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Ferrocenyliminophosphites as Easy-to-Modify Ligands for Asymmetric Catalysis

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Several N,P bidentate phosphite-type ligands derived from readily available ferrocene-based iminoalcohols were successfully used in Rh-catalysed hydrogenations and Pd-catalysed allylic substitutions of a variety of substrates. Moderate-to-high catalytic activities under standard conditions were observed, and the enantiomeric excess of the products were up to 97 %. Results obtained under systematic variation of the ligand parameters indicate that the enantioselectivity is largely determined by the nature of the phosphocentre and also by the substituent in the C*HN-fragment.

Introduction

The development of new groups of chiral ligands that can provide high activity and enantioselectivity in a wide range of asymmetric catalytic reactions remains a challenge of high importance. The minimum requirements for such a group of ligands include the following: broad reaction and substrate scope, broad variability in both steric and electronic parameters of the ligands and the direct and simple synthesis of ligands from inexpensive and readily available starting materials in a one-pot synthesis.[1] A series of optically active phosphites completely satisfies these criteria. In general, the most important advantages of chiral phosphites include their pronounced π-acidity, their oxidation stability, as well as their synthetic availability and low cost.[2] Indeed, the induction ability of a common PPh_2 fragment of phosphane-type systems can be modulated only through the introduction of an electron-donating or electron-withdrawing substituent into available positions of the phenyl ring. As for the phosphites, they provide the possibility of using a much more efficient method, that is, the replacement of carbon atoms in the first coordination sphere of the phosphorus by heteroatoms (oxygen and/or nitrogen), which allows one to modify accurately the chemical stability of the ligand, its donor–acceptor capability and steric requirements. Most phosphites can be synthesised rather simply and in high yield from a variety of optically active precursors. Usually, it is possible to perform direct one-pot phosphorylation of suitable chiral compounds, whereas the synthesis of the corresponding phosphane derivatives involves several steps. In addition, phosphites exhibit higher oxidative stability because of the absence of P–C bonds. In many cases, protocols for a catalytic process can be developed that do not involve the use of a glove box, including the ligand synthesis.

As for the variety of catalytic reactions, groups of ligands that can be equally used in both Pd-catalysed asymmetric allylic substitutions and Rh-catalysed asymmetric hydrogenations are of special interest. Indeed, allylic substitution is a versatile and widely used process in organic synthesis that can result in the enantioselective formation of carbon–carbon and carbon–heteroatom bonds; similarly, hydrogenation is a highly attractive strategy for the synthesis of optically active organic molecules that are of enormous academic and/or industrial interest. The search for multipurpose ligands has been especially fruitful among chiral bifunctional compounds incorporating P and N donor groups, in particular, oxazolinophosphites.[3] In fact, TADDOL- and diamine-based oxazolinophosphites proved to be efficient in both Pd-catalysed allylations and Ir-catalysed hydrogenations.[4]

Meanwhile, phosphites with a peripheral imino group can be supposed to present another attractive alternative. Like oxazolinophosphites, they contain a chiral unit with the sp^2-hybridised donor nitrogen atom, but, unlike hy-

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droxyoxazolines, they can be produced from a more diverse and accessible class of synthons, namely, iminoalcohols. Among the iminophosphites, of special interest are those bearing a bulky ferrocenylidene substituent on the side arm. The ferrocene nucleus makes the ligands more stable, structurally rigid and easy to modify.[5] In recent years, we have designed a wide variety of chelating ferrocenyliminophosphites (Figure 1). Optimisation of their structures has produced good and excellent results in some Pd-catalysed allylic transformations.[6] For example, the ligands afforded up to 82% *ee* in the alkylation of ethyl 3-penten-2-yl carbonate (so-called "unmanageable" substrate) and up to 97% *ee* in the alkylation of the well-known substrate 1,3-diphenyl-2-propenyl acetate.

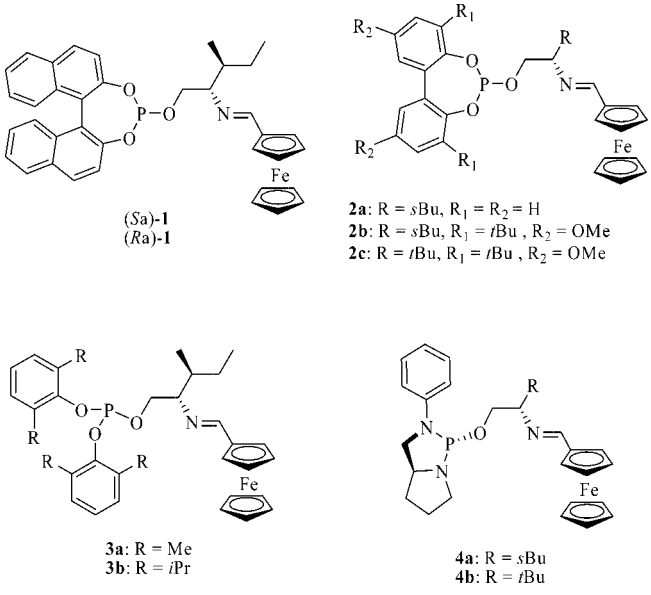


Figure 1. Some efficient N,P-bidentate chiral ferrocenyliminophosphites.

In this paper, we describe in detail the application of these and some new ligands of the same type in other benchmark tests, namely, Rh-catalysed hydrogenation of several prochiral olefins and Pd-, Rh- and Ir-catalysed allylic substitution of mono- and disubstituted substrates with different nucleophiles. The highly modular construction of the ferrocenyliminophosphites allows us to study its catalytic activity and selectivity on the basis of the contributions from the three main ligand components: (1) the effect of the configuration of the binaphthyl groups, (2) the effect of substituents at the asymmetric carbon atom in the ligand bridge and (3) the effect of substituents in the biaryl and phenyl groups. By carefully selecting these elements, we achieved high enantioselectivities for several catalytic reactions.

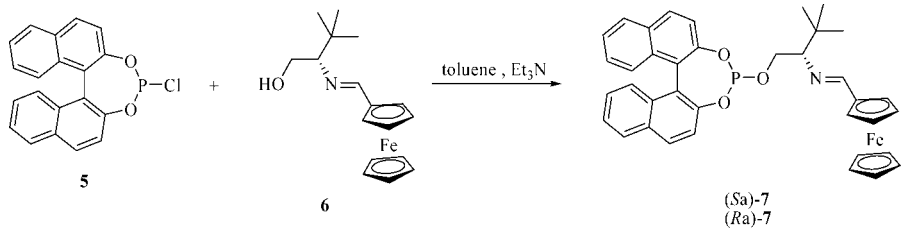
Results and Discussion

In addition to the previously reported (*S*a)-**1** and (*R*a)-**1**,[6a] new ligands were prepared to enlarge the palette of the ligand family (Scheme 1).

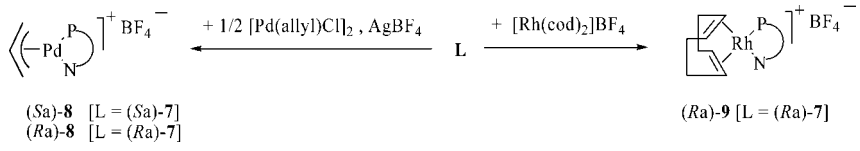
Direct phosphorylation of iminoalcohol **6** with reactant **5** readily provided ferrocenyliminophosphites (*S*a)-**7** and (*R*a)-**7**. These compounds are orange-red powders and can be exposed to the air for several months without any change to their ^{1}H or ^{31}P NMR spectra or any loss in their catalytic activity and enantioselectivity. It should be noted that compound **6**, similar to other iminoalcohols, exists in organic solvents in equilibrium with its corresponding oxazolidine tautomer.[6e,7] Nevertheless, the phosphorylation reaction proceeds selectively and no phospha derivatives of oxazolidine were detected in the reaction products.

With the intent to use ligands (*S*a)-**7** and (*R*a)-**7** in catalytic allylic substitution and hydrogenation reactions, we first studied their interaction with the appropriate catalyst precursors (Scheme 2).

As previously reported in the case of ligand (*R*a)-**1**,[6a] the reactions between $[Pd(allyl)Cl]_2$ and stoichiometric amounts of chiral iminophosphites (*S*a)-**7** or (*R*a)-**7** in the presence of a chloride scavenger such as $AgBF_4$ provided corresponding cationic complexes (*S*a)-**8** and (*R*a)-**8**. Duplication of peaks in the ^{31}P NMR spectra of compounds



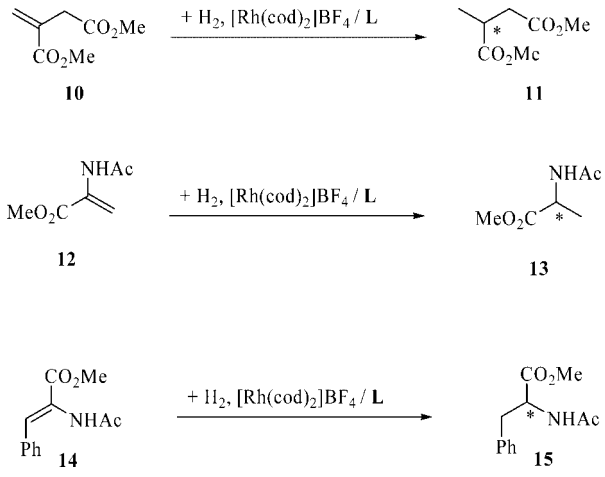
Scheme 1.



Scheme 2.

(*Sa*)-**8** and (*Ra*)-**8** [δ_P = 146.3 (28%) and 145.2 (72%); 141.8 (36%) and 140.5 (64%) ppm, respectively, in $CDCl_3$] indicates the presence of their *exo* and *endo* isomers.[6] Similarly, in the rhodium cationic complex (*Ra*)-**9**, iminophosphite (*Ra*)-**7** acts as a *cis*-chelating N,P ligand (Scheme 2). Thus, the ^{31}P NMR spectrum of (*Ra*)-**9** (in $CDCl_3$) shows a doublet at δ_P = 136.4 ppm with $^1J_{P,Rh}$ = 262.3 Hz. As shown by ^{13}C NMR spectroscopy (see Experimental Section), the 1,5-cyclooctadiene ligand is a part of complex (*Ra*)-**9**. Noteworthy is the asymmetric arrangement of this ligand, which manifests itself in the fact that each carbon atom exhibits its own signal. This seems to be due to the influence of the bulky organophosphorus ligand, which causes a distortion of the geometry of the metal complex.[6f] Comparison of the ^{13}C NMR spectral parameters of the free and coordinated (*Ra*)-**7** revealed substantial downfield coordination shifts of the signals for the CH=N carbon atom ($\Delta\delta_C$ = 12.1 ppm). As in the case of complexes (*Sa*)-**8** and (*Ra*)-**8**, chelate formation was also inferred from the MALDI TOF/TOF MS spectrum, which showed the expected $[M - BF_4^-]^+$ peak.

With ferrocenyliminophosphites in hand, we then examined the Rh-catalysed asymmetric hydrogenation of some α-dehydrocarboxylic acid esters as standard substrates (Scheme 3).



Scheme 3.

We first examined the transformation of itaconate **10** to succinate **11**. Ligands (*Sa*)-**1**, (*Ra*)-**1** and (*Sa*)-**7**, (*Ra*)-**7** containing different enantiomerically pure binaphthyl moieties were tested in detail. The cationic rhodium complexes were prepared in situ by mixing the well-known catalyst precursor $[Rh(cod)_2]BF_4$ with 1 or 2 equiv. of the ligand under an atmosphere of argon in CH_2Cl_2. As shown in Table 1, the configuration of the binaphthyl moieties determines the absolute configuration of product **11**. Ligands **1** and **7** containing (*R*)-binaphthyl moieties produced product (*R*)-**11** with enantioselectivity up to 88%, whereas the same ligands containing (*S*)-binaphthyls produced product (*S*)-**11** in lower enantioselectivity (not higher than 66%). These results indicate a cooperative effect between the configuration of the binaphthyl moieties and the configuration of the *C** stereocentre, which results in a matched combination for iminophosphites (*Ra*)-**1** and (*Ra*)-**7**. Ligand (*Ra*)-**7** with the *tert*-butyl substituent provided higher yields and *ee*'s of the product than its isomer (*Ra*)-**1** (Table 1, Entries 2, 3 and 6, 7). Variation of the ligand-to-rhodium ratio from 1 to 2 shows that no excess of the ligand is needed to reach good activities and enantioselectivities of the catalyst.

Table 1. Rh-catalysed hydrogenation of α-dehydrocarboxylic acid esters (CH_2Cl_2, 1.3 bar H_2, 20 °C, 20 h, molar ratio of substrate/metal, 1000/1).

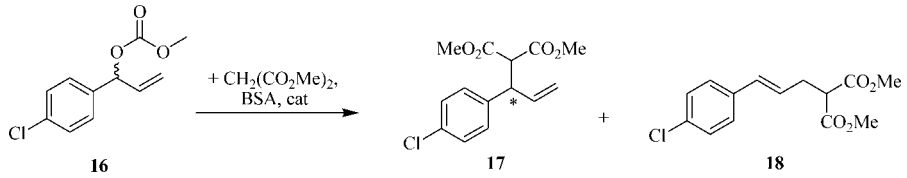
Entry	Ligand	Substrate	L/Rh	Conv. [%]	*ee* [%]
1	(*Sa*)-**1**	**10**	1	93	65 (*S*)
2	(*Ra*)-**1**	**10**	1	25	80 (*R*)
3	(*Ra*)-**1**	**10**	2	5	12 (*R*)
4	(*Sa*)-**7**	**10**	1	19	66 (*S*)
5	(*Sa*)-**7**	**10**	2	17	64 (*S*)
6	(*Ra*)-**7**	**10**	1	67	88 (*R*)
7	(*Ra*)-**7**	**10**	2	22	80 (*R*)
8	**3b**	**10**	1	11	3 (*R*)
9	**3b**	**10**	2	9	18 (*R*)
10	(*Sa*)-**1**	**12**	1	40	79 (*R*)
11	(*Ra*)-**1**	**12**	1	25	95 (*S*)
12	(*Ra*)-**1**	**12**	2	0	–
13	(*Sa*)-**7**	**12**	1	20	49 (*R*)
14	(*Sa*)-**7**	**12**	2	5	2 (*R*)
15	(*Ra*)-**7**	**12**	1	81	97 (*S*)
16	(*Ra*)-**7**	**12**	2	31	94 (*S*)
17	**3b**	**12**	1	5	5 (*R*)
18	**3b**	**12**	2	4	3 (*R*)
19	(*Ra*)-**1**	**14**	1	62	86 (*S*)
20	(*Sa*)-**7**	**14**	1	17	63 (*R*)
21	(*Sa*)-**7**	**14**	2	12	50 (*R*)
22	(*Ra*)-**7**	**14**	1	85	92 (*S*)
23	(*Ra*)-**7**	**14**	2	95	92 (*S*)
24	**3b**	**14**	1	5	5 (*R*)
25	**3b**	**14**	2	4	2 (*R*)

The same dependences were also observed in the Rh-catalysed hydrogenation of methyl 2-acetamidoacrylate **12** (Table 1, Entries 10–16). In this case, there is a matched combination of the (*R*)-binaphthyl moieties in addition to the (*S*)-*C** stereocentre in the ligand backbone. The use of iminophosphite (*Ra*)-**7** showed an excellent optical yield (97%, Table 1, Entry 15) for product **13**.

Analogously, ligands with the (*R*)-binaphthyl moieties (Table 1, Entries 19–23) were found to be the best stereoinductors in the Rh-catalysed hydrogenation of methyl (*Z*)-2-acetamido-3-phenylacrylate (**14**; Scheme 3). The highest enantioselectivity, up to 92%, was shown by ligand (*Ra*)-**7**. Unfortunately, ferrocenyliminophosphite **3b** without binaphthyl moieties produced the reaction products as an almost racemic mixture of the enantiomers, along with very poor conversions of the starting materials.

To further study the potential of ferrocenyliminophosphites, we also tested them in the Pd-catalysed allylic alkylation of the monosubstituted substrate 1-(4-chlorophenyl)-allyl methyl carbonate (**16**) with dimethyl malonate (Scheme 4).

For such substrates, as well as for controlling the enantioselectivity of the process, the regioselectivity is also of concern, because a mixture of regioisomers can be



Scheme 4.

formed. Most palladium catalysts developed to date favour the formation of the achiral linear products rather than the desired branched isomers. The development of highly regio- and enantioselective palladium catalysts is still a challenge.[8] Our results are summarised in Table 2. The efficiency of ferrocenyliminophosphites with binaphthyl moieties in Pd-catalysed allylic alkylation differs from that for Rh-catalysed hydrogenation. So, the Pd catalysts prepared from the novel ligands (*S*a)-**7** and (*R*a)-**7** exhibited moderate-to-good activity but only moderate regio- and enantioselectivity (up to 58%; Table 2, Entry 4), and (*S*a)-**7** was more enantioselective. Cationic complex [Pd(allyl){(*S*a)-**1**}]-BF_4 with the *sec*-butyl substituent provided excellent chemical and good optical yields (96 and 75%, respectively; Table 2, Entry 1), though with poor regioselectivity. Unlike this complex, its epimer, [Pd(allyl){(*R*a)-**1**}]BF_4, provided notably lower asymmetric induction (Table 2, Entry 1 vs. 3).

Excellent regioselectivity but low chemical and optical yields were found in the Rh-catalysed allylic alkylation of **16** with the use of (*R*a)-**7** (Table 2, Entries 10–12). The Ir-catalysed reactions led to the formation of isomer **17** with a moderate enantioselectivity (up to 51%; Table 2, Entries 13 and 14).

Iminophosphites **3a**,**b** with 2,6-disubstituted phenyl moieties were found to be more efficient in Pd-catalysed reactions, and they showed good activity and moderate regioselectivity. Enantioselectivity is directly governed by the substituents at the *ortho* positions. Thus, **3a** gave rise to *ee*'s up to 62% and **3b** up to 80% (Table 2, Entries 19 and 20). The nature of the counterion in the palladium complex also exerts a substantial effect, and in fact, for **3a** and **3b** it is opposite (Table 2, Entries 17 and 19, 20 and 22). Unfortunately, the presence of the biphenyl moieties in ferrocenyliminophosphite **2b** negatively effected both the regio- and enantioselectivity (Table 2, Entries 15 and 16). Interestingly,

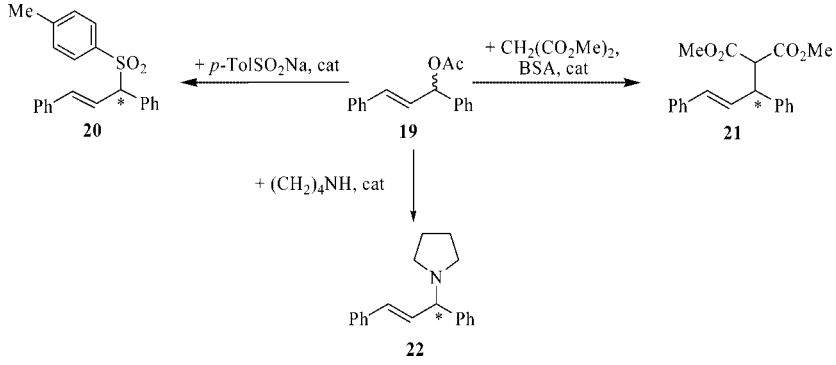
Table 2. Pd, Rh and Ir-catalysed allylic alkylation of **16** with dimethyl malonate (CH_2Cl_2, BSA, KOAc, 20 °C, 48 h, molar ratio of substrate/metal, 25).

Entry	Catalyst	L/M	Isolated yield of **17** and **18** [%]	**17**/**18**	*ee* **17** [%]
1	[Pd(allyl){(*S*a)-**1**}]BF_4	1	96	21:79	75 (*R*)
2[a]	[Pd(allyl){(*S*a)-**1**}]BF_4	1	69	17:83	4 (*R*)
3	[Pd(allyl){(*R*a)-**1**}]BF_4	1	92	56:44	47 (*R*)
4	[Pd(allyl)Cl]$_2$/(*S*a)-**7**	1	62	32:68	58 (*R*)
5	[Pd(allyl)Cl]$_2$/(*S*a)-**7**	2	85	25:75	19 (*R*)
6	(*S*a)-**8**	1	71	26:74	53 (*R*)
7	[Pd(allyl)Cl]$_2$/(*R*a)-**7**	1	92	52:48	34 (*R*)
8	[Pd(allyl)Cl]$_2$/(*R*a)-**7**	2	57	44:56	18 (*S*)
9	(*R*a)-**8**	1	91	44:56	43 (*R*)
10	[Rh(cod)Cl]$_2$/(*R*a)-**7**	1	15	95:5	16 (*R*)
11	[Rh(cod)Cl]$_2$/(*R*a)-**7**	2	34	95:5	21 (*R*)
12	(*R*a)-**9**	1	10	91:9	17 (*R*)
13	[Ir(cod)Cl]$_2$/(*R*a)-**7**	1	52	>99:1	51 (*R*)
14	[Ir(cod)Cl]$_2$/(*R*a)-**7**	2	88	99:1	45 (*R*)
15	[Pd(allyl)Cl]$_2$/**2b**	1	92	19:81	15 (*R*)
16	[Pd(allyl)Cl]$_2$/**2b**	2	84	23:77	7 (*R*)
17	[Pd(allyl)Cl]$_2$/**3a**	1	37	39:61	49 (*R*)
18	[Pd(allyl)Cl]$_2$/**3a**	2	78	37:63	47 (*R*)
19	[Pd(allyl)(**3a**)]BF_4	1	86	45:55	62 (*R*)
20	[Pd(allyl)Cl]$_2$/**3b**	1	69	41:59	80 (*R*)
21	[Pd(allyl)Cl]$_2$/**3b**	2	78	41:59	75 (*R*)
22	[Pd(allyl)(**3b**)]BF_4	1	62	54:46	56 (*R*)

[a] In THF.

the cationic complex [Pd(allyl)**(4a)**]BF_4 produced regiospecific formation of linear isomer **18** in 90% yield. So, by varying the structure of the phosphocentre in ferrocenyliminophosphites the regioselectivity of the Pd-catalysed allylic alkylation of monosubstituted substrate **16** can be controlled.

In general, an 80% optical yield of the product in the Pd-catalysed allylic alkylation of 1-(4-chlorophenyl)allyl methyl carbonate (**16**) is rather high. Indeed, only poor stereoselectivity was found in the Pd-catalysed allylic alkylation of 1-



Scheme 5.

Table 3. Pd-catalysed allylic sulfonylation of **19** with pTolSO$_2$Na (THF, 20 °C, 48 h, molar ratio of substrate/metal, 25), allylic alkylation of **19** with dimethyl malonate (CH_2Cl_2, BSA, KOAc, 20 °C, 48 h, molar ratio of substrate/metal, 25) and amination of **19** with pyrrolidine (CH_2Cl_2, 20 °C, 48 h, molar ratio of substrate/metal, 25).

Entry	Catalyst	L/Pd	Conv. [%][a]	*ee* [%]
	Allylic sulfonylation			
1	[Pd(allyl)Cl]$_2$/(*S*a)-**1**	1	41[a]	5 (*S*)
2	[Pd(allyl)Cl]$_2$/(*S*a)-**1**	2	50[a]	5 (*S*)
3	[Pd(allyl){(*S*a)-**1**}]BF$_4$	1	45[a]	2 (*S*)
4	[Pd(allyl)Cl]$_2$/(*R*a)-**1**	1	35[a]	39 (*S*)
5	[Pd(allyl)Cl]$_2$/(*R*a)-**1**	2	53[a]	40 (*S*)
6	[Pd(allyl){(*R*a)-**1**}]BF$_4$	1	72[a]	55 (*S*)
7	(*S*a)-**8**	1	12[a]	6 (*S*)
	Allylic alkylation			
8	[Pd(allyl)Cl]$_2$/(*S*a)-**1**	1	45	50 (*S*)
9	[Pd(allyl)Cl]$_2$/(*S*a)-**1**	2	5	0
10	[Pd(allyl){(*S*a)-**1**}]BF$_4$	1	73	40 (*R*)
11	[Pd(allyl)Cl]$_2$/(*R*a)-**1**	1	87	19 (*R*)
12	[Pd(allyl)Cl]$_2$/(*R*a)-**1**	2	70	0
13	[Pd(allyl){(*R*a)-**1**}]BF$_4$	1	70	36 (*R*)
14	[Pd(allyl)Cl]$_2$/(*S*a)-**7**	1	98	29 (*R*)
15	[Pd(allyl)Cl]$_2$/(*S*a)-**7**	2	95	36 (*R*)
16	(*S*a)-**8**	1	97	3 (*S*)
17	[Pd(allyl)Cl]$_2$/(*R*a)-**7**	1	99	20 (*S*)
18	[Pd(allyl)Cl]$_2$/(*R*a)-**7**	2	79	5 (*S*)
19	(*R*a)-**8**	1	42	8 (*S*)
	Allylic amination			
20	[Pd(allyl)Cl]$_2$/(*S*a)-**1**	1	60	11 (*R*)
21	[Pd(allyl)Cl]$_2$/(*S*a)-**1**	2	48	10 (*R*)
22	[Pd(allyl){(*S*a)-**1**}]BF$_4$	1	90	60 (*R*)
23	[Pd(allyl)Cl]$_2$/(*R*a)-**1**	1	90	4 (*R*)
24	[Pd(allyl)Cl]$_2$/(*R*a)-**1**	2	50	0
25	[Pd(allyl){(*R*a)-**1**}]BF$_4$	1	37	0
26	[Pd(allyl)Cl]$_2$/(*S*a)-**7**	1	40	20 (*R*)
27	[Pd(allyl)Cl]$_2$/(*S*a)-**7**	2	70	20 (*R*)
28	[Pd(allyl)Cl]$_2$/(*R*a)-**7**	1	46	17 (*R*)
29	[Pd(allyl)Cl]$_2$/(*R*a)-**7**	2	96	26 (*R*)
30	[Pd(allyl)(**2b**)]BF$_4$	1	94	73 (*R*)

[a] Isolated yield of product **20**.

(4-substituted phenyl)allyl acetates with the use of oxazolinophosphite ligands for substrates with the electron-withdrawing substituents in the *para* position of the phenyl ring.[9]

We also investigated the Pd-catalysed allylic substitution of 1,3-diphenyl-2-propenyl acetate (**19**), which is widely used as a model substrate, with S-, C- and N-containing nucleophiles by using the chiral binol-based ferrocenyliminophosphites (Scheme 5).

Moderate enantioselectivity was achieved in all cases (up to 50–60%, Table 3). Ligand (*R*a)-**1** was found to be the most efficient in the allylic sulfonylation with p-TolSO$_2$Na, whereas ligand (*S*a)-**1** was the most efficient in both the alkylation with dimethyl malonate and the amination with pyrrolidine (Table 3, Entries 6, 8 and 22). In turn, ligands (*S*a)-**7** and (*R*a)-**7** are somewhat less efficient. In general, ferrocenyliminophosphites with binaphthyl moieties were found to be less efficient than **2a**–**c** with the biphenyl backbone. So, the amination with pyrrolidine with **2b** gave *ee* values up to 73% (Table 3, Entry 30), and the alkylation with dimethyl malonate with **2a**–**c** produced *ee* values up to 88%.[6c,6d] Acyclic iminophosphites **3a**,**b** and **4a**,**b** were found to be even more efficient; they gave rise to almost quantitative chemical and optical yields in the enantioselective Pd-catalysed C*–C and C*–S bond formation reactions with substrate **19**.[6e,6f]

Conclusions

Ferrocenyliminophosphites provided good results in different types of catalytic reactions (Figure 2). Ligands with binaphthyl moieties are obvious leaders in the Rh-catalysed asymmetric hydrogenation of α-dehydrocarboxylic acid esters. In the Pd-catalysed allylic alkylation of the monosub-

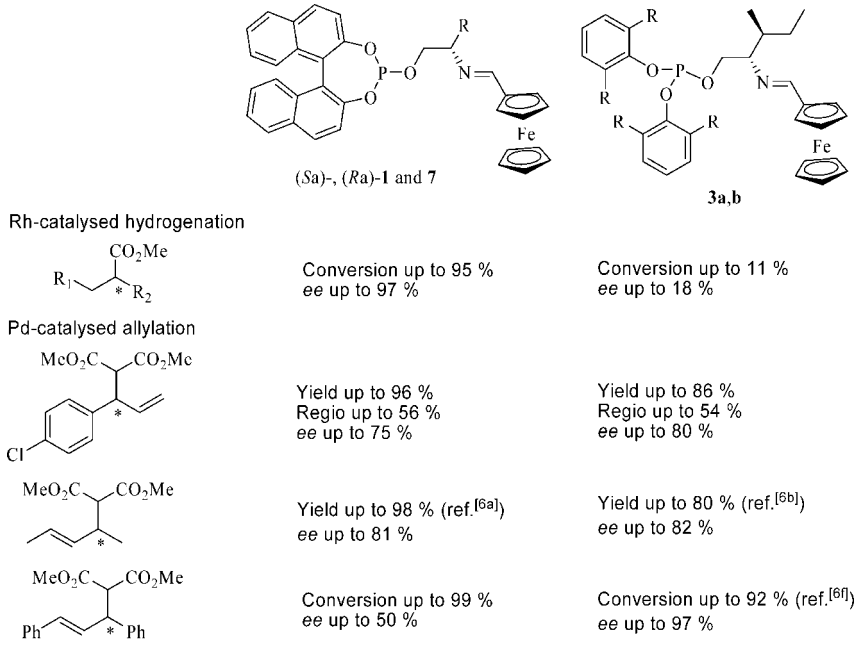


Figure 2. Summarised catalytic results for most widely investigated groups of the ferrocenyliminophosphites.

stituted substrate 1-(4-chlorophenyl)allyl methyl carbonate and the unhindered linear substrate ethyl 3-penten-2-yl carbonate the binol- and phenol-based acyclic iminophosphites produced very similar results. At the same time, in the Pd-catalysed allylic alkylation of 1,3-diphenyl-2-propenyl acetate the ligands with 2,6-disubstituted phenyl moieties were found to be much better stereoselectors and the best one was ligand **3a**.[6f] However, in contrast to the alkylation of **19**, for 1-(4-chlorophenyl)allyl methyl carbonate (**16**) enantioselectivities are higher when more sterically demanding substituents in the *ortho* positions of the phenyl rings are present (*i*Pr > Me). In addition, the iminophosphites with a biphenyl backbone **2a**–**c** were discovered to be less efficient than their binaphthyl analogues in the Pd-catalysed allylic alkylation of the monosubstituted and unhindered linear substrates and more efficient in the Pd-catalysed allylation of bulky substrate **19**.[6c,6d,6f]

In summary, we described the successful application of various ferrocenyliminophosphites in Rh-catalysed asymmetric hydrogenation and Pd-catalysed asymmetric allylic substitution reactions of several substrate types. To the best of our knowledge, this is the first example of iminophosphite-type ligands used in enantioselective Rh-catalysed hydrogenations. Ferrocenyliminophosphites have the advantage of being easily prepared in a few steps from inexpensive amino acids. In addition, they can easily be tuned so that the effect of varying the phosphocentre, different substituents and configurations of the binaphthyl moieties on the catalytic performance can be explored and adjusted. Good results can be achieved in different catalytic reactions by a careful selection of these structural components.

Experimental Section

General Remarks: ^{31}P, ^{13}C and ^{1}H NMR spectra were recorded with a Bruker AMX 400 instrument. Complete assignment of all the resonances in ^{13}C NMR spectra was achieved by DEPT techniques. Chemical shifts (ppm) are given relative to Me_4Si (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P NMR). Mass spectra were recorded with a Varian MAT 311 spectrometer (EI), a Finnigan LCQ Advantage spectrometer (electrospray ionisation technique, ESI) and a Bruker Daltonics Ultraflex spectrometer (MALDI TOF/TOF). Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow).

Conversion of substrates **10**, **12** and **14** and optical yields of products **11**, **13** and **15** were determined by using a methylsilicon column and chiral GC (column G-TA, column Hydrodex-*β*-TBDAc) and chiral HPLC (column Chiralpak-AD) according to the literature.[10] In the allylic alkylation of substrate **16**, the regioselectivity (**17**/**18** ratio) was measured by ^{1}H NMR and optical yields of product **17** were determined by HPLC (Daicel Chiralcel OD-H column) according to the literature.[11] Absolute configuration was determined by comparison with published data.[12] Optical yields of product **20** were determined by using HPLC [(*R*,*R*)-WHELK-01 column] according to the literature.[13] Conversion of substrate **19**[14] and the optical purities of products **21**[14] and **22**[15] were determined by using HPLC (Daicel Chiralcel OD-H column) as described previously.

All reactions were carried out under a dry argon atmosphere in freshly dried and distilled solvents; Et_3N and pyrrolidine were twice distilled from KOH and then over a small amount of $LiAlH_4$ before use. Ligands (*S*a)-**1**, (*R*a)-**1**,[6a] **2b**[6c]**3a**,[6b] **3b**,[6f] **4a**[6e] and their cationic *cis*-chelate complexes [Pd(allyl)(**L**)]BF_4 were prepared as described earlier. Phosphorylating reagent (*S*a)- or (*R*a)-2-chloro-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine (**5**)[16] and iminoalcohol (*2S*)-2-(ferrocenylideneamino)-3,3-dimethylbutan-1-ol (**6**)[6e] were synthesised by using literature procedures. $[Rh(cod)_2]BF_4$,[17] $[Rh(cod)Cl]_2$[18] and $[Pd(allyl)Cl]_2$[19] were prepared as described earlier. Cationic palladium complexes (*S*a)-**8** and (*R*a)-**8** were synthesised in a manner analogous to the known procedures.[6a] Catalytic experiments: allylic sulfonylation of substrate **19** with sodium *para*-toluenesulfinate, allylic alkylation with dimethyl malonate and allylic amination with pyrrolidine were performed according to the appropriate procedures.[20,21]

(*Z*)-Methyl 2-acetamido-3-phenylacrylate (**14**) was prepared as reported previously.[22] Starting substrates **16** and **19** were synthesised as published.[23,19] Dimethyl itaconate (**10**), methyl 2-acetamidoacrylate (**12**), dimethyl malonate, BSA [*N*,*O*–bis(trimethylsilyl)acetamide] and sodium *para*-toluenesulfinate were purchased from Aldrich and Acros Organics and used without further purification.

Preparation of Ligands. General Technique: A solution of iminoalcohol **6** (1.096 g, 3.5 mmol) in benzene (15 mL) was added dropwise at 0 °C to a vigorously stirred solution of chlorophosphite (*S*a)- or (*R*a)-**5** (1.228 g, 3.5 mmol) and Et_3N (0.49 mL, 3.50 mmol) in benzene (15 mL). The resulting mixture was warmed to 80 °C for a short time, then cooled down to 20 °C and filtered. The solvent was removed in vacuo (40 Torr), and the residue was extracted with boiling heptane (3 × 20 mL), filtered, evaporated and dried in vacuo (1 Torr, 2 h).

(2′*S*,*S*a)-2-[2′-(Ferrocenylideneamino)-3′,3′-dimethylbutoxy]dinaphtho[2,1-*d*:1′,2′-*f*](1,3,2)dioxaphosphepine [(*S*a)-7]: Yield: 1.603 g, 73%, orange-red solid. M.p. 87–89 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 0.89 (s, 9 H, CH_3), 2.91 (m, 1 H, NCH), 4.05 (m, 1 H, OCH_2), 4.19 (m, 1 H, OCH_2), 4.24 (s, 5 H, C_5H_5), 4.42 (br. s, 2 H, C_5H_4), 4.75 (t, ^{3}J = 1.2 Hz, 2 H, C_5H_4), 7.38 (m, 8 H, CH_{Ar}), 7.94 (m, 4 H, CH_{Ar}), 8.13 (s, 1 H, HC=N) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 161.7 (s, C=N), 149.0 (d, ^{2}J = 5.3 Hz, OC_{ipso}), 147.7, 132.3, 131.4, 130.7, 130.0, 129.8, 128.3, 128.0, 126.7, 126.4, 126.2, 124.9, 124.3, 124.1, 122.7, 122.6, 122.1, 121.9, 121.5 (C_{Ar}), 81.4 (s, $C_{Fc–ipso}$), 80.4 (d, ^{3}J = 2.9 Hz, NCH), 70.8, 69.2, 68.4, 67.7 (all s, C_{Fc}), 68.7 (s, C_{Cp}), 64.9 (d, ^{2}J = 6.6 Hz, OCH_2), 33.3 (s, C), 27.0 (s, CH_3) ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 143.4 ppm. MS (70eV, EI): *m*/*z* (%) = 627 (4) $[M]^+$, 543 (100) $[C_{31}H_{22}FeNO_3P]^+$, 268 (29) $[C_{15}H_{18}FeN]^+$. $C_{37}H_{34}FeNO_3P$ (627.2): calcd. C 70.82, H 5.46, N 2.23; found C 70.97, H 5.63, N 2.15.

(2′*S*,*R*a)-2-[2′-(Ferrocenylideneamino)-3′,3′-dimethylbutoxy]dinaphtho[2,1-*d*:1′,2′-*f*](1,3,2)dioxaphosphepine [(*R*a)-7]: Yield: 1.735 g, 79%, orange-red solid. M.p. 92–94 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 0.91 (s, 9 H, CH_3), 2.88 (m, 1 H, NCH), 4.09 (m, 1 H, OCH_2), 4.21 (s, 5H. C_5H_5), 4.23 (m, 1 H, OCH_2), 4.40 (br. s, 2 H, C_5H_4), 4.74 (t, ^{3}J = 1.2 Hz, 2 H, C_5H_4), 7.38 (m, 8 H, CH_{Ar}), 7.97 (m, 4 H, CH_{Ar}), 8.11 (s, 1 H, HC=N) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 162.0 (s, C=N), 148.9 (d, ^{2}J = 5.6 Hz, OC_{ipso}), 147.5, 132.3, 131.6, 130.4, 129.9, 129.7, 128.3, 127.8, 126.7, 126.6, 126.0, 124.6, 124.3, 123.9, 122.8, 122.4, 122.1, 121.9, 121.7 (C_{Ar}), 81.6 (s, $C_{Fc–ipso}$), 79.5 (d, ^{3}J = 2.8 Hz, NCH), 70.9, 69.2, 68.6, 68.1 (all s, C_{Fc}), 68.9 (s, C_{Cp}), 65.7 (d, ^{2}J = 6.5 Hz, OCH_2), 33.2 (s, C), 27.2 (s, CH_3) ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 142.5 ppm. MS (70eV, EI): *m*/*z* (%) = 627 (2) $[M]^+$, 543 (100) $[C_{31}H_{22}FeNO_3P]^+$, 268 (25) $[C_{15}H_{18}FeN]^+$. MS (MALDI TOF/TOF): *m*/*z* (%) = 628 (81) $[M + H]^+$, 544 (7) $[C_{31}H_{23}FeNO_3P]^+$, 314 (100) $[C_{17}H_{24}FeNO]^+$, 268 (18) $[C_{15}H_{18}FeN]^+$. $C_{37}H_{34}FeNO_3P$

(627.2): calcd. C 70.82, H 5.46, N 2.23; found C 71.02, H 5.59, N 2.35.

Palladium and Rhodium Complexes

[Pd(allyl){(*Sa*)-7}]BF_4 [(*Sa*)-8]: Yield: 92%, red powder. M.p. 108–110 °C (dec.). ^{13}C NMR (100.6 MHz, $CDCl_3$, selected data for allylic part): δ = 121.3 [d, ^2J = 9.2 Hz, CH (allyl)], 80.6 [d, ^2J = 43.1 Hz, CH_2 (allyl) *trans*-P], 54.1 [s, CH_2 (allyl) *trans*-N] ppm. MS (ESI): *m*/*z* (%) = 774 (100) $[M - BF_4]^+$, 733 (31) $[M - BF_4 -$ allyl$]^+$. MS (MALDI TOF/TOF): *m*/*z* (%) = 774 (100) $[M - BF_4]^+$, 733 (67) $[M - BF_4 -$ allyl$]^+$. $C_{40}H_{39}BF_4FeNO_3PPd$ (861.1): calcd. C 55.75, H 4.56, N 1.63; found C 55.60, H 4.28, N 1.85.

[Pd(allyl){(*Ra*)-7}]BF_4 [(*Ra*)-8]: Yield: 89%, red powder. M.p. 114–116 °C (dec.). ^{13}C NMR (100.6 MHz, $CDCl_3$, selected data for allylic part): δ = 120.9 [d, ^2J = 9.0 Hz, CH (allyl)], 80.8 [d, ^2J = 43.5 Hz, CH_2 (allyl) *trans*-P], 54.0 [s, CH_2 (allyl) *trans*-N] ppm. MS (MALDI TOF/TOF): *m*/*z* (%) = 774 (100) $[M - BF_4]^+$, 733 (51) $[M - BF_4 -$ allyl$]^+$. $C_{40}H_{39}BF_4FeNO_3PPd$ (861.1): calcd. C 55.75, H 4.56, N 1.63; found C 55.91, H 4.68, N 1.44.

(*Ra*)-9: A solution of ligand (*Ra*)-**7** (0.063 g, 0.1 mmol) in CH_2Cl_2 (5 mL) was added dropwise over 40 min to a vigorously stirred solution of $[Rh(cod)_2]BF_4$ (0.041 g, 0.1 mmol) in the same solvent (5 mL) at 20 °C. The reaction mixture was stirred at 20 °C for 1 h, concentrated under reduced pressure (40 Torr) to ca. 0.5 mL, and precipitated with ether. The obtained precipitate was separated by centrifugation, washed with diethyl ether (2 × 10 mL) and dried in air and in vacuo (1 Torr, 1 h).

[Rh(cod){(*Ra*)-7}]BF_4 [(*Ra*)-9]: Yield: 0.087 g, 94%, red-brown powder. M.p. 124–126 °C (dec.). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 174.1 (s, C=N), 149.7 (d, ^2J = 5.6 Hz, OC_{ipso}), 147.1, 132.4, 131.1, 130.5, 130.0, 129.5, 128.6, 127.1, 126.7, 126.3, 126.0, 124.5, 124.4, 123.9, 122.7, 122.4, 122.0, 121.8, 121.3 (C_{Ar}), 114.0 (dd, $^1J_{C,Rh}$ = 11.2 Hz, ^2J = 4.2 Hz) and 113.4 [dd, $^1J_{C,Rh}$ = 13.6 Hz, ^2J = 3.1 Hz, CH=(cod) *trans*-P], 81.9 (s, $C_{Fc-ipso}$), 81.1 (s, NCH), 80.2 (d, $^1J_{C,Rh}$ = 10.8 Hz), 74.8 [d, $^1J_{C,Rh}$ = 10.4 Hz, CH=(cod) *trans*-N], 69.9, 69.2, 68.4, 68.0 (all s, C_{Fc}), 68.8 (s, C_{Cp}), 66.0 (s, OCH_2), 34.7 (s, C), 34.2, 29.8, 29.3, 27.9 [all s, CH_2(cod)], 28.2 (s, CH_3) ppm. MS (MALDI TOF/TOF): *m*/*z* (%) = 838 (3) $[M - BF_4]^+$, 730 (100) $[M - BF_4 -$ cod$]^+$. $C_{45}H_{46}BF_4FeNO_3PRh$ (925.2): calcd. C 58.41, H 5.01, N 1.51; found C 58.66, H 5.13, N 1.56.

Catalytic Experiments

Rhodium-Catalysed Hydrogenation of α-Dehydrocarboxylic Acid Esters. General Procedure: A dry 50-mL Schlenk flask under an atmosphere of argon was charged with a mixture of a solution of the ligand (1.7 μM in CH_2Cl_2, 1.2 mL or 0.6 mL). A solution of $[Rh(cod)_2]BF_4$ (2.0 μM in CH_2Cl_2, 0.5 mL) was then added, and the mixture was stirred for 5 min at 20 °C. Then, a solution of the substrate (0.112 M in CH_2Cl_2, 9 mL) was added. Vacuum was applied three times until the solvent began to evaporate gently, and hydrogen was introduced. Hydrogenation was carried out at 1.3 bar for the periods given. Following dilution, conversion was determined by gas chromatography (GC). To determine the *ee* values, about 1.5 mL of the reaction solution was passed through a small amount of silica gel prior to the GC or HPLC analysis. The hydrogenation experiments were carried out in a parallel manner by using 10 or more flasks.

Pd-, Ir- and Rh-Catalysed Alkylation of 1-(4-Chlorophenyl)allyl Methyl Carbonate with Dimethyl Malonate. General Procedure: The precatalyst (0.01 mmol) and the corresponding chiral ligand (0.02–0.04 mmol) were dissolved in CH_2Cl_2 (5 mL) and stirred at 20 °C for 40 min [or a presynthesised transition metal complex with a chiral ligand (0.02 mmol) was dissolved in CH_2Cl_2 (5 mL)]. An allyl substrate (0.50 mmol) was added to the solution, and the mixture was stirred for 20 min followed by the addition of dimethyl malonate (0.75 mmol), BSA (0.75 mmol) and KOAc (2.0 mg). The reaction mixture was stirred for 48 h at 20 °C, and the solvent was evaporated. The products were separated by column chromatography (silica gel; 200 × 17 mm; hexane/EtOAc, 9:1). The fractions containing a mixture of regioisomers **17** and **18** were combined and the solvents evaporated. The residue was used for determination of the **17**/**18** ratio and optical purity of product **17** as mentioned above.

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