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Novel smart ligand for immobilizing a highly efficient Rh-catalyst

Jin-Kyu Lee,* Tae-Jong Yoon and Young Keun Chung

School of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul 151-747, Korea. E-mail: jinklee@snu.ac.kr

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Novel highly efficient Rh-based catalysts with a good regioselectivity in olefin hydroformylation have been prepared by deliberately choosing 11-mercaptoundecanoic acid as a ligating molecule to $[Rh(cod)Cl]_2$ (cod = cyclooctadiene) and a simple recovery process for their recycling was investigated.

Catalyst recovery processes are becoming more important, especially when expensive and toxic heavy metal complexes are employed. Owing to these economic and environmental factors, many attempts have been made to recover homogenous catalysts and recycle them. The homogeneous catalysts are usually recovered by thermal operations such as distillation, which normally leads to thermal stress on the catalyst and seldom yields quantitative recovery. Since the separation of catalyst from products is much simpler in two-phase (or biphasic) systems incorporating a water-soluble catalyst,[1–3] water-soluble organometallic compounds have been studied for many years. They are normally prepared by incorporating highly polar functional groups such as sulfonate salt[4,5] carboxylate salt,[1] amino,[6] or hydroxide[7] into the ligands. Recently, Rh-based catalysts have attracted much attention due to their high activity and selectivity, and some attempts to immobilize these expensive catalysts have also been reported.[6,8–13] In this communication, we will introduce a simple synthetic method of preparing novel water-soluble Rh-based hydroformylation catalysts and discuss their unique solubility and reactivity, which make catalyst recycling much simpler.

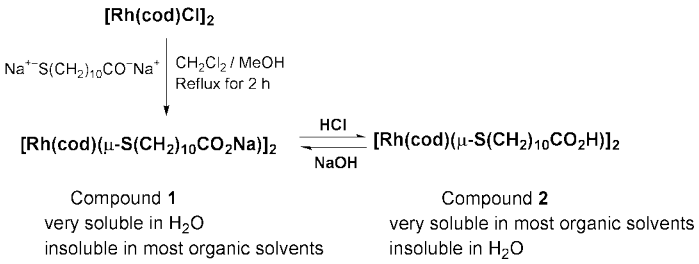
$[Rh(\mu\text{-}S(CH_2)_{10}CO_2Na)(cod)]_2$ **1** was prepared in 89% yield as a yellow–orange solid by treating $[Rh(\mu\text{-}Cl)(cod)]_2$ with 11-mercaptoundecanoic acid disodium salt† (Scheme 1). Complex **1** is a very stable solid in air and soluble in water, slightly soluble in MeOH, and insoluble in most organic solvents. This complex shows a very sensitive change of solubility in water when pH values are varied, compared to other known water-soluble organometallic compounds that usually contain sulfonate groups and show no pH-dependent solubility.[4,5] When an aqueous solution of **1** was treated with acid to $pH < 4$, $[Rh(\mu\text{-}S(CH_2)_{10}CO_2H)(cod)]_2$ **2** was quickly precipitated as a yellow–orange powder from the aqueous solution, this powder being very soluble in polar organic solvents such as THF. Complex **2** can also be quantitatively converted back into **1** by treating with a base such as NaOH aqueous solution. These interconversions between **1** and **2** can be repeated several times without any significant degradation of the complexes (Scheme 1).

The catalytic activity of both **1** and **2** for the hydroformylation of arylolefins was checked, and the large differences in their solubility (depending on the pH) were used to recover the catalyst after the reaction.‡ The water-soluble Rh catalyst **1**, in general, showed a high catalytic activity with the exception of α-methylstyrene (Table 1, entry 1), probably due to its steric bulkiness preventing the effective binding of the disubstituted styrene onto the Rh catalysts. Although the hydroformylation of aromatic olefins showed very good regioselectivity, the electron donating or withdrawing substituents on styrene (Table 1, entries 2–6) did not give rise to any further enhancement of selectivity. Unlike other reported hydroformylation catalysts,[1] compound **1** showed a very high degree of catalytic activity even towards long alkyl olefins such as oct-1-ene, undec-1-ene, and dodec-1-ene (Table 2). It is expected that the long alkyl chains in 11-mercaptoundecanoic acid themselves behave like a surfactant to enhance the solubility of the long aliphatic olefins in the aqueous catalyst phase. The low regioselectivity resulting from the hydroformylation of aliphatic terminal olefins suggests that regioselectivity is related not only to steric but also to electronic factors. After the reaction, the products were easily separated by extraction with Et_2O and the aqueous layer containing catalyst **1** could be reused without any further treatment. Reaction results from the consecutive usage (five times) of aqueous

Table 1 Hydroformylation results of substituted styrenes by employing water-soluble catalyst **1**

Entry	Olefin	*b/l*[a]	Conversion yield (%)[b]
1	α-Methylstyrene		~ 3
2	4-Bromostyrene	87/13	100
3	4-Chlorostyrene	88/12	100
4	Styrene	91/9	100
5	4-Methylstyrene	97/3	100
6	4-Vinylanisole	92/8	100

[a] Structural ratios of aldehyde products were measured by ^1H NMR spectroscopy (*b*: 9.62 ppm, *l*: 9.78 ppm); *b* stands for a branch form (*e.g.* acetophenone) and *l* for linear form (*e.g.* phenylacetaldehyde). [b] Determined by ^1H NMR spectroscopy.



Scheme 1 Synthesis of novel sulfur bridged [Rh] catalysts.

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Table 2 Hydroformylation results of long alkyl olefins by catalyst **1**

Entry	Olefin	*b*/*l*	Conversion yield (%)
1	Oct-1-ene	50/50	100
2	Undec-1-ene	48/52	100
3	Dodec-1-ene	78/22	92

Catalytic reaction and analysis process was as for Table 1.

solutions containing catalyst **1** did not indicate any differences in catalytic activity. Further detailed study on the long-term stability of catalyst **1** is under investigation.

When organic-soluble compound **2** was used as a catalyst, the reactions were carried out in homogeneous THF solution. All the reaction results were the same as for the case of catalyst **1**, thereby confirming the high catalytic activity of the new Rh-based catalysts in either a homogeneous or a heterogeneous system. However, the recovery process of catalyst **2** from THF solution was different. It was isolated by treating with NaOH solution to precipitate as **1**, followed by filtering off and dissolving it in water. It was then treated with HCl solution again to precipitate as compound **2**, then filtered off and dried for recycling. Recycled catalyst **2** showed the same activity, but there was always a small amount of weight loss during the filtration and drying procedures. From the practical point of view of recycling, therefore, it is much easier and simpler to use compound **1** in a biphasic (water/organic bilayer) system.

We are quite certain that the present catalyst should exhibit a high degree of regioselectivity toward various olefins. Further experiments to obtain a detailed mechanistic understanding and the application of these novel Rh-catalysts to other types of catalytic reactions such as hydrosilylation and stereoselective hydrogenation reactions, are currently under investigation.

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Notes and references

† A mixed solution of NaOH (3 M, 3.06 ml) and $HS(CH_2)_{10}CO_2H$ (1.00 g, 4.58 mmol) in 10 ml of THF was stirred at room temperature for 30 min to precipitate the salt $Na^{+-}S(CH_2)_{10}CO_2{}^{-}Na^{+}$. The precipitate was filtered off, and then washed with THF in order to eliminate excess NaOH. 0.53 g (2.00 mmol) of dried $Na^{+-}S(CH_2)_{10}CO_2{}^{-}\ Na^{+}$ salt was added to a stirred solution of $[Rh(\mu\text{-}Cl)(cod)]_2$ (0.49 g, 1.00 mmol) in dried MeOH (10 ml). The mixed solution was refluxed with vigorous stirring for 30 min. Solvent was evaporation to dryness, and the residual solid was rinsed with cold CH_2Cl_2 (3 × 10 ml) and crystallized from H_2O–THF mixed solvent. Solid crystals were filtered off and vacuum dried to give 0.80 g of pure complex **1** (89% yield). ^1H NMR (300 MHz, D_2O): δ 2.18 and 2.3 (br, total 8H, cod $-\mathrm{C}H_2-$), 4.3 (br, 4H, cod $=\mathrm{C}H-$), 2.19 (t, 2H, $-O_2\mathrm{CC}H_2-$), 1.27 (m, 12H, internal $-\mathrm{C}H_2-$), 2.53 (t, 2H, $-\mathrm{SC}H_2-$), 1.51(m, 4H, $-\mathrm{SCH_2C}H_2-$ and $-O_2\mathrm{CCH_2C}H_2-$). Anal. Found: C, 50.66; H, 7.16; S, 7.12%. Calc. for $C_{38}H_{64}O_4S_2Na_2Rh_2$: C, 50.69; H, 7.12%; S, 7.12%. MS (FAB, negative): 901 (M^+).

‡ Neat substituted styrenes (2.5 mmol) over 5.0 mL of the aqueous solution of catalyst **1** (1.3×10^{-3} M) were hydroformylated with pressurized H_2/CO (500 psi, 2 : 1 ratio of H_2 : CO) gas mixtures in a stainless steel autoclave reactor at 55 °C for 22 h. Structural ratios of aldehyde products were measured by ^1H NMR spectroscopy. (*b*: 9.62 ppm, *l*: 9.78 ppm)

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