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Review

Hybrid diphosphorus ligands in rhodium catalysed asymmetric hydroformylation

Samir H. Chikkali[a,b,*], Jarl Ivar van der Vlugt[a,*], Joost N.H. Reek[a,*]

[a] Supramolecular & Homogeneous Catalysis, van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands
[b] Polymer Science and Engineering Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India

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ABSTRACT

This review aims to illustrate recent advances in the application of hybrid diphosphorus ligands for the Rh catalysed hydroformylation of alkenes, discussing the most prevalent classes of hybrid systems, *i.e.* phosphine-phosphinite, phosphine-phosphonite, phosphine-phosphite, phosphite-phosphoramidite and phosphite-phosphoramidite and comparing their performance with relevant C_2 symmetric counterparts. In order to introduce the field and put the results in context, a short overview on Rh hydroformylation is provided. Available spectroscopic (*in situ*) data on the coordination modes of hybrid phosphorus ligands and the catalytic performance of these systems in asymmetric hydroformylation of vinyl arenes are reported. Potential avenues for future research are shortly discussed.

1. Introduction

The synthetically versatile and industrially very relevant "hydroformylation" reaction can be defined as the net addition of CO and H_2 [(as a formyl —CHO) and a proton] across a C—C double bond to afford aldehydes. While studying Fisher–Tropsch synthesis, Otto Roelen discovered that alkenes were converted to aldehydes containing one more carbon atom. Although alkane is the thermodynamically favoured product of this reaction (hydrogenation: $\Delta G = -88$ kJ/mol; hydroformylation $\Delta G = -42$ kJ/mol), the aldehyde is formed, as the reaction proceeds with kinetic control under judiciously chosen reaction conditions. Since this pioneering discovery, metal-catalysed hydroformylation (see Scheme 1) has become a powerful synthetic tool to construct organic compounds [1,2].

* Corresponding authors: Tel.: +31 20 5256459/+91 20 2590 3145; fax: +31 20 5255604/+91 20 25902615.
E-mail addresses: s.chikkali@ncl.res.in (S.H. Chikkali), j.i.vandervlugt@uva.nl (J.I. van der Vlugt), j.n.h.reek@uva.nl (J.N.H. Reek).

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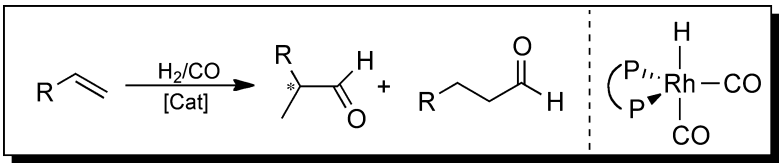

Scheme 1. General scheme for the metal catalysed hydroformylation of a prochiral alkene.

Terminal olefins can be efficiently converted into corresponding aldehydes. There are many catalysts nowadays that can form the linear aldehyde in high selectivity, but selective formation of the (chiral) branched isomers remains a challenge [3]. The same holds for the selective hydroformylation of internal olefins, although there are several examples of one-pot isomerization-hydroformylation to generate the linear aldehyde [4,5]. Branched selective hydroformylation of aromatic substrates, typically styrene, is predominant over the linear isomer due to favourable stabilization of the relevant rhodium-aryl (η^3-benzyl) intermediate. Enantioselective introduction of the aldehyde is interesting as it provides access to important intermediates for fine chemical and pharmaceutical.

Initial studies on hydroformylation were conducted using simple metal carbonyls (cobalt, rhodium) as catalysts, but interest quickly shifted to metal complexes based on monodentate phosphine ligands such as triphenyl phosphine. Ligand based metal complexes offer opportunities to tailor the properties of a catalyst by "rational ligand design". Basic parameters that govern the ligand properties include 'cone angle' and the 'bite angle'. In his landmark paper, Tolman proposed the "cone angle (Θ)" concept, which is a measure for the steric properties of a monodentate ligand (Fig. 1) [6]. The electronic properties of monodentate phosphorus ligands were also first quantified by Tolman, who came up with the χ-parameter as a measure of the electronic properties of a ligand [7].

A major breakthrough in the field was the introduction of bidentate ligands, which have been extensively investigated in hydroformylation over the last decades. Basic parameters like the "cone angle" are inadequate to describe the steric effect of such bidentate ligands on chelated metal centres. To estimate the steric properties of a bidentate ligand, Casey and Whiteker introduced the "natural bite angle" concept. The natural bite angle (β_n) can be defined as the angle at which the two donor atoms of a chelating bidentate ligand bite to a transition metal centre. Molecular mechanics forms the basis for this concept as β_n is calculated by introducing a dummy atom between the chelating phosphines of a bidentate ligand at a constant distance depending on the metal that is used, 2.315 Å in the case of rhodium (see Fig. 1 right) [8]. One should realize that the bite angle is a ligand parameter, and that the angle in the complex is actually a compromise between preference of the ligand and that of the metal. This may lead to constrained complexes that have unusual reactivity. Next to this, large bite angle ligands are sterically more demanding, which also has an influence on the catalytic properties. This bite angle has proven quite important for the regioselective hydroformylation of internal and terminal alkenes (large bite angles yield linear aldehydes preferably), as it dictates ligand coordination and thereby effectively controls the ratio between *various coordination isomers* [9]. However, it is far less established whether the bite angle plays a similar prominent role in the asymmetric hydroformylation of prochiral alkenes.

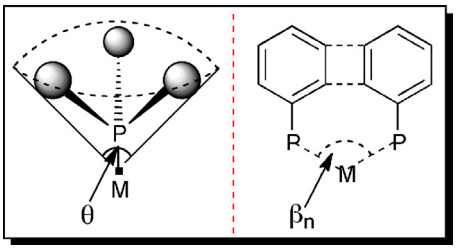

Fig. 1. Representation of cone angle (left) and natural bite angle (right).

This review summarizes the available data on coordination modes of active Rh catalysts for asymmetric hydroformylation bearing *hybrid bidentate phosphorus* ligands in relation to selectivities obtained for the conversion of alkenes and vinyl arenes. We discuss the major ligand design strategies and recent breakthroughs and identify future avenues for research.

2. Phosphorus ligands in Rh-catalysed asymmetric hydroformylation (AHF)

2.1. Hybrid diphosphorus ligands

The role of the ligand has been central to the development of asymmetric hydroformylation and different design principles have been applied. Chelating phosphorus ligand (with chirality on P/E-substituents or on backbone) systems can be broadly classified into (a) bidentate (often invoking C_2-symmetry), with additional options for chirality on P-substituents (auxiliaries) or P-stereogenic atoms), (b) C_1-symmetric (backbone chirality), (c) hybrid diphosphorus (chirality on P-substituents) and (d) mixed donor classes (chirality on P/E-substituents) (Fig. 2). The application of C_2-symmetric ligands was very successful in asymmetric hydrogenation and as such a starting point in the field of hydroformylation. The corresponding bidentate ligands are relatively easy to prepare and they often form stable, well-defined complexes. Later, a variety of different skeletons have been applied to develop C_2-symmetric diphosphines [10–14]. Many other types of chelating diphosphorus ligands have also been developed and investigated for the hydroformylation of alkenes, including diphospholanes [15], diphosphites [16] as well as amidophosphorus [17] species, while (chiral) diphosphinites [18] or diphosphonites [19] have been studied far less in (asymmetric) hydroformylation.

Although a variety of new ligand designs has been realized, many C_2-symmetric diphosphine ligands typically lead to only moderate enantioselectivity (albeit with high regio- and chemoselectivities) in the Rh catalysed *asymmetric* hydroformylation of prochiral alkenes [20]. Analogous C_2-symmetric diphosphites with chiral backbones generally result in more active catalysts and higher enantioselection for *e.g.* styrene (as well as vinyl acetate and allyl cyanide) as benchmark substrate [21].

A more recent design principle of bidentate ligands for asymmetric hydroformylation catalysis is based on C_1-symmetric ligands, either derived from a unsymmetric backbone *or* based on two different types of phosphorus donor groups, *i.e.* hybrid ligands (Fig. 2) [22]. These hybrid ligands are designed to combine the high activity displayed by one donor and the high selectivity induced by using the second donor. The performance of hybrid bidentate ligands has often been correlated to the way these ligands preferentially coordinate to a rhodium centre, which may be tunable and controllable to a certain degree. The bite angle is believed to