phosphine/phosphite



B
phosphite/phosphite



C
phosphine/phosphine

The natural bite angle concept was used to explain the regioselectivity in the hydroformylation of aliphatic olefins. According to Casey et al. [8], diphosphines with a wide bite angle near 120° favour eq–eq coordination and increase the fraction of the linear aldehyde.

The preferred coordination mode of chelating ligands also seems to be of pivotal importance for the asymmetric induction during hydroformylation [2,4].

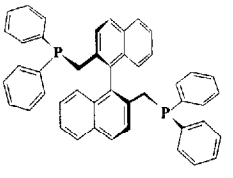
Following our earlier work on biphasic hydroformylation [9–14], we now report on enantiopure diphosphine ligands and their application in the hydroformylation of styrene.

2. Results and discussion

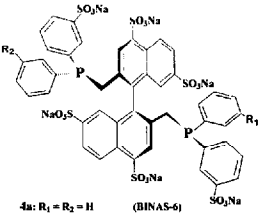
NAPHOS **1** was originally prepared by Kumada and coworkers [15] and it indeed represented the first diphosphine ligand based on the axially chiral 1,1'-binaphthyl backbone [16]. *S*-(−)-**1** has been prepared in a multi-step reaction via *S*-(−)-2,2'-bis(bromomethyl)-1,1'-binaphthalene, but the asymmetric induction of the chiral diphosphine was unsatisfactory in catalytic hydrogenation, hydrosilylation and Grignard cross-coupling.

2.1. Separation of stereoisomers

We took a simple and efficient access to both enantiomers of **1**. Several routes via asymmetric synthesis [17] or resolution [18] to optically pure precursors of NAPHOS are known, but resolution of phosphine oxides is still the most practical and promising method of preparing chiral diphosphines [19].



1 (NAPHOS)



4a: $R_1 = R_2 = H$ (BINAS-6)
4b: $R_1 = H$, $R_2 = SO_3Na$ (BINAS-7)
4c: $R_1 = R_2 = SO_3Na$ (BINAS-8)

Moreover, the highest yield synthesis of NAPHOS occurs through the *P*,*P'*-dioxide **2** [20]. We found that (±)-**2** is efficiently resolved via complexation with 2,3-di-*O*-benzoyl-tartaric acid (Section 4). The efficiency of the resolution step is proven by the X-ray structure determination of *S*-(−)-**2**-(−)-2,3-*O*-dibenzoyl-*L*-tartrate, which elucidates that crystals are made up of polymer chains and not, as one might have expected, of cyclic adducts which would correspond to a chelating way of binding (Fig. 1). The diphosphine dioxide and the tartaric acid are connected in a regularly alternating way through two intermolecular hydrogen bondings [P(1)–O(1) 1.50 Å, O(1)–O(2) 2.495 Å, O(1)–H(1)–O(2) 164°] between the oxygen atoms at the phosphorus and the hydrogen atoms of the carboxylic groups. This arrangement results in a helical polymeric

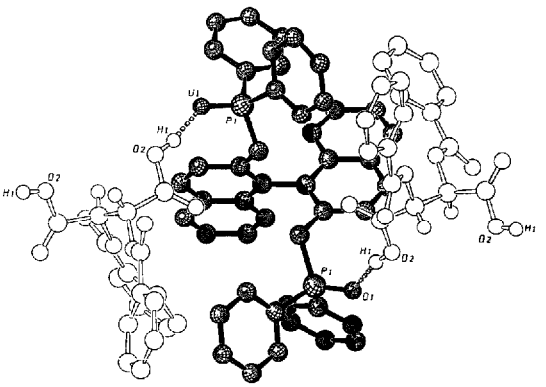
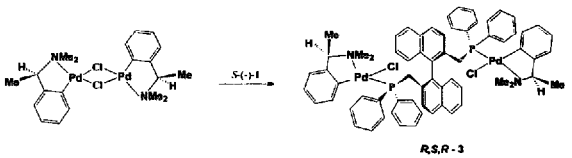


Fig. 1. SCHAKAL representation of *S*-(−)-(**2**)-(−)-2,3-*O*-dibenzoyl-*L*-tartrate. All hydrogen atoms except those contributing to hydrogen bonds or indicating chirality are omitted for clarity.

structure, to which the low solubility of this 1:1 complex can be attributed. Zhang et al. [21] obtained a similar, but non-helical, adduct by reacting Cy–BINAPO with (2*R*,3*R*)-dibenzoyltartaric acid (hydrogens were not refined). The absolute configuration of (−)-NAPHOSO was assigned as *S*, as indicated by the refinement of the enantiopole parameter [22] and by correlation with the (2*R*,3*R*)-configuration of the dibenzoyltartaric acid.

Reduction of the enantiopure *P*,*P*′-dioxides by standard procedures ($HSiCl_3$, $HNEt_2$) affords *S*-(−) and *R*-(+)-NAPHOS. The enantiomeric purity of the latter was checked by equimolar reaction with the cyclometallated dinuclear complex $[Pd_2Cl_2((R)\text{-}o\text{-}C_6H_4CHMeNMe_2)_2]$, known as 'reporter complex' (Eq. (1)) [23]. The formation of the kinetically favoured binuclear phosphine-bridged species **3** allows an easy determination of optical purity by ^1H NMR spectroscopy in this special case. Especially the diastereotopic methylene protons of **1** give rise to sufficiently separated signals in the palladium complexes *R*,*S*,*R*-**3** and *R*,*R*,*R*-**3**.



R,S,R-3

(1)

2.2. Sulfonation

Direct sulfonation of enantiopure *S*-(−)-NAPHOS under conditions reported previously [24] yields the eight-fold sulfonated species *S*-(−)-BINAS-8 **4a** (80–90% yield) accompanied by small amounts of seven- **4b** and six-fold **4c** functionalized derivatives as highly water-soluble sodium salts.

The *P*-chirality of **4b** and **4c** in addition to atropisomerism gives rise to the formation of diastereomers, thus complicating the ^{31}P NMR spectra. The precise ratios of different BINAS species **4a–c** can be determined by capillary electrophoresis [25], even traces of *P*-mono- and *P*,*P*′-dioxides (mainly due to sample preparation under atmospheric conditions) of different BINAS isomers may be detected and separated by virtue of this sensitive method.

2.3. Catalysis

The diphosphines *S*-(−)-NAPHOS **1** and *S*-(−)-BINAS **4a** were applied in homogeneous and biphasic (water/organic) rhodium-catalyzed asymmetric hydro-

Table 1
Rhodium-catalyzed hydroformylation of styrene

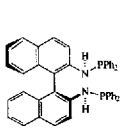
Ligand	Solvent	S/C [a]	L/[Rh]	p (bar) [b]	T (°C)	Time (h)	% Converted [c]	%i [c]	%ee
1	toluene	300	3	100	40	24	53	83	34(*S*)
1	toluene	500	3	70	40	40	89	96	32(*S*)
4	toluene MeOH, H_2O	300	4	100	40	25	92	95	18(*S*)
R-(+)-BDPAP	toluene	500	3	80	50	24	98	97	0
R-(+)-BDPAP	toluene	300	3	100	25	18	52	98	0
R-(+)-BPNAP [d]	toluene	80	1.5	7	110	20	96	100	0

[a] S/C: substrate/[Rh] ratio.
[b] 1:1 mixture of H_2 and CO.
[c] Conversion and *i*/*n* ratio determined by GLC and ^1H NMR.
[d] Ref. [28], substrate α-methylstyrene.

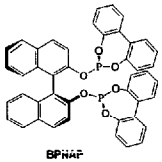
formylation of styrene. When *S*-(−)-**1** is used as catalyst ligand in the homogeneous phase (toluene, dichloromethane) the desired branched aldehyde showed up with selectivities of up to 96%, while the enantioselectivity (*S*-hydratropaldehyde) was in the range 32–34% *ee*. Although far too low for practical purposes, comparison with other diphosphines shows these values to be the highest ever achieved with a chiral diphosphine ligand. Moreover, as mentioned above, only one chiral bisphosphine with comparable large bite angle, flexibilty and chelate ring size has been tested in this reaction before.

Two-phase hydroformylation of styrene (CH_3OH–H_2O/toluene) with in situ catalysts prepared from $Rh(CO)_2(acac)$ and *S*-(−)-BINAS **4a** proceeds with good regioselectivity for 2-phenylpropionaldehyde (95%) and an enantioselectivity of 18% *ee*. This result follows the trend observed in almost all other catalytic asymmetric reactions, where application of water-soluble catalysts normally lowers optical induction [9]. However, our study shows that enantioselective hydroformylation is generally feasible in a biphasic reaction medium. Catalyst recovery and recycling is easily achieved by phase separation. Activity and asymmetric induction show no significant decrease after two runs. Asymmetric hydroformylation with a chiral sulfonated phosphine ligand was in fact attempted before [26], but only racemic aldehydes were obtained under conditions similar to those reported in the present paper.

We also prepared the axially chiral diphosphine *R*-(+)-BDPAP, which is easily obtained from commercially available *R*-(+)-2,2′-diamino-1,1′-binaphthalene. It is similar to NAPHOS in terms of bite angle and chelate ring size. Although this aminophosphine ligand provides good enantioselectivity in asymmetric hydrogenation of α-acylaminoacrylic acids and esters [27] (up to 89% *ee*), it failed in our hands with regard to asymmetric styrene hydroformylation (Table 1). Recent work of Gladfelter and coworker [28] shows poor performance of the phosphite ligand *R*-(+)-BPNAP derived from 1,1′-binaphthol in hydroformylation of vinylarenes; with α-methylstyrene as substrate 3-phenylbutyraldehyde was formed exclusively, but the product was racemic in all cases [28].



BDPAP


BPNAP

2.4. Spectroscopy of rhodium complexes

The solution structures of catalytically active hydridorhodium(I) complexes $HRh(CO)_2(P\text{–}P)$ with the diphosphine NAPHOS **1** and the water-soluble derivative **4** were established by means of NMR and infrared spectroscopy. They were prepared from equimolar mixtures of diphosphine and $Rh(CO)_2(acac)$ under typical hydroformylation conditions in appropriate solvents (Section 4). In both cases only a single rhodium species with bis-equatorially coordinating diphosphine was observed under atmospheric pressure of H_2/CO. In the

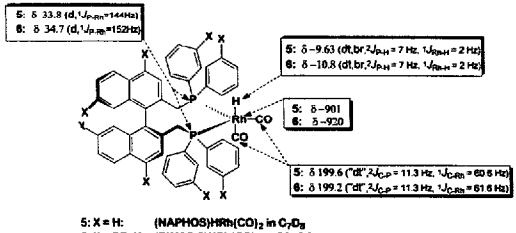


Fig. 2. ^{103}Rh{^{1}H}-^{31}P-HMQC NMR, ^{31}P{^{1}H} NMR, ^{13}C{^{1}H} NMR and ^{1}H NMR of diphosphine rhodium complexes **5** and **6**.

presence of syngas no decomposition is detected over several days. ^{31}P, ^{1}H, ^{13}C NMR and IR data of complexes of **1** and **4a** (**5** and **6**; Fig. 2) compare well with those reported for $HRh(CO)_2$(BISBI) [8], which was observed among other species after displacement of triphenylphosphine from HRh(CO)(TPP)(BISBI) with carbon monoxide.

Spectroscopic data of rhodium complexes of **1** and **4a** are quite similar; even the ^{103}Rh chemical shifts differ only a little ($\Delta\delta = 19$ ppm).

3. Conclusion

The present work provides the first example of an asymmetric hydroformylation with a water-soluble rhodium catalyst. Comparison with the non-functionalized, lipophilic diphosphine NAPHOS shows again that two-phase conditions influence the stereochemical result in a negative way. Nevertheless, NAPHOS and its water-soluble counterpart perform better than hitherto tested phosphine ligands based on the atropisomeric 1,1'-binaphthyl backbone.

4. Experimental section

All reactions were performed with standard Schlenck techniques in oxygen-free nitrogen atmosphere. Solvents were dried with standard methods and distilled under N_2. Infrared spectra were recorded on a Perkin–Elmer 1600 series FTIR spectrometer, the ^{1}H, ^{13}C and ^{31}P NMR spectra at 400, 100.5 and 161.8 MHz respectively on an FT Jeol JNM GX 400 and Bruker AMX 400 instrument. Optical rotations were measured on a Perkin–Elmer 241 polarimeter. Enantiomeric excesses of the aldehydes were measured on a Chrompack CP 9000 gas chromatograph (split/splitless injector, 50 m Lipodex A column, flame ionisation detector) after reduction to the corresponding alcohols and the absolute configuration was determined by comparison of the retention times with (*R*)-(+)-2-phenylpropanol. Hydroformylation reactions were carried out in a Roth 250 ml and Haage 200 ml stainless-steel autoclave. Commercial styrene (99%) was filtered through Al_2O_3 prior to use. [Pd_2Cl_2((*R*)-*o*-$C_6H_4CHMeNMe_2$)$_2$] [29], $Rh(CO)_2$(acac) [30] and (±)-NAPHOSO (NAPHOS-*P*,*P'*-dioxide) [15,20] were prepared as described previously. Elemental analyses were performed in the microanalytical laboratory of our institute.

4.1. Resolution of (±)-2,2'-bis(diphenyloxyphosphinomethyl)-1,1'-binaphthalene (±)-2

To a boiling solution of 30 g (43.9 mmol) racemic NAPHOSO **2** in 250 ml $CHCl_3$ was added a solution of 15.75 g (−)-*R*,*R*-Di-*O*-benzoyl-tartaric acid (43.9 mmol, 1 equiv.) in 130 ml ethylacetate. The mixture was boiled for 15 min and then concentrated on a hot plate to about 70% of its volume and allowed to cool to ambient temperature. The next day colourless crystals of *S*-(−)-NAPHOSO-*R*,*R*-(−)-dibenzoyltartrate **2a** were collected by suction filtration, washed with cold ethylacetate and dried at room temperature (0.1 mm). Yield 18.7 g (82% based on *S*-(−)NAPHOSO). M.p. 234–235 °C (decomp.). $[\alpha]_D^{25}$ −60° (c 0.5, EtOH). ^{1}H NMR ($CDCl_3$): $\delta = 3.13$–3.26 ppm (m, CH_2, 4H), 5.93 ppm (s, C*H*OCO, 2H), 6.73–7.99 ppm (m, 46H), 12.34 ppm (br, COO*H*, 2H). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 32.2$ ppm (s, 2P). IR (KBr, cm^{-1}): ν(Aryl–H): 3048(m), 745(st), 690(m); ν(Aryl–P): 1433(st). Anal. Found: H, 4.95; C, 73.36; P, 5.82. $C_{64}H_{50}O_{10}P_2$ Calc.: C, 73.84; H, 4.84; O, 15.37; P, 5.95%. This complex was suspended in 400 ml NaOH (0.8 N), extracted twice with chloroform (200 ml) and the combined organic layers washed with 100 ml of NaOH (0.8 N), twice with water and dried over anhydrous magnesium sulfate. Evaporation of solvent yielded 11.9 g *S*-(−)-NAPHOSO (white foam, 97% based on **2a**). M.p. 237–238 °C. $[\alpha]_D^{25}$ −134° (c 0.4, benzene). Analogous treatment of the mother liquor from the first crystallization to remove *R*,*R*-(−)-DBT yielded 16.8 g of *R*-(+)-**2** enriched NAPHOSO: $[\alpha]_D^{25}$

+98° (c 0.4, benzene), which was treated with 8.8 g *S,S*-(+)-Di-*O*-benzoyltartaric acid (24.6 mmol, 1 equiv.) in 60 ml ethylacetate. Work-up of crystalline material afforded 19.2 g of tartrate **2b** (84% based on **2**). M.p. 234–235 °C (decomp.). $[\alpha]_D^{25}$ +59° (c 0.5, EtOH). Separation of acid furnished 12.3 g *R*-(−)-**2** (98% based on complex **2b**). M.p. 237–238 °C. $[\alpha]_D^{25}$ +130° (c 0.4, benzene).

4.2. X-ray structure of 2a

Orthorhombic crystal system, space group $C222_1$ (No. 20), $a = 1537.7(2)$, $b = 1681.9(1)$, $c = 2137.7(2)$ pm, $V = 5528(1) \times 10^6$ pm^3, $Z = 4$, $\rho_{calc} = 1.251$ g cm^{-3}, $\mu = 1.4$ cm^{-1}, $F_{000} = 2176$; (graphite monochromated Mo Kα), measurement at −80 °C. Enraf–Nonius CAD-4, range of measurement $2° < 2\Theta < 50°$, ω-scan, scan width $(1.0 + 0.2 \tan \Theta)°$ (±25%) before and after each reflection to determine the background, $t_{max} = 60$ s, 5503 measured reflections ($h, k, \pm l$), 4581 independent reflections with $I > 0$, structure determination with direct methods and subsequent difference Fourier syntheses, empirical absorption correction based on Ψ-scan data, transmission coefficients 0.958–1.0, 443 least-squares parameters, all 38 heavy atoms with anisotropic thermal parameters, all 25 hydrogen atoms found and independently refined (isotropic), anomalous dispersions accounted for, shift/error < 0.0001, $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.044$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.023$, residual electron density +0.34 Δe Å^{-3} (87 pm besides P1)/−0.35 Δe Å^{-3}, weighting scheme according to Prince [31] with four refined parameters. All calculations were performed on a DECstation 5000/25 using the programs CRYSTALS [32] and PLATON [33]. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany on quoting the depository number CSD-406233, the names of the authors and the journal citation.

4.3. Di-μ-chloro-μ-[2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthalene)-bis[(R)-N,N-dimethyl-α-phenylethylamine-C^2,N]-dipalladium(II) (3)

^{1}H and ^{31}P NMR determination of enantiomeric purity of **1**: 15 mg (0.025 mmol) of $[Pd_2Cl_2((R)\text{-}o\text{-}C_6H_4CHMeNMe_2)_2]$ and 16 mg (0.025 mmol, 1 equiv.) of *S*-(−)-**1** or *R*-(+)-**1** were dissolved in 3 ml of $CDCl_3$. The solution was then filtered through Celite.

R,R,R-(3). ^{1}H NMR ($CDCl_3$): $\delta = 1.80$ ppm (6H, d, $^3J(H,H) = 6.0$ Hz, $CHCH_3$), 2.74 ppm (6H, s, NCH_3), 2.97 ppm (6H, s, NCH_3), 3.31 ppm (2H, "tr", $^2J(H,H) = 14.7$ Hz, $^2J(P,H) = 15.3$ Hz, CH_aH_b), 3.83 ppm (1H, m, $CHCH_3$), 4.02 ppm (2H, "tr", $^2J(H,H) = 14.7$ Hz, $^2J(P,H) = 15.3$ Hz, CH_aH_b), 6.0–7.3 ppm (m, 30H), 7.41 ppm (4H, "tr", $^3J(H,H) = 8.0$ Hz, $^3J(H,H) = 7.5$ Hz), 7.75 ppm (2H, d, $^3J(H,H) = 8.0$ Hz), 7.95 ppm (2H, d, $^3J(H,H) = 9.0$ Hz), 9.50 ppm (2H, d, $^3J(H,H) = 8.5$ Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 30.0$ ppm (s, 2P).

R,S,R-(3). ^{1}H NMR ($CDCl_3$): $\delta = 1.90$ ppm (6H, d, $^3J(H,H) = 6.0$ Hz, $CHCH_3$), 2.82 ppm (6H, s, NCH_3), 2.88 ppm (6H, s, NCH_3), 3.19 ppm (2H, "tr", $^2J(H,H) = 14.7$ Hz, $^2J(P,H) = 15.3$ Hz, CH_aH_b), 4.34 ppm (2H, "tr", $^2J(H,H) = 14.7$ Hz, $^2J(P,H) = 15.3$ Hz, CH_aH_b), 6.0–7.3 ppm (m, 48H), 7.55 ppm (4H, "tr", $^3J(H,H) = 8.0$ Hz, $^3J(H,H) = 7.5$ Hz), 7.73 ppm (2H, d, $^3J(H,H) = 8.0$ Hz), 7.91 ppm (2H, d, $^3J(H,H) = 9.0$ Hz), 9.60 ppm (2H, d, $^3J(H,H) = 8.5$ Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 30.5$ ppm (s, 2P).

4.4. Preparation of diphosphine rhodium(I) complexes

A solution of 8 mg (0.03 mmol) acetylacetonatodicarbonyl–rhodium(I) and 1.1 equiv. of the diphosphine (**1** in [$^2H_8$]-toluene; **4a** in [$^2H_4$]-methanol) in a 5 mm NMR tube (equipped with a Young valve) was degassed by three freeze–thaw cycles and afterwards purged with syngas (H_2/CO 1:1). After heating to 50 °C for 2 h, NMR spectra were recorded. Alternatively an equimolar mixture of diphosphine and $Rh(CO)_2$(acac) in an appropriate solvent was transferred into an evacuated autoclave and preformed as above. After depressurizing, NMR and infrared spectra were recorded immediately.

5 $HRh(CO)_2$(NAPHOS). ^{31}P{^{1}H} NMR (C_7D_8): $\delta = 33.8$ ppm (d, $^1J(Rh,P) = 144$ Hz). ^{1}H NMR: $\delta = -9.63$ ppm (dt, $^2J(P,H) = 7$ Hz, $^1J(Rh,H) = 2$ Hz, Rh–H), 3.8 ppm (d, 2H, CH_a, $^2J(H,H) = 12.7$ Hz), 3.99 ppm (m, 2H, CH_b), 6.5–7.7 ppm (m, 28H). ^{13}C{^{1}H} NMR: $\delta = 199.6$ ppm ("dt", $^2J(P,C) = 11.3$ Hz, $^1J(C,Rh) = 60.6$ Hz, 2C, CO). ^{103}Rh{^{1}H} NMR: $\delta = -901$ ppm ^{31}P (HMQC). IR ($CHCl_3$, cm^{-1}): ν_{CO} 2077 (vs), 2014 (vs); ν_{Rh-H} 1978 (st).

6 $HRh(CO)_2$(BINAS-8). ^{31}P{^{1}H} NMR (CD_3OD): $\delta = 34.7$ ppm (d, $^1J(Rh,P) = 152$ Hz). ^{1}H NMR: $\delta = -10.8$ ppm (dt, $^2J(P,H) = 7$ Hz, $^1J(Rh,H) = 2$ Hz, Rh–H), 3.8 ppm (d, 2H, CH_a, $^2J(H,H) = 12.7$ Hz), 3.99 ppm (m, 2H, CH_b), 6.5–7.7 ppm (m, 20H). ^{13}C{^{1}H} NMR: $\delta = 199.2$ ppm ("dt", $^2J(P,C) = 11.3$ Hz, $^1J(C,Rh) = 61.6$ Hz, 2C, CO). ^{103}Rh{^{1}H} NMR: $\delta = -920$ ppm ^{31}P (HMQC). IR (KBr, cm^{-1}): ν_{CO} 2041 (vs), 1981 (vs).

Assignments of NMR data of **5** and **6** are given in Fig. 2.

Acknowledgements

This work was supported by the Bundesministerium für Bildung und Forschung (Bonn, Germany) and Hoechst AG (Frankfurt am Main, Werk Ruhrchemie, Oberhausen, Germany). Petra Ankenbauer is gratefully

acknowledged for skilful experimental assistance and Dr. W. Baumann (Universität Rostock) is thanked for recording ^{103}Rh NMR spectra.

References

[1] F. Agbossou, J.-F. Carpentier and A. Mortreux, *Chem. Rev.*, *95* (1995) 2485; S. Gladiali, J.C. Bayon and C. Claver, *Tetrahedron Asymm.*, *6* (1995) 1453.

[2] N. Sakai, S. Mano, K. Nozaki and H. Takaya, *J. Am. Chem. Soc.*, *115* (1993) 7033; N. Sakai, K. Nozaki and H. Takaya, *J. Chem. Soc., Chem. Commun.*, (1994) 395.

[3] T. Higashizima, N. Sakai, S. Mano, K. Nozaki and H. Takaya, *Tetrahedron Lett.*, *35* (1994) 2023.

[4] G. Buisman, E.J. Vos, P.C.J. Kamer and P.W.N.M. van Leeuwen, *J. Chem. Soc., Dalton Trans.*, (1995) 405; G. Buisman, E.J. Vos, M.E. Martin, E.J. Vos, A. Klootwijk, P.C.J. Kamer and P.W.N.M. van Leeuwen, *Tetrahedron Asymm.*, *6* (1995) 719; G. Buisman, P.C.J. Kamer and P.W.N.M. van Leeuwen, *Tetrahedron Asymm.*, *4* (1993) 1625.

[5] J.E. Babin and G.T. Whiteker, *WO 93/03839*, *US*911,518, Union Carbide, 1992.

[6] T. Hayashi, M. Tanaka, Y. Ikeda and I. Ogata, *Bull. Chem. Soc. Jpn.*, *52* (1979) 2605.

[7] K. Yamamoto, S. Momose, M. Funahashi, S. Ebata, H. Ohmura, H. Komatsu and M. Miyazawa, *Chem. Lett.*, (1994) 189.

[8] C.P. Casey and G.T. Whiteker, *Israel. J. Chem.*, *30* (1990) 299; C.P. Casey, G.T. Whiteker, M.G. Melville, L.M. Petrovich, J.A. Gavney, Jr. and D.R. Powell, *J. Am. Chem. Soc.*, *114* (1992) 5535.

[9] W.A. Herrmann and C.W. Kohlpaintner, *Angew. Chem.*, *105* (1993) 1588; *Angew. Chem., Int. Ed. Engl.*, *32* (1993) 1524.

[10] W.A. Herrmann, C.W. Kohlpaintner, E. Herdtweck and P. Kiprof, *Inorg. Chem.*, *30* (1991) 4271.

[11] W.A. Herrmann, C.W. Kohlpaintner, H. Bahrmann and W. Konkol, *J. Mol. Catal.*, *73* (1992) 191.

[12] B. Cornils and W.A. Herrmann (eds.), *Applied Homogeneous Catalysis with Organometallic Complexes*, VCH, Weinheim, 1996, Chap. 4.1.

[13] W.A. Herrmann, C.W. Kohlpaintner, T. Priermeier and R. Schmid, *Organometallics*, *14* (1995) 1961.

[14] W.A. Herrmann, C.W. Kohlpaintner, R.B. Manetsberger, H. Bahrmann and H. Kottmann, *J. Mol. Catal. A: Chem.*, *97* (1995) 65.

[15] K. Tamao, H. Yamamoto, H. Matsumoto, N. Miyake, T. Hayashi and M. Kumada, *Tetrahedron Lett.*, *16* (1977) 1389.

[16] T. Hayashi, K. Hayashizaki, T. Kiyoi and Y. Ito, *J. Am. Chem. Soc.*, *110* (1988) 8153.

[17] N. Maigrot and J.-P. Mazaleyrat, *Synthesis*, (1985) 317.

[18] R. Noyori and H. Takaya, *Chem. Scri.*, *25* (1985) 83; C. Rosini, L. Franzini, A. Raffaeli and P. Salvadori, *Synthesis*, *6* (1992) 503.

[19] H. Brunner, W. Pieronczyk, B. Schönhammer, K. Streng, I. Bernal and J. Korp, *Chem. Ber.*, *114* (1981) 1137; H. Takaya, K. Mashima, K. Koyana, M. Yagi, H. Kumobayashi, T. Taketomi, S. Akutagawa and R. Noyori, *J. Org. Chem.*, *51* (1986) 629; H. Takaya, S. Akutagawa and R. Noyori, *Org. Synth.*, *51* (1989) 20.

[20] H. Bahrmann, K. Bergrath, H.-J. Kleiner, P. Lappe, C. Naumann, D. Peters and D. Regnat, *J. Organomet. Chem.*, *520* (1996) 97.

[21] X. Zhang, K. Mashima, K. Koyano, N. Sayo, H. Kumobayashi, H. Takaya and S. Akutagawa, *Tetrahedron Lett.*, *32* (1991) 7283.

[22] H. Flack, *Acta Crystallogr.*, *A39* (1983) 876.

[23] E.P. Kyba and S.P. Rines, *J. Org. Chem.*, *47* (1982) 4800; Q. Jiang, H. Ruegger and L.M. Venanzi, *J. Organomet. Chem.*, *488* (1995) 233.

[24] W.A. Herrmann, G.P. Albanese, R.B. Manetsberger, H. Bahrmann and P. Lappe, *Angew. Chem.*, *107* (1995) 893; *Angew. Chem., Int. Ed. Engl.*, *34* (1995) 811.

[25] W.A. Herrmann, G.P. Albanese and C. Schwer, *Inorg. Chem.*, in press.

[26] H. Ding, B.E. Hanson and J. Bakos, *J. Mol. Catal. A: Chem.*, *98* (1995) 117.

[27] S. Miyano, M. Nawa and H. Hashimoto, *Chem. Lett.*, (1980) 729.

[28] B. Moasser and W.L. Gladfelter, *Inorg. Chim. Acta*, *242* (1996) 125.

[29] N.K. Roberts and B.S. Wild, *J. Chem. Soc., Dalton Trans.*, (1979) 2015.

[30] Y.S. Varshavskii and T.G. Cherkasova, *Russ. J. Inorg. Chem.*, *12* (1967) 899.

[31] E. Prince, *Mathematical Techniques in Crystallography*, Springer, Berlin, 1982.

[32] D.J. Watkin, P.W. Betteridge and J.R. Carruthers, *CRYSTALS User Manual*, Oxford University Computing Laboratory, Oxford, 1986.

[33] A.L. Spek, The EUCLID Package, in D. Sayre (ed.), *Computational Crystallography*, Clarendon Press, Oxford, 1982, p. 528.