

## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gpss20>

### AROMATIC PHOSPHONATE-PHOSPHINES

Angela Köckritz<sup>a</sup>, Axel Weigt<sup>a</sup> & Michael Kant<sup>a</sup>

<sup>a</sup> Institut für Angewandte Chemie Berlin-Adlershof, Rudower Chaussee 5, 12489, Berlin, Bundesrepublik Deutschland

Published online: 24 Sep 2006.

To cite this article: Angela Köckritz, Axel Weigt & Michael Kant (1996) AROMATIC PHOSPHONATE-PHOSPHINES, *Phosphorus, Sulfur, and Silicon and the Related Elements*, 117:1, 287-292, DOI: [10.1080/10426509608038791](https://doi.org/10.1080/10426509608038791)

To link to this article: <http://dx.doi.org/10.1080/10426509608038791>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

## Communication

# AROMATIC PHOSPHONATE-PHOSPHINES

ANGELA KÖCKRITZ\*, AXEL WEIGT and MICHAEL KANT

*Institut für Angewandte Chemie Berlin-Adlershof, Rudower Chaussee 5, 12489 Berlin,  
Bundesrepublik Deutschland*

*(Received 10 April 1996; Revised 10 June 1996)*

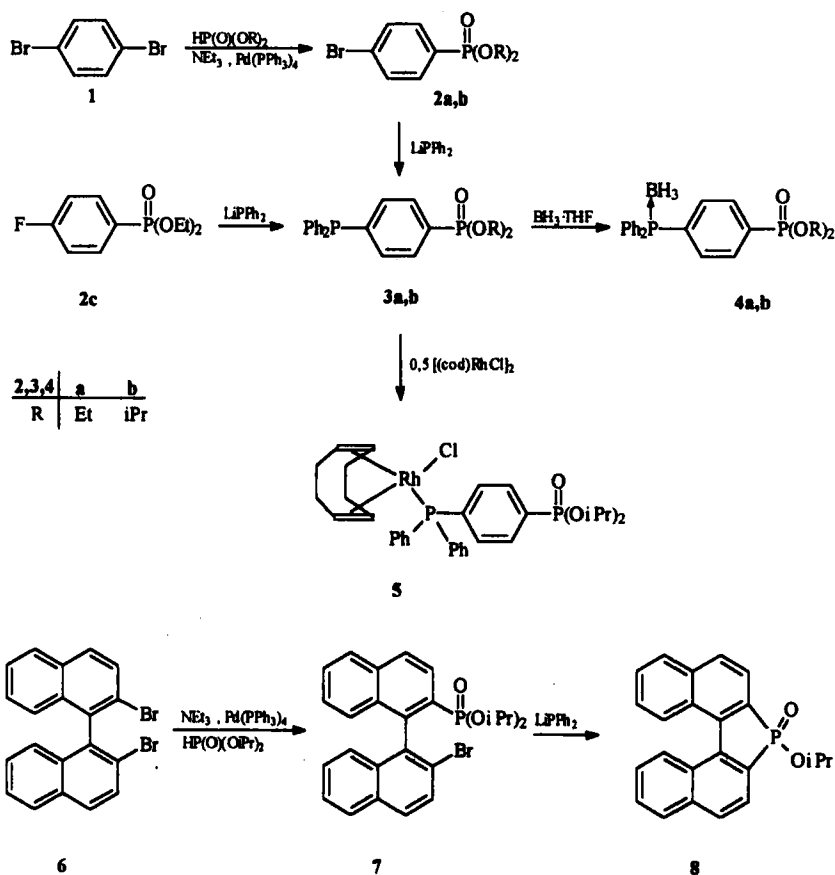
Aromatic phosphonate-phosphines **3a,b** are obtained by reaction of 4-halogen-substituted phenylphosphonates **2a,b,c** and lithium diphenylphosphide. They can be transformed into air-stable phosphine-boranes **4a,b** by co-ordination of the borane-THF complex. The reaction of the phosphonate-phosphine **3b** with  $[\text{ClRh}(\text{cod})]_2$  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,<sup>1</sup> amine-phosphines,<sup>2,3</sup> ether-phosphines,<sup>4</sup> and phosphine sulphide-phosphines<sup>5</sup> 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.<sup>1,6</sup> 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.

\*Corresponding author.

The phosphonylation of 1,4-dibromobenzene **1** succeeded with dialkyl phosphite/tetrakis(triphenylphosphine)palladium/triethylamine in analogy to the method of Hirao *et al.*<sup>7</sup> 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-phenylphosphonates **2a,b** using only one molar equivalent of dialkyl phosphite.



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<sup>8</sup> **2c** as well.

The new aromatic phosphonate-phosphines **3a,b** are air-sensitive in contrast to other triarylphosphines. However, in a smooth reaction by boronation 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.<sup>9</sup>

The reaction of the phosphonate-phosphine **3b** with  $[\text{ClRh}(\text{cod})]_2$  in  $\text{CH}_2\text{Cl}_2$  yielded the monodentate square-planar rhodium complex **5** ( $^{31}\text{P}$ -NMR:  $\delta_{\text{PRh}} = 30.9$  ppm;  $J_{\text{PRh}} = 150.8$  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.<sup>10</sup>

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.<sup>11,12</sup> 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.<sup>13</sup> 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<sup>14</sup> **6** and diethyl 4-fluorophenylphosphonate<sup>8</sup> **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<sub>2</sub>Cl<sub>2</sub> 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 bromophenylphosphonate **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 (1M solution in THF) was stirred for 2 hours. The solvent was evaporated and the air-stable products were recrystallised.).

Chloro-( $\eta^4$ -1.5-cyclooctadiene)-[4-(diisopropylphosphono)phenyl-diphenylphosphine-P]-rhodium(I) **5**. To 0.247 g (0.5 mmol) [ClRh(cod)]<sub>2</sub> in 5 ml CH<sub>2</sub>Cl<sub>2</sub> a solution of 0.426 g (1 mmol) **3b** in 5 ml CH<sub>2</sub>Cl<sub>2</sub> 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)}	<sup>1</sup> H-NMR(CDCl <sub>3</sub> ) δ (ppm), J(Hz)	<sup>13</sup> C-NMR (CDCl <sub>3</sub> ) δ (ppm), J(Hz)	<sup>31</sup> P-NMR (CHCl <sub>3</sub> ) δ (ppm), J(Hz)
<b>2a</b> <sup>15</sup>	20 [oil]	1.32 (t, 6H, CH <sub>3</sub> ); 4.11 (dq, 4H, OCH <sub>2</sub> ); 7.65 (m, 4H, CH <sub>arom</sub> )		17.7
<b>2b</b> <sup>a</sup>	34 [62–65 (iPr <sub>2</sub> O)]	1.21, 1.36 (2d, 12H, CH <sub>3</sub> ); 4.67 (dq, 2H, OCH); 7.55–7.71 (m, 4H, CH <sub>arom</sub> )	23.7, 23.8, 23.9, 24.0 (CH <sub>3</sub> ); 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 <sub>arom</sub> )	14.6
<b>3a</b>	41 [oil]	1.32, (t, 6H, CH <sub>3</sub> ); 4.20 (m, 4H, OCH <sub>2</sub> ); 7.34 (m, 12H, CH <sub>arom</sub> ), 7.75 (2dd, 2H, CH <sub>arom</sub> )	16.0, 16.1 (CH <sub>3</sub> ); 61.9, 62.0 (OCH <sub>2</sub> ); 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 <sub>arom</sub> )	–5.1 (PPh); 18.4 (P=O)

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

Product	yield (%) [m.p. (°C)] {MS (m/z)}	<sup>1</sup> H-NMR(CDCl <sub>3</sub> ) δ (ppm), J(Hz)	<sup>13</sup> C-NMR (CDCl <sub>3</sub> ) δ (ppm), J(Hz)	<sup>31</sup> P-NMR (CHCl <sub>3</sub> ) δ (ppm), J(Hz)
<b>3b</b>	59 [89–91 (iPr <sub>2</sub> O)]	1.22, 1.34 (2d, 12H, CH <sub>3</sub> ); 4.68 (dd, 2H, OCH); 7.29 (m, 12H, CH <sub>arom</sub> ); 7.72 (dd, 2H, CH <sub>arom</sub> )	23.8, 23.9, 24.0, 24.1 (CH <sub>3</sub> ); 70.7, 70.8 (OCH); 128.6 (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 <sub>arom</sub> )	–5.2 (PPh); 16.1 (P=O).
<b>4a<sup>a</sup></b>	84 [112–114 (iPr <sub>2</sub> O)]	1.34 (t, 6H, CH <sub>3</sub> ); 4.12 (dq, 2H, OCH <sub>2</sub> ); 7.68 (m, 14H, CH <sub>arom</sub> )	16.2, 16.3 (CH <sub>3</sub> ); 62.3, 62.4 (OCH <sub>2</sub> ); 128.1 (J = 58.1), 16.2, 16.3 (CH <sub>3</sub> ); 62.3, 62.4 (OCH <sub>2</sub> ); 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 <sub>arom</sub> )	16.5 (P=O, J = 3.3); 20.9 (PBH <sub>3</sub> , broad)
<b>4b<sup>a</sup></b>	96 [93–96 (iPr <sub>2</sub> O)]	1.26, 1.38 (2d, 12H, CH <sub>3</sub> ); 4.74 (dq, 2H, OCH); 7.43–7.68, 7.86 (2m, 14H, CH <sub>arom</sub> )	23.8, 23.9, 24.0, 24.1 (CH <sub>3</sub> ); 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 <sub>arom</sub> )	14.7 (P=O, J = 3.0); 21.2 (PBH <sub>3</sub> , broad)
<b>5</b>	40 [672] <sup>b</sup>		23.4, 23.5, 23.6, 23.7 (CH <sub>3</sub> ); 28.4, 32.6 (CH <sub>2</sub> ); 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 <sub>arom</sub> )	15.2 (P=O, J = 3.7); 30.87 (P-Rh, J = 150.8; 3.7) <sup>c</sup>
<b>7<sup>a</sup></b>	46 [120–121] (toluene)	0.79, 0.88, 0.95, 0.98 (4d, 12H, CH <sub>3</sub> ); 4.42 (dq, 2H, OCH); 6.93–8.15 (m, 12H, CH <sub>arom</sub> )	23.5, 23.6 (CH <sub>3</sub> ); 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 <sub>arom</sub> )	15.1
<b>8<sup>a</sup></b>	31 [207–209] (toluene) {358}	δ 1.20 (d, 6H, CH <sub>3</sub> ); 4.59 (dd, 1H, OCH); 7.50, 7.91 (2m, 12H, CH <sub>arom</sub> )	24.2 (CH <sub>3</sub> ); 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 <sub>arom</sub> )	40.5

<sup>a</sup>product gave satisfactory microanalysis<sup>b</sup>molecular weight was determined with LSIMS<sup>c</sup>in CH<sub>2</sub>Cl<sub>2</sub>

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).

### Acknowledgements

We would like to thank Prof. J. Gloede and Dr. U. Schülke for interesting discussions and constant support of this work.

### References

- [1] J. Freiberg, A. Weigt and H. Dilcher, *J. Prakt. Chem.*, **335**, 337 (1993).
- [2] C. Abu-Gnim and I. Amer, *J. Mol. Cat.*, **85**, L275 (1993).
- [3] C. Abu-Gnim and I. Amer, *J. Chem. Soc., Chem. Commun.*, **1994**, 115.
- [4] E. Lindner and B. Andres, *Chem. Ber.*, **121**, 829 (1988).
- [5] M. J. Baker, M. F. Giles, A. G. Orpen, A. G. Taylor and R. J. Watt, *J. Chem. Soc., Chem. Commun.* **1995**, 197.
- [6] A. Weigt and S. Bischoff, *Phosphorus, Sulfur, and Silicon*, **102**, 91 (1995).
- [7] T. Hirao, T. Masunaga, N. Yamada, Y. Oshiro and T. Agawa, *Bull. Chem. Soc. Jpn.*, **55**, 909 (1982).
- [8] P. Tavs, *Chem. Ber.*, **103**, 2428 (1970).
- [9] T. Imamoto, T. Ohshiki, T. Onozawa, T. Kusumoto and K. Sato, *J. Amer. Chem. Soc.*, **112**, 5244 (1990).
- [10] S. Bischoff, A. Weigt, H. Mießner and B. Lücke, *J. Mol. Cat.*, in print
- [11] S. Gladiali, J. C. Bayon, C. Claver, *Tetrahedron: Asymmetry*, **6**, 1453 (1995).
- [12] R. Noyori and H. Takaya, *Acc. Chem. Res.*, **23**, 345 (1990).
- [13] S. Gladiali, A. Dore, D. Fabbri, O. De Lucchi and G. Valle, *J. Org. Chem.*, **59**, 6363 (1994).
- [14] H. Takaya, S. Akutagawa, R. Noyori, *Organic Syntheses*, **67**, 20 (1988).
- [15] G. M. Kosolapoff, *J. Amer. Chem. Soc.*, **70**, 3465 (1948).