Easily Accessible Chiral *P,N*-Bidentate Aryl Phosphites, Their Complexation and Application in Enantioselective Allylic Alkylation, Sulfonylation and Hydrosilylation

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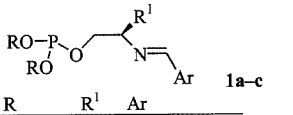
New chiral *P,N*-hybrid aryl phosphites have been obtained by one-step phosphorylation of amino and imino alcohols. Complexation of the new ligands with $[Rh(CO)_2Cl]_2$, $[Pd(COD)Cl_2]$ and $[Pd(allyl)Cl]_2$ was found to give chelate complexes $[Rh(CO)Cl(\eta^2\text{-}P^{\frown}N)]$, $[PdCl_2(\eta^2\text{-}P^{\frown}N)]$ and $[Pd(allyl)(\eta^2\text{-}P^{\frown}N)]^+Cl^-$, respectively. With these new *P,N*-ligands, up to 82% *ee* enantioselectivity was achieved in the Pd-catalysed alkylation of ethyl 3-penten-2-yl carbonate with dimethyl malonate, up to 80% *ee* in the Pd-catalysed sulfonylation of methyl 3-penten-2-yl carbonate with sodium *p*-toluenesulfinate, and up to 50% *ee* in the Rh-catalysed hydrosilylation of acetophenone with diphenylsilane.

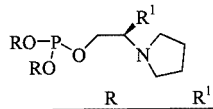
Introduction

Chiral *P,N*-bidentate compounds are one of the leading ligand groups in modern asymmetric catalysis.[1−3] Most such systems are phosphanes in nature, but phosphite-type *P,N*-hybrid ligands are acquiring progressively growing importance because of their synthetic availability, high π-acidity of the phosphorus atom and high resistance to oxidative destruction. In general, the presence of oxygen and/or nitrogen atoms in the first coordination sphere of the phosphorus atom offers the potential to tune the chemical stability of ligands, their donor/acceptor properties and steric demands. This has made it possible to achieve impressive results in catalytic enantioselective allylation, conjugate addition of organometallic compounds to enones, hydrosilylation and hydrogenation reactions.[1−9] Interestingly, each of the ligands mentioned has a phosphacyclic structure, normally constructed with the aid of effective chiral inductors such as BINOL, TADDOL, (1*R*,2*R*)-1,2-*N*,*N*′-bis(*p*-toluenesulfonylamino)-1,2-diphenylethane, (*S*)-2-(anilinomethyl)pyrrolidine etc.[1−9] Only one example[10] of the use of an achiral biphenol is known; the phosphitooxazoline derived from it is a phosphacyclic compound as well. We have recently reported syntheses of several chiral *P,N*-phosphites with acyclic phosphorus donor centres.[11,12]



1a–c

R	R^1	Ar	
*i*Pr	Et	Ph	**(1a)**
Bornyl	Et	Ph	**(1b)**
*i*Pr	*i*Pr	4-$Me_2NC_6H_4$	**(1c)**



1d–f

R	R^1	
*i*Pr	Et	**(1d)**
*i*Pr	*i*Pr	**(1e)**
2,6-Me_2Ph	Et	**(1f)**

These gave up to 57% *ee* in the Pd-catalysed alkylation of 1,3-diphenylpropen-2-yl acetate with dimethyl malonate, and up to 61% *ee* when 3-phenylpropen-2-yl acetate was used as a substrate. In this article, we describe the synthesis, complexation with Rh^I and Pd^{II} precursors and catalytic applications of a new series of *P,N*-bidentate aryl phosphites bearing distant amino or imino groups.

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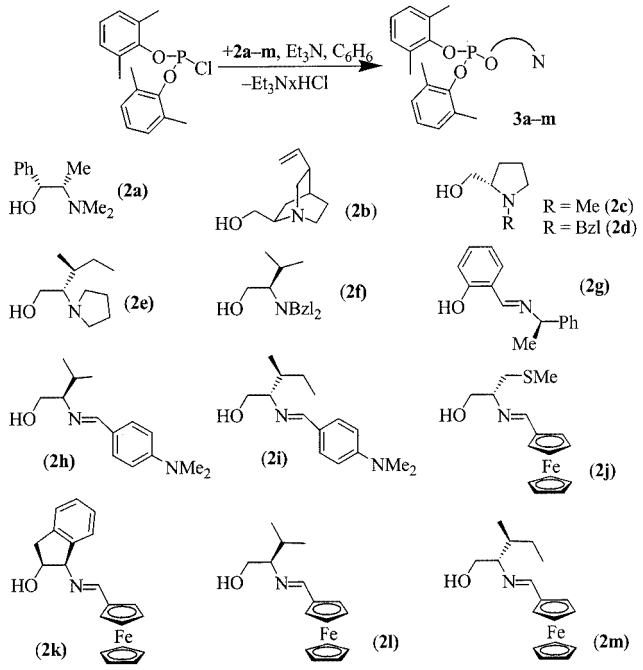
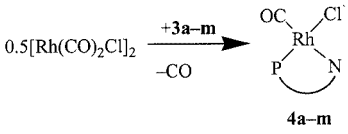
Results and Discussion

The new *P,N*-bidentate aryl phosphites were synthesized by one-step phosphorylation of the corresponding amino and imino alcohols with bis(2,6-dimethylphenyl) chlorophosphite.

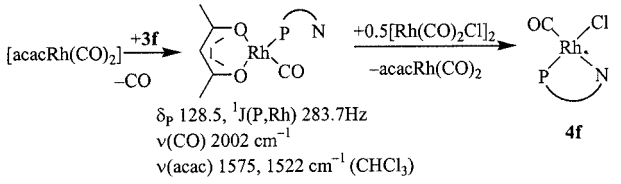


They divide into two groups: ligands **3a**−**3f**, possessing sp^3-hybridized nitrogen atoms, and ligands **3g**−**3m**, which have sp^2-hybridized nitrogen atoms. All the compounds **3a**−**m** are soluble in conventional organic solvents and stable under dry conditions for several months. On treatment with $[Rh(CO)_2Cl]_2$, their neutral carbonyl(chloro)Rh^I complexes were obtained.



The ν(CO) and $^1J_{P,Rh}$ parameters in their IR and ^{31}P NMR spectra act as sensitive indicators, which characterise the mode of complexation of the *P,N*-ligands and allow the π-acceptor ability of the phosphorus centre and the degree of electronic non-symmetry of the ligands to be estimated.[13−15]

In general, ligands **3a**−**3m** give chelate complexes. Thus, the $^1J_{P,Rh}$, $^1J_{C,Rh}$, $^2J_{C,P}$, ν(CO) and ν(Rh−Cl) data for complexes **4a**−**4m** (Tables 1 and 2) are in good agreement with the suggested structures.[13,15] Significant (9−11 ppm) coordination shifts $\Delta\delta_C$ [= δ_C(complex) − δ_C(ligand)] for the azomethine carbon atoms in complexes **4i** and **4l** (Table 2) also attest to the coordination of distant imino groups with the rhodium atom. However, complexation of some ligands displays special features. Thus, compounds **4e**−**4g**, **4j** and **4k** exist as two or more conformers (Table 1) similarly to known cationic rhodium, iridium[16] and palladium[17] *P,N*-chelates. In addition, the reactions between $[Rh(CO)_2Cl]_2$ and the compounds bearing cyclic (**3b**−**3e**) or sterically hindered acyclic (**3f**) sp^3-nitrogen donor centres produced some quantities of *trans*-$[Rh(CO)Cl(\eta^1\text{-}P^{\frown}N)_2]$ complexes, in which the compounds function as *P*-monodentate ligands. This was shown by their characteristic[13,18] IR and ^{31}P NMR spectroscopic data (the percentage of *trans* complexes determined by ^{31}P NMR is given in parentheses) for **3b**: δ_P = 122.8, $^1J_{P,Rh}$ = 204.9 Hz (8%); for **3c**: δ_P = 121.4, $^1J_{P,Rh}$ = 207.6 Hz, ν(CO) = 1995 cm^{-1} (20%); for **3d**: δ_P = 122.1, $^1J_{P,Rh}$ = 203.5 Hz, ν(CO) = 2000 cm^{-1} (45%); for **3e**: δ_P = 124.6, $^1J_{P,Rh}$ = 205.6 Hz, ν(CO) = 1994 cm^{-1} (30%); for **3f**: δ_P = 122.6, $^1J_{P,Rh}$ = 195.4 Hz, ν(CO) = 1993 cm^{-1} (54%). It was notable that, the higher the steric demands of the aza centre, the larger the amount of $[Rh(CO)Cl(\eta^1\text{-}P^{\frown}N)_2]$ complex. The reason for this seems to be an increase in steric hindrance for coordination of nitrogen atoms and, as a result, a fall in the proportion of chelate $[Rh(CO)Cl(\eta^2\text{-}P^{\frown}N)]$ products. To overcome this effect, the synthesis of complex **4f** was performed in a different way, by the exchange reaction previously developed for *P*-monodentate ligands.[19]



Imino phosphites **3g**−**3m**, independently of their steric demands, gave chelate products **4g**−**4m** only. They are therefore more typical chelate ligands than amino phosphites.

All the ligands **3a**−**3m** had highly π-acidic phosphorus centres. This was proved by the values of the ν(CO) and $^1J_{P,Rh}$ parameters for complexes **4a**−**4m**, which are significantly larger than those for the analogous amino phosphane based complexes (by 30−35 cm^{-1} and 80−100 Hz, respectively) and even their aminoalkyl phosphite counterparts (by 6−10 cm^{-1} and 10−15 Hz).[13−15] It is well known that increasing *P*-centre π-acidity in *P,N*-bidentate ligands favours high chemical and optical yields in such catalytic reactions as allylation, hydroboration/oxidation and hydrosilylation/oxidation of alkenes, and hydrosilylation of ketones.[1,2]

On the other hand, increasing σ-donor character in the *N*-centre results in higher optical yields in hydroboration/oxidation and hydrosilylation/oxidation of alkenes.[20,21] In this context, a concept of electronically non-symmetric ligands has been suggested (the higher the π-acceptor ability of the *P*-centre and the σ-donor ability of the *N*-centre, the more electronically non-symmetrical the compound).[14] This parameter can be estimated by the value of ν(CO) in the IR spectrum of the carbonyl(chloro) complex $[Rh(CO)Cl(P^{\frown}N)]$. In particular, for structurally similar complexes with identical phosphorus centres and different nitrogen centres, a compound with a lower value of ν(CO)

Table 1. IR and ^{31}P NMR spectroscopic data for complexes **4a−m** (in $CHCl_3$)

Compound	IR		^{31}P NMR	
	ν(CO) [cm^{-1}]	ν(Rh−Cl) [cm^{-1}]	δ_P	$^1J_{P,Rh}$ [Hz][a]
4a	2031	295	119.4	288.6
4b	2032	290	125.6	287.5
4c	2028	288	122.6	285.9
4d	2028	289	118.7	287.4
4e	2029	291	121.4, 122.6	290.0 (80%), 287.5 (20%)
4f	2024	280	120.1, 118.5	288.6 (70%), 288.1 (30%)
4g	2034	290	133.6, 129.7, 110.9	287.4 (83%), 273.2 (10%), 300.0 (7%)
4h	2024	288	125.8	273.4
4i	2024	287	125.3	275.5
4j	2028	287	122.8, 122.5	276.4 (85%), 278.0 (15%)
4k	2024	286	123.3, 116.4	278.4 (73%), 274.7 (27%)
4l	2026	290	121.8	279.8
4m	2025	291	121.9	279.4

[a] Percentage of each diastereomer of the complex

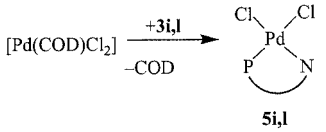
Table 2. ^{13}C NMR spectroscopic data for compounds **3i**, **4i**, **5i** and **3l**, **4l**, **5l** (in $CDCl_3$), δ_C ($J_{C,P}$ [Hz])

Compound	HC=	C_{Ar}	NCH	OCH_2	$N(CH_3)_2$	CH	CH_2	CH_3(Ar)	CH_3
3i	160.9	110.7−148.9	75.8	64.1	39.9	36.6	25.1	17.42, 17.46, 17.52, 17.58	11.0, 15.7
4i[a]	170.1	109.9−153.0	75.2	68.5	39.5	37.8	25.1	17.8, 18.2	10.2, 13.6
5i	170.8	110.4−153.6	73.7	69.2 (^2J = 2.6)	39.6	37.2	25.0	17.7, 18.1	10.2, 13.4

	HC=	C_{Ar}	NCH	Fc (*ipso*)	Fc	Fc (Cp)	OCH_2	CH	CH_3	CH_3(Ar)
3l	161.2	123.8−149.0	77.5 (^3J = 3.1)	80.6	68.3, 68.5, 69.97, 70.03	68.8	63.9	29.7	18.9, 19.9	17.59, 17.64
4l[b]	171.7	124.4−149.2	77.0	75.4	71.7, 71.8, 73.0, 75.6	69.8	67.5 (^2J = 5.0)	30.8	18.5, 20.8	18.1, 18.4
5l	173.7	125.0−148.4	76.2	74.0	70.7, 72.8, 73.9, 74.5	69.9	67.7 (^2J = 4.3)	30.0	17.6, 20.1	17.49, 17.53

[a] The resonance of the carbonyl-type carbon atom: δ_C = 187.62 ($^1J_{C,Rh}$ = 71.1, $^2J_{C,P}$ = 17.3 Hz). [b] The resonance of the carbonyl-type carbon atom: δ_C = 187.42 ($^1J_{C,Rh}$ = 71.4, $^2J_{C,P}$ = 18.1 Hz).

possesses a more active σ-donor nitrogen-containing centre and hence is more electronically non-symmetric.[14,15] From this point of view, imino phosphites are the most electronically non-symmetric ligands among compounds **3a−3m** (Table 1). The exceptions are amino phosphite **4f**, bearing an dibenzylamino group, and the imino phosphites **3g** and **3j**. However, compound **3g** has a slightly different phosphorus centre and is actually a triaryl phosphite (unlike the other ligands), while ligand **3j** has an additional sulfur atom in its structure. Analogously to complexation with Rh^I, the new *P,N*-hybrid aryl phosphites form metal chelates with Pd^{II}.



5i,l

The IR and NMR spectroscopic data for the obtained complexes, shown in Tables 2 and 3, strongly supported the suggested mode of coordination. In particular, the δ_P values for complexes **5i** and **5l** (Table 3) are typical for six-membered palladacycles based on *P,N*-bidentate phosphites with acyclic phosphorus centres.[11,22] Large coordination shifts $\Delta\delta_C$, similar to those seen in the rhodium complexes **4i** and **4l**, were observed for the azomethine carbon atoms in complexes **5i** and **5l** (Table 2). Two equally intense ν(Pd−Cl) bands in the far IR regions of **5i** and **5l** (Table 3) resulted from the *cis* configuration of chloro ligands and different *trans* influences of phosphorus and nitrogen atoms.

Table 3. IR and ^{31}P NMR spectroscopic data for palladium complexes **5i**, **5l** and **6**

Compound	ν(Pd−Cl) (nujol, CsI) [cm^{-1}]	δ_P ($CDCl_3$)
5i	342, 288	77.2
5l	336, 292	74.1
6	−	132.7

In order to investigate details of the complex geometry, complexes **4i**, **5i** and **5l** were studied by single-crystal X-ray diffraction (see Figures 1, 2 and 3, Table 4). Comparison of the crystal packings of **4i** and **5i** revealed that the two compounds were isostructural. The principal geometry of the complexes is therefore only very slightly dependent on the nature of the metal centre and the terminal ligands. In all the complexes, the metal atoms are characterized by square-planar coordination with slightly different degrees of planarity. The maximum deviations from the mean plane are 0.15, 0.12 and 0.08 Å for **4i**, **5i** and **5l**, respectively.

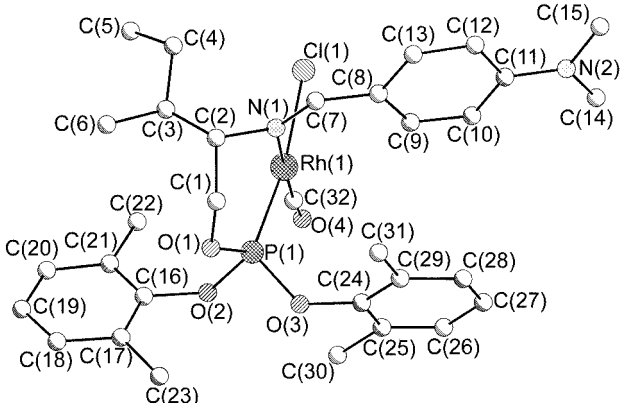


Figure 1. General view of complex **4i** and numbering scheme

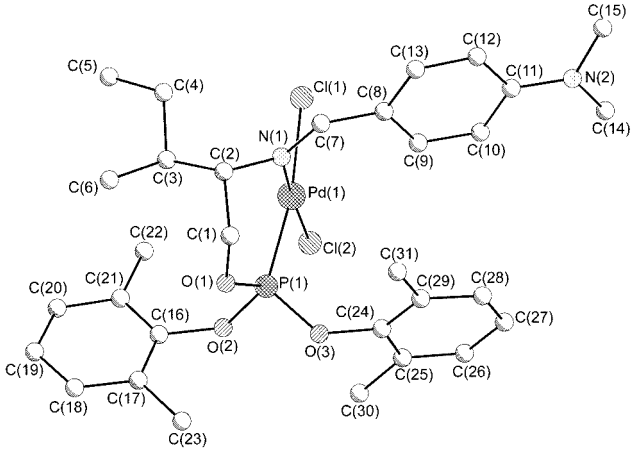


Figure 2. General view of complex **5i** and numbering scheme

The conformations of the six-membered metallacycles in the investigated compounds are far from regular, and can be described as distorted chairs in **4i** and **5i** and a distorted boat in **5l**. The difference in the conformation type seems to result from steric overcrowding due to introduction of the ferrocenyl moiety. In addition, the presence of the ferrocenyl substituent gives rise to significant changes in the mutual orientation of the 2,6-dimethylphenyl rings, with one of them approximately parallel to the Cp ring. Such an orientation of the C(8)−C(12) and C(26)−C(31) rings produces a decrease in the interplane separation to 3.32 Å, and could be regarded as an intramolecular stacking interaction. Despite this possible intramolecular stacking interaction, however, the geometry of the ferrocene moiety is actually unaffected. The ferrocene is characterized by the eclipsed conformation, with practically equal Fe(1)−centroid distances, 1.657 and 1.646 Å for the C(8)−C(12) and the C(13)−C(17) rings. In addition to the neutral dichloropalladium complexes, cationic complex **6** was obtained with ligand **3m**.

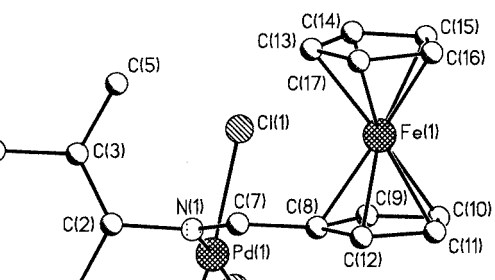
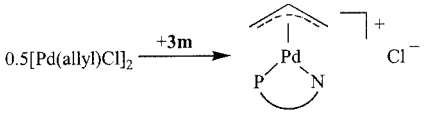


Figure 3. General view of complex **5l** and numbering scheme

Table 4. Selected bond lengths [Å] and angles [°] for **4i**, **5i** and **5l**

	4i	**5i**	**5l**
M(1)−C(32)	1.804(10)	−	−
M(1)−N(1)	2.111(7)	2.063(3)	2.027(4)
M(1)−P(1)	2.171(2)	2.1983(10)	2.2030(17)
M(1)−Cl(1)	2.3792(19)	2.3656(9)	2.3572(16)
M(1)−Cl(2)	−	2.2928(9)	2.2919(16)
P(1)−O(1)	1.580(5)	1.571(2)	1.579(4)
P(1)−O(2)	1.619(5)	1.588(2)	1.594(3)
P(1)−O(3)	1.605(4)	1.590(3)	1.576(4)
N(1)−C(7)	1.266(8)	1.282(4)	1.281(6)
C(7)−C(8)	1.426(9)	1.442(5)	1.440(7)
C(32)−M(1)−P(1)	91.3(2)	−	−
Cl(1)−M(1)−Cl(2)	−	91.15(3)	90.81(6)
N(1)−M(1)−P(1)	89.27(14)	90.60(7)	84.84(13)
N(1)−M(1)−Cl(1)	90.12(14)	90.79(7)	91.91(13)
P(1)−Pd(1)−Cl(2)	−	88.17(3)	92.49(6)
O(1)−P(1)−M(1)	116.2(2)	113.79(10)	107.35(15)
O(2)−P(1)−M(1)	117.71(17)	116.41(10)	114.59(15)
O(3)−P(1)−M(1)	120.02(16)	118.85(10)	124.67(15)
C(2)−N(1)−M(1)	115.3(5)	116.1(2)	114.7(3)
C(7)−N(1)−C(2)	115.4(7)	117.2(3)	116.0(4)
C(7)−N(1)−M(1)	129.0(4)	126.6(2)	129.0(4)

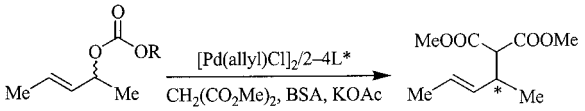


6

The ^{31}P and ^{13}C NMR spectra of complex **6** (see Exp. Sect. and Table 3) contained only one set of resonances, ex-

plicable either by the presence of only one of the possible *exo* and *endo* isomers or by their fast interconversion (see ref.[2], refs. cited therein and refs.[23,24]). It is noteworthy that the E_b(Cl2P) value of 198.4 eV in the XPS spectrum of compound **6** is close to the highest limit for chlorine anions.[25] Furthermore, the PD mass spectrum of complex **6** shows a rarely observable molecular ion peak (usually only the $[M - Cl]^+$ peak is observed). These facts allowed us to conclude that complex **6** exists as a contact ion pair.[26]

Some of the new *P,N*-(aryl phosphites) were tested in the palladium-catalysed allylic alkylation of ethyl 3-penten-2-yl carbonate with dimethyl malonate (Scheme 1, R = Et). The results are shown in Table 5. They allow the following conclusions to be made:



Scheme 1

Table 5. Enantioselective allylic alkylation of 3-penten-2-yl carbonate with dimethyl malonate according to Scheme 1 (L*/Pd = 2); DCM = dichloromethane

Entry	L*	Solvent	*T* [°C]	Yield (%)[a]	*ee* (%)[b]
1	**3b**	THF	room temp.	90	11 (*S*)
2	**3d**	THF	room temp.	35	2 (*R*)
3	**3f**	THF	room temp.	30	4 (*S*)
4	**3h**	THF	room temp.	60	24 (*S*)
5	**3i**	THF	room temp.	50	58 (*S*)
6	**3i**	DCM	room temp.	85	57 (*R*)
7	**3j**	DCM	room temp.	90	13 (*R*)
8	**3k**	THF	room temp.	65	52 (*S*)
9	**3l**	THF	room temp.	75	38 (*S*)
10	**3l**	THF	−18	40	21 (*S*)
11	**3m**	THF	65	65	49 (*R*)
12	**3m**	THF	room temp.	65	69 (*R*)
13	**3m**	THF	5	70	77 (*R*)
14	**3m**	THF	−18	25	52 (*R*)
15	**3m**	CH_3CN	room temp.	55	54 (*R*)
16	**3m**	DMF	room temp.	70	45 (*R*)
17	**3m**	$(CH_2OMe)_2$	room temp.	60	53 (*R*)
18	**3m**	toluene	room temp.	60	61 (*R*)
19	**3m**	DCM	room temp.	80	80 (*R*)
20	**3m**	DCM	5	75	81 (*R*)
21	**3m**	DCM	−18	30	76 (*R*)
22	**3m**[c]	DCM	room temp.	80	82 (*R*)

[a] Yield of analytically pure product after column chromatography. [b] The *ee* values were determined by chiral GC (fused silica capillary column DP-TFA-γ-CD, 90 °C, He, 1.8 bar). [c] L*/Pd = 1.

1. Systems with sp^3-hybridized nitrogen atoms were not effective (*ee* < 11%, Entries 1−3).

2. Among the imino phosphites, ligands **3i**, **3k** and **3m** (Entries 5, 8, 22) were the most effective (up to 82% *ee*).

3. Optical yields greatly depended on the substituent at the chiral centre, as clearly demonstrated by the homologous ligands **3h** (24% *ee*) and **3i** (58% *ee*), as well as **3l** (38% *ee*) and **3m** (82% *ee*).

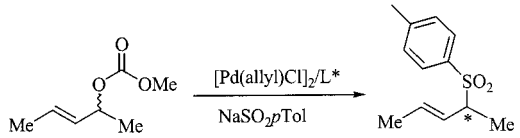
4. Optical yields depended significantly on the solvent used and the temperature. Notably, for ligand **3m** the latter correlation was nonlinear in character (Entries 11−14).

5. The L*/Pd ratio did not influence the effectiveness of a catalytic system much (compare Entries 19 and 22).

What should be discussed separately are significant increases in *ee* values on going from ligand **3h** to **3e** (by 14%, Entries 4 and 9) and, especially, from **3i** to **3m** (by 23%, Entries 6 and 19). Since the ν(CO) and $^1J_{P,Rh}$ values for their rhodium complexes [Rh(CO)Cl(η^2-P$^\frown$N)] are practically identical (Table 1), the electronic characteristics of the ligands (including the degree of electronic non-symmetry) are very much the same. Therefore, the effect is steric in nature, and the steric parameters of the ligands are indeed responsible for the difference in the optical yields in the catalytic reaction. Ligands **3i** and **3l** have similar structures and only the −N=CHR fragments are different. To estimate the bulkiness of the substituents, the cone angles θ_R for the *p*-$C_6H_4NMe_2$ and Cp_2Fe fragments were calculated by constructing appropriate computer models and from the X-ray data. The calculated cone angle for the Cp_2Fe fragment [θ_R = 159° (AM1), 157° (X-ray, complex **5l**)] is significantly larger than the angle for the *p*-$C_6H_4NMe_2$ fragment [θ_R = 133° (AM1), 129° (X-ray, complex **5i**)]. Hence, bulky substituents attached to the imine group of the *P,N*-(imino phosphite) ligands are likely to afford higher optical yields in the catalytic reaction.

The catalytic effectiveness shown by the catalytic system with ligand **3m** was comparatively high, since 1,3-dimethyl-substituted allylic substrates belong to a group termed "unmanageable".[27] There are only two known *P,N*-ligands that also give more than 80% enantioselectivity, one of the new generation phosphanyloxazolines (70−90% *ee*)[28] and a 2-(phosphanylaryl)pyridine-derived ligand (Scheme 1, R = Me, *i*Pr, Ph, 78−93% *ee*).[27] It should be noted that the mentioned high enantioselectivities were achieved by thorough optimization of the reaction conditions at a low temperature (−25 to −40 °C) and sometimes by addition of crown ethers.[27,28]

Some of the new *P,N*-bidentate aryl phosphites were tested in the Pd-catalysed allylic substitution of methyl 3-penten-2-yl carbonate with $NaSO_2p$Tol (Scheme 2). The obtained results are shown in Table 6. It is easy to see that main tendencies in this catalytic process were similar to those in the reaction with the malonate nucleophile discussed above. In particular, the highest enantioselectivities were demonstrated by the ligands with distant imino groups. It is important to note that the optical yield produced by imino phosphite **3m** (80% *ee*) was the best so far achieved in the reaction using *P,N*-ligands. Helmchen's phosphanyloxazolines, the most effective previously described *P,N*-ligands,



Scheme 2

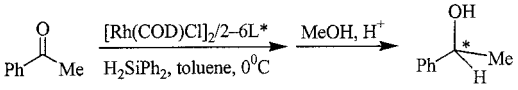
gave up to 59% *ee*.[29] Moreover, unlike phosphanyloxazolines, our ligands did not give rise to the formation of a sulfinic acid ester as a side product. To the best of our knowledge, the only ligand giving higher results in this reaction [99% *ee*, with $Pd_2(dba)_3$ as a precatalyst] is one of Trost's *P*,*P*-bidentate ligands,[30] which form 13-membered chelate palladium complexes.[31]

Table 6. Enantioselective allylic sulfonylation of 3-penten-2-yl carbonate with $NaSO_2p$Tol according to Scheme 2

Entry	L*	L*/Pd	Solvent	*T* [°C]	Yield (%)[a]	*ee* (%)[b]
1	**3b**	2:1	THF	room temp.	47	12 (*S*)
2	**3c**	2:1	THF	room temp.	22	10 (*S*)
3	**3i**	2:1	THF	room temp.	63	44 (*R*)
4	**3i**	2:1[c]	THF	room temp.	53	46 (*R*)
5	**3i**	2:1	THF	0	48	56 (*R*)
6	**3i**	1:1	THF	room temp.	65	50 (*R*)
7	**3i**	1:1	DCM	room temp.	59	50 (*R*)
8	**3k**	2:1	THF	room temp.	69	45 (*S*)
9	**3k**	2:1	THF	0	42	54 (*S*)
10	**3k**	1:1	THF	−20	20	50 (*S*)
11	**3m**	2:1	THF	room temp.	74	63 (*R*)
12	**3m**	2:1	THF	0	51	78 (*R*)
13	**3m**	2:1[c]	THF	0	38	76 (*R*)
14	**3m**	1:1	DCM	room temp.	45	76 (*R*)
15	**3m**	1:1	DCM	0	21	80 (*R*)

[a] Yield of analytically pure product after column chromatography. [b] The *ee* values were determined by chiral GC (Lipodex-γ: 2,3-di-*O*-pentyl-6-*O*-methyl-γ-cyclodextrin (25m × 0.8 mm) column). [c] $Pd_2(dba)_3 \times CHCl_3$.

Ligands **3a**−**m** were also tested in the Rh-catalysed asymmetric hydrosilylation of acetophenone with diphenylsilane (Scheme 3). However, the achieved optical yields were rather low, with amino phosphites (up to 28% *ee*) once again being less effective than imino phosphites **3i** (45% *ee*) and **3m** (50% *ee*).



Scheme 3

Experimental Section

General Comments: All reactions were performed under argon in dehydrated solvents. IR spectra were recorded with a Specord M80 or Nicolet 750 instrument. ^{31}P, ^{13}C and ^{1}H NMR spectra were recorded with a Bruker AMX 400 instrument (162.0 MHz for ^{31}P, 100.6 MHz for ^{13}C and 400.13 MHz for ^{1}H). Complete assignment of all the resonances in ^{13}C NMR spectra was achieved by use of DEPT techniques. Chemical shifts (ppm) are given relative to Me_4Si (^{1}H and ^{13}C NMR) and 85% H_3PO_4 (^{31}P NMR). Mass spectra were recorded with a Kratos MS890 spectrometer (EI), an MSVKh TOF spectrometer with ionization by Cf-252 fission fragments (plasma desorption technique, PD), and a Micromass Platform 1 mass spectrometer through an "Openlynx" system (APCI technique). Electrospray (ES) ionisation mass spectra were measured with a Micromass BioQ II-ZS mass spectrometer. Organometallic compound solutions at 5−10 pmol/μL in THF or acetonitrile were infused by syringe pump (Harvard Apparatus Model 11) at 5 μL/min. Spectra were recorded over a mass range of 200−1200 Da and were calibrated relative to a mixed PEG standard. The X-ray photoelectron spectrum (XPS) was measured with a MAC-2 Riber spectrometer calibrated against Ag lines at 901.5 and 367.9 eV, correction for the sample charging was performed at C1s = 284.6 eV; the accuracy of the line maximum determination was ±0.1 eV. Cone angles θ_R of the substituents were determined from their conformations in the structures H-R obtained by computer calculations (AM1) and in the X-ray crystal structures of the corresponding complexes by the published approach.[32] Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow). Crystallographic data and refinement parameters for compounds **4i**, **5i** and **5l** are summarized in Table 7. The experimental data were collected at 110 K with a Bruker SMART 1000 CCD area detector by using graphite-monochromated Mo-K_α radiation (λ = 0.71072 Å, ω-scans with 0.3° steps in ω and 10 s per frame exposure). The absorption correction was applied semiempirically from equivalents. All the structures were solved by direct methods and refined by the full-matrix, least-squares technique against F^2 in the anisotropic (H atoms isotropic) approximation with the SHELXTL 5.1 package. Analysis of the Fourier density synthesis in **4i** showed that the isobutyl group [C(3)−C(6)] was disordered by two positions, which were included in the refinement with equal occupancies. The absolute configurations in **4i** and **5i** were determined by use of the Flack parameter. All hydrogen atoms with the exception of the disordered group were located from the Fourier synthesis and treated by a mixture of independent and constrained refinement. CCDC-173440 (**4i**), -173441 (**5i**) and -173442 (**5l**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. $[Rh(CO)_2Cl]_2$,[33] $[Pd(COD)Cl_2]$,[34] $[Pd(allyl)Cl]_2$,[35] amino and imino alcohols **2d**,[36] **2f**,[37] **2g**,[38] **2h**,[11] **2l**[39] and bis(2,6-dimethylphenyl) chlorophosphite[12] were synthesized as published. The syntheses of compounds **2i**−**k** and **2m** were performed by techniques similar to that reported.[40] (*S*)-(+)-Isoleucinol, ferrocenecarboxaldehyde, 4-(dimethylamino)benzaldehyde and compounds **2a** and **2c** were purchased from Aldrich; (1*R*,2*S*)-(+)-*cis*-1-amino-2-indanol was purchased from Fluka. Amino and imino alcohols **2b** (quincoridine, Büchler GmbH), **2c**−**f**, **2h** and **2i** were azeotropically dried with benzene and distilled before use. Compounds **2a**, **2g** and **2j**−**2m** were dried under vacuum (2 Torr, 3 h) immediately before use.

Synthesis and Characterization

(2*S*,3*S*)-3-Methyl-2-(pyrrolidin-1-yl)pentan-1-ol (2e): A mixture of 1,4-dibromobutane (2.37 mL, 2×10^{-2} mol), (*S*)-(+)-isoleucinol (2.34 g, 2×10^{-2} mol) and K_2CO_3 (8.29 g, 6×10^{-2} mol) in acetonitrile (25 mL) was heated under reflux for 30 h. The mixture was then allowed to cool to room temp. and filtered, and the filter cake was washed with DCM (2×15 mL). The combined extracts were concentrated under vacuum (40 Torr) and the residue was distilled in high vacuum to give a yellow, paraffin-like product (2.297 g, 67% yield). B.p. 165−170 °C (0.8 Torr, kugelrohr distillation). ^{1}H NMR ($CDCl_3$): δ = 0.95 (t, ^{3}J = 7.4 Hz, 3 H, CH_2CH_3), 1.15 (d, ^{3}J = 6.8 Hz, 3 H, CH_3), 1.42 (m, 2 H, CH_2), 1.91 (m, 1 H, CH), 2.05 [m, 2 H, $(CH_2)_2$], 2.29[m, 2 H, $(CH_2)_2$], 3.00 (m, 1 H, CHN), 3.17 (m, 1 H, CH_2N), 3.22 (m, 1 H, CH_2N), 3.78 (m, 1 H, CH_2N), 3.94 (q, 1 H, CH_2N), 4.03 (m, 2 H, CH_2O), 4.27 (br. s, 1 H, OH). $C_{10}H_{21}NO$ (171.16): calcd. C 70.12, H 12.36, N 8.18; found C 69.86, H 12.12, N 7.98.

Table 7. Crystallographic data for **4i**, **5i** and **5l**

Compound	**4i**	**5i**	**5l**
Empirical formula	$C_{32}H_{41}ClN_2O_4PRh$	$C_{31}H_{41}Cl_2N_2O_3PPd$	$C_{32}H_{38}Cl_2FeNO_3PPd{\cdot}C_6H_6$
Formula mass	687.00	697.93	826.86
Crystal system, space group	orthorhombic, $P2_12_12_1$	orthorhombic, $P2_12_12_1$	orthorhombic, *Pbca*
a [Å]	12.883(8)	12.827(3)	13.826(6)
b [Å]	13.746(6)	14.333(3)	18.872(7)
c [Å]	18.178(11)	17.378(4)	27.296(9)
V [Å^3]	3219(3)	3194.9(11)	7122(5)
Z	4	4	8
D_x [Mg m^{-3}]	1.417	1.451	1.542
μ [cm^{-1}]	7.01	8.32	11.45
Crystal form, colour	prisms, yellow	prisms, yellow	needles, red
Crystal size [mm]	0.4×0.3×0.25	0.5×0.4×0.35	0.4×0.15×0.1
F(000)	1424	1440	3392
T_{min}, T_{max}	0.751, 0.839	0.653, 0.747	0.629, 0.892
θ_{max} [°]	29.00	29.06	27.00
Completeness to θ_{max}	98.1	100	99.0
No. of measured, independent and observed reflections	31319, 8280, 4952	20604, 8545, 7637	37362, 7719, 3187
R_{int}	0.0961	0.0366	0.0883
No. of parameters	417	389	430
Absolute structure parameter	0.00(4)	−0.03(2)	
wR_2 for all data	0.1321	0.0909	0.0788
R for observed data	0.0729	0.0405	0.0494
S	1.096	0.990	0.750
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	1.191, −1.672	1.376, −1.198	0.686, −0.731

(2*S*,3*S*)-2-[4-(Dimethylamino)benzylideneamino]-3-methylpentan-1-ol (2i): (*S*)-(+)-Isoleucinol (1.17 g, 1×10^{-2} mol) was dissolved in 30 mL of dichloromethane. 4-(Dimethylamino)benzaldehyde (1.49 g, 1×10^{-2} mol), Na_2SO_4 (1 g) and 15 mL of dichloromethane were added to this solution with stirring, and the mixture was heated under reflux for 3 h. After the mixture had cooled to room temperature, the Na_2SO_4 was filtered off and washed with dichloromethane. The solvent was removed and the resulting residue was distilled under vacuum. Yellow viscous oil, 1.564 g (63% yield). n_D^{20} = 1.4411. B.p. 165−167 °C (0.8 Torr, kugelrohr distillation). ^{1}H NMR ($CDCl_3$): δ = 0.83 (t, ^3J = 7.6 Hz, 3 H, CH_2CH_3), 0.92 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.04 (m, 1 H, CH), 1.46 (m, 1 H, CH_2), 1.69 (m, 1 H, CH_2), 2.41 (br. s, 1 H, OH), 2.98 (m, 1 H, CHN), 3.00 [s, 6 H, $N(CH_3)_2$], 3.78 (m, 2 H, CH_2O), 6.67 (d, ^3J = 8.8 Hz, 2 H, H_{Ar}), 7.57 (d, ^3J = 8.8 Hz, 2 H, H_{Ar}), 8.08 (s, 1 H, CH=). ^{13}C NMR ($CDCl_3$): δ_C = 10.6 (s, CH_3), 15.2 (s, CH_3), 25.1 (s, CH_2), 36.2 (s, CH), 39.5 [s, $N(CH_3)_2$], 63.6 (s, CH_2O), 76.6 (s, CHN), 110.9−151.3 (s, C_{Ar}), 161.3 (s, CH=). $C_{15}H_{24}N_2O$ (248.19): calcd. C 72.54, H 9.74, N 11.28; found C 72.36, H 9.84, N 11.15.

(2*R*)-2-(Ferrocenylidineamino)-3-(methylthio)propan-1-ol (2j): This compound was synthesized analogously to **2i**, starting from (*R*)-2-amino-3-(methylthio)propan-1-ol (1.21 g, 1×10^{-2} mol) and ferrocenecarboxaldehyde (2.14 g, 1×10^{-2} mol). Orange-red solid, 2.636 g (83% yield). ^{1}H NMR(C_6D_6): δ = 1.87 (s, 3 H, CH_3), 2.62 (m, 2 H, CH_2S), 2.85 (s, 1 H, OH), 3.24 (m, 1 H, CHN), 3.69 (m, 2 H, CH_2O), 4.10 (m, 1 H, H_{Fc}), 4.12 (m, 1 H, H_{Fc}), 4.13 (s, 5 H, H_{Fc}), 4.46 (m, 1 H, H_{Fc}), 4.80 (m, 1 H, H_{Fc}), 8.02 (s, 1 H, CH=). $C_{15}H_{19}FeNOS$ (317.05): calcd. C 56.79, H 6.04, N 4.42; found C 56.50, H 3.87, N 4.13.

(1*R*,2*S*)-1-(Ferrocenylideneamino)indan-2-ol (2k): This compound was synthesized analogously to **2i**, starting from (1*R*,2*S*)-(+)-*cis*-1-amino-2-indanol (1.49 g, 1×10^{-2} mol) and ferrocenecarboxaldehyde (2.14 g, 1×10^{-2} mol). Dark yellow solid, 85% yield (2.933 g) after recrystallisation from toluene/heptane (1:1) mixture. ^{1}H NMR ($CDCl_3$): δ = 3.21 (m, 2 H, CH_2O), 3.99 (br. s, 1 H, OH), 4.21 (s, 5 H, H_{Fc}), 4.23 (t, ^1J = 1.9 Hz, 2 H, H_{Fc}), 4.42 (t, ^1J = 1.9 Hz, 2 H, H_{Fc}), 4.60 (m, 1 H, CHO), 4.67 (d, ^1J = 5.8 Hz, 1 H, CHN), 7.18 (m, 1 H, H_{Ar}), 7.28 (m, 1 H, H_{Ar}), 7.43 (m, 1 H, H_{Ar}), 7.49 (m, 1 H, H_{Ar}), 8.45 (s, 1 H, CH=). $C_{20}H_{19}FeNO$ (345.08): calcd. C 69.58, H 5.55, N 4.06; found C 69.31, H 5.29, N 4.00.

(2*S*,3*S*)-2-(Ferrocenylideneamino)-3-methylpentan-1-ol (2m): This compound was synthesized analogously to **2i**, starting from (*S*)-(+)-isoleucinol (1.17 g, 1×10^{-2} mol) and ferrocenecarboxaldehyde (2.14 g, 1×10^{-2} mol). Orange solid, 2.685 g (81% yield). ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3), 0.94 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.24 (m, 2 H, CH_2), 1.65 (m, 1 H, CH), 2.94 (m, 1 H, CHN), 3.82 (m, 2 H, CH_2O), 3.99 (1 H, *s, br*, OH), 4.10 (s, 5 H, H_{Cp}), 4.34 (m, 1 H, H_{Fc}), 4.37 (m, 1 H, H_{Fc}), 4.51 (m, 1 H, H_{Fc}), 4.72 (m, 1 H, H_{Fc}), 8.06 (s, 1 H, CH=). ^{13}C NMR ($CDCl_3$): δ = 10.8 (s, CH_3), 15.3 (s, CH_3), 25.7 (s, CH_2), 36.0 (s, CH), 63.8 (s, CH_2O), 66.9, 68.7, 69.9, 70.2, 70.3, 80.0 (all C_{Fc}), 77.9 (s, CHN), 161.9 (s, CH=). $C_{17}H_{23}FeNO$ (313.11): calcd. C 65.19, H 7.40, N 4.47; found C 65.47, H 7.23, N 4.09.

Preparation of Ligands; General Technique: A solution of bis(2,6-dimethylphenyl) chlorophosphite (0.832 g, 2.7×10^{-3} mol) in benzene (15 mL) was added dropwise to a stirred solution of the appropriate alcohol **2** (2.7×10^{-3} mol) and Et_3N (0.4 mL, 2.7×10^{-3} mol) in the same solvent (15 mL) at 0 °C. The reaction mixture was then heated to boiling point, allowed to cool down, stirred for 1 h at 50 °C, allowed to cool to room temp. and filtered. The solvent was removed under vacuum (40 Torr), and the residue was dissolved in hexane (20 mL), filtered, concentrated and dried under vacuum (1 Torr).

(1*R*,2*S*)-2-Dimethylamino-1-phenylpropyl Bis(2,6-dimethylphenyl) Phosphite (3a): Colourless oil, 0.913 g (75% yield). ^{31}P NMR ($CDCl_3$): δ = 146.7. ^{13}C NMR ($CDCl_3$): δ = 8.6 (s, CH_3), 17.53, 17.59, 17.72, 17.78 [CH_3(Ar)], 41.6 (s, NMe_2), 65.3 (d, ^3J = 3.8 Hz, CHN), 77.4 (d, ^2J = 13.3 Hz, CHO), 119.8−149.3 (C_{Ar}). MS (EI,

70 eV): *m/z* (%) = 451 (1) $[M]^+$, 380 (5), 273 (15), 162 (67), 122 (100). $C_{27}H_{34}NO_3P$ (415.22): calcd. C 71.82, H 7.59, N 3.10; found C 72.11, H 7.43, N 3.33.

Bis(2,6-dimethylphenyl) (2*R*,4*S*,5*R*)-(5-Vinylquinuclid-2-yl)methyl Phosphite (3b): Colourless oil, 0.841 g (71% yield). ^{31}P NMR (C_6D_6): δ = 138.4. ^{13}C NMR (C_6D_6): δ = 17.96, 18.00, 18.02, 18.05 [all *C*H_3(Ar)], 24.4 (s, CH*C*H_2CH), 26.9 (s, CH_2*C*H_2CH), 28.0 (s, CH_2*C*HCH_2), 40.2 (s, CH*C*HCH=), 48.0 (s, N*C*H_2CH), 49.2 (N*C*H_2CH_2), 56.2 (d, ^3J = 3.4 Hz, CHN), 64.1 (d, ^2J = 5.2 Hz, CH_2O), 114.3 (s, CH_2=), 140.8 (s, CH=), 119.9−149.5 (C_{Ar}). MS (EI, 70 eV): *m/z* (%) = 439 (4) $[M]^+$, 318 (95), 273 (9), 166 (42), 150 (100). $C_{26}H_{34}NO_3P$ (439.22): calcd. C 71.05, H 7.80, N 3.19; found C 69.85, H 7.52, N 3.40.

Bis(2,6-dimethylphenyl) [(2*S*)-1-Methylpyrrolidin-2-yl]methyl Phosphite (3c): Colourless oil, 0.724 g (69% yield). ^{31}P NMR (C_6D_6): δ = 137.3. ^{13}C NMR (C_6D_6): δ = 17.40 [s, *C*H_3(Ar)]. 17.44 [s, CH_3(Ar)], 22.6 [s, $(CH_2)_2$], 28.4 [s, $(CH_2)_2$], 41.2 (s, NCH_3), 57.2 (s, CH_2N), 64.0 (s, CHN), 65.1 (s, CH_2O), 119.4−149.2 (C_{Ar}). MS (EI, 70 eV): *m/z* (%): 387 (3) $[M]^+$, 289 (1), 273 (42), 122 (100). $C_{22}H_{30}NO_3P$ (387.19): calcd. C 68.20, H 7.80, N 3.62; found C 68.51, H 8.07, N 3.44.

[(2*S*)-1-Benzylpyrrolidin-2-yl]methyl Bis(2,6-dimethylphenyl) Phosphite (3d): Colourless oil, 0.962 g (77% yield). ^{31}P NMR (C_6D_6): δ = 136.6. ^{13}C NMR (C_6D_6): δ = 17.4 [s, *C*H_3(Ar)], 17.6 [s, *C*H_3(Ar)], 22.7 [s, $(CH_2)_2$], 28.4 [s, $(CH_2)_2$], 54.4 (s, CH_2Ph), 59.5 (s, CH_2N), 63.5 (d, ^3J = 4.2 Hz, CHN), 65.4 (d, ^2J = 3.4 Hz, CH_2O), 119.7− 149.3 (C_{Ar}). MS (EI, 70 eV): *m/z* (%) = 463 (1) $[M]^+$, 372 (3), 342 (47), 273 (3), 122 (85), 91 (100). $C_{28}H_{34}NO_3P$ (463.23): calcd. C 72.55, H 7.39, N 3.02; found C 72.81, H 7.01, N 3.36.

Bis(2,6-dimethylphenyl) (2*S*,3*S*)-3-Methyl-2-(pyrrolidin-1-yl)pentyl Phosphite (3e): Colourless oil, 0.813 g (68% yield). ^{31}P NMR ($CDCl_3$): δ = 136.1. ^{13}C NMR (C_6D_6): δ = 12.2 (s, CH_3). 14.6 (s, CH_3), 16.9, 17.3, 17.9, 18.1, [all *C*H_3(Ar)], 23.5 [s, $(CH_2)_2$], 27.4 (s, CH_2), 36.2 (s, CH), 51.5 (s, CH_2N), 65.3 (s, CH_2O), 76.1 (s, CHN), 119.6−149.5 (C_{Ar}). MS (EI, 70 eV): *m/z* (%) = 443 (1) $[M]^+$, 273 (38), 122 (100). $C_{26}H_{38}NO_3P$ (443.26): calcd. C 70.40, H 8.64, N 3.16; found C 72.66, H 8.94, N 3.38.

(2*R*)-2-(Dibenzylamino)-3-methylbutyl Bis(2,6-dimethylphenyl) Phosphite (3f): Colourless oil, 1.184 g (79% yield). ^{31}P NMR (C_6D_6): δ = 136.9. ^{13}C NMR (C_6D_6): δ = 18.0 [s, *C*H_3(Ar)], 18.1 [s, *C*H_3(Ar)], 20.5 (s, CH_3), 21.3 (s, CH_3), 27.9 (s, CH), 55.0 (s, CH_2Ph), 60.1 (s, CH_2O), 63.4 (d, ^3J = 4.0 Hz, CHN), 119.8−149.4 (C_{Ar}). MS (EI, 70 eV): *m/z* (%) = 555 (3) $[M]^+$, 464 (13), 273 (40), 122 (100). $C_{35}H_{42}NO_3P$ (555.29): calcd. C 75.65, H 7.62, N 2.52; found C 75.31, H 7.49, N 2.67.

Bis(2,6-dimethylphenyl) 2-({[(1*R*)-1-Phenylethyl]imino}methyl)-phenyl Phosphite (3g): Green oil, 1.099 g (82% yield). ^{31}P NMR (C_6D_6): δ = 139.9. ^{13}C NMR (C_6D_6): δ = 17.8 [s, CH_3(Ar)]. 17.9 [s, CH_3(Ar)], 25.4 (s, CH_3), 70.4 (s, CHN), 120.6−152.0 (s, C_{Ar}), 153.8 (s, CH=). MS (EI, 70 eV): *m/z* (%) = 498 (2) $[M + H]^+$, 376 (56), 408 (15), 273 (52), 105 (100). $C_{31}H_{32}NO_3P$ (497.21): calcd. C 74.83, H 6.48, N 2.82; found C 75.04, H 6.22, N 3.13.

(2*R*)-2-[4-(Dimethylamino)benzylideneamino]-3-methylbutyl Bis(2,6-dimethylphenyl) Phosphite (3h): Colourless oil, 1.093 g (80% yield). ^{31}P NMR (C_6D_6): δ = 136.8. ^{13}C NMR (C_6D_6): δ = 17.94 [s, *C*H_3(Ar)], 17.98 [s, *C*H_3(Ar)], 18.5 (s, CH_3), 20.1 (s, CH_3), 30.7 (s, CH), 40.0 [s, $N(CH_3)_2$], 65.1 (d, ^2J = 11.6 Hz, CH_2O), 77.1 (d, ^3J = 2.7 Hz, CHN), 111.8−152.1 (s, C_{Ar}), 161.2 (s, CH=). MS (EI, 70 eV): *m/z* (%) = 506 (2) $[M]^+$, 316 (52), 217 (66), 122 (100). $C_{30}H_{39}N_2O_3P$ (506.27): calcd. C 71.12, H 7.76, N 5.53; found C 71.41, H 8.05, N 5.77.

(2*S*,3*S*)-2-[4-(Dimethylamino)benzylideneamino]-3-methylpentyl Bis(2,6-dimethylphenyl) Phosphite (3i): Yellow oil, 1.165 g (83% yield). ^{31}P NMR ($CDCl_3$): δ = 136.4. MS (EI, 70 eV): *m/z* (%) = 520 (1) $[M]^+$, 400 (81), 316 (28), 122 (100). $C_{31}H_{41}N_2O_3P$ (520.29): calcd. C 71.51, H 7.94, N 5.38; found C 72.84, H 8.14, N 5.16.

Bis(2,6-dimethylphenyl) (2*R*)-2-(Ferrocenylideneamino)-3-(methylthio)propyl Phosphite (3j): Dark red oil, 1.193 g (75% yield). ^{31}P NMR (C_6D_6): δ = 135.9. ^{13}C NMR (C_6D_6): δ = 16.6 (s, SCH_3), 17.9 [s, *C*H_3(Ar)], 18.0 [s, *C*H_3(Ar)], 37.2 (s, CH_2S), 65.2 (s, CH_2O), 68.8, 69.3, 70.5, 70.6 (all C_{Fc}), 69.6 (s, C_{Cp}), 71.8 (d, ^3J = 3.4 Hz, CHN), 80.9 [s, C_{Fc}(*ipso*)], 124.4−149.5 (s, C_{Ar}), 162.3 (s, CH=). MS (EI, 70 eV): *m/z* (%) = 589 (3) $[M]^+$, 542 (36), 468 (98), 300 (34), 122 (100). $C_{31}H_{36}FeNO_3PS$ (589.15): calcd. C 63.16, H 6.16, N 2.38; found C 61.89, H 6.41, N 2.63.

Bis(2,6-dimethylphenyl) (1*R*,2*S*)-1-(Ferrocenylideneamino)indan-2-yl Phosphite (3k): Red oil, 1.197 g (72% yield). ^{31}P NMR (C_6D_6): δ = 138.2. ^{13}C NMR (C_6D_6): δ = 17.97, 18.02, 18.20, 18.26 [*C*H_3(Ar)], 38.9 (s, CH_2), 68.9, 69.6, 70.4, 70.5 (all C_{Fc}), 69.4 (s, C_{Cp}), 77.2 (d, ^2J = 3.4 Hz, CHO), 77.6 (s, CHN), 81.2 [s, C_{Fc}(*ipso*)], 120.2−153.3 (s, C_{Ar}), 160.9 (s, CH=). MS (EI, 70 eV): *m/z* (%) = 617 (2) $[M]^+$, 496 (2), 328 (24), 273 (7), 122 (100). $C_{36}H_{36}FeNO_3P$ (617.18): calcd. C 70.02, H 5.88, N 2.27; found C 69.79, H 6.14, N 2.55.

Bis(2,6-dimethylphenyl) (2*R*)-2-(Ferrocenylideneamino)-3-methylbutyl Phosphite (3l): Red oil, 1.233 g (80% yield). ^{31}P NMR ($CDCl_3$): δ = 135.1. MS (EI, 70 eV): *m/z* (%) = 571 (2) $[M]^+$, 450 (76), 282 (28), 122 (100). $C_{32}H_{38}FeNO_3P$ (571.19): calcd. C 67.26, H 6.70, N 2.45; found C 67.04, H 6.87, N 2.74.

Bis(2,6-dimethylphenyl) (2*S*,3*S*)-2-(Ferrocenylideneamino)-3-methylpentyl Phosphite (3m): Dark red oil, 1.343 g (85% yield). ^{31}P NMR (C_6D_6): δ = 135.9. ^{13}C NMR (C_6D_6): δ = 10.6 (s, CH_3). 15.3 (s, CH_3), 17.2 [s, *C*H_3(Ar)], 17.23 [s, *C*H_3(Ar)], 25.0 (s, CH_2), 36.3 (s, CH), 63.6 (s, CH_2O), 68.0, 68.2, 69.78, 69.80 (all C_{Fc}), 68.6 (s, C_{Cp}), 76.0 (s, CHN), 80.0 [s, C_{Fc}(*ipso*)], 123.5−148.7 (C_{Ar}), 160.6 (s, CH=). MS (APCI): *m/z* (%) = 586 (100) $[M + H]^+$, 464 (18), 314 (42), 122 (10). $C_{33}H_{40}FeNO_3P$ (585.21): C 67.70, H 6.89, N 2.39; found C 67.96, H 6.62, N 2.74.

Preparation of Complexes

Preparation of Rhodium Complexes 4b−4f and 4j: Rhodium complexes with ligands **3b−3h** and **3j** were synthesized for the NMR and IR experiments as follows. A solution of L* (3.6×10^{-4} mol) in $CHCl_3$ (1.5 mL) was added dropwise to a stirred solution of $[Rh(CO)_2Cl]_2$ (1.8×10^{-4} mol) in the same solvent (1.5 mL). A 1-mL sample of the resulting solution was then transferred to an NMR tube or IR cuvette and spectral experiments were carried out.

General Technique for Rhodium Complexes 4a, 4i and 4k−4m: A solution of the appropriate ligand (3.6×10^{-4} mol) in DCM (20 mL) was added dropwise to a stirred solution of $[Rh(CO)_2Cl]_2$ (0.070 g, 1.8×10^{-4} mol) in the same solvent (20 mL) at 20 °C. The reaction mixture was stirred at 20 °C for 30 min. The excess solvent was then removed under vacuum (40 Torr), and 10 mL of hexane was added to the residue. The obtained precipitate was separated by centrifugation, washed with hexane (2×10 mL) and dried under vacuum (2 Torr).

[Rh(CO)Cl(3a-P^N)] (4a): Yellow solid, 0.193 g (87% yield). IR (KBr): ν(CO) 2017 cm^{-1}. $C_{28}H_{34}ClNO_4PRh$ (617.10): calcd. C 54.43, H 5.55, N 2.27; found C 54.73, H 5.69, N 2.51.

[Rh(CO)Cl(3i-P^N)] (4i): Yellow solid, 0.221 g (89% yield). IR (KBr): ν(CO) 2008 cm^{-1}. $C_{32}H_{41}ClN_2O_4PRh$ (686.15): calcd. C 55.94, H 6.02, N 4.08; found C 56.28, H 5.74, N 4.39.

[Rh(CO)Cl(3k-P^N)] (4k): Yellow-brown solid, 0.260 g (92% yield). IR (KBr): ν(CO) 2010 cm^{-1}. $C_{37}H_{36}ClFeNO_4PRh$ (783.05): calcd. C 56.69, H 4.63, N 1.79; found C 56.93, H 4.31, N 2.10.

[Rh(CO)Cl(3l-P^N)] (4l): Yellow-brown solid, 0.239 g (90% yield). IR (KBr): ν(CO) 2008 cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 702 (34) $[M - Cl]^+$, 674 (5) $[M - Cl - CO]^+$, 282 (52), 122 (100). MS (ES): *m/z* (%) = 702 (55) $[M - Cl]^+$, 300 (100). $C_{33}H_{38}ClFeNO_4PRh$ (737.06): calcd. C 53.72, H 5.19, N 1.90; found C 54.00, H 5.53, N 2.26.

[Rh(CO)Cl(3m-P^N)] (4m): Yellow-brown solid, 0.239 g (88% yield). IR (KBr): ν(CO) 2010 cm^{-1}. $C_{34}H_{40}ClFeNO_4PRh$ (751.08): calcd. C 54.31, H 5.36, N 1.86; found C 54.64, H 5.37, N 2.08.

[Rh(CO)Cl(3f-P^N)] (4f): A solution of ligand **3f** (0.200 g, 3.6×10^{-4} mol) in DCM (10 mL) was added dropwise to a stirred solution of [acacRh$(CO)_2$] (0.093 g, 1.8×10^{-4} mol) in the same solvent (10 mL) at 20 °C. The reaction solution was stirred for 30 min at room temp. to form [acacRh(CO)(η^1-P^N)] complex. A solution of [Rh$(CO)_2Cl]_2$ (0.070 g, 1.8×10^{-4} mol) in DCM (10 mL) was then added to this solution and, after the mixture had stirred for 1 h, all the volatiles were evaporated under vacuum (40 Torr). Regenerated [acacRh$(CO)_2$] was extracted from the residue with hexane (4×15 mL), and the final residue was dried under vacuum (2 Torr) to give the desired product. Yellow solid, 0.222 g (85% yield). IR (KBr): ν(CO) 2009 cm^{-1}. $C_{36}H_{42}ClNO_4PRh$ (721.16): calcd. C 59.88, H 5.86, N 1.94; found C 60.17, H 6.13, N 2.34.

General Technique for Palladium Complexes 5i and 5l: A solution of the appropriate ligand (**3i** or **3l**, 2×10^{-4} mol) in DCM (15 mL) was added dropwise to a stirred solution of [Pd(COD)Cl_2] (0.057 g, 2×10^{-4} mol) in the same solvent (15 mL) at room temp. After the mixture had been stirred for 1 h, the excess solvent was removed under vacuum (40 Torr) and 10 mL of ether was added to the residue. The obtained precipitate was separated by centrifugation, washed with ether (2×10 mL) and dried under vacuum (2 Torr).

***cis*-[PdCl$_2$(3i-P^N)] (5i):** Yellow solid, 0.126 g (91% yield). $C_{31}H_{41}Cl_2N_2O_3PPd$ (696.13): calcd. C 53.35, H 5.92, N 4.01; found C 53.62, H 6.22, N 3.87.

***cis*-[PdCl$_2$(3l-P^N)] (5l):** Yellow-brown solid, 0.135 g (90% yield). $C_{32}H_{38}FeCl_2NO_3PPd$ (747.04): calcd. C 51.33, H 5.12, N 1.87; found C 51.65, H 4.91, N 1.98.

[Pd(allyl)(3m-P^N)]$^+$Cl$^-$ (6): A solution of imino phosphite **3m** (0.234 g, 4×10^{-4} mol) in DCM (20 mL) was added dropwise to a stirred solution of [Pd(allyl)Cl]$_2$ (0.073 g, 2×10^{-4} mol) in the same solvent (20 mL) at room temp. After the mixture had been stirred for 1 h, the solvent was removed under vacuum, and the residue was washed with hexane (2×10 mL) and dried under vacuum (2 Torr). Yellow-brown solid, 0.288 g (94% yield). ^{13}C NMR (C_6D_6): δ = 11.6 (s, CH_3), 16.1 (s, CH_3), 18.7 [s, CH_3(Ar)], 18.8 [s, CH_3(Ar)], 25.1 (s, CH_2), 36.5 (s, CH), 55.0 (s, CH_2 [allyl, *trans*-N)], 67.0 (s, CH_2O), 68.2, 69.6, 70.2, 72.8 (all C_{Fc}), 69.4 (s, C_{Cp}), 75.3 (s, CHN), 80.2 [s, C_{Fc} (*ipso*)], 81.4 (d, ^2J = 42.8 Hz, CH_2 [allyl, *trans*-P)], 125.3 [d, ^2J = 8.2 Hz, CH(allyl)], 118.1−149.2 (s, C_{Ar}), 168.7 (s, CH=). MS (PD): *m/z* (%) = 767 (20) $[M]^+$, 732 (100) $[M - Cl]^+$, 690 (46), 585 (52), 121 (21). XPS: E_b [eV] = 338.2 (Pd $3d_{5/2}$), 134.0 (P 2p), 198.4 (Cl 2p), 399.6 (N 1s), 708.7 (Fe 2p). $C_{36}H_{45}FeClNO_3PPd$ (767.12): calcd. C 56.27, H 5.90, N 1.82; found C 56.58, H 6.11, N 2.02.

Catalytic Experiments

Palladium-Catalysed Alkylation of Ethyl 3-Penten-2-yl Carbonate with Dimethyl Malonate: [Pd(allyl)Cl]$_2$ (3.6 mg, 10^{-5} mol) and ligand **3** ($2-4 \times 10^{-5}$ mol) were dissolved in the appropriate solvent and the mixture was stirred at room temp. for 20 min. Ethyl 3-penten-2-yl carbonate (160 mg, 10^{-3} mol), dimethyl malonate (132 mg, 1.5×10^{-3} mol), BSA [*N,O*-bis(trimethylsilyl)acetamide] (305 mg, 1.5×10^{-3} mol) and KOAc (2.5 mg) were then added to the catalyst solution, and the mixture was stirred at room temp. for 24 h. The reaction mixture was then poured into saturated aqueous NH_4Cl solution and extracted with ether (2×50 mL). The combined organic extracts were washed with aqueous $NaHCO_3$ and water, dried (Na_2SO_4), filtered and concentrated under vacuum. Purification by flash chromatography (silica gel; petroleum ether/EtOAc, 8:1) gave the allylic alkylation product as a colourless oil. The (*S*) absolute configuration was ascribed to the product on the basis of the (−) sign of its optical rotation.[28]

Palladium-Catalysed Sulfonylation of Methyl 3-Penten-2-yl Carbonate with Sodium *p*-Toluenesulfinate: Ligand **3** ($1.1-2.2 \times 10^{-5}$ mol) was added to a solution of [Pd(allyl)Cl]$_2$ (2 mg, 5.5×10^{-6} mol) in the corresponding solvent at room temp. After the mixture had been stirred for 15 min, a solution of methyl 3-penten-2-yl carbonate (72.1 mg, 5×10^{-4} mol) in the appropriate solvent was added. Stirring was continued for 15 min and a suspension of $NaSO_2p$-Tol (178 mg, 10^{-3} mol) in the appropriate solvent was added. After the mixture had been stirred for 48 h, brine (10 mL) was added, and the mixture was extracted with THF. The organic phase was dried ($MgSO_4$) and concentrated under vacuum. Purification by flash chromatography (silica gel; hexane/EtOAc, 5:1) gave the product as a colourless oil. The (*R*) absolute configuration was ascribed to the product on the basis of the (−) sign of its optical rotation.[30]

Supporting Information: Experimental technique and catalytic results for the rhodium-catalysed hydrosilylation of acetophenone with diphenylsilane (see also footnote on the first page of this article).

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