

4.1.1.14 Effects of Metal-Containing Additives in Ruthenium Systems

Tests were continued on additional lanthanide complexes as additives. It was found that when $\text{Dy}(\text{OAc})_3$ was added to the catalyst system of ruthenium carbonyl/ $\text{P}(\text{n-Bu})_4\text{Br}$, it enhanced the formation of ethanol without much effect on the activity of the catalyst system. Results are shown in Table 13.

Other related metal complexes have also been tested as catalyst additives to the phosphonium salt system. The additives $\text{Gd}(\text{OAc})_3$, $\text{Ce}(\text{acac})_3$, $\text{Er}(\text{OAc})_3$, $\text{Nd}(\text{OAc})_3$, $\text{Tb}(\text{OAc})_3$, and $\text{Th}(\text{OAc})_3$ seemed to have either a slight positive effect or no effect on the activity and the selectivity to higher alcohols. $\text{Ho}(\text{OAc})_3$ did not affect the activity but increased the formation of ethanol moderately. $\text{Yb}(\text{OAc})_3$, $\text{Yb}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, and ZrCl_2 retarded the catalyst activity severely. Results of these experiments are also given in Table 13.

It has been found that use of the novel metal-containing additive A38 in the catalyst system of ruthenium carbonyl/iodide in NMP causes the activity of the the system to increase substantially. More interestingly, the ratio of C_2+ products increased dramatically, and the major C_2+ product, amounting to about 33%, is ethanol. In longer reaction times, the amount of methanol is only about a few percent. Initial results are presented in Table 14.

When A38 was used as an additive in the ruthenium carbonyl/ $\text{P}(\text{n-Bu})_4\text{Br}$ system, the results were similar to those carried out in NMP. The only difference may be the larger amount of other oxygenates being formed in the molten salt system. The activity of the catalyst system was also increased. Most significantly, it was found that even at 3000 psi, the system was reasonably active, as shown in Table 15.

It has also been demonstrated that by adding the precursors of A38, for example, A57/A58 or A16/A58, to the catalyst system of

$\text{Ru}_3(\text{CO})_{12}$ /molten phosphonium salt, effects similar to those of A38 itself were observed. However, A38 remains a superior additive to its precursors. Results of these experiments are presented in Table 16.

When an experiment was carried out under 2:1 H_2/CO syngas, the activity of the system dropped compared to that seen under 1:1 syngas. This suggests that a higher CO partial pressure is essential for the homologation step(s).

Modification of the ligand has not led to a further increase in the activity of the catalyst system. For example, A59, A60, and A61 are modifications of A38, but they do not provide catalytic results as good as A38. Nevertheless, one particular modification did yield some interesting results. When A62 was added to the molten salt system, it caused the system to produce more propanol than previous systems. Electron-donating groups on this ligand seem to retard the homologation steps of this particular system, while electron-withdrawing groups caused the system to produce other oxygenates. Results of these experiments are presented in Table 16.

We have also investigated the combination of organic additives of the type described in the following section with metal-containing additives; this combination can sometimes be added as a single complex. Table 17 shows the results relating to this area of research. One particular combination that deserves attention is that of Ru/A16/A92. This system is very active at 6000 psi and produces mainly methanol and methyl formate. Nevertheless, when iodide or iodine was added to the system, the formation of ethanol increased moderately and the activity of the catalyst system is not affected.

We have investigated other solvents with this particular system. Sulfolane was found to be a good solvent, probably because of the greater solubility of potassium iodide in this solvent. Compared to the results which we obtained for systems of Ru/KI/A38 or its derivatives in NMP, the overall activity is just as good or better for the A92 system in sulfolane. Most importantly, the

production of higher alcohols is better and the system produces only small amounts of the other oxygenates previously seen. Rates of higher alcohol formation are very good.

We also have carried out a few experiments in THF solvent. We found that the activity of Ru/KI/A92 is perhaps better in THF than in sulfolane. For the system of Ru/A16/KI/A92, C₂+ alcohol formation is less in THF than in sulfolane.

Since potassium iodide is more soluble in alcohols than in most other organic solvents, the alcohols could conceivably be used as solvents as well. In methanol, the system of Ru/A16/KI/A92 produces C₂+ alcohols at a rate of 1.4 M/h. Since there is a weight loss for methanol, the catalyst system no doubt is converting methanol to ethanol; but since there is also a net gain in the molar quantity of alcohols, this can be taken as evidence that the system is actually producing methanol. We also experimented in using ethanol as solvent for the same system and found that methanol is produced along with ethanol and n-propanol. A weight increase in ethanol was also noted in that experiment indicating that ethanol is being produced.

The results of the above experiments show that alcohols can be used as reaction solvents for these catalytic systems. Such a process could have practical advantages, since another solvent may not be required, and recycle of lower alcohols could lead to increased yields of the higher alcohols.

We have screened other metal complexes with the Ru/KI/A92 catalyst system. The two metal compounds Mo(CO)₆ and SmNO₃ were observed to increase the catalytic activity. Only the SmNO₃ was seen to increase the C₂+ content slightly.

Key to Tables 13 to 21

SGHAM-L-#

1 Catalyst	Catalyst precursor charged.
2 mmol	Amount of catalyst precursor used.
3 Solvent	Solvent used.
4 mL/g	Amount of solvent used, in mL or grams.
5 Additive	Additive employed.
6 mmol	Amount of additive used.
7 Press., psi	Reaction pressure in psig.
8 Temp., °C	Reaction temperature.
9 Time, hrs.	Reaction time in hours.
10 H ₂ /CO	Syngas molar ratio.
11 MeOH, g	Amount of methanol produced, in grams.
12 EtOH, g	Amount of ethanol produced, in grams.
13 n-PrOH, g	Amount of n-propanol produced, grams.
14 n-BuOH, g	Amount of n-butanol produced, grams.
15 CH ₃ CHO, g	Amount of acetaldehyde produced, grams.
16 Other Ox., g	Amount of other oxygenates produced, grams.
17 Tot. Prod., g	Weight of total products analyzed.
18 % EtOH	Wt. percent ethanol (or C ₂ + alcohols) of products formed.
19 C ₂ +/C ₁ ratio	Wt. ratio of C ₂ and higher products to methanol.

Table 13. Effects of Metal Complexes as Additives

SGHAM-L-#	2-27	2-13	3-34	4-78
1 Catalyst	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$
2 mmol	1.25	1.25	1.25	1.25
3 Solvent	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$
4 mL/g	15.0g	15.0g	15.0g	15.0g
5 Additive	$\text{Dy}(\text{OAc})_3$	$\text{Dy}(\text{OAc})_3$	$\text{Yb}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	ZrCl_2
6 mmol	0.60	2.4	1.5	1.5
7 Press., psi	5000	5000	5000	5000
8 Temp., °C	230	230	230	230
9 Time, hrs.	3.0	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0	1.0
11 MeOH, g	4.4	1.6	1.4	NA ^a
12 EtOH, g	1.3	3.4	1.5	NA ^a
13 n-PrOH, g	-	-	0.25	NA ^a
14 n-BuOH, g	-	-	trace	NA ^a
15 CH_3CHO , g	-	-	0.13	NA ^a
16 Other Ox., g	-	-	0.30	NA ^a
17 Tot. Prod., g	5.7	5.0	3.6	NA ^a
18 % EtOH	23	68	49	NA ^a
19 C_2/C_1 ratio	0.30	2.1	1.6	NA ^a

Experimental procedure: B(4); Analytical procedure: C(4); Key on page 63.

^a Not analyzed; very small amounts of products formed.

Table 13. Effects of Metal Complexes as Additives (Cont'd)

SGHAM-L-#	3-52	3-11	3-40
1 Catalyst	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$
2 mmol	1.25	1.25	1.25
3 Solvent	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$
4 mL/g	15.0g	15.0g	15.0g
5 Additive	none	$\text{Yb}(\text{OAc})_3$	$\text{Er}(\text{OAc})_3$
6 mmol	-	1.5	1.5
7 Press., psi	5000	5000	5000
8 Temp., °C	230	230	230
9 Time, hrs	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0
11 MeOH, g	3.0	1.6	2.4
12 EtOH, g	1.7	1.4	3.0
13 n-PrOH, g	0.32	0.12	0.24
14 n-BuOH, g	trace	trace	trace
15 CH_3CHO , g	0.1	trace	0.29
16 Other Ox., g	0.27	trace	0.55
17 Tot. Prod., g	5.4	3.1	6.4
18 % C_2+ alcohols	39	-	51
19 C_2+/C_1 ratio	0.8	-	1.7

Experimental procedure: B(4); Analytical procedure: C(4); Key on page 63.

Table 13. Effects of Metal Complexes as Additives (Cont'd)

SGHAM-L-#	3-44	3-46	3-50
1 Catalyst	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$
2 mmol	1.25	1.25	1.25
3 Solvent	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$
4 mL/g	15.0g	15.0g	15.0g
5 Additive	$\text{Gd}(\text{OAc})_3$	$\text{Nd}(\text{OAc})_3$	$\text{Ce}(\text{acac})_3$
6 mmol	1.5	1.5	1.2
7 Press., psi	5000	5000	5000
8 Temp., °C	230	230	230
9 Time, hrs	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0
11 MeOH, g	2.5	2.7	2.7
12 EtOH, g	3.1	3.3	3.0
13 n-PrOH, g	0.24	0.23	0.2
14 n-BuOH, g	trace	trace	trace
15 CH_3CHO , g	0.29	0.35	0.28
16 Other Ox., g	0.55	0.69	0.52
17 Tot. Prod., g	6.7	7.3	6.7
18 % C_2+ alcohols	50	48	48
19 C_2+/C_1 ratio	1.7	1.7	1.5

Experimental procedure: B(4); Analytical procedure: C(4); Key on page 63.

Table 13. Effects of Metal Complexes as Additives (Cont'd)

SGHAM-L-#	4-82	3-56	3-62
1 Catalyst	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$
2 mmol	1.25	1.25	1.25
3 Solvent	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$
4 mL/g	15.0g	15.0g	15.0g
5 Additive	$\text{Tb}(\text{OAc})_3$	$\text{Th}(\text{OAc})_3$	$\text{Ho}(\text{OAc})_3$
6 mmol	1.5	1.5	1.5
7 Press., psi	5000	5000	5000
8 Temp., °C	230	230	230
9 Time, hrs	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0
11 MeOH, g	2.7	3.4	1.8
12 EtOH, g	2.9	2.1	2.9
13 n-PrOH, g	0.18	0.19	0.27
14 n-BuOH, g	trace	0.0	0.0
15 CH_3CHO , g	0.26	0.20	0.31
16 Other Ox., g	0.73	0.40	0.50
17 Tot. Prod., g	6.8	6.3	5.8
18 % C_2+ alcohols	45	36	55
19 C_2+/C_1 ratio	1.5	0.9	2.2

Experimental procedure: B(4); Analytical procedure: C(4); Key on page 63.

Table 14. Effects of Additive A38 in NMP Solvent

SGHAM-L-#	3-33	2-41	2-49
1 Catalyst	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$
2 mmol	1.25	1.25	1.25
3 Solvent	NMP	NMP	NMP
4 mL/g	50.0g	30.0g	30.0g
5 Additive	KI	KI/A38	KI/A38
6 mmol	11	11/1.5	11/3.0
7 Press., psi	6000	6000	6000
8 Temp., °C	230	230	230
9 Time, hrs.	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0
11 MeOH, g	3.1	3.4	2.3
12 EtOH, g	0.3	2.7	4.3
13 n-PrOH, g	0.0	0.3	0.3
14 n-BuOH, g	0.0	0.0	0.0
15 CH_3CHO , g	trace	1.4	2.0
16 Other Ox., g	trace	0.4	1.6
17 Tot. Prod., g	3.4	8.2	10.5
18 % EtOH	9.0	33	41
19 C_2+C_1 ratio	0.1	1.4	3.6

Experimental procedure: B(5); Analytical procedure: C(4); Key on page 63.

Table 15. Effects of Additive A38 in Phosphonium Salt Solvent

SGHAM-L-#	2-55	2-63	2-67	1-115
1 Catalyst	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$
2 mmol	1.25	1.25	1.25	1.25
3 Solvent	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$
4 mL/g	15.0g	15.0g	15.0g	15.0g
5 Additive	A38	A38	A38	A38
6 mmol	3.0	3.0	3.0	3.0
7 Press., psi	5000	4000	4000	3000
8 Temp., °C	230	230	230	230
9 Time, hrs.	3.0	3.0	6.0	3.0
10 H_2/CO	1.0	1.0	1.0	1.0
11 MeOH, g	2.8	1.3	1.7	2.0
12 EtOH, g	5.4	3.5	5.2	2.3
13 n-PrOH, g	1.1	0.9	1.2	0.7
14 n-BuOH, g	0.0	0.0	0.0	0.0
15 CH_3CHO , g	trace	0.2	0.3	0.1
16 Other Ox., g	7.0	4.6	6.8	2.9
17 Tot. Prod., g	16.3	10.5	15.0	8.0
18 % EtOH	33	33	35	29
19 C_2+C_1 ratio	4.8	7.1	7.8	3.0

Experimental procedure: B(4); Analytical procedure: C(4); Key on page 63.

Table 16. Effects of Metal-Containing Additives

SGHAM-L-#	1-123	1-129	1-119
1 Catalyst	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$
2 mmol	1.25	1.25	1.25
3 Solvent	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$
4 mL/g	15.0g	15.0g	15.0g
5 Additive	A16	A16/A58	A57
6 mmol	3.0	3.0/3.0	3.0
7 Press., psi	5000	5000	5000
8 Temp., °C	230	230	230
9 Time, hrs	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0
11 MeOH, g	0.89	2.7	0.15
12 EtOH, g	1.70	3.1	0.26
13 n-PrOH, g	0.59	1.0	trace
14 n-BuOH, g	0.0	0.26	0.0
15 CH_3CHO , g	trace	0.25	trace
16 Other Ox., g	9.4	5.7	3.4
17 Tot. Prod., g	12.6	13.0	3.8
18 % C_2+ alcohols	18	34	6.8
19 C_2+/C_1 ratio	13	3.8	-

Experimental procedure: B(4); Analytical procedure: C(4); Key on page 63.

Table 16. Effects of Metal-Containing Additives (Cont'd)

SGHAM-L-#	1-131	2-79	3-29
1 Catalyst	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$
2 mmol	1.25	1.25	1.25
3 Solvent	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$
4 mL/g	15.0g	15.0g	15.0g
5 Additive	A57/A58	A59	A60
6 mmol	3.0/3.0	3.0	3.0
7 Press., psi	5000	5000	5000
8 Temp., °C	230	230	230
9 Time, hrs	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0
11 MeOH, g	1.0	1.9	2.5
12 EtOH, g	2.7	3.3	3.1
13 n-PrOH, g	0.80	1.2	0.96
14 n-BuOH, g	0.36	0.38	0.30
15 CH_3CHO , g	0.20	0.26	0.31
16 Other Ox., g	5.4	5.3	4.1
17 Tot. Prod., g	10.5	12.3	11.2
18 % C_2+ alcohols	37	40	39
19 C_2+/C_1 ratio	9.5	5.5	3.4

Experimental procedure: B(4); Analytical procedure: C(4); Key on page 63.

Table 16. Effects of Metal-Containing Additives (Cont'd)

SGHAM-L-#	2-81	3-19	2-55 ^a	2-103 ^a
1 Catalyst	Ru ₃ (CO) ₁₂	Ru ₃ (CO) ₁₂	Ru ₃ (CO) ₁₂	Ru ₃ (CO) ₁₂
2 mmol	1.25	1.25	1.25	1.25
3 Solvent	NMP	NMP	P(n-Bu) ₄ Br	P(n-Bu) ₄ Br
4 mL/g	30.0 mL	30.0 mL	15.0g	15.0g
5 Additive	KI/A59	KI/A61	A38	A38
6 mmol	9.0/3.0	9.0/3.0	3.0	3.0
7 Press., psi	6000	6000	5000	5000
8 Temp., °C	230	230	230	230
9 Time, hrs	3.0	3.0	3.0	3.0
10 H ₂ /CO	1.0	1.0	1.0	1.0
11 MeOH, g	2.3	2.5	2.8	3.71
12 EtOH, g	3.3	2.4	5.4	3.48
13 n-PrOH, g	0.41	0.14	1.1	0.43
14 n-BuOH, g	trace	trace	0.34	trace
15 CH ₃ CHO, g	1.9	1.4	0.10	0.25
16 Other Ox., g	1.9	1.4	7.7	2.5
17 Tot. Prod., g	9.9	7.9	17.8	10.4
18 % C ₂ + alcohols	37	32	38	38
19 C ₂ +/C ₁ ratio	3.3	2.2	5.4	1.8

Experimental procedure: B(5); Analytical procedure: C(4); Key on page 63.

^a Experimental procedure B(4).

Table 16. Effects of Metal-Containing Additives (Cont'd)

SGHAM-L-#	3-24	3-28	2-106
1 Catalyst	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$
2 mmol	1.25	1.25	1.25
3 Solvent	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$
4 mL/g	15.0g	15.0g	15.0g
5 Additive	A62	A79	A80
6 mmol	3.5	3.0	3.5
7 Press., psi	5000	5000	5000
8 Temp., °C	230	230	230
9 Time, hrs	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0
11 MeOH, g	1.76	2.03	0.56
12 EtOH, g	3.55	2.69	1.21
13 n-PrOH, g	1.47	0.92	0.36
14 n-BuOH, g	0.58	0.32	0.41
15 CH_3CHO , g	0.18	0.23	0.16
16 Other Ox., g	5.8	4.52	7.2
17 Tot. Prod., g	13.3	10.7	9.86
18 % C_2+ alcohols	42	37	20
19 C_2+/C_1 ratio	6.6	4.3	17

Experimental procedure: B(4); Analytical procedure: C(4); Key on page 63.

Table 17. Effects of Metal-Containing Additives

SGHAM-L-#	3-54	3-70
1 Catalyst	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$
2 mmol	2.2	2.2
3 Solvent	NMP	NMP
4 mL/g	50.0g	50.0g
5 Additive	A16/A94	A99
6 mmol	1.5/3.7	1.0
7 Press., psi	6000	6000
8 Temp., °C	230	230
9 Time, hrs	3.0	3.0
10 H_2/CO	1.0	1.0
11 MeOH, g	2.2	3.5
12 EtOH, g	2.8	1.7
13 n-PrOH, g	0.2	0.26
14 n-BuOH, g	trace	0.0
15 CH_3CHO , g	1.0	0.61
16 Other Ox., g	0.2	0.6
17 Tot. Prod., g	6.4	6.7
18 % C_2+ alcohols	47	29
19 C_2+/C_1 ratio	1.9	0.91

Experimental procedure: B(5); Analytical procedure: C(4); Key on page 63.

Table 17. Effects of Metal-Containing Additives (Cont'd)

SGHAM-L-#	3-60	4-98	4-84	4-90
1 Catalyst	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$	$\text{Ru}_3(\text{CO})_{12}$
2 mmol	1.8	1.8	1.8	1.8
3 Solvent	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$	$\text{P}(\text{n-Bu})_4\text{Br}$
4 mL/g	15.0g	15.0g	15.0g	15.0g
5 Additive	A100/A16	A94/C6	A101	A99
6 mmol	3.0/3.0	4.1/0.82	3.0	1.0
7 Press., psi	5000	5000	5000	5000
8 Temp., °C	230	230	230	230
9 Time, hrs	3.0	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0	1.0
11 MeOH, g	0.13	0.61	0.60	0.77
12 EtOH, g	0.36	1.8	1.8	2.0
13 n-PrOH, g	0.17	0.94	0.69	0.54
14 n-BuOH, g	0.74	1.3	0.82	0.18
15 CH_3CHO , g	trace	0.10	0.18	0.32
16 Other Ox., g	6.8	12.3	8.0	0.7
17 Tot. Prod., g	8.1	17.1	12.1	4.5
18 % C_2+ alcohols	16	24	27	60
19 C_2+/C_1 ratio	61	27	11	4.8

Experimental procedure: B(4); Analytical procedure: C(4); Key on page 63.

Table 17. Effects of Metal-Containing Additives (Cont'd)

SGHAM-L-#	2-129	4-117	4-119
1 Catalyst	Ru ₃ (CO) ₁₂	Ru ₃ (CO) ₁₂	Ru ₃ (CO) ₁₂
2 mmol	2.2	2.2	2.2
3 Solvent	Toluene	Toluene	Toluene
4 mL/g	40.0g	40.0g	40.0g
5 Additive	A16/A92	A16/A92/I ₂	A16/A92/PPNI ^a
6 mmol	93/1.5	93/1.5/2.0	93/1.5/19
7 Press., psi	6000	6000	6000
8 Temp., °C	230	230	230
9 Time, hrs	3.0	3.0	3.0
10 H ₂ /CO	1.0	1.0	1.0
11 MeOH, g	11.2	10.2	8.7
12 EtOH, g	0.20	1.4	1.6
13 n-PrOH, g	0.0	0.0	0.0
14 n-BuOH, g	0.0	0.0	0.0
15 CH ₃ CHO, g	0.0	0.0	0.0
16 Other Ox., g	4.4	2.9	2.1
17 Tot. Prod., g	15.8	14.5	12.4
18 % C ₂ + alcohols	1.3	10	13
19 C ₂ +C ₁ ratio	0.13	0.18	0.25

Experimental procedure: B(5); Analytical procedure: C(4); Key on page 63.

^a PPNI = bis(triphenylphosphine)iminium iodide.

Table 17. Effects of Metal-Containing Additives (Cont'd)^a

SGHAM-L-#	6-19	6-17	6-20
1 Catalyst	Ru ₃ (CO) ₁₂	Ru ₃ (CO) ₁₂	Ru ₃ (CO) ₁₂
2 mmol	2.20	2.20	2.20
3 Solvent	Sulfolane	Sulfolane	Sulfolane
4 mL	40.00	40.00	40.00
5 Additive	A16/KI	A16/KI/A92	A16/KI/A92
6 mmol	3.4/30	3.4/30/93	4.6/30/93
7 Press., psi	6000	6000	6000
8 Temp., °C	230	230	230
9 Time, hr.	3.00	3.00	3.00
10 H ₂ /CO	1.00	1.00	1.00
11 MeOH, g	1.40	5.90	2.60
12 EtOH, g	0.75	8.40	7.00
13 n-PrOH, g	0.00	1.60	1.60
14 n-BuOH, g	0.00	0.00	0.00
15 CH ₃ CHO, g	0.00	0.00	0.00
16 Other Ox., g	2.15	0.78	0.00
17 Tot. Prod., g	4.30	16.68	11.20
18 % C ₂ + alcohols	17	60	77
19 C ₂ +C ₁ ratio	2.1	1.8	3.3

Experimental procedure: B(16); Analytical procedure: C(10); Key on page 63.

^a Experiments conducted in last quarter of contract.

Table 17. Effects of Metal-Containing Additives (Cont'd)^a

SGHAM-L-#	4-124	4-134	4-136
1 Catalyst	Ru ₃ (CO) ₁₂	Ru ₃ (CO) ₁₂	Ru ₃ (CO) ₁₂
2 mmol	2.20	2.20	2.20
3 Solvent	Sulfolane	Sulfolane	Sulfolane
4 mL	40.00	40.00	40.00
5 Additive	A16/KI/A92	A16/KI/A92	A16/KI/A92
6 mmol	3.4/30/93	3.4/30/93	3.4/30/93
7 Press., psi	5000	4000	3000
8 Temp., °C	230	230	230
9 Time, hr.	2.00	3.00	3.00
10 H ₂ /CO	1.00	1.00	1.00
11 MeOH, g	2.40	1.60	3.70
12 EtOH, g	4.60	3.40	1.30
13 n-PrOH, g	0.71	0.42	0.00
14 n-BuOH, g	0.00	0.00	0.00
15 CH ₃ CHO, g	0.00	0.00	0.00
16 Other Ox., g	0.00	0.00	0.00
17 Tot. Prod., g	7.71	5.42	5.00
18 %C ₂ + alcohols	69	70	26
19 C ₂ +/C ₁ ratio	2.2	2.4	0.35

Experimental procedure: B(16); Analytical procedure: C(10); Key on page 63.

^a Experiments conducted in last quarter of contract.

Table 17. Effects of Metal-Containing Additives (Cont'd)^a

SGHAM-L-#	6-42	6-45
1 Catalyst	Ru ₃ (CO) ₁₂	Ru ₃ (CO) ₁₂
2 mmol	2.2	2.2
3 Solvent	THF	THF
4 mL	45	45
5 Additive	KI/A92	A16/KI/A92
6 mmol	30/93	3.4/30/93
7 Press., psi	5000	5000
8 Temp., °C	230	230
9 Time, hr.	3.0	3.0
10 H ₂ /CO	1.0	1.0
11 MeOH, g	13.10	11.20
12 EtOH, g	2.40	5.00
13 n-PrOH, g	0.20	0.29
14 n-BuOH, g	0.00	0.00
15 CH ₃ CHO, g	0.00	0.00
16 Other Ox., g	1.71	1.47
17 Tot. Prod., g	17.41	17.96
18 % C ₂ + alcohols	15	29
19 C ₂ +C ₁ ratio	0.21	0.47

Experimental procedure: B(16); Analytical procedure: C(10); Key on page 63.

^a Experiments conducted in last quarter of contract.

Table 17. Effects of Metal-Containing Additives (Cont'd)^a

SGHAM-L-#	6-27	6-43	6-44
1 Catalyst	Ru ₃ (CO) ₁₂	Ru ₃ (CO) ₁₂	Ru ₃ (CO) ₁₂
2 mmol	2.2	2.2	2.2
3 Solvent	Methanol	Ethanol	Ethanol
4 mL	40	50	50
5 Additive	A16/KI/A92	KI/A92	A16/KI/A92
6 mmol	1.0/30/93	30/93	4.7/30/93
7 Press., psi	6000	5000	5000
8 Temp., °C	230	230	230
9 Time, hr.	3.0	3.0	3.0
10 H ₂ /CO	1.0	1.0	1.0
11 MeOH, g	-5.0 ^b	6.90	11.50
12 EtOH, g	8.80	-1.5 ^b	3.6 ^b
13 n-PrOH, g	1.10	1.73	2.12
14 n-BuOH, g	0.00	0.00	0.35
15 CH ₃ CHO, g	0.00	0.00	0.00
16 Other Ox., g	1.82	0.25	0.75
17 Tot. Prod., g	6.72	7.38	18.32
18 % C ₂ + alcohols	na	na	31
19 C ₂ +/C ₁ ratio	1.20	0.25	0.75

Experimental procedure: B(16); Analytical procedure: C(10); Key on page 63.

^a Experiments conducted in last quarter of contract.

^b This alcohol was used as solvent; based on weight gain or loss.

Table 17. Effects of Metal-Containing Additives (Cont'd)^a

SGHGAM-L-#	6-16	3-113
1 Catalyst	Ru ₃ (CO) ₁₂	Ru ₃ (CO) ₁₂
2 mmol	2.2	2.2
3 Solvent	Toluene	Sulfolane
4 mL	30	40
5 Additive	Mo(CO) ₆ /A92	SmNO ₃ /KI/A92
6 mmol	30/93	8.5/17/93
7 Press., psi	5000	5000
8 Temp., °C	230	230
9 Time, hr.	3.0	3.0
10 H ₂ /CO	1.0	1.0
11 MeOH, g	16.00	8.60
12 EtOH, g	0.00	1.70
13 n-PrOH, g	0.00	0.73
14 n-BuOH, g	0.00	0.00
15 CH ₃ CHO, g	0.00	0.00
16 Other Ox., g	2.11	3.92
17 Tot. Prod., g	18.11	14.95
18 % C ₂ + alcohols	0	16
19 C ₂ +/C ₁ ratio	0.02	0.70

Experimental procedure: B(16); Analytical procedure: C(10); Key on page 63.