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Rhodium Catalysts Bearing Mixed Thioether–Phosphine Ligands for Carbonylation of Methanol

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Two kinds of thioether–trialkylphosphine ligands and their Rh complexes were synthesized and applied to the carbonylation of methanol to acetic acid to reveal that one of the two complexes showed higher activity compared to Rh catalyst without any ligands.

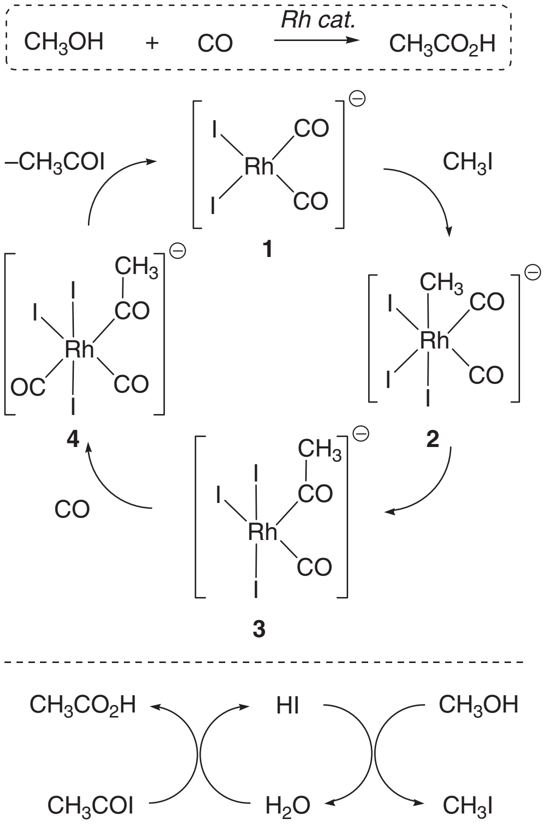
The metal–catalyzed carbonylation of methanol is a process of great importance because of overwhelming global acetic acid production.[1,2] However, since the first report of the catalyst, there has been little improvement on the intrinsic activity of the rhodium catalyst $[RhI_2(CO)_2]^-$. Thus, drastic improvement on the catalytic activity is desirable.

The overall reaction mechanism is described in Scheme 1. The rate-determining step of the catalytic cycle is the oxidative addition of CH_3I (From **1** to **2** in Scheme 1) and thus the catalyst design focused on the improvement of this oxidative addition step. The basic idea was that ligands which increase the electron density at the metal should promote oxidative addition, and consequently increase the overall rate of the reaction. For this purpose, a variety of rhodium complexes have been synthesized in the past, and they have been shown to be active catalysts of comparable or better performance compared to rhodium carbonyl species without donor ligands.[1]

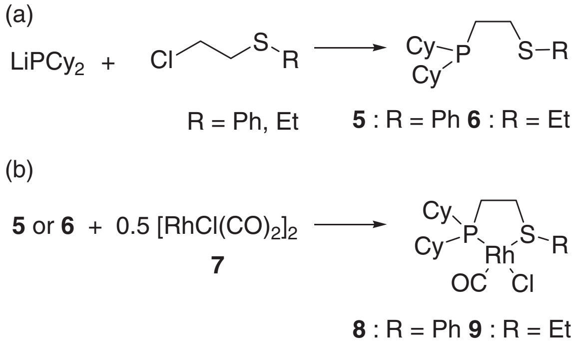
Mixed P–S ligands, such as phosphine–phosphine sulfide $Ph_2PCH_2P(=S)Ph_2$ (dppms) and phosphine–thiolate $Ph_2PC_2H_4S^-$ (dppes), are particularly attractive for incorporating an electron-rich sulfur anion together with a neutral phosphorus atom to accelerate oxidative addition and enhance activity of the catalytic carbonylation of methanol.[3–5]

On the other hand, thioether ligands have higher stability, allowing easy storage and handling. In addition, the synthetic pathway to thioether-bearing phosphine ligands is a simple one and thus both their electronic states and steric states can be easily varied,[6] compared to dppms[7] and dppes derivatives.[8,9]

Herein we report syntheses of thioether-bearing phosphine ligands, their Rh complexes, and their application to the carbonylation of methanol.



Scheme 1. Rh-catalyzed methanol carbonylation.



Scheme 2. Phosphine–thioether ligands and Rh complexes.

Since the electron-donating ability of thioether (R_2S) is clearly lower than that of thiolate (RS^-) or sulfide ($R_3P{=}S$), we focused on thioethers-bearing trialkylphosphines which are much more electron-rich than triarylphosphines.[10] Thus, the introduction of a trialkylphosphine moiety was expected to make up for the modest electron-donating ability of thioether ligands so that the overall electron-donating ability would be comparable to dppms and dppes. The new ligands **5** and **6** were easily prepared by the reaction of 2-chloroethyl sulfides with $LiPCy_2$ (Scheme 2a). The complexes **8** and **9** were prepared from ligands **5** and **6** and $[RhCl(CO)_2]_2$ **7** (Scheme 2b).

Single-crystal X-ray analyses of **8** and **9** revealed their structures and their ORTEP views are shown in Figures 1 and 2. Judging from their bond angles and bond lengths (See CIF files), all the local geometries at the palladium atoms of **8** and **9** are square planar with Rh, P, S, C, and Cl. The CO groups and phosphorus atoms of **8** and **9** are coordinated cis on the rhodium centers. Complexes **8** and **9** have ν(CO) absorption centered around 1975 (**8**) and 1979 cm^{-1} (**9**). The small

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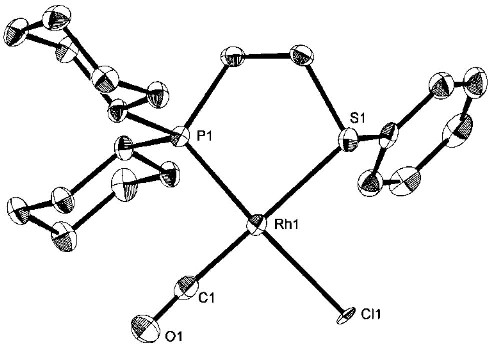

Figure 1. ORTEP drawing of **8** (all H atoms are omitted for clarity).

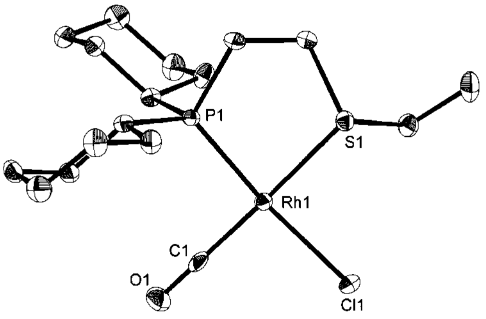

Figure 2. ORTEP drawing of **9** (all H atoms are omitted for clarity).

difference of ν(CO) absorption between **8** and **9** indicates little difference of electron-donating ability between phenyl sulfide and alkyl sulfide. Naturally, both rhodium centers of **8** and **9** are more electron-rich than the rhodium complex with triarylphosphine–thioether, $Ph_2P(o\text{-}MeSC_6H_4)$: ν(CO) 1998 cm^{-1}.[3] Furthermore, no difference in stability between **8** and **9** was seen, judging from decomposition points: **8** (177.2 to 179.3 °C) and **9** (178.2 to 180.2 °C).

The application of the rhodium complexes **8** and **9** to the carbonylation of methanol was investigated as shown in Table 1. At 120 °C for 1 h,[11] catalyst precursor $[RhCl(CO)_2]_2$ (**7**) provided 2.78 mmol of $CH_3CO_2CH_3$ and CH_3CO_2H (Run 1). Under the same conditions, catalyst precursor **8** catalyzed the carbonylation of MeOH to yield 7.13 mmol of $CH_3CO_2CH_3$ and CH_3CO_2H which is more than double the rate (Run 2), of $[RhCl(CO)_2]_2$ (**7**). However, the ^{31}P NMR spectrum of the inorganic residue indicated that some amount of ligand **5** remained bound to the Rh center after 1 h at 120 °C in the presence of large excess of MeI, while the dissociation and degradation of ligand **5** occurred.[12] The phosphine ligand would result in phosphine oxide and/or phosphonium iodide.[13] On the other hand, another precursor **9** showed slightly higher catalytic activity than $[RhCl(CO)_2]_2$ (**7**) (Run 3). Thus, significant difference in catalytic activity between **8** and **9** was seen although complexes **8** and **9** have nearly the same ν(CO) absorption values indicating negligible difference of the electron center on the Rh centers in **8** and **9**. At 180 °C, all the complexes **7**–**9** provided nearly the same amount of $CH_3CO_2CH_3$ and CH_3CO_2H (Runs 4–6). At 180 °C, the dissociation of ligands would be promoted to give phosphine oxide and phosphonium iodide. Judging from no ^{31}P NMR spectra of Rh–P bonds with ligands **5** and **6**,[14] ligands **5** and **6** did not possess enough stability under the industrial conditions (180 °C, CO 5.2 MPa), while other thioether-bearing phosphine ligands such as $Ph_2P(2\text{-}MeSC_6H_4)$ and $Ph_2PC_2H_4SMe$ can increase catalytic activity under the harsh conditions (185 °C, CO 70 bar).[3] It should be noted that the ratio of CH_3CO_2H to $CH_3CO_2CH_3$ was greatly enhanced at 180 °C, compared to 120 °C. In order to confirm that the enhanced activity was achieved by not phosphine oxide and/or phosphonium iodide derived from **5** but ligand **5**, phosphine oxide and phosphonium iodide were added to **7** (Runs 7 and 8). Addition of $[PBu_3Me]^+I^-$ to $[RhCl(CO)_2]_2$ (**7**) inhibited catalytic activity (Run 7), compared with the result of $[RhCl(CO)_2]_2$ (**7**) (Run 1). The dissociation and degradation of phosphine ligand into phosphonium iodide would retard the catalytic cycle.[4] Finally, addition of phosphine oxide $O{=}POct_3$ to $[RhCl(CO)_2]_2$ (**7**) showed no influence on catalytic activity (Run 8). Results of Runs 7 and 8 indicate that enhanced catalytic activity (Run 2) results from coordination of ligand **5** on the Rh center.

Table 1. Carbonylation Experiments[a)]

Run	Rh cat.	T/°C	t/h	$CH_3CO_2CH_3$ /mmol	CH_3CO_2H /mmol
1	**7**	120	1.0	2.48	0.300
2	**8**	120	1.0	6.24	0.891
3	**9**	120	1.0	2.81	0.491
4	**7**	180	0.5	5.15	4.77
5	**8**	180	0.5	5.00	5.10
6	**9**	180	0.5	6.24	3.80
7[b)]	**7**	120	1.0	1.88	0.276
8[c)]	**7**	120	1.0	2.48	0.362

a) Experiments were carried out in a 50-cm^3 autoclave equipped with a vessel. Reaction conditions after 15 min at room temperature: Rh catalyst (0.0280 mmol), MeOH (10.5 mL), H_2O (2.28 mL), MeI (1.74 mL, 28.0 mmol), and CO 2.5 MPa at rt (3.2 MPa at 120 °C, 5.2 MPa at 180 °C). Yield was determined by NMR spectra with internal standard ($CHCl_2CHCl_2$). b) $[PBu_3Me]^+I^-$ (0.0280 mmol) was added. c) $O{=}POct_3$ (0.0280 mmol) was added.

In conclusion, new mixed phosphine–thioether ligands **5** and **6** and their rhodium complexes **8** and **9** were synthesized and applied to the carbonylation of methanol. Rhodium complex **8** demonstrated higher yield of $CH_3CO_2CH_3$ and CH_3CO_2H at 120 °C than $[RhCl(CO)_2]_2$ (**7**), while rhodium complex **9** gave slightly higher catalytic activity. On the other hand, at 180 °C, all the complexes **7**–**9** provided nearly the same amount of $CH_3CO_2CH_3$ and CH_3CO_2H. This may be due to the dissociation of ligands which were converted into phosphine oxide and phosphonium iodide.

Experimental

Carbonylation of MeOH. A solution of Rh catalyst (28.0 µmol) and MeI (28.0 mmol) in MeOH (10.5 mL) and H_2O (2.28 mL) was added to a 50-cm^3 autoclave equipped with a vessel. All reactor valves were closed. The solution was stirred at room temperature for 15 min under CO pressure (2.5 MPa at room temperature). The solution in the autoclave was stirred at an assigned temperature. After the reactor was rapidly cooled to room temperature, the reactor valve was opened to release CO gas. As an internal standard, $CHCl_2CHCl_2$ was added to the resultant solution to determine yield of AcOH and AcOMe.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-724017 and -724018 for compounds **8** and **9**, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information

Experimental procedures and identification data of newly synthesized compounds. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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11 Before the carbonylation of MeOH carried out at high temperature, resultant solution of all material was stirred at room temperature for 15 min (See experimental section). No acetic acid or methyl acetate were detected for 15 min at room temperature.

12 The amount of phosphine ligand bound to the Rh center can not be measured precisely, because an unidentified broad peak was detected. Moreover, it should be noted that the difference of the activity between **7** and **8** decreased for 2 h, compared with 1 h (**8**: $CH_3CO_2CH_3$ 8.77 mmol and CH_3CO_2H 2.15 mmol, **7**: $CH_3CO_2CH_3$ 5.72 mmol and CH_3CO_2H 1.10 mmol.).

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14 ^{31}P NMR spectrum of the residue in Run 5 showed only one singlet peak at 56.5 ppm.