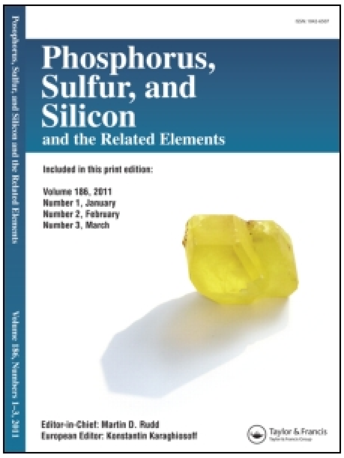

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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

Ronald G. Cavell[a]; Chih Y. Wong[a]; Robert McDonald[a]
[a] Department of Chemistry, University of Albena, Edmonton, AB, Canada

To cite this Article Cavell, Ronald G. , Wong, Chih Y. and McDonald, Robert(1996) 'Neutral Hexacoordinate Phosphorus(V) Compounds Containing Tridentate Dianionic Ligands Obtained from Salicylideneamines, 2,2'-Azodiphenol and a Thio(Diphenol)', Phosphorus, Sulfur, and Silicon and the Related Elements, 111: 1, 151

To link to this Article: DOI: 10.1080/10426509608054780

URL: http://dx.doi.org/10.1080/10426509608054780

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 151
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Amsterdam B.V. Published in The Netherlands
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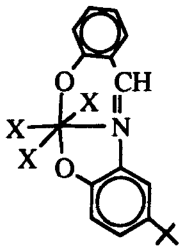
Publishers SA
Printed in Malaysia

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

RONALD G. CAVELL, CHIH Y. WONG AND ROBERT MCDONALD
Department of Chemistry, University of Alberta, Edmonton, AB,
Canada T6G 2G2

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**).

A


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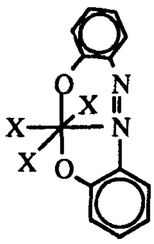
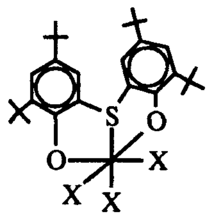


C


NMR spectra of $(CF_3)F_2PL^I$ show exclusive *cis* conformation in solution but $(CF_3)F_2PL^{IV}$ 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.

We thank the Natural Sciences and Engineering Research Council of Canada for support.

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