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New non-C_2-symmetric phosphine-phosphonites as ligands in asymmetric metal catalysis

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Abstract

Starting from 1,2-dibromobenzene, the synthesis of *N*,*N*,*N*′,*N*′-tetraethyl-[2-(diphenylphosphino)phenyl]phosphonous acid tetraamide is possible in two simple steps. This key compound reacts with a variety of chiral diols such as (*R*)- and (*S*)-binaphthol, 1,2:5,6-diisopropylidene-D-mannitol or (1*R*,2*R*)-1,2-diphenyl-1,2-ethane diol to form the corresponding non-C_2-symmetric phosphine-phosphonite compounds. These ligands react with $Rh(COD)_2BF_4$ to form bidentate Rh-complexes which serve as catalysts in the asymmetric hydrogenation of dimethyl itaconate with *ee* values of up to 88%.

1. Introduction

Interest in chiral non-C_2-symmetric bidentate organophosphorus compounds as ligands in asymmetric transition metal catalyzed reactions is increasing,[1] phosphine-phosphite[2] and phosphine-phosphinite[3] compounds being prominent examples. Less is known concerning chiral phosphine-phosphonite ligands.[3] Recently, we reported the highly enantioselective Rh-catalyzed hydrogenation of olefins using a chiral diphosphonite based on (*R*)- and (*S*)-binaphthol, the backbone being ferrocene.[4] This development arose from previous work relating to the synthesis of chiral phosphine-phosphonites derived from chiral diols.[5] A recent communication by Knight[6] described the synthesis of one of these ligands, namely compound **6**, and prompts us to report our data at this time. Specifically, we describe the synthesis of the chiral non-C_2-symmetric ligands **6**, **8** and **10**, as well as their use in transition metal catalyzed asymmetric hydrogenation.

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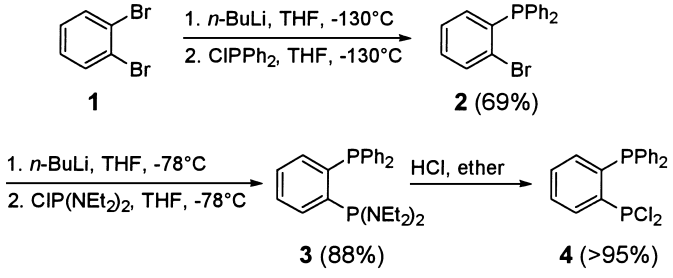
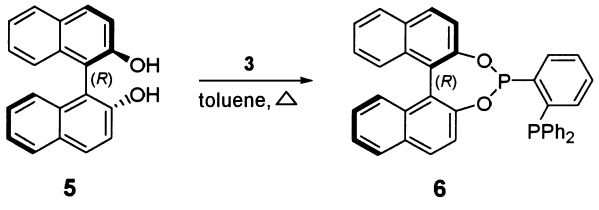
2. Results and discussion

We envisioned *N*,*N*,*N*′,*N*′-tetraethyl-[2-(diphenylphosphino)phenyl]phosphonous acid diamide **3** or [2-(diphenylphosphino)phenyl]phosphonous acid dichloride **4** as the key intermediates in the synthesis of ligands **6**, **8** and **10**. Accordingly, the known (2-bromophenyl)diphenylphosphine[7] **2** was first prepared by lithiation/phosphorylation of 1,2-dibromobenzene **1** (Scheme 1). Lithiation of **2** with *n*-butyllithium followed by in situ reaction with $ClP(NEt_2)_2$ (accessible in excellent yield from $PCl_3/HNEt_2$)[8] afforded the desired new compound **3** in 88% yield following isolation by high-vacuum distillation. This demonstrates that the use of two equivalents of *tert*-butyllithium, as recently described,[6] is not necessary, one equivalent of the cheaper *n*-butyllithium being perfectly suitable. Reaction of **3** with dry HCl in ether provided the dichloride **4** in almost quantitative yield.[5]



Scheme 1.

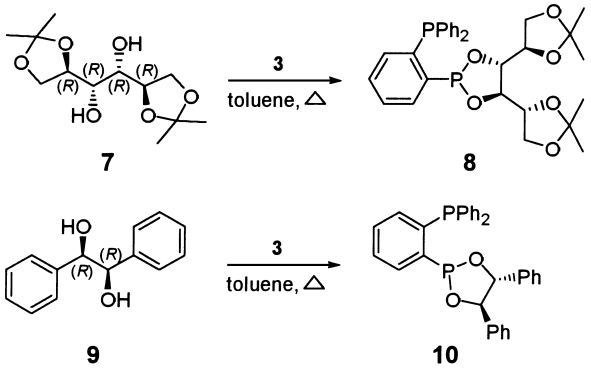
Upon treating **3** with the equivalent amount of (*R*)-binaphthol **5** in refluxing toluene, the desired ligand **6** was formed in excellent yield (Scheme 2). Removal of the solvent and Et_2NH, trituration with pentane and filtration afforded a white-beige analytically pure solid (88–90%) which was characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy, mass spectrometry (MS) and elemental analysis.[5] The analogous result was obtained using (*S*)-binaphthol.



Scheme 2.

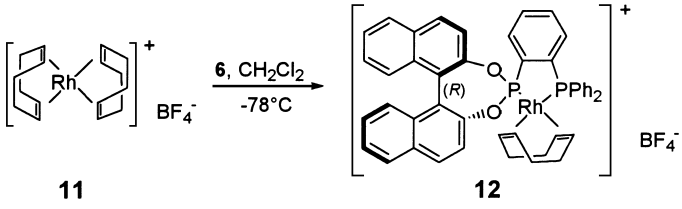
The analogous exchange reactions using 1,2:5,6-diisopropylidene-D-mannitol **7** or (1*R*,2*R*)-1,2-diphenyl-1,2-ethane diol (**9**) turned out to be slower (Scheme 3). Removal of Et_2NH during the synthesis led to excellent up to almost quantitative yields of **8** and **10**. Ligands **6**, **8** and **10** were also accessible by reaction of the dichloride **4** with the corresponding diols in the presence of a base, although this appeared to be less direct.[5]

Although compound **6** was prepared by Knight et al. from **4** and (*R*)-binaphthol **5**, no catalytic data were reported.[6] In principle, a wide variety of transition metal complexes can be prepared on the basis of ligands **6**, **8** and **10**. We began by attempting to synthesize a Rh-complex. However, upon injecting a CH_2Cl_2 solution of bis[η^2,η^2-(*Z*,*Z*)-1,5-cyclooctadiene]rhodium(I) tetrafluoroborate [$Rh(COD)_2BF_4$] **11** into a solution of ligand **6** at room temperature, a mixture of phosphorus-containing compounds was formed as judged by the ^{31}P NMR spectrum of the crude product (Scheme 4).[5] In contrast, a clean reaction took place by using an inverse reaction mode at low temperatures,[5] i.e. by adding a solution of the ligand **6** to a solution of $Rh(COD)_2BF_4$ in CH_2Cl_2 at −78°C. Complex **12** was formed in essentially



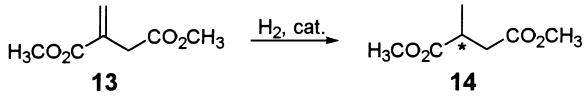
Scheme 3.

quantitative yield as judged by the ^{31}P NMR spectrum of the crude product. Following workup, the complex was isolated in analytically pure form in 95% yield and fully characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, and elemental analysis. The ^{31}P NMR spectrum revealed two doublets of doublets at δ=182.4 and 58.9, in line with the structure shown (cf. **12**).



Scheme 4.

As far as catalysis is concerned, either preformed complex **12** or an in situ reaction mode can be used. In the case of ligands **8** and **10**, only the in situ method was applied. Most of the initial efforts[5] concentrated on the Rh-catalyzed hydrogenation of dimethyl itaconate (**13**–**14**) (Scheme 5). In the literature, this reaction was most often carried out in methanol.[1] In the present case, methanol could not be used due to instability of the ligands in this medium.



Scheme 5.

The results summarized in Table 1 show that of the three ligands compound **6** is the most effective, delivering an *ee* value of 88% in favor of the (*R*)-configured product **14** in the optimal case of an in situ reaction mode. This competes favorably with some of the ligands previously reported in the literature, but others are clearly more effective (*ee* >95%).[1,4] It is interesting to note that BINAP,[1a] when used in CH_2Cl_2, leads to an *ee* value of only 76%,[8] whereas in methanol enantioselectivity is much higher (*ee* >95%).[1a] These and other observations[1,8] show that solvent effects are extremely important in asymmetric hydrogenation.

3. Summary

The synthesis of the non-C_2-symmetric ligands **6**, **8** and **10** is possible in three simple steps starting from 1,2-dibromobenzene allowing for a simple variation of the ligands chirality and steric nature. This

Table 1
Asymmetric hydrogenation of dimethyl itaconate (**13**→ **14**) in CH_2Cl_2 (Lig/Rh=1.0, 22°C, 1.3 bar H_2)

Entry	Catalyst	S/C	Reaction time (h)	Conversion (%)	% *ee* (configuration of **14**)
1	**6**/Rh(COD)$_2$BF$_4$[a]	1000	2.5	100	88 (*R*)
2	**6**/Rh(COD)$_2$BF$_4$[a]	2000	3.2	93	87 (*R*)
3	**12**[b]	1000	1.5	100	82 (*R*)
4	**8**/Rh(COD)$_2$BF$_4$[a]	1000	2.5	100	52 (*S*)
5	**8**/Rh(COD)$_2$BF$_4$[a]	2000	2.8	90	60 (*S*)
6	**10**/Rh(COD)$_2$BF$_4$[a]	1000	1.5	100	77 (*S*)
7	**10**/Rh(COD)$_2$BF$_4$[a]	2000	1.5	100	79 (*S*)

[a] *In situ* reaction mode.

[b] Preformed catalyst.

synthetic scheme makes phosphine-phosphonites with an *ortho*-phenylene backbone easily accessible in an analytically pure form. Initial studies directed towards their use as chiral ligands in the asymmetric Rh-catalyzed hydrogenation of dimethyl itaconate reveal appreciable degrees of enantioselectivity (up to 88% *ee*). It remains to be seen if further ligand tuning can improve the efficiency of these types of ligands. Studies are also under way to test them in C–C bond forming reactions.

4. Experimental

4.1. General

All manipulations were carried out under strict exclusion of air and humidity using standard Schlenk-type techniques. NMR spectra were recorded at room temperature on Bruker AC 200, AM 200 and AMX 300 spectrometers. Chemical shifts are given in ppm relative to TMS or 85% H_3PO_4 as external standards, and coupling constants are given in hertz. Electron ionization (70 eV) mass spectra were recorded on a Finnigan MAT 8200 instrument using fractional evaporation. High resolution electron ionization (70 eV) mass spectra were recorded on a Finnigan MAT 95 instrument. Fourier transform IR spectra were recorded on a Nicolet Magna-IR 750 spectrometer. Elemental analyses were carried out by Mikroanalytisches Labor H. Kolbe, Mülheim an der Ruhr. GC analyses were carried out on Carlo Erba 5300 and Hewlett–Packard 5890 instruments (conditions given below). The assignment of absolute configuration of product **14** was done by comparison with a commercial sample of (*R*)-(+)-2-methyl dimethyl succinate (Aldrich).

4.2. Materials

Ether, THF, pentane, benzene and toluene were all distilled from sodium tetraethylalanate. Dichloromethane and trichloromethane were distilled from calcium hydride. Ethanol was dried

with magnesium or sodium ethanolate and diethyl phthalate and distilled. Solvents were stored under argon until use. *n*-Butyllithium was obtained from Chemetall GmbH as a 1.6 M solution in hexane. Chlorodiphenylphosphine was obtained from Aldrich and distilled prior to use. 1,2:5,6-Diisopropylidene-D-mannitol was obtained from Fluka; (*R*)- and (*S*)-binaphthol (*R*: 98% *ee*, *S*: 99% *ee*) and 1,2-dibromobenzene were purchased from Aldrich and used without further purification. Bis(diethylamino)chlorophosphine,[9a] (1*R*,2*R*)-1,2-diphenyl-1,2-ethane diol **9**[9b] and bis[η^2,η^2-(*Z*,*Z*)-1,5-cyclooctadiene]rhodium(I) tetrafluoroborate[9c] **11** were all prepared according to literature procedures. The density of bis(diethylamino)-chlorophosphine was determined to be 0.978 kg l^{-1}. Dimethyl itaconate was obtained from Fluka and distilled under reduced pressure prior to use.

4.3. Improved synthesis of (2-bromophenyl)diphenylphosphine **2**

The synthesis follows a protocol published by Ravindar et al.[7b] A 1 l three-necked round-bottom flask equipped with a 500 ml dropping funnel and an overhead stirring device was charged with 125 ml of a 1.6 M solution of *n*-butyllithium in hexane (200 mmol) and 500 ml THF. This mixture was cooled down to −130°C (pentane/liq. N_2) and a solution of 24.0 ml (199 mmol) of 1,2-dibromobenzene in 200 ml THF was slowly added within 2 h under vigorous stirring. After completely adding the 1,2-dibromobenzene, the reaction mixture was stirred for a further 20 min at −130°C before a solution of 36.8 ml (200 mmol) of chlorodiphenylphosphine in 200 ml THF was added. The resulting mixture was then allowed to slowly warm to room temperature affording a slightly yellow solution from which any insoluble residues were filtered off. It was necessary to carefully avoid too intensive cooling, i.e. by adding too much liquid nitrogen to the cooling bath.

The solvent was then removed in vacuo yielding a yellow-green, oily residue. Methanol (100 ml) was immediately added to this and the suspension was stirred overnight. The yellow solution was filtered off and the solid residue was washed twice with 100 ml of methanol. The crude product was then recrystallized from ethanol to afford a crystalline, slightly greenish solid which was dried in vacuo (46.84 g, 69%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.15–7.05 (*m*, 5H), 6.83–6.76 (*m*, 6H), 6.63 (*m*, 1H), 6.51 (*m*, 1H), 6.43 (*m*, 1H). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ −4.1 (*s*). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 133.8 (*d*, $^1J_{CP}$=11.4 Hz, *C*PAr_2), 131.7 (*d*, $^1J_{CP}$=10.7 Hz, *C*PC_6H_4-*o*-Br), 129.3 (*s*), 128.9 (*d*, $^2J_{CP}$=20.2 Hz, C_6H_5-*o*-PAr), 127.8 (*d*, $^2J_{CP}$=2.4 Hz, C_6H_4-*o*-Br), 125.0 (*s*), 124.8 (*d*, $^2J_{CP}$=31.1 Hz, *C*Br), 123.9 (*s*, C_6H_5-*p*-PAr), 123.5 (*d*, $^3J_{CP}$=7.2 Hz, C_6H_5-*m*-PAr), 122.3 (*s*). MS (EI, 70 eV, pos. ions): *m/z*=340 (85%, M^+), 339 (87%, $[M-H]^+$), 260 (17%, $[M-Br]^+$), 183 (82%, [9-phosphafluorenyl]$^+$).

4.4. Synthesis of N,N,N′,N′-tetraethyl-[2-(diphenylphosphino)phenyl]phosphonous acid diamide **3**

A 250 ml three-necked round-bottom flask equipped with a 50 ml dropping funnel was charged with 10.55 g (30.92 mmol) of (2-bromophenyl)diphenylphosphine **2** and 150 ml THF. The solution was cooled down to −78°C and 21.5 ml of a 1.6 M solution of *n*-butyllithium in hexane (34.4 mmol) was added within 10 min via a syringe. The resulting orange solution was then stirred for another 30 min at this temperature.

To this mixture was added, over a period of 30 min, a solution of 7.3 ml (34 mmol) of bis(diethylamino)chlorophosphine in 45 ml THF. The reaction mixture was then allowed to slowly warm up to room temperature. Removal of the solvent in vacuo afforded a viscous brown residue to which 150 ml of pentane was added. The resulting suspension was filtered over Celite and the solvent evaporated in vacuo. Fractional distillation of the brown and very viscous raw product under high vacuum afforded two fractions (43°C and 130°C/$<10^{-6}$ mbar) containing side products and a bright yellow, very viscous oil

(bp 170–180°C/$<10^{-6}$ mbar) as the pure product (11.66 g, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (*m*, 1H), 7.31 (*m*, 1H), 7.27–7.22 (*m*, 10H), 7.15 (*m*, 1H), 7.05 (*m*, 1H), 3.07–2.82 (*m*, 8H, NCH_2), 0.97 (*t*, $^{3}J_{HH}$=18.3 Hz, 12H, CH_3). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 149.0 (*dd*, $^{1}J_{CP}$=42 Hz, $^{2}J_{CP}$=13 Hz, $C_6H_4PN_2$), 139.9 (*dd*, $^{2}J_{CP}$=29.6 Hz, $^{1}J_{CP}$=14.8 Hz, $C_6H_4PAr_2$), 138.1 (*dd*, $^{1}J_{CP}$=14 Hz, $^{4}J_{CP}$=4.4 Hz, $C_6H_5PAr_2$), 135.1 (*dd*, $^{2}J_{CP}$=4.4 Hz, $^{3}J_{CP}$=1.5 Hz, C_6H_4-*m*-PN_2-*o*-PAr_2), 133.4 (*d*, $^{2}J_{CP}$=19.6 Hz, C_6H_5-*o*-PAr_2), 129.9 (*dd*, $^{2}J_{CP}$=8 Hz, $^{3}J_{CP}$=4 Hz, C_6H_4-*o*-PN_2-*m*-PAr_2), 128–127.7 (*m*), 127.4 (*s*), 43.1 (*d*, $^{2}J_{CP}$=18.3 Hz, CH_2), 43.06 (*d*, $^{2}J_{CP}$=18.3 Hz, CH_2), 14.4 (*d*, $^{3}J_{CP}$=3.4 Hz, CH_3). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 93.5 (*d*, $^{3}J_{PP}$=135 Hz, PN_2), −14.5 (*d*, PPh_2). MS (EI, 70 eV, pos. ions): *m/z*=436 (18%, M^+), 364 (100%, $[M-C_4H_{10}N]^+$), 293 (40%, $[M-C_8H_{19}N_2]^+$), 183 (11%, [9-phosphafluorenyl]$^+$). HRMS (EI, 70 eV, pos. ions): *m/z*=436.2192 (5) (436.2197 calcd). IR (capillary): $\tilde{\nu}$=ν(=C−H) 3069, 3050 (*s*), ν(C=C) 1434 (*s*, br.), ν(C–N) 1185 (*s*, br.), ν(P–N) 919 (*s-m*, br.) cm^{-1}.

*4.5. Synthesis of [2-(diphenylphosphino)phenyl]phosphonous acid dichloride **4***

A round-bottom flask was charged with 817 mg (2.25 mmol) of *N*,*N*,*N*′,*N*′-tetraethyl-[2-(diphenylphosphino)phenyl]phosphonous acid diamide **3** and 50 ml of diethyl ether. To this solution was added 10 ml of a 5.8 M solution of hydrogen chloride in diethyl ether at room temperature, affording a colorless suspension. The colorless precipitate was filtered off and the solvent evaporated from the clear filtrate under reduced pressure, yielding a greenish solid which was dried in vacuo (910 mg, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13 (*m*, 1H), 7.59 (*m*, 1H), 7.45 (*m*, 1H), 7.33 (*m*, 1H), 7.27–7.16 (*m*, 10H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 146.0 (*dd*, $^{1}J_{CP}$=55 Hz, $^{2}J_{CP}$=29 Hz, $C_6H_4PCl_2$), 140.8 (*dd*, $^{1}J_{CP}$=9.51 Hz, $^{2}J_{CP}$=33.2 Hz, $C_6H_4PAr_2$), 134.9 (*dd*, $^{1}J_{CP}$=9 Hz, $^{3}J_{CP}$=9 Hz, $C_6H_5PAr_2$), 133.4 (*d*, $^{2}J_{CP}$=2.4 Hz), 133.3 (*d*, $^{2}J_{CP}$=18.5 Hz, C_6H_5-*o*-PAr_2), 132.1 (*s*), 130.2 (*dd*, $^{2}J_{CP}$=8 Hz, $^{3}J_{CP}$=4 Hz), 130.1 (*s*), 128.8 (*s*), 128.4 (*d*, $^{3}J_{CP}$=6.1 Hz). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 157.1 (*d*, $^{3}J_{PP}$=336 Hz, PCl_2), −19.6 (*d*, PPh_2). MS (EI, 70 eV, pos. ions): *m/z*=362 (48%, M^+), 327 (100%, $[M-Cl]^+$), 183 (73%, [9-phosphafluorenyl]$^+$). IR (KBr): $\tilde{\nu}$=ν(=C–H) 3067, 3051 (*s*), ν(C=C) 1583, 1478, 1434 (*s*), ν(P–Cl) 481 cm^{-1}. Anal. calcd for $C_{18}H_{14}Cl_2P_2$: C, 59.53; H, 3.88; Cl, 19.52; P, 17.06. Found: C, 58.20; H, 4.36; Cl, 19.42; P, 17.18.

4.6. Synthesis of phosphine-phosphonites

4.6.1. General procedure for the synthesis of phosphine-phosphonites

A 100 ml round-bottom flask equipped with a reflux condenser was charged with a weighed amount of the appropriate diol. Added to this was an equimolar amount of *N*,*N*,*N*′,*N*′-tetraethyl-[2-(diphenylphosphino)phenyl]phosphonous acid diamide **3** as a solution in toluene (usually about 45–145 mmol l^{-1}) and the mixture was heated to reflux. The reaction can be followed by ^{31}P NMR and was usually complete within 24 to 48 h (mmolar scale). After cooling to room temperature, the solvent was removed under reduced pressure and the oily residue was stirred in 20–50 ml of pentane overnight. The liquid phase was then filtered off and the solid residue washed again with pentane. Finally, the powdery solid was dried in vacuo. ^{31}P NMR did not indicate the formation of side products and isolated yields typically ranged from 80 to 95%.

*4.6.2. Synthesis of (*R*)-2-[2-(diphenylphosphino)phenyl]-1,3,2-dinaphtho[*d^{1,2},f^{1,2}*]dioxaphosphepine **6***

(*R*)-Binaphthol (378 mg, 1.32 mmol) and 9.10 ml of a 0.145 M solution of *N*,*N*,*N*′,*N*′-tetraethyl-2-(diphenylphosphino)phenylphosphonous acid diamide (**3**) (1.32 mmol) were reacted as outlined above, affording a white-beige powder (606 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (*m*, 1H), 7.83 (*m*,

1H), 7.72 (*m*, 1H), 7.5–7.4 (*m*, 4H), 7.4–7.32 (*m*, 4H), 7.32–7.0 (*m*, 13H), 6.96 (*m*, 1H), 6.07 (*d*, J_{HP}=8.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 135.1 (*s*), 134.8 (*s*), 133.8 (*d*, J_{CP}=4 Hz), 133.5 (*s*), 133.2 (*s*), 131.4 (*s*), 130.5 (*s*), 129.3 (*s*), 129.1 (*s*), 128.8 (*s*), 128.7 (*s*), 128.6 (*s*), 128.5 (*s*), 128.4 (*s*), 128.2 (*s*), 126.9 (*s*), 126.1 (*s*), 125.9 (*s*), 124.8 (*s*), 124.6 (*s*), 121.9 (*s*), 121.7 (*s*); (75 MHz, $D_5C_6CD_3$): δ 152.3 (*s*), 149.5 (*d*, J_{CP}=1.9 Hz), 148.2 (*d*, J_{CP}=7.1 Hz), ca. 143 (*m*). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 174.6 (*d*, $^3J_{PP}$=212 Hz, PO_2), −19.2 (*d*, $^3J_{PP}$=212 Hz, PPh_2). MS (EI, 70 eV, pos. ions): *m/z*=576 (100%, M^+), 575 (92%, $[M-H]^+$), 499 (98%, $[M-C_6H_5]^+$), 449 (64%, $[M-C_{10}H_7]^+$), 435 (30%, $[M-C_{10}H_5O]^+$), 252 (8%, $[C_{20}H_{12}]^+$), 183 (41%, [9-phosphafluorenyl]$^+$). IR (KBr): $\tilde{\nu}$=ν(aryl–O) 1230 (*s*), ν(P–O) 951 (*s*) cm^{-1}. Anal. calcd for $C_{38}H_{26}O_2P_2$: C, 79.16; H, 4.54; P, 10.74. Found: C, 78.98; H, 4.64; P, 10.65.

*4.6.3. Synthesis of (4*R,*5*R*)-4,5-bis[(4*R*)-2,2-dimethyl-1,3-dioxolan-4-yl]-2-[2-(diphenylphosphino)-phenyl]-1,3,2-dioxaphospholane* ***8***

1,2:5,6-Diisopropylidene-D-mannitol (236 mg, 900 μmol) and 20.0 ml of a 45.0 M solution of *N,N,N′,N′*-tetraethyl-[2-(diphenylphosphino)phenyl]phosphonous acid diamide **3** (900 μmol) were reacted as outlined above affording a white-beige powder (434 mg, 87%). In some cases it was necessary to remove the solvent completely after 48 h reflux and redissolve the residue in fresh toluene to afford complete conversion upon further heating. In one case this procedure had to be carried out twice (96 h reaction time in this case). ^1H NMR (300 MHz, $CDCl_3$): δ 7.53 (*m*, 1H), 7.37–7.23 (*m*, 7H), 7.23–7.06 (*m*, 6H), 4.31 (*dd*, J_{HH}=5.8 Hz, J_{HH}=6 Hz, 1H, *anti-H*COPO), 4.14 (*ddd*, $^3J_{HH}$=6 Hz, $^3J_{HH}$=5 Hz, $^3J_{HH}$=5 Hz, 1H, OCH_2CHO), 3.95 (*dd*, $^3J_{HH}$=5 Hz, $^2J_{HH}$=6.3 Hz, 2H, OCH_2CHO), 3.68 (*ddd*, $^3J_{HH}$=9 Hz, $^3J_{HP}$=8.9 Hz, $^3J_{HH}$=5.8 Hz, 1H, *anti-H*COPO), 3.31 (*dd*, $^3J_{HH}$=4 Hz, $^2J_{HH}$=8.9 Hz, 1H, OCH_2CHO), 3.21 (*ddd*, $^3J_{HH}$=9 Hz, $^3J_{HH}$=4 Hz, $^3J_{HH}$=6 Hz, 1H, OCH_2CHO), 2.94 (*dd*, $^2J_{HH}$=8.9 Hz, $^3J_{HH}$=6 Hz, 1H, OCH_2CHO), 1.37 (*s*, 3H), 1.28 (*s*, 3H), 1.21 (*s*, 3H), 1.03 (*s*, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 150.5 (*dd*, $^1J_{CP}$=55.9 Hz, $^2J_{CP}$=30.4 Hz, $C_6H_4PO_2$), 138.6 (*dd*, $^1J_{CP}$=11.2 Hz, $^2J_{CP}$=22.2 Hz, $C_6H_4PAr_2$-*o*-PO_2), 136.5 (*dd*, $^1J_{CP}$=9.1 Hz, $^4J_{CP}$=5 Hz, $C_6H_5PAr_2$), 134.4 (*dd*, $^1J_{CP}$=8 Hz, $^4J_{CP}$=2 Hz, $C_6H_5PAr_2$), 134.3 (*s*), 133.1 (*d*, $^2J_{CP}$=19.6 Hz, C_6H_5-*o*-PAr_2), 132.0 (*d*, $^2J_{CP}$=18 Hz, C_6H_5-*o*-PAr_2), 129.1 (*s*), 128.3 (*s*), 128.1 (*s*), 127.6 (*d*, $^3J_{CP}$=7.6 Hz, C_6H_5-*m*-PAr_2), 127.3 (*d*, $^3J_{CP}$=6.2 Hz, C_6H_5-*m*-PAr_2), 127.3 (*s*), 126.5 (*dd*, $^2J_{CP}$=13.3 Hz, $^3J_{CP}$=7.5 Hz, C_6H_4-*o*-PO_2-*m*-PAr_2), 108.7 (*s*, $O_2C(CH_3)_2$), 108.5 (*s*, $O_2C(CH_3)_2$), 80.1 (*d*, $^3J_{CP}$=9.4 Hz, PO*C*H), 79.5 (*d*, $^3J_{CP}$=9.8 Hz, PO*C*HR_2), 75.3 (*d*, $^4J_{CP}$=3.2 Hz, O*C*HCH_2O), 74.9 (*s*, O*C*HCH_2O), 65.8 (*s*, $OCHCH_2O$), 64.4 (*s*, $OCHCH_2O$), 25.7 (*s*, CH_3), 25.4 (*s*, CH_3), 24.3 (*s*, CH_3), 24.1 (*s*, CH_3). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 171.1 (*d*, $^3J_{PP}$=132 Hz, PO_2), −20.8 (*d*, PPh_2). MS (EI, 70 eV, pos. ions): *m/z*=552 (100%, M^+), 537 (24%, $[M-CH_3]^+$), 325 (83%, $[M-C_{12}H_{19}O_4]^+$), 228 (1%, $[C_{12}H_{20}O_4]^+$), 183 (12%, [9-phosphafluorenyl]$^+$), 43 (21%, $[CH_3CO]^+$). IR (KBr): $\tilde{\nu}$=ν(=C–H) 3056 (*s*), $\delta_s(CH_3)$ 1368 (*s*), ν(O–C–O) 1146, 1086, 1056 (*s*, br.) cm^{-1}. Anal. calcd for $C_{30}H_{34}O_6P_2$: C, 65.21; H, 6.20; P, 11.21. Found: C, 65.36; H, 6.19; P, 11.31.

*4.6.4. Synthesis of (4*R,*5*R*)-4,5-diphenyl-2-[2-(diphenylphosphino)phenyl]-1,3,2-dioxaphospholane* ***10***

(1*R*,2*R*)-1,2-Diphenyl-1,2-ethane diol (482 mg, 2.2 mmol) and 50.0 ml of a 45 M solution of *N,N,N′,N′*-tetraethyl-[2-(diphenylphosphino)phenyl]phosphonous acid diamide **3** (2.25 mmol) were reacted as outlined above affording a white-beige powder (993 mg, 88%). In some cases it was necessary to remove the solvent completely after 48 h reflux and redissolve the residue in fresh toluene to afford complete conversion upon further heating. This procedure had to be carried out up to two times (96 h reaction time in this case). ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (*m*, 1H), 7.36 (*m*, 21H), 6.69 (*dd*, J_{HP}=1 Hz, J_{HH}=7.4 Hz, 2H), 4.76 (*dd*, $^3J_{HH}$=9.3 Hz, $^3J_{HP}$=1.1 Hz, 1H, *anti*-POC*H*), 4.65 (*d*, $^3J_{HH}$=9.3 Hz, 1H, *syn*-POC*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.2 (*dd*, $^1J_{CP}$=55 Hz, $^2J_{CP}$=31.1 Hz, $C_6H_4PO_2$), 139.2 (*dd*, $^1J_{CP}$=21 Hz, $^2J_{CP}$=11.6 Hz, $C_6H_4PAr_2$), 136.0 (*dd*, $^1J_{CP}$=8.4 Hz, $^4J_{CP}$=3.6 Hz, $C_6H_5PAr_2$),

135.0 (*s*, C_6H_5CHO), 135.1 (*dd*, $^1J_{CP}$=13.3 Hz, $^4J_{CP}$=3.5 Hz, $C_6H_5PAr_2$), 134.2 (*s*), 132.9 (*d*, $^2J_{CP}$=18.9 Hz, C_6H_5-*o*–PAr_2), 132.3 (*d*, $^2J_{CP}$=18.1 Hz, C_6H_5-*o*-PAr_2), 129.0 (*s*), 128.1 (*s*), 127.6 (*s*), 127.4 (*s*), 127.3 (*s*), 127.23 (*s*), 127.17 (*s*), 127.0 (*s*), 126.8 (*dd*, $^2J_{CP}$=13.5 Hz, $^3J_{CP}$=8 Hz, C_6H_4-*o*-PO_2-*m*-PAr_2), 126.4 (*s*), 126.0 (*s*), 86.1 (*d*, $^2J_{CP}$=8.6 Hz, O*C*HCHO), 83.2 (*d*, $^2J_{CP}$=7.2 Hz, O*C*HCHO). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 173.1 (*d*, $^3J_{PP}$=120 Hz, PO_2), −19.4 (*d*, PPh_2). MS (EI, 70 eV, pos. ions): *m/z*=504 (3%, M^+), 324 (32%, $[M-C_{14}H_{12}]^+$), 323 (42%, $[M-C_{14}H_{13}]^+$), 183 (22%, [9-phosphafluorenyl]$^+$), 180 (100%, $[C_{14}H_{12}]^+$). IR (KBr): $\tilde{\nu}$=ν(C=C) 1433 (m-s), ν(P–O) 985, 963 (*s*) cm^{-1}. Anal. calcd for $C_{32}H_{26}O_2P_2$: C, 76.18; H, 5.19; P, 12.28. Found: C, 76.07; H, 5.15; P, 12.12.

*4.6.5. Synthesis of {(*R*)-2-[2-(diphenylphosphino)phenyl]-1,3,2-dinaphtho[d^{1,2},f^{1,2}]dioxaphosphepine}-[η^2,η^2-(Z,Z)-1,5-cyclooctadiene]rhodium(I) tetrafluoroborate **12***

A 100 ml Schlenk tube was charged with 16.0 ml of a 29.1 M solution of bis[η^2,η^2-(*Z*,*Z*)-1,5-cyclooctadiene]rhodium(I) tetrafluoroborate **11** (466 μmol) in dichloromethane. At −78°C a solution of 271 mg (470 μmol) of (*R*)-2-[2-(diphenylphosphino)phenyl]-1,3,2-dinaphtho[$d^{1,2}$,$f^{1,2}$]dioxaphosphepine **6** in 20 ml of dichloromethane was added over a period of 70 min via a syringe pump. The orange solution was allowed to warm up to room temperature and the solvent was removed under reduced pressure. The orange, slightly oily residue was then suspended in 25 ml of pentane and stirred overnight at room temperature. Finally the liquid phase was filtered off and the residue was dried in vacuo, affording a bright orange powder (385 mg, 95%). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.26 (*d*, J_{HH}=8.8 Hz, 1H), 8.10 (*d*, J_{HH}=8.2 Hz, 1H), 8.03 (*d*, 1H, J_{HH}=9.4 Hz, 1H), 8.00 (*d*, J_{HH}=9.1 Hz, 1H), 7.95–7.48 (*m*, 15H), 7.4–7.2 (*m*, 5H), 7.12–6.90 (*m*, 2H), 5.77 (*m*, 1H, CH_2CH=C), 5.46 (*m*, 1H, CH_2CH=C), 5.21 (*m*, 1H, CH_2CH=C), 4.98 (*m*, 1H, CH_2CH=C), 2.65–2.00 (*m*, 8H, CH_2CH=C). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 148.5 (*d*, J_{CP}=13.7 Hz), 147.8 (*d*, J_{CP}=7.3 Hz), 144.8 (*ddd*, *J*=56.0 Hz, *J*=39.9 Hz, *J*=8.4 Hz), ca. 140 (*m*), 135.7 (*d*, *J*=5.8 Hz), 133.7–133.5 (*m*), 132.9 (*m*), 132.6–132.5 (*m*), 132.2–132.0 (*m*), 132.1 (*s*), 131.5 (*s*), 130.7 (*s*), 130.5 (*s*), 130.3–130.0 (*m*), 129.1 (*s*), 129.0 (*s*), 127.5 (*s*), 127.3 (*s*), 127.3 (*s*), 127.2 (*s*), 126.3 (*s*), 126.0 (*s*), 122.7 (*dd*, *J*=82.7 Hz, *J*=3.0 Hz), 121.1–120.7 (*m*), 111.8 (*dd*, *J*=27.8 Hz, *J*=33.4 Hz, CH_2CH=), 111.3 (*dd*, *J*=4.9 Hz, *J*=11.0 Hz, CH_2CH=), 105.2 (*m*, CH_2CH=), 100.4 (*m*, CH_2CH=), 31.6–28.4 (*m*, CH_2). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ 182.4 (*dd*, $^1J_{PRh}$=227.2 Hz, $^2J_{PP}$=32.8 Hz, PO_2), 58.9 (*dd*, $^1J_{PRh}$=153.0 Hz, PPh_2). Anal. calcd for $C_{46}H_{38}BF_4O_2P_2Rh$: C, 63.18; H, 4.38; P, 7.08; Rh, 11.78. Found: C, 63.08; H, 4.38; P, 7.04; Rh, 11.66.

*4.7. General procedure for the hydrogenation of dimethyl itaconate **13***

Hydrogenations were carried out in 25 or 50 ml round-bottom flasks which were charged with 1 ml dimethyl itaconate **13** 1 M in dichloromethane and measured volumina of solutions of bis[η^2,η^2-(*Z*,*Z*)-1,5-cyclooctadiene]rhodium(I) tetrafluoroborate **11** [$Rh(cod)_2BF_4$] 1 M in dichloromethane as well as one of the ligands **6**, **8** and **10** 1 M in dichloromethane according to the ligand-to-rhodium ratio (L:Rh) and the substrate-to-catalyst ratio (S:C), i.e. 1 ml [$Rh(cod)_2BF_4$] (**11**) 1 M in dichloromethane and 1 ml ligand 1 M in dichloromethane for L:Rh=1 and S:C=1000. To the mixture thus obtained, dichloromethane was added to a total volume of 10 ml, the argon atmosphere was replaced by hydrogen (1.3 bar) and the mixture was stirred for a given period of time (1–20 h). An aliquot of the mixture was then filtered over silica and analyzed via capillary GC: 30 m RTX-1 100% dimethylpolysiloxane (0.25 mm), 0.6 bar H_2, 60°C/5°C min^{-1}−300°C/4 min; t_R=7.2 min, 2-methyl dimethyl succinate (**14**); 7.9 min, dimethyl itaconate (**13**). 30 m GT-A, trifluoroactyl γ-cyclodextrin (0.25 mm), 0.9 bar H_2, 60°C/0.8°C min^{-1}−87°C/5°C min^{-1}−127°C; t_R=24.0 min, (*S*)-**14**; 25.0 min, (*R*)-**14**.

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