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Journal of Organometallic Chemistry 690 (2005) 1166–1171
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Highly enantioselective catalytic asymmetric ring opening reaction employing the Daniphos ligand

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Received 24 September 2004; accepted 3 November 2004
Available online 29 December 2004

Abstract

A set of the recently published planar-chiral Daniphos diphosphine ligands, based on an arene chromium tricarbonyl scaffold, has been applied to the rhodium-catalyzed asymmetric ring opening (ARO) reaction of 1,4-dihydro-1,4-epoxynaphthalene with methanol as the nucleophile. Enantioselectivities of up to 97.5% *ee* at satisfactory conversions have been obtained. The most successful ligand showed to be a $PPh_2/P(t\text{-}Bu)_2$-substituted derivative. An X-ray structure of this ligand is presented and discussed.

Keywords: Diphosphines; Rhodium; Asymmetric catalysis

1. Introduction

The search for new effective ligands for application in homogeneous transition-metal mediated asymmetric transformations remains one of the most prominent fields in organometallic chemistry. Recently we have reported on the synthesis and application of a novel planar-chiral diphosphine ligand for asymmetric catalysis based on an α-chiral arene chromium tricarbonyl scaffold, which can be synthesized in a modular, consecutive manner. It is referred to as Daniphos-ligand, the general structure is depicted in Fig. 1 [1,2].

After testing it in common enantioselective catalytic reactions like hydrogenation, hydrovinylation, allylic sulphonation and others [2], we searched for a new application of that ligand.

While the discovery of new reactions for stereoselective organometallic catalysis is somewhat rare, it is especially noteworthy that Lautens and co-workers [3] have reported recently on the development of a nucleophilic asymmetric ring opening (ARO) reaction of oxabenzonorbornadienes, achieving excellent results with different substrates and various kinds of nucleophiles. It reveals an interesting new application for chiral diphosphine ligands. Lautens had successfully employed the ferrocene-based Josiphos [4] class of ligands [5], which are structurally related to ours, so we found it challenging to test the Daniphos ligands with one of these substrates as well.

2. Results and discussion

We applied a choice of our ligands in the asymmetric ring opening of oxanorbornadiene using methanol as the nucleophile. It proceeds rhodium-catalyzed at a substrate-to-ligand ratio of 100:1 and a reaction time of 5 h at 80 °C. The reaction scheme is depicted in Scheme 1.

Fig. 2 summarizes the ligands that were employed in this investigation. For an easy nomenclature we use the

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doi:10.1016/j.jorganchem.2004.11.023

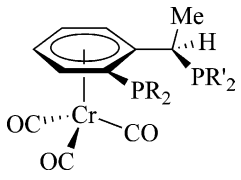


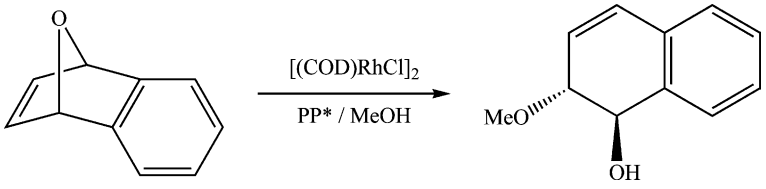
Fig. 1. The "Daniphos"-ligand.

following acronym system: PX_2/PY_2, in which PX_2 denotes the donor group in the *ortho*-position and PY_2 that in the α-position at the stereogenic center. According to that ligand **3** for instance is abbreviated to $PPh_2/P(i\text{-Bu})_2$ (see also Table 1). The ferrocene ligand **7** (*Josiphos*), which was also employed for reasons of comparison, is denoted as $Fc/PPh_2/PCy_2$.

The results obtained in this survey are depicted in Table 1 below.

As can be seen from the table the enantioselectivities achieved range from moderate to very good, with the best value of 97.5% *ee* obtained with ligand **4**. Taking into account that ligands were used that have the same backbone and differ only in the nature of the second donor group in the α-chain, it appears noteworthy that the values vary in a considerable range. This manifests the sensitivity of the reaction towards the steric and electronic properties of the ligands. Some striking effects can be found: while the "mother compound" PPh_2/PPh_2 **1** gives a respectable *ee* of 80.3% with a yield of 69%, these values drop dramatically when changing to ligand **2** $PPh_2/P(p\text{-FPh})_2$, which differs only in the fluorine substituent in *para*-position of the phenyl groups in the α-chain. This underlines vividly the outstanding effect that such an electron-withdrawing group has and one can conclude that this reaction prefers ligands which are more electron-rich. As the rest of the ligands are all alkyl-substituted no greater differences in their electron-donor ability are to be expected. Nonetheless their catalytic performance differs remarkably. So it might be assumed that this finding is due to steric effects, as the spatial demands of these alkyl-chains are dissimilar. This is best illustrated by a comparison of ligands **3** and **4**: while the sterically demanding and rigid $PPh_2/P(t\text{-Bu})_2$ **4** gives an excellent value of 97.5% *ee*, its isomer $PPh_2/P(i\text{-Bu})_2$ **3** produces a significantly lower value of 75.0%. This is probably due to the fact that the rather flexible *iso*-butyl chains cannot enforce a rigid environment in the catalytically active complex to induce a satisfactory selectivity.

To get a closer insight into that we were interested in obtaining an X-ray structure of the $PPh_2/P(t\text{-Bu})_2$ ligand **4**. Luckily we were able to grow a crystal suitable for X-ray crystallography of that compound by crystallization



Scheme 1. The nucleophilic asymmetric ring opening of oxanorbomadiene.

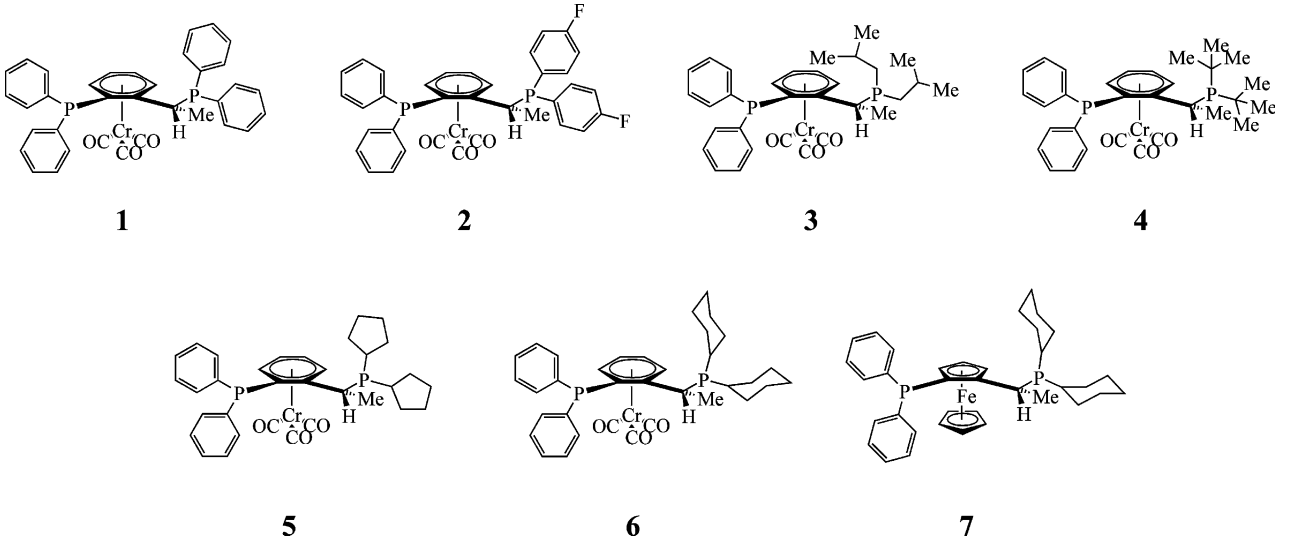


Fig. 2. Overview of the ligands employed in this investigation.

Table 1
Results of the ARO reactions

Ligand (ortho/alpha)	Yield (%)	*ee* (%)
PPh_2/PPh_2 (**1**)	69	80.3
$PPh_2/P(p\text{-}FPh)_2$ (**2**)	10	50.9
$PPh_2/P(i\text{-}Bu)_2$ (**3**)	20	75.0
$PPh_2/P(t\text{-}Bu)_2$ (**4**)	59	97.5
PPh_2/Pcyclpent (**5**)	79	84.7
PPh_2/PCy_2 (**6**)	53	93.1
$Fc/PPh_2/PCy_2$ (**7**) "Josiphos"	36	92.4

from acetone. The experimental X-ray diffraction parameters and the crystal data are summarized in Table 2.

Fig. 3 shows an ORTEP plot of ligand **4**. Clearly visible are the elements of planar and central chirality, both configured *R*. Moreover it can be seen that, in the free ligand, the α-chain adopts a conformation in which the hydrogen atom points towards the bulky chromium tricarbonyl group and the $P(t\text{-}Bu)_2$-group is directed upward, away from the complexed arene ring. We know from other structures we have examined [1b–d,2c] that this assembly has to undergo a considerable conformational change to enable a coordination to a metal center, so that the phosphorus atom is turned inwards (to the left from the viewers direction).

For a more quantitative conformational description of the ligand some selected bond lengths and angles

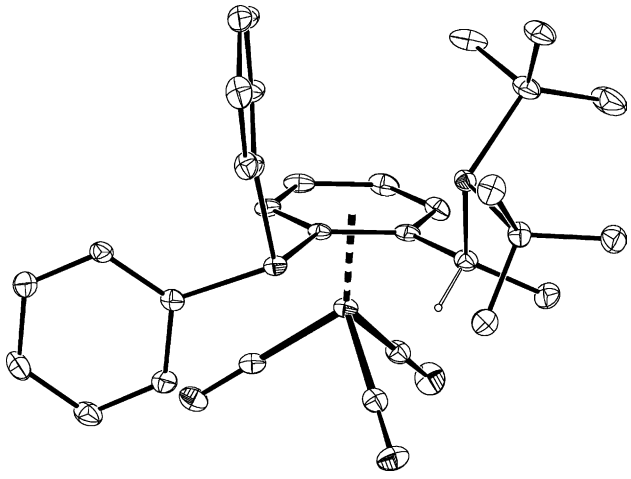


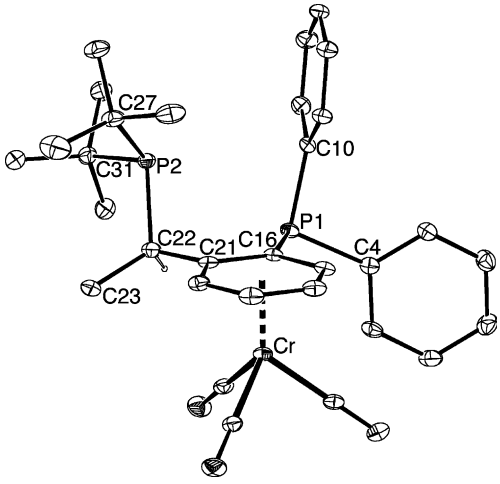
Fig. 3. Displacement elipsoids plot (30%) of **4**. The H attached to the chiral centre is shown with arbitrary radius, others have been omitted for clarity.

are summarized in Table 3. A number of characteristic torsion angles have also been calculated, which are given in Table 4. As a typical feature for this kind of complexes the dihedral angle between the planes defined by P1–C16–C21–C22 and P2–C22–C21 can be considered, which is 69.3(2)° in this case. This is in the same range as for other examples of ligands we have examined by X-ray diffraction [1b–d,2c].

Table 2
Experimental X-ray diffraction parameters and crystal data for **4**

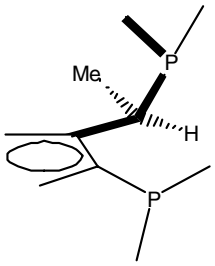
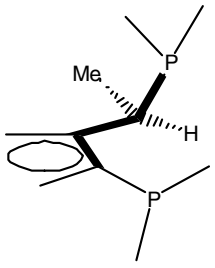
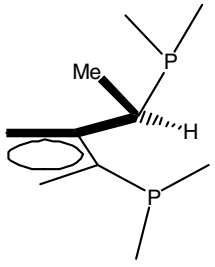
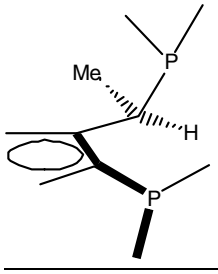
	Compound **4**
Empirical formula	$C_{31}H_{36}CrO_3P_2 \times C_3H_6O$
Formula mass	628.62
Crystal habit, color	Block, orange
Crystal dimension (mm)	$0.65 \times 0.55 \times 0.50$
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	8.7443(13)
b (Å)	10.8826(16)
c (Å)	17.249(3)
β (°)	90.742(3)
V (Å^3)	1641.3(4)
Z	2
D (g cm^{-1})	1.272
F(0 0 0)	664
μ(Mo Kα) (cm^{-1})	0.481
Diffractometer	Bruker Smart CCD
T (K)	110 (2)
θ Range	1.18–27.44
Reflections collected	26,374
Unique reflection	7494
R_{int}	0.0510
Reflections used	7494
Parameters refined	379
R_1	0.0410
wR_2	0.0897
Flack's parameter	0.013(16)
Goodness-of-fit	1.039
Differential peak/hole (e/Å^3)	0.50/−0.22

Table 3
Selected distances and angles for compound **4**



Distances (Å)			
P1–C4	1.839(3)	P2–C31	1.901(3)
P1–C10	1.833(3)	P2–C27	1.902(3)
P1–C16	1.861(2)	P2–C22	1.893(3)
Angles (°)			
C10–P1–C16	100.85(11)	C27–P2–C22	108.72(12)
C4–P1–C16	101.52(11)	C31–P2–C22	103.36(12)
P2–C22–C23	120.77(19)	P2–C22–C21	108.51(17)

Table 4
Characteristic torsion angles for compound **4**

Torsion angle	Complex **4**
	−75.7(2)
	−69.3(2)
	−25.8(3)
	101.19(19)

In this context it is informative to view the structure from another direction, from the "side" of the molecule along the arene ring (see Fig. 4). From this view it can be anticipated that the sterically very demanding and rigid P(*t*-Bu)$_2$-group, together with the "propellers" of the PPh$_2$-group, enforces a chiral cavity to achieve an effective optical induction in the coordinated prochiral substrate. In this respect it is interesting to note that Lautens obtained excellent results with the analoguous ferrocene ligand PPF-P^{t}Bu$_2$ as well, which exhibits the same substitution pattern (97.0% *ee* for the reaction examined here) [3a–d]. The other cases under consideration might be too flexible in conformation (especially the *i*-butyl and phenyl groups in the α-side chain) to do so.

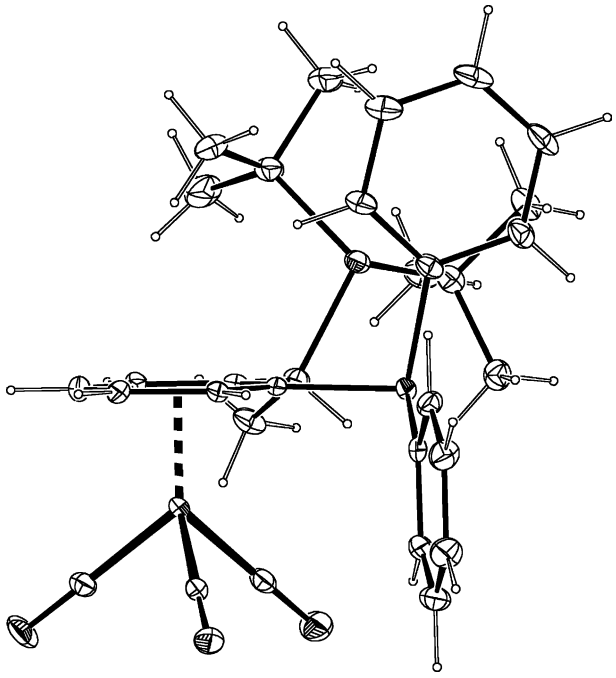


Fig. 4. Displacement elipsoids plot (30%) of **4**. H atoms are shown with arbitrary radius.

3. Conclusion

We have applied our young class of planar-chiral complex ligands to a fairly new and interesting asymmetric catalytic reaction with satisfactory and, in part, very good enantioselectivities. The results obtained so far are very encouraging and further experiments for improvement and the application of other substrates and ligands are currently being carried out in our laboratories.

4. Experimental

The ligands were synthesized according to our published method [1,2]. Analytical data is given below for those candidates that did not appear elsewhere until now (compounds **3** and **5**). For the catalytic experiments all flasks were dried by application of heat, vacuum and argon for three times and cooled before use. Solvents were purified applying standard procedures. All substances were handled under argon atmosphere using standard inert gas techniques. NMR spectra were recorded on Bruker Ultrashield 400 (^{1}H: 400 MHz, ^{13}C: 400 MHz) and Varian Unity 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz, ^{31}P: 200 MHz) spectrome-

ters at ambient temperature. IR spectra were recorded on a Perkin–Elmer FT-IR model 1720 X spectrometer. Determinations of *ee* values were carried out using HPLC. The analyses were performed on a Waters DELTA 600 system with a Chiracel OJ-H column (25 cm; Ø 0.46 cm), $\lambda = 254$ nm, hexane:isopropanol = 9:1, 1 ml/min. Analytical TLC was carried out on Merck aluminum sheets silica gel $60F_{254}$. Flash chromatography was performed using Merck grade silica gel 60 (0.04–0.063 mm).

4.1. 2-Methoxy-1,2-dihydro-naphthalene-1-ol

In a dry Schlenk tube equipped with a stirring bar were placed 0.008 mmol $[(COD)RhCl]_2$, 0.017 mmol PX_2/PY_2 and 0.0017 mol 1,4-dihydro-1,4-epoxynaphthalene and 0.75 ml THF and 0.5 ml methanol were added. The mixture was heated for 5 h under stirring and after that the solvent as well as the excess of the nucleophile were removed under vacuum. The resulting residue was purified by flash chromatography (ethyl acetate:hexane = 1:4) to result the product as a white powder. The *ee* was determined by HPLC. The retention times were 9.9 min (major) and 11.75 min (minor). m.p. = 85.5 °C; $[\alpha]_D^{25} = 220.242°$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.51 - 7.49$ (1H, m), $7.20 - 7.12$ (2H, m), $7.00 - 6.97$ (1H, m), $6.39 - 6.36$ (1H, dd, $J = 10.0$, 2.0 Hz), $5.97 - 5.94$ (1H, dd, $J = 9.9$, 2.4 Hz) ppm; ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 127.34$, 126.96, 126.81, 125.69, 125.29, 124.05, 81.19, 71.44, 55.75 ppm.

4.2. $[\eta^6$-(*R,R*)-{(*Pi-Bu*$_2$)*CHMe*}$C_6H_4PPh_2$)$]Cr(CO)_3$ (**3**)

Compound **3** was prepared according to the method published in [1,2] from the corresponding chloro derivative $[\eta^6$-(*R,R*)-{(Cl)CHMe}$C_6H_4PPh_2$)$]Cr(CO)_3$ (1.00 g, 2.17 mmol), diisobutylphosphine (0.34 g, 2.41 mmol) and $TIPF_6$ (0.76 g, 2.17 mmol). It was purified by column chromatography (silica, CH_2Cl_2:hexane = 1:3). Yield: 0.65 g (1.14 mmol, 55%). IR ($CHCl_3$): ν_{max} 1968, 1897 (CO) cm^{-1}. ^{31}P NMR (200 MHz, C_6D_6) $\delta = 17.02$ (d, $J_{PP} = 32.96$ Hz, α-P), −19.25 (d, $J_{PP} = 32.96$ Hz, *ortho*-P) ppm. ^{1}H NMR (500 MHz, C_6D_6) $\delta = 7.61$ (td, 2H, $J = 7.6$ Hz, $J_{PH} = 1.4$ Hz), 7.36 (td, 2H, $J = 7.4$ Hz, $J_{PH} = 1.0$ Hz), $7.15 - 7.02$ (m, 6H) (*Ph*), 4.98 (dd, 1H, $J = 6.3$ Hz, $J_{PH} = 1.2$ Hz), 4.70 (t, 1H, $J = 6.4$ Hz), 4.45 (dd, 1H, $J = 6.4$ Hz, $J_{PH} = 3.5$ Hz), 4.23 (t, 1H, $J = 6.3$ Hz) (H_{ar}), 4.00 (dq, 1H, $J = 7.2$ Hz, $J_{PH} = 7.2$ Hz, C*H* CH_3), $1.58 - 1.42$ (m, 1H), $1.37 - 1.22$ (m, 2H) (PCH_2CH Me_2), 1.20 (dd, 3H, $J = 7.0$ Hz, $J_{PH} = 4.9$ Hz, $CHCH_3$), $1.04 - 0.98$ (m, 1H), $0.97 - 0.84$ (m, 2H) (PCH_2CHMe_2), 0.82 (dd, 6H, $J = 6.7$ Hz, $J_{PH} = 4.0$ Hz), 0.78 (dd, 6H, $J = 6.8$ Hz, $J_{PH} = 22.7$ Hz), (PCH_2CHMe_2) ppm. ^{13}C NMR (125 MHz, C_6D_6) $\delta = 232.90$ (CO), 137.73 (d, $J_{CP} = 6.6$ Hz, $C_{ipso}PPh_2$), 137.13 (dd, $J_{CP} = 13.7$ Hz, $J_{CP} = 3.3$ Hz, $C_{ipso}PPh_2$), 135.14 (d, 2C, $J_{CP} = 20.8$ Hz, $C_{ar}PPh_2$), 133.85 (dd, 2C, $J_{CP} = 18.9$ Hz, $J_{CP} = 2.2$ Hz, $C_{ar}PPh_2$), 129.67, 128.81 (d, 2C, $J_{CP} = 6.5$ Hz, $C_{ar}PPh_2$), 128.55 (d, 2C, $J_{CP} = 6.6$ Hz, $C_{ar}PPh_2$), 128.23 ($C_{ar}PPh_2$), 125.37 (dd, $J_{CP} = 23.3$ Hz, $J_{CP} = 16.7$ Hz, $C_{ar,ipso}$), 103.38 (dd, $J_{CP} = 23.3$ Hz, $J_{CP} = 3.0$ Hz, $C_{ar,ipso}$), 99.98 (d, $J_{CP} = 2.8$ Hz), 94.54, 89.39, 87.51 (dd, $J_{CP} = 3.8$ Hz, $J_{CP} = 3.8$ Hz) (C_{ar}), 37.79 (d, $J_{CP} = 20.3$ Hz, CH_2), 33.02 (d, $J_{CP} = 22.5$ Hz, CH_2), 32.86 (dd, $J_{CP} = 23.0$ Hz, $J_{CP} = 20.3$ Hz, *C*HCH_3P), 26.74 (d, $J_{CP} = 17.6$ Hz, PCH_2C HMe_2) 26.39 (d, $J_{CP} = 14.8$ Hz, PCH_2CHMe_2), 24.68 (d, $J_{CP} = 8.8$ Hz, PCH_2CHMe_2), 24.40 (d, $J_{CP} = 9.3$ Hz, PCH_2CHMe_2), 24.32 (dd, $J_{CP} = 9.2$ Hz, $J_{CP} = 1.1$ Hz, $CHCH_3P$), 23.94 (d, $J_{CP} = 9.9$ Hz, PCH_2CHMe_2), 12.94 (PCH_2CHMe_2) ppm.

4.3. $[\eta^6$-(*R,R*)-{(*PCyclopentyl*$_2$)*CHMe*}$C_6H_4PPh_2$)$]$-$Cr(CO)_3$ (**5**)

Compound **5** was prepared according to the method published in [1,2] from the corresponding chloro derivative $[\eta^6$-(*R,R*)-{(Cl)CHMe}$C_6H_4PPh_2$)$]Cr(CO)_3$ (0.85 g, 1.85 mmol), dicyclopentylphosphine (0.36 g, 2.12 mmol) and $TIPF_6$ (0.65 g, 1.85 mmol). It was purified by column chromatography (silica, ethyl acetate:hexane = 1:8). Yield: 0.69 g (1.16 mmol, 63%). IR ($CHCl_3$): ν_{max} 1966, 1896 (CO) cm^{-1}. ^{31}P NMR (200 MHz, C_6D_6) $\delta = 20.11$ (d, $J_{PP} = 46.9$ Hz, α-P), −19.61 (d, $J_{PP} = 47.0$ Hz, *ortho*-P) ppm. ^{1}H NMR (500 MHz, C_6D_6) $\delta = 7.63$ (td, 2H, $J = 7.6$ Hz, $J_{PH} = 1.2$ Hz), 7.35 (td, 2H, $J = 7.3$ Hz, $J_{PH} = 1.2$ Hz), 7.07 (td, 4H, $J = 7.0$ Hz, $J_{PH} = 1.5$ Hz), 7.02 (t, 2H, $J = 7.3$ Hz) (Ph), 5.06 (dd, 1H, $J = 6.3$ Hz, $J_{PH} = 1.2$ Hz), 4.73 (t, 1H, 6.3 Hz) 4.53 (dd, 1H, $J = 6.3$ Hz, $J_{PH} = 3.5$ Hz) (H_{ar}), 4.20 (m, 2H, H_{ar}), $1.88 - 1.73$ (m, 2H, PC*H*), $1.67 - 1.52$ (m, 2H, CH_2), $1.54 - 1.30$ (m, 10H, CH_2), $1.28 - 1.24$ (dd, 3H, $J = 7.0$ Hz, $J_{PH} = 3.7$ Hz, $CHCH_3P$), $1.17 - 0.99$ (m, 2H, CH_2), $0.93 - 0.82$ (m, 2H, CH_2) ppm. ^{13}C NMR (125 MHz, C_6D_6) $\delta = 233.00$ (CO), 138.54 (dd, $J_{CP} = 7.2$ Hz, $J_{CP} = 2.8$ Hz, $C_{ipso}PPh_2$), 137.71 (dd, $J_{CP} = 14.3$ Hz, $J_{CP} = 5.0$ Hz, $C_{ipso}PPh_2$), 135.33 (d, 2C, $J_{CP} = 20.8$ Hz, $C_{ar}PPh_2$), 133.81 (dd, 2C, $J_{CP} = 18.1$ Hz, $J_{CP} = 2.7$ Hz, $C_{ar}PPh_2$), 129.66, 128.80 (d, $J_{CP} = 7.1$ Hz), 128.31, 128.28, 128.11, 128.00 ($C_{ar}PPh_2$), 126.06 (dd, $J_{CP} = 17.6$ Hz, $J_{CP} = 5.5$ Hz, $C_{ar,ipso}$), 103.41 (dd, $J_{CP} = 3.0$ Hz, $J_{CP} = 2.3$ Hz, $C_{ar,ipso}$), 100.92 (d, $J_{CP} = 3.3$ Hz), 94.70, 89.15, 87.97 (dd, $J_{CP} = 3.0$ Hz, $J_{CP} = 3.0$ Hz) (C_{ar}), 36.41 (d, $J_{CP} = 19.2$ Hz, *C*HCH_3P), 33.89 (dd, $J_{CP} = 23.6$ Hz, $J_{CP} = 20.3$ Hz, P*C*H), 33.19 (dd, $J_{CP} = 22.2$ Hz, $J_{CP} = 2.5$ Hz, P*C*H), 32.57 (d, $J_{CP} = 21.4$ Hz, CH_2), 32.02 (d, $J_{CP} = 23.0$ Hz, CH_2), 31.61 (d, $J_{CP} = 15.3$ Hz, CH_2), 31.14 (dd, $J_{CP} = 13.2$ Hz, $J_{CP} = 3.8$ Hz, CH_2), 26.66 (d, $J_{CP} = 7.7$ Hz, CH_2), 26.35 (d, $J_{CP} = 7.7$ Hz, CH_2), 26.25 (d, $J_{CP} = 6.6$ Hz, C H_2), 25.95 (d, $J_{CP} = 6.5$ Hz, CH_2), 13.25 ($CHCH_3P$) ppm.

4.4. X-ray structure determination

Crystal data and details of the structure determination are listed in Table 2. Data collection was performed with a Bruker Smart CCD (Mo Kα radiation, $\lambda = 0.71073$ Å, graphite monochromator) area detector. The unit cell parameters were obtained by the least-squares refinement of 8096 reflections. The structure was solved by direct methods (SHELXS-97) [6] and refined by full matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-97) [7]. The SADABS [8] program was used for absorption correction of the structures. All non-hydrogen atoms were refined anisotropically. All H atom positions were introduced at their idealized positions (d(CH) = 0.98Å) and were refined using a riding model. The absolute configuration was confirmed by evaluation of the Flack [9] parameter.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-248343. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: int. code +(1223) 336 033; e-mail: deposit@ccdc.cam.ac.uk; web: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors acknowledge financial support by the Deutsche Forschungsgemeinschaft DFG within the Collaborative Research Centre (SFB 380) ''Asymmetric Synthesis with Chemical and Biological Methods'' and by the ''Fonds der Chemischen Industrie''. We thank Dipl.-Chem. Jutta Knuppertz for preparative assistance. B.C. is grateful to the Graduiertenkolleg: ''Methods of asymmetric synthesis'' for a scholarship.

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