



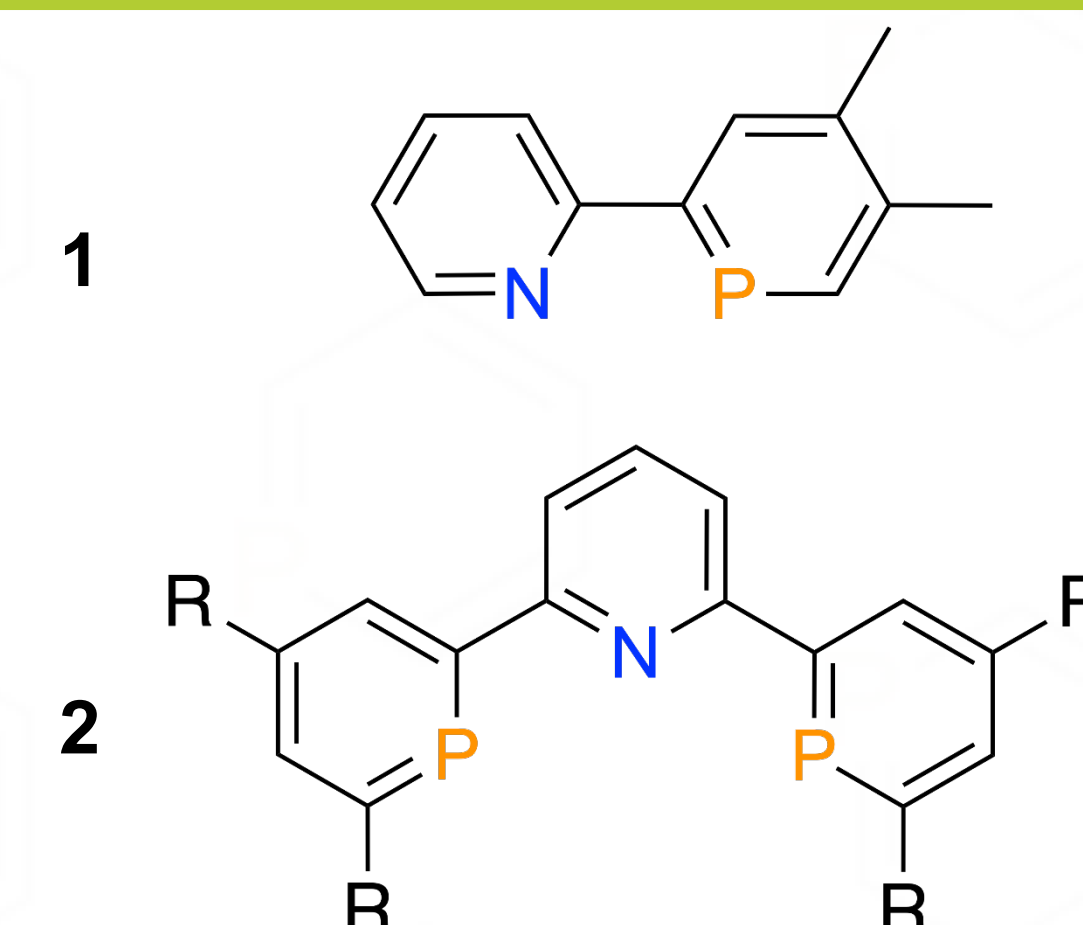
# Highly selective, reversible water activation by P,N-cooperativity in pyridyl-functionalized phosphinines

Richard. O. Kopp, S. L. Kleynemeyer, L. J. Groth, M. J. Ernst, S. M. Rupf, M. Weber, L. J. Kershaw Cook, N. T. Coles, S. E. Neale, C. Müller<sup>[1]</sup>

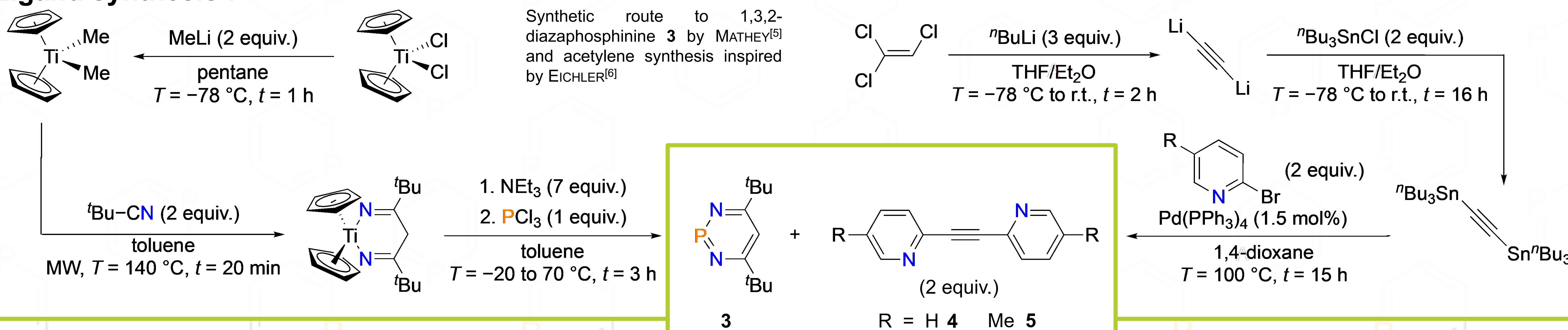
Freie Universität Berlin, Institute of Chemistry and Biochemistry, Fabeckstr. 34/36, 14195 Berlin, Germany  
richard.kopp@fu-berlin.de, christian.mueller@fu-berlin.de

## 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.<sup>[2]</sup> While the coordination chemistry of pyridyl-functionalized phosphinines,<sup>[3]</sup> for example NIPHOS (1), has been extensively studied, their reactivity towards small molecules is barely explored. During the synthesis of phosphorus-containing terpyridine derivatives (2),<sup>[4]</sup> we discovered that these novel NPN-heterocycles (6 and 7) react highly selectively with water. In addition to presenting the coordination chemistry of these heterocycles, we highlight here the fully reversible activation of water under ambient conditions to form the corresponding 1,2-dihydrophosphinine oxides 8 and 9 via the corresponding λ<sup>5</sup>-phosphinin-1-ols.<sup>[1]</sup>

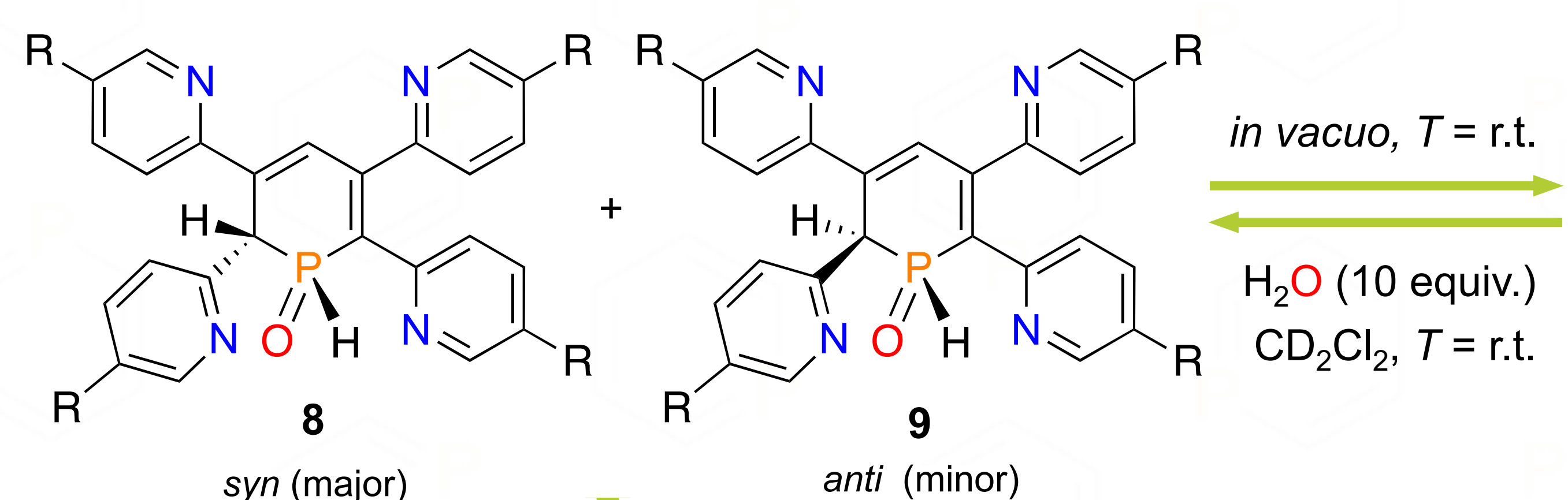
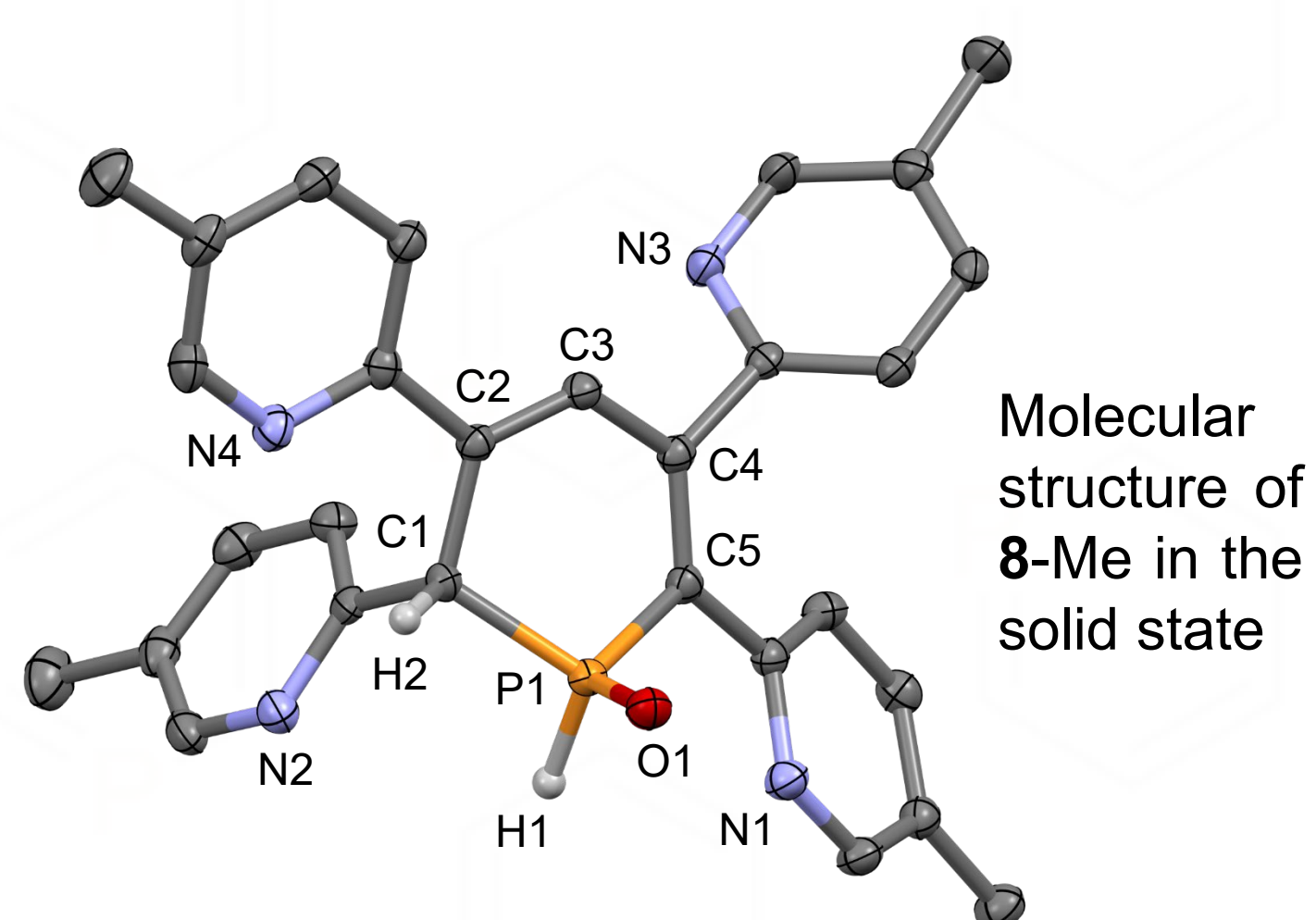


## Ligand synthesis:

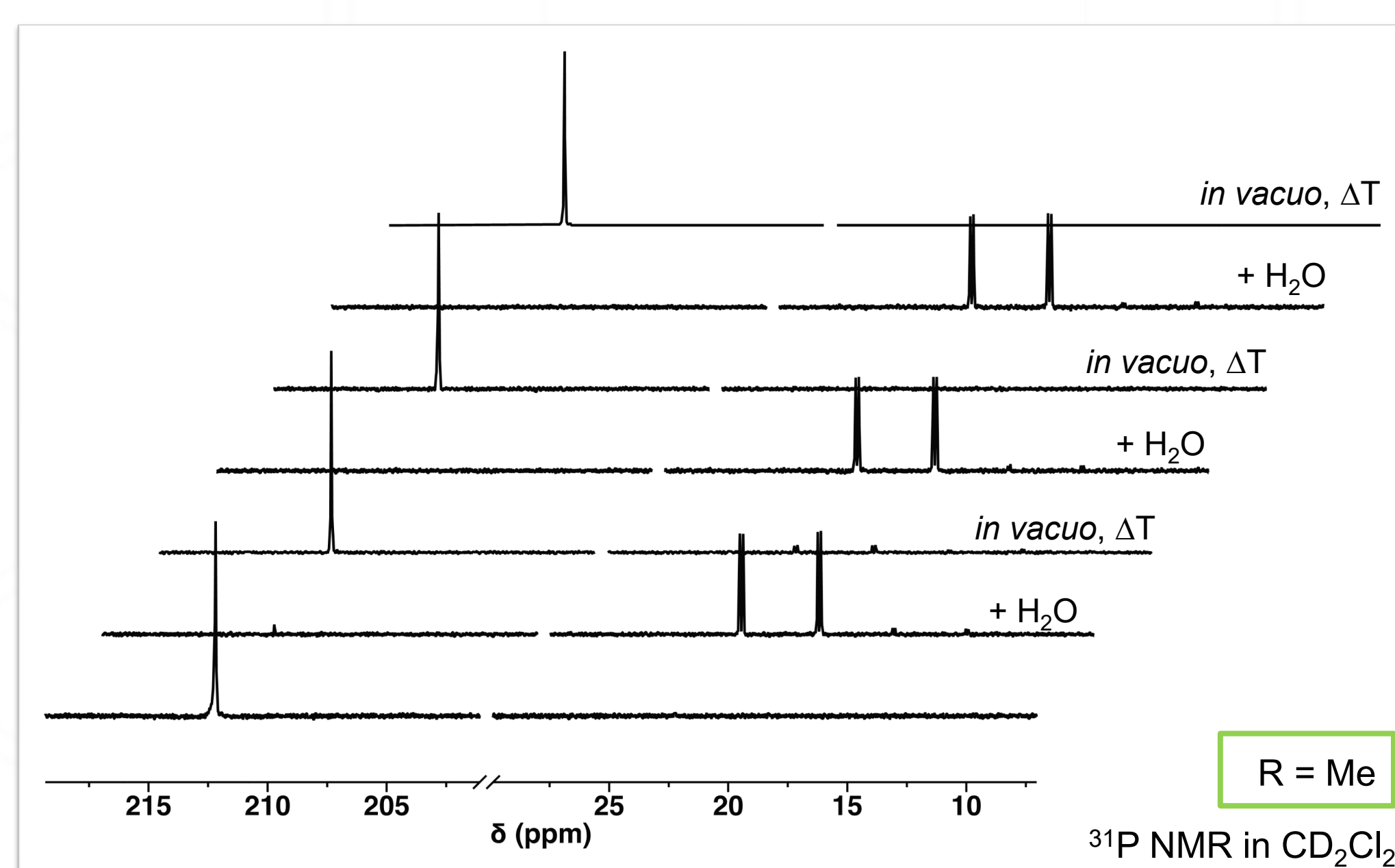


## Small molecule activation

Both phosphinines 6 and 7 react fully reversibly 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 H<sub>2</sub>O. As an intermediate a λ<sup>5</sup>-phosphinin-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-aromatization to the phosphinine.



Ratio of 8 to 9 (97:3) not influenced by solvent, temperature or R-group.



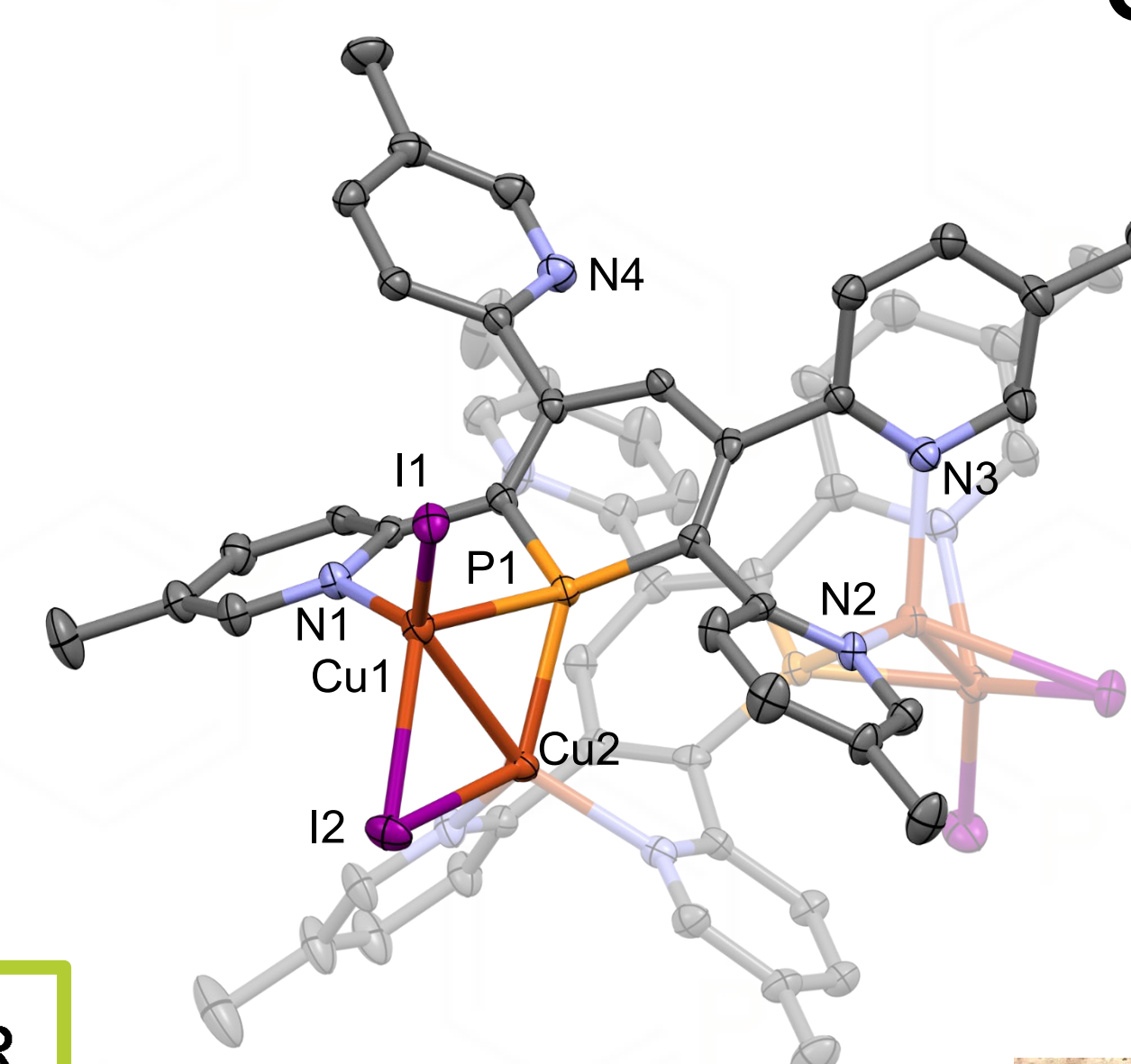
<sup>31</sup>P NMR in CD<sub>2</sub>Cl<sub>2</sub> [ppm]:

Compound	Chemical Shift (ppm)	Assignment	<sup>1</sup> J <sub>PH</sub> (Hz)	<sup>2</sup> J <sub>PH</sub> (Hz)
6	213.9			
7	211.3			
8-H	(dd) 21.7		529	22
9-H	(dd) 15.3		495	18

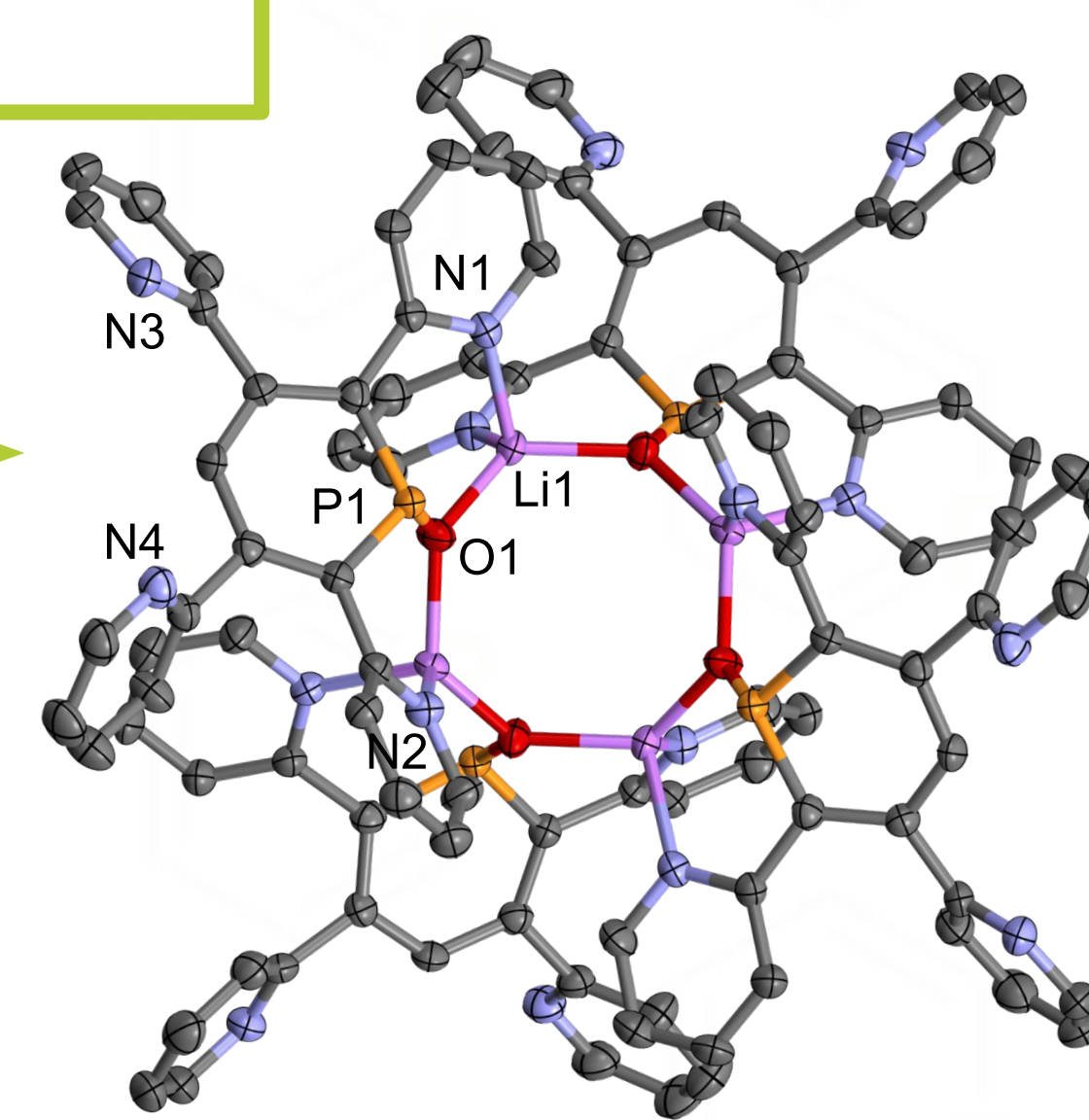
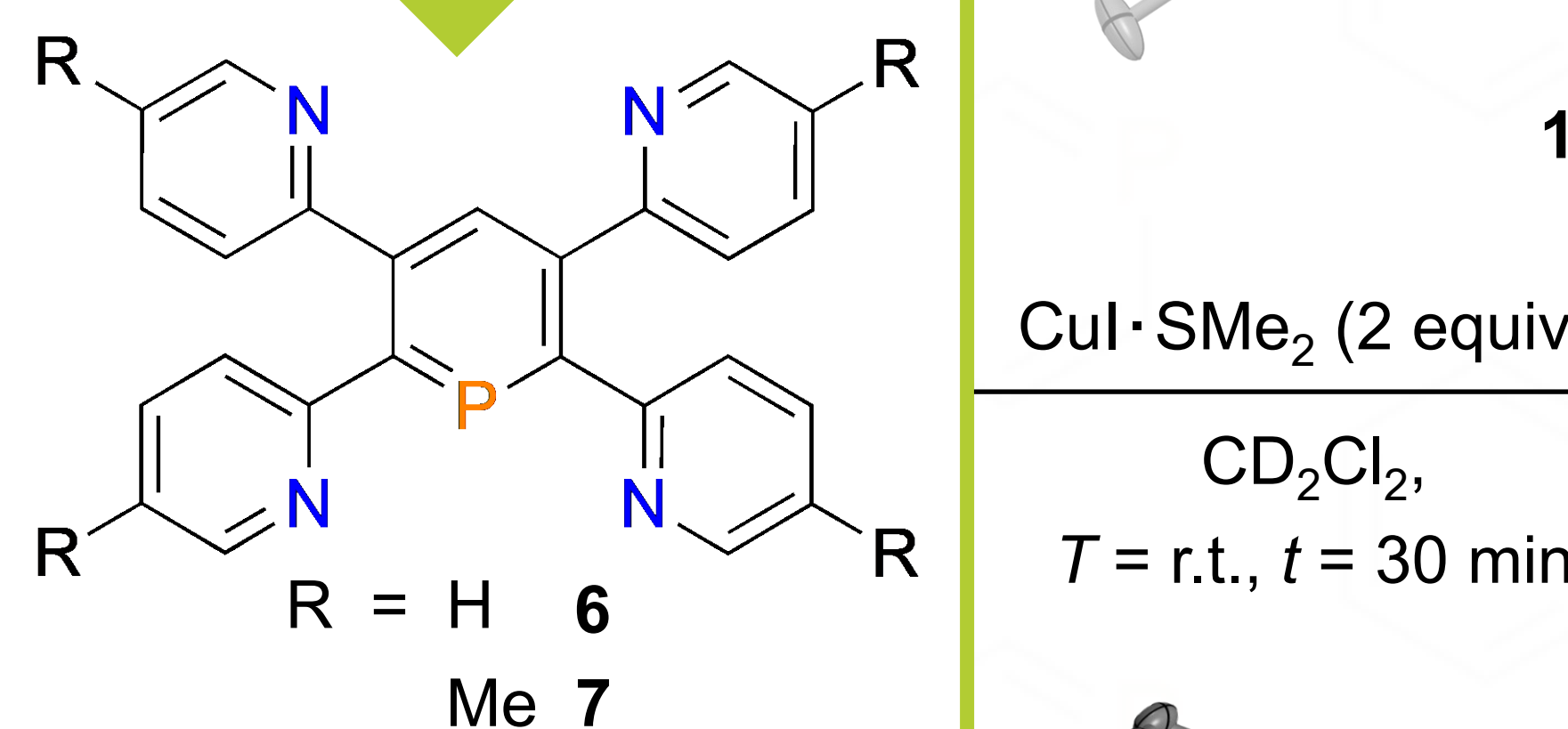
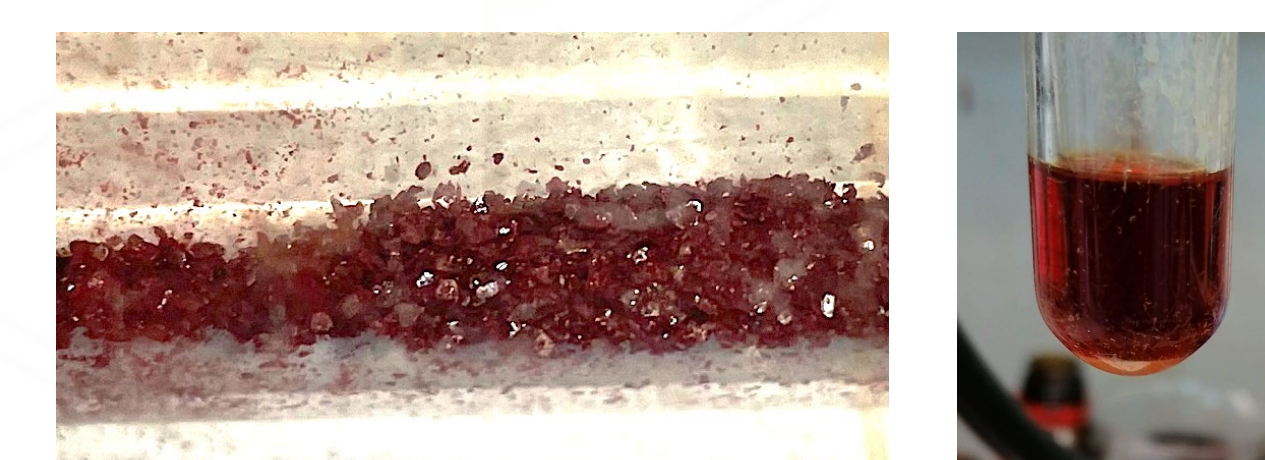
The removal of H<sub>2</sub>O *in vacuo* takes place already at room temperature. The addition and removal can be repeated several times. All dihydrophosphinine oxides show a characteristic doublet in the <sup>31</sup>P NMR spectra.

## Coordination chemistry

6 bridges two copper dimer, with support of three pyridyl groups. The Cu-Cu distance with 2.561(1) Å in the η<sup>1</sup>-μ<sub>2</sub> complex (12) is unusually short.



Quantitative formation of the dark red (PP(CuI))<sub>2</sub> dimer 12.



<sup>31</sup>P NMR in Et<sub>2</sub>O [ppm]:

Compound	Chemical Shift (ppm)	<sup>1</sup> J <sub>PH</sub> (Hz)
10 (R = H)	(d) 9.7	527
11 (R = Me)	(d) 7.7	529

Deprotonation of 8 and 9 with MeLi results into a tetrameric structure with a lithium-oxygen octagon (10).



Solid and solution of 10 (right NMR tube) show intense fluorescence under UV-light at λ = 230 nm. Compared to a solution of 8 and 9 (left NMR tube).

## 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 λ<sup>5</sup>-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 got introduced into the coordination sphere of Cu(I). Two phosphinines coordinate to a (CuI)<sub>2</sub>-dimer by involvement of three pyridyl moieties. This results in dimeric coordination compounds.

## Acknowledgements:

The authors thank the Freie Universität Berlin and the DFG for financial support.



- [1] R. O. Kopp, S. L. Kleynemeyer, L. J. Groth, M. J. Ernst, S. M. Rupf, M. Weber, L. J. Kershaw Cook, N. T. Coles, S. E. Neale, C. Müller, *Chem. Sci.* **2024**, 15, 5496–5506
- [2] J. M. Alcaraz, A. Breque, F. Mathey, *Tetrahedron Lett.* **1982**, 23, 1565–1568.
- [3] N. T. Coles, A. Sofie Abels, J. Leidl, R. Wolf, H. Grützmaier, C. Müller, *Coord. Chem. Rev.* **2021**, 432, 4–21.
- [4] C. Müller, E. A. Pidko, M. Lutz, A. L. Spek, D. Vogt, *Chem. Eur. J.* **2008**, 14, 8803–8807.
- [5] N. Avarvari, P. Le Floch, C. Charrier, F. Mathey, *Heteroat. Chem.* **1996**, 7, 397–402.
- [6] A. E. Brown, B. E. Eichler, *Tetrahedron Lett.* **2011**, 52, 1960–1963.



*Chem. Sci.* **2024**, 15, 5496–5506.