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Quasi-Thermoneutral P → B Interactions within Di- and Tri-Phosphine Boranes

Sébastien Bontemps,[†] Ghenwa Bouhadir,[†] Philip W. Dyer,[‡] Karinne Miqueu,[*,§] and Didier Bourissou[*,†]

Laboratoire Hétérochimie Fondamentale et Appliquée (UMR CNRS 5069),
Université Paul Sabatier, 118, route de Narbonne, 31062 Toulouse Cedex 09, France,
Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, U.K.,
Equipe de Chimie-Physique (UMR 5254-IPREM), and Université de Pau et des Pays de l'Adour,
Avenue de l'Université, BP 1155, 64013 Pau Cedex, France

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Spectroscopic, structural, and theoretical evidence is provided for both *open* (no intramolecular P → B interaction) and *closed* (with intramolecular P → B interaction) forms of the di- and tri-phosphine boranes [*o*-(*i*Pr$_2$P)C$_6$H$_4$]$_2$BPh (**2**) and [*o*-(*i*Pr$_2$P)C$_6$H$_4$]$_3$B (**3**).

Ambiphilic compounds combining both donor and acceptor functionalities have attracted increasing interest over the past 20 years as multi-center catalysts,[1] molecular probes,[2] and nonlinear optical materials.[3] Notably, recent investigations on phosphine−borane (PB) derivatives have further extended the synthetic interest of ambiphilic compounds, with PB-containing species having been demonstrated to be (i) versatile ligands for transition metals[4] affording unusual M → B interactions;[5] (ii) metal-free systems capable of reversible dihydrogen activation under mild conditions;[6] (iii) direct precursors for photoisomerizable heterodienes;[7] and (iv) readily tuneable fluorescent systems.[8]

Depending on the disposition of the donor and acceptor moieties about an organic backbone, ambiphilic compounds may adopt *closed* or *open* forms in which there is, or is not, an intramolecular donor → acceptor interaction, respectively.[9] Chemical interconversion between these two forms has been quite extensively studied for amine−borane (NB) systems, with its pivotal role in chemosensing having been recognized, for example.[10] In contrast, P → B interactions in PB derivatives have been scarcely investigated; only the limiting cases that either have or do not have an interaction have been described to date.[11]

Here we report on the unusual behavior encountered in *o*-(di- and tri-phosphine)-substituted triarylboranes **2** and **3**. Spectroscopic analyses reveal the coexistence in solution of the *open* and *closed* forms for both compounds **2** and **3**, with the *open* form **2o** and *closed* form **3c** having been structurally authenticated. These observations are supported by DFT calculations, which substantiate the propensity of the *o*-phenyl spacer to induce quasi-thermoneutral intramolecular P → B interactions in these systems.

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[*] To whom correspondence should be addressed. Email: dbouriss@chimie.ups-tlse.fr. Fax: +33 5 6155 8204.

[†] University Paul Sabatier (Toulouse).

[‡] Durham University.

[§] Université de Pau et des Pays de l'Adour.

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10.1021/ic7006556 CCC: $37.00

Scheme 1. Synthesis and *Open*/*Closed* Structures of the Di- and Tri-Phosphine-Boranes **2** and **3**

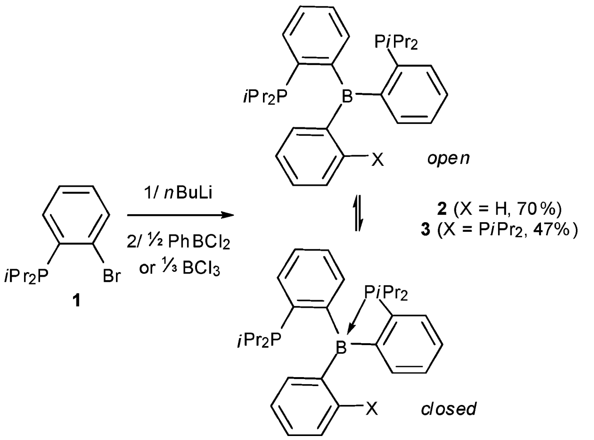

Table 1. Experimentally Determined and Calculated ^{31}P and ^{11}B NMR Chemical Shifts (in ppm) at 298 K unless Otherwise Stated

	exptl/theor	conditions	^{11}B	^{31}P
2	exptl	THF	+43.1	+11.0
2o	exptl	solid	+71.0	−2.0
2o	theor	−	+64.4	+13.4, +12.3
2c	theor	−	+12.1	+25.5 (P → B), +9.8
3	exptl	THF	+50.1	+4.9
3c	exptl	THF[a]	−	+26.1 (P → B), −2.9
3c	exptl	solid	+13.0	+28.5 (P → B), +1.0, −1.1
3c	theor	−	+14.5	+25.8 (P → B), +8.0, +4.0
3o	theor	−	+65.4	+15.1, +10.5, +8.6

[a] At 173 K.

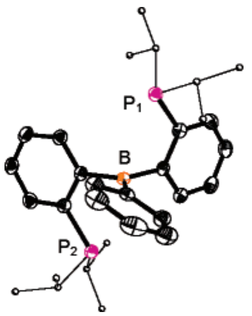

Figure 1. Thermal ellipsoid diagrams (50% probability) for the *open* form **2o**. Thermal ellipsoid for *i*Pr groups and hydrogen atoms are omitted for clarity.

The diphosphine borane **2** was prepared as previously described[4a] by bromine−lithium−boron exchange starting from the readily available (*o*-bromophenyl)phosphine **1**[12] and $PhBCl_2$ (Scheme 1). Following the same strategy with BCl_3, the related triphosphine-borane **3** was obtained in 47% isolated yield.[13] The solution-state (THF-d_8) multinuclear NMR data (Table 1) for **2** and **3** are very similar and merit little comment, except for the ^{11}B NMR chemical shifts (**2**, +43.1 ppm; **3**, +50.1 ppm), which are in between those of free triarylboranes (δ ^{11}B ≈ 70 ppm)[14] and of the few phosphine adducts thereof (δ ^{11}B ≈ 0 ppm).[15] Comparison of all these ^{11}B NMR data suggests that compounds **2** and **3** exist in solution either in rapid equilibrium between the *open* and *closed* forms or as intermediate structures. In order to probe this unusual behavior, DFT calculations were performed on the complete systems **2** and **3** at the BP86/6-31G* level of theory. In both cases, two minima of similar energy (ΔG < 3 kcal/mol at 25 °C), associated with the *open* and *closed* forms, were located on the potential hypersurface.[16] These calculations support the hypothesis that there exists an equilibrium between the *open* and *closed* forms in solution at room temperature, with negligible ring strain being induced by the *o*-phenyl spacer.[17]

To explore these P → B interactions further, NMR studies of the *open*/*closed* equilibrium were carried out in solution at low temperature and in the solid state.[13] Interestingly, in THF-d_8 at −100 °C, the ^{31}P NMR signal for **3** splits into two signals at δ ^{31}P = +26.1 (P → B) and −2.9 (free P) ppm, in a 1:2 relative ratio by integration, respectively. A rather similar ^{31}P NMR pattern was obtained for a solid-state sample with three signals of near-identical relative integration being observed at +28.5, +1.0, and −1.1 ppm. Combined with the ^{11}B NMR signal observed at +13.0 ppm in the solid state,[18] these data are most likely attributable to a frozen *closed* form of **3**. This has been further corroborated by computing the ^{11}B and ^{31}P NMR chemical shifts for the optimized *open* and *closed* forms of **3** via the GIAO method (Table 1). Notably, the experimental data are in excellent agreement with those predicted for the *closed* form **3c**, but differ significantly from those of the *open* form **3o**.

For the related diphosphine-borane **2**, the two phosphorus atoms remain equivalent upon cooling a THF solution to −100 °C, and only a slight broadening of the ^{31}P NMR signal (δ^{31}P = +11 ppm) was noticed. In the solid state, a single resonance was observed at δ^{31}P = −2 ppm. More significantly, the solid-state ^{11}B NMR resonance at +71.0 ppm strongly suggests that unlike **3**, the diphosphine-borane **2** adopts the *open* form in the solid state. This difference in behavior is supported by the computed NMR data, ^{11}B NMR chemical shifts of +64.4 and +12.1 ppm being predicted for the *open* and *closed* forms **2o** and **2c**, respectively.

Intrigued by the different spectroscopic data obtained for **2** and **3** in the solid state, single crystals suitable for X-ray diffraction analyses were grown for both compounds. In agreement with the conclusions drawn from the NMR investigations, the di- and tri-phosphine-boranes were found to adopt the *open* (**2o**) and *closed* (**3c**) forms, respectively (Figures 1 and 2, Table 2). As would be expected, rather

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(12) Tamm, M.; Dressel, B.; Baum, K.; Lügger, T.; Pape, T. *J. Organomet. Chem.* **2003**, *677*, 1.

(13) See Supporting Information for details.

(14) (a) Brown, N. M. D.; Davidson, F.; Wilson, J. W. *J. Organomet. Chem.* **1981**, *209*, 1. (b) Brown H. C.; Racherla, U. S. *J. Org. Chem.* **1986**, *51*, 427.

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(16) For both compounds, the absence of P → B interaction in the *open* forms **2o** and **3o** is supported by the long PB distances (>3 Å), while the corresponding *closed* forms **2c** and **3c** feature short PB distances (∼2.2 Å).

(17) A very similar P−B distance (2.22 Å) and a near identical P−B bonding energy (ΔE with ZPE correction = 2.8 kcal/mol) were predicted for the related *unconstrained* intermolecular adduct *i*Pr_2-PPh → BPh_3.[13]

(18) No ^{11}B NMR signals could be detected for low-temperature solutions of **2** and **3**.

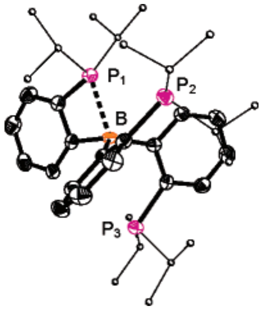

Figure 2. Thermal ellipsoid diagrams (50% probability) for the *closed* form **3c**. Thermal ellipsoid for *i*Pr groups and hydrogen atoms are omitted for clarity.

long B−P distances (∼3.0 Å) and a planar environment around boron (ΣBα = 359.9°) were observed for **2o**. The two phosphino-substituted phenyl rings are orientated almost perpendicularly to the boron coordination plane, while the unsubstituted ring is rotated out of the plane by 31.5°. This latter observation, combined with the slightly shortenened B−C$_{ipso}$ bond length (1.56/1.59 Å), may indicate some stabilization of the Lewis acid via π-donation. The presence of an intramolecular P → B interaction in the related triphosphine-borane **3c** is apparent from the short PB distance (2.15[19] vs 3.27 and 3.31 Å for the two other P atoms) and the noticeable pyramidalization of the boron environment (ΣBα = 348.9°).[20]

Table 2. Computed and Experimentally Determined Selected Geometric Data for **2** and **3** (Bond Lengths in Å, Bond Angles in deg)

	BP_1	BP_2	BP_3	$\Sigma B\alpha$	$\Sigma P_1\alpha$	$\Sigma P_2\alpha$	$\Sigma P_3\alpha$
2o (exptl)	2.993	2.993	−	359.9	309.8	309.8	−
2o (theor)	3.081	3.053	−	360.0	310.5	311.1	−
2c (theor)	2.154	3.318	−	350.7	328.3	303.5	−
3c (exptl)	2.154	3.307	3.267	348.9	328.4	301.0	302.7
3c (theor)	2.221	3.428	3.317	349.6	327.5	307.4	303.9
3o (theor)	3.376	3.232	3.259	359.8	306.8	317.1	308.4

In conclusion, the characterization of both the *open* and *closed* forms of the di- and tri-phosphine boranes **2** and **3** provides evidence for quasi-thermoneutral P → B interactions. Future development of PB systems as molecular probes and activators[21] should greatly benefit from such investigations on P → B interactions. Through modulation of the organic backbone and substitution pattern, we are currently trying to identify new PB systems that would adopt the *closed*, protected, form in the ground state, but whose related *open*, reactive, form would remain accessible energetically.

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Supporting Information Available: Experimental and computational details, crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) This value is in the upper range of those observed in phosphine−borane adducts [2.05 Å in (−PhNCH$_2$CH$_2$NPhPPh−)BPh$_3$^{15a} and 2.18 Å in Ph$_3$P → B(C$_6$F$_5$)$_3$^{15b}], including in four-membered rings: Breen, T. L.; Stephan, D. W. *Organometallics* **1997**, *16*, 365.

(20) The related triphosphine-alane [*o*-(Ph$_2$PCH$_2$)C$_6$H$_4$]$_3$Al exhibits a pentacoordinate aluminium (C$_3$P$_2$) center and trigonal-bipyramidal geometry: Müller, G.; Lachmann, J.; Rufińska, A. *Organometallics* **1992**, *11*, 2970.

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