Journal of Organometallic Chemistry, 239 (1982) 11—15
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

ON THE REUSE OF RHODIUM(I) BISPHOSPHINE COMPLEXES IN CATALYTIC HOMOGENEOUS HYDROGENATION OF 2-ACETAMIDOACRYLIC ACID *

AKIRA UEHARA and JOHN C. BAILAR, Jr.
School of Chemical Sciences, University of Illinois, Urbana, IL 61801 (U.S.A.)

(Received in India November 20th, 1981; in Amsterdam May 25th, 1982)

Summary

The cationic rhodium(I) complexes having the general formulas, [Rh(cod)-(p-p)]Cl and $[Rh(p\text{-}p)Cl]_2$, were prepared and investigated as homogeneous catalysts for the hydrogenation of 2-acetamidoacrylic acid: (cod is 1,5-cyclooctadiene and p-p is one of bisphosphines such as bis(1,2-diphenylphosphino)-ethane (diphos), 2,2'-bis(diphenylphosphino)biphenyl (bpbp) and (—)-2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ((—)-diop)). It was found that these catalysts can be used repeatedly in the above hydrogenations and that the chloride ion plays an important role in the repetitive utilization because these complexes are probably maintained as $[Rh(p\text{-}p)Cl]_2$ during and after the work-up procedures of the product.

Introduction

Rh^I-phosphine complexes are useful homogeneous catalysts for the hydrogenation of unsaturated organic compounds containing C=C [1,2], C=N [3] and C=O [4] bonds. The complexes containing chiral phosphines have recently been found to be useful as asymmetric hydrogenation catalysts [1,3,4]. Little information has, however, been reported on the possibilities of the repetitive utilization of these catalysts. Heterogeneous catalysts such as insoluble polymer-supported metal complexes can be employed repeatedly, but they are not as active as homogeneous catalysts [5,6]. Homogeneous catalysts are, in general, more active, but they are more difficult to recover. It is therefore worthwhile to learn something about homogeneous catalysts which are readily recovered from reaction mixtures and can be used repeatedly.

---

* Dedicated to Prof. R.C. Mehrotra on the occasion of his 60th birthday (February 16th, 1982).

0022-328X/82/0000—0000/$02.75

We recently found that the chloride of the Rh^I complexes having general formulas [Rh(cod)(p-p)]Cl and $[Rh(p\text{-}p)Cl]_2$, (cod is 1,5-cyclooctadiene and p-p is one of the biphosphines such as bis(1,2-diphenylphosphino)ethane (diphos), 2,2′-bis(diphenylphosphino)biphenyl (bpbp) and (—)-2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ((—)-diop)) can be used repeatedly as homogeneous catalysts for the reduction of 2-acetamidoacrylic acid to *N*-acetylalanine.

Experimental

Materials

Rhodium(III) chloride trihydrate ($RhCl_3 \cdot 3H_2O$), diphos, and (—)-diop were purchased from Strem Chemicals, Inc., and 2-acetamidoacrylic acid from Aldrich Chemical Co. bpbp was prepared as described previously [7]. Di-μ-chlorobis(1,5-cyclooctadiene)dirhodium(I) ($[Rh(cod)Cl]_2$) was prepared by a known procedure [8].

Preparation of optically inactive complexes

[Rh(cod)(diphos)]Cl. 493 mg (1 mmol) of $[Rh(cod)Cl]_2$ and 796 mg (2 mmol) of diphos were each separately suspended in 10 ml of acetone. The suspensions were mixed and stirred until no residue remained. After the resulting solution stood overnight, a yellow precipitate was obtained. This was collected by filtration, washed with ether, and air-dried. Yield 940 mg (73%). Recrystallization was carried out by dissolving the precipitate in CH_2Cl_2 and adding ether.

Found: C, 62.86; H, 5.31; P, 9.67; Cl, 5.37. Calcd. for $C_{34}H_{36}P_2ClRh$: C, 63.32; H, 5.62; P, 9.60; Cl, 5.50%.

$[Rh(diphos)Cl]_2$. Hydrogen was bubbled for one hour through a solution of 128 mg (0.2 mmol) of [Rh(cod)(diphos)]Cl in 10 ml of CH_2Cl_2. Evaporation of the solution gave a crude product, which was purified by precipitation by ether (4 ml) from CH_2Cl_2 (2—3 ml). Yield, 50 mg (43%).

Found: C, 57.70; H, 4.71; P, 11.74; Cl, 6.61. Calcd. for $C_{52}H_{48}P_4Cl_2Rh_2$: C, 58.18; H, 4.50; P, 11.54; Cl, 6.60%.

[Rh(cod)(bpbp)]Cl. This was prepared as reported previously [7].

$[Rh(bpbp)Cl]_2$. Hydrogen was bubbled through a solution of 153 mg (0.2 mmol) of [Rh(cod)(bpbp)]Cl in 5 ml of acetone and the solution was evaporated to dryness to give a brown, oily product. The oil was diluted with 2—3 ml of acetone, to which 4 ml ether was added dropwise to precipitate a brown product. Yield 30 mg (11%).

Found: C, 64.65; H, 4.40; P, 9.18; Cl, 5.15. Calcd. for $C_{72}H_{56}P_4Cl_2Rh_2$: C, 65.42; H, 4.27; P, 9.37; C, 5.36%.

Preparation of optically active complexes

(+)-[Rh(cod)(bpbp)]Cl. This was prepared as reported previously [7].

(+)-[Rh(cod)(—)-diop)]Cl. 493 mg (1 mmol) of $[Rh(cod)Cl]_2$ was suspended in 10 ml of acetone and 996 mg of (—)-diop was added. The orange-red solution was evaporated to dryness. The residue was dissolved in 5 ml of acetone, to

which 5 ml of ether was gradually added to precipitate a brown complex. Yield, 620 mg (83%). $[d]_D^{25} = 10.2°$ (in acetone).

Found: C, 62.69; H, 5.62; P, 8.34; Cl, 4.78. Calcd. for $C_{39}H_{44}O_2P_2ClRh$: C, 62.87; H, 5.95; P, 8.31; Cl, 4.76%.

(+)-[Rh((—)-diop)Cl]₂. Hydrogen was passed through a solution of 149 mg (0.2 mmol) of [Rh(cod)((—)-diop)]Cl in 5 ml of acetone for 1 h and the solution was evaporated to dryness. The brown product thus obtained was dissolved in 2—3 ml of acetone and 5 ml of ether was added to precipitate the pure complex. Yield 20 mg (16%). $[d]_D^{25} = +12.3°$ (in acetone).

Found: C, 57.96; H, 4.92; P, 9.65; Cl, 5.49. Calcd. for $C_{62}H_{64}O_4P_4Cl_2Rh_2$: C, 58.46; H, 5.06; P, 9.72; Cl, 5.56%.

Apparatus

The same apparatus was used as described earlier [7].

Hydrogenation and work-up

To 3—4 mmol samples of 2-acetamidoacrylic acid (AAA) a solution of each catalyst (0.05—0.1 mmol) in 5 ml of acetone was added (in the case of diphos catalyst, CH_2Cl_2 was used in place of acetone) and the mixture was hydrogenated [7]. The solutions were evaporated to dryness. The residues were dissolved in 10 ml of water and separated from the insoluble catalysts by filtration; the latter were washed with water (3 × 20 ml), dried over P_2O_5 and used again. The organic products were obtained by evaporation of the filtrate and were identified by their melting points, analytical data, IR spectra, PMR spectra and optical rotations [7].

Results and discussion

Derivation of [Rh(p-p)Cl]₂ from [Rh(cod)(p-p)]Cl

In the previous paper [7], we reported that only the chloride of the complexes [Rh(cod)(bpbp)]A (A = Cl, PF_6, $B(C_6H_5)_4$ or *d*-α-bromocamphor-π-sulfonate ion) can be reused as the homogeneous catalyst for the hydrogenation of 2-acetamidoacrylic acid, probably because the complex would be kept as the dimer [(bpbp)Rh(Cl)₂Rh(bpbp)] even during and after the work-up steps. This is also true for the diphos and (—)-diop complexes. Therefore, various attempts were made to obtain the complexes [Rh(p-p)Cl]₂ from the following reaction system, and their catalytic activities were evaluated.

$$[Rh(cod)(p\text{-}p)]Cl + 2\,H_2 \rightarrow 1/2\,[Rh(p\text{-}p)Cl]_2 + \text{cyclooctane}$$

Catalytic activities of diphos, bpbp and (—)-diop complexes

Table 1 summarizes typical results of catalytic hydrogenation of 2-acetamidoacrylic acid. New catalysts were used in the 1st run and the recovered catalysts were used in the 2nd run. The yields at atmospheric pressure were essentially zero for [Rh(cod)(diphos)]Cl and [Rh(diphos)Cl]₂ (exps. 1 and 4), but were in the order of 70 and 90% when 100 and 200 psi were applied (exps. 2, 3, 5 and 6). However, control experiments showed that about 5% and 38% of 2-acetamidoacrylic acid are hydrogenated at 100 psi for 120 min and 200 psi for 120

TABLE 1

RESULTS OF CATALYTIC HYDROGENATION OF 2-ACETAMIDOACRYLIC ACID

Exp.	Hydrogenation conditions			Products					
	Catalysts	Hydrogen		Chemical yield (%) [a]		$[\alpha]_D^{25}$ (°)		Optical yield (%) [c]	
		Press. (psi)	Time (min)	1st run [b]	2nd run [b]	1st run	2nd run	1st run	2nd run
	Optically inactive complexes								
1	$[Rh(cod)(diphos)]Cl$	Atm.	360	~0	~0				
2	$[Rh(cod)(diphos)]Cl$	100	120	75	74				
3	$[Rh(cod)(diphos)]Cl$	200	120	95	94				
4	$[Rh(diphos)Cl]_2$	Atm.	360	~0	~0				
5	$[Rh(diphos)Cl]_2$	100	120	73	73				
6	$[Rh(diphos)Cl]_2$	200	120	95	95				
7	$[Rh(cod)(bpbp)]Cl$	Atm.	300	97	96				
8	$[Rh(bpbp)Cl]_2$	Atm.	300	95	95				
	Optically active complexes								
9	$(+)$-$[Rh(cod)(bpbp)]Cl$	Atm.	300	95	95	7.6	7.2	11.4	10.8
10	$(+)$-$[Rh(cod)((-)$-$diop)]Cl$	Atm.	300	94	94	40.8	40.2	61.3	60.4
11	$(+)$-$[Rh((-)$-$diop)Cl]_2$	Atm.	300	95	95	41.2	40.6	61.9	61.0

[a] Chemical yield is the yield of the product. [b] New catalysts were used in the 1st run, and the catalysts recovered after work-up of the 1st runs were reused in the 2nd run. [c] Optical yields were calculated with respect to the value $[\alpha]_D = 66.5°$ for the optically pure *N*-acetyl-(*R*)-alanine [9].

min even with no catalyst. These results indicate that diphos complexes are not good catalysts for the hydrogenation of 2-acetamidoacrylic acid. On the other hand, bpbp and (—)-diop complexes afford yields of the order of 90% even at atmospheric pressure (exps. 7 through 11), suggesting that they are very active for hydrogenation. The comparison of the data for [Rh(cod)(p-p)]Cl and $[Rh(p\text{-}p)Cl]_2$ reveals that their catalytic abilities are almost the same. The chemical yields in the 1st runs and the 2nd runs are comparable in all cases, indicating that the reuse of the catalysts is quite possible. Optical yields are in the order of 60 and 11% for (—)-diop and bpbp complexes, respectively (exps. 9 through 11). Optical yields for the 2nd runs are almost the same as those for the 1st runs.

Acknowledgment

The work reported in this paper was done under ACS-PRF Grant #11390-AC1,3, for which the authors express their thanks.

References

1 H.B. Kagan and T.P. Dang, J. Amer. Chem. Soc., 94 (1972) 6429.
2 R.R. Schrock and J.A. Osborn, J. Amer. Chem. Soc., 98 (1976) 4450.
3 A. Levi, G. Modena and G. Scorrano, J. Chem. Soc. Chem. Commun., (1975) 6.
4 P. Bonvicini, A. Levi, G. Modena and G. Scorrano, J. Chem. Soc. Chem. Commun., (1972) 1188.
5 a) K. Ohkubo, K. Fujimori and K. Yoshinaga, Inorg. Nucl. Chem. Lett., 15 (1979) 231.
b) K. Ohkubo, M. Haga, K. Yoshinaga and Y. Motozato, Inorg. Nucl. Chem. Lett., 16 (1980) 155.
6 W. Dumont, J.C. Poulin, T.P. Dang and H.B. Kagan, J. Amer. Chem. Soc., 95 (1973) 8295.
7 A. Uehara and J.C. Bailar, Jr., J. Organometal. Chem., 239 (1982) 1.
8 J. Chatt and L.M. Venanzi, J. Chem. Soc., (1957) 4735.
9 S.M. Birnbaum, L. Levintow and R.B. Kingsley, J. Biol. Chem., 194 (1952) 455.
10 Recently [Rh(diphos)(mac)]BF_4 was isolated and the structure was determined (mac is methyl-α-acetamidocinnamic acid): see a) A.S.C. Chan, J.J. Pluth and J. Halpern, Inorg. Chim. Acta, 37 (1979) L477.
b) J. Halpern, D.P. Riley, A.S.C. Chan, and J.J. Pluth, J. Amer. Chem. Soc., 99 (1977) 8055.