SCIENTIFIC PROGRAM

9:00
Prof. Jozef Drabowicz/Prof. Anna Wypych-Gawrońska, Rector JDU
OPENING

Chairman: Dr Tomasz Girek

9:10
Prof. Christian V. Stevens
AZAHETEROCYCLIC SYNTHESES FOR PLANT APPLICATIONS THROUGH GOLD CATALYSIS

9:55
Prof. John D. Protasiewicz
IMPACT OF STABLE CARBENES ON THE PHOTOPHYSICS OF HETEROCYCLIC NITROGEN AND PHOSPHORUS COMPOUNDS

10:40
Prof. Jacek Skarżewski
CHIRAL β-AMINO ALCOHOLS. SYNTHESES AND THEIR STRUCTURAL MODIFICATIONS WITH NEIGHBORING GROUP PARTICIPATION

11.25 – 11:45
Coffee break

Chairman: Prof. Wojciech Ciesielski

11:45
Prof. Mao Minoura
RECENT ASPECTS OF CHEMISTRY OF HYPER- AND HYPOVALENT MAIN GROUP ELEMENT COMPOUNDS: TETRAARYLTELLURIUM, Ar_4Te^{IV} AND DIALKYLGERMANIUM, R_2Ge^{II}

12:30
Prof. Pr. Marc Gingras
A TOUCH OF SULFUR FOR EXOTIC POLYAROMATIC ARCHITECTURES

13:15
Prof. Derek P. Gates
CAN PHOSPHORUS MAKE A POLYMER "SMART"?

14:00
Prof. Jozef Drabowicz
CLOSING

XIX INTERNATIONAL SYMPOSIUM

on

SELECTED PROBLEMS OF CHEMISTRY OF ACYCLIC AND CYCLIC HETEROORGANIC COMPOUNDS

Jan Dlugosz University in Czestochowa
(JDU)

CZĘSTOCHOWA, November 21ST, 2019

XIX INTERNATIONAL SYMPOSIUM
on
SELECTED PROBLEMS
OF CHEMISTRY OF ACYCLIC AND CYCLIC HETEROORGANIC COMPOUNDS

organized by

Team of Organic Chemistry
Institute of Chemistry
Jan Dlugosz University in Czestochowa

Division of Organic Chemistry
Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz

Section of Heteroorganic Chemistry, Polish Chemical Society

Polish Chemical Society, Czestochowa Branch

Scientific and Organizing Committe
Prof. Józef DRABOWICZ (CBMM PAN Lodz; JDU Czestochowa)
Dr hab. prof. JDU Robert BICZAK (JDU Czestochowa)
Dr hab. prof. JDU Wojciech CIESIELSKI (JDU Czestochowa)
Dr Tomasz GIREK (JDU Czestochowa)

Date
November 21ST, 2019

Location
Institute of Chemistry
lecture hall 139,
Armii Krajowej 13/15 Ave.,
42-200 Częstochowa

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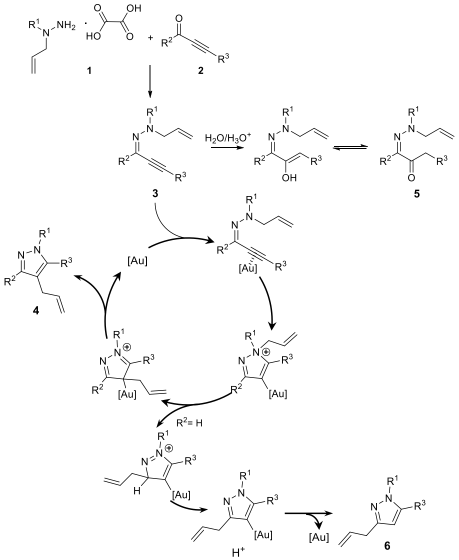
AZAHETEROCYCLIC SYNTHESES FOR PLANT APPLICATIONS THROUGH GOLD CATALYSIS

Arno Verlee,*[1] *Thomas Heugebaert,*[1] *Tom van der Meer,*[2] *Pavel Kerchev,*[2] *Frank van Breusegem*[2]*,
<u>Christian V. Stevens</u>[1]

[1]*Department of Green Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium.*
[2]*Department of Plant Systems Biology, VIB, Ghent University, Technologiepark 927, B-9000 Ghent, Belgium.*

A number of azaheterocyclic classes of compounds could be prepared by a gold catalyzed ringclosure and rearrangement of appropriately substituted alkynes. Gold catalysts were used to activate the alkyne function towards nucleophilic attack by an internal amine function, leading to ammonium intermediates. These rearranged through an allyl group migration to functionalized azaheterocycles. The rearrangement could be developed for isoindoles, benzothiophenes, oxazolones and pyrazoles. Pyrazoles are present in different pharmaceuticals and agrochemicals. As an example, the synthesis of regioselective polysubstituted pyrazoles is depicted. For the synthesis of these polysubstituted pyrazoles, *N*-allyl-*N*-aryl/alkyl hydrazine oxalate and an alkynyl aldehyde or ketone were used. These pyrazoles were prepared by a one-pot procedure through a domino reaction which includes imine formation, a gold-catalyzed 5-*endo-dig* cyclization and a subsequent sigmatropic rearrangement [1]. This method can be used for both the synthesis of 1,4,5-tri– or 1,3,4,5-tetrasubstituted pyrazoles and allows the efficient construction of functionalized pyrazoles with the possibility to vary at least three substituents [2]. Furthermore, these pyrazole analogues proved to reduce oxidative stress in plants.



Scheme 1. Gold catalyzed synthesis of polysubstituted pyrazole analogues.

References

1. W. Debrouwer, T.S.A. Heugebaert, B.I. Roman, C.V. Stevens, *Adv. Synth. & Catalysis*, 2015*, 357*, 2975 – 3006; W. Debrouwer, R.A.J. Seigneur, T.S.A. Heugebaert, C.V. Stevens, *Chem. Comm.*, 2015, *51*, 729 – 732; T. Heugebaert, C.V. Stevens, *Org. Lett*., 2009, *11*, 5018-5021.
2. A. Verlee, T. Heugebaert, T. Van Der Meer, P. Kerchev, F. Van Breusegem, C.V. Stevens, *Org. Biomol. Chem.*, 2018, 16, 9359 - 9363. A. Verlee, T. Heugebaert, T. van der Meer, P. Kerchev, K. Van Hecke, F. Van Breusegem, C.V. Stevens, *ACS Catalysis*, 2019, 9, 7862 - 7869.

IMPACT OF STABLE CARBENES ON THE PHOTOPHYSICS OF HETEROCYCLIC NITROGEN AND PHOSPHORUS COMPOUNDS

John D. Protasiewicz

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2-R-1,3-benzoxaphospholes (**R-BOPs**) and 2-R-1,3-benzazaphospholes (**R-BAPs**) are rare examples of low coordinate phosphorus compounds that display photoluminescence (PL).[1,2] While examining the reactions of these materials with isolable carbenes such as *N*-heterocyclic carbenes (NHCs) or cyclic (alkyl)(amino)carbenes (CAACs) we uncovered three distinct ways in which carbenes can modulate the photoluminescence of π-conjugated nitrogen and phosphorus fluorophores. For example, reaction of the *N*heterocyclic carbene 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (**IPr**) with carbazole leads to formation of a strong C•••HN hydrogen bonded dimer in which leads to reversible PL quenching (Figure 1). Detailed solution, solid state, and computational studies have been conducted to understand how these systems respond to interactions with isolable carbenes.

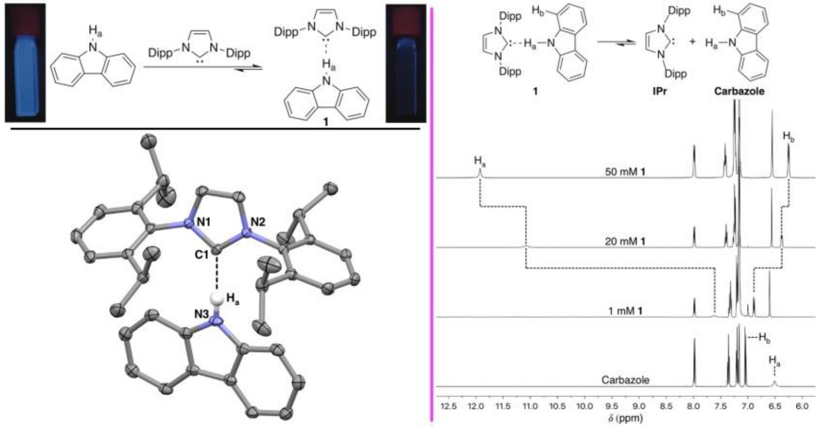

Figure 1. Hydrogen bonding between carbazole and IPr.

References

1. Kieser, J. M.; Kinney, Z. J.; Gaffen, J. R.; Evariste, S.; Harrison, A. M.; Rheingold, A. L.; Protasiewicz, J. D. "Three Ways Isolable Carbenes Can Modulate Emission of NH- Containing Fluorophores", *J. Am. Chem. Soc.* 2019, *141*, 12055−12063
2. Simpson, M. C.; Protasiewicz, J. D. "Phosphorus as a Carbon Copy and as a Photocopy: New Conjugated Materials Featuring Multiply Bonded Phosphorus" *Pure Appl. Chem.*, 2013, *85*, 801-815.
3. Sarkar, S.; Protasiewicz, J. D.; Dunietz, B.D., *J. Phys. Chem. Lett.* 2018, *9*, 3567-3572.

NOTES

CAN PHOSPHORUS MAKE A POLYMER “SMART”?

Derek P. Gates

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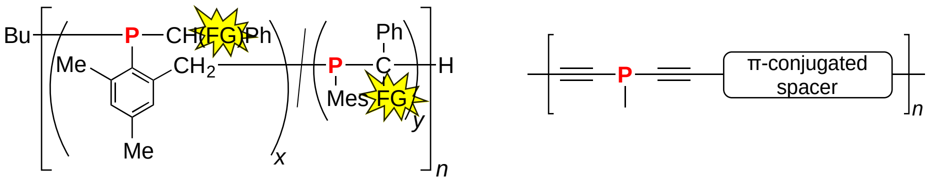
The incorporation phosphorus into the main chain or side chain of a macromolecule is a rapidly growing interdisciplinary area of research. The unique oxidation states and coordination numbers of phosphorus in the main chain impart chemical functionality, semi-conducting, optoelectronic and physical properties that are often quite different from their organic counterparts. Of particular interest is their prospect to change properties in response to an external stimuli, either chemical or physical. This presentation will focus on our development of a polymerization chemistry for the P=C bonds of phosphaalkenes which is at the same time both analogous and very different to olefin polymerization. The resultant phosphine polymers, poly(methylenephosphine)s or PMP's, are highly chemically functional. Also discussed will be our development of conjugated polymers featuring phosphine-alkyne moieties in the main chain, poly(p-phenylenediethynylene phosphines)s (PPYP's). PPYP's have emissive properties that are highly sensitive to the chemical environment at phosphorus and are therefore attractive as sensors. A case will be made that some of these new materials should be considered as “smart” polymers.



PMP **PPYP**

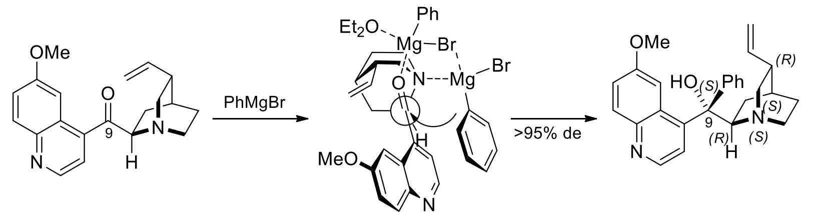
Figure 1. Chemical structures of classes of fluorescent polymers to be discussed: poly(methylenephosphine)s (**PMP**) and poly(p-phenylenediethynylene phosphine)s (**PPYP**).

CHIRAL β-AMINO ALCOHOLS. SYNTHESES AND THEIR STRUCTURAL MODIFICATIONS WITH NEIGHBORING GROUP PARTICIPATION

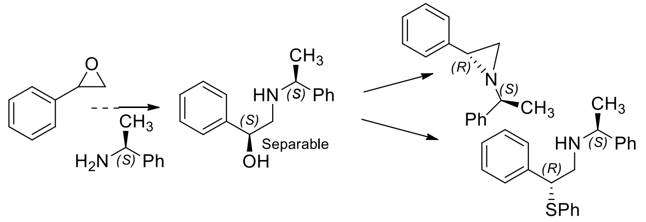
Jacek Skarżewski

Department of Organic Chemistry, Faculty of Chemistry, Wrocław University of Science and Technology, Wrocław, Poland

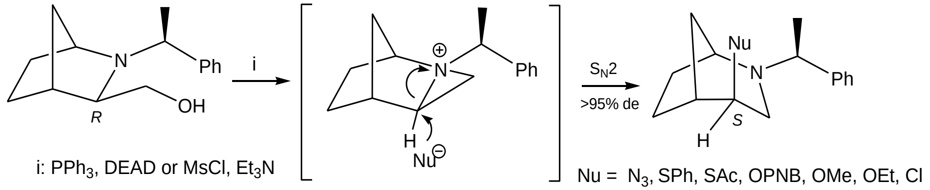
Enantiomeric β-amino alcohols belong to a group of easily available chiral building blocks. Some of them are commercially offered natural products (e.g. *Cinchona* alkaloids), the others are obtainable in a few simple synthetic steps. The selective modification of Cinchona alkaloids is often challenging due to a multitude of reactive functions and interplay of steric interactions and neighboring group participation. However, these specific interactions may also lead to very stereoselective reactions. For instance, due to the magnesium complexation, we have observed the highly diastereoselective reaction of cinchoninone with Grignards.



Catalyzed epoxide ring openings with chiral amines offer an effective route to the separable diastereomeric β-amino alcohols. Their further transformations usually require the substitution of the hydroxyl group, but this reaction is often complicated by the participation of the neighboring amino group. Under Mitsunobu or Appel reaction conditions, the respective aziridines were furnished, but with aryl disulfide and Bu_3P as well as aryl selenecyanide and Bu_3P the respective sulfides and selenides were formed. The desired transformation into the diamino-derivative was achieved by an indirect method.



Earlier we have observed similar amino group participation in the attempted transformation of primary alcohol derived from the 2-azanorbornyl system. The reaction resulted in the formation of stereoselectively rearranged products.



The above examples, as well as their general background, will be discussed in detail.

RECENT ASPECTS OF CHEMISTRY OF HYPER- AND HYPOVALENT MAIN GROUP ELEMENT COMPOUNDS: TETRAARYLTELLURIUM, Ar_4Te^{IV} AND DIALKYLGERMANIUM, R_2Ge^{II}

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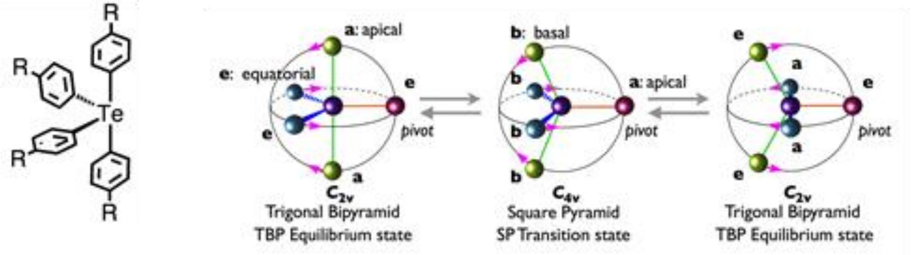
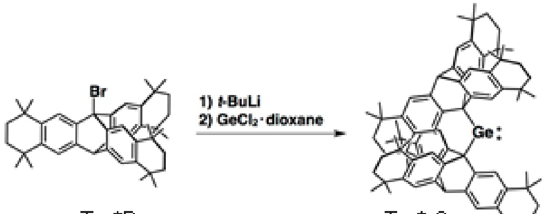
Recent years have witnessed important progress in the heteroatom chemistry, especially on the hyper- and hypovalent compounds due to their unique properties.

Hypervalent compounds are of interest in the study of the heteroatom chemistry because of their intriguing bonding characters and structures. The chemistry of hypervalent organochalcogen compounds opened from tellurium when Wittig prepared tetraphenyltellurium(IV) Ph_4Te in 1952. In R_4Te^{IV} molecules (R = monodentate substituent), the central Te^{IV} atom is considered to have a trigonal bipyramidal (TBP) geometry with an equatorial lone pair at the global minimum structure. Actually, X-ray structural analyses on R_4Te^{IV} have been investigated in the past, only TBP geometry was found around the Te^{IV} with two apical and two equatorial substituents. On the other hand, in solution-state NMR, the fluxional behavior of R_4Te^{IV} has been known as the Berry Pseudorotation (BPR) process containing interconversion of two TBP structures via square pyramidal (SP) structure as the transition state. Here, we present the systematic synthesis and structural comparison of hypervalent organotellurium(IV) compounds, $(p\text{R-}C_6H_4)_4Te$, (R = H, H_3C, F_3C, H_3CO, H_3CS, *t*-Bu, etc.), and the first SP structure for tetraorgano-heteroatom compound in the solid state.



Berry Pseudorotation Process

Hypo- or low-valent heavier carbene (R_2C:) analogs of group 14 element compounds, such as silylene (R_2Si:) and germylene (R_2Ge:), have been known as very reactive species although some electronically perturbed stable compounds are isolated.Recently, we designed and synthesized Trp*, a novel triptycene (Trp)-base aliphatic bulky group that bears bulky fused ring-type substituents at the periphery of Trp framework. In this paper, we took advantage of the steric protection ability of Trp* group to synthesize the thermally stable germylene, Trp^*_2Ge:, in which the divalent germanium atom is bound to aliphatic carbon ligands. The structure and reactivity of Trp^*_2Ge: will also be discussed.



Trp*Br Trp^*_2Ge:

A TOUCH OF SULFUR FOR EXOTIC POLYAROMATIC ARCHITECTURES

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Sulfur-rich polyaromatic architectures(1) of various topologies, their exalted properties and their applications in chemical-biology,(2) materials science and nanoscience will be presented. They comprise asterisks,(1) oligomers and dendrimers,(3) which often incorporate thiophenylene units and persulfurated aromatic cores, leading to some molecular semi-rigidity. These architectures often have exalted supramolecular, chiroptical and electronic properties, which can be modulated from the interactions with metallic species, cation interactions and □□□ complexes. Polysulfuration is often responsible for multiple redox states,(3) metal-ion coordination,(4) aggregation-induced phosphorescence (AIP).(5-7) Applications as asymmetric catalysts, the most phosphorescent organic crystals (□□~100%),(7) cation-selective membranes, cations and anions sensors in coordination polymers,(5,6) electrochromic switches,(3) glycosylated inhibitors of lectins,(2) and organic ligands for stabilizing small metal nanoparticles will be discussed.(8)

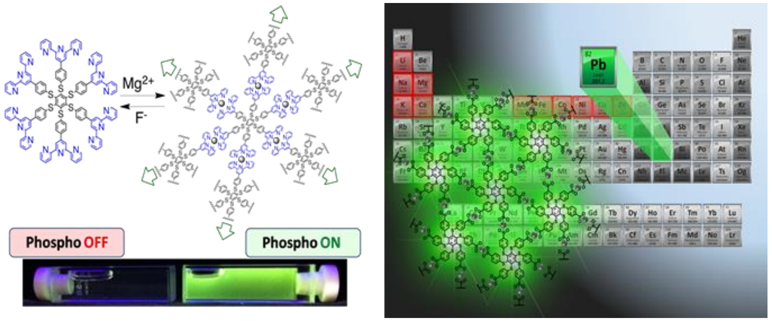

Figure 1. Cation sensors by AIP.

References

1. Gingras, M.; Raimundo, J.-M.; Chabre, Y. M. *Angew. Chem. Int. Ed.* (2006), *45*, 1686.
2. (a) Sleiman, M.; Varrot, A.; Raimundo, J.-M.; Gingras, M.; Goekjian, P.G. *Chem. Commun.* (2008), 6507; (b) Smadhi, M.; de Bentzmann, S.; Imberty, A.; Gingras, M.; Abderrahim, R.; Goekjian, P.G. *Beilstein J. Org. Chem.* (2014), *10*, 1981; (c) Gingras, M.; Chabre, Y.M.; Roy, M.; Roy, R. *Chem. Soc. Rev.* (2013), *42*, 4823.
3. (a) Gingras, M.; Placide, V.; Raimundo, J.-M.; Bergamini, G.; Ceroni, P.; Balzani, V. *Chem. Eur. J.* (2008), *14*, 10357; (b) Valenti, G.; Fiorani, A.; Di Motta, S.; Bergamini, G.; Gingras, M.; Ceroni, P.; Negri, F.; Paolucci, F.; Marcaccio, M. *Chem. Eur. J.* (2015), *21*, 2936.
4. Fermi, A.; Ceroni, P.; Roy, M.; Gingras, M.; Bergamini, G. *Chem. Eur. J.* (2014), *14*, 10357 (back cover).
5. (a) Fermi, A.; Bergamini, G.; Roy, M.; Gingras, M.; Ceroni, P. *J. Am. Chem. Soc.* (2014), 136, 6395; Article highlighted as one of the 6 publications of the week among all ACS journals on May 26, 2014, as "Notewhorthy Chemistry", http://www.acs.org/content/acs/en/noteworthy-chemistry/2014-archive/may-26.html#nc3. CNRS press:
http://www.cnrs.fr/inc/communication/direct_labos/gingras.htm June 30, 2014.
6. Villa, M.; Roy, M.; Bergamini, G.; Gingras, M.; Ceroni, P. *Dalton Trans.* (2019), 48, 3815 (front cover).
7. (a) G. Bergamini, A. Fermi, C. Botta, U. Giovanella, S. Di Motta, F. Negri, R. Peresutti, M. Gingras, P. Ceroni, *J. Mater. Chem. C* (2013), *1*, 2717 (web selection 2013); (b) A. Fermi, G. Bergamini, R. Peresutti, E. Marchi, M. Roy, P. Ceroni, M. Gingras, *Dyes and Pigments* (2014), *110*, 113.
8. Bergamini, G.; Ceroni, P.; Balzani, V.; Gingras, M.; Raimundo, J.-M.; Morandi, V. Merli. P.G. *Chem. Commun.* (2007), 4167.