APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 335–337
Materials, Nanoscience and Catalysis
Published online 27 March 2006 in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.1057

A new rhodium complex with a nitrogen-containing bis(phosphine oxide) ligand as an efficient catalyst for the hydroformylation of styrene

Evangelos I. Tolis, Kalliopi A. Vallianatou, Fotini J. Andreadaki and Ioannis D. Kostas*

National Hellenic Research Foundation, Institute of Organic and Pharmaceutical Chemistry, Vas. Constantinou 48, 116 35 Athens, Greece

Received 5 December 2005; Accepted 3 February 2006

A new rhodium complex with a nitrogen-containing bis(phosphine oxide) ligand has been synthesized. The complex was applied to hydroformylation of styrene and displayed high activity and regioselectivity towards the branched aldehyde, which was found to be higher than those of the tertiary bis(phosphine) analogue. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: amino phosphine oxide; bis(phosphine oxide); hemilabile ligand; rhodium complex; hydroformylation; homogeneous catalysis

INTRODUCTION

Hydroformylation is one of the most extensively studied homogeneous catalytic reactions with enormous industrial interest, and thus the development of new catalysts which provide high activity and selectivity remains a challenge of high importance.[1,2] Ligands with mixed donors of different coordination abilities, so-called hemilabile ligands, such as phosphines containing nitrogen, oxygen or sulfur, have received much attention due to the improved catalytic activity of their transition-metal complexes.[3–5] It has also been reported that mixed amino phosphine oxide ligands display high reactivity and regioselectivity in the hydroformylation of aryl alkenes to branched aldehydes as compared with the phosphine analogs.[6–8]

In recent years, we have engaged in preparing ligands with phosphorus and nitrogen, oxygen or sulfur donors, which were found to lead to improved systems for homogeneous catalysis.[9–16] In one of these papers, a rhodium complex with the nitrogen-containing bis(phosphine) ligand **1** was successfully applied in the hydroformylation of styrene.[11] In the present work, we report a new rhodium complex with the nitrogen-containing bis(phosphine oxide) ligand **2**, easily prepared from **1**, and its application to the hydroformylation of styrene.

*Correspondence to: Ioannis D. Kostas, National Hellenic Research Foundation, Institute of Organic and Pharmaceutical Chemistry, Vas. Constantinou 48, 116 35 Athens, Greece.
E-mail: ikostas@eie.gr
Contract/grant sponsor: General Secretariat of Research and Technology of Greece.

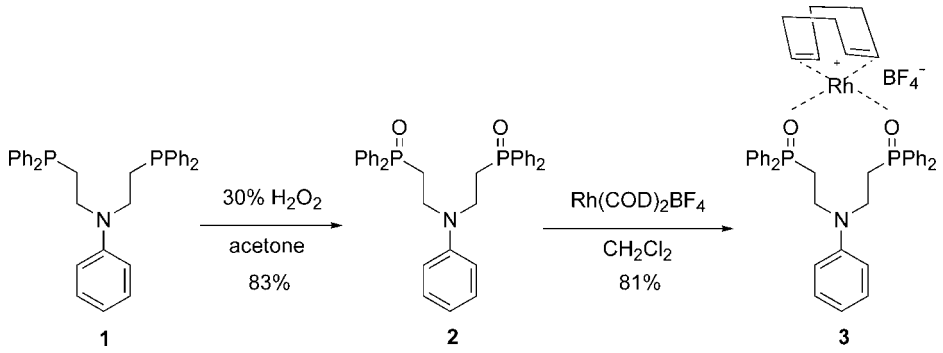
RESULTS AND DISCUSSION

Synthesis of the ligand and the rhodium complex

Oxidation of bis(phosphine) **1** by hydrogen peroxide resulted the bis(phosphine oxide) ligand **2** in an 83% yield (Scheme 1). The presence of only one singlet at δ 30.02 in the ^{31}P NMR spectrum of the ligand clearly indicates the equivalence of the two phosphorus atoms. Treatment of $[Rh(COD)_2]BF_4$ in dichloromethane solution with one equivalent of ligand **2** yielded the cationic rhodium complex **3**. The ^{31}P NMR spectrum of **3** shows a singlet at δ 41.16; this resonance is shifted 11 ppm to low field compared with the corresponding resonance in the free ligand, indicative of electron donation from the P=O group to Rh. No coupling was observed between Rh and P═O, showing that $^2J_{Rh,P}$ is very small. The ^{13}C NMR spectrum of **3** shows two singlets for the CH_2NCH_2 carbons and two doublets (due to P–C coupling) for the two CH_2P carbons, indicating the non-equivalence of the $CH_2CH_2NCH_2CH_2$ carbons. The singlets for the CH_2NCH_2 carbons (δ 44.87 and 44.39) are almost in the same position as that of the free ligand (δ 44.07), indicating the absence of Rh–N coordination.

Hydroformylation

The catalytic activity of the rhodium complex **3** was tested on the hydroformylation of styrene, under variable conditions of pressure and temperature (Scheme 2, Table 1). The catalyst displays a high chemoselectivity to aldehydes (over 99%), a high activity, and a high regioselectivity (up to 97%) towards the branched aldehyde. The variation

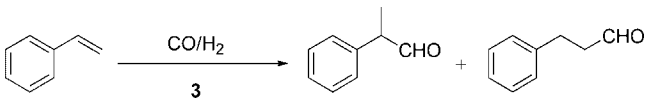


Scheme 1. Synthesis of rhodium complex with a nitrogen-containing bis(phosphine oxide) ligand

Table 1. Hydroformylation of styrene catalyzed by rhodium complex **3**[a]

Entry	*P* (bar)	*T* (°C)	Time (h)	Conversion (%)[b]	R_c (%)[b]	R_{br} (%)[b]	TON[c]
1	100	30	22	98.3	99.6	96.9 (96.0)[d]	1425 (1236)[d]
2	100	40	4	79.6	99.0	96.5 (95.0)[d]	1147 (1107)[d]
3	100	60	1	93.0	99.3	88.3 (87.0)[d]	1344 (1415)[d]
4	30	40	68	99.7	99.5	88.3 (87.9)[d]	1443 (1429)[d]
5	20	40	72	91.4	99.5	85.9 (87.0)[d]	1323 (715)[d]

[a] Reactions were carried out using a 4 mM solution of **3** in CH_2Cl_2. Styrene : **3** = 1455 : 1.
[b] Conversions, chemoselectivities towards aldehydes (R_c) and regioselectivities towards the branched aldehyde (R_{br}) were determined by GC.
[c] Turnover no. (TON) = aldehydes fraction × substrate/catalyst ratio.
[d] Rhodium complex [Rh(**1**)(COD)]BF_4 was used as catalyst.[11]



Scheme 2. Hydroformylation of styrene

observed in this work in the conversions of styrene and the regioselectivities in the resulting branched aldehyde, under variable conditions of pressure and temperature, was as expected for hydroformylation of styrene using rhodium systems. In most experiments, complex **3** displays a higher activity and regioselectivity compared with the tertiary bis(phosphine) **2**,[11] and this observation is in accordance with the results obtained by other authors for phosphine oxide ligands compared with the phosphine analogs.[6–8]

EXPERIMENTAL

General

N,N-Bis[2-(diphenylphosphino)ethyl]-benzenamine (**1**) was prepared as described previously.[11] Complex [$Rh(COD)_2$]BF_4 was prepared from rhodium trichloride according to a literature procedure.[17–19] Hydroformylation using syngas ($CO–H_2$, 1 : 1) was performed in a stainless steel autoclave (300 ml) with magnetic stirring. The NMR measurements were made using a Bruker AC 300 (300.13, 75.47 and 121.50 MHz for ^1H, ^{13}C and ^{31}P, respectively); ^1H and ^{13}C NMR shifts were referenced to the solvent and the ^{31}P NMR shifts were referenced to external 85% H_3PO_4 in H_2O. Distinction of the CH, CH_2 and CH_3 carbons in the ^{13}C-NMR spectra was performed by DEPT-NMR experiments. Gas chromatography was undertaken using a Varian Star 3400 CX with a 30 m × 0.53 mm DB5 column. Electron impact gas chromatography–mass spectrometry was carried out using a Varian Saturn 2000 with a 30 m × 0.25 mm DB5-MS column.

Syntheses

*N,N-Bis[2-(diphenylphosphinyl)ethyl]-benzenamine (**2**)*

To a solution of **1** (2.00 g, 3.87 mmol) in acetone (45 ml), 30% H_2O_2 (0.9 ml, 8.81 mmol) was added dropwise and the mixture was refluxed for 1 h. The solvents were then removed by evaporation, and by addition of a mixture CH_3CN–ether, product **2** (1.76 g, 3.21 mmol, 83%) was isolated as a white solid; m.p. 181–182 °C. ^1H NMR ($CDCl_3$): δ 7.72–7.66 (m, 8H, Ar); 7.53–7.44 (m, 12H, Ar); 7.13 (t, J = 7.4 Hz, 2H, Ar); 6.69 (t, J = 6.7 Hz, 1H, Ar); 6.46 (d, J = 7.4 Hz, 2H, Ar); 3.58–3.50 (m, 4H, CH_2); 2.52–2.47 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 145.91–113.30 (Ar); 44.07 (s, CH_2N); 27.33 (d, $J_{P,C}$ = 65.9 Hz, CH_2P). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.02 (s).

*Rhodium(1+)-[(1,2,5,6-η)-1,5-cyclooctadiene]-[N,N-Bis[2-(diphenylphosphinyl)ethyl]-benzenamine]-tetrafluoroborate(1-) (**3**)*

A solution of the ligand **2** (0.15 g, 0.27 mmol) in dichloromethane (10 ml) was added dropwise to the dark red solution of $[Rh(COD)_2]BF_4$ (0.11 g, 0.27 mmol) in dichloromethane (5 ml) using a dry ice–acetone cooling bath. The reaction mixture was warmed slowly to room temperature within 2 h and stirred at this temperature overnight. The resulting orange solution was evaporated under reduced pressure to ca. 0.5 ml, and addition of ether (20 ml) caused the precipitation of an orange solid. The supernatant solution was decanted, the solid was washed with ether (3 × 10 ml) and dried by vacuum, yielding rhodium complex **3** (0.19 g, 0.22 mmol, 81%). ^{1}H NMR (CD_2Cl_2): δ 7.82–7.53 (m, 20H, Ar); 7.19 (t, $J = 7.9$ Hz, 2H, Ar); 6.76 (t, $J = 7.3$ Hz, 1H, Ar); 6.48 (d, $J = 6.1$ Hz, 2H, Ar); 6.24–6.18 (m, 1H, COD-CH); 4.46 (br s, 1H, COD-CH); 3.83 (br s, 2H, COD-CH); 3.74–3.66 (m, 2H, CH_2); 3.60–3.52 (m, 2H, CH_2); 2.92–2.86 (m, 2H, CH_2); 2.66–2.45 (m, 4H, CH_2); 2.32 (br m, 4H, CH_2); 2.18 (br m, 2H, CH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 146.42–113.94 (Ar); 103.65, 86.05, 77.82 and 76.38 (COD-CH); 44.87 (s, CH_2N); 44.39 (s, CH_2N); 31.77 and 30.61 (s, COD-CH_2); 27.76 (d, $J_{P,C} = 68.4$ Hz, CH_2P); 27.50 (d, $J_{P,C} = 68.4$ Hz, CH_2P). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 41.16 (sl br s).

Hydroformylation

In a typical experiment, styrene (2 ml, 17.456 mmol) and a 4 mM solution of rhodium complex **3** in dichloromethane (3 ml, 0.012 mmol) were placed under argon in an oven-dried autoclave, which was then closed, pressurized with syngas ($CO–H_2$, 1 : 1) and brought to the required temperature. After the required reaction time, the autoclave was cooled to room temperature, the pressure was carefully released and the solution was passed through celite and analyzed by GC and GC–MS. Conversions were determined by GC.

Acknowledgment

This work was supported by the General Secretariat of Research and Technology of Greece.

REFERENCES

1. Frohning CD, Kohlpaintner CW. Hydroformylation. In *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 1, Cornils B, Herrmann WA (eds). VCH: Weinheim, 1996; 29–104.
2. van Leeuwen PWNM, Claver C. *Rhodium Catalyzed Hydroformylation*. Kluwer Academic: Dordrecht, 2000.
3. Slone CS, Weinberger DA, Mirkin CA. *Prog. Inorg. Chem.* 1999; **48**: 233.
4. Börner A. *Eur. J. Inorg. Chem.* 2001; 327.
5. Braunstein P, Naud F. *Angew. Chem. Int. Ed* 2001; **40**: 680.
6. Abu-Gnim C, Amer I. *J. Chem. Soc., Chem. Commun.* 1994; 115.
7. Abu-Gnim C, Amer I. *J. Organomet. Chem.* 1996; **516**: 235.
8. Basoli C, Botteghi C, Cabras MA, Chelucci G, Marchetti M. *J. Organomet. Chem.* 1995; **488**: C20.
9. Kostas ID, Screttas CG. *J. Organomet. Chem.* 1999; **585**: 1.
10. Kostas ID. *J. Chem. Res. (S)* 1999; 630.
11. Kostas ID. *J. Organomet. Chem.* 2001; **626**: 221.
12. Kostas ID. *J. Organomet. Chem.* 2001; **634**: 90.
13. Kostas ID. *Inorg. Chim. Acta* 2003; **355**: 424.
14. Kostas ID, Steele BR, Terzis A, Amosova SV. *Tetrahedron* 2003; **59**: 3467.
15. Kostas ID, Steele BR, Andreadaki FJ, Potapov VA. *Inorg. Chim. Acta* 2004; **357**: 2850.
16. Kostas ID, Vallianatou KA, Holz J, Börner A. *Appl. Organomet. Chem.* 2005; **19**: 1090.
17. Giordano G, Crabtree RH. *Inorg. Syntheses* 1990; **28**: 88.
18. Bennett MA, Saxby JD. *Inorg. Chem.* 1968; **7**: 321.
19. Green M, Kuc TA, Taylor SH. *J. Chem. Soc. A* 1971; 2334.