P-Chiral Monodentate Diamidophosphites – New and Efficient Ligands for Palladium-Catalysed Asymmetric Allylic Substitution

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Keywords: Allylic substitution / Asymmetric catalysis / P ligands / Palladium / Rhodium

Novel *P**-monodentate diamidophosphite ligands have been prepared by a one-step phosphorylation of alcohols or amines. Both the electronic and the steric demands of the ligands have been estimated quantitatively. Neutral [Pd(allyl)Cl(L)] and cationic $[Pd(allyl)(L)_2]^+ BF_4^-$ complexes have been obtained by starting from $[Pd(allyl)Cl]_2$. The new ligands have demonstrated high enantioselectivity in the Pd-catalysed allylic substitution reactions of 1,3-diphenylallyl acetate with $NaSO_2p$Tol (up to 97% *ee*), $PhCH_2NH_2$ (up to 95% *ee*) and $CH_2(CO_2Me)_2$ (up to 97% *ee*). Application of the *P**-monodentate diamidophosphites to the asymmetric catalytic synthesis of chiral carborane derivatives has also been demonstrated.

Introduction

The last five years have been characterized by significant progress in the use of chiral phosphites in asymmetric metal complex catalysis.[1–3] First and foremost this relates to monodentate phosphites and phosphoramidites of the types depicted in Figure 1.

Almost quantitative enantioselectivity has been achieved in the Rh-catalysed hydrogenation of prochiral unsaturated substrates in the presence of $\mathbf{L}_a$[4–6,7] and $\mathbf{L}_b$.[8,9] At present, these BINOL-derived ligands compete successfully with the *P*,*P*-bidentate phosphanes that previously dominated in this field. Notably, $\mathbf{L_a}$ is 50 times cheaper than BINAP.[5]

Some more impressive results have been provided by phosphoramidites $\mathbf{L_b}$ in the Cu-catalysed conjugate addition of organometallic reagents to enones[10] and in Ni-catalysed hydrovinylation.[11] In the Pd-catalysed hydrosilylation–oxidation of vinyl arenes, $\mathbf{L_b}$ afforded the highest enantioselectivity so far – up to 99% *ee* in the case of styrene.[12]

The design of $\mathbf{L_c}$ and $\mathbf{L_d}$ put into practice an attractive idea to replace the BINOL chiral scaffold with cheap and easily available biphenols. Compound $\mathbf{L_c}$ provided a 99% *ee* in the Cu-catalysed conjugate addition of R_2Zn to cyclohexenone,[13,14] and $\mathbf{L_d}$ yielded up to 75% *ee* in the Rh-catalysed hydrogenation of dimethyl itaconate.[15]

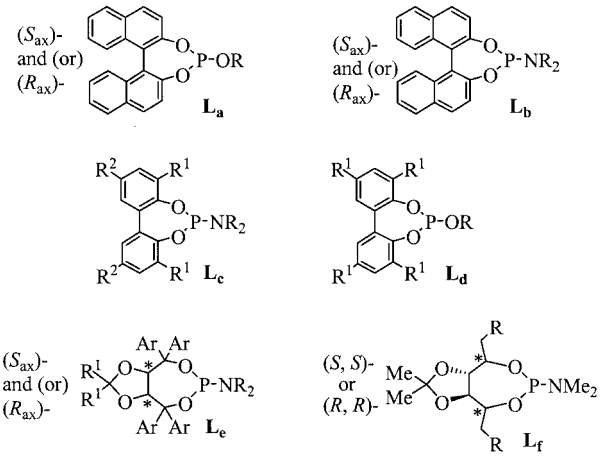

Figure 1. Some well-known efficient *P*-monodentate chiral phosphites and phosphoramidites

TADDOL-derived phosphoramidites $\mathbf{L_e}$ have been applied to good effect in Cu-catalysed conjugate addition[16] and Pd-catalysed intramolecular Heck reactions.[17] High *ee*s were also achieved in the Rh-catalysed hydrogenation of unsaturated carboxylic acids with the phosphacyclanes $\mathbf{L_f}$, derived from D-mannitol and closely related to $\mathbf{L_e}$.[18]

Of particular interest is the contribution of monodentate phosphites and phosphoramidites to the catalytic allylic

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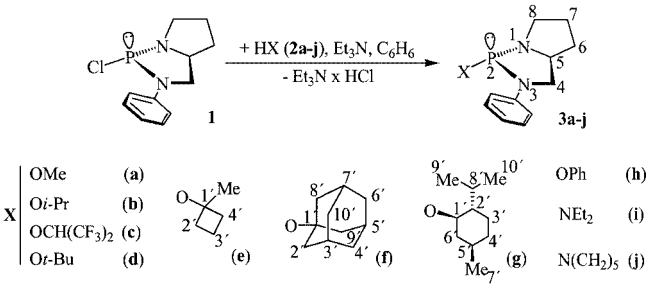
substitution processes. Ir-catalysed alkylations of a variety of dissymmetrical substrates with dimethyl malonate were reported to give up to 86% *ee* with $\mathbf{L_b}$ and 96% *ee* with $\mathbf{L_a}$.[19−21] Slightly better results (up to 97% *ee*) have been obtained with phosphoramidites $\mathbf{L_b}$ by use of amines[22] or phenoxides[23] as nucleophiles. To the best of our knowledge, there have been no reports on efficient catalytic applications of monodentate phosphites or phosphoramidites bearing a *P**-stereogenic atom. Monodentate chiral phosphites and phosphoramidites have also never been employed in Pd-catalysed allylic substitution reactions, even though palladium is usually the metal of choice in catalytic allylation.[24] Since ligands bearing chiral donor atoms are reputed to be good stereoselectors,[25] we present here a series of new *P**-chiral ligands and the results of their application in various Pd-catalysed allylic substitution reactions.

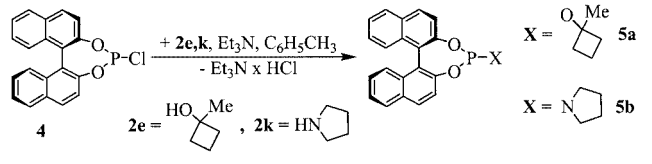
Results and Discussion

Monodentate diamidophosphites **3a**−**j** were synthesized by a one-step phosphorylation of the corresponding alcohols or amines **2a**−**j** with (2*R*,5*S*)-1,3-diaza-2-chloro-3-phenyl-2-phosphabicyclo[3.3.0]octane (**1**) (Scheme 1).



Scheme 1

In addition, new BINOL-based ligands **5a** and **5b** of structural types $\mathbf{L_a}$ and $\mathbf{L_b}$ were obtained in order to compare their effectiveness in Pd-catalysed allylation reactions with ligands **3a**−**j** (Scheme 2).



Scheme 2

Compounds **3a**−**j** are stable on prolonged storage and, if needed, can easily be purified either by vacuum distillation or by extraction with hexane. Since compound **1** is readily available,[26] ligands **3a**−**j** can be prepared on multigram scales.

Table 1. ^{31}P NMR chemical shifts ($CDCl_3$) and cone angles θ (deg.) of ligands **3a**−**j**

Ligand	δ_P	θ
(R_P)-**3a**	123.1	122
(R_P)-**3b**	123.9	134
(R_P)-**3c**	133.3	152
(R_P)-**3d** (82%)[a]	128.4	156
(S_P)-**3d** (18%)	114.5	
(R_P)-**3e** (91%)	127.1	137
(S_P)-**3e** (9%)	114.9	
(R_P)-**3f** (74%)	126.7	168
(S_P)-**3f** (26%)	112.3	
(R_P)-**3g** (93%)	129.5	163
(S_P)-**3g** (7%)	121.7	
(R_P)-**3h** (98%)	123.5	163
(S_P)-**3h** (2%)	114.4	
(R_P)-**3i**	117.3	137
(R_P)-**3j** (97%)	114.8	149
(S_P)-**3j** (3%)	95.2	

[a] Percentage of *P** epimers.

The ^{31}P NMR spectroscopic data for **3a**−**j** are summarized in Table 1. While ligands **3a**−**c** and **3i** are formed as single stereoisomers, **3d**−**h** and **3j** each contain from 2 to 26% of the second stereoisomer. In all cases, the major stereoisomer has a pseudoequatorial orientation of the exocyclic substituent at the phosphorus atom (i.e., the *R* configuration at the *P** stereocenter). This was concluded from the characteristic[26,27] $^2J_{C(8),P}$ values (34.3−41.2 Hz) in the ^{13}C NMR spectra of **3a**−**j** (see Table 2 and the Exp. Sect.). There is a correlation between the $^2J_{C(8),P}$ values and the dihedral angle between the lone pair (LP) of the phosphorus atom and C(8).[28] If the LP of the phosphorus atom and C(8) are *cis* to each other (i.e., the substituent X has a pseudoequatorial orientation, Scheme 1), the $^2J_{C(8),P}$ value is maximum. In contrast, the minimum values of the $^2J_{C(8),P}$ correspond to *trans* orientations of the phosphorus LP to C(8) in the minor S_P epimers (Table 2).

To estimate the steric demands of ligands **3a**−**j**, we calculated their Tolman's angles[29] by the reported method, by use of semiempirical quantum mechanical AM1 techniques with full optimization of geometrical parameters.[30] The obtained results (Table 1) show that the steric demands of **3a**−**j** vary over a rather wide range between 122° and 168°, peaking at compounds **3g** and **3f**, bearing bulky menthyl or adamantyl groups.

The electronic demands of the novel ligands were determined from the ^{31}P NMR and IR spectroscopic data (Table 3) of their dimeric rhodium(I) chlorocarbonyl complexes (Scheme 3).

The dimeric structures of complexes **6a**−**c** and **6i** are supported by the intensive molecular ion peak *m*/*z* (%) = 805 (40) $[M]^+$ in the FAB mass spectrum of **6a**. The IR spectrum of **6a** contains a characteristic ν(Rh−Cl) band at 273 cm^{-1}, attributable to the bridging chloro ligand. Further treatment of **6a** with additional **3a** gave the mononuclear product **7** (Scheme 4).

The spectroscopic data for the rhodium chlorocarbonyl complexes (Table 3) show that diamidophosphites **3a**−**j** lie

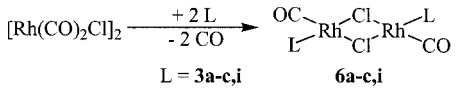
Table 2. ^{13}C NMR spectroscopic data for ligands **3d** and **3f**, in $CDCl_3$ (δ_C, $J_{C,P}$, [Hz])

Carbon atom	Ligand		Carbon atom	Ligand	
	(R_P)-**3d**	(S_P)-**3d**		(R_P)-**3f**	(S_P)-**3f**
C_{Ar}	145.8 (^2J = 14.1)	148.0 (^2J = 13.0)	C_{Ar}	145.7 (^2J = 14.5)	147.5 (^2J = 13.2)
	128.6, 118.3	128.1, 118.7		128.6, 118.2	128.0, 118.8
	115.5 (^3J = 12.5)	116.4 (^3J = 13.3)		115.3 (^3J = 12.1)	116.6 (^3J = 13.3)
C (*t*Bu)	74.3 (^2J = 7.2)	72.6 (^2J = 5.7)	1′	73.8 (^2J = 6.9)	72.3 (^2J = 5.3)
5	64.5 (^2J = 8.0)	64.8 (^2J = 10.4)	5	62.3 (^2J = 7.6)	65.0 (^2J = 10.6)
4	52.5 (^2J = 6.5)	50.6 (^2J = 6.6)	4	52.5 (^2J = 6.5)	50.8 (^2J = 6.4)
8	47.8 (^2J = 35.5)	43.7 (^2J = 2.9)	8	47.7 (^2J = 35.5)	44.1 (^2J = 3.4)
6	31.6	31.7	2′,8′,9′	44.6 (^2J = 8.8)	44.9 (^2J = 8.3)
CH_3(*t*Bu)	30.7 (^3J = 8.4)	30.6 (^3J = 7.6)	4′,6′,10′	35.9	35.8
7	26.0 (^3J = 4.6)	27.6	6	31.4	32.1
			3′,5′,7′	30.7	30.6
			7	25.9 (^3J = 4.6)	27.7

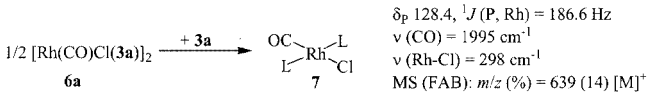
Table 3. Selected spectroscopic data for metal complexes **6a−c**, **6i**, **8f**, **8g**, **9a** and **9c-g** (in $CHCl_3$)

Complex	^{31}P NMR, δ_P	IR, [cm^{-1}]
(R_P)-**6a**	125.2, $^1J_{P,Rh}$ = 250.5 Hz	2000[a]
(R_P)-**6b**	120.1, $^1J_{P,Rh}$ = 250.4 Hz	1998[a]
(R_P)-**6c**	130.3, $^1J_{P,Rh}$ = 267.1 Hz	2016[a]
(R_P)-**6i**	114.2, $^1J_{P,Rh}$ = 222.5 Hz	1992[a]
(R_P)-**8f**	111.3 (73%)[b]	268[c]
(S_P)-**8f**	98.9 (27%)	
(R_P)-**8g**	120.1 (52%), 119.5 (48%)[d]	270[c]
(R_P)-**9a**	118.9	
(R_P)-**9c**	98.6 (66%), 95.5 (34%)[d]	
(R_P)-**9d**	106.2 (93%)[b]	
(S_P)-**9d**	89.4 (7%)	
(R_P)-**9e**	107.5 (88%)[b]	
(S_P)-**9e**	84.6 (12%)	
(R_P)-**9f**	106.2 (97%)[b]	
(S_P)-**9f**	89.6 (3%)	
(R_P)-**9g**	113.0 (14%), 110.9 (86%)[d]	

[a] ν(CO) [cm^{-1}]. [b] Percentage of *P** epimers. [c] ν(Pd-Cl) [cm^{-1}]. [d] Percentage of *exo* and *endo* isomers.



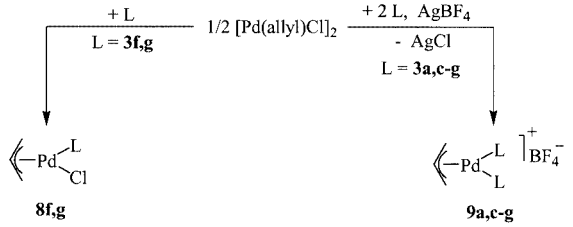
Scheme 3



Scheme 4

between phosphanes and phosphites in the spectrochemical row of phosphorus ligands. Thus, the $^1J_{P,Rh}$ values for **6a−c** and **6i** are 70−80 Hz higher than the $^1J_{P,Rh}$ values for their phosphane analogues[31] and 30−60 Hz lower than those for the corresponding phosphites.[32,33] The increases both in $^1J_{P,Rh}$, from 222.5 to 267.1, and in ν(CO), from 1992 to 2016 cm^{-1}, in the sequence of complexes **6i−6a, 6b−6c** reflects the increase in the π-acidity of the ligands in the same direction.[32]

Both neutral and cationic palladium(II) complexes with the new *P**-monodentate ligands were prepared from $[Pd(allyl)Cl]_2$ (Scheme 5):

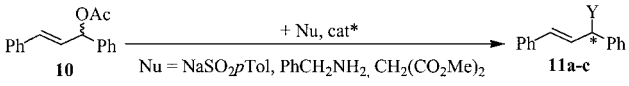


Scheme 5

Their spectroscopic data are shown in Table 3. It should be noted that, as a rule, the ratios of the *P** epimers in the palladium complexes were the same as in the free ligands (Tables 1 and 3). The only exception is **9f**, which contains less minor epimer than the starting ligand **3f**. According to the $^2J_{C(8),P}$ values in the ^{13}C NMR spectra of the complexes (e.g., **8f** and **9e**, see Exp. Sect.), the major epimers have R_P configurations, analogously to the free ligands.

Signals of both *exo* and *endo* isomers of **8g**, **9c** and **9g** are visible in their ^{31}P NMR spectra (Table 3). This was not the case for other palladium complexes, due either to fast interconversion of the isomers or to the absence of one of them (see ref.[34] and references cited therein). The IR (Table 3),[35] ^{13}C NMR (for the allyl ligand),[36] and MS spectroscopic data (see Exp. Sect.) were also in a good agreement with the proposed structures for **8f**, **8g**, **9a** and **9c−g**.

The novel ligands were tested in the asymmetric Pd-catalysed allylic substitution reactions with 1,3-diphenylallyl acetate **10** as substrate (Scheme 6).



Scheme 6

The results are given in Tables 4−6. Most of the ligands showed good enantioselectivity (about 80% *ee*) in the allylic

Table 4. Enantioselective allylic sulfonylation of 1,3-diphenylallyl acetate with sodium *p*-toluenesulfinate

Entry	Precatalyst	L	L/[Pd]	Yield, [%]	*ee*, [%]
1	$[Pd(allyl)Cl]_2$	**3a**	1:1	17	83 (*S*)
2	$[Pd(allyl)Cl]_2$	**3a**	2:1	16	81 (*S*)
3	$[Pd_2(dba)_3]\cdot CHCl_3$	**3a**	1:1	37	78 (*S*)
4	**9a**		2:1	98	64 (*S*)
5	$[Pd(allyl)Cl]_2$	**3b**	1:1	72	84 (*S*)
6	$[Pd(allyl)Cl]_2$	**3b**	2:1	80	80 (*S*)
7	$[Pd_2(dba)_3]\cdot CHCl_3$	**3b**	1:1	53	80 (*S*)
8	$[Pd(allyl)Cl]_2$	**3c**	1:1	28	13 (*S*)
9	$[Pd(allyl)Cl]_2$	**3c**	2:1	30	44 (*S*)
10	$[Pd_2(dba)_3]\cdot CHCl_3$	**3c**	1:1	23	13 (*R*)
11	$[Pd(allyl)Cl]_2$	**3d**	1:1	32	94 (*S*)
12	$[Pd_2(dba)_3]\cdot CHCl_3$	**3d**	1:1	16	80 (*S*)
13	**9d**		**2:1**	**44**	**97** (*S*)
14	$[Pd(allyl)Cl]_2$	**3e**	1:1	83	79 (*S*)
15	$[Pd(allyl)Cl]_2$	**3e**	2:1	97	86 (*S*)
16	$[Pd_2(dba)_3]\cdot CHCl_3$	**3e**	1:1	23	78 (*S*)
17	**9e**		2:1	20	85 (*S*)
18	$[Pd(allyl)Cl]_2$	**3f**	1:1	27	83 (*S*)
19	$[Pd_2(dba)_3]\cdot CHCl_3$	**3f**	1:1	35	30 (*S*)
20	**9f**		2:1	53	90 (*S*)
21	$[Pd(allyl)Cl]_2$	**3g**	1:1	45	83 (*S*)
22	$[Pd(allyl)Cl]_2$	**3g**	2:1	50	78 (*S*)
23	$[Pd_2(dba)_3]\cdot CHCl_3$	**3g**	1:1	22	80 (*S*)
24	$[Pd(allyl)Cl]_2$	**3h**	1:1	27	76 (*S*)
25	$[Pd(allyl)Cl]_2$	**3h**	2:1	92	78 (*S*)
26	$[Pd_2(dba)_3]\cdot CHCl_3$	**3h**	1:1	47	78 (*S*)
27	**9h**		2:1	27	73 (*S*)
28	$[Pd(allyl)Cl]_2$	**3i**	1:1	16	15 (*S*)
29	$[Pd(allyl)Cl]_2$	**3i**	2:1	16	13 (*S*)
30	$[Pd_2(dba)_3]\cdot CHCl_3$	**3i**	1:1	15	1 (*S*)
31	$[Pd(allyl)Cl]_2$	**3j**	1:1	17	61 (*S*)
32	$[Pd(allyl)Cl]_2$	**3j**	2:1	18	59 (*S*)
33	$[Pd_2(dba)_3]\cdot CHCl_3$	**3j**	1:1	17	9 (*R*)
34	$[Pd(allyl)Cl]_2$	**5a**	1:1	21	72 (*R*)
35	$[Pd(allyl)Cl]_2$	**5a**	2:1	21	70 (*R*)
36	$[Pd_2(dba)_3]\cdot CHCl_3$	**5a**	1:1	28	63 (*R*)
37	$[Pd(allyl)Cl]_2$	**5b**	1:1	35	46 (*S*)
38	$[Pd(allyl)Cl]_2$	**5b**	2:1	0	–
39	$[Pd_2(dba)_3]\cdot CHCl_3$	**5b**	1:1	13	7 (*S*)

sulfonylation reaction (Table 4, ligands **3a**, **3b**, **3e**, **3g**, **3h**). Notably, the additional C*-stereogenic centres in the menthyl substituent of **3g** did not provide any improvement. Ligand **3f** bearing a bulky adamantyl substituent gave up to 90% *ee*, while the best result (97% *ee*) was obtained with **3d**, which has an average θ value as high as 156° (Table 1). It is important to note that all the efficient ligands mentioned have moderate π-acidity. Meanwhile, both more and less π-acidic ligands, such as **3c** and **3i**, respectively, provided much lower chemical and especially optical yields. The *ee*s did not exceed 44% for **3c** and 15% for **3i**. The notable increase in the enantioselectivity on going from **3i** to **3j** (up to 61%) is likely to be due to an increase in the θ value from 137 to 149°. Nevertheless, the chemical yields for both ligands were poor.

The use of $[Pd_2(dba)_3]\cdot CHCl_3$ instead of $[Pd(allyl)Cl]_2$ as the palladium precursor provided no essential advantages. Furthermore, notable reduction in enantioselectivity or even an inversion of the absolute configuration of **11a** was observed in some cases (Table 4, entries 10,12,30, and 33).

Table 5. Enantioselective allylic amination of 1,3-diphenylallyl acetate with benzylamine

Entry	Precatalyst	Solvent	L	θ, (°)	L/[Pd]	Yield, [%]	*ee*, [%]
1	$[Pd(allyl)Cl]_2$	THF	**3a**	122	1:1	62	46 (*R*)
2	$[Pd(allyl)Cl]_2$	CH_2Cl_2	**3a**		2:1	90	59 (*R*)
3	**9a**	CH_2Cl_2			2:1	74	47 (*R*)
4	$[Pd(allyl)Cl]_2$	THF	**3b**	134	1:1	68	78 (*R*)
5	$[Pd(allyl)Cl]_2$	CH_2Cl_2	**3b**		1:1	67	81 (*R*)
6	$[Pd(allyl)Cl]_2$	CH_2Cl_2	**3b**		2:1	92	70 (*R*)
7	$[Pd(allyl)Cl]_2$	CH_2Cl_2	**3c**	152	2:1	65	92 (*R*)
8	$[Pd(allyl)Cl]_2$	CH_2Cl_2	**3d**	156	2:1	31	90 (*R*)
9	**9d**	CH_2Cl_2			2:1	37	93 (*R*)
10	$[Pd(allyl)Cl]_2$	THF	**3e**	137	1:1	59	90 (*R*)
11	$[Pd(allyl)Cl]_2$	CH_2Cl_2	**3e**		1:1	38	81 (*R*)
12	$[Pd(allyl)Cl]_2$	CH_2Cl_2	**3e**		2:1	90	92 (*R*)
13	**9e**	CH_2Cl_2			2:1	94	90 (*R*)
14	$[Pd(allyl)Cl]_2$	CH_2Cl_2	**3f**	168	2:1	18	94 (*R*)
15	**9f**	**CH_2Cl_2**			**2:1**	**76**	**95** (*R*)
16	$[Pd(allyl)Cl]_2$	THF	**3h**	163	1:1	64	77 (*R*)
17	$[Pd(allyl)Cl]_2$	CH_2Cl_2	**3h**		2:1	92	83 (*R*)
18	$[Pd(allyl)Cl]_2$	CH_2Cl_2	**3i**	137	2:1	0	–
19	$[Pd(allyl)Cl]_2$	THF	**3j**	149	1:1	18	51 (*R*)
20	$[Pd(allyl)Cl]_2$	CH_2Cl_2	**3j**		1:1	0	–
21	$[Pd(allyl)Cl]_2$	CH_2Cl_2	**3j**		2:1	0	–
22	$[Pd(allyl)Cl]_2$	THF	**5a**		1:1	0	–
23	$[Pd(allyl)Cl]_2$	CH_2Cl_2	**5a**		1:1	32	36 (*R*)
24	$[Pd(allyl)Cl]_2$	CH_2Cl_2	**5a**		2:1	31	33 (*R*)
25	$[Pd(allyl)Cl]_2$	THF	**5b**		1:1	26	24 (*R*)
26	$[Pd(allyl)Cl]_2$	CH_2Cl_2	**5b**		1:1	62	23 (*R*)
27	$[Pd(allyl)Cl]_2$	CH_2Cl_2	**5b**		2:1	73	24 (*R*)

Remarkably, in the allylic amination reaction, the *ee*s of **11b** roughly correlate with the steric demands of the ligand expressed in terms of the cone angle θ (Table 5). The best result (95% *ee*) was obtained with the bulkiest ligand **3f**, and even the most π-accepting diamidophosphite **3c** did not violate the correlation (Table 5, entry 7). The amide-type ligands **3i** and **3j** appeared to be inefficient though, due to miserable chemical yields. When THF was used as a solvent instead of CH_2Cl_2 the results were substantially the same.

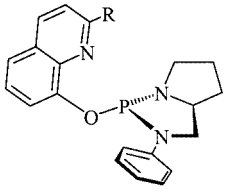
The general trends in allylic alkylation have much in common with the sulfonylation reaction discussed above. As in the sulfonylation, most of the ligands demonstrated good enantioselectivity (about 80% *ee*) in the alkylation of 1,3-diphenylallyl acetate with dimethyl malonate (Table 6, ligands **3b**, **3d**–**f**, **3h**). Similarly, low conversion and moderate optical yields of **11c** were obtained with the ligands of marginal π-acidity (up to 66% *ee* with **3c**, up to 62% *ee* with **3i**). Application of $[Pd_2(dba)_3]\cdot CHCl_3$ as a precatalyst again resulted mainly in reduction in the enantioselectivity. The main distinctive feature of the allylic alkylation is that the least bulky **3a** provided the best stereoinduction (97% *ee*).

To summarize, the most efficient ligands in the three discussed reactions are compounds with moderate π-acidity. They outperformed the BINOL-derived **5a** and **5b**, which provided only moderate chemical and optical yields in the Pd-catalysed allylic substitution reactions of **10** (Scheme 6, Tables 4–6).

Even more interesting is that the novel *P**-monodentate diamidophosphites were found to be superior stereoselec-

Table 6. Enantioselective allylic alkylation of 1,3-diphenylallyl acetate with dimethyl malonate

Entry	Precatalyst	L	Conversion, [%]	*ee*, [%]
1	**[Pd(allyl)Cl]$_2$**	**3a**	**98**	**97** (*S*)
2	[Pd$_2$(dba)$_3$]·CHCl$_3$	**3a**	65	94 (*S*)
3	[Pd(allyl)Cl]$_2$	**3b**	16	70 (*S*)
4	[Pd$_2$(dba)$_3$]·CHCl$_3$	**3b**	92	77 (*S*)
5	[Pd(allyl)Cl]$_2$	**3c**	29	55 (*R*)
6	[Pd$_2$(dba)$_3$]·CHCl$_3$	**3c**	9	66 (*R*)
7	[Pd(allyl)Cl]$_2$	**3d**	35	82 (*S*)
8	[Pd$_2$(dba)$_3$]·CHCl$_3$	**3d**	9	36 (*S*)
9	[Pd(allyl)Cl]$_2$	**3e**	62	78 (*S*)
10	[Pd$_2$(dba)$_3$]·CHCl$_3$	**3e**	45	80 (*S*)
11	[Pd(allyl)Cl]$_2$	**3f**	28	86 (*S*)
12	[Pd$_2$(dba)$_3$]·CHCl$_3$	**3f**	4	32 (*S*)
13	[Pd(allyl)Cl]$_2$	**3h**	82	78 (*S*)
14	[Pd$_2$(dba)$_3$]·CHCl$_3$	**3h**	90	74 (*S*)
15	[Pd(allyl)Cl]$_2$	**3i**	20	62 (*R*)
16	[Pd$_2$(dba)$_3$]·CHCl$_3$	**3i**	10	55 (*R*)
17	[Pd(allyl)Cl]$_2$	**3j**	1	31 (*S*)
18	[Pd$_2$(dba)$_3$]·CHCl$_3$	**3j**	2	9 (*S*)
19	[Pd(allyl)Cl]$_2$	**5a**	8	9 (*S*)
20	[Pd$_2$(dba)$_3$]·CHCl$_3$	**5a**	3	22 (*S*)
21	[Pd(allyl)Cl]$_2$	**5b**	20	60 (*S*)
22	[Pd$_2$(dba)$_3$]·CHCl$_3$	**5b**	58	52 (*S*)



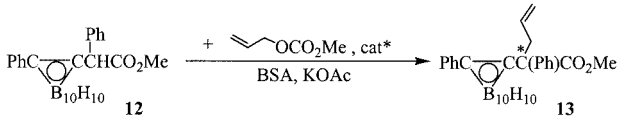
QUIPHOS, R = H

Figure 2. Well-known *P**,*N*-bidentate diamidophosphite ligand QUIPHOS

tors to the well-known *P**,*N*-bidentate ligand QUIPHOS and its derivatives (Figure 2).

Specifically, while the *ee*s of product **11b** in the allylic amination reaction were roughly equal (94% *ee* for QUIPHOS[27] and 95% *ee* for **3f**), in the allylic alkylation reaction between **10** and dimethyl malonate, QUIPHOS (85% *ee*[27]) and its analogues (R = Me, Ph, *t*Bu, CN, etc.[37]) were outplayed by **3a** (97% *ee*). Therefore, removal of the nitrogen donor centre and essential simplification of the ligand structure resulted in increased enantioselectivity and seem to represent a fruitful trend in chiral ligand design.

The synthetic availability and high efficiency of the *P**-monodentate diamidophosphites make it feasible to consider them promising ligands for catalytic processes of practical importance in, as one example, the Pd-catalysed asymmetric alkylation step in the recently reported elegant synthesis of enantiomerically pure anti-inflammatory agent *Ibuprofen*.[38] Another possible field of their application is the synthesis of chiral carborane derivatives. Carboranes are objects of sustained interest as potential B-10 carriers in Boron Neutron Capture Therapy (BNCT).[39] We tested ligands **3a−i** in the Pd-catalysed allylic alkylation of the



Scheme 7

Table 7. Enantioselective allylic alkylation of methyl (2-phenyl-*ortho*-carboran-1-yl)phenyl acetate with methyl prop-2-enyl carbonate

Entry	Precatalyst	L	*ee* [%]
1	[Pd(allyl)Cl]$_2$	**3a**	50
2	**9a**		51
3	[Pd(allyl)Cl]$_2$	**3b**	72
4	[Pd(allyl)Cl]$_2$	**3c**	48
5	[Pd(allyl)Cl]$_2$	**3d**	70
6	**9d**		**73**
7	[Pd(allyl)Cl]$_2$	**3e**	61
8	[Pd(allyl)Cl]$_2$	**3f**	16
9	[Pd(allyl)Cl]$_2$	**3g**	72
10	[Pd(allyl)Cl]$_2$	**3h**	49
11	[Pd(allyl)Cl]$_2$	**3i**	44

carborane compound **12** and achieved enantioselectivities of up to 73% *ee* (Scheme 7, Table 7).

Ligands **3b, 3d** and **3g** were found to be the most efficient. Notably, this is the first direct asymmetric reaction in the carborane series. The obtained *ee*s are fairly high for this specific case of allylation reactions in which the arising chiral centre is situated at the attacking nucleophile.[40]

Experimental Section

General Remarks: All reactions were carried out under dry argon atmospheres. The solvents were dried before use according to the methods described.[41] Methyl, isopropyl, *tert*-butyl and 1-methylcyclobutyl alcohols were dried by heating at reflux over Mg/I$_2$, followed by distillation. Hexafluoroisopropyl alcohol was distilled from over Na$_2$SO$_4$. Removal of moisture from phenol was achieved by azeotropic distillation with benzene followed by distillation. Adamantan-1-ol (Merck) and (1*R*,2*S*,5*R*)-(−)-menthol (Fluka) were sublimed at reduced pressure (1 Torr). Diethylamine, triethylamine, pyrrolidine, piperidine and benzylamine were freshly distilled from over LiAlH$_4$. Phosphorylating reagents **1** and **4** were prepared by the reported methods,[26,42] as were the complexes [Rh(CO)$_2$Cl]$_2$, [Pd(allyl)Cl]$_2$ and [Pd$_2$(dba)$_3$]·CHCl$_3$.[43−45] Both ligand **3d** and complex **9d** have been reported by us.[46] 1,3-Diphenylallyl acetate **10**, methyl (2-phenyl-*ortho*-carboran-1-yl)phenyl acetate **12** and methyl prop-2-en-1-yl carbonate were prepared by the methods described earlier.[40,44,47] Sodium *p*-toluenesulfinate (Acros Organics) was dried in vacuo (2 h, 80 °C, 1 Torr). *N*,*O*-Bis(trimethylsilyl)acetamide (BSA) and dimethyl malonate (Acros Organics) were used as received.

IR spectra were recorded on Specord M-80 or Nicolet 750 devices in CHCl$_3$ (polyethylene cuvette) or in Nujol (CsI plates). ^{13}C NMR (100.61 MHz) and ^{31}P NMR (161.98 MHz) spectra were measured in CDCl$_3$ on a Bruker AMX 400 device. ^{19}F NMR (188.3 MHz) spectra were measured in CDCl$_3$ on a Bruker WP 200 SY instrument. Chemical shifts (δ scale) are given in ppm relative to internal

$CDCl_3$ (δ = 76.91 ppm for ^{13}C NMR) or external 85% aqueous H_3PO_4 solution (δ = 0 ppm for ^{31}P NMR) or CF_3COOH (δ = 0 ppm for ^{19}F NMR). The ^{13}C NMR peaks were ascribed by the DEPT techniques. Mass spectra were recorded on Varian MAT-311 (EI, 70 eV), AMD-402 FAB, or Finnigan LCQ electrospray spectrometers. The analytical data were obtained in the Organic Microanalysis Laboratory at the A. N. Nesmeyanov Institute of Organoelement Compounds. The *ee*s of **11a−c** and **13** were measured by HPLC on a Bruker LC 41 apparatus, with use of (*R*,*R*)-WHELK-01 chiral columns for **11a** and **13**[48,49] and Daicel Chiralcel OD-H for **11b** and **11c**.[50]

Preparation of the Ligands

(2*R*,5*S*)-1,3-Diaza-2-chloro-3-phenyl-2-phosphabicyclo[3.3.0]octane (1): A solution of (*S*)-2-(anilinomethyl)-pyrrolidine (0.722 g, 4.1 mmol) in benzene (20 mL) was added dropwise at 0 °C over 15 min to a vigorously stirred solution of PCl_3 (0.36 mL, 4.1 mmol) and Et_3N (1.12 mL, 8.2 mmol) in benzene (40 mL). The mixture was then briefly heated to boiling point and cooled down to 20 °C. Solid $Et_3N{\cdot}HCl$ was filtered off, and the filtrate was concentrated in vacuo (40 Torr). The residue was dried for 30 min at 10 Torr and distilled in vacuo (1 Torr). White crystalline powder (0.70 g, 71%), m.p. 110−111 °C, b.p. 156−158 °C (1 Torr). ^{13}C NMR ($CDCl_3$): δ_C = 27.48 [s, C(7)], 30.83 [s, C(6)], 44.08 [s, C(8)], 52.22 [s, C(4)], 65.97 [s, C(5)], 116.96−142.74 (C_{Ph}) ppm. ^{31}P NMR ($CDCl_3$), δ_P = 153.66. MS (EI, 70 eV): *m*/*z* (%) = 240 (56) $[M]^+$, 205 (100) $[M - Cl]^+$, 174 (12) $[M - PCl]^+$. $C_{11}H_{14}ClN_2P$ (240.0): calcd. C 54.90, H 5.86, N 11.64; found C 55.27, H 5.58, N 11.95.

General Procedure for Preparation of 3a−j: A solution of Et_3N (0.6 mL, 4.2 mmol) and the relevant alcohol or amine (4.2 mmol) in benzene (10 mL) was added dropwise at 0 °C over 15 min to a vigorously stirred solution of **1** (1 g, 4.2 mmol) in benzene (10 mL). The mixture was then briefly heated to boiling point and allowed to cool to 20 °C. Solid $Et_3N{\cdot}HCl$ was filtered off, and the filtrate was concentrated in vacuo (40 Torr) at 50 °C. Products **3a−e** and **3i** were distilled in vacuo. Products **3f−h** and **3j** were extracted with hexane.

(2*R*,5*S*)-1,3-Diaza-2-methoxy-3-phenyl-2-phosphabicyclo[3.3.0]-octane (3a): Colourless oil, (0.9 g, 92%), b.p. 81−82 °C (0.8 Torr). ^{13}C NMR ($CDCl_3$): δ_C = 25.8 [d, ^3J = 3.4 Hz, C(7)], 31.8 [s, C(6)], 48.3 [d, ^2J = 38.9 Hz, C(8)], 48.6 (s, CH_3), 54.7 [d, ^2J = 6.9 Hz, C(4)], 63.0 [d, ^2J = 8.8 Hz, C(5)], 114.4 (d, ^3J = 11.8 Hz), 118.5 (s), 128.7 (s), 145.3 (d, ^2J = 15.7 Hz) (C_{Ar}) ppm. MS (EI, 70 eV): *m*/*z* (%) = 236 (44) $[M]^+$, 205 (45), 131 (100), 116 (95). $C_{12}H_{17}N_2OP$ (236.1): calcd. C 61.01, H 7.25, N 11.86; found C 61.22, H 7.37, N 11.52.

(2*R*,5*S*)-2-Isopropyloxy-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]-octane (3b): Colourless oil, (0.9 g, 82%), b.p. 76−77°C (0.8 Torr). ^{13}C NMR ($CDCl_3$): δ_C = 24.2 (s, CH_3), 24.6 (s, CH_3), 26.0 [d, ^3J = 4.2 Hz, C(7)], 31.8 [s, C(6)], 48.1 [d, ^2J = 37.8 Hz, C(8)], 54.0 [d, ^2J = 7.2 Hz, C(4)], 62.6 [d, ^3J = 8.8 Hz, C(5)], 66.1 (s, CH), 114.7 (d, ^3J = 11.8 Hz), 118.4 (s), 128.7 (s), 145.6 (d, ^2J = 16.0 Hz) (C_{Ar}) ppm. MS (EI, 70 eV): *m*/*z* (%) = 264 (87) $[M]^+$, 221 (68), 205 (72), 116 (100). $C_{14}H_{21}N_2OP$ (264.1): calcd. C 63.62, H 8.01, N 10.60; found C 63.31, H 8.24, N 10.37.

(2*R*,5*S*)-2-(Hexafluoroisopropyloxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (3c): Colourless oil, (1.25 g, 81%), b.p. 92−93°C (0.8 Torr). ^{13}C NMR ($CDCl_3$): δ_C = 26.4 [d, ^3J = 4.5 Hz, C(7)], 31.7 [s, C(6)], 47.3 [d, ^2J = 34.3 Hz, C(8)], 53.4 [d, ^2J = 7.2 Hz, C(4)], 63.0 [d, ^2J = 8.1 Hz, C(5)], 68.9 (qt, ^2J = 3.6, $^2J_{C,F}$ = 33.2 Hz, CH), 115.3 (d, ^3J = 12.9 Hz), 120.0 (s), 121.5 [q, $^1J_{C,F}$ = 280 Hz, CF_3], 129.0 (s), 144.3 (d, ^2J = 16.4 Hz) (C_{Ar}) ppm. ^{19}F NMR ($CDCl_3$): δ_F = 4.1 (dq), 3.7 (dq) ($^4J_{F,F}$ = 7.5, $^4J_{F,P}$ = 3.3 Hz) ppm. MS (EI, 70 eV): *m*/*z* (%) = 372 (44) $[M]^+$, 267 (55), 205 (32), 116 (100). $C_{14}H_{15}F_6N_2OP$ (372.0): calcd. C 45.17, H 4.06, N 7.53; found C 44.98, H 4.27, N 7.24.

(2*R*,5*S*)-2-(1′-Methylcyclobutyl-1′)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (3e): Colourless oil, (1.12 g, 93%), b.p. 121−122°C (0.8 Torr). ^{13}C NMR ($CDCl_3$): δ_C = 13.0 [s, C(3′)], 25.9 [d, ^3J = 4.6 Hz, C(7)], 26.7 [d, ^3J = 7.2 Hz, CH_3], 31.6 [s, C(6)], 36.1 [d, ^3J = 9.5 Hz, C(4′)], 36.9 [d, ^3J = 7.6 Hz, C(2′)], 47.9 [d, ^2J = 35.6 Hz, C(8)], 54.2 [d, ^2J = 6.9 Hz, C(4)], 62.5 [d, ^2J = 8.0 Hz, C(5)], 75.7 [d, ^2J = 7.6 Hz, C(1′)], 115.3 (d, ^3J = 12.5 Hz), 118.4 (s), 128.6 (s), 145.3 (^2J = 14.5 Hz) (C_{Ar}) ppm. MS (EI, 70 eV): *m*/*z* (%) = 290 (10) $[M]^+$, 221 (53), 205 (90), 116 (100). $C_{16}H_{23}N_2OP$ (290.2): calcd. C 66.19, H 7.98, N 9.65; found C 65.97, H 7.76, N 9.32.

(2*R*,5*S*)-2-(Tricyclo[3.3.1.1.$^{3',7'}$]dec-1′-yloxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (3f): Colourless, viscous oil solidifying on storage, (1.41 g, 95%), m.p. 61−62°C. MS (EI, 70 eV): *m*/*z* (%) = 356 (20) $[M]^+$, 221 (47), 205 (37), 135 (100). $C_{21}H_{29}N_2OP$ (356.2): calcd. C 70.76, H 8.20, N 7.86; found C 70.49, H 8.42, N 7.57.

(2*R*,5*S*,1′*R*,2′*S*,5′*R*)-2-(2′-Isopropyloxy-5′-methyl-cyclohex-1′-yloxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (3g): Colourless, very viscous oil, (1.4 g, 93%). ^{13}C NMR ($CDCl_3$): δ_C = 15.1 [s, C(10′)], 21.0 [s, C(9′)], 22.1 [s, C(7′)], 22.7 [s, C(3′)], 24.9 [s, C(8′)], 26.1 [d, ^3J = 3.8 Hz, C(7)], 31.7 [s, C(6)], 31.8 [s, C(5′)], 34.2 [s, C(4′)], 43.7 [s, C(6′)], 48.5 [d, ^2J = 36.2 Hz, C(8)], 48.8 [d, ^3J = 1.9 Hz, C(2′)], 54.3 [d, ^2J = 6.9 Hz, C(4)], 62.6 [d, ^2J = 8.4 Hz, C(5)], 74.2 [d, ^2J = 9.2 Hz, C(1′)], 114.9 (d, ^3J = 13.3 Hz), 118.4 (s), 128.7 (s), 145.7 (d, ^2J = 15.3 Hz) (C_{Ar}) ppm. MS (EI, 70 eV): *m*/*z* (%) = 360 (10) $[M]^+$, 221 (73), 205 (59), 116 (100). $C_{21}H_{33}N_2OP$ (360.2): calcd. C 69.97, H 9.23, N 7.77; found C 69.58, H 8.96, N 7.41.

(2*R*,5*S*)-2-Phenoxy-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]-octane (3h): White solid, (1.15 g, 93%), m.p. 94−95°C. ^{13}C NMR ($CDCl_3$): δ_C = 26.2 [d, ^3J = 4.2 Hz, C(7)], 31.2 [s, C(6)], 47.6 [d, ^2J = 35.1 Hz, C(8)], 53.7 [d, ^2J = 7.6 Hz, C(4)], 62.5 [d, ^2J = 8.8 Hz, C(5)], 114.9−153.4 (C_{Ar}) ppm. MS (EI, 70 eV): *m*/*z* (%) = 298 (10) $[M]^+$, 205 (100), 136 (78). $C_{17}H_{19}N_2OP$ (298.1): calcd. C 68.44, H 6.42, N 9.39; found C 68.16, H 6.57, N 9.62.

(2*R*,5*S*)-2-Diethylamino-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]-octane (3i): Colourless, viscous oil, solidifying on storage, (1.0 g, 90%), b.p. 118−119°C (0.8 Torr), m.p. 38−39°C. ^{13}C NMR ($CDCl_3$): δ_C = 14.6 (d, ^3J = 2.7 Hz, CH_3), 25.4 [d, ^3J = 3.8 Hz, C(7)], 32.3 [s, C(6)], 39.5 [d, ^2J = 18.7 Hz, NCH_2], 49.6 [d, ^2J = 41.2 Hz, C(8)], 53.9 [d, ^2J = 5.7 Hz, C(4)], 61.8 [d, ^2J = 7.6 Hz, C(5)], 114.6 (d, ^3J = 12.1 Hz), 117.2 (s), 128.5 (s), 146.5 (d, ^2J = 14.5 Hz) (C_{Ar}) ppm. MS (EI, 70 eV): *m*/*z* (%) = 277 (8) $[M]^+$, 221 (23), 205 (52), 58 (100). $C_{15}H_{24}N_3P$ (293.2): calcd. C 64.96, H 8.72, N 15.15; found C 65.17, H 8.63, N 14.93.

(2*R*,5*S*)-2-Piperidino-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]-octane (3j): Colourless oil, (1.1 g, 88%). ^{13}C NMR ($CDCl_3$): δ_C = 24.9 (s, CH_2), 25.4 [d, ^3J = 3.8 Hz, C(7)], 26.7 [d, ^3J = 5.0 Hz, CH_2], 32.1 [s, C(6)], 45.7 [d, ^2J = 15.6 Hz, NCH_2], 50.0 [d, ^2J = 40.1 Hz, C(8)], 54.1 [d, ^2J = 5.3 Hz, C(4)], 62.2 [d, ^2J = 7.6 Hz, C(5)], 114.6 (d, ^3J = 11.8 Hz), 117.3 (s), 128.6 (s), 145.6 (d, ^2J = 13.7 Hz) (C_{Ar}) ppm. MS (EI, 70 eV): *m*/*z* (%) = 289 (55) $[M]^+$, 205 (100), 136 (81), 84 (78). $C_{16}H_{24}N_3P$ (305.2): calcd. C 66.41, H 8.36, N 14.52; found C 66.23, H 8.52, N 14.66.

General Procedure for Preparation of 5a and 5b: A solution of Et_3N (0.2 mL, 1.4 mmol) and the relevant alcohol or amine (1.4 mmol) in toluene (7 mL) was added dropwise at 0 °C over 15 min to a vigorously stirred solution of **4** (0.5 g, 1.4 mmol) in toluene (7 mL). The mixture was then briefly heated to boiling point and allowed to cool to 20 °C. Solid Et_3N·HCl was filtered off, and hexane (15 mL) was added to the filtrate. The resulting mixture was filtered, the solvent was evaporated at reduced pressure (40 Torr), and the product was dried in vacuo (1 Torr) for 2 h.

(R_{ax})-2-(1′-Methylcyclobut-1′-yloxy)-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]-dioxaphosphepine (5a): Colourless tar, (0.55 g, 97%). ^{13}C NMR ($CDCl_3$): δ_C = 13.2 [s, C(3′)], 27.4 (d, ^3J = 6.9 Hz, CH_3), 36.8 [d, ^3J = 6.9 Hz, C(4′)], 36.9 [d, ^3J = 6.1 Hz, C(2′)], 78.5 [d, ^2J = 14.1 Hz, C(1′)], 121.7−147.6 (C_{Ar}) ppm. ^{31}P NMR ($CDCl_3$): δ_P = 153.1 ppm. MS (EI, 70 eV): *m*/*z* (%) = 400 (41) $[M]^+$, 332 (97), 268 (98), 239 (100). $C_{25}H_{21}O_3P$ (400.1): calcd. C 74.99, H 5.29; found C 75.18, H 5.07.

(R_{ax})-2-(3-Pyrrolidin-1′-yl)-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine (5b): White solid, (0.52 g, 95%), m.p. 119−120°C. ^{13}C NMR ($CDCl_3$): δ_C = 25.6 (d, ^3J = 4.2 Hz, CH_2), 45.4 (d, ^2J = 16.0 Hz, NCH_2), 121.2−150.1 (C_{Ar}) ppm. ^{31}P NMR ($CDCl_3$): δ_P = 150.7 ppm. MS (EI, 70 eV): *m*/*z* (%) = 385 (48) $[M]^+$, 315 (64), 268 (72), 70 (100). $C_{24}H_{20}NO_2P$ (385.1): calcd. C 74.80, H 5.23, N 3.63; found C 74.62, H 4.99, N 3.35.

Preparation of the Complexes

General Procedure for Preparation of Rh Complexes 6a−c, 6i and 7: Rhodium(I) chlorocarbonyl complexes with ligands **3a−c** and **3i** were prepared for ^{31}P NMR, IR, and FAB mass spectral experiments as follows. A solution of the relevant ligand (0.18 mmol) in $CHCl_3$ (1.5 mL) was added dropwise over 20 min to a vigorously stirred solution of $[Rh(CO)_2Cl]_2$ (0.035 g, 0.09 mmol) in $CHCl_3$ (1.5 mL). An aliquot portion of the solution (1 mL) was used for the appropriate experiment.

Complex **7** was prepared similarly, by starting from ligand **3a** (0.36 mmol) in a $CHCl_3$ solution.

General Procedure for Preparation of Pd Complexes 8f and 8g: A solution of the relevant ligand (0.4 mmol) in $CHCl_3$ (15 mL) was added dropwise over 40 min to a vigorously stirred solution of $[Pd(allyl)Cl]_2$ (0.073 g, 0.20 mmol) in $CHCl_3$ (15 mL). The mixture was stirred for an additional 1 h and the solvent was evaporated at reduced pressure (40 Torr). The residue was washed with diethyl ether (2 × 10 mL) and dried in vacuo (1 Torr) for 1 h.

[Pd(allyl)(3f)Cl] (8f): Light brown powder, (0.20 g, 92%), m.p. 165−167 °C (dec.), ^{13}C NMR ($CDCl_3$): δ_C = 26.9 [d, ^3J = 5.7 Hz, C(7)], 30.9 [s, C(3′), C(5′), C(7′)], 31.6 [d, ^3J = 1.9 Hz, C(6)], 35.7 [s, C(4′), C(6′), C(10′)], 43.9 [d, ^3J = 5.0 Hz, C(2′), C(8′), C(9′)], 47.4 [d, ^2J = 23.3 Hz, C(8)], 54.2 [s, C(4)], 60.5 [s, C(5)], 61.7 [s, $CH_{2(allyl,\ trans\text{-}Cl)}$], 77.9 [d, ^2J = 46.9 Hz, $CH_{2(allyl,\ trans\text{-}P)}$], 82.4 [d, ^2J = 20.6 Hz, C(1′)], 115.7 (d, ^3J = 8.0 Hz), 117.5 (d, ^2J = 9.5 Hz, CH_{allyl}), 119.7 (s), 128.5 (s), 143.9 (d, ^2J = 12.6 Hz) (C_{Ar}) [for (R_P)-**8f**] ppm. ^{13}C NMR ($CDCl_3$): δ_C = 27.4 [d, ^3J = 4.9 Hz, C(7)], 31.2 [s, C(3′), C(5′), C(7′)], 31.5 [d, ^3J = 1.5 Hz, C(6)], 35.4 [s, C(4′), C(6′), C(10′)], 44.2 [d, ^3J = 4.6 Hz, C(2′), C(8′), C(9′)], 50.2 [s, C(8)], 55.7 [d, ^2J = 6.5 Hz, C(4)], 59.8 [s, $CH_{2(allyl,\ trans\text{-}Cl)}$], 63.0 [d, ^2J = 1.9 Hz, C(5)], 78.4 [d, ^2J = 44.2 Hz, $CH_{2(allyl,\ trans\text{-}P)}$], 81.4 [d, ^2J = 17.4 Hz, C(1′)], 117.7 (d, ^2J = 7.6 Hz, CH_{allyl}), 118.1 (d, ^3J = 9.5 Hz), 121.0 (s), 128.7 (s), 145.4 (d, ^2J = 8.2 Hz) (C_{Ar}) [for (S_P)-**8f**] ppm. MS (FAB): *m*/*z* (%) = 539 (3) $[M]^+$, 503 (10) $[M - Cl]^+$, 462 (14), 135 (100). $C_{24}H_{34}ClN_2OPPd$ (538.1): calcd. C 53.44, H 6.35, N 5.19; found C 53.29, H 6.52, N 5.52.

[Pd(allyl)(3g)Cl] (8g): Yellow-orange powder, (0.19 g, 89%), m.p. 176−178 °C (dec.). MS (FAB): *m*/*z* (%) = 543 (5) $[M]^+$, 508 (8) $[M - Cl]^+$, 467 (27), 116 (100). $C_{24}H_{38}ClN_2OPPd$ (542.1): calcd. C 53.05, H 7.05, N 5.16; found C 53.34, H 6.73, N 5.44.

General Procedure for Preparation of Pd Complexes 9a and 9c−g: A solution of the relevant ligand (0.8 mmol) in $CHCl_3$ (15 mL) was added dropwise over 40 min to a vigorously stirred solution of $[Pd(allyl)Cl]_2$ (0.073 g, 0.20 mmol) in $CHCl_3$ (15 mL). The mixture was stirred for an additional 1 h, followed by dropwise addition of $AgBF_4$ (0.078 g, 0.4 mmol) in THF (15 mL) over 20 min. The mixture was stirred for 1 h, and precipitated AgCl was filtered off. The filtrate was concentrated at reduced pressure to the volume of ca. 0.5 mL, and diethyl ether (15 mL) was added. The precipitated solid was separated by centrifugation, washed with diethyl ether (2 × 10 mL) and dried in vacuo (1 Torr) for 1 h.

$[Pd(allyl)(3a)_2]^+$ BF_4^- (9a): White powder, (0.27 g, 95%), m.p. 178−180 °C (dec.). MS (FAB): *m*/*z* (%) = 619 (91) $[M - BF_4]^+$, 578 (63), 131 (100). $C_{27}H_{39}BF_4N_4O_2P_2Pd$ (706.2): calcd. C 45.88, H 5.56, N 7.93; found C 45.52, H 5.21, N 8.11.

$[Pd(allyl)(3c)_2]^+$ BF_4^- (9c): Brown powder, (0.35 g, 90%), m.p. 177−179 °C (dec.). MS (FAB): *m*/*z* (%) = 891 (82) $[M - BF_4]^+$, 850 (54), 116 (100). $C_{31}H_{35}BF_{16}N_4O_2P_2Pd$ (978.1): calcd. C 38.04, H 3.60, N 5.72; found C 38.30, H 3.29, N 5.57.

$[Pd(allyl)(3e)_2]^+$ BF_4^- (9e): Yellow powder, (0.32 g, 96%), m.p. 166−168 °C (dec.). ^{13}C NMR ($CDCl_3$): δ_C = 13.4 [s, C(3′)], 25.5 [s, C(7)], 27.1 (s, CH_3), 31.8 [s, C(6)], 36.2 [s, C(4′)], 37.1 [s, C(2′)], 48.2 [d, ^2J = 23.6 Hz, C(8)], 53.5 [d, ^2J = 24.4 Hz, C(4)], 60.8 [s, C(5)], 70.1 [t, ^2J = 52.7 Hz, $CH_{2(allyl)}$], 82.2 [s, C(1′)], 115.8 (d, ^3J = 14.4 Hz), 120.6 (s), 123.6 (t, ^2J = 8.4 Hz, CH_{allyl}), 129.2 (s), 142.7 (d, ^2J = 11.3 Hz) (C_{Ar}) ppm. MS (ESI): *m*/*z* (%) = 727 (25) $[M - BF_4]^+$, 437 (100), 174 (14). $C_{35}H_{51}BF_4N_4O_2P_2Pd$ (814.3): calcd. C 51.58, H 6.31, N 6.87; found C 51.32, H 6.52, N 6.68.

$[Pd(allyl)(3f)_2]^+$ BF_4^- (9f): Light brown powder, (0.33 g, 88%), m.p. 189−191 °C (dec.). MS (FAB): *m*/*z* (%) = 859 (89) $[M - BF_4]^+$, 818 (50), 135 (100). $C_{45}H_{63}BF_4N_4O_2P_2Pd$ (946.4): calcd. C 57.06, H 6.70, N 5.92; found C 56.82, H 6.52, N 5.81.

$[Pd(allyl)(3g)_2]^+$ BF_4^- (9g): White powder, (0.34 g, 90%), m.p. 173−175 °C (dec.). MS (FAB): *m*/*z* (%) = 867 (94) $[M - BF_4]^+$, 826 (48), 205 (100). $C_{45}H_{71}BF_4N_4O_2P_2Pd$ (954.4): calcd. C 56.58, H 7.49, N 5.87; found C 56.31, H 7.20, N 6.11.

Catalytic Experiments

Palladium-Catalysed Allylic Sulfonylation of 1,3-Diphenylallyl Acetate with Sodium *p*-Toluenesulfinate: A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) or $[Pd_2(dba)_3]$·$CHCl_3$ (0.0103 g, 0.01 mmol) and the appropriate ligand (0.02−0.04 mmol) in THF (5 mL) was stirred for 40 min [alternatively, the presynthesized appropriate complex (0.02 mmol) was dissolved in THF (5 mL)]. 1,3-Diphenylallyl acetate **10** (0.1 mL, 0.5 mmol) was added to the solution and the reaction mixture was stirred for 15 min. Sodium *p*-toluenesulfinate (0.178 g, 1.00 mmol) was added, and the reaction mixture was stirred for 48 h, quenched with brine (10 mL) and extracted with THF (3 × 7 mL). The organic layer was washed with brine (2 × 7 mL) and dried over $MgSO_4$. The solvent was evaporated at reduced pressure (40 Torr). Crystallization of the residue from EtOH, followed by desiccation in vacuo (10 Torr, 12 h), gave the product **11a** as white crystals. All spectroscopic data for compound **11a** were in good agreement with the literature.[48]

Palladium-Catalysed Allylic Amination of 1,3-Diphenylallyl Acetate with Benzylamine: A solution of $[Pd(allyl)Cl]_2$ (0.0037 g,

0.01 mmol) and the appropriate ligand (0.02−0.04 mmol) in THF or CH_2Cl_2 (5 mL) was stirred for 40 min [alternatively, the presynthesized appropriate complex (0.02 mmol) was dissolved in CH_2Cl_2 (5 mL)]. 1,3-Diphenylallyl acetate **10** (0.1 mL, 0.5 mmol) was added to the solution, and the reaction mixture was stirred for 15 min. Benzylamine (0.11 mL, 1.00 mmol) was added, and the reaction mixture was stirred for 48 h and concentrated at reduced pressure (40 Torr). The product **11b** was obtained as a light yellow oil after column chromatography (silica gel, hexane/ethyl acetate, 3:1). All spectroscopic data for compound **11b** were in good agreement with the literature.[25]

Palladium-Catalysed Allylic Alkylation of 1,3-Diphenylallyl Acetate with Dimethyl Malonate: A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) or $[Pd_2(dba)_3]\cdot CHCl_3$ (0.0103 g, 0.01 mmol) and the appropriate ligand (0.02 mmol) in THF (5 mL) was stirred for 40 min. 1,3-Diphenylallyl acetate **10** (0.1 mL, 0.50 mmol) was added to the solution, and the reaction mixture was stirred for 15 min. Dimethyl malonate (0.10 mL, 0.87 mmol), BSA (0.22 mL, 0.87 mmol) and sodium acetate (0.002 g) were added. The reaction mixture was stirred for 48 h, diluted with THF (5 mL) and filtered through Celite. The filtrate was evaporated at reduced pressure (40 Torr) giving after desiccation in vacuo (10 Torr, 12 h) product **11c** as a colourless oil, solidifying upon standing. All spectroscopic data for compound **11c** were in good agreement with the literature.[25]

Palladium-Catalysed Allylic Alkylation of Methyl (2-Phenyl-*ortho*-carboran-1-yl)phenyl Acetate with Methyl Prop-2-enyl Carbonate: A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) and the appropriate ligand (0.04 mmol) in THF (5 mL) was stirred for 40 min [alternatively, the presynthesized appropriate complex (0.02 mmol) was dissolved in THF (5 mL)]. Methyl (2-phenyl-*ortho*-carboran-1-yl)-phenyl acetate **12** (0.185 g, 0.50 mmol), methyl prop-2-enyl carbonate (0.12 mL, 1.00 mmol), BSA (0.15 mL, 0.60 mmol), and potassium acetate (0.003 g) were then added to the solution, and the reaction mixture was stirred for 96 h. The solvent was evaporated at reduced pressure (40 Torr), and the residue was dissolved in diethyl ether (30 mL), washed with 5% HCl (2 × 20 mL), saturated $NaHCO_3$ (20 mL) and water (20 mL), dried over Na_2SO_4, filtered and concentrated in vacuo (40 Torr). The product **13**[40] was obtained as a yellow oil after column chromatography (silica gel, petroleum ether/ethyl acetate, 7:1). ^1H NMR ($CDCl_3$), δ = 3.15 +3.22 (AB system, J = 14.4, 7.2, 5.6, 1.4, 1.2 Hz, 2 H), 3.53 (s, 3 H), 4.87 (dm, J = 10.2 Hz, 1 H), 4.95 (dm, J = 17 Hz, 1 H), 5.18 (m, 1 H), 7.05 −7.40 (m, 10 H) ppm. MS (EI, 70 eV): *m*/*z* (%) = 408 (100) $[M]^+$.

Acknowledgments

The authors gratefully acknowledge receiving the chiral HPLC columns (*R*,*R*) WHELK-01 from Regis Technologies (USA) and Chiralcel OD-H from Daicel Chemical Industries, Ltd. (Japan). The authors thank Dr. A.V. Korostylev (Leibniz-Institut für Organische Katalyse, Rostock, Germany) for his assistance in preparation of the manuscript. This work was partially supported by the Russian Foundation for Basic Research (Grant No. 03−03−32181) and a Grant of the President of the Russian Federation for Young Doctors of Sciences (No. MD−21.2003.03).

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Received October 31, 2003

