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Review

Phosphinidene-bridged binuclear complexes

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ABSTRACT

This article contains a comprehensive review of the work carried out within the last three decades on the synthesis, structural studies and reactivity of the binuclear complexes of transition and lanthanide elements bearing bridging phosphinidene (PR) ligands. The latter are grouped into three different classes according to their geometry and electronic distribution: pyramidal, symmetric planar trigonal and asymmetric planar trigonal. Different reactivity patterns can be then outlined for each of these classes of metal complexes, which differ in many ways from those characterizing the extensively studied chemical behaviour of mononuclear phosphinidene complexes.

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1. Introduction

The chemistry of transition-metal phosphinidene complexes (PR; *phosphanylidenes* according to IUPAC recommended nomenclature) has emerged during the last decades as an active area of research within the organometallic field, this being in part due to its direct analogy with the ubiquitous carbene complexes [1]. This relationship holds particularly well for mononuclear compounds with bent phosphinidene ligands, which can be roughly divided in two groups, displaying either electrophilic or nucleophilic behaviour reminiscent of that observed for Fischer or Schrock carbenes, respectively. In turn, these analogies can be traced back, in a simplified manner, to two different extreme descriptions of the M–P bond in these compounds, as single dative or double bond, respectively (**A** and **B** in Chart 1). Then, it is not surprising that these compounds show an extraordinary reactivity derived from the combined presence of multiple M–P bonding, a phosphorus lone pair and a low lying P-centred LUMO. Such a chemical versatility makes these compounds to act as valuable synthons for the preparation of diverse organophosphorus derivatives or novel metal complexes, and their chemistry has been the focus of several excellent reviews [2].

In contrast to the "carbene-like" chemistry, the presence of a lone electron pair at the phosphorus atom of phosphinidene complexes opens up the possibility for these ligands to act as four-electron donors, thus enabling them to bind efficiently up to four metal atoms with a wide variety of coordination modes (**D**–**H**, Chart 1). Obviously, the nature of the M–P bonds changes dramatically among the different coordination modes so does the corresponding reactivity. In particular, the M–P bonds are essentially single for ligands bound to three or four metals (modes **G** and **H**), a situation for which little reactivity can be expected. Indeed, μ_3- or μ_4-PR groups are good supporting ligands in clusters, efficient to maintain their nuclearity in the course of reactions, although a limited number of examples exists in which an alteration of the M–P bond occurs for these compounds. In contrast, binuclear compounds retain either M–P bond multiplicity (types **D** or **E**) or a chemically active phosphorus lone pair (type **F**), therefore high reactivity can be anticipated for these systems. Indeed, after the pioneering work carried out in the late seventies and early eighties (mainly centred on type **D** complexes and reviewed by Huttner in 1986) [3], the chemistry of binuclear phosphinidene complexes has expanded exponentially to include complexes of almost every transition-metal element. More recently, even some rare-earth elements have been added to the panoply of phosphinidene complexes, in spite of the less favoured M–P interactions in these cases (hard-soft combinations). Recent work from several research groups has highlighted the great versatility of all these compounds, which proved to be quite reactive towards an immense variety of organic molecules, transition metal complexes and *p*-block compounds. Expectedly, the chemical reactivity of these molecules is substantially influenced by the coordination mode attained by the phosphinidene ligand, with the pyramidal complexes (type **F**) exhibiting a marked nucleophilicity at the phosphorus position, while that of the symmetric and asymmetric trigonal planar complexes (types **D** and **E**) is more unpredictable, especially for systems also having M–M multiple bonds.

The main goal of this contribution is to review comprehensively the last decades of work (from 1986 to mid 2016) on binuclear complexes having bridging phosphinidene ligands. We will discuss the most common routes used for their synthesis, the main structural parameters associated to the three coordination modes known to date (**D**–**F**), and the reactivity studies carried out on these complexes, with particular attention to the processes in which the phosphinidene group is directly involved, and not a mere spectator. Thus, we aim to provide a global vision of the state-of-the-art in the chemistry of these versatile complexes, thus setting a concise reference which will be of use for further progress in the field to follow in the near future. Finally, we must note that some minor parts

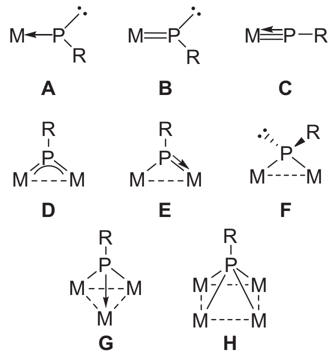

Chart 1. Coordination modes of the phosphinidene ligand.