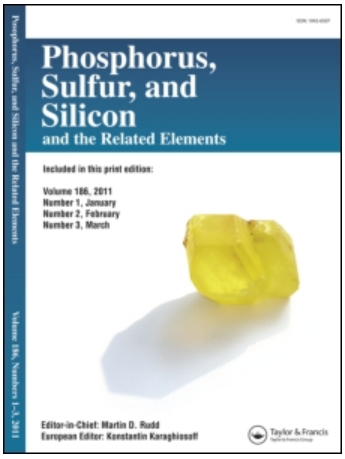

Phosphorus, Sulfur, and Silicon and the Related Elements

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Conformational Studies of Organophosphines

Hubert Schmidbaur[a]; Rudolf Herr[a]; Thomas Pollok[a]; Gabriele Reber[a]; Annette Schier[a]; Gerhard Müller[a]
[a] Anorganisch-chemisches Institut der Technischen Universität München, Garching, West Germany

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CONFORMATIONAL STUDIES OF ORGANOPHOSPHINES

HUBERT SCHMIDBAUR, RUDOLF HERR, THOMAS POLLOK, GABRIELE REBER, ANNETTE SCHIER, and GERHARD MÜLLER

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, D-8046 Garching, West Germany.

Abstract The crystal and molecular structures of a series of mono- and polytertiary phosphines with bridging alkyl, cyclopropyl, vinyl, and allyl substituents have been determined: Bis(diphenylphosphino)methane, and -cyclopropane, cis-1,2-, trans-1,2-, and 1,1-bis(diphenylphosphino)ethene, 1,1,2-tris- and 1,1,2,2-tetrakis(diphenylphosphino)allene, triphenylphosphonium[bis(diphenylphosphino)methylide]. The results are compared with the structural data (where available) of the corresponding aminals, enamines, allylamines, and amino-ylides. Molecular parameters are also available for some of the re-related phosphine oxides and a few metal complexes.

INTRODUCTION

Aminals, enamines, and aminoallenes are extremely important synthones in Organic Chemistry. A knowledge of their structures is of prime importance for an understanding of any selectivity in the chemical reactions of these

compounds. While for aminals (geminal diamino-alkanes) only the relative conformation of the functional groups is to be considered, the structure of enamines with an olefinic double bond next to the amino group(s) is a much more sophisticated problem. Recent X-ray data have illustrated the predominant structural features of enamines[1]. It appears from these studies that the assumption of a virtually planar configuration at nitrogen due to the mesomeric system $C{=}C{-}\underline{N} \longleftrightarrow \underline{C}^{-}{-}C{=}N^{+}$ is basically correct, though significant deviations from this geometry may occur. For allene derivatives much less structural information is available[2], but the same concept appears to be valid. Observations regarding the reactivity patterns of enamines and aminoallenes confirm these suggestions[3].

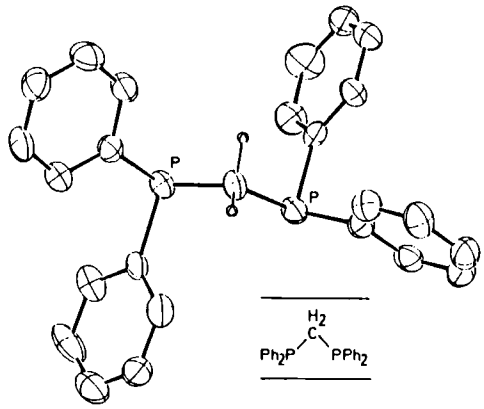
Enphosphines (vinylphosphines) and phosphinoallenes were less thoroughly studied, and structural details in particular are lacking even for simple prototypes. Standard bonding theory makes it unlikely that a mesomeric system of the above type would describe realistically the ground state of compounds containing C=C-P or C=C=C-P moieties. There is fact little evidence for an activation of the C=C bond in vinylphosphines comparable to the phenomena in enamines. An effect of this type does show up in the corresponding enphosphonium cations (or complexes)[4-6], however, where ylidic systems can be invoked for the description of bonding: $C{=}C{-}P^{+} \longleftrightarrow {}^{+}C{-}C{=}P$.

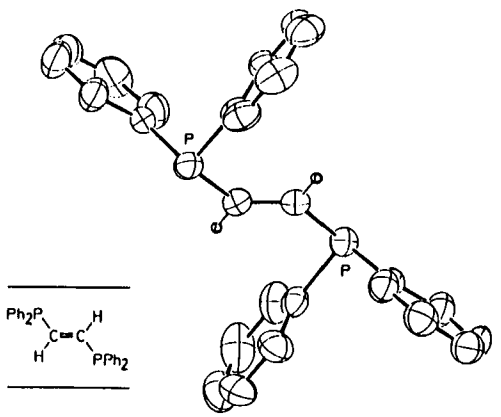
In an attempt to contribute to the discussion of these complex questions from the structural point of view, a series of molecular geometries have been determined by X-ray diffraction. Some of the results have been included in previous papers[7-9], but most of the structures presen-

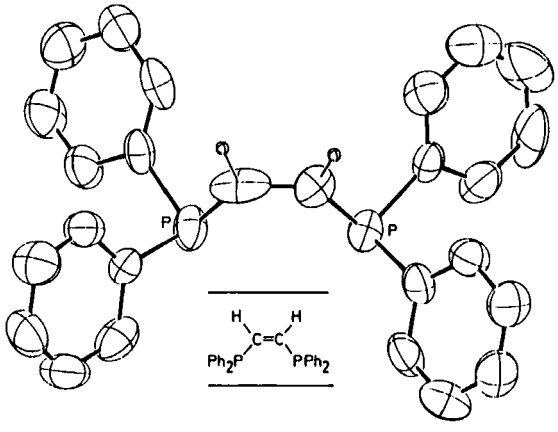
ted below are either unpublished or in press elsewhere [10,11]. Numerical data will be available also from the crystallographic data centers in due course.

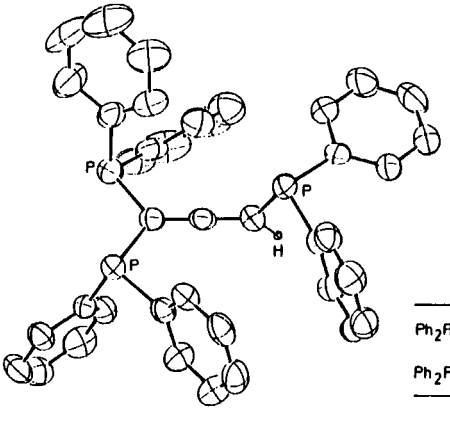
RESULTS

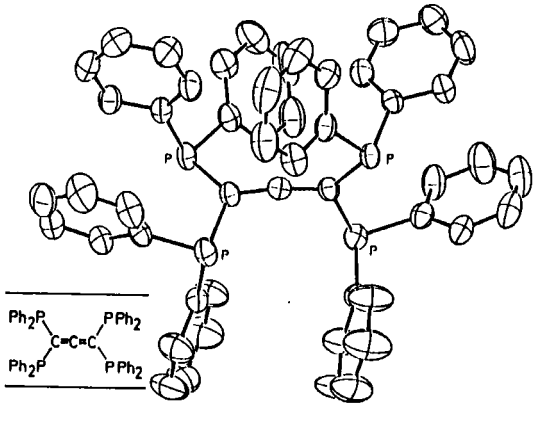
The individual structures of five molecules with their structural formulae are shown in Figures 1-5. 50% probability ellipsoids were chosen for these presentations. Phenyl hydrogen atoms were omitted for clarity.
Figure 1 shows the structure of bis(diphenylphosphino)methane, while Figures 2 and 3 depict two endiphosphines. Figures 4 and 5 finally show the structures of two poly(phosphino)allenes.











In summary the structures show the following important common features: 1) All phosphorus atoms are in a pyramidal configuration. There is virtually no evidence for an unusual widening of the C-P-C angles. 2) The P-C distances are quite normal in all cases. No increase in bond order is detectable from structural parameters. 3) The molecular conformations do not show a uniform pattern and are determined by a number of factors, including steric interactions of phenyl groups, lone pair repulsions, and sp^2 versus sp^3 adaption of neighbouring atoms.

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