Chiral Sulfonated Phosphines. Syntheses and Use as Ligands in Asymmetric Hydrogenation Using an Aqueous–Organic Two-Phase Solvent System

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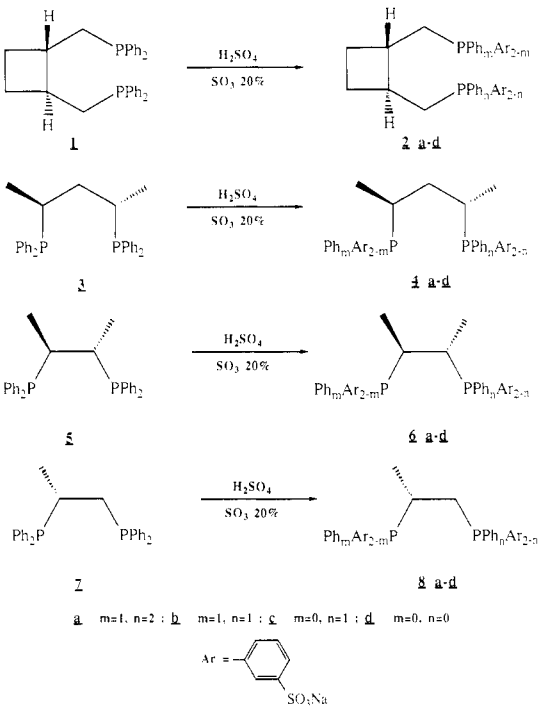
Sulfonation of chiral phosphines (*S,S*)-cyclobutanediop (**1**), (*S,S*)-BDPP (**3**), (*S,S*)-Chiraphos (**5**), and (*R*)-Prophos (**7**) results in water-soluble ligands. The course of the reaction has been studied by using $^{31}P\{^1H\}$ NMR. While the proper choice of the conditions permits the synthesis of tetrasulfonated cyclobutanediop **2d**, BDPP **4d**, and Chiraphos **6d**, Prophos **7** gives a mixture of tetrasulfonated **8d** and trisulfonated phosphine **8c**. Treatment of $[Rh(diene)Cl]_2$ with these novel ligands (L) results in chloride bridge splitting to give $[Rh(diene)L]^+$ (**9**), which in turn reacts with hydrogen or water to give $[Rh(L)(H_2O)_2]^+$ (**10**). Addition of (*Z*)-enamide, $PhCH{=}CH(NHCOCH_3)COOH$ (**13a**), to the aqua complex in water produces a substrate chelate complex **12**. Rhodium(I) catalysts formed with sulfonated diphosphines are efficient catalysts for the asymmetric hydrogenation of carbon–carbon (88% ee), carbon–oxygen (28% ee), and carbon–nitrogen double bonds (58% ee) in aqueous–organic two-phase solvent systems. Sulfonated ligands afford a catalyst system, which can be reused without loss of enantioselectivity.

Introduction

One of the most recent and important advances in asymmetric synthesis is the use of a soluble chiral catalyst.[1,2] However, in the use of a soluble catalyst, one of the central problems is the separation of the catalyst from the reaction products. One way to solve this problem involves the attachment of the catalyst onto an insoluble polymeric support in a way that the advantages observed in solution are retained.[3] Such chiral systems have been used most not only in enantioselective hydrogenation[4-21] but also in hydrosilylation,[22] hydroformylation,[23-26] and formation of carbon–carbon bonds using Grignard reagents;[27] reuse of the catalyst was possible and showed no loss in enantioselectivity.

A quite different approach has involved the use of metal complexes of water-soluble ligands. The water solubilization of phosphines is usually achieved via introduction of a highly polar functional group such as an amino, car-

Scheme I. Sulfonation of the Chiral Diphosphines



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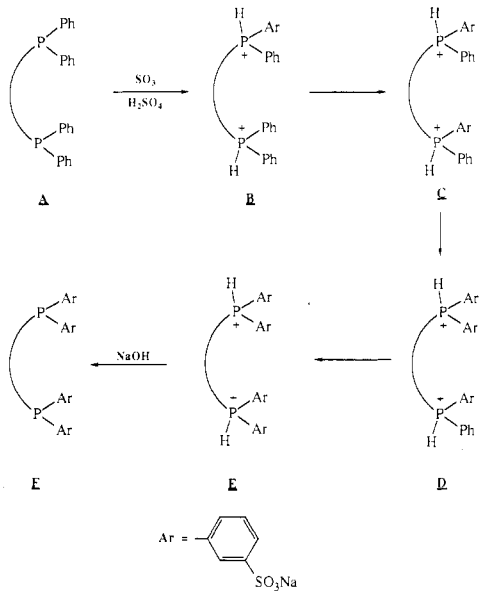
Scheme II. Sequence of Sulfonation of a Diphosphine



boxylic acid, hydroxide, or sulfonate.[28,29] The catalytic properties of complexes with sulfonated triphenylphosphines,[30-37] derivatives of bis(2-(diphenylphosphino)ethyl)amine,[38-40] or amphos[41-44] have been studied and compared with the more typical nonfunctionalized phosphines. We and others reported the synthesis of asymmetric water-soluble disphosphines and their use in enantioselective hydrogenation using water as a solvent.[45-47] We have earlier described some preliminary results concerning the use of sulfonated chiral phosphines as ligands in enantioselective hydrogenation in an aqueous–organic two-phase solvent system.[48] We now describe in detail the synthesis of the chiral sulfonated phosphines and their use in asymmetric hydrogenation.

Results and Discussion

Sulfonation of Ligands. The sulfonation of the chiral phosphines (*S,S*)-cyclobutanediop (**1**), (*S,S*)-BDPP (**3**), (*S,S*)-Chiraphos (**5**), and (*R*)-Prophos (**7**)[49] (Scheme I) was carried out in concentrated sulfuric acid containing 20% SO_3 in the manner described for triphenylphosphine.[36] To know the time and the conditions necessary for tetrasulfonation of the diphosphines, we followed the reaction by $^{31}P\{^1H\}$ NMR by using various concentrations of the phosphine in oleum. The sequence of sulfonation of a diphosphine is quite complex (Scheme II). Protonation of the phosphorus is followed by the successive sulfonation of the phenyl ring giving rise to the formation of monosulfonated, disulfonated, trisulfonated, and tetrasulfonated diphosphines. To avoid the formation of diastereomers with different configuration at the phosphorus in the case of chiral phosphines (compounds B, C, and D), it is desirable to prepare tetrasulfonated diphosphines (compound F).

The $^{31}P\{^1H\}$ NMR spectrum with the time of an oleum solution containing 0.147 M or 0.22 M of (*S,S*)-cyclobutanediop (**1**), a 1,4-diphosphine, showed only two signals at 6.4 and 5.5 ppm which could be assigned to the protonated PPh_2, PPhAr and to the protonated PAr_2 groups, resectively. However, oxidation of the phosphines gives new five signals (in D_2O) corresponding to the five possibilities: a monosulfonated PPh_2 facing a nonsulfonated group, a monosulfonated group facing a disulfonated one, a monosulfonated group facing a monosulfonated one, a disulfonated group facing a disulfonated one, and a disulfonated group facing a monosulfonated one at 38.8, 38.5, 38.2, 37.5, and 37.3 ppm, respectively. Tetrasulfonated diphosphine **2d** could be obtained after only 24 h. Carrying out the reaction at 50 °C slightly increased the rate, but mainly oxides were obtained; the use of sulfuric acid containing 60% SO_3 afforded only the oxide of tetrasulfonated phosphine **2d**.

In the case of (*S,S*)-BDPP (**3**), a chiral 1,3-diphosphine, tetrasulfonation is slower. Three signals at 20.2, 19.6, and 19.0 ppm arising from protonated PPh_2, PAr_2, and PPhAr were observed. Tetrasulfonation required 50 h in a 0.5 M solution. On the other hand, increasing the amount of oleum decreases the time necessary for tetrasulfonation (30 h for a 0.25 M solution).

Sulfonation of (*S,S*)-Chiraphos (**5**) (0.25 M or 0.125 M in sulfuric acid containing 20% SO_3) is much slower than for (*S,S*)-BDPP. We observed three signals at 16.8, 16.4, and 15.6 ppm which could be attributed again to protonated PPh_2, PPhAr, and PAr_2. Monosulfonation is quite slow compared to (*S,S*)-cyclobutanediop (**1**) and (*S,S*)-BDPP (**3**); with use of a 0.125 M solution, tetrasulfonation is complete in 4 days. Increasing the amount of oleum (0.064 M in **5**) allowed us to perform the tetrasulfonation in 2 days. The same features have been found for the (*R*)-Prophos (**7**), although the spectrum is more complex with signals at approximately 20 and 5 ppm.

In conclusion, we observe that the reactivity order of tetrasulfonation of the diphosphines is 1,4 > 1,3 > 1,2.

When the chiral diphosphines were treated with 20% SO_3 in H_2SO_4 during 1 week and eventually some more oleum was added, we obtained tetrasulfonated diphosphines **2d** and **4d** (δ(P) −20.2 and 0.7, respectively) without traces of oxides. When the reaction time was

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(49) Abbreviations: (*S,S*)-cyclobutanediop = (*S,S*)-1,2-bis((diphenylphosphino)methyl)cyclobutane; (*S,S*)-BDPP = (*S,S*)-2,4-bis(diphenylphosphino)pentane; (*S,S*)-Chiraphos = (*S,S*)-2,3-bis(diphenylphosphino)butane; (*R*)-Prophos = (*R*)-1,2-bis(diphenylphosphino)propane.

Table I. $^{31}P\{^1H\}$ NMR Data

compound	δ(P) (D_2O)[a]	J_{Rh-P}	δ(P) (D_2O + H_2O_2)[a]	Δ[b]
2d	−20.2		38.0	
$[Rh(C_2H_4)_2Cl]_2$ + **2d** (**9**)	14.0 (d)	143		34.2
$[Rh(COD)Cl]_2$ + **2d** (**9**)	20.2 (d)	144		40.4
$[Rh(COD)Cl]_2$ + **2d** + KPF_6 (**9**)	20.2 (d)	144		40.4
$[Rh(COD)_2]PF_6$ + **2d** (**9**)	20.2 (d)	144		40.4
$[Rh(\mathbf{2d})(H_2O)_2]^+$ (**10**)	43.5 (d)	182		63.7
4d	0.7		45.0	
$[Rh(COD)Cl]_2$ + **4d** (**9**)	29.3 (d)	144		28.6
$[Rh(NBD)_2]BF_4$ + **4d** (**9**)	28.5 (d)	149		27.8
$[Rh(\mathbf{4d})(H_2O)_2]^+$ (**10**)	53.2 (d)	185		52.5
$[Rh(NBD)(\mathbf{4d})]BF_4$ + **4d** (**11**)	24.9 (d)	131		24.2
$[Rh(\mathbf{4d})(H_2O)_2]^+$ + **13a** (**12**)	56.2 (dd)	169 (43)[c]		55.5
	43.6 (dd)	157 (43)[c]		42.9
6d	−9.6		43.2	
6c	−9.6 and −8.3		43.2 and 43.5	
$[Rh(COD)Cl]_2$ + **6d** (**9**)	57.4 (d)	148		67.0
8c	−0.6 (d) and −19.9 (d) (32)[c]		38.7 (d) and 43.1 (d) (50)[c]	
	0.4 (d) and −21.1 (d) (31)[c]		37.8 (d) and 43.8 (d) (50)[c]	
8d	−0.5 (d) and −20.7 (d) (36)[c]		37.7 (d) and 43.0 (d) (50)[c]	

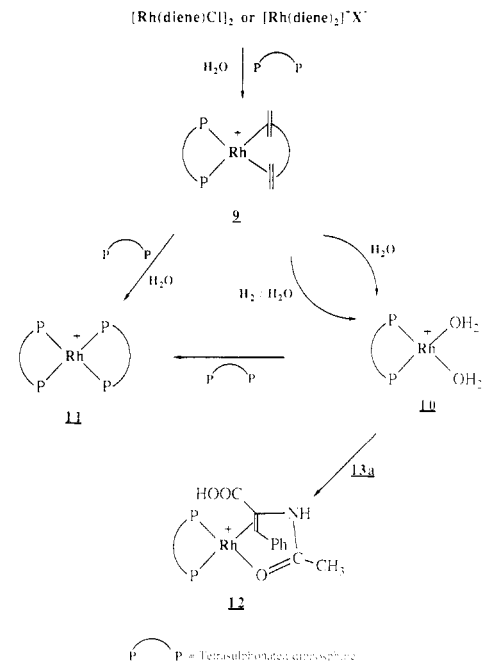
[a] In ppm relative to external H_3PO_4; downfield shifts positive; coupling constant in hertz. [b] Coordination shift = $\delta(P_{complex}) - \delta(P_{ligand})$. [c] J_{P-P}.

decreased, sulfonation of (*S,S*)-BDPP (**3**) gave a mixture containing 23% mono- (**4a**), 68% di- (**4b**), and 9% trisulfonated phosphine (**4c**) as determined by $^{31}P\{^1H\}$ NMR. Sulfonation of (*S,S*)-Chiraphos (**5**) gave the tetrasulfonated diphosphine **6d** (δ(P) − 9.6) and another sample consisting of 40% tri- (**6c**) and 60% tetrasulfonated phosphine (**6d**) [δ(P) −9.6 (80%) and −8.3 (20%) as determined by $^{31}P\{^1H\}$ NMR]. Attempts to obtain pure tetrasulfonated (*R*)-Prophos **8d** were unsuccessful owing to the formation of phosphine oxide. However, a mixture of tetrasulfonated **8d** (55%) and trisulfonated **8c** (35%) phosphines contaminated with 10% of oxides could be prepared. The $^{31}P\{^1H\}$ NMR spectra of this sample exhibit two doublet resonances at −20.7 and −0.5 ppm (J = 36 Hz) for the tetrasulfonated species **8d**, four doublets resonances at −19.9, −0.6 ppm (J = 32 Hz) and −21.1, +0.4 ppm (J = 31 Hz) for the two trisulfonated species and also four doublet resonances at 43.1, 38.7 ppm (J = 50 Hz) and 43.8, 37.8 ppm (J = 50 Hz) for the oxidized trisulfonated species. The $^{31}P\{^1H\}$ NMR data of all these phosphines are compiled in Table I. In all cases, residual amounts of sodium sulfate (5–10%) remained with the phosphines, but without damage to the catalytic activity of the ligands.

Catalytic Studies. These ligands were used in asymmetric hydrogenation of prochiral substrates like amino acids precursors in a two-phase system. The catalysts were prepared by reacting the sulfonated phosphine with $[Rh(COD)Cl]_2$ or $[Rh(NBD)_2]BF_4$, respectively, in the appropriate ratio in water, the reaction occurred slowly because of the insolubility of the diene precursor in water. The $^{31}P\{^1H\}$ NMR parameters obtained using $[Rh(COD)Cl]_2$ (Table I), and particularly J_{Rh-P} = 143–148 Hz, are characteristic of the cationic species **9**.[50] Reaction of $[Rh(COD)_2]PF_6$ or $[Rh(NBD)_2]BF_4$ with **2d** and **4d** gave identical spectra, and the same pattern was observed by using $[Rh(COD)Cl]_2$ + **2d** in the presence of KPF_6.

In the case of $[Rh(COD)Cl]_2$ + **2d**, a new species appeared after 12 h and at a concentration of 40% after 60 days. Since the chemical shift at the lower field (43.5 Hz), the coordination shift Δ (63.7 Hz), and the coupling constant J_{Rh-P} (182 Hz) are very similar to those of $[Rh(L)(MeOH)_2]^+$ (L = nonsulfonated diphosphine),[50] structure **10** (Scheme III) was therefore attributed to this species. Bubbling hydrogen through these solutions also gave very easily complex **10**. These phosphino complexes in water are quite stable under argon for months, with no appearance of phosphine oxide. Addition of 1 equiv of **4d** to the complex $[Rh(NBD)(\mathbf{4d})]BF_4$ gave, as expected, the bis(diphosphine) complex $[Rh(\mathbf{4d})_2]BF_4$ showing characteristic ^{31}P NMR parameters.[50]

Scheme III



Addition of an excess of the (*Z*)-enamide PhCH=C(NHCOCH$_3$)COOH (**13a**) to the aqua complex $[Rh(\mathbf{4d})(H_2O)_2]^+$ in water produced a significant change in the $^{31}P\{^1H\}$ NMR spectrum: the doublet signal of the aqua complex (δ 56.2 (J_{Rh-P} = 185 Hz)) disappeared and two sets of double doublets signals appeared at δ 56.2 (J_{Rh-P} = 169 Hz, J_{P-P} = 43 Hz)) and 43.6 (J_{Rh-P} = 157 Hz (J_{P-P} = 43 Hz)) (at +36 °C) indicating for the first time the formation of a substrate chelate complex in aqueous solution. We

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Table II. Reduction of α-Acetamidocinnamic Acid Methyl Ester 13b Using [Rh(COD)Cl]$_2$ + Ligand[a]

ligand	P_{H_2}, atm	solvent	ee, % (config)
2d	1	AcOEt/H_2O (1/1)	20 (*S*)
2d	1	CH_2Cl_2/H_2O (1/1)	12 (*S*)
2d	1	CH_2Cl_2/H_2O (1/1)	16 (*S*)[b]
2d	1	C_6H_6/H_2O (1/1)	12 (*S*)
6d	10	AcOEt/H_2O (1/1)	81 (*R*)
6d	10	CH_2Cl_2/H_2O (1/1)	89 (*R*)
6c (40%) + **6d** (60%)	10	CH_2Cl_2/H_2O (1/1)	82 (*R*)
6c (40%) + **6d** (60%)	10	CH_2Cl_2/H_2O (1/1)	86 (*R*)[b]
6d	10	C_6H_6/H_2O (1/1)	70 (*R*)

[a] Conditions: 25 °C; [substrate] = 1 M; [substrate]:[ligand]:[Rh] = 100:1.1:1;10 mL of H_2O; 10 mL of organic solvent; chemical yield quantitative. [b] Catalyst reused.

assume a square-planar structure **12**, as a similar coordination of an enamide in methanol to Rh(I) is well-known.[51] Although we have not determined the formation constant, it must be fairly large, as the ^{31}P NMR spectrum indicated the absence of the doublet signal at δ 53.2.

Asymmetric reduction of some prochiral precursors was studied in a two-phase system with the catalyst derived from [Rh(COD)Cl]$_2$ and the sulfonated chiral diphosphines. The phosphine **2d** based catalyst works generally under 1 atm of hydrogen, but the other phosphine-based catalysts give a less active system and higher pressure is needed.

Reduction of the methyl ester of α-acetamidocinnamic acid **13b** in various two-phase systems using tetrasulfonated (*S,S*)-cyclobutanediop **2d**, tetrasulfonated (*S,S*)-Chiraphos **6d**, or a mixture of tri- and tetrasulfonated (*S,S*)-Chiraphos **6c** + **6d** based catalyst produced interesting results (Table II). The hydrogenation was carried out under mild conditions, with the greatest enantioselectivity being observed by using the ligand **6d** in ethyl acetate (ee = 81%) or dichloromethane (ee = 89%) and the lowest in benzene cosolvent (ee = 70%). It was found that the aqueous catalyst system could be reused without loss of enantioselectivity (ee = 86% versus 82% on reusing the catalyst in the system dichloromethane–water). Ligand **2d** based catalyst, which had the highest activity, gave disappointingly very low enantioselectivity (only 12–20% ee). For the following experiments, we choose ethyl acetate as the cosolvent, since the esters of the amino acid precursors are soluble in dichloromethane, but not the amino acid precursors.

The results obtained in the reduction of various amino acid precursors are summarized in Table III. It appears clearly that tetrasulfonated (*S,S*)-Chiraphos **6d** or the mixture of tri- and tetrasulfonated (*S,S*)-Chiraphos **6c** + **6d** leads to a very efficient catalyst, giving enantioselectivity up to 88% in the reduction of the acid **13a**, 82% for the methyl ester **13b**, 86% for the acid **13c**, and 88% for the precursor of Dopa **13d**. Reuse of the catalyst solution is possible with no loss of enantioselectivity: the catalyst obtained from the ligand **6c** + **6d** gave ee of 88% and 87%, respectively, in the reduction of the methyl ester **13b**, being reused once and twice. It was then advisable to use the tetrasulfonated derivative as the different configurations of the phosphorus atom in the diastereomers of mono-, di-, and trisulfonated phosphines could decrease the enantioselectivity. Surprisingly, using a mixture of tri- and tetrasulfonated (*S,S*)-Chiraphos **6c** + **6d** (40% and 60%, respectively) instead of the tetrasulfonated has no influence on the enantioselectivity: 87% versus 88% in the reduction of the acid **13a** and 81% versus 82% for the methyl ester **13b**.

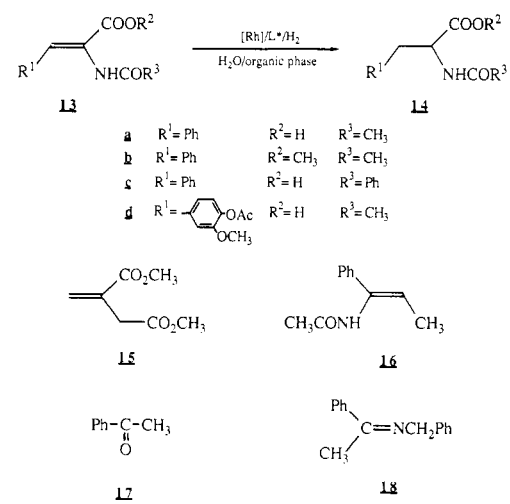
Tetrasulfonated (*S,S*)-BDPP **4d** based catalyst gave lower enantioselectivity (ee = 44–65%) than the catalyst modified by the analogous ligand tetrasulfonated (*S,S*)-Chiraphos **6d**. A surprising consequence of our experiments is the increase of the optical yield in going from the

Table III. Reduction of Various Enamides Using [Rh(COD)Cl]$_2$ + Ligand[a]

substrate	ligand	P_{H_2}, atm.	AcOEt/H_2O	ee, % (config)
13a	**2d**	1	1/1	34 (*S*)
		1	1/1	37 (*S*)[b]
	4d	15	1/1	65 (*R*)
	4a + **4b** + **4c**[c]	15	1/1	80 (*R*)
	6d	10	2/1	87 (*R*)
	6c + **6d**[d]	10	2/1	88 (*R*)
	8c + **8d**[e]	10	2/1	70 (*S*)
13b	**2d**	1	1/1	20 (*S*)
		1	1/1	23 (*S*)
	4d	15	1/1	45 (*R*)
	4a + **4b** + **4c**[c]	15	1/1	67 (*R*)
	6d	10	1/1	81 (*R*)
	6c + **6d**[d]	10	1/1	82 (*R*)
		10	1/1	88 (*R*)[b]
		10	1/1	87 (*R*)[f]
	8c + **8d**[e]	10	1/1	67 (*S*)
13c	**2d**	1	2/1	13 (*S*)
	4d	15	1/1	44 (*R*)
	4a + **4b** + **4c**[c]	15	1/1	76 (*R*)
	6c + **6d**[d]	10	2/1	86 (*R*)
	8c + **8d**[e]	10	2/1	70 (*S*)
13d	**2d**	1	2/1	37 (*S*)
	4c	10	2/1	58 (*R*)
	4a + **4b** + **4c**[c]	10	2/1	71 (*R*)
	6c + **6d**[d]	10	2/1	88 (*R*)
	8c + **8d**[e]	10	2/1	80 (*S*)
15	**2d**	1	1/1	43 (*S*)
	4d	1	1/1	8 (*R*)
	6c + **6d**[d]	1	1/1	29 (*S*)
	8c + **8d**[e]	1	1/1	7 (*R*)
16	**2d**	10	1/1	26 (*S*)
	4d	5	1/1	13 (*R*)
	6c + **6d**[d]	10	1/1	39 (*S*)
	8c + **8d**[e]	10	1/1	18 (*R*)
17	**4a** + **4b** + **4c**[c]	70	1/1	22 (*S*) [22]
18	**4d**	70	1/1	34 (*R*)
	4a + **4b** + **4c**[c]	70	1/1	58 (*R*)

[a] Conditions: 25 °C; [substrate] = 1 M; [substrate]:[ligand]:[Rh] = 100:1.1:1; 10 mL of H_2O; quantitative chemical yield unless otherwise indicated in brackets. [b] Catalyst reused. [c] Mixture of 23% **4a** + 68% **4b** + 9% **4c**. [d] Mixture of 40% **6c** and 60% **6d**. [e] Mixture of 35% **8c** + 55% **8d**. [f] Catalyst twice reused.

Scheme IV. Structure of the Unsaturated Substrates



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tetrasulfonated (*S,S*)-BDPP **4d** to a mixture of mono- (**4a**), di- (**4b**), and trisulfonated phosphine (**4c**) (respectively 23% **4a**, 68% **4b**, and 9% **4c**); we obtained an enantioselectivity of 65% versus 80% in the reduction of the acid **13a**, 45% versus 67% for the methyl ester **13b**, 44% versus 76% for the acid **13c**, and 58% versus 71% for the precursor of Dopa **13d**.

Sulfonated (*R*)-Prophos based catalyst, although the ligand is a mixture of tri- and tetrasulfonated phosphine **8c + 8d** and phosphine oxides, gave ee up to 70%, 68%, and 80%, respectively, in the reduction of the acid **13a**, the methyl ester **13b**, and the precursor of Dopa **13d**.

The catalyst obtained from tetrasulfonated (*S,S*)-cyclobutanediop **2d**, although the most active, gave lower enantioselectivity than the others; all the values are in the range of 20–35%; here again, reuse of the catalyst gave the same ee.

Other substrates were reduced in presence of these catalytic system. As shown in Table III, the dimethyl ester of itaconic acid **15** undergoes a facile reduction with all ligands, giving 2-methylsuccinic acid dimethyl ester with ee up to 43% in the case of tetrasulfonated (*S,S*)-cyclobutanediop **2d**. The simple enamide **16** is reduced only under pressure and generally with poor selectivity (ee up to 39% with ligand **6d**).

Preliminary experiments were also carried out with the sulfonated (*S,S*)-BDPP **4a + 4b + 4c** based catalyst for the hydrogenation of carbon–oxygen and carbon–nitrogen double bonds. Thus, the asymmetric hydrogenation of the carbon–oxygen double bond in acetophenone **17** at 30 °C (70 bar) gave the 2-phenylethanol in a chemical yield of 22% and a optical yield of up to 22%. The hydrogenation of the carbon–nitrogen double bond in Schiff base **18** gave optical yields in the range of 34–58% under the same conditions. Although the optical yields are rather modest, this is the first time that such a water-soluble ligand has been successfully used in a two-phase system for the asymmetric hydrogenation of carbon–oxygen and carbon–nitrogen double bonds.

Conclusion

In conclusion, sulfonation of chiral 1,2-, 1,3-, and 1,4-diphosphines afforded water-soluble ligands. The reactivity order of tetrasulfonation was found to increase by increasing the chain length between the two phosphorus atoms. Asymmetric hydrogenation occurred in an aqueous–organic two-phase solvent system using rhodium complexes of these sulfonated phosphines: ee's up to 88% are obtained. The primary advantages of this catalytic system are the ease of the workup and the ability to recover and reuse both the rhodium and the optically active ligand. Since the different configurations of the phosphorus atom in the diastereomers of mono-, di-, and trisulfonated phosphines could decrease the enantioselectivity, therefore, the tetrasulfonated diphosphines were expected to give the most effective catalysts. However, a mixture of tri- and tetrasulfonated (*S,S*)-Chiraphos gave same optical yields, as the tetrasulfonated one; furthermore, the tetrasulfonated (*S,S*)-BDPP-based catalyst gave lower enantioselectivity than a mixture of mono-, di-, and trisulfonated phosphines. The work is actually in progress to obtain pure mono-, di-, and trisulfonated diphosphines and to evaluate the effectiveness of their catalytic activity.

Experimental Section

Operations were normally carried out under nitrogen unless otherwise described. Solvents were distilled from appropriate drying agents and stored under nitrogen. The 80-MHz ^{1}H NMR spectra and the ^{31}P spectra (all ^{1}H decoupled) were run on a Brucker W.P.80 CW or a Varian XL 100 spectrometer. Optical rotation were recorded on a Perkin-Elmer 241 polarimeter. High-performance liquid chromatography (HPLC) was performed on a Chromatem 380 high-performance liquid chromatograph (Touzard Matignon). The detector used was an SP 8200 detector optical unit with a single wavelength (254 nm).

(*S,S*)-Cyclobutanediop (**1**) was a gift from Rhône-Poulenc Recherches. (*S,S*)-BDPP (**3**),[52] (*S,S*)-Chiraphos (**5**),[53] and (R)-Prophos (**7**)[54] were prepared as previously described.

Preparation of Sulfonated Phosphines. To 2×10^{-3} Mol of diphosphine dissolved in 1 mL of sulfuric acid in a Schlenk tube under argon was added slowly 10 mL of sulfuric acid containing 20% SO_3 at 0 °C. After 2–5 days, the mixture was poured very slowly onto 100 g of ice and neutralized with 50% sodium hydroxide at 0 °C. After decantation, the liquid phase was poured into 100 mL of methanol and the solid washed again with 100 mL of methanol. After evaporation, the residue was dissolved in the minimum amount of water and poured into methanol. Filtration of the solid and evaporation of the liquid gave the crude diphosphine. Yields are generally quantitative. The extent of sulfonation was determined by ^{31}P{^{1}H} NMR and by HPLC using the technique called "soap chromatography".[55] Analytical separation was carried out on a 250 × 4.6 mm i.d. stainless-steel column packed with 5 μm Hypersil SAS (C_1) silica or with 10 μm Hypersil SAS (C_8) silica and water–propanol (5:2) containing various amounts of cetrimide or water–acetonitrile containing 0.5% of $(NH_4)_2CO_3$, respectively. In the latter case an eluent program was used: the starting eluent contained 5% CH_3CN and 95% water and the amount of CH_3CN was increased to 100% for 8 min. The percentage of phosphorus in the sample determined by microanalysis gave the content of the sulfonated phosphine in the crude mixture. To obtain authentic samples of the tetrasulfonated phosphines, the crude product was repeatedly recrystallized from aqueous methanol.

Tetrasulfonated (*S,S*)-cyclobutanediop 2d: ^{31}P NMR (D_2O) δ −20.2; ^{13}C NMR (D_2O) δ 28.1 (d, CH_2, $^3J_{PC}$ = 12 Hz), 31.5 (d, CH_2–P, $^1J_{PC}$ = 15 Hz), 41.4 and 41.6 (2 × d, CH, $^2J_{PC}$ = 12.5 Hz), 132 (d, C-4 ar, $^4J_{PC}$ = 2 Hz), 132.7 (d, C-5 ar, $^3J_{PC}$ = 7.5 Hz), 138.5 (d, C-6 ar, $^2J_{PC}$ = 15 Hz), 138.3 and 138.5 (2 × d, C-1 ar, $^1J_{PC}$ = 11 Hz), 146.7 and 146.8 (2 × d, $^3J_{PC}$ = 6 Hz). Anal. Calcd for $C_{30}H_{42}O_{20}P_2S_4Na_4 \cdot 8H_2O$: C, 35.9; H, 4.2; P, 6.2. Found: C, 36.2; H, 4.2; P, 6.4.

Tetrasulfonated (*S,S*)-BDPP 4d: ^{31}P NMR (D_2O) δ 0.7; ^{13}C NMR (D_2O) δ 17.4 (d, CH_3, $^2J_{PC}$ = 16.7 Hz), 27.4 (ps t, CH, $^1J_{PC}$ + $^3J_{PC}$ = 19.2 Hz), 38.3 (br s, CH_2), 128.8 (d, C-4 ar, $^4J_{PC}$ = 2.6 Hz), 131.7 (d, C-5 ar, $^3J_{PC}$ = 6.8 Hz), 132.4 (d, C-2 ar, $^2J_{PC}$ = 21.7 Hz), 138.6 (d, C-6 ar, $^2J_{PC}$ = 21.3 Hz), 138.7 (d, C-1 ar, $^1J_{PC}$ = 14.2 Hz), 139.1 (d, C-1 ar, $^1J_{PC}$ = 13.8 Hz), 145.4 (d, C-3 ar, $^3J_{PC}$ = 7.1 Hz). Anal. Calcd for $C_{29}H_{26}O_{12}P_2S_4Na_4 \cdot 8H_2O$: C, 35.1; H, 4.2; P, 6.2; S, 12.9. Found: C, 35.1; H, 4.1; P, 6.1; S, 13.0.

Tetrasulfonated (*S,S*)-Chiraphos 6d: ^{31}P NMR (D_2O) δ −9.6; ^{13}C NMR ($D_2O + H_2O_2$) δ 14.5 (d, CH_3, $^2J_{PC}$ = 16.6 Hz), 33.5 (d, CH, $^1J_{PC}$ = 71 Hz), 130.6 (d, C-2 ar, $^2J_{PC}$ = 9.1 Hz), 132.9 (s, C-4 ar), 132.9 (d, C-1, $^1J_{PC}$ = 97.6 Hz), 133.2 (d, C-5 ar, $^3J_{PC}$ = 12 Hz), 135.9 (d, C-6, $^2J_{PC}$ = 9.9 Hz), 146.0 (d, C-3 ar, $^3J_{PC}$ = 10.3 Hz). Anal. (as the oxide). Calcd for $C_{28}H_{24}O_{14}P_2S_4Na_4 \cdot 8H_2O$: C, 33.2; H, 4.0; P, 6.1; S, 12.7. Found: C, 33.0; H, 3.7; P, 5.9; S, 12.6.

Tetrasulfonated (*R*)-Prophos 8d (as the oxide): ^{31}P NMR (D_2O) δ 37.7 and 43.0 (J_{PP} = 50 Hz); ^{13}C NMR (D_2O) δ 16.2 (d, CH_3, $^2J_{PC}$ = 15 Hz), 28.9 (d, CH, $^1J_{PC}$ = 69.6 Hz), 30.2 (d, CH_2, $^1J_{PC}$ = 69.4 Hz), 130.6 (d, C-2 ar, $^2J_{PC}$ = 8.5 Hz), 132.8 (s, C-4 ar), 132.8 (d, C-1, $^1J_{PC}$ = 93.2 Hz), 133.1 (d, C-5, $^3J_{PC}$ = 11 Hz), 136.0 (d, C-6, $^2J_{PC}$ = 8.7 Hz), 146.3 (d, C-3, $^3J_{PC}$ = 10.2 Hz). Anal. Calcd for $C_{27}H_{22}O_{14}P_2S_4Na_4 \cdot 8H_2O$: C, 32.5; H, 3.8; P, 6.2. Found: C, 32.2; H, 3.8; P, 6.1.

Aqua Complex 10. A suspension of chloro(cyclooctadiene)-rhodium(I) dimer (7.8 mg, 20 μmol) and tetrasulfonated di-

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phosphine (22 μmol) in H_2O (3 mL) in a Schlenk tube was stirred under argon for 1 h. The tube was attached to the vacuum line, and hydrogen was admitted. The tube was then agitated at room temperature under a positive pressure of hydrogen for 2 h. The hydrogen was then removed, the tube sealed under argon, and the ^{31}P NMR spectrum recorded.

Tetrasulfonated BDPP Rhodium(I) Adduct of (*Z*)-α-Acetamidocinnamic Acid, 12. The aqua complex **10** was prepared as above from **4d** (78 mg, 20 μmol) in H_2O (3 mL). This solution was carefully transferred under argon into an NMR tube containing (*Z*)-α-acetamidocinnamic acid (30 mg, 30 μmol) in water (0.5 mL). The tube was sealed under argon and the ^{31}P NMR spectrum recorded.

Hydrogenation. $[Rh(COD)Cl]_2$ and an appropriate amount of the sulfonated phosphine were mixed together in water (5 or 10 mL) for 2 h. This solution was added to the unsaturated substrate dissolved in the organic solvent (ethyl acetate, methylene chloride, or benzene). The two-phase liquid mixtures were transferred to hydrogenation apparatus and shaken until absorption of the theoretical amount of hydrogen when working under atmospheric pressure or for 12 h when working under hydrogen pressure. The organic phase was separated, and in the case of recycling, a solution of the unsaturated substrate was again injected into the apparatus. After reaction, the organic solvent was evaporated, the reaction products were analyzed by ^1H NMR, and the ee was determined by polarimetry using the following rotations for the optically pure compounds: *N*-acetyl-(*S*)-phenylalanine, $[\alpha]^{20}_D = +46.0°$ (*c* = 1, EtOH);[56] *N*-acetyl-(*S*)-phenylalanine methyl ester, $[\alpha]^{20}_D = 101.3°$ (*c* = 1, $CHCl_3$);[57] *N*-benzoyl-(*S*)-phenylalanine, $[\alpha]^{20}_D = -40.3°$ (*c* = 1, MeOH);[53] *N*-acetyl-3-(4-acetoxy-3-methoxyphenyl)-(*S*)-alanine, $[\alpha]^{20}_D = 40.7°$ (*c* = 1, MeOH);[58] (*S*)-methylsuccinic acid dimethyl ester, $[\alpha]^{20}_D = 6.75°$ (*c* = 6, EtOH);[59] *N*-acetyl-(*S*)-phenyl-1-propylamine, $[\alpha]^{20}_D = -137.8°$ (*c* = 2.4, MeOH);[60] (*R*)-1-phenylethyl-*N*-benzylamine, $[\alpha]^{20}_D = +56.2°$ (*c* = 1.07, EtOH);[61] (*S*)-1-phenylethanol, $[\alpha]^{20}_D = -52.5°$ (*c* = 2.27, CH_2Cl_2).[62]

Registry No. **1**, 72689-88-4; **2a**, 117897-88-8; **2b**, 117957-31-0; **2c**, 117957-32-1; **2d**, 102806-81-5; **3**, 77876-39-2; **4a**, 117897-89-9; **4b**, 117897-90-2; **4c**, 117897-91-3; **4d**, 117957-30-9; **5**, 64896-28-2; **6a**, 117897-92-4; **6b**, 117897-93-5; **6c**, 117897-94-6; **6d**, 102806-82-6; **6d**(oxide), 118013-34-6; **7**, 67884-32-6; **8a**, 117897-95-7; **8b**, 117897-96-8; **8c**, 117897-97-9; **8d**, 117897-87-7; **8d**(oxide), 117897-98-0; [**10**(P-P = **2d**)]$^+$, 117939-75-0; [**10**(P-P = **4d**)]$^+$, 117939-79-4; [**11**(P-P = **4d**)]BF_4, 117939-81-8; [**12**(P-P = **4d**)]$^+$, 117939-82-9; **13a**, 55065-02-6; **13b**, 60676-51-9; **13c**, 26348-47-0; **13d**, 55739-56-5; (*R*)-**14a**, 10172-89-1; (*S*)-**14a**, 2018-61-3; (*R*)-**14b**, 21156-62-7; (*S*)-**14b**, 3618-96-0; (*R*)-**14c**, 37002-52-1; (*S*)-**14c**, 2566-22-5; (*R*)-**14d**, 33043-31-1; (*S*)-**14d**, 31269-52-0; **15**, 617-52-7; **16**, 97305-96-9; **17**, 98-86-2; **18**, 14428-98-9; $[Rh(C_2H_4)_2Cl]_2$, 12122-73-5; $[Rh(COD)Cl]_2$, 12092-47-6; $[Rh(COD)_2]PF_6$, 62793-31-1; $[Rh(NBD)_2]BF_4$, 36620-11-8; $[Rh(C_2H_4)_2(\mathbf{2d})]^+$, 117939-73-8; [Rh(COD)(**2d**)]$^+$, 117939-74-9; [Rh(COD)(**2d**)](PF_6), 118015-57-9; [Rh(COD)(**4d**)]$^+$, 117939-76-1; [Rh(NBD)(**4d**)]BF_4, 117939-78-3; [Rh(COD)(**3d**)]$^+$, 117939-83-0; (*R*)-$CH_3CH(CO_2Me)CH_2CO_2CH_3$, 22644-27-5; (*S*)-$CH_3CH(CO_2Me)CH_2CO_2Me$, 63163-08-6; (*R*)-$PhCH(NHCCO)CH_3)CH_2CH_3$, 57680-92-9; (*S*)-$PhCH(NHCOCH_3)CH_2CH_3$, 20306-86-9; (*S*)-$PhCH(OH)CH_3$, 1445-91-6; (*R*)-$PhCH(CH_3)NHCH_2Ph$, 38235-77-7.

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Communications

Synthesis and Characterization of Binuclear Zirconocenophane Hydrides. The Molecular Structure of $[SiMe_2(C_5H_4)_2][(\eta^5\text{-}C_5H_5)ZrCl(\mu\text{-}H)]_2$

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Summary: The reactions of $[SiMe_2(C_5H_4)_2][(C_5H_5)ZrCl_2]_2$ and $[SiMe_2(C_5H_4)_2][(C_5H_5)ZrCl]_2(\mu\text{-}O)$ with stoichiometric amounts of $LiAl(O\text{-}t\text{-}Bu)_3H$ and $LiAlH_4$, respectively, in THF afford convenient routes for the preparation of the corresponding binuclear zirconocenophane hydrides $[SiMe_2(C_5H_4)_2][(C_5H_5)ZrCl(\mu\text{-}H)]_2$ (**1**) and $[SiMe_2(C_5H_4)_2][(C_5H_5)ZrH(\mu\text{-}H)]_2$ (**2**). The molecular structure of **2** has been established by X-ray diffraction. Preliminary results obtained from reactivity studies of **1** with C_2H_4 and ^{13}CO are described.

The bridged bis(cyclopentadienyl) ligand $[X(C_5R_4)_2]^{2-}$ [X = $(CH_2)_n$ (*n* = 1–3), $SiMe_2$; R = H, Me] has been employed as both a chelating[1] and a bridging[2] ligand in organometallic chemistry. An effort has been undertaken in our laboratories to prepare binuclear zirconocenophane

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