Carbenoid routes to substituted phosphaalkenes and phosphabenzenes

Friedrich Bickelhaupt

Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands

Abstract - Convenient syntheses of C-halogen-substituted phosphaalkenes and of 2-iodophosphabenzenes have been developed. Under certain conditions, the halogen in these compounds can be replaced by metals such as lithium or zinc. The resulting organometallics open in principle an entry to other functionalized derivatives. In the phosphaalkene series, examples of mercury and Group 14 substitution are presented, as well as attempts to obtain phosphorus analogues of isocyanides. Phosphabenzenes have been substituted at the 2-position by elements from Groups 11, 12, 14 and 15.

INTRODUCTION

Since the 1960's, a rich chemistry has developed of heteroatoms such as phosphorus, silicon and their heavier analogues, in which these elements are involved in multiple bonding, either localized, as illustrated for the phosphalkene 1 (ref. 1) or delocalized as in the phosphabenzenes (or phosphinines) 2 (ref. 2, 3). This development is remarkable against the background that multiple bonding - which is quite normal in the Second Period - was previously believed not to occur in higher Periods. Even at the present state of knowledge, however, it remains valid that higher row elements in the multiple bonded (= low coordinated) state need protection against decomposition either by steric hindrance (kinetic stabilization) or delocalization (thermodynamic stabilization). In phosphorus chemistry, the advances in this area have been recently summarized (ref. 4).

Inspite of the impressive developments, there are certain aspects which have so far received less attention. One of them is the synthesis and investigation of derivatives carrying "normal" organic functionalities or metals. Halogen derivatives of phosphaalkenes or phosphabenzenes might be considered to be useful synthons to obtain such functional derivatives if one succeeds, by methodology wellknown in organic chemistry, to convert them to organometallic derivatives of strongly positive metals such as lithium, magnesium or zinc which in turn may lead to a variety of substitution products on reaction with electrophilic substrates.

In this paper, two aspects of this general strategy will be discussed. The first one concerns the halosubstituted compounds of diccordinated phosphorus. Several representatives of this class have been known for some time, especially in the phosphaalkene series, but their synthesis was either tedious or it involved divergent approaches (ref. 4). Using carbenoid intermediates, we developed an easy and general access to C-halogen substituted phosphaalkenes; in the phosphabenzene series, 2-iodophosphabenzenes were obtained via carbenoids by a strategy developed by Mathey and Le Floch for analogous 2-chloro- and 2-bromophosphabenzenes (ref. 5). The second aspect to be reported here concerns our initial results in converting the halogen functions, in particular the iodides, to other organic and organometallic functions.

SYNTHESIS OF C-HALOSUBSTITUTED PHOSPHAALKENES

Initially, our approach (ref. 6) to C-halophosphaalkenes consisted in the addition of two equivalent of n-butyllithium at -100 °C to a solution of supermesityldichlorophosphine (Mes $^{+}$ PCl₂; Mes $^{+}$ =

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2,4,6-tri-tert-butylphenyl) and a haloform in THF. Depending on the halogen, a mono- or a dihalo derivative was obtained (3, or 4, respectively).

Mes*PCl₂ + HCX₃
$$\frac{2 \text{ } n\text{-BuLi}}{\text{Mes}^*\text{P=CHX}}$$
 $\frac{3b \text{ } (X = \text{Br})}{3c \text{ } (X = \text{I})}$ $\frac{3b \text{ } (X = \text{Br})}{4c \text{ } (X = \text{I})}$

Two extreme cases can be distinguished. For chloroform, the reaction proceeds via the carbenoid LiCCl₃ which couples to give Mes*PCl-CCl₃; subsequent lithium-chlorine exchange and elimination of LiCl completes the formation of 4a.

In contrast, iodoform undergoes iodine-lithium exchange to give the carbenoid LiCHI2; coupling to Mes*PCl-CHI2, followed by a second iodine-lithium exchange etc. furnishes <u>3c</u>, which is obtained as an *E*,*Z*-mixture (80:20).

Although some effort has been invested in elucidating the more complicated mechanisms behind the bromoform reaction which gives a 1:1 mixture of 3b and 4b, some aspects still need furnther investigation. However, the mechanistic insight in these investigations so far guided us in devising attractive syntheses of 4b and 4c as follows (LDA = lithium diisopropylamide):

$$Mes^*PCl_2 + 2LiCHBr_2 \longrightarrow Mes^*P=CBr_2$$
 4b
 $Mes^*PCl_2 + CHI_3 + 2LDA \longrightarrow Mes^*P=Cl_2$ 4c

With less success, the latter reaction was also tried for analogues of $\underline{4c}$ which carry smaller groups on phosphorus and are therefore less sterically protected. Thus $\underline{5}$ (Is = 2,4,6-triisopropylphenyl) was obtained in 15% yield only, whereas $\underline{6}$ (Es = 2,4,6-triethylphenyl) and $\underline{7}$ were only identified in the reaction mixtures by their ${}^{31}P$ chemical shifts (δ = 340 ppm, δ = 345 ppm, respectively); in these two latter cases, substitution at phosphorus by LDA was the dominant reaction.

$$RPCl_2 + CHI_3 + 2 LDA \longrightarrow RP=CI_2 \qquad \begin{array}{c} 5: R = Is (15\%) \\ \underline{6}: R = Es \\ \underline{7}: R = Mes \end{array}$$

The dihalophosphaalkenes $\underline{4}$ showed an unexpectedly low reactivity. Thus, $\underline{4b}$ and $\underline{4c}$ were inert towards iodine; $\underline{4b}$ did not react with HCl, but with the more reactive HBr, there is evidence that addition took place. Bromine successively substituted the iodines of $\underline{4c}$ - presumably via adducts such as $\underline{8}$ (tentatively identified by its $\delta(^{3}{}^{1}P) = 78$ ppm), and $\underline{9}$ - to give $\underline{4b}$ (and further products).

CARBON-FUNCTIONALIZED P-SUPERMESITYLPHOSPHAALKENES

Reaction of *n*-butyllithium with 3c (- 80 °C) or 4c (-120 °C) gave the expected lithium derivatives 10 and 11; the specific substitution of the *trans*-iodine in 4c, leading to Z-11 is remarkable and is presumably caused by steric factors. Compounds 10 and 11 gave 12 and 13 on reaction with Me₃MCl; 13 was converted to 14 by a second sequence involving metallation and subsequent reaction with Me₃MCl (M = Ge, Sn).

Similarly, $\underline{10}$ was converted to E- or Z- $\underline{15a}$ and - $\underline{15b}$, of which only the Z-isomers were stable, inspite of greater steric hindrance. An X-ray crystal structure determination of Z- $\underline{15b}$ revealed the reason for this unexpected trend: its mercury atom undergoes an attractive interaction with the π -cloud of the aryl ring.

Mes
$$^{\circ}$$
P=CHHgCl $\xrightarrow{\text{HgCl}_2}$ Mes $^{\circ}$ P=CHLi $\xrightarrow{0.5 \text{ HgCl}_2}$ 0.5 [Mes $^{\circ}$ P=CH]₂Hg 15a 15b

Incidentally, the availability of a several E,Z-isomers such as 3, 12-15 and others allowed to clearly define the validity of the "cis-rule" which states that in phosphaalkenes RP=CXY, nuclei X cis to the phosphorus lone pair have a larger $^2J(PX)$ than trans nuclei, if X is more positive than Y (ref. 6); this rule is convenient for the determination of the configuration around the P=C bond of phosphaalkenes.

DO PHOSPHORUS ANALOGUES OF ISONITRILES EXIST?

Carbenoid Z-11, discernable by its phosphorus chemical shift (δ = 288 ppm) decomposed at -85 °C under formation of supermesitylphosphaacetylene Mes*C=P (16; δ = 35 ppm). It is tempting to postulate the intermediacy of the phosphinidenemethylene Mes*P=C: (17), a phosphorus analogue of an isonitrile; however, intermediate ³¹P NMR signals pointing to the occurrence of 17 were never observed, which indicates that the barrier for the rearrangement $17 \rightarrow 16$ is either extremely low or even - in line with theoretical predictions (ref. 7) - nonexistent. Analogous experiments starting with complex-stabilized derivatives such as 18 have not yet been quite conclusive; thus, 19 gave at -75 °C in rapid sequence new unstable phosphorus compounds with signals at δ = -1 ppm, 21 ppm and finally 33 ppm which are tentatively assigned to 20, 21 and 16, respectively.

Mes*
$$P = CI_2$$
 $CO)_4Fe$
 $P = CI_2$
 $CO)_4Fe$
 $P = CILi$
 $CO)_4Fe$
 $P = CILi$
 $CO)_4Fe$
 $P = CILi$
 $CO)_4Fe$
 $P = C$
 $CO)_4Fe$
 $CO)_4Fe$

These results need confirmation. It should be pointed out, however, that very recently, a diplatinum complex 22 of 17 has been reported (ref. 8); interestingly, both the phosphorus chemical shift (δ = 151.3 ppm) and the P=C bond length (d = 167 pm) characterize 22 essentially as a dimetallated phosphaalkene comparable in its spectral and structural properties to compounds such as 14.

2-SUBSTITUTED PHOSPHABENZENES

Encouraged by the high reactivity of iodine in phosphaalkenes of type 4c, we expected 2-iodophosphabenzenes 23 to be good candidates for similar functionalizations. For the synthesis of 23 (ref. 9), we followed the strategy developed by Mathey and Le Floch for the analogous 2-chloro-and 2-bromo derivatives (ref. 5). In the first step of our synthesis, it was essential to use the carbenoid ClMgCHI₂ (rather than LiCHI₂) to produce 24 in good yield; reaction of 24 with triethylamine gave the unstable trihalophosphaalkene 25 which was intercepted with (2,3-dimethyl)-1,3-butadiene to furnish 26, which in turn finally gave 23.

Relative to iodoform, the (nonoptimized) yield of $\underline{23a}$ was 10%, that of $\underline{23b}$ 33%; therefore the further investigations were mainly conducted with $\underline{23b}$. A considerable number of attempts to derivatize $\underline{23b}$ were unsuccessful, but two routes look rather promising. Reactive organometallic

derivatives were obtained with Zn (either in DMF or in THF/TMEDA) to give 27; or, after complexation to pentacarbonyltungsten, with n-butyllithium to furnish 28; 28 has also been prepared from the analogous 2-bromo complex (ref. 5).

Illustrative for the accessible functionalities at the 2-position of the phosphabenzene system are the reactions of 27 shown in the following scheme (ref. 9).

CONCLUSION

Iodo-substituted phosphaalkenes and phosphabenzenes such as 3c, 4c, and 23 are easily accessible by means of carbenoid intermediates. Via transformations to organometallic intermediates they promise to be useful synthons for the preparation of other functional derivatives.

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REFERENCES

- 1. Th. C. Klebach, R. Lourens and F. Bickelhaupt, J. Am. Chem. Soc., 100, 4886 (1978).
- 2. G. Märkl, Angew. Chem. 78, 907 (1966).
- 3. A.J. Ashe, III, J. Am. Chem. Soc. 93, 3293 (1971).

4. M. Regitz and O.J. Scherer, Eds. Multiple Bonds and Low Coordination in Phosphorus

Chemistry, Thieme, Stuttgart, 1990.

5. (a) P. Le Floch, D. Carmichael, L. Picard and F. Mathey, <u>J. Am. Chem. Soc. 113</u>, 667 (1991); (b) P. Le Floch, D. Carmichael and F. Mathey, Organometallics, 10, 2432 (1991); and references cited).

6. S.J. Goede and F. Bickelhaupt, Chem. Ber. 124, 2677 (1991).

7. (a) K.K. Lehmann, S.C. Ross, and L.L. Lohr, <u>J. Chem. Phys.</u> 82, 4460 (1985). (b) M.T. Nguyen, and T.K. Ha, J. Mol. Struct. (Thermochem). 139, 145 (1986). (c) W.W. Schoeller in ref. 4, chapter B.4.1.

8. K. Jun, V.G. Young and R.J. Angelici, <u>J. Am. Chem. Soc. 113</u>, 9379 (1991).

9. H.T. Teunissen and F. Bickelhaupt, Tetrahedron Lett. and Bull. Soc. Chim. Belges, in press