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Bulky *P**-Chirogenic Diazaphospholidines as Monodentate Ligands for Asymmetric Catalysis

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A series of easily prepared bulky *P**-chiral diamidophosphites based on (2*R*,5*S*)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane and (2*R*,5*S*)-3-(*p*-bromophenyl)-1,3-diaza-2-phosphabicyclo[3.3.0]octane backbones have been designed and developed. Ligands of this type exhibited high enantioselectivities in Pd-catalysed allylic substitution reactions of (*E*)-1,3-diphenylallyl acetate with $NaSO_2p$Tol (up to 87 % *ee*), $CH_2(CO_2Me)_2$ (up to 92 % *ee*), $(C_3H_7)_2NH$ (up to 93 % *ee*) and $(CH_2)_4NH$ (up to 99 % *ee*). These novel stereoselectors have also been successfully employed in Rh-catalysed asymmetric hydrogenations of dimethyl itaconate (up to 76 % *ee*), methyl (*Z*)-2-acetamido-3-phenylacrylate (up to 73 % *ee*) and methyl 2-acetamidoacrylate (up to 98 % *ee*). Cu-catalysed conjugate addition of diethylzinc to cyclohexenone leads to a maximum of 70 % *ee* with quantitative conversion.

Introduction

Asymmetric catalysis now provides one of the most cost-effective and environmentally responsible methods for the production of a truly vast array of structurally diverse, enantiomerically pure compounds. In addition to well-known pharmaceutical applications, asymmetric catalytic methods are being employed to great effect in the flavour and fragrance, agrochemical, animal health, polymer and liquid-crystal industries.[1] Rh-catalysed enantioselective hydrogenation, Pd-catalysed allylic substitution and Cu-catalysed conjugate addition represent a number of the major catalytic processes. Asymmetric catalytic hydrogenation of unsaturated bonds, employing dihydrogen and small amounts of transition-metal complexes modified intrinsically by chiral ligands, is now recognized as the most promising strategy for the synthesis of large amounts of optically pure products, and enormous progress has been achieved in this area.[2] Asymmetric allylic substitution has also been very intensely investigated. Besides a high level of asymmetric induction, the advantages of this method include its tolerance of a wide range of functional groups and a great flexibility in the type of bonds that can be formed. For example, H-, C-, N-, O-, and S-centred nucleophiles can be employed.[3] Enantioselective Cu-catalysed conjugate addition represents another powerful carbon–carbon bond-forming method. Significant advantages of this process are its high compatibility with many functional groups, the low cost of the copper salts and the often high regio- and enantioselectivities.[4] Because the design of chiral ligands plays a key role in the development of these metal-catalysed reactions, many recent studies have addressed the tuning of existing ligands and/or the development of novel chiral ligands. Optically active phosphite-type compounds play important roles here, because of their intrinsic electronic properties and steric variability. Indeed, various P–O and/or P–N bond containing phosphorus ligands may be constructed in large quantities through the use of relatively simple condensation processes, and from inexpensive starting materials. In addition, they are characterized by pronounced π-acidity and high oxidative stability.[5]

Phosphite-type ligands, in which the chiral centre exists at the phosphorus atom itself, are very promising. In their complexes, the chirogenic phosphorus atoms bind directly to the metal atom. This factor eliminates potentially inefficient secondary transfer of chirality from the ligand backbone and thus provides more efficient chiral environments at the sites where the enantioselection takes place.[2] Excel-

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lent results have thus been achieved in the Rh-catalysed hydrogenation of functionalized olefins with *P**-stereogenic phosphoramidites derived from *ortho*-substituted BINOL and (*S*)-diphenylprolinol.[6]

Note that *P**-chiral diazaphospholidines are one of the most attractive groups of optically active diamidophosphite ligands. In general, diazaphospholidines are good π-acceptor ligands, thanks to the availability of low-lying π^*_{PN} orbitals, and good σ-donor ligands. The inclusion of the phosphorus atom in a cyclic structure, in particular a five-membered ring, is a key feature, because it increases stability towards air and moisture. In addition, these ligands are modular in nature because the substituents at the nitrogen and the phosphorus atom can be varied.[7] Buono and co-workers, and more recently Gavrilov et al., have reported QUIPHOS-type ligands $\mathbf{L_A}$ and some other *P**,*N*-bidentate compounds (such as the iminophosphites $\mathbf{L_B}$ in Figure 1) derived from C_1-symmetric (2-anilinomethyl)pyrrolidine, which induced excellent enantioselectivities in Pd-catalysed allylic substitution.[8] At the same time, it was shown that mixed donor ligands containing heterodonor atoms with nitrogen and phosphorus functional moieties are not necessary for achieving high enantioselectivity, and that the *P**-monodentate diazaphospholidine stereoselectors $\mathbf{L_C}$ could also provide very good *ee*s in asymmetric allylation.[9] Nevertheless, such ligands with small exocyclic OR substituents (R = Me, *i*Pr) provide only disappointing stereodiscrimination (no more than 20% *ee*s) in the Cu-catalysed conjugate addition of diethylzinc to cyclohexenone and the Rh-catalysed hydrogenation of dimethyl itaconate.[10] Accordingly, careful selection and design of the novel $\mathbf{L_C}$-type monodentate ligands is currently a very relevant task. Here we examine whether the presence of bulky organic groups and/or chiral axes in the exocyclic substituents may be useful for improving catalytic outcomes in asymmetric reactions.

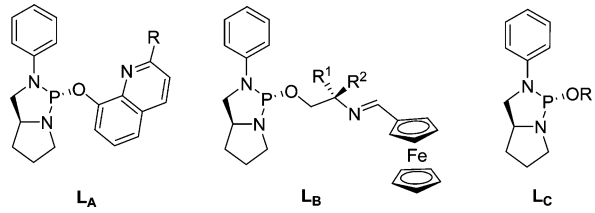
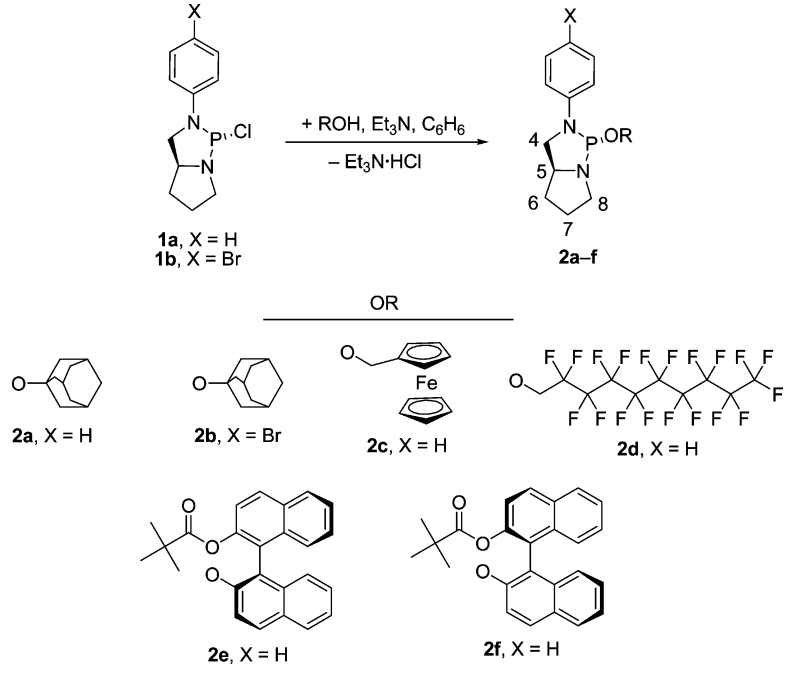


Figure 1. Examples of *P**,*N*-bidentate and *P**-monodentate diazaphospholidine ligands.

Results and Discussion

Novel *P**-monodentate diamidophosphites can be readily obtained in two steps from (*S*)-2-(anilinomethyl)pyrrolidine or (*S*)-2-(*p*-bromoanilinomethyl)pyrrolidine. In turn, these optically active diamines are easily accessible (in two and three steps, respectively) from L-glutamic acid.[11] The pyrrolidine compounds react with PCl_3 in benzene to yield the phosphorylating reagents **1a** and **1b**.[9a] Subsequent treatment of chlorodiamidophosphites **1a** or **1b** with appropriate alcohols in benzene leads to the desired compound **2a**–**f** (Scheme 1). The reactions require the presence of Et_3N as a base because of the concomitant formation of HCl. The starting alcohols are commercially available, with the exception of (*S*)- and (*R*)-1-(2-hydroxynaphthalen-1-yl)-naphthalen-2-yl pivalates, which are conveniently obtained by direct interaction between the appropriate enantiomer of



Scheme 1. Synthesis of *P**-chiral diazaphospholidines **2a**–**f**.

BINOL and pivaloyl chloride.[12] The novel ligands are stable enough to allow manipulation in open air and can be stored under dry conditions at room temperature over several months without any degradation. In addition, they are fairly stable in solutions in common organic solvents. For instance, the ^1H and ^{31}P NMR spectra of compound **2d**, recorded two months after its dissolution in $CDCl_3$, showed no signals of any decomposition products.

During the phosphorylation process, exclusive formation of the stereoindividual diamidophosphites **2c** and **2d** takes place, although the other ligands contain 16–33% of the second *P** epimers (Table 1). According to the literature data, compounds **2c** and **2d** and the major epimers of **2a**, **2b**, **2e** and **2f** each have the pseudoequatorial orientation of the exocyclic substituent at the phosphorus atom and a *cis* orientation between the lone pair of the phosphorus atom and C(8) [i.e., (*R*) configuration at the *P** stereocenter]. This was concluded from the large $^2J_{C(8),P}$ values (32.7–38.2 Hz) in their ^{13}C NMR spectra (see Experimental Section).[9a,11a,13] The minor (S_P) epimers of compounds **2a**, **2b**, **2e** and **2f** (Table 1) are each characterized by a *trans* orientation of the phosphorus lone pair to C(8) and, in consequence, minimal values of $^2J_{C(8),P}$ (3.4–4.4 Hz for **2a**, **2e** and **2f**; see ref.[9a] and Experimental Section).

Table 1. ^{31}P NMR chemical shifts ($CDCl_3$) and cone angles θ of ligands **2a**–**f**.

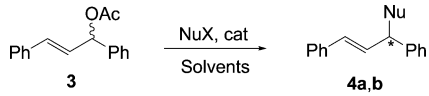
Ligand	δ_P [ppm]	θ [°]
(R_P)-**2a** (74%)[a]	126.7	168[b]
(S_P)-**2a** (26%)	112.3	
(R_P)-**2b** (84%)	125.7	170
(S_P)-**2b** (16%)	111.6	
(R_P)-**2c**	121.9	165
(R_P)-**2d**	124.1	174
(R_P)-**2e** (67%)	125.9	177
(S_P)-**2e** (33%)	117.9	
(R_P)-**2f** (73%)	129.7	197
(S_P)-**2f** (27%)	119.6	

[a] Percentage of *P** epimers. [b] Published data.[9a]

With a view to an estimation of the steric demands of **2a**–**f**, we calculated their Tolman cone angles[14] by the reported method using a semiempirical quantum-mechanical AM1 method with full optimization of geometrical parameters.[15] The obtained results show that **2a**–**e** are very bulky diazaphospholidines and that their steric parameters (θ) vary within the rather narrow interval of 165°–177° (Table 1). It is interesting that **2f** is an extremely bulky ligand (θ = 197°). For comparison, the Tolman angle for $P(C_6F_5)_3$ is 184° and that for P(*o*-Tol)$_3$ is 194°.[15,16]

With these sterically congested ligands to hand, we first chose to explore their reactivities and enantioselectivities in the Pd-catalysed allylic amination of (*E*)-1,3-diphenylallyl acetate (**3**, Table 2). On the one hand, this is a common benchmark test for novel groups of stereoselectors. On the other, it is also a highly efficient procedure for the preparation of optically active aromatic amines with stereocentres α to their nitrogen atoms. Such amines are important structural motifs in a number of biologically active compounds.[17] We first tested the new diazaphospholidines in the asymmetric allylic amination of **3** with dipropylamine as N-nucleophile, under standard conditions and in CH_2Cl_2 as solvent (Table 2). The catalysts were generated in situ from [Pd(allyl)Cl]$_2$ and the ligands at 1:1 and 2:1 ligand/palladium ratios. Compounds **2b** and **2c** displayed mediocre efficiency (no more than 67% *ee* and 41% conversion), whereas **2a** produced higher levels of reactivity and asym-

Table 2. Pd-catalysed allylic amination of (*E*)-1,3-diphenylallyl acetate (**3**).[a]



Nu = N(Pr)$_2$, X = H, **4a**
Nu = N(CH$_2$)$_4$, X = H, **4b**

Entry	Ligand	L/Pd	Solvent	Conv. [%]	*ee* [%]
Allylic amination with dipropylamine[b]					
1	**2a**	1:1	CH_2Cl_2	100	76 (+)
2	**2a**	2:1	CH_2Cl_2	100	74 (+)
3	**2b**	1:1	CH_2Cl_2	29	47 (+)
4	**2b**	2:1	CH_2Cl_2	41	67 (+)
5	**2c**	1:1	CH_2Cl_2	14	45 (+)
6	**2c**	2:1	CH_2Cl_2	21	46 (+)
7	**2d**	*1:1*	*CH_2Cl_2*	*99*	*93 (+)*
8	**2d**	2:1	CH_2Cl_2	100	90 (+)
9	**2e**	1:1	CH_2Cl_2	57	91 (+)
10	**2e**	2:1	CH_2Cl_2	68	90 (+)
11	**2f**	1:1	CH_2Cl_2	73	26 (+)
12	**2f**	2:1	CH_2Cl_2	93	59 (+)
Allylic amination with pyrrolidine[c]					
13	**2a**	1:1	CH_2Cl_2	100	85 (*R*)
14	**2a**	2:1	CH_2Cl_2	100	87 (*R*)
15	**2a**	1:1	THF	64	86 (*R*)
16	**2a**	2:1	THF	92	90 (*R*)
17	**2b**	1:1	CH_2Cl_2	70	74 (*R*)
18	**2b**	2:1	CH_2Cl_2	88	79 (*R*)
19	**2b**	1:1	THF	25	43 (*R*)
20	**2b**	2:1	THF	40	85 (*R*)
21	**2c**	1:1	CH_2Cl_2	100	75 (*R*)
22	**2c**	2:1	CH_2Cl_2	100	74 (*R*)
23	**2c**	1:1	THF	53	67 (*R*)
24	**2c**	2:1	THF	100	70 (*R*)
25	**2d**	1:1	CH_2Cl_2	100	94 (*R*)
26	**2d**	2:1	CH_2Cl_2	100	91 (*R*)
27	**2d**	1:1	THF	35	69 (*R*)
28	**2d**	2:1	THF	63	90 (*R*)
29	**2e**	1:1	CH_2Cl_2	73	74 (*R*)
30	**2e**	2:1	CH_2Cl_2	97	76 (*R*)
31	**2e**	1:1	THF	22	39 (*R*)
32	**2e**	2:1	THF	88	67 (*R*)
33	**2f**	*1:1*	*CH_2Cl_2*	*96*	*99 (R)*
34	**2f**	2:1	CH_2Cl_2	100	73 (*R*)
35	**2f**	1:1	THF	98	89 (*R*)
36	**2f**	2:1	THF	32	88 (*R*)

[a] All reactions were carried out with 2 mol-% of [Pd(allyl)Cl]$_2$ at room temperature over 48 h. [b] The conversion of the substrate **3** and the enantiomeric excess of **4a** were determined by HPLC [Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH/HN(Et)$_2$, 1000:1:1, 0.4 mL min^{-1}, 254 nm, t(+) = 8.2 min, t(–) = 9.1 min]. [c] The conversion of the substrate **3** and the enantiomeric excess of **4b** were determined by HPLC [Daicel Chiralcel OD-H, OD-H, C_6H_{14}/*i*PrOH/HN(Et)$_2$, 200:1:0.1, 0.9 mL min^{-1}, 254 nm].

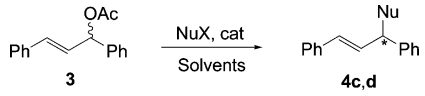
metric induction (up to 76% *ee*). The best stereoselector was diamidophosphite **2d**, bearing a fluorous ponytail. It provided up to 93% *ee* and quantitative conversion (Table 2, Entries 7, 8). Similar enantioselectivity, but lower activity was demonstrated by **2e** (Table 2, Entries 9, 10). Note that its epimer **2f** is a significantly poorer stereoinductor (only up to 59% *ee*) as a result of the mismatched (2*R*,5*S*) phosphorus centre/(S_a)-Piv-BINOL combination. The use of pyrrolidine as N-nucleophile allows higher stereoselectivity to be achieved. In this case, diazaphospholidines **2a**–**e** provide up to 90, 85, 75, 94 and 76% *ee*s, respectively (Table 2, Entries 16, 20, 21, 25 and 30). As a rule, CH_2Cl_2 is the optimum solvent, and in this medium the enantioselectivity is almost independent of the ligand/palladium ratio. It should be noted that the fluorous diamidophosphite **2d** produced more than 90% optical yields of products **4a** and **4b** in both allylic amination reactions. It is interesting that, in contrast with the allylic amination in the presence of dipropylamine, in the pair of epimers **2e** and **2f**, **2f** is more efficient [up to 99% *ee*, (Table 2, Entry 33)]. It is possible to assume that this is the consequence of a matched (2*R*,5*S*) phosphorus centre/(S_a)-Piv-BINOL combination and the much greater value of the Tolman cone angle for **2f** (Table 1).

We have also tested novel *P**-stereogenic diazaphospholidines in the enantioselective Pd-catalysed allylic sulfonylation of **3** with $NaSO_2pTol$ as S-nucleophile (Table 3). As well as in allylic aminations, these processes are also powerful tools in the total synthesis of natural products.[3b] Earlier we reported that ligand **2a** provided up to 90% *ee* in this reaction.[9a] Compounds **2b**–**e** also displayed moderate to good enantioselectivities (63–87%). As stated above, the fluorous diamidophosphite **2d** is a powerful stereoinductor in allylic amination, but in allylic sulfonylation, like the similar $\mathbf{L_C}$-type ligand with strong π-acidity [R = $CH(CF_3)_2$],[9a] **2d** provided rather moderate optical and mediocre chemical yields of product (*S*)-**4c** (Table 3, Entries 5 and 6). Diazaphospholidine **2e**, containing the (R_a)-Piv-BINOL unit, was found to be a good stereoselector, whereas its epimer **2f** was much less efficient (up to 87 and 24% *ee*s, respectively, Table 3, Entries 7–10).

Previously we had established that in the allylic alkylation of **3** with dimethyl malonate as C-nucleophile, catalytic systems based on the *P**-chirogenic diamidophosphite **2a** and $[Pd(allyl)Cl]_2$ or $[Pd_2(dba)_3]\cdot x CHCl_3$ allowed up to 87% optical yields of product (*S*)-**4d** to be achieved.[9a] The use of $Pd(CF_3CO_2)_2$ as a precatalyst led to an increase in enantioselectivity up to 92% (Table 3, Entries 11–14). The enantiomeric excess depended on the solvent used: CH_2Cl_2 is the optimal solvent (Table 3, Entry 12).

In the second set of experiments, the new *P**-chiral diazaphospholidines were applied in Rh-catalysed hydrogenations of common benchmark substrates: namely dimethyl itaconate (**5a**), methyl (*Z*)-2-acetamido-3-phenylacrylate (**5b**) and methyl 2-acetamidoacrylate (**5c**). In all cases the cationic rhodium catalysts were prepared in situ by treating $[Rh(cod)_2]BF_4$ with 2 equiv. of the corresponding monodentate ligand; the results are summarized in Table 4. For substrates **5a**–**c**, the low or moderate enantioselectivity varied within rather similar ranges between 33–76, 13–73 and 31–68% *ee*, respectively. The exception is the excellent result achieved in the hydrogenation of methyl 2-acet-

Table 3. Pd-catalysed allylic sulfonylation and alkylation of (*E*)-1,3-diphenylallyl acetate (**3**).[a]



3 **4c,d**

Nu = SO_2pTol, X = Na, **4c**
Nu = $CH(CO_2Me)_2$ X = H, **4d**

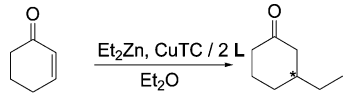
Entry	Ligand	Precatalyst	L/Pd	Solvent	Time [h]	Conv. [%][b]	*ee* [%]
Allylic sulfonylation with sodium *p*-toluenesulfinate[c]							
1	**2b**	$[Pd(allyl)Cl]_2$	1:1	THF	48	46	66 (*S*)
2	**2b**	$[Pd(allyl)Cl]_2$	2:1	THF	48	95	77 (*S*)
3	**2c**	$[Pd(allyl)Cl]_2$	1:1	THF	48	54	74 (*S*)
4	**2c**	$[Pd(allyl)Cl]_2$	2:1	THF	48	66	81 (*S*)
5	**2d**	$[Pd(allyl)Cl]_2$	1:1	THF	48	33	63 (*S*)
6	**2d**	$[Pd(allyl)Cl]_2$	2:1	THF	48	26	74 (*S*)
7	**2e**	$[Pd(allyl)Cl]_2$	1:1	THF	48	48	75 (*S*)
8	**2e**	*$[Pd(allyl)Cl]_2$*	*2:1*	*THF*	*48*	*51*	*87 (S)*
9	**2f**	$[Pd(allyl)Cl]_2$	1:1	THF	48	38	21 (*S*)
10	**2f**	$[Pd(allyl)Cl]_2$	2:1	THF	48	27	24 (*S*)
Allylic alkylation with dimethyl malonate (BSA, KOAc)[d]							
11	**2a**	$Pd(CF_3CO_2)_2$	1:1	PC[e]	14	79	91 (*S*)
12	**2a**	*$Pd(CF_3CO_2)_2$*	*1:1*	*CH_2Cl_2*	*14*	*87*	*92 (S)*
13	**2a**	$Pd(CF_3CO_2)_2$	1:1	THF	14	92	80 (*S*)
14	**2a**	$Pd(CF_3CO_2)_2$	1:1	toluene	14	82	84 (*S*)

[a] All reactions were carried out with 2 mol-% of $[Pd(allyl)Cl]_2$ (allylic sulfonylation) and with 1 mol-% of $Pd(CF_3CO_2)_2$ (allylic alkylation) at room temperature. [b] Isolated yield of **4c** in allylic sulfonylation. [c] Enantiomeric excess of **4c** was determined by HPLC (Daicel Chiralcel OJ, C_6H_{14}/*i*PrOH, 4:1, 0.5 mL min^{-1}, 254 nm). [d] The conversion of substrate **3** and enantiomeric excess of **4d** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH, 99:1, 0.6 mL min^{-1}, 254 nm). [e] Propylene carbonate.

amidoacrylate (**5c**) with the participation of ligand **2a**: a 98% optical yield of the product (*R*)-**6c** and quantitative conversion of the starting substrate (Table 4, Entry 14). This stereoselector also provided the best enantioselectivities (up to 73–75%) in the cases of substrates **5a** and **5b** (Table 4, Entries 2 and 9). For dimethyl itaconate (**5a**), analogous asymmetric induction (76% *ee*) was also observed with the participation of the fluorous diamidophosphite **2d** (Table 4, Entry 5). Optical yields strongly depended on the nature of the solvent: they increased dramatically on replacement of propylene carbonate with CH_2Cl_2 (Table 4, Entries 1, 2 and 8, 9). In contrast with the allylic substitution, in all hydrogenation experiments the epimeric ligands **2e** and **2f** caused the formation of products **6a**–**c** with opposite absolute configurations, as a consequence of the determining influence of the Piv-BINOL fragment. For comparison it should be noted that catalytic systems based on the known *P**,*N*-bidentate diazaphospholidines $\mathbf{L_B}$ (R^1, R^2 = Me and R^1 = *s*Bu, R^2 = H)[8g] and $[Rh(cod)_2]BF_4$ (L/Rh molar ratio = 1:1 and 2:1) provided only low enantioselectivities (13–26%) in the hydrogenation of **5a** and no more than 50% conversions. In the case of substrate **5c** its conversion has not exceeded 4%.

In the third step, we screened several *P**-chiral diazaphospholidines in the Cu-catalysed conjugate addition of diethylzinc to cyclohexenone **7** (Table 5). Copper catalysts were prepared by treatment of copper(I) thiophenecarboxylate (CuTC) with 2 equiv. of the ligand in Et_2O. With participation of diamidophosphite **2a**, **2e** and **2f**, nearly quantitative conversion of **7** (>99%) was achieved, but with disappointing enantioselectivities (16–21%). In contrast, diazaphospholidine **2d** with the fluorous ponytail was quite efficient and gave a 70% optical yield of product **8** with com-

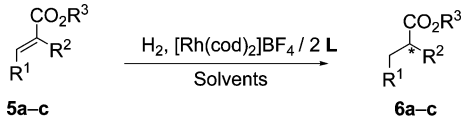
Table 5. Cu-catalysed conjugate addition of Et_2Zn to cyclohexenone.[a]



Entry	Ligand	Conv. [%]	*ee* [%][b]
1	**2a**	>99	21 (*S*)
2	**2d**	*>99*	*70 (S)*
3	**2e**	99	16 (*S*)
4	**2f**	>99	18 (*S*)

[a] All reactions were carried out with 2 mol-% of CuTC at –30 °C over 3 h. [b] The conversion of substrate **7** and the enantiomeric excess of **8** were determined by GC (Lipodex E, 25 m × 0.25 mm, 60 °C, 1 mL min^{-1}).

Table 4. Rh-catalysed hydrogenation of α-dehydrocarboxylic acid esters.[a]



5a–c **6a–c**

R^1 = H, R^2 = CH_2CO_2Me, R^3 = Me, **5a** and **6a**
R^1 = Ph, R^2 = NHAc, R^3 = Me, **5b** and **6b**
R^1 = H, R^2 = NHAc, R^3 = Me, **5c** and **6c**

Entry	Substrate	Ligand	Solvent	Time [min]	Conv. [%]	*ee* [%][b–d]
1	**5a**	**2a**	PC[e]	35	100	45 (*S*)
2	**5a**	**2a**	CH_2Cl_2	30	100	75 (*S*)
3	**5a**	**2b**	CH_2Cl_2	1440	100	67 (*S*)
4	**5a**	**2c**	CH_2Cl_2	1440	35	33 (*S*)
5	**5a**	**2d**	*CH_2Cl_2*	*1200*	*100*	*76 (S)*
6	**5a**	**2e**	CH_2Cl_2	1440	100	55 (*S*)
7	**5a**	**2f**	CH_2Cl_2	1440	100	47 (*R*)
8	**5b**	**2a**	PC[e]	80	100	13 (*R*)
9	**5b**	**2a**	*CH_2Cl_2*	*1200*	*100*	*73 (R)*
10	**5b**	**2b**	CH_2Cl_2	1440	75	50 (*R*)
11	**5b**	**2d**	CH_2Cl_2	1440	100	34 (*R*)
12	**5b**	**2e**	CH_2Cl_2	1440	100	45 (*R*)
13	**5b**	**2f**	CH_2Cl_2	1440	100	27 (*S*)
14	**5c**	**2a**	*CH_2Cl_2*	*1200*	*100*	*98 (R)*
15	**5c**	**2b**	CH_2Cl_2	1440	85	68 (*R*)
16	**5c**	**2c**	CH_2Cl_2	1440	0	–
17	**5c**	**2d**	CH_2Cl_2	1200	62	46 (*R*)
18	**5c**	**2e**	CH_2Cl_2	1440	100	40 (*R*)
19	**5c**	**2f**	CH_2Cl_2	1440	100	31 (*S*)

[a] All reactions were carried out with 1 mol-% of $[Rh(cod)_2]BF_4$ at 25 °C and 1 bar H_2. [b] The conversion of substrate **5a** and the enantiomeric excess of **6a** were determined by GC (Lipodex E, 25 m × 0.25 mm, 80 °C, 1 mL min^{-1}) or HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH, 98:2, 0.8 mL min^{-1}, 220 nm, *t*(*R*) = 9.1 min, *t*(*S*) = 16.1 min). [c] The conversion of the substrate **5b** and the enantiomeric excess of **6b** were determined by GC (Lipodex E, 25 m × 0.25 mm, 145 °C, 1 mL min^{-1}). [d] The conversion of substrate **5c** and the enantiomeric excess of **6c** were determined by GC [XE-valin(*tert*-butylamide) 4 × 0.25 mm, 85 °C, 1 mL min^{-1}]. [e] Propylene carbonate.

plete conversion of the starting substrate. As in the case of Rh-catalysed hydrogenation, the *P**,*N*-bidentate diazaphospholidines $\mathbf{L_B}$ (R^1, R_2 = Me and R^1 = *s*Bu, R^2 = H) provided only low asymmetric induction (13–15% *ee*) under the same conditions. Note that the monodentate ligand **2d** as stereoselector also surpasses QUIPHOS-type *P**,*N*-bidentate ligands $\mathbf{L_A}$, which in this reaction allow no more than 55% *ee*s to be achieved.[8e]

Conclusions

We have described the successful application of various easily accessible sterically congested (θ = 165–197°) monodentate *P**-chirogenic diazaphospholidines in Pd-catalysed asymmetric allylic substitution and Rh-catalysed asymmetric hydrogenation reactions of several substrate types, as well as in the Cu-catalysed conjugate addition of diethylzinc to cyclohexenone. It has been shown that in the two last catalytic processes such ligands can afford enantioselectivities superior to those of their chelating $\mathbf{L_A}$ and small monodentate $\mathbf{L_C}$ (OR = OMe, O*i*Pr) analogues, whereas in the Pd-catalysed allylation all three groups of stereoselectors show comparable efficiencies. Novel diazaphospholidines can be considered modular, and because the bulky exocyclic moieties can be varied, a large library of these ligands is readily available. Accordingly, our ongoing experiments are focused on the fine-tuning of the structures of *P**-chiral diazaphospholidines to improve the optical yields in various asymmetric transformations and will be reported in due course.

Experimental Section

General: IR spectra were recorded with a Specord M-80 spectrophotometer in $CHCl_3$ (KBr cuvette). ^{31}P, ^{13}C, ^1H and ^{19}F NMR spectra were recorded with a Bruker AMX 400 instrument (162.0 MHz for ^{31}P, 100.6 MHz for ^{13}C, 400.13 MHz for ^1H and 282.4 MHz for ^{19}F). Complete assignment of all the ^{13}C NMR resonances was achieved by the use of DEPT techniques. Chemical shifts (ppm) are given relative to Me_4Si (^1H and ^{13}C), 85% H_3PO_4 (^{31}P NMR) and CCl_3F (^{19}F). Mass spectra were recorded with a Varian MAT 311 spectrometer (EI). Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow). All reactions were carried out under dry argon in freshly dried and distilled solvents; triethylamine, pyrrolidine and dipropylamine were distilled from KOH and then from a small amount of $LiAlH_4$ before use. Phosphorylating reagents, (2*R*,5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]-octane (**1a**) and (2*R*,5*S*)-2-chloro-3-*para*-bromophenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**1b**), were prepared analogously to a known procedure.[9a] The synthesis of ligand **2a** was described by us earlier.[9a] $[Pd(allyl)Cl]_2$,[18] $Pd(CF_3CO_2)_2$[19] and $[Rh(cod)_2]BF_4$[20] were prepared as described earlier. Pd-catalysed allylic substitution: amination of substrate **3** with dipropylamine and pyrrolidine, sulfonylation with sodium *p*-toluenesulfinate and alkylation with dimethyl malonate were performed according to the appropriate procedures.[9a,9b,21] Rh-catalysed hydrogenation of α-dehydrocarboxylic acid esters **5a**–**c** was performed as published.[22,23] Cu-catalysed 1,4-addition of diethylzinc to cyclohexenone **7** was performed according to a known procedure.[24] Starting substrates **3** and **5b** were synthesised as published.[18,25] Adamantan-1-ol, ferrocenemethanol, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-nonadecafluorodecan-1-ol, (*R*)- and (*S*)-2,2′-dihydroxy-1,1′-binaphthyl [(*R*)- and (*S*)-BINOL], dimethyl malonate, BSA [*N*,*O*-bis(trimethylsilyl)acetamide], sodium *p*-toluenesulfinate, dimethyl itaconate, methyl 2-acetamidoacrylate, cyclohexenone, Et_2Zn solution in hexane (1 M) and CuTC [copper(I) thiophenecarboxylate] were purchased from Aldrich and Acros Organics and used without further purification.

General Procedure for Preparation of the Ligands 2b–f: A solution of Et_3N (0.27 mL, 1.9 mmol) and the appropriate alcohol (1.8 mmol) in benzene (8 mL) were added dropwise to a vigorously stirred solution of phosphorylating reagent **1a** or **1b** (1.8 mmol) in benzene (8 mL). The mixture was heated to the boiling point with stirring and was then allowed to cool to 20 °C. Solid $Et_3N{\cdot}HCl$ was filtered off; benzene was removed under reduced pressure (40 Torr). Products **2d**, **2e** and **2f** were extracted with hexane. The residue was dissolved in hexane (3 × 15 mL; boiling hexane in the case of **2e** and **2f**) and the mixture filtered, concentrated and dried in vacuo (1 Torr) for 2 h. Compounds **2b** and **2c** were purified by flash chromatography on silica gel with use of non-degassed eluents (ethyl acetate/hexane, 1:10 and 1:6, respectively).

(2*R*,5*S*)-2-(Tricyclo[3.3.1.1.$^{3',7'}$]dec-1′-yloxy)-3-(*p*-bromophenyl)-1,3-diaza-2-phosphabicyclo[3.3.0]octane (2b): White amorphous solid (0.60 g, 76%), ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ_C = 26.0 [d, ^3J = 4.4 Hz, C(7)], 30.8 [s, C(3′,5′,7′)], 31.5 [s, C(6)], 35.9 [s, C(4′,6′,10′)], 44.7 [d, ^2J = 8.8 Hz, C(2′,8′,9′)], 47.7 [d, ^2J = 35.0 Hz, C(8)], 52.9 [d, ^2J = 5.9 Hz, C(4)], 62.4 [d, ^2J = 8.1 Hz, C(5)], 74.2 [d, ^2J = 6.6 Hz, C(1′)], 110.4 (s, C_{Ar}), 117.0 (d, ^3J = 12.5 Hz, CH_{Ar}), 131.4 (s, CH_{Ar}), 144.9 (d, ^2J = 14.7 Hz, C_{Ar}) ppm. MS (EI, 70 eV): *m*/*z* (%) = 435 (12) $[M]^+$, 251 (93), 205 (32), 135 (84), 95 (100). $C_{21}H_{28}BrN_2OP$ (434.1): calcd. C 57.94, H 6.48, N 6.43; found C 58.22, H 6.62, N 6.32.

(2*R*,5*S*)-2-(Ferrocenylmethoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0]octane (2c): Yellow powder (0.50 g, 66%), m.p. 65–66 °C. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ_C = 26.0 [d, ^3J = 3.9 Hz, C(7)], 31.8 [s, C(6)], 48.6 [d, ^2J = 38.2 Hz, C(8)], 54.9 [d, ^2J = 7.1 Hz, C(4)], 60.1 (d, ^2J = 2.9 Hz, CH_2O), 63.0 [d, ^2J = 8.7 Hz, C(5)], 68.2 (s, C_{Cp}), 68.0, 68.1, 68.4, 68.6 (4 s, C_{Fc}), 84.6 [d, ^3J = 1.5 Hz, $C_{Fc(ipso)}$], 114.6 (d, ^3J = 11.6 Hz, CH_{Ar}), 118.7 (s, CH_{Ar}), 128.9 (s, CH_{Ar}), 145.6 (d, ^2J = 16.1 Hz, C_{Ar}) ppm. MS (EI, 70 eV): *m*/*z* (%) = 420 (92) $[M]^+$, 355 (100), 199 (75). $C_{22}H_{25}FeN_2OP$ (420.1): calcd. C 62.87, H 6.00, N 6.67; found C 63.0, H 5.95, N 6.58.

(2*R*,5*S*)-2-(2′,2′,3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,8′,8′,9′,9′,10′,10′,10′-Nonadecafluorodecyloxy)-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0]octane (2d): Colourless, viscous oil solidifying on storage (1.03 g, 81%), m.p. 62–63 °C. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ_C = 26.4 [d, ^3J = 3.7 Hz, C(7)], 31.8 [s, C(6)], 48.3 [d, ^2J = 37.2 Hz, C(8)], 54.9 [d, ^2J = 6.6 Hz, C(4)], 58.6 (m, ^2J = 5.3 Hz, CH_2O), 63.2 [d, ^2J = 8.8 Hz, C(5)], 109.4 [br. m, C(2′)–C(10′)], 115.0 (d, ^3J = 11.7 Hz, CH_{Ar}), 119.7 (s, CH_{Ar}), 129.2 (s, CH_{Ar}), 145.1 (d, ^2J = 16.8 Hz, C_{Ar}) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$, 25 °C): δ_F = –79.1 to –79.35 (m, 3 F), –117.92 (s, 2 F), –120.25 (s, 8 F), –121.15 (s, 2 F), –121.4 (s, 2 F), –124.55 (s, 2 F) ppm. MS (EI, 70 eV): *m*/*z* (%) = 704 (10) $[M]^+$, 484 (8), 222 (100), 205 (82). $C_{21}H_{16}F_{19}N_2OP$ (704.3): calcd. C 35.81, H 2.29, N 3.98; found C 36.04, H 2.37, N 3.79.

(2*R*,5*S*,R_a)-2-[1-(2-Pivaloxynaphthalen-1-yl)naphthalen-2-yloxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (2e): White powder (0.72 g, 70%), m.p. 63–64 °C. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ_C = 25.7 [d, ^3J = 4.4 Hz, C(7)], 26.1, 26.4 (s, CH_3), 31.2 [s, C(6)], 38.5 (s, 1 C), 46.9 [d, ^2J = 35.7 Hz, C(8)], 53.3 [d, ^2J = 7.3 Hz,

C(4)], 62.3 [d, ^2J = 8.8 Hz, C(5)], 114.8 (d, $^3J_{C,P}$ = 13.1 Hz), 118.6, 119.5, 122.8, 122.9, 123.2, 123.9, 124.1, 125.5, 125.7, 125.8, 125.9, 127.4, 127.7, 128.5, 128.7, 128.9, 129.2, 130.2, 133.7, 133.9, 147.0 (d, ^2J = 20.4 Hz), 150.0 (d, $^2J_{C,P}$ = 5.8 Hz), 155.2 (all CH_{Ar} and C_{Ar}), 176.1 (s, C=O, major epimer); 26.2, 26.3 (s, CH_3), 27.4 [s, C(7)], 31.5 [s, C(6)], 38.3 (s, 1 C), 42.5 [d, ^2J = 4.4 Hz, C(8)], 50.9 [d, ^2J = 5.8 Hz, C(4)], 65.3 [d, ^2J = 10.2 Hz, C(5)], 117.0 (d, $^3J_{C,P}$ = 13.1 Hz), 118.4, 119.8, 122.8, 123.0, 123.5, 123.9, 124.1, 125.1, 125.6, 125.8, 126.2, 127.5, 127.7, 128.3, 128.7, 128.9, 129.0, 130.5, 132.6, 134.2, 144.9 (d, ^2J = 15.3 Hz), 150.6 (d, $^2J_{C,P}$ = 2.8 Hz), 155.0 (all CH_{Ar} and C_{Ar}), 175.9 (s, C=O, minor epimer) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1744 (C=O) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 575 (4) $[M]^+$, 473 (25), 370 (40), 286 (81), 205 (100). $C_{36}H_{35}N_2O_3P$ (574.2): calcd. C 75.24, H 6.14, N 4.87; found C 75.40, H 6.21, N 4.79.

(2*R*,5*S*,S_a)-2-[1-(2-Pivaloxynaphthalen-1-yl)naphthalen-2-yloxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (2f): White powder (0.78 g, 75%), m.p. 59–60 °C. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ_C = 26.0 [d, ^3J = 3.8 Hz, C(7)], 26.2, 26.3 (s, CH_3), 31.0 [s, C(6)], 38.5 (s, 1 C), 47.1 [d, ^2J = 32.7 Hz, C(8)], 53.1 [d, ^2J = 6.8 Hz, C(4)], 62.0 [d, ^2J = 8.0 Hz, C(5)], 115.0 (d, $^3J_{C,P}$ = 12.4 Hz), 118.2, 120.5, 122.7, 122.9, 123.6, 123.9, 124.0, 124.9, 125.7, 125.8, 126.2, 127.4, 127.7, 128.3, 128.7, 128.9, 129.2, 130.9, 133.5, 133.9, 146.0 (d, ^2J = 17.7 Hz), 151.0 (d, $^2J_{C,P}$ = 5.1 Hz), 154.6 (all CH_{Ar} and C_{Ar}), 176.1 (s, C=O, major epimer); 26.4, 26.5 (s, CH_3), 27.3 [s, C(7)], 31.6 [s, C(6)], 38.3 (s, 1 C), 43.0 [d, ^2J = 3.8 Hz, C(8)], 51.0 [d, ^2J = 6.5 Hz, C(4)], 65.2 [d, ^2J = 10.7 Hz, C(5)], 117.2 (d, $^3J_{C,P}$ = 13.1 Hz), 118.0, 120.6, 122.7, 122.9, 123.3, 123.9, 124.7, 124.9, 125.1, 125.9, 126.0, 127.5, 127.7, 128.4, 128.6, 128.9, 129.5, 130.8, 133.7, 133.9, 146.8 (d, ^2J = 16.7 Hz), 151.5 (d, $^2J_{C,P}$ = 3.1 Hz), 155.6 (all CH_{Ar} and C_{Ar}), 176.0 (s, C=O, minor epimer) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1742 (C=O) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 575 (5) $[M]^+$, 473 (28), 370 (34), 286 (92), 205 (100). $C_{36}H_{35}N_2O_3P$ (574.2): calcd. C 75.24, H 6.14, N 4.87; found C 75.50, H 6.04, N 5.01.

Supporting Information (see footnote on the first page of this article): General experimental procedures for asymmetric catalytic reactions and ^1H NMR spectroscopic data for ligands **2b**–**f**.

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