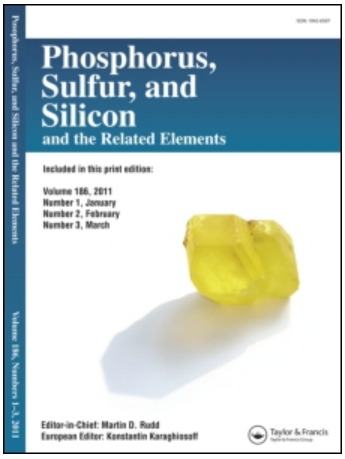

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Synthesis and Reactivity of 2-Iodophosphinines

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SYNTHESIS AND REACTIVITY OF 2-IODOPHOSPHININES

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Abstract. With the aim of synthesizing novel functionalized derivatives of phosphinine (phosphabenzene), we investigated Diels-Alder approaches to 2-iodophosphinines. The precursor Cl_2P-CHI_2 reacted with triethylamine in the presence of 1,3-butadiene or its 2,3-dimethyl derivative to furnish 2-iodophosphinines **6** which, directly or after formation of their pentacarbonyltungsten complexes, underwent a number of interesting functionalization reactions. Useful for reaction with a number of electrophiles were the organozinc reagent 4,5-dimethyl-2-iodozincophosphinine (**9**) which could be obtained directly from the corresponding 2-iodophosphinine **6b** and zinc either in DMF or in THF/TMEDA, and the pentacarbonyltungsten coordinated 2-lithio derivative **18**.

INTRODUCTION

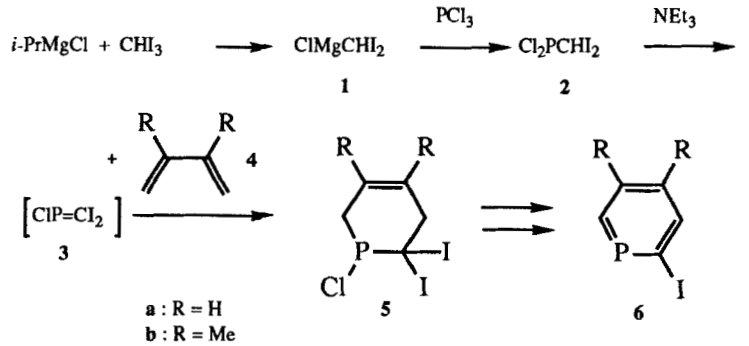
While a considerable number of phosphinines with alkyl or aryl substituents or with annelated rings have been reported, the number of functionalized derivatives is rather limited, and a general approach has not yet been devised[1]. In principle, halo-substituted phosphinines might furnish a general access to other functionalities via the corresponding organometallic derivatives. This concept has been explored quite successfully by the group of Mathey and Le Floch[2], who prepared derivatives of 2-chloro- and 2-bromophosphinines by a Diels-Alder approach and investigated their synthetic potential. Initially, problems were encountered due to the unexpectedly low reactivity of these halo derivatives, but by a number of successful routes, these problems have largely been overcome[2c].

Our own work in this area was directed in particular towards the synthesis and investigation of 2-iodophosphinines **6** which were expected to have a higher reactivity than their chloro and bromo analogues and might be useful in general for the functionalization of the phosphabenzene system.

SYNTHESIS

The synthesis of 2-iodophosphinines by the Diels-Alder strategy[2a] requires the reaction of a diene - butadiene (**4a**) or 2,3-dimethylbutadiene (**4b**), respectively - with the unstable phosphaalkene **3**; the latter was obtained from **2** ($\delta(^{31}P)$ = 155.1 ppm) with triethylamine (Scheme 3). Reaction of **1**[4] with phosphorus trichloride gave crude **2** in good yield which could be directly converted with **4** (via **3** and **5**) to **6a** ($\delta(^{31}P)$ = 233.1 ppm; 10 % relative to iodoform) and **6b** ($\delta(^{31}P)$ = 216.2 ppm; 33 % relative to iodoform), respectively.

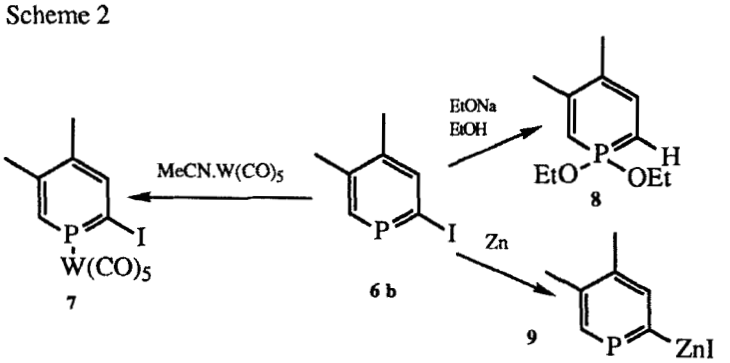
Scheme 1



REACTIONS

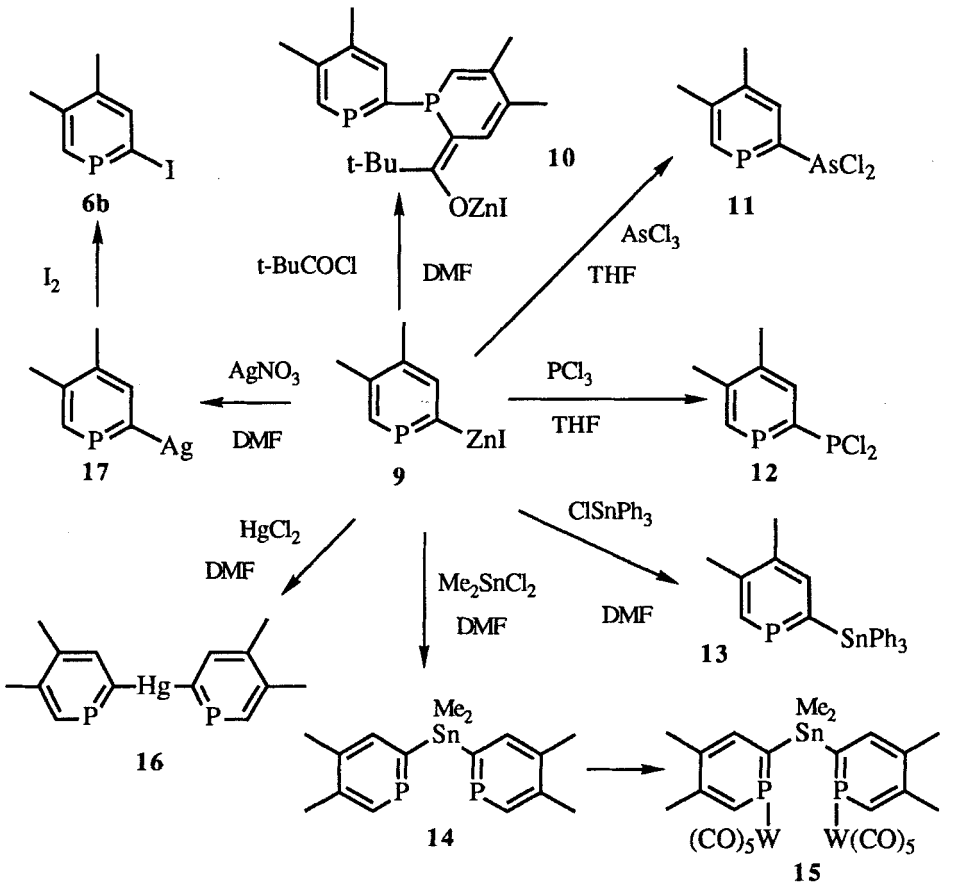
The reactivity of 2-iodophosphinines was so far investigated mainly for the dimethyl derivative **6b** (Scheme 2).

Scheme 2



Complexation with $MeCN{\cdot}W(CO)_5$ gave the tungsten complex **7** ($\delta(^{31}P)$ = 184.6 ppm). Of mechanistic interest is the conversion of **6b** to the λ^5-phosphinine **8** ($\delta(^{31}P)$ = 68.9 ppm). The organozinc reagent **9** ($\delta(^{31}P)$ = 222.6 ppm) was obtained in good yield by two methods: reaction with metallic zinc either in DMF (this solvent was recently recommended for aryl iodides[5]) or, more recently, in THF in the presence of TMEDA; the latter solvent is more convenient for further conversions of **9**. The synthetic potential as well as certain limitations of **9** follow from the reactions described in Scheme 3. The number of organic electrophiles tested so far is limited. In DMF only pivaloyl chloride gave an identified product (**10**). Other electrophiles like phosphorus and arsenic trichloride reacted with **9** in THF to give the respective monosubstitution products.

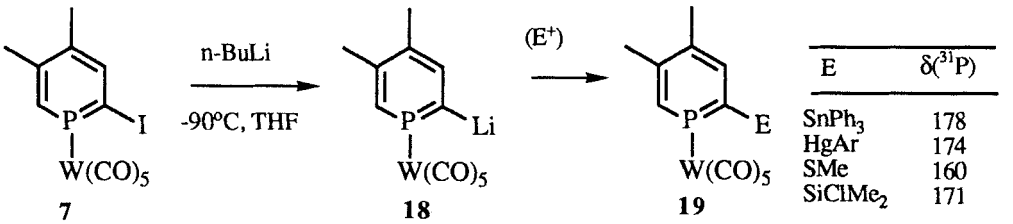
Scheme 3



Many of the (organo)metallic electrophiles investigated gave the expected phosphinine derivative (Scheme 3; cf. **13** - **17**); of these, **16** ($\delta(^{31}P)$ = 213.1 ppm) and **14** ($\delta(^{31}P)$ = 218.5 ppm) were of special interest as potential bidentate ligands with various bite angles. However, with the exception of **13** ($\delta(^{31}P)$ = 222.0 ppm) and the bis-tungsten complex **15** ($\delta(^{31}P)$ = 176.8 ppm) derived from **14**, the thermal stability of these compounds at room temperature was found to be low. Thus, the unstable organosilver compound **17** could only be identified by ^{31}P NMR spectroscopy (δ= 201 ppm) and a quench reaction with I_2 to give **6b**.

Quite promising is the recently initiated investigation of the lithiated tungsten complex **18** (Scheme 4); it is accessible from **7** with *n*-butyllithium at - 90 C and has also been prepared from its bromo analogue[2c]. Reagent **18** ($\delta(^{31}P)$ = 163 ppm) is only stable at low temperatures. Reaction of **18** with several electrophilic substrates gave the derivatives **19** (Scheme 4).

Scheme 4



E	$\delta(^{31}P)$
$SnPh_3$	178
HgAr	174
SMe	160
$SiClMe_2$	171

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