

Carbenoid routes to substituted phosphalkenes and phosphabenzenes

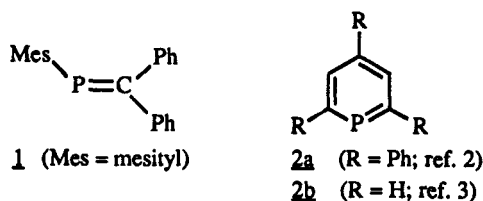
Friedrich Bickelhaupt

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

Abstract - Convenient syntheses of C-halogen-substituted phosphalkenes 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 phosphalkene 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).



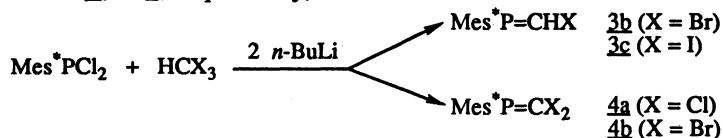
In spite of the impressive developments, there are certain aspects which have so far received less attention. One of them is the synthesis and investigation of derivatives carrying "normal" organic functionalities or metals. Halogen derivatives of phosphalkenes or phosphabenzenes might be considered 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 dicoordinated phosphorus. Several representatives of this class have been known for some time, especially in the phosphalkene 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 phosphalkenes; 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-halophosphalkenes consisted in the addition of two equivalent of *n*-butyllithium at -100 °C to a solution of supermesityldichlorophosphine (Mes^*PCl_2 ; $\text{Mes}^* =$

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).



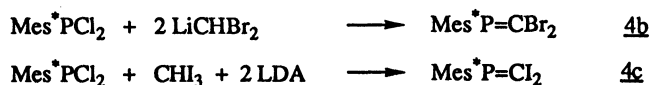
Two extreme cases can be distinguished. For chloroform, the reaction proceeds via the carbenoid LiCCl_3 which couples to give $\text{Mes}^*\text{P}(\text{Cl})\text{CCl}_3$; subsequent lithium-chlorine exchange and elimination of LiCl completes the formation of **4a**.



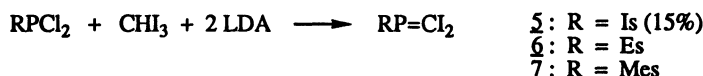
In contrast, iodoform undergoes iodine-lithium exchange to give the carbenoid LiCHI_2 ; coupling to $\text{Mes}^*\text{P}(\text{Cl})\text{CHI}_2$, followed by a second iodine-lithium exchange etc. furnishes **3c**, which is obtained as an *E,Z*-mixture (80:20).



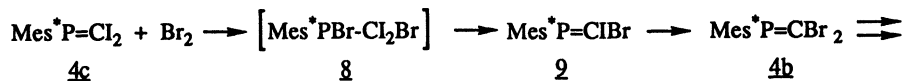
Although some effort has been invested in elucidating the more complicated mechanisms behind the bromoform reaction which gives a 1:1 mixture of **3b** and **4b**, some aspects still need further investigation. However, the mechanistic insight in these investigations so far guided us in devising attractive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



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

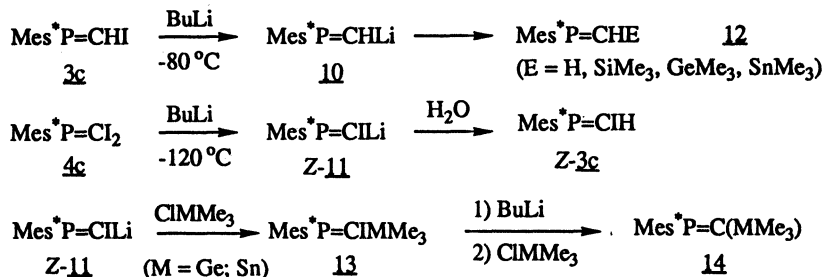


The dihalophosphaalkenes **4** showed an unexpectedly low reactivity. Thus, **4b** and **4c** were inert towards iodine; **4b** did not react with HCl , but with the more reactive HBr , there is evidence that addition took place. Bromine successively substituted the iodines of **4c** - presumably via adducts such as **8** (tentatively identified by its $\delta(^{31}\text{P}) = 78$ ppm), and **9** - to give **4b** (and further products).

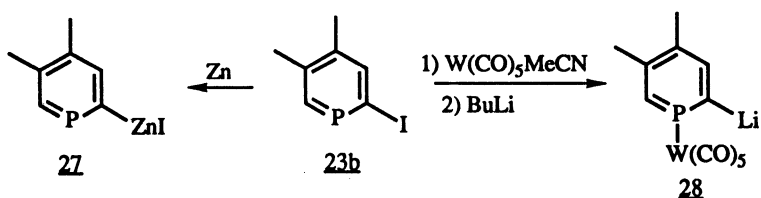


CARBON-FUNCTIONALIZED P-SUPERMESITYLPHOSPHAALKENES

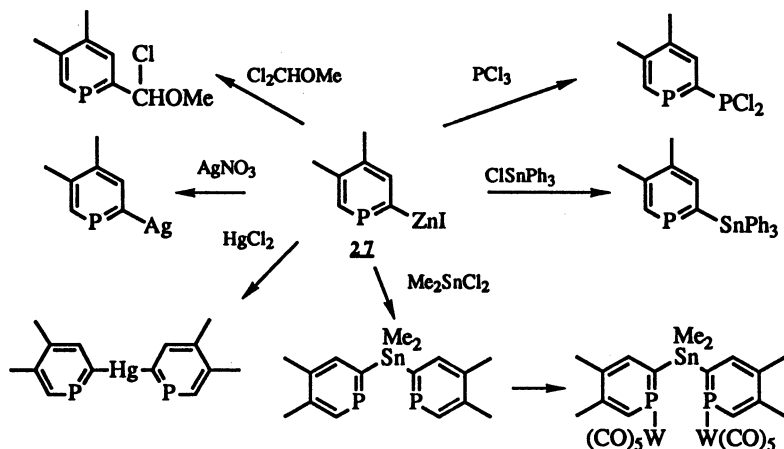
Reaction of *n*-butyllithium with **3c** (-80 °C) or **4c** (-120 °C) gave the expected lithium derivatives **10** and **11**; the specific substitution of the *trans*-iodine in **4c**, leading to *Z*-**11** is remarkable and is presumably caused by steric factors. Compounds **10** and **11** gave **12** and **13** on reaction with Me_3MCl ; **13** was converted to **14** by a second sequence involving metallation and subsequent reaction with Me_3MCl (*M* = Ge, Sn).



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 phosphalkenes and phosphabenzene derivatives 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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