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Highly Enantioselective or Not?—Chiral Monodentate Monophosphorus Ligands in the Asymmetric Hydrogenation

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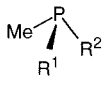
The development was over before it had really begun—this was certainly true for the use of monodentate chiral monophosphorus ligands in rhodium(I) catalysts for enantioselective hydrogenation reactions. Initially everything seemed very promising. In 1965 Wilkinson and co-workers discovered that $[RhCl(PPh_3)_3]$ catalyzes the hydrogenation of olefins.[1] Only a few months later Vaska and Rhodes reported the use of *trans*-coordinated bis(monophosphane) iridium complexes in the reduction of alkenes.[2] Monophosphane ligands were also prominent in other newly discovered metal catalysts, whereas *cis*-chelating diphosphanes, such as bis(diphenylphosphanyl)-ethane greatly reduced the rate of hydrogenation. Mechanistic studies showed that the dissociation of a phosphane from Wilkinson's complex is essential for the initiation of the catalytic cycle. For this reason bidentate diphosphane ligands were regarded as unsuitable since the chelate effect enhances their binding to the metal center.[3]

In 1968, the suggestion from Horner and co-workers to employ chiral monophosphanes for the enantioselective hydrogenation of prochiral olefins was both timely and logical.[4] Two Monsanto chemists, Knowles and Sabacky, realized this idea only a few months later through the use of a rhodium complex with the P-chiral ligands PAMP (*o*-anisylmethylphenylphosphane **1a**) and CAMP (*o*-anisylcyclohexylmethylphosphane **1b**) for the hydrogenation of atropic acid.[5] They generated hydratropic acid in a 15% optical yield. With this report itaconic acid (ItH_2) began its career as a prochiral test substrate, it was reduced with a 3% optical yield.

1a: R^1 = *o*-$MeOC_6H_4$, R^2 = Ph (PAMP)
1b: R^1 = *o*-$MeOC_6H_4$, R^2 = *cyc*-C_6H_{11} (CAMP)
1c: R^1 = Ph, R^2 = *n*-C_3H_7



Still in the same year Horner et al., now showed that prochiral styrene could be hydrogenated in up to 8% optical yield by using an in situ formed Rh^I complex of methylphenyl-*n*-propylphosphane (**1c**).[6] Clearly the disappointingly low enantioselectivities were a deciding factor that greatly hindered the rapid adoption of the new hydrogenation method.

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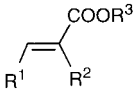
In addition came the blinkered focus on P-chiral phosphane ligands, the synthesis of which, at that time, was relatively complicated and did not always proceeded without racemization.

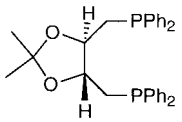
The situation changed drastically in 1971 when Dang and Kagan reported the synthesis and use of (*R*,*R*)-DIOP, the first

ItH$_2$: R^1 = H, R^2 = CH_2COOH, R^3 = H
ItMe$_2$: R^1 = H, R^2 = CH_2COOMe, R^3 = Me
aH: R^1 = H, R^2 = NHAc, R^3 = H
aMe: R^1 = H, R^2 = NHAc, R^3 = Me
AH: R^1 = Ph, R^2 = NHAc, R^3 = H
AMe: R^1 = Ph, R^2 = NHAc, R^3 = Me



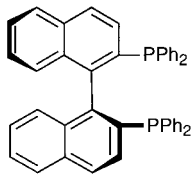
chiral diphosphane ligand.[7] The corresponding Rh^I complex was used for the hydrogenation of (*Z*)-*N*-acetylaminocinnamic acid (AH) and promptly gave an optical yield of 72% and almost quantitative conversion—all this with the rhodium complex of a diphosphane! Three requirements were central to the design of DIOP 1) maximum conformational rigidity of the ligand, 2) strong coordination to the metal center 3) use of a ligand with chemically equivalent phosphorus atoms.[8]

It remains for chemical historians to analyze the reasons in all their complexity for the change in the direction of research, from mono- to diphosphane ligands, that now followed. The simple preparation of enantiomerically pure (*R*,*R*)-DIOP from naturally occurring (+)-tartaric acid, the typically short hydrogenation times with seven-ring chelates, and the, for that time, impressive enantioselectivities even for the reduction of other substrates no doubt played an important role and stimulated the search for similarly effective (diphosphane) ligands. In the following years huge numbers of this type of ligand were prepared and tested in particular in the normal-pressure hydrogenation of the substrates itaconic acid (ItH$_2$), *N*-acetylaminoacrylic acid (aH), and (*Z*)-*N*-acetylaminocinnamic acid (AH), or their methylesters (ItMe$_2$, aMe, AMe)—substrates which are still the standards against which hydrogenation catalysts are measured.[9]

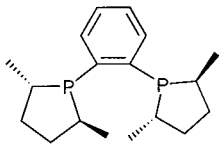


(*R*,*R*)-DIOP

Milestones in the development of the diphosphane family include the establishment of BINAP[10] and DuPHOS.[11] The potential offered by the chiral diphosphane complexes of



(*S*)-BINAP



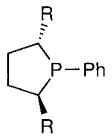
(*S*,*S*)-DuPHOS

ruthenium[12] and iridium[13] in hydrogenation was also recognized. In parallel investigations into the mechanism of the enantioselective hydrogenation[14] and the influence of the ligand parameters on it were carried out.[15] Diphosphinites[16] and more recently diphosphonites[17] and diphosphites[18] as well as hybrid ligands[19] have also been shown to be similarly effective to diphosphanes.

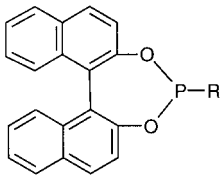
That in 1972 Knowles and co-workers achieved an optical yield of 90% in the hydrogenation of unsaturated *N*-acetylphenylalanine precursors with an Rh catalyst containing the monophosphane CAMP, was completely lost in the euphoria over the bidentate ligands.[20] In the subsequent 30 years as far as enantioselective hydrogenation is concerned monophosphorus ligands have been living in the shadows. Of course, every now and then chiral monophosphane ligands would be prepared, but usually only as intermediates on the road towards more efficient and hopefully unpatented diphosphorous ligands.

Almost ironically it is Kagan, who with DIOP initiated the rapid development of the chelating diphosphane ligands and who has had such a lasting influence on this area, who recently in a retrospective over monophosphanes, with regard to enantioselective hydrogenation, came to the following conclusion: "We can expect that they [monophosphanes] will play a role of increasing importance in many aspects of organometallic catalysis. We hope that this review will encourage practitioners of asymmetric catalysis to consider the potential of chiral monodentate phosphines and to investigate this area which has been quite neglected till now".[21]

This impulse from such a respected source found an unexpectedly rapid response. In the last few months several groups have reported the use of monophosphorus ligands in highly enantioselective hydrogenation reactions, whereby different oxidation states of the trivalent phosphorus atom have received attention. Leading the way Guillen and Fiaud reported as early as 1999 a rhodium complex of 1,2,5-triphenylphospholane (**2a**), a monodentate species of the DuPHOS-type, that reduces AMe with 82% *ee* (Table 1).[22, 23] Incidentally this ligand is closely related to 2,5-dimethylphospholane **2b** the compound that stands at the beginning of the development of the bidentate DuPHOS by Burk et al., but on grounds of its poor enantioselectivity in hydrogenation



2a: R = Ph
2b: R = Me



3a: R = *t*Bu
3b: R = Et
3c: R = (*R*)-OCH(Me)Ph
3d: R = NMe_2

Table 1. Highly enantioselective Rh-catalyzed hydrogenation with monophosphorus ligands.

Ligand	Substrate	*ee* [%]	Author(s), Ref.
2a	AMe	82–92 (*S*)	Fiaud[22, 23]
(*S*)-**3a**	aMe	92 (*R*)	Orpen and Pringle[26]
(*R*)-**3b**	aMe	94 (*S*)	Reetz[27]
(*R*)-**3b**	ItMe$_2$	90 (*R*)	Reetz[27]
(*S*)-**3c**	ItMe$_2$	>99 (*S*)	Reetz[28]
(*S*)-**3d**	AMe	98.4 (*R*)	de Vries and Feringa[30]
(*S*)-**3d**	AH	97.1 (*R*)	de Vries and Feringa[30]
(*S*)-**3d**	aMe	>99 (*R*)	de Vries and Feringa[30]
(*S*)-**3d**	aH	98.7 (*R*)	de Vries and Feringa[30]
(*S*)-**3d**	ItH$_2$	96.6 (*S*)	de Vries and Feringa[30]

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reactions (maximum 60 % *ee*)[24] has since only been used as a synthetic building block on the way to bidentate ligands.[25]

In 2000 Orpen, Pringle, and co-workers attained the hydrogenation of aMe in 92 % *ee* with the asymmetric monophosphonite **3a** and thus a higher enantioselectivity than is possible with comparable C_2-symmetric diphosphonite analogues.[26] With this publication the widely accepted dominance of the bidentate diphosphorus ligands was questioned for the first time. Reetz and Sell showed in response that through the exchange of the *tert*-butyl group for an ethyl group (→**3b**) the enantioselectivity can be increased further.[27] With the same catalyst $ItMe_2$ was also hydrogenated with a respectable 90 % *ee*. However, in spite of this a related diphosphonite ligand when tested delivered >99 % *ee*. The old rule that chelating diphosphorus ligands are superior still appeared to hold.

A clear tie in regard to performance, with enantioselectivities that could not be topped, was achieved with the use of monodentate binaphtholphosphites and phosphoramidites. Reetz and Mehler prepared the monophosphite **3c**.[28] The corresponding catalyst induces >99 % *ee* in the hydrogenation of $ItMe_2$. Particularly noteworthy is the high substrate:rhodium ratio of up to 5000:1, that still guarantees complete conversion in 20 h under normal pressure. Surprisingly the configuration of the chiral carbon atom of the benzyl ether does not play any kind of role. The enantioselectivity of this type of ligand is dominated by the chiral binaphthyl unit, in complete contrast to other P substituents, for example, sterically demanding aryloxy groups, that have a very significant influence on the enantioselectivity and conversion.

Phosphoramidites, a ligand class that has only recently been introduced into asymmetric hydrogenation, in the form of hybrid chelate ligands,[29] induce excellent enantioselectivity as monodentate ligands. Thus de Vries, Feringa, and coworkers could reduce standard substrates in >96 % *ee* with a rhodium complex based upon the binaphtholphosphoramidite **3d**, once the solvent and reaction temperature had been optimized.[30]

It is noticeable that all the ligands that induce a high enantioselectivity are phosphorus derivatives of binaphthol. Based on the crystal structure of a Pt^{II} complex with monophosphonite ligands Orpen and Pringle have proposed a plausible explanation that could be helpful in the development of other selective monophosphorus ligands.[26] Through the *cis* coordination both the sterically demanding monophosphonite ligands take up an exceptionally stable configuration around the metal center, through which rotation about the P–O bond is reduced. In this conformation the two biaryl fragments point out of the plane of the projection in what is described as edge-on arrangement. In a virtual coordination system two diagonally opposing squares are occupied (Figure 1 A). The squares at the top left and bottom right are not effectively occupied, because of the planar arrangement of the two phenyl groups in the plane of the projection (face-on). From investigations with chelating diphosphorus ligand complexes it is known that such an alternating edge/face arrangement[31] can support the diastereo-differentiating coordination of a prochiral substrate through the minimization of repulsive interactions.[32] In

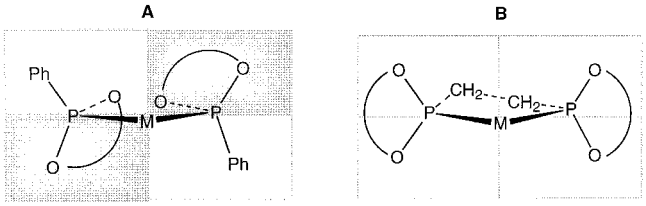

Figure 1. Monodentate (A) and chelating (B) binaphthyl ligands on a metal center and their effect on the stereoselective occupation of the squares.

contrast, by the *cis* coordination of the diphosphonite ligands the rotamer stabilized is that in which the biaryl units are in the face-on orientation; none of the squares is favored (Figure 1 B). Thus the chances of diastereomeric recognition of the prochiral substrate are greatly reduced.

On the basis of this general model[33] and supported by first semiempirical calculations from de Vries and Feringa[30] it is clear that for the mechanism of chiral transfer in asymmetric hydrogenation, mono- and diphosphorus ligands do not necessarily fundamentally differ.[34] The requirement originally laid down by Kagan, that the catalyst must be conformationally rigid, is clearly also achievable with two appropriate monodentate monophosphorus ligands. As a consequence of these results the strategic decision as to whether one should favor mono- or diphosphorus ligands comes down to the principle question asked of every asymmetric catalyst: is it highly enantioselective or not?

Clearly the potential that chiral monophosphorus ligands have in hydrogenation reactions is far from exhausted, a hypothesis that is supported by the well known and excellent results from other asymmetric catalytic reactions.[21] Naturally the demands for the design of monophosphorus ligands that effect high enantioselectivity are higher, something that should stimulate the search for new principles for the selective stabilization of diastereomeric catalysis intermediates, for example, by secondary interactions between the ligand and the metal or substrate.[35] The synthesis of monophosphorus ligands is often simpler than that of diphosphorus compounds, which is justification enough to look closer at these types of ligands that in the past were often undervalued.

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[34] In contrast to the hydrogenation measurements reported in ref. [26, 27, 30], Reetz et al. in ref. [28] used predominately an Rh:ligand ratio of 1:1, although with a 1:2 ratio no significantly different enantioselectivity was observed. Unpublished NMR spectroscopy experiments indicate that 1:2 precatalyst complexes are formed in the in situ reaction of $[Rh(cod)_2]BF_4$ (cod = 1,5-cyclooctadiene) with the monophosphites. In addition the hydrogenation reactions show a strong (positive) nonlinear effect, an indication that two monophosphite groups are also involved in the transition state. (M. T. Reetz, personal communication).
[35] Review see: A. Börner, *Eur. J. Inorg. Chem.* **2001**, 327 – 337.

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