Optically Active Phospholanes as Substituents on Ferrocene and Chromium-Arene Complexes

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In memoriam Othmar Stelzer

Keywords: Iron / Chromium / Sandwich complexes / P ligands / Asymmetric catalysis

An improved synthesis of (*R*,*R*)- and (*S*,*S*)-hexane-2,5-diol is presented. The (*S*,*S*)-derivative was converted into a cyclic sulfate, which on treatment with $NaPH_2$ in liquid ammonia ultimately gave the secondary (*R*,*R*)-2,5-dimethylphospholane. This phospholane can be introduced into the side chain of chiral tricarbonylchromium and ferrocene derivatives to give new bidentate ligands of the Josiphos and Daniphos type. Both the ferrocene- and tricarbonylchromium-based diphosphanes have been characterized by X-ray diffraction analysis. A discussion of their structural features is included. The new ligands were successfully applied to the enantioselective hydrogenation of itaconic acid esters.

Introduction

Enantioselective homogeneous catalysis remains one of the most challenging topics in organic and organometallic chemistry. Continuous improvements are being made, largely due to the development of new families of ligands. The Nobel committee recognized this by awarding the 2001 Nobel Prizes in chemistry for achievements in this field.[1]

In the search for novel catalysts and ligands, chemists have used all types of organic backbones, natural as well as unnatural. Whereas earlier research focused on ligands derived from the "chiral pool", e.g. tartaric acid, terpenes, amino acids, and sugars, the emphasis has shifted somewhat towards other ligand systems not derived from natural sources. This is largely due to the enormous success of such ligand families as BINAP and its derivatives, the DUPHOS ligands,[2,3] as well as the "Josiphos" family of ligands.[4,5] It should be noted that these ligands contain unusual elements of chirality, such as planar and axial chirality. The Josiphos ligands are also special in that they incorporate a transition metal containing unit as the central core around which the ligand framework is constructed. This transition metal itself is not involved in the catalysis, but is part of the scaffold to which the ligand functions are attached. The function of the metal is to create a chiral environment, the spatial and dynamic properties of which could not be achieved by an organic framework alone.

We have recently described a similar class of metal complexes, known as "Daniphos" complexes, which are based on chiral arenetricarbonylchromium complexes.[6−10] In many aspects, these ligands are similar to the Josiphos ligands but differ both in steric as well as electronic properties. They also match the ferrocene ligands in enantioselectivity in a number of catalytic applications. The major advantage of the chromium systems is their easy availability in an optically active form without any need for resolution, because the organic ligand itself (phenylethylamine), is commercially available in both enantiomers and with a variety of functional derivatives. Furthermore, the simple and straightforward synthetic route to the Daniphos ligands allows the construction of these diphosphanes in a modular fashion, a concept that has attracted considerable attention in the last decade.[11]

We sought to combine the advantages of both the metal-containing chiral frameworks of ferrocene and chromium-arene derivatives with the chirality of the phospholane units used in DUPHOS ligands. A necessary prerequisite was the availability of the secondary chiral phospholane (*R*,*R*)-2,5-dimethylphospholane, which has been briefly mentioned in

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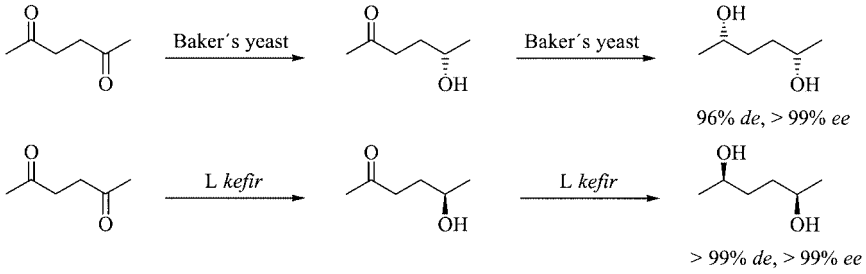


Scheme 1

the literature but was not isolated or fully characterized.[12] We therefore sought a route to prepare this phospholane directly from PH_3, and to incorporate it into both Josiphos and Daniphos ligands.

Results and Discussion

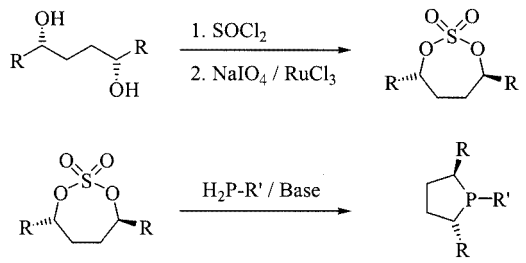
Optically active 2,5-hexanediol can be prepared by several routes, preferably by asymmetric homogeneous hydrogenation or enzymatic methods. Due to the commercial success of the DUPHOS ligands, larger quantities of this chemical in both the (*R*,*R*)- and (*S*,*S*)-forms are now in demand, and therefore we tried to scale the enzymatic route to allow the synthesis of kilogram amounts. The synthesis of both enantiomers could be achieved with quantitative conversion and with excellent diastereo- and enantioselectivities (> 96% *de*, > 99% *ee* for the (*R*,*R*)-isomer and 99% *de*, > 99% *ee* for the (*S*,*S*)-isomer) (Scheme 1).[13] Both enantiomers prepared by this route are now also commercially available.[13c]

The introduction of phospholane units into suitable organic frameworks remains a synthetic challenge even nowadays. The standard method employed today for the synthesis of the various DUPHOS ligands starts from a bis(primary)phosphane [e.g. the benzene derivative *o*-$C_6H_4(PH_2)_2$], which has to be synthesized by an elaborate route. This compound is then deprotonated and treated with the cyclic sulfate derived from hexanediol (Scheme 2).[3] A possible alternative is the reductive cleavage of a phenylphospholane with lithium metal, which then can be treated with organic halides.[14] Once again, however, this method is quite elaborate and (with larger substituents) can result in epimerization at C-2 and C-5. A third route has recently been described by Börner et al., in which *P*-(trimethylsilyl)phospholane, prepared from $P(TMS)_3$ in a two-step cyclization, undergoes nucleophilic addition to dichloromaleic anhydride.[15]

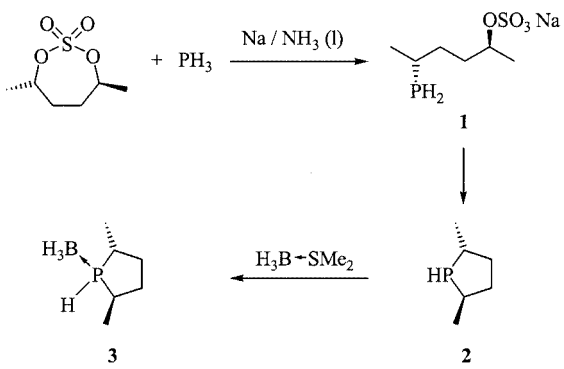
A fourth possible alternative is the use of a secondary phospholane, which proved to be difficult to isolate and characterize due to its volatility and extreme sensitivity. It was stabilized as a borane adduct, which however restricted its use to the synthesis of ligands with remote phospholane groups.[12]

Unfortunately, none of the above-mentioned reagents can be used for the introduction of phospholane units into the side-chain of Josiphos or Daniphos ligands. We therefore sought a route to prepare the secondary phospholane directly from PH_3. $NaPH_2$ was generated by deprotonation of PH_3 with sodium in liquid ammonia, and then treated with the cyclic sulfate of (*S*,*S*)-2,5-hexanediol. By following the reaction with ^{31}P and ^{1}H NMR spectroscopy, we were able to show that the ring-opening phosphination of the cyclic sulfate proceeded much faster than the second insertion step. The intermediate primary phosphane **1** (δ_P = −110.7 ppm) can be isolated and appears to be quite stable. By using two equivalents of $NaPH_2$, the reaction can be driven to completion, and after 48 h at −35 to −40 °C the secondary phospholane **2** (δ_P = −27.7 ppm) was isolated in the (*R*,*R*)-form with no evidence of epimerization, as the substitution proceeds cleanly by double inversion. The phospholane **2** can be purified by distillation, but due to its high volatility and pyrophoric nature, we were not able to obtain an elemental analysis. This compound can be stabilized as a BH_3 adduct **3**, as described earlier (Scheme 3).[12]

The standard method of introducing phosphanes onto the side chain of chiral (*R*,*R*)-1-[1-(dimethylamino)ethyl]-2-diphenylphosphanylferrocene is by refluxing this compound

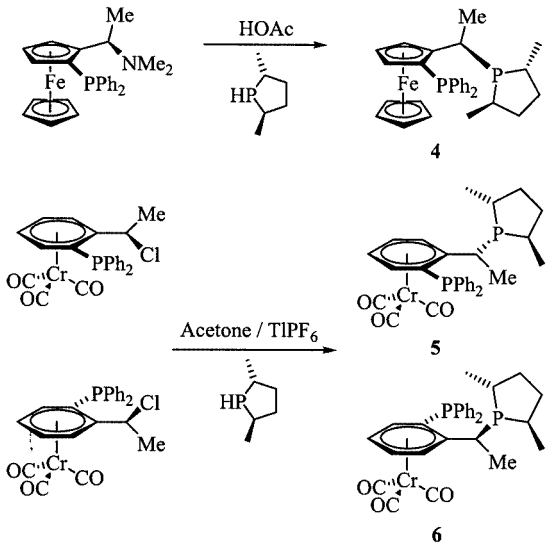


Scheme 2



Scheme 3

with a secondary phosphane in glacial acetic acid.[16] With the phospholane **2**, this reaction gave the desired diphosphane **4** in 55% yield. A somewhat different reaction path is necessary for the chromium complexes — an acetone solution of (*R*,*R*)-[1-(1-chloroethyl)-2-diphenylphosphanyl-η^6-benzene]chromium tricarbonyl was treated with **2**. An acetone solution of $TlPF_6$ was then slowly added to this mixture over one hour by an automatic syringe. The same reaction was also performed with the (*S*,*S*)-chromium com plex and the two diastereomeric products **5** and **6** were isolated in 80% and 96%, respectively (Scheme 4).



Scheme 4

Table 1. Comparison of characteristic torsion angles [°]

Torsion angle	4	7	10	9
	55.6(3)	74.1(3)	63.3(4)	179.1(4)	58.2(2)
	-113.3(3)	44.7(4)	33.9(6)	-69.9(5)	71.1(3)
	-60.2(4)	80.1(4)	74.6(6)	-28.2(9)	20.6(4)
	-149.1(3)	-134.9(3)	-148.4(4)	-69.1(4)	81.6(3)

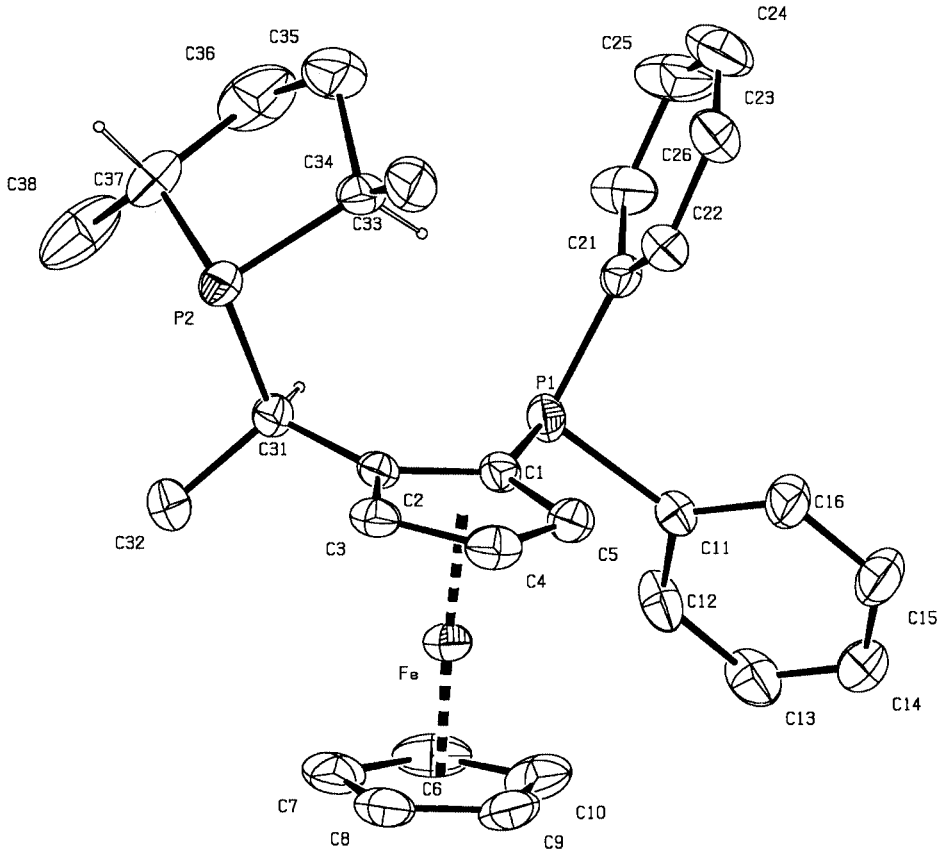


Figure 1. Displacement ellipsoids plot (PLATON[17]) of **4**; ellipsoids are at the 30% probability level; all H atoms except for those on the asymmetric carbon atoms have been omitted for clarity.

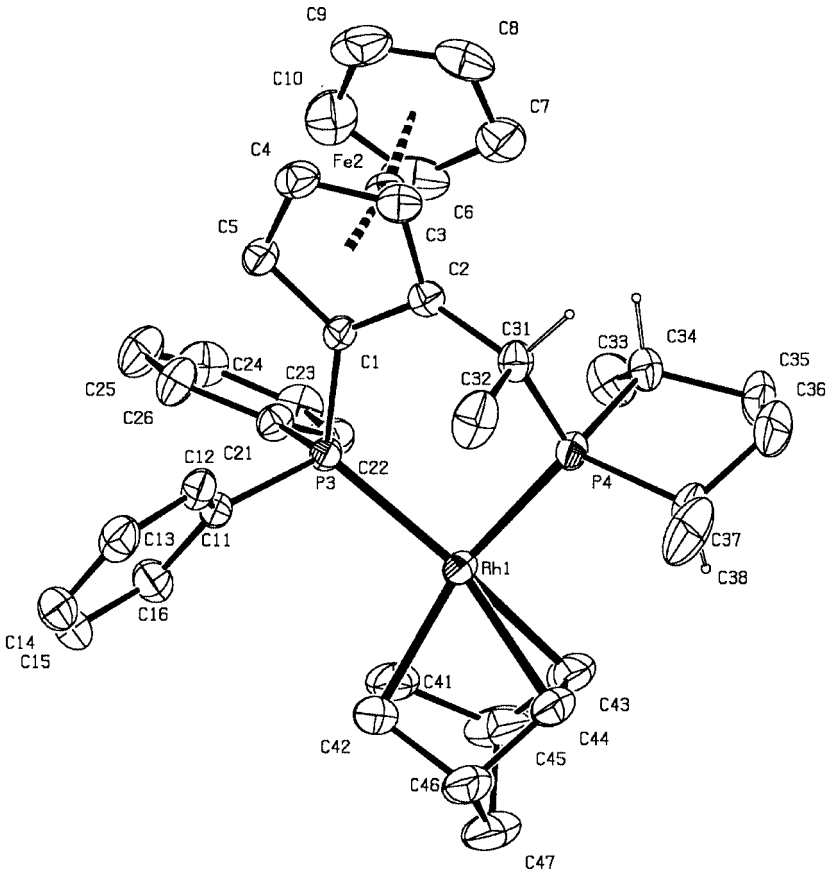


Figure 2. Displacement ellipsoids plot (PLATON[17]) of the cation of **7**; ellipsoids are at the 30% probability level; all H atoms except for those on the asymmetric carbon atoms have been omitted for clarity

We were able to grow single crystals of the ferrocene derivative **4** (Figure 1). Not surprisingly, **4** adopts a conformation in which the bulky phospholane is above the plane of the cyclopentadienyl ring. Some relevant dihedral angles are shown in Table 1.

For applications to catalysis, we also prepared the (norbornadiene)Rh complexes of both the iron and chromium compounds (**7**−**9**). Again, we were fortunate to obtain single crystals of the Fe−Rh complex **7** (Figure 2) and the Cr−Rh complex **9** (Figure 3). We also synthesized and structurally characterized the bis(ferrocene) rhodium complex **10** (Figure 4). Experimental crystallographic and crystal data are collected in Table 7.

As expected, the diphosphane **4**, on coordination to the square-planar environment of rhodium, has to undergo a considerable conformational change (Figures 1, 2 and 4). By comparing rhodium complexes of both Josiphos and Daniphos ligands, we were able to show that this conformational change is even more severe for the chromium complexes than for the iron complexes (Table 1), possibly due to the narrower bite angle of the benzene ring relative to the cyclopentadienyl ring.[9] Some selected bond lengths and angles for complexes **4**, **7**, **9** and **10** are summarized in Tables 2−5.

Table 2. Selected distances for **4**

Distances, Å			
P1−C1	1.814(3)	P2−C31	1.882(3)
P1−C11	1.841(3)	P2−C34	1.867(4)
P1−C21	1.845(4)	P2−C37	1.868(4)

Table 3. Selected distances and angles for **7**

Distances, Å			
Rh1−P3	2.3098(1)	Rh1−P4	2.3020(10)
Rh1−C41	2.214(5)	Rh1−C43	2.195(4)
Rh1−C42	2.226(4)	Rh1−C44	2.220(4)
P3−C1	1.801(3)	P4−C31	1.853(4)
P3−C11	1.832(3)	P4−C34	1.874(4)
P3−C21	1.832(3)	P4−C37	1.877(3)
Angles, deg			
P3−Rh1−P4	92.98(3)		
P3−Rh1−C41	97.90(13)	P4−Rh1−C43	98.75(16)
P3−Rh1−C42	100.34(11)	P4−Rh1−C44	97.39(13)
C42−Rh1−C44	64.75(17)	C41−Rh1−C43	65.8(2)

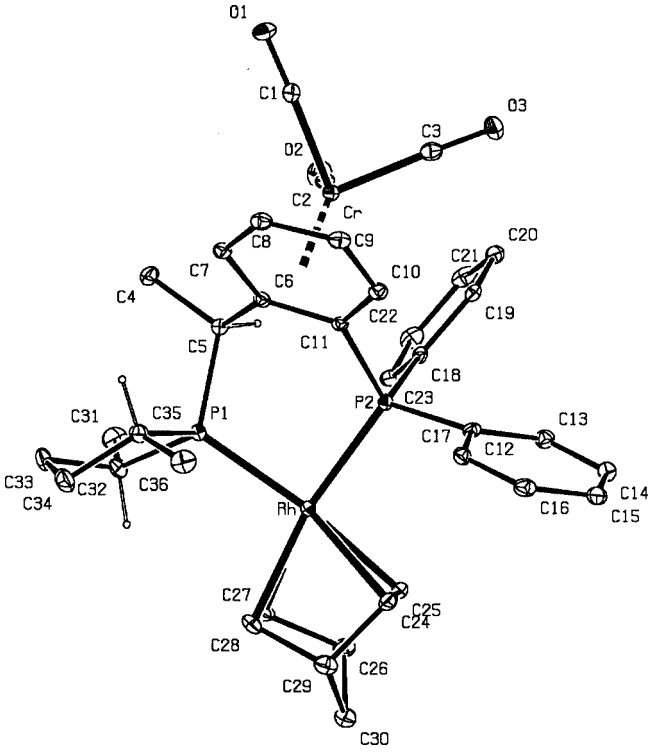


Figure 3. Displacement ellipsoids plot (PLATON[17]) of the cation of **9**; ellipsoids are at the 30% probability level; all H atoms except for those on the asymmetric carbon atoms have been omitted for clarity

Table 4. Selected distances and angles for **10**

Distances, Å			
Rh−P11	2.3281(12)	Rh−P21	2.3213(12)
Rh−P12	2.3056(11)	Rh−P22	2.4008(13)
P11−C101	1.811(5)	P21−C201	1.823(5)
P11−C111	1.840(5)	P21−C211	1.823(5)
P11−C121	1.847(5)	P21−C221	1.836(5)
P12−C132	1.865(5)	P22−C232	1.870(6)
P12−C134	1.843(5)	P22−C234	1.864(6)
P12−C137	1.887(5)	P22−C237	1.868(7)
Angles, deg			
P11−Rh−P12	89.21(4)	P12−Rh−P21	95.15(4)
P21−Rh- P22	89.71(4)	P11−Rh−P22	93.21(5)
P11−Rh−P21	156.83(5)	P12−Rh−P22	161.75(5)

The respective conformations of each ligand are also manifested by the P,P coupling constants in the ^{31}P NMR spectra. This is normally governed by the orientation of the lone pairs on the phosphorus atoms with respect to each other and the accompanying dihedral angle.[18] As can be seen from Figure 1, the phospholane moiety in compound **4** adopts a position away from the bulky diphenylphosphane group, so that the two phosphorus atoms are almost anti-periplanar. As a consequence, no P,P coupling constant can

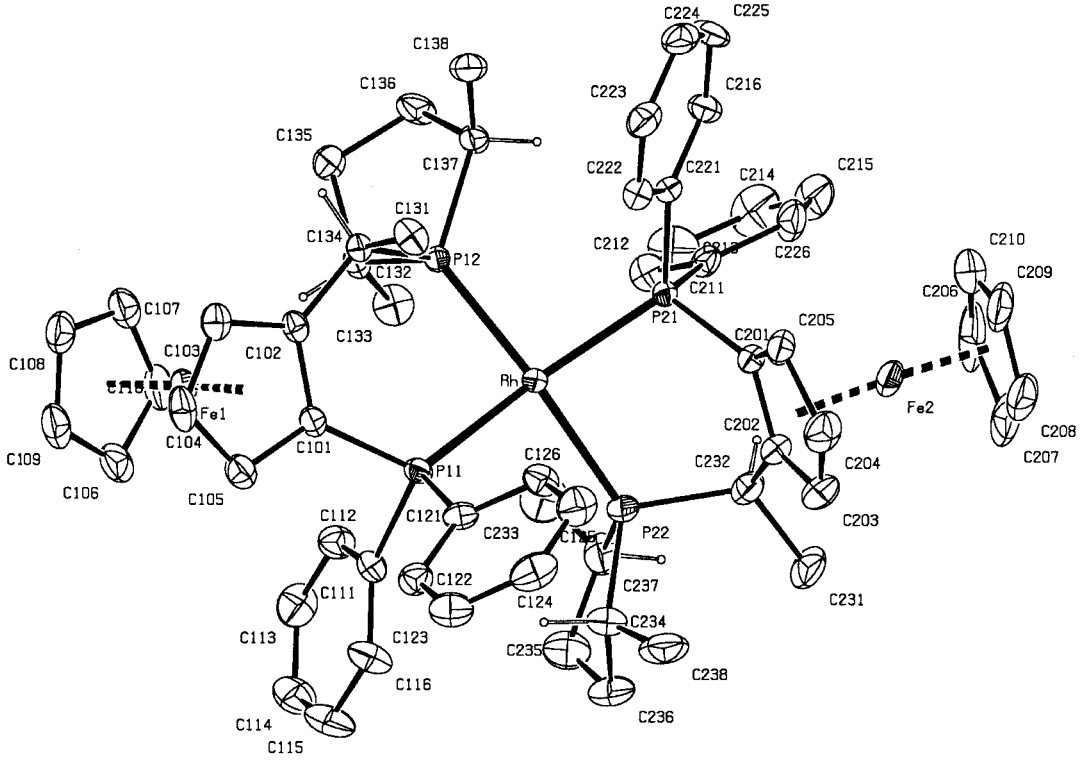


Figure 4. Displacement ellipsoids plot (PLATON[17]) of the cation of **10**; ellipsoids are at the 30% probability level; all H atoms except for those on the asymmetric carbon atoms have been omitted for clarity

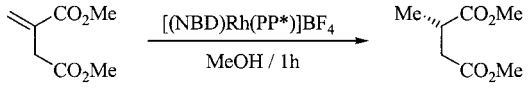
Table 5. Selected distances and angles for **9**

Distances, Å			
Rh−P1	2.2806(8)	Rh−P2	2.2794(8)
Rh−C27	2.215(3)	Rh−C24	2.210(3)
Rh−C28	2.218(3)	Rh−C25	2.220(3)
P1−C5	1.863(3)	P2−C11	1.839(3)
P1−C32	1.853(3)	P2−C12	1.818(3)
P1−C35	1.855(3)	P2−C18	1.814(3)
Angles, deg			
P1−Rh−P2	91.48(3)		
P1−Rh- C27	100.82(8)	P2−Rh−C24	99.58(9)
P1−Rh- C28	98.79(9)	P2−Rh−C25	97.57(8)
C25−Rh−C27	65.25(11)	C24−Rh−C26	53.25(12)

be observed in the ^{31}P NMR spectrum of **4**. In contrast, when the ligand is attached to rhodium, it has to undergo a severe conformational change (as mentioned above). The two phosphorus atoms are now synperiplanar, and consequently the NMR spectrum shows a clear set of two double doublets, revealing a P,P coupling constant of 45.8 Hz ($J_{P,Rh}$ = 150.2 Hz). The same can be said for the chromium ligands: whereas the (*R*,*R*)-diastereomer **5** as the free ligand shows only singlets, a set of two double doublets is observed for its rhodium complex **8**. In contrast, the (*S*,*S*)-diastereomer **6** shows "normal" behaviour in its uncomplexed form, with two doublets and a set of two double doublets in the rhodium complex **9**.

Hydrogenation of Dimethyl Itaconate

For an assessment of the catalytic performance of the ligands, some preliminary hydrogenations were carried out, using dimethyl itaconate as the substrate (Scheme 5). The results are summarized in Table 6.



Scheme 5

Table 6. Results of the hydrogenation of itaconate (reaction time = 1 h)

Ligand	Conversion [%]	chemical yield [%]	*ee* [%][a]	Configuration	TOF [1/h]
4	100	100	> 99	*S*	200
5	12	12	25	*S*	24
6	53	53	86	*S*	106

[a] Determined by GC on a Lipodex *E* column at 100 °C.

It should be noted that the experiments were stopped after one hour in order to get an insight into the reaction rate of each ligand, which explains the incomplete conversions in some cases. Taking into account that a relatively high substrate-to-catalyst ratio of 200 was chosen, it can be concluded that the ferrocene ligand **4** is working quite efficiently, whereas its chromium analogues are somewhat slower. It also shows excellent enantioselectivity, whereas the enantiomeric excess is considerably lower for the chromium ligands. It is noteworthy that diastereomer **6** results in a much higher *ee* than diastereomer **5**. This exemplifies vividly that the stereochemical outcome of a catalysis is very sensitive to the steric as well as the electronic features of the employed ligand, because the ferrocene derivative **4** possesses the same stereochemical features as chromium ligand **5**, but a different backbone, whereas the stereochemistry in the backbone of **6** is reversed. (It should be noted that, due to its carbonyl ligands, the chromium tripod is strongly electron-withdrawing, whereas the ferrocene unit is a potent electron donor). In this context it seems desirable to have an analogous ferrocene diastereomer in hand for comparison.

In conclusion, it seems likely that the *ee* value of the product is not governed by the phospholane unit alone, but that the configuration (and nature) of the planar chiral backbone plays an important role as well. More detailed investigations in that respect are currently being carried out.

Conclusion

A novel method for preparing the secondary (*R*,*R*)-dimethylphospholane has been elaborated, making it available in moderate-to-good yields from enantiopure (*S*,*S*)-hexanediol, itself synthesized on a large scale by an improved enzymatic route. The phospholane has been successfully introduced onto ligand scaffolds both of the Daniphos and the Josiphos type. These have been structurally studied in detail by X-ray analyses. Preliminary catalytic studies on the hydrogenation of itaconic acid esters showed encouraging results. Further studies on catalysis employing these ligands are currently under investigation and are due to be published soon.

Experimental Section

General Remarks: All manipulations were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and deoxygenated by standard procedures. Chromatography was carried out with Merck alumina 90. NMR spectra were recorded with Varian Mercury 200 (^1H: 200 MHz, ^{13}C: 50 MHz, ^{31}P: 81 MHz), Varian Unity 500 (^1H: 500 MHz, ^{13}C: 125 MHz, ^{31}P: 202 MHz), Bruker AC 250 (^1H: 250 MHz, ^{13}C: 63 MHz, ^{31}P: 101 MHz) and Bruker AMX 400 (^1H: 400 MHz, ^{13}C: 100 MHz, ^{31}P: 162 MHz) spectrometers at ambient temperature. IR spectra were recorded with a Perkin−Elmer FT-IR model 1720 X spectrometer. Mass spectra were obtained with a Finnigan MAT 95 spectrometer, using CI (with isobutane as the reactant gas) and SIMS recording techniques for the chromium and rhodium complexes, respectively.

(2*S*,5*S*)-Hexanediol and (2*R*,5*R*)-Hexanediol: In a thermostatted vessel (30 °C) glucose (169.2 g, 0.858 mol glucose) was dissolved in distilled water (1.5 L). Baker's yeast (*Saccharomyces cerevisiae*) (271.5 g) was then added portionwise. The pH was adjusted to 6

with 4 N NaOH, and 2,5-hexanedione (4.63 mL, 25 mmol) added. Quantitative conversion was achieved after 24 h (96% *de*, > 99% *ee*). The biomass was separated by centrifugation (20 min, 5000 *g*). The resulting supernatant liquid was extracted with ethyl acetate (3 L) and the organic phase evaporated. (2*S*,5*S*)-hexanediol crystallized overnight at 4 °C and was recrystallized from 1-octanol (75% yield). For a detailed description of the synthesis of (2*R*,5*R*)-hexanediol see ref.[13]

(2*R*,5*R*)-Dimethylphospholane (2): Ammonia (300 mL) was condensed into a three-necked flask at −78 °C. Sodium (5.4 g, 234 mmol) was added in small portions. Using a slight pressure excess (0.1 bar), PH_3 was added until the solution was saturated (yellow colour). The cyclic sulfate of (2*S*,5*S*)-hexanediol (21.1 g, 117 mmol) was added. After complete evaporation of the ammonia, the residue was dissolved in Et_2O (300 mL) and stirred for two days. The sodium sulfate was then filtered off and washed with Et_2O (100 mL). The solvent was removed by distillation and the remaining residue distilled at ambient pressure. Yield 7.4 g (63.8 mmol, 55%). ^{1}H NMR (C_6D_6): δ = 2.75 (ddd, $J_{P,H}$ = 181.8, $J_{H,H}$ = 11.2, $J_{H,H}$ = 8.9 Hz, 1 H, PH), 2.55−2.45 (m, 1 H, CH), 1.92−1.82 (m, 1 H, CH), 2.05 −1.82 (m, 2 H, CH_2), 1.22−1.02 (m, 2 H, CH_2), 1.10 (dd, $J_{P,H}$ = 17.6, $J_{H,H}$ = 7.6 Hz, 3 H), 1.11 (dd, $J_{P,H}$ 11.4, $J_{H,H}$ = 6.3 Hz, 3 H) ppm. ^{13}C NMR (C_6D_6): δ = 40.75 (d, $J_{P,C}$ = 6.1 Hz, CH_2), 38.70 (d, $J_{P,C}$ = 3.1 Hz, CH_2), 32.46 (d, $J_{P,C}$ = 8.6 Hz, CH), 29.31 (d, $J_{P,C}$ = 6.6 Hz, CH), 21.65 (d, $J_{P,C}$ = 31.0 Hz, CH_3*cis*P(l.p.)], 19.43 (s, CH3*trans*P(l.p.)] ppm. ^{31}P NMR (C_6D_6): δ = −27.7 (d, $^1J_{P,H}$ = 181.1 Hz) ppm.

(2*R*,5*R*)-Dimethylphospholane−BH_3 Adduct: Equimolar amounts of the phospholane **2** and borane−dimethylsulfide complex (10.0 M solution in dimethyl sulfide) were stirred at room temperature for 4 h. All volatile components were then removed in vacuo to provide the adduct (quantitative conversion). ^{1}H NMR (C_6D_6): δ = 4.34 (m, $J_{P,H}$ = 349.3 Hz, PH), 2.71−2.56 (m, 1 H, CH_2−CH_2), 2.29−2.11 (m, 3 H, CH_2−CH_2), 1.48−1.32 (m, 2 H, CH), 1.27 (dd, $J_{P,H}$ = 15.5, $J_{H,H}$ = 6.9 Hz), 1.16 (dd, $J_{P,H}$ = 17.0, $J_{H,H}$ = 7.4 Hz), 0.49 (m, $J_{B,H}$ = 98.0 Hz) ppm. ^{13}C NMR (C_6D_6): δ = 37.04 (d, $J_{P,C}$ = 3.1 Hz, CH_2), 36.79 (s, CH_2), 33.77 (d, $J_{P,C}$ = 36.6 Hz, CH), 28.15 (d, $J_{P,C}$ = 34.6 Hz, CH), 17.52 (d, $J_{P,C}$ = 3.1 Hz, CH_3), 16.04 (d, $J_{P,C}$ = 5.1 Hz, CH_3) ppm. ^{31}P{^{1}H} NMR: δ = 24.0 (d, $J_{P,B}$ = 44.3 Hz) ppm. ^{31}P NMR: δ = 24.0 (d, $J_{P,H}$ = 349.3 Hz) ppm. $C_6H_{16}BP$ (129.97): calcd. C 55.34, H 12.39; found C 53.47, H 12.16.

For convenience, in the following experimental descriptions, the abbreviation "DMP" is used for the structural unit "2,5-dimethylphospholane".

(*R*,*R*)-[(C_5H_5)Fe{C_5H_3(CHMe{(*R*,*R*)-DMP})(PPh_2)}] (4): (*R*,*R*)-2,5-Dimethylphospholane (0.14 g, 1.20 mmol) was added to a stirred solution of (*R*,*R*)-[(C_5H_5)Fe{C_5H_3(CHMeNMe_2)(PPh_2)}] (0.53 g, 1.20 mmol) in glacial acetic acid (7 mL), and heated to 75 °C for 1 h. The solvent was removed in vacuo and the resulting solid was washed with ethanol twice. The pure product was obtained as an orange solid by recrystallization from ethanol. Yield 0.34 g (0.66 mmol, 55%). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.72 (m, 2 H, arom. H), 7.55 (m, 2 H, arom. H), 7.03 (m, 6 H, arom. H), 4.40 (m, 1 H, Cp), 4.19 (m, 2 H, Cp), 3.83 (s, 5 H, Cp), 3.29 (m, 1 H, Fc-C*H*CH_3), 1.90 (m br., 1 H, PC*H*CH_3), 1.76 (dd, $J_{H,H}$ = 6.7, J_{PH} = 16.2 Hz, 3 H, Fc-CHCH_3), 1.44 (m br., 1 H, PC*H*CH_3), 1.40−0.80 (m br., 4 H, CH_2), 1.21 (t, $J_{H,H}$ = 8.1 Hz, 3 H, PCHCH_3), 0.96 (dd, $J_{H,H}$ = 7.0, $J_{P,H}$ = 17.1 Hz, 3 H, PCHCH_3) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 135.68, 135.50, 133.49, 133.34, 129.14 (PPh_2), 70.21 (*Cp*), 69.64 (*Cp*), 69.12 (CpC_{ipso}), 36.63 (*Me*-Phospholane), 36.49 (*Me*-Phospholane), 34.85 (CH_2), 31.68 (CH_2), 25.43 [d, $J_{C,P}$ = 31.3 Hz, PCH(Me)CH_2], 24.27 [d, $J_{C,P}$ = 14.2 Hz, PCH(Me)CH_2], 21.13 (d, $J_{C,P}$ = 13.7 Hz, *C*HMe), 14.33 (CH*Me*) ppm. ^{31}P NMR (80 MHz, C_6D_6): δ = 20.22 (α-P), −30.49 (*ortho*-P) ppm. $C_{30}H_{34}FeP_2$ (512.4): calcd. C 70.32, H 6.69; found C 69.95, H 6.67.

General Procedure for the Synthesis of the Chromium Tricarbonyl Ligands 5 and 6: (*R*,*R*)-2,5-Dimethylphospholane (1 equiv.) was added to a stirred solution of the appropriate chloride-substituted chromium complex[8,10] (1 equiv.) in dry acetone (20 mL/mmol). Subsequently, $TlPF_6$ (1 equiv.), dissolved in 20 mL/mmol of acetone, was added dropwise over a period of one hour with an automatic syringe. The reaction mixture was stirred overnight at ambient temperature, quenched by adding NEt_3, filtered, evaporated and subjected to column chromatography (Al_2O_3, pentane followed by Et_2O).

[η^6-(*R*,*R*)-{[(*R*,*R*)-DMP]CHMe}$C_6H_4PPh_2$]Cr(CO)$_3$ (5'): Compound **5** was made from (*R*,*R*)-2,5-dimethylphospholane (0.25 g, 2.15 mmol), [η^6-(*R*,*R*)-{(Cl)CHMe}$C_6H_4PPh_2$]Cr(CO)$_3$ (0.99 g, 2.15 mmol) and $TlPF_6$ (0.71 g, 2.04 mmol) according to the general procedure described above. Yield: 0.93 g (1.72 mmol, 80%). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.63−7.53 [m, 2 H, $H_{ar.}$(PPh_2)], 7.43−7.34 [m, 2 H, $H_{ar.}$ (PPh_2)], 7.14−6.99 [m, 6 H, $H_{ar.}$(PPh_2)], 5.17 (ddt, $J_{H,H}$ = 6.5, $J_{H,P}$ = 3.2, $J_{H,H}$ = 1.1 Hz, 1 H, $H_{ar.}$), 4.69 (dt, *J* = 6.1, *J* = 1.3 Hz, $H_{ar.}$), 4.52 (t, *J* = 6.5 Hz, $H_{ar.}$), 4.29 (td, *J* = 6.3, *J* = 1.1 Hz, $H_{ar.}$), 3.64 (sext, *J* = 6.7, *J* = 1.1 Hz, 1 H, C*H*Me), 1.77 [m, 1 H, PC*H*(Me)CH_2], 1.63 (dd, $J_{H,P}$ = 15.6, $J_{H,H}$ = 6.8 Hz, 3 H, CH*Me*), 1.42−1.34 (m br., 2 H, CH_2), 1.20 [m, 1 H, PC*H*(Me)CH_2], 0.95 [dt, *J* = 8.1, *J* = 1.5 Hz, 3 H, PCH(*Me*)CH_2], 0.77 (d, *J* = 7.0 Hz, *J* = 17.0 Hz, 3 H, PCH(*Me*)CH_2], 0.58 (m, 1 H, CH_2), 0.48 (m, 1 H, CH_2) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 233.18 (*C*O), 135.24−127.12 [12 C, $C_{ar.}$(PPh_2)], 127.54 (d, *J* = 21.1 Hz, $C_{ipso,ar.}$), 104.53 (d, *J* = 20.1 Hz, $C_{ipso,ar.}$), 96.32 (d, *J* = 2.0 Hz, $C_{ar.}$), 92.95 (dd, $^2J_{C,P}$ = 15.4, $^4J_{C,P}$ = 3.8 Hz, $C_{ar.}$), 92.55 ($C_{ar.}$), 91.55 ($C_{ar.}$), 37.49 (d, *J* = 2.9 Hz, CH_2), 36.44 (s, CH_2), 36.28 (d, *J* = 17.2 Hz, *Me*-phospholane), 34.26 (d, *J* = 12.4 Hz, *Me*-phospholane), 24.85 [d, *J* = 28.8 Hz, PC*H*(Me)CH_2], 20.82 [d, *J* = 36.1 Hz, PC*H*(Me)CH_2], 15.19 (*C*HMe), 5.67 (CH*Me*) ppm. ^{31}P NMR (80 MHz, C_6D_6): δ = 29.16 (s, α-P), −20.63 (s, *ortho*-P) ppm. IR (C_6D_6): ν_{CO} = 1967, 1893 cm^{-1}. $C_{29}H_{30}CrO_3P_2$ (540.5): calcd. C 64.44, H 5.59; found C 64.22, H 5.69.

[η^6-(*S*,*S*)-{[(*R*,*R*)-DMP]CHMe}$C_6H_4PPh_2$]Cr(CO)$_3$ (6): Compound **6** was made from (*R*,*R*)-2,5-dimethylphospholane (0.227 g, 1.953 mmol), [η^6-(*S*,*S*)-{(Cl)CHMe}$C_6H_4PPh_2$]Cr(CO)$_3$ (0.90 g, 1.953 mmol) and $TlPF_6$ (0.648 g, 1.855 mmol) according to the general procedure described above. Yield: 1.01 g (1.77 mmol, 96%). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.64 [m, 2 H, $H_{ar.}$ (PPh_2)], 7.42 [m, 2 H, $H_{ar.}$ (PPh_2)], 7.15−7.05 [m, 6 H, $H_{ar.}$ (PPh_2)], 4.87 (dt, *J* = 6.1, *J* = 1.2 Hz, $H_{ar.}$), 4.63 (t, *J* = 6.4 Hz, $H_{ar.}$), 4.56 (m, 1 H, $H_{ar.}$), 4.26 (dt, *J* = 6.4, *J* = 0.9 Hz, $H_{ar.}$), 4.01 (q, *J* = 7.0 Hz, 1 H, C*H*Me), 1.91 [m, 1 H, PC*H*(Me)CH_2], 1.74 [m, 1 H, PC*H*(Me)CH_2], 1.62 (m, 1 H, CH_2), 1.50 (m, 1 H, CH_2), 1.41 (m, 1 H, CH_2), 1.33 (dd, *J* = 7.0, *J* = 4.0 Hz, 3 H, CH*Me*), 1.00 [PCH(*Me*)CH_2], 0.96 [PCH(*Me*)CH_2], 0.82 (m, 1 H, CH_2) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 233.10 (*C*O), 136.58 [d, *J* = 6.5 Hz, $C_{ipso,ar.}$(PPh_2)], 136.36 [d, *J* = 13.7 Hz, $C_{ipso,ar.}$(PPh_2)], 135.26−125.30 (10 C, P*Ph*$_2$), 127.00 (d, *J* = 23.0 Hz, $C_{ipso,ar.}$), 103.62 (d, *J* = 17.5 Hz, $C_{ipso,ar.}$), 98.74 ($C_{ar.}$), 93.80 ($C_{ar.}$), 90.23 ($C_{ar.}$), 88.45 (dd, *J* = 6.9 Hz; *J* = 3.6 Hz, $C_{ar.}$), 37.80 (d, *J* = 3.8 Hz, CH_2), 36.95 (s, CH_2), 35.65 [d, *J* = 18.1 Hz, PC*H*(Me)CH_2], 30.65 [d, *J* = 18.7 Hz, PC*H*(Me)CH_2], 21.50 [PCH(*Me*)CH_2], 21.23 [PCH(*Me*)CH_2], 18.18 (*C*HMe), 14.78 (CH*Me*) ppm. ^{31}P NMR

(80 MHz, C_6D_6): δ = 19.96 (d, $J_{P,P}$ = 20.1 Hz, α-P), −18.99 (d, $J_{P,P}$ = 20.1 Hz, *ortho*-P) ppm. IR (C_6D_6): $\tilde{\nu}_{CO}$ = 1968, 1898 cm^{-1}. $C_{29}H_{30}CrO_3P_2$ (540.5): calcd. C 64.44, H 5.59; found C 64.25, H 5.71.

General Procedure for the Synthesis of the Rhodium Complexes: $[NBDRhCl]_2$ (1 equiv.) and $AgBF_4$ (2 equiv.) were dissolved in THF (10 mL) in a Schlenk flask and the solution was stirred vigorously for 30 minutes at ambient temperature. The clear solution was removed from the precipitated AgCl by a syringe equipped with a filter needle, and dripped into a solution of the diphosphane (2 equiv.) in THF (5 mL). After stirring for 10 minutes, the product [(diene)Rh(PP*)]BF_4 was precipitated by adding Et_2O. The ethereal solution was discarded and the solid dried in vacuo.

[(NBD)Rh{(*R*,*R*)-(C_5H_5)Fe[C_5H_3(CHMe{(*R*,*R*)-DMP})(PPh_2)]}]-BF_4 (7): Compound **7** was obtained by treating complex **4** (44 mg, 0.085 mmol) with $[NBDRhCl]_2$ (20 mg, 0.043 mmol) and $AgBF_4$ (17 mg, 0.085 mmol), according to the general procedure described above. Yield: 50 mg (0.063 mmol, 74%). ^{31}P NMR (200 MHz, $CDCl_3$): δ = 61.03 (dd, $J_{P,P}$ = 45.8, $J_{P,Rh}$ = 150.2 Hz, α-P), 20.08 (dd, $J_{P,P}$ = 45.8, $J_{P,Rh}$ = 150.2 Hz, *ortho*-P) ppm. MS (SIMS): *m*/*z* (rel. int.) = 86.8 (100) $[BF_4]^-$, 707.5 (3.2) [(NBD)-Rh{(*R*,*R*)-(C_5H_5)Fe[C_5H_3(CHMe{(*R*,*R*)-DMP})(PPh_2)]}]$^+$.

[(NBD)Rh{[η^6-(*R*,*R*)-{[(*R*,*R*)-DMP]CHMe}$C_6H_4PPh_2$]Cr($CO)_3$}]-BF_4 (8): Compound **8** was obtained by treating complex **5** (125 mg, 0.232 mmol) with $[NBDRhCl]_2$ (53 mg, 0.116 mmol) and $AgBF_4$ (45 mg, 0.232 mmol), according to the general procedure described above. Yield: 122 mg (0.150 mmol, 64%). ^{31}P NMR (200 MHz, $CDCl_3$): δ = 68.92 (dd, $J_{P,P}$ = 38.5, $J_{P,Rh}$ = 130.0 Hz, α-P), 30.87 (dd, $J_{P,P}$ = 38.5, $J_{P,Rh}$ = 130.0 Hz, *ortho*-P) ppm. MS (SIMS): *m*/*z* (rel. int.) = 86.9 (100) $[BF_4]^-$, 734.8 (8.0) [(NBD)Rh{[η^6-(*R*,*R*)-{[(*R*,*R*)-DMP]CHMe}$C_6H_4PPh_2$]Cr($CO)_3$}]$^+$.

[(NBD)Rh{[η^6-(*S*,*S*)-{[(*R*,*R*)-DMP]CHMe}$C_6H_4PPh_2$]Cr($CO)_3$}]-BF_4 (9): Compound **9** was obtained by treating complex **6** (140 mg, 0.260 mmol) with $[NBDRhCl]_2$ (60 mg, 0.130 mmol) and $AgBF_4$ (51 mg, 0.260 mmol), according to the general procedure described above. Yield: 130 mg (0.160 mmol, 61%). ^{31}P NMR (200 MHz, $CDCl_3$): δ = 61.07 (dd, $J_{P,P}$ = 43.0, $J_{P,Rh}$ = 156.6 Hz, α-P), 28.66 (dd, $J_{P,P}$ = 43.0, $J_{P,Rh}$ = 156.6 Hz, *ortho*-P) ppm. MS (SIMS): *m*/*z* (rel. int.) = 87.0 (100) $[BF_4]^-$, 734.8 (20) [(NBD)Rh{[η^6-(*S*,*S*)-{[(*R*,*R*)-DMP]CHMe}$C_6H_4PPh_2$]Cr($CO)_3$}]$^+$.

{(*R*,*R*)-[C_5H_5]Fe[C_5H_3(CHMe{(*R*,*R*)-DMP})(PPh_2)]}$_2BF_4$ (10): Compound **10** was obtained by treating complex **4** (30.0 mg, 0.0586 mmol) with $[(NBD)_2Rh]BF_4$ (11.0 mg, 0.0293), according to the general procedure described above. Recrystallization from MeOH afforded single crystals suitable for X-ray diffraction.

Hydrogenation of Dimethyl Itaconate: Hydrogenations were carried out by putting a weighed amount of the [(NBD)Rh(PP*)]BF_4 complex (approx. 3 mg) in a glass vial and adding (under argon) the appropriate amount of a stock solution of the substrate in methanol (0.25 mmol/mL), in order to give a substrate-to-catalyst ratio of 200. After purging with hydrogen three times, the reaction was left to run for one hour.

X-ray Crystallographic Study: Single crystals suitable for X-ray analyses were grown from dry methanol. Crystal data and details of the structure determination are listed in Table 7. Data set for **4** was collected with an Enraf Nonius CAD4 diffractometer (Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator). The unit cell parameters were obtained by the least-squares refinement of 25 re-

Table 7. Crystallographic data for compounds **4**, **7**, **9** and **10**

Compound	**4**	**7**	**10**	**9**
Empirical formula	$C_{30}H_{34}P_2Fe$	$[C_{37}H_{42}P_2FeRh]BF_4$	$[C_{60}H_{68}Fe_2P_4Rh]BF_4$	$[C_{36}H_{38}O_3P_2CrRh]$ BF_4·CH_3OH
Formula mass	512.36	794.22	1214.44	854.37
Crystal habit, color	blocks, orange	blocks, red	blocks, red	rods, cognac
Crystal dimensions (mm)	0.4 × 0.32 × 0.2	0.51 × 0.32 × 0.16	0.32 × 0.23 × 0.2	0.41 × 0.1 × 0.04
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
Space Group	$P2_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	8.594(3)	9.614(3)	15.1856(19)	10.7121(10)
b (Å)	10.830(3)	17.084(4)	15.692(2)	12.6034(12)
c (Å)	14.631(4)	10.950(3)	25.684(3)	26.471(2)
β [°]	102.78(2)	104.545(8)	90.00	90.00
V (Å^3)	1328.1(7)	1740.8(8)	6120.4(13)	3573.9(6)
Z	2	2	4	4
D [g·cm^{-1}]	1.281	1.515	1.318	1.588
*F*000	540	812	2504	1744
μ (Mo-K_α) [cm^{-1}]	0.704	1.030	0.886	0.916
Diffractometer	Enraf−Nonius CAD4	Bruker−Smart CCD	Bruker−Smart CCD	Bruker−Smart CCD
T [K]	221(2)	293(2)	293(2)	110(2)
θ range	2.36−26.90	2.19−28.27	2.05−28.46	1.79−28.37
Reflections collected	7812	23873	85295	49337
Unique reflections	5773	8499	15370	8912
R_{int}	0.0284	0.0226	0.0715	0.0662
Reflections used	4429	8202	14441	8912
Parameters refined	301	418	655	459
R_1	0.0451	0.0347	0.0615	0.0339
wR_2	0.0910	0.0868	0.1546	0.0744
Flack's parameter	−0.008(16)	−0.012(15)	0.04(2)	0.001(17)
GooF	1.003	1.105	1.258	1.013
Diff. peak/ hole [e/Å^3]	0.29/−0.20	0.69/−0.40	1.35/−0.70	0.79/−0.34

flections. The data collection for **7**, **9** and **10** was performed with a Bruker Smart CCD (Mo-K_α radiation, λ= 0.71073 Å, graphite monochromator) area detector. The unit cell parameters were obtained by the least-squares refinement of 8096 reflections. All structures were solved by direct methods (SHELXS-97)[19] and refined by full-matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-97.[19] The SADABS[20] program was used for absorption correction of the structures **7**, **9** and **10**. All non-hydrogen atoms were refined anisotropically. All H atom positions were introduced at their idealized positions (d_{C-H} = 0.96 Å) and were refined using a riding model. The absolute configuration was confirmed by evaluation of the Flack[21] parameter. CCDC-217865, -217866, -217867 and -21786 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The authors wish to gratefully 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 Dr. Felix Spindler of Solvias for his help with the catalytic experiments. B. C. is grateful to the Graduiertenkolleg: "Methods of Asymmetric Synthesis" for a scholarship.

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Received September 30, 2003
Early View Article
Published Online April 1, 2004

