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Account/Revue

Recent developments in the chemistry of donor-functionalized phosphinines

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This review provides an overview of the most significant strategies developed in recent years for the preparation of donor-functionalized phosphinines and new developments in this field are highlighted. Selected synthetic procedures for the introduction of additional sulfur-, oxygen-, phosphorus-, and nitrogen-donor groups into the heterocyclic framework are presented. Examples of their coordination chemistry and potential applications in homogeneous catalysis and phosphorus containing molecular materials will be given.

1. Introduction

A milestone in the chemistry of low-coordinated phosphorus compounds was set with the first successful preparation of λ^3-2,4,6-triphenylphosphinine (**1**) by Märkl in 1966 and the parent phosphinine C_5H_5P (**2**) by Ashe, III in 1971 (Fig. 1) [1,2]. The stabilization of reactive P═C double bonds by incorporation into aromatic systems opened up the access to formally sp^2-hybridized phosphorus systems with significantly different electronic and steric properties compared to classical ligands based on trivalent phosphorus [3]. Long regarded as “chemical curiosities”, state-of-the-art synthetic methodologies developed mainly by the groups of Mathey and Le Floch allow nowadays specific derivatization and functionalization, including the introduction of additional donor-functionalities (**3**) [4,5]. This is an important aspect for potential applications, because it can lead to polydentate systems with interesting coordination and functional properties, not accessible by monodentate phosphinines [6]. In the last few years, we have focused on the design of functionalized and chiral [7] 2,4,6-triaryl-substituted phosphinines, which turned out to be accessible *via* the original pyrylium salt route. These derivatives often show a significant kinetic stability and are considerably inert towards water, oxygen and many acids and bases, which often facilitates their preparation and functionalization.

2. Phosphinines – electronic properties

Phosphinines are planar, aromatic systems. Recent calculations employing bond separation and homodesmic reaction energies suggest their aromaticity to be as high as 88% of benzene [8]. The electronic properties of phosphinines differ significantly from pyridines, as shown by photoelectron and electron transmission spectroscopy as well as by theoretical calculations [9]. The HOMO^{-2} orbital has a large coefficient at the phosphorus atom and represents essentially the lone-pair at the heteroatom. The phosphorus lone-pair occupies a more diffuse, partly delocalized, and less directional orbital than that of pyridine. While the HOMO^{-1} and HOMO orbitals contribute to π-donation, the LUMO orbital, with a large coefficient at the phosphorus atom, enables the heterocy-

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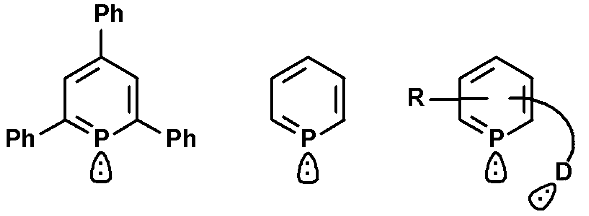

1 **2** **3**

Fig. 1. First reported phosphinines and donor functionalized system.

cle to act as a π-acceptor ligand, once coordinated to the metal center via the phosphorus atom (Fig. 2). In pyridines, the LUMO is located higher in energy compared to phosphinines, while the HOMO represents the lone pair located at the nitrogen atom. Consequently, phosphinines are much better π-acceptor ligands, but less good σ-donors compared to pyridines. The phosphorus atom in λ^3-phosphinines has a strong 3s-orbital character, which is about 63.8%, versus 29.1% found for the nitrogen atom in pyridines [10]. This reflects the poor hybridization ability of phosphorus, which leads to a very low basicity of the phosphorus center (pK_a ($C_5H_6P^+$) = -16.1 ± 1.0 in aqueous solution), and consequently, phosphinines are relatively inert towards electrophilic attack [11]. Based on Tolman's electronic parameter χ, a comparison of phosphinines with classical phosphorus-based ligands, such as phosphines and phosphites, suggests that phosphinines are electron-withdrawing ligands with electronic properties similar to phosphites as already anticipated from the corresponding MO scheme (Fig. 2).

Due to their particular electronic properties, phosphinines are especially suitable for the stabilization of

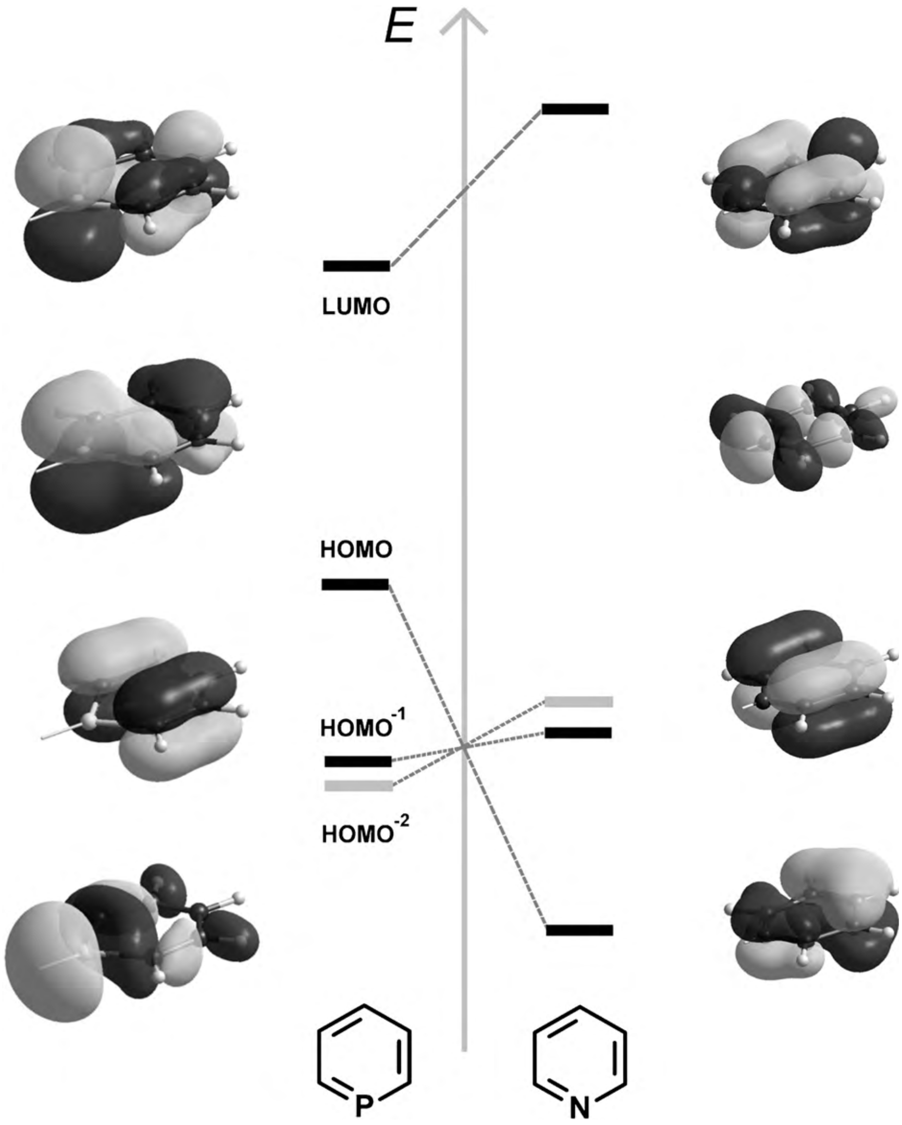

Fig. 2. Qualitative MO-diagram of the frontier orbitals of phosphinine and pyridine. Light grey: MO representing the lone-pair.