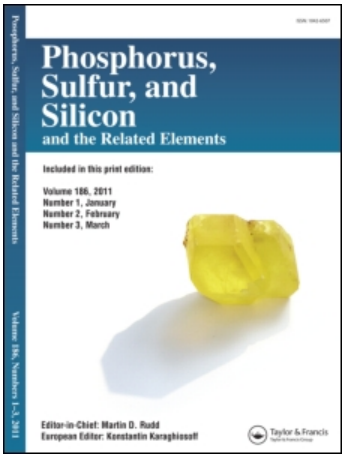

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New Routes to (*E*)-Halophosphaalkenes

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NEW ROUTES TO *(E)*-HALOPHOSPHAALKENES

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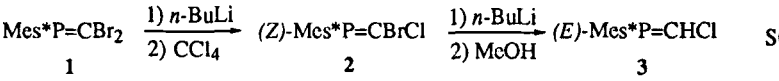
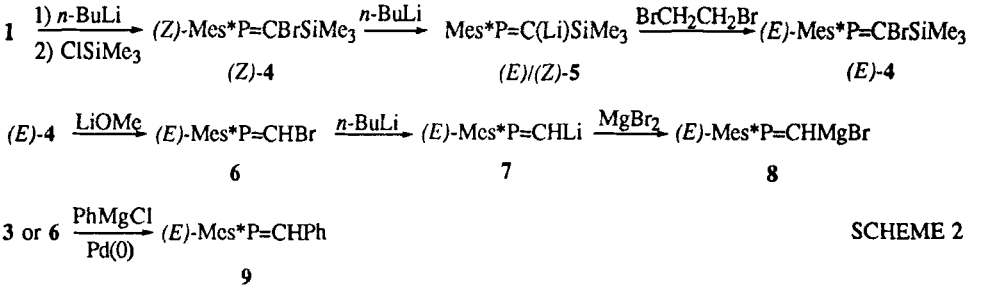
Starting from dihalophosphaalkenes Mes*P=CHal$_2$ (Hal = Cl, Br, I) we have been developing methodologies for the synthesis of *(E)*-Mes*P=CHHal, which can be converted to reactive phosphaalkenyl metal reagents. Dibromophosphaalkene **1** was reacted with *n*-butyllithium at -120 °C, furnishing **2** after chlorination of the intermediate carbenoid. Compound **2** was transformed to the *(E)*-chlorophosphaalkene **3** as shown (SCHEME 1).



1 **2** **3** SCHEME 1

(E)-Bromophosphaalkene **6** was obtained from **1** via **4** and *(E)/(Z)*-**5** as illustrated in Scheme 2. Compound **6** was obtained in 54 % yield with respect to **1**.



SCHEME 2

Halogen-lithium exchange of **6** furnished **7** which was converted to the stable phosphaalkenyl-Grignard reagent **8**. Phosphaalkenes **3** and **6** were subjected to Stille-type cross coupling reactions with phenylmagnesium chloride; *trans*-phosphastilbene **9** was isolated in 76% yield from **3** and in 90% yield from **6**. In both cases, **9** was obtained with 100% isomeric purity (SCHEME 2).