A first *P*,*N*-bidentate phosphite with a chiral ketimine fragment. Catalytic properties of its Rh^{I} and Pd^{II} complexes in comparison with those of phosphine analogs

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A chiral *P*,*N*-bidentate aryl phosphite ligand containing peripheral (*R*)-(+)-camphor-derived ketimine and its rhodium(I) and palladium(II) chelate complexes were synthesized for the first time. These compounds were found to be suitable for asymmetric allylic substitution. The Pd-catalyzed sulfonylation of 1,3-diphenylallyl acetate with sodium *p*-toluenesulfinate gave the product in 73% *ee*; in the alkylation of the same substrate with dimethyl malonate, the *ee* was 94%. These *ee* values are higher than the enantioselectivity achieved with the known phosphine analogs.

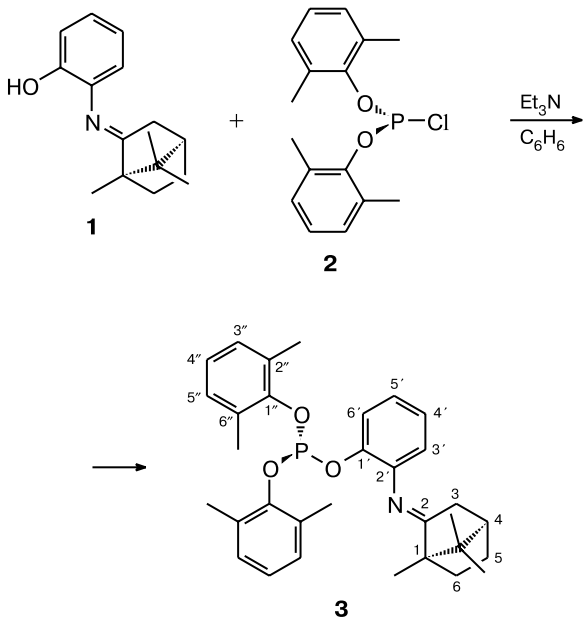
Key words: *P*,*N*-ligands, chiral iminoaryl phosphites, rhodium, palladium, asymmetric allylation.

Imino phosphines constitute an important group of chiral *P*,*N*-bidentate ligands for asymmetric catalysis by metal complexes.[1—3] The vast majority of such compounds contain an aldimine fragment, whereas systems with ketimine units are fairly uncommon.[4—6] Since recently, imino phosphites have been successfully used in enantioselective catalysis because of their high π-acidity, resistance to oxidation, synthetic accessibility, and low cost (see Refs 3 and 7 and references cited therein and Ref. 8). However, all these ligands contain a peripheral aldimine group; no phosphite with a ketimine fragment has been documented to date. In the present work, a first chiral aryl phosphite containing a ketimine substituent based on (*R*)-(+)-camphor was synthesized and successfully used in Pd-catalyzed asymmetric allylation.

Results and Discussion

A new *P*,*N*-bidentate chiral aryl phosphite was easily obtained by phosphorylation of camphor *N*-(*o*-hydroxyphenyl)imine (**1**) with accessible reagent **2** (Scheme 1).

Scheme 1



It should be noted that imino phosphite **3** is stable when stored in a dry atmosphere. For instance, the ^{31}P NMR spectrum of compound **3** recorded several months after it has been synthesized shows no signals for decomposition products. In addition, the starting reagents, including (*R*)-(+)-camphor, are inexpensive. As regards the complexation character, ligand **3** is a typical chelating agent. In particular, its reactions with $[Pd(All)Cl]_2$ in the presence of $AgBF_4$ and with $[Rh(CO)_2Cl]_2$ gave cationic and neutral metal chelates **4** and **5** with *cis*-orientation of the P and N atoms (Scheme 2).

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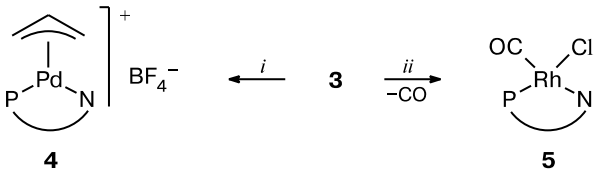
Table 1. ^{13}C NMR data ($CDCl_3$) for compounds **3** and **4**

Compound	δ_C (*J*/Hz)											
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C_{Ar}	Me	Me_{Ar}	CH_2 (allyl)	CH (allyl)
3	54.2	186.8	36.9	43.7	27.1	31.5	47.4	121.1—148.5	10.8, 18.8, 19.5	17.2, 17.4, 17.5, 17.6	—	—
4	55.3	200.3	38.1	42.3	29.0	32.0	48.0	121.2—149.9	9.5, 18.1, 18.5	17.1, 17.5, 17.6, 17.8	51.2 (*trans*-N), 81.5 (*trans*-P, $^2J_{C,P}$ = 41.2)	120.3 ($^2J_{C,P}$ = 8.9)

Scheme 2



4 5

Reagents: *i*. 1/2 $[Pd(All)Cl]_2$, $AgBF_4$; *ii*. 1/2 $[Rh(CO)_2Cl]_2$.

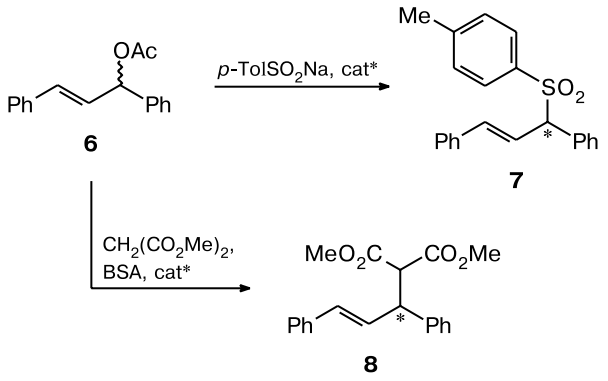
This is evident from ^{31}P NMR data for complexes **4** and **5**. The ^{31}P NMR spectrum of complex **4** contains two singlets at δ_P 143.5 (54%) and 141.5 (46%) assigned to its *exo*- and *endo*-isomers, respectively.[9] The averaged coordination shift $\Delta\delta_P = \delta_P(\text{complex}) - \delta_P(\text{ligand}) = 2.7$ ppm indicates the presence of a P—Pd bond in complex **4**. The large coordination shift $\Delta\delta_C = \delta_C(\text{complex}) - \delta_C(\text{ligand}) = 13.5$ ppm for the signal of the imino C atom in the ^{13}C NMR spectrum of complex **4** (Table 1) suggests coordination of the peripheral imino group to palladium. FAB MS data (see Experimental) are consistent with the mononuclear structure of complex **4**.

The parameters of the ^{31}P NMR and IR spectra of compound **5** (δ_P: 137.8, $^1J_{P,Rh}$ = 297.6 Hz; ν(CO) = 2026 cm^{-1} ($CHCl_3$)) suggest (see Ref. 10 and references cited therein) the pronounced π-withdrawing ability of ligand **3** typical of aryl phosphites, which is substantial for attaining high chemical and optical yields in some areas of asymmetric catalysis.[2,3] Note that complex **5** is stable in solution (NMR data).

Iminoaryl phosphite **3** (L), its complex **4**, and systems $[Pd(All)Cl]_2$/2L and $[Pd(All)Cl]_2$/4L generated *in situ* were used in Pd-catalyzed enantioselective reactions of allylic substitution (Scheme 3).

The results obtained are summarized in Tables 2 and 3. In particular, good chemical and optical yields (up to 80 and 73%, respectively; see Table 2, entry *1*) were attained in the sulfonylation of 1,3-diphenylallyl acetate (**6**) with sodium *p*-toluenesulfinate. Even better results (up to 94% *ee* and a nearly stoichiometric conversion) were obtained in the alkylation of allyl acetate **6** with methyl malonate (see Table 3, entry *3*). The yields were found to depend on the nature of both the nucleophile and the

Scheme 3



catalyst and on the solvent. For instance, in both catalyzed reactions, the asymmetric induction increases significantly when passing from complex **4** to the catalytic system $[Pd(All)Cl]_2$/2L (see Table 2, entries *1, 2* and Table 3, entries *1, 4*, *3*, *5*). This favorable effect can be associated with replacement of the outer-sphere BF_4^- anion

Table 2. Results of the Pd-catalyzed allylic sulfonylation of 1,3-diphenylallyl acetate (**6**) in THF (Nu = *p*-$TolSO_2Na$) in the presence of complexes with ligand **3**

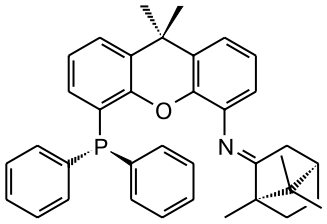
Entry	Catalyst	Yield of **7** (%)	*ee* (%)
1	$[Pd(All)Cl]_2$/2L	80	73 (*R*)
2	Complex **4**	41	65 (*R*)

Table 3. Results of the Pd-catalyzed allylic alkylation of 1,3-diphenylallyl acetate (**6**) (Nu = $CH_2(CO_2Me)_2$) in the presence of complexes with ligand **3**

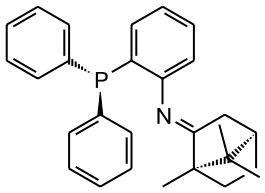
Entry	Catalyst	Solvent	Conversion of **6** (%)	*ee* (%)
1	$[Pd(All)Cl]_2$/2L	THF	98	82 (*R*)
2	$[Pd(All)Cl]_2$/4L	THF	97	92 (*R*)
3	$[Pd(All)Cl]_2$/2L	CH_2Cl_2	99	94 (*R*)
4	Complex **4**	THF	54	51 (*R*)
5	Complex **4**	CH_2Cl_2	43	78 (*R*)

by Cl^-. It is not less interesting that the enantioselectivity of allylic alkylation in dichloromethane is appreciably higher than in THF (see Table 3, entries *1*, *3*, *4*, *5*).

Now let us compare the efficiencies of iminoaryl phosphite **3** and related iminoarylphosphine ligands **9** and **10** as stereoselectors.



9



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Under conditions of catalyzed allylic alkylation comparable with those described for compound **3**, xanthene-containing ligand **9** [11] yields racemate **8**, while phosphine **10**, which is the closest analog of phosphite **3**, ensures up to 51% *ee* and a noticeably lower degree of conversion (74—80%).[4] In addition, the syntheses of ligands **9** and **10** are more complicated than that of compound **3** and their chemical yields are significantly lower (48% and 45%, respectively).[4,11] Therefore, iminoaryl phosphite **3** is obviously superior to arylphosphines **9** and **10**, thus confirming that chiral phosphites represent a new generation of phosphorus-containing ligands for metal complex asymmetric catalysis.[2,3,12]

Experimental

^{31}P and ^{13}C NMR spectra were recorded on a Bruker AMX-400 instrument (161.98 and 100.61 MHz) with reference to 85% H_3PO_4 in D_2O and $CDCl_3$ (δ_C: 76.91), respectively. Signals in the ^{13}C NMR spectra were assigned with the DEPT procedure; assignment of signals for the coordinated allyl ligand in the spectrum of complex **4** was based on the previously published data.[13] FAB mass spectra were recorded on an AMD 402 instrument. IR spectra were recorded in $CHCl_3$ on a Specord M-80 instrument (polyethylene cell). The optical yields of compound **7**, the degree of conversion of substrate **6**, and the optical yield of product **8** (chiral columns (*R*,*R*)-WHELK-01[9] for (**7**) and Daicel Chiralcel OD-H for (**6**) and (**8**)[14]) were determined by HPLC as described earlier.

All reactions were carried out in an atmosphere of dry argon in anhydrous solvents. Triethylamine was distilled over KOH and $LiAlH_4$ immediately before use. Phosphorylating reagent **2** was prepared according to a known procedure.[15] Iminophenol **1** [16] was dried *in vacuo* (1 h, 1 Torr) before the reaction. The starting complexes $[Rh(CO)_2Cl]_2$ and $[Pd(All)Cl]_2$ were prepared as described earlier.[17,18] Complex **4** was synthesized according to a known procedure.[9] Rhodium complex **5** was prepared and characterized *in situ* by spectroscopy in $CHCl_3$ as described earlier.[19]

Catalyzed alkylation of allyl acetate **6** with methyl malonate and its catalyzed sulfonylation with sodium *p*-toluenesulfinate were carried out according to the corresponding procedures.[20] The starting substrate **6** was prepared according to a known procedure.[18] Sodium *p*-toluenesulfinate, *N*,*N*-bis(trimethylsilyl)acetamide (BSA), and methyl malonate (Acros Organics Co.) were used without additional purification.

Bis(2,6-dimethylphenyl) {2-[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylideneamino]phenyl} phosphite (3). Iminophenol **1** (0.657 g, 2.7 mmol) was added at 0 °C to a vigorously stirred solution of reagent **2** (0.833 g, 2.7 mmol) and Et_3N (0.4 mL, 2.7 mmol) in 20 mL of benzene. The resulting solution was stirred for 10 min, brought to boiling, and then cooled to 20 °C. The precipitate of $Et_3N \cdot HCl$ was filtered off and the filtrate was concentrated *in vacuo* (40 Torr). The residue was kept at 1 Torr for 1 h. The yield of compound **3** was 1.211 g (87%), light yellow oil. Found (%): C, 74.33; H, 7.58; N, 2.54. $C_{32}H_{38}NO_3P$. Calculated (%): C, 74.54; H, 7.43; N, 2.72. ^{31}P NMR ($CDCl_3$), δ: 139.8. FAB MS, m/z (I_{rel} (%)): 515 $[M]^+$ (7), 394 $[M - Me_2C_6H_3O]^+$ (10), 290 $[(Me_2C_6H_3O)_2POH]^+$ (24), 243 $[M - (Me_2C_6H_3O)_2P + H]^+$ (27), 122 $[Me_2C_6H_3OH]^+$ (100).

Bis(2,6-dimethylphenyl){2-[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylideneamino]phenyl}phosphito-*P*,*N*)(π-allyl)palladium(2+) tetrafluoroborate (4) was obtained as a yellow powder in 88% yield, m.p. 152—154 °C (decomp.). Found (%): C, 55.87; H, 5.57; N, 2.06. $C_{35}H_{43}BF_4NO_3PPd$. Calculated (%): C, 56.06; H, 5.78; N, 1.87. FAB MS, m/z (I_{rel} (%)): 662 $[M - BF_4]^+$ (100), 621 $[M - BF_4 - All]^+$ (12), 515 $[L]^+$ (15).

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