



Review

The unusual coordination chemistry of phosphorus-rich linear and cyclic oligophosphanide anions

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ARTICLE INFO

Article history:

Received 31 August 2010

Accepted 9 November 2010

Available online 19 November 2010

The authors wish to dedicate this work to the memory of Prof. Dr. H.C. Hans-Georg von Schnering, an outstanding scientist and distinguished colleague.

Keywords:

Oligophosphanides

P ligands

Phosphorus-rich anions

Phosphorus

Metal phosphides

ABSTRACT

In this review, the synthesis, reactivity and properties of linear and cyclic oligophosphanides are described. Specifically the structures and versatile reactivity of the anionic ligands (P₄R₄)²⁻ (R = Bu^t, Ph, Mes), (P₄HR₄)⁻ (R = Ph and Mes) and *cyclo*-(P₅Bu^t₄)⁻ towards main group and transition metal complexes is elucidated. In addition, potential application of metal oligophosphanides as precursors for the preparation of metal phosphides is also briefly discussed.

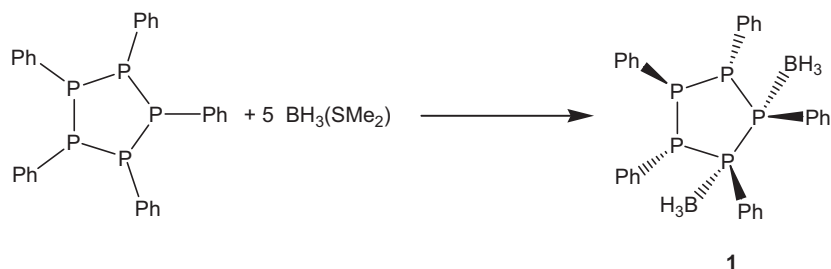
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1. Introduction

The reports by Baudler and some other authors on their extensive investigations on cyclooligophosphanes *cyclo*-(PR)_n [1] and catenated polyphosphanes (with hydrogen, organic or even organometallic substituents) [2] have shown that the chemistry of these compounds is analogous to that of related carbon com-

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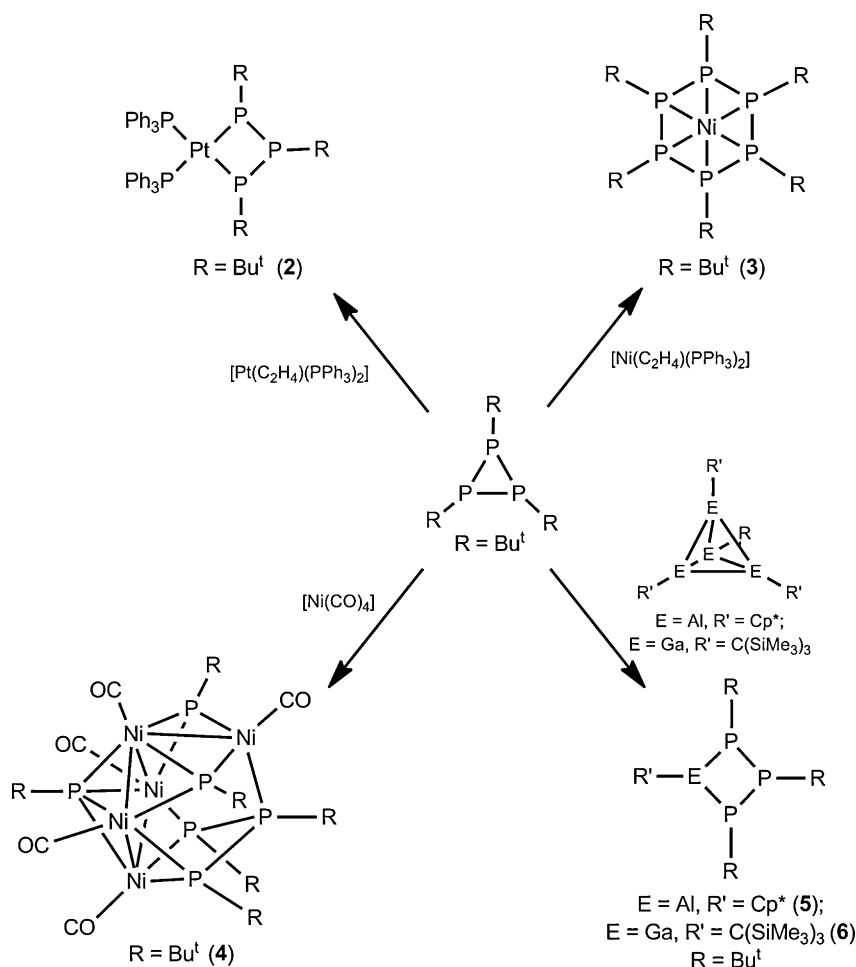


Scheme 1. Reaction of *cyclo*-P₅Ph₅ with BH₃.

pounds [3]. Among other things, this analogy is due to the existence of constitutional and configurational isomerism and valence tautomerism, as well as the existence of mixed P–C ring systems, and is rationalized by the isolobality of the fragments P/CR, PR/CR₂ and PR₂/CR₃ [1–3]. Like carbon, phosphorus shows a notable propensity to form a wide variety of P_n frameworks due to the comparatively high bond energy of P–P single bonds (ca. 200 kJ/mol, the highest value within group 15) [4].

While the chemistry of catena and cyclic polyphosphanes has been studied in depth, especially with the help of ³¹P NMR spectroscopy and X-ray crystallography, less is known about metal complexes of these species. Only a few examples have been described, and all of them have shown that cyclic [5] and catenated oligophosphanide anions [6] exhibit a rich coordination chemistry, because each P atom may be involved in coordination *via* its free electron pair.

On the other hand, the coordination chemistry of oligophosphanide anions has hardly been explored until recently, as selective and facile syntheses were mostly unknown for the corresponding oligophosphanide anions. Besides the academic challenge, metal complexes with anionic polyphosphorus ligands are of interest as potential precursors for the development of rational syntheses of binary metal phosphides (M_xP_y), which are compounds with rare structures and interesting properties for materials science [7], such as corrosion resistance [8], catalysts for hydrodesulfurization and hydrodenitrogenation of petroleum fuels [9], oxygen barriers in capacitors [10], and magnetic properties [11]. Even today, the number of accessible metal complexes with linear and cyclic oligophosphanide ligands is still relatively small. Thus, this article will review the synthetic methods and reactivity for the preparation of metal complexes with anionic polyphosphorus rings and chains, as well as their structural and spectroscopic properties.



Scheme 2. Synthesis of metal oligophosphanide complexes using *cyclo*-P₃Bu^t₃ as starting material.

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