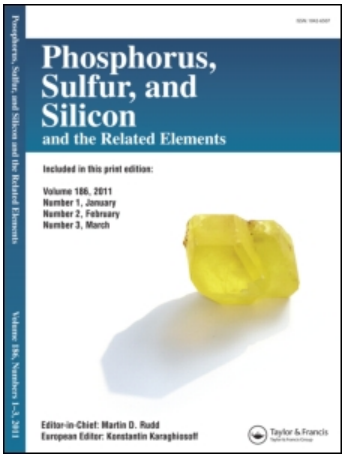

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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Bernard Garrigues[a]; Lydia Lamandé[a]; Aurelio Munoz[a]
[a] UA au CNRS No 454-Université Paul, Toulouse, Cedex, France

To cite this Article Garrigues, Bernard , Lamandé, Lydia and Munoz, Aurelio(1988) 'AN EQUILIBRIUM BETWEEN SPIROPHOSPHORANIC AND TETRACOORDINATED PHOSPHORUS COMPOUNDS HAVING THE PHOSPHORUS-BORON BOND', Phosphorus, Sulfur, and Silicon and the Related Elements, 35: 3, 309 — 310
To link to this Article: DOI: 10.1080/03086648808074334
URL: http://dx.doi.org/10.1080/03086648808074334

Phosphorus and Sulfur, 1988, Vol. 35, pp. 309–310
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AN EQUILIBRIUM BETWEEN SPIROPHOSPHORANIC AND TETRACOORDINATED PHOSPHORUS COMPOUNDS HAVING THE PHOSPHORUS–BORON BOND

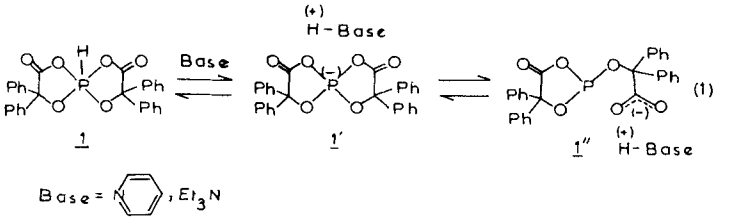
BERNARD GARRIGUES,* LYDIA LAMANDÉ and AURELIO MUNOZ
UA au CNRS No 454–Université Paul Sabatier–118 route de Narbonne–31062 Toulouse Cedex–France

(Received June 25, 1987; in final form August 26, 1987)

A new adduct was isolated from the reaction of borane–dimethyl-sulfide complex and conjugate bases of spirophosphorane prepared from benzilic acid. In solution, it exists as equilibrium between a spirophosphorane and a tetracoordinated phosphorus compound bearing a phosphorus–boron bond.

It is known that phosphoranes prepared from diethanolamines and tetraethylene-tetramines react with borane. Adducts have been isolated where complexations take place on phosphorus and nitrogen atoms. Nevertheless, in all cases phosphorus pentacoordinance is not kept and tetracoordinated phosphorus compounds are obtained.[1a–d] We report here the isolation of an adduct between a spirophosphorane prepared from benzilic acid and the borane–dimethylsulfide complex.

A few years ago, we demonstrated that spriophosphorane **1** reacts, at room temperature, with bases like pyridine or triethylamine, according to Equation (1).[2]



Conjugated bases **1'**, **1"** show interesting nucleophilic properties towards various electrophiles.[3] Reacting with borane, they can lead to a spirophosphorane with a P–B bond.

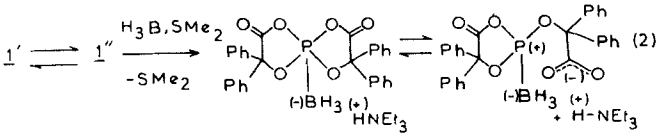
In fact, the phosphorane **1**, dissolved in THF, reacts easily with the borane–dimethylsulfide complex, in presence of triethylamine. A powder was obtained whose elemental analysis and mass spectrum (desorption under ionisation) are consistent with formulae **2** or **3** (Equation (2)). The ^{11}B NMR spectrum (CH_2Cl_2, 25.71 Mhz, ^1H decoupled) shows a doublet at $\delta = -35.6$ (Reference BF_3, Et_2O), corresponding to a tetracoordinated boron compound with a P–B bond ($^1J_{B-P} = 130$ Hz).

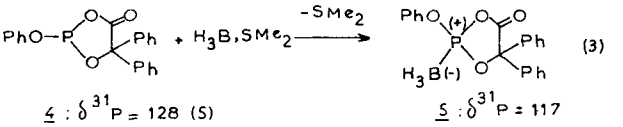
In ^{31}P NMR spectroscopy (CH_2Cl_2, 32,44 Mhz, Reference H_3PO_4) a broad

signal is observed at $\delta = 35$. This parameter allows us to discard the presence of only the pentacoordinated compound **2** or the tetracoordinated derivative **3**. Effectively, the α-hydroxyacid spirophosphoranes show signals at higher fields ($\delta^{31}P = -35$).[4a,b] On the other hand, the adduct **5**, homologous of **3** presents a singlet at $\delta = 117$. It was prepared via the reaction 3.[5]

Thus, the more likely situation is an equilibrium between compounds **2** and **3** (Equation (2)). This interpretation is supported by the IR spectrum (nujol, CaF_2) which exhibits two $\nu_{C=O}$ absorption bands at 1730 cm^{-1} ($\nu_{C=O}$ of the ring part) and 1620 cm^{-1} ($\nu_{C=O}$ of the carboxylate anion). The ^{13}C NMR spectrum ($CDCl_3$, 20,1 MHz) does not allow to observe any signal for the O=C atoms. This phenomenum is connected to the fast (towards the NMR time) exchange between **2** and **3** species. We must remark that in ^{31}P NMR spectroscopy the singlet position does not vary at low temperatures. A similar fact was observed with the equilibrium 1, the chemical shift varying only by 10 ppm in the temperature range from −20°C to −60°C[2].

In conclusion, a new adduct between organophosphorus compound and borane was isolated. Its originality among the numerous compounds with a P–B bond, consists in the coordination isomerism $P^{IV} \rightleftharpoons P^{V}$. To our knowledge no P–B adduct of this type has yet been published.





4 : $\delta^{31}P$ = 128 (S)

5 : $\delta^{31}P$ = 117

ACKNOWLEDGEMENTS

We thank G. Pelletier and B. Montsarrat for their technical help in the recording of NMR and Mass Spectrometry and the "Service Général d'Analyse du CNRS" for microanalyses.

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