

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

György Keglevich,¹ Helga Szelke,² Andrea Kerényi,¹ Tímea Imre,³ Krisztina Ludányi,³ József Dukai,⁴ Ferenc Nagy,⁴ and Péter Arányi⁴

¹Department of Organic Chemical Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary

²Research Group of the Hungarian Academy of Sciences at the Department of Organic Chemical Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary

³Hungarian Academy of Sciences, Chemical Research Center, 1525 Budapest, Hungary

⁴NIKE 2000, 8175 Balatonfüzfő, Hungary

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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 ³¹P 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 chlorodibenzo-oxaphosphorine 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

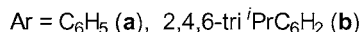
*IUPAC name of 2-aryl-dibenzo-1,2-oxaphosphorine is 1,2-oxaphosphinine.

Correspondence to: György Keglevich; e-mail: gkeglevich@mail.bme.hu.

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SCHEME 1



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 $\text{tri}^i\text{PrC}_6\text{H}_2\text{MgBr}$, as the by-product from double arylation was formed only in the first case (**4**).

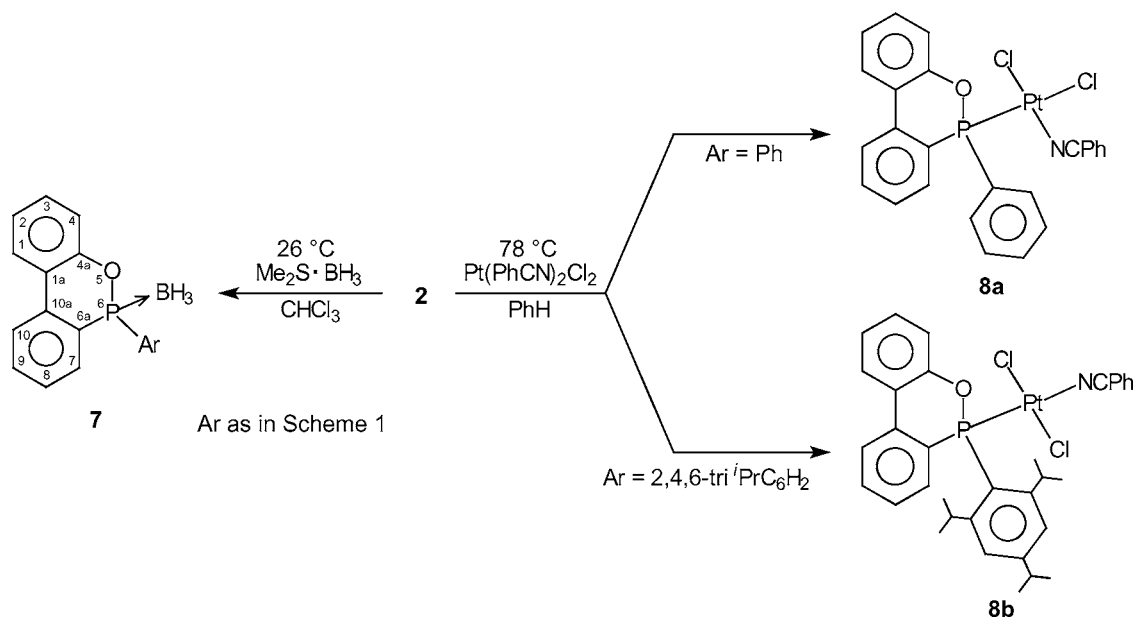
To prepare a more stable derivative, phosphinite **2b** was converted to phosphinate **3b** by oxidation and was isolated in 66% after column chromatography (Scheme 1).

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 ^1H 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 phosphiniteboranes (**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 $J_{\text{Pt-P}}$ of 4240 Hz and at δ 84.6 with a $J_{\text{Pt-P}}$ 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 $J_{\text{Pt-P}}$ 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 triisopropylphenyl 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 ^1H 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 ^1H 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 , $\text{F}_3\text{B}\cdot\text{OEt}_2$ 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 ($^3J = 4.2$, $\text{C}_{3'}$), 129.4 (CH=), 129.6 (CH=), 130.7 (CH=), 130.9 ($\text{C}_{2'}$), 131.5 ($\text{C}_{4'}$), 131.9 ($^1J = 13.9$, C_{6a})^b, 133.5 (C_{10a})^a, 138.9 ($^1J = 30.1$, $\text{C}_{1'}$)^b, 151.3 ($^2J = 10.8$, C_{4a})^a, ^{a,b}may be reversed; FAB-MS, 277 ($\text{M}+\text{H}$); ($\text{M}+\text{H}$)_{found}⁺ = 277.0782, $\text{C}_{18}\text{H}_{14}\text{OP}$ requires 277.0755.

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

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 (Na₂SO₄), 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); ³¹P NMR (CDCl₃) δ 25.0 (99%); ¹³C NMR (CDCl₃) δ 120.4 (²J = 6.0, C₇)^a, 121.8 (³J = 11.1, C_{1a})^b, 123.5 (³J = 9.6, C₁₀)^a, 124.5 (C₃)^c, 124.7 (¹J = 128.1, C_{6a})^d, 124.9 (C₁)^c, 128.1 (³J = 14.1, C₄)^a, 128.4 (³J = 14.2, C₃)^c, 129.3 (¹J = 143.6, C₁)^d, 130.3 (C₄)^a, 130.7 (³J = 12.2, C₈)^a, 131.9 (²J = 11.0, C₂)^e, 132.8 (C₉)^c, 132.9 (C₂)^c, 135.5 (²J = 5.3, C_{10a})^b, 148.9 (²J = 8.5, C_{4a}), ^{a–e}tentative assignment; ¹H NMR (CDCl₃) δ 7.27–8.07 (m, 13H, Ar); FAB-MS, 293 (M+H); M_{found}⁺ = 292.0601, C₁₈H₁₄O₂P requires 292.0653.

5: ³¹P NMR (CDCl₃) δ 32.7 (1%); ¹H NMR (CDCl₃) 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: ³¹P NMR (CDCl₃) δ 93.7 (broad); ¹¹B NMR (CDCl₃) δ –36.2 (broad); ¹³C NMR (CDCl₃) δ 120.8 (²J = 4.5, C₇)^a, 123.1 (¹J = 59.9, C₁)^b, 123.4 (³J = 10.0, C_{1a})^c, 124.3 (³J = 6.0, C₁₀)^a, 124.8 (C₃)^d, 125.4 (C₁)^d, 128.7 (³J = 10.0, C₃)^e, 128.8 (³J = 13.3, C₄)^a, 129.8 (¹J = 41.0, C_{6a})^b, 130.7 (C₄)^a, 131.3 (²J = 11.5, C₂)^e, 131.7 (³J = 18.9, C₈)^a, 132.4 (C₉)^d, 133.3 (C₂)^d, 135.0 (C_{10a})^c, 149.4 (²J = 12.6, C_{4a}), ^{a–e}tentative assignment; ¹H NMR (CDCl₃) δ 7.06–7.96 (m, 13H, Ar); FAB-MS, 277 (M–BH₃+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%); ³¹P NMR (CDCl₃) δ 112.0; ¹³C NMR (CDCl₃) δ 23.3, 23.7, 26.0 (CH(CH₃)₂), 31.4 (C₂–CHMe₂), 34.7 (C₄–CHMe₂), 120.9 (CH=), 122.3 (CH=), 122.6 (³J = 3.6, C₃)^a, 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, C₁)^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 (C₄)^a, 156.5 (C₂)^a, ^{a,b}may be reversed; ¹H NMR (CDCl₃) δ 1.12 (d, ³J_{HH} = 6.5, 6H, CH(CH₃)₂), 1.26 (d, ³J_{HH} = 7.0, 6H, CH(CH₃)₂), 1.37 (d, ³J_{HH} = 7.0, 6H, CH(CH₃)₂), 2.97 (sept, ³J_{HH} = 7.0, 1H,

C₄–CHMe₂), 3.99 (m, 2H, C₂–CHMe₂), 6.85–8.15 (m, 10H, Ar); FAB-MS, 403 (M+H); (M+H)_{found}⁺ = 403.2124, C₂₇H₃₁OP requires 403.2191.

3b: Yield: 1.11 g (76%); could be separated as a crystalline compound, m.p. 155–157°C (acetone); ³¹P NMR (CDCl₃) δ 25.6; ¹³C NMR (CDCl₃) δ 23.8, 24.4, 25.3 (CH(CH₃)₂), 30.4 (³J = 3.6, C₂–CHMe₂), 34.6 (C₄–CHMe₂), 118.7 (¹J = 140.7, C')^c, 120.9 (²J = 5.9, C₇)^a, 121.7 (³J = 11.3, C_{1a})^d, 123.0 (³J = 13.4, C₃)^a, 123.7 (³J = 8.9, C₁₀)^a, 124.2 (C₃)^b, 125.0 (C₁)^b, 127.0 (³J = 14.6, C₄)^a, 129.1 (¹J = 125.3, C_{6a})^c, 129.4 (³J = 13.9, C₈)^a, 130.2 (C₂)^b, 132.0 (C₉)^b, 133.8 (²J = 4.3, C_{10a})^d, 148.4 (²J = 8.2, C_{4a}), 153.9 (C₄)^a, 156.5 (²J = 13.3, C₂)^a, ^{a–d}tentative assignment; ¹H NMR (CDCl₃) δ 1.00 (d, ³J_{HH} = 7.0, 6H, CH(CH₃)₂), 1.22 (d, ³J_{HH} = 6.5, 6H, CH(CH₃)₂), 1.31 (d, ³J_{HH} = 7.0, 6H, CH(CH₃)₂), 2.96 (sept, ³J_{HH} = 7.0, 1H, C₄–CHMe₂), 3.89 (m, 2H, C₂–CHMe₂), 7.20–8.07 (m, 10H, Ar); FAB-MS, 419 (M+H); M_{found}⁺ = 418.1982, C₂₇H₃₁O₂P requires 418.2062.

6–2: ³¹P NMR (CDCl₃) δ 15.3; FAB-MS, 420 (M+H)

7b: Yield: ~100%; ³¹P NMR (CDCl₃) δ 101.9 (broad); ¹¹B NMR (CDCl₃) δ –30.0 (broad); ¹³C NMR (CDCl₃) δ; 23.9, 24.6, 25.7 (CH(CH₃)₂), 31.0 (³J = 6.3, C₂–CHMe₂), 34.5 (C₄–CHMe₂), 120.9 (²J = 5.4, C₇)^a, 121.5 (¹J = 50.5, C₁)^b, 123.2 (³J = 9.8, C_{1a})^a, 123.4 (³J = 8.8, C₃)^a, 124.0 (³J = 6.4, C₁₀)^a, 124.2 (C₃)^d, 125.1 (C₁)^d, 128.2 (³J = 11.7, C₄)^a, 128.6 (¹J = 55.5, C_{6a})^b, 130.0 (³J = 14.7, C₈)^a, 130.6 (C₂)^d, 131.8 (C₉)^d, 134.2 (C_{10a})^c, 149.2 (²J = 9.1, C_{4a}), 153.7 (C₄)^a, 156.1 (²J = 12.0, C₂)^a, ^{a–d}tentative assignment; ¹H NMR (CDCl₃) δ 1.02 (d, ³J_{HH} = 6.5, 6H, CH(CH₃)₂), 1.10 (d, ³J_{HH} = 7, 6H, CH(CH₃)₂), 1.23 (d, ³J_{HH} = 7.0, 6H, CH(CH₃)₂), 2.87 (m, 1H, C₄–CHMe₂), 3.82 (m, 2H, C₂–CHMe₂), 7.08–7.85 (m, 10H, Ar); FAB-MS, 417 (M+H), 403 (M–BH₃+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%; ³¹P NMR (CDCl₃) δ 76.8 (J_{Pt–P} = 4239); ¹H NMR (CDCl₃) δ 6.11–7.97 (m, 18H, Ar).

8b: Yield: 50 mg (31%); in a purity of ca. 75%; ³¹P NMR (CDCl₃) δ 84.6 (J_{Pt–P} = 2900); ¹H NMR (CDCl₃) δ 0.90 (d, ³J_{HH} = 6.5, 6H, CH(CH₃)₂), 1.02 (d, ³J_{HH} = 6.0, 6H, CH(CH₃)₂), 1.15 (d, ³J_{HH} = 6.5, 6H, CH(CH₃)₂), 2.77 (sept, ³J_{HH} = 7.0, 1H, C₄–CHMe₂), 4.28 (m, 2H, C₂–CHMe₂), 6.93–8.03 (m, 15H, Ar).

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