Available online at www.sciencedirect.com

SCIENCE DIRECT®

Inorganica Chimica Acta 358 (2005) 303–309

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Rhodium(I) complexes with phosphinooxathiane (POT) and phophinooxazolidine (POZ) ligands: the crystal structures of [(POT)Rh(CO)Cl] and [(POZ)Rh(CO)Cl]

Gustavo Ríos-Moreno [a], Rubén A. Toscano [a], Rocío Redón [b], Hiroto Nakano [c], Yuko Okuyama [c], David Morales-Morales [a,*]

[a] *Instituto de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, Circuito Exterior, Coyoacán, 04510 México, D.F.*
[b] *Centro de Ciencias Aplicadas y Desarrollo Tecnológico (CCADET), UNAM. Cd. Universitaria, Circuito Exterior, Coyoacán, 04510 México, D.F.*
[c] *Tohoku Pharmaceutical University, 4-4-1 Komatsushima, Aoba-ku, Sendai 981-8558, Japan*

Received 7 May 2004; accepted 7 September 2004
Available online 7 October 2004

Abstract

The reactions of two equivalents of the ligands POT or POZ with one equivalent of the rhodium complex $[Rh(\mu\text{-}Cl)(CO)_2]_2$ afford the complexes [(POT)Rh(CO)Cl] (**1**) and [(POZ)Rh(CO)Cl] (**2**), respectively. The crystal structures of both complexes have been determined showing the rhodium centers to be into slightly distorted square planar environments. Preliminary screening of the catalytic systems POT/Rh and POZ/Rh in the asymmetric hydroformylation of styrene has been carried out.

Keywords: Phosphorus–sulfur ligands; Phosphorus–nitrogen ligands; Asymmetric hydroformylation; Rhodium complexes; Crystal structures; Catalysis

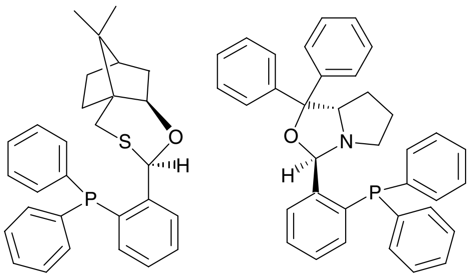
1. Introduction

The rhodium-catalyzed hydroformylation reaction is one of the most important and highly used reactions at the industrial level [1]. It is precisely due to the high importance of this reaction that in the last decades it has been the topic of continuous study at all levels for several research groups around the world. These studies include the design of new ligands and thus the design of new and more active and selective species able to provide a specific product, mechanistic studies to better understand the behavior of the reaction, *in situ* identification of the active species and intermediates involved in the process, etc. Moreover, in the last decade a growing interest has been focused in the design of new ligands and their rhodium complexes for application as enantioselective catalysts in the hydroformylation process [2]. This research, has led to the design of numerous species which have found important applications in the pharmaceutical industry for instance. Furthermore, attention has increasingly been paid to the coordination chemistry of polydentate ligands incorporating both an heteroatom and tertiary phosphine donor ligands, as their combination is likely to confer unusual structures and reactivities on their metal complexes [3]. These complexes have shown an intriguing variety of structures [4] or unusual oxidation states and enhanced solubility, [5] making these species excellent candidates for further studies in reactivity. In the specific case of compounds with elements of the groups 8–10, these may be suitable species for catalytic screening. In addition, the presence of these ligands in the coordination sphere of transition

---

[*] Corresponding author. Tel.: +525556224514; fax: +525556162217.
E-mail address: damor@servidor.unam.mx (D. Morales-Morales).

0020-1693/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2004.09.006



Scheme 1. Structure of the ligands POT and POZ.

metal complexes may render interesting behaviors in solution as these ligands can be capable of full or partial de-ligation (hemilability), [6] being able to provide important extra coordination sites for incoming substrates during a catalytic process [6]. Thus, following our continuous interest [7] in the design and synthesis of new complexes for its application in potentially relevant industrial applications, we would like to report our findings on the reactivity of the ligands POT [1] and POZ [2] with $[Rh(\mu\text{-}Cl)(CO)_2]_2$ and its application in the rhodium catalyzed asymmetric hydroformylation of styrene (see Scheme 1).

2. Experimental

2.1. Materials and methods

Unless stated otherwise, all reactions were carried out under an atmosphere of dinitrogen using conventional Schlenk glassware, and solvents were dried using established procedures and distilled under dinitrogen immediately prior to use. The IR spectra were recorded on a Nicolet-Magna 750 FT-IR spectrometer as nujol mulls. The ^1H NMR (300 MHz) spectra were recorded on a JEOL GX300 spectrometer. Chemical shifts are reported in ppm downfield of TMS using the solvent ($CDCl_3$, $\delta = 7.27$) as internal standard. $^{31}P\{^1H\}$ NMR (121 MHz) spectra were recorded with complete proton decoupling and are reported in ppm using 85% H_3PO_4 as external standard. Elemental analyses were determined on a Perkin–Elmer 240. Positive-ion FAB mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer operated at an accelerating voltage of 10 kV. Samples were desorbed from a nitrobenzyl alcohol (NOBA) matrix using 3 keV xenon atoms. Mass measurements in FAB are performed at a resolution of 3000 using magnetic field scans and the matrix ions as the reference material or, alternatively, by electric field scans with the sample peak bracketed by two (polyethylene glycol or cesium iodide) reference ions. The ligands (1*R*,3*R*,5*R*,8*S*)-11,11-Dimethyl-4-oxa-5-(2-diphenylphosphino)phenyl-6-thiatricyclo[6.2.1.0]undecane (POT), [8] (2*R*, 5*R*)-1-Aza-2-(2-diphenylphosphino)phenyl-3-oxa-4,4-diphenylbicyclo[3.3.0]octane (POZ) [9] and the starting material $[Rh(\mu\text{-}Cl)(CO)_2]_2$ [10] were synthesized according to the published procedures.

2.2. Synthesis of the complexes [(POT)Rh(CO)Cl](**1**) and [(POZ)Rh(CO)Cl](**2**)

2.2.1. Synthesis of [(POT)Rh(CO)Cl](**1**)

A toluene solution (5 mL) of the ligand POT (50.0 mg, 0.109 mmol) and $[Rh(\mu\text{-}Cl)(CO)_2]_2$ (21.2 mg, 0.055 mmol) was stirred for 24 h. After the prescribed reaction time, the pale yellow solution was concentrated under vacuum and the product precipitated from hexane (5 mL). The yellow precipitate was filtered off, washed twice with hexane and dried under vacuum to afford complex **1** as a yellow microcrystalline powder (64.0 mg). Yield 94%. Yellow crystals suitable for single crystal X-ray diffraction analysis were obtained from a toluene/hexane (1:1) solvent system at 0 °C. Mp = 248–250 °C. $[\alpha]_D^{24} = -172.14$ (*c* 1.40 M, $CHCl_3$). IR(KBr): $\nu(CO) = 1999\ cm^{-1}$. ^1H NMR (300 MHz, $CDCl_3$), δ 7.77 (*m*, 1H), 7.54–7.00 (*m*, 12H), 6.92 (*m*, 1H), 6.62 (*m*, 1H), 3.58 (*m*, 1H), 3.37 (*m*, 1H), 3.31 (*m*, 1H), 1.70–1.58 (*m*, 4H), 1.53 (br,s, 3H), 1.20–0.92 (*m*, 2H), 0.80 (*m*, 3H); ^{31}P NMR (121 MHz, $CDCl_3$), δ 35.0 (*s*), $J_{Rh-P} = 158$ Hz. Elem. *Anal.* Calc. for $[C_{37}H_{32}ClNO_2\text{-}PRh]$: C, 64.22; H, 4.66. Found: C, 64.15; H, 4.62%. MS-FAB$^+$ $[M^+ - CO] = 664$ *m*/*z*.

2.2.2. Synthesis of [(POZ)Rh(CO)Cl](**2**)

A toluene solution (5 mL) of the ligand POZ (50.0 mg, 0.095 mmol) and $[Rh(\mu\text{-}Cl)(CO)_2]_2$ (18.5 mg, 0.048 mmol) was stirred for 24 h. After the prescribed reaction time the brown yellow solution was concentrated under vacuum and the product precipitated from hexane (5 mL). The brown yellow precipitate was filtered off, washed twice with hexane and dried under vacuum to afford complex **2** as a yellow microcrystalline powder (60.5 mg). Yield 92%. Yellow crystals suitable for single crystal X-ray diffraction analysis were obtained by slow vapor diffusion of pentane into a concentrated solution (CH_2Cl_2) of **2** at room temperature. Mp = 253–254 °C. $[\alpha]_D^{24} = -225.4$ (*c* 1.22 M, $CHCl_3$). IR(KBr): $\nu(CO) = 1988\ cm^{-1}$. ^1H NMR (300 MHz, $CDCl_3$), δ 7.38–7.63 (*m*, 1H), 7.28–6.92 (*m*, 22H), 6.88 (*m*, 1H), 6.23 (*m*, 1H), 5.06 (s, 1H), 3.97 (*m*, 1H), 2.59 (*m*, 1H), 2.38 (*m*, 1H), 1.52–1.07 (*m*, 4H); ^{31}P NMR (121 MHz, $CDCl_3$), δ 41.7 (*s*), $J_{Rh-P} = 179$ Hz. Elem. *Anal.* Calc. for $[C_{30}H_{31}ClO_2PSRh]$: C, 57.65; H, 5.00. Found: C, 57.60; H, 5.02%. MS-FAB$^+$ $[M^+ - CO] = 596$ *m*/*z*.

---

[1] (1*R*, 3*R*, 5*R*, 8*S*)-11,11-dimethyl-4-oxa-5-(2-diphenylphosphino)phenyl-6-thiatricyclo[6.2.1.0]undecane.

[2] (2*R*, 5*R*)-1-aza-2-(2-diphenylphosphino)phenyl-3-oxa-4,4-diphenylbicyclo[3.3.0]octane.