Phosphorus Special Issue in Honor of Koop Lammertsma and Edgar Niecke

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Guest Editorial

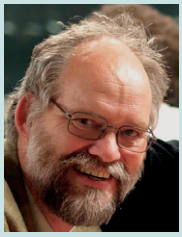
Phosphorus Special Issue in Honor of Koop Lammertsma and Edgar Niecke

Dietrich Gudat,*[a] Andreas Orthaber,*[b] J. Chris Slootweg,*[c] and Rainer Streubel*[d]

Two very prominent researchers of the European community of phosphorus chemists are celebrating their 70th and 80th birthdays: congratulations to Professors Koop Lammertsma and Edgar Niecke (Figure 1).

Figure 1. Koop Lammertsma and Edgar Niecke.

As university teachers, supervisors to numerous PhD students and postdoctoral fellows, and as researchers throughout their scientific work, Koop Lammertsma and Edgar Niecke had and still have a great influence on the phosphorus chemistry community, and beyond. Their combined oeuvre includes more than 500 research papers, review articles, and so on. Prof. Niecke was one of the pioneers in the field of low-coordinate phosphorus compounds, which contributed vitally to the "Renaissance of main group chemistry" during the 1970s and 1980s, and his seminal work on 1,3-diphosphacyclobutane-2,4-yls[1] set off a boom in the chemistry of inorganic biradicaloids that is still continuing. Prof. Lammertsma brought a physical organic chemistry perspective to the phosphorus community and challenged everyone to include quantum chemical computations in their own research. He investigated a large variety of topics, the activation, functionalization, and fragmentation of P_4 as well as the spectroscopic characterization of a metal-free phosphinidene[2] being his greatest achievements. To celebrate their birthdays and as a tribute to their accomplishments, the *European Journal of Inorganic Chemistry* has collected a special issue guest edited by Rainer Streubel, Dietrich Gudat, J. Chris Slootweg, and Andreas Orthaber, whose academic tree can be directly traced back to either of the two.



Dietrich Gudat was born in Düsseldorf (Germany) and finished his undergraduate education at the Universities of Düsseldorf and Bielefeld with a Diploma degree in 1984. After earning a Ph.D. in 1987 under the supervision of Edgar Niecke, he pursued postdoctoral studies at the Universities of Bonn and Sussex with Edgar Niecke and John F. Nixon, respectively, and at Iowa State University with John G. Verkade. He completed his habilitation in 1995 and became Professor at the University of Stuttgart in 2002. He was appointed Dr. h.c. at the Budapest University of Technology and Economics in 2017. His research is devoted to molecular compounds of main group elements, with a strong focus on phosphorus.

Andreas Orthaber was born in 1979. He received his undergraduate education from Karl-Franzens Universität Graz (Austria) and obtained a Ph.D. under the supervision of Prof. R. Pietschnig (Dept. Inorg. Chem. KFU Graz). After postdoctoral studies with Prof. O. Kunert (Dept. Pharm. Chem., KFU Graz) and Prof. S. Ott (Uppsala University, Sweden) he started his independent work, in 2014. Since 2019, he is a Senior Lecturer in synthetic molecular chemistry at Uppsala University.

The European phosphorus chemistry community is deeply connected with the annual "*European Workshop in Phosphorus Chemistry*" (EWPC). This workshop was first organized in Kaiserslautern in 2004 with a national focus. This was followed by two further workshops in Germany, one in Bonn (2005), which included international researchers for the first time, and the other in Leipzig (2006), which continued to broaden the participant

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scope. Since then it has travelled through Europe including the Netherlands, Italy, Hungary, France, Bulgaria, Romania, Sweden, and now crosses the Channel for the 16th EWPC in Bristol in 2019. These workshops have traditionally focused on supporting and promoting early stage researchers, giving the word to PhD students to present and discuss their work. The programs are usually complemented with keynote lectures from internationally renowned speakers. The workshop has also brought the industrial and academic worlds together by inviting representatives from various phosphorus chemical companies to participate in round table discussions, to give presentations, and to be included as exhibitors. This tradition is now continued in a back-to-back organization of the IndPhos (Industrial Phosphorus Chemistry Symposium) and EWPC-16, organized by Paul Pringle and J. Chris Slootweg. Rooted in and originating from these events, this research community has constantly grown in size and collaborations. In 2008, the European COST action PhoSciNet chaired by Prof. Hey-Hawkins and Prof. Lammertsma was accepted and included for the first time during the EWPC 2009 in Florence. From 2013 to 2017, the European Training Network "SusPhos" chaired by J. Chris Slootweg established an additional dissemination and exchange platform, also by organizing the ICSPC (International Conferences on Sustainable Phosphorus Chemistry) in Florence (2014) and Berlin (2017), back-to-back with EWPC-13.

Undeniably, the (European) phosphorus chemistry community is in its diversity spanning organic, inorganic, polymer, materials chemistry and biological chemistry, including very fundamental research questions at one end of the spectrum, and touching applied and industrially relevant processes and developments at the other end. In the past years, various topics have emerged, others have been lifted from fundamental to applied research questions, and some aspects of phosphorus chemistry have been rediscovered and are now in their second bloom. This double issue gives a cross-section of timely fields by leading groups from Europe and beyond. It comprises 21 articles and 7 reviews. The front cover is designed by Robert Wolf and coworkers and the cover features are provided by the working group of Christian Müller and by Ian Teasdale.

Romero-Nieto and coworkers describe in their review article fused six-membered phosphorus heterocycles, highlighting their use as biomarkers, in responsive systems, and for other optoelectronic applications. The groups of Baumgartner and Orthaber report new synthetic and optoelectronic properties of the dithienoheterole motifs of phosphorus and arsenic, respectively. Slootweg and coworkers report a facile synthesis of azophosphonium> salts: Aryl–N=N–$P^{+}(t\mathrm{Bu})_3$, with highly tunable electronic properties with potential applications as one-electron acceptors or dyes.

Six- and twelve-membered P,N-heterocyclic carborane derivatives and their use as ligands in Rh-catalyzed hydrogenations are reported by Hey-Hawkins. In contrast, the electron-rich N-heterocyclic boryl substituted phosphines by the Gudat group are applied to Pd-mediated C–N coupling reactions. Müller and coworkers have investigated new rhenium complexes of 2-pyridylphosphinines and their reactivities at the PC double bond, while Wolf and coworkers have studied the reactivity of the anionic triphenylphosphinine ferrate anion $[Cp^*Fe(\eta^4\text{-}PC_5Ph_3H_2)]^-$ in electrophilic halogenation reactions. Espinosa Ferao and Streubel elucidate the reaction of a Li/Cl phosphinidenoid $Fe(CO)_4$ complex with ammonia and primary/secondary amines to give 1,1′-bifunctional aminophosphanes via a formal N–H bond insertion. Oxidative addition of P–P bonds at a metal carbonyl fragment, as well as insertion of acetonitrile, is reported by Hey-Hawkins and coworkers. Frison, Carmichael, and coworkers have studied the pH responsiveness of a metallocene coordination compound via reversible hydroxide coordination to a cationic P-center. Rozhenko and Kostyuk elucidate the complex transformations involving N–($P^{III/V}$)-substituted acyclic diaminocarbenes. Optically active phosphophosphidites as P–P analogues to the well-explored phosphoramidites display significantly higher reactivity for P–P and P–O cleavage. The integrity of the ligands is maintained during BH_3 and Mo^0 coordination, as reported by Pringle and coworkers. Efficient catalytic hydrophosphination of different alkenes have been reported by Waterman using a triamidoamine/zirconium catalyst giving improved results under irradiation.

Fundamental reactivity questions of phosphaalkenes have been answered by Arkhypchuk and Ott looking at the equilibria involving triphenylphosphaethene, as well as by Gates and Streubel exploring the synthesis and reactivity of *P*-thiazol-2-thione-functionalized phosphaalkenes. Compton and Goicoechea have studied the electrochemistry of the phospha- and arsaethynolate anions. Pietschnig describes a bisplumbylene

Chris Slootweg was born in Haarlem (The Netherlands) in 1978 and received his undergraduate education from Vrije Universiteit Amsterdam in 2001. After earning his Ph.D. in 2005 under the supervision of Prof. Koop Lammertsma, he pursued postdoctoral studies at the ETH Zürich with Peter Chen. In 2006, he returned to VU to initiate his independent career. He was promoted to Associate Professor in 2014 and moved to the University of Amsterdam in 2016. The mission of his laboratory is to educate students at the intersection of fundamental physical organic chemistry, main group chemistry and circular chemistry.

Rainer Steubel received his undergraduate education at University of Bonn (Germany), where he also obtained his Ph.D. (summa cum laude) under the guidance of Prof. Edgar Niecke. After postdoctoral studies with Prof. François Mathey at the Ecole Polytechnique (Paris, 1990–1992), he pursued a habilitation at the Technical University Braunschweig, Germany (1992–1997). In 2003, he returned to Bonn as a Full Professor in Inorganic Chemistry. His group is working amongst many other topics on phosphorus heterocycles, phosphinidene complexes with a focus on reactive intermediates using a wide range of experimental, spectroscopic, and theoretical methods.

embedded in a phosphorus-containing [3]-ferrocenophane scaffold and its cationic derivative obtained by chloride abstraction. Krossing and coworkers contribute with their work to understand the different coordination behaviors of the P_4Se_3 and As_4S_3 cages toward Ag^I salts. The groups of Schreiner and Schulz describe the syntheses and structures of carbene-stabilized stibinidenes.

Polymer aspects have been discussed by Troev, reporting the synthesis and spectroscopic characterization of a hybrid phosphorus/silicon inorganic polymer, poly(dimethyl-H-phosphonate). The review by Peruzzini deals with 2D materials and summarizes the role of phosphorene in this emerging area of research. Two new polymorphs of lithium pyrophosphate $Li_4P_2O_7$ were obtained by Glaum and studied by X-ray diffraction and solid-state ^{31}P NMR spectroscopy.

Contributions by Schoeller and Heinicke review the progressive work on the Niecke biradicals (and congeners) and the chemistry of α-phosphanyl α-amino acids, respectively. Phosphorhydrazones $RP(X)(NMeNH_2)_2$ and $Cl_2P(X)NMeNH_2$ and their role as fundamental building blocks for dendrimers and macrocycles is reviewed by Majoral and Caminade, while Teasdale focuses in his review on the responsive properties of polyphosphazenes and polyphosphoesters to various triggers. Finally, Romerosa reviews the medicinal, in particular the antiproliferative, properties of PTA-derived coordination compounds (PTA = 1,3,5-triaza-7-phosphaadamantane).

We feel privileged that, with this collection of articles, we had the opportunity to combine a timely report on current developments in phosphorus chemistry with a look into the past and the future. In our opinion, this collection of articles honors the birthday boys Prof. Lammertsma and Prof. Niecke and demonstrates their legacy, as many of their ideas still influence us and have contributed to bringing us where we are today. Looking into the future, there are many prospects for finding useful applications of the chemistry developed so far, and there is plenty of opportunity for new discoveries, which we think will continue to offer scientific challenges. Thus, we are confident that phosphorus chemistry will continue to be a fruitful and relevant research field, and we hope that this special issue of the *European Journal of Inorganic Chemistry* can help to increase its attractiveness, which is felt by all the contributors to this article, to younger colleagues and newcomers.

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