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Modification of Rhodium Catalyst with Stibines for Hydroformylation of 1-Pentene

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Homogeneous hydroformylation of 1-pentene under synthesis gas experimental conditions was studied using $RhClCO(PPh_3)_2$ complex with different triarylstibines. Three different stibine ligands SbR_3 [where R = 2,4,6-mesityl (TMS), 2-furyl (TFS), 2-N,N-dimethylbenzylamine (TDMBAS)], have been tested. It is interesting to note that 2:1 addition of these stibine ligands to the $RhClCO(PPh_3)_2$ complex catalyst increases the aldehydes yields with an appreciable n:iso ratio. The catalytic activity of the system shows a TDMBAS > TMS > TFS pattern which indicates that not only basicity of the ligand alone is playing a role in the activity but the steric effect is also very important, and it is combination of these two factors that contributes to the resulting catalytical activity. The maximum yield of aldehydes obtained were 98.7% with n/iso = 1.4 when $RhClCO(PPh_3)_2$ + TFS system was used and 93.7% with n/iso = 2.43 when TDMBAS ligand was studied.

Keywords: Stibines; Hydroformylation; Rhodium catalyst.

INTRODUCTION

There exist a number of reports on modification of rhodium catalyst by different phosphines ligands;[1,2] however, there are a few reports on the modification of these catalysts with stibine ligands.[4,5] Recently our group has reported the modification of Rh and Co catalysts by different arylstibines for hydroformylation and amidocarbonylation reactions.[6-8] In view of the scanty reports on the modification of Rh with antimony ligands in hydroformylation reactions, this work was undertaken. This paper presents the modification of rhodium catalyst viz. $RhClCO(PPh_3)_2$ with different stibines in the hydroformylation of 1-pentene.

MATERIALS

All the solvents used were purified, dried and deoxygenated. $RhCOCl(PPh_3)_2$ was purchased from Strem Chemicals Company. 1-Pentene, $SbCl_3$, were obtained from Aldrich. CO, H_2 were obtained from Matheson and Aga Gas Inc., respectively, and used without further purification. The ligands SbR_3 (where R = 2,4,6-mesityl, 2-furyl, 2-N,N-dimethylbenzylamine) were prepared according to the literature.[9-11]

Measurements

The reaction products were analyzed on JEOL JMS-AX505 HA GC-MS equipment with a 25 m × 10.3 mm glass column packed with 5% phenylsilicone and compared with pure Aldrich samples, quantified by GC using hexane as an internal standard (added after the reaction and just before analyzation) in a Hewlett Packard 5890 analyzer with a 20 m × 0.2 mm glass column packed with Carbowax 20 M. The IR spectra were obtained by using a Nicolet FTIR Magna 750 spectrometer.

General Catalytic Procedure

In a Schlenck tube, 9.143×10^{-5} mol of catalyst $[RhCOCl(PPh_3)_3]$ and 2×10^{-4} mol of ligand (1:2 molar ratio) were dissolved in 5 mL of benzene. This mixture was stirred for three minutes and 9.143×10^{-3} mol of 1-pentene was added. The solution was transferred through a syringe to a stainless steel reactor previously closed and purged 2 or 3 times with CO. After this the pressure reactor was used until the desired pressure (800 psig CO/H_2, 1:1) and then

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Table 1. Reaction effect of several parameters on the hydroformylation of 1-pentene with $RhClCO(PPh_3)_2$ using different stibines ligands

Run	Ligand	Ratio Cat/ligand	Ratio Pressures[a]	Temperature (°C)	Time (hrs)	Yield	1-pentene	iso-aldehyde	n-aldehyde	Ratio n/iso
1	TMS	1/2	3/1	120	4	88.46	11.54	29.53	58.93	1.99
2	TMS	1/2	1/1	120	4	91.47	8.53	28.18	63.32	2.25
3	TMS	1/2	1/3	120	4	78.02	21.98	26.29	51.73	1.97
4	TFS	1/2	3/1	120	4	98.07	1.93	40.84	57.23	1.40
5	TFS	1/2	1/1	120	4	37.90	62.10	14.47	23.42	1.62
6	TFS	1/2	1/3	120	4	48.17	51.83	19.49	28.68	1.47
7	TDMBAS	1/2	3/1	120	4	92.21	7.30	26.88	65.33	2.43
8	TDMBAS	1/2	1/1	120	4	93.74	3.43	27.77	65.97	2.37
9	TDMBAS	1/2	1/3	120	4	89.22	10.28	22.88	6.34	2.90
10	TMS	1/2	3/1	120	2	77.30	22.70	26.61	50.69	1.92
11	TMS	1/2	3/1	120	3	83.51	16.49	30.98	52.52	1.70
12	TMS	1/2	1/1	120	2	86.68	13.40	28.78	57.82	2.00
13	TMS	1/2	1/1	120	3	88.63	11.64	28.32	60.04	2.12
14	without	1/0	1/1	120	4	65.10	34.90	19.50	45.60	2.30
15	TMS	1/2	1/3	120	2	73.64	26.36	21.55	52.09	2.42
16	TMS	1/2	1/3	120	3	76.46	23.54	23.01	53.45	2.32
17	TMS	1/2	1/3	150	2	57.47	42.53	19.14	38.33	2.00
18	TMS	1/2	1/3	150	3	63.90	36.10	20.90	43.00	2.06
19	TMS	1/2	1/3	150	4	77.30	22.70	26.61	50.69	1.91
20	TMS	1/2	1/3	150	6	83.44	15.56	24.20	59.24	2.45
21	TMS	1/2	1/1	150	4	88.36	11.64	28.32	60.04	2.12
22	TMS	1/2	3/1	150	4	75.46	25.54	22.01	52.45	2.32

Experimental conditions: 1-pentene 9.14 × 10^{-3} mol; $RhClCO(PPh_3)_2$ 9.14 × 10^{-5} mol; ligand 2 × 10^{-4} mol; benzene 5 mL; 800 psig CO/H_2 total pressure.

[a] CO/H_2 ratios: 3/1 = P_{CO} 600 psig and P_{H2} 200 psig; 1/1 = P_{CO} 400 psig and P_{H2} 400 psig; 1/3 = P_{CO} 200 psig and P_{H2} 600 psig.

Table 2. Reaction effect of several parameters on the hydroformylation of 1-pentene with $RhClCO(PPh_3)_2$ using different stibines ligands

Run	Ligand	Ratio Cat/ligand	Ratio Pressures[a]	Temperature (°C)	Time (hrs)	Yield	1-pentene	iso-aldehyde	n-aldehyde	Ratio n/iso
23	without	1/0	3/1	120	4	69.15	30.85	48.70	20.45	0.42
24	TFS	1/1	3/1	120	4	53.38	47.62	18.84	34.54	1.83
25	TFS	3/1	3/1	120	4	42.63	57.37	14.60	28.03	1.92
26	TFS	1/1	3/1	80	4	22.10	1.93	8.03	14.07	1.75
27	TFS	1/1	3/1	100	4	70.00	3.00	27.27	42.23	1.52
28	without	1/0	3/1	120	4	69.15	30.85	48.70	20.45	0.42
29	TDMBAS	1/1	1/3	120	2	79.40	20.15	20.82	58.58	2.81
30	TDMBAS	1/1	1/3	120	4	89.59	10.33	23.80	65.79	2.76
31	TDMBAS	1/1	1/3	120	5	94.55	4.98	25.28	69.27	2.74
32	TDMBAS	1/1	1/3	120	6	88.63	10.95	24.18	64.45	2.67

Experimental conditions: 1-pentene 9.14 × 10^{-3} mol; $RhClCO(PPh_3)_2$ 9.14 × 10^{-5} mol; ligand 1 × 10^{-4} mol; benzene 5 mL; 800 psig CO/H_2 total pressure.

[a] CO/H_2 ratios: 3/1 = P_{CO} 600 psig and P_{H2} 200 psig; 1/1 = P_{CO} 400 psig and P_{H2} 400 psig; 1/3 = P_{CO} 200 psig and P_{H2} 600 psig.

warmed in an oil bath at 120 °C for 4 h.; at the end of this time, the reactor was cooled, (final pressure was 650 psig) and the gas was liberated. The solution was percholated through a column packed with alumina and the resulting yellow solution was analyzed using GC and GC-MS. In the case of reactions at different time intervals, several experiments in the same conditions were performed.

RESULTS AND DISCUSSION

From runs 1 to 9, it was observed that Rh/TDMBAS in a 1:2 ratio produces a catalytic system which is very active and is independent of synthesis gas partial pressures. It also produces higher selectivity in comparison to the other two systems. The catalytic system Rh/TMS is more active and selective in comparison to the Rh/TFS system. The last system exhibits very good activity depending on CO and H_2 partial pressures. It is to be mentioned that none of the catalytic systems favors the hydrogenation reaction, and formation of pentane is less than 2%.

Runs 10 to 16 show the variation of aldehydes yield as a time function at different partial pressures using Rh/TMS as catalytic system. The highest yield of aldehydes was obtained at a partial pressure ratio of CO/H_2 1:1. Run 14 shows that without the stibine ligand, the aldehyde yield is lower. It was also observed that though H_2 partial pressure is higher, the system does not favour the formation of pentane.

In runs 17 to 20, on comparing the conversions in run 3, it was observed that there is a decrease in the product conversion with the increase of temperature. This indicates that reaction favours 120 °C, and at a higher temperature of 150 °C probably uncoordination of the stibine ligand favors producing an inactivated species in the Rh/TMS system.

On comparing run 4 with runs 23 to 25 it was observed that the optimum ligand/catalyst TFS/Rh ratio is 2/1 and gives higher yields with high selectivity for linear aldehydes. An increase in ligand/catalyst ratio produces a less active catalytic species than without the modified catalyst. Reactions 1 and 7 show that Rh/TMS and Rh/TDMBAS catalytic systems are less active under these conditions, although these appear more selective toward the linear aldehyde.

Runs 26 and 27 shows that the reaction does not proceed practically < 100 °C using the Rh/TFS catalytic system. The formation of aldehyde increases notably at 120 °C. Reaction carried out without the ligand exhibits less conversion with low selectivity toward linear aldehyde in comparison to run 4. This comparison indicates that catalytic precursor $RhClCO(PPh_3)_2$ is less active than the Rh/TFS catalytic system. It is to be mentioned here that these experimental conditions do not give reduction products.

Runs 29 to 31 shows that Rh/TDMBAS, in a ratio 1/1, is an active catalytic system even at 1:3 CO/H_2 pressure ratio and produces an appreciable yield of aldehyde in less time. This study also confirms that a Rh/TDMBAS catalytic system is independent of CO/H_2 partial pressures.

On comparing the catalytic precursors viz. $RhClCO(PPh_3)_2$, $RhClCO(PPh_3)_2$ + TMS, $RhClCO(PPh_3)_2$ + TFS, $RhClCO(PPh_3)_2$ + TDMBAS, it was observed that ligand effect on the catalytic activity of the system shows a (2-N,N-dimethylbenzylamine)stibine > (2,4,6-mesityl)stibine > (2-furyl)stibine pattern which indicates that not only basicity of the ligand alone is playing role in the activity but steric effect is also very important and it is a combination of these two factors which explain the resulting catalytic activity.[6,7] It was concluded that the better acceptor character of stibines is responsible for its important trans effect and in the homogeneously catalyzed hydroformylation process.[6-8] The trans effect[12,13] of these stibine ligands may be responsible for the enhancement of exchange of ligands.

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