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Structure and Reactions of Benzo-4-diphenylphosphino-2-phenyl-1,3,2-dioxaborinane

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ABSTRACT

The crystal structure of 5,6-benzo-4-diphenylphosphino-2-phenyl-1,3,2-dioxaborinane **1** *indicates the occurrence of an interaction between the π-systems of the 1,3,2-dioxaborinane ring and the appropriate phenyl group of the diphenylphosphino group. Complexes of compound* **1** *with $PtCl_2$, $PdCl_2$, and CuI were synthesized. Compound* **1** *and its complexes are readily hydrolyzed in solution to give diphenylphosphine and its corresponding complexes (NMR).*

INTRODUCTION

Chemical properties of compounds containing tri-coordinated phosphorus and boron atoms are to a great extent determined by their electronic nature. Three types of interaction are possible in the system P–X–Y–B, where X and Y are carbon or heteroatoms: intramolecular through-bond, intramolecular *trans*-annular and intermolecular interactions [1,2].

Chemical properties and conformational behavior of cyclic boryloxyalkyl phosphines are fairly well interpreted in terms of intramolecular donor-acceptor through-bond interactions (n-σ^*) [3]. The second type of interaction (trans-annular) was demonstrated with *cis*-1,2-borylphosphinoethenes [4]. Intermolecular interactions of tri-coordinated phosphorus and boron, resulting in formation of dimers and oligomers, are also well known [5]. The type of interaction depends on the fragment separating the P and B atoms, on their substituents, and on the spatial structure of the molecule. For example, 1,3,2,5-dioxaboraphosphorinanes having the P–C–O–B fragment in a heterocyclic ring are stable, while diphenylboryloxymethyl-(methyl)phenylphosphine, containing the acyclic P–C–O–B fragment, is an unstable compound capable of oxidation, hydrolysis, and intermolecular disproportionation [1,2].

RESULTS AND DISCUSSION

Previously [6], we described the synthesis of an O–B–O–C–C = C type of heterocycle, also having an exocyclic 4-phosphino group, from secondary phosphines, aromatic aldehydes containing an ortho-hydroxy group, and boronic acid esters.

In the IR spectrum of crystalline **1**, the absorption bands of hydroxyl groups are absent. The mass spectrum of **1** contains molecular ion peaks with m/z 394 (3.2%) and 393 (0.8%), $C_{25}H_{20}{}^{11,10}BO_2P$, as well as intensive peaks m/z 209 (100%) and 208 (25.5%) assigned to the ions of M^+–PPh_2 and $C_{13}H_{10}{}^{11,10}BO_2$.

The properties of the compound that was obtained appeared to be different from those expected for compounds containing the P–C–O–B fragment. In contrast to 1,3,2,5-dioxaboraphosphorinanes, they exhibit typical properties of tertiary phosphines and a boronic acid, e.g., a high

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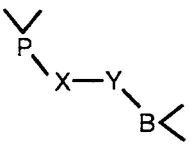

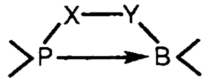

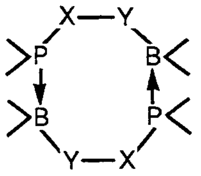

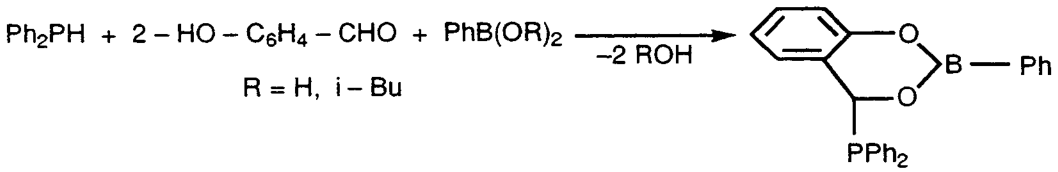

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sensitivity to oxidation and hydrolysis, respectively.

X-Ray Structure Determination

A single crystal of **1** was obtained from acetone-acetonitrile (1:1). Structure determination data are given in Table 1. Selected bond lengths and angles are listed in Table 2 and the torsion angles in Table 3. Coordinates of non-H-atoms are listed in Table 4, and the atom numbering scheme (for the X-ray determination) is given in Figure 1. Compound **1** contains two independent molecules **1A** and **1B** in a crystalline cell ($Z = 4$). The bicyclic system is approximately planar (within 0.15 Å), and the distance of the P atom from this plane is −1.807(1) Å in **1A** and 1.728(1) Å in **1B**. The six-membered heterocycle has a slightly distorted planar conformation, with the fragment O(1)B(2)C(4)C(5) being planar within 0.026(6) Å in molecule **1A** and 0.012(7) Å in **1B**, and the deviations of atoms O(3) and C(6) from this plane being equal to −0.047(4) and −0.207(5) Å, respectively, in molecule **1A** and 0.070(4) and 0.168(5) Å in **1B**.

The B-phenyl substituent is coplanar with the mean-square plane of the bicyclic fragment (the dihedral angles between these planes being 4.3° in **1A** and 7.4° in **1B**). This conformation is determined by the conjugation of the ring π-system and the oxygen lone pairs with the vacant *p*-orbital of boron. The O–B bond lengths in molecules **1** are slightly different, the average values being equal to 1.346(6) Å for O(1)–B(2) and 1.367(7) Å for O(3)–B(2). The smaller contribution of the O(3) lone electron pairs into conjugation with a vacant boron orbital due to its interaction with the π-system of the condensed benzene ring may account for such a difference. The shortening of the O(3)–C(4) bond in comparison with the O(1)–C(6) bond can also be cited in favor of this supposition. In general, the O–B bond lengths in molecules **1** are close to these observed in 4,6-dimethyl-2-phenyl-1,3,2-dioxaborinane (1.362 Å av) [7] and in 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane (1.360 Å av) [8]. The C(Ph)–B(2) bond length in **1** is close to the value of 1.554(3) Å found in 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane and in 2-phenyl-1,3,2-dioxaborolane 1.555(2) Å [9]. In these molecules, the plane of the phenyl substituent at the boron atom coincides with that of the bonds formed by the boron atom.

The diphenylphosphino group in molecule **1** has the usual geometry. Parallel orientation of one of the phenyl substituents and the heterocyclic system should be mentioned, short contacts between the atoms of the phenyl ring, O(1), and boron atoms being observed. The following distances were found: C(17) . . . B(2) 3.306 Å, C(22) . . . B(2) 3.210 Å, and O(1) . . . C(17) 3.052 Å in molecule **1A** and C(17) . . . B(2) 3.477 Å, C(22) . . . B(2) 3.280 Å, and O(1) . . . C(17) 3.112 Å in molecule **1B**, the sum of the van der Waals and radii being equal to 3.5 Å for C–B and 3.1 Å for O–C distances [10]. These short contacts do not result in an increase of the corresponding valence angles at phosphorus. On the contrary, the C(6)PC(17) angle in molecule **1A** and **1B** is smaller than the other angles at phosphorus. Thus, there is no repulsion between the two planar fragments and the interaction between them likely results from dispersion forces [11]. This is probably the first example of a "stacking interaction" with the participation of the boronic ester fragment. Less probable is the interaction between the π-system of the ring and a vacant boron orbital (the boron atom having an undistorted planar trigonal configuration).

Behavior of **1** in Solutions

The value of the chemical shift $\delta P = 10$ (THF, benzene, DMF) significantly differs from that of similar tertiary phosphines, *e.g.*, (diphenylbenzyl)diphenylphosphine ($\delta P = -14$ [12]). At the same

TABLE 1 Structure Determination Summary for **1** at 20°C

Empirical formula	$C_{24}H_{20}O_2BP$
Color, habit	colorless prisms
Crystal size	0.3 × 0.2 × 0.1 mm
Crystal system	triclinic
Space group	p_1
Unit cell dimensions (from 25 high-angle reflections)	a = 10.814(4) Å b = 11.517(5) Å c = 19.013(6) Å α = 102.45(3)° β = 99.641(3)° γ = 110.41(3)°
Volume V	2089(5) Å^3
Z	4 (two independent molecules)
Formula weight	381.20
Density (calcd)	1.21 g/cm^3
Absorption coefficient	1.42 cm^{-1}
F(000)	1200 e
Diffractometer used	Enraf-Nonius CAD-4
Radiation	Mo K_α (λ = 0.71073 Å) graphite monochromator
2θ range	4–50°
Scan mode	$\omega/(5/3\theta)$
Scan speed	variable: 2–20° min^{-1} in σ(I)
Scan range	variable: ω = (1.35 + 0.35 tgθ)°
Standard reflections	two intensity and two orientation control reflections measured after every 200 reflections
Index range	$-10 < h < 10$, $-11 < k < 11$, $0 < l < 20$
Reflections collected	7573
Observed reflections	2695 ($F^2 > 3\sigma$)
System	SDP-PLUS PDP-11/23
Solution	direct methods
Refinement method	full-matrix least squares (on F_s)
Quantity minimized	$\Sigma\omega\ (\lvert F_o\rvert - \lvert F_c\rvert)^2$
Hydrogen atoms	from Fourier, not refined, fixed, B_{iso} = 4 Å
Weighting scheme	$\omega = 4\ \lvert F_o\rvert^2/((\sigma(I))^2 + (0.07\lvert F_o\rvert^2)^2)$
Final R indices (observed data)	R = 0.048, R_w = 0.69
Goodness of fit	1.42
Largest Δ/τ	0.2
Data to parameter ratio	1:5.15
Largest difference peak	0.1 e/Å^3

time, the chemical shift of **1** in pyridine is nearly δP = −4.

The NMR signals of the phenyl and 1,2-phenylene protons are at δH = 7.56–6.11, and the doublet corresponding to the protons of the methyne group is at δH = 5.61, ($^2J_{PH}$ = 9 Hz). The $^2J_{PH}$ constant depends on the dihedral angle between the phosphorus lone electron pair and the C–H bond. This angle should be equal to 50–60° in compound **1** as derived from the Albrand curve [13]. Two conformers **a** and **b** of three possible ones for compound **1** have the appropriate dihedral angle.

The conformer **a** with *trans*-orientation of the phosphorus lone pair with respect to the C–O bond is the most stable conformation. The conformer **a** is observed also in the crystals, due to two stabilizing donor-acceptor interactions; the n-σ^* interaction of phosphorus with the C–O bond and that of the π-systems of the borinane ring and the appropriate phenyl ring. Moreover, steric hindrance is smaller in this conformation. The extraordinary structure of **1** with its parallel orientation of borinane and phenyl rings, fixed in crystals, is also preserved in solutions resulting in an anomalous value of the chemical ^{31}P NMR shift. Because the interaction of two π-systems is absent in a complex with pyridine, the chemical shift becomes typical of tertiary phosphines.

In solution, compound **1** is easily oxidized by oxygen of the air and also adds sulfur and selenium. The oxide, sulfide, and selenide of **1** form stable complexes with pyridine [6]. At the same time, unlike the behavior of borylphosphinoalkenes, reactions with compounds containing polar multiple bonds—aldehydes, isocyanates, isothiocyanates, thiocyanates, and carbodiimides—do not take place. Moreover, compound **1** easily undergoes hydrolysis even with traces of water. Thus, the

TABLE 2 Selected Distances (Å) and Angles (°) with Estimated Standard Deviations in Parentheses for **1**

	A	*B*		*A*	*B*
P–C6	1,884(5)	1,871(5)	O3–C4	1,400(5)	1,393(6)
P–C17	1,822(5)	1,822(5)	O3–B2	1,368(5)	1,365(7)
P–C23	1,828(5)	1,833(5)	C4–C5	1,376(6)	1,390(6)
O1–C6	1,440(5)	1,430(5)	C5–C6	1,494(6)	1,508(6)
O1–B2	1,345(6)	1,347(6)	C11–B2	1,573(7)	1,562(8)
C6PC17	98.4(2)	102.9(2)	C4C5C10	118.0(5)	117.7(5)
C6PC23	102.5(2)	100.2(2)	C6C5C10	121.3(4)	121.7(5)
C17PC23	103.4(2)	102.8(2)	PC601	110.9(3)	112.2(3)
C6O1B2	121.4(4)	122.(4)	PC8C5	110.3(3)	110.2(3)
C4O3B2	119.4(4)	119.6(4)	O1C6C5	112.9(4)	112.6(4)
O3C4C5	120.2(4)	120.1(5)	O1B2O3	122.5(5)	122.6(5)
O3C4C7	116.8(4)	118.4(5)	O1B2C11	118.8(5)	118.4(5)
O5C4C7	122.9(4)	121.5(5)	03B2C11	118.6(5)	119.0(5)
C4C5C6	120.7(4)	120.6(5)			

TABLE 3 Torsion Angles (°) for **1**

	A	*B*		*A*	*B*
C6O1B2O3	−12.7	6.9	C4O3B2C11	175.9	173.9
O1B2O3C4	−1.8	5.6	O1B2C11C12	−10.8	−169.8
B2O3C4C5	6.8	−7.7	O1C6PC17	54.2	51.6
O3C4C5C6	3.3	−2.0	O1C6PC23	−51.6	−54.1
C4C5C6O1	−15.0	12.8	C5C6PC17	−71.6	177.9
C5C6O1B2	20.1	−15.3	C5C6PC23	−177.4	72.2
B2O1C6P	−104.3	109.7	C6PC17C18	92.9	20.7
C4C5C6P	109.7	−113.3	C6PC23C24	174.3	−103.7
C6B1O2C11	169.6	−173.6			

formation of diphenylphosphine oxide ($\delta P = 26$), diphenylphosphine ($\delta P = -42$, ${}^1J_{PH} = 209$ Hz) or diphenyldeuterophosphine ($\delta P = -42.9$, in the presence of D_2O), and aldehyde ($\upsilon_{C-O} = 1650\ cm^{-1}$) was observed after some time by ${}^{31}P$ NMR and IR spectroscopy. The hydrolysis is the reverse of the formation of **1**. The subsequent dissociation of the hydrolysis product, containing an α-oxyalkyl fragment, is well known.

Compound **1** *with Transition Metals*

Compound **1** reacts with $PtCl_2(PhCN)_2$ or $PdCl_2$ in MeCN to form white **2** and bright yellow **3** crystalline complexes, respectively, which are poorly soluble in organic solvents. The spectroscopic values of $\upsilon = 700–1700$, 346 (Pt–Cl) for **2** and 360 (Pd–Cl) for **3** constitute evidence for the *trans*-configurations in the Pt and Pd products. The elemental analysis results coincide with the addition of two ligand molecules to one metal atom in each case. Similar complexes with the *trans*-configuration about the central atom have been obtained for 4,6-disubstituted 1,3,2,5-dioxaboraphosphorinane [14], these complexes being hydrolytically stable. Crystalline compounds **2** and **3** are stable even when refluxed in ethanol, in which they are almost insoluble. Complex **2** is decomposed into cis-$(Ph_2PH)_2PtCl_2$ when dissolved in DMF. The ${}^{31}P$ NMR signals of solutions of **2** in pyridine or **3** in DMF belong to $(Ph_2PH)_2(\mu\text{-}Ph_2P)_2Pt_2Cl_2$ and $(Ph_2PH)_2(\mu\text{-}Ph_2P)_2Pd_2Cl_2$, respectively. The σ-phosphine-μ-phosphino complex of platinum was isolated, its physical constants being in accordance with known data [15].

Compound **1** reacts with CuI in pyridine to give the crystalline colorless complex **4** in high yield. An IR study of **4** showed the presence of bonds assigned to skeletal vibrations of ligand **1** in the spectrum and the absence of absorptions attributable to decomposition products (e.g., OH, P–H, P = O). Immediately after preparation, the NMR spectra of the solution contains only the signal with $\delta P = 8.9$ ($CHCl_3$), close to that of the initial ligand. Elemental analysis results of this complex indicate the presence of three pyridine and one ligand molecule per CuI moiety. However, after several minutes, the signal with $\delta\ {}^{31}P = -36$ and ${}^1J_{PH} = 306$ Hz ($CHCl_3$), corresponding to the formation of the complex of the diphenylphosphine with CuI, appears in the spectrum of the solution. At the same time, the C = O absorption of salicylaldehyde ap-

TABLE 4 Coordinates of Nonhydrogen Atoms for Structure (**1**) and Its Equivalent Isotropic Temperature Factors

$$B_{iso}^{equiv} = \sum_{i=1}^{3}\sum_{j=1}^{3}(a^*_i a^*_j)B(ij)$$

Atom	*X*	*Y*	*Z*	*B*
Molecule A				
P	0.2122(1)	0.4208(1)	0.6054(8)	3.75(3)
O1	0.3169(3)	0.3355(3)	0.4923(2)	3.76(9)
O3	0.5050(3)	0.2979(3)	0.5518(2)	4.48(9)
C4	0.5586(5)	0.4216(4)	0.6034(3)	3.8(1)
C5	0.4858(5)	0.4986(4)	0.6042(3)	3.4(1)
C6	0.3466(5)	0.4499(4)	0.5522(3)	3.6(1)
C7	0.6850(5)	0.4603(5)	0.6515(3)	5.0(2)
C8	0.7425(5)	0.5850(5)	0.7001(4)	5.3(2)
C9	0.6731(6)	0.6651(5)	0.7019(3)	5.1(2)
C10	0.5449(5)	0.6212(5)	0.6546(3)	4.1(1)
C11	0.3333(5)	0.1242(5)	0.4366(3)	3.7(1)
C12	0.2053(6)	0.0726(5)	0.3860(3)	4.7(2)
C13	0.1560(6)	−0.0479(6)	0.3354(4)	5.7(2)
C14	0.2352(6)	−0.1199(5)	0.3312(3)	5.1(2)
C15	0.3631(6)	−0.0694(5)	0.3810(3)	4.5(1)
C16	0.4144(5)	0.0529(5)	0.4330(3)	4.1(1)
C17	0.2207(5)	0.2771(4)	0.6276(3)	3.4(1)
C18	0.3076(6)	0.2959(5)	0.6956(3)	5.1(2)
C19	0.3264(7)	0.1901(6)	0.7138(3)	6.7(2)
C20	0.2613(6)	0.0683(5)	0.6673(4)	6.1(2)
C21	0.1731(6)	0.0478(5)	0.5993(4)	5.3(2)
C22	0.1545(5)	0.1506(5)	0.5797(3)	4.3(1)
C23	0.0533(5)	0.3555(4)	0.5311(3)	3.8(1)
C24	−0.0664(5)	0.3131(5)	0.5545(3)	5.1(2)
C25	−0.1937(6)	0.2696(5)	0.5028(4)	6.0(2)
C26	−0.2009(6)	0.2724(5)	0.4305(4)	5.7(2)
C27	−0.0849(6)	0.3163(5)	0.4078(3)	5.7(2)
C28	0.0455(5)	0.3584(5)	0.4577(3)	4.2(1)
B2	0.3867(6)	0.2598(5)	0.4973(3)	3.8(2)
Moleccule B				
P	−0.3883(1)	0.3055(1)	0.90121(8)	3.46(3)
O1	−0.1794(3)	0.3282(3)	1.0151(2)	4.04(9)
O3	−0.0410(3)	0.2350(3)	0.9598(2)	5.0(1)
C4	−0.0367(5)	0.3039(5)	0.9077(3)	4.3(1)
C5	−0.1131(5)	0.3789(5)	0.9049(3)	3.7(1)
C6	−0.2097(5)	0.3831(4)	0.9563(3)	4.0(1)
C7	0.0478(5)	0.2998(5)	0.8621(3)	4.7(2)
C8	0.0596(6)	0.3719(6)	0.8124(3)	5.3(2)
C9	−0.0166(6)	0.4473(5)	0.8081(3)	5.2(2)
C10	−0.0999(5)	0.4510(5)	0.8541(3)	4.4(1)
C11	−0.0989(5)	0.1863(5)	1.0763(3)	4.5(3)
C12	−0.0086(6)	0.1242(5)	1.0852(4)	5.4(2)
C13	0.0004(6)	0.0683(5)	1.1441(4)	6.5(2)
C14	−0.0789(7)	0.0725(6)	1.1933(4)	6.6(2)
C15	−0.1664(7)	0.1330(6)	1.1830(3)	6.9(2)
C16	−0.1758(6)	0.1928(5)	1.1279(3)	5.0(2)
C17	−0.4127(5)	0.1347(4)	0.8751(3)	3.1(1)
C18	−0.1451(6)	0.0805(5)	0.8037(3)	4.7(2)
C19	−0.4312(7)	−0.0495(5)	0.7774(3)	6.5(2)
C20	−0.4426(7)	−0.1209(5)	0.8269(4)	6.7(2)
C21	−0.4422(6)	−0.0697(5)	0.8987(3)	5.4(2)
C22	−0.4257(5)	0.0602(5)	0.9243(3)	4.2(1)
C23	−0.4793(5)	0.3155(4)	0.9732(3)	3.3(1)
C24	−0.4203(5)	0.4027(5)	1.0455(3)	4.6(2)
C25	−0.5019(6)	0.4139(5)	1.0930(3)	5.6(2)
C26	−0.6390(6)	0.3433(5)	1.0719(3)	5.6(2)
C27	−0.6982(6)	0.2561(6)	1.0010(4)	5.9(2)
C28	−0.6194(5)	0.2433(5)	0.9523(3)	4.6(2)
B2	−0.1073(6)	0.2534(6)	1.0135(4)	4.0(2)

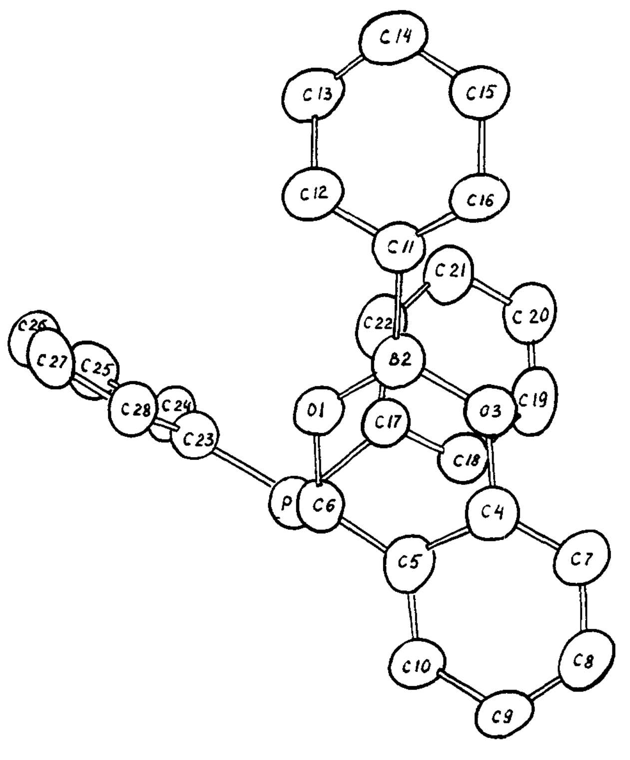


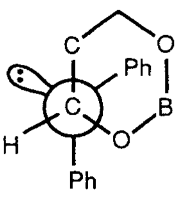
FIGURE 1 The molecular structure of **1A** showing the atom numbering scheme. Hydrogen atoms have been omitted.

pears at 1680 cm^{-1}. Crystalline complex **4** is also unstable and easily decomposes with the formation of the oxide of **1** and its complex with pyridine, as determined by ^{31}P NMR (δP = 29.4 and 28) spectroscopy [6] and mass spectrometry. The mass spectrum contains the peaks of the molecular ion of the oxide $C_{25}H_{20}\,{}^{11}BO_3P$ with *m/z* 410 (27%) as well as intense peaks with *m/z* 209 (100%) M^+-Ph_2PO and 201 (6%) Ph_2PO.

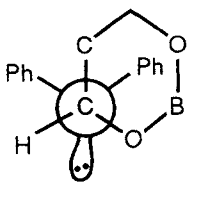
EXPERIMENTAL

The synthesis of compound **1** has been previously reported [6]. Colorless crystals of **1** were obtained from a mixture of acetone and acetonitrile (1:1). Reactions and manipulation were carried out under an atmosphere of dry argon. Solvents were dried using standard procedures.

^{1}H and ^{31}P NMR spectra were recorded on a



a



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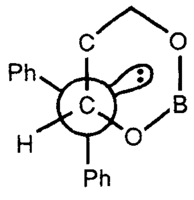

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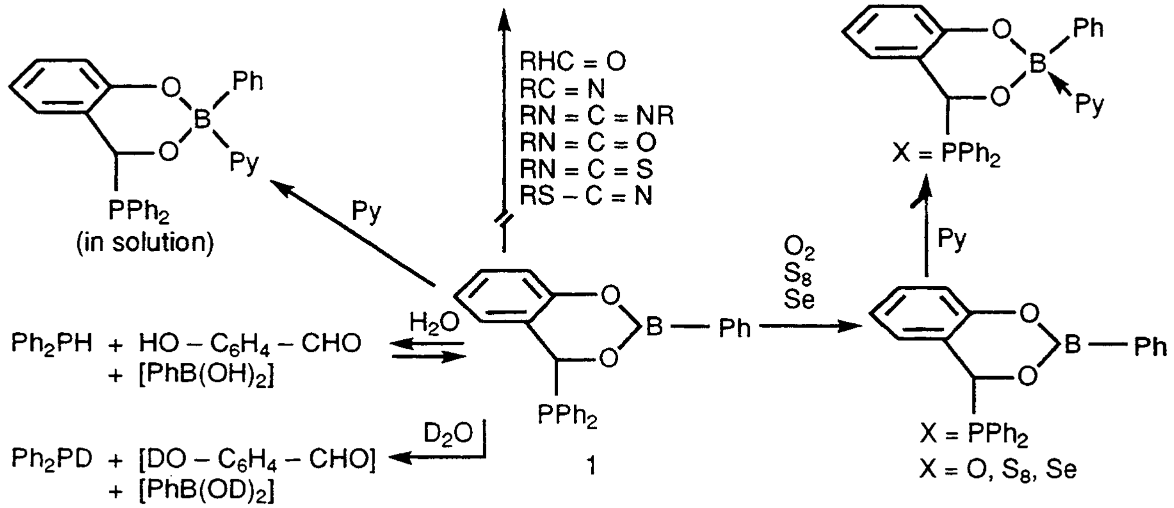
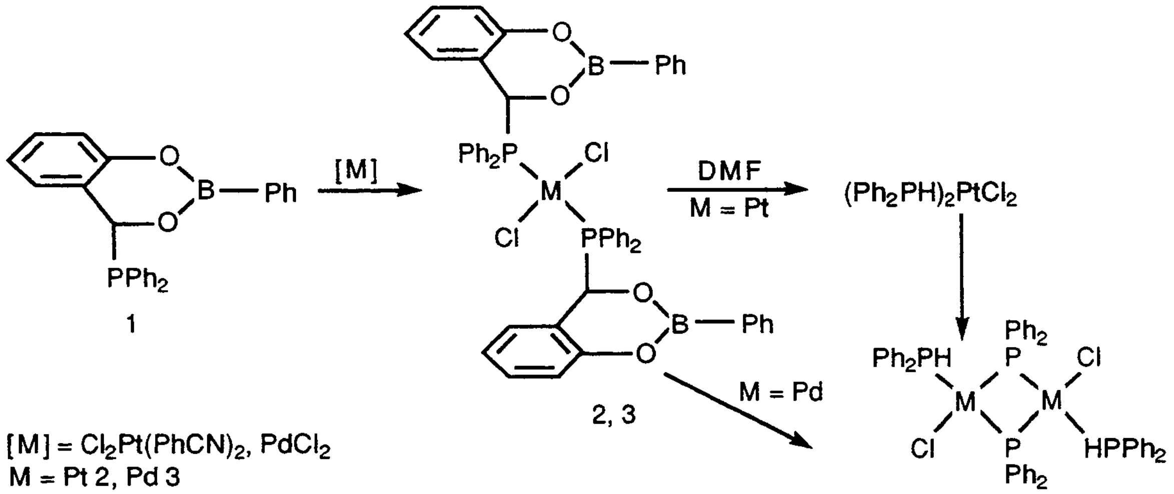
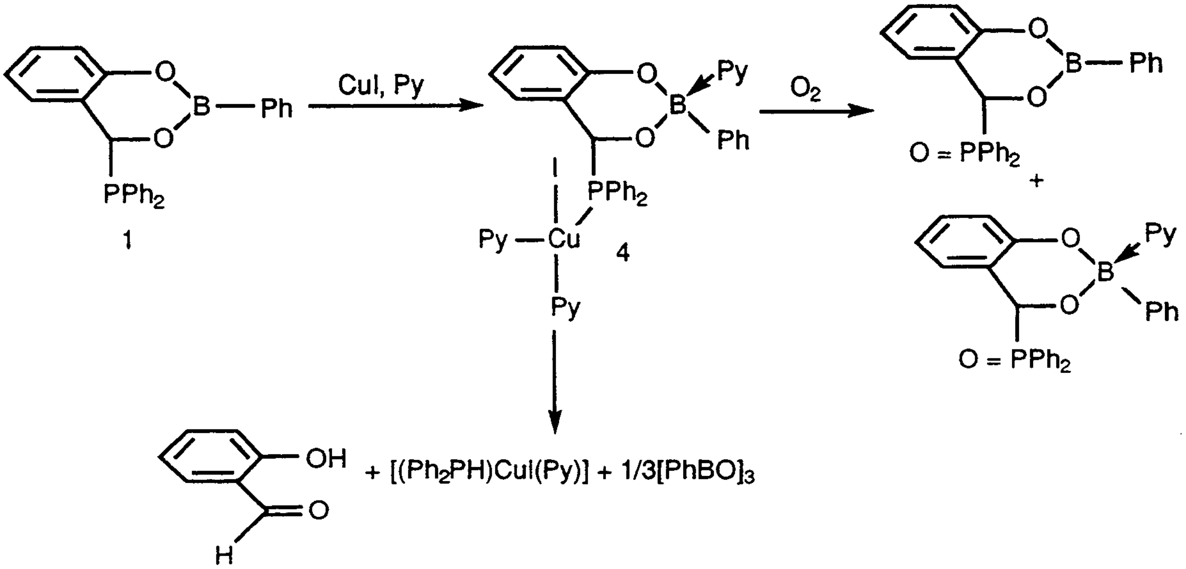

Ph
B
Py
PPh2
(in solution)
Py
RHC = O
RC = N
RN = C = NR
RN = C = O
RN = C = S
RS – C = N
Ph
B
Py
X = PPh2
Py
O2
S8
Se
Ph2PH + HO – C6H4 – CHO
+ [PhB(OH)2]
H2O
B — Ph
PPh2
1
B — Ph
X = PPh2
X = O, S8, Se
Ph2PD + [DO – C6H4 – CHO]
+ [PhB(OD)2]
D2O


B — Ph
PPh2
1
[M]
B — Ph
Ph2P
Cl
M
Cl
PPh2
B — Ph
2, 3
DMF
M = Pt
(Ph2PH)2PtCl2
M = Pd
Ph2PH
Ph2
P
Cl
M
M
Cl
P
Ph2
HPPh2
[M] = Cl2Pt(PhCN)2, PdCl2
M = Pt 2, Pd 3


B — Ph
PPh2
1
CuI, Py
Py
B
Ph
PPh2
Py — Cu
Py
4
O2
B — Ph
O = PPh2
+
Py
B
Ph
O = PPh2
OH
O
H
+ [(Ph2PH)CuI(Py)] + 1/3[PhBO]3

WM-250 Bruker spectrometer. IR spectra were obtained on a "Specord M-80" spectrometer. Mass spectra were recorded on an MX-1310 instrument at 50 eV.

trans-Bis(5,6-benzo-4-diphenylphosphino-1,3,2-dioxaborinane)-dichloroplatinum(II) (**2**)

A solution of **1** (0.58 g, 1.5 mmol) in 10 mL of MeCN was mixed with a solution of $PtCl_2(PhCN)_2$ (0.35 g, 0.75 mmol) in 20 mL of MeCN. The mixture was allowed to stand for 2 hours with continual mixing. A yellow precipitate of the air stable solid **2** was isolated by filtration: 0.51 g (65%), mp > 350°C. IR (CsI): v = 346 cm^{-1} (Pt–Cl). $^{31}P\{^1H\}$ NMR (DMF): $\delta = -10.2$, $^1J_{PtP} = 3416$ Hz, $^1J_{PH} = 430$ Hz ($Cl_2Pt(HPPh_2)$). Anal. calcd for $C_{50}H_{40}P_2O_4B_2PtCl_2$: C, 56.93; H, 3.80; P, 5.88. Found: C, 56.50; H, 3.78; P, 6.05.

trans-Bis(5,6-benzo-4-diphenylphosphino-1,3,2-dioxaborinane)-dichloropalladium(II) (**3**)

Compound **1** (0.5 g, 1.3 mmol) was mixed with $PdCl_2$ (0.11 g, 0.6 mmol) in 35 mL of MeCN. After 1 day, the reaction mixture was filtered and the filtrate concentrated to about 1 mL. The yellow solid **3** (air stable) formed was collected by filtration and washed with ether: 0.27 g (44%), mp 201–205°C. IR (CsI): v = 360 (Pd–Cl) cm^{-1}. $^{31}P\{^1H\}$ NMR (DMF) $\delta = -5.2$, $^1J_{PH} = 440$ Hz, $\delta = -141.2$, $^1J_{PP} = 370$ Hz ($(Ph_2PH)ClPd(\mu\text{-}PPh_2)_2PdCl(Ph_2PH)$). Anal. calcd for $C_{50}H_{40}P_2O_4B_2PdCl_2$: C, 55.22; H, 4.17; P, 8.91. Found: C, 54.76; H, 4.20; P, 8.91.

(5,6-Benzo-4-diphenylphosphino-1,3,2-dioxaborinane)*tris(pyridine)iodocopper(I)* (**4**)

Compound **1** (0.43 g, 1.1 mmol) was mixed with CuI (0.19 g, 1.0 mmol) in 15 mL of pyridine. After 1 day, the solvent was removed *in vacuo* from the reaction mixture. Acetone (2 mL) was added to produce a white, air-sensitive solid **4**: 0.5 g (61%), mp 90–92°C. MR: δ = $^{31}P\{^1H\}$ ($CHCl_3$) 8.9 (immediately after solution); $\delta = -36.5$, $^1J_{PH} = 306$ Hz, ($(Ph_2PH)CuIPy_2$) (after 1 hour). Anal. calcd for $C_{40}H_{35}PO_2N_3BCuI$: C, 58.39; H, 4.26; P, 3.77; N, 5.11. Found: C, 57.89; H, 4.23; P, 3.37; N, 5.10.

SUPPLEMENTARY MATERIAL AVAILABLE

Atomic coordinates and anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Database. Copies may be obtained through the Executive Secretary, 12 Union Road of Cambridge CB2 1EZ, England.

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