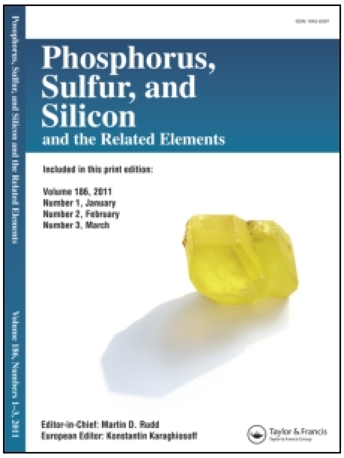

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Fluorinated Derivatives of 4-Phosphino- and 4-Iminophosphorano-2,5-Dimethyl-2*H*-1,2,3-Diazaphospholes and Their Metal Complexes

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FLUORINATED DERIVATIVES OF 4-PHOSPHINO- AND 4-IMINOPHOSPHORANO-2,5-DIMETHYL-2*H*-1,2,3-DIAZAPHOSPHOLES AND THEIR METAL COMPLEXES

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Although there has been considerable interest in the chemistry and metal complexation of low coordinate phosphines, there are very few examples of bisphosphine systems where both phosphorus atoms are trivalent and only one of the centers is two-coordinate[1,2]. An example of such a system is the 4-phosphino-2,5-dimethyl-1,2,3-diazaphosphole obtained from acetone methylhydrazone and phosphorus trichloride[3]. This bisphosphine contains a two-coordinate endocyclic phosphorus and a three-coordinate exo phosphorus center. The exo phosphorus preferentially coordinates to metals but under certain conditions the two-coordinate phosphorus will also coordinate[4].

The reaction of 4-dichlorophosphino-2,5-dimethyl-1,2,3-diazaphosphole in acetonitrile with sodium fluoride in the presence of 15-crown-5 ether gave the 4-difluorophosphino derivative. The analogous fluoroalcohol derivatives, dimethyldiazaphosphole-PE_2 ($E = OCH_2CF_3$, OC_6F_5, and $OCH_2C_6F_5$) were obtained from the reaction of the fluorinated alcohol in diethyl ether in the presence of triethylamine acting as base. The oxidation of the exo phosphorus to iminophosphorano derivatives of these phospholes was achieved with the usual Staudinger azide reaction. These oxidized phosphorus centers showed large upfield ^{31}P NMR shifts with a shift of over 200 ppm in the case of the 4-{difluoro(*p*-cyanotetrafluoro-phenyl)iminophosphorano}diazaphosphole. These iminophosphorano-phospholes may act as bidentate as well as monodentate ligands with metal complexes. The 4-phosphinophospholes however typically act as mono-dentate ligands toward $Mo(CO)_4$, Cp*Rh, $PtCl_2$, and $PdCl_2$ with the 4-phosphino group coordinated to the metal.

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REFERENCES:

1. M. REGITZ, O.J. SCHERER, (Eds.) *Multiple Bonds and Low Coordination in Phosphorus Chemistry,* Thieme Verlag, Stuttgart, p. 149-286 (1990).
2. J.F. NIXON, Chem. Rev.*88*, 1327 (1988).
3. J. LUBER, A. SCHMIDPETER, *J. Chem. Soc., Chem. Commun.* 887.(1976).
4. J.H. WEINMAIER, G. BRUNNHUBER, A. SCHMIDPETER, *Chem. Ber.* (1980), *113*, 1178.