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

The Mechanism of Reactive Group Exchange at Tri-Coordinate Phosphorus Centre

M. Cypryk^a; J. Chojnowski^a; W. Fortuniak^a

^a Centre of Molecular and Macromolecular Studies of the Polish Academy of Sciences, Lódź, Poland

To cite this Article Cypryk, M., Chojnowski, J. and Fortuniak, W.(1990) 'The Mechanism of Reactive Group Exchange at Tri-Coordinate Phosphorus Centre', Phosphorus, Sulfur, and Silicon and the Related Elements, 51: 1, 305

To link to this Article: DOI: 10.1080/10426509008040839 URL: http://dx.doi.org/10.1080/10426509008040839

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.

THE MECHANISM OF REACTIVE GROUP EXCHANGE AT TRI-COORDINATE PHOSPHORUS CENTRE

M.CYPRYK, J.CHOJNOWSKI, and W.FORTUNIAK Centre of Molecular and Macromolecular Studies of the Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lódź, Poland

Compounds of tricoordinate phosphorus are well known to have the ability to exchange some reactive groups bound to the P(III) centre (scheme 1) or they may exchange reactive groups in result of the interaction with compounds of other heteroatoms like silicon (scheme 2)

$$R_{1}'R_{2}'PX + R_{1}'R_{2}'PY \Longrightarrow R_{1}'R_{2}'PY + R_{1}'R_{2}'PX$$
 (1)

$$R_1$$
, R_2 , R_1 , R_2 = Alk, Ar, OAlk, OAr, NAlk₂

Particularly remarkable reactivity and often amazingly high selectivity are exhibited by systems involving R_1 and R_2 substituents increasing nucleophilicity of the phosphorus centre like dialkylamine groups. It was shown that in these systems ionic complexes are formed (scheme 3,4) which are stable on the NMR time scale at low temperatures. Variant temperature ^{31}P and ^{29}Si NMR studies of these complexes proved that they are true intermediates in the ligand exchange processes.

$$R_1 R_2 PX + R_1 R_2 PY = [R_1 R_2 XP - PR_1 R_2]^{+Y^{-}}$$
 (3)

$$R_1 R_2 PX + R \equiv SiY \Longrightarrow [R_1 R_2 XP \longrightarrow Si \equiv]^+ Y^-$$
 (4)

The mechanism of the decomposition of these intermediates to the exchange products is discussed.