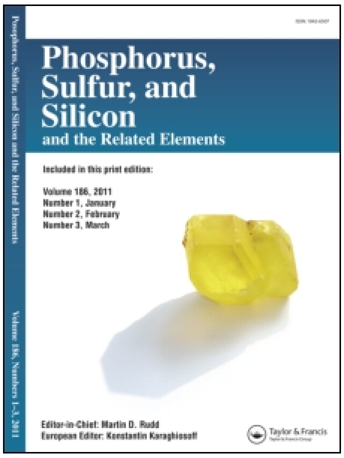

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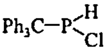
The Triphenylmethyl Group- a Kinetically Stabilizing Substituent and Protecting Group in Organophosphorus Chemistry

VOLKER PLACK and REINHARD SCHMUTZLER

Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D- 38023 Braunschweig, Germany

The introduction of sterically demanding substituents at phosphorus leads to the protection of reactive centres, and consequently to the kinetic stabilization of molecules. Yoshifuji has demonstrated such possibilities, by using the 2,4,6-tri-t-butylphenyl substituent [1]. Although the dichlorophosphine Ph_3CPCl_2 was already described in 1933 [2], this principle has now been extended to numerous other systems containing the triphenylmethyl (Ph_3C) group as a substituent at phosphorus, and the stable compounds, e.g. **1**- **6** [3],



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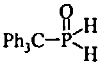

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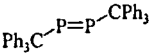

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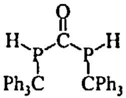

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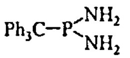

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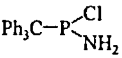

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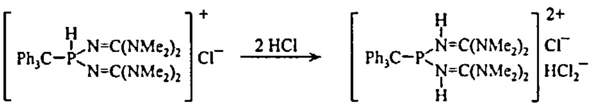
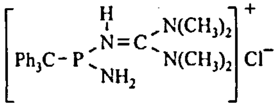
serve to illustrate the possibilities (Eq. 1).



7 **8** (1)

The use of the tetramethylguanidine substituent at phosphorus [4] furnished the first $\sigma^3\lambda^3$-phosphorus-containing ammonium salts; the stability of **8** was sufficient to permit a single X-ray structure determination [5].

Also, in the precursors of compounds 9 and 10, the imino nitrogen atoms were found to be the nucleophilic centres, and treatment with HCl led to stable ammonium salts in which the amino group (9) and the P-P-bond (10) were protected against attack by HCl [3].



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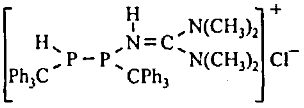

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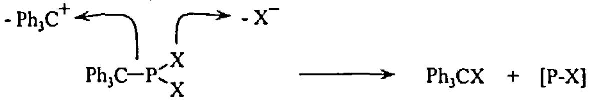
The efficient charge delocalization in species such as Ph_3C^- and Ph_3C^+ is reflected in the reactivity of the appropriately substituted $\sigma^3\lambda^3$ phosphorus compounds towards both nucleophiles and electrophiles. Also, it may explain the instability of the primary phosphine Ph_3CPH_2 [6] and the stability of the corresponding halogenophosphines at room temperature (Eq. 2).



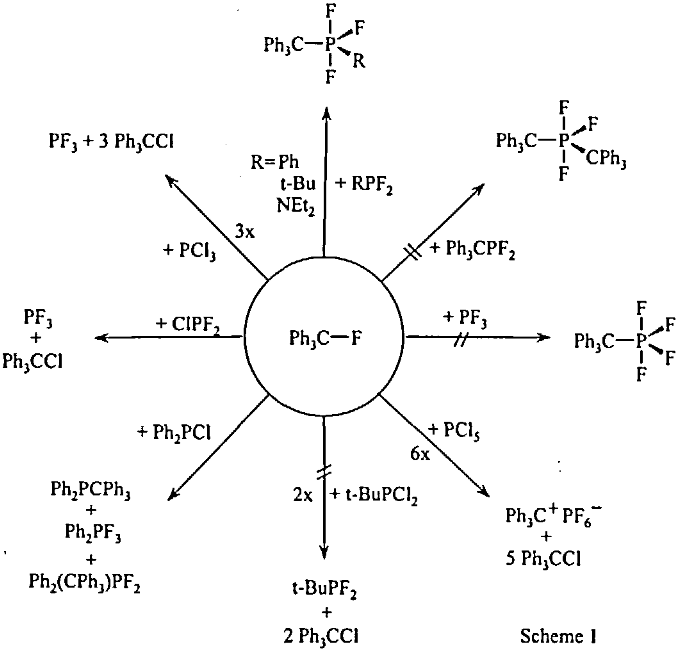
(2)

stable			unstable
Ph_3CPF_2	Ph_3CPCl_2	Ph_3CPBr_2	Ph_3CPI_2
Ph_3CPHF	Ph_3CPHCl	Ph_3CPHBr	Ph_3CPHI

Phosphonium compounds of the type $[Ph_3CPR_{3-n}Cl_n]^+Cl^-$ (R= hydrocarbon group or halogen atom) are stable only for n = 0, whereas for values of n > 0 spontaneous loss of Ph_3CCl with formation of $PR_{3-n}Cl_n$ is observed. This synthetic principle permits the use of the triphenylmethyl group as a protecting group in organophosphorus chemistry (Eq. 3) [7].

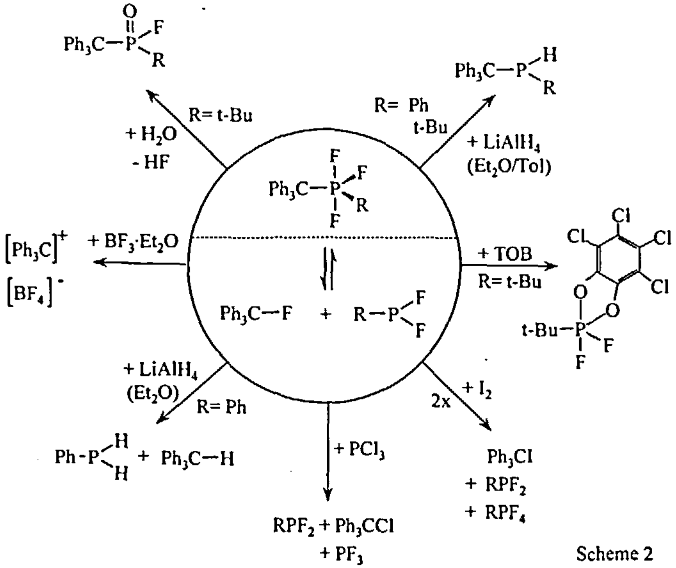
$$Ph_3CPF_2 + PCl_5 \longrightarrow Ph_3CCl + ClPF_2 \qquad (3)$$

Ph_3CF acts as a fluorinating agent towards chlorophosphines and chlorophosphoranes [7], whereas treatment with organodifluorophosphines RPF_2 leads to the stable trifluorophosphoranes ($Ph_3C(R)PF_3$) (Scheme 1).



Scheme 1

The bond parameters of the solid trifluorophosphoranes with R= t-Bu, Ph and NEt_2 were obtained, for the first time, by X-ray diffraction [8]. The reactivity of these compounds is illustrated by the equilibrium shown in Scheme 2.



Scheme 2

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