
1. Introduction	1
2. The reaction of Na(OCP) with carbon dioxide: Formation of anionic four-membered rings.....	8
2.1 Introduction	8
2.2 Synthesis and structure	11
2.3 VT-NMR experiments.....	17
2.4 Mechanistic investigations	18
2.5 Reactivity studies.....	21
2.6 Conclusion	24
3. Experimental proof for the ambident character of the (OCP)⁻ anion: Reactions of Na(OCP) with triorganyl tetrel compounds.....	25
3.1 Introduction	25
3.2 Oxyphosphaalkynes (R ₃ E–O–C≡P) vs. phosphaketenes (R ₃ E–P=C=O)	27
3.3 Silylphosphaketenes – Siloxyphosphaalkynes	28
3.4 Heavier tetrel substituted phosphaketenes, Ph ₃ E–P=C=O (Ge, Sn, Pb)	34
3.5 The stability of phosphaketenes	37
3.6 Conclusion	40
4. Synthesis of phosphorus heterocycles from hetero-phosphaketenes	42
4.1 Introduction	42
4.2 The “decomposition” of stannylphosphaketene in dimethyl sulfoxide	42

4.3 X-ray structures	44
4.4 Investigations on the reaction mechanism.....	45
4.5 The reaction of $\text{Ph}_3\text{Ge-P=C=O}$ with Na(OCP)	49
4.6 Synthesis of a siloxy substituted 1,2,4-triphospholide	49
4.7 Reactivity of the siloxy substituted 1,2,4-triphospholide.....	51
4.8 Conclusion	52
5. A simple access to 1,2,4-oxadiphospholes.....	53
5.1 Introduction	53
5.2 Synthesis of ester-functionalized 1,2,4-oxadiphospholes	54
5.3 X-ray structure of the 1,2,4-oxadiphosphole.....	55
5.4 Investigations on the reaction mechanism.....	57
5.5 Conclusion	64
6. Interconversion of a monocyclic phosphide anion and an annulated diazaphospholenium cation	65
6.1 Introduction	65
6.2 Reaction of Na(OCP) with dicyclohexylcarbodiimide (DCC).....	66
6.3 Mechanistic studies on the formation of the 1,3,5-diazaphosphinane anion	66
6.4 Oxidation of the anionic 1,3,5-diazaphosphinane	68
6.5 X-ray structures	71
6.6 Computational investigations on the rearrangement reactions.....	72
6.7 Conclusion	75

7. Oligorization of isocyanates around a P⁻ anion: the reaction of (OCP)⁻ with isocyanates	76
7.1 Introduction	76
7.2 Reaction of Na(OCP) with 2,6-diisopropylphenyl isocyanate	77
7.3 Reaction of Na(OCP) with sterically less demanding isocyanates (PhNCO, CyNCO, <i>n</i> -BuNCO)	79
7.4 Catalytic activity of anionic species in the trimerization process of isocyanates.....	80
7.5 Single crystal X-ray diffraction studies	83
7.6 VT-NMR study of a 2,6-difluorophenyl substituted phosphoranide..	85
7.7 Exchange of isocyanate moieties on a P ⁻ anion	86
7.8 Reaction of Na(OCP) with diisocyanates.....	87
7.9 Conclusion.....	88
8. Summary and Outlook	89
9. Experimental procedures	91
9.1 General remarks.....	91
9.2 Experimental procedures for Chapter 2.....	93
9.3 Experimental procedures for Chapter 3.....	99
9.4 Experimental procedures for Chapter 4.....	104
9.5 Experimental procedures for Chapter 5.....	110
9.6 Experimental procedures for Chapter 6.....	113
9.7 Experimental procedures for Chapter 7.....	119
10. Appendix	124

Table of contents

10.1 Measured and simulated NMR spectra of selected compounds.....	124
10.2 Crystallographic tables	131
10.3 Abbreviations	140
10.4 Curriculum Vitae	143
11. Literature	144