Summary

Electrophilic phosphinidenes are versatile, transient intermediates that have been highly valuable in the synthesis of a plethora of organophosphorus compounds. However, some questions about their identity remained, which inspired us to undertake an in-depth investigation in both the formation and reactivity of the in-situ generated metal-complexed phosphinidenes. The particular focus of this study was the newly, in house-developed phosphepines 1 (X = P; Scheme 1) that can be applied as phosphinidene precursors via thermal expulsion of the low-valent fragments from phosphanorcaradienes 2 (X = P).

\[
\begin{align*}
\text{1} & \rightleftharpoons \text{2} \\
X &= \text{C, O, S, N or P}
\end{align*}
\]

Scheme 1. Valence isomerization.

The first chapter (Chapter 1) of this thesis concerns a literature study explaining the general concept of the valence isomerization of the phosphepines (1 → 2) and their analogues that leads to the electron deficient transients. The study starts with the rearrangement of the all-carbon cyclohepta-1,3,5-triene into the corresponding bicyclo[4.1.0]hepta-2,4-diene (X = C) and is followed by reviewing the chemistry of the parent seven-membered ring systems bearing the elements O, S, N and P (Scheme 1).

Chapter 2 presents a detailed investigation of the reaction of the transient, electrophilic phosphinidenes [R–P=W(CO)_5] (R = Me, Ph), thermally generated from the corresponding benzophosphepines 3, with a 1-phosphallene that affords methylenediphosphirane complexes 5 (Scheme 2). Phosphiranes 5 are accessible in a remarkable diastereoselective manner in which only the anti-isomer is formed. A detailed DFT analysis at the B3PW91/6-31G(d) level of theory...
shows that the ring closure of the initially formed syn and anti P,P-ylides 4 is mostly influenced by the bulky Mes* and W(CO)₅ groups, causing a negative activation energy for syn-ring closure and a high diastereoselective outcome of the reaction. This case study shows that the 3-benzophosphene complexes 3 are powerful phosphinidene precursors, generating the transients at lower temperatures (≥ 60 °C) then normally (110 °C) is the case for the traditional 7-phosphanorbornadiene complexes, making the more strained and thermally less stable phosphiranones accessible as well.

Scheme 2. Formation of methylenediphosphiranones 5.

Although the phosphinidenes [R–P=W(CO)₅] have emerged as versatile intermediates that are highly valuable in the synthesis of a plethora of organophosphorus compounds, their existence has never been unequivocally established.

Scheme 3. Phosphinidene formation from phosphene 3.

In Chapter 3 we illustrate our quest to determine if these transients are indeed scientific objects or perhaps fictional characters by employing electrospray ionization tandem mass spectrometry (ESI-MS/MS). We were able to detect the electrophilic phosphinidene complex [R–P=W(CO)₅] 6, carrying a cationic
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$p$-trimethylammoniumphenyl substituent in the gas-phase, and show that the generated reactive intermediate provides the same benchmark [1+2]-cycloadducts with olefins as is reported for the established solution phase chemistry, thereby giving credence to the claimed intermediacy of neutral phosphinidene complexes that are involved in the synthesis of numerous organophosphorus compounds. The gas-phase studies further illustrate that W(CO)$_5$-complexed PCC-rings can undergo demetalation or [1+2]-retroaddition depending on the nature of the phosphirane ring and its substituents expanding the chemistry of low-valent phosphorus intermediates.

In Chapter 4 the valence isomerization of phosphepines 1 into phosphanorcaradienes 2 has been studied computationally at the B3PW91/6-311+G(d,p) (LANL2DZ for W) level of theory to facilitate the development of novel, metal-free phosphinidene precursors that controllably release singlet phosphinidenes upon heating. This target becomes viable by benzannulation of the seven-membered phosphepine ring and the introduction of P-amino substituents (R = NR$_2$; Scheme 4).

![Scheme 4](image)

**Scheme 4.** Valence isomerization of phosphepines.

Finally, Chapter 5 deals with the BABAR-Phos family that normally represents remarkable stable polycyclic phosphiranes bearing different $N$-substituents. Interestingly, only the sterically unencumbered MeBABAR-Phos can be alkylated with methyl triflate, resulting in the formation of the novel salt [N,N-dimethyl-BABAR-Phos]OTf 7 (Scheme 5). This BABAR-Phos salt can undergo various nucleophilic additions with lithium organonyl species, resulting in $P$-substituted phosphiranes (8, 9). These phosphiranes are thermally unstable and give rise to products which formally correspond to phosphinidene extrusion reactions; however, calculations predict that formation of the free species costs ~50
kcal·mol\(^{-1}\). In addition, 7 reacts with neutral nucleophiles like \(N\)-heterocyclic carbenes such as 13 resulting in the NHC-stabilized phosphiranylium cation 14. Calculations show that both \([N,N\text{-dimethyl-BABAR-Phos}]\text{OTf}\) 7 and \([(\text{Me}_2N\text{-trop})\text{P}(\text{iPr}_2\text{Me}_2)]\text{OTf}\) 14 may be regarded as the first isolated examples of intra- and inter-molecular amino- or carbene-stabilized phosphiranylium salts, respectively.

**Scheme 5.** Reactivity of the amino phosphiranylium salt 7.