Synthesis of a 1-boratabenzene-(2,3,4,5-tetramethylphosphole): towards a planar monophosphole

Guillaume Bélanger-Chabot,[a] Philippe Rioux,[a] Laurent Maron*[b] and Frédéric-Georges Fontaine*[a]

[a] Département de Chimie, Université Laval, Cité Universitaire, Québec (Québec), Canada, G1K 7P4

[b] Université de Toulouse, INSA, UPS, LPCNO, 135 avenue de Rangueil, 31077 Toulouse (France) and CNRS, LPCNO, UMR 5215 CNRS-UPS-INSA 31077 Toulouse (France)

Email:

frederic.fontaine@chm.ulaval.ca

Synthesis of a 1-boratabenzene-(2,3,4,5-tetramethylphosphole): towards a planar monophosphole[1]

Guillaume Bélanger-Chabot,[a] Philippe Rioux,[a] Laurent Maron*[b] and Frédéric-Georges Fontaine*[a]

Novel boratabenzene-phosphole complexes have been prepared and structurally characterized. The electronic communication between the two heterocyclic rings linked by a P-B bond and the aromaticity of these systems were probed using crystallographic and density functional studies.

The coordination chemistry of the boratabenzene[2] and phospholyl ligands,[3] both isoelectronic to the ubiquitous cyclopentadienyl anion, has been extensively studied in the last 40 years. Although each moiety has individually drawn interest for applications in the synthesis of chiral molecules or assemblies,[4,5] unusual metal complexes,[6,7] E-H bond activation (E = H, N, Si),[8,9] olefin polymerization,[10,11] and for unusual electronic properties,[12] no species involving both boratabenzene and phosphole rings has been reported yet.

Although borabenzene, boratabenzene, and the phospholyl anion are all aromatic fragments, the phosphorus atom in neutral phospholes has a strong tendency towards pyramidalization, thus reducing its aromaticity.[13] With the exception of few polyphospholes that are fully aromatic,[14] the highest aromatic character in a monophosphole was observed when a very bulky aryl substituent was present on the phosphorus atom. Indeed, Keglevich *et al.* reported that Bird's index (BI)[15] and the summation of the angles around the phosphorus atom (ΣP), the most important structural parameters for quantifying the aromaticity of a phosphole, were of 56.5 and 331°, respectively, for 1-(2,4,5-tris-*tert*-butylphenyl)-3-methylphosphole, indicative of significant aromatic character.[16] It was also predicted that good σ donors bound to phosphorus atom would favour planarity of the phosphole.[17] Therefore, based solely on electronic considerations, a phosphole having the -BH$_2$ substituent on the phosphorus atom was predicted to have very high aromatic character. However, the propensity of boryl phospholes to form Lewis acid-base adducts and to oligomerize, prevents their isolation.[18] In our search for novel borabenzene species, we sougth to synthesize a boratabenzene-phosphole, which would be the first example of a monomeric phosphole having a divalent boron bound to the phosphorus atom. This species could then provide additional insight in the long-standing debate on the aromaticity of phospholes. This report describes such a species.

The synthesis of the desired boratabenzene-phosphole species was carried out using two different strategies, which are depicted in Scheme 1. The first pathway is based on the methodology developed by Fu, involving a nucleophilic substitution at boron on a borabenzene-trimethylphosphine adduct.[19] The 2,3,4,5-tetramethylpholyl lithium-TMEDA adduct (**1**) was added to a borabenzene-trimethylphosphine solution to afford the 1-boratabenzene-(2,3,4,5-tetramethylphosphole) lithium-TMEDA adduct (**2**) in 80% yield. An alternative strategy, inspired by the work of Piers,[12b] involved the use of the phospholyl as a Brönsted base that effected dehydrochlorination of 1-chloro-2-TMS-boracyclohexadiene (TMS = trimethylsilyl) en route to the formation of a B-P bond. This reaction, very sensitive to experimental conditions, yielded several products including **2**, and more importantly, the 2-TMS-boratabenzene-(2,3,4,5-tetramethyl-phosphole) (**3**).
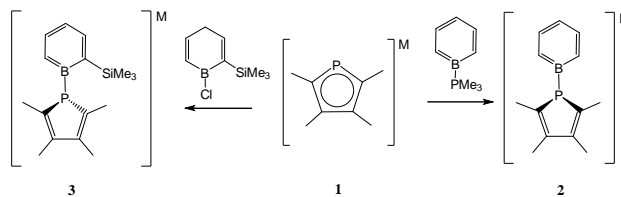
Scheme 1. Synthesis of boratabenzene-phospholes **2** and **3**. M is Li.(TMEDA)$^+$ (TMEDA = tetramethylethylenediamine)
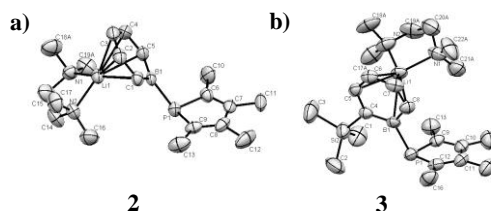
Figure 1. ORTEP diagrams (50% probability ellipsoids) of **2-Mo** and **3**. The hydrogen atoms were removed for clarity.

The solid state structures of compounds **2** and **3** are shown in Figure 1 and confirm that these bicyclic systems are indeed boratabenzene-phospholes and not Lewis acid-base adducts involving the participation of the lone pair of the phosphorus atom. This is demonstrated by the pyramidalization of the phosphorus atom and the negative charge localized on the electrophilic boratabenzene ring, which is bound to Li. The alternative borabenzene-phospholyl structures, where the negative charge is centered on the phospholyl moiety instead of being on the boratabenzene, were determined to be less stable by 8.3 and 14.1 kcal/mol for **2** and **3**, respectively, using DFT (density-functional theory) calculations.[20] A list of important structural parameters from both solid state and computational studies are given in Table 1. The resolution of structures of two crystals of **2** obtained by different

crystallization procedures and analyzed using two different X-ray radiations (**2-Mo** and **2-Cu**) has been carried out.

Table 1. Geometrical parameters for the crystallographic data of **2**, **3**, and **4** and for the structures minimized using DFT (*)

	2-Mo	2-Cu	2*	2'	3	3*	4	4*
P-B	1.939(4)	1.953(3)	1.956	1.949	1.975(6)	1.972	1.942(3)	1.952
P-C_α	1.774(4);	1.777(3);	1.799	1.798;	1.787(5);	1.794;	1.795(3);	1.817;
	1.779(4)	1.782(3)	1.807	1.798	1.800(5)	1.790	1.798(3)	1.817
C_α-C_β	1.351(5);	1.345(4);	1.365	1.366;	1.361(6);	1.370	1.354(4);	1.368;
	1.363(5)	1.354(4)	1.364	1.367	1.346(6)	1.372	1.358(4)	1.370
C_β-C_β	1.443(5)	1.474(4)	1.462	1.460	1.449(7)	1.455	1.460(3)	1.464
ΣP	313.3(5)	312.6(4)	304.9	314.2	300.9(7)	321.0	310.0(4)	309.3
BI	43.2	36.4	33.1	36.3	33.9	40.9	33.0	28.3

Similar to Fu's report of a boratabenzene-diphenylphosphide adduct,[21] little π-overlap is observed between phosphorus and boron. The P-B distances in **2-Mo**, **2-Cu**, and **3** are 1.939(5) Å, 1.953(3) Å and 1.975(6) Å, respectively, which are within 3σ to the P-B distance observed for Fu's boratabenzene-diphenylphosphide (1.968(7) Å). The presence of a trimethylsilyl group on the boratabenzene fragment significantly affects the conformation of the boratabenzene-phosphole in **3**. The pholpholyl is rotated by 118.3° around the P-B axis, deviating from the expected mirror plane that would pass through the boratabenzene-phosphole if electronic communication between the lone pair of phosphorus and the empty p_z orbital on boron would be present.[22] However, complex **2** is rotated only slightly, by 12.7°, which would not prevent such orbital overlap. The BI (36.4-43.2) and ΣP (312.6-313.3°) are both relatively high,[23] suggesting some degree of planarization, even though the presence of methyl groups on the backbone of the phosphole is known to disfavor aromatization in phospholes.[24] A structural comparison of **2** with the data for all 96 phospholes stored in the Cambridge Crystallographic Database indicates that only five of the phospholes have greater BI and ΣP.[25] Three of these molecules have an aryl moiety with large substituants in the *ortho* position bound to the phosphorus atom[16,26] and one other molecule has part of the phosphole backbone fused with another ring system.[27] The other species is Cp(CO)₂W(3,4-dimethylphosphole) (BI and ΣP are 50.9 and 319.6°, respectively) where the aromatization of the phosphole is likely favoured by a higher nucleophilicity at phosphorus, which gives it a phospholyl character, and the bulk of the complex.[28] These data suggest that the presence of a secondary borane on phosphorus helps, albeit modestly, promote the planarization of the phosphole.

In order to support the presence of electronic overlap, DFT calculations were done on both **2** and **3**. Surprisingly, the optimized minimum for these species (**2*** and **3***, respectively) both have significant out-of-the-axis rotation, 29.3° and 52.4°, respectively.[29] Whereas for **3*** the data suggest some degree of planarization, probably caused by the steric hindrance of the TMS moiety, the BI (33.1) and ΣP (304.9°) for **2*** are both lower than observed in the solid state structure. Although they are not absolute minima, several low-energy rotamers of **2** can be observed. Among those structures, **2'** has a mirror plane passing through the P-B bond and is structurally closer to the solid-state conformation

observed for **2**. With this model, the BI (36.3) and ΣP (314.2°) are both more important than in **2*** and the P-B bond length is shorter (1.949 Å vs 1.956 Å). Since the effect is marginal, it suggests that the stronger σ donation of the boratabenzene, rather than an electronic communication between the electron lone pair on phosphorus and the empty p_z orbital on boron, causes this phenomenon. Also, the planarization might be favoured by solid state packing, although the shielding of the phosphole resonances in the ¹³C NMR spectra by an average of 2 ppm in **2** as compared to **3** is an indication that these slight deviations are likely present in solution.[16]

A careful analysis of the frontier orbitals on an artificially planarized structure of **2** was done in order to better explain the marginal π-donation. Surprisingly, it can be observed that the orbital expected to be the HOMO for a planar boratabenzene-phosphole, which represents the π interaction between the boron and the phosphorous, is instead the LUMO. Indeed, the HOMO corresponds to an anti-bonding orbital between the π system of the boratabenzene and the p orbital on phosphorus, which destabilizes the planarity greatly. Therefore, a logical strategy for destabilizing the latter orbital and increasing the Lewis acidity on boron is to coordinate the π system of borabenzene on a transition metal. Indeed, Fu reported that the coordination of the borabenzene moiety on chromium significantly enhanced the Lewis acidity of the borabenzene and increased the B-O double bond character between the boron center and aldehydes.[30] In the work described herein, reaction of two equivalents of **3** with FeCl₂ in THF yielded an orange powder corresponding to bis(1-boratabenzene-(2,3,4,5-tetramethyl-phosphole)) iron(II) (**4**). This sandwich complex displays a single broad resonance in the ³¹P{¹H} NMR spectrum at -11.5 ppm and borabenzene resonances in the ¹H NMR spectrum that are significantly shielded compared to the starting material, which is expected from a coordination of a boratabenzene moiety to iron.[31] The connectivity of compound **4** was confirmed using X-Ray diffraction studies (Scheme 2).
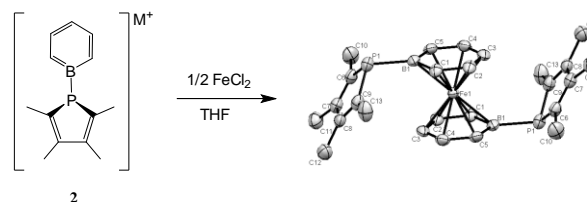
Scheme 2. Synthesis of boratabenzene-phosphole iron(II) complex **4** and its ORTEP diagram (50% probability ellipsoids).

Surprisingly, coordination of the boratabenzene on iron(II) does not seem to have an impact on the planarization of the phosphole, as the relevant structural parameters point against it (BI of 33.0 and ΣP of 310.0°). Indeed, it can be calculated using DFT that the empty p_z orbital does become more electrophilic, but that it interacts very strongly with the filled $3d_{xy}$ orbital on the iron atom (HOMO-4) rather than with the lone pair on the phosphorus atom, the former orbital gaining stabilization by more than 50 kcal/mol.

Conclusions

We succeeded in characterizing the first boratabenzene-phosphole adduct and in coordinating it to iron(II). These species represent the first "free" borylphospholes. The structure of **2**, having strongly σ-donor boratabenzene group on the phosphorus atom, proved to demonstrate some degree of planarization for the phosphole, as demonstrated by relatively large BI and ΣP. Electronic repulsions between the aromatic system on the borabenzene and the lone pair on the phosphorus atom prevent the formation of a P-B bond with a double bond character. The coordination of **2** on iron(II) is possible, but does not increase the P-B bond strength, since the Lewis acidic p_z orbital on boron is electronically compensated by the filled $3d_{xy}$ Fe(II) orbital. In order to reduce such metal-to-ligand interaction, we are currently investigating the coordination of **2** on d^0 metal species, which may induce a larger planarization of the phosphole.

Notes and references

Guillaume Bélanger-Chabot,[a] Philippe Rioux , [a] Laurent Maron[b] and Frédéric-Georges Fontaine*[a]

[a] Département de chimie, Université Laval, 1045 Avenue de la Médecine Cité Universitaire, Québec, Qc, G1V0A6 (Canada).
Fax :+1 418 6565140; E-mail : frederic.fontaine@chm.ulaval.ca

[b] Université de Toulouse, INSA, UPS, LPCNO, 135 avenue de Rangueil, 31077 Toulouse (France) and CNRS, LPCNO, UMR 5215 CNRS-UPS-INSA 31077 Toulouse (France)

1   This article is dedicated *in memoriam* to Pascal Le Floch.
2   (a) G. C. Fu, *Adv. Organomet. Chem.*, 2000, **47**, 101-119; (b) G. E. Herberich and H. Ohst, *Adv. Organomet. Chem.*, 1986, **25**, 199-236.
3   (a) P. Le Floch, *Coord. Chem. Rev.*, 2006, **250**, 627-681; (b) F. Mathey, *Acc. Chem. Res.*, 2004, **37**, 954-960; (c) F. Mathey, *J. Organomet. Chem.*, 1994, **475**, 25-30.
4   Few examples of chiral complexes based on phosphole moieties: a) W. Shen, S. Graule, J. Crassous, C. Lescop, H. Gornitzka, R. Reau, *Chem. Commun.*, 2008, 850-852; b) D. Carmichael, L. Ricard, N. Seeboth, *Organometallics*, 2007, **26**, 3552-3558; c) S. Mourgues, D. Serra, F. Lamy, S. Vincendeau, J.-C. Daran, E. Manoury, M. Gouygou, *Eur. J. Inorg. Chem.*, 2003, 2820-2826.
5   Chiral complexes based on boratabenzene moieties: (a) A. J. Ashe III, S. Al-Ahmad, X. Fang and J. W. Kampf, *Organometallics*, 2001, **20**, 468-473; (b) J. Tweddell, D. A. Hoic and G. C. Fu, *J. Org. Chem.*, 1997, **62**, 8286-8287.
6   Some phospholyl low-valent complexes: (a) F. Jaroschik, F. Nief, X.-F. Le Goff and L. Ricard, *Organometallics*, 2007, **26**, 3552-3558; (b) D. Turcitu, F. Nief and L. Ricard, *Chem.--Eur. J.*, 2003, **9**, 4916-4923; (c) K. T. Hollis, Y. J. Ahn and F. S. Tham, *Organometallics*, 2003, **22**, 1432-1436.
7   Some unusual borabenzene bonding modes : (a) A. Languérand, S. S. Barnes, G. Bélanger-Chabot, L. Maron, P. Berrouard, P. Audet and F.-G. Fontaine, *Angew. Chem., Int. Ed.*, 2009, **48**, 6695-6698; (b) P.

Cui, Y. Chen, G. Li and X. Wei, *Angew, Chem., Int. Ed.,* 2008, **47**, 9944-9947; (c) D. A. Hoic, W. M. Davis and G. C. Fu, *J. Am. Chem. Soc.*, 1996, **118**, 8176-8177.
8   Activation of E-H bonds by phospholyl complexes: (a) G. Mora, B. Deschamps, S. Van Zutphen, X.-F. Le Goff, L. Ricard and P. Le Floch, *Organometallics*, 2007, **26**, 1846-1855; (b) M. Ogasawara, A. Ito, K. Yoshida and T. Hayashi, *Organometallics*, 2006, **25**, 2715-2718; c) J.-J. Brunet, H. Hajouji, J.-C. Ndjanga and D. Neibecker, *J. Mol. Cat.*, 1992, **475**, 25-30.
9   Activation of E-H bonds by boratabenzene complexes: (a) Y. Yuan. Y. Chen, G. Li and W. Xia, *Organometallics*, 2008, **27**, 6307-6312; (b) D. H. Woodmansee, X. Bu and G. C. Bazan, *Chem. Commun.*, 2001, 619-620.
10   Some examples of phospholyl complexes used for alkene polymerization: (a) G. Mora, S. Van Zutphen, C. Klemps, L. Ricard, Y. Jean and P. Le Floch, *Inorg. Chem.*, 2007, **46**, 10365-10371; (b) F. Jaroschik, T. Shima, X. Li, K. Mori, L. Ricard, X.-F. Le Goff, F. Nief and Z. Hou, *Organometallics*, 2007, **26**, 5654-5660; (c) C. Janiak, K. C. H. Lange and P. Marquardt, *J. Mol. Cat. A.*, 2002, **180**, 43-58.
11   Some examples of boratabenzene complexes used for alkene polymerization: (a) P. Cui, Y. Chen, X. Zeng, J. Sun, G. Li and W. Xia, *Organometallics*, 2007, **26**, 6519-6521; (b) J. S. Rogers, X. Bu and G. C. Bazan, *J. Am. Chem. Soc.*, 2000, **122**, 730-731; (c) G. C. Bazan, G. Rodriguez, A. J. Ashe III, S. Al-Ahmad and C. Muller, *J. Am. Chem. Soc.*, 1996, **118**, 2291-2292.
12   (a) C. A. Jaska, D. J. H. Emslie, M. J. D. Bosdet, W. E. Piers, T. S. Sorensen and M. Parvez, *J. Am. Chem. Soc.*, **128**, 10885-10896; (b) D. J. H. Emslie, W. E. Piers and M. Parvez, *Angew. Chem., Int Ed.*, 2003, **42**, 1252-1255.
13   L. Nyulászi, *Chem. Rev.*, 2001, **101**, 1229-1246, and references therein.
14   F. G. N. Cloke, P. B. Hitchcock, P. Hunnable, J. F. Nixon, L. Nyulászi, E. Niecke and V. Thelen, *Angew. Chem., Int. Ed.* 1998, **37**, 1083-1086.
15   C. W. Bird, *Tetrahedron*, 1985, **41**, 1409-1414.
16   G. Keglevich, Z. Böcskei, G. M. Keserü, K. Ujszaszy and L. D. Quin, *J. Am. Chem. Soc.* 1997, **119**, 5095-5099.
17   (a) L. Nyulászi, *J. Phys. Chem.*, 1995, **99**, 586-591; (b) D. Delaere, A. Dransfeld, M. T. Nguyen and L. G. Vanquickenborne, *J. Org. Chem.*, 2000, **65**, 2631-2636.
18   N.-N. Pham-Tran, N.-H. Tran Huy, P.-C. Nam, L. Ricard, M. T. Nguyen, *J. Organomet. Chem.*, 2006, **691**, 4058-4064.
19   S. Qiao, D. A. Hoic and G. C. Fu, *J. Am. Chem. Soc.,* 1996, **118**, 6329-6330.
20   See Supporting Information for more details on DFT.
21   D. A. Hoic, M. DiMare, G. C. Fu, *J. Am. Chem. Soc.,* 1997, **119**, 7155.
22   More detailed explanations on the various geometrical parameters described are given in the Supporting Information.
23   The average values for B.I and ΣP, according to CCDC, are of 31.4 and 299.6º, respectively.
24   E. Mattmann, F. Mathey, A. Sevin and G. Frison, *J. Org. Chem.*, 2002, **67**, 1208-1213.
25   Including, in some instances, more than one of each phosphole when several independent molecules are present in a unit cell.
26   (a) G. Keglevich, L. D. Quin, Z. Böcskei, G. M. Keserü, R. Kalgutkar and P. M. Lahti, *J. Organomet. Chem.* 1997, **532**, 109-116; (b) G. Keglevich, L. D. Quin, Z. Böcskei, G. M. Keserü, R. Kalgutkar and P. M. Lahti, *J. Organomet. Chem.* 1997, **532**, 109-116.
27   G. Märkl, R. Hennig and H. Nöth, *Tetrahedron Lett.*, 1995, **36**, 6655-6658.
28   F. Mercier, L. Ricard and F. Mathey, *Organometallics*, 1993, **12**, 98-103.
29   In the case of **3***, the lone pair on P points toward the Si atom, contrarily to the structure of **3** where the lone pair points away from the Si atom (see Supporting Information).
30   M. Amendola, K. E. Stockman, D. A. Hoic, W. M. Davis and G. C. Fu, *Angew. Chem, Int. Ed.*, 1997, **36**, 267-269.
31   A. J. Ashe III, E. Meyers, P. Shu, T. Von Lehmann, *J. Am. Chem. Soc.*, 1975, **97**, 6865-6866.