

This article was downloaded by:

On: 29 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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>

Electrophilic Substitutions on Tris(Pyridyl)Phosphine

Yuzuru Uchida; Shigeru Oae

To cite this Article Uchida, Yuzuru and Oae, Shigeru(1996) 'Electrophilic Substitutions on Tris(Pyridyl)Phosphine', Phosphorus, Sulfur, and Silicon and the Related Elements, 109: 1, 605 – 608

To link to this Article: DOI: 10.1080/10426509608545226

URL: <http://dx.doi.org/10.1080/10426509608545226>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

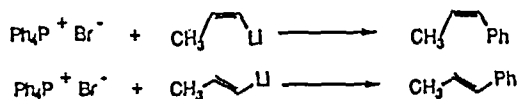
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

ELECTROPHILIC SUBSTITUTIONS ON TRIS(PYRIDYL)PHOSPHINE

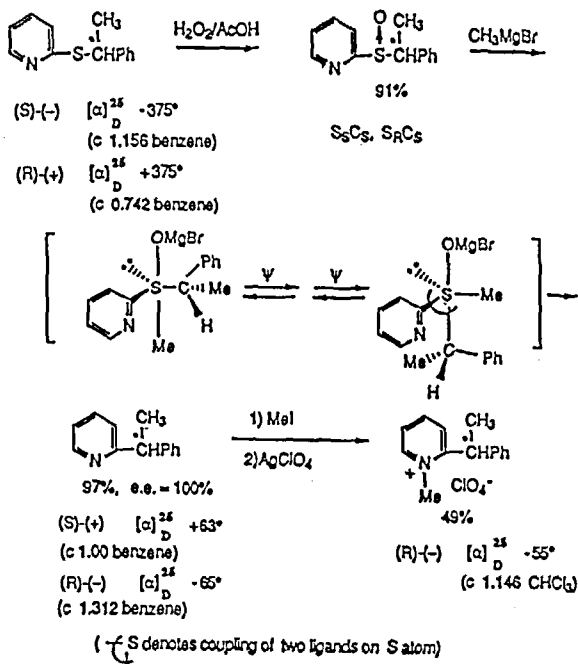
Yuzuru Uchida, Department of Applied Chemistry, Osaka Institute of Technology, Osaka 535 and

Shigeru Oae, Institute of Heteroatom Chemistry, 2509 Hirao Minami-kawachi-gun, Osaka-fu 587 Japan.

Eversince Seyferth ran the very odd reaction which he did 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)



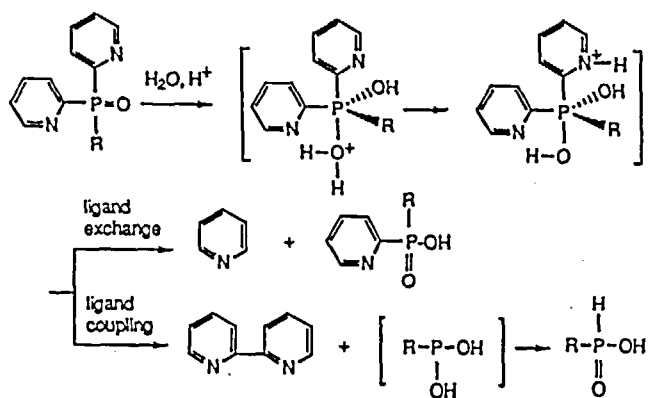
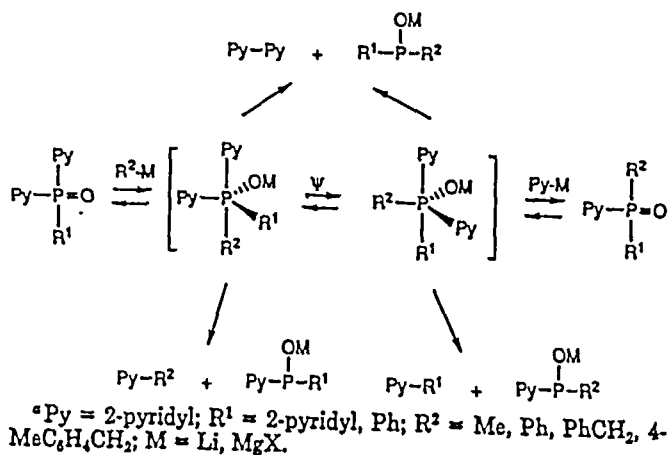
The yield of the reactions are good while the stereochemistry in both cases are nearly 100 %. This means that the coupling between an apical and an equatorial ligands is both intramolecular and concerted, as in the case of the sulfur species which we have shown earlier.(2)



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)

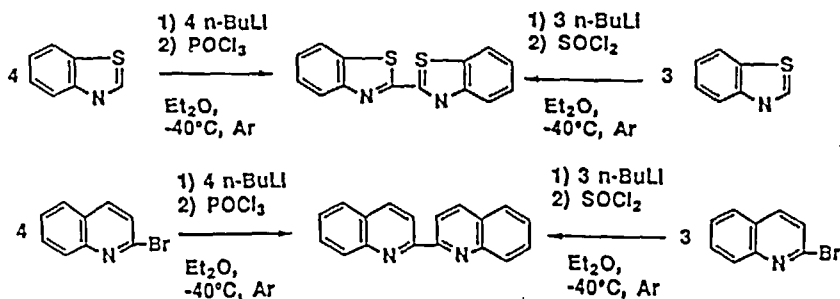
The early work of Hey and Ingold,(4) who claimed to have obtained hydrocarbons by coupling of alkyl groups by the treatment of quaternary phosphonium

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)

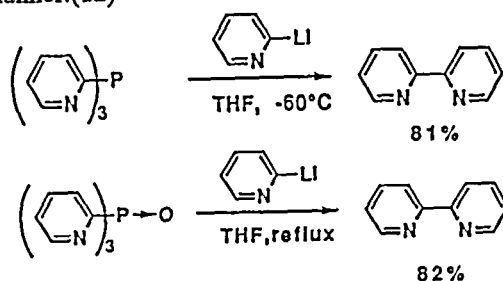


All these reactions are ligand couplings forming pentacoordinated phosphorus intermediates and do not require any alkaline condition(10) nor quaternary phosphorus compounds.

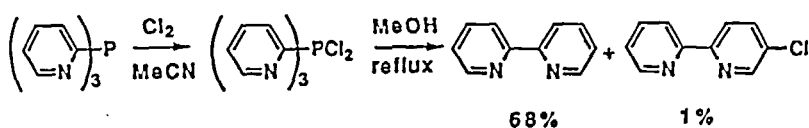
The uses of phosphorus trichloride, phosphorus oxychloride and thionyl chloride were found to undergo coupling reaction with the following heterocycles.(11)



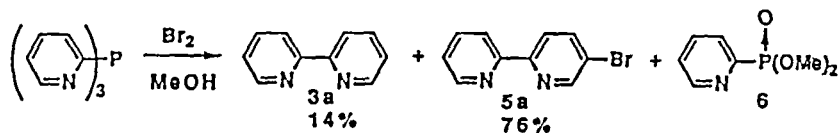
2-Pyridyllithium is known to react with either tris(2-pyridyl)phosphine or its oxide in the following manner.(12)



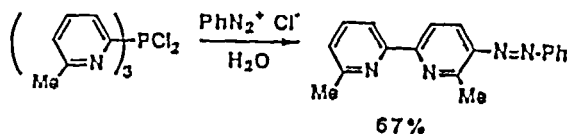
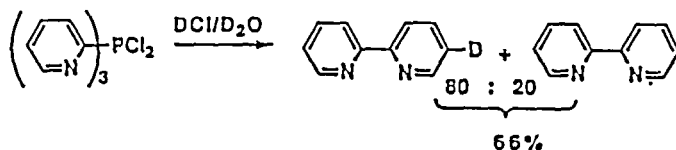
In the meantime, the following electrophilic substitution by chlorine was found to take place.(13)



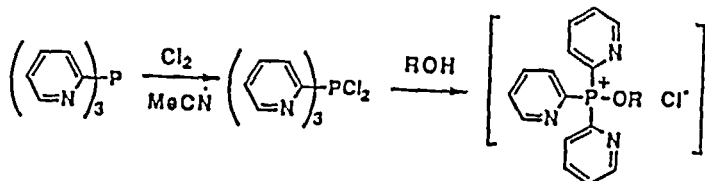
The use of methanol was found to be much more effective and even bromine in methanol was quite effective in the electrophilic substitution. The normal ligand coupling was also observed to some extent.

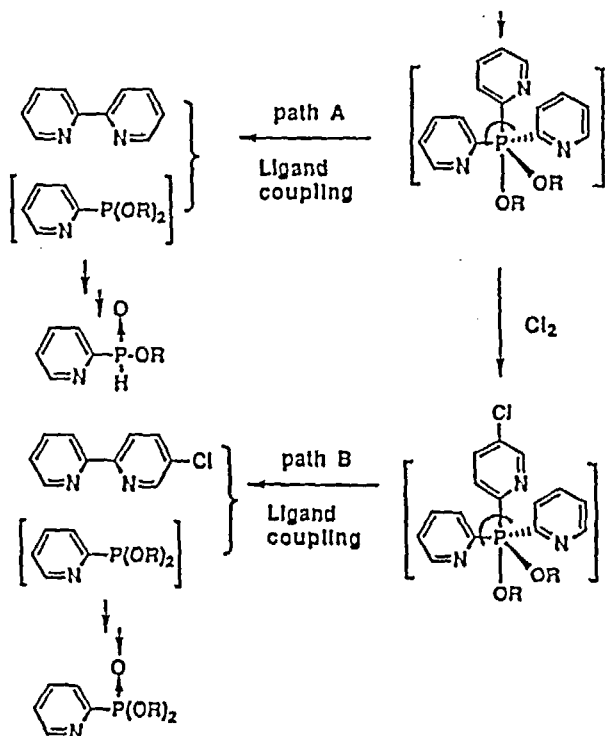


Not only halogenations, but also the deuteration and diazo-coupling reaction took place, as shown below.



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, *Tetrahedron 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.