ONLINE WORKSHOP ON PHOSPHORUS CHEMISTRY

BOOK of ABSTRACTS



Welcome to OWPC

We cordially invite you to participate at the Online Workshop on Phosphorus Chemistry (OWPC), an online conference aimed at PhD students in the field of phosphorus chemistry.

The OWPC was created to shorten the wait until the next "regular" iteration of the European Workshop on Phosphorus Chemistry (EWPC), which had to be postponed to 2022 due to the Covid-19 pandemic. Like the EWPC, the online workshop offers early-stage researchers an opportunity to communicate their work to the leading European and international research groups in phosphorus chemistry. The aspects of phosphorus chemistry covered by this workshop span organic, inorganic, polymer, materials chemistry, and biological chemistry.

We are quite overwhelmed with the positive resonance we received while organizing this online event. With 24 talks, including two "how-to" lectures, and 37 poster presentations, that is, a total of 61 scientific contributions, the OWPC has become quite a lot bigger than we anticipated. Contributions were submitted from Asia, North America and Europe, so the OWPC will truly be an international conference.

Thus, special thanks are due to our contributors, without whom this conference would and could not take place. We are grateful that all of you are open to the idea of an online workshop, and that by participating at the OWPC, we can come together albeit staying apart in an effort to fight the pandemic.

We wish us all a successful meeting and fruitful exchange of ideas!

Warmest regards,

Jonas Bresien Christian Hering-Junghans Christian Müller Axel Schulz

We thank our sponsors and supporters:









How can I listen to the talks?

All talks will be streamed via **Zoom**. The link to the meeting will be posted <u>on our webpage</u> on March 29. The Zoom meeting will be opened at 08:30 CET every morning and stay open until the end of the sessions each day.

How can I join the discussions?

There will be time for questions **after each talk**. If you want to ask a question, please "raise your hand". One of the moderators of the meeting will then unmute you, so you can ask your question(s). Alternatively, you may use the "Questions and Answers" (Q&A) tab in the Zoom meeting to type your question. The session chair will then read your question to the audience.

You will also have the opportunity to ask questions **during the breaks**. To this end, we have configured a conference chat room on GWDG Rocket.Chat. Registration is free of charge:

https://www.gwdg.de/registration

After registration, please join our OWPC chat room:

https://chat.gwdg.de/invite/g6oP4n

There are separate chat rooms for every presentation, which you can access by clicking the "Chat" links in the online programme, or by clicking the chat icons (P) in the timetable below.

Where can I see the posters?

All posters can be viewed <u>on our website</u> throughout the conference. They are sorted into **poster sessions 1 and 2**, according to when the poster presenters will be available for questions in a live video meeting.

How can I discuss the posters?

The poster presenters will be available for discussions in a live video meeting during the poster sessions: **Posters 1-18 on Monday**, 29 March, 16:30–17:30 CET, and **posters 19-37 on Tuesday**, 30 March, 16:30–17:30 CET. To discuss a poster, just click the button "Join video meeting", which can be found next to each poster.

Alternatively, each poster has an individual chat room, where questions can be asked throughout the conference. Click the button "Discuss in chat" to enter the chat room.



Monday, 29 March 2021

09:00–10:00 CET Session 1
09:00 Welcome to OWPC
Keynote lecture
09:15 KL Angela Marinetti Gif-sur-Yvette, Paris Design of chiral phosphorus ligands for gold catalysis
10:30–11:30 CET Session 2
10:30 O1 Roman Franz Kassel P P-P bond activation in phosphorus rich ferrocenophanes P
10:50 O2 Joey Feld Oxford Place A Phosphanyl-Phosphagallene that Functions as a Frustrated Lewis Pair
11:10 Q3 Thomas D. Hettich Stuttgart Synthesis and ambiphilic reactivity of metalated diorganophosphonite boranes
13:30–14:30 CET Session 3
13:30 O4 Priyanka Gupta Rostock Priyanka Gupta Rostock New Avenues in Phospha-Wittig Chemistry Priyanka Gupta Rostock Priyanka Gupta Rostock
13:50 O5 Volker Eilrich Leipzig P Versatile Chemistry of Phosphorus-Rich Compounds P
14:10 O6 How-to lecture Debora Thöny Zürich Image: Comparison of the safely work with PH3
15:00–16:00 CET Session 4
15:00 Q7 Harish S. Kunchur Mumbai Pd ^{II} , and Pt ^{II} assisted 1,2-azaphosphole formation in a functionalized bisphosphine: Synthesis, mechanistic studies and catalytic <i>N</i> -alkylation reactions
15:20 <u>O8</u> Anne S. Abels Zurich The coordination chemistry of 2,4,6-oxy functionalised 1,3,5-triphosphinines
15:40 O9 Gen Li Cambridge, MA Intermolecular Reductive C–N Cross-Coupling of Nitro Compounds and Boronic Acids by P ^{III} /P ^V =O Catalysis
16:30–17:30 CET Poster session 1

Posters 1-18. See our website https://www.ewpc18.uni-rostock.de/owpc/poster-session-1/



Tuesday, 30 March 2021

09:00-	10:00 C	CET Paul Kamer Colloquium		
09:00		Christian Müller Berlin		
		J. Chris Slootweg Amsterdam		
		Hans de Vries Rostock		
		Paul Pringle Bristol		
10:30-	11:30 C	CET Paul Kamer Colloquium		
10:30		David J. Cole-Hamilton St Andrews		
		Peter J. Deuss Groningen		
		Dieter Vogt Dortmund		
		Matthias Beller Rostock		
13:30-	14:30 (CET Session 5		
13:30	<u>010</u>	Antonio García Alcaraz Murcia	3	
13:50	<u>011</u>	Gabriele Hierlmeier RegensburgReactivity of Di-tert-butyldiphosphatetrahedrane	3	
14:10	<u>012</u>	How-to lecture Andryj M. Borys Bern Scalable Synthesis of P(SiMe ₃) ₃ – An Illustrated Tutorial	3	
15:00-	16:00 C	CET Session 6		
15:00	<u>013</u>	Gernot Weinberger GrazFSyntheses of 2,4-functionalized diphosphapentasilanes as precursors for low-valent tin and germanium compoundsF	3	
15:20	<u>014</u>	Nicolas Ledos Rennes # Aggregation Induced Emission: organic and hybrids fluorophores #	1	
15:40	<u>015</u>	Kendahl L. Walz Mitra SeattleSurface functionalization of black phosphorus nanosheets with nitrenes:Identification of P=N bonds using isotopic labelling	3	
16:30–17:30 CET Poster session 2				
	10.07			

Posters 19-37. See our website https://www.ewpc18.uni-rostock.de/owpc/poster-session-2/



Wednesday, 31 March 2021

09:00-	10:00 C	CET Session 7				
09:00	<u>016</u>	Philipp C. Brehm BonnPhilipp C. Brehm BonnInspecting new cyclic diheterophospholane complexes as potentialphosphanoxyl complex precursors				
09:20	<u>017</u>	Tim Görlich BerlinImage: ComplexesA new synthetic pathway towards cyaphide complexes				
09:40	<u>018</u>	Maria Haimerl Regensburg Image: Complexes Towards Polypnictogen Compounds Reactivity of Cu(I) Nacnac Complexes Towards Polypnictogen Compounds				
10:30–	11:30 C	CET Session 8				
10:30	<u>019</u>	Callum Branfoot BristolPDynamic diphosphanesP				
10:50	<u>020</u>	Christian Ritter MarburgPreparation of Multinary Interpnictogen Molecules				
11:10	<u>021</u>	Omar Alami Toulouse Graphene oxide functionalized by phosphorus dendrons and dendrimers for oncology applications				
13:30–14:50 CET Session 9						
13:30	<u>022</u>	Jan Rosenboom RostockμA radical mechanism for the addition of bromoalkanes to [P(μ-NTer)]2 and synthesis of a novel P-centered persistent radical				
13:50	<u>023</u>	Alicia Rey Planells MurciaHigh-Coordinate Phosphasiliranes: Do they exist?				
14:10	<u>024</u>	Julien Aujard-Catot ToulousePSynthesis of a new series of phosphorus dendrimers				
14:30		Awards and Closing Remarks				



Poster sessions

Mond	ay, 16:30–17:30 CET
<u>P1</u>	Nicholas Birchall StuttgartPN-Heterocyclic Phosphenium Ions and their Noble Contribution to a Base Metal
<u>P2</u>	David Biskup Bonn Image: Complex Adducts Formation and Reactions of Isonitrile-to-Phosphinidene Complex Adducts Image: Complex Adducts
<u>P3</u>	Nathan T. Coles BerlinSynthesis and coordination chemistry of phosphinine-based hybrid ligands
<u>P4</u>	Heidar Darmandeh BochumImage: Synthesis and Isolation of the Metalated Ylides [Cy3P-C-SO2Tol] M (M = Li, K) and their Application in Main Group Chemistry
<u>P5</u>	Lea Dettling BerlinTrimethylsilyl-substituted triazaphospholes: formation of an unprecedentedphosphorus-containing mesoionic carbene
<u>P6</u>	Sebastian Hauer RegensburgSelective Activation and Functionalization of White Phosphorus by a Highly Sterically Demanding α-Diimine Cobalt Complex
<u>P7</u>	Tim Kalisch BonnA thiazole-2-thione-based 1,4-diphosphinine anion and its conversion into a derivative with mixed P-valency
<u>P8</u>	Katrin Klimov Berlin Particular 2-(Dimethylamino)phosphinine: A Phosphorus-Containing Aniline Derivative
<u>P9</u>	Nils König LeipzigReductive Rearrangement of 1-Phospha-2-azanorbornenes
<u>P10</u>	Rachel E. Nuttall BristolUnexpected zwitterion formation during a Pt(0)-catalysed Hydrophosphination
<u>P11</u>	Yannic Pilopp RostockPilophilosSynthesis of Bulky Secondary Phosphides and Diphosphanes
<u>P12</u>	Christoph Riesinger Regensburg Sover Polyphosphorus Architectures from Polyphosphorus Ligand Complexes and Cationic p-Block Electrophiles
<u>P13</u>	Selina Schneider Marburg Image: Comparison of the section of th
<u>P14</u>	Karolina Trabitsch RegensburgReactivity Studies of an Anionic Cyclotriphosphido Cobalt Complex



Monday, 16:30-17:30 CET P15 Jose M. Veiga del Pino | Almería Bipyridyl-Ru(II) complexes containing 1,3,5-Triaza-7-phosphaadamantane (PTA) vs. plasmid DNA (pKSII) P16 Chendong Xu | Rennes Cu(I)-phosphine pre-assembled precursors for selective adaptive coordinationdriven supramolecular syntheses of new polymetallic Cu(I) luminescent assemblies P17 Jiaying Yang | Seattle •••• Characterization and Properties of Covalently Functionalized Black Phosphorus P18 Jana-Alina Zur | Bochum ••• From Ylide-Phosphine Tautomers to Carbanionic Phosphines Tuesday, 16:30–17:30 CET Andrés Alguacil Alarcón | Almería ••• <u>P19</u> Synthesis, characterization and antiproliferative properties of [RuCl₂(p-cymene)(HdmoPTA)] <u>P20</u> Jose Cammarata | Regensburg Simple and Practical Functionalisation of P₄ Mediated by Bu₃SnH P21 Adam Carrick | Durham Catalytic Alkene Carbonylation: Design, Synthesis and Application of Multi-functional Ligands P22 ••• David Decker | Rostock Highly E-selective transfer-semihydrogenation of internal alkynes with ammonia borane and a Co(II) PNN pincer catalyst P23 Shahriar Kermanshahian | Bonn A P-functional TTF-fused 1,4-diphosphinine precursor P24 ••• Ingo Köhne | Kassel Functionalised Phosphonate Esters in Lanthanide Model Complexes and ^RPOSSsupported Lanthanide Coordination P25 Mridhul R. K. Ramachandran | Bonn Synthesis and redox chemistry of anionic imidazole-2-thione-fused 1,4-dihydro-1,4diphosphinines •••• P26 Sébastien Lapointe | Bochum Exploring the chemistry of novel phosphorous ylides and their main group complexes ••• P27 Grégoire Le Corre | Zürich

Cyano(triphenylsilyl)phosphanide, an ambident PCN building block



Tuesc	day, 16:30–17:30 CET	
<u>P28</u>	Jinxiong Lin BerlinSynthesis, Electronic Properties and OLED Devices of Chromophores Based on λ5-Phosphinines	
<u>P29</u>	Pawel Löwe MünsterPawel Löwe MünsterTowards metathesis reactions with three-coordinate phosphorus cations	
<u>P30</u>	Andrey Petrov Berlin Sodium Pentaphospholide as a Versatile Precursor for the Synthesis of Phosphorus Heterocycles	
<u>P31</u>	Axel Straube Leipzig Redox-switchable tris(ferrocenyl)arene-based gold(I) complexes for multi-state- switchable catalysis	
<u>P32</u>	Lilian S. Szych RostockImage: Constraint of the second seco	
<u>P33</u>	Tatjana Terschüren Bonn Investigating the donor ability of P ^{III} - vs P ^V -bridged Janus bis(NHCs) towards main group element chlorides	
<u>P34</u>	Jan Tönjes Rostock Poly(methylhydrosiloxane) as a green reductant in the catalytic base-free Wittig reaction via PIII/PV catalysis	
<u>P35</u>	Martin Weber Regensburg	
<u>P36</u>	Edgar Zander RostockPAza-diphospha-indane-1,3-diyls: A class of resonancestabilized biradicals	
<u>P37</u>	Daniel Tofan Seattle Surface Modification of Black Phosphorus with Group 13 Lewis Acids for Ambient Protection and Electronic Tuning	



Talks 01-024

P-P bond activation in phosphorus rich ferrocenophanes

R. Franz, S. Nasemann, R. Pietschnig*

University of Kassel, Institute of Chemistry, Chemical Hybrid Materials, Kassel, Germany

pietschnig@uni-kassel.de

Phosphorus bridged [n]ferrocenophanes are attractive building blocks with implications for ferrocenylene based polymers containing phosphorus in the backbone or asymmetric catalysis.^[1,2] To this end we obtained a variety of functional triphospha [3]ferrocenophanes in preliminary work.^[3,4] Beside the preparation of functionalized triphospha [3]ferrocenophanes, we were able to combine several such systems to phosphorus-rich bisferrocenophanes.^[5]

These phosphorus-rich ferrocenophanes are suitable model systems for achieving thermal or electrochemical activation of P-P bonds. Bisferrocenophane **1** can be thermally activated under homolysis of the central P-P bond to generate the phosphorus centered radical **2**. Regarding P-P bond activation particular attention should also be paid to diphospha [2]ferrocenophanes, since the increased ring strain also leads to an increased reactivity of the P-P bond. Thus the primary phosphanylphosphoranes **3** show thermal conversion into the thermodynamically preferred chalcogenophosphinous anhydrides **4**, which constitute novel diphospha [3]ferrocenophanes with stereogenic phosphorus centers.^[6]



Acknowledgement. The authors gratefully acknowledge financial support by SFB 1319 (ELCH).

- [1] D. Herbert, U. Mayer, I. Manners, *Angew. Chem. Int. Ed.* **2007**, *46*, 5060.
- [2] R. Šebesta, A. Almassy, I. Císařová, Š. Toma, *Tetrahedron: Asymmetr.* 2006, 17, 2531.
- [3] S. Borucki, Z. Kelemen, M. Maurer, C. Bruhn, L. Nyulászi, R. Pietschnig, *Chem. Eur. J.* **2017**, *23*, 10438.
- [4] S. Isenberg, L.-M. Frenzel, C. Bruhn, R. Pietschnig, *Inorganics*, **2018**, *6*, 67.
- [5] S. Isenberg, S. Weller, D. Kargin, S. Valić, B. Schwederski, Z. Kelemen, C. Bruhn, K. Krekić, M. Maurer, C. M. Feil, M. Nieger, D. Gudat, L. Nyulászi, R. Pietschnig, *ChemistryOpen* **2019**, *8*, 1235.
- [6] R. Franz, S. Nasemann, C. Bruhn, Z. Kelemen, R. Pietschnig, Chem. Eur. J. 2021, 27, 641.

A Phosphanyl-Phosphagallene that Functions as a Frustrated Lewis Pair

Joey Feld,^a Daniel W. N. Wilson,^b Jose. M. Goicoechea^{*a}

^aDepartment of Chemistry, Chemistry Research Laboratory, University of Oxford, Oxford, United Kingdom

joey.feld@chem.ox.ac.uk

Multiple bonds are common in compounds featuring elements such as carbon, nitrogen, oxygen and boron. By contrast, heavier p-block elements form weaker multiple bonds, partly due to the ineffective p_{π} - p_{π} orbital overlap, resulting in significantly different reactivity to that of their lighter counterparts.

We present the first example of a gallium–phosphorus double bond. Similar to the synthesis of main group imides from the reaction of low valent group 13 species and sterically encumbered organic azides,^[1] our phosphagallene synthesis exploits the decarbonylation of phosphaketenes with the addition of a suitable nucleophile.^[2] In this case, upon the addition of Ga(NacNac) (NacNac = HC[C(Me)N(2,6-

 $(Pr_2C_6H_3)]_2$), CO was displaced from [P]PCO ([P] = $(H_2C)_2[N(2,6-Pr_2C_6H_3)]_2P)$ to form a phosphanyl phosphagallene species.

In this presentation, the reactivity of this phosphanyl phosphagallene towards a number of small molecule substrates such as H_2 , CO_2 , silanes and amines will be discussed.



Figure 1: H_2 and CO_2 activation of a phosphanyl phosphagallene.

- [1] N. J. Hardman, C. Cui, H. W. Roesky, W. H. Fink, P. P. Power, *Angew. Chem. Int. Ed.* **2001**, *40*, 2172–2174.
- [2] M. M. Hansmann, G. Bertrand, J. Am. Chem. Soc. 2016, 138, 15885–15888.
- [3] J. Possart, W. Uhl, Organometallics, **2018**, 37, 1314–1323.

Synthesis and ambiphilic reactivity of metalated diorganophosphonite boranes

<u>Thomas D. Hettich</u>,^a Richard Rudolf,^a Christoph M. Feil,^a Nicholas Birchall,^a Martin Nieger,^b Dietrich Gudat^a

^a Institute of Inorganic Chemistry, University of Stuttgart, Germany. ^b Department of Chemistry, University of Helsinki, Finland.

thomas.hettich@iac.uni-stuttgart.de

Salt methatesis of metal phosphides with various types of electrophiles is a common approach of the synthesis of phosphines. This approach is usually applied to alkyl-, and arylphosphines restricted by the low accessibility to nucleophilic synthons of N-, and O-substituted phosphines. Pioneering work by Knochel et al.^[1] demonstrated the *in situ* metalation and electrophilic substitution of secondary diaminophosphines via the borane adduct of diaminochlorophosphine and lithium-naphthalenide inspiring recent efforts depicting spectroscopic and structural data of metalated diaminophosphine boranes.^[2,3]

Despite their widespread application as ligands in transition metal catalysis, there are only sparse records of P-metalated diorganophosphonites and its borane adducts.^[4–6] We report here on new phosphinite boranes and the investigation of their unique reactivity. Reaction of alkali metal hexamethylsilazides with phosphinite boranes cleanly afforded metalated phosphides M[**1a-c**], which easily undergo nucleophilic substitution of Ph₃SnCl. In addition, P-O bond cleavage was observed with other nucleophiles or under intermolecular self-condensation, demonstrating ambiphilic behaviour.



R =Ethyl (a), Isopropyl (b), 2,6-Diisopropylphenyl (c), M = Li, K, Nu = Li[a,b], Bu

Figure 1: Schematic overview of the amphiphilic reactivity of P-metalated phosphonite boranes

- [1] A. Longeau, P. Knochel, *Tetrahedron Letters* **1996**, *37*, 6099–6102.
- [2] M. Blum, J. Kappler, S. H. Schlindwein, M. Nieger, D. Gudat, Dalton Trans. 2018, 47, 112–119.
- [3] M. Blum, T. Dunaj, J. A. Knöller, C. M. Feil, M. Nieger, D. Gudat, *Chemistry A European Journal* 2020, 26, 15190–15199.
- [4] Y. Belabassi, M. I. Antczak, J. Tellez, J.-L. Montchamp, *Tetrahedron* 2008, 64, 9181–9190.
- [5] L. F. Centofanti, *Inorg. Chem.* **1973**, *12*, 1131–1133.
- [6] E. Rivard, A. J. Lough, I. Manners, J. Chem. Soc., Dalton Trans. 2002, 2966–2972.

New Avenues in Phospha-Wittig Chemistry

Priyanka Gupta, Jan-Erik-Siewert, Tim Wellnitz, Malte Fischer, Wolgang Baumann, Torsten Beweries,* Christian Hering-Junghans*

Leibniz Institute for Catalysis Rostock Albert-Einstein-Straße 29a, 18059 Rostock, Germany priyanka.gupta@catalysis.de, christian.hering-junghans@catalysis.de

Phosphanylidenephosphoranes



Scheme 1. Reactivity of phospha-Wittig reagents towards NHCs and NHOs.

The term "Phospha-Wittig" reaction was originally introduced by Mathey for the reaction $(RO)_2P(O)-P^{(-)}[W(CO)_5]R'$ ketones (CO)₅W-coordinated of with to give phosphaalkenes.¹ Later, investigating the reactivity of [Cp₂Zr(PR₃)P^{Mes}Ter] Protasiewicz and co-workers noted the formation of MesTerP=PR₃ which showed that phospha-Wittig reagents can be isolated when the group R on phosphorus is kinetically stabilizing and to date four examples of ArP=PMe₃ (Ar = Mes*, MesTer, TipTer, EIND) have been described in the literature.^{2,3} Phospha-Wittig reagents are generally obtained by the combination of the respective dichlorophosphine Ar-PCl₂ with Zn powder and an excess of PMe₃.⁴ Using ArP=PMe₃ in the reaction with aldehydes, phosphaalkenes, ArP=CR'H, are obtained, with the concomitant formation of Me₃P=O.

Phospha-Wittig reagents, ArP=PMe₃, can also be considered as phosphine-stabilized phosphinidenes. Thus, in this study we show that the phosphine, PMe₃, can be displaced by NHCs or NHOs. Phospha-Wittig reagents are moreover isovalence electronic to carbene phosphinidene adducts,⁵ thus, should be easily converted into such by replacement of the phosphine with a carbene. N-heterocyclic olefins (NHOs) replace PMe₃ as well, however, further react in a C-H activation to afford phosphine-substituted NHOs. This concept was further extended to allyl-appended NHOs, which furnishes phosphine-substituted allyl species. These reactions clearly show the potential of phospha-Wittig reagents beyond the formation of phosphaalkenes and offer access to bulky phosphines that could be of interest as ligands in homogeneous catalysis.

^{1.} A. Marinetti and F. Mathey, Angew. Chem., Int. Ed. Engl., 1988, 27, 1382–1384.

^{2.} Protasiewicz, J.D. Coordination-Like Chemistry of Phosphinidenes by Phosphanes. *Eur. J. Inorg. Chem.* **2012**, 4539-4549.

^{3.} R. C. Smith, S. Shah, J. D. Protasiewicz, J. Organomet. Chem. 2002, 646, 255.

^{4.} R. C. Smith, S. Shah, E. Urnezius and J. D. Protasiewicz, J. Am. Chem. Soc., 2003, 125, 40-41.

^{5.} T. Krachko and J. C. Slootweg, *Eur. J. Inorg. Chem.*, **2018**, 2018, 2734–2754.

Versatile Chemistry of Phosphorus-Rich Compounds

V. Eilrich,^a T.Grell,^b E. Hey-Hawkins*^a

^a Universität Leipzig, Institut für Anorganische Chemie, Johannisallee 29, 04103 Leipzig, Germany. ^b Dipartimento di Chimica, Università degli Studi di Milano, Via Camillo Golgi 19, 20131 Milano, Italy

volker_jens.eilrich@uni-leipzig.de

Phosphanes can exhibit similar constitutions and conformations as their analogous carbon compounds. These similarities can be explained by the isolobal principle. However, due to the presence of lone pairs of electrons, phosphanes can for example act as ligands in complexes.

Phosphorus-rich transition metal or main group metal complexes are promising candidates as precursors for phosphorus-rich metal phosphides, some of which show interesting catalytic properties.^[1,2] Although ³¹P NMR spectra of phosphorus-rich compounds are often very complex, the spectral analysis and, if possible, simulation offer a powerful tool to acquire structural information about these compounds.^[3-6]



Figure 1: Compounds employed in complexation reactions.

We recently reported various complexes of two isomers of hexa-*tert*-butyloctaphosphane (Figure 1).^[3–5] Rational syntheses to these^[5] and other phosphorusrich organophosphorus compounds have been developed and are presented.

- [1] Y. Shi, B. Zhang, Chem. Soc. Rev. 2016, 45, 1529–1541.
- [2] A. Kircali, R. Frank, S. Gómez-Ruiz, B. Kirchner, E. Hey-Hawkins, *ChemPlusChem* **2012**, 77, 341–344.
- [3] T. Grell, E. Hey-Hawkins, Chem. Eur. J. 2020, 26, 1008–1012.
- [4] T. Grell, E. Hey-Hawkins, *Inorg. Chem.* **2020**, *59*, 7487–7503.
- [5] T. Grell, E. Hey-Hawkins, Eur. J. Inorg. Chem. 2020, 2020, 732–736.
- [6] V. Eilrich, E. Hey-Hawkins, Coord. Chem. Rev., in print, https://doi.org/10.1016/j.ccr.2020.213749.

How to safely work with PH₃

Debora Thöny^a, Hansjörg Grützmacher^a

^a Laboratory of Inorganic Chemistry, ETH Zurich, Switzerland.

dthoeny@inorg.chem.ethz.ch

Phosphane PH₃ is the well-known analogue to ammonia NH₃. However, these derivatives show completely different properties. The E-H bonds of ammonia are best described using sp³ hybridized orbitals at the nitrogen center. On the contrary, phosphorous belongs to the "hybridization-reluctant" elements and the P-H bonds in PH₃ have a significantly higher p-orbital contribution which results in narrow H-P-H angles close to 90°.^[1] Another important difference is the ability to engage in E-H···A hydrogen bonding (A = hydrogen acceptor). While ammonia is highly soluble in water (up to 25 wt%) due to a high solvation energy caused by strong N-H···O bonds, phosphane is only soluble with 0.39 g L⁻¹.^[1] The aqueous solution of ammonia is safe to handle in the laboratory. Also, NH₃ gas can be liquified by the use of a dry ice bath. Handling phosphane on a laboratory scale is much more challenging.

Phosphane gas is toxic and is immediately dangerous to life and health (IDLH) at 50 ppm. It acts on the central nervous system and lungs, leading to pulmonary oedema.^[2] Ultra-pure phosphane is odorless, though it is mostly known for its garlic or rotten-fish smell, which originates from the dimer P_2H_4 .^[2] Phosphane is spontaneously flammable at air. The boiling point of phosphane is at -87.7°C, which is below the one of commonly used cooling baths.^[1]

We build a setup for the safe handling of PH_3 in our laboratory at ETHZ. This setup was improved over the years in order to gain a safe and easy way in handling phosphane. The setup is shown in Fig. 1 and 2 and will be explained in detail in the presentation.



Figure 2: PH₃ setup in the fume hood including the quenching system.



Figure 1: PH₃ cupboard.

[1] D. Corbridge, in Studies in Inorganic Chemistry, Vol. 20, Elsevier, 1995, p. 1172.

[2] Md. S. Khan, *Chem Phys. Lett.*, **2015**, 636, 103-109.

Pd^{II}, and Pt^{II} assisted 1,2-azaphosphole formation in a functionalized bisphosphine: Synthesis, mechanistic studies and catalytic *N*-alkylation reactions

Harish S. Kunchur and Maravanji S. Balakrishna*

^a Phosphorus Laboratory, Department of Chemistry, IIT Bombay, Mumbai 400076, INDIA

e-mail: harishkunchur@gmail.com & krishna@chem.iitb.ac.in

The chemistry of phosphines, especially tertiary phosphines, is studied to an extent that the systematic fine-tuning of the steric and electronics attributes can now be achieved with certain degree of predictability. ^[1-3] Herein, we describe a novel bisphosphine with additional donor functionalities, $o-Ph_2PC_6H_4QC_6H_4PPh_2-o$, which showed unique reactivity towards Pd^{II} and Pt^{II} precursors. Reaction of bisphosphine with palladium afforded an 1,2-azaphosphole complex, whereas in a similar reaction with Pt^{II}, a complex containing a Pt-Ph bond was isolated. By varying metal to ligand ratios and metal precursors, several interesting complexes including pincers were isolated and structurally characterized. Mechanistic studies for the formation of palladium complex were investigated using NMR spectroscopy, DFT calculations and by SCXRD analysis. It involves reductive elimination to form a phosphonium salt followed by the oxidative addition. The palladium complex showed exceptional catalytic activity towards *N*-alkylation of amines with alcohols with a very low catalyst loading (0.05 mol %). The details of reactions, synthesis, metal chemistry and catalytic aspects will be presented in detail.

- S. D. Walker, T. E. Barder, J. R. Martinelli, S. L. Buchwald, *Angew. Chem., Int. Ed.* 2004, 43, 1871-1876.
- [2] M. K. Pandey, M. S. Balakrishna, J. T. Mague, Inorg. Chem. 2018, 57, 7468-7480.
- [3] F. Rekhroukh, L. Estevez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* **2016**, *138*, 11920-11929.

The coordination chemistry of 2,4,6-oxy functionalised 1,3,5-triphosphinines

<u>Anne Sofie Abels</u>,^a Grégoire Le Corre,^a Pascal Jurt,^a Frederik Eiler,^a René Verel,^a Hansjörg Grützmacher^{*a}

^a Department of Chemistry and Applied Biosciences, ETH Zürich, Switzerland.

abelsa@inorg.chem.ethz.ch

2,4,6-Oxy functionalised 1,3,5-triphosphinines are phosphorus containing heterocyclic ligands that can readily be tuned by changing the substituent on the oxygen centre and coordinated in a η^6 -binding mode through the π -system of the ring to form stable metal complexes with different group 6 metals.[1] This type of P₃C₃(OR)₃ (R =H, BR₂, SiR₃) ligands act as significantly stronger π -electron acceptors compared to benzene.[2] A series of group 6 metal complexes with various oxy functionalised P₃C₃ rings was synthesised to systematically study the electronic and structural characteristics of this new type of compounds. The π -electron accepting properties of the ligand increases in the following order: P₃C₃(OH)₃ < P₃C₃(OSi⁷BuPh₂)₃ < P₃C₃(OB(ipc)₂)₃. This trend is reflected in X-ray crystallography, IR spectroscopy, and ³¹P-, ¹³C- and ¹⁸³W-NMR spectroscopy. The tunability of these triphosphinine ligands is of interest for the rational design of new catalysts. In addition, the formation of stable P₃C₃(OH)₃ molecules, as η^6 -coordinated ligands, offers great potential to use these complexes as building blocks for hydrogen-bonded coordination polymers.



Figure 1: Structure of η^6 -coordinated $P_3C_3OH_3$ molybdenum complex, with tert-butanol as hydrogen bond acceptor.

- [1] Suter, R., Mei, Y., Baker, M., Benkő, Z., Li, Z., Grützmacher, H., Angew. Chem. Int. Ed. 2017, 56 (5), 1356-1360.
- [2] Falconer, R. L., Russell, C. A., Coord. Chem. Rev., 2015, 297-298, 146-167.

Intermolecular Reductive C-N Cross-Coupling of Nitro

Compounds and Boronic Acids by P^{III}/P^V=O Catalysis

Gen Li, Alexander T. Radosevich*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, 02139, United States

genli@mit.edu

Intermolecular C–N cross coupling has emerged as a powerful technology for the preparation of aromatic amines in both academia and industry. The prevailing strategy for the C–N bond construction is currently shaped by transition metal-catalyzed methods (e.g., Buchwald-Hartwig, Ullmann, and Chan-Lam couplings) from parent amines. Orthogonal to current strategies, new methods that transform readily available nitro compounds into value-added products by organophosphorus-catalyzed reductive C–N bond formation will be described in this presentation.

Though nitro compounds are frequently reduced to the amine coupling-partner, utilizing nitro compounds as an amine surrogate in C–N cross-coupling proves challenging with current methods due to poor compatibility between reducing reagents and coupling catalysts. In our work, a simple organophosphorus catalyst is shown to catalyze the deoxygenative coupling of nitro compounds with boronic acids to form secondary amines. This strategy has been further extended to various heteroarenes syntheses; starting with *ortho*-functionalized nitroarenes, organophosphorus-catalyzed reductive C–N cross coupling with boronic acids, followed by intramolecular cyclization provides a regiospecific approach to *N*-substituted benzimidazoles and quinoxalinediones.

- 010 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Tackling the chemistry of 1,2-oxaphosphetanes via theoretical calculations

Antonio García Alcaraz,ª Arturo Espinosa Ferao,*ª Rainer Streubel*b

^aDepartamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Spain. ^bInstitut für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Germany

antonio.garcia47@um.es

In recent years, $1,2\sigma^3\lambda^3$ -oxaphosphetanes κP -metal carbonyl complexes (I, Figure 1) were successfully prepared through ring expansion of epoxides using Li/Cl phosphinidenoid complexes.^[1] However, the mechanistic aspects of this reaction have never been investigated. On the other hand, free $1,2\sigma^3\lambda^3$ -oxaphosphetanes (II) could be accessed from their ligated counterparts using a decomplexation strategy, and first investigations towards *P*-oxidation were conducted.^[2] More recently, new *C*-substituted derivatives of II were prepared and oxidation to the corresponding *P*-chalcogenides III (E = O, S, Se) was achieved,^[3] thus entering the rather elusive area of $1,2\sigma^4\lambda^5$ -oxaphosphetanes.

Herein, the mechanism and regiochemical outcome of the formation of C^3 - and C^4 -phenyl substituted $1,2\sigma^3\lambda^3$ -oxaphosphetane κP -Mo(CO)₅ complexes by means of DFT calculations are presented using styrene oxide and a model Li/Cl phosphinidenoid complex as starting materials *in silico*. In addition, ring strain energies (RSEs), isomerization reactions leading to $1,2\sigma^4\lambda^5$ -chalcogenaphosphetane *P*-oxides (**IV**) or $1,3,2\sigma^3\lambda^3$ -oxachalcogenaphospholanes (**V**) were calculated, and the potential retro-[2+2] cycloaddition reactions of **III** analysed.



Figure 1: $1,2\sigma^{3}\lambda^{3}$ -oxaphosphetane metal complexes (I), $1,2\sigma^{3}\lambda^{3}$ -oxaphosphetanes (II), $1,2\sigma^{4}\lambda^{5}$ -oxaphosphetanes (III), $1,2\sigma^{4}\lambda^{5}$ -chalcogenaphosphetanes (IV) and $1,3,2\sigma^{3}\lambda^{3}$ -oxachalcogenaphospholanes (V).

- a) A. W. Kyri, V. Nesterov, G. Schnakenburg, R. Streubel, *Angew. Chem. Int. Ed.* 2014, 53, 10809–10812; b) A. W. Kyri, G. Schnakenburg, R. Streubel, *Organometallics*, 2016, 35, 563-568.
- [2] A. W. Kyri, F. Gleim, A. García Alcaraz, G. Schnakenburg, A. Espinosa Ferao, R. Streubel, *Chem. Commun.* **2018**, *54*, 7123-7126.
- [3] F. Gleim, G. Schnakenburg, A. García Alcaraz, A. Espinosa Ferao, R. Streubel, *unpublished results.*

Reactivity of Di-tert-butyldiphosphatetrahedrane

<u>Gabriele Hierlmeier</u>,^a Peter Coburger,^b Roger-Jan Kutta,^c Hans-Georg Stammler,^d Norbert Mitzel,^d Robert Wolf^{*a}

^a Institute of Inorganic Chemistry, University of Regensburg, Germany. ^b Institute of Inorganic Chemistry, ETH Zürich, Switzerland. ^c Institute of Physical Chemistry, University of Regensburg, Germany. ^d Institute of Inorganic Chemistry, University of Bielefeld, Germany

gabriele.hierlmeier@ur.de

Tetrahedranes have long fascinated the chemical community due their simple structure and typically high reactivity.^[1] While purely carbon-based tetrahedranes are wellknown, the first mixed C/P tetrahedranes were only reported last year.^[2] We recently showed that the 'hybrid' of (tBuC)₄ and P₄, di-*tert*-butyldiphosphatetrahedrane (tBuCP)₂ (**1**), can be synthesised in a simple nickel-catalysed dimerisation reaction of *tert*-butylphosphaalkyne, tBuCP.^[3] Shortly after our report, the synthesis of tri-*tert*butylphosphatetrahedrane (tBuC)₃P was published by Cummins and co-workers.^[4]



Figure 1: Reactivity of 1.

We now present the remarkable reactivity of **1** towards carbenes,^[5] metalloradicals,^[6] and metalates. Moreover, the photochemistry of **1** is highlighted. Our investigations show the distinct reactivity of **1** compared to its monomer *t*BuCP and give access to new unsaturated organophosphorus compounds and unusual (*t*BuCP)_n (n = 2, 4) ligand frameworks.

- [1] G. Maier, Angew. Chem. Int. Ed. **1988**, 27, 309–332.
- [2] A. R. Jupp, J. C. Slootweg, Angew. Chem. Int. Ed. 2020, 59, 10698–10700.
- [3] G. Hierlmeier, P. Coburger, M. Bodensteiner, R. Wolf, *Angew. Chem. Int. Ed.* **2019**, *58*, 16918–16922.
- [4] M.-L. Y. Riu, R. L. Jones, W. J. Transue, P. Müller, C. C. Cummins, Sci. Adv. 2020, 6, eaaz3168.
- [5] G. Hierlmeier, M. K. Uttendorfer, R. Wolf, Chem. Commun. DOI: 10.1039/d0cc07103j
- [6] G. Hierlmeier, R. Wolf, Angew. Chem. Int. Ed. DOI: 10.1002/anie.202015680

Scalable Synthesis of P(SiMe₃)₃ – An Illustrated Tutorial

Andryj M. Borys*a

^a Departement für Chemie und Biochemie, Universität Bern, Switzerland.

andryj.borys-smith@dcb.unibe.ch

Tris(trimethylsilyl)phosphine,^[1] P(SiMe₃)₃, is a versatile reagent that is widely used to prepare a number of metal clusters and low-coordinate organophosphorus compounds such as phosphaalkynes.^[2] It is often exploited as an 'easy to handle' alternative to PH₃ gas and it is a covalent synthon for the P³⁻ anion.

 $P(SiMe_3)_3$ is a highly pyrophoric, air- and moisture-sensitive, oily liquid that hydrolyses to produce toxic PH₃ gas. Although it is commercially available, its high cost means that it is instead more commonly prepared on a multigram scale in the laboratory. This 'how to' presentation will detail how to safely synthesise $P(SiMe_3)_3$ on a large scale with the aid of illustrated guides from the Schlenk Line Survival Guide.^[3]



Figure 1: Synthesis of P(SiMe₃)₃.

- [1] S. A. Kosarev, S. J. Collier. *e-EROS*, **2011** (*doi: 10.1002/047084289X.rn01332*)
- [2] C. A. Russell, N. S. Townsend. *Phosphorus(III) Ligands in Homogenous Catalysis: Design and Synthesis.* **2012**, *Chapter 11 (doi: 10.1002/9781118299715.ch11)*
- [3] A. M. Borys. schlenklinesurvivalguide.com/psime₃₃/

- 013 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Syntheses of 2,4-functionalized diphosphapentasilanes as precursors for low-valent tin and germanium compounds

Gernot Weinberger,^a Ana Torvisco,^a and Michaela Flock*^a

^aInstitute of Inorganic Chemistry, Graz University of Technology, Austria

g.weinberger@tugraz.at

In contrast to diphosphanes with carbon backbones, the number of 1,2-diphosphadisilanes is rather small.^[1] Diphosphasilanes with longer chain lengths do not exist with the exception of three 1,3-diphosphatrisilanes.^[2-3] However, similar to their carbon analogues, diphosphatrisilanes are expected to offer a wide range of uses in organometallic synthesis and as ligands in complex chemistry.

Our main interest is their possible application for the formation of low-valent group 14 compounds, namely diphosphagermylenes and -stannylenes.^[4]

The aim of the presented work is the preparation and characterization of 2,4-diphosphapentasilanes, $SiMe_2[Si(SiMe_3)_2PRR']_2$ with R,R' = H, Ph, SiMe_3, and R = SiMe_3, R' = Si(SiMe_3)_3, and C(SiMe_3)_3. The formation and characteristics of these silanes is compared to related carbon compounds, namely 1,2-diphosphaethanes and 1,3-diphosphapropanes. Experimental work is accompanied by DFT calculations aiding the characterization of these compounds and supporting a better comprehension of the reaction mechanism depending on the substitution pattern on the phosphorus atoms.

Molecular structures obtained by single crystal X-Ray diffraction, where feasible, and DFT calculations show an optimal preorientation of the diphosphapentasilanes regardless of the size and kind of the substituents. This characteristic qualifies them as ideal candidates for the formation of monomeric cyclic diphosphatetrylenes.



Figure 1: Reaction Pathways

[1] L.-C. Liang, P.-S Chien, Y.-L Huang, J. Am. Chem. Soc. 2006, 128, 15562-15563.

[2] K. Hassler, S. Seidl, Monatsh. Chem. 1988, 119, 1241-1244.

[3] G. Weinberger, F. Sommer, A. Torvisco, R. C. Fischer, M. Flock *Eur. J. Inorg. Chem.*, **2020**, 39, 3778-3785.

[4] (a) M. Driess, R. Janoschek, H. Pritzkow, S. Rell, U. Winkler, *Angew. Chem. Int. Ed.*, **1995**, *34*, 1614-16; (b) E. Schwarz, S. K. Mueller, G. Weinberger, A. Torvisco, M. Flock Organometallics, **2018**, *37*,2950-2960.

Aggregation Induced Emission: organic and hybrids fluorophores

<u>Nicolas Ledos</u>^a, Pierre-Antoine Bouit^a, Jonathan Phelipot^b, Olivier Margeat^b, Denis Tondelier^c, Bernard Geffroy^d, Jörg Ackerman^b, Muriel Hissler^{a*}

^a Univ Rennes, CNRS, ISCR - UMR 6226, ScanMAT - UMS 2001, F-35000 Rennes. ^b Aix-Marseille Univ, CNRS, CINaM UMR 7325, 13288 Marseille.^c LPICM, CNRS, Ecole Polytechnique, IPParis, 91128 Palaiseau. ^d LICSEN, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur- Yvette Cedex.

nicolas.ledos@univ-rennes1.fr

Some organic molecules show Aggregation Induced Emission (AIE), this property has been used to prepare Organic Light Emitting Diodes (OLEDs) or biologic fluorescent sensors.¹ Benzophospholes derivatives (**1**, Fig 1b, π = Ph) are known to present the AIE property and thus can be used to design highly emissive materials in solid state.² Moreover, this structure present a strong advantage: the P atom is reactive and can be functionalized to bring several properties to the molecule.³ Here, the P atom was functionalized with POOEt group in order to maximize the luminescence properties. In addition this offers the possibility for further grafting on different inorganic nanoparticles (ZnO and HgS), through the POOH group .⁴ The preparation of hybrid nanoparticles allowed us to combine luminescent properties from the organic part and new properties coming from the inorganic part (charge transport, chirality...). Several fluorophores have been synthesized in order to tune the emission properties in the visible range and adapt the HOMO and LUMO levels. The synthesis and the photophysical properties of those new AIE fluorophores will be presented as well as their recent use in OLEDs or for the preparation of new hybrid materials showing circularly polarized luminescence (CPL).



Figure 1: a) effect of aggregation on the luminescence of organic compounds; b) structure of synthesized benzophospholes.

- ¹ B. Z. Tang, et al. , Chem. Soc. Rev. **2011**, *40*, 5361.
- ² B. Z. Tang, et al. , J. Mater. Chem. C, **2017**, *5*, 1836
- ³ M. Hissler, et al. , Chem. Soc. Rev. **2016**, *45*, 5296
- ⁴ M. Hissler et al. Intern. Patent 2014 WO2015EP53859 20150224

- 015 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Surface functionalization of black phosphorus nanosheets with nitrenes: Identification of P=N bonds using isotopic labeling

<u>Kendahl L. Walz Mitra</u>,^a Christine H. Chang,^b Michael P. Hanrahan,^c Jiaying Yang,^a Daniel Tofan,^a William M. Holden,^d Niranjan Govind,^e Gerald T. Seidler,^d Aaron J. Rossini,^c and Alexandra Velian^{*a}

^a Department of Chemistry, University of Washington, USA. ^b Department of Materials Science and Engineering, University of Washington, USA. ^c US DOE Ames Laboratory and Department of Chemistry, Iowa State University, USA. ^d Department of Physics, University of Washington, USA. ^e Pacific Northwest National Laboratory, USA.

kwalz@uw.edu

Surface functionalization of two-dimensional nanosheets provides a facile path to tune their fundamental physical, chemical, and electronic properties. However, methods to directly probe new bond formation at modified surfaces are scarce. Materials characterization techniques often cannot distinguish between intentional surface functionalization and adventitious side reactions (e.g., oxidation) with sufficient resolution, making the assignment of surface binding motifs circumstantial and challenging to distinguish.

To circumvent these limitations, we applied techniques from molecular phosphorus chemistry to directly observe deliberate surface functionalization on black phosphorus. Black phosphorus (bP), a 2D van der Waals material composed entirely of tricoordinate phosphorus atoms, is particularly suited to mild and highly specific surface modification protocols due to the availability of lone pairs in its basal plane. While previous efforts to covalently functionalize bP rely primarily on harsh conditions traditionally used for less reactive nanosheets, a mild, surface-specific protocol is used to functionalize fewlayer bP with a family of nitrenes (RN) photolytically generated from the corresponding azides. Functional groups with embedded spectroscopic tags installed on the bP surface allowed the chemical structure to be examined in detail with a multitude of characterization techniques including vibrational, X-ray (photoelectron, emission), NMR, and UV-vis spectroscopies. Bonds between functional groups and the bP surface were directly probed using infrared spectroscopy and ¹⁵N labeling experiments in conjunction with DFT methods. Diagnostic P=N vibrational stretches were observed, allowing for conclusive identification of iminophosphorane units on the nanosheet surface.

[1] Walz Mitra, K.L.; Chang, C.H.; Hanrahan, M.P.; Yang, J.; Tofan, D.; Holden, W.M.; Govind, N.; Seidler, G.T.; Rossini, A.J.; Velian, A. Angew. Chem. Int. Ed. 2020, just accepted. Doi: 10.1002/anie.202016033

- 016 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Inspecting new cyclic diheterophospholane complexes as potential phosphanoxyl complex precursors

Philipp C. Brehm,^a Rainer Streubel*^b

^aInstitut für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Germany

PhilippBrehm@uni-bonn.de

In 2012, we had first speculated about the presence of phosphanoxyl complexes I in the decomposition of *P*-2,2,6,6-tetramethylpiperidinoxyl (TEMPO) substituted phosphane complexes II.^[1] In the following years, we achieved to get further evidence for transient phosphanoxyl complexes I using *P*-TEMPO substituted complexes II, the latter being stable up to 60 °C.^[2] First studies using a 1,3,2-diazaphospholane complex had revealed a significant decrease in thermal stability.^[3] Therefore, a new study on synthesis and reactivity of diheterophospholane complexes III was launched.



Figure 1: Phosphanoxyl complex I, 2,2,6,6-Tetramethylpiperidinoxyl (TEMPO) substituted phosphan complex II, diheterophospholan complexes III, with E = 0, R = Me, E = NR, R = H.

Herein, a new multi-step synthetic protocol to access a family of diheterophospholane complexes **III** and their conversion into the *P*-TEMPO derivatives **IV** will be described.^[4] The suitability of the latter to form transient phosphanoxyl complexes was experimentally and theoretically investigated, and the transient open-shell complexes were used to polymerize various common monomers.^[4]

- a) V. Nesterov, S. Schwieger, G. Schnakenburg, S. Grimme, R. Streubel, *Organometallics* 2012, 31, 3457 b) V. Nesterov, Z.-W. Qu, G. Schnakenburg, S. Grimme, R. Streubel, *Chem. Commun.* 2014, *50*, 12508.
- [2] a) T. Heurich, Z.-W. Qu, S. Nozinovic, G. Schnakenburg, H. Matsuoka, S. Grimme, O. Schiemann, R. Streubel, *Chem. Eur. J.* 2016, *22*, 10102 b) T. Heurich, V. Nesterov, G. Schnakenburg, Z.-W. Qu, S. Grimme, K. Hazin, D. P. Gates, M. Engeser, R. Streubel, *Angew. Chem. Int. Ed.* 2016, *55*, 14439 c) T. Heurich, Z.-W. Qu, G. Schnakenburg, Y. NejatyJahromy, O. Schiemann, S. Grimme, R. Streubel, *Organometallics* 2017, *56*, 2877.
- [3] T. Heurich, Z.-W. Qu, R. Kunzmann, G. Schnakenburg, M. Engeser, S. Nožinović, R. Streubel, *Chem. Eur. J.* **2018**, *24*, 6473-6478.
- [4] P. C. Brehm, A. S. Müller-Feyen, G. Schnakenburg, R. Streubel, unpublished results.

A new synthetic pathway towards cyaphide complexes

Tim Görlich,^a Nico Boback,^a Manuela Weber,^a William D. Jones,^b Christian Müller*^a

^a Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany. ^b Department of Chemistry, University of Rochester, USA.

tim.goerlich@fu-berlin.de

Since the introduction of the first Pt(II)-cyaphide complex by Angelici *et al.* in 1992,^[1] there have been many attempts to isolate cyaphide (C=P⁻) complexes. In 2006, Grützmacher *et al.* reported on the first crystallographically characterized Ru(II) complex containing a terminally bound cyaphide ligand.^[2] This was achieved by desilylation and rearrangement of an η^1 -coordinated-silylphosphaalkyne. This method was adopted by several groups and lead to a variety of similar transition metal-cyaphide complexes.^[3–4] Unfortunately, none of these complexes undergo any consecutive reactions, due to the sterically demanding substituents on the co-ligands.

Jones *et al.* demonstrated that $C(sp^2)$ -C(sp) bonds of aryl-nitriles and aryl-alkynes can be activated by Ni(0)- and Pt(0)-complexes.^[5] Based on the valence isoelectronic relationship between nitriles and phosphaalkynes, we synthesized and characterized a selection of η^2 -phosphaalkyne complexes of different low-valent transition metals bearing chelating diphosphine ligands (Scheme 1). The isolated M(0) π -complexes were then reacted under various conditions (thermal, photochemical or Lewis acid promoted activation) to achieve C-C=P-bond activation, forming the desired M(II) σ cyaphide complexes by oxidative addition. The obtained cyaphide complexes, were then subjected to consecutive reactions to prove the existence of the cyaphide moiety.



Scheme 1: Synthesis and activation of transition-metal-phosphaalkyne complexes.

- [1] H. Jun, V. G. Young, R. J. Angelici, J. Am. Chem. Soc. 1992, 114, 10064.
- [2] J. G. Cordaro, D. Stein, H. Rüegger, H. Grützmacher, Angew. Chem. Int. Ed. 2006, 45, 6159.
- [3] N. Trathen, M. C. Leech, I. R. Crossley, V. K. Greenacre, S. M. Roe, Dalton Trans. 2014, 43, 9004.
- [4] S. M. Mansell, M. Green, C. A. Russell, *Dalton Trans.* 2012, 41, 14360.
- [5] a) J. J. Garcia, W. D. Jones, Organometallics, 2000, 19, 5544; b) C. Müller, C. N. Iverson, R. J. Lachicotte, W. D. Jones, J. Am. Chem. Soc., 2001, 123, 9718; c) Brett D. Swartz, W. W. Brennessel, W. D. Jones, Synlett, 2018, 29, 747.

- 018 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Reactivity of Cu(I) Nacnac Complexes Towards Polypnictogen Compounds

<u>Maria Haimerl</u>,^a Martin Piesch,^a Gabor Balázs,^a Piero Mastrorilli,^b Werner Kremer^c and Manfred Scheer^{*a}

^a Institute of Inorganic Chemistry, University of Regensburg, Germany. ^b DICATECh, Politecnico die Bari, Italy. ^c Institute of Biophysics and Physical Biochemistry, University of Regensburg, Germany.

maria.haimerl@chemie.uni-regensburg.de

The conversion of white phosphorus and yellow arsenic, respectively, in the coordination sphere of transition metals was studied extensively within the last decades yielding a plethora of polypnictogen (E_n) ligand complexes (E = P, As).^[1] The most prominent derivative is [Cp*Fe(η^5 -E₅)] (E = P (**1a**), As (**1b**), Cp* = η^5 -C₅Me₅) which contains a *cyclo*-E₅ ligand that is isolobal to the well-known Cp ligand.^[2] In our group, compounds **1** and its derivatives are of central interest to explore their reactivity.^[3] Current investigations focus on the reactivity of [LCu(NCMe)] (**2**, L = [{N(C₆H₃Me₂-2,6)C(Me)}₂CH]⁻) towards E_n ligand complexes such as **1** which leads to [(Cp*Fe)($\mu_3,\eta^{5:2:1}$ -E₅)(LCu)₂] (**3**) and [(Cp*Fe)($\mu,\eta^{5:2:-}$ E₅)(LCu)] (**4**), respectively (Figure 1). These complexes prefer a η^2 -side-on coordination over an η^1 -end-on coordination of the *cyclo*-E₅-ligand, in which the coordinated bond is still intact according to DFT calculations. Its dynamic behaviour was examined by different NMR techniques. Furthermore, the reactivity of **2** towards other *cyclo*-E_n ligand complexes was investigated and the results are discussed.



Figure 1. Reaction of $[Cp*Fe(n^5-E_5)]$ with one or two equivalents of [LCu(NCMe)].

- [1] a) O. J. Scherer, Angew. Chem. Int. Ed. Engl. 1990, 29, 1104-1122; b) O. J. Scherer, Acc. Chem. Res. 1999, 32, 751-762; c) B. M. Cossairt, N. A. Piro, C. C. Cummins, Chem. Rev. 2010, 110, 4164-4177; d) M. Scheer, G. Balázs, A. Seitz, Chem. Rev. 2010, 110, 4236-4256; e) M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, Chem. Rev. 2010, 110, 4178-4235.
- a) O. J. Scherer, T. Brück, Angew. Chem. Int. Ed. Engl. 1987, 26, 59-59; b) O. J. Scherer, C. Blath, G. Wolmershäuser, J. Organomet. Chem. 1990, C21, 387.
- [3] a) E. Mädl, M. V. Butovskii, G. Balázs, E. V. Peresypkina, A. V. Virovets, M. Seidl, M. Scheer, *Angew. Chem.* 2014, 126, 7774-7777; b) M. Fleischmann, S. Welsch, H. Krauss, M. Schmidt, M. Bodensteiner, E. V. Peresypkina, M. Sierka, C. Gröger, M. Scheer, *Chem. Eur. J.* 2014, 20, 3759-3768; c) E. Peresypkina, C. Heindl, A. Virovets, H. Brake, E. Mädl, M. Scheer, *Chem. Eur. J.* 2018, 24, 2503-2508.

- 019 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Dynamic diphosphanes

Callum Branfoot,^{a,b} Paul Pringle,*a and Tom Young^c

^a School of Chemistry, University of Bristol, UK. ^b Bristol Composites Institute, University of Bristol, UK. ^c Department of Chemistry, University of Oxford, UK.

callum.branfoot@bristol.ac.uk

Dynamic and reversible chemical reactions have garnered increasing attention in medicine and biology, supramolecular chemistry and materials science, and they are key to the rapidly growing field of dynamic combinatorial chemistry (DCC). One of the most widely studied of such systems is disulfide metathesis, which by virtue of the weak (~260 kJ/mol) and reactive S–S bond, are capable of various exchange mechanisms both in solution and polymer melts.^[1]

Amongst the main group E–E bonds not explored in DCC, the P–P bond of diphosphanes is a potentially interesting candidate because of its relative weakness (~220 kJ/mol). Moreover, diphosphanes undergo many reactions that involve P–P scission,^[2] including "diphosphane scrambling".^[3]

In this study, through a combination of experimental and computational techniques, new insights into the metathesis of tetra-aryldiphosphanes (see Figure 1 for an example) have emerged, revealing parallels with radical-mediated disulfide exchange.^[4]



Figure 1: ${}^{31}P{}^{1}H$ NMR spectrum of the equilibrium mixture obtained from $(p-Tol)_2P-P(p-Tol)_2$ and $(p-Anisyl)_2P-P(p-Anisyl)_2$.

- [1] I. Azcune and I. Odriozola, *Eur. Polym. J.*, 2016, **84**, 147–160.
- (a) A. Gorman, J. Cross, R. Doyle, T. Leonard, P. Pringle and H. Sparkes, *Eur. J. Inorg. Chem.*, 2019, 1633–1639. (b) N. Szynkiewicz, L. Ponikiewski and R. Grubba, *Chem. Commun.*, 2019, 55, 2928–2931.
- [3] (a) A. Molloy, G. Sanchez-Sanz and D. Gilheany, *Inorganics*, 2016, **4**, 36–45. (b) R. Harris, E. Norval and M. Fild, *Dalton Trans.*, 1979, 825–831.
- [4] S. Nevejans, B. Ballard, J. Miranda, B. Reck and J. Asua, *Phys. Chem. Chem. Phys.*, 2016, **18**, 39, 27577–27583.

- 020 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Preparation of Multinary Interpnictogen Molecules

Christian Ritter,^a Carsten von Hänisch*^a

^a Department of Chemistry and Wissenschaftliches Zentrum für Materialwissenschaften (WZMW), Philipps University Marburg, Germany.

christian.ritter@chemie.uni-marburg.de

Recently, our group investigated the preparation of solely *tert*-butyl substituted molecules with several different pnictogen atoms being attached to another.^[1] In the course of this study it was possible to integrate the heaviest homologue bismuth to these chains.^[2] However, di-*tert*-butyl substituted bismuthanes suffer from high sensitivity against light and even moderate temperatures leading to rapid decomposition. Based on this knowledge it seemed to be a hard challenge to prepare even longer chains with four or five different adjacent pnictogen atoms. To overcome this issue we decided to synthesise multinary interpnictogen molecules with bismuth being stabilised by intramolecular nitrogen coordination which has proven to enhance the stability of such compounds.^[3]



Scheme 1: Building up interpnictogen molecules with a bis(amido)diazadiarsetidine structural motive.

- [1] B. Ringler, M. Müller, C. von Hänisch, Eur. J. Inorg. Chem. 2018, 2018, 640–646.
- [2] C. Ritter, B. Ringler, F. Dankert, M. Conrad, F. Kraus, C. von Hänisch, *Dalton Trans.* **2019**, *48*, 5253–5262.
- [3] C. Ritter, F. Weigend, C. von Hänisch, *Chem. Eur. J.* **2020**, *26*, 8536–8540.

- 021 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Graphene oxide functionalized by phosphorus dendrons and dendrimers for oncology applications

<u>Omar Alami</u>,^{a,b,c} Régis Laurent,^{a,b} Nabil El Brahmi,^c Said El Kazzouli,^c Anne-Marie Caminade^{a,b}

^a Laboratoire de Chimie de Coordination, CNRS, 205, route de Narbonne, Toulouse 31077, Cedex 04, France.

^b LCC-CNRS, Université de Toulouse, CNRS, Toulouse, France.

^c Euromed Research Center, Engineering School of Biomedical & Biotechnology, Euromed. University of Fes (UEMF), Route de Meknes, 30000 Fez, Morocco.

omar.alami@lcc-toulouse.fr

The use of nanomaterials based on dendrimers functionalizing graphene oxide in the biological field has recently attracted more and more attention of the scientific community, including chemists and biologists, because of their characteristics and unique properties[1-2].



Figure 1:different synthesis strategy

In this communication, we will present a new series of phosphorus dendrons and dendrimers which contain on their surface metal complexes [3] or small anticancer molecules to functionalize graphene oxide *via* two strategies (Figure 1).

- [1] Ma, X.; Tao, H.; Yang, K.; Feng, L.; Cheng, L.; Shi, X.; Li, Y.; Guo, L.; Liu, Z. A. Nano Res., 2012, 5, 199–212.
- [2] El Brahmi, N.; Mignani, S.M.; Caron, J.; El Kazzouli, S.; Bousmina, M.M.; Caminade, A.-M.; Cresteil, T.; Majoral, J.-P. Nanoscale, 2015, 7, 3915–3922.

[3] Alami, O.; Laurent, R.; Majoral, J.P.; El Brahmi, N.; El Kazzouli, S.; Caminade, A.M. *Inorg. Chim. Acta*, **2020**, *517*, 120212

- 022 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

A radical mechanism for the addition of bromoalkanes to $[P(\mu-NTer)]_2$ and synthesis of a novel P-centered persistent radical

Jan Rosenboom,^a Jonas Bresien,^a Jabor Rabeah,^b Alexander Villinger,^a Axel Schulz*^{a,b}

^a Institute of Chemistry, University of Rostock, Germany. ^b Leibniz Institute for Catalysis at the University of Rostock (LIKAT), Rostock, Germany.

jan.rosenboom@uni-rostock.de

According to the IUPAC definition biradicals are molecular entities with an even number of electrons with two (possibly delocalized) radical centres which act nearly independently of each other. ^[1] They may show a radical reactivity but can also react in a similar way as closed-shell molecules.^[2] So far, for the biradical $[P(\mu-NTer)]_2$, first synthesized in our group in 2011, only concerted reactions and insertions into the N_2P_2 four-membered ring have been observed. ^{[3],[4]}



Figure 2: Structure of the novel P-centered persistent radical as determined by single crystal X-ray diffraction.

In this study we present proof for a radical mechanism during the addition of bromoalkanes to $[P(\mu-NTer)]_2$ as well as report the synthesis and isolation of a novel persistent phosphorus-centered radical.

This radical was successfully identified as the radical intermediate of the bromoalkane addition to $[P(\mu-NTer)]_2$ using EPR-spectroscopy and single crystal X-ray diffraction.

- M. Abe, Chem. Rev. 2013, 113, 7011-7088. [1]
- T. Stuyver, B. Chen, T. Zeng, P. Geerlings, F. De Proft, R. Hoffmann, Chem. Rev. 2019. 119. [2] 11291-11351.
- T. Beweries, R. Kuzora, U. Rosenthal, A. Schulz, A. Villinger, Angew. Chem., Int. Ed. 2011, 50, [3] 8974-8978.
- [4] A. Hinz, A. Schulz, Phosphorus, Sulfur Silicon Relat. Elem. 2016, 191, 578–581.

High-Coordinate Phosphasiliranes: Do they exist?

Alicia Rey Planells,^a Arturo Espinosa Ferao,*^a Rainer Streubel*^b

^aDepartamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Spain. ^bInstitut für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Germany.

alicia.rey@um.es

A fundamental discovery in *p*-block chemistry has been the development of FLPs (frustrated Lewis pairs).^[1] Those derived from 1,3-zwitterionic species could form the corresponding three-membered ring isomers. These are systems composed of a Lewis acidic and basic centres that, generally, are not likely to form a stable adduct due to steric factors. Therefore, it could be envisaged that such systems could activate small molecules^[2] through a synergistic action of both centres.

The following reactions have been studied: *a priori* stable X₃P=E species react with coordinatively saturated (and stable) SiY₄ species to give dipolar species **3** with a hypervalent (pentacoordinate) silicon centre (Scheme 1), which could eventually form phosphasiliranes **6** bearing a hexacoordinate silicon and pentacoordinate phosphorus atom.^[3] But both species **3** and **6** could also enable a E-group transfer giving rise to X₃P (**4**) and E=SiY₄ (**5**), finally.



Scheme 1: Studied interconversions (E = CH₂, SiH₂, NH, PH, O or S; X, Y = Me, NH₂, Tms, F, CF₃).

As it turned out, the choice of substituents is key to finding stable species in these interconversions (Scheme 1), *i.e.*, donors X at P and acceptors Y at Si should favour acyclic zwitterionic structures **3**. The opposite electronic nature of X and Y could eventually favour a cyclic structure **6** which would represent the first example of a three-membered heterocyclic ring with two hypercoordinate centres.^[3]

- [1] D. W. Stephan, J. Am. Chem. Soc, 2015, 137, 10018–10032.
- [2] G. C.Welch. R. R. San Juan, J. D. Masuda, D. W. Stephan, Science, 2006, 314, 1124–1126.
- [3] A. Rey Planells, A. Espinosa Ferao, R. Streubel, to be published.

Synthesis of a new series of phosphorus dendrimers

Julien Aujard-Catot^{ab*}, Abdelouahd Oukhrib^{ab}, Anne-Marie Caminade^{ab}, Cédric-Olivier Turrin^{ab*}

^a Laboratoire de Chimie de Coordination du CNRS, UPR 8241, 205 route de Narbonne, F-31077, Toulouse, France
^b Université de Toulouse, UPS, INP, LCC, F-31077, Toulouse, France.

julien.aujard@lcc-toulouse.fr, cedric-olivier.turrin@lcc-toulouse.fr

Dendrimers are perfectly designed and highly branched macromolecules with a globular 3D shape. A dendrimer is made of a core, attach to the core are branches and at the end of branches are terminal functions. The synthesis of dendrimers follows iterative processes.

Since the first neutral phosphorus dendrimers were reported in 1994¹, the number of patents and publications in this field has grown exponentially. The thiophosphohydrazone (PPH) skeleton designed and reported by Caminade's team in France has been thoroughly studied. This family of dendrimers offers a very wide range of applications² in fields like biology³, materials and catalysis. However, because of the nature of the skeleton, PPH dendrimers maybe prone to undergo hydrolytic degradation at the hydrazone function, even at physiological pH. This drawback is possibly among the reasons why PPH dendrimers did not have a successful industrial fate.

To answer this problem, we have developed a new kind of phosphorus dendrimers based on a thiophosphoramidate skeleton (PTPAm). These new dendrimers series were prepared up to the fifth generation. The stability in water at various pH values was found to be dramatically increased in the case of polyanionic dendrimers. Moreover, the highly versatile synthetic approach is compatible with large-scale production and offers a wide range of modifications that are really helpful for layerblock approaches and multifunctional molecular platforms.



- (1) Launay, N.; Caminade, A.-M.; Lahana, R.; Majoral, J.-P. A General Synthetic Strategy for Neutral Phosphorus-Containing Dendrimers. *Angewandte Chemie International Edition in English* **1994**, 33 (15–16), 1589–1592.
- (2) Caminade, A. M.; Turrin, C. O.; Laurent, R.; Ouali, A.; Delavaux-Nicot, B. *Dendrimers: Towards Catalytic, Material and Biomedical Uses*; Wiley, 2011.
- (3) Caminade, A. M.; Turrin, C. O.; Majoral, J. P. *Phosphorous Dendrimers in Biology and Nanomedicine: Syntheses, Characterization, and Properties*; Jenny Stanford Publishing, 2018.



Posters P1-P37

N-Heterocyclic Phosphenium lons and their Noble Contribution to a Base Metal.

Nicholas Birchall,^a Christoph M. Feil,^a Mark R. Ringenberg,^a Dietrich Gudat*^a

^a Institute of Inorganic Chemistry, University of Stuttgart, Germany.

nicholas.birchall@iac.uni-stuttgart.de

The catalytic transfer and activation of H₂, mainly found for late transition metals, plays an important role in both synthetic and applied chemistry.^[1] The often required two electron oxidative addition/reductive elimination steps are less favoured for base metals.^[2] As an emerging solution in this field, **M**etal-Ligand-Cooperativity (**MLC**) has shown to provide some noble character to base metals.^[3] In contrast to the well described *NNN- NPN-* and *PNP-* Pincer systems, MLC involving diamino phosphenium ions was confined to a few rare examples.^[4]

Recently we reported on reversible H₂ addition across a Cr=P double bond involving a phosphenium stabilized non-classical H₂ complex as the intermediate. Crucially relying on the cooperative interplay between metal and ligand, as well as its redox-non-innocence, the mechanism of H₂ binding can be seen as an unprecedented form of MLC.^[5]

Our current studies focus on more comprehensive investigations of the underlying redox-non-innocence in these systems as well as its impact on hydrogen binding and catalytic transfer (Figure 1).



Figure 1: Current studies include investigations on the underlying redox-non-innocent behaviour and its impact on H₂ binding and catalytic transfer.

- [1] J. R. Khusnutdinova and D. Milstein, *Angew. Chem. Int. Ed.* **2015**, *54*, 12236-12273
- [2] J. I. van der Vlugt, Eur. J. Inorg. Chem. 2012, 363-375, O. R. Luca, R. H. Crabtree, Chem. Soc. Rev. 2013, 42, 1440-1459.
- [3] W. I. Dzik, J. I. van der Vlugt, J. N. H. Reek, B. de Bruin, *Angew. Chem. Int. Ed.* **2011**, *50*, 3356-3358
- [4] M. Gediga, S. H. Schlindwein, J. Bender, M. Nieger, D. Gudat, Chem. Eur, J. 2017, 23 (48), 11728
- [5] N. Birchall, C. M. Feil, M. Gediga, M. Nieger, D. Gudat, Chem. Sci. 2020, 11, 9571-9576
Formation and Reactions of Isonitrile-to-Phosphinidene Complex Adducts

David Biskup,^a Rainer Streubel*^a

^a Institut für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany.

d.biskup@uni-bonn.de

To date, electrophilic terminal phosphinidene metal(0) complexes could not be isolated experimentally and remain subject of theoretical calculations.^[1] The first stable isonitrile-to-phosphinidene complex adducts **3** were isolated via strongly strained 3-iminoazaphosphiridine tungsten(0) complexes **1** by Streubel *et al.* in 2016.^[2]



Scheme 1: Synthesis and decomposition reactions of phosphinidene complex adducts (M = Cr, W; NMIm: N-methylimidazole).

A more facile route to the adducts 3-5 is the reaction of ligands L with the *in situ* formed Li/Cl phosphinidenoid complex starting from the dichlorophosphane complex 2.^[3]

The isonitrile-to-phosphinidene complex adduct **3a** unveiled a low stability towards strong Lewis acids under formation of the cyanidophosphane complex **6** and elevated temperatures forming white phosphorus **7**.^[3] Further attempts to trap thermally generated intermediates are currently persued.

- a) Recent review: F. Mathey, *Dalton Trans.* 2007, 1861–1868. b) A. Özbolat, G. von Frantzius, J. M. Pérez, M. Nieger, R. Streubel, *Angew. Chem. Int. Ed.* 2007, *46*, 9327–9330. c) M. Bode, J. Daniels, R. Streubel, *Organometallics* 2009, *28*, 4636–4638. d) A. Espinosa Ferao, R. Streubel, *Chem. Eur. J.* 2017, 8632–8643. e) A. Espinosa Ferao, A. García Alcaraz, S. Zaragoza Noguera, R. Streubel, *Inorg. Chem.* 2020, *59*, 12829–12841.
- [2] J. M. Villalba Franco, G. Schnakenburg, A. Espinosa Ferao, R. Streubel, *Dalton Trans.* **2016**, *45*, 13951–13956.
- [3] D. Biskup, R. Streubel, *unpublished results*.

Synthesis and coordination chemistry of phosphininebased hybrid ligands

Nathan T. Coles, a Richard O. Kopp, a Christian Müller*a

^a Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany.

n.t.coles@fu-berlin.de

Hybrid ligands, as defined by Braunstein and Nord,¹ are ligands encompassing both a hard and soft binding motif. This can be used to exploit the binding properties of various metals and potentially extend the principle to synthesise complexes bearing differing metal centres. Phosphinines are an attractive candidate for this purpose as it is possible to synthesise highly functionalised molecules with the donor atoms separated, allowing for selective coordination.

To this end, we have synthesised a pyridyl-containing phosphinine and investigated the coordination chemistry of this species. It was shown that varying the amount of CuBr used led to a number of different structures, including coordination polymers. Crystal structures of all compounds, starting from the acetylene to the final complexes have been obtained and will be presented.



Figure 1: Schematic structures of the phosphinine based hybrid ligand and the complexes isolated.

[1] P. Braunstein, F. Naud, Angew. Chemie Int. Ed. 2001, 40, 680–699.

Synthesis and Isolation of the Metalated Ylides $[Cy_3P-C-SO_2Tol]M$ (M = Li, K) and their Application in Main Group Chemistry

Heidar Darmandeh^a, Viktoria H. Gessner*^a

^a Chair of Inorganic Chemistry II, Faculty of Chemistry and Biochemistry Ruhr-University Bochum Universitätsstraße 150, 44801 Bochum, Germany

heidar.darmandeh@rub.de

Metalated Ylides or so called yldiides are a special class of monoanionic ylidic compounds, in which the central carbon atom bears two lone pairs of electrons. These metalated vides potentially serve as strong σ - and π -donors, making them promising reagents for the stabilization and isolation of highly reactive main group element species. Our group recently reported on the facile synthesis of a metalated ylide, which is structurally based on a triphenylphosphonium group and a neutral sulfonyl substituent.^[1a] This reagent showed exceptional reactivity towards low valent main group element compounds. For example, the first di-ylide substituted germylene and stannylene^[1b] as well as boron cations^[1c] were prepared. Furthermore, we reported on the strong electron-donating properties of ylide-functionalized phosphines (YPhos) and applied them as powerful ligands in transition-metal catalysis^[2]. However, due to the incorporated triphenylphosphonium moiety, we observed $C(sp^2)$ -P as well as $C(sp^2)$ -H bond activation reactions^[3], thus limiting the stability and applicability of these new compounds. To further investigate the properties of metalated ylides and their applicability in main group chemistry, we aimed at the synthesis of tricyclohexylphosphonium substituted yldiides ^{Cy}Ys-M (M=Li, K) directly from their protonated precursor (^{Cy}Y_s-H) by deprotonation with strong metal bases^[4]. Here, we present the synthesis of novel tetrylenes (CyYs)₂E via the reaction of CyYs-M with ECl₂ (E=Ge, Sn) precursors^[5].



Figure 1: Synthesis of the metalated ylides $^{Cy}Y_{s}$ -M (M=Li, K) and subsequent preparation of tetrylenes via reaction with ECl₂ (E= Ge, Sn).

- a) T. Scherpf, R. Wirth, S. Molitor, K.-S. Feichtner, V. H. Gessner, *Angew. Chem. Int. Ed.* 2015, 54, 8542-8546 b) C. Mohapatra, L. Scharf, T. Scherpf, B. Mallick, K.-S. Feichtner, C. Schwarz, V. H. Gessner, *Angew. Chem. Int. Ed.* 2019, 58, 22, 7459-7463, c) T. Scherpf, K.-S. Feichtner, V. H. Gessner, *Angew. Chem. Int. Ed.* 2017, 56, 3275-3279.
- a) T. Scherpf, C. Schwarz, L. T. Scharf, J.-A. Zur, A. Helbig, V. H. Gessner, *Angew. Chem.* 2018, 130,13041, b) P. Weber, T. Scherpf, I. Rodstein, D. Lichte, L. T. Scharf, L. J. Gooßen, V. H. Gessner, *Angew. Chem. Int. Ed.* 2019, 58, 3203.
- [3] T. Scherpf, I. Rodstein, M. Paaßen, V. H. Gessner, Inorg. Chem. 2019, 58(12), 8151-8161.
- [4] H. Darmandeh, T. Scherpf, K.-S. Feichtner, C. Schwarz, V.H. Gessner, Z. Anorg. Allg. Chem. 2020, 646, 835–841.
- [5] C. Mohapatra, H. Darmandeh, H. Steinert, B. Mallick, K.-S. Feichtner, V. H. Gessner, Chem. Eur. J. 2020, 26, 15145–15149

Trimethylsilyl-substituted triazaphospholes: formation of an unprecedented phosphorus-containing mesoionic carbene

L. Dettling,^a M. Papke,^a D. Frost,^a M. Weber,^a C. Müller*^a

^a Institute of Chemistry, Freie Universität Berlin, Germany.

leadettling@zedat.fu-berlin.de

3H-1,2,3,4-triazaphospholes can be considered as the phosphorus analogues of 1,4-disubstituted 1,2,3-triazoles due to the isolobal relationship between a trivalent P-atom and a C-H fragment. These $\lambda^3\sigma^2$ -phosphorus heterocycles can be synthesized in a [3+2] cycloaddition reaction starting from organic azides and phosphaalkynes.^[1] Lately we reported on the successful synthesis of 3H-1,2,3,4-triazaphospholenium salts (1).^[2] According to the principle of valence isoelectronicity these compounds represent the formal phosphorus analogues of the well-known mesoionic 1,2,3-triazolylidenes (2).^[3]



Figure 1: Left: Mesoionic carbenes (**2**, **4**) and their phosphorus analogues (**1**, **3**). Right: Molecular structure of **3** in the crystal.

While originally only tert-butyl-substituted 3H-1,2,3,4-triazaphosphole derivatives were alkylated with Meerwein's reagent to obtain compounds of type **1** (R = ^{*t*}Bu) we were now able to access also Si(CH₃)₃-substituted 3H-1,2,3,4-triazaphospholenium salts (R = Si(CH₃)₃, TMS). Much to our surprise, while investigating protodesilylation reactions, we observed the formation of a product which can be described as a BF₃-adduct of a phosphorus-containing mesoionic carbene (**3**). This compound fits perfectly into the gap between 3H-1,2,3,4-triazaphospholenium salts (**1**) and the mesoionic 1,2,3 triazolylidenes (**2**). Using the isolobal concept, it can be described as a phosphorus derivative of **2**, or simply as a phosphorus derivative of tetrazolylidenes (**4**).^[4]

- [1] W. Rosch, M. Regitz, Angew. Chem. 1984, 11, 898.
- [2] M. Papke, L. Dettling, J. A. W. Sklorz, D. Szieberth, L. Nyulászi, C. Müller, *Angew. Chem. Int. Ed.* **2017**, *56*, 16484.
- [3] G. Guisado-Barrios, J. Bouffard, B. Donnadieu, G. Bertrand, Angew. Chem. Int. Ed. 2010, 49, 4759.
- [4] L. Schaper, X. Wei, P. J. Altmann, K. Öfele, A. Pöthig, M. Drees, J. Mink, E. Herdtweck, B. Bechlars, W. A. Herrmann, F. E. Kühn, *Inorg. Chem.* **2013**, *52*, 7031–7044.

Selective Activation and Functionalization of White Phosphorus by a Highly Sterically Demanding α-Diimine Cobalt Complex

Sebastian Hauer,^a Robert Wolf*a

^a Institute of Inorganic Chemistry, University of Regensburg, 93040 Regensburg, Germany.

sebastian.hauer@ur.de

Redox active α -diimine ligands have been found to be effective at stabilizing highly reactive metallate species, allowing for unprecedented reactivity.^[1] One such example is the reaction of the anionic complex **1**, with white phosphorus affording the dinuclear complex [{(^{Dipp}BIAN)Co}₂(μ - η^4 : η^4 -P₄)]²⁻ **(2)** [(^{Dipp}BIAN)Co(cod)]⁻ (^{Dipp}BIAN = 1,2-bis(2,6-diisopropylphenylimino)acenaphthene, cod = 1,5-cyclooctadiene; Figure 1).^[2] However, further functionalization of the *cyclo*-P₄ fragment in **2** with electrophiles results only in undesired outer sphere electron transfer reactions. Such selective transformations of P₄ are highly sort after in contemporary research.^[3]

Our recent research has focused on increasing the steric demand of the BIAN-ligand to suppress the formation of dinuclear species such as **2**. In contrast to **1**, the reaction of the bulkier **3** with P₄ selectively yields the mononuclear complex **4** with a terminal cyclo-P₄ unit. Herein, we present its further functionalization with electrophiles and the subsequent rearrangement of the polyphosphorus ligand.



Figure 1: Selective Activation of white Phosphorus by α -diimine cobalt complexes **1** and **3**, further functionalization of **4** and rearrangement by isonitriles (Dipp = 2,6-diisopropylpheny, N-N = bis(N-arylimino) acenaphthene).

- [1] X. Wang, Y. Zhao, S. Gong, B. Liu, B. Wu, X. Yang, Chem. Eur. J., 2015, 21, 13302.
- [2] S. Pelties, T. Maier, D. Herrmann, B. de Bruin, C. Rebreyend, S. Gärtner, I. Shenderovich, R. Wolf, Chem. Eur. J., 2017, 23, 6094.
- [3] C. M. Hoidn, D. J. Scott, R. Wolf, Chem. Eur. J. DOI:10.1002/chem.202001854

A thiazole-2-thione-based 1,4-diphosphinine anion and its conversion into a derivative with mixed P-valency

Tim Kalisch,^a Rainer Streubel*^a

^a Institute for Inorganic Chemistry, University of Bonn, Germany.

tim.kalisch@uni-bonn.de

For over 40 years only one example of a 1,4-diphosphinine – described by Kobayashi *et al.*^[1] – was known, until this field of research was reopened by the synthesis of tricyclic 1,4-diphosphinines by Streubel and co-workers.^[2] Manifold reactivity studies such as addition reactions^[3] and anion formations^[2b] have since been conducted regarding the chemistry of these heteroaromatic systems.

Herein, addition reactions like the formation of a thermochromic monoanion of a thiazole-2-thione-based 1,4-diphosphinine and subsequent conversions are presented.^[4] But also decomposition reactions to yield the starting material were found.



Acknowledgement: T.K. is grateful to the Studienstiftung des deutschen Volkes for a PhD fellowship.

- [1] Y. Kobayashi, I. Kumadaki, A. Ohsawa, H. Ohsawa, *Tetrahedron Lett.* **1976**, *41*, 3715–3716.
- (a) A. Koner, G. Pfeifer, Z. Kelemen, G. Schnakenburg, L. Nyulászi, T. Sasamori, R. Streubel, *Angew. Chem. Int. Ed.* 2017, 56, 9231–9235; (b) I. Begum, G. Schnakenburg, Z. Kelemen, L. Nyulászi, R. T. Boeré, R. Streubel, *Chem. Commun.* 2018, 54, 13555–13558.
- [3] A. Koner, Z. Kelemen, G. Schnakenburg, L. Nyulászi, R. Streubel, *Chem. Commun.* **2018**, *54*, 1182–1184.
- [4] T. Kalisch, R. Streubel, *unpublished results*.

2-(Dimethylamino)phosphinine: A Phosphorus-Containing Aniline Derivative

<u>Katrin Klimov</u>,^a S. Giese, A. Mikeházi, Z. Kelemen, D. S. Frost,^a S. Steinhauer,^a P. Müller, L. Nyulászi, Christian Müller^{*a}

^a Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany.

katrin.klimov@fu-berlin.de

Recently, we could achieve the synthesis of the first phosphorus-containing 2-anilinederivatives 2-(CH₃)₂N-6-Si(CH₃)₃-phosphinine and 2-(CH₃)₂N-phosphinine.^[1] Functionalized phosphinines can act as μ_2 -bridging 2-electron ligands (μ_2 -P-2e) to metal centers while a highly π -donating substituent in the 2-position (e.g. 2phosphinolate) enables the μ_2 -bridging 4-electron (μ_2 -P-4e) coordination motif.^[2] With the nitrogen being less electronegative than oxygen, we expected a significant electronic interaction of its lone pair with the π -accepting system of the heterocycle impacting the coordination chemistry of those phosphinines.

We started to investigate the properties, synthesis and coordination chemistry of the yet unknown 2-aminophosphinines. The theoretical investigations reveal two resonance structures with two lone pairs at the phosphorus atom and a fully planar dimethylamino group, which is in accordance with the described π -electronic interaction between the lone pair of the nitrogen atom and the heterocycle increasing the π -electron density at the phosphorus atom in the ring. The 2-dimethylaminophosphinines are accessible *via* the classical pyrone-route starting from 2-dimethylamino-3-pyrone and TMS-C=P. Their coordination chemistry with CuBr·SMe₂ show indeed the rare μ_2 -P-4e bridging coordination mode which is so far unprecedented for neutral phosphinines.



Figure 1: Illustration of theoretical properties of 2-(dimethylamino)phosphinine

- [1] S. Giese, K. Klimov, A. Mikeházi, Z. Kelemen, D. S. Frost, S. Steinhauer, P. Müller, L. Nyulászi, C. Müller, *Angew. Chem. Int. Ed.* **2020**, *59*, 1-7.
- [2] X. Chen, S. Alidori, F. F. Puschmann, G. Santiso-Quinones, Z. Benkó, Z. Li, G. Becker, H.-F. Grützmacher, H. Grützmacher, *Angew. Chem. Int. Ed.* **2014**, *53*, 1641-1645.

- P9 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Reductive Rearrangement of 1-Phospha-2-azanorbornenes

Peter Wonneberger,^a <u>Nils König</u>,^a Menyhárt B. Sárosi,^a Peter Lönnecke and Evamarie Hey-Hawkins^{*a}

^a Faculty of Chemistry and Mineralogy, Institute for Inorganic Chemistry, University of Leipzig, Germany.

nk97hubo@studserv.uni-leipzig.de

Phospholes are phospha-cyclopentadienes which can form different tautomers.^[1] *In situ* generated 2*H*-phospholes are highly reactive dienes and undergo DIELS-ALDER reactions with a variaty of dienophiles resulting in 1-phosphanorbornenes.^[2] Recently, we reported the phospha-aza-DIELS-ALDER reaction between 2*H*-phospholes and an electron-poor *N*-sulfonyl- α -iminoester resulting in 1-phospha-2-azanorbornenes (PANs).^[3] The reduction of 1-phospha-2-azanorbornene derivate *endo-1* with lithium aluminium hydride leads to an unprecedented 1-phosphabicyclo[3.2.1]octa-2,5-diene **2**. Reduction of *endo-1* with elemental lithium leads to phospholide anion **3** that reacts with water to an unusual 2*H*-phosphole dimer. Subsequent sulfurisation gave 2*H*-phosphole sulfide dimer *endo-4* which could be characterised via X-ray crystallography.



Scheme 1. Synthesis of compounds **2** (*i*) and endo-**4** (*ii*) and their corresponding molecular structures (hydrogen atoms other than NH and OH have been omitted for clarity).

- [1] F. Mathey, Chem. Rev. 1988, 88, 429-453.
- [2] F. Mathey, Acc. Chem. Res. 2004, 37, 954–960.
- [3] P. Wonneberger, N. König, F. B. Kraft, M. B. Sárosi, E. Hey-Hawkins, *Angew. Chem. Int. Ed.* **2019**, 58, 3208-3211.

- P10 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Unexpected zwitterion formation during a Pt(0)-catalysed Hydrophosphination

Rachel E. Nuttall,^a M. Carmen Galan,^a Michelle T. Ma,^b Paul G. Pringle*^a

^a School of Chemistry, University of Bristol, UK. ^b Imaging Sciences, St. Thomas' Hospital, King's College London, UK.

rachel.nuttall@bristol.ac.uk

Hydrophosphination, the addition of a P–H bond across a multiple bond, is an important and atom-efficient method for the synthesis of organophosphorus compounds.¹ Recent work has shown that in the case of activated alkenes Pt(0) catalysis is a very efficient and selective route to synthesise air-stable, functionalised unsymmetrical diphosphines, despite the potential for chelation to inhibit catalysis.² By incorporating a glucose moiety into the activated alkene, diphosphine carbohydrate conjugates can be synthesised in this way (Scheme 1). These diphosphine glycoconjugates have been synthesised with the aim of producing new, more targeted ^{99m}Tc radioimaging agents.³



Scheme 1: Pt(0)-catalysed hydrophosphination by a chelating diphosphine and the competitive phospha-Michael addition, where Glc = glucose moiety.

Varying the glucose substrates has enabled conjugation at different positions of the glucose moiety. In most cases, the hydrophosphination step is an extremely reliable, highly chemoselective process. However, an unexpected side reaction was observed with some glucose substrates, which we believe is the formation of a zwitterion by a phospha-Michael addition (Scheme 1). Investigations into the factors which lead to this aberrant behaviour are ongoing, as well as the synthetic opportunities it presents.

The diphosphine glycoconjugates readily form complexes with Re, which are valence isoelectronic with the radioactive ^{99m}Tc.

- [1] C. A. Bange, R. Waterman, Chem. Eur. J. 2016, 22, 12598–12605.
- [2] A. C. Chadwick, M. A. Heckenast, J. A. Race, P. G. Pringle, H. A. Sparkes, Organometallics 2019, 38, 3871–3879.
- [3] M. L. Bowen, O. Orvig, *Chem. Commun.* **2008**, 5077–5091.

- P11 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Synthesis of Bulky Secondary Phosphides and Diphosphanes

<u>Yannic Pilopp</u>,^a Jonas Bresien,^a Lilian Sophie Szych,^a Alexander Villinger,^a Ronald Wustrack,^a Axel Schulz^{*a, b}

^a Institute of Chemistry, University of Rostock, D-18059 Rostock, Germany. ^b Leibniz-Institut für Katalyse eV at the University of Rostock, D-18059 Rostock, Germany.

yannic.pilopp@uni-rostock.de

Over the past years the metal-free activation of small molecules gained a lot of attention.^[1-3] On this account certain trivalent diphosphanes were found to activate *e.g.* CS₂, which can be used as a building block in synthetic chemistry.^[1-3] The Terbased (Ter = 2,6-bis(2,4,6-trimethylphenyl)phenyl) secondary phosphanes **1** can be deprotonated by the use of KH, yielding the corresponding secondary potassium phosphides **2**.^[4] Conversion of these compounds with secondary chlorophosphanes leads to formation of sterically demanding diphosphanes **3**.^[4] The reaction behaviour of the diphosphanes **3** towards H₂O and CS₂ was investigated, showing differences between fully *C*-substituted diphosphanes **3a**-**3f** and partly *N*-substituted diphosphanes **3g** and **3h**.^[4]



Figure 1: Synthesis of sterically demanding secondary phosphides 2 and diphosphanes 3.^[4]

The experimentally estimated P–P bond lengths from the diphosphanes in the single crystal (**3b**, **3c**, **3e**, **3g** and **3h**) were compared with the corresponding theoretically estimated ones obtained from quantum chemical calculations.^[4] While the fully *C*-substituted diphosphanes show bond lengths that are similar to the sum of the covalent radii of a P–P bond ($\Sigma r_{cov}(P-P) = 2.22 \text{ Å}$), the partly *N*-substituted species bear slightly elongated P–P bonds (2.28–2.29 Å).^{[4], [5]} All species mentioned were fully characterized.

- [1] F. R. Hartley, *The Chemistry of Organophosphorus Compounds Volume 1*, John Wiley & Sons, Inc., **1990**.
- [2] N. A. Giffin, A. D. Hendsbee, J. D. Masuda, Dalton Trans. 2016, 45, 12636-12638.
- [3] N. Szynkiewicz, L. Ponikiewski, R. Grubba, Chem. Commun. 2019, 55, 2928-2931.
- [4] J. Bresien, Y. Pilopp, A. Schulz, L. S. Szych, A. Villinger, R. Wustrack, *Inorg. Chem.* **2020**, *42* (*18*), 13561–13571.
- [5] P. Pyykkö, M. Atsumi, Chem. Eur. J. 2009, 15, 12770 12779.

- P12 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Novel Polyphosphorus Architectures from Polyphosphorus Ligand Complexes and Cationic p-Block Electrophiles

Christoph Riesinger,^a Manfred Scheer*a

^a Institute of Inorganic Chemistry, University of Regensburg, Germany.

christoph.riesinger@chemie.uni-regensburg.de

The chemistry of cationic polyphosphorus frameworks has been an active research topic for several decades. While manifold intriguing structural motifs could be obtained utilizing phosphenium cations $[R_2P]^+$,^[1] the formal oxidation of P₄ yielded the first homopolyatomic phosphorus cation $[P_9]^+$.^[2] The reactivity of unsubstituted polyphosphorus ligand complexes has been intensively studied over the past years.^[3] However, their reactivity towards cationic electrophiles has barely been explored.^[4] Herein, we evaluate the reactivity of two selected polyphosphorus ligand complexes $[Cp'''Ni(\eta^3-P_3)]$ (1)^[5] and $[Cp^*Fe(\eta^5-P_5)]$ (2)^[6] towards different electrophiles. The reaction of 1 with phosphenium cations yields the ring-expanded cations $[Cp'''Ni(\eta^3-P_4R_2)]^+$ (3), bearing the unprecedented *cyclo*-P₄R₂ unit. Subsequently, the P₄ ring in 3 can be opened nucleophilically to yield dinuclear complexes $[(Cp'''Ni)_2P_4R_2X]^+$ (4).^[7] In contrast, the reaction of 2 with group 14 electrophiles yields the first structurally characterized complexes of pentaphospholes. The controlled hydrolysis of the silylated derivative $[Cp^*Fe(\eta^5-P_5SiEt_3)]^+$ (5) provides access to the parent compound $[Cp^*Fe(\eta^5-P_5H)]^+$ (6).^[8]



Figure 1: Reactivity of the polyphosphorus ligand complexes **1** and **2** towards cationic p-block electrophiles.

- a) N. Burford, T. S. Cameron, P. J. Ragogna, *J. Am. Chem. Soc.* 2001, *123*, 7947; b) J. J. Weigand,
 M. Holthausen, R. Fröhlich, *Angew. Chem. Int. Ed.* 2009, *48*, 295.
- [2] T. Köchner, T. A. Engesser, H. Scherer, D. A. Plattner, A. Steffani, I. Krossing, *Angew. Chem. Int. Ed.* **2012**, *51*, 6529.
- [3] C. M. Hoidn, D. J. Scott, R. Wolf, Chem. Eur. J. 2021, doi.org/10.1002/chem.202001854.
- [4] a) G. Capozzi, L. Chiti, M. Di Vaira, M. Peruzzini, P. Stoppioni, Chem. Commun. 1986, 24, 1799.
- [5] E. Mädl, G. Balázs, E. V. Peresypkina, M. Scheer, Angew. Chem. Int. Ed. 2016, 55, 7702.
- [6] O. J. Scherer, T. Brück, Angew. Chem. Int. Ed. Engl. 1987, 26, 59.
- [7] C. Riesinger, L. Dütsch, G. Balázs, M. Bodensteiner, M. Scheer, Chem. Eur. J. 2020, 26, 17165.
- [8] C. Riesinger, G. Balázs, M. Bodensteiner, M. Scheer, Angew. Chem. Int. Ed. 2020, 59, 23879.

- P13 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Oxidative addition reactions of low valent [Dipp₂NacNac]Ga with group 15 hydrides

Selina Schneider,^a Sergei Ivlev,^b Carsten von Hänisch*^a

^a Institute of Chemistry, Philipps-Universität Marburg, Germany. ^b Department of Xray crystallography, Philipps-Universität Marburg, Germany.

selina.schneider@chemie.uni-marburg.de

In the last years, stabilization and reaction behaviour of low-valent metal compounds has become a great interest. Some of the most used ligands not only in transition metal Chemistry but also in main group Chemistry are the β -diketiminates better known as '[NacNac]-' ligands.^[1] Low-valent group 13-NacNac complexes are analogous to NHC's and can react both nucleophilic and electrophilic.^[2,3]

One focus on reactions with low valent group 13-NacNac complexes are oxidative addition reactions. For the compound $[(Dipp_2NacNac)Ga]^{[4]}$ (Dipp = di-*iso*-propyl-phenyl), multiple oxidative addition reactions with hydrogen-element bonds are described.^[5]

On this poster, we present a row of oxidative addition reactions with [(Dipp₂NacNac)Ga] and group 15 hydrogen compounds with the main focus on the simplest representative phosphine and its heavy homologous (s. figure 1 for examples).^[6]



Figure 1: Molecular structure of [(Dipp₂NacNac)GaH(PH₂)] (left) and the bridged arsenic homologous (right).

- [1] L. Bourget-Merle, M. F. Lappert, J. R. Severn, *Chem. Rev,* **2002**, *10*2, 3031-3065.
- [2] M. Asay, C. Jones, M. Driess, Chem. Rev., 2011, 111, 354-396.
- [3] Y. Tsai, Coord. Chem. Rev., 2012, 256, 722-758.
- [4] N. J. Hardman, B. E. Eichler, P.P. Power, *Chem. Commun.*, **2000**, 1991-1992.
- [5] A.Seifert, D. Scheid, G. Linti, T. Zessin, Chem. Eur. J., 2009
- [6] S. Schneider, S. Ivlev, C. von Hänisch manuscript in preparation.

- P14 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Reactivity Studies of an Anionic Cyclotriphosphido Cobalt Complex

K. Trabitsch,^a R. Wolf*a

^a Institut für Anorganische Chemie, Universität Regensburg, 93040 Regensburg, Germany.

karolina.trabitsch@chemie.uni-regensburg.de

The anionic cyclotetraphosphido cobalt complex **1** (Figure 1) is an excellent precursor for the construction of larger polyphosphido ligands by reacting **1** with diorganochlorophosphanes. Cyanide anions cleave the pentaphosphorus unit of the resulting complexes **2-R** into a cyclotriphosphido complex **3** and 1-cyanodiphosphan-1-ide anions **4-R**.^[1]

Our recent research has focused on the reactivity of **3** toward main group electrophiles. A regioselective attack on the two different reaction sites in compound **3**, i.e. *cyclo*-P₃ ring and cyanide ligand, was observed, leading to different structural motifs, depending on the electrophile. Herein, we report the synthesis of neutral cobalt complexes **5-R** containing a *cyclo*-P₄R₂ ligand by reaction of **3** with diorganochlorophosphanes. By contrast, group 14 electrophiles, MeOTf and Me₃SiOTf, afford isocyanide complexes **6-E**.



Figure 1: Reactivity of the cyclotriphosphido complex **3** toward main group electrophiles; [LCo] = [(PHDI)Co]; PHDI = Bis(2,6-diisopropylphenyl)phenanthrene-9,10-diimine.

 C. M. Hoidn, T. M. Maier, K. Trabitsch, J. J. Weigand, R. Wolf, Angew. Chem. 2019, 131, 19107– 19112; Angew. Chem. Int. Ed. 2019, 58, 18931–18936.

Bipyridyl-Ru(II) complexes containing 1,3,5-Triaza-7phosphaadamantane (PTA) vs. plasmid DNA (pKSII)

<u>J. M. Veiga del Pino</u>,^a A.Romerosa Nievas, ^a F. Scalambra, ^a F. García Maroto ^a, A. Hernández Zanoletty, ^a

^a Department of Chemistry and Physics-CIESOL, Faculty of Experimental Sciences University of Almería, Spain.

jvd270@ual.es

The researching on less toxic antitumoral drugs with a higher activity spectrum against cancer has led to the study of new complexes with metals different to Pt. Among them, Ru(II) complexes has showed to display significant antiproliferative activity that can be activate when irradiated by a specific wavelength, such as those containing bipyridyl ligands.^[1] In this communication is presented the synthesis and characterization of ruthenium complex *cis*-[Ru(Dcbpy)₂(PTA)₂]Cl₂ (1), containing carboxyl-bipyridyl (Dcbpy) and PTA ligands, which display a large solubility in water and significant optical properties. The photoactivation of this complex together with the previously published ^[2] parent complex containing bipyridine and PTA, *cis*-[Ru(bpy)₂(PTA)₂]Cl₂ (2), *trans*-[Ru(bpy)₂(PTA)₂](CF₃SO₃)₂ (3) and *cis*-[Ru(bpy)₂(PTA)(H₂O)](CF₃SO₃)₂ (4) (bpy = 2,2'-bipiridina), was evaluated against plasmid DNA under UV-Vis irradiation. The reaction products were analysed by electrophoresis on agarose gels. The resulting changes in plasmid mobility revealed those complexes that interacts with DNA and how strong is this interaction.

The obtained results show that complex **4** is active both in the dark and under visible irradiation while **1** and **3** only are active against DNA when irradiated with visible light, while **2** is inactive. The most active complexes were **3** and **4**, which require the presence of oxygen for being actives.

- [1] D. Gopalakrishnan, S. Srinath, B. Baskar, S. Bhuyanesh, M. Ganeshpandian, *Appl. Organometal Chem.* **2020**, 33, 1-16.
- [2] F. Scalambra, M. Serrano-Ruiz, S. Nahim-Granados, A. Romerosa, *European Journal of Inorganic Chemistry*. **2016**, *10*, 1528-1540

Acknowledgements. We acknowledge the Ministerio de Economía y Competitividad (MINECO) and the FEDER program for jointly funding the Project CTQ2015-67384-R, also thanks are provided to the PAI group FQM-317.

Cu(I)-phosphine pre-assembled precursors for selective adaptive coordination-driven supramolecular syntheses of new polymetallic Cu(I) luminescent assemblies

<u>C. Xu,</u> A. M. Khalil, M. El Sayed Moussa, S. Evariste, G. Calvez, K. Costuas, C.Lescop*

Univ Rennes, INSA Rennes, CNRS, ISCR "Institut des Sciences Chimiques de Rennes", F¬35708 Rennes, France

Chendong.Xu@insa-rennes.fr

An increasing interest is devoted to Cu(I) metal complexes as new multifunctional molecular materials for lighting and sensors applications.¹ Using a synthetic approach inspired by the general coordination-driven supramolecular (CDS) chemistry strategy,² we present herein the straightforward syntheses and solid state characterizations of a novel series of polymetallic Cu(I) supramolecular assemblies.³ Their specific solid-state luminescent are also reported. These results highlight that, the typical labile, flexible and low-directional coordination sphere of the Cu(I) ion, initially regarded as strongly restrictive in conventional CDS chemistry, turned out to be very valuable to conduct the adaptive and selective preparation of original polymetallic derivatives.



- a) V. W.-W. Yam, V. K.-M. Au, S. Y.-L. Leung, *Chem. Rev.* 2015, *115*, 7589; b) R. Czerwieniec, M. J. Leitl, H.H.H. Homeier, H. Yersin, *Coord. Chem. Rev.* 2016, *325*.
- [2] a) C. Lescop, Acc. Chem. Res., **2017**, 50, 885; C. Lescop, Chemical Record, **2021**, DOI : <u>https://doi.org/10.1002/tcr.202000144</u>.
- [3] a) M. El Sayed Moussa, S. Evariste, H.-L. Wong, L. Le Bras, C. Roiland, L. Le Polles, B. Le Guennic, K. Costuas, V. W.-W. Yam, C. Lescop, *Chem. Commun.* 2016, *52*, 11370; b) S. Evariste, A.M. Khalil, M. Elsayed Moussa, A. K.-W. Chan, E. Y.-H. Hong, H.-L. Wong, B. Le Guennic, G. Calvez, K. Costuas, V. W.-W. Yam, C. Lescop, *J. Am. Chem. Soc.*, 2018, *140*, 12521. c) M. El Sayed Moussa, A.K. Khaliil, S. Evariste, H.-L. Wong, V. Delmas, B. Le Guennic, G. Calvez, K. Costuas, V. W.-W. Yam, C. Lescop, *Inorg. Chem. Front.*, 2020, *7*, 1334.

- P17 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Characterization and Properties of Covalently Functionalized Black Phosphorus

<u>Jiaying Yang</u>,^a Kendahl L. Walz Mitra,^a Daniel Tofan,^a Christine H. Chang,^b Ruoming Peng,^c Mo Li,^c Alexandra Velian^{*a}

^a Department of Chemistry, University of Washington, USA. ^b Department of Materials Science and Engineering, University of Washington, USA. ^c Department of Electrical Engineering, University of Washington, USA.

jiay2858@uw.edu

Surface modification can tune the electronic, chemical, and physical properties of two-dimensional materials. However, methods to chemically modify the surface and directly probe the interactions between the material and the added fragments are not adequately developed.

The surface of black phosphorus (bP), with a lone pair on each P atom, is chemically reactive and suitable for facile surface functionalization. In this work, two surface functionalization strategies of thin-layer black phosphorus were demonstrated: mild functionalization with nitrenes and organometallic fragments, respectively. Functionalized nanosheets were characterized through a variety of techniques including vibrational, X-ray (photoelectron, emission), NMR, and UV-Vis spectroscopies. For the first time, the chemical bond between black phosphorus and covalently attached species can be directly probed through infrared spectroscopy (IR). By isotopically labelling the nitrenes, diagnostic P=¹⁵N stretches appear in IR. For bP functionalized with organometallic fragments, significant shifts of v(CO) were observed suggesting changes in electron density at the metal centers. Systematic studies of electronic and steric properties of black phosphorus as ligand towards metal centers were performed through ligand exchange experiments. Molecular phosphines were added with metalated nanosheets to test if bP would be displaced.



Figure 1: Overview of the characterization and electronic/steric properties of surface-modified black phosphorus.

[1] K. L. Walz Mitra, C. H. Chang, M. P. Hanrahan, J. Yang, D. Tofan, W. M. Holden, N. Govind, G. T. Seidler, A. J. Rossini, A. Velian, Angew. Chem. Int. Ed. 2021, 60, 2–10.

From Ylide-Phosphine Tautomers to Carbanionic Phosphines

Jana-Alina Zur, a, Viktoria H. Gessner *a

^a Chair of Inorganic Chemistry II, Ruhr-University Bochum, 44780 Bochum, Germany jana-alina.zur@rub.de

Phosphines are a privileged class of ligands in homogenous catalysis. In many transformations electron-rich phosphines are particularly efficient, e.g. in C–C and C– X coupling reactions^[1, 2], where strong donors are required to facilitate the oxidative addition of the aryl halide. For example, powerful catalytic systems are based on dialkyl-biaryl ^[3] phosphines or the structurally related ylide-functionalized phosphines (YPhos).^[4] In the latter, an ylidic moiety is bound to the phosphorus atom and increases its donor strength. As most of these ligand systems are neutral compounds, we became interested in the development of anionic phosphines with the charge located at the carbanionic moiety adjacent to the phosphorus atom. These functionalized phosphines should likewise give rise to highly electron-rich ligands with novel donor properties interesting for catalytic applications. Here, we present first studies on bis(sulfonyl)methane-substituted phosphines, which led to interesting phosphine-ylide tautomers and the isolation of carbanionic phosphines:



Scheme 1: top: tautomerism depending on **R/R'**, bottom: exemplary molecular structures of a phosphine (left), an ylide (middle), and a carbanionic functionalized phosphine (right) formed in solid state.

- a) R. F. Heck and J. P. Nolley, J. Org. Chem. 1972, 37, 2320. b) Stille J. K., Angew. Chem. Int. Ed. 1986, 25, 508.
- [2] D. W. Old, J. P. Wolfe, S. L. Buchwald, J. Am. Chem. Soc. 1998, 120, 9722.
- [3] J. Carreras, A. Pereira, M. Zanini, A. M. Echavarren, Organometallics 2018, 37, 3588.
- [4] T. Scherpf, R. Wirth, S. Molitor, K.-S. Feichtner, V. H. Gessner, Angew. Chem. Int. Ed. 2015, 54, 8542. b) T. Scherpf, C. Schwarz, L. T. Scharf, J.-A. Zur, A. Helbig, V. H. Gessner, Angew. Chem. Int. Ed. 2018, 12859.

Synthesis, characterization and antiproliferative properties of [RuCl₂(p-cymene)(HdmoPTA)]

<u>Andrés Alguacil Alarcón</u>,^{a,b} Nazanin Kordestani,^{a,b} Franco Scalambra,^{a,b} Antonio Manuel Romerosa Nievas^{*a,b}

^a Department of Chemistry and Physics, University of Almeria, Almeria, 04120, Spain ^b Inorganic Chemistry Lab-CIESOL, University of Almeria, Almeria, 04120, Spain

aaa518@ual.es

Our research group has investigated the possibilities of the ligand dmPTA (*N*,*N*'dimethyl-1,3,5-triaza-7-phsophadamantane) and its parent ligand dmoPTA (3,7dimethyl-1,3,7-triaza-5-phosphabyciclo[3.3.1]nonane), which shows interesting coordinative properties by having a soft coordination position, the phosphorus atom, and two hard coordination positions, nitrogen atoms, with the ability to form chelate rings.^[1] This ligand was useful for obtain interesting Ru-M bimetallic complexes of general formula [RuCp(PPh₃)₂- μ -dmoPTA-1 κ P:2 κ ²N,NMCl₂] (M = Co, Ni, Zn), that displayed significant antiproliferative activity, some of them up 600 bigger than cisplatin.^[2,3]

A next step in the use of this ligand is to check how can modify the antiproliferative properties of the known RAPTA family. With the aim of synthesizing a first representative ruthenium complex containing p-cymene and dmoPTA ligand, [RuCl₂ (p-cymene)(HdmoPTA)] complex was synthesized (Scheme 1) and fully characterized by single-crystal X-ray diffraction and their antiproliferative properties were studied against a panel of cancer cells.



Scheme 1. Synthesis of [RuCl₂(p-cymene)(HdmoPTA)].

Acknowledgements: We acknowledge the Ministerio de Economía y Competitividad (MINECO) and the FEDER program for jointly funding the Project CTQ2015-67384-R, also thanks are provided to the PAI group FQM-317.

- [1] A. Mena-Cruz, P. Lorenzo-Luis, A. Romerosa, M. Saoud, M. Serrano-Ruiz, *Inorg. Chem.*, **2007**, 46 6120-6128.
- [2] A. Mena-Cruz, P. Lorenzo-Luis, A. Romerosa, M. Serrano-Ruiz, *Inorg. Chem.*, **2008**, 47, 2246-2248
- [3] M. Serrano-Ruiz, L.M. Aguilera-Sáez, P. Lorenzo-Luis, J.M. Padrón, A. Romerosa, *Dalton Trans.*, **2013**, 42, 11212-11219

- P20 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Simple and Practical Functionalisation of P₄ Mediated by Bu₃SnH

Jose Cammarata, Daniel Scott, Robert Wolf*

Institute of Inorganic Chemistry, University of Regensburg, 93040 Regensburg, Germany.

Jose-Ricardo.Camarata-Paredes@ur.de

White phosphorus, P₄, is by far the most reactive and industrially relevant allotrope of the element. Its production is currently estimated to be above one million tons per year and it serves as the synthetic precursor for all organophosphorus compounds worldwide.^[1] Unfortunately, the industrial preparation of the desired organophosphorus derivatives from P₄ typically consists of a multistep process that involves hazardous reactants and intermediates such as chlorine gas, phosphorus chlorides and/or PH₃, with the additional generation of stoichiometric amounts of chlorinated waste.^[1,2] Alternative strategies for the transformation of P₄ into valuable organophosphorus compounds are therefore highly desirable.

Many efforts in academia have been focused on the activation and transformation of P₄ using reactive main group and transition metal compounds.^[3,4] A comparatively underexplored approach is the functionalisation of P₄ using radical reagents.^[5,6] We have found a simple procedure for the degradation of P₄ into P₁ species using the radical reagent Bu₃SnH. The initially-formed hydrostannylation products (Bu₃Sn)_xPH_{3-x} (x = 1-3) serve as P³⁻ equivalents, and can be treated with various electrophiles to directly afford industrially relevant monophosphorus compounds in a one pot procedure (Figure 1).^[7] We also demonstrate facile and efficient recycling and ultimately even catalytic use of the tributyltin reagent, thereby avoiding the formation of significant Sn-containing waste.^[7]



Figure 1. Synthesis of Monophosphines Directly from White Phosphorus.

- [1] Corbridge D. E. C., *Phosphorus. Chemistry, Biochemistry and Technology*, Elsevier, **2000**.
- [2] Ullmann's Encyclopedia of Inorganic Chemistry, Wiley-VCH, Weinheim, 2012.
- [3] Hoidn, C.; Scott, D. J.; Wolf, R. Chem. Eur. J. DOI:10.1002/chem.202001854.
- [4] Wang, Y.; Szilvási, T.; Yao, S.; Driess, M. *Nat. Chem.* **2020**, *12*, 801-807.
- [5] Cossairt, B. M.; Cummins, C. C. New J. Chem. 2010, 34, 1533-1536.
- [6] Lennert, U.; Arockiam, P. B.; Streitferdt, V.; Scott, D. J.; Rödl, C.; Gschwind, R. M.; Wolf, R. *Nat. Catal.* **2019**, *2*, 1101-1106.
- [7] Scott, D.; Cammarata, J.; Schimpf, M.; Wolf, R. Nat. Chem., accepted for publication.

Catalytic Alkene Carbonylation: Design, Synthesis and Application of Multi-functional Ligands

Adam Carrick,^a Andrei Batsanov,^a Philip Dyer*^a

^a Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK. Email: adam.carrick@durham.ac.uk

Alkoxycarbonylation converts an olefin/alkyne, CO and an alcohol into an ester, often using a palladium-based bidentate phosphine catalyst.¹ The rate of reaction can be increased by using complexes with pendant pyridyl moieties, which behave as *in situ* non-coordinating bases.² To further explore this effect, an array of diphosphinoamines of the form RN(PPh₂)₂ (R is pyridyl-based) have been synthesised as potential ligand candidates. Reaction of diphosphinoamines with [PdCl₂(MeCN)₂] affords complexes of the form [RN(PPh₂)₂PdCl₂], containing strained four-membered chelates with κ^2 -P,P coordination (∠PPdP ~72°) and a non-coordinating pyridyl nitrogen atom. Reaction of diphosphinoamines with CoBr₂ affords products with differing coordination modes.



Scheme 1. Reactions of two diphosphinoamine ligands L1 and L6 with PdCl₂(MeCN)₂ and CoBr₂, showing molecular structures obtained by single crystal XRD analysis.

- [1] T. Fanjul, G. Eastham, N. Fey, A. Hamilton, A. G. Orpen, P. G. Pringle, M. Waugh, *Organometallics*, **2010**, *29*, 2292-2305.
- [2] K. Dong, R. Sang, Z. Wei, J. Liu, R. Dühren, A. Spannenberg, H. Jiao, H. Neumann, R. Jackstell, R. Franke, M. Beller, *Chem. Sci.*, **2018**, *9*, 2510-2516.

Highly E-selective transfer-semihydrogenation of internal alkynes with ammonia borane and a Co(II) PNN pincer catalyst

David Decker,^a Jabor Rabeah,^a Hans-Joachim Drexler,^a Torsten Beweries^{*a}

^a Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany; E-Mail: torsten.beweries@catalysis.de

David.Decker@catalysis.de

Alkenes are versatile building blocks for a broad range of applications in organic chemistry that can be synthesised by semi-hydrogenation of alkynes. The selective formation of E- or Z-alkenes however still represents a major challenge, especially when considering functional or aliphatic substrates. While Z-selective hydrogenation can be conveniently achieved using a multitude of catalyst systems, including the Lindlar catalyst as the most prominent example, *E*-selectivity is more difficult to obtain and one of the most common routes still is Birch-reduction using alkali metals in ammonia, producing stoichiometric amounts of waste. The use of suitable hydrogen transfer reagents instead of gaseous hydrogen is a practical and safe alternative.^[1]

We present two Co(II) PNN complexes^[2] as active catalysts in the dehydrogenation of ammonia borane and the semihydrogenation of different substituted internal alkynes in methanol at exceptionally low catalyst concentration in less than 30 minutes. This mild system shows an excellent *E*-selectivity due the isomerization of the initially formed Z-alkene. Furthermore, labeling experiments with deuterated ammonia borane and methanol showed that H-transfer to the substrate occurs from the B-H bond of H₃B·NH₃ and the O-H of MeOH. A reliable method to determine the end point of the reaction is the monitoring of the H₂ evolution, which takes place due to the dehydrogenation of the ammonia borane mediated by the catalyst during the transfer semihydrogenation, using a gas burette.^[3]



Figure 1: Transfer semihydrogenation of internal alkynes using a cobalt(II) catalyst.

- [1] a) D. Decker, H.-J. Drexler, D. Heller, T. Beweries, Catal. Sci. Technol. 2020, 10, 6449-6463; b) W. Bonrath, J. A. Medlock and M.-A. Müller, Catalytic Reduction of Alkynes and Allenes, in Catalytic Reduction in Organic Synthesis 1, 2018, ed. J. G. de Vries, Georg Thieme Verlag, Stuttgart, 2018.
- [2] [3] A. V. Polezhaev, C.-H. Chen, Y. Losovyj, K. G. Caulton, Chem. Eur. J. 2017, 23, 8039-8050.
- D. Decker, J. Rabeah, H.-J. Drexler, T. Beweries, manuscript in preparation.

A P-functional TTF-fused 1,4-diphosphinine precursor

Shahriar Kermanshahian, Rainer Streubel*

Institut für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Bonn, Germany shk2018@uni-bonn.de

During the past 10 years, we have used the methodology of stepwise lithiation and phosphanylation of various five-membered ring systems, *i.e.*, 1,3-imidazol-2-thione^[1,2]. 1,3-thiazol-2-thione^[3] and and 1,3-dithiole-2-thione^[4]. These heterocycles can be converted into tricyclic compounds containing a 1,4-dihydro-1,4-diphosphinine ring which were reduced to access 1,4-diphosphinines.^[5] On the other hand Fourmigué and coworkers reported first on TTF-fused 1,4-dihydro-1,4-diphosphines bearing P-Ph groups using bis-lithiation of o-dimethyltetrathiafulvalene (o-DMTTF) with LDA, followed by reaction of the dianion with one equivalent of PhPCl₂.^[6]

Herein, we present results on synthesis and conversion of P-chloro tetrathiafulvalenes 2 into 1,4-dihydro-1,4-diphosphinines 3 fused to two TTF units^[7]. Also by using ortho-ⁿPr₂-TTF to overcome insolubility problem, related 1,4-dichloro-1,4-dihydro-1,4-diphosphinine 4 could be synthesized. Currently, we are on the way to establish the corresponding 1,4-diphosphinine, thus pushing the boundaries of molecular electronics.



Scheme 1: Synthetic route to TTF-fused P-functional 1,4-dihydro-1,4-diphosphinine derivatives.

[1] S. Sauerbrey, P. K. Majhi, G. Schnakenburg, A. J. Arduengo III, R. Streubel, Dalton Trans., 2012, 41, 5368-5376.

- [2] P. K. Majhi, G. Schnakenburg, R. Streubel, Dalton Trans., 2014, 43, 16673-16679.
- [3] I. Begum, G. Schnakenburg, R. Streubel, Dalton Trans., 2016, 45, 2955–2962.
- [4] A. Gese, M. Akter, G. Schnakenburg, A. García Alcaraz, A. Espinosa Ferao, R. Streubel, New. J. Chem. 2020, 44, 17122-17128.
- [5] a) A. Koner, R. Streubel, Z. Kelemen, G. Schnakenburg, L. Nyulaszi, T. Sasamori, G. Pfeifer, [5] a) A. Koner, N. Oreaber, Z. Kelemen, G. Schnakenburg, Z. Kyuazzi, T. Oddanieri, C. Fleiner, Angew. Chem. 2017, 56, 9231-9235; b) I. Begum, G. Schnakenburg, Z. Kelemen, L. Nyulászi, R. T. Boeré, R. Streubel, Chem. Commun. 2018, 54, 13555-13558.
 [6] N. Avarvari, M. Fourmigué, Chem. Commun. 2004, 24, 2794-2795.
- [7] S. Kermanshahian, Z. Kelemen, L. Nyulászi, R. T. Boeré, R. Streubel, manuscript in preparation.

Functionalised Phosphonate Esters in Lanthanide Model Complexes and ^RPOSS-supported Lanthanide Coordination

I. Köhne,^a M. Gerstel,^b C. Bruhn,^a J. P. Reithmaier,^b M. Benyoucef^b and R. Pietschnig^{*a}

^a Institute of Chemistry and Centre for Interdisciplinary Nanostructure Science and Technology (CINSaT), University of Kassel, Germany. ^b Institute of Nanostructure Technologies and Analytics (INA) and CINSaT, University of Kassel, Germany.

ikoehne@uni-kassel.de

Owing to their outstanding photoluminescence properties, lanthanide ions already find widespread application in lighting, sensing and display technologies.¹⁻³ In comparison to their carboxylic acid counterparts, the advantage of phosphonate esters initiates from their lower vibrational frequencies resulting in diminished non-emissive excited state quenching and improved quantum yields.⁴ Our group has focused on these ligands in recent years synthesising several highly luminescent lanthanide-based MOF's⁵⁻⁷ as well as mono- and dimeric lanthanide complexes showing interesting splitting features in their NIR emission spectra.⁸ To obtain distinct molecular complexes with enhanced excited state lifetimes in the context of a future immobilisation on semi-conductor surfaces, our research focusses on preparation of POSS cage-supported lanthanide complexes coordinated by functionalised aromatic phosphonate esters.⁹



Figure 1: Bromo- and azido-functionalised phosphonate esters (top). Lanthanide model complexes (bottom, left). POSS cage- and phosphonate ester-supported lanthanide complexes (bottom, right).

- [1] O. Guillou, C. Daiguebonne, G. Calvez, K. Bernot, Acc. Chem. Res. 2016, 49, 844-856.
- [2] J.-C. Bünzli, Nat. Chem. 2010, 2, 696-696.
- [3] B. Samson, A. Carter, K. Tanaka, *Nat. Photonics* **2011**, *5*, 466-467.
- [4] Y.Hasegawa, Y. Kimura, T. Yamanaka, S. Yanagida, J. Phys. Chem. 1996, 24, 10201-10205.
- [5] K. Krecić, D. Klintuch, R. Pietschnig, Chem. Commun. 2017, 53, 11076-11079.
- [6] K. Krecić, E. Käkel, D. Klintuch, D. Bloß, R. Pietschnig, Z. Anorg. Allg. Chem 2018, 644, 149-154.
- [7] K. Krecić, D. Klintuch, C. Lescop, G. Calvez, R. Pietschnig, Inorg. Chem. 2019, 58, 382-390.
- [8] I. Koehne, A. Lik, M. Gerstel, C. Bruhn, J.-P. Reithmaier, M Benyoucef, R. Pietschnig, *Dalton Trans.* **2020**, *49*, 16683-16692.
- [9] I. Koehne, M. Gerstel, C. Bruhn, J. P. Reithmaier, M Benyoucef, R. Pietschnig, *Inorg. Chem.* **2021**, submitted.

Synthesis and redox chemistry of anionic imidazole-2thione-fused 1,4-dihydro-1,4-diphosphinines

Mridhul. R. K. Ramachandran^a and Rainer Streubel^{*a}

^aInstitut für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany. s6mrkott@uni-bonn.de

The synthesis of the first stable and isolable 1,4-diphosphinine **1** by Streubel and coworkers in 2017^[1] enabled synthesis and isolation of mono anionic 1,4-dihydro-1,4diphosphinines, which were initially targeted with limited success.^[2] Herein, the synthesis of the blue, anionic 1,4-dihydro-1,4-diphosphinines **2a-c** will be described as well as reactions with iodomethane thus leading to P-methylated compounds **3a-c**.^[3]



Figure 1: Synthesis and reactions of anionic 1,4-dihydro-1,4-diphosphinines 2a-c.

An oxidation/reduction cycle was examined and successfully established, *i.e.*, starting from anion **2a** via P-P coupled product **4a** and back to **2a**, thus representing a new reversible molecular 2-electron battery material. Additional cyclovoltammetric studies corroborate these results; the latter will be also discussed.^[3]

- [1] A. Koner, G. Pfeifer, Z. Kelemen, G. Schnakenburg, L. Nyulászi, T. Sasamori, R. Streubel, *Angew. Chem. Int. Ed.* **2017**, *56*, 9231-9235.
- [2] A. Koner, M. Kunz, G. Schnakenburg, R. Streubel, Eur. J. Inorg. Chem. 2018, 3778-3784.
- [3] M. Ramachandran, G. Schnakenburg, M. Majumdar, Z. Kelemen, D. Gál, L. Nyulászi, R. T. Boeré, R. Streubel, **2021**, *submitted*.

- P26 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Exploring the chemistry of novel phosphorous ylides and their main group complexes

Dr. Sébastien Lapointe,^a Prof. Dr. Viktoria Däschlein-Gessner*^a

^a Chair of Inorganic Chemistry II, Ruhr-Universität Bochum, 44780, Bochum, Germany.

sebastien.lapointe@rub.de

Our group's focus is to develop unique and new types of carbenoid compounds that can be used in fundamental research from reactivities to catalysis. Amongst those, we have been focusing on carbene complexes that deviate from the traditional Fischer or Schrock-type carbenes, also called methandiides. Methandiides are highly reactive carbenoid moieties that bind to elements through s and p donor interactions, in contrast with the usual carbenes that either coordinate through s-donor and p-acceptor interactions (Fischer-type carbenes) or through covalent bonding (Schrock-type carbenes). The reactive nature of methandiide species makes their isolation and manipulation usually difficult. However, the introduction of phosphorous(V) substituents on the ligands, usually result in their stabilization.

We have decided to explore the bis(iminophosphorano)methandiide (BIPM) ligand framework, which has been intensively studied in transition metal chemistry but less with the main group elements. In initial experiments we focused on the reactivity towards phosphorus compounds and uncovered the unexpected formation of the novel ylide **1** (Scheme 1). Here, we describe its synthesis, further reactivity, and coordination chemistry studies.



Scheme 1: (left) Reactivity of BIPM ligands with different chlorophosphines to form novel ylides **1**. (Right) ORTEP representation of one of the ylides **1**.

- P27 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Cyano(triphenylsilyl)phosphanide, an ambident PCN building block

<u>Grégoire Le Corre</u>,^a Juan José Gamboa Carballo,^{a,b} Frederik Eiler,^a Hansjörg Grützmacher^a

^a Department of Chemistry and Applied Biosciences ETH Zürich, Switzerland. ^b Higher Institute of Technologies and Applied Sciences (InSTEC), University of Havana, Ave. S Allende 1110, 10600 Havana (Cuba)

lecorreg@inorg.chem.ethz.ch

Despite the significant impact that anionic PCN building blocks would have on synthetic organophosphorus chemistry, only a handful of cyanophosphides and anionic PCN species have been reported to this day^[1-5] and their chemistry remains relatively unexplored.

The [Ph₃SiPCN]⁻ anion was recently synthesized by our group and we sought to explore its potential as a nucleophilic PCN building block. Reactions of the novel anion with carbodiimides and isocyanates provided phosphorus analogs of guanidines and ureas respectively, demonstrating the P-nucleophilicity of this anion. On the other hand, reactivity at nitrogen was evidenced spectroscopically and by single crystal X-Ray diffraction in reactions with heavier group 14 electrophiles and boron-based Lewis acids. These results are in line with ab initio calculations which predict significant contribution of the 1-aza-3-phosphaallenide resonance form in [Ph₃SiPCN]⁻.



Figure 1: Reactivity of the [Ph₃SiPCN]⁻ anion with main group electrophiles

- [1] A. Schmidpeter, F. Zwaschka, Angewandte Chemie International Edition **1977**, *16*, 704-705.
- [2] A. Schmidpeter, K. H. Zirzow, G. Burget, G. Huttner, I. Jibril, *Chemische Berichte* **1984**, *117*, 1695-1706.
- [3] G. Becker, H. Brombach, S. T. Horner, E. Niecke, W. Schwarz, R. Streubel, E. U. Wurthwein, *Inorganic Chemistry* **2005**, *44*, 3080-3086.
- [4] C. M. Hoidn, T. M. Maier, K. Trabitsch, J. J. Weigand, R. Wolf, *Angewandte Chemie* International Edition **2019**, *58*, 18931-18936.
- [5] Z. Li, J. E. Borger, F. Müller, J. R. Harmer, C. Y. Su, H. Grützmacher, *Angewandte Chemie International Edition* **2019**, *58*, 11429-11433.

Synthesis, Electronic Properties and OLED Devices of

Chromophores Based on λ5-Phosphinines

<u>J. Lin</u>,^a G. Preifer,^a F. Chahdoura,^b M. Papke,^a M. Weber,^a R. Szűcs,^c B. Geffroy,^d D. Tondelier,^d L. Nyulászi,^{*c} M. Hissler,^{*b} C. Müller^{*a}

^a Institut für Chemie und Biochemie, Freie Universität Berlin, Germany. ^b ISCR-UMR CNRS, Univ Rennes, France. ^c Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Hungary, ^d LISCEN; NIMBE; CEA, CNRS, Université, Paris-Saclay, France.

Jinxiol93@zedat.fu-berlin.de

In general, 6-membered aromatic phosphinines have received little attention as building blocks for the construction of emissive π -conjugated systems as it has been shown that 2,4,6-triaryl- λ^3 -phosphinines are mostly non-emissive at room temperature.^[1] However, the emission of phosphinines can be restored by introducing additional substituents at the P-atom of λ^3 -phosphinines, to form λ^5 -phosphinines, or by coordination of the heterocycle to a transition metal center.^[2-3]

We will present the emissive properties of compounds of type **1**, in addition to crystallographic characterisation, electrochemical behavior and theoretical calculations. Furthermore, we report the first OLED based on a blue λ^5 -phosphinine emitter.



Figure 1. Left, the structure of type **1** λ^5 -phosphinines. Right: example of an emissive λ^5 -phosphinine.

These novel λ^5 -phosphinines exhibit moderate to high quantum yields in solution. The fabricated OLEDs devices were found to have current and power efficiencies of 1.87 cd A⁻¹ and 0.58 lm W⁻¹, respectively. As the emitter in OLED devices, the external quantum efficiency was found to be 0.96 %. These experiments show that λ^5 -phosphinines can be used to produce optical functional materials, which encourages us to design, synthesise and fabricate further λ^5 -phosphinines of this type.^[4]

- [1] C. Müller, D. Wasserberg, J. J. M. Weemers, E. A. Pidko, S. Hoffmann, M. Lutz, A. L. Spek, S. C. J. Meskers, R. A. J. Janssen, R. A. van Santen, D. Vogt, *Chem. Eur. J.* **2007**, *13*, 4548-4559.
- [2] K. Dimroth, Top. Curr. Chem. 1973, 38, 1-147.
- [3] P. Roesch, J. Nitsch, M. Lutz, J. Wiecko, A. Steffen, C. Müller, *Inorg. Chem.* **2014**, *53*, 9855-9859.
- [4] G. Preifer, F. Chahdoura, M. Papke, M. Weber, R. Szűcs, B. Geffroy, D. Tondelier, L. Nyulászi, M. Hissler, C. Müller, *Chem. Eur. J.* **2020**, *26*, 10534-10543.

- P29 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Towards metathesis reactions with three-coordinate phosphorus cations

Pawel Löwe,^a Milica Feldt,^b Maike B. Röthel,^{a,c} Lukas F. B. Wilm,^a Fabian Dielmann*^{a,c}

^a Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Germany.

^b Theoretische Organische Chemie, Organisch-Chemisches Institut and Center for Multiscale Theory and Computation, Westfälische Wilhelms-Universität Münster, Germany.

^c Institute of General, Inorganic and Theoretical Chemistry, Leopold-Franzens-Universität Innsbruck, Austria.

p.loewe@uni-muenster.de

While transition metal catalyzed metathesis reactions are widely utilized to make and brake a variety of bonds, heavy main-group elements are rarely involved. This contribution shows the potential of three-coordinate phosphorus cations as tools for metathesis reactions.



Figure 1: Reactivity of three-coordinate phosphorus cations with polar double bonds.

We show that three-coordinate phosphorus cations undergo cycloaddition reactions with polar double and triple bonds to either form stable four-membered rings or to rearrange into new products (Figure 1). Detailed computational analysis on the reaction mechanisms and the influence of the substituents were carried out.

Sodium Pentaphospholide as a Versatile Precursor for the Synthesis of Phosphorus Heterocycles

Andrey Petrov, Prof. Dr. Christian Müller

Institute of Inorganic Chemistry, Free University of Berlin, Germany.

andrey.petrov@fu-berlin.de

Non-chlorine-based methods for the transformation of white phosphorus (**P**₄) into organophosphorus compounds have been a continuous interest for ecological, safety and economic reasons.^[1] It has been reported by Baudler that **P**₄ reacts with two equivalents of sodium in refluxing diglyme to give sodium pentaphospholide (**1**).^[2] Coordination properties of the pentaphospholide anion are well studied. Due to the isolobal relationship with the cyclopentadienide anion, η^{5} -type complexes are found to be preferable.^[3] However, η^{1} -coordination *via* the lone pair electrons on the phosphorus has also been observed.^[3] Besides that, little is known about the chemistry of pentaphospholide because of its high reactivity towards electrophiles.^[4]



Scheme 1: Reactivity of the pentaphospholide anion.

We present here the reactivity of the pentaphospholide anion towards different C=E triple bonds: alkynes, nitriles and phosphaalkynes. Based on these experiments, new synthetic pathways to rarely explored 1,2,3- and 1,2,4-triphospholides (**3-4**), 1,2,3,4-tetraphospholides (**5**), as well as to an hitherto unknown 1,2,3-azatriphospholide (**2**), are reported (Scheme 1).

[1] M. Scheer, G. Balázs, A. Seitz, Chem. Rev. 2010, 110, 4236-4256.

- [2] M. Baudler, D. Düster, D. Ouzounis, Z. Anorg. Allg. Chem. 1987, 544, 87-94.
- [3] V. A. Milyukov, Yu. H. Budnikova, Russ. Chem. Rev. 2005, 74, 781-805.
- [4] M. Baudler, S. Akpapoglou, D. Ouzounis, Angew. Chem. Int. Ed. 1988, 27, 280-281.

- P31 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Redox-switchable tris(ferrocenyl)arene-based gold(l) complexes for multi-state-switchable catalysis

Axel Straube,^a Peter Coburger,^b Evamarie Hey-Hawkins^{*a}

^a Institute of Inorganic Chemistry, Leipzig University, Germany. ^b Department of Chemistry and Applied Biosciences, ETH Zürich, Switzerland.

axel.straube@uni-leipzig.de

Adorning catalysts with functionality beyond the pure conversion of a substrate by including stimuli-responsive moieties has been a prominent area of ligand design ever since the groundbreaking discoveries by Wrighton^[1a] and Allgeier/Mirkin^[1b] who showed their catalysts to differentiate between substrates in response to a change of oxidation state in the ligand backbone. Switching between more than two activity states as showcased by the groups of Feringa and Chen yet remains a scientific challenge.^[2]



Figure 1: Yield-over-time plot of the conversion of **2** to **3**, employing gold(I) complex **1** (1 mol% Au), and switching between different activity states by stepwise oxidation (Ox = 1, 1'-diacetylferrocenium tetrakis(perfluoro-tert-butoxy)aluminate) and reduction (**Red** = decamethylferrocene) as indicated by the arrows.

To that end, gold(I) complex **1** of our modular tris(1-phosphanyl-1'-ferrocenylene)arene ligand system^[3a] was found to be reversibly oxidisable in four distinct steps, differing in respective catalytic activity towards the cyclisation of propargyl amide **2** to yield oxazoline **3**.^[3b] Syntheses, catalytic profiles, and insights into the switching behaviour of **1** and its congeners will be presented.

- a) I. M. Lorkovic, R. R. Duff, M. S. Wrighton, *J. Am. Chem. Soc.* 1995, *117*, 3617–3618; b) A. M. Allgeier, C. A. Mirkin, *Angew. Chem. Int. Ed.* 1998, *37*, 894–908.
- [2] a) J. Wang, B. Feringa, *Science* **2011**, *331*, 1429–1432; b) M. Zhao, C. Chen, *ACS Catal.* **2017**, *7*, 7490–7494.
- [3] a) A. Straube, P. Coburger, M. R. Ringenberg, E. Hey-Hawkins, *Chem. Eur. J.* 2020, 26, 5758–5764; b) A. Straube, P. Coburger, L. Dütsch, E. Hey-Hawkins, *Chem. Sci.* 2020, *11*, 10657–10668.

Synthesis and Investigation of Terphenyl-stabilized Phosphanyl Esters of Dithioformic Acid

L. S. Szych^a, J. Bresien^a, Y. Pilopp^a, A. Schulz^{*a,b}, A. Villinger^a and R. Wustrack^a.

^a Institute of Chemistry, University of Rostock, Germany. ^b Leibniz-Institut für Katalyse, Germany.

lilian.szych@uni-rostock.de

Sterically demanding, trivalent secondary phosphanes show an interesting reaction behaviour and are therefore of great interest for synthetic chemistry, catalysis and molecular chemistry.^[1-3] Deprotonation of secondary phosphanes with strong bases such as KH yields the corresponding potassium phosphides, for example **1**. Compound **1** reacts with CS₂ to form the disubstituted phosphanyl dithioformates **2**. The conversion of **2** with secondary halophosphanes CIP(R¹)₂ provides a hitherto unknown route towards some of the few known examples of phosphanyl esters of dithioformic acid **3a-d**.^[4,5]



Figure 1: Synthesis of phosphanyl derivatives of dithioformic acid **3a-d** *and migration reaction yielding* **4a;** Ter = 2,6-Bis-(2,4,6-trimethylphenyl)-phenyl.

One of these thioesters (**3a**) was found to undergo a $(R^1)_2P$ -migration reaction, which is accompanied by oxidation of one phosphorus atom from $P^{(III)}$ to $P^{(V)}$. The migration reaction is resulting in the formation of a phosphanylthioketone with an additional phosphanylthiolate group **4a**, which was used as chiral ligand in gold coordination chemistry.

The phosphanyl-migration reaction was investigated by spectroscopic and theoretical methods, revealing a first-order reaction *via* a cyclic transition state. All species mentioned were fully characterized.

- [1] Hartley F.R.; *The Chemistry of Organophosphorus Compounds Volume 1*, John Wiley & Sons, Inc., **1990**.
- [2] Kamer, P. C. J.; van Leeuwen, P. W. N. M.; *Phosphorus(III) Ligands in Homogeneous Catalysis: Design and Synthesis*, John Wiley & Sons, Inc., **2012**.
- [3] Murphy, P. J.; Organophosphorus Reagents A Practical Approach in Chemistry, Oxford University Press, **2004**.
- [4] Giffin, N. A.; Hendsbee, A. D.; Masuda, J. D.; Dalton Trans. 2016, 45, 12636–12638.
- [5] Szynkiewicz, N.; Ponikiewski, Ł.; Grubba, R.; Chem. Commun. 2019, 55, 2928–2931.

- P33 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Investigating the donor ability of P^{III}- vs P^v-bridged Janus bis(NHCs) towards main group element chlorides

Tatjana Terschüren,^a Rainer Streubel*^a

^a Institute of Inorganic Chemistry, University of Bonn, Germany.

t.terschueren@uni-bonn.de

After the synthesis of the first 1,4-diphosphinine in 1976^[1] and the discovery of new, facile routes to tricyclic imidazole- and thiazole-based 1,4-diphosphinines dithiones^[2] and diselones^[3] in 2017, the quest for P-bridged Janus bis(NHCs) **1** arose and was fulfilled only recently.^[3,4] While their reactivity towards coinage metal complexes was explored^[4], reactions towards main group element halides were not investigated as yet.



Figure 1: Reactivity studies on the formation of main group element chloride adducts or salts.

Herein, we present preliminary results on the formation of group 13 to 15 element chloride adducts **2**, **3** vs their corresponding salts **2'**, **3'** using the P^{III}- or P^V-bridged bis(NHCs), respectively. This is part of a comparative study of the donor ability of these C²-carbene centres towards main group element compounds. Furthermore, first attempts to access bent bis(NHCs), subsequent to a [4+2]-cycloadduct formation of 1,4-diphosphinine diselones, will be presented.

- [1] Y. Kobayashi, I. Kumadaki, A. Ohsawa, H. Hamana, *Tetrahedron Lett.* **1976**, *17*, 3715–3716.
- [2] a) A. Koner, G. Pfeifer, Z. Kelemen, G. Schnakenburg, L. Nyulászi, T. Sasamori, R. Streubel, Angew. Chem. Int. Ed. 2017, 56, 9231–9325 b) I. Begum, G. Schnakenburg, Z. Kelemen, L. Nyulászi, R. T. Boeré, R. Streubel, Chem. Commun. 2018, 54, 13555–13558.
- [3] N. Rauf Naz, G. Schnakenburg, Z. Kelemen, D. Gál, L. Nyulászi, R. T. Boeré, R. Streubel, *Dalton Trans.* **2021**, *50*, 689–695.
- [4] N. Rauf Naz, G. Schnakenburg, A. Mikeházi, Z. Kelemen, L. Nyulászi, R. T. Boeré, R. Streubel, *Chem. Commun.* **2020**, *56*, 2646–2649.

Poly(methylhydrosiloxane) as a green reductant in the catalytic base-free Wittig reaction via PIII/PV catalysis

Jan Tönjes,^a Lars Longwitz,^b Thomas Werner*^a

^a Leibniz-Institute for Catalysis (LIKAT), Rostock, Germany ^b University of Antwerp, Antwerp, Belgium

jan.toenjes@catalysis.de

The Wittig reaction and related olefinations are well-established in both lab scale organic synthesis and industrial applications. Over the years numerous modifications affecting the selectivity as well as a variety of different reagents were reported. Still, the formation of stoichiometric amounts of phosphine oxide waste and its associated difficulties in work-up remained a disadvantage. The catalytic Wittig reaction developed by O'Brien *et al.* in 2009 shows an alternative strategy by avoiding the phosphine oxide waste through PIII/PV redox cycling catalysis with silanes as a terminal reductant.^[1] Several contributions to this field of research have been made by our group, including the first enantioselective catalytic Wittig reaction, a base-free catalytic Wittig reaction and a room temperature catalytic Wittig reaction with low catalyst loading using a highly active phosphetane catalyst.^[2-4]



Figure 1: The catalytic base-free Wittig reaction with PMHS as terminal reductant.

Previously used acyclic phosphane or phospholane catalysts required highly active and costly silanes, such as phenylsilane, as terminal reductants, mostly in combination with cocatalysts. polymethylhydrosiloxane (PMHS) as a by-product of silicone production is cheap, non-toxic and stable to air and water, though its low reactivity without an additional catalyst hampers its use in synthetic chemistry.^[5] The highly active phosphetane catalyst was shown to react under neutral conditions in the basefree catalytic Wittig reaction in renewable solvents with PMHS as the terminal reductant and without additional cocatalyst. A method for the synthesis of highly functionalized olefins from electron deficient alkenes with high yields und improved E/Z-selectivity was developed and a broad scope of substrates was converted. Also, the formation of water by dimerization of the oxidized reductant forming siloxanes was studied.

- [1] C. J. O'Brien et al. Angew. Chem. Int. Ed. 2009, 48, 6836–6839.
- [2] L. Longwitz et al. ACS Catal. 2019, 9, 9237–9244.
- [3] M.-L. Schirmer et al. Chem. Eur. J. 2016, 22, 2458–2465.
- [4] T. Werner et al. Eur. J. Org. Chem. 2014, 2014, 6630–6633.
- [5] N. J. Lawrence et al. J. Chem. Soc., Perkin Trans. 1 1999, 3381–3391.

- P35 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Reactivity of magnesium reagents towards [Cp*Fe(η^5 -P₅)]

Martin Weber,^a Ravi Yadav,^b Peter W. Roesky,^b Manfred Scheer^a

^a Institute of Inorganic Chemistry, University of Regensburg, Universitätsstrasse 31, 93040 Regensburg (Germany).

^b Institute of Inorganic Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstraße 15, 76131 Karlsruhe (Germany).

Martin2.Weber@ur.de

During the last decade, the dimeric magnesium (I) compound $({}^{Dipp}nacnacMg)_2$ (1), synthesized by the group of Cameron Jones,^[1] was used as an versatile reduction agent. This magnesium compound can be reacted with $[Cp^*Fe(\eta^5-P_5)]$ at room temperature or at -80 °C to form selectively **2**. If the mesityl substituted magnesium reagent **3** is used, the reaction at -80 °C yields **4**. The products are highly sensitive towards oxidation as well as hydrolysis and were characterized by X-ray diffraction and NMR spectroscopy. The structure of **2** shows similarities to the P_5^{2-} moiety in $K_2[Cp^*Fe(\eta^4-P_5)]$, but is no longer symmetric. The structure of **4** is comparable by its P_{10}^{2-} moiety with $K_2[\{Cp^*Fe\}_2(\mu^2,\eta^8-P_{10})]$.^[2] By reacting $({}^{Dipp}nacnacMg(CH_3)_2$ ^[3] with $[Cp^*Fe(\eta^5-P_5)]$, the supramolecular wheel **5**, containing four methylated $[Cp^*Fe(\eta^4-P_5CH_3)]$ units connected by a ${}^{Dipp}nacnacMg$ fragment each, can be isolated upon self-assembly during crystallization.



- [1] S. P. Green, C. Jones, A. Stasch, Science, 2007, 318, 1754-1757
- [2] M. V. Butovskiy, G. Balazs, M. Bodensteiner, E. V. Peresypkina, A. V. Virovets, J. Sutter, M. Scheer, Angew. Chem. Int. Ed., 2013, 52, 2972–2976
- [3] A. P. Dove, V. C. Gibson, P. Hormnirun, E. L. Marshall, J. A. Segal, A. J. P. White, D. J. Williams, *Dalton Trans.* **2003**, 15, 3088–3097.

- P36 -

Online Workshop on Phosphorus Chemistry, March 29-31, 2021

Aza-diphospha-indane-1,3-diyls: A class of resonancestabilized biradicals

<u>Edgar Zander</u>,^a Jonas Bresien,^{a,*} Piérre Friedel,^a Dirk Michalik,^a Axel Schulz,^{a,*} Alexander Villinger^a

^a Institute of Chemistry, University of Rostock, Germany.

edgar.zander@uni-rostock.de

Pnictogen centered, cyclic biradicals have been in the focus of our research over the last decade.^[1] Four-membered biradicals can be easily synthesized by reduction of halogenated precursors, while stable five-membered biradicals have thus far only been synthesized by reversible insertion of CO or isonitriles into four-membered biradicals. Hence, reactions of four- and five-membered biradicals often yield the same reaction products due to the elimination of the CO or isonitrile.^[2,3]



Scheme 1: Synthesis of substituted 2-aza-1,3-diphosphaindane-1,3-diyls. Their stability depends on R (Dmp = 2,6-dimethylphenyl, Ter = 2,6-dimesitylphenyl, ^{tBu}Bhp = 2,6-bis(benzhydryl)-4-tert-butylphenyl).

Because of this elimination problem, we prepared a new class of stable five-membered biradicals by a reductive approach similar to the four-membered systems. A suitable halogenated precursor (**A**, Scheme 1) was obtained by the conversion of 1,2-bis(dichlorophosphanyl)benzene with sterically demanding amines (R = Dmp, Ter, $t^{Bu}Bhp$). Reduction leads to the formation of the corresponding 2-aza-1,3-diphosphaindane-1,3-diyls (**B**), whose stability depends on the size of the substituent R (Scheme 1).^[4] First activation experiments towards small molecules (e.g. I₂, tolane, Se_x) were successful.

- [1] A. Schulz, *Dalton Trans.* **2018**, *47*, 12827–12837.
- [2] A. Hinz, A. Schulz, A. Villinger, Angew. Chem., Int. Ed. 2015, 54, 2776–2779.
- [3] A. Hinz, A. Schulz, A. Villinger, J. Am. Chem. Soc. 2015, 137, 9953–9962.
- [4] J. Bresien, D. Michalik, A. Schulz, A. Villinger, E. Zander, Angew. Chem., Int. Ed. 2021, 60, 1507– 1512.

Surface functionalization of 2D semiconductors promises a rational entry into tuning their physical and chemical properties, but strategies to accomplish this are scarce. We sought to uncover a facile, solution-phase protocol to modify the Lewis basic surface of few-layer black phosphorus (bP) and demonstrate its effectiveness at providing ambient stability and tuning electronic properties. A family of commercially available group 13 Lewis acids that range in electrophilicity, steric bulk, and Pearson hard/soft-ness were evaluated. The nature of the interaction between the Lewis acids and the bP lattice was investigated using a range of microscopic and spectroscopic methods. The resilience of bP field-effect transistors treated with Lewis acids was demonstrated in IV characteristics, photocurrent, and an ambient stability comparable to those demonstrated with metal oxide encapsulation, as well as significant p-doping of bP and complete suppression of n-type conductivity. This simple solution-phase functionalization protocol, chemically matched to the bP surface and compatible with device fabrication, enables a path for deterministic and persistent tuning of the electronic properties of bP.

