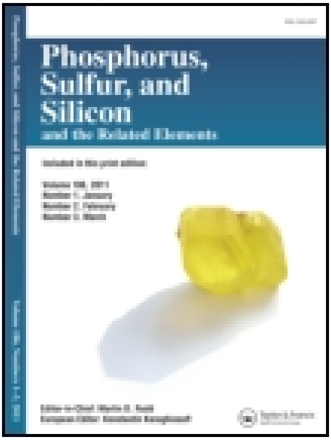

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Diphosphene and Phosphoranylidenephosphin Formation from a Terminal Phosphinidene Complex

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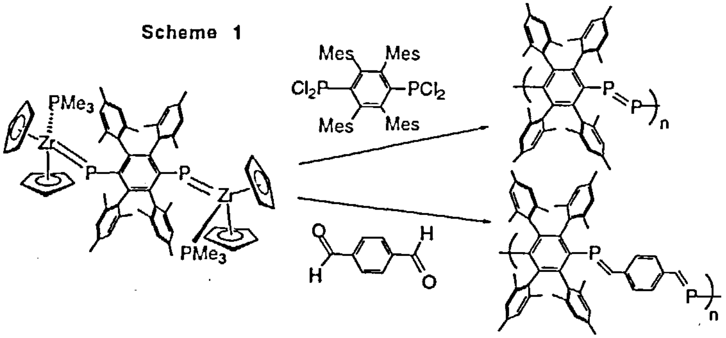
The zirconium phosphinidene complexes $[Cp_2Zr{=}PDmp(PR_3)]$ (Dmp = 2,6-$Mes_2C_6H_3$; R = Me: **1a**; R = Bu: **1b**) form the diphosphene DmpP=PDmp, $[Cp_2ZrCl_2]$, and the phosphoranylidenephosphines $DmpP{=}PR_3$ (**3a**, **3b**) upon reaction with $DmpPCl_2$.

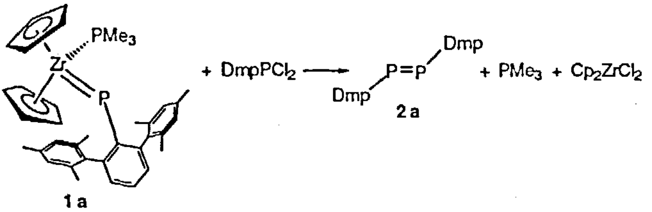
Keywords: phosphinidene complex; phosphoranylidenephosphine

Our research is directed to the synthesis of new materials having P=P and P=C multiple bonds (Scheme 1). Our particular approach features bis-phosphinidene complexes for synthesis of extended materials. Zirconium phosphinidene complexes, such as $[Cp_2Zr{=}PMes^*(PMe_3)]$ (Mes^* = 2,4,6-$^tBu_3C_6H_2$) have been established as

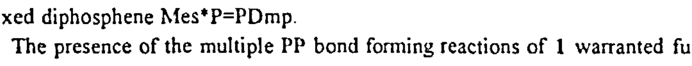
Scheme 1



efficient phosphinidene precursors for synthesis of new materials.[1] Owing to the need to simultaneously provide steric shelter for two low coordinate phosphorus atoms, we must move from aromatics having protective *ortho-tert*-butyl groups (2,3,5,6-^{t}Bu$_4$C$_6$X$_2$ aromatic systems would be very difficult or impossible to prepare) to 2,3,5,6-Ar$_4$C$_6$X$_2$ aromatic linking units. We have developed phosphorus systems containing the sterically encumbered group Dmp (Dmp = 2,6-Mes$_2$C$_6$H$_3$) which represents half of this linking group,[2,3] and prepared the analogous zirconium phosphinidene complex [Cp$_2$Zr=PDmp(PMe$_3$)] (1a) and tested its efficacy for diphosphene synthesis (eq. 1). Quite unexpectedly, the reaction actually produces a mixture of three species (eq. 2), including the anticipated diphosphene DmpP=PDmp (2a). The two new species, the phosphoranylidenephosphine DmpP=PMe$_3$ (3a)[4] and the dichlorodiphosphine DmpP(Cl)P(Cl)Dmp (4a), have been independently prepared and characterized. The reaction of 1a with Mes*PCl$_2$ (Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$) reveals another level of complexity for these reactions, for not only is Mes*P=PMes*, Mes*P=PMe$_3$, and [Cp$_2$ZrCl$_2$], produced, but also 2a, 3a, and the mixed diphosphene Mes*P=PDmp.



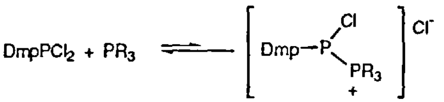
(1)


$$\mathbf{1a} + \mathrm{DmpPCl_2} \longrightarrow \mathbf{2a} + \underset{\mathbf{3a}}{\mathrm{DmpP{=}PMe_3}} + \underset{\mathbf{4a}}{\mathrm{Dmp(Cl)P{-}P(Cl)Dmp}} + \mathrm{PMe_3} + \mathrm{Cp_2ZrCl_2} \qquad (2)$$

The presence of the multiple PP bond forming reactions of 1 warranted further investigation prior to our successful use of Zr=P bonds as described in Scheme 1. Phosphoranylidenephosphine formation in these reactions beckoned for experiments to be performed in the presence of added PMe$_3$. Furthermore, previous work has suggested that the reactivity of 1a may require initial PMe$_3$ dissociation.[1] Early studies, however, revealed that a slow direct reaction occurs between excess PMe$_3$ and DmpPCl$_2$ to yield DmpP=PMe$_3$ and Me$_3$PCl$_2$. Solutions of excess PBu$_3$ and DmpPCl$_2$ do not show any evidence for reaction. In order to probe the mechanism between **1a** and $DmpPCl_2$ in more detail and in the presence of excess PR_3, we have also prepared $[Cp_2Zr{=}PDmp(PBu_3)]$ (**1b**).

Compound **1b** reacts analogously with $DmpPCl_2$ to produce **1a** and forms **2a**, $DmpP{=}PBu_3$ (**3b**), and **4a**. Upon addition of increasing amounts of PBu_3, the *reaction produces greater amounts of* **3b**. *Upon adding 10 equivalents of* PBu_3, **3b** is produced in ≥95% yield. Under these conditions the rate of reaction is promoted by at least tenfold.

No evidence for electrophilic behavior for **1** was found by ^{31}P NMR spectroscopic examination of solutions of **1** and PR_3. We thus propose that the mechanism for phosphoranylidenephosphine formation involves initial activation of the dichlorophosphine $DmpPCl_2$ by PR_3 (eq. 3).



(3)

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