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Ditopic ligands featuring [P,S], [P,P] or [P,B] chelating pockets housed on a protected *o*-hydroquinone core

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ABSTRACT

1,2-Dibromo-4,5-dimethoxybenzene was explored as a platform for the buildup of ditopic ligands. Low temperature reactions with *n*-butyllithium followed by quenches with various electrophiles led to the syntheses (2-bromo-4,5-dimethoxyphenyl)diphenylphosphine (**1**), (4,5-dimethoxy-2-(methylthio)phenyl) diphenylphosphine (**2**), 1,2-bis(diphenylphosphino)-4,5-dimethoxybenzene (**3**), and (2-(dicyclohexylboryl)-4,5-dimethoxyphenyl)diphenylphosphine (**4**). Oxidation of **3** produced 1,2-bis(diphenylphosphoryl)-4,5-dimethoxybenzene (**5**). All compounds were characterized by multinuclear ($^{1}H/^{13}C/^{31}P\{^{1}H\}$) NMR spectroscopy and by high resolution mass spectrometry. In addition, single crystal X-ray diffraction characterizations of **1**, **3**, **4**, and **5** were also carried out. Reactivity of *o*-phosphinophenylborane **4** toward molecular hydrogen was also probed.

1. Introduction

Polydentate phosphine ligands are ubiquitous in coordination chemistry [1]. Phosphine groups ($-PR_2$) are also common building blocks for constructing chelating ligand architectures, particularly when combined with other donor functionalities [2–5]. More recently chelating phosphine compounds where the $-PR_2$ group is adjacent to electron accepting borane $-BR_2$ functionality have been characterized. Various derivatives of *o*-phosphinophenylboranes have attracted attention as ligands for coordination chemistry [6–9], as units for small molecule activation [10–13], and as platforms for developing new catalysts [14–16]. The properties of the phosphine ligand are usually set at the stage of synthesis, by varying the nature of the substituents on the phosphorus center. Possibilities for post-synthetic modifications of steric or electronic properties are rather limited. One avenue for such modification is available if $-PR_2$ group is mounted onto suitable redox active platforms. Thus, tetrathiafulvalenes [17,18] and ferrocene [19] appended by phosphines have been successfully utilized for the coordination chemistry of selected transition metals. Another common redox-active molecular platform suitable for such purposes is *o*-hydroquinone. Several phosphine derivatives bearing this functional group have been investigated, but the studies have been mostly limited to monodentate *o*-hydroquinone–PR_2 derivatives [20–23].

Herein we report on the syntheses and characterizations of several new phosphine derivatives where 1,2-dimethoxy-benzene unit (a methyl-protected *o*-hydroquinone) is appended by adjacent $-PPh_2$/X groups (X = –Br, $-SCH_3$, $-BCy_2$, or $-PPh_2$). We obtained (2-bromo-4,5-dimethoxyphenyl)diphenylphosphine (**1**) from 1,2-dibromo-4,5-dimethoxybenzene. The compound was used to synthesize (4,5-dimethoxy-2-(methylthio)phenyl)diphenylphosphine (**2**), 1,2-bis(diphenylphosphino)-4,5-dimethoxybenzene (**3**), and (2-(dicyclohexylboryl)-4,5-dimethoxyphenyl)diphenylphosphine (**4**). Oxidation of **3** led to 1,2-bis(diphenylphosphoryl)-4,5-dimethoxybenzene (**5**). Single crystal X-ray diffraction characterizations of compounds **1**, **3**, **4**, and **5**·H_2O are also reported.

2. Experimental

2.1. General procedures

All reactions and manipulations requiring exclusion of air were carried out under nitrogen atmosphere, utilizing standard Schlenk techniques involving a double manifold vacuum line, or in a glovebox (Innovative Technologies). Low temperature (−100 °C) reactions were carried out in Schlenk flasks immersed into shallow Dewar flasks filled with isopropanol/liquid N_2. Once a required temperature of the cooling mixture was attained, the flasks

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containing reaction mixtures were maintained at that temperature for at least 1 h before the addition of other reagents. Diethyl ether, THF, heptane, hexanes and pentane were distilled from Na/benzophenone. Methylene chloride was distilled from CaH_2. Starting materials were purchased from commercial suppliers and were used as received except for $ClPPh_2$ (distilled in vacuum), and dimethyldisulfide (dried over activated 4A molecular sieves).

NMR measurements were carried out on Varian INOVA or Varian-MR spectrometers operating at 400 (^{1}H), 100 (^{13}C), and 161 (^{31}P) MHz, respectively. ^{1}H and ^{13}C spectra were referenced to tetramethylsilane; ^{31}P{^{1}H} spectra were referenced to 85% H_3PO_4 as an external reference. High resolution mass-spectrometry measurements were carried out at the Mass Spectrometry Facility of Michigan State University (East Lansing, MI 48829-1319).

2.2. Syntheses and characterizations

2.2.1. (2-Bromo-4,5-dimethoxyphenyl)diphenylphosphine, **1**

A solution of 2.96 g (10 mmol) of 1,2-dibromo-4,5-dimethoxybenzene in diethyl ether (100 mL) and THF (10 mL) was cooled to −100 °C, and a solution of *n*-BuLi (1.6 M in hexanes, 6.25 mL, 10 mmol) was slowly (over 15 min) added via syringe. The reaction mixture (white suspension) was stirred for 1 h while the temperature was maintained at −100 °C. A solution of $ClPPh_2$ (1.8 mL, 10 mmol) in 10 mL of diethyl ether was added over a period of 5 min. The reaction mixture (yellow/orange solution) was stirred while warming up to room temperature overnight. Workup and purification were carried out exposing the reaction mixture to air. All volatiles were removed under reduced pressure (rotary evaporator), yielding a pale yellow waxy solid. Crystallization from boiling ethanol (70 mL) yielded pure **1** as white needles. Selected crystals were suitable for single crystal X-ray diffraction experiments. Yield: 3.267 g (81.5%). Melting point: 133–135 °C. ^{1}H NMR (acetone-d_6) δ 7.41 (m, 6H), 7.29 (m, 4H), 7.21 (d, 1H, $^3J_{HP}$ = 9 Hz), 6.29 (d, 1H, $^4J_{HP}$ = 6 Hz), 3.87 (s, 3H), 3.43 (s, 3H). ^{13}C NMR (acetone-d_6) δ 160.0 (s), 148.9 (s), 136.9 (s), 136.7 (s), 133.6 (d, $^2J_{CP}$ = 20 Hz), 128.8 (d, $^1J_{CP}$ = 27 Hz), 128.6 (s), 120.5 (d, $^1J_{CP}$ = 33 Hz), 117.4 (s), 117.3 (d, $^2J_{CP}$ = 10 Hz), 55.6 (s), 54.9 (s). ^{31}P NMR (acetone-d_6) δ −3.4 (s). HRMS (ESI): 401.0315 (MH^+); calcd. for $C_{20}H_{19}BrO_2P$ (MH^+): 401.0306.

2.2.2. (4,5-Dimethoxy-2-(methylthio)phenyl)diphenylphosphine, **2**

Compound **1** (2.690 g, 6.7 mmol) was dissolved in diethyl ether (100 mL). The solution was cooled to 0 °C, and a solution of *n*-BuLi (1.6 M in hexanes, 4.2 mL, 6.72 mmol) was slowly added. The reaction mixture became a creamy suspension, and was stirred at 0 °C for 1 h. A solution of dimethyldisulfide (0.67 mL, 7.5 mmol) in 10 mL of diethyl ether was added, producing a yellow–orange suspension. Reaction mixture was stirred overnight while warming to room temperature. Workup and purification were carried out exposing the reaction mixture to air. (*Caution*! Reaction mixture typically has very strong and unpleasant odor, thus it is best to handle it in the fume hood.) All volatiles were removed under reduced pressure (rotary evaporator), yielding a yellow oil. This was dissolved in diethyl ether (20 mL); cooling the solution to −28 °C overnight produced a white solid **2** (1.109 g) which was isolated by filtration. The volume of the filtrate was reduced in vacuum, and repeated crystallization yielded another 0.405 g of compound **2**. Combined yield: 1.514 g (61.2%). Melting point: 67–69 °C. ^{1}H NMR (C_6D_6) δ 7.42 (m, 4H), 7.03 (m, 6H), 6.89 (d, 1H, $^3J_{PH}$ = 4 Hz), 6.49 (d, 1H, $^4J_{PH}$ = 3 Hz), 3.29 (s, 3H), 3.13 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (C_6D_6) δ 150.9 (s), 149.2 (s), 138.4 (d, $^1J_{CP}$ = 14 Hz), 135.2 (d, $^1J_{CP}$ = 30 Hz), 133.9 (d, $^2J_{CP}$ = 20 Hz), 133.6 (d, $^2J_{CP}$ = 18 Hz), 131.5 (d, $^2J_{CP}$ = 9 Hz), 128.5 (s), 128.4 (d, $^3J_{CP}$ = 3 Hz), 115.4 (d, $^3J_{CP}$ = 4 Hz), 55.3 (s), 55.0 (s), 19.1 (d, $^4J_{CP}$ = 6 Hz). ^{31}P NMR (C_6D_6) δ −12.1 (s). HRMS (ESI): 369.1074 (MH^+); calcd. for $C_{21}H_{22}O_2PS$ (MH^+): 369.1078.

2.2.3. 1,2-Bis(diphenylphosphino)-4,5-dimethoxybenzene, **3**

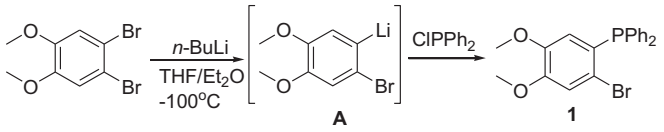
Compound **3** was prepared by two methods; descriptions of both are provided.

Method A: From **1** by single lithium-halogen exchange. The reaction leading to Li–Br exchange was carried out in an analogous

Table 1
Summary of crystallographic data for **1**, **3**, **4** and **5**·H_2O.

Compound reference	**1**	**3**	**4**	**5**·H_2O
Chemical formula	$C_{20}H_{18}Br_1O_2P_1$	$C_{32}H_{28}O_2P_2$	$C_{32}H_{40}B_1O_2P_1$	$C_{32}H_{30}O_5P_2$
Formula mass	401.24	506.48	498.42	556.54
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
a/Å	11.6091(5)	9.5793(4)	9.247(5)	14.7204(5)
b/Å	7.3074(2)	10.5801(4)	9.275(3)	16.1482(7)
c/Å	22.5063(10)	14.0265(4)	19.243(13)	12.1826(5)
α/°	90.00	97.646(3)	101.83(3)	90.00
β/°	101.252(4)	95.735(3)	93.12(5)	99.698(4)
γ/°	90.00	109.790(3)	115.14(3)	90.00
Unit cell volume/Å^3	1872.56(13)	1309.62(8)	1443.5(13)	2854.5(2)
Temperature/K	297(2)	150(2)	291(2)	299(2)
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
No. of formula units per unit cell, *Z*	4	2	2	4
Absorption coefficient, μ/mm^{-1}	2.289	0.194	0.121	0.192
No. of reflections measured	19,376	15,295	4035	14,366
No. of independent reflections	5698	8026	3753	6910
R_{int}[a]	0.0435	0.0213	0.0263	0.0244
Final R_1 values ($I > 2\sigma(I)$)[b]	0.0335	0.0354	0.0446	0.0899
Final $wR(F^2)$ values ($I > 2\sigma(I)$)[c]	0.0524[d]	0.0729[e]	0.1183[f]	0.2018[g]
Final R_1 values (all data)	0.1026	0.0513	0.0636	0.1003
Final $wR(F^2)$ values (all data)	0.0549	0.0753	0.1294	0.2070
Goodness of fit on F^2 [h]	1.001	1.005	1.081	1.011

[a] $R_{int} = \sum|F_o^2 - < F_o^2 >| / \sum|F_o^2|$.
[b] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$.
[c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$.
[d] $w = 1/[\sigma^2(F_o^2) + (0.0130P)^2 + 0.0000P]$.
[e] $w = 1/[\sigma^2(F_o^2) + (0.0250P)^2 + 0.2800P]$.
[f] $w = 1/[\sigma^2(F_o^2) + (0.0627P)^2 + 0.6365P]$.
[g] $w = 1/[\sigma^2(F_o^2) + (0.0250P)^2 + 15.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$.
[h] GooF $= S = [\sum[w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2}$.



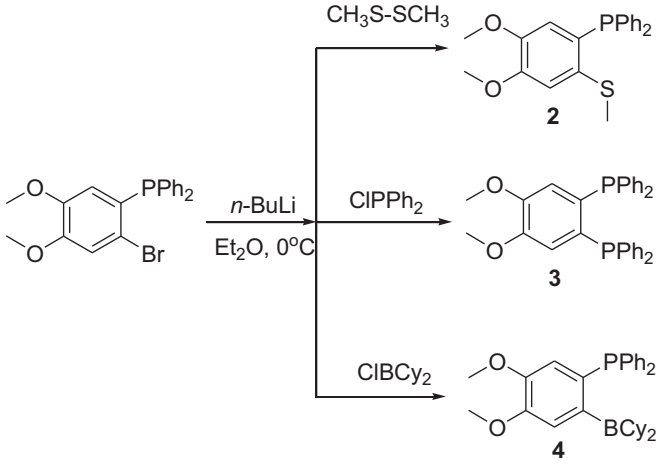
Scheme 1. Generation of organolithium intermediate **A** and synthesis of compound **1**.

manner to the procedure described for the synthesis of **2** (2.106 g, (5.25 mmol) of (2-bromo-4,5-dimethoxyphenyl)diphenylphosphine was used). The generated aryl lithium compound was reacted with a solution of $ClPPh_2$ (1.131 mL, 6.1 mmol) in 15 mL of diethyl ether. The reaction mixture was allowed to warm to room temperature while being stirred overnight. Workup and purification were carried out by exposing the reaction mixture to air. All volatiles were removed under vacuum (rotary evaporator), and the resulting pale yellow paste was extracted with 100 mL of boiling ethanol. Compound **3** precipitated in the form of white crystals upon cooling the solution to room temperature. Selected crystals were suitable for single crystal X-ray diffraction experiments. Yield: 2.617 g (52%).

Method B: One-step procedure via double lithium–halogen exchange. A solution of 1,2-dibromo-4,5-dimethoxybenzene (2.96 g, 10 mmol) in 100 mL of Et_2O/THF (1:1) was cooled to −100 °C, and a solution of *n*-BuLi (1.6 M in hexanes, 13.1 mL, 21 mmol) was added to it. The pale brown reaction mixture was stirred at −100 °C for 45 min, after which a solution of $ClPPh_2$ (4.63 g, 21 mmol, in 15 mL of THF) was slowly added to it. The temperature of the reaction flask was maintained at −100 °C during the addition. The reaction mixture was further stirred at −100 °C for 2 h and was then allowed to warm to room temperature overnight. Workup of the reaction mixture and isolation of the product were analogous to the ones described in *Method A*. Yield: 1.417 g (53%). Melting point: 157–159 °C. ^{1}H NMR (C_6D_6) δ 7.36 (m, 8H), 6.99 (m, 12H), 6.77 (m, 2H), 3.14 (s, 6H). ^{13}C NMR (C_6D_6) δ 149.7 (s), 137.6 (m), 134.8 (m), 132.8 (m), 127.2 (m), 127.1 (s), 116.3 (m), 53.7 (s). ^{31}P NMR (C_6D_6) δ −12.9 (s). HRMS (ESI): 507.1646 (MH^+); calcd. for $C_{32}H_{29}O_2P_2$ (MH^+): 507.1643.

2.2.4. (2-(Dicyclohexylboryl)-4,5-dimethoxyphenyl) diphenylphosphine, *4*

A solution of compound **1** (0.802 g, 2 mmol) in ether (40 mL) was cooled to 0 °C, and a solution of *n*-BuLi (1.6 M in hexanes, 1.3 mL, 2.1 mmol) was added. The reaction mixture (beige suspension) was stirred at 0 °C for 1 h, and a solution (1 M in hexanes) of $ClBCy_2$ was added (2.1 mL, 2.1 mmol). The reaction mixture was allowed to attain room temperature and was stirred for 14 h. This solution was filtered, and all volatiles were removed under reduced pressure (Schlenk line). The remaining white solid was extracted with hot heptane (~40 mL), and the solution was kept at −28 °C. Crystals of **4** (large light yellow cubes; suitable for X-ray analysis) formed upon standing for 6 days, and were isolated by filtration. Yield: 0.310 g (31%). Melting point: 114–116 °C. ^{1}H NMR (C_6D_6) δ 7.51 (m, 4H), 7.11–6.97 (m, 7H), 6.56 (m, 1H), 3.44 (s, 3H), 3.30 (s, 3H), 2.03 (m, 4H), 1.81–1.67 (m, 8H), 1.43–1.15 (m, 10H). ^{13}C NMR (C_6D_6) δ 151.7 (s), 149.4 (s), 138.8 (d, J_{CP} = 9 Hz), 133.3 (d, J_{CP} = 16 Hz), 128.5 (s), 128.4 (s), 128.3 (s), 125.0 (s), 116.7 (s), 110.1 (s), 109.8 (s), 55.3 (s), 55.2 (s), 29.4 (s), 29.3 (s), 28.2 (s), 27.2 (s). ^{31}P NMR (C_6D_6) δ −6.7 (s). HRMS (APCI): 499.2959 (MH^+); calcd. for $C_{32}H_{41}BO_2P$ (MH^+): 499.2937.



Scheme 2. Syntheses of compounds **2**, **3**, and **4**.

2.2.5. 1,2-Bis(diphenylphosphoryl)-4,5-dimethoxybenzene *5*

To a stirred solution of **3** (0.506 g, 1 mmol) in 10 mL of acetone was added 1 mL of 30% H_2O_2 and the reaction mixture was stirred overnight. All the volatiles were removed under reduced pressure (rotary evaporator), and compound **5** (white solid) was obtained in quantitative yield as a water adduct, **5**·H_2O. X-ray quality crystals of **5**·H_2O were obtained by crystallization from acetone. Melting point: 135–140 °C. H NMR ($CDCl_3$) δ 7.44 (m, 12 H), 7.31 (m, 10H), 3.75 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 154 (m), 132.9 (d, $^1J_{CP}$ = 107 Hz), 132.1 (m), 131.5 (s), 128.7 (d, $^2J_{PC}$ = 9 Hz), 127.8 (m), 118.7 (m), 56.0 (s). ^{31}P NMR ($CDCl_3$) δ 34.7 (s). HRMS (ESI): 539.1548 (MH^+); calcd. for $C_{32}H_{29}O_4P_2$ (MH^+): 539.1541.

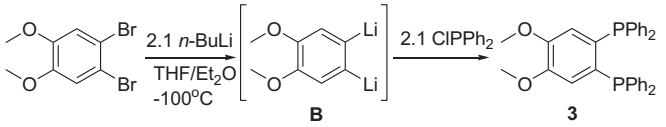
2.3. Single crystal X-ray diffraction studies

Compounds **1**, **3** and **5**·H_2O were characterized at the University of Portland Diffraction Facility. A typical experimental procedure is described below. A small specimen was retrieved and affixed to a fine glass fiber attached to a stout glass fiber mounted on a pin; the pin was placed on a goniometer head. The crystallographic properties and data were collected using MoKα radiation and the charge-coupled area detector (CCD) on an Oxford Diffraction Systems Gemini S diffractometer. A preliminary set of cell constants was calculated from reflections observed on three sets of 5 frames which were oriented approximately in mutually orthogonal directions of reciprocal space. Data collection was carried out using MoKα radiation (graphite monochromator) with a crystal-to-CCD distance of 50 mm, and a strategy to achieve a resolution of 0.7 Å. Crystals of compounds **1** and **4** were characterized at Michigan Technological University following previously described procedures [24]. In both cases, in the final cycles of refinement, all non-H atoms were refined with anisotropic thermal parameters with all H atoms constrained to the atoms to which they were attached. Crystallographic data and details about the refinements are given in Table 1.

3. Results and discussion

3.1. Syntheses and characterizations

Chemical attributes of 1,2-dibromo-4,5-dimethoxybenzene (4,5-dibromoveratrole) render it a useful starting material for the design and syntheses of various ditopic ligands. The compounds



Scheme 3. Generation of the organodilithio intermediate **B** and synthesis of bisphosphine **3**.

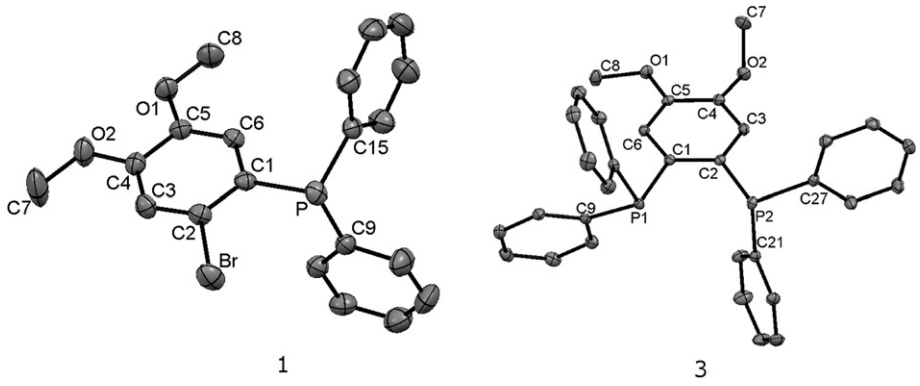


Fig. 1. Thermal ellipsoid plots of compounds **1** and **3**.

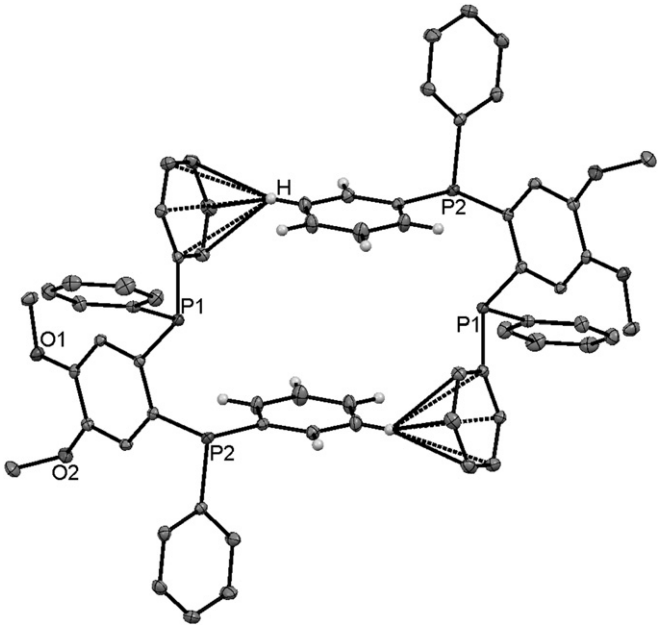


Fig. 2. Thermal ellipsoid plot of **3** illustrating intermolecular H–aryl interactions.

possess a methyl-protected *o*-hydroquinone functionality which can be transformed into [O,O] chelating pocket. Another chelating pocket can be constructed by replacing bromines with various ligating groups. This strategy has been successfully utilized for the syntheses of the 4,5-dithiocatecholate ligand and of transition metal complexes based on it [25]. Given our interest in phosphine-appended hydroquinone ligands [26] we decided to explore 1,2-dibromo-4,5-dimethoxybenzene as a platform for phosphine ligands containing the *o*-hydroquinone unit.

Reactions of 1,2-dibromo-4,5-dimethoxybenzene with an equivalent of *n*-BuLi led to a single lithium–bromine exchange and formation of the thermally unstable organolithium intermediate **A** (Scheme 1). Similar *o*-bromo-phenyllithium intermediates derived from 1,2-dibromo-4,5-dialkoxybenzene were reported [27]. It is critical to maintain a low temperature of the reaction media (~ -100 °C), since reaction mixtures reaching ~ -90 °C and higher temperatures led to significant darkening of the solution, presumably due to the formation of benzyne intermediates. Reactions of **A** with chlorodiphenylphosphine at ~ -100 °C led to the formation of (2-bromo-4,5-dimethoxyphenyl)diphenylphosphine **1** (Scheme 1) in high yields (up to 80%). Phosphine **1** is an air-stable crystalline solid that is soluble in common organic solvents. It displays a singlet in ^{31}P NMR spectrum, with a chemical shift value (δ −3.4) which is very close to that of (2-bromophenyl)diphenylphosphine (δ −4.5) [28]. The presence of a bromine substituent at the position *ortho* to a $-PPh_2$ group makes it a valuable starting material for the syntheses of other phosphine derivatives. Subjecting the solution of **1** in diethyl ether to *n*-BuLi at 0 °C led to facile lithium–bromine exchange. Quenching such reaction mixtures with electrophiles MeS–SMe, $ClPPh_2$, or $ClBCy_2$ led to the formation of **2**, **3**, or **4**, respectively (Scheme 2). All three compounds were isolated as air-stable crystalline solids. The ^{31}P NMR features of compounds **2** (δ −12.1) and **3** (δ −12.9) resemble those reported for

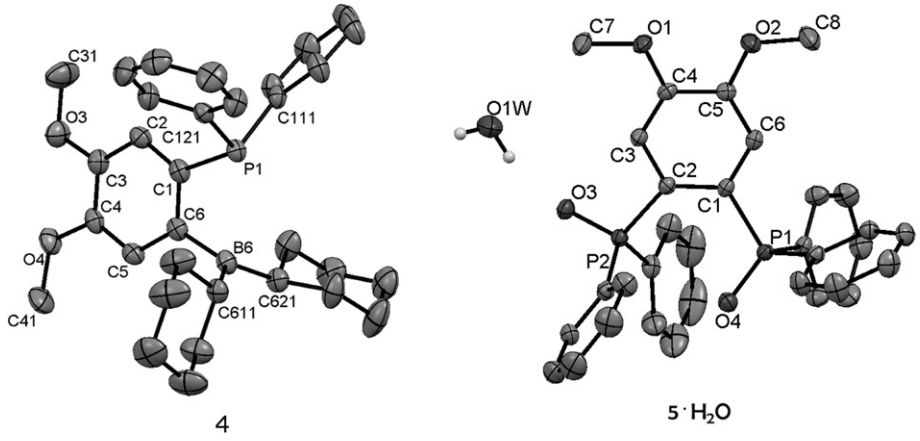


Fig. 3. Thermal ellipsoid plots of **4** and **5**·H_2O.

Table 2
Selected relevant bond distances for crystallographically characterized compounds.

1		**3**		**4**		**5**·H_2O	
C1–P	1.8384(17)	C1–P1	1.8463(11)	C1–P1	1.806(3)	C1–P1	1.817(3)
C1–C6	1.399(2)	C2–P2	1.8391(12)	C1–C6	1.382(4)	C2–P2	1.825(3)
C1–C2	1.378(2)	C1–C2	1.4022(16)	C6–C5	1.411(4)	C1–C2	1.410(4)
C2–Br	1.9048(16)	C2–C3	1.4059(15)	C6–B6	1.589(4)	P2–O3	1.495(2)
O1–C5	1.3676(19)	C1–C6	1.4035(16)	O3–C3	1.369(3)	P1–O4	1.481(2)
		C5–C6	1.3914(15)	C611–B6	1.584(4)	C2–C3	1.397(4)
		O1–C5	1.3634(14)			C3–C4	1.375(4)
		O2–C4	1.3773(13)			C4–C5	1.400(4)
						C4–O1	1.363(3)

o-diphenylphosphinothioanisole (δ −14.4) [29] and 1,2-bis(diphenylphosphino)benzene (δ −13.0) [30]. While bisphosphine **3** is air-stable in the solid state, oxidation of its phosphorus centers is facile in solution (acetone) when excess of hydrogen peroxide is used. The product, bis(phosphine-oxide) **5** is a white crystalline solid. The solid is hygroscopic, as evident from the presence of a water signal in the ^{1}H NMR spectrum of vacuum dried crystals. X-ray structural analysis also revealed water present in the lattice (**5**·H_2O). A sharp singlet in the ^{31}P NMR spectrum (δ 34.1) suggests that bulky adjacent diphenylphosphoryl groups in **5** are equivalent in solution. Similar observations have been reported for 1,2-bis(diphenylphosphoryl)benzene [31].

A notable feature of compound **4** is the presence of adjacent phosphine and borane groups. Structural motifs consisting of a donor/acceptor pair mounted onto the same molecular frame have been extensively explored recently, mainly for pursuing activation of dihydrogen or other small molecules [32]. The extent of intermolecular donor/acceptor interactions in these compounds is determined by the steric bulk around the donor/acceptor atoms and by the overall molecular geometry [32]. Spectroscopic data for compound **4** suggests that there is little, if any, interaction between the $-PPh_2$ and $-BCy_2$ groups in solution, as the chemical shift value (^{31}P NMR, δ −6.7 (*s*)) is characteristic to the derivatives of uncoordinated triphenyl phosphine. The data is consistent with spectroscopic observations reported for other *o*-phosphinophenylboranes [13,33–35], although similar compounds with pronounced P–B interactions in solution are also known [36,37]. The spectral signature remained unchanged upon exposure of the solutions of **4** to H_2, leading us to conclude that compound **4** does not react with H_2 under normal conditions. This is not surprising, as reactivity of phosphine/borane combinations toward H_2 is heavily dependent on steric and electronic properties of the pair [38,39]. When in crystalline state, compound **4** is stable in air.

We also briefly explored 1,2-dibromo-4,5-dimethoxybenzene for double lithium–bromine exchange (intermediate **B**, Scheme 3) reactions. Such exchange is facile when the starting material is subjected to slight excess of *n*-butyllithium, and 1:1 mixture of diethylether/THF is used as a solvent. Quenching the reaction mixture with equimolar amount of chlorodiphenylphosphine led to the synthesis and isolation of **3** in 52% yield.

3.2. Structural studies

In addition to spectroscopic characterizations we have succeeded in obtaining high quality single crystals of compounds **1**, **3**, **4** and **5**·H_2O, and characterized them by single crystal diffraction methods (Table 1). Thermal ellipsoid plots for these compounds are displayed in Figs. 1–3 while the selected bond distances and angles are shown in Tables 2 and 3.

Most of the structural parameters for **1** (Fig. 1) are unremarkable, as bond distances and angles involving phosphorus and bromine atoms are similar to those reported for (2-bromophenyl)diphenylphosphine [40]. The strain resulting from accommodating Br and $-PPh_2$ groups on the adjacent positions of the central phenyl ring is rather minimal, as the torsion angle Br–C2–C1–P is only 4.12°.

The most interesting structural parameters of bisphosphine **3** (Fig. 1) are those involving the –OMe and $-PPh_2$ groups, as these functionalities define the compound's capacity to function as a [P,P] and [O,O] bis-chelating ligand. The bond lengths and angles around the central phenyl ring are typical for an aromatic ring, and the arrangement of the $-PPh_2$ groups is similar to that reported for *o*-$C_6H_4(PPh_2)_2$ [30]. The phosphorus atoms are moved toward each other, as can be judged from the values of the inner bond angles P1–C1–C2 (117.69(8)°) and C2–C2–P2 (118.33(8)°). Peripheral phosphorus and oxygen atoms are also slightly bent out of the plane of the central phenyl ring (deviations ranging from 0.055 to 0.129 Å), with all of the atoms bent to the same side of the parent ring. These deviations from the ideal geometries are probably due to the packing of molecules in the crystal. In the crystalline state of **3**, intermolecular H–aryl interactions [41] are observed, as shown in Fig. 2. The distance between the interacting hydrogen atom and the calculated centroid of the aryl ring in another molecule is estimated at 2.491 Å.

Structural characterization of **4** was carried out in order to assess the extent of phosphorus–boron interactions in the solid state. Both groups ($-PPh_2$ and $-BCy_2$) are clearly tilted toward each other, as can be judged from the values of the bond angles at their points of attachment to the central phenyl ring (C6–C1–P1 109.01(19)° and C1–C6–B6 116.3(2)°). Phosphorus and boron atoms are slightly tilted out of the plane of the central phenyl ring (0.101 Å for P1, and 0.122 Å for B6), resulting in a torsion angle P1–C1–C6–B6 value of 6.98°. The geometry around the boron center is planar, as can be judged by the sum of the bond angles around the boron center (357.7°). There are no intermolecular P–B interactions, as well as no interactions between the boron center and the oxygen atoms of the methoxy groups of another molecule of **4**. The phosphorus–boron distances reported for other structurally characterized *o*-phosphinophenylboranes range from 3.0 to 3.3 Å (no interaction) [35,36] to 2.154 Å (donor–acceptor interaction) [36]. The intramolecular phosphorus–boron distance in **4** was determined at 2.695 Å. It is significantly longer than the distance expected for a P(III)–B coordinate covalent bond, where the sum of covalent radii of P and B atoms is estimated at 1.98 Å. The extent of P–B interaction in **4** is probably limited both by the geometry of the molecule and by the

Table 3
Selected relevant bond angles for crystallographically characterized compounds.

1		**3**		**4**		**5**·H_2O	
P–C1–C2	120.54(13)	P1–C1–C2	117.69(8)	C6–C1–C2	121.3(2)	P2–C2–C1	129.2(2)
C1–C2–Br	120.75(13)	C1–C2–P2	118.33(8)	C6–C1–P1	109.01(19)	C2–C1–P1	121.5(2)
C1–C2–C3	122.85(15)	P2–C2–C3	122.95(9)	C2–C1–P1	129.6(2)	C2–P2–O3	108.68(12)
C2–C3–C4	119.88(16)	C2–C3–C4	121.52(11)	C1–C6–B6	116.3(2)	C1–P1–O4	111.58(13)
P–C1–C6	123.19(13)	P1–C1–C6	122.46(9)	C621–B6–C611	120.2(2)	P2–C2–C3	112.5(2)
C3–C2–Br	116.36(13)	C1–C6–C5	121.02(11)	C621–B6–C6	116.6(2)	C2–C3–C4	122.0(3)
		C6–C5–O1	124.80(11)	C611–B6–C6	120.9(2)	C3–C4–C5	119.7(3)
		C5–C4–O2	120.70(10)	C5–C6–B6	125.5(2)	C3–C4–O1	125.1(3)

steric restrictions of the Ph and Cy substituents. Similar observations on donor–acceptor interactions between adjacent groups on the same phenyl ring have been reported for structurally related *o*-aminophenylboranes [42,43].

Bis(phosphine) oxide **5** crystallizes with one molecule of water (Fig. 2), which is bound via hydrogen bonding to one of the P═O groups (distance H–O–H···O═P is 1.989 Å), and to the oxygen atom of the methoxy group (distance H–O–H···O–CH_3 is 2.318 Å) of the other molecule of **5**. The phosphoryl groups are not equivalent in the solid state. One of them (O3═P2) is engaged in hydrogen bonding to water and rotated away from the central ring, whereas the other one (O4═P1) has its oxygen atom pointing toward P2 atom. The phosphoryl group involved in hydrogen bonding also has a longer P═O bond (by 0.014 Å). It also displays significant distortions from the ideal molecular geometry at the attachment point to the central phenyl ring (angle values: C1–C2P2 129.2(2)° and C3–C2–P2 112.5(2)°). Similar structurally characterized compound, *o*-$C_6H_4(P(O)PPh_2)_2\cdot CH_2Cl_2$ [44] shows different orientation of the phosphoryl groups as well as equal (within experimental error) P═O bond lengths. Since P═O groups in the later compound are not engaged in hydrogen bonding, we attribute the differences in structural features seen in **5** to the inclusion of water in the crystal. Analysis of the difference maps for **5**·H_2O revealed additional density located nearby the oxygen atom of water, but we have not been able to model a disorder. It is also possible that the crystals could be slightly desolvated since the data was collected at room temperature.

4. Conclusions

New phosphine derivatives bearing methyl-protected *o*-hydroquinone functionality were synthesized and characterized. The compounds are being explored for coordination chemistry of bimetallic compounds, and for activation of selected small molecules.

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Appendix A. Supplementary material

CCDC 890210, 890692, 890211, 890693 and 890212 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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