



Research Article

Synthesis of a water-soluble thio-triazole ligand for biphasic rhodium catalyzed hydroformylation of styrene

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Abstract

An environmentally safe water-soluble new ligand (2-(1-(2-(methylthio)ethyl)-1H-1,2,3-triazol-4-yl)ethanol) (ligand **1**) has been synthesized by the click reaction between (2-azidoethyl)(methyl)sulfane and 3-butyn-1-ol. The structure of the novel ligand was confirmed by NMR spectroscopy. In situ combination of ligand **1** with [Rh(COD)Cl]₂ and [Rh(CO)₂(acac)] (Rh: ligand = 1: 4) successfully employed for the biphasic catalytic hydroformylation of styrene. The formation of branched 2-phenylpropanol was confirmed by gas chromatographic analysis. The recycled catalytic aqueous phase can be used three runs with remarkable catalytic efficiency.

Keywords Hydroformylation · Triazole ligand · Rhodium catalysts · Biphasic catalysis · Phenylpropanol

1 Introduction

Hydroformylation is a general reaction in which the introduction of both hydrogen and formyl group into the olefin bonds is carried out. This industrial process catalyzed by homogeneous catalysts is widely used for the synthesis of *aldehydes* from *alkenes* [1]. There are many different approaches that aim to make effective hydroformylations.

A wide variety of water-soluble rhodium catalysts have been employed in biphasic hydroformylation [2–8]. Particularly, water-organic biphasic methods have been employed for preferential catalyst separation [9, 10]. In association, the use of water as a solvent makes noticeable interest from an environmental and economical points of view. The organometallic complexes containing water-soluble ligands could be the best tool for biphasic systems [11, 12]. Besides hydroformylation reaction, several reactions like hydrogenation reactions [13], Suzuki coupling reaction [14] etc. were catalyzed by catalyst containing water soluble ligand. In the past, the water/organic phase

hydroformylation of olefine using highly water-soluble rhodium catalyst was reported by Uwe Ritter et al. [15]. The use of in situ catalysts assembled by mixing Rh(CO)₂(acac) and naturally available water-soluble ligand, *L*-tryptophan was reported by Paganelli [9, 10]. The two phase hydroformylation reaction experienced difficulties in catalyst separations even the ligand is water-soluble. The complete leaching of catalyst ingredients into the organic phase indicates the weak metal–ligand coordination in the aqueous phase. However, rhodium coordinated with thiol ligands showed effective hydroformylations [16] indicating the greater interaction of sulfur containing ligands with “soft” metal rhodium.

Recently, we reported the biphasic hydroformylation [17] catalyzed by rhodium catalyst containing a water-soluble N donating pyridyl-triazole ligand. The success of this reaction, encourage us to replace N by S in the ligand structure and the authors successfully synthesized and characterized water-soluble (2-(1-(2-(methylthio)ethyl)-1H-1,2,3-triazol-4-yl)ethanol) (ligand **1**). According

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to our literature review, no research work have published on the hydroformylation using water-soluble (methylthio)ethyl-triazole as ligand. The authors decided to use water soluble ligand **1** in combination with rhodium for hydroformylation of styrene because of its synthetic path, expected coordination with a variety of metal centers. Moreover, some examples of the interaction of rhodium with S of human serum albumin (HSA) to form Rh–HSA complex were reported. The catalytic activity of Rh–HAS complexes have been broadly studied [18–22].

2 Experimental

2.1 General methods

The solvents (Sigma Aldrich) with high degree of purity were purchased directly from the market and used without further purification. In case where it is necessary to handle the reaction in absence of oxygen and water, solvents and reagents were distilled and dried according to the procedure reported in the literature [28]. [Rh(CO)₂(acac)] and styrene were purchased from Sigma-Aldrich. [Rh(COD)Cl]₂ was laboratory made [29] or purchased from Alfa Aesar. The ligand **1**, (2-(1-(2-(methylthio)ethyl)-1*H*-1,2,3-triazol-4-yl)ethanol) was synthesized as described in the literature method [23]. Duplicate or triplicate hydroformylation reactions were carried out under inert atmosphere using Schlenk techniques [13]. The obtained results generally agreeing within 5%. The resulting catalytic solutions were analyzed by gas chromatography on a Agilent Technologies 6850 gas chromatograph fitted with an HP-5 column (30 m × 0.32 μm × 0.25 μm). ¹H NMR and ¹³C NMR spectra were recorded on Bruker Avance-300 spectrometer.

2.2 Synthesis of ligand 1

In a 50.0 mL round bottom flask, sodium azide (0.54 g, 8.35 mmol) was dissolved in a mixture of 16.0 mL of a *tert*-BuOH and 4.0 mL of water. (2-chloroethyl)(methyl)sulfane (0.42 mL, 4.17 mmol) was slowly added to the reaction vessel under inert atmosphere. After overnight stirring, (2-azidoethyl)(methyl)sulfane was collected into a nitrogen refrigerated vessel by high vacuum pump. When the system returned to room temperature, 0.158 mL (2.086 mmol) of 3-butyn-1-ol was added to the azido solution. Then, 1.0 mL aqueous solution of a mixture of CuSO₄ × 5H₂O (0.2086 mmol) and Na-ascorbate (0.4172 mmol) was added to the reaction vessel. The mixture was left for additional 24 h under stirring. After filtration and vacuum evaporation to dryness, a pale yellow oil was obtained. Extraction with CHCl₃ (5 mL × 2) and dried over vacuum gave a yellow oil (85%) which was characterized by ¹H-NMR and ¹³C-NMR

in CDCl₃. ¹H NMR (300 MHz, CDCl₃, 298 K): δ 7.51 [s, 1H(4)], 4.52 [t, 2H(3), *J* = 7.0 Hz], 3.93 [t, 2H(7), *J* = 5.9 Hz], 3.15 [br, s, 1H(8)], 2.96 [m, 4H(2,6)], 2.07 [s, 3H(1)] ppm. ¹³C NMR (300 MHz, CDCl₃, 298 K): δ 145.45 (C5), 122.30 (C4), 61.44 (C7), 49.57 (C3), 34.11 (C6), 28.72 (C2), 15.59 (C1) ppm.

2.3 Preparation of [RhCl(COD)]₂ precursor complex

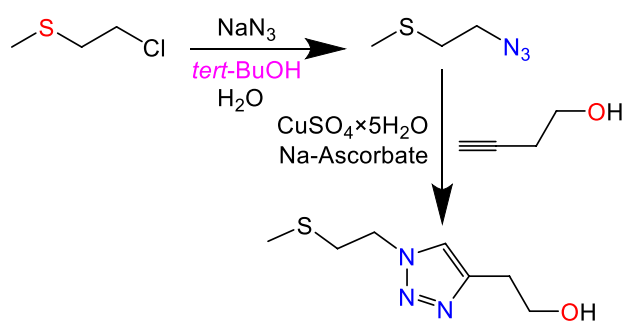
In a 100.0 mL two-neck round bottom flask, 2.00 g (7.6 mmol) rhodium trichloride trihydrate was dissolved in 20.0 mL mixture (5:1) of ethanol–water. 3.0 mL of cyclooctadiene was added to the flask. After overnight reflux, the obtained yellow-orange solid precipitate was immediately filtered. The product was washed with pentane and then with methanol–water (1:5) until the washing no longer contain chloride ion. Yield 90%. ¹H NMR (300 MHz, CDCl₃, 298 K): δ 4.24 (s, 1H), 4.12 (br, m, 2H), 1.75 (d, 2H, *J* = 8.6 Hz) ppm.

2.4 Hydroformylation experiments with in situ prepared rhodium-ligand **1** catalyst

As an example the experimental details relevant to Entry 2 in Table 2, in a Schlenk tube, 2.4 mg (4.81 × 10⁻³ mmol) of [Rh(COD)Cl]₂ and 7.2 mg (0.039 mmol) of ligand **1** were stirred under nitrogen in 2.0 mL of deaerated water until complete dissolution of the complex (about 30 min). A 2.0 mL toluene solution of styrene (1.0 g, 9.62 mmol) was then added to the aqueous phase. The Schlenk tube was then transferred into a 150.0 mL stainless steel autoclave under nitrogen, pressurized with syngas (CO/H₂ = 1) and magnetically stirred for 5 h at 80 °C. The reactor was then cooled to room temperature and the residual gas vented off. The organic phase was separated (extracted with Et₂O), dried on MgSO₄ and analyzed by GC (HP5 column 30 m × 0.32 μm × 0.25 μm). The catalytic aqueous phase was reused for recycle experiments.

3 Results and discussion

The synthesis of (methylthio)ethyl-triazole ligand (ligand **1**) was carried according to Rostovtsev et al. [23]. The synthesis consists of two steps. First, the reaction of sodium azide with (2-chloroethyl)(methyl)sulfane in *tert*-BuOH/water (4:1) solvent mixture, was analyzed by GC. When the conversion was complete (monitored by GC analysis), the highly volatile (2-azidoethyl)(methyl)sulfane was collected in closed vessel. The large excess of sodium azide ensured the complete conversion of chloride into the corresponding azide.



Scheme 1 Synthesis of water-soluble triazole ligand **1** (2-(1-(2-(methylthio)ethyl)-1H-1,2,3-triazol-4-yl)ethanol)

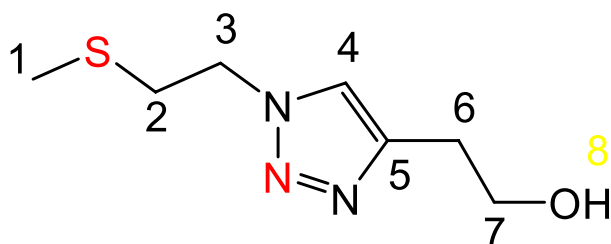


Fig. 1 Structure of (2-(1-(2-(methylthio)ethyl)-1H-1,2,3-triazol-4-yl)ethanol) (ligand **1**)

Second, 3-butyn-1-ol is added to the closed vessel followed by the addition of copper catalyst ($\text{CuSO}_4 \times 5\text{H}_2\text{O}$ and Na-ascorbate). After 24 h stirring at room temperature, a pale yellow oil was obtained (see Scheme 1). Extraction with chloroform gave yellow oil in 85% yield.

3.1 Characterization of ligand **1** by NMR spectroscopy

The ligand **1** (Fig. 1) is highly soluble in water and methanol and its structure is confirmed by ^1H NMR and ^{13}C NMR spectroscopy. In the ^1H NMR spectrum (Fig. 2), the strong singlet H(4) at 7.51 ppm indicates the formation of triazole moiety. This result is consistent with the formation of 1–4 disubstituted triazole ligand [14]. The chemical shift of ligand H(6) is shifted to higher δ value (2.96) compared to their corresponding value (2.45) in 3-butyn-1-ol. The ^{13}C NMR spectrum (Fig. 3) exhibits the resonance for the carbons on the pyridine ring at 145.45 (C5), 122.30 (C4), 61.44 (C7), 49.57 (C3), 34.11 (C6), 28.72 (C2), 15.59 (C1) ppm. Upon the formation of ligand, the δ value of C5 and C6 significantly shifted to higher values compared to their corresponding value in 3-butyn-1-ol. These data are good agreement with other triazole ligands [14, 24, 25, 30].

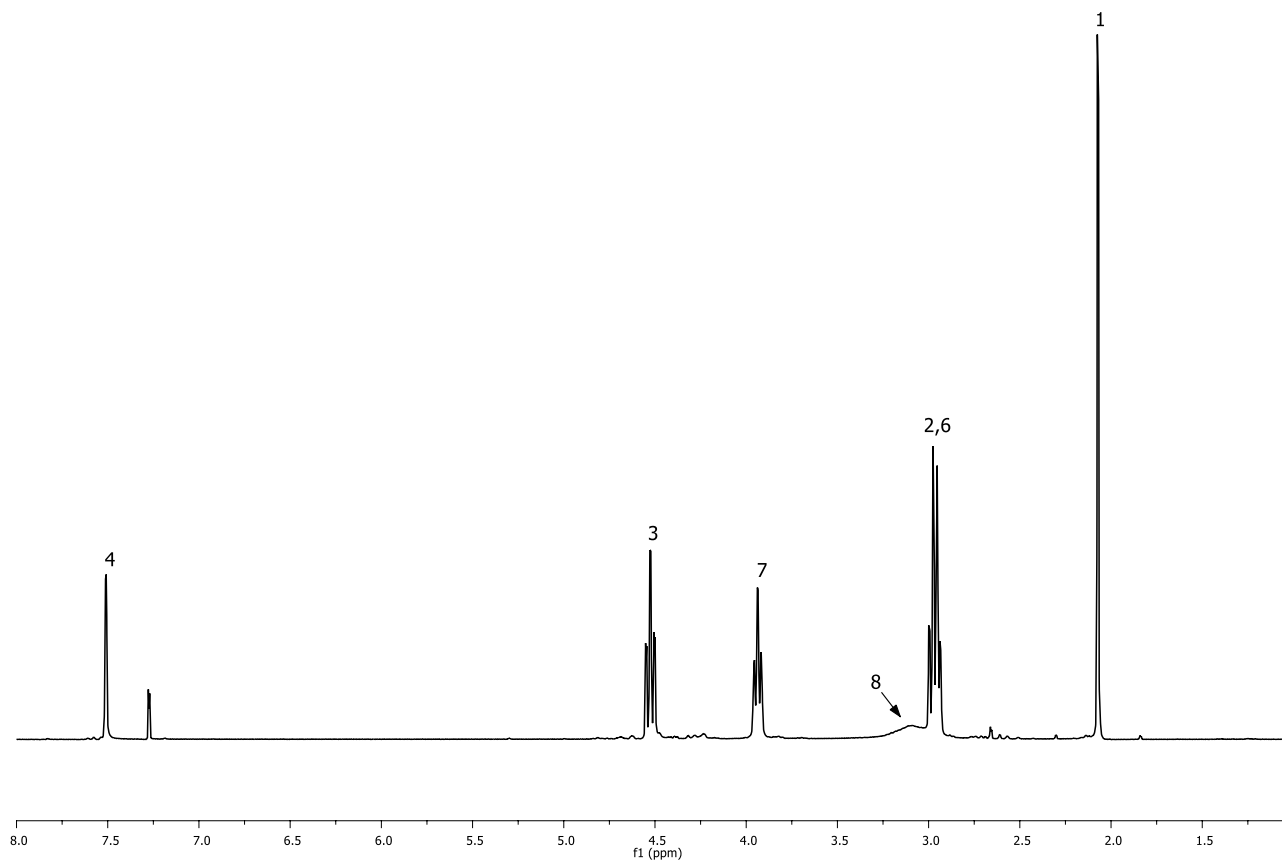
3.2 Catalysis study

Styrene is an important model substrate frequently used to test the catalytic activity of new catalyst and ligands in the hydroformylation reaction. The use of styrene does not have a great industrial importance but it is still used as a standard substance because it is a less volatile liquid. The main products which were formed by the hydroformylation of styrene (see scheme 2) are 2-phenylpropanal (2) and 3-phenylpropanal (3). The first isomer is a branched aldehyde (2), comes from the attack of $-\text{CHO}$ group into the 2 position of the double bond of styrene while the second one is a linear aldehyde (3), derived from the attack of $-\text{CHO}$ group into the 1 position of the double bond of styrene. The third possible product is ethyl benzene (4) which comes from the partial hydrogenation of styrene.

The catalytic hydroformylation of styrene in aqueous biphasic system was carried out according to the procedure reported by Paganelli et al. [10–16]. The precursor used is either $[\text{Rh}(\text{CO})_2(\text{acac})]$ or $[\text{RhCl}(\text{COD})]_2$. Although both precursors are commercially available, we prepared $[\text{RhCl}(\text{COD})]_2$ in our laboratory (see the experimental section). The simple stirring of $[\text{Rh}(\text{COD})\text{Cl}]_2$ and ligand **1** in deaerated water at room temperature in about 10 min provides a clear orange-yellow solution. Before starting this reaction, we carried out several experiments to understand the activity of two different precursors $[\text{Rh}(\text{COD})\text{Cl}]_2$, and $[\text{Rh}(\text{CO})_2(\text{acac})]$ in combination with water-soluble ligand **1**. We found both of them have same catalytic activity (Table 1) under same condition. Upon lowering of pressure (80 to 20 atm) and time (18 to 5 h), the conversion drastically decreases with producing some hydrogenation product. This result indicates that higher pressure and temperature are favorable for this catalysis reaction. The precursor $[\text{Rh}(\text{COD})\text{Cl}]_2$ has comparatively better solubility in water than $[\text{Rh}(\text{CO})_2(\text{acac})]$, therefore $[\text{Rh}(\text{COD})\text{Cl}]_2$ was used in all the hydroformylation experiments.

Exploratory experiments revealed that the activity of the catalytic system depends on the rhodium to ligand ratio. The best results obtained using 8 mol of ligand for mole of $[\text{Rh}(\text{COD})\text{Cl}]_2$ ($\text{Rh}/\text{ligand } \mathbf{1} = 1/4$). Therefore this Rh/ligand **1** ratio was used in all the catalytic experiments. The most significant results obtained for styrene hydroformylation (see Scheme 2) are reported in Table 2.

The first reaction was carried out at 80 atm ($\text{CO}/\text{H}_2 = 1/1$) in 18 h provides complete conversion of the reactants and the products obtained from the organic phase are 81% of 2-phenylpropanal (2) and 19% of 3-phenylpropanal (3). The branched to linear ratio (B/L) is 3. Upon lowering of reaction time to 5 h (Entry 2), the conversion remains 100% with an increase of branched/linear (B/L) ratio into 4. Recycle experiments (Entry 2a) were carried out in condition of entry 2 affords 99%

Ligand 1**Fig. 2** ^1H NMR spectrum of ligand **1** in CDCl_3

conversion with a modest enlargement in the selectivity towards branched product. Further recycling experiment shows gradual decreases in conversion 84% (Entry 2b), and 40% (Entry 2c). Interestingly, all the recycle experiments maintain the same B/L ratio and in all cases no ethyl benzene is formed. Therefore, it is important to conclude that the rhodium-ligand **1** catalytic system displayed better activity compared to the precursor catalyst.

Generally, the hydroformylation of an unsaturated substrate produced linear product as the major product [26, 27]. Instead, in our case the hydroformylation of styrene gave the reverse result, the branched aldehyde (**2**) is the major product. This peculiarity can be explained by observing the expected intermediate formations (see Scheme 3). The branched intermediate is more stable compared to linear intermediate because in the branched intermediate the partial negative charge on the carbon atom adjacent to the rhodium centre is delocalized onto the aromatic ring. It is anticipated that to complete

resonance, need a threshold time which is higher than 5 h. This is supported by recycle experiments.

4 Conclusions

The ligand **1**, namely (2-(1-(2-(methylthio)ethyl)-1*H*-1,2,3-triazol-4-yl)ethanol) was synthesized using copper catalyzed cycloaddition (CuAAC) reaction. The water soluble ligand **1** in combination with $[\text{RhCl}(\text{COD})]_2$ displaying a good catalytic activity in styrene hydroformylation. Instead of linear 3-phenylpropanol, the hydroformylation of styrene gives branched 2-phenylpropanol. The biphasic water/toluene catalytic system works under inert atmosphere, is air sensitive and used for three consecutive runs with sufficient catalytic activity. Finally it is important to note that ligand **1** can be considered a new type of water-soluble ligand. The properties of the ligand **1** can be tuned by taking the advantages of the modular nature of the azide-alkyne cycloaddition reaction.

Ligand 1

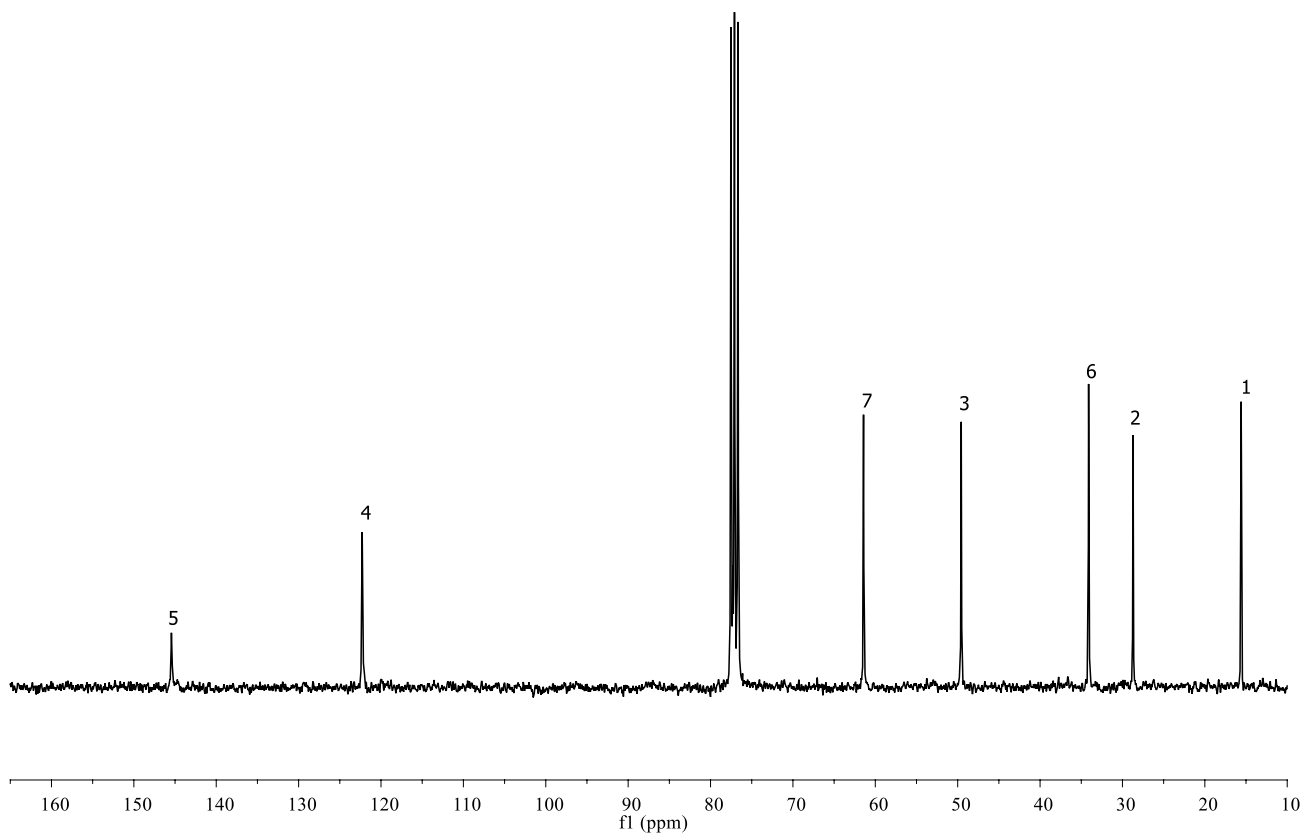


Fig. 3 ^{13}C NMR spectrum of ligand **1** in CDCl_3

Scheme 2 Hydroformylation of styrene

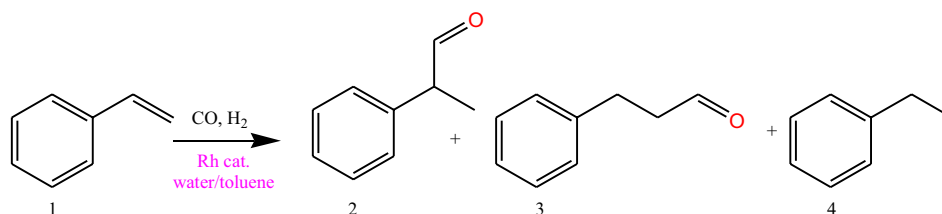


Table 1 Biphasic hydroformylation of styrene catalyzed by Rh/ligand **1** in-situ catalytic system [20, 21]

Entry	Precursor	P(CO + H ₂) atm	Time (h)	^a Conv. (%)	(2) ^a	(3) ^a	(4) ^a
1	[Rh(COD)Cl] ₂	80	18	100	81	19	0
2	[Rh(CO) ₂ (acac)]	80	18	100	79	21	0
3	[Rh(COD)Cl] ₂	20	5	17	53	45	2
4	[Rh(CO) ₂ (acac)]	20	5	13	48	50	2

Reaction conditions: Styrene/Rh = 1000; styrene = 9.62 mmol; [Rh(COD)Cl]₂ = 4.81 × 10⁻³ mmol (2.40 mg); [Rh(CO)₂(acac)] = 9.62 × 10⁻³ mmol (2.49 mg); Rh/ligand **1** = 1/4, T = 80 °C; H₂O = 2.0 mL; toluene = 2.0 mL.

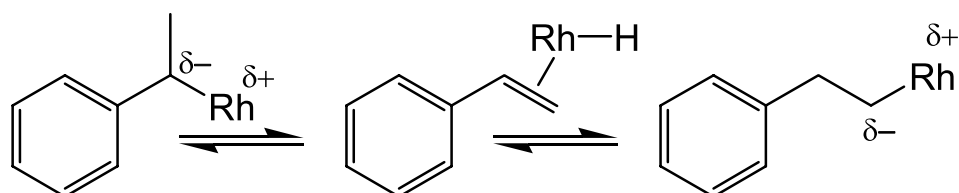
^aBy GLC

Table 2 Biphasic hydroformylations of styrene catalyzed by [Rh(COD)Cl]₂-ligand **1** catalyst [20, 21]

Entry	Time (h)	Conv.(%)	(2)	(3)	(4)	B/L(2/3)
1	18	100	81	19	0	4
2	5	100	75	24	Trc	3
2a	"	99	81	19	0	4
2b	"	84	81	19	0	4
2c	"	40	82	18	0	4

Reaction conditions: Styrene/Rh = 1000; styrene = 9.62 mmol; [Rh(COD)Cl]₂ = 4.81 × 10⁻³ mmol (2.40 mg); ligand **1** = 7.2 mg (0.039 mmol); Rh/ligand **1** = 1/4, P = 80 atm (CO/H₂ = 1/1); T = 80 °C; H₂O = 2.0 mL; Toluene = 2.0 mL

(a) 1st recycle; (b) 2nd recycle; (c) 3rd recycle experiment

Scheme 3 Formation of intermediates via coordination of rhodium into styrene

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Compliance with ethical standards

Conflict of interest This manuscript has not been published and is not under consideration for publication elsewhere. We have no conflict of interest to disclose.

References

- Ojima I, Tsai CY, Tzamarioudaki M, Bonafoux D (2000) The hydroformylation reaction. *Org React* 56:2–4. <https://doi.org/10.1002/0471264180.or056.01>
- Goedheijt MS, Kamer PCJ, Van Leeuwen PWNM (1998) A water soluble diphosphine ligand with large natural bite angle for two-phase hydroformylation of alkenes. *J Mol Catal A Chem* 134:243–249. [https://doi.org/10.1016/S1381-1169\(98\)00042-9](https://doi.org/10.1016/S1381-1169(98)00042-9)
- Joo' F, Katho' A (1997) Recent developments in aqueous organometallic chemistry and catalysis. *J Mol Catal A Chem* 116:3–26. [https://doi.org/10.1016/S1381-1169\(96\)00075-1](https://doi.org/10.1016/S1381-1169(96)00075-1)
- Kuntz EG (1987) Homogeneous catalysis in water. *ChemTech* 17:570
- Cornils B, Herrmann WA (1996) Applied homogeneous catalysis with organometallic compounds. Wiley
- Ding H, Kang J, Hanson BE, Kohlpaintner CW (1997) New water soluble chelating phosphines for aqueous phase catalysis. *J Mol Catal A: Chem* 124:21–28. [https://doi.org/10.1016/S1381-1169\(97\)00063-0](https://doi.org/10.1016/S1381-1169(97)00063-0)
- Herrmann WA, Kohlpaintner CW, Manetsberger RB, Bahrmann H, Kottmann H (1995) Water-soluble metal complexes and catalysts. Part 7. New efficient water-soluble catalysts for two-phase olefin hydroformylation: BINAS-Na, a superlative in propene hydroformylation. *J Mol Catal A Chem* 97:65–72. [https://doi.org/10.1016/1381-1169\(94\)00076-X](https://doi.org/10.1016/1381-1169(94)00076-X)
- Paganelli S, Zanchet M, Marchetti M, Mangano G (2000) Hydroformylation of functionalized olefins catalyzed by water-soluble rhodium carbonyl complexes. *J Mol Catal A Chem* 57:1–8. [https://doi.org/10.1016/S1381-1169\(99\)00437-9](https://doi.org/10.1016/S1381-1169(99)00437-9)
- Marchetti M, Mangano G, Paganelli S, Botteghi C (2000) A protein-rhodium complex as an efficient catalyst for two-phase olefin hydroformylation. *Tetrahedron Lett* 41:3717–3720. [https://doi.org/10.1016/S0040-4039\(00\)00473-1](https://doi.org/10.1016/S0040-4039(00)00473-1)
- Paganelli S, Marchetti M, Bianchin M, Bertucci C (2007) Aqueous biphasic hydroformylation catalyzed by rhodium carbonyl complexes modified with bioligands. *J Mol Catal A Chem* 269:234–239. <https://doi.org/10.1016/j.molcata.2007.01.027>
- Melean LG, Rodriguez M, Romero M, Alvarado ML, Rosales M, Baricelli PJ (2011) Biphasic hydroformylation of substituted allylbenzenes with water-soluble rhodium or ruthenium complexes. *Appl Catal A* 394:117–123. <https://doi.org/10.1016/j.apcata.2010.12.037>
- Paganelli S, Ciappa A, Marchetti M, Scrivanti A, Matteoli U (2006) Hydroformylation of m-diisopropenylbenzene and 1-isopropyl-3-isopropenylbenzene for the preparation of the fragrance. *Florhydral J Mol Catal A Chem* 247:138–144. <https://doi.org/10.1016/j.molcata.2005.10.032>
- Paganelli S, Alam MdM, Beghetto V, Scrivanti A, Amadio E, Bertoldini M, Matteoli U (2015) A pyridyl-triazole ligand for ruthenium and iridium catalyzed C=C and C=O hydrogenations in water/organic solvent biphasic systems. *Appl Catal A* 503:20–25. <https://doi.org/10.1016/j.apcata.2014.11.013>
- Amadio E, Scrivanti A, Beghetto V, Bertoldini M, Alam MdM, Matteoli U (2013) A water-soluble pyridyl-triazole ligand for aqueous phase palladium catalyzed Suzuki–Miyaura coupling. *RSC Adv* 3:21636–21640. <https://doi.org/10.1039/c3ra44740e>
- Borrmann T, Roesky HW, Ritter U (2000) Biphasic hydroformylation of olefins using a novel water soluble rhodium polyethylene glycolate catalyst. *J Mol Catal A Chem* 153:31–48. [https://doi.org/10.1016/S1381-1169\(99\)00353-2](https://doi.org/10.1016/S1381-1169(99)00353-2)

- Paganelli S, Piccolo O, Pontini P, Tassini R, Rathod VD (2015) Aqueous-phase hydrogenation and hydroformylation reactions catalyzed by a new water-soluble [rhodium]-thioligand complex. *Catal Today* 247:64–69. <https://doi.org/10.1016/j.cattod.2014.05.038>
- Scrivanti A, Beghetto V, Alam MdM, Paganelli S, Canton P, Bertoldini M, Amadio E (2017) Biphasic hydroformylation catalyzed by rhodium in combination with a water-soluble pyridyl-triazole ligand. *Inorg Chim Acta* 455:613–617. <https://doi.org/10.1016/j.ica.2016.05.011>
- Giraldi T, Sava G, Mestroni G, Zassinovich G, Stolfa D (1978) Antitumour action of rhodium (I) and iridium (I) complexes. *Chem Biol Interact* 22:231–238. [https://doi.org/10.1016/0009-2797\(78\)90128-X](https://doi.org/10.1016/0009-2797(78)90128-X)
- Lo JM, Pillai MR, John CS, Tranter DE (1990) Labeling of human serum albumin with ^{105}Rh cysteine complexes. *Int J Rad Appl Instrum* 41:63–67. [https://doi.org/10.1016/0883-2889\(90\)90131-Y](https://doi.org/10.1016/0883-2889(90)90131-Y)
- Trynda L, Pruchnik F (1995) Interaction of tetra- μ -acetatodirrhodium(II) with human serum albumin. *J Inorg Biochem* 58:69–77. [https://doi.org/10.1016/0162-0134\(94\)00040-H](https://doi.org/10.1016/0162-0134(94)00040-H)
- Trynda L, Pruchnik F (1997) Studies on the interaction between human serum albumin and $[\text{Rh}_2(\text{OAc})_2(\text{bpy})_2(\text{H}_2\text{O})_2](\text{OAc})_2$. *J Inorg Biochem* 66:187–192. [https://doi.org/10.1016/S0162-0134\(96\)00202-4](https://doi.org/10.1016/S0162-0134(96)00202-4)
- Espósito BP, Faljoni-Alário A, de Menezes JFS, de Brito HF, Najjar RA (1999) Circular dichroism and fluorescence quenching study of the interactions between rhodium(II) complexes and human serum albumin. *J Inorg Biochem* 75:55–61. [https://doi.org/10.1016/S0162-0134\(99\)00032-X](https://doi.org/10.1016/S0162-0134(99)00032-X)
- Rostovtsev VV, Green LG, Fokin VV, Sharpless KB (2002) A step-wise Huisgen cycloaddition process: copper(I)-catalyzed regioselective “ligation” of azides and terminal alkynes. *Angew Chem Int Ed* 41:2596–2599. [https://doi.org/10.1002/1521-3773\(20020715\)41:14<2596::AID-ANIE2596>3.0.CO;2-4](https://doi.org/10.1002/1521-3773(20020715)41:14<2596::AID-ANIE2596>3.0.CO;2-4)
- Amadio E, Scrivanti A, Chessa G, Matteoli U, Beghetto V, Bertoldini M, Rancan M, Dolmella A, Venzo A (2012) Synthesis, characterization and low temperature self assembling of (η^3 -allyl)palladium complexes with 2-pyridyl-1,2,3-triazole bidentate ligands. Study of the catalytic activity in Suzuki–Miyaura reaction. *J Organomet Chem* 716:193–200. <https://doi.org/10.1016/j.jorganchem.2012.06.018>
- Brotherton WS, Michaels HA, Simmons JT, Clark RJ, Dalal NS, Zhu L (2009) Apparent copper(II)-accelerated, azide-alkyne cycloaddition. *Org Lett* 11:4954–4957. <https://doi.org/10.1021/ol9021113CCC>
- Herrmann N, Bianga J, Palten M, Riemer T, Vogt D, Dreimann JM, Seidensticker T (2019) Improving aqueous biphasic hydroformylation of unsaturated oleochemicals using a jet-loop-reactor. *Eur J Lipid Sci Technol* 122:1900166. <https://doi.org/10.1002/ejlt.201900166>
- Alsalahi W, Trzeciak AM (2019) Hydroformylation of unsaturated esters and 2,3-dihydrofuran under solventless conditions at room temperature catalysed by rhodium *N*-pyrrolyl phosphine catalysts. *New J Chem* 43:16990–16999. <https://doi.org/10.1039/C9NJ04438H>
- Armarego WLF, Perrin DD (1998) Purification of laboratory chemicals, 3rd edn. Pergamon Press, Oxford
- Giordano G, Crabtree RH, Heintz RM, Forster D, Morris DE (1990) Di- μ -chloro-bis(η^4 -1,5-cyclooctadiene)-dirrhodium(I). *Inorg Synth* 28:88–90. <https://doi.org/10.1002/9780470132593.ch22>
- Alam MdM, Beghetto V, Scrivanti A, Bertoldini M, Salim M (2020) Preparation and characterization of a mononuclear cobalt complex containing a water-soluble triazole ligand. American Association for Science and Technology (AASCIT). *J Chem* 1:1–6

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