

## Review

## 1,3-P,N hybrid ligands in mononuclear coordination chemistry and homogeneous catalysis

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## ABSTRACT

1,3-P,N-ligands are prominent hybrid ligands which provide valuable mononuclear transition metal complexes, due to their varied bonding modes with an inherent usefulness in cooperative processes such as ligand-assisted substrate activation and both homogeneous and heterogeneous catalysis. Reviewed are recent developments in an expanding number of applications, including coordination chemistry, catalysis, and bio-inorganic applications.

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## 1. Introduction

The translation of the activity and reactivity of the less abundant second and third row transition metal systems to cheaper, more available, but generally less reactive first row metals, requires successfully combining metal- with ligand-based reactivity [1]. This approach of ‘ligand cooperativity’, or ‘non innocence’ for redox active ligands, can be pursued with hybrid ligands, which combine the distinctive bonding preferences of different donor atoms to provide cooperative metal-ligand interactions such as hemilability, ligand assisted substrate recognition, substrate activation and proton shuttling (Fig. 1) [2,3], and have found prominent applications in homogeneous catalysis [4].

Since their introduction in 1972 [5], the hybrid 1,3-P,N-ligands (Fig. 2) have provided rich coordination chemistry, due to the fruitful combination of a soft phosphorus donor with a hard nitrogen [6,7]. Besides rich multinuclear chemistry in which the ligands coordinate in a bridging mode between (hetero)metals to facilitate the formation of metal-metal bonds [8,9], they also form *N*-monodentate [10], *P*-monodentate [11,12], and bidentate mononuclear complexes [12] (Fig. 3), which are active in catalytic reactions including the Ru(II)-catalyzed hydration of nitriles [12f], the Ru(II)-catalyzed hydrogenation of alkynes and transfer hydrogenation of ketones [12e], the Ru(II)-catalyzed hydrogenation of alkenes [12d], the Rh(I)- and Ir(I)-catalyzed hydroformylation of alkenes [8c,12a], the Pd(II)-catalyzed carbonylation of alkynes [11b,12b,c], and the Pd(II)-catalyzed

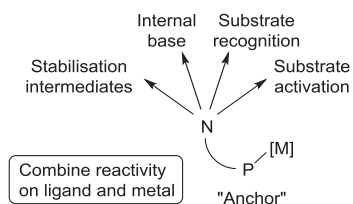


Fig. 1. Cooperative P,N-ligands.

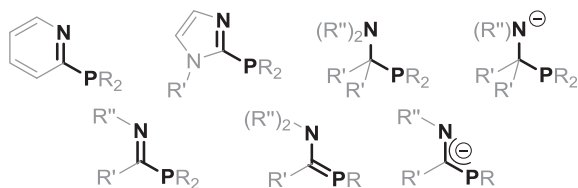


Fig. 2. 1,3-P,N-ligands in recent mononuclear complexes.

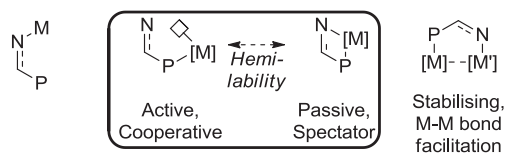


Fig. 3. 1,3-P,N-ligands as hemilabile cooperative ligands.

Buchwald-Hartwig and Suzuki-Miyaura cross-coupling reactions [13]. The number of catalytic applications is still growing.

To provide insight into why these ligands are so valuable, we review recent developments in mononuclear 1,3-P,N chemistry from 2009 [6,7] to mid-2017 with a focus on catalysis and coordination chemistry. Excluded are systems in which one of the donors is unavailable (e.g., *P*-oxidized systems, 2-pyrrolyl-phosphanes, *P*- or *N*-cationic *P,N*-systems) [14,15], those that contain an additional donor atom that can actively participate (e.g., bis-/tris-(pyridyl) phosphanes, ClickPHOS, *N,N'*-coordinating phosphaguandinates, 1,3,5-P,N,X-ligands) [16,17] or ligands that are conformationally restricted in such a fashion that their chemistry is not comparable to the titular compounds (e.g., benzaphospholes, 1,3,5-triaza-7-phosphaadamantate (PTA) ligands) [18]. After an overview of synthetic developments, recent 1,3-P,N-containing mononuclear complexes will be discussed in ascending Group number.

## 2. Synthesis

Recent synthetic developments are discussed first to provide background for the ligands discussed in Sections 2–7.

### 2.1. 2-Pyridyl- and 2-imidazolylphosphanes

Most reports improve on the syntheses and expand on the substituent scope of known ligand systems. To overcome the limited access to substituted 2-pyridylphosphanes (PyPPh<sub>2</sub>) [7a,12c], cross-coupling reactions have been developed to selectively access their 6-substituted precursors **1.2** by using Cu(I)-catalysis for *t*-alkyl groups (Scheme 1; five examples, 74–92%, cat. loading 3.5–10 mol%) or a Ni(II)-catalysis/POCl<sub>3</sub> sequence for others (eight examples; step 1: 53–98%, cat. loading 0.3–3 mol%; step 2: 60–94%) [19]. Subsequent couplings provide **1.3** (10 examples, 58–86%). Nickel was also used to cross couple 2-pyridyl nitrile with HPPH<sub>2</sub> to PyPPh<sub>2</sub> (40%; 10 mol% Ni(COD)<sub>2</sub>+8-hydroxyquinoline, 90 °C, 16 h) [20]. A primary 2-pyridylphosphane has been cyclocondensed to phospholane **2.1** (Scheme 2) [21].

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