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Iminophosphorane–phosphines: Versatile ligands for homogeneous catalysis

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ABSTRACT

Iminophosphoranes $R_3P{=}NR$ are nitrogen analogues of phosphorus ylides that can coordinate transition metals using the lone pair on the nitrogen atom. The integration of supplementary donor sites into the iminophosphorane backbone yields polydentate ligands of increasing interest in both coordination chemistry and catalysis. Herein, a comprehensive account of the applications of mixed ligands featuring both a phosphine and an iminophosphorane moiety in homogeneous catalysis is presented. Among others, metal-catalyzed hydrogenation and transfer hydrogenation reactions, C–C cross-couplings, olefin oligomerization and cyclopropanation processes, allylic alkylation and oxidation reactions, Meyer–Schuster rearrangements and cycloisomerization processes are discussed.

1. Introduction

Iminophosphoranes, also referred to as phosphoranimines, phosphinimines or phosphazenes, are organic compounds of general composition $R_3P{=}NR$. Although the discovery of these nitrogen analogues of phosphorus ylides dates back to 1919 [1], the chemistry of iminophosphoranes has only been explored in depth during the last three decades. However, the maturity reached is such that these compounds find now a wide range of relevant applications [2], which include their use as versatile intermediates in organic synthesis (*e.g.* aza-Wittig reaction) [3], as "superbases" [4], or as building blocks for P–N-backbone polymers (*e.g.* polyphosphazenes) [5]. Several methods of synthesis of iminophosphoranes are known, but the so-called Staudinger and Kirsanov reactions are by far the most general and widely used (Scheme 1) [2]. In both cases a phosphine (PR_3) is used as the starting material, with the Staudinger reaction involving its direct oxidation with an organic azide [1,6], and the Kirsanov one its initial bromination and subsequent treatment of the resulting P(V) phosphine-dibromide with a primary amine in the presence of a base [7,8].

Iminophosphoranes possess a highly polarized P=N bond, and are best described as resonance hybrids of the two extreme canonical forms **A** and **B** (Fig. 1). In addition, they are able to coordinate transition metals *via* the lone pair of the approximately sp^2-hybridized nitrogen atom to give stable complexes **C** (Fig. 1) [9]. However, we must note that the intrinsic coordinating ability of iminophosphoranes, which are predominantly σ-donor ligands with only minor π-acceptor properties, is relatively weak as they can be easily exchanged by other ligands. This point was evidenced for the first time by Fukui and co-workers in 1975 while studying the reactivity of the chloride-bridged dinuclear Pd(II) complexes $[\{PdCl(\mu\text{-}Cl)(Ph_3P{=}NR)\}_2]$ (R = 4-$C_6H_4CO_2Et$, 4-C_6H_4Me) towards triphenylphosphine, triphenylphosphite and 2,2′-bipyridine. All these ligands were able to displace rapidly the coordinated iminophosphoranes $Ph_3P{=}NR$ under very mild reaction conditions (room temperature) [10]. Despite this inherent lability, organometallic and coordination compounds comprising iminophosphorane ligands are being actively studied and found increasing applications in homogeneous catalysis. The most recent breakthroughs in the field are, among others, the development of highly active systems for the polymerization of olefins [11] and *rac*-lactide [12], or the design of robust water-soluble iminophosphoranes for catalytic transformations in environmentally friendly aqueous media [13]. This last point deserves to be highlighted given the sensitivity of P=N bonds towards hydrolysis [2].

The integration of supplementary donor sites into the iminophosphorane substituents yields polydentate mixed ligands, as those included in the generic metal complexes structures **D**–**G**

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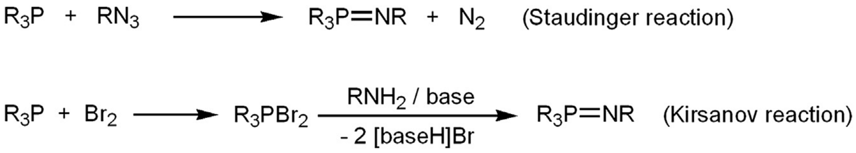

$$R_3P + RN_3 \longrightarrow R_3P{=}NR + N_2 \quad \text{(Staudinger reaction)}$$

$$R_3P + Br_2 \longrightarrow R_3PBr_2 \xrightarrow[\text{- 2 [baseH]Br}]{RNH_2\text{ / base}} R_3P{=}NR \quad \text{(Kirsanov reaction)}$$

Scheme 1. General methods of synthesis of iminophosphoranes.

depicted in Fig. 2, capable of stabilizing a wider range of metal ions in comparison with their monodentate $R_3P{=}NR$ counterparts. The proper selection and fine tuning of these additional donor sites, as well as the corresponding linkers, allows also the on-demand modulation of the reactivity of the metal centre, a key point to achieve high activities and selectivities in catalysis. In addition, in these compounds, the weak iminophosphorane–metal bond may dissociate reversibly without the complete detachment of the ligand, thus opening a vacant coordination site on the metal for substrate binding while maintaining the catalyst integrity, *i.e.* they can present a hemilabile behaviour [14].

Complexes bearing such polydentate ligands, particularly those featuring *P,N*-donor sets of type **H**–**L** (see Fig. 3), have found several uses in homogeneous catalysis in recent years. Herein, an overview of the catalytic applications of these mixed iminophosphorane–phosphine ligands is given [15–17].

2. Hydrogenation and transfer hydrogenation reactions

Metal-catalyzed hydrogenation reactions are among the most frequently encountered transformations in laboratories and industry, appearing as a core technology for the production of a large variety of commodity and fine chemicals, as well as pharmaceutical substances. Concerning the homogeneous version of these reactions, it is now well-accepted that high rates and selectivities are only attainable by the coordination of electronically and structurally well-defined ligands to the metal centre [18]. In this sense, several Rh and Ir complexes containing iminophosphorane–phosphine ligands have been checked as potential catalysts for the selective hydrogenation of C=C bonds.

First examples were described by Cavell and co-workers in 1994, who used the rhodium(I) complexes **1** and **2**, in combination with NEt_3, for the homogeneous hydrogenation of 1-hexene under mild conditions, *i.e.* at room temperature under a H_2 pressure of 1.1 atm (Scheme 2) [19]. Thus, while isolated cationic species **1** gave only poor results (turnover frequency TOF = 0–9.5 h^{-1}), catalytic solutions derived from freshly prepared mixtures of $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ (cod = 1,5-cyclooctadiene) and two equivalents of the appropriate iminophosphorane–phosphine ligand $Ph_2P{-}X{-}P({=}NR)Ph_2$ showed a moderate reactivity (TOF = 14.5–88 h^{-1}). This improvement in the catalytic activity was attributed by the authors to the higher solubility in ethanol of the complexes formed *in situ* as compared to the preformed hexafluophosphate salts **1**.

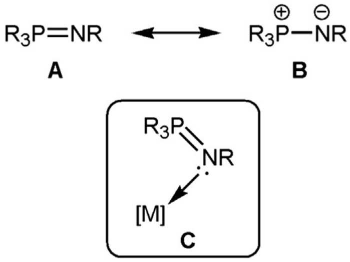

Fig. 1. The two canonical forms of an iminophosphorane and its coordination to a metallic fragment.

Better results were obtained with the neutral complexes **2**, generated *in situ* from $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ and the *N*-silylated ligands $Ph_2P{-}X{-}P({=}NSiMe_3)Ph_2$ (X = CH_2, $(CH_2)_2$, N^nPr) *via* Me_3SiCl elimination, which showed catalytic activities (TOF values up to 570 h^{-1}) comparable with those of the more classical systems $[Rh(cod)(PPh_3)_2][PF_6]$ (TOF = 236 h^{-1}), $[RhCl(PPh_3)_3]$ (TOF = 380 h^{-1}) and $[Rh(cod)(dppb)][PF_6]$ (dppb = 1,4-bis(diphenylphosphino)butane; TOF = 570 h^{-1}) tested under identical reaction conditions. Using the catalytic system $[\{Rh(\mu\text{-}Cl)(cod)\}_2]/Ph_2PCH_2P({=}NSiMe_3)Ph_2/NEt_3$, for which the best activity was found, the authors also investigated the effect of the solvent, ligand to rhodium ratio, and the role of the amine additive and co-solvents. The use of pure ethanol as solvent, a Rh/ligand ratio of 1:1, and an excess of the amine NEt_3 (Rh/NEt_3 ratio of 1:18) led to the highest catalytic activity. Under these optimal conditions, other olefins, such as cyclohexene and styrene, were also hydrogenated (TOF = 660 and 285 h^{-1}, respectively) by the $[\{Rh(\mu\text{-}Cl)(cod)\}_2]/Ph_2PCH_2P({=}NSiMe_3)Ph_2$ combination [19].

The hydrogenation of styrene catalyzed by the cationic rhodium(I) complex **3**, containing a *N*-phosphorylated iminophosphorane–phosphine ligand coordinated in a chelating κ^2-(*P,O*) manner, was described by Balakrishna and co-workers some years later (Scheme 3) [20]. In this case, using 0.0005 mol% of **3** in combination with triethylamine (10 mol%), styrene could be converted quantitatively into ethylbenzene after 80 min in THF under mild conditions (*i.e.* H_2 pressure of 4 atm at room temperature). This result implies a turnover number (TON) of 200,000 and a turnover frequency (TOF) of 300,000 h^{-1} (calculated at 50% conversion, *i.e.* TOF_{50}), values that largely surpass those achieved by the Wilkinson's catalyst $[RhCl(PPh_3)_3]$, for which complete conversion at a low metal loading was observed under the following conditions: 0.0008 mol% of $[RhCl(PPh_3)_3]$, $T = 80\ ^\circ C$, $P(H_2) = 28$ atm, $t = 2$ h [21]. Moreover, the activity of **3** could be improved by increasing the H_2 pressure to 10 atm and the temperature to 70 °C, leading to a TOF_{50} value of 600,000 h^{-1} under these new reaction conditions. Note that good results in terms of activity and selectivity were also reached in the catalytic hydrogenation of other olefins and terminal alkynes (α-methylstyrene, 4-methylstyrene and phenylacetylene) using the Rh(I) complex **3** [20].

Although to date little attention has been paid to the design of optically active iminophosphorane–phosphines [22,23], Kim and co-workers have demonstrated the enormous potential of this type of compounds in asymmetric catalysis. In particular, they described the preparation of the *P,N*-donor ligands **4a**–**c** and **5a**–**b** derived from planar–chiral ferrocenyl–diphosphines, anticipating that, as sterically demanding and robust chelating agents, they should accomplish high optical inductions in asymmetric reactions (Fig. 4) [24]. Thus, in a first set of experiments, they performed the Rh-catalyzed asymmetric hydrogenation of the activated olefins (*E*)-2-methylcinnamic acid, (*Z*)-2-acetamidocinnamate and (*Z*)-2-acetamidoacrylate (see Scheme 4) [24a]. Reactions were conducted in methanol at 40 °C, under a H_2 pressure of 1 bar, and in the presence of 2 mol% of the corresponding rhodium catalyst generated *in situ* from $[Rh(nbd)_2][BF_4]$ (nbd = norbornadiene) and a slight excess of **4a**–**c** or **5a**–**b**. The results obtained under these conditions are quite remarkable since high