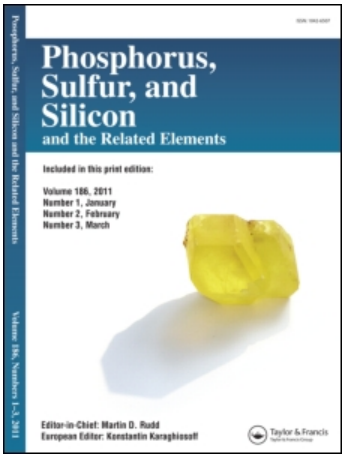

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Electrophilic Substitutions on Tris(Pyridyl)Phosphine

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ELECTROPHILIC SUBSTITUTIONS ON TRIS(PYRIDYL)PHOSPHINE

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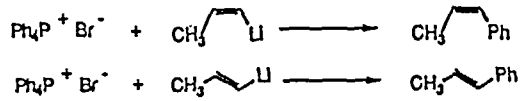
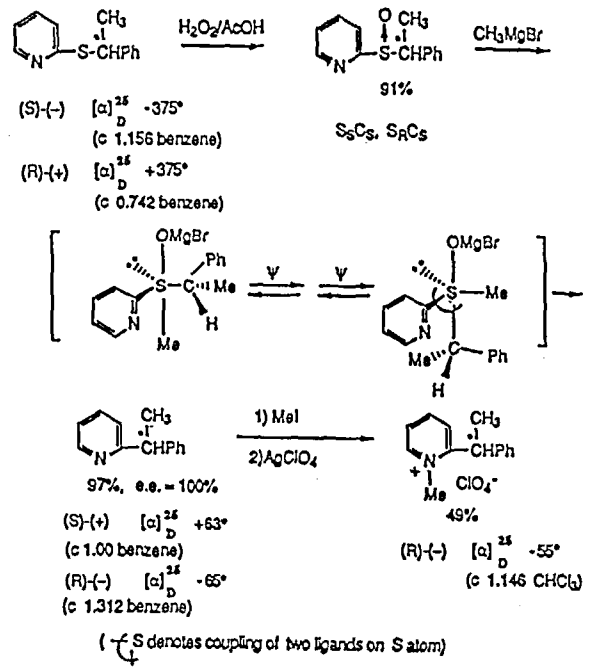
Eversince Seyferth ran the very odd reaction which he dit not add any word, this has remained as the first example of stereochemistry of phosphorus atom centered ligand coupling reaction in the hypervalent species and the reaction is the following.(1)



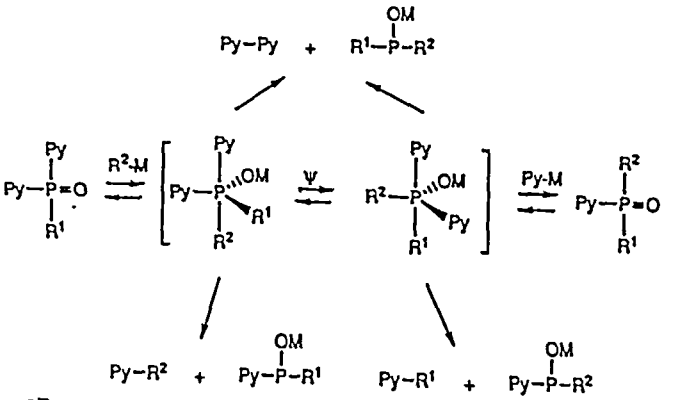
The yield of the reactions are good while the stereochemistry in both cases are nearly 100 %. This means that the coupling between an apical and an eqatorial ligands is both intramolecular and concerted, as in the case of the sulfur species which we have shown earlier.(2)



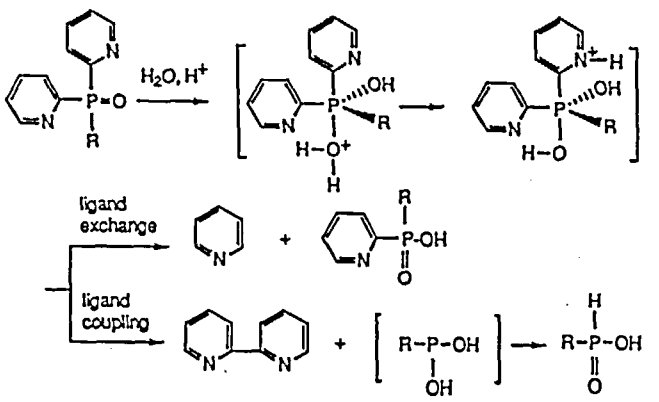
In the meantime, the M. O. calculation, performed on hypervalent chalcogen species has shown that there are certain amounts of interactions between the apical and the equatorial ligands.(3)

The early work of Hey and Ingold,(4) who claimed to have obtained hydrocarbons by coupling of alkyl groups by the treatment of quaternary phosphonium

salts with alkoxides was recently found to be wrong.(5) We have shown many examples of ligand coupling involving 2-pyridyl groups as shown below. (6, 7, 8, 9)

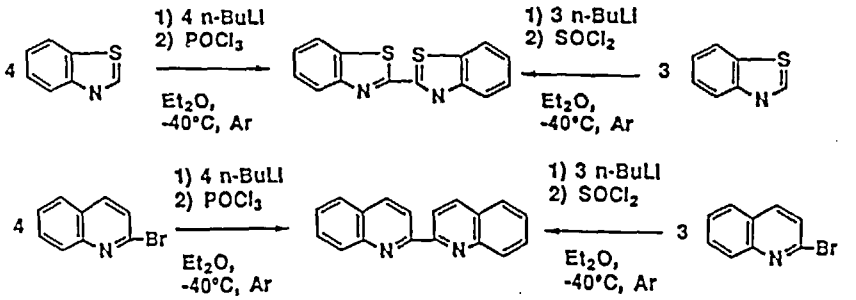


[a] Py = 2-pyridyl; R^1 = 2-pyridyl, Ph; R^2 = Me, Ph, $PhCH_2$, 4-$MeC_6H_4CH_2$; M = Li, MgX.

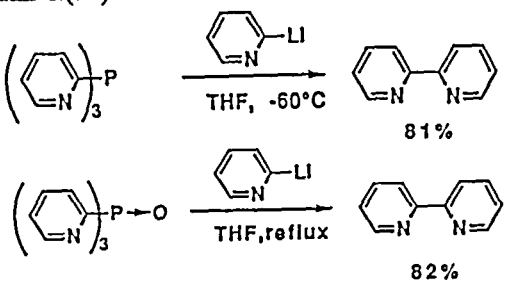


All these reactions are ligand couplings forming pentacoordinated phosphorus intermediates and do not require any alkaline condition(10) nor quaternay phosphorus compounds.

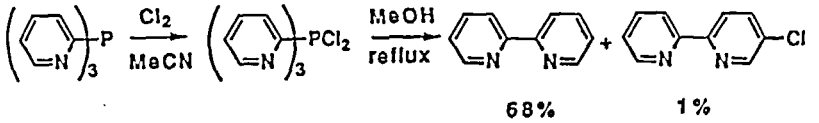
The uses of phosphorus trichloride, phosphorus oxychloride and thionyl chloride were found to undergo coupling reaction with the following heterocycles.(11)



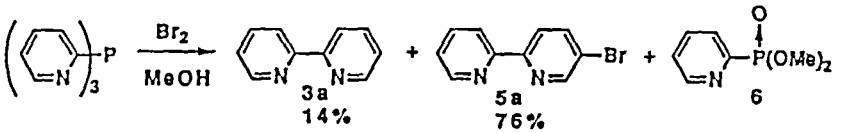
2-Pyridyllithium is known to react with either tris(2-pyridyl)phosphine or its oxide in the following manner.(12)



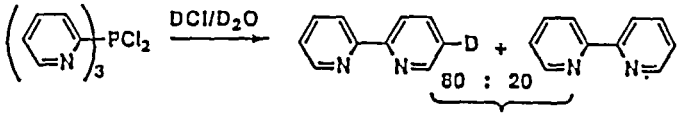
In the meantime, the following electrophic substution by chlorine was found to take place.(13)

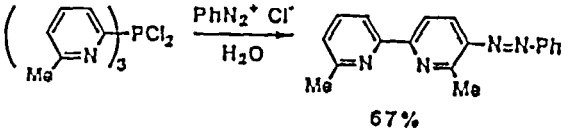


The use of methanol was found to be much more effctive and even bromine in methanol was quite effective in the electrophilic substitution. The normal ligand coupling was also observed to some extent.

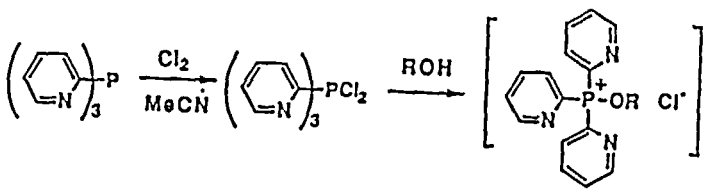


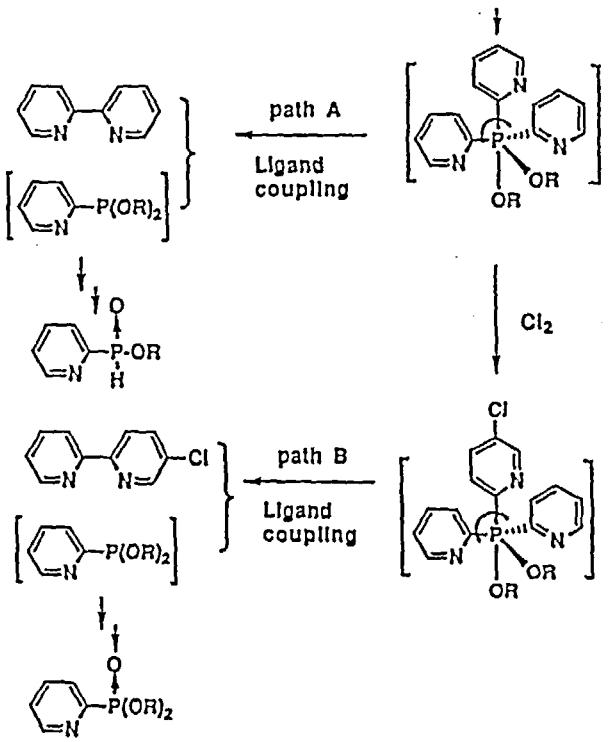
Not only halogenations, but also the deuteration and diazo-coupling reaction took place, as shown below.





The following is our tentative scheme of the path. In other words, the phosphorus atom in the hypervalent species is prone to an electrophilic substitution.





REFERENCES

(1) D. Seyferth, J. Fogel and J. K. Heeren, J. Am. Chem. Soc., 88 (1966) 2207.

(2) S. Oae, T. Kawai and N. Furukawa, Teterahedron Lett, 25 (1984) 69; S. Oae, T. Kawai, N. Furukawa and F. Iwasaki, J. Chem. Soc., Perkin Trans. 2, (1987) 405.

(3) J. Moe, A. E. Dorigo and K. Morokuma, Chem. Phys. Lett., 204 (1993) 65.

(4) L. Hey and C. K. Ingold, J. Chem. Soc. 1933, 531.

(5) Y. Uchida and S. Oae, unpublished.

(6) Y. Uchida, K. Onoue, N. Tada, F. Nagao and S. Oae, Tetrahedron Lett. 30, (1998) 567.

(7) Y. Uchida, H. Kozawa and S. Oae, Tetrahedron Lett., 30 (1989) 6365: Y. Uchida, Y. Takaya and S. Oae, Heterocycles 30 (1990) 347.

(8) Y. Uchida, K. Onoue, N. Tada, F. Nagao, H. Kozawa and S. Oae, Heteroatom Chem., 1 (1990) 295.

(9) S. Oae and Y. Uchida, Acc. Chem. Res., 24 (1991), 202.

(10) G. R. Newkome and D. C. Hager, J. Am. Chem. Soc., 100 (1978) 5567.

(11) Y. Uchida, N. Echikawa and S. Oae, Heteroatom Chem. 5 (1994) 409.

(12) Y. Uchida, M. Kawai, H. Masauji and S. Oae, Heteroatom Chem.4 (1993) 421.

(13) Y. Uchida, R. Kajita, Y. Kawasaki and S. Oae, Phosphorus,Sulfur and Silicon, 93(1-4) & 94(1-4) (1994) 403.