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Application of alkane-diyl based chiral phosphine-aminophosphine (P-NP) and thioether-aminophosphine (S-NP) ligands in Rh-catalyzed asymmetric hydrogenation

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ABSTRACT

Rhodium(I)-complexes of five new alkane-diyl based phosphine-aminophosphine (P,NP) type chiral ligands ($Ph_2PCH(CH_3)(CH_2)_nCH(CH_3)N(R^1)PR^2_2$ (n = 0-2, R^1 = Me, Et, *i*Pr, R^2 = Ph, Cy)) and a thioether-aminophosphine type compound ((*S,S*)-$PhSCH(CH_3)(CH_2)CH(CH_3)N(iPr)PPh_2$) have been synthesized. The investigation of the coordination chemistry of structurally analogous systems by NMR and IR spectroscopy and in one case by X-ray crystallography enabled the comparison of the effect of (i) the ligand backbone length, (ii) the N-substituent, (iii) the type of the coordinating functionality and (*iv*) the P-substituent in aminophosphine moiety on the stereo-electronic properties of the complexes. The novel Rh-compounds were tested in the asymmetric hydrogenation of a broad range of prochiral substrates including dimethyl itaconate, dehydroaminoacid derivatives and α,β-unsaturated enol ester phosphonates. Catalysts modified by the pentane-2,4-diyl based phosphine-aminophosphine ligands provided superior catalytic performance compared to the analogous butane- and hexane-diyl based systems and thioether containing compound. Most importantly, by the proper choice of the N-substituent outstanding enantioselectivities could be obtained in the asymmetric hydrogenation of acetamidocinnamic acid derivatives (up to 98% *ee*) and enol ester phosphonates (up to 97% *ee*).

1. Introduction

The precise control of molecular chirality plays an important role in chemistry, life sciences, and materials engineering [1]. Transition metal catalyzed asymmetric synthesis is one of the most useful strategies to produce enantioenriched chiral compounds [2]. High activity, selectivity and stability, readily accessible chiral ligands, and enzyme-like stereocontrol are amongst the main features of an ideal transition metal catalyst [3]. In the past several decades, the exploration of ligand effects in transition metal catalysis has proven to be an extremely powerful tool for fine tuning the efficiency of the catalytic systems in homogeneous catalysis. Variation of electronic and steric features [4] and the „natural" bite angle [5] for bidentate ligands has been used to optimize many catalytic reactions. Consequently, the development of tunable chiral ligands and their highly modular synthetic methodologies are extremely important in efficient catalyst design. At the early stages of such research, C_2 symmetry diphosphines dominated the field that proved to be extremely successful in certain catalytic transformations [6,7]. Later, C_1 symmetry hybrid phosphorus ligands (eg. phosphine-phosphites, -phosphoramidites, -aminophosphines, -phosphonites, etc.) emerged as valuable chiral selectors in transition metal catalyzed asymmetric syntheses providing, in many cases, even higher efficiency compared to their C_2 symmetry analogues [8]. The success of hybrid phosphorus ligands rests upon the presence of a unique stereoelectronic environment due to their distinct phosphorus-containing binding sites [9]. Additionally, the non-identical nature of the coordinating functionalities facilitates their independent modification that enables subtle changes in the catalyst structure. Based on these facts, it is not surprising that recently, the development of novel hybrid phosphorus-containing ligands gained a central role in asymmetric catalysis [10].

Chiral phosphine-phosphoramidites [11] and phosphine-aminophosphines (P,NP ligands) represent a particularly interesting class of chiral stereoselectors amongst hybrid phosphorus ligands

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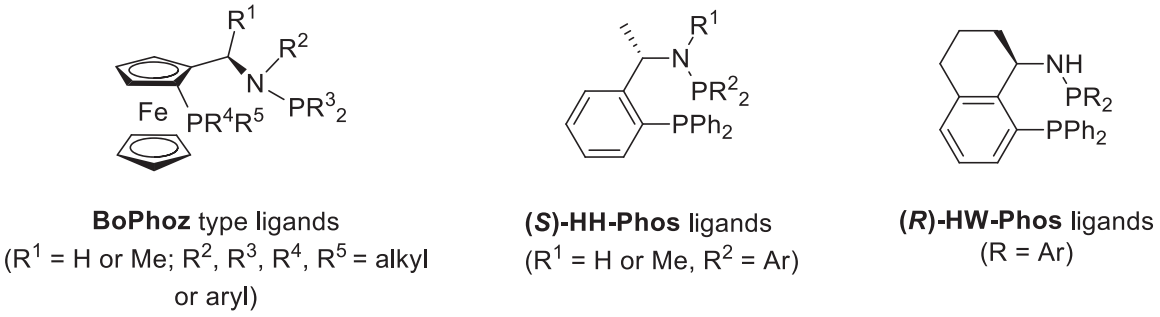


BoPhoz type ligands (R^1 = H or Me; R^2, R^3, R^4, R^5 = alkyl or aryl)

(*S*)-HH-Phos ligands (R^1 = H or Me, R^2 = Ar)

(*R*)-HW-Phos ligands (R = Ar)

Fig. 1. Chiral phosphine-aminophosphine ligands.

due to the presence of the trivalent nitrogen atom in one of their coordinating moieties. The nitrogen atom further increases the tunability of the ligand as it can strategically be functionalized to enhance steric or electronic control. More specifically, the variation of the N-substituent is a useful tool to tune the steric bulk around the phosphorus in the NP moiety or to regulate the conformational rigidity of the chelate ring, a key element in chiral ligand design. Furthermore, in phosphine-aminophosphines the steric and electronic properties of the NP moiety can easily be varied in the reaction of the precursor aminoalkyl-phosphine (P,N) with a wide array of chlorophosphine reagents. Based on the above unique features, phosphine-aminophosphine ligands provided exceptionally high activity and enantioselectivity in a number of catalytic transformations. Boaz and coworkers developed a ferrocene based P,NP ligand library (BoPhoz ligands, Fig. 1) that was used in Rh- and Ru-catalyzed asymmetric hydrogenation reaction of a variety of prochiral substrates: dehydroaminoacids, itaconates, hydroxyketones and α- and β-ketoesters were converted to valuable chiral products with high optical yield [12]. Later on, the structural modification of the parent BoPhoz ligand by the introduction of fluorinated P-substituents (R^3 = 3,5-bis(trifluoromethyl)phenyl or $R^4 = R^5$ = 3,5-bis(trifluoromethyl)phenyl) [13] or a P-chiral donor site ($R^4 \neq R^5$) [14] further enhanced catalytic efficiency in the asymmetric hydrogenation of enamides and dehydroaminoacid esters. Hu and Zheng synthesized 1-phenylethylamine- (HH-Phos) and 1,2,3,4-tetrahydro-1-naphthylamine-derived (HW-Phos) P,NP ligands that provided high activity and enantioselectivity not only in the asymmetric hydrogenation of dehydroaminoacids and enamides [15] but also in the reduction of α,β-unsaturated enol ester phosphonates and α-enamido phosphonates [16]. Furthermore, these ligands were also highly effective in the asymmetric hydrogenation of various 3-aryl-2H-1,4-benzoxazines [17].

Interestingly, the skeleton of privileged P,NP ligands prepared so far is based on a rather narrow scope of rigid aromatic subunit as important element in successful chirality transfer (Fig. 1) [12–17]. Additionally, these rigid P,NP frameworks are less suitable for structural modifications even though the alteration of the ligand backbone may induce dramatic improvements both in catalyst activity and enantioselectivity [18]. The introduction of (multiple) chirality centers into a simple aliphatic backbone, however, also represents a beneficial approach to enhance conformational rigidity of bidentate aminophosphines. In addition, this strategy significantly increases the modularity of the ligand design.

Recently, we have reported on the synthesis of thioether-aminophosphine (S,NP) **L7** and phosphine-aminophosphine (P,NP) **L3** (Fig. 2) and their application in Pd-catalyzed asymmetric allylic etherification reactions [19]. Although **L3** proved to be less effective in this reaction, preliminary catalytic results forecasted its successful application in Rh-catalyzed asymmetric hydrogenation.

Motivated by these experiments and literature findings, we envisaged to synthesize a new family of phosphine-aminophosphine type ligands based on simple alkane-diyl backbone to exploit (i) the high modularity of their synthesis, (ii) their exceptional stereoelectronic tunability and (iii) the potential of a conformationally rather rigid aliphatic backbone. Our additional aim was to systematically modify the ligand's structure to investigate its effect both in catalysis and rhodium coordination chemistry.

2. Results and discussion

2.1. Synthesis of the new ligands

Earlier, we described the preparation of a class of simple alkane-diyl based aminophosphine (P,N) type chiral ligands having secondary amino functionality starting from optically pure cyclic sulfate esters [20]. These P,N ligands could successfully be utilized in asymmetric allylic alkylation and amination reactions [21] but gave only poor selectivity in Rh-catalyzed asymmetric hydrogenation reactions. A useful feature of these ligands, however, is the possibility of a subsequent functionalization step due to the presence of the secondary amino group. Indeed, the addition of 1.5 equiv. of the corresponding chlorophosphine to the P,N compound in the presence of a base resulted in the formation of the desired P,NP type hybrid phosphorus ligands **L1**-**L6** (Fig. 2). Most importantly, no tedious workup procedures are required as passing the reaction mixture through a pad of activated alumina affords the product with generally high yield in a pure form.

It is important to note that the preparation of the pentane-2,4-diyl based P,NP ligand with R^1 = *t*Bu was unsuccessful even at elevated temperatures and by using a stronger base (eg. DABCO (1,4-diazabicyclo [2.2.2]octane)). Analogously, the yield of the synthesis of ligand **L5** was considerably lower (37%) than that of the other compounds (67–85%). These effects can be explained by the strong steric crowding around the NH moiety in these cases that clearly hampers the formation of the P-N bond. Nevertheless, based on the diversity of the available alkane-diyl based P,N (or S,N) compounds, a highly modular procedure has been developed that allows the modification of the P- and N-substituents and the structure of the backbone as well.

The $^{31}P\{^1H\}$ NMR spectra of ligands **L1**-**L6** exhibit two signals in the expected chemical shift range for the two phosphorous atoms of different chemical environments. The ^{31}P signals of compounds **L1, L4** and **L5** showed ^{31}P-^{31}P coupling, with magnitudes of 2.5, 1.3 and 9.5 Hz, respectively [22].

2.2. Coordination chemistry

The coordination chemistry of the novel ligands has been evaluated through the analysis of their $[Rh(COD)(\mathbf{L})]BF_4$ and $[Rh(CO)_2(\mathbf{L})]BF_4$ type complexes by NMR and IR methods, respectively. $[Rh(COD)(\mathbf{L})]BF_4$ complexes could easily be synthesized in the reaction of the free ligand with one molar equivalent

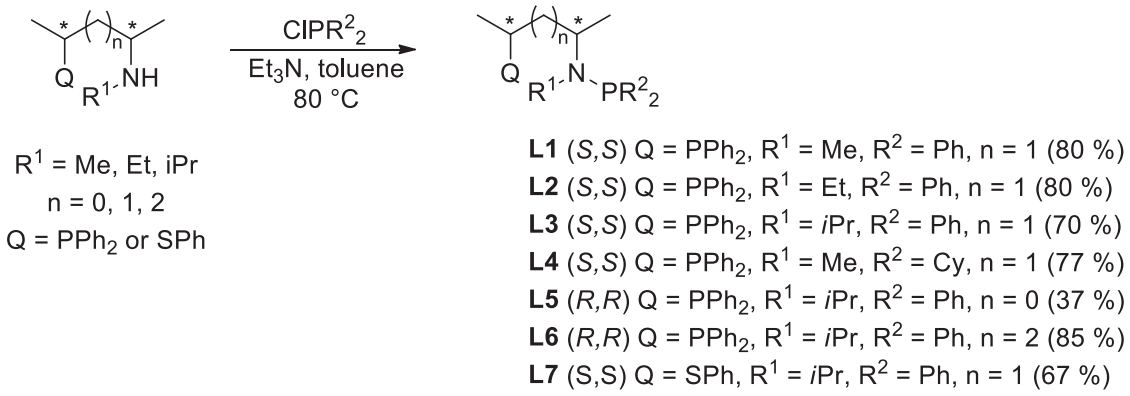


Fig. 2. Synthesis of the novel alkane-diyl based bidentate ligands L1-L7.

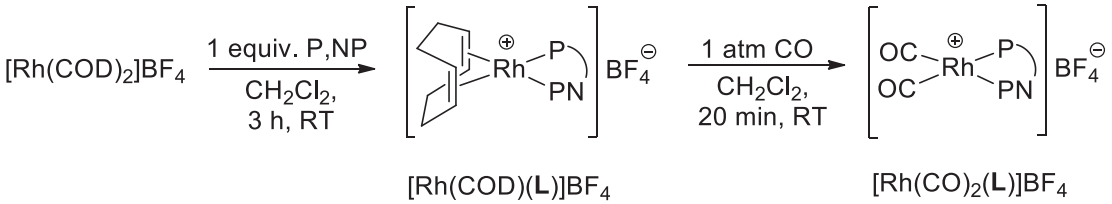


Fig. 3. Synthesis of [Rh(COD)(**L**)]BF_4 and [Rh(CO)$_2$(**L**)]BF_4 complexes.

of [Rh(COD)$_2$]BF_4 in CH_2Cl_2 at room temperature (Fig. 3). Compounds [Rh(COD)(**L1-L5**)]BF_4 exhibit two doublet of doublets in their $^{31}P\{^1H\}$ NMR spectra arising from the ^{31}P-^{31}P and ^{103}Rh-^{31}P couplings, indicating the formation of *cis* chelate complexes (Fig. 3). The low temperature ^1H and $^{31}P\{^1H\}$ NMR spectra of [Rh(COD)(**L3**)]BF_4 recorded at 193 K still exhibit one signal set. Based on this experimental observation, the presence of rapid conformational equilibria between different seven-membered chelate species seems to be highly unlikely.

In compounds [Rh(COD)(**L1-L4**)]BF_4, having 7-membered chelate ring, the ligand backbones adopt identical conformation that can be deduced from the very similar chemical shifts and coupling patterns of the backbone protons. Compound **L7** also forms 7-membered chelate upon coordination to the Rh(I)-center. This is most obvious from the significant coordination shift of the corresponding signals relative to the free ligand in the ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra and the characteristic $^1J(^{103}Rh$-$^{31}P)$ = 153.2 Hz coupling constant. Additionally, a single crystal suitable for X-ray diffraction analysis could be grown by the slow evaporation of solution of [Rh(COD)(**L7**)]BF_4 in CD_2Cl_2. The coordination sphere of the seven-membered Rh-S,NP chelate has a strongly distorted square planar geometry (Fig. 4).

A search of the Cambridge Structural Database (Ver. 5.43, Update November, 2022) [23] for [Rh(COD)(P,S)]$^+$ type coordination compounds showed that our structure has somewhat longer Rh-S and Rh-P distances, 2.3809(19) and 2.3111 (18) Å, respectively, compared to the average values 2.35(3) and 2.29(3) Å, respectively.

The large differences in the Rh-carbon bond distances *trans* to the P and S atoms (~0.1 Å) illustrate the distinct *trans* influence of the aminophosphine and thioether sites. In the distorted boat-like seven-membered chelate ring the coordinated sulfur donor has (*S*)-configuration with pseudo axially disposed Ph-substituent. The nitrogen atom has a trigonal planar geometry with bond angles of C5-N5-P6 120.0(5)°, C5-N5-C4 122.0(6)° and C4-N5-P6 117.9(5)° around it and the P-N bond length is 1.666(6) Å. These are clear indications that the P-N bond has a considerable double bond character. The torsion angles C20-C2-C3-C4 (176.96°) and C40-C4-C3-C2 (179.23°) in the pentane-2,4-diyl moiety are very close to 180° (Fig. 4). In other words, the pentane-2,4-diyl

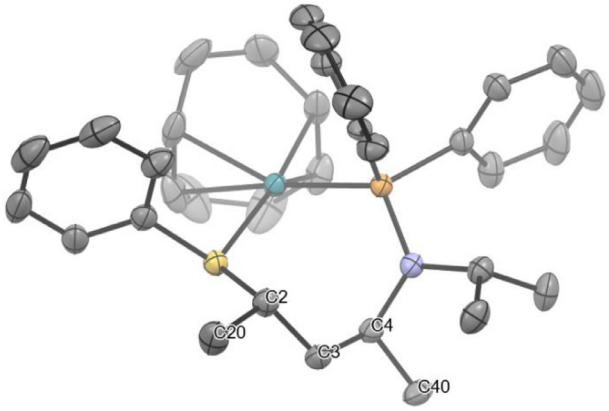


Fig. 4. X-ray structure of [Rh(COD)(L7)]BF4 (ORTEP view at 30% probability level, hydrogen atoms and BF4– counter anion are omitted for clarity).

framework adopts a nearly planar zig-zag conformation so that both methyl groups are directed pseudo equatorially in the chelate. It is important to note that the same arrangement of the backbone has been observed for an uncoordinated pentane-2,4-diyl based phosphine-phosphoramidite ligand in the solid phase [24] and for the [Pd(**L**)Cl_2] type complex of ligand **L7** both in the solid and solution phases [19]. Based on these observations, it is reasonable to assume that the nearly planar backbone conformation is an intrinsic feature of bidentate pentane-2,4-diyl based systems containing P-N moiety and therefore also preferred in [Rh(COD)(**L**)]$^+BF_4^-$ type complexes of phosphine-aminophosphines **L1**-**L4**.

Interestingly, the reaction of ligand **L6** with one molar equiv. of [Rh(COD)$_2$]BF_4 in CH_2Cl_2 resulted in the formation of a mixture complexes. It is most obvious from the $^{31}P\{^1H\}$ NMR spectrum that exhibits four signals at 92.98, 91.61, 67.13 and 22.06 ppm, instead of two resonances as was observed for compounds [Rh(COD)(**L1-L5**)]BF_4. The signals are relatively well-resolved doublet of doublets except for the one at 91.61 ppm that is considerably broader displaying a doublet coupling pattern. The significant chemical shift difference between the ^{31}P resonances

Table 1
ν(CO) values of $[Rh(CO)_2(L)]^+BF_4^-$ type dicarbonyl complexes[a].

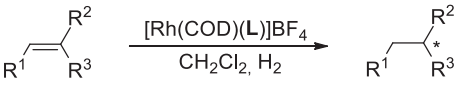
$[Rh(CO)_2(\mathbf{L})]^+BF_4^-$	ν(CO) (cm^{-1})	ν(CO) (cm^{-1})
L1	2098	2052
L2	2097	2052
L3	2096	2051
L4	2091	2041
L5	2098	2054
L7	2106	2052

[a] The IR spectra were recorded in CH_2Cl_2 as solvent.

relative to the free ligand and the multiplicity of the signals indicate that the phosphorus atoms are involved in coordination to the metal. Furthermore, the coupling pattern of the signals strongly suggests the presence of multiple species in solution. (Obviously, the formation of multimetallic species cannot be excluded either.) Unfortunately, the exact structural characterization of these species could not be performed due to the significant overlap of the signals in the ^{1}H NMR spectrum. Nevertheless, it is clearly proved that unlike ligands **L1**-**L5**, compound **L6** having five atoms between its coordinating phosphorus donors does not take part in a similar selective complex formation with $[Rh(COD)_2]BF_4$.

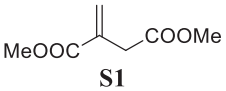
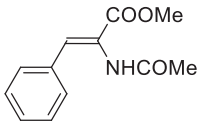
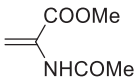
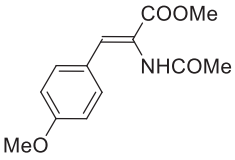
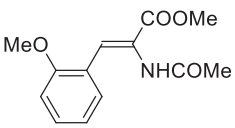
In order to estimate the electronic effect of the ligands on the Rh(I) center, infrared analysis of the ν(CO) bands of ionic $[Rh(CO)_2(\mathbf{L})]BF_4$ complexes was performed [25]. The Rh-carbonyl compounds were prepared by treating the corresponding $[Rh(COD)(\mathbf{L})]BF_4$ complex with 1 atm CO in CH_2Cl_2. The substitution of the diene by two CO ligands occurred smoothly within minutes that was shown by a color change of the solutions from orange (or bright yellow in the case of $[Rh(COD)(\mathbf{L7})]BF_4$) to pale yellow. As compounds $[Rh(CO)_2(\mathbf{L})]BF_4$ proved to be stable only under a protective CO atmosphere, their IR analysis was carried out in CH_2Cl_2 solution without any workup. The IR spectra of the complexes showed two strong ν(CO) bands of similar intensity in the ranges of 2091-2106 and 2041-2054 cm^{-1}, corresponding to the symmetric and antisymmetric vibrational modes of the CO ligands, respectively (Table 1). The number, position and intensity of the

Table 2
Asymmetric hydrogenation of dimethyl itaconate (S1) and dehydroaminoacid derivatives (S2-S5)[a]



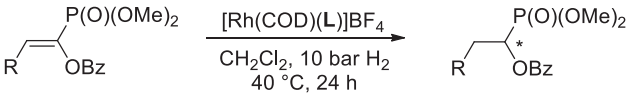
S1-S5

S1 R^1 = H; R^2 = CH_2COOMe; R^3 = COOMe
S2 R^1 = Ph; R^2 = COOMe; R^3 = NHCOMe
S3 R^1 = H; R^2 = COOMe; R^3 = NHCOMe
S4 R^1 = 4-MeO-C_6H_4; R^2 = COOMe; R^3 = NHCOMe
S5 R^1 = 2-MeO-C_6H_4; R^2 = COOMe; R^3 = NHCOMe.

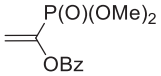
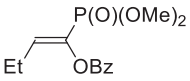
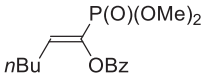
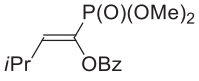
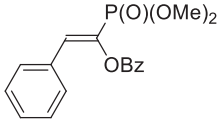
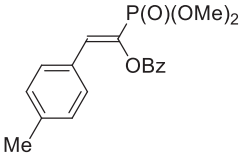
Entry	Ligand	Substrate	Conv. (%)[b]	Ee (%) (config.)[b]
1	**L1**	 **S1**	>99	30 (*R*)
2	**L2**		>99	6 (*R*)
3	**L3**		>99	24 (*R*)
4	**L4**		>99	57 (*R*)
5	**L5**		95	7 (*S*)
6	**L6**		9	36 (*S*)
7	**L7**		1	n.d.
8	**L1**	 **S2**	>99	91 (*R*)
9	**L2**		>99	92 (*R*)
10	**L3**		>99	93 (*R*)
11	**L4**		>99	92 (*R*)
12	**L5**		>99	74 (*R*)
13	**L6**		23	12 (*R*)
14	**L7**		2	n.d.
15	**L1**	 **S3**	>99	72 (*R*)
16	**L2**		>99	63 (*R*)
17	**L3**		>99	68 (*R*)
18	**L4**		>99	83 (*R*)
19	**L3**	 **S4**	>99	98 (*R*)
20	**L3**	 **S5**	>99	98 (*R*)

[a] Reaction conditions: catalyst: 0.0025 mmol of $[Rh(COD)(\mathbf{L})]BF_4$, substrate: 0.25 mmol, solvent: 1 mL CH_2Cl_2, temperature: RT, H_2 pressure: 5 bar, reaction time: 1 h.
[b] Conversion and *ee* was determined by chiral GC.

Table 3
Asymmetric hydrogenation of α,β-unsaturated enol ester phosphonates[a]



S6 R = H
S7 R = Et
S8 R = *n*Bu
S9 R = *i*Pr
S10 R = Ph
S11 R = 4-Me-C_6H_4.

Entry	Ligand	Substrate	Conv. (%)[b]	Ee (%)[b]
1	**L1**	 **S6**	>99	97
2	**L2**		>99	97
3	**L3**		>99	89
4	**L4**		>99	68
5	**L5**		>99	47
6	**L1**	 **S7**	>99	88
7	**L1**	 **S8**	>99	91
8	**L1**	 **S9**	42	85
9	**L1**	 **S10**	95	64
10	**L1**	 **S11**	82	55

[a] Reaction conditions: catalyst: 0.0025 mmol of [Rh(COD)(**L**)]BF_4, substrate: 0.25 mmol, solvent: 1 mL CH_2Cl_2, temperature: 40°C, H_2 pressure: 10 bar, reaction time: 24 h.
[b] Conversions were determined by NMR, enantioselectivities were determined by chiral HPLC. The configuration of the predominant enantiomer is (*S*).

carbonyl stretching frequencies confirm the formation of square planar [$Rh(CO)_2$(**L**)]BF_4 complexes and support the *cis* disposition of the CO ligands (Fig. 3) [25]. As was expected, the CO stretching frequencies are lower in the carbonyl complex containing **L4** with PCy_2 moiety (2091, 2041 cm^{-1}) compared to **L1** having PPh_2 group (2098, 2052 cm^{-1}) in the aminophosphine moiety. These are consistent with the higher electron donating ability of **L4** compared to **L1**. In a similar manner, the observed values for the thioether functionalized system [$Rh(CO)_2$(**L7**)]BF_4 (2106, 2052 cm^{-1}) suggest a less electron rich metal compared to the complex containing **L3** (2096, 2051 cm^{-1}). Interestingly, neither the structure of the N-substituent nor the size of the chelate ring influenced the electron-donating properties of the ligands significantly.

2.3. Asymmetric hydrogenation

In the first set of experiments the Rh-catalysts were screened in the asymmetric hydrogenation of dimethyl itaconate (**S1**) and methyl acetamidocinnamate (**S2**) as benchmark substrates (Table 2, entries 1-14). The catalytic tests were carried out in dichloromethane as solvent using 1 mol% of [Rh(COD)(**L**)]BF_4 at room temperature under 5 bar hydrogen pressure. Generally, the catalysts provided much higher enantioselectivities in the asymmetric hydrogenation of **S2** compared to the reactions of **S1**. The highest enantioselectivities (>90%) could be achieved with pentane-2,4-diyl based complexes [Rh(COD)(**L1-L4**)]BF_4. Additionally, catalysts containing ligands with pentane-2,4- or butane-2,3-diyl based ligands (**L1**-**L4** or **L5**) gave full conversion in almost every case. Ligand **L7** with less electron donating SPh subunit or **L6** with non-selective coordinating ability formed less active and enantioselective catalysts in the above hydrogenation processes.

As phosphine-aminophosphine complexes [Rh(COD)(**L1-L4**)]BF_4 with pentane-2,4-diyl backbone afforded promising catalytic results in the hydrogenation of **S2**, we decided to broaden the scope of prochiral substrates. Although the hydrogenation of methyl acetamidoacrylate (**S3**) could be realized with complete conversion

(Table 2, entries 15-18), the enantioselectivity of the reactions were only moderate. The best *ee* (83%) in this reaction was achieved by **L4** containing PCy_2 coordinating moiety (entry 18). In contrast to **S3**, dehydroaminoacid esters **S4** and **S5** could be hydrogenated with complete conversion and excellent enantioselectivities (98% *ee* for both substrates) were obtained (entries 19 and 20). The comparison of the selectivities achieved in the hydrogenation of **S1**-**S5** suggest that the catalytic system is highly sensitive to the steric and electronic features of the substrate.

In order to test our newly synthesized catalysts in the reaction of a more challenging substrate class, the asymmetric hydrogenation of α,β-unsaturated enol ester phosphonates was investigated. An interesting feature of these substrates is the presence of a tetrahedrally arranged phosphorus moiety bonded to the olefinic carbon that makes hydrogenation reactions even more sensitive towards steric effects [26]. The hydrogenated products can be used as starting materials to the synthesis of optically active 1-hydroxyalkylphosphonates, an attractive class of biologically active compounds which have received a lot of attention in pesticide and enzyme chemistry [27].

The hydrogenation of **S6** with 1 mol% [Rh(COD)(**L1-L5**)]BF_4 took place smoothly in CH_2Cl_2 at 40°C under 10 bar hydrogen pressure (Table 3, entries 1-5). The catalysts with sterically less demanding N-substituent (**L1** and **L2** with Me and Et groups, respectively) provided outstanding enantioselectivities (97% *ee*) compared to that having *i*Pr subunit (**L3**). As the N-substituent seems to have no significant effect on the electronic properties of the Rh-center or the chelate ring conformation in Rh-COD complexes, the distinct enantioselectivities achieved by ligands **L1**/**L2** and **L3** can be explained by flexibility differences in the aminophosphine moiety. A similar relationship between the *ee* and the size of the N-substituent was found by Zheng and coworkers using BoPhoz and HHPhos type ligands in the asymmetric hydrogenation of phoshonates [16]. In our case, increasing the bulkiness of the aminophosphine moiety by changing the PPh_2 group to PCy_2 unit (**L1** vs. **L4**) or the reduction of the chelate size (**L3** vs. **L5**) resulted in a drop in enantioselectivity.

Encouraged by the high enantioselectivity achieved with **L1** we performed further catalytic studies in the asymmetric hydrogenation of phosphonate esters **S7**–**S11** (Table 3, entries 6-10). Interestingly, increasing the size of the β-substituent resulted in a decrease in both activity and enantioselectivity. According to these observations the catalytic system is highly sensitive towards the steric nature of the substrate. This is somewhat consistent with the fact that increasing the steric demand of the PR_2 unit in the aminophosphine moiety (PPh_2 vs. PCy_2) also results in a drop in enantioselectivity (Table 3, entries 1 and 4). Consequently, subtle changes in the steric demand of both the ligand and the substrate significantly affect the stereochemical outcome and activity of the catalytic reaction. The high modularity of this ligand class, however, may serve to overcome this difficulty and provide a useful tool to find the matching substrate-ligand combination as is exemplified by entries 1 and 2 in Table 3.

3. Conclusions

A highly modular synthetic approach suitable for the preparation of phosphine-aminophosphine (**L1**-**L6**) and thioether-aminophosphine (**L7**) ligands has been presented. The new ligands were prepared in the reaction of the parent aminophosphine with the corresponding chlorophosphine and the yield of the reaction proved to be strongly dependent on the steric congestion around the secondary amine functionality. The coordination chemistry of the ligands was studied by the NMR and IR analysis of their [Rh(COD)(**L**)]BF_4 and [$Rh(CO)_2$(**L**)]BF_4 type complexes, respectively, and in the case of [Rh(COD)(**L7**)]BF_4 by X-ray crystallography. It has been observed that the size of the chelate ring (6- vs. 7-membered) and the N-substituent do not significantly influence the electronic properties of the metal. Furthermore, the N-substituent seems to have no effect on the ring conformation either, that is assumed to be determined primarily by the planar arrangement of the homochiral pentane-2,4-backbone. Interestingly, ligand **L6** with hexane-2,5-diyl provided two complex species in its reaction with [$Rh(COD)_2$]BF_4. The novel Rh-complexes were tested in the asymmetric hydrogenation of a broad range of prochiral substrates including dimethyl itaconate, dehydroaminoacid derivatives and α,β-unsaturated enol ester phosphonates. For substituted acetamidocinnamic acid esters *ee*'s up to 98% could be obtained by using pentane-2,4-diyl based systems. In the case of phosphonate esters containing a sterically more demanding tetrahedral P(V) moiety catalysts with less bulky N-substituents provided good-to-high enantioselectivities (up to 97%).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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