Journal of Organometallic Chemistry, 346 (1988) 267–275
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Synthesis and properties of crown ether-modified phosphines and their use as ligands in transition metal catalysts

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(Received October 1st, 1987)

Abstract

A novel series of crown ether-modified triarylphosphines, 1,2-diphenylphosphino-2,3,5,6,8,9-hexahydro-1,4,7,10-benzotetraoxacyclodecin (IIIa) and its higher homolog (III) (common nomenclature is $3n$-diphenylphosphinobenzo-[$3n$-crown-n]ethers ($n = 4$, 5, 6, and 7)), is reported. The thermodynamic parameters for the extraction of alkali metal picrates are evaluated. Phosphines III ($n = 5$ and 6) form 1 : 1 stoichiometric crown-type complexes with Na^+ and K^+. The observed extractability is in good agreement with the cavity size selectivity concept. The thermodynamic parameters $\Delta H°$ and $T\Delta S°$ for the extractive complexation at 25 °C are -63 to -58 kJ/mol and -41 to -35 kJ/mol, respectively, thus $\Delta G°$ is governed by the enthalpy term. These phosphines are applied to reactions in liquid-liquid or liquid-solid phases, as the auxiliary ligands of homogeneous palladium and rhodium catalysts. The catalytic activities correlate well with the extractabilities of the phosphine ligands. The compound $[RhCl(cod)]_2$, combined with IIIc and IIId, shows high activities toward catalytic hydrogenation of potassium and caesium cinnamates, respectively. Replacement of allyl bromide with powdered sodium or potassium iodide in benzene to give allyl iodide are catalyzed by $(\pi\text{-}C_3H_5PdCl)_2$ in the presence of phosphines III.

Introduction

Tertiary phosphines are among the most widely used ligands of homogeneous organotransition metal catalysts. Aryl- or alkyl-substituted phosphines, however, are hydrophobic. Consequently, transition metal catalysts possessing such ligands can hardly be applied to the reaction of hydrophilic reagents which are insoluble in common organic solvents. In this case, combined use of a phase transfer catalyst and a hydrophobic organotransition metal catalyst effects the reaction [1]. For example, the use of tetrakis(triphenylphosphine)palladium in conjunction with

0022-328X/88/$03.50

1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) smoothly catalyzes the nucleophilic substitution of vinyl halides with solid potassium cyanide in benzene despite the fact that neither component independently catalyzes the reaction [2]. The combined use of the two catalysts, however, is not necessarily applicable to all reactions which occur in liquid-liquid or liquid-solid phases, because the concentrations of both catalysts are low and the catalytic efficiency is proportional to the product of their concentrations.

To multify this defect, to some extent, we have reported briefly the synthesis of phosphines containing polyether chains [3], and pointed out that the combination of the features of both transition metal complexes and phase transfer catalysts in the same molecule constitutes a bifunctionalization for double-concerted catalysis. Moreover, we demonstrated the counter or inverse phase transfer catalysis by water-soluble phosphine palladium complexes [4]. In addition to our work, several reports on the preparations of phosphine ligands combined with crown or pseudo-crown rings have appeared viz. diphenylphosphinomethyl-substituted benzo-crowns [5], chelating phosphites containing polyether chains [6], and uni- or bidentate phosphines having azo-crowns [7]. Each of these phosphines, however, has disadvantages in that laborious synthetic routes are necessary or that the bonds between the phosphorus and the polyether moieties, are unstable.

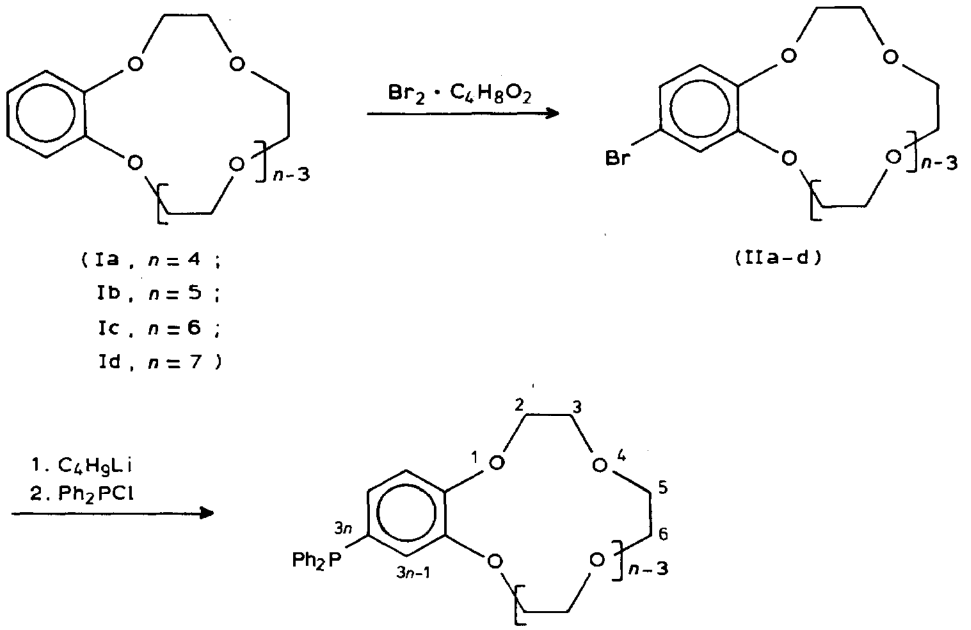
We report here on the preparation of crown ether-modified triaryl phosphines which have chemically stable bonds, their preferential cation binding properties, and their use as ligands in phase transfer organotransition metal catalysts.

Results and discussion

Synthesis of crown ether-modified phosphines

2,3,5,6,8,9-Hexahydro-1,4,7,10-benzotetraoxacyclododecin (Ia) and its homologous series (I) were used. Hereafter, the common nomenclature "crown" will be used. Shaw et al. [5] have attempted to prepare 14- or 15-diphenylphosphino-substituted benzo-[15-crown-5] through metalation of benzo-[15-crown-5], followed by the reaction with R_2PCl. They could find no evidence for the formation of R_2P-alternative route.

We have succeeded in introducing the Ph_2P group into the $3n$-position of benzo-[$3n$-crown-n] by bromination and lithiation, followed by the reaction with Ph_2PCl as shown in Scheme 1. In the abbreviations (bc-n) of the benzo crown moiety, n refers to the number of oxygen atoms in the cyclic polyether chain. Therefore, $3n$ indicates the size of the ring. The bromination was performed with 1,4-dioxane bromine complex in the dark. The use of an excess of brominating agent led to the dibromination. Brominated benzo crown ethers II were soluble in benzene, tetrahydrofuran (THF), ethanol, and ether. It should be emphasized that compound II was successfully lithiated below $-90\,^\circ C$, and subsequent reaction with diphenylchlorophosphine gave the crown ether-modified triarylphosphines (III). Since the lithiated crown ethers are thermally unstable, it is necessary to keep the temperature below $-90\,^\circ C$ during the addition of n-BuLi and Ph_2PCl (See Experimental). The ^{13}C NMR spectra of each phosphine suggested that the diphenylphosphino group was bound to the $3n$ carbon atom. The absorption peak appeared at 129.1δ [3c]. These phosphines showed solubilities similar to those of brominated benzo crown ethers II in common organic solvents. They were stable in



(Ia, $n = 4$;
Ib, $n = 5$;
Ic, $n = 6$;
Id, $n = 7$)

(IIa-d)

(IIIa, $n = 4$, Ph_2P(bc-4);
IIIb, $n = 5$, Ph_2P(bc-5);
IIIc, $n = 6$, Ph_2P(bc-6);
IIId, $n = 7$, Ph_2P(bc-7))

Scheme 1

air in the solid state, but oxidized slowly in solutions. The crown ether-modified phosphines could be stored under nitrogen in a refrigerator for months.

Extractability for metal picrates. In order to assess the ability to transfer ionic compounds, we measured the extractability for alkali metal picrates from an aqueous phase into benzene. The crown ether-modified phosphines (III) were scarcely soluble in water. The distribution constants (defined as $[Ph_2P(bc\text{-}n)]_{aq}/[Ph_2P(bc\text{-}n)]_{org}$) of IIIb and IIIc were 3.7×10^{-3} and 4.8×10^{-3} in benzene at 30 °C, respectively. Consequently, the stoichiometric number (m) of the extractive

$$m\{Ph_2P(bc\text{-}n)\}_{org} + M^+_{aq} + A^-_{aq} \overset{K_e}{\rightleftharpoons} \{Ph_2P(bc\text{-}n)_m MA\}_{org} \quad (1)$$

complexation was calculated from eq. 1, in which the terms $Ph_2P(bc\text{-}n)_{aq}$ and $[Ph_2P(bc\text{-}n)_m M^+]_{aq}$ were neglected [8]. In the extractions of sodium picrate with IIIb and potassium picrate with IIIc, each plot of $\log[\{Ph_2P(bc\text{-}n)_m MA\}_{org}]/[M^+_{aq}][A^-_{aq}]$ against $\log[Ph_2P(bc\text{-}n)_{org}]$ in benzene gave a good straight line. The slopes were 1.0 for IIIb/Na^+ and 1.1 for IIIc/K^+. Since both stoichiometric numbers were close to unity, 1 : 1 stoichiometric crown-type complexes were considered to be formed under these conditions. Accordingly, the extraction equilibrium constant (K_{ex}) was calculated from eq. 2 for the 1 : 1 complexes [9].

$$K_{ex} = \left[\{Ph_2P(bc\text{-}n)MA\}_{org}\right] / \left[M^+_{aq}\right]\left[A^-_{aq}\right]\left[\{Ph_2P(bc\text{-}n)\}_{org}\right] \quad (2)$$

The results in benzene at 6 °C are summarized in Table 1, which includes the data of benzo-[15-crown-5] and -[18-crown-6] for comparison. Table 1 shows that

Table 1

Logarithmic equilibrium constants for the extraction of metal picrates

Crown compound		Li^+	Na^+	K^+	Cs^+
Ph_2P(bc-4)	(IIIa) [a]	1.5	1.3	0.9	
Ph_2P(bc-5)	(IIIb) [b]	1.5	3.59	2.7	1.3
Ph_2P(bc-6)	(IIIc)	1.9	3.39	5.45	3.55
Ph_2P(bc-7)	(IIId)		2.9	4.12	4.76
benzo-[15-crown-5]	(Ib)	1.1	3.48	2.3	1.1
benzo-[18-crown-6]	(Ic)	1.9	3.36	5.11	3.54

Extraction was carried out in water (10 ml)-benzene (10 ml) at 6 °C under following conditions; picric acid, 7.0×10^{-5} mol/l; metal hydroxide, 0.1 mol/l; crown ether, 3.5×10^{-4} mol/l.

[a] 3.5×10^{-3} mol/l. [b] 1.75×10^{-3} mol/l.

IIIa exhibits the highest extractability for Li^+, IIIb for Na^+, IIIc for K^+ and IIId for Cs^+. These facts are in good agreement with the criterion of cavity size selectivity [10]. The equilibrium constant (log K_{ex}) of IIIc for K^+ was 5.45 at 6 °C and decreased to 4.50 at 25 °C. This value is somewhat lower than the 4.65 of dibenzo-[18-crown-6] at 25 °C [11]. On the whole, the K_{ex} values were slightly higher than those of the corresponding benzo-crown ethers.

The thermodynamic parameters, $\Delta G°$, $\Delta H°$, and $T\Delta S°$ for the extractions of Na^+ with IIIb, K^+ with IIIc, and Cs^+ with IIId were calculated by use of the Frensdorff-Toei method [11,12]. The plots of log K_{ex} against the reciprocal of absolute temperature are linear over the range of 6 to 35 °C. The results are shown in Table 2. The change in enthalpy increases slightly with the number of the crown oxygen atoms, and is greater than $T\Delta S°$ in all cases. Therefore, the free energy change is governed by the enthalpy terms.

Palladium complexes with crown ether-modified phosphines and some catalytic reactions under the solid-liquid two-phase system. Palladium dichloride complexes $PdCl_2[Ph_2P(bc\text{-}n)]_2$ (IVa–d) could be prepared readily by reaction of $PdCl_2(PhCN)_2$ with III in benzene at 80 °C for 5 min. On addition of methanol to the benzene solution, the reaction mixtures gave analytically pure orange crystals. The orange crystals of IVd which recrystallized from dichloromethane-methanol are formulated as $PdCl_2L_2$ $1/2CH_2Cl_2$. The *trans* configuration is suggested by the presence of a single infrared band in the Pd–Cl stretching region from 351 to 358 cm^{-1}.

Complexes IV readily underwent halogen exchange reactions. When complex IVb was treated with 50 equivalents of powdered sodium bromide in chloroform at 40 °C for 1 h, the corresponding dibromide complex, *trans*-$PdBr_2L_2$ (V, L = IIIb), was obtained quantitatively. On the other hand, the exchange reaction of

Table 2

Thermodynamic parameters (kJ/mol) for the extractive complexation at 25 °C [a]

System	$\Delta G°$	$\Delta H°$	$T\Delta S°$
Ph_2P(bc-5)-Na^+	−17	−58	−41
Ph_2P(bc-6)-K^+	−27	−59	−32
Ph_2P(bc-7)-Cs^+	−23	−63	−40

[a] Conditions are the same as shown in Table 1.

$PdCl_2(Ph_3P)_2$ with sodium bromide was very slow and only 30% was estimated to exchange for 10 h. These results indicate that the bromide anion is able to approach the coordination sphere of palladium by pairing with the sodium cation captured by the crown moiety and thus is able to undergo rapid substitution to give complex V. It has been reported already that the palladium complexes (IV) act as catalysts for the reduction of 1-chloromethylnaphthalene in benzene with solid or aqueous sodium formate [3c]. In this reduction, the complexes (IV) have higher catalytic activities than that of the mixed catalyst $PdCl_2(Ph_3P)_2$/benzo-[18-crown-6]. We reasoned that these high activities arise from an intramolecular reaction of the naphthylmethyl group on palladium with the formate extracted by the crown moiety of the phosphine ligand.

Hydrogenation by rhodium catalysts containing crown ether-modified phosphines under aqueous-organic two-phase system

As described above the crown ether-modified phosphines have size-selective extractability cavities for alkali metal picrates. To see the relationship between the extractability of the phosphines and the catalytic activity of the metal complexes with these phosphine ligands (III), the hydrogenation of alkali metal cinnamates with a rhodium catalyst in a benzene-water bilayer system was undertaken. A mixture of $[RhCl(cod)]_2$ (VI) and III (2.2 equivalents to Rh atom) was used as the catalyst, and the initial rate of hydrogen uptake was measured with vigorous stirring. The rates corresponded to the extractabilities of the phosphine ligands as shown in Table 3. Although we expected a remarkable selectivity for the reduction of lithium and sodium cinnamates by the VI-IIIa and -IIIb systems, respectively, it was hardly discernible. Inspection of Table 3 reveals that the rhodium complexes (VI) combined with IIIc and IIId possess the highest activity toward potassium and caesium cinnamates owing to the respective preferential cation binding. These results suggest that the extraction of cinnamates from water into benzene is an important step in this two-phase hydrogenation. This interpretation was supported by the fact that the activity of the catalyst system VI/IIIc was increased by the addition of KF, because an increase in the potassium ion concentration elevates the concentration of extracted cinnamate in the benzene phase. On the other hand, the temperature effect was not correlated with the thermodynamic estimation of the extractability. The rate increased with elevated temperatures, though the extractabil-

Table 3

Initial hydrogen uptake rates (mmol/min) during rhodium-catalyzed hydrogenation of alkali metal cinnamates in a benzene-water bilayer phase at 30 °C [a]

Phosphine Ligand		Cinnamate			
		Li^+	Na^+	K^+	Cs^+
Ph_2P(bc-4)	(IIIa)	1.2	1.6	1.3	
Ph_2P(bc-5)	(IIIb)	1.4	1.9	1.4	1.7
Ph_2P(bc-6)	(IIIc)	1.5	1.7	7.4	3.7
Ph_2P(bc-7)	(IIId)		1.9	2.1	5.4

[a] Conditions: $[RhCl(cod)]_2$, 0.05 mmol; Ph_2P(bc-*n*), 0.22 mmol; cinnamate, 3 mmol; H_2, 760 mmHg; benzene, 3 ml; water, 7 ml.

Table 4

The replacement of allyl bromide with iodides by $[C_3H_5PdCl]_2$-ligand (III) systems [a]

Ligand	Additive [b]	Phase [c]	Yield, %
–	Ic	C_6H_6–solid KI	16
Ph_3P	Ic	C_6H_6–solid KI	17
IIIc	–	C_6H_6-solid KI	84
IIIb	–	C_6H_6–solid NaI	32
–	Ic	C_6H_6–1.2 *M* aq KI	21
IIIb	–	C_6H_6–1.2 *M* aq NaI	18
IIIc	–	C_6H_6–1.2 *M* aq NaI	15
IIIc	–	C_6H_6–1.2 *M* aq KI	42
IIIc	–	C_6H_6–2.4 *M* aq KI	73
Ph_3P	Ic	C_6H_6–1.2 *M* aq KI	38
IIIc	–	$CHCl_3$–1.2 *M* aq KI	49
IIIc	–	CH_2Cl_2–1.2 *M* aq KI	54

[a] Catalyst, $[C_3H_5PdCl]_2$ (0.05 mmol)-phosphine (0.1 mmol); additive, 0.1 mmol; allyl bromide, 10 mmol; reaction, 25 °C for 2 h. [b] 0.1 mmol. [c] Organic solvent, 10 ml; solid NaI or KI, 20 mmol; aqueous solution, 10 ml.

ity was lower at high temperatures. This fact indicates that the kinetic factors are naturally important in the catalytic reaction.

It is interesting to note that the catalyst system of VI/IIIc was 50 times as active as the mixed catalyst system of PPh_3 and benzo-[18-crown-6]. This high efficiency of the crowned phosphine complex can possibly be ascribed to its facile hydrogenation step, which is an intramolecular reaction between the captured cinnamate with the crown moiety and the hydrogenated rhodium, similar to the "proximity effect" in the enzymatic reactions.

Catalytic substitution reactions. The crown ether-modified phosphines can also be used as the auxiliary ligand in the palladium catalyst for the nucleophilic substitution reactions. The substitution of allyl bromide with sodium or potassium iodide was studied. It is well known that palladium complexes catalyze allylic substitutions with various nucleophiles, where a π-allyl complex is a key intermediate [14,15]. Therefore, π-allylpalladium chloride, $[\pi\text{-}C_3H_5PdCl]_2$ (VII), combined with phosphines was used as the catalyst. The use of benzo-[18-crown-6] (Ic) itself or a mixture of VII/Ph_3P/Ic for the reaction with solid potassium or sodium iodide in benzene resulted in poor conversion of allyl bromide, and allyl iodide was obtained in yields of less than 20%.

Catalysis in the presence of IIIb or IIIc resulted in the substitution as shown in Table 4. It can be seen that there is a correlation between the catalytic activity and the metal ion extractability of the phosphine ligands. The palladium complex in combination with crown ether-modified phosphines was superior to the mixed catalyst system.

Upon changing nucleophiles from iodide ion to organic reagents such as ethyl acetoacetonate, phenolate, or ethyl malonate in benzene-5*M* KOH (aqueous), the substitution of allyl bromide proceeded smoothly with ligand III, and the expected allylic compounds were obtained in 45–70% yields at 25 °C for 1 h. In these reactions, however, the use of triphenylphosphine instead of III as the added ligand is of similar consequence in terms of yields. This is presumably due to the fact that even in the absence of a phase transfer catalyst these organic nucleophiles dissolve moderately in benzene where the substitution takes place.

Experimental

Methods and materials. All commercially available reagents were used without further purification. Solvents were dried in the usual way, distilled under a stream of nitrogen and then stored under nitrogen. 1,4-Dioxane bromine complex was prepared by a published procedure [16]. NMR spectra were recorded on Varian T-60 and JEOL GX 270 spectrometers.

Bromination of benzo-[3n-crown-n] [17]. The bromination of Ib is typical. A solution of 15 g (55.9 mmol) of Ib in 240 ml of tetrahydrofuran (THF) was cooled in an ice bath, and then 16.9 g (68.2 mmol) of dioxane bromine complex was added to it, all at once, in the dark. After stirring for 10 min, the solution was neutralized by saturated aqueous sodium hydrogencarbonate. Resulting salts were removed by filtration and THF was removed under reduced pressure. The residue was extracted with dichloromethane. The crude product was recrystallized from hot n-hexane to give IIb in a 76% yield, mp 69–71° C. Bromination of Ia, Ic, and Id was performed in a similar manner to give IIa (in 78% yield; mp, 37.5–38.9° C), IIc (78%, 72.5–73.5° C), and IId (62%, 40.5–41.5° C), respectively. These crude products were purified by recrystallization except IIa which was distilled under 1 Torr at 130–150° C and dried over P_4O_{10} under reduced pressure.

Preparation of crown ether-modified phosphines (III). Preparation of IIIb is representative. In a three-necked flask equipped with a thermometer 41 g (118 mmol) of IIb was placed, and then the system was placed under nitrogen. Dry THF (800 ml), which was distilled from sodium benzophenone ketyl, was added. The temperature was lowered to −97° C by a liquid nitrogen-methanol bath. n-Butyllithium (142 mmol, 88 ml of 1.61 *M* hexane solution) was added slowly by cold syringe over a period of 12 min, keeping the temperature below −90° C. After stirring for 15 min at the same temperature, 27.5 ml (153 mmol) of chlorodiphenylphosphine dissolved in 50 ml of THF was added gradually to the solution over a period of 15 min while the temperature was maintained below −90° C, and the

Table 5

Data of crown ether-modified phosphines III and $PdCl_2L_2$ (L = III)

Compd.	Yield [a] (%)	M.p. (° C)	Elemental analysis (Found (calc) (%))			Spectral data
			C	H	Cl	
IIIa	76	62.5–63.5	70.81(70.58)	6.22(6.17)		^{13}C NMR See ref. 8.
IIIb	92	102.5–103.0	68.78(69.01)	6.48(6.46)		
IIIc	66	81.5–82.5	67.49(67.73)	6.68(6.70)		
IIId	65	oily	66.89(66.65)	6.62(6.90)		
IVa	87	191.0–194.0	58.34(57.99)	4.92(5.07)	7.00(7.13)	358 ν(Pd–Cl) (cm^{-1})
IVb	95	196.0–198.0	57.65(57.71)	5.31(5.40)	6.84(6.55)	355
IVc	70	171.0–172.0	57.64(57.47)	5.63(5.68)	6.02(6.06)	356
IVd [b]	74	102.0–105.0	55.83(55.86)	5.81(5.81)	8.18(8.18)	351

[a] Yields of III are based on II. [b] Calcd values are for $PdCl_2L_2 \cdot 1/2CH_2Cl_2$.

mixture was then allowed to warm gradually to room temperature over a period of 3.5 h. After this period 0.2 mol of triethylamine was added. Stirring was continued for a while, and then the reaction mixture was hydrolyzed with 20% aqueous ammonium chloride. The resulting mixture was concentrated under reduced pressure, and extracted with benzene. The benzene layer was dried over sodium sulfate. After filtration, the solvent was removed under reduced pressure, and the crude product was recrystallized from ethanol. Yield, 39.9 g. The other phosphines were prepared and purified similarly, except for IIId, which was purified by silica gel (Wakogel) chromatography using benzene and benzene-THF (9–15 : 1) as the developing solvents. See Table 5 for analytical data.

Distribution coefficient between benzene and water. To a 1 : 1 mixture (100 ml) of benzene and water was added 0.2 mmol of IV and stirring was continued for 10 min at 30 ° C. The aqueous solution (20 ml) was pipetted and evaporated to dryness. The amount of IV dissolved was determined by UV spectroscopy (in ethanol, 214 nm): IVb, 28800; IVc, 29100.

Extractability of phosphines toward picrates. A mixture (20 ml : 20 ml) of aqueous picrate solution and a benzene solution of the phosphines was stirred for 10 min in a thermostat and equilibrated. The mixture was allowed to stand for 5 min, then the concentration of picrate in the aqueous layer was determined by UV spectroscopy at 354 nm.

Preparation of palladium complexes $PdCl_2L_2$. The following illustrates a typical example. Bis(benzonitrile)palladium chloride (191.8 mg, 0.5 mmol) was placed in a two-necked flask equipped with a condenser and three-way stopcock. The system was placed under nitrogen, 5 ml of benzene was added, and then the solution was refluxed for 2 min. Phosphine IVc (546 mg, 1.1 mmol) was added rapidly at room temperature and the resulting solution was refluxed for 5 min. After addition of methanol, the mixture was allowed to cool to room temperature. Filtration gave the crude product, which was recrystallized from CH_2Cl_2-methanol. See Table 5 for the yields and elemental analysis.

Catalytic hydrogenation of cinnamates in bilayer phase. Rhodium complex $[RhCl(cod)]_2$ (0.05 mmol) and phosphine IV (0.22 mmol) were placed in a 10 ml flask which was connected to a gas buret. The flask was thermostated at 30 ° C and the system was placed under hydrogen. Cinnamate (3.0 mmol) dissolved in 7 ml of degassed water and 3 ml of benzene were introduced into the flask by a syringe. With vigorous stirring the initial rate of hydrogen uptake at room temperature (below 10% conversion) was measured.

Substitution of allyl bromide with iodide ion. In a 30 ml flask were placed $[C_3H_5PdCl]_2$ (0.05 mmol) and phosphine III (0.1 mmol). The system was placed under nitrogen and thermostated at 25 ° C. Organic solvent (10 ml) was added. After stirring for 5 min, allyl bromide (10 mmol) and solid potassium (or sodium) iodide (20 mmol) or 10 ml of aqueous solution of potassium (or sodium) iodide were added, and the mixture was stirred for 2 h. Then anisole (1 mmol) was added as an internal standard. After filtration the resulting solution was analyzed by gas chromatography on a PEG 20M column 3 m, at 90–150 ° C.

Replacement of allyl bromide with other nucleophiles. These substitution reactions were carried out similar as to those described above, using the active hydrogen compounds (20 mmol) and 5 ml of 5 *M* potassium hydroxide. The products were identified spectroscopically.

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