Advances in organophosphorus chemistry

Synthesis, reactivity and recycling

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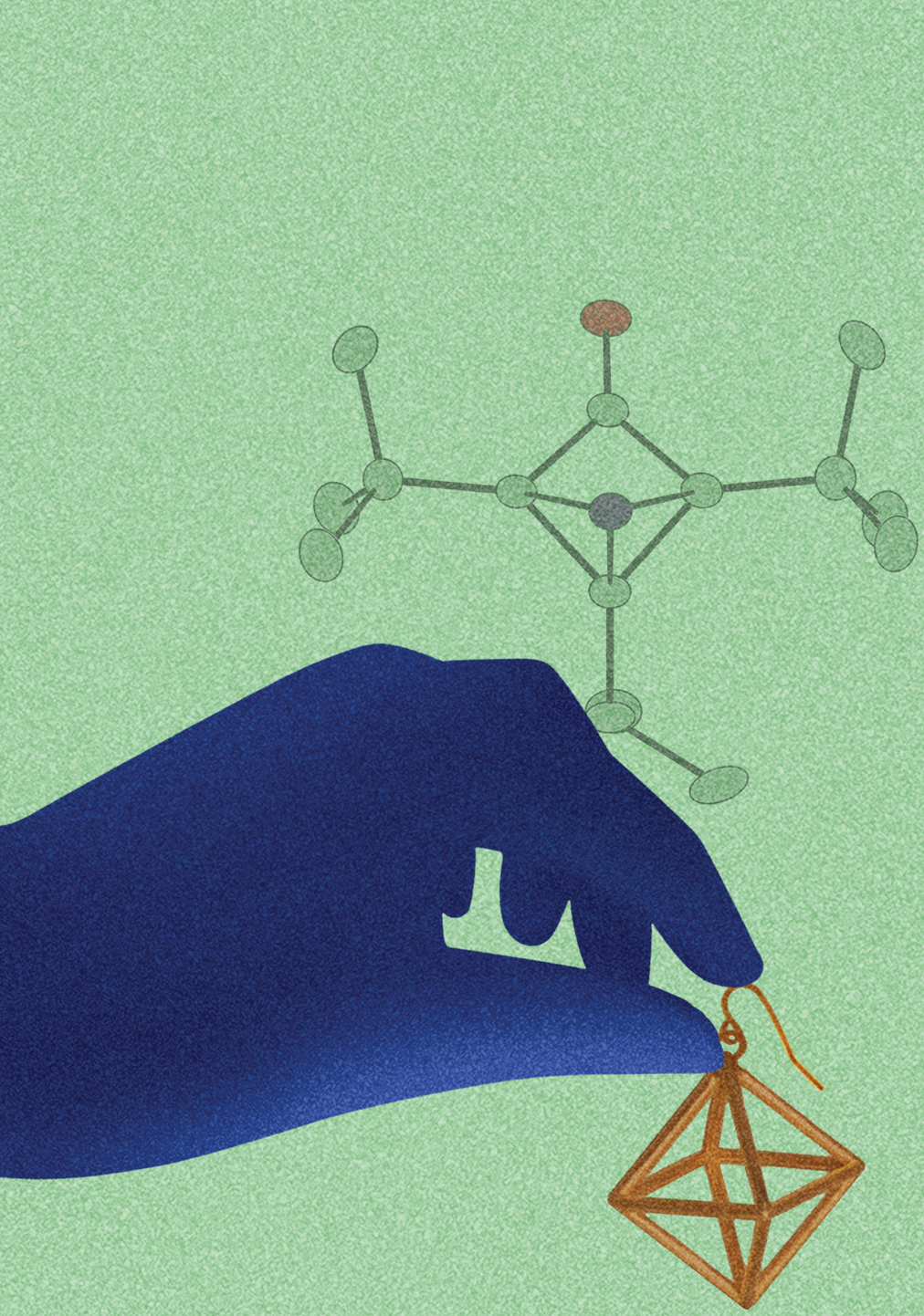
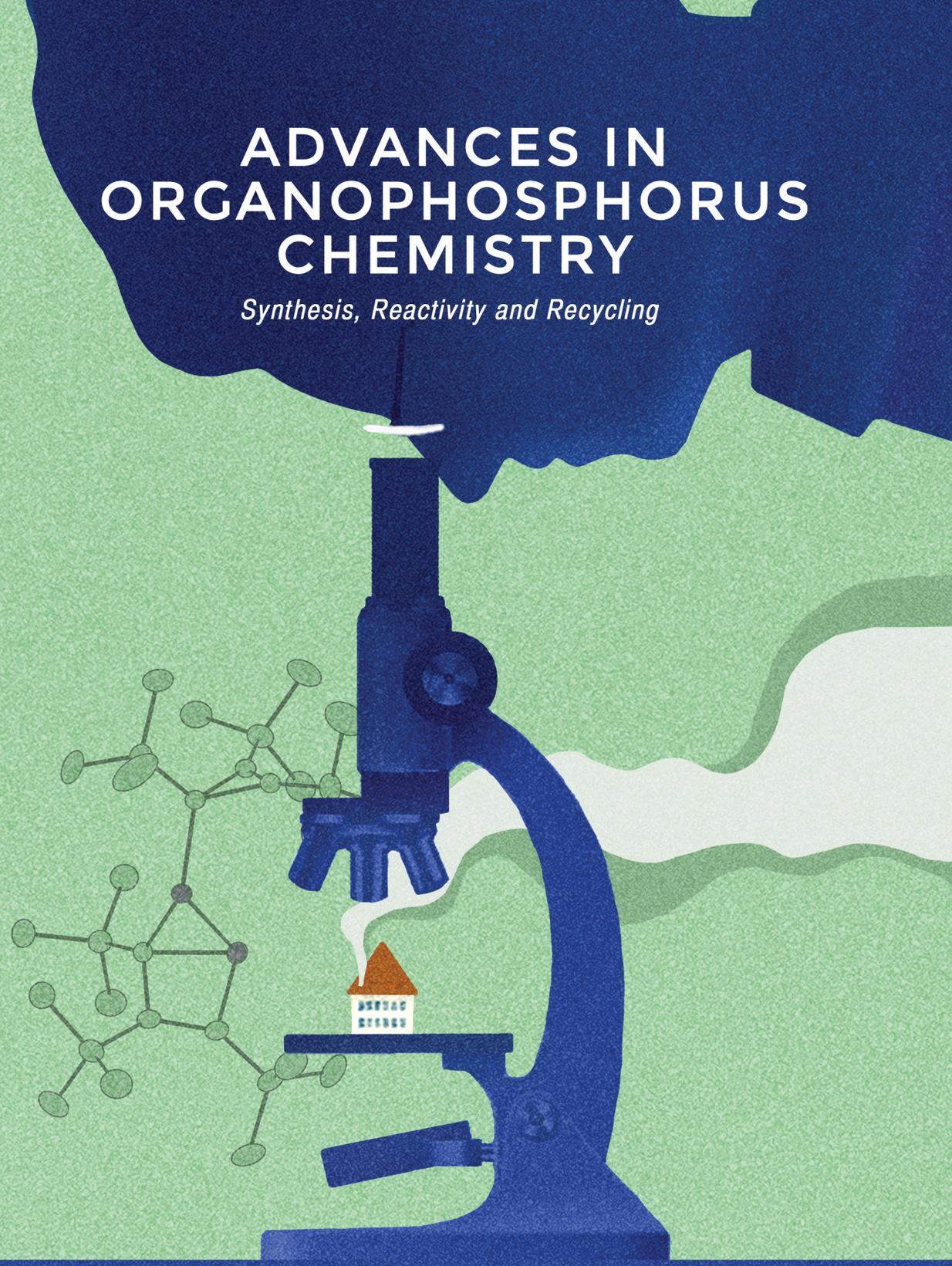


ADVANCES IN ORGANOPHOSPHORUS CHEMISTRY • Tetiana Krachko

ADVANCES IN ORGANOPHOSPHORUS CHEMISTRY

Synthesis, Reactivity and Recycling



Tetiana Krachko

ADVANCES IN ORGANOPHOSPHORUS CHEMISTRY:

Synthesis, Reactivity and Recycling

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2018

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Advances in Organophosphorus Chemistry: Synthesis, Reactivity and Recycling

ACADEMISCH PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Universiteit van Amsterdam
op gezag van de Rector Magnificus
prof. dr. ir. K. I. J. Maex
ten overstaan van een door het College voor Promoties ingestelde commissie,
in het openbaar te verdedigen in de Agnietenkapel
op dinsdag 19 juni 2018, te 12.00 uur

door

Tetiana Krachko

geboren te Zaporizhia Oblast, Oekraïne

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For my parents

“In framing an ideal we may assume what we wish, but should avoid impossibilities.”

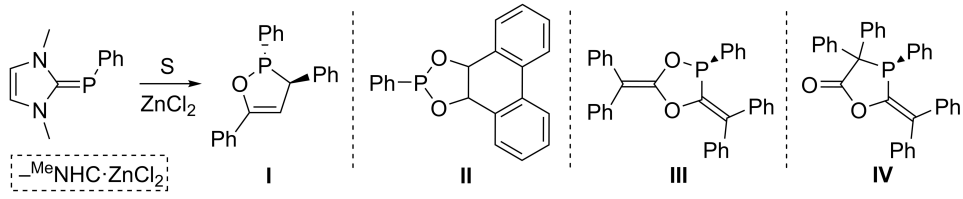
Aristotle

Table of Contents

Preface

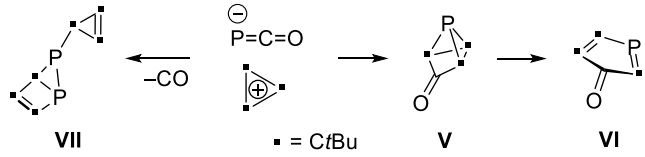
Phosphorus, in many respects, is one of the most important elements in both nature and synthetic chemistry. Thus, phosphate rock, the industrial source of phosphorus fertilizers, is required for food production and is a limiting nutrient for crops, and at the same time, organophosphorus compounds are widely used in organic synthesis. While the natural life cycle of phosphate rock takes 10s to 100s of million years, the synthetic life cycle of organophosphorus compounds can be much faster. Therefore, novel atom-economical methodologies towards the synthesis of organophosphorus compounds, studies on their reactivity and recycling schemes for the regeneration of phosphorus compounds are of great importance. In this thesis, we address these three aspects: how to make, use and reuse organophosphorus compounds.

First, we provide a complete overview of the chemistry of N-heterocyclic carbene (NHC)-phosphinidene adducts (**Chapter 1**) and demonstrate a possible application of the sterically accessible carbene-phosphinidene adduct ^{Me}NHC=PPh as phenylphosphinidene transfer agent upon functionalization with $ZnCl_2$ (**Chapter 2**). This Lewis acid protection enabled the synthesis of the new uncomplexed phosphorus heterocycles **I**–**IV** upon treatment with the electron-poor heterodienes (S) 9,10-phenanthrenequinone, diphenylketene and *trans*-chalcone, while $ZnCl_2$ trapped the remaining carbene as an insoluble coordination polymer.

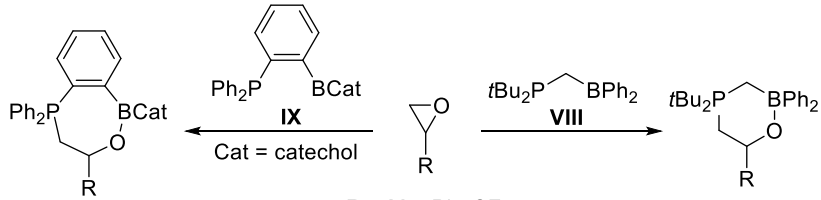


In **Chapter 3**, we show that incorporation of a phosphorus atom to a carbon scaffold can also be achieved with sodium phosphaethynolate (NaOCP), and

describe its reactivity with a cyclopropenium cation, which after a number of pericyclic reactions provides access to the phosphorus analogues of tricyclopentanone (**V**), cyclopentadienone (**VI**), and housene (**VII**).



In **Chapter 4** we explore the stoichiometric reactivity of frustrated P/B Lewis pairs (**VIII**, **IX**) towards epoxides resulting in epoxide ring-opening and study this reactivity in detail using DFT calculations and kinetic analyses.



Finally, **Chapter 5** focuses on the mechanistic studies of the Brønsted acid mediated reduction of tertiary phosphine oxides to phosphines. We investigate the stoichiometric protonation of triphenylphosphine oxide and fully characterize the formed products, and subsequently, study the reduction of the protonated phosphine oxides with readily available hydrosiloxanes.