Spontaneous Dissociation of Phosphoniumylidyl-chlorophosphines to Ionic Phosphenium Chlorides

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Abstract The products from the replacement of two chlorofunctions of PCl₃ by a pair of phosphoniumylidyl substituents or by both a phosphoniumylidyl and an amino substituent are ionic phosphenium chlorides and not covalent chlorophosphines

The formal insertion of two methine units into a diaminophosphenium ion A^{1a} produces a 1,3diamino-2-phosphaallylic cation B^{1b} A 1,3 diphosphonio-2-phosphapropenide **D** may be derived from triphosphenium ion C^{1c} by the similar insertion of two methine centers. The central phosphorus atom of all four types of compounds may be regarded as ambiphilic with nucleophilic character predominating at the central P-atom in **B** and **C** and electrophilic character dominating at this P-atom in **A** and **D**, regardless of the net positive charge present in each of these species. Consequently the formal chain extension reactions $A \rightarrow B$ and $C \rightarrow D$ are accompanied by an inversion of the electronic character of the central P-atom. Thus, the following structure-reactivity correlation should exist for the central phosphorus atoms of **A**, **B**, **C** and **D**



This correlation has been confirmed^{1b,c} with known compounds of types A, B and C However, representative species of type D have not yet been reported², although they might be prepared from a phosphorus trihalide using a twofold substitution sequence with a phosphonium yhd

Phosphonium ylids have repeatedly been reacted with chlorophosphines³ Twice, to our knowledge, reactions of this type were performed with phosphorus trichloride, which resulted in either a mono-³¹ or a trisubstitution product^{3b} Neither of these products was fully characterized

Equal molar amounts of phosphorus trichloride and a benzyltriphenylphosphonium bromide 1 in dichloromethane solution in the presence of triethylamine undergo a smooth condensation reaction at room temperature (15 h) The resulting ylidyldichlorophosphines $3c_{,d,e}$ with R = aryl (Table 1) are readily soluble in non-polar solvents and are thus easily separated from the triethylammonium halides, also formed in these reactions. For this purpose the residue which remains following the evaporation of

the dichloromethane solvent is extracted eight times with toluene. From these combined extracts the solvent is evaporated and the crude product is recrystallized from a dichloromethane/benzene/petrol ether mixture.

Proceeding in the same way phosphorus trichloride can be condensed with two equivalents of 1 The desired reaction products in this case cannot be separated from the co-product triethylammonium halides since they are not soluble in non-polar solvents. This observation gave a first hint to the ionic nature of the reaction products. In fact, they are not bis(yhdyl)chlorophosphines 4 as expected but bis(yhdyl)phosphenium chlorides 5. The latter species are better obtained from phosphorus trichloride and two equivalents of a trimethylsilvlyhd 2^4 in benzene and precipitate in pure form from the reaction mixture. Besides 5c. R = Ph, alkyl derivatives 5a,b (Table 1) have also been prepared this way Reaction of phosphorus trichloride with one equivalent of 2 yields the alkyl derivatives 3a,b (Table 1). These species are not accessible using the base condensation employed for the aryl derivatives 3c,d,e. The trimethylsilyl derivative 3f, which is obtained in the same way, could not be converted to a disubstituted product 4/5. For the sake of simplicity, the ylid formulae are given without the use of formal charges



The ³¹P NMR spectra of compounds 5 represent AB₂ spin systems (Table 1) and the chemical shift of the A part to low-field confirms their phosphenium character Parallel to these chemical shift data $^{2}J_{PP}$ has decreased in value in comparison to that of **3** Furthermore the addition of aluminium chloride to the solution does not influence the ³¹P NMR spectra and thus demonstrates complete dissociation

In its absence An X-ray investigation of 5c confirms a lack of interaction of the phosphenium center and the chloride ions⁵ Compounds 5 are the first (acyclic⁶) ionic chlorophosphines i.e. the first phosphenium *chlorides* As suggested by the resonance formulae used above, the cationic charge will reside to a large extent at the terminal phosphorus atoms thus resembling a phosphonium charge rather than a phosphenium charge^{7,8}

In contrast to the spontaneous dissociation of the bis(ylidyl)chlorophosphines 4 to give cations of type **D** the formation of a diaminophosphenium ion **A** always necessitates the presence of a chloride ion acceptor^{1a} Compounds which resemble both **A** and **D** can be obtained from **3** by the substitution of one of its chloro functions by a secondary amine



The diethylamino derivative obtained from 3c, is not a covalent chlorophosphine 6 but an ionic phosphenium chloride 7 This is clearly indicated by a low field shift of the PCl₃-derived phosphorus and a small coupling constant ${}^{2}J_{PP}$ similar to those of 5 (Table 1) To effect the spontaneous dissociation of a chlorophosphine the presence of one ylidyl combined with one amino substituent is seen to provide ample driving force Tetrafluoroborate and tetraphenyloborate salts of cations of the same type have recently been described^{7b}

	R	Spin system	$\delta_A{}^a$	$\delta_{\mathbf{B}}{}^{\mathbf{b}}$	$J_{AB}[Hz]$
3a	Me	AB	191 1	23 5	215 9
3 b	Et	AB	$188 \ 6$	2 3 6	228 9
3c	Ph	AB	$170 \ 8$	20.6	228 9
3d	$3-\mathrm{MeC}_6\mathrm{H}_4$	AB	$171\ 7$	20~7	$227\ 4$
3e	$4\text{-NO}_2C_6H_4$	AB	164.6	$20\ 0$	224 3
3f	S_1Me_3	AB	$217\ 6$	22 3	224 3
5a	Me	AB_2	303 5	31 9	170 9
5b	Et	AB_2	295 5	$30\ 5$	16 9 4
5c	\mathbf{Ph}	AB_2	2910	$25\ 4$	$165 \ 3$
7c	Ph	AB	279 3	24 7	169 4

Table 1 ³¹P NMR Data of Compounds 3, 5 and 7 (in CD_2Cl_2)

* Phosphorus derived from PCl₃, ^b Ph₃P group

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References and Notes

- (a) M Sanchez, M -R Mazieres, L Lamandé and R Wolf in Multiple Bonds and Low Coordination in Phosphorus Chemistry, eds M Regitz and O J Scherer, Thieme, Stuttgart, 1990 p 129,
 (b) A Schmidpeter, ibid p 149, (c) A Schmidpeter, ibid p 346
- 2 Diphosphonio-isophosphindoles contain a fragment of type D A Schmidpeter and M Thiele, Angew Chem, 1991, 103, 333. Angew Chem Int Ed Engl., 1991, 30, 308
- 3 (a) K Issleib and R Lindner, Liebigs Ann Chem, 1966, 699, 40 (b) K Issleib and M Lischewski, J prakt Chem, 1969, 311, 857, (c) K Issleib and M Lischewski, ibid 1970, 312, 135, (d) G Märkl and W Bauer, Angew Chem, 1989, 101, 1698, Angew Chem Int Ed Engl., 1989, 28, 1695, (e) H Schmidbaur and W Tronich, Chem Ber, 1968, 101, 3545, (f) H Schmidbaur, Acc Chem Res, 1975, 8, 62, (g) H Schmidbaur S Strunk and C E Zybill, Chem Ber, 1983, 116, 3559, (h) H Grutzmacher, Z Naturforsch, Teil B, 1990, 45, 170,
 (i) D R Mathiason and N E Miller, Inorg Chem, 1968, 7, 709 The addition of chlorophosphines to carbodiphosphoranes has also been reported
- 4 H J Bestmann and A Bomhard, Angew Chem, 1982, 94, 562, Angew Chem Int Ed Engl., 1982, 21, 545, A Ricci, M Fiorenza, A Degl'Innocenti, G Seconi, P Dembech, K Witzgall and H J Bestmann, ibid 1985, 97, 1068 and 1985, 24, 1068
- 5 A Schmidpeter, G Jochem and Ch Robl, to be published
- 6 The only known exceptions refer to cases where the two-coordinate phosphorus arising from the dissociation of the chlorophosphine becomes a member of an aromatic ring P Friedrich, G Huttner, J Luber and A Schmidpeter, Chem Ber, 1978, 111, 1558 and ref 2
- 7 Cf (a) H H Karsch, H-U Reisacher and G Muller, Angew Chem, 1986, 98, 467, Angew Chem Int Ed Engl, 1986, 25, 454, (b) H Grutzmacher and H Pritzkow, Angew Chem, 1989, 101, 768, Angew Chem Int Ed Engl, 1989, 28, 740, U Fleischer, H Grutzmacher and U Kruger, J Chem Soc, Chem Commun, 1991, 302
- 8 The cations in 5 are 2-phospha-analogues of the "phosphocyanines" R₃P(CH)₃PR₃⁺ Habilitationsschrift G Markl, Universitat Wurzburg 1964, as quoted by S Hunig, Neuere farbige Systeme, in Optische Anregung organischer Systeme, Verlag Chemie, Weinheim, 1966, p 184 More C-unsubstituted representatives are mentioned in ref 3b, 2-sustituted representatives have recently been reported H Schmidbaur, Ch Paschalidis, O Steigelmann and G Muller, Angew Chem, 1989, 101, 1739, Angew Chem Int Ed Engl, 1989, 28 1700, H J Bestmann and L Kisielowski, Tetrahedron Lett, 1990, 31, 3301

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