Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Organometallic Chemistry 664 (2002) 1–4

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Communication

Polyether phosphine oxide induced phase separable homogeneous catalysis for hydroformylation of higher olefins

Liu Xiaozhong [a,b,*], Li Hongmei [b], Kong Fanzhi [a]

[a] Department of Organic Chemistry, Dalian University of Technology, Dalian 116012, People's Republic of China
[b] Department of Chemistry, Institute of Organic Chemistry, Peking University, Beijing 100871, People's Republic of China

Received 11 July 2002; received in revised form 24 September 2002; accepted 28 September 2002

Abstract

Triarylphosphine oxide bearing polyether group (PETAPO) gives high activity and allows easy separation of the catalyst for hydroformylation of 1-decene. PETAPO induces phase separable homogeneous catalysis for aqueous organic biphasic and non-aqueous hydroformylation reaction.

Keywords: Phosphine oxide; Hydroformylation; Catalyst separation

Phosphine oxides, proved to be weak coordinating ligands to metal center and long believed to be one of reasons for deactivation of hydroformylation catalysts, have received some special attention in hydroformylation and found their industrial application [1]. Triphenylphosphine oxide (TPPO) was employed industrially as ligand in Rh-catalyzed hydroformylation of higher olefins such as octenes and nonenes [1b,1c]. Triphenylphosphine (TPP) was added in need to stabilize rhodium before separation of products by distillation and oxidized to TPPO before reuse of the separated catalyst. Meanwhile TPPO presented higher activity in hydroformylation of octenes than TPP [1d]. Bidentate analogues of phosphine oxides such as P(O)–N, P(O)–O, P(O)–P, which containing two coordinating sites (O–N, O–O, O–P) to metal center, [1e,1f,1g] were also reported to be promoting ligands in rhodium catalyzed hydroformylation reactions.

An ever-increasing consideration in hydroformylation of higher olefins has been taken by using aqueous organic biphasic catalysis mainly in tackling with catalyst separation [2]. Water-soluble phosphines, mostly ionic phosphines have been believed to be an important factor in controlling selectivity, activity and catalyst separation. Recently introduction of polyether group to phosphines has become an available approach to prepare water-soluble ligands [2b,2c]. Polyether triarylphosphine analogues were successfully demonstrated for aqueous organic biphasic hydroformylation, selective hydrogenation and water gas shift reactions etc [2b,2c,2e].

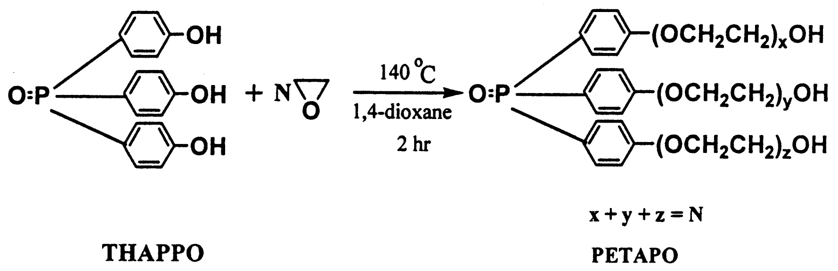
Herein for the first time we report a new triarylphosphine oxide bearing polyether moiety (polyether triarylphosphine oxide, PETAPO) for hydroformylation of 1-decene. PETAPO gave high activity for rhodium catalyzed aqueous organic biphasic hydroformylation of 1-decene and the separated aqueous solution containing catalyst was employed in several successive reactions without obvious loss in activity. Meanwhile in the absence of water, quantitative catalyst precipitated from reaction mixture on cooling to room temperature, which also provides another potential approach to catalyst separation.

PETAPO was prepared by ethoxylation reaction of tri-(*p*-hydroxyphenyl)phosphine oxide (THPPO) as follows [3,4].

---

* Corresponding author. Tel.: +86-10-6275-9643; fax: +86-10-6275-1708
E-mail address: xzchem@hotmail.com (L. Xiaozhong).

0022-328X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(02)01980-0



(1)

PETAPO turns to be yellow or brown viscous oil after removing solvent. *N* value was determined by area of H of glycol moiety to that of H of Ph group from its ^{1}H-NMR spectra. From ^{31}P-NMR spectra of PETAPO, it has a characteristic peak at 29.6 ppm. PETAPOs are presented to be water soluble when *N* over or equal to 7 and give increasing water solubility with longer polyether chain.

Table 1 collects catalytic experimental results of hydroformylation of 1-decene with rhodium catalyst formed in situ with ligand **L1**–**L3.** Entries 1–7 give good activity of PETAPO's rhodium complexes. The aqueous solution containing catalysts is easily separated by decantation, hence as entries 1–5 revealed, the separated aqueous solution is recycled four times without loss in activity. Table 1 also indicated about 0.6–3.1% of loaded rhodium and less than 1.0% phosphine loss in organic product phase in the first reaction run. From point of catalyst retentation, longer polyether moiety benefits rhodium and phosphine recovery, which is ascribed to higher water solubility of PETAPO with longer moiety.

In order to get some insight into where this reaction carries on, we took an analysis of PETAPO's ($\mathbf{L}_1$ $N = 22$ as a model) solubility in heptane at 25, 100 (reaction temperature) and 150 °C. Upon reaction conditions 1.8, 2.7 and 3.5 ppm of phosphines in heptane were detected at room temperature, 100 and 150 °C, respectively. That means that only 0.224% of loaded phosphine dissolves in heptane event at 150 °C. As a result, PETAPO turns to be another phase immiscible with heptane between room temperature and 150 °C. These results exclude role of Thermoregulated Phase-Transferred Catalysis in the above biphasic catalysis [2e,5]. Since molecules with polyether moiety has long considered as amphiphilic group and easily induces micelles or vesicles in its aqueous dispersion, [6] hence micellar catalysis is proposed for the above aqueous organic hydroformylation. In aqueous media, these polyether phosphine oxides form micelles or vesicles incorporating substrate and catalysts in it, inducing catalytic active microreactors in which reaction goes on. Further study about its formation of vesicles is in progress experimentally.

As described above, only a little PETAPO, e.g. 0.115% of $\mathbf{L}_1$, dissolves in heptane at room temperature, which means potential easy separation of the catalyst after reaction. Table 2 reveals catalytic results on non-aqueous hydroformylation of 1-decene with in situ formed Rh/PETAPO complexes as catalysts. Experimentally Rh/PETAPO precipitated quantitatively as viscous oil from reaction mixture at room temperature

Table 1
Aqueous–organic biphasic hydroformylation of 1-decene with PETAPO/Rh complexes as catalyst

Entry [a]	Ligand	Conv.(%)	Aldehyde yield (%)	*n*/iso	TOF [b] (h^{-1})	Rh loss [c](%/ppm)	P loss [c] (%/ppm)
1	$\mathbf{L}_1$, $N = 22$	92	90	32:68	225	2.5/6.5	0.22/3.4
2	2nd run	90	87	32:68	223	2.3/6.0	0.21/3.3
3	3rd run	91	88	33:67	231	1.5/3.9	0.19/3.0
4	4th run	89	87	32:68	232	1.3/3.4	0.17/2.7
5	5th run	89	86	33:67	233	1.1/2.8	0.13/2.0
6	$\mathbf{L}_2$ $N = 30$	95	93	32:68	225	0.8/2.1	0.10/1.6
7	$\mathbf{L}_3$ $N = 45$	96	93	32:68	230	0.6/1.6	0.08/1.3

[a] 10 mmol 1-decene, 0.10 mol% [Rh(acac)(CO)$_2$], 2.0 mol% ligand **L1**–$\mathbf{L}_4$, 4.0 ml solution (heptane + internal standard), 6.0 ml H_2O, 7.0 Mpa CO–H_2 (1:1), Temperature 100 °C, $t = 4$ h.

[b] Moles 1-decene converted to aldehydes per mole Rh per hour.

[c] Rhodium and phosphine loss to the organic product as percentage loaded Rh or P and ppm as corresponding concentration of Rh and P in the organic product.

Table 2
Non-aqueous hydroformylation of 1-decene with PETAPO/Rh complexes as catalyst

Entry [a]	Ligand	P/Rh (mol mol^{-1})	Conv.(%)	Aldehyde yield (%)	*n*/iso	TOF [b]	Rh loss [b] (%/ppm)	P loss [b] (%/ppm)
8	$\mathbf{L}_1$, $N = 20$	20	83	81	35:65	202	4.5/11.1	1.7/26.5
9	2nd run		81	78	32:68	204	3.0/7.83	1.6/25.0
10	3rd run		81	79	33:67	213	2.5/6.5	1.4/21.9
11	4th run		80	78	34:66	216	2.5/6.5	1.2/18.7
12	5th run		79	78	35:65	222	2.1/5.4	1.0/15.6
13	$\mathbf{L}_2$ $N = 30$	20	88	86	35:65	215	5.0/13	3.0/46.8
14	$\mathbf{L}_3$ $N = 45$	20	91	90	33:67	228	8.0/20.7	6.5/101.5
15	$\mathbf{L}_1$	40	76	74	34:66	185	2.1/5.4	3.1/48.4
16	$\mathbf{L}_1$	60	59	58	36:64	170	1.5/3.9	3.9/60.8

[a] 10 mmol 1-decene, 0.10 mol% [Rh(acac)(CO)$_2$], 4.0 ml solution (heptane + internal standard), 7.0 Mpa CO/H$_2$ (1:1), Temperature 100 °C, $t = 4$ h.

[b] Indicated the same as in Table 1.

and the catalyst could be employed in the successive reaction runs by decanting organic product phase (entries 8–12 in Table 2). About 4.5–8.0% of Rh and 1.7–6.5% of phosphine leached in organic product phase after the first reaction. From entry 8, 15 and 16, higher P/Rh ratio supports retentation of rhodium and phosphine from reaction mixture. This may be reasoned by that more PETAPO promote in stabilizing rhodium complex. Upon reaction conditions, PETAPO turns to be an mobile fluid immiscible with heptane at temperature over 40 °C and only 0.224% of $\mathbf{L}_1$ dissolves in heptane even at 150 °C. It is made sense that this reaction takes place in liquid phosphine phase in which, PETAPO acts as ligand and reactant medium as well. In comparison of Table 1 with Table 2, PETAPO give lower activity in non-aqueous system than that in aqueous organic biphasic system.

From the above results, the catalyst with the longer hydrophilic part shows the higher activity irrespective of the solvent. In aqueous organic biphasic system, phosphine with longer polyether moiety may easily induce micelles, improving mass transfer of substrates. This work is still in progress. Unexpectedly, we observed that PETAPO with longer polyether moiety has more solubility in heptane, toluene, and mixture of heptane and aldehydes, very different from popular polyether derivatives such as polyethylene glycol's and their corresponding alkyl ether which are less soluble in heptane with longer polyether moiety. Hence it is made sense that the catalyst with the longer polyether moiety showed the larger Rh loss during the non-aqueous hydroformylation (Table 2).

In conclusion, a novel water-soluble phosphine oxide PETAPO, first prepared by introduction of polyether group to triarylonosphine oxide, proves to be an efficient ligand for rhodium catalyzed hydroformylation of 1-decene. The catalyst appears to be phase separable from reaction mixture in aqueous organic system and non-aqueous system after reaction.

Acknowledgements

The research was partially supported by the National Nature Science Foundation of China. The authors thank Professor Dr Jin Zilin for his advice in catalysis and thanks are also given to Dr Li Ji for his ICP-AES analysis.

References

[1] (a) B. Cornils, J. Mol. Catal. A. 104 (1995) 17;
(b) T. Onoda, Chemtechnology 23 (9) (1993) 34;
(c) K. Sato, C. Miyazawa, K. Wada, T. Onoda, Nippon Kagaku Kaish 94 (1994) 681;
(d) D. He, D. Pang, T. Wang, Y. Chen, Y. Liu, J. Liu, Q. Zhu, J. Mol. Catal. A: Chem. 174 (2001) 21;
(e) C. Abu-Gnim, I. Amer, J. Chem. Soc. Chem. Commun. (1994) 115;
(f) C. Basoli, C. Botteghi, M.A. Cabras, G. Chelucci, M. Marchetti, J. Organomet. Chem. 488 (1995) C20;
(g) C. Abu-Gnim, I. Amer, J. Organomet. Chem. 516 (1996) 235.

[2] (a) B. Cornils, W.A. Herrmann (Eds.), Aqueous-phase Organometallic Catalysis Concepts and Applications, Wiley-VCH, Weinheim, 1998;
(b) W.A. Herrmann, C.W. Kohlpainter, Angew. Chem. Int. Ed. Engl. 32 (1993) 1524;
(c) X. Liu, Y. Wang, Q. Miao, Z. Jin, Chin. J. Org. Chem. 21 (2001) 191 (and references therein);
(d) S. Haber, H.J. Kleiner, US Patent 6160, 180, 2000;
(e) Z. Jin, X. Zheng, B. Fell, J. Mol. Catal. A: Chem. 116 (1997) 55.

[3] Tri-(*p*-hydroxyphenyl)phosphine oxide was prepared by Ref. [7].

[4] Preparation of PETAPO with $\mathbf{L}_2$ ($\mathbf{N = 22}$) as model: 2.92 g (90 mmol) THPPO, 0.016 g (1.8 mmol) anhydrous NaAc and 4.0 ml 1,4-dioxane were added to a 100 ml stainless autoclave. About 14 ml ethylene oxide was injected. The system was stirred for 2 h with magnetic stirrer at 140 °C in an oil bath. The product was obtained as brown viscous liquid after removing solvent. $N = 22$. FTIR (cm^{-1}) 3346, 3064, 2872, 1958, 1736, 1641, 1596, 1569, 1502, 1455, 1407, 1352, 1292, 1255, 1119, 950, 835. δ_H (300 MHz, solvent CDCl$_3$) 6.97–7.59 (m, 12H), 3.56–4.17 (m(br), 86H, C$_2$H$_4$O); δ_C (300 MHz, solvent CDCl$_3$) 161.54, 133.82, 133.67, 114.5, 114.7, 72.76, 72.66, 70.69, 70.67, 70.35, 70.32, 70.21, 70.15, 70.10, 69.96, 69.34, 67.44, 67.22, 61.33, 61.24, 61.12; δ_P (200 MHz, solvent CDCl$_3$, 85% H$_3$PO$_4$ as standard) 29.60 (s). MS-APCI [M+Na$^+$]:

745, 789, 833, 877, 921, 965, 1009, 1053, 1097, 1141, 1185, 1229, 1273, 1317, 1361, 1405, 1449, 1493, 1537, 1581, 1625, 1669.

[5] X. Liu, H. Li, Y. Wang, Z. Jin, J. Organomet. Chem. 654 (2002) 83.

[6] (a) G. Oehme, I. Grassert, S. Ziegler, R. Meisel, H. Fuhrmann, Catal. Today 42 (1998) 459;
(b) G. Oehme, I. Grassert, E. Paetzold, R. Meisel, K. Drexler, H. Fuhrmann, Coord. Chem. Rev. 185–186 (1999) 585 (and references therein);
(c) B.E. Hanson, Coord. Chem. Rev. 185–186 (1999) 795 (and references therein);
(d) G.M. Whitaker, K.L. Kott, R.J. McMahon, J. Org. Chem. 60 (1999) 3499.

[7] B.P. Friedrichsen, D.R. Powell, H.W. Whitlock, J. Am. Chem. Soc. 112 (1990) 8931.