Since the 1960s the question, whether electron-rich alkenes (especially tetraaminoalkenes) can dissociate at the double-bond\cite{99}\cite{100}, is a controversial issue. The products of this dissociation would be diaminocarbenes, which are believed to be in an equilibrium with the dimer (Wanzlick-equilibrium). Phosphaalkenes, in which one CR$_2$-unit of an alkene is replaced by the isoelectronic PR$_2$-unit, frequently react like their organic analogues. Inversely polarized phosphaalkenes have electronic properties similar to the tetraaminoalkenes involved in the Wanzlick-type-chemistry. By analogy such phosphaalkenes should dissociate at the double-bond into a carbene and a phosphinidene.

\[
\begin{align*}
 & \text{R-P=NMe}_2 \\
\rightarrow & \text{R-P} + \text{C=NMe}_2
\end{align*}
\]

Thus, inversely polarized phosphaalkenes may be expected to be a convenient source of these two reactive molecules in organic synthesis.

In this work reactions are investigated, in which inversely polarized phosphaalkenes R-P=C(NR’R”)$_2$ show the reactivity of carbenes and/or phosphinidenes. The question, whether a Wanzlick-type-equilibrium also can be encountered with phosphaalkenes is of concern.

The reaction of the phosphaalkene tBu-P=C(NMe$_2$)$_2$ 2 with (Ph$_3$P)AuCl 3 yields the decanuclear gold cluster [Au$_6$(AuCl)$_2$(µ$_3$-P-tBu)$_2$(tBu-P=C(NMe$_2$)$_2$)$_6$]$^{4+}$(Cl)$_4$ 1. In 1 two of the employed eight molecules 2 decompose to tert-butyl-phosphinidene units. The ion [(Me$_2$N)$_2$CCl]Cl 14 can be detected as further product. A degradation of phosphaalkenes by (in this case heterolytical) cleavage of the double-bond was not known before.
The by-product [(Au(PPh₃))₄(AuCl)₂(μ₃-P-tBu)₂] 15 also contains tert-butylphosphinidene ligands.
Reactions of similar phosphaalkenes R-P=C(NMe₂)₂ (R= Cyh 6, Ad 7, Ph 8, Mes 9) and tBu-P=C(NEt₂)₂ 11 with (Ph₃P)AuCl 3 only yield mononuclear complexes [(R-P=C(NR'₂)₂)₂Au]Cl.

Phosphaalkenes R-P=C(NMe₂)₂ (R= tBu 2, Cyh 6, Ad 7, Ph 8, Mes 9) react with three equivalents of diphenylketene 17 to afford the dipolar bisdimethylamino-carbene-ketene adduct 28 and 2-substituted 3,5-dibenzhydrylidene-1,4,2-dioxaphospholanes (R= tBu 2, Cyh 30, Ad 31, Ph 32, Mes 33). Each of the two products contains one half of the phosphaalkene employed. This conversion is the first example of a reaction where phosphaalkenes show the reactivity of carbenes and phosphinidenes. Formally, the double-bond is cleaved homolytically like in the genuine Wanzlick-equilibrium.
During the formation of the 3,5-dibenzhydrylidene-1,4,2-dioxaphospholanes (R= tBu 29, Cyh 30, Ad 31, Ph 32, Mes 33) both molecules of diphenylketene 17 react via the C-O-bond. Under different reaction conditions in the case of R= tBu the isomeric product 5-benzhydrylidene-2-tert-butyl-4,4-diphenyl-1,2-oxaphospholan-3-one 35 is found. In 35 one molecule of diphenylketene 17 has reacted via the C-C-bond. A mechanism explaining the formation of all products is proposed.
The reaction of tBu-P=C(NEt) \textsubscript{2} \textbf{11} with diphenylketene \textbf{17} yields the bisdiethylaminocarbene-ketene addition product \textbf{38} and \textbf{29}. Under similar conditions phosphaalkene Mes*-P=C(NMe) \textsubscript{2} \textbf{10} shows no reaction, H-P=C(NMe) \textsubscript{2} \textbf{12} yields decomposition products. Me\textsubscript{3}Si-P=C(NMe) \textsubscript{2} \textbf{13} undergoes an addition reaction with the C-O-bond of the diphenylketene \textbf{17}, whereby the P-Si-bond is cleaved and 1,1-Bis-dimethylamino-3-trimethylsiloxy-4,4-diphenyl-2-phosphabutadiene \textbf{39} is formed. The ketenes RCH=C=O (R= SiEt\textsubscript{3} \textbf{40}, SiMe\textsubscript{2}tBu \textbf{41}) do not react with phosphaalkene tBu-P=C(NMe) \textsubscript{2} \textbf{2}; with MeO\textsubscript{2}C-C≡C-CO\textsubscript{2}Me \textbf{42} the 1-tert-butyl-1H-phosphole-2,3,4,5-tetracarboxylic-acid-tetramethylester \textbf{43} is formed. \textbf{43} contains a tert-butyl-phosphinidene unit as well. It can be derived that free carbenes and free phosphinidenes do not appear during the reactions mentioned. Obviously a more complicated mechanism seems to be responsible for the observed product pattern.
The 1,4,2-dioxaphospholane 29 is also formed in the reaction of the phosphinidene source tri-tert-butyl-cyclotriphosphane 44 with diphenylketene 17. The stable Arduengo-carbene 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene 48 reacts with 17 giving the carbene-ketene adduct 49 which is comparable to 28.
For further studies the less stable phosphaalkene 2-tert-butyl-phosphanyliden-1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1H-imidazol 51 is synthesized.
51 cannot be isolated due to slow decomposition at room temperature. The tert-butylphosphinidene initially formed oligomerizes to tri-tert-butyl-cyclotriaphosphane 44 and tetra-tert-butyl-cyclotetraphosphane 45. The carbene unit of 51 is detected as its conjugate acid 54. Phosphaalkene tBu-P=C(NEt$_2$)$_2$ 11 decomposes upon prolonged heating to products 44 and 45 as disclosed by $^{31}$P-NMR-spectroscopy. These transformations are the first examples of reactions in which the homolytical cleavage of P-C-double-bonds like in the Wanzlick-equilibrium is observed.

In this work a new reaction pattern of inversely polarized phosphaalkenes R-P=C(NR'R'')$_2$ is established. The P-C-double-bonds may be cleaved homolytically or heterolytically depending on the reaction conditions. The resulting fragments were trapped by metal complexes or by ketenes and can be used for synthetic purposes. More stable phosphaalkenes show bond cleavage in presence of suitable reactants only, free carbenes and phosphinidenes are not present at any time. This behaviour is comparable to that of tetraaminoalkenes, whose reactivity points to the presence of free carbenes$^{[101][102][103]}$. Less stable phosphaalkenes undergo bond cleavage at room temperature or upon heating, the carbenes and phosphinidenes formed undergo further reactions like protonation or oligomerisation respectively. This behavior is comparable to that of less stable tetraaminoalkenes, which show in fact homolytical decomposition into carbenes$^{[107][108]}$ as proven by NMR-spectroscopy. Thus, most of our knowledge about the genuine Wanzlick-equilibrium can be transferred to electron-rich inversely polarized phosphaalkenes. The similar reactivity of alkenes and phosphaalkenes which can be expected from the diagonal-relationship between phosphorus and carbon was confirmed by experiments.