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Neutral Hexacoordinate Phosphorus(V) Compounds Containing Tridentate Dianionic Ligands Obtained from Salicylideneamines, 2,2'-Azodiphenol and a Thio(Diphenol)

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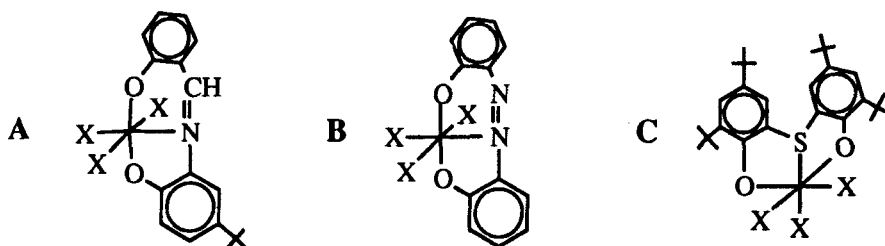
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NEUTRAL HEXACOORDINATE PHOSPHORUS(V) COMPOUNDS CONTAINING TRIDENTATE DIANIONIC LIGANDS OBTAINED FROM SALICYLIDENEAMINES, 2,2'-AZODIPHENOL AND A THIO(DIPHENOL).

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Neutral hexacoordinate phosphorus(V) compounds of a number of univalent bidentate ligands are known.^{1,2} The silylated forms of tridentate, dianionic Schiff base ligands: *N*-(2-hydroxyphenyl)salicylideneamine H_2L^I , *N*-(4-*tert*-butyl-2-hydroxyphenyl)salicylideneamine H_2L^{II} , *N*-(2-hydroxy-4-nitrophenyl)salicylidene-amine H_2L^{III} , and 2,2'-azodiphenol H_2L^{IV} gave, with halogeno- and (trifluoromethyl)halogenophosphoranes, neutral hexa-coordinate derivatives with bis-chelate structures. The ligands form bicyclic five- and six-membered chelate rings in a meridional conformation, with two P-O bonds and one N→P donor bond. Hexacoordinate structures were evidenced by high-field ^{31}P NMR chemical shifts (-136 to -148 ppm), characteristic J_{PF} coupling patterns and was further substantiated by crystal structures of Cl_3PL^{II} (A) and F_3PL^{IV} (B).



NMR spectra of $(CF_3)_2F_2PL^I$ show exclusive *cis* conformation in solution but $(CF_3)_2F_2PL^{IV}$ formed an approximate 1:1 ratio of *cis:trans* isomers. The sulfur ligand, 2,2'-thiobis(4,6-ditertbutylphenol), H_2L^V , formed a *fac* bis-chelate, Cl_3PL^V (structure C), with a relatively short P-S bond (2.331(1) Å). A similar structure, reported by Holmes *et al.*³ for a derivative of the same ligand, has a longer P-S bond.

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