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Synthesis of New Chiral Bicyclic Aminophosphoranes and of Rhodium(I) Chelates Derived from Their Open-Form Tautomers. Isolation and Characterization of an Optically Pure Rhodium(I) N/P Chelate

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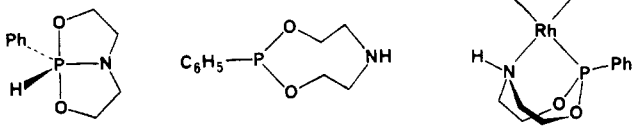
We have previously shown that, in the presence of rhodium(I) derivatives, bicyclic aminophosphoranes of type **2**[2] develop into monocyclic bidentate phosphorus-nitrogen chelating ligands **3** to give adducts of type **4**,[3] the structures of several of which, with diverse substitutions on the cycles, have been established by X-ray crystallography.[4]



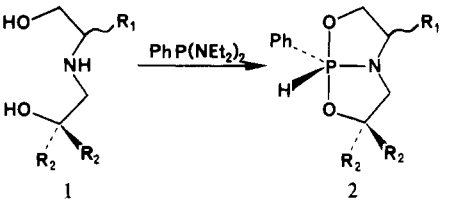
2 3 4

Among the original features of **4** that are propitious to catalytic activity should be mentioned the location of the rhodium atom in a cradle-shaped ligand, to which it is bound by both the π-accepting phosphorus atom and the solely σ-donating nitrogen atom. The latter can contribute toward increasing the electron density at the metal, and hence its nucleophilicity, while its lack of π-accepting capability should labilize the N–Rh bond, i.e. should constitute an additional, potential vacant site on the metal. In addition, the hydrophilic character of the N–H site within the coordination sphere of the metal was expected to contribute to regioselective control in catalysis.

Preliminary tests showed complexes of type **4** to be active as hydrogenation and hydroformylation catalysts.[5] In view of these results, and because it is easy to render the cradle asymmetric, we undertook the preparation of new chiral rhodium adducts of type **4**. This paper reports the synthesis of several new bicyclic aminophosphoranes, the isolation of their chlorocarbonylrhodium derivatives, and the separation of an optically pure diastereoisomer; a preliminary evaluation of their catalytic activity and enantioselectivity in the hydrogenation of α-acetamidocinnamic acid is also given.

Results and Discussion

Bicyclic Aminophosphoranes. The new asymmetric bicyclic aminophosphoranes **2a–d**, which contain the optically pure (+)-(*S*)-2-amino-1-propanol (L-alaninol) or (−)-(*R*)-2-amino-1-butanol (D-ethylalaninol) residues in one of their cycles, were obtained in 40–85% yield by allowing the optically active amino diols **1a–d** to react with bis(diethylamino)-phenylphosphanes, according to the scheme established by Houalla et al.[2]

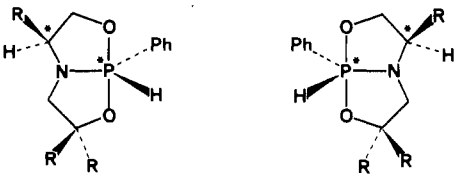


1 2

	a	b	c	d
R_1	CH_3	C_2H_5	CH_3	C_2H_5
R_2	H	H	CH_3	CH_3

The elemental analysis and mass, IR, ^1H, and ^{31}P NMR spectroscopic data for **2a–d** (Tables I and II) are consistent with the above formulation and with those previously published for other bicyclic aminophosphoranes.[2]

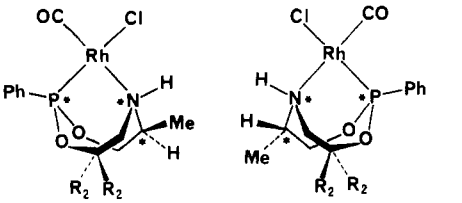
Compounds of type **2** bear a chiral center at the P atom, which is characterized by the different natures of the equatorial ligands as well as by the differing substitution of the two cycles.[6] The introduction of an asymmetric carbon atom into one of the cycles thus provokes the existence of two diastereoisomers, **2A** and **2B**, which give rise to two distinct singlets



2A 2B

in the $^{31}P\{^1H\}$ NMR spectra. The ^1H NMR spectra also exhibit two distinct sets of signals for the methyl or ethyl groups of the alaninol fragments, as well as two doublets for the proton attached to phosphorus. The diastereoisomeric ratio, which can easily be determined by means of ^{31}P NMR spectroscopy, is usually close to 50:50. No assignment of the absolute configuration at the phosphorus atom has been achieved so far.

Asymmetric Rhodium Chelates 4: Separation of an Optically Pure Diastereoisomer. When bicyclic aminophosphoranes **2** were allowed to react with $^1/_2$ equiv of $[Rh(CO)_2Cl]_2$ in toluene at room temperature, the immediate evolution of carbon monoxide was observed and the yellow crystalline adducts **4a–d** precipitated. They were isolated in 40–93% yields. Each diastereoisomeric pair of phosphoranes gives rise to a diastereoisomeric pair of rhodium adducts **4A** and **4B**; for the L-alaninol one has for example



4a,cA 4a,cB

The nitrogen atom, which is probably coplanar with its substituents in **2**, becomes pyramidal and asymmetric in **4**, but

(1) (a) Université de Nice. (b) Universität Regensburg.
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Table I. ^1H and ^{31}P NMR Spectra of Compounds **2a–d** and **4a–d**[a]

compd	K,[b] %	$\delta(^1H)$ (J_{CH-H}) $CH_3(R_1)$	$CH_3(R_2)$	CH_3(Et)	CH_2(Et)	CH_2N	CH_2O	P-H	NH	C_6H_5	$\delta(^{31}P)$ (J) pV	pIII	solvent
2aA	52	1.15 d (5.9)				3.14 m	3.81	7.32 d		7.38 m, 7.67 m	−41.3 m (693)		$CDCl_3$
2aB	48	1.19 d (6.2)						7.38 d			−45.8 m (703)		
2bA	53			0.89 d (7.0), 0.95 d (7.4)	1.55 m	2.95 m	3.78 m	7.32 d		7.34 m, 7.60 m	−41.3 m (700)		$CDCl_3$
2bB	47							7.32 d			−45.0 m (714)		
2cA	56	1.17 d (6.5)	1.09 s, 1.31 s			2.99 m	3.71 m	7.35 d		7.33 m, 7.63 m	−42.9 m (703)		$CDCl_3$
2cB	44	1.15 d (6.5)	1.21 s, 1.31 s					7.42 d			−48.1 m (715)		
2dA	56		1.04 s, 1.25 s	0.88 d (7.6), 0.83 d (7.1)	1.65 m	2.98 m	3.71 m	7.31 d		7.30 m, 7.64 m	−43.3 m (690)		$CDCl_3$
2dB	44		1.15 s, 1.25 s	0.80 d (7.1), 0.75 d (7.6)				7.30 d			−47.1 m (709)		
4aA[c]	39	1.32 d (6.6)				3.05 m	4.47 m		4.90 m	7.54 m		161.0 d (191)	Me_2SO-d_6 (60 °C)
4aB	61	1.05 d (7.1)				2.97 m, 3.67 m	4.17 m, 4.68 m					160.1 d (191)	
4bA	53			0.99 d (7.0)	1.37 m	3.06 m, 3.46 m	4.43 m		4.85 m	7.65 m		160.7 d (187.5)	Me_2SO-d_6 (60 °C)
4bB	47			0.93 d (7.0)	1.75 m							160.0 d (190.5)	
4cA	55	1.46 d (6.6)	1.40 s, 2.22 s			3.03 m	4.25 m		5.17 m	7.55 m		148.9 d (182)	Me_2SO-d_6 (60 °C)
4cB	45	1.07 d (6.1)	1.42 s, 2.22 s									148.0 d (188)	
4dA	52		1.39 s, 2.21 s	0.94 d (7.0), 0.96 d (7.0)	1.91 m	2.90 m, 3.29 m	4.29 m		5.13 m	7.55 m		154.4 d (185)	Me_2SO-d_6 (60 °C)
4dB	48		1.40 s, 2.23 s	1.02 d (7.0), 1.13 d (7.0)								150.6 d (188)	

[a] The spectra were recorded at 90 and 35.45 MHz for ^1H and ^{31}P, respectively, on a Bruker WH-90 DS spectrometer; the Rh complexes are broad-band decoupled for ^{31}P. Chemical shifts are given in ppm downfield from Me_4Si (internal) and 85% H_3PO_4 (external); coupling constants are in Hz; s = singlet, d = doublet, m = multiplet. [b] Ratio of diastereoisomers after formation of the product. [c] Data taken from a mixture enriched with 64% of **A**.

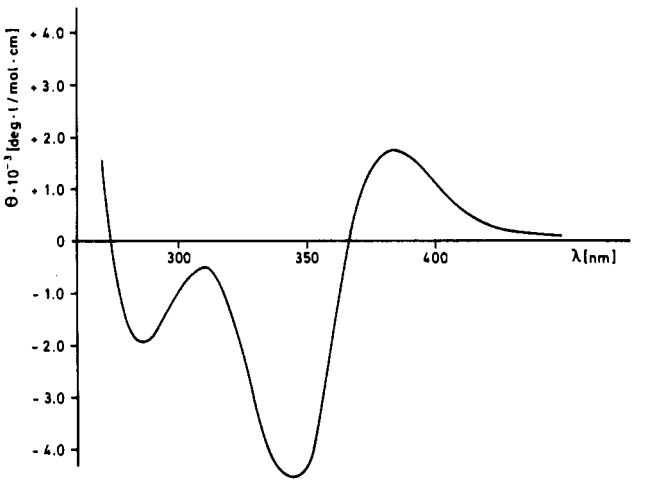

Figure 1. Molecular ellipticity of $(-)_{365}$-**4aB** (10^{-3} *m* in CH_3CN solution) as measured on a Jasco J-40A instrument.

since its configuration is not independent of that of the phosphorus atom, it does not give rise to additional stereoisomers.

The coordination of phosphorus to the metal in **4** is evidenced in the ^{31}P NMR spectra by the presence of signals in the range 148–161 ppm, the disappearance of the J_{P-H} coupling, and the appearance of a J_{P-Rh} coupling constant of 180–190 Hz (Table I). The coordination of nitrogen to the metal is established by the disappearance of the ν(P–H) vibration in the infrared spectra (Table II), to the profit of a low ν(N–H) vibration around 3200 cm^{-1}. A trans location of the phosphorus and chlorine ligands on the metal, consistent with the antisymbiotic rule, is proposed by analogy with related structures that have been established by X-ray diffraction studies.[3] The substitution of the remaining carbon monoxide and chloride ligands by a second phosphorane molecule was not observed even in the presence of an excess of the latter.

The presence of two diastereoisomers is evidenced by two signals in the $^{31}P\{^1H\}$ and by distinct sets of ^1H signals for the alkyl groups of the alaninol residues. All the complexes [4] with ^{31}P resonances at lower fields should belong to the same type of stereoisomer, called **A**, whereas the high-field resonances should belong to the opposing diastereoisomers, **B**. The absolute configuration at the P atom can however not be determined. In complexes **4b–d** no significant change in the diastereomic ratio was found upon coordination, whereas some optical induction leading to an **A**:**B** ratio of 39:61 was observed in the case of **4a**, even when starting with an approximately 50:50 mixture of the two diastereoisomers of **2a**.

In the case of **4a**, separation of one diastereoisomer was successfully and reproducibly achieved by two fractional crystallization steps in CH_3CN. No noticeable changes in the diastereomeric ratio were observed in the other cases, even upon repeated and very slow recrystallization. The originally predominant diastereoisomer **B** formed in **4a** could thus very easily be separated as the sparingly soluble isomer, in optically pure quality ($[\alpha]^{20}_{365} = -435°$, 0.9 mg/3 mL of CH_3CN). The molecular ellipticity of **4aB** is shown in Figure 1. The mixture could be enriched in the case of the more readily soluble isomer **4aA** only to an optical purity of 64%, as shown by ^1H NMR.

The significant difference between the two diastereoisomers of **4a** and **4c**, found in their ^1H NMR spectra for the CH_3 group R_1 (0.27 and 0.29 ppm, respectively), may be due either to distinct orientation of the methyl groups with respect to the phosphonite cycle (exo/endo) or to an interaction with the metal.

The catalytic hydrogenation of several unsaturated substrates with phosphorane-based rhodium(I) catalysts of type

Table II. Selected Properties of Compounds 2a–d and 4a–d

compd	yield, %	mp, °C	anal.[c] mol wt[b]	% C	% H	% N	% P	% Cl	% Rh	infrared peaks,[a] cm^{-1} ν_{NH}	ν_{PH}	ν_{CO}	ν_{RhCl}
2a	60		225.2	58.72	7.17	6.22	13.76				2295		
			225	58.20	7.19	5.82	13.67						
2b	90		239.2	60.24	7.58	5.86	12.94				2310		
			239	60.21	7.47	5.80	12.17						
2c	68		253.3	61.65	7.96	5.53	12.23				2320		
			253	61.64	8.22	5.34	12.34						
2d	85		267.3	62.90	8.30	5.24	11.59				2320		
			267	61.56	8.43	5.05	11.12						
4a	58	225 dec	391.5	36.81	4.12	3.58	7.92	9.05	26.28	3201 m		2001 vs	295 w
			391	36.91	4.21	3.57	8.11	9.59	26.10				
4b	42	215 dec	405.6	38.52	4.44	3.46	7.65	8.64	25.37	3190 m		1996 vs	285 w
			405	38.79	4.46	3.50	7.70	8.68	25.43				
4c	93	228 dec	419.6	40.12	4.81	3.34	7.40	8.47	24.55	3203 m		1998 vs	295 w
			419	40.19	4.90	3.58	7.50	8.54	24.27				
4d	83	225 dec	433.7	41.54	5.11	3.23	7.14	8.17	23.37	3190 m		1998 vs	280 w
			433	41.07	5.05	3.18	7.16	7.81	23.76				

[a] Films (2a–d) or KBr disks (4a–d) measured on a Beckman 4240 or a Perkin-Elmer 577 instrument. [b] Mass spectroscopy. [c] Top row of data for each compound gives calculated values; bottom row, found values.

4 has previously been reported.[5] In contrast to these reactions, which took place at an initial pressure of 1 bar when cyclohexene was the substrate, a drastic increase in H pressure was required for the hydrogenation of (*Z*)-α-acetamidocinnamic acid; this pressure is moreover dependent on the solvent. In a typical run, the acid could be hydrogenated in the presence of (−)-**4aB** under 100 bar of H_2 in 92% yield but with only an 18% enantiomeric excess.

Experimental Section

Elemental analyses (Service Central d'Analyses du CNRS) are shown, together with melting points, yields, and infrared data, in Table II. All procedures were carried out under nitrogen with dry, N_2-saturated solvents. The optically active amino diols $HOCH_2CH(R_1)NHCH_2C(R_2)_2OH$ were prepared according to published methods.[7] The preparation of the phosphoranes **2a–d** in general follows the procedure given by Houalla et al.[2] with some modifications.

General Operation Mode for Bicyclic Aminophosphoranes 2a–d. A mixture of carefully distilled bis(diethylamino)phenylphosphane (5.04 g, 20 mmol) was heated with an equivalent amount of the amino diol in 100 mL of toluene at 140 °C for 24 h. The diethylamine was distilled as it formed. The solution was concentrated to 20 mL and filtered through SiO_2 (5 × 2 cm). After evaporation of the solvent, the phosphoranes were isolated as colorless, viscous oils. **2a** was obtained as white crystals on cooling a saturated pentane solution to −35 °C.

Preparation of the Rh Complexes 4a–d. A solution of 1 mmol of phosphorane **2** in 10 mL of benzene was added at room temperature to a solution of $[Rh(CO)_2Cl]_2$ (194 mg, 0.5 mmol) in 10 mL of benzene. The mixture immediately darkened, and a bright yellow solid precipitated with evolution of CO. The solid was filtered and washed twice with small portions of benzene to give the crude product in 60–90% yield, from which the optical inductions were examined by means of ^{31}P and ^1H NMR spectroscopy.

Isolation of $(-)_{365}$-4aB. A 572-mg sample of complex **4a** was dissolved in 15 mL of CH_3CN at 60 °C. The solution was filtered and then slowly cooled to 0 °C over 2 days. The resulting yellow crystals were again recrystallized, to give 57 mg (8% yield) of the optically pure compound $(-)_{365}$-**4aB**.

Catalytic Hydrogenation of (*Z*)-α-Acetamidocinnamic Acid. A solution of $(-)_{365}$-**4aB** (35 mg, 0.09 mmol) in 10 mL of CH_3CN was added to a solution of (*Z*)-α-acetamidocinnamic acid (506 mg, 2.4 mmol) in 10 mL of CH_3OH. The mixture was transferred into a 100-mL autoclave. After being purged three times with 50 bar of H_2, the solution was stirred under 100 bar of H_2 for 24 h at 35 °C. Workup of the dark solution and determination of the enantiomeric excess were accomplished as described in the literature.[8]

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Registry No. 1a, 91239-52-0; **1b**, 74572-06-8; **1c**, 91239-53-1; **1d**, 91239-54-2; **2aA**, 91239-48-4; **2aB**, 91280-11-4; **2bA**, 91239-49-5; **2bB**, 91280-12-5; **2cA**, 91239-50-8; **2cB**, 91280-13-6; **2dA**, 91239-51-9; **2dB**, 91280-14-7; **4aA**, 91239-55-3; **4aB**, 91280-15-8; **4bA**, 91239-56-4; **4bB**, 91280-16-9; **4cA**, 91239-57-5; **4cB**, 91280-17-0; **4dA**, 91239-58-6; **4dB**, 91280-18-1; $[Rh(CO)_2Cl]_2$, 14523-22-9; $PhP(NEt_2)_2$, 1636-14-2; (*Z*)-α-acetamidocinnamic acid, 55065-02-6.

Supplementary Material Available: Tables of selected ions from mass spectra of phosphoranes **2a–d** and rhodium adducts **4a–d**. Preliminary data on hydrogenation of (*Z*)-α-acetamidocinnamic acid with $(-)_{365}$-**4aB** (2 pages). Ordering information is given on any current masthead page.

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