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2-Diphenylphosphino-2′-hydroxybiphenyl-based P-ligands and their platinum(II) complexes

György Keglevich [a,*], Andrea Kerényi [a], Helga Szelke [b],
Krisztina Ludányi [c,d], Tamás Körtvélyesi [e]

[a] Department of Organic Chemical Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary
[b] Research Group of the Hungarian Academy of Sciences at the Department of Organic Chemical Technology,
Budapest University of Technology and Economics, 1521 Budapest, Hungary
[c] Semmelweis University, Faculty of Pharmacy, Department of Pharmaceutics, 1092 Budapest, Hungary
[d] Hungarian Academy of Sciences, Chemical Research Center, 1525 Budapest, Hungary
[e] Department of Physical Chemistry, University of Szeged, 6701 Szeged, Hungary

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Abstract

2-Diphenylphosphino-2′-hydroxybiphenyl (**2**), become readily available via a ring opening reaction of a dibenzo[*c.e*][1,2]oxaphosphorine, was utilized as P-ligand in complexation with dichlorodibenzonitrile platinum to give a $Cl_2Pt\mathbf{2}_2$ complex (**4**) with *trans* geometry. The *O*-benzyl derivative (**5**) could not be involved in complexation. A bidentate P-ligand (**7**) obtained by the interaction of hydroxydiphenylphosphinobiphenyl **2** with chloro-dibenzo[*c.e*][1,2]oxaphosphorine (**1**) formed an 8-ring transition metal complex ($Cl_2Pt\mathbf{7} = \mathbf{9}$) in reaction with $PtCl_2(PhCN)_2$. Under the conditions of chromatography, separation of the diastereomers of **7** was not possible due to a partial isomerisation by rotation around the biphenyl axis of the molecule that is justified by the average barrier height of 6.0 kcal/mol.

The stereostructure of P-ligands **2** and **7**, as well as platinum complexes **4** and **9** was evaluated by B3LYP quantum chemical calculations.

Keywords: Mono and bidentate P-ligands; Transition metal complex; Stereospecific coupling; Stereostructure; Quantum chemical calculations

1. Introduction

These days, a great variety of P-ligands is known, from among the P-heterocyclic derivatives form a special group [1]. These may be components in transition metal complexes that, in turn, are potential catalysts [1]. Hence, driven by green chemistry, the development of new monodental and bidental P-ligands and their complexes remains a challenge for organic chemists. The family of dibenzo[*c.e*][1,2]oxaphosphorines with a P(III) function represents a typical class [2–4]. Recently, *P*-aryl-, *P*-alkoxy- and *P*-amino derivatives, as well as their platinum complexes including chiral derivatives have been introduced [5–7]. A hydroxyaryl-aryloxydibenzooxaphosphorine along with its rhodium(I) complex has also been described [8]. In the course of the preparation of phenyl-dibenzo[*c.e*][1,2]oxaphosphorine from the corresponding *P*-chloro species and phenylmagnesium bromide, a ring opening side-reaction resulting in 2-diphenylphosphino-2′-hydroxybiphenyl was observed [5]. We decided to make use of this reaction in order to synthesize biaryl-related P-ligands and their complexes.

2. Results and discussion

After an optimisation, it was found that using 2.5 equiv. of the Grignard reagent, chloro-dibenzo[*c.e*][1,2]oxa-

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[*] Corresponding author. Tel.: +36 1 4631111/5883; fax: +36 1 4633648.
E-mail address: keglevich@mail.bme.hu (G. Keglevich).

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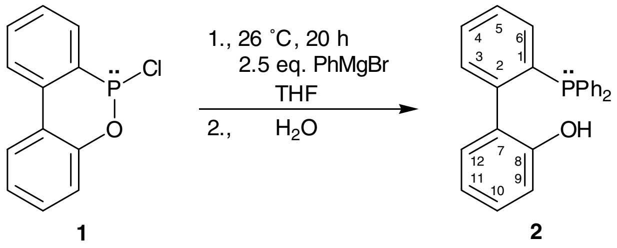
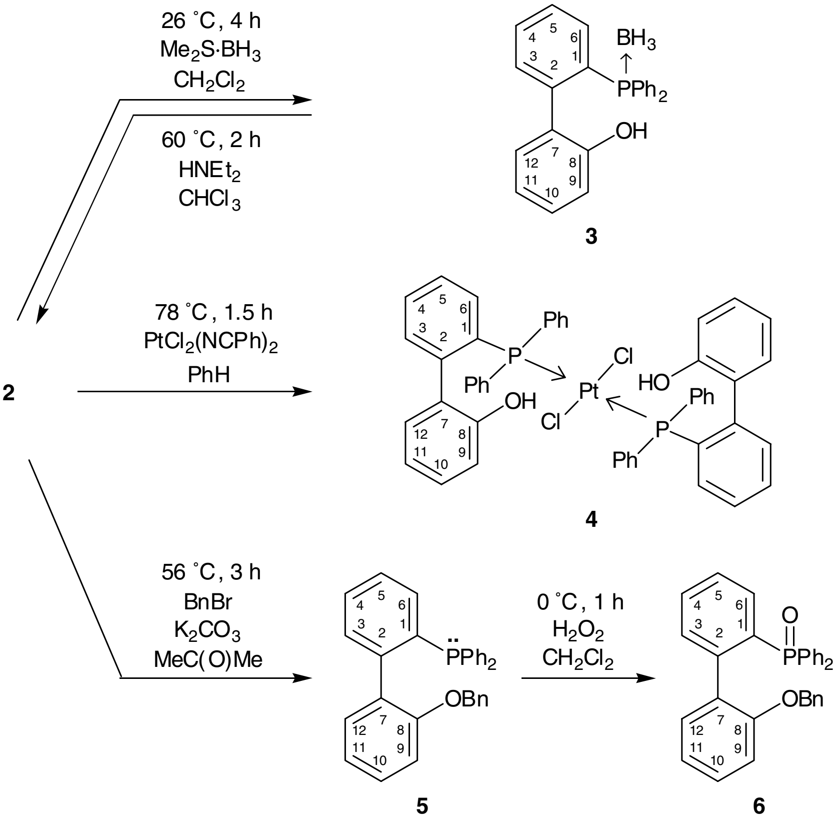


Scheme 1.

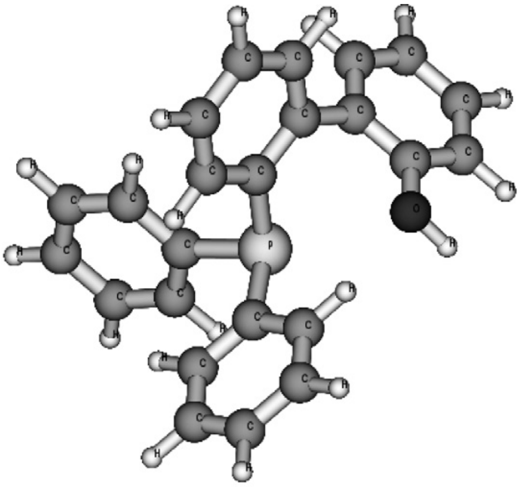
phosphorine **1** was efficiently transformed at 26 °C to 2-diphenylphosphino-2′-hydroxybiphenyl **2** (Scheme 1). The yield of 90% seemed to be competitive with that of other procedure [9]. The biaryl P-ligand (**2**) was protected against oxidation as its borane complex (**3**) from which the phosphine (**2**) was regenerated by a standard procedure applying diethylamine [10] (Scheme 2). The interaction of biaryldiphenylphosphine **2** with dichlorodibenzonitrile platinum in a molar ratio 2:1, at benzene reflux afforded complex **4** exhibiting the P-ligands, on the basis of the stereospecific $J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ coupling [5,11] of 2621 Hz, in *trans* disposition (Scheme 2). It is noteworthy that the similar reaction of P-substituted dibenzo[*c.e*][1,2]oxaphosphorines led to the formation of the corresponding *cis* complexes [7].

The stereostructure of P-ligand **2** was evaluated by B3LYP/3-21G* calculations, while that of platinum complex was **4** determined by B3LYP/3-21G* and B3LYP/LANL2DZ calculations. The perspective views are shown in Figs. 1 and 2, respectively. It was found that in the case of ligand **2**, there may be a stabilizing H-bond between the proton of the phenolic hydroxy function and the phosphorus atom of the PPh$_2$ group. In complex **4**, an intramolecular interaction between one of the two phenolic hydroxy groups and a suitable chlorine atom bond to the central platinum atom was substantiated. The H···P and H···Cl distances in the above complexes (**2** and **4**) were found to be 3.082 and 2.186 Å, respectively. Nevertheless, the H-bond in **2** did not prevent the complexation of the phosphorus atom. An NMR study including record of the ^{1}H NMR spectrum of **4** on a 250 and 500 MHz spectrometer suggested that the phenolic hydroxy lines at δ_{H} 5.30 and 5.57 are not the consequences of a coupling, but are distinct signals due to some kind of asymmetry of the molecule that may be explained with the intramolecular interaction at only one side of the complex mentioned above. At the 3-21G* basis set, relative stability of **4** and the symmetric version with two H-bonds cannot be established reliably due to the overestimation of the H-bond energy.

Then, the *ortho*-arylphenol P-ligand was modified by benzylation. The benzylether (**5**) obtained was identified as its *P*-oxide (**6**) due to its high sensitivity towards air (Scheme 2). It was a surprising experience that the diphenylphosphinophenylphenol ether (**5**) could not be involved in complexation with PtCl$_2$(PhCN)$_2$ that may be, on one hand, due to steric hindrance caused by the benzyl substituent (Fig. 3).



Scheme 2.



2

Fig. 1. Perspective view of **2** with bond lengths (Å), bond angles (°) and torsion angles (°) obtained at the B3LYP/3-21G* level of theory. C(1)–P: 1.850, C(2)–C(7): 1.497, C(8)–O: 1.382, P–C(1′): 1.844, P–C(1″): 1.841, C(1′)–P–C(1″): 101.24, C(7)–C(8)–O(H): 122.44, C(1)–C(2)–C(7): 121.21, C(2)–C(7)–C(8): 118.96, C(1)–C(2)–C(7)–C(8): −74.05, C(7)–C(2)–C(1)–P: −1.78, C(2)–C(1)–P–C(1′): 170.38, C(2)–C(1)–P–C(2′): −85.82, O–C(8)–C(7)–C(2): 2.66.

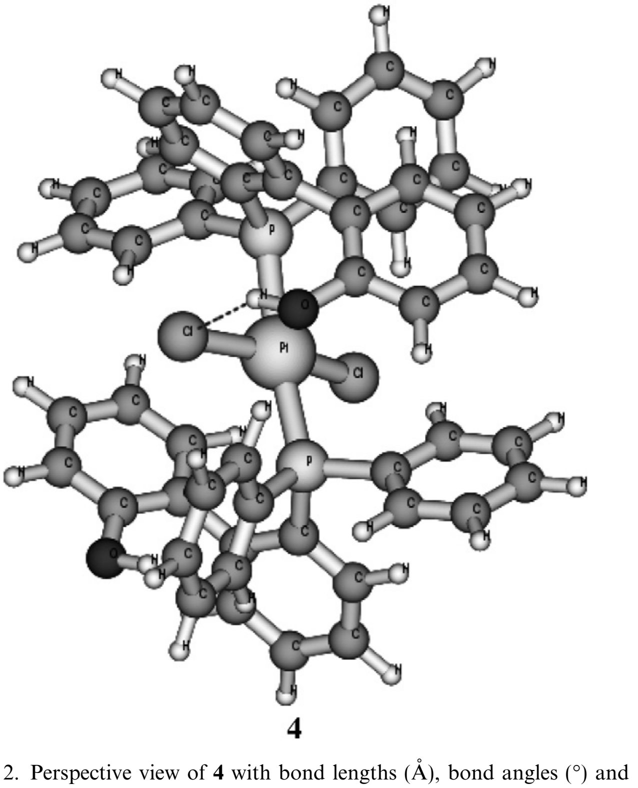


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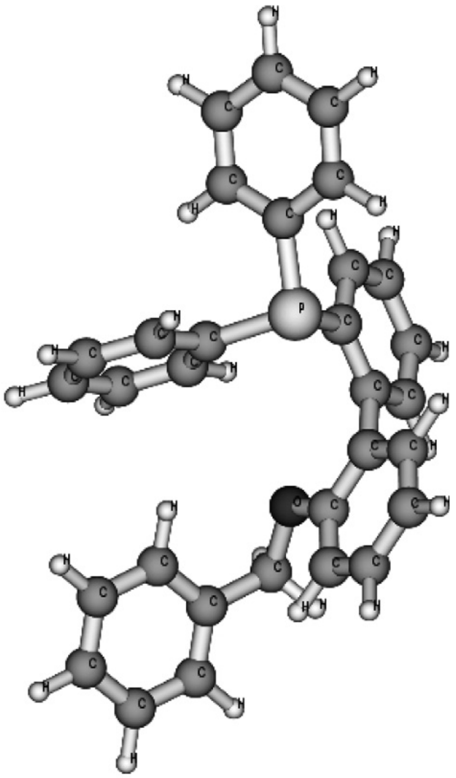
Fig. 2. Perspective view of **4** with bond lengths (Å), bond angles (°) and torsion angles (°) obtained at the B3LYP/3-21G* and B3LYP/LANL2DZ level of theory. Pt–P(1): 2.399, Pt–P(2): 2.384, P(1)–C(1): 1.842, P(1)–C(1′): 1.835, P(1)–C(1″): 1.835, P(2)–C(1*): 1.844, P(2)–C(1′*): 1.826, P(2)–C(1″*): 1.846, C(2)–C(7): 1.500, C(2*)–C(7*): 1.495, Pt–P(1)–C(1): 113.04, Pt–P(1)–C(1′): 123.42, C(1)–P(1)–C(1′): 101.39, C(1)–P(1)–C(1″): 104.23, C(1*)–P(2)–C(1′*): 102.39, C(1*)–P(2)–C(1″*): 105.74, C(1)–C(2)–C(7): 124.47, C(1*)–C(2*)–C(7*): 124.97, C(1)–C(2)–C(7)–C(8): −102.51, C(1*)–C(2*)–C(7*)–C(8*): −105.55, O···Cl: 3.096, O–H···Cl: 149.63, C(8)–O–H···Cl: 103.84, C(2)–C(1)–P(1)–Pt: 60.74, C(2*)–C(1*)–P(2)–Pt: −51.45. *: Numbering of the second P-ligand in the complex.

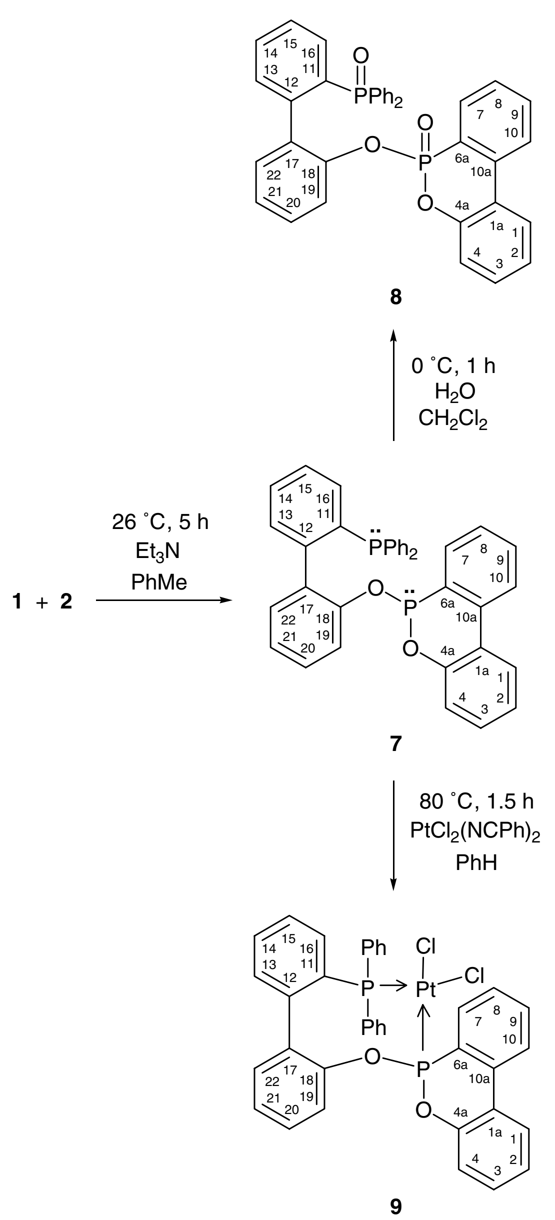


5

Fig. 3. Perspective view of **5** with bond lengths (Å), bond angles (°) and torsion angles (°) obtained at the B3LYP/3-21G* level of theory. P–C(1): 1.850, C(2)–C(7): 1.495, C(8)–O: 1.397, O–C(CH$_2$): 1.469, C(1′)–P: 1.846, C(1″)–P: 1.844, C(1)–C(2)–C(7): 122.36, C(2)–C(7)–C(8): 120.13, C(7)–C(8)–O: 116.18, C(8)–O–C(CH$_2$): 117.88, C(1)–C(2)–C(7)–C(8): 113.48, C(2)–C(7)–C(8)–O: −3.66, C(7)–C(8)–O–C(CH$_2$): 156.49, C(1′)–P–C(1)–C(2): 169.82, C(1″)–P–C(1)–C(2): −86.98.

As molecular mechanics (PCMODEL/MMX) calculations suggested, benzyl substitution results in a structure with possible clashes with the other parts of the molecules. On the other hand, it is also possible that only some conformations may enable the formation of the complex. As an analogy, 2-(anisylphenylphosphino)-2′-methoxy-1,1′-binaphthyl has been described that was obtained from the corresponding phosphine oxide by deoxygenation using phenylsilane. It is worthy of mention that after a reduction over 3 days at 80 °C, partial epimerisation of the P-centrum occurred [12].

As an interesting modification, the *ortho*-arylphenol (**2**) was reacted with chloro-dibenzo[*c.e*][1,2]oxaphosphorin (**1**) to afford a novel bidental P-ligand (**7**) that was obtained as a 64–36% mixture of two diastereomers (Scheme 3). The phosphine–phosphonite (**7**) was fully characterized as its dioxide (**8**) obtained by oxidation with 30% hydrogen peroxide (Scheme 3). Attempts on the separation of the two diastereomers by column chromatography failed, even an enrichment of the major component was not possible. In all cases, the ∼64–36% mixture of isomers was regenerated. This experience suggests that the diastereomers of **7** are not stable enough at room temperature to be separated that

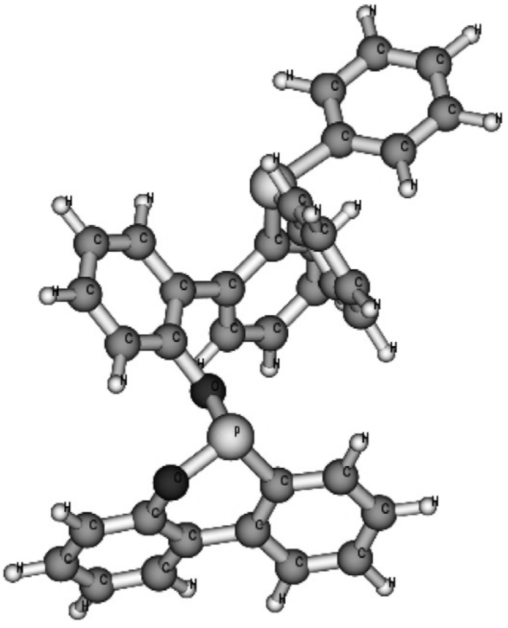


Scheme 3.

may be due to a partial isomerisation by rotation around the biphenyl axis of **7**. It is also clear that, in this particular case, the rotation around the C–C bond in solution is slower than the NMR time scale. A similar situation was found for the diastereomers of 2-diphenylphosphino-2′-(1″,1‴-binaphthyl-2″,2‴-phosphito-)1,1′-biphenyl by *Nozaki* et al. [13,14]. They experienced, however, that the presence of additional *ortho* substituents (even methyl groups) prevented the rotation around the C–C axis. Analogous binaphthol derivatives, such as 2-diphenylphosphino-2′-(1″,1‴-binaphthyl-2″,2‴-phosphito-)1,1′-binaphthol were, of course stable species [14].

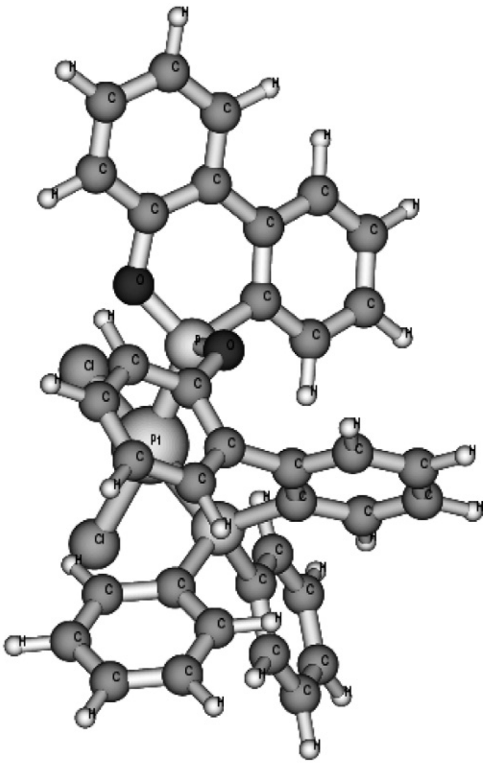
The barrier heights for the interconversion of the atrop isomers (diastereomers) of **7** were found to be 6.9 and 5.1 kcal/mol by PM3 calculations suggesting that the relative energy of one isomer to the other one is 1.8 kcal/mol. A somewhat larger barrier height (10.0 and 9.6 kcal/mol) was predicted for the atrop isomers of the diphenylphosphino-binaphthylphosphito-biphenyl mentioned above [14]. This energy value should allow at least a partial isomerisation by rotation around the C–C axis of the biphenyl moiety. For this reason, it is more appropriate to call the isomers under discussion “tropos” rather than “atropos” [15]. Methyl substitution in the corresponding *ortho* positions of the above molecules (**7** and the literature molecule [14]) prevents, however, the rotation as it was suggested by the PM3 calculations. This is in a good agreement with the experimental results [14].

The interaction of bidental P-ligand **7** with dichlorodibenzonitrile platinum led to the formation of cyclic platinum complex **9**. Starting from the diastereomeric mixture of the bidental P-ligand (**7**), the transition metal complex (**9**) was also formed as isomers (62–38%). The $^{2}J_{P(1)P(2)}$ of 15.7 Hz detected on both phosphorus atoms, as well as the $^{1}J_{^{195}Pt-^{31}P(1)}$ of 5093 Hz and $^{1}J_{^{195}Pt-^{31}P(2)}$ of 3400 Hz confirmed the *cis* position of the P-moieties. It is recalled that the second coupling should be around 2620 Hz (as it is in **4**) in case of a *trans* relationship of the ligands. Due to the low solubility of complex **9** in the usual solvents, it was not possible to obtain ^{13}C NMR data. The stereostructure of the



7

Fig. 4. Perspective view of **7** with bond lengths (Å), bond angles (°) and torsion angles (°) obtained at the B3LYP/3-21G* level of theory. C(6a)–P(1): 1.821, C(6a)–C(10a): 1.415, C(10a)–C(1a): 1.481, P(1)–O(5): 1.667, O(5)–C(4a): 1.409, P(1)–O: 1.679, O–C(18): 1.397, C(12)–C(17): 1.496, C(11)–P(2): 1.844, P(2)–C(1′): 1.843, P(2)–C(1″): 1.845, O(5)–P(1)–O: 98.30, O(5)–P(1)–C(6a): 97.59, C(6a)–P(1)–O: 99.01, C(4a)–O(5)–P(1): 123.80, C(10a)–C(6a)–P(1): 122.08, P(1)–O–C(18): 123.79, C(18)–C(17)–C(12): 120.99, C(11)–P(2)–C(1′): 101.70 C(11)–P(2)–C(1″): 101.41, C(4a)–C(1a)–C(10a)–C(6a): −16.87, C(11)–C(12)–C(17)–C(18): 79.28, C(12)–C(11)–P(2)–C(1′): 85.67, C(12)–C(11)–P(2)–C(1″): −170.50, C(4a)–O(5)–P(1)–O: 60.46, C(4a)–O(5)–P(1)–C(6a): −39.87.



9

Fig. 5. Perspective view of **9** with bond lengths (Å), bond angles (°) and torsion angles (°) obtained at the B3LYP/3-21G* and B3LYP/LANL2DZ level of theory. P(1)–Pt: 2.247, P(2)–Pt: 2.328, C(6a)–P(1): 1.788, C(6a)–C(10a): 1.418, C(10a)–C(1a): 1.482, P(1)–O(5): 1.628, O(5)–C(4a): 1.409, P(1)–O: 1.639, O–C(18): 1.416, C(12)–C(17): 1.493, C(11)–P(2): 1.847, P(2)–C(1′): 1.834, P(2)–C(1″): 1.826, P(1)–Pt–P(2): 102.05, O(5)–P(1)–O: 101.78, O(5)–P(1)–C(6a): 102.30, C(6a)–P(1)–O: 101.18, C(4a)–O(5)–P(1): 124.93, C(10a)–C(6a)–P(1): 120.96, P(1)–O–C(18): 122.70, C(18)–C(17)–C(12): 118.69, C(11)–P(2)–C(1′): 101.58, C(11)–P(2)–C(1″): 102.80, C(4a)–C(1a)–C(10a)–C(6a): −14.21, C(11)–C(12)–C(17)–C(18): −76.41, C(12)–C(11)–P(2)–C(1′):−58.55, C(12)–C(11)–P(2)–C(1″): −167.46, C(4a)–O(5)–P(1)–O: 74.89, C(4a)–O(5)–P(1)–C(6a): −29.48, O(5)–P(1)–Pt–P(2): −146.88, C(6a)–P(1)–Pt–P(2): 91.97, P(1)–Pt–P(2)–C(1′): −126.68, P(1)–Pt–P(2)–C(1″): 114.72.

more stable isomer of the bidentate P-ligand **7**, as well as that of the deriving transition metal complex (**9**) was calculated by the B3LYP/3-21G* method and, in respect of the platinum atom, also by the B3LYP/LANL2DZ method; the perspective views are shown in Figs. 4 and 5, respectively. As a not too far analogy, a cyclic palladium complex derived on a phosphine–phosphinite bidental P-ligand was also described [16].

To summarize our results, novel platinum complexes based on 2-diphenylphosphino-2′-hydroxybiphenyl and on its O-dibenzo[*c.e*][1,2]oxaphosphorine derivative have been introduced whose stereostructure was evaluated by stereospecific NMR couplings and B3LYP calculations. The situation regarding the atrop isomerism of one of the P-ligands was clarified experimentally and by quantum chemical calculations. Theory and practice seem to be in agreement.

3. Experimental

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 couplings are given in Hertz. Mass spectrometry was performed on a ZAB-2SEQ instrument. The starting chloro-dibenzo[*c.e*][1,2]oxaphosphorine **1** was prepared as described earlier [2].

*3.1. (2′-Hydroxy-biphenyl-2-yl)-diphenylphosphane **2***

To 1.0 g (4.3 mmol) of chlorooxaphosphorine **1** in 10 ml tetrahydrofuran was added dropwise 8.5 mmol of phenylmagnesium bromide in 10 ml tetrahydrofuran (prepared from 1.5 g (9.8 mmol) of bromobenzene and 0.20 g (8.5 g atom) of magnesium in 10 ml tetrahydrofuran) 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 10 ml of chloroform, 10 ml of water and 0.8 ml (4.3 mmol) of 37% hydrochloric acid. The organic phase was dried (Na_2SO_4) and concentrated to afford 1.6 g crude product. ^{31}P NMR ($CDCl_3$) δ −12.4 (δ_P lit. [8] −12.3), [5].

*3.2. (2′-Hydroxy-biphenyl-2-yl)-diphenylphosphane borane **3***

To the 20 ml dichloromethane solution of 1.0 g (2.8 mmol) of phosphine **2** was added 2.1 ml (4.2 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 gave 1.0 g (100%) of **3** as an oil. ^{31}P NMR ($CDCl_3$) δ 20.7; ^{11}B NMR ($CDCl_3$) δ −33.1; ^{13}C NMR ($CDCl_3$) δ 116.3 $(C_9)^a$, 119.8 $(C_{11})^a$, 127.4 ($^2J = 3.1$, C_2), 128.2 ($J = 9.3$, $C_3)^b$, 128.7 ($J = 10.2$, $C_{3'}$ and $C_{3''})^c$, 128.9 ($^1J \sim 30$, $C_{1'})^e$, 129.3 ($J = 10$, $C_5)^b$, 129.7 ($^1J = 34.0$, $C_{1''}$, 129.8 $(C_{10})^a$, 130.4 ($^1J = 29.8$, $C_{1'})^e$, 131.0 $(^4J = 2.2)^d$, 131.1 $(C_{12})^a$, 131.2 $(^4J = 2.3)^d$, 131.6 $(^4J = 2.2)^d$, [133.2 ($J = 9.7$, $C_{2''}$) ,133.6 ($J = 9.7$, $C_{2'}$)]^c, 135.6 ($J = 9.2$, $C_6)^b$, 142.2 ($^3J = 9.6$, C_7), 152.9 $(C_8)^{a–d}$; ^{1}H NMR ($CDCl_3$) δ 0.66–1.34 (m, 3H, BH_3), 6.47–6.55 (m, 2H, Ar), 6.65 (d, $J = 8.0$, 1H, OH), 7.03–7.08 (m, 1H, Ar), 7.18–7.61 (m, 15H, Ar).

*3.3. Bis((2′-hydroxy-biphenyl-2-yl)-diphenylphosphine)-dichloro-platinum(II) **4***

To 0.15 g (0.42 mmol) of phosphine **2** in 30 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 crystallisation from the benzene solution furnished **4** as a yellow powder-like material. ^{31}P NMR ($CDCl_3$) δ 16.9 ($J_{Pt–P} = 2621.4$); ^{1}H NMR ($CDCl_3$) δ 5.30 (s, OH), 5.57 (s, OH), δ 6.51–7.84 (m, 23H, Ar).

FAB-MS, 902 $[\mathrm{M{-}2HCl{+}H}]^+$; $[\mathrm{M-2HCl+H}]^+_{\mathrm{found}} = 902.1881$, $\mathrm{C_{48}H_{37}O_2P_2Pt}$ requires 902.1917; Elem. Anal., C, 58.86; H, 3.83, $\mathrm{C_{48}H_{38}Cl_2O_2P_2Pt}$ requires C, 59.14; H, 3.93.

3.4. *(2′-Benzyloxy-biphenyl-2-yl)-diphenylphosphine* **5**

To the 20 ml dichloromethane solution of 0.85 mmol of phosphine **2** was added 20 mg (0.085 mmol) of TEBAC and 0.15 ml (1.27 mmol) of benzyl bromide and 5% aqueous sodium hydroxide containing of 0.04 g (1.02 mmol) of sodium hydroxide at room temperature under nitrogen and the mixture was stirred for 8 h. The organic phase was dried ($\mathrm{Na_2SO_4}$) and concentrated to give 0.38 g of product **5** quantitatively. ^{31}P NMR ($\mathrm{CDCl_3}$) δ 23.3.

Compound **5** was characterized as its oxide (**6**) (obtained by oxidation using 30% aqueous $\mathrm{H_2O_2}$ according to a standard procedure [6]): ^{31}P NMR ($\mathrm{CDCl_3}$) δ 27.5; ^{13}C NMR ($\mathrm{CDCl_3}$) δ 110.7 $(\mathrm{C_9})^{\mathrm{a}}$, 119.6 $(\mathrm{C_{11}})^{\mathrm{a}}$, 126.3 $(\mathrm{C_\gamma})^{\mathrm{b}}$, 126.7 $(J = 12.3, \mathrm{C_3})^{\mathrm{c}}$, 127.5 $(\mathrm{C_{10}})^{\mathrm{a}}$, 127.6 $(J = 12.4, \mathrm{C_{3''}})^{\mathrm{d}}$, 128.2 $(J = 11.8, \mathrm{C_{3'}})^{\mathrm{d}}$, 128.5 $(\mathrm{C_\beta})^{\mathrm{b}}$, 129.0 $(^2J = 4.5, \mathrm{C_2})$, 129.3 $(\mathrm{C_{12}})^{\mathrm{a}}$, 130.7 $(^4J = 2.6, \mathrm{C_4})$, 131.0 $(J = 9.8, \mathrm{C_{2''}})^{\mathrm{d}}$, 131.2 $(^4J = 2.5, \mathrm{C_{4''}})^{e}$, 131.3 $(^4J = 2.5, \mathrm{C_{4'}})^{\mathrm{e}}$, 132.2 $(J = 9.1, \mathrm{C_{2'}})^{\mathrm{d}}$, 132.7 $(^1J = 150.3, \mathrm{C_1})$, 133.0 $(^1J = 103.8, \mathrm{C_{1'}}, \mathrm{C_{1''}})$, 133. 0 (d, $J = 9.9$, $\mathrm{C_6})^{\mathrm{c}}$, 133.0 $(\mathrm{C_\delta})$, 134.0 $(J = 12.0, \mathrm{C_5})^{\mathrm{c}}$, 137.5 $(\mathrm{C_\alpha})$, 143.7 $(^3J = 8.6, \mathrm{C_7})$, 154.8 $(\mathrm{C_8})$,$^{\mathrm{a–e}}$ tentative assignment; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 4.57 (d, $J = 12.5$, 1H), 4.80 (d, $J = 12.5$, 1H), 6.40 (d, $J = 8.0$, 1H, Ar), 6.82 (t, $J = 7.5$, 1H, Ar) 6.99–7.73 (m, 21H, Ar); FAB-MS, 461.2 $(\mathrm{M{+}H})^+$; $(\mathrm{M+H})^+_{\mathrm{found}} = 461.1631$, $\mathrm{C_{31}H_{26}O_2P}$ requires 461.1670.

3.5. *(2′-Diphenylphosphino-biphenyl-2-yl)-oxy-dibenzo[c.e][5,6]oxaphosphorine 7*

To 1.0 g (4.3 mmol) of chloro-oxaphosphorine **1** in 20 ml of toluene was added 1.5 g (4.3 mmol) biphenyl derivative **2** and 0.60 ml (4.3 mmol) of triethylamine. Contents of the flask were stirred at 26 °C for 3 h under nitrogen. The reaction mixture was filtrated and the filtrate concentrated. The crude product so obtained was refined by column chromatography (silica gel, 3% methanol in chloroform) to give 1.1 g (72%) of product **7** as a 64:36% mixture of two isomers. It was not possible to enrich the proportion of the major component by repeated column chromatography. FAB-MS, 553 $(\mathrm{M{+}H})^+$; $(\mathrm{M+H})^+_{\mathrm{found}} = 553.1447$, $\mathrm{C_{36}H_{26}O_2P_2}$ requires 553.1486.

Compound $\mathbf{7_1}$: ^{31}P NMR ($\mathrm{CDCl_3}$) −12.4 and 129.9.
Compound $\mathbf{7_2}$: ^{31}P NMR ($\mathrm{CDCl_3}$) −13.1 ($J_{\mathrm{PP}} = 10.5$), 128.9 ($J_{\mathrm{PP}} = 10.8$).

The major isomer ($\mathbf{7_1}$) of **7** was characterized as its oxide ($\mathbf{8_1}$) (obtained by oxidation using 30% $\mathrm{H_2O_2}$ according to a standard procedure [6]): ^{31}P NMR ($\mathrm{CDCl_3}$) 5.9 and 27.5; ^{13}C NMR ($\mathrm{CDCl_3}$) δ 119.2 $(J = 2.4, \mathrm{C_4})^{\mathrm{a}}$, 120.0 $(J = 6.7, \mathrm{C_{19}})^{\mathrm{a}}$, 121.6 $(^1J = 183.0, \mathrm{C_{6a}})$, 122.6 $(^2J = 12.2, \mathrm{C_{10a}})$, 123.8 $(\mathrm{C_{21}})^{\mathrm{b}}$, 124.0 $(J = 12.3, \mathrm{C_{10}})^{\mathrm{a}}$, 125.3 $(\mathrm{C_2})^{\mathrm{b}}$, 126.8 $(J = 12.1, \mathrm{C_{13}})^{\mathrm{a}}$, 127.6 $(J = 12.3, \mathrm{C_{2''}})^{\mathrm{c}}$, 128.1 $(J = 11.8, \mathrm{C_{2'}})^{\mathrm{c}}$, 128.1 $(J \sim 13, \mathrm{C_8})^{a}$, 129.3 $(\mathrm{C_1})^{\mathrm{b}}$, 130.3 $(J = 9.9, \mathrm{C_7})^{\mathrm{a}}$, 130.5 $(\mathrm{C_{20}})^{\mathrm{b}}$, 130.6 $(J = 9.9, \mathrm{C_{3''}})^{\mathrm{c}}$, 130.8 $(^4J = 2.6, \mathrm{C_{4'}}, \mathrm{C_{4''}})$, 131.0 $(^4J = 1.9, \mathrm{C_{14}})$, 131.4 $(\mathrm{C_{22}})^{\mathrm{b}}$, 131.6 $(^2J = 9.6, \mathrm{C_{12}})$, 131.9 $(J = 9.2, \mathrm{C_{3'}})^{\mathrm{c}}$, 131.9 $(J \sim 10, \mathrm{C_{16}})^{\mathrm{a}}$, 133.0 $(\mathrm{C_3})^{\mathrm{b}}$, 133.4 $(J = 11.5, \mathrm{C_{15}})^{\mathrm{a}}$, 133.8 $(\mathrm{C_9})^{\mathrm{b}}$, 136.9 $(^3J = 6.8, \mathrm{C_{1a}})$, 141.3 $(^3J = 8.3, \mathrm{C_{17}})$, 146.4 $(^2J = 8.1, \mathrm{C_{4a}})$, 149.7 $(^2J = 8.4, \mathrm{C_{18}})$; $(\mathrm{M+H})^+_{\mathrm{found}} = 585.1339$, $\mathrm{C_{36}H_{26}O_4P_2}$ requires 585.1385.

3.6. *[(2′-Diphenylphosphino-biphenyl-2-yl)-oxi-dibenzo[c.e][5,6]oxaphosphorine]dichloro-platinum(II)* **9**

To 0.12 g (0.21 mmol) of phosphine **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 crystallisation from the benzene solution furnished 0.12 g (71%) of **9** as a white powder-like material consisting of a 62:38 mixture of two isomers; $(\mathrm{M\text{-}Cl+H})^+_{\mathrm{found}} = 783.0782$, $\mathrm{C_{36}H_{27}ClO_2P_2Pt}$ requires 783.0823, $(\mathrm{M\text{-}HCl+H})^+_{\mathrm{found}} = 782.0709$, $\mathrm{C_{36}H_{26}ClO_2P_2Pt}$ requires 782.0745.

Compound $\mathbf{9}_1$: ^{31}P NMR (DMSO) 10.4 ($J_{\mathrm{PP}} = 15.7$, $J_{\mathrm{Pt–P}}$ 3399.5), 105.6 ($J_{\mathrm{PP}} = 15.6$, $J_{\mathrm{Pt–P}}$ 5062.6).
Compound $\mathbf{9}_2$: ^{31}P NMR (DMSO) 11.3 ($J_{\mathrm{PP}} = 17.1$, $J_{\mathrm{Pt–P}}$ 3414.7), 96.1 ($J_{\mathrm{PP}} = 17.2$, $J_{\mathrm{Pt–P}}$ 5092.7).

4. Calculations

The structures of the molecules were built up and optimized by PCMODEL [17] with MMX force field. The optimized geometries of the molecules were reoptimized at the level of *ab initio* quantum chemical method implemented in GAUSSIAN'03 [18], where B3LYP/3-21G* basis was applied for the C, H, O and P atoms and B3LYP/LANL2DZ (LANL2DZ effective core potential) for the Pt atom. The force matrices were always positive definite in the minima. The barrier height of the atrop isomerisms was calculated by the PM3 semiempirical quantum chemical method implemented in MOPAC93 [19]. The structure of the molecules was described by MOLDEN [20].

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