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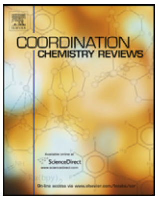

Review

H-spirophosphoranes—Promising ligands in transition metal chemistry, an outlook of their coordination and catalytic properties

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ABSTRACT

The paper gives a short survey on the coordination properties of H-spirophosphoranes towards transition metals. The emphasis is on the application of H-spirophosphorane complexes in catalysis. Spirophosphoranes supported by transition metals, palladium or rhodium, have been identified as ligands in metal-catalysed enantioselective catalysis; connected to palladium centres, they exhibit catalytic properties in cross-coupling reactions. Rhenium complexes incorporating spirophosphoranes appear to act as excellent co-catalysts in oxidation reactions. It is demonstrated how fine tuning within the structure of phosphorus ligands can determine the catalytic properties of transition metal complexes.

1. Introduction

Hydridospirophosphoranes (HSPs) constitute a class of phosphorus compounds (oxidation state +3) with the P—H bond frequently emphasized in their names (Scheme 1) [1,5]. The unique feature of H-phosphoranes is the fact that in solution they exist as equilibrium mixtures of two tautomeric forms [2,5]. H-spirophosphoranes exhibit a tautomeric equilibrium of pentacoordinate hydridophosphorane $\lambda^5\sigma^5$ and tricoordinate hydroxyalkyl (aryl)phosphite or aminoalkyl (aryl)phosphite $\lambda^3\sigma^3$ (λ and σ indicate respectively the valency and the coordination number of the phosphorus atom). The distribution of the tautomers depends on several factors, such as the solvent, the temperature, the ring size and the type of substituents that the rings carry [3]. An increase in temperature and the presence of basic solvents favour the presence of the $\lambda^3\sigma^3$ form over the $\lambda^5\sigma^5$ form. Moreover, symmetry factors and unsaturation also affect the tautomer composition. The presence of aromatic cycles (catechols, *o*-aminophenols) favours $\lambda^5\sigma^5$ structure, whereas $\lambda^3\sigma^3$ is mainly observed for unsymmetrical spirophosphoranes having two different heteroatoms in equatorial positions. Steric factors also play a crucial role: the appearance of one to eight aromatic or aliphatic substituents in the rings shift the equilibrium towards the $\lambda^5\sigma^5$ form. The equilibrium and the presence of a P—H bond in the spirophosphorane form affect the reactivity of hydridospirophosphoranes. In the phosphorane form $\lambda^5\sigma^5$, phosphorus exhibits electrophilic properties; however, in the tricoordinated $\lambda^3\sigma^3$ form, the phosphorus atom and the EH; E = O, NH group exhibit

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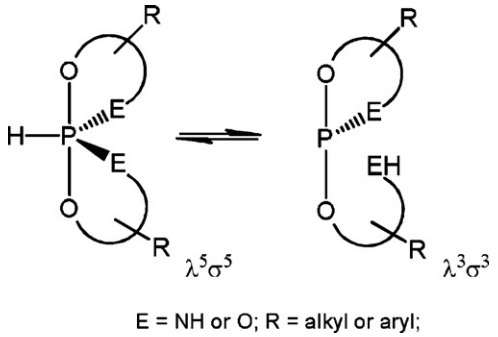
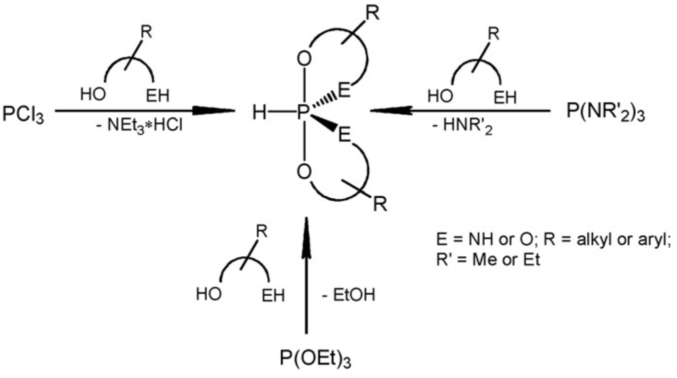


Scheme 1. Schematic structure of hydridospirophosphoranes (HSPs).

nucleophilic properties. The reactivity of hydridospirophosphoranes to some extent depends on: (i) the nature of the heteroatoms coordinated to the phosphorus atom; (ii) the size of phosphorus cycles; and (iii) the kind of substituents within the cycles [4].

Hence, spirophosphoranes containing even one nitrogen atom within the ring are more reactive than tetraoxaspirophosphoranes. To date, most of the interest in H-spirophosphoranes has focused on their synthetic and structural properties. The synthesis of the vast majority of HSPs can be accomplished by two main routes. One is provided by the reaction of diols or aminoalcohols with phosphorus trichloride PCl_3 in the presence of amine as hydrochloride scavenger (Scheme 2). The other approach relies on the reaction of diol or aminoalcohol with hexamethyl(ethyl)phosphorus triamide $P(NR_2)_3$ (R = Me, Et) connected with the evolution of dialkylamine [5]. Besides, there are some examples of a third procedure, which is based on the reaction of triethylphosphite with a corresponding aminoalcohol [6].

The limited X-ray data indicate that H-spirophosphoranes in a solid state show a trigonal bipyramidal TBP molecular geometry with the hydrogen atom located in one of the equatorial positions [7], whereas the two remaining equatorial positions are occupied by heteroatoms: oxygen or nitrogen. Dioxadiazaspirophosphoranes greatly stabilise the arrangement in which two equatorial locations are occupied by nitrogen atoms, whereas two axial locations are occupied by oxygen atoms [8]. This architecture surrounding the P atom is in agreement with the VSEPR rules stating that the more electronegative atoms tend to go to axial positions where the bonds are more ionic [9]. Though the pentacoordinate form is favoured for HSPs, there are some exceptions, such as tetrazaspirophosphorane $HP(NHCH_2CH_2NH)_2$, which exists wholly in the tricoordinate phosphite form. A useful method for determining the structure of H-spirophosphoranes is provided by ^{31}P NMR spectroscopy, which makes it possible to estimate the $P(\lambda^3\sigma^3) \leftrightarrow P(\lambda^5\sigma^5)$ equilibrium (Scheme 1), common in solutions of hydrogen-bearing spirophosphoranes. The typical range of phosphorus shift relevant to the $P(\lambda^5\sigma^5)$ tautomeric form is ca. −60 to −40 ppm, whereas the presence of the $P(\lambda^3\sigma^3)$ form, if any, is observed in the range ~130–140 ppm. The signal of the phosphorus $P(\lambda^5\sigma^5)$ atom exists as a doublet due to interaction between the phosphorus nucleus and the proton, with the $^1J(PH)$ value of 700–900 Hz [2a,b, 10]. The presence of the P—H bond also finds reflection in IR spectroscopy in the form of a characteristic medium-intensity band attributed to the stretching vibration ν(P—H) at ca. 2300 cm^{-1}.



Scheme 2. Formation of hydridospirophosphoranes.

The interest in the chemistry of hydridospirophosphoranes, especially chiral ones, arises from their applications as reagents in the synthesis of phosphorus acid surfactants, in the diastereoselective addition reaction of the P—H bond in tetraoxaspirophosphoranes to symmetrical prochiral bis-imine linkers, followed by the hydrolysis reaction of bis-spirophosphorane intermediates with P*—C* bonds [11]. Spirophosphoranes also act as peptide coupling agents; e.g. 2,2′-spirobi(1,3,2-benzodioxaphosphole) can easily induce the formation of peptide bonds in the construction of dipeptide, polypeptide and protein. Used in conjunction with different bases and additives, they cause the suppression of racemization, exemplified by the Izumiya test based on the condensation of Z-Gly-LAla-OH with H-LLeu-OBzl [12]. Moreover, hydridospirophosphoranes derived from amino acids inhibit the activity of tyrosinase, the enzyme responsible for the production of the melanin pigment found in plants and animals [13]. A spirophosphorane containing an isoleucine residue shows a 96% rate of inhibition, better than the whitening reagent Arbutin (88%) used in cosmetology.

Despite the fact that H-spirophosphoranes have been present in laboratories for almost half a century, there has not been much interest in the coordination properties of these compounds [14]. Even less attention has been paid to their catalytic activity. Consequently, this micro review is concerned solely with the coordination and catalytic properties of these phosphorus compounds. The literature reports presented in this article have been assigned to individual sections based on the collection of transition metals incorporating H-spirophosphoranes.

2. Coordination properties of H-spirophosphoranes

Several factors must be taken into account when using specific H-spirophosphoranes as ligands: (i) they are synthesised simply and with considerable yields; (ii) they are stable enough to be oxidized to derivatives with phosphorus in the 5+ oxidation state; (iii) they exhibit π-acceptor properties due to the presence of P—O or P—N bonds; (iv) by modifying the kind of heteroatom and the nature and bulkiness of substituents within phosphorus cycles, it is possible to control the stability as well as the electronic and steric properties of the ligands. The feasible interplay between the electronic and the steric properties of the ligands can play a crucial role in determining the properties of the complexes and even small changes in ligand architecture might entirely alter the properties of the metal.

2.1. *Metallophosphorane complexes*

So far H-spirophosphoranes have been seen to coordinate to transition metals as monodentate – κ^1 or bidentate κ^2 chelating or bridging ligands. One of the first examples of the coordination abilities of spirohosphoranes towards transition metals was reported by the research group of professor Lattman et al. [15]. In the reported complexes, spirophosphorane ligands coordinate *via* the phosphorus atom in monodentate κ^1 fashion yielding metallophosphorane arrangements **1, 2, 4, 6**. Generally, there are two synthetic methods to obtain κ^1 metallophosphorane complexes: replacement of the