

This article was downloaded by:

On: 30 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## 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>

### Mixed-valence diphosphorus compounds

Gerhard Bettermann<sup>a</sup>; Horst Buhl<sup>a</sup>; Reinhard Schmutzler<sup>a</sup>; Dietmar Schomburg<sup>a</sup>; Ulrich Wermuth<sup>a</sup>

<sup>a</sup> Institut für Anorganische Chemie der Technischen Universität, Braunschweig, ALLEMAGNE

**To cite this Article** Bettermann, Gerhard , Buhl, Horst , Schmutzler, Reinhard , Schomburg, Dietmar and Wermuth, Ulrich(1983) 'Mixed-valence diphosphorus compounds', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 18: 1, 77 – 80

**To link to this Article:** DOI: 10.1080/03086648308075971

**URL:** <http://dx.doi.org/10.1080/03086648308075971>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

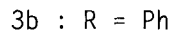
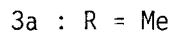
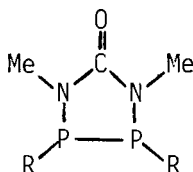
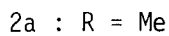
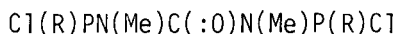
This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

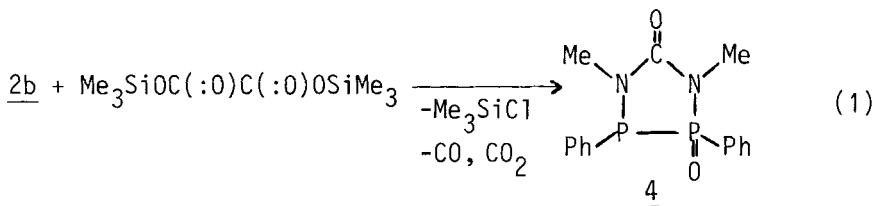
## MIXED-VALENCE DIPHOSPHORUS COMPOUNDS

GERHARD BETTERMANN, HORST BUHL, REINHARD SCHMUTZLER\*,  
DIETMAR SCHOMBURG, and ULRICH WERMUTH  
Institut für Anorganische Chemie der Technischen Universität,  
Pockelsstrasse 4, 3300 Braunschweig, ALLEMAGNE

We have reported in 1981/82<sup>1,2</sup> the symmetric diphosphorylation of N,N'-dimethyl-N,N'-bis(trimethylsilyl)urea, 1, with methyl dichlorophosphine. Dechlorination of the resulting product, 2a, led to the formation of a bridged diphosphine, 3a, which, in turn, served as a precursor to the synthesis of various mixed valence ( $\lambda^3\text{P}\lambda^4\text{P}$  and  $\lambda^3\text{P}\lambda^5\text{P}$ ) diphosphorus compounds, as a result of selective oxidative addition at one of the two  $\lambda^3$  phosphorus atoms which leaves the P-P bond intact,

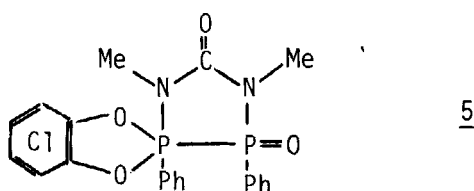


We have now prepared the P,P'-diphenyl analogue of 2a, 2b by the reaction of 1 with  $\text{PhPCl}_2$ . An attempt at the preparation of the N,N'-dimethyl urea-bridged diphosphine, 3b, by treating 2b with a reagent newly introduced into phosphorus chemistry, oxalic acid bis(trimethylsilyl)ester, surprisingly furnished the previously known  $\lambda^3\text{P}\lambda^4\text{P}$  mixed valence diphosphorus compound, 4, in one step:

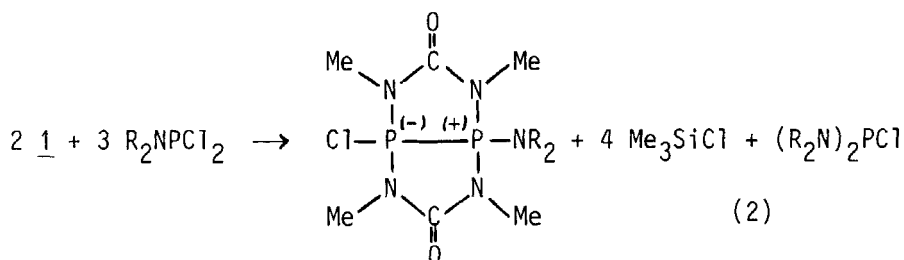


The new synthesis is superior to the previous one, providing 4 in good yield and high purity. Its identity has been confirmed by a single crystal X-ray diffraction study<sup>4</sup>.

Oxidative addition of tetrachloro-o-benzoquinone (TOB) at the  $\lambda^3$  phosphorus atom in 4 was found to provide an easy access to a  $\lambda^5\text{P}\lambda^4\text{P}$  diphosphorus compound, 5.

5

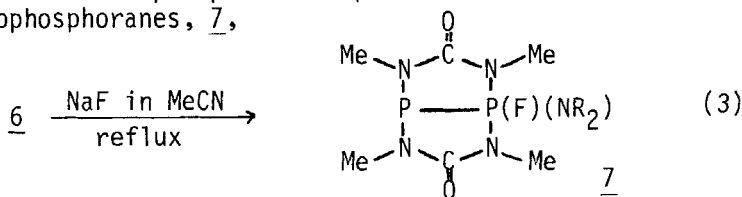
Several new classes of organophosphorus compounds involving a phosphorus-phosphorus bond have become accessible via simple one-step syntheses by an extension of the phosphorylation of 1, employing dialkyl-amino dichlorophosphines,  $R_2NPCl_2$ . The overall reaction proceeds in accord with eq. (2),



6a: R = Me; 6b: R = Et; 6c:  $R_2 = (\text{CH}_2)_4$ ; 6d:  $R_2 = \text{O}(\text{CH}_2\text{CH}_2)_2$

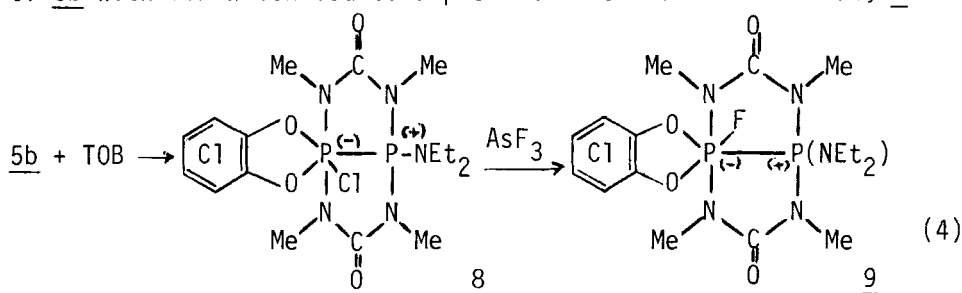
While the mechanism of the formation of 6 has not been elucidated it must, clearly, involve a sequence of Si-N cleavage reactions, as well as a scrambling reaction, producing  $(R_2N)_2\text{PCl}$ . The facile formation of the P-P bond in 6 may probably be rationalized in terms of the ideas advanced by Sišler and his co-workers<sup>5</sup>. Compounds of type 6 involve an entirely novel structural element in phosphorus chemistry, viz. the direct and stable combination of a phosphonium ( $P^+$ ) and a phosphoranide ( $P^-$ ) phosphorus atom. The identity of compounds 6 is clearly established by their  $^1\text{H}$  and, especially,  $^{31}\text{P}$  n.m.r. spectra (with  $J(\text{PP})$  of the order of 160 Hz). For 6b (R = Et) a single crystal X-ray diffraction study has been conducted which has revealed, for the solid state, the presence both of molecules of type 6b ( $r(\lambda^4\text{P}^{(+)}, \lambda^4\text{P}^{(-)})$  2.195(1) Å), as well as of chlorine-bridged dimers of 6b in which the two phosphoranide ( $\lambda^4\text{P}^{(-)}$ ) phosphorus atoms and two chlorine atoms form a planar ring with bond angles near  $90^\circ$ .

Chlorine-fluorine exchange in 6, using the simple reagent, sodium fluoride in acetonitrile, has furnished a novel type of mixed valence diphosphorus compound, viz.  $\lambda^3\text{P}$ -substituted ( $\lambda^5\text{P}$ )-fluorophosphoranes, 7,

7

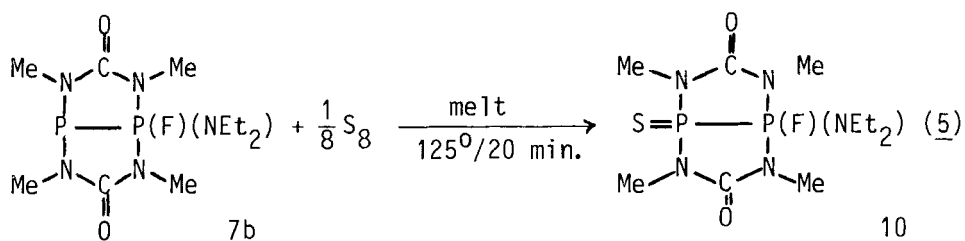
This class of compounds, although evidence for its transient existence has been obtained <sup>6</sup>, has resisted all previous attempts at its isolation and complete characterization <sup>7</sup>. A number of fluorophosphoranes of type 7 have now been obtained. The crystal structure of 7 (R = Et) has been determined, and has revealed a butterfly-type arrangement of the  $\lambda^3\text{P}[(\text{Me})\text{NC}(\text{:O})\text{N}(\text{Me})]_2$  group at largely trigonal-bipyramidal, penta-coordinate phosphorus, with F and  $\lambda^3\text{P}$  occupying one axial position each.

The lower-valent phosphorus atom in compounds of type 6 was found to display characteristic reactivity, e.g. in the reaction of 6b with TOB which led to a product of oxidative addition, 8:



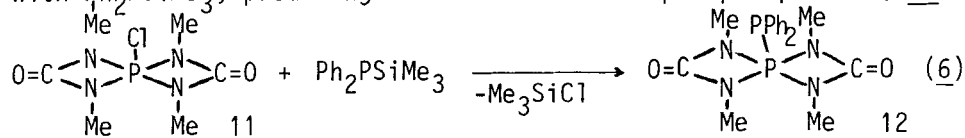
Chlorine-fluorine exchange in 8 with  $\text{AsF}_3$  (but not with  $\text{NaF}/\text{MeCN}$ ) has furnished another new type of zwitterionic phosphorus compound, 9 which has been characterized by  $^{19}\text{F}$  and  $^{31}\text{P}$  n.m.r. spectroscopy.

The preparation of a  $\lambda^5\text{P}\lambda^4\text{P}$  mixed valence diphosphorus compound, 10, from 7b by addition of elemental sulfur at  $\lambda^3\text{P}$  is also noteworthy,



The identity of 10, as a novel,  $\lambda^4\text{P}$ -substituted monofluorophosphorane, has been established on the basis of its  $^{19}\text{F}$  and  $^{31}\text{P}$  n.m.r. spectra.

Finally, a first substitution reaction at a five-coordinate phosphorus atom by a lower-valent phosphorus substituent has been achieved, in the reaction of the spiro-monochlorophosphorane, 11, with  $\text{Ph}_2\text{PSiMe}_3$ , producing a  $\lambda^3\text{P}$ -substituted spirophosphorane, 12:



Characterization of 12, aside from n.m.r. ( $^1J(PP)$  269 Hz) and mass spectrometry, was by single crystal X-ray diffraction<sup>9</sup>.

As has previously been noted by Weferling<sup>10</sup>, the P-P bond in all our mixed valence diphosphorus compounds is of strikingly constant length, regardless of the oxidation state and/or coordination number of the two phosphorus atoms. Four new values of  $r_{PP}$ , obtained in the course of the present work (for compounds 4, 6b, 7 ( $R = Et$ ), and 12 further serve to illustrate this point, with only the number for the  $\lambda^3P$ -substituted fluorophosphorane, displaying a slight deviation from the "standard" value, of the order of 2.2 Å.

Acknowledgements: Thanks are due to Bayer AG, Hoechst AG, and Stauffer Chemical Co. for gifts of chemicals. Also, support by Fonds der Chemischen Industrie, Frankfurt am Main, is gratefully acknowledged.

## REFERENCES

1. N. Weferling and R. Schmutzler, Am. Chem. Soc., Symposium Series No. 171 (Phosphorus Chemistry); L.D. Quin and J.G. Verkade, Eds., p. 425 (1981).
2. N. Weferling, R. Schmutzler, and W.S. Sheldrick, Liebigs Ann. Chem., 1982, 167.
3. W.S. Sheldrick, S. Pohl, H. Zamankhan, M. Banek, D. Amirzadeh-Asl, and H.W. Roesky, Chem. Ber., 114, 2132 (1981).
4. U. Thewalt (University of Ulm, Germany), unpublished work.
5. H.H. Sisler and co-workers, in: "Compounds containing Phosphorus-Phosphorus Bonds"; A.H. Cowley, Edit.); Dowden, Hutchinson, and Ross, Inc., Stroudsburg, Pa., 1973; pp. 45, 48, and references quoted therein.
6. F. Seel and K. Rudolph, Z. anorg. allg. Chem., 359, 233 (1968).
7. M. Murray and R. Schmutzler, Chem. and Ind., 1968, 1730.
8. R.E. Dunmur, Ph.D. Thesis, University of Technology, Loughborough, Leics., England, 1970.
9. U. Wermuth, D. Schomburg, and R. Schmutzler, Z. Naturf., 38b, 702 (1983).
10. N. Weferling, Ph.D. Thesis, Technische Universität, Braunschweig, 1981.