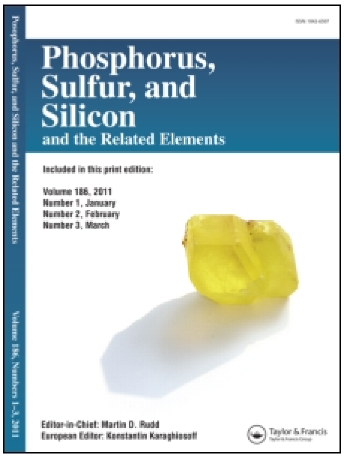


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Structural Characterization of the Solvate Complexes of the Lithium Salts of Diorganophosphides and Phosphinideneborates; A Pathway to Phosphorus-Boron Double Bonds

R. A. Bartlett[a]; X. Feng[a]; M. M. Olmstead[a]; P. P. Power[a]
[a] Department of Chemistry, University of California, Davis, California

To cite this Article Bartlett, R. A. , Feng, X. , Olmstead, M. M. and Power, P. P.(1987) 'Structural Characterization of the Solvate Complexes of the Lithium Salts of Diorganophosphides and Phosphinideneborates; A Pathway to Phosphorus-Boron Double Bonds', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 1, 245 — 248

To link to this Article: DOI: 10.1080/03086648708080568

URL: http://dx.doi.org/10.1080/03086648708080568

Phosphorus and Sulfur, 1987, Vol. 30, pp. 245-248
Photocopying permitted by license only

STRUCTURAL CHARACTERIZATION OF THE SOLVATE COMPLEXES OF THE LITHIUM SALTS OF DIORGANOPHOSPHIDES AND PHOSPHINIDENEBORATES; A PATHWAY TO PHOSPHORUS-BORON DOUBLE BONDS

R. A. BARTLETT, X. FENG, M. M. OLMSTEAD, P. P. POWER*
Department of Chemistry, University of California,
Davis, California 95616

Abstract

The structures of several solvated lithium diorganophosphides are described. These may take a variety of structures including chain-like polymers with alternating Li^+ and PR_2^- groups, dimeric species with PR_2^- groups bridging two Li^+ ions or mononuclear species having terminal $^-PR_2$ groups which have pyramidal geometries at phosphorus. The Li^+ ions in all structures are solvated by either THF or Et_2O bases. Separation of the Li^+ can be effected using 12-crown-4 to coordinate Li^+ as $[Li(12\text{-crown-}4)_2]^+$ affording free $[PR_2]^-$ counterions. An extension of these techniques has led to the synthesis of the first compounds which have B-P double bonds. These are the compounds $[Li(Et_2O)_2PRBMes_2]$ and $[Li(12\text{-crown-}4)_2][PRBMes_2]$(R=Ph, C_6H_{11},Mes) which have B-P bond lengths of 1.82 - 1.83Å.

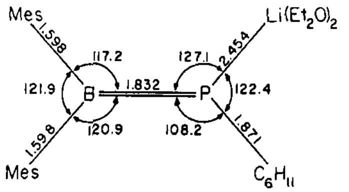
The most widely used transfer agents for diorganophosphide (and arsenido) groups are their lithium salts. However these compounds, which are themselves inherently interesting, have received scant attention. Recent work in this laboratory has concentrated on the crystallization and structural characterization of the solvated and solvent separated ion pair salts LiPR'R'' (R', R'' = Ph,Ph; C_6H_{11}; Mes, Mes; H, Mes)[1,2,3] The major structural probes used were X-ray diffraction and ^{31}PNMR.

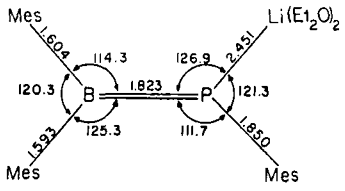
The compounds $[(Li(Et_2O)PPh_2)_\infty]$,[2,3] 1, $[(Li(THF)_2PPh_2)_\infty]$,[2,3] 2, $[(Li(THF)P(C_6H_{11})_2)_\infty]$,[3,4] 3, are all chain polymers in solution with an alternating -Li-P-Li-P-Li backbone. The addition of 12-crown-4 to these results in a <u>ca</u>. 30 ppm downfield shift in their ^{31}P NMR spectra and crystallization affords the solvent separated free ions $[PPh_2]^-$ and $[P(C_6H_{11})_2]^-$ with $[Li(12\text{-crown-}4)_2]^+$ counter cations. Their As[1] and Sb[3] congeners have also been obtained in this manner. More bulky phosphides give lower aggregates than the polymeric chains. For example the tetrameric couplex $[\{Li_2(\mu_3\text{-}t\text{-}Bu_2P)(\mu\text{-}t\text{-}Bu_2P)(THF)\}_2]$[4] of Jones and the dimers $[\{Li(THF)PMes_2\}_2]$[5] 4 and $[(LiP\{CH(SiMe_3)_2\}_2)_2]$[6]. The ^{31}P NMR spectrum 4 complex also undergoes a 30 ppm downfield shift when 12-crown-4 is added.[6]

A unique monomeric structure for a lithium phosphide is observed in the compounds $[Li(THF)_3 PHMes]$[5]. The most conspicuous feature of this structure is the pyramidal nature of the phosphorus atom, $\sum$P angles = 301°. The arsenic species $[Li(1,4\text{-dioxane})_3AsPh_2]$[3] is also pyramidal, $\sum$As angles = 292°. These structures are in sharp contrast to those of the terminal lithium amides $[Li(12\text{-crown-}4)NR_2]$(R = Ph[3] or $SiMe_3$[7]) which are planar at nitrogen.

If one of the alkyl or aryl groups on the lithium phosphide $LiPR_2$ (R=alkyl or aryl) is replaced by the $-BMes_2$ group a complex of formula $[Li(Et_2O)_2PRBMes_2]$

(R=Ph,C_6H_{11} or Mes) can be isolated.[8] The structures of two of these complexes are illustrated below.





Yellow crystals mp 92-94°C

Yellow crystals, orange at mp. 127-135°C

Twist angle between B + P planes 11.7°(C_6H_{11}) 3.8°(Mes)

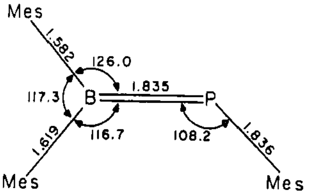
δ ^{31}P NMR	R	PPM
	Ph	+73.1
	C_6H_{11}	+70.05
	Mes	+55.5

δ ^{11}B NMR	R	PPM
	Ph	+65.4
	C_6H_{11}	+65.6
	Mes	+63.7

can be seen that both molecules have planar boron and phosphorus centers with very small twist angles between these planes. This is contrary to what is expected on steric grounds. The B-P bond lengths 1.82-1.83Å are much shorter than the BP distance (1.96Å) in boron-phosphide. These strucutres support a B-P double bond formulation, a moiety which had not been previously characterized structurally. The addition of 12-crown-4 as shown[8]

Free Phosphinidene Borate Anions

$$Mes_2BPMesLi\cdot 2Et_2O \xrightarrow{2\ \text{12-crown-4}} [Li(\text{12-crown-4})_2][Mes_2BPMes]$$



δ ^{31}P NMR	R	PPM
	Ph	+103.6
	C_6H_{11}	+113.6
	Mes	+91.3

Yellow crystals

Twist angle 0°

complexes the lithium giving a free $[Mes_2BPMes]^-$ ion. The removal of the Li^+ ion has little effect on the B=P double bond. The formulation of the compounds above as having BP double bonds gives rise to the speculation that compounds such as Mes_2BPR_2 should perhaps also be planar with an essentially P-B double bond. However the structure of Mes_2BPPh_2 shows that although the boron remains planar the coordination at phosphorus is intermediate between that seen in phosphines (e.g. PPh_3) and a planar geometry. The P-B distance ≈ 1.86Å which also lies in between the double bonded and single bond distance.[9]

REFERENCES

1. H. Hope, M. M. Olmstead, P. P. Power, X. Xu. J. Am. Chem. Soc., 106, 819 (1983).
2. R. A. Bartlett, M.M. Olmstead, P. P. Power. Inorg. Chem., 25, 1325 (1986).
3. R. A. Bartlett, H. V. R. Dias, H. Hope, B. D. Murray, M.M. Olmstead, P. P. Power. J. Am. Chem. Soc. in press.
4. R. A. Jones, A. L. Stuart, T. C. Wright. J. Am. Chem. Soc., 105, 7459 (1983).
5. R. A. Bartlett, M. M. Olmstead, P. P. Power, G. E. Sigel. unpublished results.
6. P. B. Hitchcock, M. F. Lappert, P. P. Power, S. J. Smith. J. Chem. Soc. Chem.Commun., 1669 (1984).
7. P. P. Power, X. Xu. J. Chem.Soc. Chem. Commun., 358 (1984).
8. R. A. Bartlett, X. Feng, P. P. Power. J. Am. Chem. Soc., in press.
9. X. Feng, M. M. Olmstead, P. P. Power. Inorg. Chem., submitted.