Evidence for Surface Phosphinidene Intermediates [RP $\rightarrow$ Mg] in the Heterogeneous Dechlorination of Alkyldichlorophosphanes $RPCl_2$ by Mg Metal[1]

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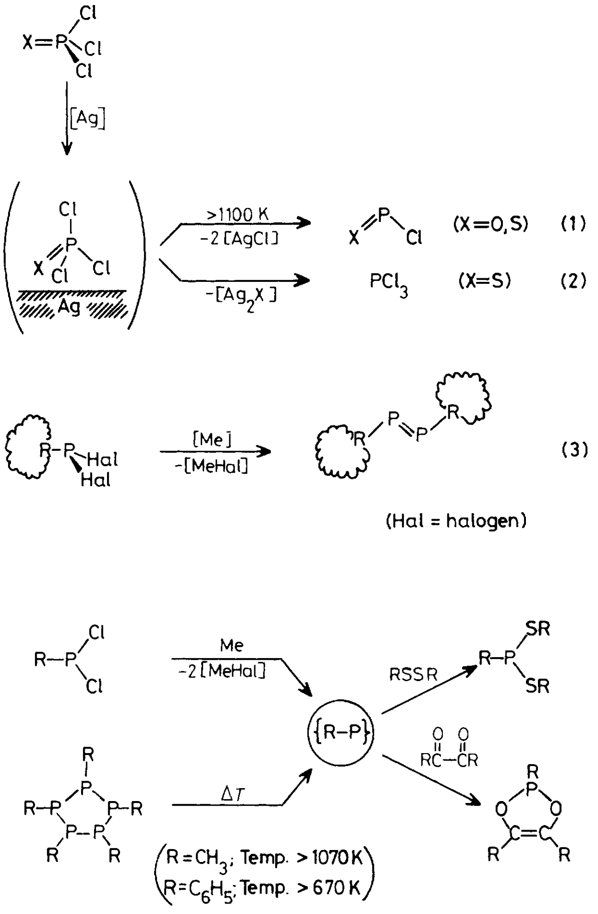
The heterogeneous dechlorination of alkyldichlorophosphanes by Mg metal at 600 K yields chemidesorbed products which include penta-alkylcyclopentaphosphanes $(RP)_5$, in addition to R_nPH_{3-n}, $R_2P–PR_2$, P_4, RH, and R–R, and thus provides evidence for surface phosphinidene intermediates [RP $\rightarrow$ Mg].

In recent years, heterogeneous dehalogenation of a variety of phosphorus compounds with geminal halogens (Hal) has made numerous unsaturated molecules containing phosphorus centres of low co-ordination number accessible [*e.g.* equations (1)—(3)].[2,3] In contrast to the dechlorination of $OPCl_3$ [equation (1)], which is based on the thermal instability of $[Ag_2O]$ above 620 K, and therefore exclusively yields OPCl, the reaction of $SPCl_3$ due to the higher decomposition temperature of $[Ag_2S]$, produces a mixture of SPCl and PCl_3 [equation (2)].[2] Whereas there is a lack of analogous evidence for a chemisorbed surface intermediate in the synthesis of kinetically stabilised diphosphenes RP=PR in solution,[3] the suspected phosphinidene intermediates RP, generated *e.g.* by $RPHal_2$ dehalogenation or by $(RP)_5$ pyrolysis can be either traced mass spectroscopically or trapped *e.g.* with disulphides or α,β-diketones[4] (Scheme 1). According to *ab initio* calcula-



Scheme 1

tions,[5] the triplet ground state $^3(H_3C–P)$ is expected to be stabilised by 138 kJ mol^{-1} relative to the excited singlet state $^1(H_3C–P)$.

In an attempt to generate the still unknown $H_3CP{=}PCH_3$ under nearly unimolecular gas-phase conditions, we have passed a stream of $H_3C–PCl_2$ over Mg powder under photoelectron spectroscopic (PES) real-time gas analysis.[6] The reaction takes place in the rather narrow temperature range between 570 and 620 K and yields a product mixture (Figure 1), from which $P(CH_3)_3$, CH_4, $(H_3C)_2P–P(CH_3)_2$, and $(PCH_3)_5$ can be isolated by fractionation, using intense cooling traps fitted with bypasses, and identified either by their PES ionisation or mass fragmentation patterns (Figure 1).

The product distribution suggests an intermediate formation of chemisorbed phosphinidenes at the Mg metal surface (Scheme 2). The driving force is the thermodynamically favourable formation of $[MgCl_2]$. The presumably low activation barrier for H_3CP surface migration should allow oligomerisation, *e.g.* to the isolated and spectroscopically characterised pentamer $(H_3CP)_5$. The dissociation of $[H_3CP \rightarrow Mg]$ to a surface phosphide $[Mg_3P_2]$ and chemisorbed $[H_3C \rightarrow Mg]$ as indicated by the considerable amount of CH_4 observed, would be consistent with mechanistic studies for alkyl Grignard RMgHal formation[7] as well as with ultrahigh vacuum investigation results for the reaction of H_3CBr at Mg [001] surfaces.[8] It also would explain, *via* radical alkylation of $[H_3CP \rightarrow Mg]$ to $[(H_3C)_2P^{\bullet} \rightarrow Mg]$ and $[(H_3C)_3P \rightarrow Mg]$, how both $P(CH_3)_3$ and the dimer $(H_3C)_2P–P(CH_3)_2$ are formed as unequivocally identified products (Figure 1) in the heterogeneous reaction of H_3CPCl_2 at magnesium powder.

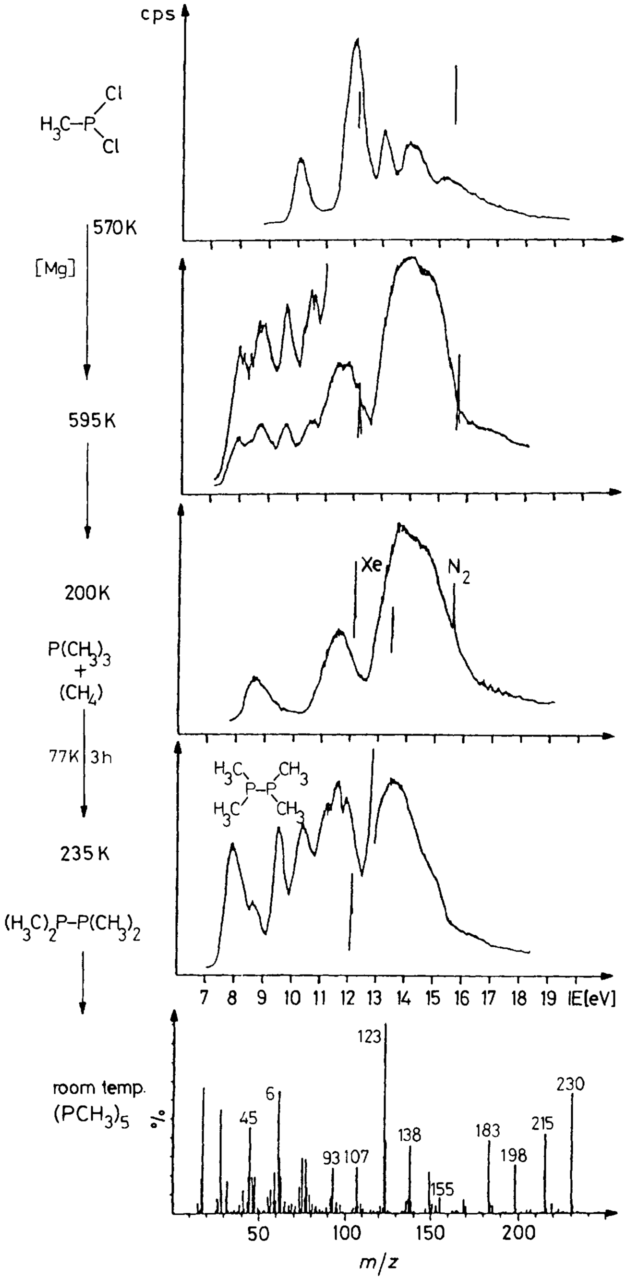
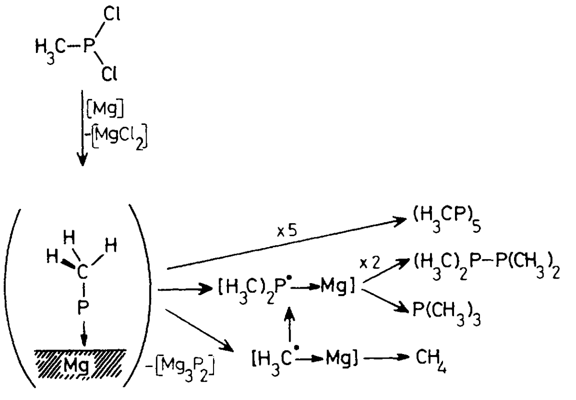


Figure 1. Reaction of gaseous H_3CPCl_2 with Mg in a flow reactor with intense cooling traps connected to a high vacuum line (HV) and the PE spectrometer, yielding a product mixture, from which after fractionation at the temperatures indicated, $P(CH_3)_3$, CH_4, $(H_3C)_2P–P(CH_3)_2$, and $(PCH_3)_5$ have been identified by the PES ionisation and mass fragmentation patterns shown.

The product mixture obtained analogously from ethyldichlorophosphane at 150 K higher temperature [equation (4)] suggests the following. The detection of n-butane as a $H_3CH_2C^{\bullet}$-dimer confirms the likely presence of $[H_3CH_2C^{\bullet} \rightarrow Mg]$ as a source also for H_3CCH_3 and $H_2C{=}CH_2$. The latter indicates [HP – – – Mg] as chemisorbed species, which in turn allows the rationalisation of the formation of $H_3CH_2CPH_2$, $(H_3CH_2C)_2PH$, and also of P_4. Again the oligomer $(H_3CH_2CP)_5$ can be isolated and identified mass spectroscopically.



Scheme 2

$$H_3CH_2CPCl_2 \xrightarrow[>720\,K]{[Mg]} \left\{ \begin{array}{l} H_3CH_2CPH_2 + (H_3CH_2C)_2PH + \\ (H_3CH_2C)_3P + (H_3CH_2P)_5 + P_4 + \\ H_2C{=}CH_2 + H_3CCH_3 + \\ H_3CH_2CCH_2CH_3 \end{array} \right. \qquad (4)$$

Iso(valence)electronic nitrenes on metal surfaces [RN → Me] can be generated more elegantly by catalytically splitting off thermodynamically favourable leaving groups like N_2 from alkyl azides $RN{-}N_2$ [9] or CO from alkyl isocyanates RNCO.[1,10] Depending on their alkyl substituents and the respective metal surface, various secondary reactions lead to chemidesorbed products such as $[(H_3C)_2HCN \rightarrow Ni] \rightarrow CH_4 + H_3CCN$[1,10] or $[(H_3C)_3CN \rightarrow Ni] \rightarrow (H_3C)_2C{=}CH_2 + NH_3 + N_2$,[10] *i.e.*, presumably involving a surface nitrene [HN → Ni], which disproportionates into NH_3 and N_2. Therefore, the above assumptions for [equation (4)], *i.e.* formation of $[H_3CH_2CP \rightarrow Mg]$, its ethene elimination to [HP → Mg] and the disproportionation to elemental P_4 do have a close analogy at least, and it is hoped that our results will stimulate further research in surface phosphinidenes.

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