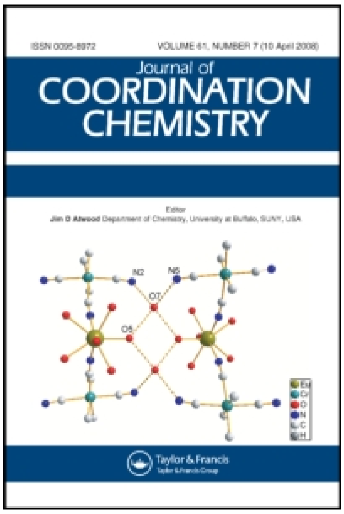

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POLYTERTIARY PHOSPHINES AND ARSINES II: Systematics of Polytertiary Phosphines and their Metal Complexes

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POLYTERTIARY PHOSPHINES AND ARSINES II
Systematics of Polytertiary Phosphines and their Metal Complexes[1]

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The geometries of possible polytertiary phosphine networks containing trivalent phosphorus atoms and bridging groups are shown to be completely analogous to the geometries of acyclic planar networks of linked sp^2 carbon atoms.[2] The bridging groups between pairs of phosphorus atoms in such polytertiary phosphines may be classified into the following three types on the basis of coordination properties: (1) Bridges which allow the two bridged phosphorus atoms to bond both to a single metal atom but not to different metal atoms (type 1); (2) Bridges which allow the two bridged phosphorus atoms to bond to two different metal atoms but not both to a single metal atom (type 2); and (3) Bridges which allow the two bridged phosphorus atoms to bond either to two different metal atoms or both to a single metal atom (type 3). The numbers of possible polytertiary phosphines with up to six phosphorus atoms and various combinations of these three types of bridges are determined. The modes of coordination of the possible tritertiary phosphines and the possible tripod and linear tetratertiary phosphines to one or more metal atoms are given.

INTRODUCTION

The additions of phosphorus-hydrogen and arsenic-hydrogen bonds across the carbon-carbon double bonds of vinylphosphines and the carbon-carbon triple bonds of ethynylphosphines[1] provide for the first time a rational and efficient method for the preparation of polytertiary phosphines and arsines with relatively complex structures. This new development in synthetic chemistry makes relevant the following three-step theoretical investigation, which is discussed briefly in this paper:

1) The generation of possible polytertiary phosphine networks containing tertiary phosphorous atoms and bridging groups.
2) The investigation of possible combinations of different bridging groups within the polytertiary phosphine networks obtained in the first step.
3) An investigation of the possible modes for metal complex formation by the polytertiary phosphines obtained in the second step.

For the sake of clarity the discussion in this paper is limited to polytertiary phosphines. Extension of the principles and method to polytertiary arsines is trivial except for a consideration of numbers of possible mixed phosphine-arsines of various structures; discussion of the latter appears premature until more data becomes available.

GENERATION OF POSSIBLE NETWORKS OF TERTIARY PHOSPHORUS ATOMS AND BRIDGING GROUPS

Consider a polytertiary phosphine to be represented by a network containing P tertiary phosphorus atoms and b bridges between pairs of tertiary phosphorus atoms. Of the phosphorus atoms in this network, p_0 will be connected to three bridges (type P), p_1 will be connected to two bridges (type RP), and p_2 will be connected to only one bridge (type R_2P). (In this discussion R represents a non-bridging group such as the phenyl groups in the polytertiary phosphines prepared in the first paper of this series.)[1] Obviously, $p_0 + p_1 + p_2 = P$. Since each tertiary phosphorus atom has exactly three bonds like an sp^2 carbon atom, the set of networks representing polytertiary phosphines is identical to the set of acyclic planar unsaturated carbon systems[2] with the phosphorus atoms corresponding to the sp^2 carbon atoms, and the bridges corresponding to the carbon-carbon bonds. Networks representing macrocyclic polytertiary phosphines corresponding to *cyclic* planar unsaturated carbon systems[2] are excluded from consideration in this paper since there is no experimental evidence to date that such macrocyclic polytertiary phosphines can be prepared.[3] The following conditions similar to, but more restrictive than, conditions for planar networks of unsaturated carbon systems[2] apply to networks for polytertiary phosphines:

(1) *Relationship between the types of phosphorus atoms and the number of bridges*:

$$\sum_{n}(3 - n)p_n = 2b$$

(2) *Presence of the minimum number of bridges to hold the molecule together*:

$$p_2 \leq p_1 + 2p_0 \text{ if } p_0 + p_1 > 1$$

(3) *Exclusion of cyclic structures with two bridges between any pair of phosphorus atoms*:

$$b = P - 1$$

Table 1 lists the possible networks for polytertiary phosphines with up to six phosphorus atoms. These correspond to the indicated planar unsaturated carbon networks[2] with the consideration of analogues of two isomeric methylenepentadienyl networks (18 and 18A in Figure 1). Figure 1 depicts the geometries of the networks considered in Table I with vertices representing phosphorus atoms and edges representing bridges. Of the ten possible networks for polytertiary phosphines listed in Table 1, half are known in actual compounds.[1]

POSSIBLE COMBINATIONS OF DIFFERENT BRIDGING GROUPS IN VARIOUS POLYTERTIARY PHOSPHINES

Several different types of bridges between pairs of phosphorus atoms in polytertiary phosphines are known as exemplified by the following: (1) Polymethylene bridges as in the compounds

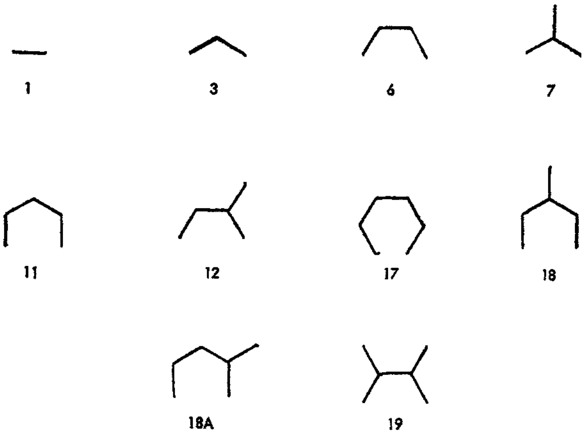

FIGURE 1 Geometries of networks considered in Table 1. The numbering of these structures corresponds to the numbering of planar unsaturated carbon systems in R. B. King, *J. Am. Chem. Soc.*, **91**, 7217 (1969).

TABLE I

Possible networks for polytertiary phosphines with up to six phosphorus atoms

P	b	p_0	p_1	p_2	Analogous planar unsaturated carbon network[a]	Symmetry elements[b]	I_3	Known (1970)
2	1	0	0	2	Ethylene (1)	—	3	Yes
3	2	0	1	2	Allyl (3)	C_2	6	Yes
4	3	0	2	2	Butadiene (6)	C_2	18	Yes
4	3	1	0	3	Trimethylenemethane (7)	C_3	10	Yes
5	4	0	3	2	Pentadienyl (11)	C_2	45	No
5	4	1	1	3	2-Methylenebutadiene (12)	C_2	54	No
6	5	0	4	2	Hexatriene (17)	C_2	135	No
6	5	1	2	2	sym-Methylenepentadienyl (18)	C_2	135	No
6	5	1	2	2	asym-Methylenepentadienyl (18A)	C_2	162	No
6	5	2	0	4	Diallylene (19)[c]	C_2	63	Yes

[a] For a more detailed discussion of the systematics of planar unsaturated carbon networks see R. B. King, *J. Am. Chem. Soc.* **91**, 7217 (1969). The numbers in parentheses refer to structures in Figure I.

[b] Only symmetry elements contributing to making phosphorus atoms equivalent are considered here.

[c] The structure (19) depicted for the diallylene system in Figure I of R. B. King, *J. Am. Chem. Soc.* **91**, 7217 (1969), has one line missing. See structure 19 of Figure 1 of this paper for a correct structure of the diallylene network.

$(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$;[4] (2) Substituted trimethylene bridges as in $CH_3C[CH_2P(C_6H_5)_2]_3$;[4] (3) Olefinic bridges as in the *cis*- and *trans*-isomers of $(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$;[5] (4) Acetylenic bridges as in the rigid $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$[6] and the more flexible $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$.[7] These diverse bridging groups in polytertiary phosphines can be divided into the following three types on the basis of the complexing behaviors towards transition-metal derivatives: of the ditertiary phosphines containing these bridging groups:

Type 1 Bridges which place the two phosphorus atoms sufficiently close together for bonding both to a single metal atom but too close together for bonding to two different metal atoms because of steric interference. This is the rarest of the three types of bridges but has been established[8, 9] for the rigid *cis*-CH=CH bridge as found in *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$.

Type 2 Bridges which place the two phosphorus atoms sufficiently far apart for bonding to two different metal atoms without steric interference but which are sufficiently rigid that the two bridged phosphorus atoms cannot approach each other closely enough to bond both to a single metal atom. Examples of this type of bridge include the *trans*-CH=CH bridge in *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$, the C≡C bridge in $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$, and the $CH_2C{\equiv}CCH_2$ bridge in $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$.

Type 3 Bridges which are sufficiently flexible so that the two bridged phosphorus atoms can be either close enough together for bonding both to a single metal atom or far enough apart for bonding to two different metal atoms. Phosphorus atoms separated by this type 3 bridge can bond to metal atoms in the manners characteristic of both type 1 and type 2 bridges. The type 3 bridge is best exemplified by the CH_2CH_2 bridge in $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$; CH_2 and $CH_2CH_2CH_2$ bridges also exhibit type 3 characteristics.

The classification of the diverse types of bridging groups found in polytertiary phosphines into three basic types differing in their possible modes of coordination to metal atoms makes manageable the systematics of polytertiary phosphines of complexities comparable to those prepared in the first paper of this series.[1] This classification based on coordinating properties is justified by the general interest in the transition metal complexes of polytertiary phosphines and their importance in catalysis.

In order to determine the numbers and types of polytertiary phosphines with distinctly different coordination properties that can be prepared, the number of ways the three different types of bridges listed above can be located in the polytertiary phosphine networks (Table 1) is examined. For a given polytertiary phosphine network this number is designated as I_3. For a polytertiary phosphine network with no symmetry elements the number of ways three different types of bridges can be arranged is 3^b provided that any of the three types of bridges can be in any location relative to any other of the three types of bridges; this certainly seems to be the case. Elements of symmetry, particularly C_n axes, will make identical some of the 3^b arrangements of three different types of bridges in a polytertiary phosphine network such that the number of arrangements of the three different types of bridges leading to distinguishable polytertiary phosphines from a given network will be less than 3^b. Thus for a polytertiary phosphine network with a C_2 axis, the number of arrangements of the three different types of bridges which lead to different polytertiary phosphines (I_3 in Table 1) may be obtained by the following formula:

$$I_3 = 3^b - \sum_{i=1}^{r} 3^{(b-i)} \qquad (1)$$

In this formula *b*, as before, refers to the number of bridges and refers to the number of pairs of bridges that are interchanged in the C_2 symmetry operation.

POSSIBLE MODES OF COORDINATION OF THE POLYTERTIARY PHOSPHINES

In discussing the coordination characteristics of polytertiary phosphines it is useful to distinguish between the following series of terms:

(1) *Monodentate, bidentate, tridentate, etc.* As when discussing other chelate derivatives these terms refer to the number of phosphorus or other donor atoms that bond to a single metal atom in a given complex.

(2) *Monoligate, biligate, triligate, etc.* These terms refer to the total number of phosphorus or other donor atoms in a ligand that bond to metal atoms in a given complex (abbreviated as L in Tables 2, 3, and 4 and subsequently in the text). All of the

TABLE II

Possible modes of coordination of tritertiary phosphines

Mode of Coordination[a]		Tritertiary phosphine[a]					
L	M	P(33)	P(32)	P(31)	P(22)	P(21)	P(11)
1	1	2	3	3	2	3	2
2	1	1	1	2	0	1	1
2	2	2	3	2	2	2	1
3	1	1	0	1	0	0	1
3	2	1	1	1	0	1	0
3	3	1	1	0	1	0	0
TOTAL		8	9	9	5	7	5
Z′(LM)[a]		6	5	5	3	4	4

[a] See the text for an explanation of these symbols.

donor atoms need not necessarily bond to the same metal atom.

(3) *Monometallic, bimetallic, trimetallic, etc.* These terms refer to the total number of metal atoms to which the ligand bonds in a given complex (abbreviated as M in Tables 2, 3, and 4 and subsequently in the text).

The meaning of these terms monoligate, biligate, triligate, etc., as used in this and succeeding papers is identical to the meaning of the terms monodentate, bidentate, tridentate, etc., as used in some of the author's previous work;[8, 9] however, the distinction between these two series of terms as outlined above is a potentially useful one which will be followed in future publications.

In the absence of any constraints imposed by limitations on the coordination of phosphorus atoms separated by type 1 and type 2 bridges, the number of ways a given polytertiary phosphine can coordinate to one or more metal atoms is $\frac{1}{2}P(P+1)$ or $\sum_{i=1}^{P} i$ if any differences arising from the non-equivalence of phosphorus atoms in the polytertiary phosphines are ignored. Constraints imposed by the inabilities of phosphorus atoms linked by type 1 bridges to bond to different metal atoms and of phosphorus atoms linked by type 2 bridges to bond both to the same metal atom will reduce the number of ways a given polytertiary phosphine can coordinate to one or more metal atoms. On the other hand, non-equivalence of the phosphorus atoms in most polytertiary phosphines will often generate more than one non-equivalent mode of coordination for a given set of L and M values. These effects are summarized in Table 2 for tritertiary phosphines (allyl analogues corresponding to structure 3 in Figure 1), in Table 3 for tripod tetratertiary phosphines (trimethylenemethane analogues corresponding to structure 7 in Figure 1), and in Table 4

TABLE III

Possible modes of coordination of tripod tetratertiary phosphines

Mode of coordination[a]		Tripod tetratertiary phosphine[a]									
L	M	P(333)	P(332)	P(331)	P(322)	P(321)	P(311)	P(222)	P(221)	P(211)	P(111)
1	1	2	3	3	3	4	3	2	3	3	2
2	1	1	1	2	1	2	2	0	1	1	1
2	2	2	4	3	4	5	3	2	3	3	1
3	1	1	1	2	0	1	2	0	0	1	1
3	2	1	2	2	1	3	1	0	1	1	0
3	3	2	3	1	3	2	1	2	1	1	1
4	1	1	0	1	0	0	1	0	0	0	1
4	2	1	1	1	0	1	1	0	0	1	0
4	3	1	1	1	1	1	0	0	1	0	0
4	4	1	1	0	1	0	0	1	0	0	0
TOTAL		13	17	16	14	19	13	7	10	11	7
Z′ (LM)		10	9	9	7	8	7	4	6	7	6

See the text for an explanation of these symbols

TABLE IV

Possible modes of coordination of linear tetratertiary phosphines

Mode of coordination[a]		Linear tetratertiary phosphine[a]								
L	M	P(333)	P(323)	P(313)	P(233)	P(232)	P(223)	P(222)	P(213)	P(212)
1	1	2	2	2	4	2	4	2	4	2
2	1	2	1	2	3	1	1	0	2	1
2	2	4	4	3	6	4	6	4	5	3
3	1	1	0	1	1	0	0	0	1	0
3	2	3	2	2	4	1	2	0	3	1
3	3	2	2	1	4	2	4	2	2	1
4	1	1	0	1	0	0	0	0	0	0
4	2	2	1	1	1	1	0	0	1	0
4	3	2	2	1	2	0	1	0	1	1
4	4	1	1	0	1	0	1	1	0	1
TOTAL		20	15	14	26	11	19	9	19	10
Z′ (LM)*r*		10	8	9	9	6	7	4	8	7

TABLE IV (Continued)

Mode of coordination[a]		Linear tetratertiary phosphine[a]								
L	M	P(133)	P(132)	P(131)	P(123)	P(122)	P(121)	P(113)	P(112)	P(111)
1	1	4	4	2	4	4	2	4	4	2
2	1	3	2	2	2	1	1	3	2	2
2	2	5	5	4	5	5	4	4	4	3
3	1	2	1	1	0	0	0	2	1	1
3	2	5	4	2	4	2	2	3	2	1
3	3	2	2	0	2	2	0	1	1	0
4	1	1	0	1	0	0	0	1	0	1
4	2	2	1	1	1	0	1	1	1	0
4	3	1	1	0	1	1	0	0	0	0
4	4	0	0	0	0	0	0	0	0	0
TOTAL		25	20	13	19	15	10	19	15	10
Z′ (LM)[a]		9	8	7	7	6	5	8	7	6

[a] See the text for an explanation of these symbols.

for linear tetratertiary phosphines (butadiene analogues corresponding to structure 6 in Figure 1). In order to make these tables more readable the polytertiary phosphines are abbreviated as P(abc... where *a*, *b*, *c*, etc., indicate the types of the bridges in the polytertiary phosphine under consideration by 1, 2, or 3 as defined above. Thus the polytertiary phosphines $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ and $[(C_6H_5)_2PCH_2CH_2]_3P$ discussed in the first paper of this series[1] would be abbreviated as P(33) and P(333), respectively. In the cases of linear polytertiary phosphines the numbers of the types of bridges are cited in the order the bridges appear along the chain. The entries in Tables 2, 3, and 4 refer to the number of distinguishable modes of coordination for the P(abc. . .) polytertiary phosphine listed at the head of the column with the L and M values listed at the beginning of the row. An entry of zero means that this mode of coordination is not possible because of the constraints imposed by type 1 and/or type 2 bridges. The row designated as Z′(LM) at the bottom of each table refers to the number of different L and M pairs which are possible (i.e. non-zero entries) modes of coordination for the P(abc) polytertiary phosphine listed at the head of the column.

One of the polytertiary phosphines described in the first paper of this series[1] is the hexatertiary phosphine $[(C_6H_5)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(C_6H_5)_2]_2$ with a polytertiary phosphine network analogous to the diallylene system (structure 19 in Figure 1). However, a table describing the possible modes of coordination of hexatertiary phosphines analogous to the diallylene system is not presented in this paper since such a table would have 21 × 63 = 1323 entries and therefore would be too unwieldy to be of much value at the present stage of development of this field.

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