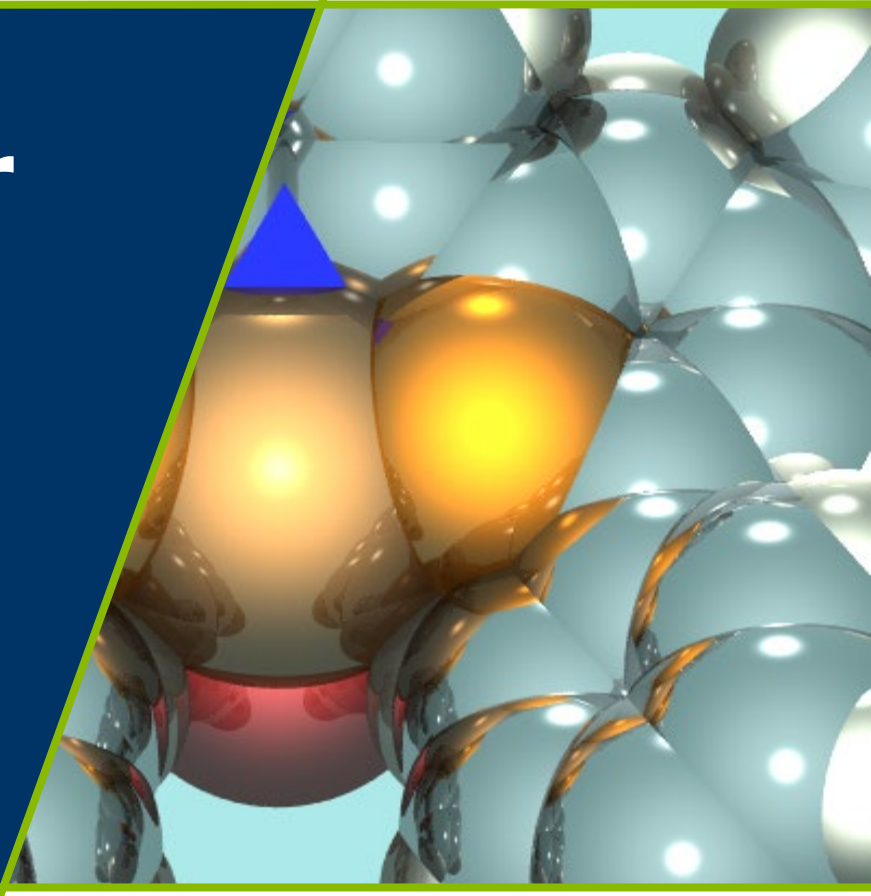
Phosphorus & Catalysis
AK Müller

AK Prof. Dr. Christian Müller

Molecular Inorganic Chemistry



Freie Universität Berlin, Germany
Institut für Chemie und Biochemie

www.bcp.fu-berlin.de/chemie/chemie/forschung/InorgChem/agmueller

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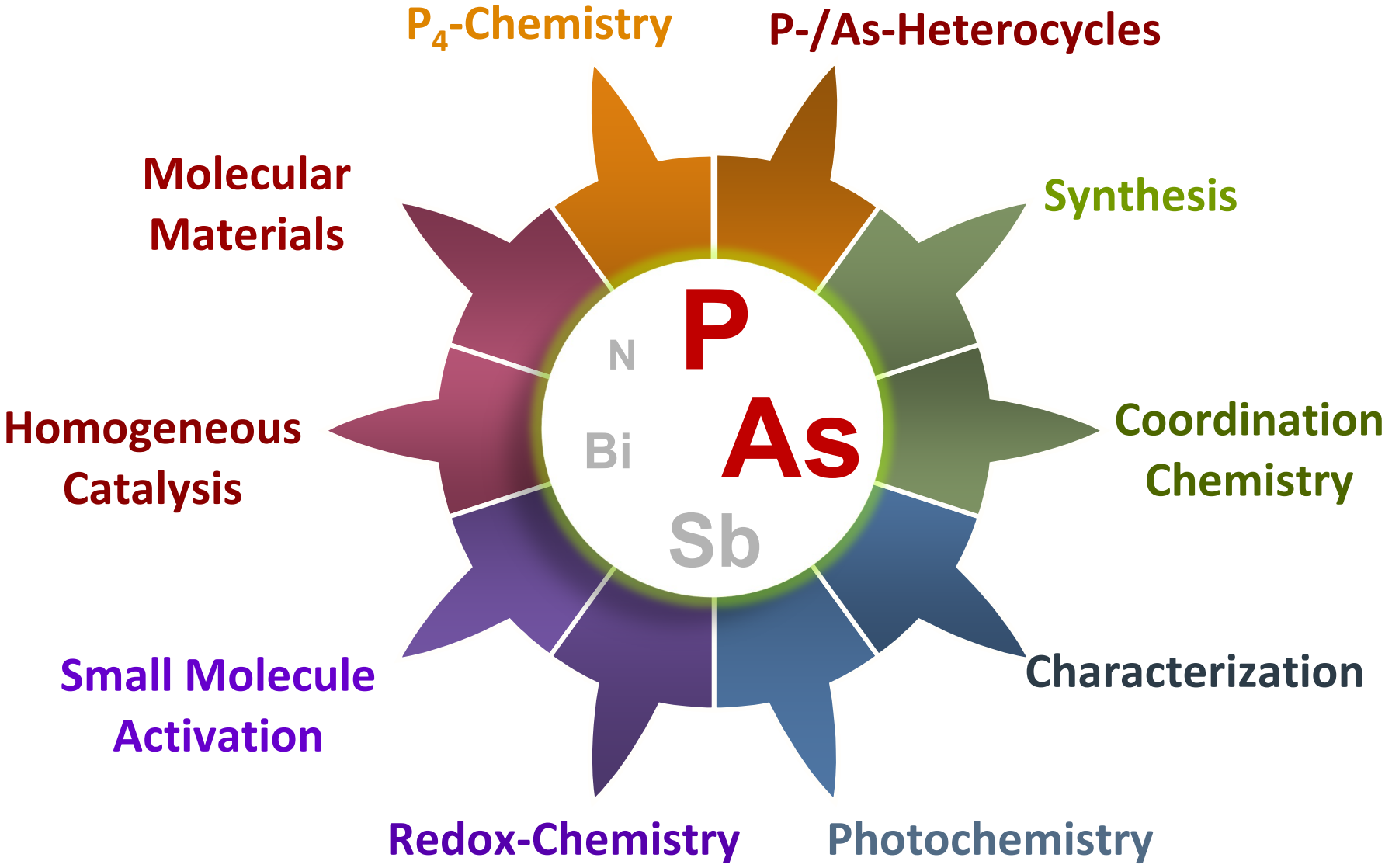
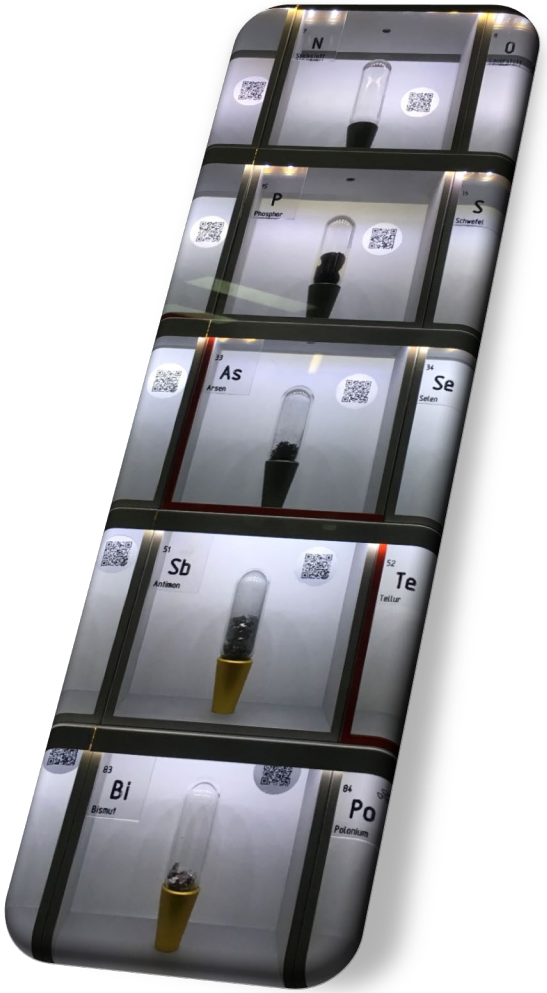
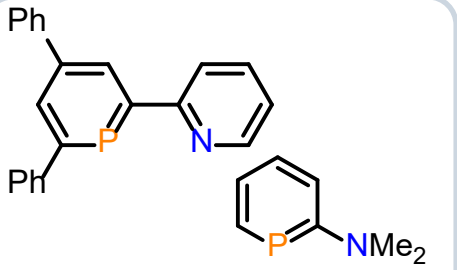
Chemistry of Group-15-Elements: Fundamental Aspects and Applications



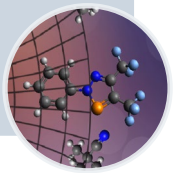


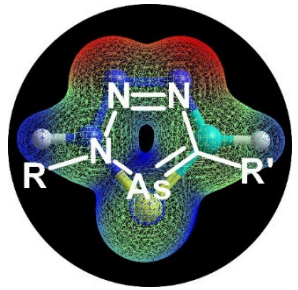
Molecular Inorganic Chemistry of Group-15-Elements: From Fundamental Aspects to Applications



Angew. Chem. Int. Ed. **2019**, *58*, 15407
Angew. Chem. Int. Ed. **2021**, *133*, 3625

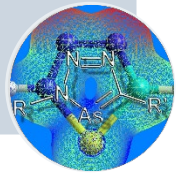
P-Heterocycles

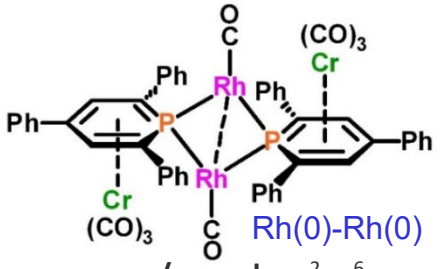




Angew. Chem. Int. Ed. **2016**, *55*, 11760

As-Heterocycles



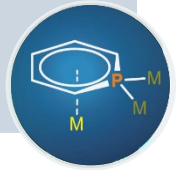


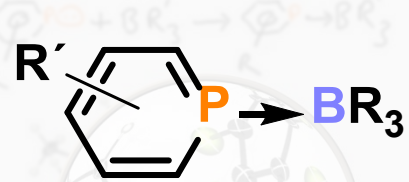
Rh(0)-Rh(0)

σ-/π-mode; μ^2, η^6;

Chem. Commun. **2022**, *58*, 6184

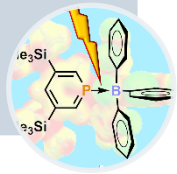
Coordination Chemistry

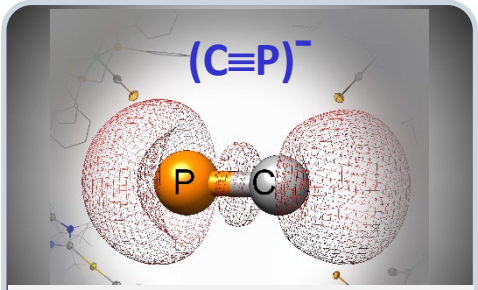




Angew. Chem. Int. Ed. **2019**, *58*, 15407
Chem. Commun. **2022**, *58, 13580*
Chem. Sci. **2024**, *15*, 5496

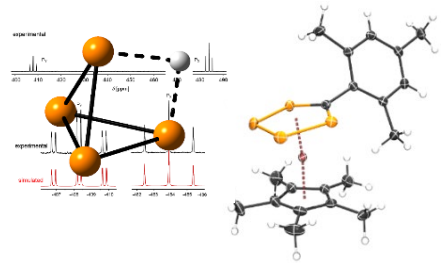
Activation of Small Molecules





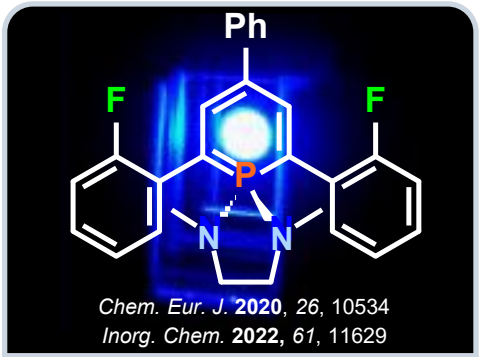
J. Am. Chem. Soc. **2021**, *143*, 19365
Angew. Chem. Int. Ed. **2023**, e202217749

Photochemistry



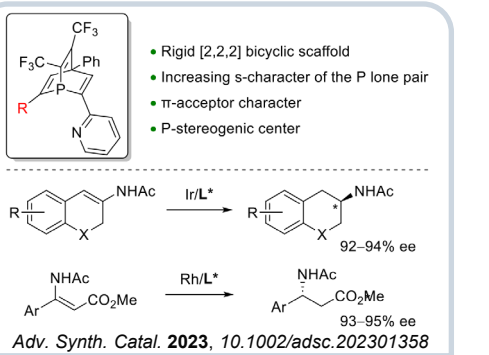
Chem. Sci. **2018**, *9*, 7169-7173
Chem. Commun. **2024,**
DOI: 10.1039/D4CC04319G

P_4-Chemistry



Chem. Eur. J. **2020**, *26*, 10534
Inorg. Chem. **2022,** *61*, 11629

Luminescent Molecular Materials



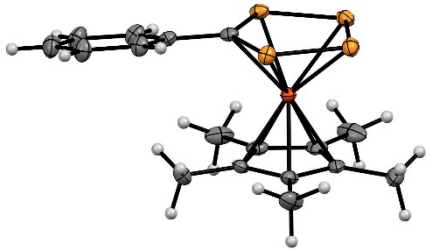
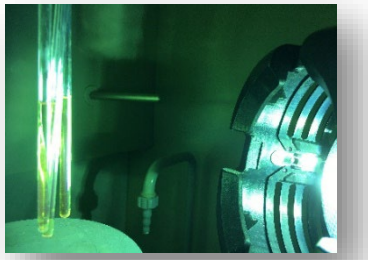
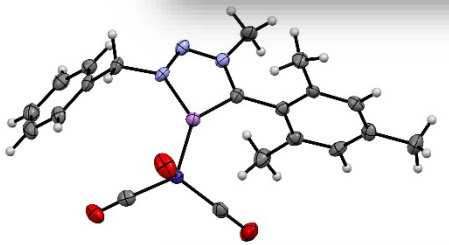
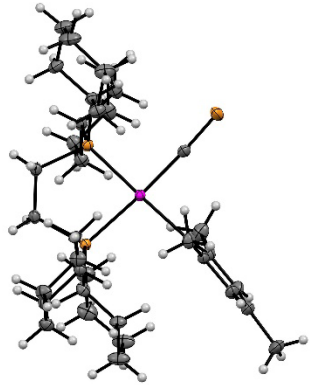
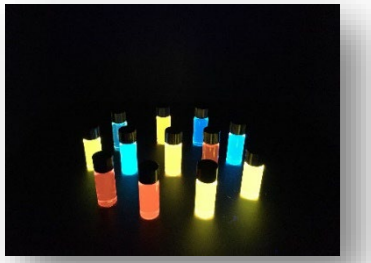
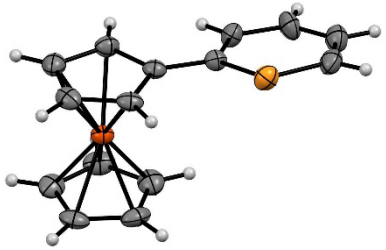
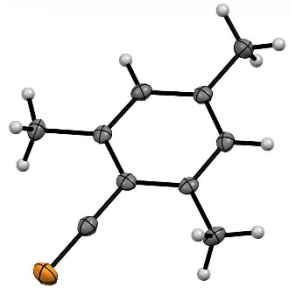
Adv. Synth. Catal. **2023**, *10.1002/adsc.202301358*

Homogeneous Catalysis

Molecular Inorganic Chemistry of Group-15-Elements: From Fundamental Aspects to Applications

Topics we offer:

- New transformations of white phosphorus with pericyclic reactions
- The chemistry of the cyaphide and cyarside anion $(C{\equiv}P)^-$; $(C{\equiv}As)^-$
- Photochemistry
- Click-chemistry with phospha- and arsaalkynes: new P- and As-heterocylces
- New ligands for homogeneous catalysis, P-derivatives of bipy and terpy
- P- and As-heterocycles in optoelectronic devices
- Highly reduced P-based metal complexes for small molecule activation
- small molecule activation with aromatic phosphorus- and arsenic heterocycles

Molecular Inorganic Chemistry of Group-15-Elements: From Fundamental Aspects to Applications

What we request from you:

- being motivated and interested
- being creative
- being a team-player
- having practical skills for working under inert reaction conditions (Schlenk-lines)
- being fluent in English
- „full-time job“

Molecular Inorganic Chemistry of Group-15-Elements: From Fundamental Aspects to Applications

A Phosphinine-Borane Adduct activates Water

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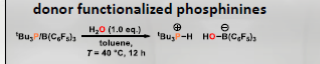
Introduction

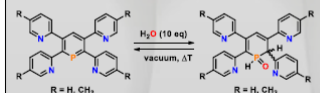
The interest in transition metal free activation of small molecules increased drastically in the past years. Especially FLPs allow a metal free approach to activate small molecules such as H_2 or H_2O for catalytic organic reactions.[1] In addition, two *ortho*-donor functionalized phosphinines have proven to activate water selectively, whereas a third pyridyl-phosphinine activates water upon coordination to a rhodium metal center.[2] We have recently reported for the first time on a 3,5-bis(trimethylsilyl)-phosphinine-$B(C_6F_5)_3$ Lewis pair (**1**).[3] Even though **1** is not a classical FLP and does not contain *ortho* functional groups, we observed the activation of H_2O upon equimolar conversion.

$^{31}P\{^1H\}$ NMR: δ = 176.6 ppm d(P1-B1) = 2.0415(12) Å

H_2O activation with FLPs and donor functionalized phosphinines

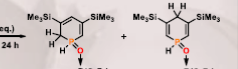


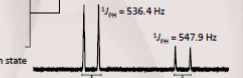
ROSENTHAL, *Acta Cryst.* **2012**



MÜLLER, *Chem. Sci.* **2024**

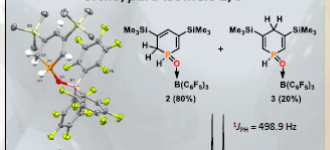
H_2O activation with phosphinine borane adduct 1





^{31}P NMR spectrum (CH_2Cl_2)

ortho/para isomers 2/3



HOMO of **2** (level of theory: PBE0 def2-svp)

^{31}P NMR spectra of isomers **2**/**3** in CH_2Cl_2 and CH_3OH

Reactivity of phosphinine oxide 2/3 with bases

$^{31}P\{^1H\}$ NMR spectrum (CH_2Cl_2)

Conclusion and outlook

We present here that phosphinine-borane adduct **1** activates water in an equimolar reaction. Unlike the published examples, **1** activates water without cooperation with *ortho* functional groups in the phosphinine. In addition to the isolated *ortho* isomer **2**, a hitherto unknown *para* isomer **3** is observed by means of NMR spectroscopy. Furthermore, **2**/**3** reacts with bases differently. Depending on the base, deprotonation, intermolecular hydrophosphination and formal reversibility were observed. Further investigations on the mechanism concerning the activation of water are currently in process.

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

References:
[1] D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed. Engl.* **2010**, *49*, 46–76. [2] a) M. Doux, N. Mézailles, L. Ricard, P. Le Floch, *Eur. J. Inorg. Chem.* **2003**, *2003*, 3878–3894; b)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; c) I. de Krom, E. A. Pidko, M. Lutz, C. Müller, *Chem. Eur. J.* **2013**, *19*, 7523–7531. [3] J. Lin, F. Wossidlo, N. T. Coles, M. Weber, S. Steinhauer, T. Böttcher, C. Müller, *Chem. Eur. J.* **2022**, *28*, e202104135.