

## Review

## Coordination chemistry of the main group elements with phosphine, arsine and stibine ligands



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## ABSTRACT

Complexes of Group 2, 12, 13, 14, 15 and 16 elements with mono-, bi-, and poly-dentate phosphine and arsine ligands (and including the very few examples of stibine and bismuthine donor ligands) are described. Polydentate ligand complexes containing neutral or charged N, O, C, or S donor groups in addition to phosphino or arsino donor groups are included, but charged P or As (phosphides, arsenides, phosphinomethanides etc.) ligands are excluded. Emphasis is placed upon the X-ray structures, multinuclear NMR data and reactions. The major differences of this class of complexes compared to the familiar d-block phosphine/arsine complexes are discussed and rationalised in terms of the E–M bonding

*Abbreviations:* E, P, As, Sb or Bi; M, Lewis acid atom usually metal or metalloid; X, F, Cl, Br or I; R, alkyl or aryl; DMPP, tris(2,6-dimethoxyphenyl)phosphine; TMPP, tris(2,4,6-trimethoxyphenyl)phosphine; HCB, *closo*-2-((dimethylphosphino)methyl)-1,2-dicarbaborane; MOCVD, metal organic chemical vapour deposition; AACVD, aerosol assisted chemical vapour deposition.

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## 1. Introduction

Phosphine and arsine ligands have continued to play a major role in transition metal (d-block) coordination and organometallic chemistry over several decades, forming a wide range of complexes with different metal oxidation states [1–3], and transition metal phosphine complexes are also widely used in catalysis [4]. The weaker donor stibines have a more restricted chemistry and relatively few bismuthine complexes are known [5]. These Group 15 neutral donor ligands are described in standard texts as  $\pi$ -acids or  $\sigma$ -donor  $\pi$ -acceptor ligands, which bond to d-block metals by  $\sigma$ -donation of the lone pair on the pnictogen (E) centre, supplemented in many cases by  $\pi$ -acceptance of d-electron density into E–C  $\sigma^*$ - (or a combination of E–C  $\sigma^*$ - and empty E d-) orbitals. The relative importance of the  $\sigma$  and  $\pi$  components varies with the metal oxidation state and d-electron density [6]. Main group elements also form complexes with phosphines and arsines, and more rarely with stibines, although these have received much less research effort than the d-block analogues, and have fundamentally different properties. This article reviews recent research on the synthesis and properties of phosphine, arsine and stibine complexes of the s- and p-block metals, metalloids and non-metals, specifically complexes of Groups 2, 12, 13, 14, 15 and 16 elements. The area has been reviewed twice before [7,8], the last article having been published in 1995, and thus we will concentrate on work published in the last 20 years, although the fragmented nature of the field necessitates some reference to older work. Group 12 complexes have sometimes been included in reviews of transition metal phosphines [9] and refs therein. Phosphine boranes have been reviewed twice in the recent past [10,11] and thus are not included in the present article. A number of weak adducts between  $\text{PH}_3$  or  $\text{PMe}_3$  and p-block Lewis acids formed at low temperatures and characterised using matrix isolation techniques have been discussed in a very recent comprehensive review of the field [12].

The present article describes the complexes of mono-, bi- and multi-dentate phosphine, arsine, stibine and bismuthine ligands, and includes examples (but not exhaustive coverage) of hybrid ligands where other donors, mostly neutral or charged O-, N- or S-groups are incorporated in the ligand. Coverage here is focused on complexes of interest from the point of view of the pnictogen ligand. Charged pnictogen ligands such as phosphides, arsenides, phosphinomethanides etc. are not included in this article. Literature coverage is on work published up to early 2013.

## 2. Bonding

The traditional  $\sigma$ -donor  $\pi$ -acceptor bonding model [6] used for d-block metal phosphine complexes needs to be revised for p-block adducts. In the p-block the Lewis acid has ns and three np orbitals available for  $\sigma$  bonding, the filled  $(n-1)d$  orbitals are essentially core orbitals and unavailable for  $\pi$ -donation, and the nd orbitals are empty and too high in energy to make any significant contributions to bonding. Thus the Lewis acid-phosphine(arsine) bond must be based upon  $\sigma$ -donation alone (this is also true for  $d^0$  transition metal acceptors such as Ti(IV) or Nb(V) which form stable complexes with phosphine and arsine ligands). For compounds with four electron pair donor ligands ( $8e^-$  systems), the traditional model using either  $sp^3$  hybridisation or symmetry allowed MO's derived from the central atom ns and 3 np orbitals is adequate and this is used, for example, for four coordinate Cd(II) or Hg(II)

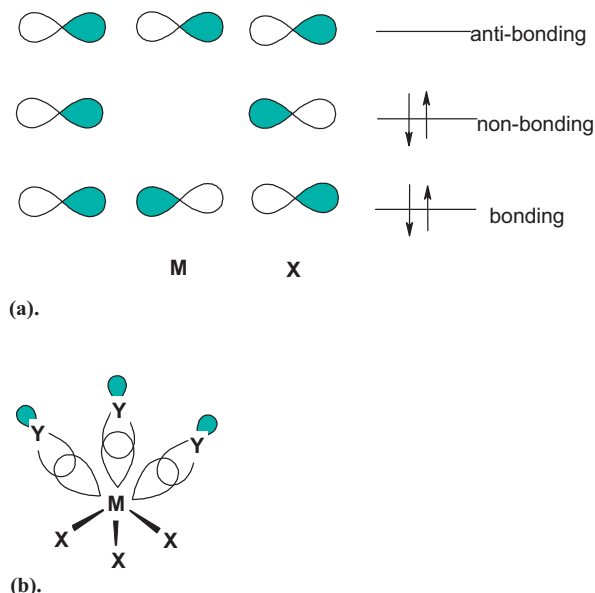


Fig. 1. (a) 3c–4e bonding model. (b) M–Y  $\sigma$ -bonding using M–X  $\sigma^*$  orbitals as acceptor orbitals.

adducts. However, the unavailability of d orbitals for bonding raises problems when the central atom exceeds an octet of electrons in its valence shell. This *hypervalency* is common in p-block chemistry and requires a different bonding model. The popular model currently used to describe such bonding is the 3c–4e bond [13–18].

For a linear X–M–X unit, the central M uses one empty np orbital, and combining this with one filled donor orbital on each X results in three molecular orbitals: bonding, non-bonding and anti-bonding (in order of increasing energy). The two donor electron pairs are then placed in the first two MOs (Fig. 1(a)). For an octahedron this model uses three orthogonal p orbitals on M to form three 3c–4e bonds. When the groups around the central M are different (X–M–Y), the model describes an M–X bond with the bonding orbital polarised towards X, and the M–X antibonding orbital ( $\sigma^*$ ) polarised towards M. The M–X  $\sigma^*$  orbital is empty and can therefore act as an acceptor orbital towards an electron pair from Y (Fig. 1(b)). If the X–M bonding dominates (primary bond) and M–Y is weak the latter is often termed “secondary bonding”.

It is also possible to use a mixture of the models. For example, for a trigonal bipyramid,  $sp^2$  hybrid orbitals can be used for the equatorial  $\text{MX}_3$  donors (conventional 2c–2e bonding), while the  $p_z$  orbital is used for the axial X–M–X unit (3c–4e). However, for cases where the coordination number of the central atom exceeds six, which is the case in many crown ether complexes for example, problems of insufficient orbitals for covalent bonding remain, and currently such high coordination numbers lack a generally satisfactory detailed model.

A second issue in main group chemistry is that of lone pairs, which arise when the p-block element is in its  $(n-2)$  oxidation state, e.g. As(III) or Ge(II). The “extra” electron pair may be stereochemically active whereby it occupies one of the central element’s “bonding” orbitals, or it may be stereochemically inactive, in which case it is assumed to occupy the spherically symmetric ns orbital (which is then unavailable for bonding to ligands). Similarly in the 3c–4e bonding model, a stereochemically active lone pair occupies

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