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PEGPHOT: A New Well-Defined Molecular Weight Polyether-Substituted Triphenylphosphite and its Application in Biphasic Hydroformylation

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Abstract This work describes the synthesis and characterization of PEGPHOT (tri-(4-triethylenoglycol-monomethyletherphenyl)phosphite) and its use in the rhodium-catalyzed hydroformylation of different olefins. In the hydroformylation of 1-hexene, it was possible to carry out 10 recycles of the catalytic system without significant loss in activity.

Keywords Biphasic catalytic system · Hydroformylation · Rhodium · PEO · PEG

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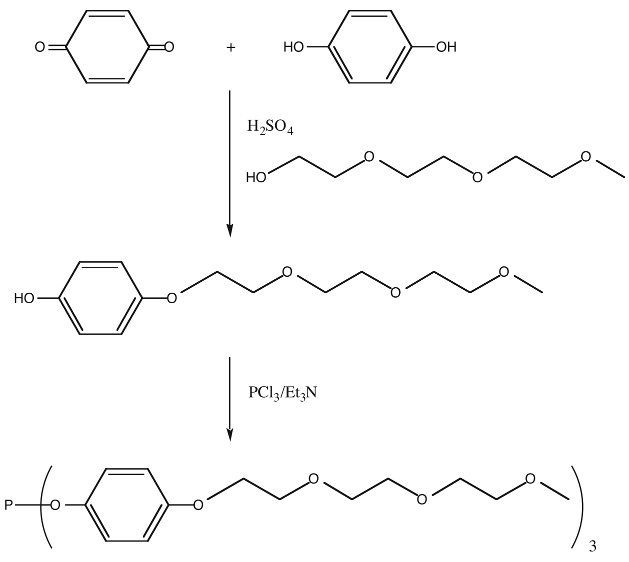
1 Introduction

Hydroformylation is an important and clean process to produce aldehydes, which are important intermediates in the chemical industry [1]. A major drawback of this reaction is the catalyst recovery. The most successful strategy to overcome this problem is the use of liquid–liquid biphasic systems [2–8]. An example of these systems is the combination of a nonpolar organic phase and a high polarity solvent like poly(ethylene-oxide) (PEG) [9, 10]. This polymer has shown good performance in segregating some metal catalysts from low polarity products, allowing recovery and recycling of the metal complex. Many examples of PEG-based biphasic systems using Rh, Ru and Pd catalysts have been recently reported [11–18]. As in other liquid–liquid biphasic systems, the recovery efficiency of the catalyst depends on the difference between the polarity of the products and the catalyst. These polarity requirements could be a problem when the products of a particular reaction show a medium to high polarity, like aldehydes produced in the oxo process. To circumvent this problem, we herein present the synthesis of tri-(4-triethylenoglycolmonomethyletherphenyl)phosphite (PEGPHOT). To the best of our knowledge, this ligand is the first ever described bearing PEG tails with a well-defined molecular weight.

The phosphite PEGPHOT was synthesized in a purity higher than 98% in two steps according to Scheme 1.

To evaluate the ligand as a modifier for the rhodium-based catalytic system, we performed the hydroformylation of 1-hexene (model substrate), 1-decene, styrene and methyl oleate using PEG-400 as a solvent, which is liquid at room temperature.



Scheme 1 Synthesis of PEGPHOT

2 Experimental

2.1 General

All operations were performed under an argon atmosphere using standard Schlenk flask techniques. Solvents were dried and distilled before use. The gases H_2 (AGA, 99.999%) and CO (Air Products, 99%) were used without purification.

Gas chromatography–mass spectrometry experiments were carried out with a G1800A Hewlett Packard gas chromatograph and the ionization mode was electron impact. Separations were accomplished on an HP-5 capillary column (30 m × 0.25 mm × 0.25 µm). ^{31}P, ^{1}H and ^{13}C NMR spectra were obtained with a Bruker Avance-250 instrument (s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet). Chemical shifts of the ^{1}H and ^{13}C NMR spectra are reported in ppm (δ) relative to tetramethylsilane (TMS) using $CDCl_3$ as an internal reference. The ^{31}P NMR spectra were recorded with 85% H_3PO_4 as an external reference.

The conversion and selectivity of the hydroformylation reactions were determined using a gas chromatographic technique on a Shimadzu 17A GC system equipped with a DB-5 column (30 m × 0.25 mm × 0.25 µm) and FID detector. Helium was the carrier gas. For methyl oleate, these parameters were determined by ^{1}H NMR, as described below.

2.2 General Procedure for the Preparation of 4-triethyleneglycolmonomethyletherphenol (HPEG)

The precursor 4-triethyleneglycolmonomethyletherphenol (HPEG) was prepared according to a modified published procedure [19]. Under argon, a mixture of 3.00 g (27.3 mmol) of the hydroquinone, 0.31 g (2.85 mmol) of the quinone, 4.47 g (27.3 mmol) of triethyleneglycolmonomethylether and 0.33 mL of concentrated H_2SO_4 was prepared. The mixture was vigorously stirred at 80 °C for 24 h. After this time, the sample was dissolved in dichloromethane and washed with water. The organic phase was then dried with $MgSO_4$ and the solvent was removed. The viscous dark residue was purified by distillation under reduced pressure (230 °C, 1 mmHg) to give a 60% yield of a 98% purity product. The intermediate was characterized as follows:

^{1}H NMR ($CDCl_3$, 250 MHz): 7.06 (s, 1H), 6.78–6.65 (m, 4H), 3.97 (t, 2H), 3.77 (t, 2H), 3.59–3.73 (m, 6H), 3.53 (t, 2H), 3.34 (s, 3H).

^{13}C NMR ($CDCl_3$, 63 MHz): 152.2, 150.4, 116.0, 115.6, 71.7, 70.5, 70.4, 69.8, 67.9, 58.8.

MS [m/z (relative intensity)]: 256 (M^+, 16%); 147 (14%); 110 (37%); 103 (19%); 59 (100%); 45 (11%); 29 (9%).

2.3 Ligand Synthesis

The phosphite PEGPHOT was prepared according to the following procedure: 4.68 g of 4-triethyleneglycolmonomethyletherphenol (18.3 mmol), previously dried twice by azeotropic distillation with toluene, and 2.55 mL of triethylamine (18.3 mmol) were dissolved in 20 mL of dry THF. The solution was cooled by means of an ice bath and a solution of 0.92 g (6.7 mmol) of PCl_3 in 20 mL of THF was added dropwise over 30 min. The ice bath was removed and the mixture was stirred overnight and then refluxed for 2 h. The resulting mixture was filtered from the ammonium salt through a small silica column (dried at 130 °C overnight) and the solvent was evaporated under vacuum to furnish PEGPHOT as a clear oil in 80% yield. The final ligand was characterized as follows:

^{1}H NMR ($CDCl_3$, 250 MHz): 7.00 (d, 6H), 6.86 (d, 6H), 4.07 (t, 6H), 3.81 (t, 6H), 3.59–3.75 (m, 18H), 3.49-3.56 (m, 6H), 3.35 (s, 9H).

^{13}C NMR ($CDCl_3$, 63 MHz): 155.1, 144.8, 121.4, 115.2, 71.6, 70.5, 70.3, 69.4, 67.6, 58.7.

^{31}P NMR {^{1}H} ($CDCl_3$, 101.3 MHz): 129.2.

ESI$^+$: 796.34; calculated 796.84 (along with this signal, another peak at 819.3 due to the sodium adduct was observed).

2.4 Hydroformylation and Recycling of the Catalytic System

Under an argon atmosphere, a mixture of $RhCl_3.3H_2O$ (1.92×10^{-2} mmol), PEG-400 (4 g) and PEGPHOT (0.192 mmol) was stirred at room temperature. After

30 min, 1-hexene (2.4 mL, 19.2 mmol) was added and the resulting mixture was transferred to an argon purged stainless steel mini-reactor (100 mL) by a cannula without additional solvent and under an argon atmosphere. The reactions were carried with magnetic stirring. The reactor was sealed, purged three times with H_2 and pressurized with H_2 and CO as described below (Tables 1, 2, 3). The reactor was heated by means of an oil bath and the temperature was monitored with an adapted thermocouple. The catalytic reactions were cooled to room temperature and the reactor was vented. Next, the homogeneous reaction mixture was transferred by cannula to a Schlenk tube under argon. The unconverted substrate and products were quantitatively (within experimental GC error) extracted with vigorous magnetic stirring using 3 × 3 mL of dry *n*-heptane. The extracts were analyzed by GC. For recycling experiments, the polar phase containing the catalytic system was dried under vacuum and transferred back to the reactor, and then fresh alkene was added. For methyl oleate, the procedure was similar, but the analysis was made by ^{1}H NMR and APT on a small sample; the remaining sample was passed through silica-gel (using dichloromethane as an eluent), dried under vacuum and stocked.

3 Results and Discussion

The starting operational conditions were based on the literature [20–28]: 100 °C, 40 bar, 5 h, L/Rh = 10, substrate/Rh = 1000 and CO/H_2 = 1. We observed excellent conversions from the 1st to the 7th cycles. However, despite the high yields in total aldehydes, the system showed different product distributions along the recycles (Table 1). This was likely due to some thermal decomposition of either the solvent (PEG) or ligand, which was reinforced by the presence of the catalyst's color in the *n*-heptane phase after some recycles.

To overcome the thermal decomposition problems described above, the reaction temperature was lowered to 80 °C. Table 2 shows that at this temperature, the catalytic activity and selectivity were retained after a greater number of recycles, which implied an increase in the TON.

Using this modification, we were able to perform four recycles (five reactions) while maintaining the same aldehyde linearity ratio (> 72%), and no loss in conversion or total aldehyde selectivity was observed (Fig. 1). We also noticed that by lowering the temperature, the catalyst leaching (observed during the extraction procedure for reactions performed at 100 °C) was no longer visible, as observed previously [11]. The formation of branched aldehydes should come from the tandem isomerization-hydroformylation process, which was considerable, especially after the 4th recycle. This behavior should be related to phosphite inactivation during each recycle workup due to some PEG's residual water. Indeed, the oxidation of both phosphines and phosphites by water under similar reaction conditions has been already demonstrated [29]. Also, the aldehydes generated as products could react with phosphites modifying their coordination behavior [30, 31].

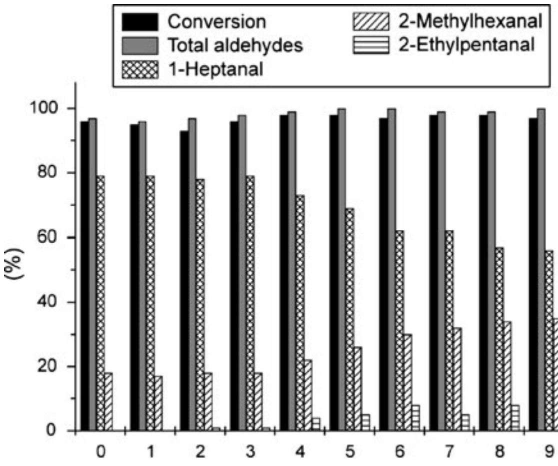


Fig. 1 Product distribution along the recycles for the hydroformylation of 1-hexene under the reaction conditions in Table 2

Table 1 Preliminary results of the hydroformylation of 1-hexene using PEGPHOT and the biphasic system PEG-400/*n*-heptane

Number of recycles	C (%)[a]	Isomers (%)[a, b]	Hexane (%)[a]	1-Heptanal (%)[a]	2-MH (%)[a]	2-EP (%)[a]	TON
0	96	0	1	72	22	5	960
1	96	0	1	68	25	6	960
2	98	0	1	60	29	10	980
3	100	0	2	53	34	11	1000
4	100	0	1	52	36	11	1000
5	98	0	0	52	37	11	980
6	98	0	0	51	37	12	980
7	80	0	5	51	35	9	800

Reaction conditions $RhCl_3.3H_2O$ (0.01923 mmol); substrate/Rh = 1000; ligand/Rh = 10; PEG-400 (4 g); 100 °C; 5 h; 40 bar (CO/H_2 = 1:1);
[a] *C* Conversion, *2-MH* 2-methylhexanal, *2-EP* 2-ethylpentanal, data calculated by GC; [b] 2-hexene and 3-hexene. See text for recycling details

Table 2 Hydroformylation of 1-hexene with $RhCl_3.3H_2O$/PEGPHOT using the biphasic system PEG-400/alkene

Number of recycles	C (%)[a]	Isomers (%)[a, b]	Hexane (%)[a]	1-Heptanal (%)[a]	2-MH (%)[a]	2-EP (%)[a]	TON
0	97	3	4	76	17	0	960
1	96	3	5	76	16	0	950
2	96	3	3	76	17	1	930
3	98	2	4	75	17	1	960
4	98	1	2	72	21	4	980
5	98	0	0	69	26	5	980
6	97	1	2	62	30	6	970
7	98	1	2	61	31	5	980
8	98	1	2	56	33	8	980
9	97	1	1	56	35	7	970
10	97	1	2	56	35	6	970

Reaction conditions $RhCl_3.3H_2O$ (0.01923 mmol); substrate/Rh = 1000; ligand/Rh = 10; PEG-400 (4 g); 80 °C; 5 h; 40 bar (CO/H_2 = 1:1); [a] *C* Conversion, *2-MH* 2-methylhexanal, *2-EP* 2-ethylpentanal, data calculated by GC; [b] 2-hexene and 3-hexene. See text for recycling details

Table 3 Hydroformylation of different olefins with $RhCl_3.3H_2O$/PEGPHOT using the biphasic system PEG-400/alkene

Olefin	Conversion (%)	Aldehydes (%)	Isomers (%)	Hydrogenation (%)	*n*/*iso*
1-Hexene	97	93	3[a]	4	4.4
1-Decene	90	86	10[a]	4	5.0
Styrene	85	82	–	18	0.2
Methyl oleate[b]	92[c]	50[c]	ND	50[c]	ND

Reaction conditions $RhCl_3.3H_2O$ (0.01923 mmol); substrate/Rh = 1000; ligand/Rh = 10; PEG-400 (4 g); 80 °C; 5 h; 40 bar; CO/H_2 = 1:1. Product distribution calculated by GC, except when indicated; [a] 2-hexene and 3-hexene or 2-decene and 3-decene, respectively; [b] Reaction performed using the following conditions: 100 °C; ligand/Rh = 10. Double bonds/Rh = 745; 40 bar; CO/H_2 = 2:1; 5 h; [c] Calculated by ^1H NMR, see text

Table 3 shows the versatility of the present system for different kinds of olefins. $RhCl_3.3H_2O$/PEGPHOT was an excellent catalyst for the hydroformylation of 1-hexene, but also 1-decene, styrene and methyl oleate in PEG-400. For 1-decene, the only hydroformylation products observed were 1-undecanal and 2-methydecanal, aside from 2-decene and 3-decene, which were formed by substrate isomerization. For styrene, some hydrogenation was observed and a typical *n*/*iso* ratio of the aldehydes was achieved with this substrate.

Methyl oleate was hydroformylated under the optimized reaction conditions previously described [32]. In this case, even in the presence of an excess of CO, a significant amount of the hydrogenation product was observed. Furthermore, because the conversion was measured by ^1H NMR [32], it was not possible to quantify the amount of 9- and 10-formylestearate or other aldehydes formed from previously isomerized substrate. Although the catalytic system $RhCl_3.3H_2O$/PEGPHOT proved to be very efficient for the hydroformylation of terminal olefins, it needs to be optimized for internal ones. It is important to emphasize that the reactions conditions are very mild compared to most of the previously published reports on related catalytic systems [15, 20–28].

4 Conclusions

In summary, PEGPHOT is a well-defined phosphite ligand that can be easily prepared from readily accessible reagents. Its use with an Rh-based catalyst in liquid PEG-400 media for the biphasic hydroformylation of alkenes has been demonstrated. Further work to investigate the evolution of the catalytic species in the recycling experiment, as well as to extend this strategy to other phosphorus ligands and reactions are in progress.

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References

1. Frohning CD, Kohlpaintner CW, Gauß M, Seidel A, Torrence P, Heymanns P, Höhn A, Beller M, Knifton JF, Klausener A, Jentsch J-D, Tafesh AM (2008) In: Cornils B, Herrmann WA. Applied homogeneous catalysis with organometallic compounds,

chap. 2.1, A comprehensive handbook in two volumes, vol. I, Wiley-VCH, Weinheim
2. Kuntz, EG (1987) ChemTech, 17:570
3. Brasse, CC, Salzer, A, Bahrmann, H WO 99/16737
4. Brasse, CC, Salzer, A WO 99/16776
5. Behr A, Henze G, Schomäcker R (2006) Adv Synth Catal 348:1485
6. Riisager A, Fehrmann R, Haumann M, Wasserscheid P (2006) Eur J Inorg Chem 4:695
7. Yoshida A, Hao X, Yamazaki O, Nishikido J (2006) Molecules 11:627
8. Pollet P, Hart RJ, Eckert CA, Liotta CL (2010) Acc Chem Res 43:1237
9. da Silva LHM, Loh W (1998) Chem Commun 7:787
10. Ji ZJ, Jiang JY, Wang YH (2010) Chinese Chem Lett 21:515
11. da Rosa RG, Martinelli L, da Silva LHM, Loh W (2000) Chem Commun 1:33
12. Heldebrant DJ, Jessop PG (2003) J Am Chem Soc 125:5600
13. Nobre SM, Wolke SI, da Rosa RG, Monteiro AL (2004) Tetrahedron Lett 45:6527
14. Corma A, García H, Leyva A (2005) Tetrahedron 61:9848
15. Feng C, Wang Y, Jiang J, Yang Y, Yu F, Jin Z (2006) J Mol Catal A: Chem 248:159
16. Tavares A, Wolke SI, da Rosa RG (2008) J Catal 254:374
17. Lu YD, Wang YH, Jin ZL (2010) Chinese Chem Lett 21:1067
18. Terashima T, Ouchi M, Ando T, Sawamoto M (2010) J Polym Sci Part A: Polym Chem 48:373
19. Bellas M, Cahill R, Hayes L (1979) Brit Patent 1557237
20. Zheng X, Jiang J, Liu X, Jin Z (1998) Catal Today 44:175
21. Jiang J, Wang Y, Liu C, Han F, Jin Z (1999) J Mol Catal A: Chem 147:131
22. Chen R, Jiang J, Wang Y, Jin Z (1999) J Mol Catal A: Chem 149:113
23. Liu C, Jiang J, Wang Y, Cheng F, Jin Z (2003) J Mol Catal A: Chem 198:23
24. Liu X, Kong F, Zheng X, Jin Z (2003) Catal Commun 4:129
25. Breuzard JAJ, Tommasino L, Bonnet MC, Lemaire M (2000) J Organomet Chem 616:37
26. Karakhanov EA, Kardasheva YS, Runova EA, Semernina VA (1999) J Mol Catal A: Chem 142:339
27. Borrmann T, Roesky HW, Ritter U (2000) J Mol Catal A: Chem 153:31
28. Jin Z, Zheng X, Fell B (1997) J Mol Catal A: Chem 116:55
29. da Rosa RG, de Campos JDR, Buffon R (2000) J Mol Catal A: Chem 153:19
30. Ginsburg VA, Yakubovitch AY (1960) Zh Obshch Khim 30:3979
31. Abramov VS (1954) Dokl Akad Nauk SSSR 95:991
32. Mendes ANF, Gregório JR, da Rosa RG (2005) J Braz Chem Soc 16:1124