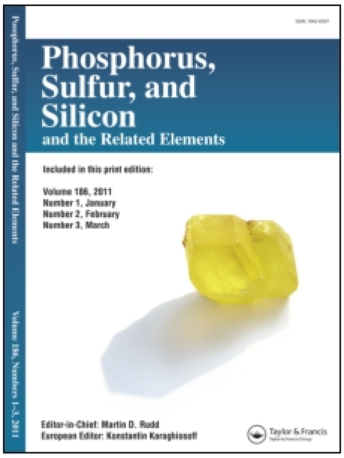

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Preparation, structures, and reactivities of compounds with double bonding between the heavier group 5A elements

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To cite this Article Cowley, Alan H. , Kilduff, Jan E. , Lasch, Jonathan G. , Mehrotra, Sushil K. , Norman, Nicholas C. , Pakulski, Marek and Stewart, Constantine A.(1983) 'Preparation, structures, and reactivities of compounds with double bonding between the heavier group 5A elements', Phosphorus, Sulfur, and Silicon and the Related Elements, 18: 1, 3 — 6

To link to this Article: DOI: 10.1080/03086648308075953

URL: http://dx.doi.org/10.1080/03086648308075953

Phosphorus and Sulfur, 1983, Vol. 18 pp. 3-6
0308-664X/83/1801-0003/$18.50/0

PREPARATION, STRUCTURES, AND REACTIVITIES OF COMPOUNDS WITH DOUBLE BONDING BETWEEN THE HEAVIER GROUP 5A ELEMENTS

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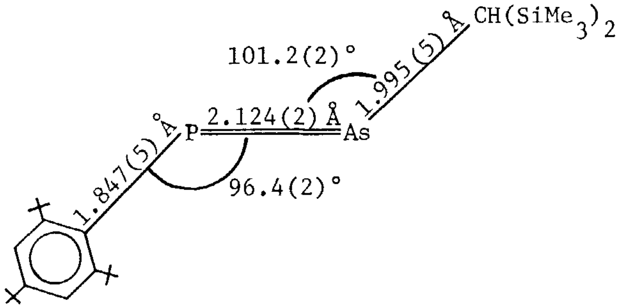
Abstract The synthesis of diphosphenes (RP=PR'), phosphaarsenes (RP=AsR'), phosphastibenes (RP=SbR'), and diarsenes (RAs=AsR') is discussed. X-ray crystallographic studies have been performed on representative double-bonded compounds. The reactivities and coordination chemistry of selected compounds have been explored.

Diphosphenes (RP=PR) have been recognized as reactive intermediates for some time.[1] However, following the isolation of the stable diphosphene, $(2,4,6\text{-}(\underline{t}\text{-Bu})_3C_6H_2)P{=}P(2,4,6\text{-}(\underline{t}\text{-Bu})_3C_6H_2)$ (1) by Yoshifuji et al.,[2] research in this area has grown dramatically.[3] Our own work focussed initially on the sterically protected alkyl derivative, $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (2). X-ray crystallographic studies[4,5,6] reveal that 2 adopts a trans planar skeletal arrangement, and the phosphorus-phosphorus bond length is close to the sum of Pauling's double-bond covalent radii (2.00 Å).[7] The average P-P-C bond angle is 108.5(4)°.

The fact that 2 is not a particularly reactive compound prompted our synthesis of unsymmetrical diphosphenes. The initial strategy involved cross-coupling of the appropriate dichlorides using sodium naphthalenide and afforded 20% yields of $(2,4,6\text{-}(\underline{t}\text{-Bu})_3C_6H_2)P{=}PC(SiMe_3)_3$ (3).[8] A new approach involving the base-promoted dehydrochlorination of $RPH_2/R'PCl_2$ mixtures resulted in excellent yields of $(2,4,6\text{-}(\underline{t}\text{-Bu})_3C_6H_2)P{=}PCH(SiMe_3)_2$ (4).[9]

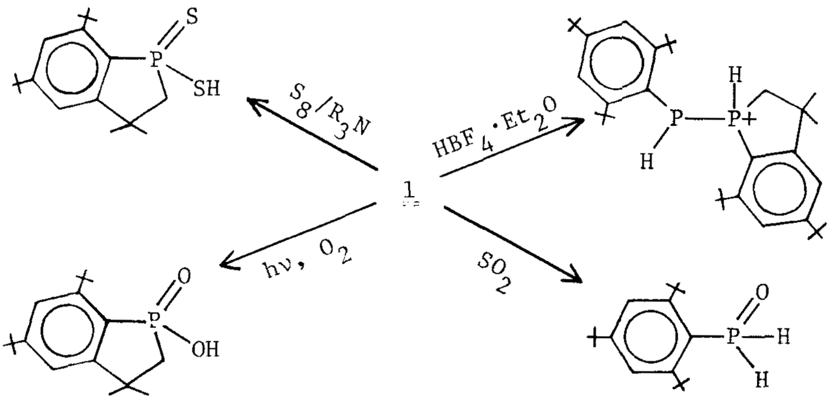
Realizing that the dehydrochlorination route might provide access to the first phosphorus-arsenic double bond, (2,4,6-(t-Bu)$_3C_6H_2$)PH_2 was treated with $(Me_3Si)_2CHAsCl_2$ and DBU (1,5-diazabicyclo[5.4.0] undec-5-ene) in THF solution. Structural details for the resulting phospha-arsene, 5, are summarized below:[10]



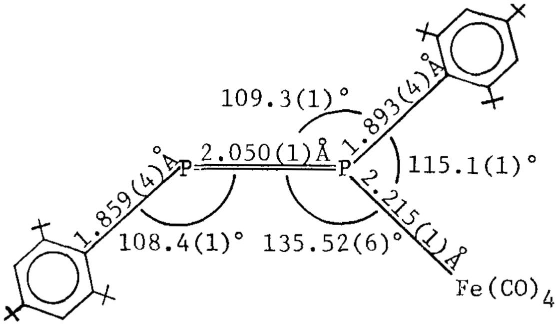
A similar reaction with the corresponding stibine, $(Me_3Si)_2CHSbCl_2$, afforded the first (marginally stable) phosphastibene, (2,4,6-(t-Bu)$_3C_6H_2$)P=SbCH$(SiMe_3)_2$ (6).[10]

In order to synthesize a diarsene, a route to the arsine, (2,4,6-(t-Bu)$_3C_6H_2$)AsH_2 (7) had to be found. Compound 7 was prepared by $LiAlH_4$ reduction of (2,4,6-(t-Bu)$_3C_6H_2$)AsF_2, and in turn, treatment of 7 with $(Me_3Si)_2CHAsCl_2$ in the presence of DBU resulted in the diarsene, (2,4,6-(t-Bu)$_3C_6H_2$)As=AsCH$(SiMe_3)_2$ (8).[11] An X-ray study of 8 revealed that, as for 2 and 5, the central bond length (2.224(2) Å) is close to the sum of the double-bond covalent radii, and the conformation is trans planar. The As-As-C angles are 93.6(3) and 99.9(3)°.

To date, reactivity studies have focussed on electrophiles. For example, treatment of 2 with a stoichiometric quantity of HCl at -78°C results in $(Me_3Si)_3CP(H)P(Cl)C(SiMe_3)_3$, thus affording an interesting parallel with alkene chemistry.[5] Some reactions of 1 are summarized below:[12]

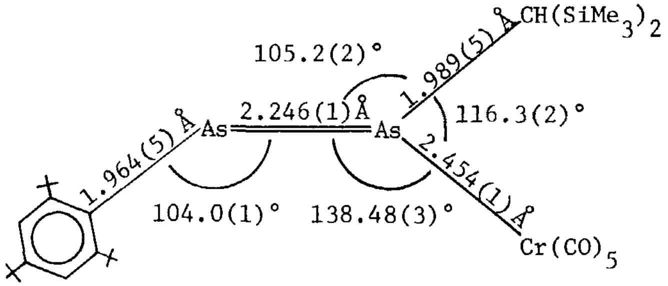


The coordination behavior of diphosphenes, phospha-arsenes, and diarsenes depends critically on the steric demands of both the ligand and the organometallic fragment. Thus 2 fails to react with $Ni(CO)_4$, $Fe_2(CO)_9$ or $Cr(CO)_5(THF)$. On the other hand, 1, featuring a somewhat smaller ligand, reacts with $Ni(CO)_4$ or $Fe_2(CO)_9$, but not $Cr(CO)_5(THF)$. Spectroscopic evidence indicates that one $Ni(CO)_3$ or $Fe(CO)_4$ moiety is attached to the diphosphene, thus representing a new mode of coordination for this type of ligand. X-ray crystallographic data have been obtained for the iron complex and are summarized below:[13]



The unsymmetrical diphosphene, 4, and the phospha-arsene, 5, also react with $Fe_2(CO)_9$ to afford the corresponding $(Me_3Si)_2CHP$-bound $Fe(CO)_4$ complexes.[13] In order to accomodate the larger $Cr(CO)_5$ moiety, we have found it necessary to take advantage of the longer arsenic-arsenic double bond. Thus, 8 reacts readily with

$Cr(CO)_5(THF)$ to afford the diarsene-$Cr(CO)_5$ complex, X-ray data for which are summarized below:[14]



ACKNOWLEDGMENT

The authors are grateful to the National Science Foundation (Grant No. CHE-8205871) and the Robert A. Welch Foundation for generous financial support.

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