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2-Aryl-dibenzo-1,2-oxaphosphorine as a Ligand in Borane and in Pt(II) Complexes*

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ABSTRACT: *Optimum conditions for the synthesis of aryl-dibenzo-oxaphosphorines (***2***) from the corresponding phosphonous chloride (***1***) were explored to avoid the formation of by-products (e.g.,* **4–6***). The aryl-dibenzo-oxaphosphorines (***2***) were converted to the P-oxides (***3***), and were utilized in the synthesis of phosphinite-boranes* **7** *and Pt(II) complexes* **8**. *Depending on the aryl substituent, the Pt(II) complex (***8***) was formed with cis and trans geometry.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:459–463, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20042

INTRODUCTION

The P-ligands are widely applied in transition metal complexes that may be useful catalysts. The heterocyclic P-ligands including five- and six-membered P-cycles form a special class [1]. The dibenzo-1,2-oxaphosphorines with phosphorous function represent a group that attracted much attention [2–4]. The P-aryl derivatives were not, however, studied in detail, mainly their oxides were described [5]. For this, we decided to examine the synthesis and complexing properties of aryl-dibenzo-1,2-oxaphosphorines.

The chloro derivative (**1**) available via the cyclization of ortho-hydroxybiphenyl by phosphorus trichloride [2] was first reacted with phenylmagnesium bromide in tetrahydrofuran at 0 → 26°C under nitrogen. After the work-up procedure including hydrolysis, a mixture of phosphinite **2a** (83%) and 2-diphenylphosphino-2′-hydroxybiphenyl **4** (17%) formed by ring opening with a second equivalent of Grignard reagent was obtained according to ^{31}P NMR and mass spectroscopic analysis of the crude mixture. The two components were obtained in a pure form as their oxides (**3a** and **5**, respectively) after oxidation and purification by column chromatography (Scheme 1). A similar side reaction was also observed in the reaction of the P-oxide of the chlorodibenzooxaphosphorine with methylmagnesium bromide [5]. The substitution was extended to the preparation of triisopropylphenyl phosphinite **2b** (Scheme 1). The product (**2b**) was formed in a neat reaction, under the conditions of the hydrolysis

*IUPAC name of 2-aryl-dibenzo-1,2-oxaphosphorine is 1,2-oxaphosphinine.

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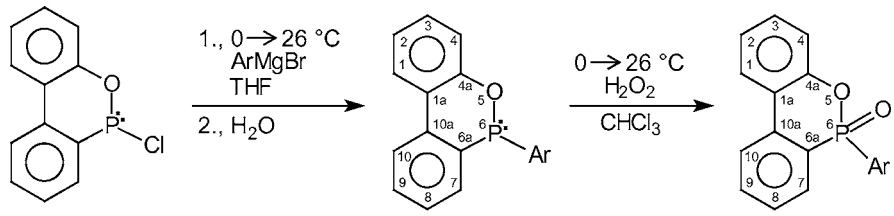
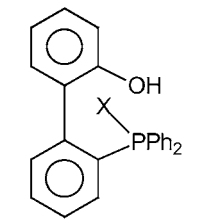


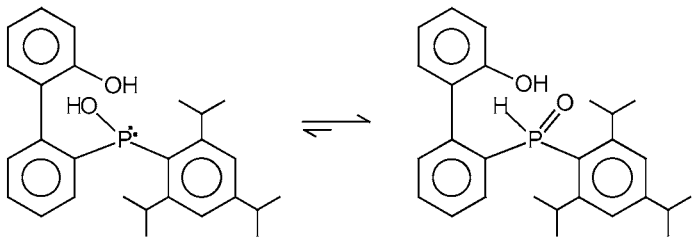
1 **2** **3**

Ar = C_6H_5 (**a**), 2,4,6-tri $^{i}PrC_6H_2$ (**b**)

SCHEME 1



X	
electron pair	**4**
O	**5**



6-1 **6-2**

applying 0.15 M hydrochloric acid; the oxaphosphorine ring of **2b** was, however, opened up partially to afford 2-aryl-*H*-phosphinoxido-2′-biphenyl **6-2** (as the predominant component of a tautomeric equilibrium). According to ^{31}P NMR and MS, the crude mixture consisted of 80% of phosphinite (**2b**) and 20% of by-product **6-2**. Performing the hydrolysis in the absence of hydrochloric acid, the ring opening side reaction could be avoided. It can be seen that the oxaphosphorine ring of the triisopropylphenyl compound (**2b**) is more sensitive under the conditions of acidic hydrolysis than that of the phenyl derivative (**2a**) is. At same time, the oxaphosphorine ring in **2** is more vulnerable toward PhMgBr than to tri$^{i}PrC_6H_2MgBr$, as the by-product from double arylation was formed only in the first case (**4**).

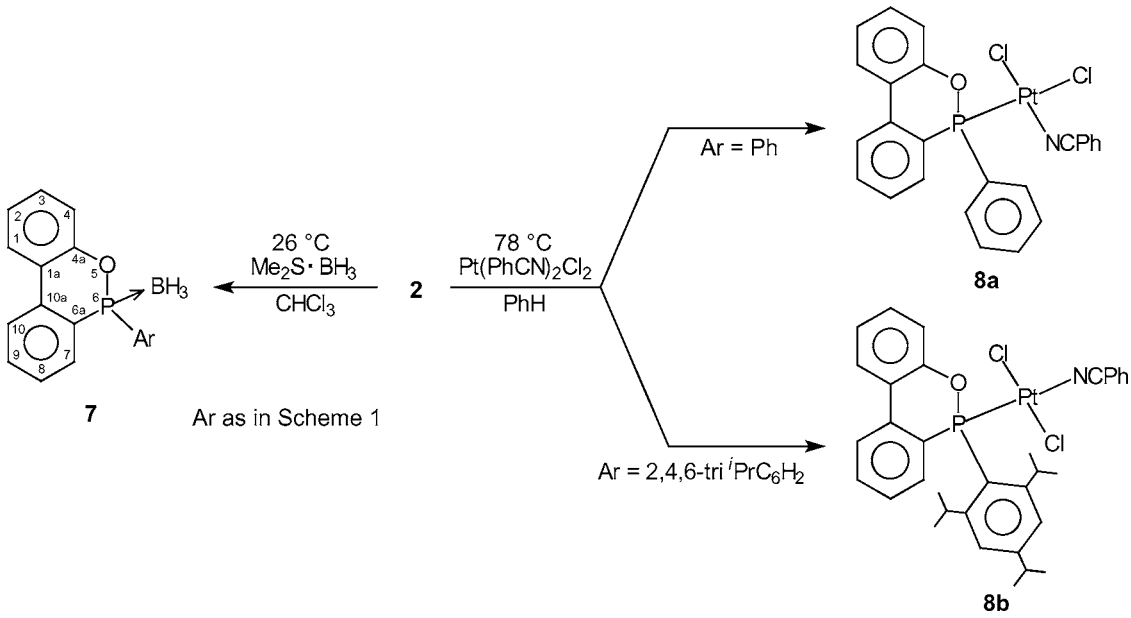
To prepare a more stable derivative, phosphinite **2b** was converted to phosphinate **3b** by oxidation and was isolated in 66% after column chromatography (Scheme 1).

Phosphinites **2a** and **2b** and phosphinates **3a** and **3b** were characterized by ^{31}P and ^{13}C NMR, as well as mass spectroscopy, the P-oxides (**3a** and **3b**) also by ^{1}H NMR spectral data. By-products **4**, **5**, and **6-1** were identified by ^{31}P NMR and MS.

The P-ligands are usually protected against oxidation as borane complexes [6]. The arylphosphinites (**2a** and **2b**) were reacted with dimethylsulfide borane to give the phosphiniteboranes (**7a** and **7b**, respectively) that were characterized after purification by ^{31}P, ^{11}B, and ^{13}C NMR spectral parameters (Scheme 2). The phosphinite boranes (**7a** and **7b**) were of a ca. 95% purity.

Finally, arylphosphinites **2a** and **2b** were reacted with dichlorodibenzonitrile platinum in boiling benzene. On cooling, the products were precipitated and identified as complexes **8a** and **8b** (Scheme 2).

The ^{31}P NMR spectra of the complexes **8a** and **8b** revealed a signal at δ 76.8 with a J_{Pt-P} of 4240 Hz and at δ 84.6 with a J_{Pt-P} of 2900 Hz, respectively. Both



SCHEME 2

signals were accompanied by a pair of satellites resulting from the presence of the ^{195}Pt isotope. The *cis* and *trans* orientation of the ligands in complexes **8a** and **8b**, respectively, is in accord with the stereospecific J_{Pt-P} couplings detected. It is known that within a *cis* and *trans* diastereomer pair, the larger coupling belongs to the *cis* isomer, while the smaller one to the *trans* form [7]. The outcome of the complexation can be explained well with the role of steric factors; with the smaller phenyl group, the orientation of the ligands in the usual *cis*, while with the sterically more demanding tri*iso*propylphenyl substituent, the ligands are in the more favorable *trans* relationship. A similar situation was reported for the corresponding phospholes [7,8].

Complex **8a** was also characterized by ^{1}H NMR spectroscopic data. The solubility of complexes **8a** and **8b** in chloroform is very poor. Moreover, compound **8b** was found to be unstable in $CHCl_3$ ($CDCl_3$) solution.

In summary, two arylphosphines together with the corresponding boranes and the two kinds of platinum complexes based on the dibenzooxaphosphorine skeleton were prepared and characterized.

EXPERIMENTAL SECTION

The ^{31}P, ^{11}B, ^{13}C, and ^{1}H NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4, 160.4 125.7, and 500 MHz, respectively. Positive chemical shifts are downfield relative to 85% H_3PO_4, $F_3B \cdot OEt_2$ or TMS. The coupling constants are given in Hz. Mass spectrometry was performed on a ZAB-2SEQ instrument.

The Preparation of Phenyl-oxaphosphorines **2a, 3a**, *and* **7a**

To 1.0 g (4.26 mmol) of chlorooxaphosphorine **1** in 10 mL of tetrahydrofuran was added dropwise 5.54 mmol of phenylmagnesium bromide in 10 mL of diethyl ether (prepared from 0.86 g (5.54 mmol) of bromobenzene and 0.14 g (5.54 mmol) of magnesium in 10 mL of ether) at 0°C with stirring. After addition was complete, content of the flask was stirred at 26°C for 20 h under nitrogen. Solvent was evaporated and the residue taken up in the mixture of 20 mL of chloroform and 5 mL of water. The organic phase was dried (Na_2SO_4) and concentrated. 0.82 g crude product containing 99% of **2a** and 1% of **4** was obtained.

2a: Yield: 70%; ^{31}P NMR ($CDCl_3$) δ 84.6; ^{13}C NMR ($CDCl_3$) δ 120.8 (CH=), 123.1 (CH=), 124.0 ($^3J = 5.8$, C_{1a})[a], 124.1 ($^3J = 1.5$, CH=), 125.0 (CH=), 127.5 (CH=), 128.1 ($^3J = 4.2$, $C_{3'}$), 129.4 (CH=), 129.6 (CH=), 130.7 (CH=), 130.9 ($C_{2'}$), 131.5 ($C_{4'}$), 131.9 ($^1J = 13.9$, C_{6a})[b], 133.5 (C_{10a})[a], 138.9 ($^1J = 30.1$, $C_{1'}$)[b], 151.3 ($^2J = 10.8$, C_{4a}), [a,b]may be reversed; FAB-MS, 277 (M+H); $(M+H)^+_{found}$ = 277.0782, $C_{18}H_{14}OP$ requires 277.0755.

4: ^{31}P NMR ($CDCl_3$) δ–11.8; FAB-MS, 355 (M+H).

The crude product was taken up in 20 mL of chloroform and was treated with 1.3 mL (12.8 mmol)

of 30% hydrogen peroxide at 0°C for 2 h on stirring. The organic phase was washed with 3 × 10 mL of water and dried (Na_2SO_4), and finally concentrated. The main component was obtained by column chromatography (silica gel, 3% methanol in chloroform) to afford 0.69 g (80%) of **3a** as a white solid.

3a: m.p. 156–158°C (acetone); ^{31}P NMR ($CDCl_3$) δ 25.0 (99%); ^{13}C NMR ($CDCl_3$) δ 120.4 ($^2J = 6.0$, C_7)[a], 121.8 ($^3J = 11.1$, C_{1a})[b], 123.5 ($^3J = 9.6$, C_{10})[a], 124.5 (C_3)[c], 124.7 ($^1J = 128.1$, C_{6a})[d], 124.9 (C_1)[c], 128.1 ($^3J = 14.1$, C_4)[a], 128.4 ($^3J = 14.2$, $C_{3'}$)[e], 129.3 ($^1J = 143.6$, $C_{1'}$)[d], 130.3 ($C_{4'}$), 130.7 ($^3J = 12.2$, C_8)[a], 131.9 ($^2J = 11.0$, $C_{2'}$)[e], 132.8 (C_9)[c], 132.9 (C_2)[c], 135.5 ($^2J = 5.3$, C_{10a})[b], 148.9 ($^2J = 8.5$, C_{4a}), [a-e]tentative assignment; ^{1}H NMR ($CDCl_3$) δ 7.27–8.07 (m, 13H, Ar); FAB-MS, 293 (M+H); $M^+_{found} = 292.0601$, $C_{18}H_{14}O_2P$ requires 292.0653.

5: ^{31}P NMR ($CDCl_3$) δ 32.7 (1%); ^{1}H NMR ($CDCl_3$) δ 6.46–8.04 (m, 18H, Ar), 9.03 (s, 1H, OH); FAB-MS, 371 (M+H).

To the 20 mL dichloromethane solution of 4.26 mmol of phosphine **2a** was added 2.6 mL (5.12 mmol) of 2 M tetrahydrofuran solution of dimethylsulfide borane at room temperature under nitrogen and the mixture was stirred for 24 h. Evaporation of the volatile components led to **7a** as pale yellow solid. Yield: ∼100%.

7a: ^{31}P NMR ($CDCl_3$) δ 93.7 (broad); ^{11}B NMR ($CDCl_3$) δ –36.2 (broad); ^{13}C NMR ($CDCl_3$) δ 120.8 ($^2J = 4.5$, C_7)[a], 123.1 ($^1J = 59.9$, $C_{1'}$)[b], 123.4 ($^3J = 10.0$, C_{1a})[c], 124.3 ($^3J = 6.0$, C_{10})[a], 124.8 (C_3)[d], 125.4 (C_1)[d], 128.7 ($^3J = 10.0$, $C_{3'}$)[e], 128.8 ($^3J = 13.3$, C_4)[a], 129.8 ($^1J = 41.0$, C_{6a})[b], 130.7 ($C_{4'}$), 131.3 ($^2J = 11.5$, $C_{2'}$)[e], 131.7 ($^3J = 18.9$, C_8)[a], 132.4 (C_9)[d], 133.3 (C_2)[d], 135.0 (C_{10a})[c], 149.4 ($^2J = 12.6$, C_{4a}), [a-e]tentative assignment; ^{1}H NMR ($CDCl_3$) δ 7.06–7.96 (m, 13H, Ar); FAB-MS, 277 (M–BH_3+H).

The Preparation of Triisopropylphenyl-Oxaphosphorines **2b, 3b**, *and* **7b**

2b, 3b, and **7b** were prepared from **1** as described for the **1**→**2a**→**3a**→**7a** transformation.

2b: Yield: 1.4 g (82%); ^{31}P NMR ($CDCl_3$) δ 112.0; ^{13}C NMR ($CDCl_3$) δ 23.3, 23.7, 26.0 (CH(CH_3)$_2$), 31.4 ($C_{2'}$–CHMe$_2$), 34.7 ($C_{4'}$–CHMe$_2$), 120.9 (CH=), 122.3 (CH=), 122.6 ($^3J = 3.6$, $C_{3'}$), 123.2 (CH=), 123.6 (CH=), 125.3 (CH=), 125.8 ($^3J = 9.7$, C_{1a})[a], 128.0 (CH=), 129.1 (CH=), 129.7 ($^1J = 31.3$, $C_{1'}$)[b], 130.1 (CH=), 134.5 ($^2J = 12.6$, C_{10a})[a], 138.6 ($^1J = 26.4$, C_{6a})[b], 152.5 (C_{4a}), 152.9 ($C_{4'}$), 156.5 ($C_{2'}$), [a,b]may be reversed; ^{1}H NMR ($CDCl_3$) δ 1.12 (d, $^3J_{HH} = 6.5$, 6H, CH(CH_3)$_2$), 1.26 (d, $^3J_{HH} = 7.0$, 6H, CH(CH_3)$_2$), 1.37 (d, $^3J_{HH} = 7.0$, 6H, CH(CH_3)$_2$), 2.97 (sept, $^3J_{HH} = 7.0$, 1H, $C_{4'}$–CHMe$_2$), 3.99 (m, 2H, $C_{2'}$–CHMe$_2$), 6.85–8.15 (m, 10H, Ar); FAB-MS, 403 (M+H); $(M+H)^+_{found} = 403.2124$, $C_{27}H_{31}OP$ requires 403.2191.

3b: Yield: 1.11 g (76%); could be separated as a crystalline compound, m.p. 155–157°C (acetone); ^{31}P NMR ($CDCl_3$) δ 25.6; ^{13}C NMR ($CDCl_3$) δ 23.8, 24.4, 25.3 (CH(CH_3)$_2$), 30.4 ($^3J = 3.6$, $C_{2'}$–CHMe$_2$), 34.6 ($C_{4'}$–CHMe$_2$), 118.7 ($^1J = 140.7$, C′)[c], 120.9 ($^2J = 5.9$, C_7)[a], 121.7 ($^3J = 11.3$, C_{1a})[d], 123.0 ($^3J = 13.4$, $C_{3'}$), 123.7 ($^3J = 8.9$, C_{10})[a], 124.2 (C_3)[b], 125.0 (C_1)[b], 127.0 ($^3J = 14.6$, C_4)[a], 129.1 ($^1J = 125.3$, C_{6a})[c], 129.4 ($^3J = 13.9$, C_8)[a], 130.2 (C_2)[b], 132.0 (C_9)[b], 133.8 ($^2J = 4.3$, C_{10a})[d], 148.4 ($^2J = 8.2$, C_{4a}), 153.9 ($C_{4'}$), 156.5 ($^2J = 13.3$, $C_{2'}$), [a-d]tentative assignment; ^{1}H NMR ($CDCl_3$) δ 1.00 (d, $^3J_{HH} = 7.0$, 6H, CH(CH_3)$_2$), 1.22 (d, $^3J_{HH} = 6.5$, 6H, CH(CH_3)$_2$), 1.31 (d, $^3J_{HH} = 7.0$, 6H, CH(CH_3)$_2$), 2.96 (sept, $^3J_{HH} = 7.0$, 1H, $C_{4'}$–CHMe$_2$), 3.89 (m, 2H, $C_{2'}$–CHMe$_2$), 7.20–8.07 (m, 10H, Ar); FAB-MS, 419 (M+H); $M^+_{found} = 418.1982$, $C_{27}H_{31}O_2P$ requires 418.2062.

6-2: ^{31}P NMR ($CDCl_3$) δ 15.3; FAB-MS, 420 (M+H)

7b: Yield: ∼100%; ^{31}P NMR ($CDCl_3$) δ 101.9 (broad); ^{11}B NMR ($CDCl_3$) δ −30.0 (broad); ^{13}C NMR ($CDCl_3$) δ; 23.9, 24.6, 25.7 (CH(CH_3)$_2$), 31.0 ($^3J = 6.3$, $C_{2'}$–CHMe$_2$), 34.5 ($C_{4'}$–CHMe$_2$), 120.9 ($^2J = 5.4$, C_7)[a], 121.5 ($^1J = 50.5$, $C_{1'}$)[b], 123.2 ($^3J = 9.8$, C_{1a})[c], 123.4 ($^3J = 8.8$, $C_{3'}$), 124.0 ($^3J = 6.4$, C_{10})[a], 124.2 (C_3)[d], 125.1 (C_1)[d], 128.2 ($^3J = 11.7$, C_4)[a], 128.6 ($^1J = 55.5$, C_{6a})[b], 130.0 ($^3J = 14.7$, C_8)[a], 130.6 (C_2)[d], 131.8 (C_9)[d], 134.2 (C_{10a})[c], 149.2 ($^2J = 9.1$, C_{4a}), 153.7 ($C_{4'}$), 156.1 ($^2J = 12.0$, $C_{2'}$), [a-d]tentative assignment; ^{1}H NMR ($CDCl_3$) δ 1.02 (d, $^3J_{HH} = 6.5$, 6H, CH(CH_3)$_2$), 1.10 (d, $^3J_{HH} = 7$, 6H, CH(CH_3)$_2$), 1.23 (d, $^3J_{HH} = 7.0$, 6H, CH(CH_3)$_2$), 2.87 (m, 1H, $C_{4'}$–CHMe$_2$), 3.82 (m, 2H, $C_{2'}$–CHMe$_2$), 7.08–7.85 (m, 10H, Ar); FAB-MS, 417 (M+H), 403 (M–BH_3+H).

The Preparation of Pt-Complexes **8a** *and* **8b**

To 0.21 mmol of phosphinite **2** in 20 mL of benzene, 0.10 g (0.21 mmol) of dichlorodibenzonitrile-platinum was added and the mixture was stirred at reflux for 1.5 h under nitrogen. Fractional crystallization from the benzene solution furnished **8** as pale yellow powder-like crystal.

8a: Yield: 60 mg (44%); in a purity of ca. 90%; ^{31}P NMR ($CDCl_3$) δ 76.8 ($J_{Pt-P} = 4239$); ^{1}H NMR ($CDCl_3$) δ 6.11–7.97 (m, 18H, Ar).

8b: Yield: 50 mg (31%); in a purity of ca. 75%; ^{31}P NMR ($CDCl_3$) δ 84.6 ($J_{Pt-P} = 2900$); ^{1}H NMR ($CDCl_3$) δ 0.90 (d, $^3J_{HH} = 6.5$, 6H, CH(CH_3)$_2$), 1.02 (d, $^3J_{HH} = 6.0$, 6H, CH(CH_3)$_2$), 1.15 (d, $^3J_{HH} = 6.5$, 6H, CH(CH_3)$_2$), 2.77 (sept, $^3J_{HH} = 7.0$, 1H, $C_{4'}$–CHMe$_2$), 4.28 (m, 2H, $C_{2'}$–CHMe$_2$), 6.93–8.03 (m, 15H, Ar).

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