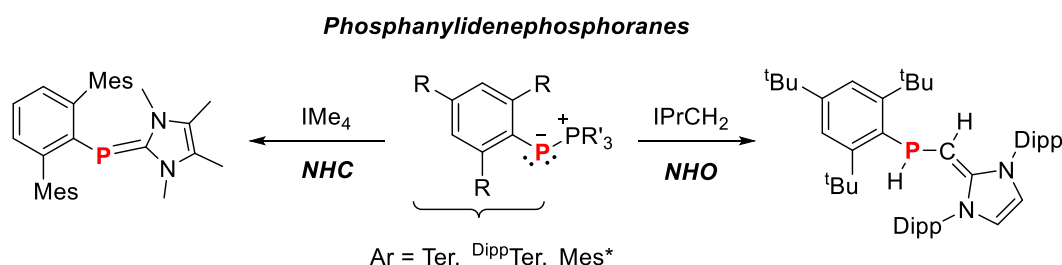


New Avenues in Phospha-Wittig Chemistry

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Scheme 1. Reactivity of phospha-Wittig reagents towards NHCs and NHOs.

The term “Phospha-Wittig” reaction was originally introduced by Mathey for the reaction of $(RO)_2P(O)-P^{(-)}[W(CO)_5]R'$ with ketones to give $(CO)_5W$ -coordinated phosphalkenes.¹ Later, investigating the reactivity of $[Cp_2Zr(PR_3)P^{Mes}Ter]$ Protasiewicz and co-workers noted the formation of $^{Mes}TerP=PR_3$ which showed that phospha-Wittig reagents can be isolated when the group R on phosphorus is kinetically stabilizing and to date four examples of $ArP=PMe_3$ ($Ar = Mes^*$, ^{Mes}Ter , ^{Tip}Ter , EIND) have been described in the literature.^{2,3} Phospha-Wittig reagents are generally obtained by the combination of the respective dichlorophosphine $Ar-PCl_2$ with Zn powder and an excess of PMe_3 .⁴ Using $ArP=PMe_3$ in the reaction with aldehydes, phosphalkenes, $ArP=CR'H$, are obtained, with the concomitant formation of $Me_3P=O$.

Phospha-Wittig reagents, $ArP=PMe_3$, can also be considered as phosphine-stabilized phosphinidenes. Thus, in this study we show that the phosphine, PMe_3 , can be displaced by NHCs or NHOs. Phospha-Wittig reagents are more over isovalence electronic to carbene phosphinidene adducts,⁵ thus, should be easily converted into such by replacement of the phosphine with a carbene. N-heterocyclic olefins (NHOs) replace PMe_3 as well, however, further react in a C-H activation to afford phosphine-substituted NHOs. This concept was further extended to allyl-appended NHOs, which furnishes phosphine-substituted allyl species. These reactions clearly show the potential of phospha-Wittig reagents beyond the formation of phosphalkenes and offer access to bulky phosphines that could be of interest as ligands in homogeneous catalysis.

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