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Review

Recent developments in the chemistry of metallophosphaalkenes

Lothar Weber*

Fakultät für Chemie der Universität Bielefeld, Universitätsstraße 25, D-33615 Bielefeld, Germany

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Contents

Abstract

The chemistry of low-valent organophosphorus compounds such as phosphaalkenes has undergone rapid development in the last three decades. These developments also include the organometallic and coordination chemistry of such species. Metallophosphaalkenes are compounds in which one or more of the organic substituents on the P=C unit are replaced by metal fragments. *P*- and *C*-metallophosphaalkenes have emerged from laboratory curiosities to versatile and useful synthons in organoelement chemistry. Particular examples are *C*-lithiophosphaalkenes and *C*-magnesiophosphaalkenes (phospha-Grignard reagents).

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Keywords: Metallophosphaalkenes; Lithiophosphaalkenes; Phospha-Grignard reagents; Organoelement derivatives

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* Tel.: +49 521 1066169; fax: +49 521 1066146.
E-mail address: lothar.weber@uni-bielefeld.de.

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1. Introduction

The chemistry of compounds with low-coodinate phosphorus atoms involved in phosphorus–carbon multiple bonding has been rapidly developed since the discovery of thermolabile HC≡P by Gier in 1961 [1,2]. Shortly after, cationic phosphamethyne cyanines were synthesized by Dimroth and Hofmann [3], while Märkl [4] reported on the first representative of phosphabenzene. In the latter species, the P=C multiple bonds are stabilized by extensive π-delocalization (Scheme 1).

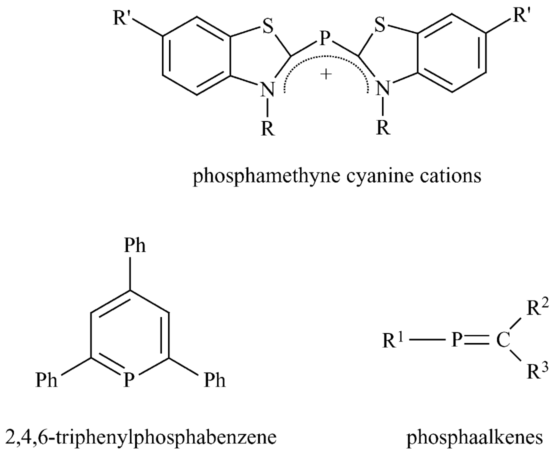
The formal replacement of one methylene group in alkenes $R^2R^3C{=}CR^4R^5$ by the phosphanediyl unit R^1P leads to the class of phosphaalkenes $R^1P{=}CR^2R^3$, the first representatives of which were presented by Becker in 1976. Numerous papers on phosphaalkenes have highlighted the remarkable ability of phosphorus to mimic the chemistry of carbon [2].

The rapid development of phosphaalkene chemistry during the last three decades also includes their coordination chemistry. Five types of complexes are now known featuring phosphaalkene ligands (**A**–**E**) (Scheme 2).

In metallophosphaalkenes, one or more of the substituents R at the P=C backbone are replaced by transition metal complex fragments or main group metals; thus five basically different types of compound (**I**–**V**) can be differentiated (Scheme 3).

The first metallophosphaalkenes of the types **I** and **II** were synthesized in 1985 by our group [5]. In 1996, a review article gave an account on synthesis, structure, bonding and reactivity of the various classes of phosphaalkenes **I**–**IV** [6]. It is now evident that the vast majority of metallophosphaalkenes belong to the classes **I** and **II**, whereas representatives of type **V** still remain elusive. First investigations on their reactivity disclosed metallophosphaalkenes as valuable and versatile starting materials for a wide range of chemical transformations.

Whereas the previous review provided an overview of metal-functionalized P=C systems with particular emphasis placed on synthetic and structural aspects, this report highlights the remarkable richness of the chemistry exhibited by such species and covers the literature of the years 1996–2003. Almost all papers published in that period of time are restricted to metallophosphaalkenes of the types **I** and **II.**

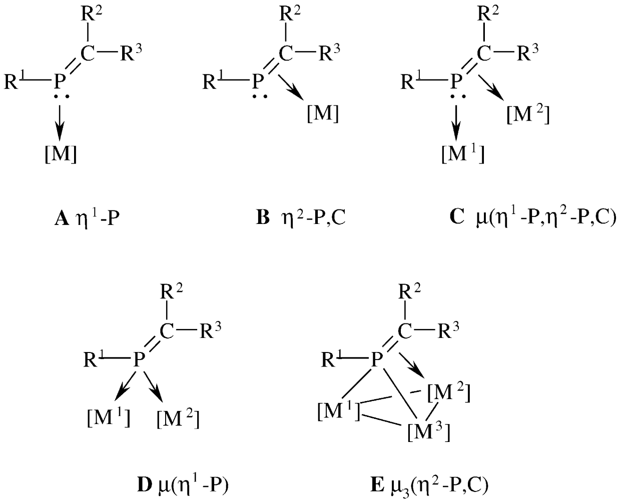


phosphamethyne cyanine cations

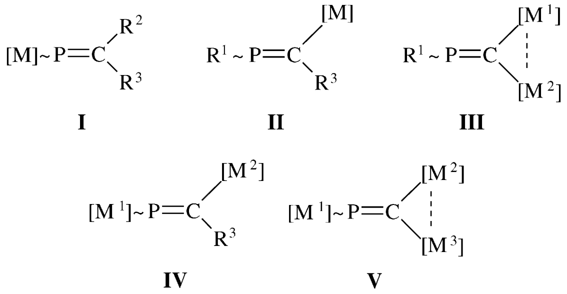
2,4,6-triphenylphosphabenzene

phosphaalkenes

Scheme 1. Molecules featuring P=C multiple bonding.



Scheme 2. Basic types of phosphaalkene transition metal complexes.



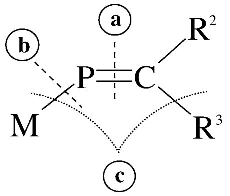
Scheme 3. Basic types of metal-functionalized phosphaalkenes (metallophosphaalkenes).

2. Synthetic methods

2.1. *P*-Metallophosphaalkenes

For the synthesis of *P*-metallophosphaalkenes, three general principles (a–c) are discernable (Scheme 4).

In syntheses following route (a), the P=C bond is constructed from precursors such as metallophosphanes. In route (b), a metal–phosphorus bond is formed between a *P*-



Scheme 4. Routes to metallophosphaalkenes of type **I**.

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