Convenient Access to π-Conjugated 1,3-Azaphospholes from Alkynes via [3+2]-Cycloaddition and Reductive Aromatization

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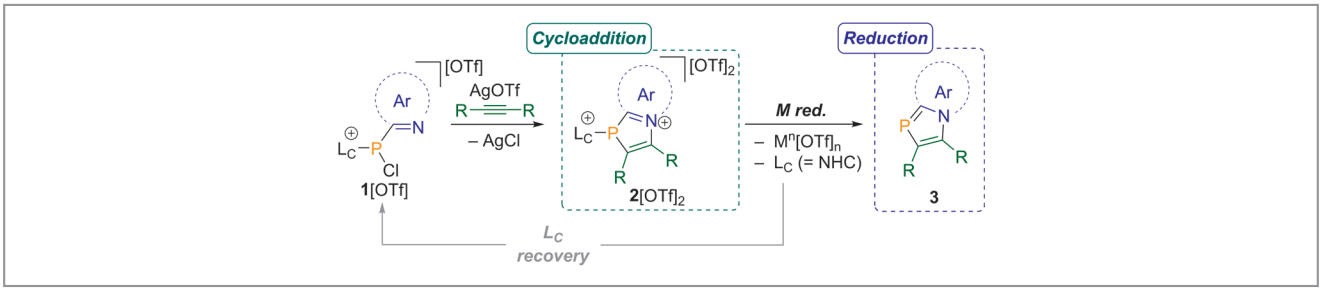
The chemistry of phosphorus-containing heterocycles is well established and in recent years a significant number of *P*-heterocycles have been successfully used in various applications related to organic semiconductors, such as OLEDs, OPVs and OFETs, or as ligands in transition-metal complexes. A recent article in *Chem* from the group of Professor Jan J. Weigand at the Technische Universität Dresden (Germany) describes a new method for the synthesis of annelated 1,3-azaphospholes (**3**) in a two-step procedure from a conveniently accessible phosphorus building-block. The described method provides access to a wide range of compounds, which allows study of their physical and chemical properties. "Initially, 1,3-dipolar triflatophosphanes are formed that readily engage in 'click-type' [3+2]-cycloaddition reactions with alkynes to afford 1,3-azaphospholium cations **2**$[OTf]_2$ as their respective triflate salts," said Professor Weigand. He continued: "Subsequent reduction reactions lead to the formation of 1,3-azaphospholes (**3**, Scheme 1), a substance class that was only accessible to a limited extent due to inconvenient synthetic access pathways. Interestingly, the imidazoliumyl substituent is reductively cleaved to yield an *N*-heterocyclic carbene as the leaving group, an approach that we have developed in our group over the past years (*J. Am. Chem. Soc.* **2023**, *145*, 10364–10375)."

The Weigand group's approach originates from a previous contribution in which highly electrophilic fluorophosphonium ions with a donor atom in the 3-position were used as frustrated Lewis pairs for the activation of small molecules (*Chem. Eur. J.* **2021**, *27*, 13709–13714). Professor Weigand explained: "We adapted this method slightly to phosphenium ions, which in turn led to the formation of phosphorus ring systems with tri-coordinate phosphorus atoms. During our investigations, we noticed that due to the coordination of one triflate anion, triflatophosphanes are the reactive species in the cycloaddition reactions. After standard electrochemical screening of a model compound, it was determined that the cycloaddition products could be reduced to afford neutral 1,3-azaphospholes (**3**). Due to convenience and ease of handling, we used zinc dust in most of our syntheses."

What particularly stands out with this approach is its convenience and scope (Scheme 2). "The range of usable alkynes has been expanded to 19 derivatives, achieving yields of up to 99%. Typically, such 1,3-azaphospholes are prepared either from phosphaalkynes or other phosphorus building-blocks, both of which have lacked sufficient scope and have only been scarcely explored in recent years," remarked Professor Weigand. He went on: "Furthermore, we believe that the simplicity of this approach will appeal to a large segment of the research community, as the main precursors can be synthesized from readily available starting materials using common Schlenk techniques in quantitative yields (*J. Am. Chem. Soc.* **2010**, *132*, 16321–16323). The range of potential alkynes is undoubtedly vast." Professor Weigand concluded: "We aim to establish 1,3-azaphospholes as a new and promising substance class and have therefore investigated some fundamental structure–property relationships, deriving some general design rules to influence their optoelectronic properties. Given the expanded scope behind our method, we anticipate that these compounds can be specifically adapted targeting



Scheme 1 Two-step synthesis of 1,3-azaphospholes (**3**) involving a 1,3-dipolar cycloaddition of **1**[OTf] with alkynes in the presence of AgOTf to form azaphospholium salts **2**$[OTf]_2$, which are subsequently reduced to yield 1,3-diazaphopsholes (**3**).

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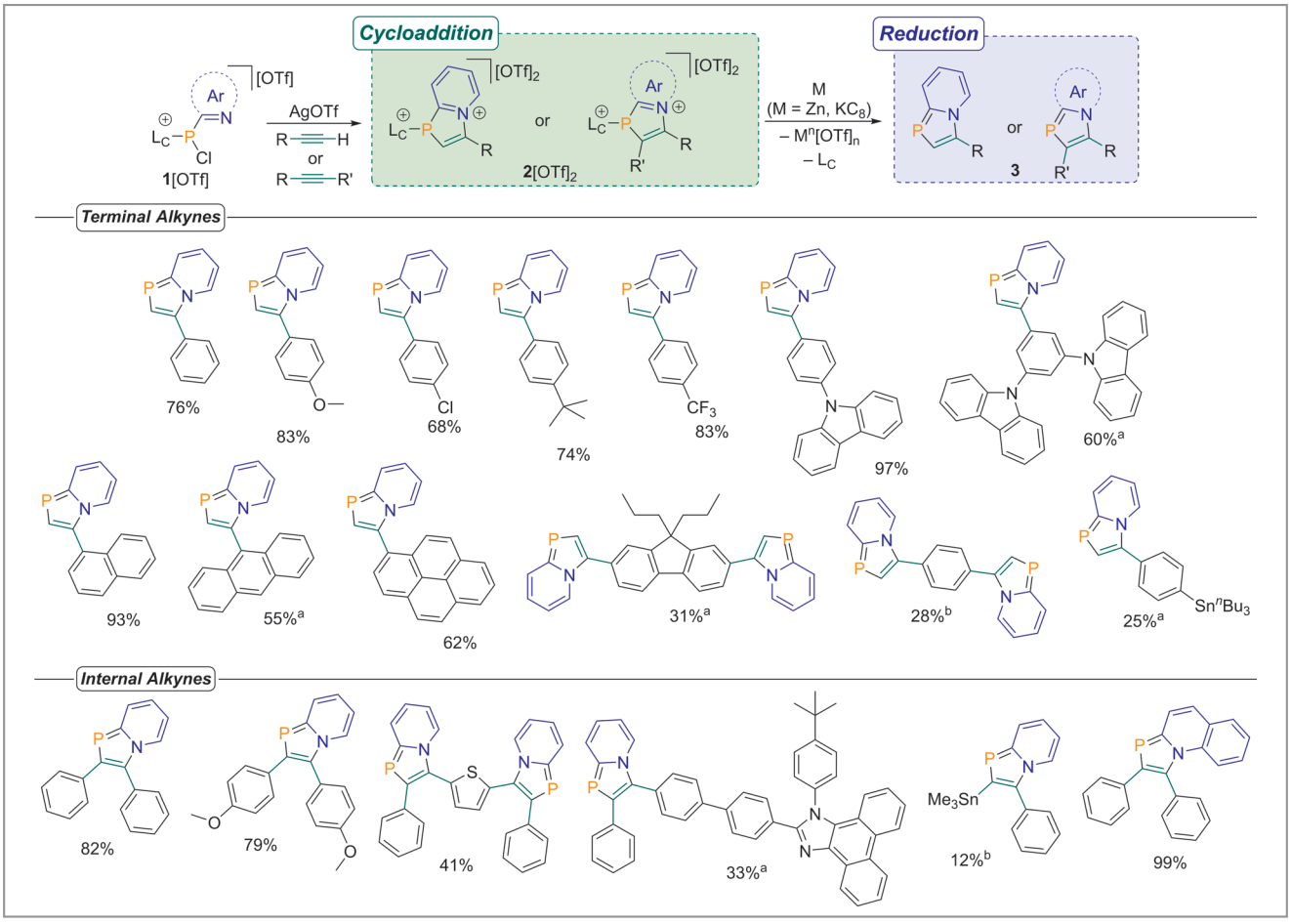
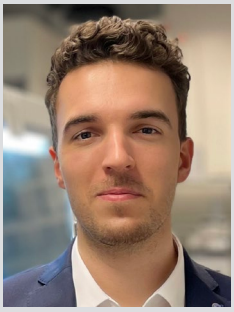
favorable optoelectronic characteristics, potentially making them suitable for innovative applications including organic semiconductors, OLEDs, OPVs, and OFETs."



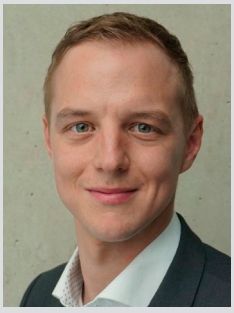
Scheme 2 Scope of 1,3-azaphospholes (**3**) prepared using the described method. [a] Yield from crude starting material. [b] Yield from **1**[OTf].

About the authors



J. Fidelius

Jannis Fidelius received his B.Sc. in chemistry from the Dresden University of Technology (Germany) in 2017 under the supervision of Prof. Dr. Peter Metz. He then completed his M.Sc. degree in Dresden in 2019. He is currently pursuing his Ph.D. under the supervision of Prof. Dr. Jan J. Weigand, focusing on the development of novel methods for the synthesis of phosphorus-containing ring systems and their application as novel molecular materials, with a special focus on optoelectronic properties.



Dr. K. Schwedtmann

Kai Schwedtmann received his diploma degree from the WWU Münster (Germany) in 2012 and started his Ph.D. studies under the supervision of Prof. Jan J. Weigand. In 2013, he moved to TU Dresden (Germany), where he received his Dr. rer. nat. in 2016. During his Ph.D. studies, he was a visiting researcher in the group of Prof. Neil Burford in 2014 at the University of Victoria (Canada). Today, he is senior researcher at TU Dresden, focusing on reactive phosphorus compounds and sustainable phosphorus chemistry.

Prof. J. J. Weigand

Jan J. Weigand obtained his diploma in chemistry in 2002 and his Dr. rer. nat. in 2005 from the LMU in Munich (Germany). Awarded the Bavarian Culture Prize in 2005, he received a Lynen Scholarship from the Alexander von Humboldt (AvH) Foundation for postdoctoral research at Dalhousie University in Halifax (Canada). He returned to Germany with a Lynen Return Fellowship and began his habilitation at WWU Münster in 2007 under the supervision of Prof. Hahn. Shortly thereafter, he was awarded the Liebig scholarship of the Fonds der Chemischen Industrie (FCI), allowing him to start his independent career in 2008. In April 2010, he became a fellow of the prestigious Emmy Noether research program awarded by the DFG, and received the Wöhler Young Scientist Research Award. In July 2012, he was granted an ERC Starting Grant by the European Council (EC). Since January 1, 2013, he has been a full professor at TU Dresden (Germany). His research focuses on molecular inorganic and phosphorus chemistry, including the development of sustainable methods for extraction, technical applications, and novel recycling strategies. This encompasses innovative catalyst systems for use in the petrochemical industry and resource conversion into biogenic and fossil residues. In 2023, he received Reinhardt Koselleck funding from the DFG for the project 'Blueprint for a Modern Sustainable Phosphorus Chemistry'.

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