Introduction:

Phosphinines are intriguing ligands in coordination chemistry due to the possibility to realize highly diverse substitution pattern. In particular, pyridyl-functionalized phosphinines can exhibit interesting binding motifs in transition metal complexes due to their hard N- and soft P-donor properties. While the coordination chemistry of pyridyl-functionalized phosphinines, for example NIPHOS, has been extensively studied, their reactivity towards small molecules is barely explored. During the synthesis of phosphorus-containing terpyridine derivatives, we discovered that these novel NPN-heterocycles react fully reversible with small molecule activation of H₂O. As an intermediate a 1,2-dihydrophosphinine oxide can be generated. This is a sign for the involvement of three pyridyl moieties. This results in dimeric coordination compounds.

Both phosphinines 6 and 7 react fully reversible with water. DFT calculations showed, that for the formation of the 1,2-dihydrophosphinine oxides the ortho pyridyl moieties play a crucial role in the activation of H₂O. As an intermediate a 1-phosphinine-1-ol is possibly formed. The interplay of multiple water molecules lowers the reaction barrier and allows the reaction to occur even at room temperature. The driving force of the reverse reaction is due to a small energy difference between the molecules and the re-organization to the phosphinines.

Small molecule activation

Both phosphinines 6 and 7 react fully reversible with water. DFT calculations showed, that for the formation of the 1,2-dihydrophosphinine oxides the ortho pyridyl moieties play a crucial role in the activation of H₂O. As an intermediate a 1-phosphinine-1-ol is possibly formed. The interplay of multiple water molecules lowers the reaction barrier and allows the reaction to occur even at room temperature. The driving force of the reverse reaction is due to a small energy difference between the molecules and the re-organization to the phosphinines.

Ligand synthesis:

**Synthetic route to 1,3,2-diazaphosphinine 3 by Manay**

R = H 4  Me 5

Coordination chemistry

12 bridges two copper dimer, with support of three pyridyl groups. The Cu-Cu distance with 2.561(1) Å in the 1-μ-C₂ complex (12) is unusually short.

Conclusion:

The two tetrapyridyl functionalized phosphinines (6 and 7) undergo a fully reversible addition of water to the C=P bond forming syn- and anti-1,2-dihydrophosphinine oxides at ambient condition which can be repeated several times. A subsequent deprotonation of the mixture of 8 and 9 results in the formation of a tetrameric structure (10), wherein the ortho pyridyl groups and newly formed 1-phosphinine encapsulate a lithium-oxygen octagon. The C-H acidity and driving force of the deprotonation are primarily attributed to the re-aromatization of the phosphinine ring. The tetrapyridyl phosphinines get introduced into the coordination sphere of Cu(I). Two phosphinines coordinate to a (Cu)₂-dimer by involvement of three pyridyl moieties. This results in dimeric coordination compounds.

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**References:**


