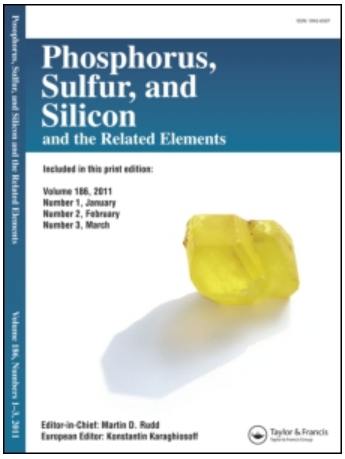

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AROMATIC PHOSPHONATE-PHOSPHINES

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Communication

AROMATIC PHOSPHONATE-PHOSPHINES

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Aromatic phosphonate-phosphines **3a,b** are obtained by reaction of 4-halogen-substituted phenylphosphonates **2a,b,c** and lithium diphenylphosphide. They can be transformed into air-stable phosphine-boranes **4a,b** by co-ordination of the borane-THF complex. The reaction of the phosphonate-phosphine **3b** with $[ClRh(cod)]_2$ affords the corresponding rhodium phosphine complex **5**. The cyclic phosphinate **8** with a binaphthalene skeleton can be obtained by a new cyclisation reaction of 2-bromo-2′-diisopropylphosphono-binaphthalene **7** with lithium diphenylphosphide.

Keywords: phosphonate-phosphines; rhodium phosphine complex; phosphine-boranes

Transition metal complexes with bidentate ligands having groups of different donor character, e.g. phosphonate-phosphines,[1] amine-phosphines,[2,3] ether-phosphines,[4] and phosphine sulphide-phosphines[5] are known to enhance catalytic reactions with carbon monoxide and hydrogen (carbonylation, hydroformylation, hydrogenation and others). We reported already on the synthesis and complexation behaviour of hemilabile aliphatic phosphonate-phosphines and on catalytic properties of the corresponding rhodium complexes in carbonylation of methanol.[1,6] Activation parameters measured for several phosphonate-phosphines indicated that the arrangement between phosphonate and phosphine moiety strongly affects the transition between open-chain and chelate complex structures. Therefore we tried to prepare ligands where both the phosphino and the phosphonato group are bond to aromatic rings in different positions.

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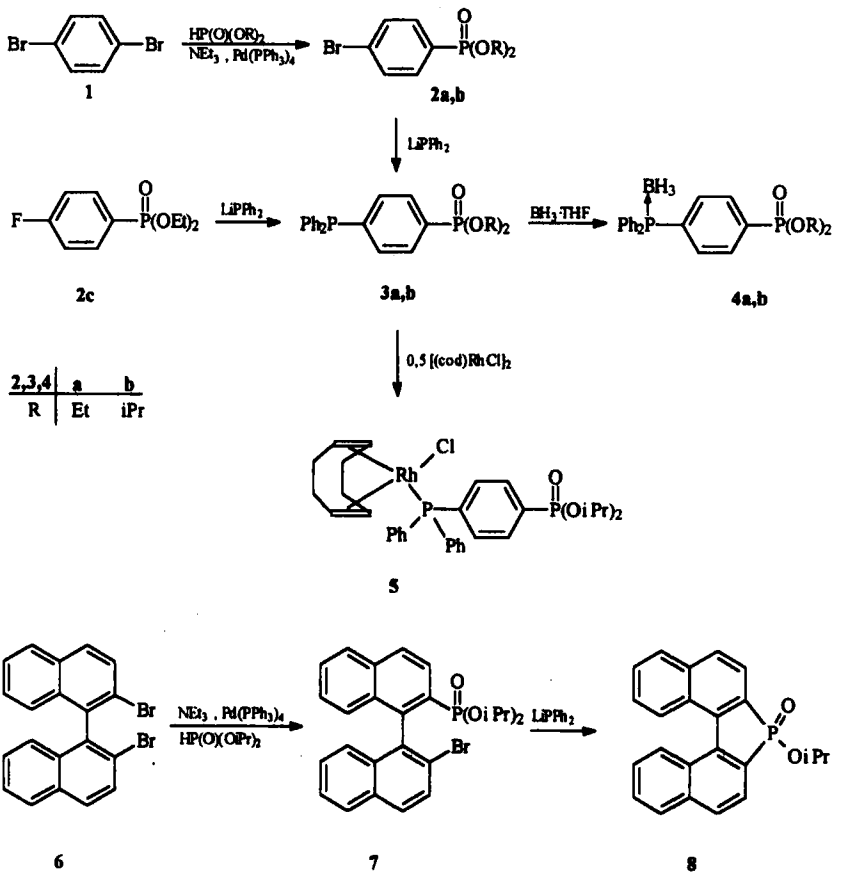
The phosphonylation of 1,4-dibromobenzene **1** succeeded with dialkyl phosphite/tetrakis(triphenylphosphine)palladium/triethylamine in analogy to the method of Hirao et al.,[7] who described the synthesis of 1,4-bis(diethylphosphono)benzene by reaction of **1** with two molar equivalents of diethyl phosphite. We obtained the monosubstituted 4-bromo-phenyl-phosphonates **2a,b** using only one molar equivalent of dialkylphosphite.



The introduction of the phosphino group into the 4-position of the aromatic ring succeeded with lithium diphenylphosphide in the cases of 4-bromo-phenylphosphonates **2a,b** and 4-fluoro-phenylphosphonate[8] **2c** as well.

The new aromatic phosphonate-phosphines **3a,b** are air-sensitive in contrast to other triarylphosphines. However, in a smooth reaction by boranation of the phosphino group of **3a,b** the air-stable phosphine-boranes **4a,b** were obtained. This conversion is reversible in the presence of amines and can be used therefore for the protection of the phosphino group.[9]

The reaction of the phosphonate-phosphine **3b** with $[ClRh(cod)]_2$ in CH_2Cl_2 yielded the monodentate square-planar rhodium complex **5** (^{31}P-NMR: δ_{PRh} = 30.9 ppm; J_{PRh} = 150.8 Hz) in which the phosphine-phosphorus is co-ordinated to the rhodium whereas the phosphonate group as second potential donor function of the ligand remains uncoordinated. This complex was found to be an active catalyst in the carbonylation of methanol.[10]

Our attempts to synthesise 2- and 3-phosphino-substituted phenylphosphonates failed. The reaction of the corresponding 2- and 3-halophosphonates with various phosphinylating agents such as lithium diphenylphosphide or butyl lithium/halodiphenylphosphine gave only the products of dealkylation or cleavage of the phosphonate group.

The binaphthalene skeleton is used as a structure controlling the enantioselectivity of various effective catalysts.[11,12] Therefore, we included a binaphthyl-substituted phosphonate into our investigations. The monophosphonylation of the starting racemic dibromo-binaphthalene **6** to the racemic phosphonate **7** was carried out according to the method mentioned above. Reaction of **7** with lithium diphenylphosphide did not lead to the desired phosphonate-phosphine but to the cyclic phosphinate **8** in addition to unreacted **7**. The formation of **8** can be explained by an attack of the phosphide at the phosphonate group, splitting off an alkoxy group followed by cyclization. Recently Gladiali et al.[13] obtained a phosphinate similar to **8** by reaction of **6** with butyl lithium/methyl dichlorophosphate. All efforts to introduce the phosphino substituent into **7** with butyl lithium/halodiphenylphosphine failed.

EXPERIMENTAL

All reactions and operations were carried out under argon atmosphere. Dibromobinaphthalene[14] **6** and diethyl 4-fluorophenylphosphonate[8] **2c** were prepared according to common procedures.

Dialkyl 4-bromo-phenylphosphonates **2a, 2b**; *2-bromo-2'-diisopropylphosphono-1,1'-binaphthalene* **7**. A mixture of 50 mmol dibromoarene **1** or **6** (in the latter case 10 ml toluene were added), 50 mmol dialkylphosphite, 55 mmol triethylamine and 2.5 mmol tetrakis(triphenylphosphine)palladium was heated to

90°C (**2a**: 12 hrs, **2b**: 16 hrs, **7**: 70 hrs). After cooling the mixture was dissolved in 100 ml CH_2Cl_2 and extracted twice with 30 ml water. The organic phase was dried with sodium sulphate, the solvent was evaporated and the residue purified on a silica gel column (acetone/hexane 1:4).

(4-Dialkylphosphono)phenyl-diphenylphosphines **3a,b**. A solution of 10 mmol lithium diphenylphosphide in 10 ml THF was added to 10 mmol bromo-phenylphosphonate **2a** or **2b** or fluoro-phenylphosphonate **2c** dissolved in 20 ml THF, at 0°C. The mixture was stirred for 2 hours at this temperature and then allowed to stand overnight at room temperature. Then 1 ml water was added, the solvent evaporated, and the residue washed with ethyl acetate/hexane 1:1. Compound **3a** was chromatographed on a short column (benzene/THF gradient). For crystallisation the oily **3b** was dissolved in diisopropyl ether and some drops of hexane were added.

(4-Dialkylphosphono)phenyl-diphenylphosphine-boranes **4a,b**. A mixture of 3 mmol of **3a** or **3b** in 15 ml THF and 6 mmol of borane (1*M* solution in THF) was stirred for 2 hours. The solvent was evaporated and the air-stable products were recrystallised.).

Chloro-(η^4-1.5-cyclooctadiene)-[4-(diisopropylphosphono)phenyl-diphenyl-phosphine-P]-rhodium(I) **5**. To 0.247 g (0.5 mmol) $[ClRh(cod)]_2$ in 5 ml CH_2Cl_2 a solution of 0.426 g (1 mmol) **3b** in 5 ml CH_2Cl_2 was dropped at 0°C. After cooling the mixture in the refrigerator for 16 hours, it was filtrated twice, the solvent evaporated and the residue recrystallised from toluene/hexane.

TABLE I Physical and spectroscopical data of prepared compounds

Product	*yield (%) [m.p. (°C)] {MS (m/z)}*	*^{1}H-NMR($CDCl_3$) δ (ppm), J(Hz)*	*^{13}C-NMR ($CDCl_3$) δ (ppm), J(Hz)*	*^{31}P-NMR ($CHCl_3$) δ (ppm), J(Hz)*
2a[15]	20 [oil]	1.32 (t, 6H, CH_3); 4.11 (dq, 4H, OCH_2); 7.65 (m, 4H, CH_{arom})		17.7
2b[a]	34 [62–65 (iPr_2O)]	1.21, 1.36 (2d, 12H, CH_3); 4.67 (dq, 2H, OCH); 7.55–7.71 (m, 4H, CH_{arom})	23.7, 23.8, 23.9, 24.0 (CH_3); 70.9, 71.0 (OCH); 127.1 (J = 3.9), 129.0 (J = 191.0), 131.5 (J = 15.2), 133.2 (J = 10.4)(CH_{arom})	14.6
3a	41 [oil]	1.32, (t, 6H, CH_3); 4.20 (m, 4H, OCH_2); 7.34 (m, 12H, CH_{arom}), 7.75 (2dd, 2H, CH_{arom})	16.0, 16.1 (CH_3); 61.9, 62.0 (OCH_2); 128.6 (J = 7.5), 129.1, 131.4 (J = 6.3; 10.3), 133.1 (J = 14.9; 18.3), 133.9 (J = 20.6), 134.3 (J = 9.2; 11.5), 136.0 (J = 10.4), 143.4 (J = 3.1; 14.6) (C_{arom})	−5.1 (PPh); 18.4 (P═O)

TABLE I Physical and spectroscopical data of prepared compounds (continued)

Product	*yield (%) [m.p. (°C)] {MS (m/z)}*	*^{1}H-NMR($CDCl_3$) δ (ppm), J(Hz)*	*^{13}C-NMR ($CDCl_3$) δ (ppm), J(Hz)*	*^{31}P-NMR ($CHCl_3$) δ (ppm), J(Hz)*
3b	59 [89–91 (iPr_2O)]	1.22, 1.34 (2d, 12H, CH_3); 4.68 (dd, 2H, OCH); 7.29 (m, 12H, CH_{arom}), 7.72 (dd, 2H, CH_{arom})	23.8, 23.9, 24.0, 24.1 (CH_3); 70.7, 70.8 OCH); 1 28.6 (J = 7.1), 129.1, 131.3 (J = 10.0; 6.5), 133.0 (J = 18.4; 15.0), 133.9 (J = 19.9), 136.1 (J = 10.6), 142.8 (J = 14.0) (C_{arom})	−5.2 (PPh); 16.1 (P═O).
4a[a]	84 [112–114 (iPr_2O)]	1.34 (t, 6H, CH_3); 4.12 (dq, 2H, OCH_2); 7.68 (m, 14H, CH_{arom})	16.2, 16.3 (CH_3); 62.3, 62.4 (OCH_2); 128.1 (J = 58.1), 16.2, 16.3 (CH_3); 62.3, 62.4 (OCH_2); 128.1 (J = 58.1), 128.8 (J = 10.2), 131.7 (J = 187.5), 131.5 (J = 2.2), 136.6 (J = 9.8), 132.9 (J = 15.3; 9.7), 133.1 (J = 9.8), 134.5 (J = 54.9; 3.2) (CH_{arom})	16.5 (P═O, J = 3.3); 20.9 (PBH_3, broad)
4b[a]	96 [93–96 (iPr_2O)]	1.26, 1.38 (2d, 12H, CH_3); 4.74 (dq, 2H, OCH); 7.43–7.68, 7.86 (2m, 14H, CH_{arom})	23.8, 23.9, 24.0, 24.1 (CH_3); 71.2, 71.3 (OCH); 127.9, 128.7, 128.9, 129.0, 131.5, 131.6, 131.8, 132.7, 132.8, 132.9, 133.0, 133.2, 133.3 (CH_{arom})	14.7 (P═O, J = 3.0); 21.2 (PBH_3, broad)
5	40 {672}[b]		23.4, 23.5, 23.6, 23.7 (CH_3); 28.4, 32.6 CH_2); 70.4, 70.5, 70.6, 70.7 (OCH + CH=); 105.1 (J = 11.8; 6.9); 127.7, 127.8, 127.9, 128.1, 128.3, 128.5, 130.0, 130.4, 130.5, 130.7, 131.5, 132.7, 133.8, 133.9 (J = 14.9), 134.2, 134.4, 136.1 (J = 39.2), 137.2 (C_{arom})	15.2 (P═O, J = 3.7); 30.87 (P-Rh, J = 150.8; 3.7)[c]
7[a]	46 [120–121] (toluene)	0.79, 0.88, 0.95, 0.98 (4d, 12H, CH_3); 4.42 (dq, 2H, OCH); 6.93–8.15 (m, 12H, CH_{arom})	23.5, 23.6 (CH_3); 70.1, 70.2, 70.3, 70.4 (OCH); 123.3, 125.8, 126.4, 126.8, 127.1, 127.2, 127.6 (CP, J = 190.6), 127.7, 127.9, 128.0, 128.1, 128.2, 128.3, 129.4, 129.7, 131.9, 132.1, 134.8 (J = 6.9), 136.6 (J = 4.8), 141.8 (J = 9.0)(C_{arom})	15.1
8[a]	31 [207–209] (toluene) {358}	δ 1.20 (d, 6H, CH_3); 4.59 (dd, 1H, OCH); 7.50, 7.91 (2m, 12H, CH_{arom})	24.2 (CH_3); 70.9, 71.0 (OCH); 123.2, 125.7, 127.5, 127.9, 128.5, 128.7, 130.3, 137.3, 140.6 (J = 27.8) (CH_{arom})	40.5

[a]product gave satisfactory microanalysis
[b]molecular weight was determined with LSIMS
[c]in CH_2Cl_2

7-Isopropoxy-dinaphtho[2,1-b:1',2'-d]phosphole oxide **8**. 4 mmol) of **7** were dissolved in 10 ml THF and 4.6 mmol lithium diphenylphosphide in 10 ml THF were added to the phosphonate solution at 0°C. Stirring at this temperature was continued for 2 hours. The solvent was evaporated, the residue was dissolved in 50 ml ethyl acetate and extracted twice with 20 ml water. The ethyl acetate phase was dried over sodium sulphate, the solvent was evaporated and the residue chromatographed on a silica gel column (acetone/hexane 1:3.

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