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

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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 Ph₃CPCl₂ was already described in 1933 [2], this principle has now been extended to numerous other systems containing the triphenylmethyl (Ph₃C) group as a substituent at phosphorus, and the stable compounds, e.g. 1-6 [3],

serve to illustrate the possibilities (Eq. 1).

$$\begin{bmatrix} H \\ Ph_3C - P < N = C(NMe_2)_2 \\ N = C(NMe_2)_2 \end{bmatrix} Cl^{-} \xrightarrow{2 \text{ HCl}} \begin{bmatrix} H \\ Ph_3C - P < N = C(NMe_2)_2 \\ H \end{bmatrix} Cl^{-} \xrightarrow{R} \begin{bmatrix} Ph_3C - P < N = C(NMe_2)_2 \\ H \end{bmatrix} Cl^{-}$$
(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 HCI led to stable ammonium salts in which the amino group (9) and the P-P-bond (10) were protected against attack by HCI [3].

$$\begin{bmatrix} P_{h_3C-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix} P_{h_3C} > P_{-P} < N(CH_3)_2 \\ N(CH_3)_2 \end{bmatrix}^+ C \begin{bmatrix}$$

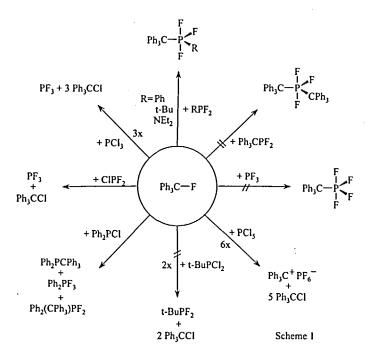
The efficient charge delocalization in species such as Ph_3C^- and Ph_3C^+ is reflected in the reactivity of the appropriately substituted $\sigma^3\lambda^3$ phosphorus compounds towards both nucleophiles and electrophiles. Also, it may explain the instability of the primary phosphine Ph_3CPH_2 [6]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

Phosphonium compounds of the type $[Ph_3CPR_{3-n}CI_n]^*CI^-$ (R= hydrocarbon group or halogen atom) are stable only for n = 0, whereas for values of n > 0 spontaneous loss

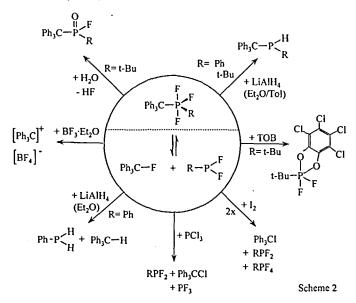
of Ph₃CCl with formation of PR_{3-a}Cl_a is observed. This synthetic principle permits the use of the triphenylmethyl group as a protecting group in organophosphorus chemistry (Eq. 3) [7].

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

Ph₃CF acts as a fluorinating agent towards chlorophosphines and chlorophosphoranes [7], whereas treatment with organodifluorophosphines RPF₂ leads to the stable trifluorophosphoranes (Ph₃C(R)PF₃) (Scheme 1).



The bond parameters of the solid trifluorophosphoranes with R= t-Bu, Ph and NEt₂ 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.



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