Journal of Organometallic Chemistry, 288 (1985) C37—C39
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

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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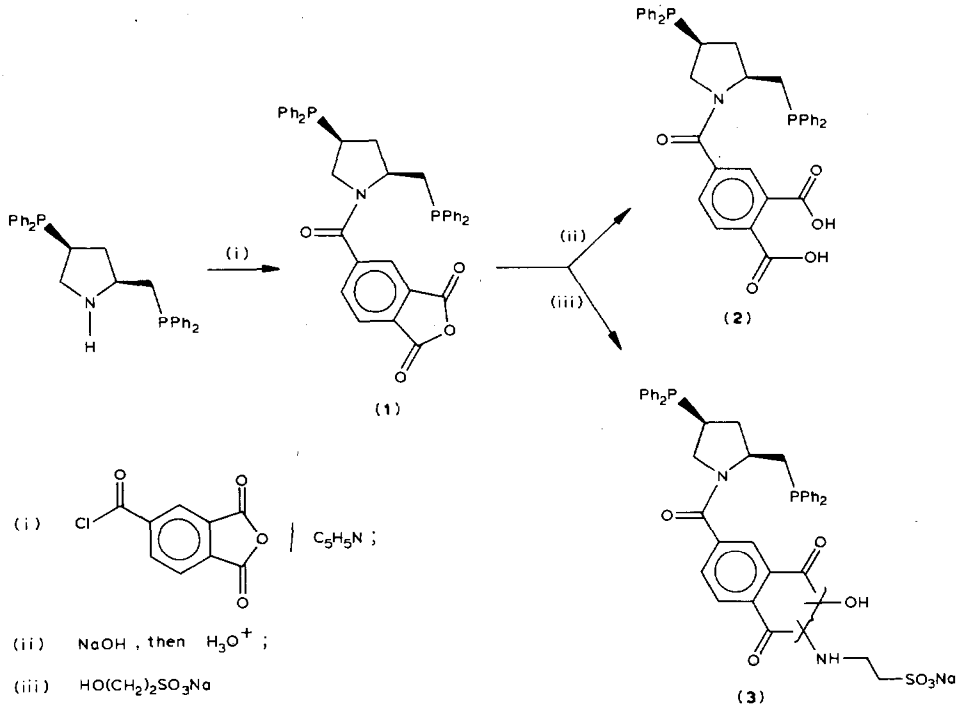
(Reçu le 25 février 1985)

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.

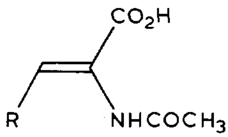
Acylation of PPM [14] with trimellitic anhydride acid chloride gives diphosphine 1 in high yield (80% after recrystallisation) ($[\alpha]_D^{20}$ −33° (c = 0.5, $CHCl_3$); δ P($CDCl_3$) −9.7 and −24.1 ppm). Treatment of this diphosphine with sodium hydroxyde or sodium taurinate using Whiteside's procedure [7] gives the diphosphine 2 ($[\alpha]_D^{20}$ −28° ($c = 0.5, C_2H_5OH$)) or 3 ($[\alpha]_D^{20}$ −6.4° (c = 0.5, water)). The corresponding cationic rhodium complexes [Rh(COD)-(ligand)]$^+$ ClO_4^- (COD = cyclooctadiene) were prepared by known methods [15]. Phosphine 2 and its rhodium complex are soluble in an aqueous solution



(i) | C_5H_5N ;

(ii) NaOH , then H_3O^+ ;

(iii) $HO(CH_2)_2SO_3Na$



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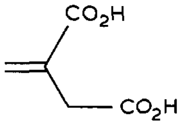

(5)

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

of Na_2HPO_4 (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 $[\mathrm{Rh(COD)}](\mathrm{ligand})]^+ \mathrm{ClO_4}^-$ [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_2O/Na_2HPO_4	31	*(R)*	5
4a	3	EtOH	57	*(R)*	0.2
4a	3	H_2O	34	*(R)*	0.3
4b	1	EtOH	87	*(R)*	0.2
4b	2	EtOH	82	*(R)*	1.5
4b	2	H_2O/Na_2HPO_4	60	*(R)* [b]	24
4b	3	EtOH	No reduction		
4b	3	H_2O	No reduction		
5	1	EtOH	74	*(S)*	0.2
5	2	EtOH	58	*(S)*	0.2
5	2	H_2O/Na_2HPO_4	16	*(S)*	24
5	3	EtOH	65	*(S)*	0.2
5	3	H_2O	59	*(S)*	24

[a] [Rh] = 1 mmol; [substrate]/[Rh] = 100; Temperature: 25°C; $P(H_2)$ 1 atm; chemical yield quantitative. [b] $P(H_2)$ 5 atm.

Acknowledgements. We are grateful to the C.N.R.S. for financial support (A.T.P. No. 8187; applications chimiques des complexes de coordination).

References

1 F. Joó and Z. Tóth, J. Mol. Catal., 8 (1980) 369.
2 Y. Dror and J. Manassen, J. Mol. Catal., 2 (1977) 219.
3 A.F. Borowski, D.J. Cole-Hamilton and G. Wilkinson, Nouv. J. Chim., 2 (1978) 137.
4 F. Joó, Z. Tóth and M.T. Beck, Inorg. Chim. Acta., 25 (1977) L61.
5 M.E. Wilson, R.G. Nuzzo and G.M. Whitesides, J. Am. Chem. Soc., 100 (1978) 2269.
6 R.G. Nuzzo, D. Feitler and G.M. Whitesides, J. Am. Chem. Soc., 101 (1979) 3683.
7 R.G. Nuzzo, S.L. Haynie, M.E. Wilson and G.M. Whitesides, J. Org. Chem., 46 (1981) 2861.
8 R.T. Smith and M.C. Baird, Trans. Met. Chem., 6 (1981) 197.
9 R.T. Smith and M.C. Baird; Inorg. Chim. Acta, 62 (1982) 135.
10 R.T. Smith, R.K. Ungar and M.C. Baird, Trans. Met. Chem., 7 (1982) 288.
11 R.T. Smith, R.K. Ungar, L.J. Sanderson and M.C. Baird, Organometallics, 2 (1983) 1138.
12 Y. Amrani and D. Sinou, J. Mol. Catal., 24 (1984) 231.
13 M.E. Wilson and G.M. Whitesides, J. Am. Chem. Soc., 100 (1978) 306.
14 a. I. Ojima, T. Kogure and N. Yoda, J. Org. Chem., 45 (1980) 4728.
b. G.L. Baker, S.J. Fritschel, J.R. Stille and J.K. Stille, J. Org. Chem., 46 (1981) 2954.
15 R.R. Schrock and J.A. Osborn, J. Am. Chem. Soc., 94 (1972) 6429.