

Acceptor Properties of Triphenyl Derivatives of Group V

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TERVALENT phosphorus and arsenic compounds behave as σ -donors to protons and other electron acceptors, and their π -acceptor properties contribute to the stability of complexes formed with

certain transition metals. These synergic bonding effects are also important in mechanisms involving oxygen transfer from dimethyl sulphoxide to tervalent phosphorus compounds.¹ Holmes has

reported association between trimethylamine and phosphorus trihalides,² which presumably involves nitrogen \rightarrow halogen³ or nitrogen \rightarrow phosphorus bonding.

Investigations of compound formation between hexamethylbenzene, a typical strong π -donor, and triphenyl derivatives of the Group V elements, using phase-diagram techniques, are reported here. Solid 1:1 complexes are formed with triphenylphosphine, triphenylarsine, and triphenylstibine, but not with triphenylamine (see Table), and there is no indication of a complex with triphenylbismuth. Compound formation is consistent with donation of electrons from hexamethylbenzene to vacant orbitals of the central atom. Nitrogen has no d -orbitals available, bismuth rarely uses them.

Binary mixtures of hexamethylbenzene with triphenylphosphine oxide and triphenylphosphine sulphide, in which the lone-pair of electrons is replaced by oxo- and thiono-groups respectively, have also been investigated. Hexamethylbenzene

forms a 2:1 complex with triphenylphosphine oxide, but no complex is formed with triphenylphosphine sulphide under similar conditions (see Table). This behaviour is in general agreement with that expected from the contraction of the d -orbitals of Group V elements and the increase in acceptor power caused by electron-withdrawing substituents.

TABLE

Complexes of hexamethylbenzene

				Complex	M.p. °C.
NPh ₃	—	—
PPh ₃	1:1	145
AsPh ₃	1:1	144
SbPh ₃	1:1	137
BiPh ₃	—	—
Ph ₃ PO	2:1	154
Ph ₃ PS	—	—

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¹ E. H. Amonoo-Neizer, S. K. Ray, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1965, 4296.

² R. R. Holmes, *J. Phys. Chem.*, 1960, **64**, 1295; *J. Amer. Chem. Soc.*, 1960, **82**, 5285.

³ O. Hassel and C. Rømming, *Quart. Rev.*, 1962, **16**, 1; S. K. Das, R. A. Shaw, and B. C. Smith, *Chem. Comm.*, 1965, 176.