

Preliminary communication

SYNTHESIS AND APPLICATION OF RHODIUM COMPLEXES OF ASYMMETRIC WATER-SOLUBLE DIPHOSPHINE DERIVED FROM 2-[(DIPHENYLPHOSPHINO)METHYL]-4-(DIPHENYLPHOSPHINO)-PYRROLIDINE

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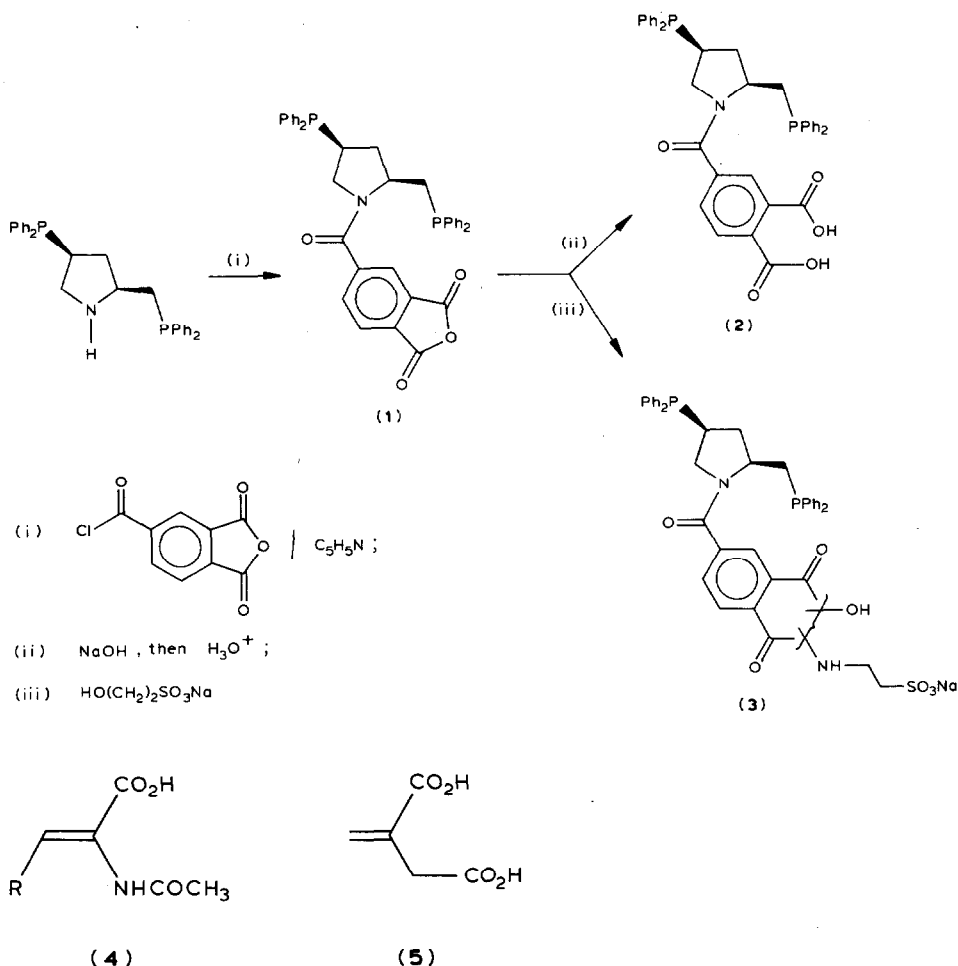
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Summary

Optical yields of up to 60% are obtained in the hydrogenation in water of prochiral compounds in the presence of rhodium complexes of asymmetric water-soluble diphosphines derived from 2-[(diphenylphosphino)methyl]-4-(diphenylphosphino)pyrrolidine.

Water solubilization of transition metal catalytic complexes has become an area of increasing interest. It is generally achieved via coordination of water soluble ligands [1]. The catalytic properties of complexes with sulfonated triphenylphosphine [2–4], derivatives of bis(2-diphenylphosphinoethyl)amine [5–7] or the [(2-diphenylphosphino)ethyl]trimethylammonium cation (AMPHOS) [8–11] have been studied in water and in two phase systems. Asymmetric water-soluble phosphines have recently been used in hydrogenation of prochiral substrates in water [12,13]. We describe below some preliminary results on the synthesis of asymmetric water-soluble diphosphines derived from 2-[(diphenylphosphino)methyl]-4-(diphenylphosphino)pyrrolidine (PPM) and their use in hydrogenation.

Acylation of PPM [14] with trimellitic anhydride acid chloride gives diphosphine 1 in high yield (80% after recrystallisation) ($[\alpha]_D^{20} -33^\circ$ ($c = 0.5$, CHCl_3); $\delta \text{P}(\text{CDCl}_3) -9.7$ and -24.1 ppm). Treatment of this diphosphine with sodium hydroxyde or sodium taurinate using Whiteside's procedure [7] gives the diphosphine 2 ($[\alpha]_D^{20} -28^\circ$ ($c = 0.5$, $\text{C}_2\text{H}_5\text{OH}$)) or 3 ($[\alpha]_D^{20} -6.4^\circ$ ($c = 0.5$, water)). The corresponding cationic rhodium complexes $[\text{Rh}(\text{COD})\text{-(ligand)}]^+ \text{ClO}_4^-$ (COD = cyclooctadiene) were prepared by known methods [15]. Phosphine 2 and its rhodium complex are soluble in an aqueous solution



(a: R = H; b: R = Ph)

of Na₂HPO₄ (0.1 M), and phosphine 3 and its rhodium complex are soluble in water alone.

Results of catalytic hydrogenation using 4 and 5 as prochiral substrates are summarized in Table 1. They show that reduction occurs in water with enantioselectivity as high as 34% for α -acetamido acrylic acid, 60% for α -acetamido cinnamic acid, and 59% for itaconic acid. These values are the highest yet obtained in enantioselective reduction in water and are only a little lower than those found in ethanol; this observation contrasts with those when 1,4-polyoxadiphosphines were used [12]. The rate of hydrogenation is lower in water than in ethanol. Surprisingly, α -acetamido cinnamic acid 4b is not reduced in ethanol or water using 3 as ligand even under 5 bars of hydrogen.

Studies are currently in progress on 1,2- and 1,4-analogues and their use in a two-phase system.

TABLE 1

ASYMMETRIC HYDROGENATION CATALYZED BY $[\text{Rh}(\text{COD})(\text{ligand})]^+ \text{ClO}_4^-$ ^a

Substrate	Ligand	Solvent	Optical yield (%)	Configuration	Time (h)
4a	1	EtOH	34	(R)	0.3
4a	2	EtOH	35	(R)	0.3
4a	2	H ₂ O/Na ₂ HPO ₄	31	(R)	5
4a	3	EtOH	57	(R)	0.2
4a	3	H ₂ O	34	(R)	0.3
4b	1	EtOH	87	(R)	0.2
4b	2	EtOH	82	(R)	1.5
4b	2	H ₂ O/Na ₂ HPO ₄	60	(R) ^b	24
4b	3	EtOH	No reduction		
4b	3	H ₂ O	No reduction		
5	1	EtOH	74	(S)	0.2
5	2	EtOH	58	(S)	0.2
5	2	H ₂ O/Na ₂ HPO ₄	16	(S)	24
5	3	EtOH	65	(S)	0.2
5	3	H ₂ O	59	(S)	24

^a $[\text{Rh}] = 1 \text{ mmol}$; $[\text{substrate}]/[\text{Rh}] = 100$; Temperature: 25°C ; $P(\text{H}_2) = 1 \text{ atm}$; chemical yield quantitative. ^b $P(\text{H}_2) = 5 \text{ atm}$.

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