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## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

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### A SYSTEMATIC CLASSIFICATION OF FREE AND COORDINATED PHOSPHORUS COMPOUNDS

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**To cite this Article** Dupart, Jean-Marc(1987) 'A SYSTEMATIC CLASSIFICATION OF FREE AND COORDINATED PHOSPHORUS COMPOUNDS', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 33: 1, 15 – 23

**To link to this Article:** DOI: 10.1080/03086648708074277

**URL:** <http://dx.doi.org/10.1080/03086648708074277>

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# A SYSTEMATIC CLASSIFICATION OF FREE AND COORDINATED PHOSPHORUS COMPOUNDS

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*(Received October 1, 1986; in final form December 27, 1986)*

A classification is presented which aims at organizing the numerous valence states of phosphorus, known or as yet unknown, according to the number of free electrons remaining on the phosphorus atom in a phosphorus compound. The chemical relationships described in the classification link any given phosphorus compound to known species, and to species as yet inexistent, by mono- and bielectronic transfers. We propose a new code number which allows a complete unambiguous description of any phosphorus species of the classification. The use of the classification is illustrated by some examples.

## INTRODUCTION

The chemistry of phosphorus is characterized by a great variety of valence states, bonding patterns and geometries.<sup>1</sup> In the last twenty years, numerous new organic and inorganic compounds have succeeded in disconcerting the experts because of a phosphorus atom in a stable, hitherto unknown, valence state which was formally considered as particularly unstable or elusive. Some examples are given in Figure 1.<sup>2-6</sup>

The ever-increasing diversity of bonding patterns and possible structural situations has become such that a systematic classification is highly necessary.

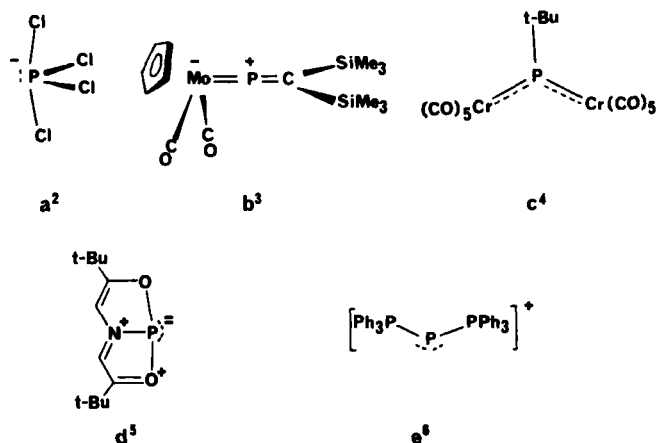
So far the best known attempt at classification is probably the cube designed by Wolf,<sup>7</sup> in which the three apparent faces contain species derived from  $\text{:P:}^+$ ,  $\text{:P:}^{\cdot}$  and  $\text{:P:}^-$  (exclusive of polycharged species). A face is obtained in varying the coordination number of the phosphorus atom vs its number of valence electrons.

Our approach complements Wolf's by including mono- and polycharged species and because it is based upon the number of free electrons remaining on the phosphorus atom in the phosphorus species, which allows immediate recognition of the way in which any species is formally related to the others by mono- and bielectronic transfers. From this point of view it may have heuristic value, since non-existent species can be easily predicted and derived from known ones.

We also propose a new code number which allows a complete, unambiguous description of any phosphorus species comprised in the classification.

## PRINCIPLE OF THE CLASSIFICATION

All the valence states of phosphorus are grouped according to the number of free electrons (NFE) remaining on the phosphorus atom in the phosphorus species.

FIGURE 1 Some examples of new phosphorus compounds.<sup>2-6</sup>

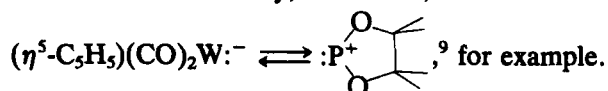
Since the NFE may vary from 0 to 8 (a completed octet of electrons) there are nine groups of phosphorus species and nine subtables in the classification. Each subtable matches a face of the staircase representation shown in Figure 2.

Phosphoranes  $\text{PR}_5$ <sup>8</sup> and phosphonium salts  $\text{PR}_4^+$  which have no free electrons on phosphorus (NFE = 0) are classified in group 0. Species with a lone pair such as phosphines  $:\text{PR}_3$  or phosphonium cations  $:\text{PR}_2^+$ <sup>1c</sup> belong to group 2 (NFE = 2), while phosphides  $::\text{PR}_2^-$  with 2 free electron doublets (NFE = 4), will be found in group 4. The monoatomic species  $:\text{P}^+$ ,  $:\text{P}^\cdot$  and  $::\text{P}^-$  belong to groups 4, 5 and 6, respectively.

## NATURE OF THE BONDING BETWEEN THE PHOSPHORUS ATOM AND ITS SUBSTITUENTS

In molecular compounds such as  $:\text{PMe}_3$  the phosphorus shares bonding electrons with its three substituents; in species such as  $\text{Me}_3\text{P}:\rightarrow\text{BH}_3$  phosphorus acts as a Lewis base and all its electrons are involved in bonding, while in species such as  $\text{F}_5\text{P}\leftarrow:\text{NC}_5\text{H}_5$  phosphorus acts as a Lewis acid and accepts electrons from a ligand in its vacant orbitals.

According to the commonly accepted bonding schemes one could thus make a distinction between covalent compounds and coordination compounds, the latter class including "phosphorbasic" species in which one at least of the bonds around the phosphorus derives from the donation of a phosphorus lone pair and "phosphoracid" species in which one at least of the bonds around the phosphorus originates from the donation of a ligand's lone pair to the phosphorus. The three kinds of behavior may, of course, exist on the same phosphorus atom, as in



However, the formal character of these distributions must be emphasized. They

are based upon the pathway used for the formation of the species. It is possible to imagine a species which could be formed either from the donation of a phosphorus lone pair or from the donation of a ligand's lone pair to the phosphorus. In this case, covalent, phosphorbasic and phosphoracid species are no longer really differentiable.<sup>10</sup>

Both covalent and coordination species are dealt with in a single table if we replace the conventional formalism for a coordination bond, i.e. the arrow, by a non-directional bond with formal charges distributed equally on the donor and the acceptor atoms:  $\text{Me}_3\text{P}:\rightarrow\text{BH}_3$  will then be written as  $\text{Me}_3\text{P}^+-\text{BH}_3^-$ , and will belong to the phosphonium  $\text{PR}_4^+$  group;  $\text{F}_5\text{P}\leftarrow:\text{NC}_5\text{H}_5$  will become  $\text{F}_5\text{P}^--\text{N}^+\text{C}_5\text{H}_5$ , which can be considered as a  $\text{PR}_6^-$  species. In compound  $(\text{Ph}_3\text{P}:\rightarrow:\text{P}:\leftarrow:\text{PPh}_3)^+$ ,<sup>6</sup> the phosphorus atoms will be formally considered as two phosphoniums around a central phosphide  $\text{Ph}_3\text{P}^+-:\text{P}:-\text{P}^+\text{Ph}_3$ .

In all cases, the charge  $Q$  of the phosphorus (left of Figure 2) is related to its NFE by Equation 1:

$$Q = 5 - \text{NFE} - \sum B \quad (1)$$

where  $\sum B$  is the sum of its bonds ( $\sigma$  and/or  $\pi$ ). In the classification, we do not distinguish effective charge (anion, cation) from the effect of a charge transfer: partial charges are formally considered as effective charges.

## AN UNEQUIVOCAL NOMENCLATURE

We propose to complement Martin's N P L naming system<sup>11</sup> by a NFE(N P L)D code number, which then allows a complete, unambiguous description of phosphorus in any species of the classification. In this code, the number of valence shell electrons (N) formally associated with the phosphorus atom (left of Figure 2) and the coordination number (L) are completed by the NFE of the phosphorus atom, and by the number of doublets (D) donated and/or accepted by the phosphorus when it acts as a Lewis base or a Lewis acid, D being negative or positive, respectively (two D numbers may be necessary, one for the donated, the other for the accepted electrons. D can be omitted when it equals to 0 or when the pathway for the formation of the species is not clear).

Thus for example a phosphine  $:\text{PR}_3$  and a phosphonium  $\text{E} = \text{PR}_2^+$  which have the same code number 8 P 3 according to Martin's system will be differentiated by our system, where they will be described as 2(8 P 3) and 0(8 P 3), respectively. Coordination compounds will be differentiated from similar covalent compounds with the D number:  $\text{PMe}_4^+$ , 0(8 P 4)0;  $\text{Me}_3\text{P}:\rightarrow\text{BH}_3$ , 0(8 P 4)-1;  $\text{PF}_6^-$ , 0(12 P 6);  $\text{F}_5\text{P}\leftarrow:\text{NC}_5\text{H}_5$ , 0(12 P 6)+1.

## CONSTRUCTION OF THE TABLE

The classification of the phosphorus species (Figure 2) contains 9 subtables, each corresponding to a NFE. We adopt a "staircase" representation to distinguish the

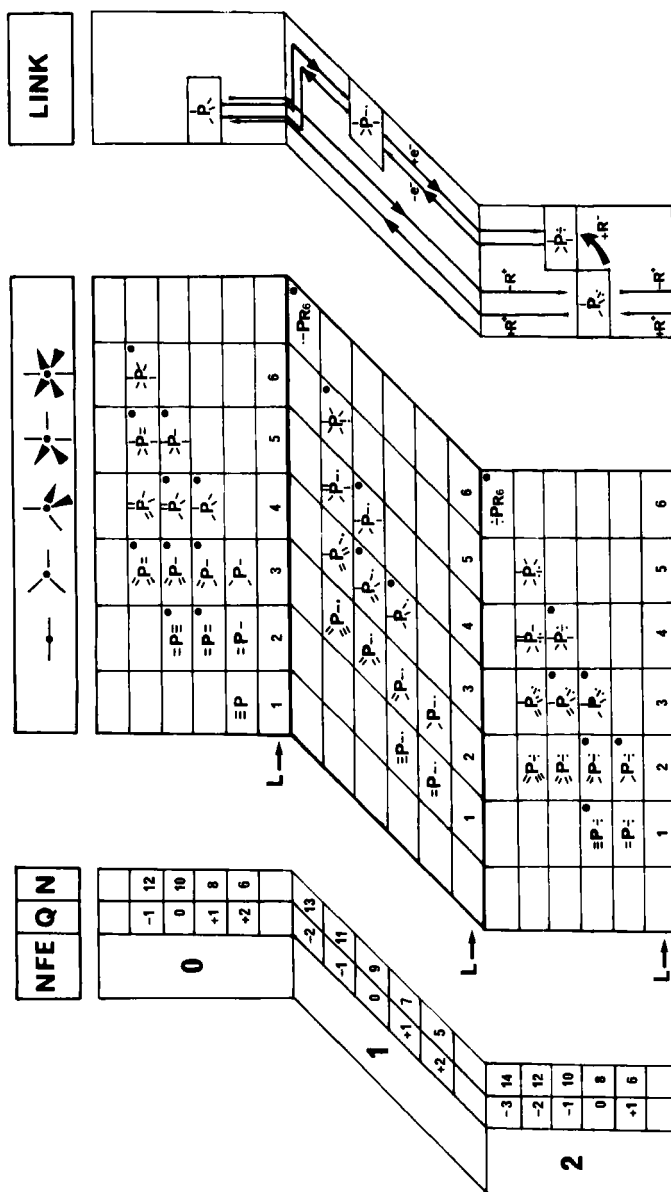


FIGURE 2 The classification of the phosphorus species contains 9 subtables, each corresponding to a NFE (Number of Free Electrons remaining on the phosphorus atom in the phosphorus species; left of the table). Each subtable is generated by varying the coordination number  $L$  of the phosphorus atom ( $X$ -axis) vs its number of valence electron  $N$  ( $Y$ -axis). A same  $N$  and a same charge  $Q$  are kept in a given line of the table. A same idealized geometry is kept in a given column. The squares marked with a dot correspond to situations for which species have been detected or isolated. The right part of the table shows the chemical relationships between the various species as mono- and bielectronic transfers.

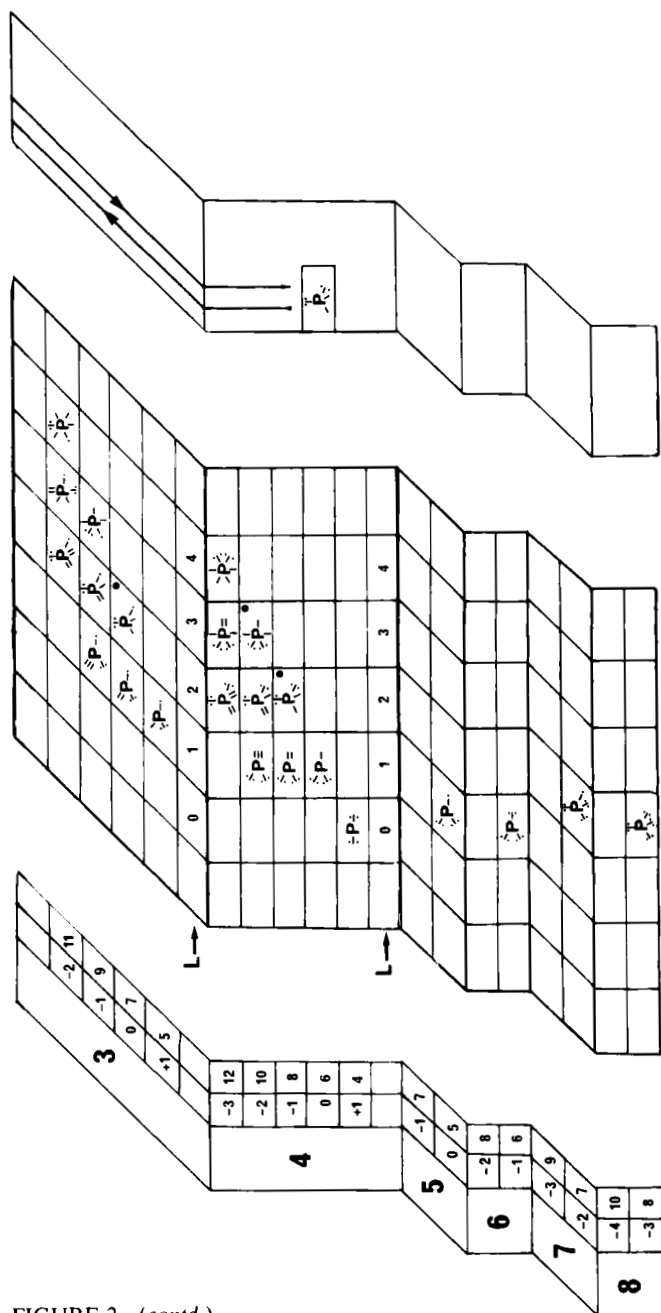


FIGURE 2 (contd.)

non-radical species from the radical ones: the vertical surfaces between the steps (the risers) are occupied by non-radical species (even NFE), whereas radical compounds (odd NFE) occupy the horizontal surface of each step (the tread).

For a given NFE, the subtable is generated by varying the coordination number  $L$  of the phosphorus atom ( $X$ -axis) vs its number of valence electrons  $N$  ( $Y$ -axis). In each subtable, all the species located on the same diagonal are related by the addition (in ascending) or subtraction (in descending) of one or several  $R^-$  groups.

When several isomers are possible for a given species ( $=P^+ =$  and  $-P^+ \equiv$ , and hence have the same code number 0(8 P 2)), only one is represented, in the cause of clarity.

The VSEPR model may be used to assign the most probable geometry to each species. To simplify the table, we have kept the same idealized geometry in a given column, ignoring the distortions that may take place in each particular case. So the position of a species in a given column of the table gives a rough idea of its geometry (free doublets or single electrons have to be considered as substituents).

Finally, the squares marked with a dot correspond to situations for which species have been detected or isolated.

## HOW TO MAKE USE OF THE CLASSIFICATION AND THE NOMENCLATURE

Since chemistry relies largely on the transfers of electrons among atoms, our classification, based upon the different possible NFE of phosphorus, depicts *chemical* relationships between the various species as mono- and bielectronic transfers (right of Figure 2). One goes from a riser to the adjacent upper or lower tread by, respectively, subtraction or addition of one electron. We can go directly from a tread (or a riser) of the staircase to the next one by addition (in ascending) or subtraction (in descending) of a  $R^+$  group, which is equivalent to a bielectronic transfer. In all cases a change of column involves a change of the geometry at phosphorus.

The diagram shown in Figure 3 numbers all the ways leading to a target phosphorus species, here a phosphoranide anion,<sup>2</sup> 2(10 P 4), from known species (marked with a dot) or from as yet inexistent species through monoelectronic,  $R^+$  and  $R^-$  transfers.<sup>12</sup> A bold line-drawing between two species indicates that the pathway is known.<sup>13</sup> Such a chart can be quickly established with the help of the classification. Its predictive value is clearly shown.

Furthermore, a convenient use of the NFE(N P L)D code is for designating compounds in which phosphorus belongs to a delocalized system. Each resonance structure can be named easily by a code number. Such a use of the nomenclature is illustrated in Figure 4 with a two metallic centers bound phosphinidene.<sup>14</sup>

Although this classification is not exhaustive, it does cover almost all the presently known phosphorus species. Among the exceptions, we can list the compounds in which phosphorus belongs to a multicentric bond system with a coordination number higher than the number of electrons involved in bonding

## NFE

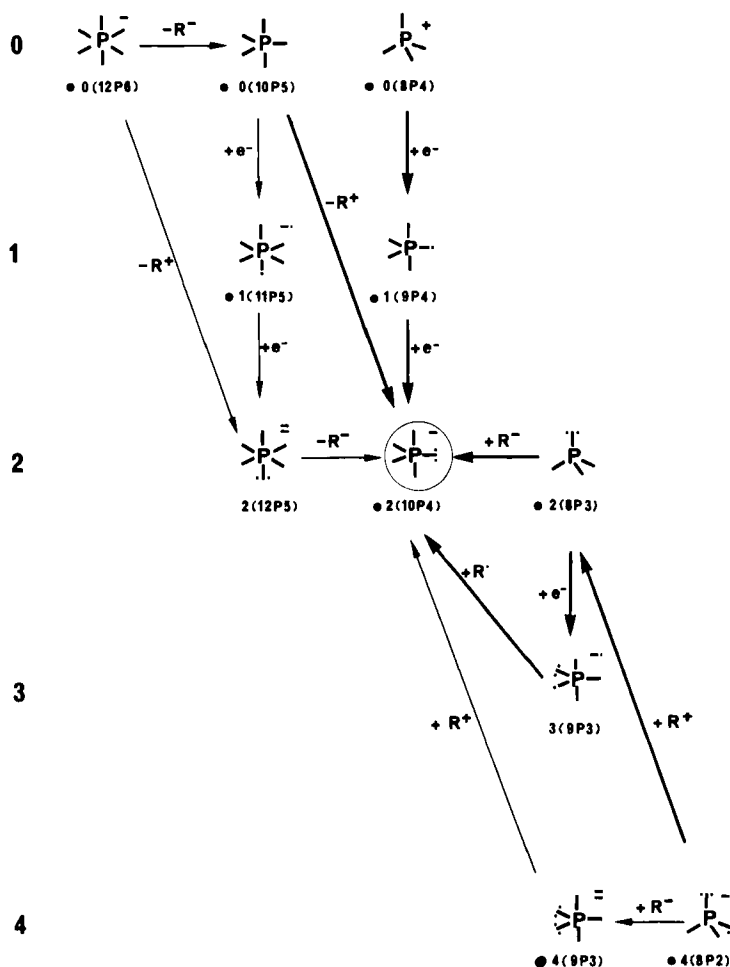


FIGURE 3 Example of a flow-chart showing the ways formally leading to a new phosphorus species, here a phosphoranide anion 2(10 P 4); the known species are marked with a dot; a bold arrow between two species indicates that the pathway is known.<sup>13</sup>

(Figure 5). As examples one can quote some polyhedral phosphaboranes such as  $B_{11}H_{11}PC_6H_5$ <sup>14</sup> in which the phosphorus contributes only two electrons to the polyhedral framework, the encapsulation of phosphorus by transition metal clusters such as  $(Rh_9(CO)_{21}P)^{-2}$ <sup>15</sup> or the hexaphosphabenzene  $P_6$  moiety present in the triple decker complex  $((\eta^5-Me_5C_5)Mo)_2(\mu, \eta^6-P_6)$ .<sup>16</sup>

In conclusion, we hope that this systematic classification of phosphorus compounds will meet with specialist and non-specialist favor because of its heuristic and didactic advantages. This approach may, of course, be extended to other elements of the periodic table.



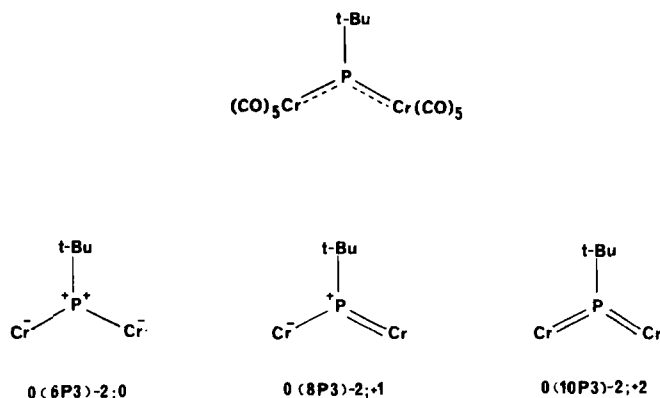


FIGURE 4 Use of the code number NFE(N P L) D for the description of the resonance structures of a two-metallic-centers-bound phosphinidene.

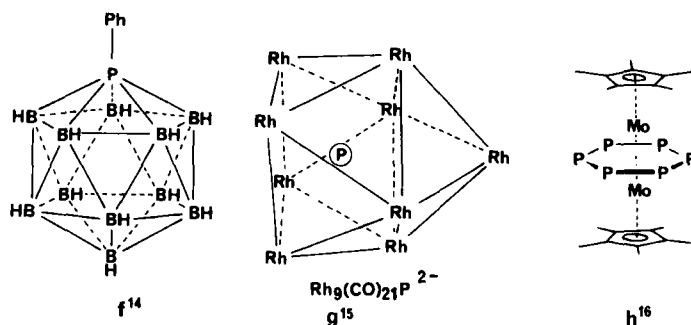


FIGURE 5 Some compounds in which phosphorus belongs to a multicentric bond system.<sup>14-16</sup>

## ACKNOWLEDGMENTS

I wish to acknowledge the constructive criticisms and other helpful suggestions offered by J. Riess, B. Devallez, L. Hubert and P. Vierling while preparing this paper.

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