

## Efficient Carbonylation of Methanol Catalyzed by Rhodium(I) Cyclooctadiene Complexes with Triphenylphosphinechalcogenide Ligands

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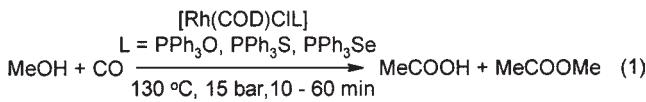
Rhodium(I) complexes of the type,  $[\text{Rh}(\text{COD})\text{Cl}]$  ( $\text{COD} = 1,5\text{-cyclooctadiene}$  and  $\text{L} = \text{Ph}_3\text{PO}$ ,  $\text{Ph}_3\text{PS}$  and  $\text{Ph}_3\text{PSe}$ ) have been synthesized. The complexes show higher efficiency as catalyst for carbonylation of methanol to acetic acid and methyl acetate at  $130^\circ\text{C}$  and 15 bar pressure than the industrially used species  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ .

Rhodium catalyzed carbonylation of methanol is a commercially important route for the production of acetic acid and methyl acetate. Since the first report,<sup>1</sup> the species  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ , has been used as preferred commercial catalyst. Research activities are continued to replace the existing rhodium catalyst either by incorporating different types of electron donating ligands in the metal complex species<sup>2</sup> or by changing the metal center.<sup>3</sup> Recently, BP chemicals has introduced<sup>4</sup> a new catalytic process for acetic acid synthesis in which rhodium is replaced by iridium (Cativa process).

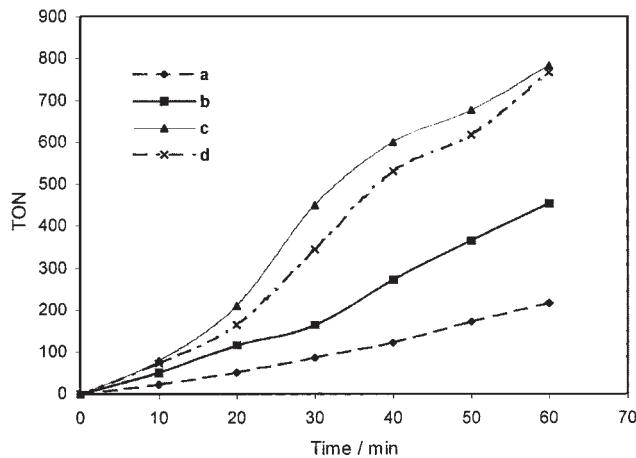
As a part of our work<sup>5</sup> i.e., the effects of various ligands on rhodium catalyzed carbonylation of methanol, we report here synthesis and catalytic activity of rhodium(I) complexes containing 1,5-cyclooctadiene and triphenylphosphinechalcogenide ligands.

The dimeric complex,  $[\text{Rh}(\text{COD})\text{Cl}]_2$ , undergoes bridge splitting reaction with two equivalent of triphenylphosphinechalcogenide in dichloromethane under refluxing condition for 30 min to yield complexes of the type  $[\text{Rh}(\text{COD})\text{ClL}]$  ( $\text{L} = \text{Ph}_3\text{PO}$ ,  $\text{Ph}_3\text{PS}$  and  $\text{Ph}_3\text{PSe}$ ). The IR spectra of the complexes show  $\nu(\text{P}=\text{O})$ ,  $\nu(\text{P}=\text{S})$  and  $\nu(\text{P}=\text{Se})$  bands at 1170, 600 and  $540\text{ cm}^{-1}$  respectively which are 30, 33 and  $18\text{ cm}^{-1}$  less compared to the corresponding free ligands indicating complexation through chalcogen donor. The complexes have also been characterized<sup>6</sup> by elemental analysis,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectroscopy.

The results of batch carbonylation of methanol<sup>7</sup> to acetic acid and methyl acetate in the presence of complexes  $[\text{Rh}(\text{COD})\text{Cl}]$  as catalyst precursors (eq 1) are shown in Figure 1 and 2.

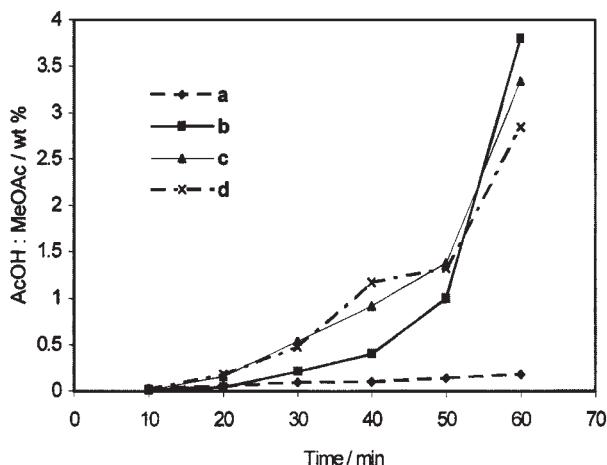


The Figure 1 indicates that for any reaction time, the complexes  $[\text{Rh}(\text{COD})\text{Cl}]$  show higher turn over number (TON) compared to the well known species,  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  generated *in-situ* from the added  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ .<sup>2c,8</sup> With the progress of reaction time, the TON of the catalyst increases and at 60 min, maximum TON of 453, 782 and 766 with corresponding conversion of 58, 100 and 98% have been obtained for the complexes containing phosphineoxide, phosphinesulfide and phosphineselenide, respectively. Such a high TON shown by the complexes  $[\text{Rh}(\text{COD})\text{Cl}]$  over  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  as catalyst

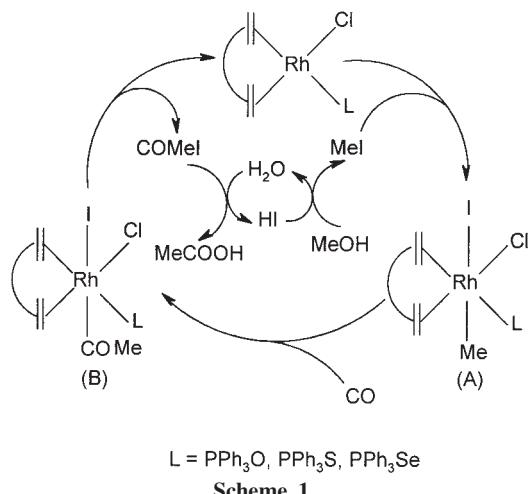


**Figure 1.** The TON with corresponding time of carbonylation reaction of methanol in the presence of (a)  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ ; (b)  $[\text{Rh}(\text{COD})\text{Cl}(\text{PPh}_3\text{O})]$ ; (c)  $[\text{Rh}(\text{COD})\text{Cl}(\text{PPh}_3\text{S})]$ ; (d)  $[\text{Rh}(\text{COD})\text{Cl}(\text{PPh}_3\text{Se})]$  as catalyst precursors.  $\text{TON} = \frac{\text{Moles of product}}{\text{Moles of catalyst} \times \text{reaction time}}$  Moles of product have been calculated from GC analysis.

precursors may be attributed to the high nucleophilicity of the rhodium center caused by the presence of (i) COD group which has a lesser  $\pi$ -acceptor capacity compared to CO group and (ii)  $\text{Ph}_3\text{PX}$  ( $\text{X}=\text{O}$ ,  $\text{S}$  and  $\text{Se}$ ) group, which are stronger donor than iodide. It is interesting to note that the complexes containing phosphinesulfide and phosphineselenide ligand show much higher activity compared to that containing phosphineoxide ligand. This higher activity may be attributed to the soft nature of Rh(I) which interacts strongly with soft S or softer Se atom and thus provides more electron density on the rhodium centre as compared to hard oxygen. It may be mentioned here that the present complexes  $[\text{Rh}(\text{COD})\text{Cl}]$  (except  $\text{L} = \text{PPh}_3\text{O}$ ) showed much higher catalytic activity for carbonylation of methanol even under milder reaction conditions and within shorter reaction time compared to our earlier work<sup>5a</sup> where the complexes of the type  $[\text{Rh}(\text{CO})_2\text{Cl}]$  ( $\text{L} = \text{PPh}_3\text{O}$ ,  $\text{PPh}_3\text{S}$ ,  $\text{PPh}_3\text{Se}$ ) exhibited a maximum conversion of 72–75% methanol at  $150^\circ\text{C}$  and 20 bar pressure within a period of 1.5 h. It is clear (Figure 2) that with the progress of the reaction, the selectivity of the catalyst changes i.e. initially the major product was methyl acetate but near the end of the reaction acetic acid was the major yield (in our earlier work<sup>5a</sup> methyl acetate was the major yield). Among the complexes, the one containing phosphineoxide ligand shows the lowest  $\text{AcOH} : \text{MeOAc}$  ratio upto about 50 min reaction time and thereafter the ratio changes steeply to the highest value during 60 min. After completion of reaction (60 min run) the catalysts have been recovered and on recycling<sup>9</sup> for second time, almost same amount of conversion was obtained indicating longer durability as well as



**Figure 2.** The ratio of acetic acid and methyl acetate with time for carbonylation of methional in the presence of (a)  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ ; (b)  $[\text{Rh}(\text{COD})\text{Cl}(\text{PPh}_3\text{O})]$ ; (c)  $[\text{Rh}(\text{COD})\text{Cl}(\text{PPh}_3\text{S})]$ ; (d)  $[\text{Rh}(\text{COD})\text{Cl}(\text{PPh}_3\text{Se})]$  as catalyst precursors.



**Scheme 1.**

stability of the catalyst.

A possible pathway (Scheme 1) has been proposed for the above mentioned reaction where a Rh(III) alkyl complex (A) and Rh(III) acyl complex (B) act as intermediates. The acyl species (B) on subsequent reductive elimination of MeCOI gives back the parent complex and thus completes the cycle. This mechanism is similar to the cycle for catalysis by  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ .<sup>10</sup> The above mechanistic route is proposed on the basis of separately done model reaction of  $[\text{Rh}(\text{COD})\text{Cl}(\text{Ph}_3\text{PS})]$  with MeI, which leads to the formation of  $[\text{Rh}(\text{COD})\text{Cl}(\text{Me})(\text{Ph}_3\text{PS})](\text{A})$ .<sup>11</sup> The complex A in methanol reacts with CO gas (6 bar) at 130 °C and 15 bar pressure for 1 h converts to a rhodium acyl complex  $[\text{Rh}(\text{COD})\text{Cl}(\text{COMe})(\text{Ph}_3\text{PS})](\text{B})$ .<sup>12</sup>

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- 6 Analytical and spectroscopic data of the complexes,  $[\text{Rh}(\text{COD})\text{Cl}(\text{PPh}_3\text{O})]$ : yield: 98%; Anal. Calcd for  $\text{C}_{26}\text{H}_{27}\text{ClPORh}$ : C, 59.54; H, 5.15%; Found: C, 59.41; H, 5.13%. IR (KBr/cm<sup>-1</sup>): 1170 (ν PO). NMR (300 MHz, in  $\text{CDCl}_3$ , δ, <sup>1</sup>H): 7.70–7.27 (m,  $\text{C}_6\text{H}_5$ ), 4.22 (-CH=CH), 2.49 (-CH<sub>2</sub>-C); <sup>13</sup>C{<sup>1</sup>H}: 133.13–128.40 (m,  $\text{C}_6\text{H}_5$ ), 78.76 (-CH=CH), 30.11 (-CH<sub>2</sub>-C); <sup>31</sup>P{<sup>1</sup>H}: 29.81.  $[\text{Rh}(\text{COD})\text{Cl}(\text{PPh}_3\text{S})]$ : Yield: 99%; Anal. Calcd for  $\text{C}_{26}\text{H}_{27}\text{ClPSRh}$ : C, 57.77; H, 5.00%; Found: C, 57.91; H, 5.02%. IR (KBr/cm<sup>-1</sup>): 600 (ν PS). NMR (300 MHz, in  $\text{CDCl}_3$ , δ, <sup>1</sup>H): 7.75–7.41 (m,  $\text{C}_6\text{H}_5$ ), 5.30 (-CH=CH), 2.48 (-CH<sub>2</sub>-C); <sup>13</sup>C{<sup>1</sup>H}: 132.44–128.41 (m,  $\text{C}_6\text{H}_5$ ), 78.57 (-CH=CH), 30.85 (-CH<sub>2</sub>-C); <sup>31</sup>P{<sup>1</sup>H}: 43.87.  $[\text{Rh}(\text{COD})\text{Cl}(\text{PPh}_3\text{Se})]$ : Yield: 98%; Anal. Calcd for  $\text{C}_{26}\text{H}_{27}\text{ClPSeRh}$ : C, 53.15; H, 4.59%; Found: C, 53.03; H, 4.62%. IR (KBr/cm<sup>-1</sup>): 540 (ν PSe). NMR (300 MHz, in  $\text{CDCl}_3$ , δ, <sup>1</sup>H): 7.76–7.26 (m,  $\text{C}_6\text{H}_5$ ), 4.23 (-CH=CH), 2.46 (-CH<sub>2</sub>-C); <sup>13</sup>C{<sup>1</sup>H}: 134.87–128.66 (m,  $\text{C}_6\text{H}_5$ ), 78.79 (-CH=CH), 33.10 (-CH<sub>2</sub>-C); <sup>31</sup>P{<sup>1</sup>H}: 31.81 (d,  $J_{\text{PSe}} = 364$  Hz).
- 7 Catalytic experiment: MeOH (3.1 ml, 0.077 mol); MeI (1 ml, 0.006 mol);  $\text{H}_2\text{O}$  (1 ml, 0.055 mol) and the complex  $[\text{Rh}(\text{COD})\text{Cl}(\text{PPh}_3\text{O})]$  (24 mg, 0.046 mmol) or  $[\text{Rh}(\text{COD})\text{Cl}(\text{PPh}_3\text{S})]$  (25 mg, 0.046 mmol) or  $[\text{Rh}(\text{COD})\text{Cl}(\text{PPh}_3\text{Se})]$  (27 mg, 0.046 mmol) was charged into the reactor. The reactor was purged with CO gas for about 5 min and then pressurized with CO gas (6 bar, 0.036 mol) at about 30 °C. The pressure in the reactor was maintained at 15 bar by increasing the temperature to 130 °C.
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- 9 Catalyst recycle experiment: recycle experiments were done by maintaining the same experimental condition as described in Ref. 7.
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- 11  $[\text{Rh}(\text{COD})\text{Cl}(\text{Me})(\text{PPh}_3\text{S})]$ : Yield: 68%; Anal. Calcd for  $\text{C}_{27}\text{H}_{30}\text{ClIPh}_3\text{SRh}$ : C, 47.50; H, 4.39%; Found: C, 47.61; H, 4.37%. IR (KBr/cm<sup>-1</sup>): 593 (ν PS). NMR (300 MHz, in  $\text{CDCl}_3$ , δ, <sup>1</sup>H): 7.82–7.36 (m,  $\text{C}_6\text{H}_5$ ), 5.18 (-CH=CH), 2.43 (-CH<sub>2</sub>-C), 1.91 (-CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H}: 131.97–127.90 (m,  $\text{C}_6\text{H}_5$ ), 78.01 (-CH=CH), 31.01 (-CH<sub>2</sub>-C), 11.1(CH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H}: 44.26.
- 12  $[\text{Rh}(\text{COD})\text{Cl}(\text{COMe})(\text{PPh}_3\text{S})]$ : Yield: 72%; Anal. Calcd for  $\text{C}_{28}\text{H}_{30}\text{ClIPh}_3\text{SRh}$ : C, 47.32; H, 4.22%; Found: C, 47.20; H, 4.20%. IR (KBr/cm<sup>-1</sup>): 595 (ν PS), 1700 (ν CO). NMR (300 MHz, in  $\text{CDCl}_3$ , δ, <sup>1</sup>H): 7.76–7.27 (m,  $\text{C}_6\text{H}_5$ ), 5.07 (-CH=CH), 2.46 (-CH<sub>2</sub>-C), 3.01 (-COCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H}: 132.07–128.01 (m,  $\text{C}_6\text{H}_5$ ), 78.49 (-CH=CH), 30.87 (-CH<sub>2</sub>-C), 209.10 (-CO), 37.10 (-CH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H}: 44.06.