Journal of Organometallic Chemistry, 222 (1981) 143—153
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

PROMOTION BY PHOSPHORUS COMPOUNDS OF RUTHENIUM-CATALYZED METHYL FORMATE HOMOLOGATION

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(Received June 24th, 1981)

Summary

Trivalent phosphorus compounds are promoters for methyl formate homologation to ethanol and ethyl formate catalyzed by ruthenium compounds in the presence of iodide at 220°C and 27 MPa of synthesis gas. Under these conditions the phosphines are quaternized, but decomposition of phosphonium salts occurs during the reaction. Promotion is also observed for methyltriphenylphosphonium bromide and triphenylphosphine sulfide, but benzyltrimethylammonium bromide, triphenylarsine, and triphenylantimony are not effective. The major ruthenium species present is $Ru(CO)_3I_3^-$ but with triphenylantimony a trimethylantimony complex, $Ru(CO)_2(Sb(CH_3)_3)_2I_2$, can be isolated in high yield.

Introduction

As petroleum resources dwindle, methanol and other chemicals readily derivable from carbon monoxide and hydrogen (so-called synthesis gas) will increasingly replace ethylene as basic petrochemical feedstocks. Thus, processes for C_2 chemicals from such feedstocks are of special interest. A number of catalysts have been reported for the homologation of methanol to acetaldehyde and ethanol [1]. The most effective are based upon soluble Co compounds with phosphine ligands and iodide promoters [2]. Selectivity to ethanol over acetaldehyde is enhanced by the addition of a Ru cocatalyst [3].

Catalysts for the production of C_2 chemicals from methyl esters have also been reported. Methyl acetate is converted to acetic anhydride and ethylidene diacetate with Rh catalysts and iodide promoters [4], and catalysts based upon

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0022-328X/81/0000—0000/$02.50

Ni and iodide carbonylate methyl acetate to acetic anhydride [5]. Homologation of methyl acetate to ethyl acetate is achieved using Co [6] and Ru [7] compounds, again with iodide promotion. The Ru system has more recently been reported to homologate methyl formate to ethyl formate under the same conditions [8]. A related report concerning Ru/I catalysis of homologation of carboxylic acids has recently appeared [9].

Methyl formate, although not currently a large-volume chemical, is another feedstock readily derivable from synthesis gas, either directly [10] or by carbonylation of methanol [11]. Moreover, methyl formate homologation to ethanol, unlike methanol homologations, does not require energy-intensive removal of water from the product.

From methanol:

$$2\ CO + 4\ H_2 \rightarrow CH_3OH + CO + 2\ H_2 \rightarrow C_2H_5OH + H_2O$$

From methyl formate:

$$3\ CO + 3\ H_2 \rightarrow HCO_2CH_3 + CO + H_2 \rightarrow C_2H_5OH + CO_2$$

For these reasons we have examined catalysts for the homologation of methyl formate to ethanol, emphasizing Co and Ru catalysts previously found effective for methanol and methyl acetate homologation.

Results

The most active catalysts for methanol homologation to ethanol consist of mixtures of soluble Co and Ru compounds with phosphines and iodide-containing compounds as promoters. Methanol homologations with these catalysts are typically performed at 175—220°C and 14—35 MPa * of synthesis gas [4]. In our initial trials for methyl formate homologation, we used cobalt(II) acetylacetonate, ruthenium(III) acetylacetonate ($Ru(acac)_3$), triphenylphosphine, and lithium iodide in molar ratios of 1 : 1 : 2 : 4 and operated at 220°C and 27 MPa of 1/1 CO/H_2 with methyl formate as solvent. This system was indeed catalytic for methyl formate homologation to primarily ethanol and ethyl formate. However, in subsequent experiments we observed that the mixed Co-Ru system was no more active than the Ru component alone. By contrast, for methanol homologation the Co component is more active and the Ru compound is added to improve selectivity to ethanol. We were also surprised to find that the $Ru/PPh_3/I$ catalyst system was considerably more active than $Ru(acac)_3$ with methyl iodide [12] alone, which had previously been reported [9], (compare runs 1 and 2 in Table 1). Consequently, we systematically studied the effects of added Lewis bases upon the activity and selectivity of Ru-catalyzed methyl formate homologation.

For all catalysts studied (see Table 1) the major liquid products were methanol, ethanol, and ethyl formate with smaller amounts of dimethyl acetal and methyl acetate. In most cases methyl ethers were present in only trace amounts. These results differ from those of a previous study of methyl formate homologation by $Ru(acac)_3$ and methyl iodide at 200°C and 15 MPa, which

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* 1 MPa = 9.87 atmospheres.

found 14% conversion after 17.5 h to a mixture of ethyl formate (33.5%), methyl acetate (36.0%), and acetic acid (13.0%) [9]. In our hands only low yields of acetates were formed.

The stoichiometry for methyl formate homologation to ethanol is given by eq. 1:

$$HCO_2CH_3 + CO + H_2 \rightarrow CO_2 + C_2H_5OH \qquad (1)$$

Methanol is formed by reaction between methyl formate and ethanol and also by decarbonylation of methyl formate (eq. 2):

$$HCO_2CH_3 \rightarrow CO + CH_3OH \qquad (2)$$

A significant and highly undesirable reaction is decarboxylation of methyl formate, according to eq. 3:

$$HCO_2CH_3 \rightarrow CO_2 + CH_4 \qquad (3)$$

This last reaction occurred to a large extent in all of our runs (average ca. 10—15% conversion of methyl formate), but the relative proportion of methyl formate decarboxylated to methane varied considerably from run to run, even under identical conditions. It is possible that small amounts of the metal may be responsible for some of the methane formed, since it is known that metallic Ru catalyzes hydrogenolysis of alkyl halides, methyl iodide being the presumed organic intermediate. Since the overall molar yields of homologated products were reproducible for identical runs, regardless of the amount of methane formed, it seems likely that eq. 3 represents a side reaction rather than a competing path for the same intermediate species. In any case, because of carbon dioxide and methane production via eqs. 1 and 3, the partial pressures of carbon monoxide and hydrogen dropped during the reaction and the rate of homologation fell off accordingly. Because liquid sampling during a run required the introduction of some additional synthesis gas, methyl formate conversion was increased for sampled runs and all comparisons of yields are for batch reactions or for identically sampled runs.

Of the Lewis bases tested as promoters, significant yield enhancements for ethanol and ethyl formate were only observed for trivalent phosphorus ligands or for triphenylphosphine sulfide (see Table 1). For the phosphines PR_3 little variation with the nature of R was observed, but 1,2-bis(diphenylphosphino)ethane was not a promoter [13]. It soon became clear that, although phosphine ligands were effective promoters, they were not stable under the reaction conditions (vide infra), and after a single 5 h run catalyst activity decreased significantly. The original activity could be restored by the addition of more phosphine.

The fate of the phosphorus ligand was investigated by ^{31}P NMR spectroscopy. Product solutions were evaporated to dryness and then spectra were obtained of the residues as deuterochloroform solutions. With triphenylphosphine as promoter, the spectrum of the catalyst residue (run 2) displayed over 27 resonances between —29 and +32 ppm downfield from 1 *M* phosphoric acid with the most intense resonance at 18.8 ppm assigned to the methyltriphenylphosphonium cation (cf. $CH_3P(C_6H_5)_3I$, 18.6 ppm). However, quaternization was not the mechanism for catalyst deactivation because methyltriphenylphos-

TABLE 1

PRODUCT YIELDS FROM HOMOLOGATION OF METHYL FORMATE[a]

Run no.	Catalyst (mmol)	Ligand (mmol)	Product (mol)					
			CH_3OH	HCO_2CH_3	C_2H_5OH	$HCO_2C_2H_5$	$CH_3CO_2CH_3$	$CH_3CH(OCH_3)_2$
1	$Ru(acac)_3(0.55)$	—	0.23	2.55	—	0.04	—	—
2[b]	$Ru(acac)_3(0.55)$	$PPh_3(2.2)$	0.44	1.45	0.15	0.26	0.03	0.02
3	$Ru(acac)_3(0.55)$	$PMe_2Ph(2.2)$	0.26	1.69	0.05	0.16	0.02	0.03
4	$Ru(acac)_3(0.55)$	$PBu_3(2.2)$	0.34	1.29	0.10	0.18	0.04	0.09
5	$Ru(acac)_3(0.55)$	$SPPh_3(2.2)$	0.54	1.45	0.12	0.29	—	0.03
6	$Ru(acac)_3(0.55)$	$MePPh_3I(2.2)$	0.38	1.41	0.07	0.35	0.02	—
7[c]	$Ru(acac)_3(0.55)$	$MePPh_3Br(2.2)$	0.68	1.41	0.17	0.35	—	0.03
8	$Ru(acac)_3(0.55)$	$BzNMe_3Br(2.2)$	0.32	2.23	—	0.06	—	—
9	$Ru(acac)_3(0.55)$	$AsPh_3(2.2)$	0.38	2.36	—	0.06	0.01	—
10	$Ru(acac)_3(0.55)$	$SbPh_3(2.2)$	0.26	2.21	—	0.04	—	—
11[d]	$Ru(CO)_3(PPh_3)_2(0.55)$	$PPh_3(1.1)$	0.31	1.69	0.09	0.20	—	0.01
12	—	$PPh_3(2.2)$	0.12	2.45	—	—	—	—

[a] Reaction conditions: Initial charge of methyl formate, 2.84 mol; methyl iodide, 5.4 mmol; 220°C; 27 MPa of 1/1 CO/H_2; 4 h after catalyst injection. [b] Final gas analysis (mol percent): Methane (24%), carbon dioxide (16%), carbon monoxide (29%), hydrogen (24%). [c] Final gas analysis (mol percent): Methane (26%), carbon dioxide (18%), carbon monoxide (23%), hydrogen (29%). [d] Source of iodide: Methyl iodide (2.1 mmol), lithium iodide (2.2 mmol).

phonium iodide was as effective as triphenylphosphine for promotion of methyl formate homologation catalyzed by $Ru(acac)_3$ and methyl iodide [14]. Indeed, the ^{31}P NMR spectrum of the catalyst residue from run 6 displayed not only the resonance due to the methyltriphenylphosphonium cation (18.7 ppm, rel. int. 55) but also resonances at −19.3 (rel. int. 12), 7.8 (17), 17.7 (58), and 25.3 ppm (11), as well as many other less intense peaks. In fact, the spectrum of the triphenylphosphine sulfide-promoted catalyst residue (run 5) was very similar to that of the triphenylphosphine-promoted run; after 10 h of operation no triphenylphosphine sulfide remained. These results show that triphenylphosphine, triphenylphosphine sulfide and methyltriphenylphosphonium iodide all decompose under the reaction conditions, with the most abundant single species during these runs being the methyltriphenylphosphonium cation.

The formation of phosphonium salts does not, however, eliminate the possibility that in all of these cases small amounts of trivalent phosphorus compounds might be present and might promote methyl formate homologation through generation of a very active ruthenium complex. Relevant to this aspect, it is significant that neither triphenylarsine, which forms the methyltriphenylarsonium cation under the reaction conditions, nor benzyltrimethylammonium bromide were promoters for methyl formate homologation [15]. Since these Group V cations should behave similarly to phosphonium cations, it is very unlikely that a simple cation effect is responsible for promotion.

To gain insight into the role of the phosphorus compound in promotion of homologation, the triphenylphosphine-promoted catalyst system was sampled during the course of the run. Liquid products were analyzed by gas chromatography and after evaporation of solvent the infrared spectra of the catalyst residues were recorded as dichloromethane solutions. For all additives, other than triphenylantimony, the infrared spectra of the final reaction solutions contained absorptions at 2106s, 2036s, and 1988m to s cm^{-1}. This spectrum was also observed in the absence of a promoter. Other absorptions were sometimes observed at 2118 and 2066 cm^{-1} of varying relative intensities [16]. The bands at 2106 and 2036 cm^{-1} are attributed to $Ru(CO)_3I_3^-$, previously reported to be present in the homologation catalyst systems based upon $Ru(acac)_3$ and methyl iodide alone [7]. Indeed, we were able to isolate in low yield from the final solution from a run with tricyclohexylphosphine as the added ligand a yellow, crystalline compound identified as $[CH_3P(C_6H_{11})_3][Ru(CO)_3I_3]$ (IR(CH_2Cl_2): 2105s, 2036s cm^{-1} cf. IR(H_2O) for $Cs[Ru(CO)_3I_3]$: 2112s, 2051 vs cm^{-1} [18]; ^{31}P NMR (CD_2Cl_2): 31.62 ppm cf. 31.42 ppm for $[CH_3P(C_6H_{11})_3]I$; Anal. Found: I, 45.25; P. 3.39; Ru, 11.82. Calcd. for $C_{22}H_{36}I_3PO_3Ru$: I, 44.21; P, 3.60; Ru, 11.74%). However, the relative intensities of the infrared absorptions of the product mixtures suggest additional species to account for the bands at 2036 and 1988 cm^{-1}. Since these bands are also present in the absence of phosphine, this species does not contain phosphorus.

When $Ru(acac)_3$ was used as the source of Ru, the infrared spectrum of the catalyst residue from a sample taken immediately after injection of $Ru(acac)_3$ and triphenylphosphine into the autoclave at reaction conditions showed only two carbonyl absorptions at 2060s and 1987vs cm^{-1}, which are attributed to $Ru(CO)_2(acac)_2$ [19]. This complex was still one of the major species observed in the spectrum after 1 h. Absorptions at 2106 and 2038 cm^{-1}, assigned to Ru-

$(CO)_3I_3^-$, grew in next but the band at 2106 cm^{-1} then diminished relative to the intensity of the 1988 cm^{-1} band, with concurrent shift in the absorption maximum from 2038 to 2046 cm^{-1}. By the end of the 5 h run the bands attributed to the $Ru(CO)_3I_3^-$ had increased again in relative intensity.

When $Ru(CO)_3(PPh_3)_2$ or $Ru(CO)_2(PPh_3)_2I_2$ were used as catalyst precursors, the infrared spectra of samples taken immediately after injection into the autoclave at 220°C showed bands at 2106s, 2036vs, and 1988s cm^{-1}. Spectra remained essentially unchanged throughout the 5 h run. When $Ru(acac)_3$, lithium iodide, and triphenylphosphine were treated in tetrahydrofuran at 220°C under 27 MPa of 1 : 1 synthesis gas, the isolated species were $Ru(CO)_2(PPh_3)_2I_2$ and $Ru(CO)_4(PPh_3)$. Thus, methyl iodide is an essential factor for removal of the phosphine ligands under reaction conditions.

With phosphine ligands, which are rapidly quaternized, no reliable evidence has been obtained for the existence of complexes with ruthenium under catalytic conditions. However, the use of triphenylantimony, not easily quaternized with methyl iodide, does result in formation of an isolable complex of an antimony ligand. Upon introduction of $Ru(acac)_3$ and triphenylantimony to a solution of methyl iodide and methyl formate under reaction conditions the first species observed in the infrared spectrum was $Ru(CO)_2(acac)_2$. Then smooth conversion to a species characterized by two infrared absorptions at 2036s and 1979s cm^{-1} was observed over ca. 1 h. After 5 h a pale yellow, crystalline complex could be isolated in 75% yield after chromatography on silica gel. Based upon elemental analysis, infrared and ^1H NMR spectroscopy, and mass spectrometry this species is characterized, not as the expected triphenylantimony complex, but as $Ru(CO)_2(Sb(CH_3)_3)_2I_2$. Under the reaction conditions, complete replacement of phenyl groups on antimony by methyl groups has occurred. A similar result may be expected with phosphine promoters, although phosphine complexes are not stable in the presence of methyl iodide. However, $Ru(CO)_2(Sb(CH_3)_3)_2I_2$ is no more effective as a catalyst for methyl formate homologation than $Ru(acac)_3$ and methyl iodide alone; the addition of lithium iodide as a source of free iodide ion has no effect upon the activity of this species. Trivalent arsenic and antimony ligands have been claimed as promoters for Co-catalyzed methanol homologation [3] and Rh-catalyzed methyl acetate carbonylation [4], but neither triphenylarsine nor triphenylantimony were effective for Ru-catalyzed methyl formate homologation.

Since methanol was present even before catalyst injection, we considered the possibility that methanol, rather than methyl formate, was the precursor to ethanol. However, for $Ru(CO)_3(PPh_3)_2$, which shows no induction period for decomposition to the steady-state catalyst solution, no induction period for formation of ethyl formate was observed. By contrast, for $Ru(acac)_3$, which forms moderately stable $Ru(CO)_2(acac)_2$ upon injection, an induction period of ca. 30 min was observed, approximately the time required for significant decomposition of $Ru(CO)_2(acac)_2$. In neither case was an induction period noted for methanol formation. Moreover, adding methanol to the reactor had no effect upon the quantity of C_2 products formed but did increase slightly the amount of dimethyl acetal. Others have found that Ru-catalyzed homologation of methanol is quite slow [20], and methyl iodide formation from methyl formate is more likely than from methanol under our reaction conditions.

The presumed organic intermediate in the homologation reaction is methyl iodide, generated by reaction of methyl formate with HI (eq. 4):

$$HCO_2CH_3 + HI \rightarrow HCO_2H + CH_3I \qquad (4)$$

The formic acid thus formed must decompose to carbon dioxide and hydrogen to maintain the stoichiometry of eq. 1. Contrary to a previous report of catalytic decarbonylation of formic acid under reaction conditions for methyl formate homologation with Ru(acac)$_3$ and sodium iodide [8], we found that decarboxylation was induced at temperatures as low as 130°C with the catalyst residue from run 1 in tetrahydrofuran. Analysis of the gas phase by mass spectrometry showed only carbon dioxide and hydrogen, no carbon monoxide. This result was previously reported using RuHBr(CO)(PEt$_2$Ph)$_3$ and RuHCl-(Et$_2$PC$_2$h$_4$PEt$_2$)$_2$ [21]. However, non-catalytic decarbonylation of formic acid has been used for the synthesis of Ru(CO)$_2$I$_2$ and other carbonyl complexes from Ru^{III} compounds [18,22].

Discussion

Enhancement of catalytic activity by the addition of phosphine ligands has been observed for a number of iodide-promoted homologations, including Co-catalyzed methanol homologation, Rh-catalyzed methyl acetate carbonylation, and now Ru-catalyzed methyl formate homologation. In all these systems the phosphines are expected to be quaternized under the reaction conditions. In fact, for methanol homologation above 200°C with Co and mixed Co-Ru catalysts it is unlikely that the ligands are stable for long periods under the reaction conditions. We have found that methyltriphenylphosphonium salts, triphenylphosphine, and triphenylphosphine sulfide all decompose to a complex mixture of products, with the phosphonium cation being the predominant species present in all three cases during the course of a catalyst run. Triphenylphosphine oxide, expected to be much more stable than triphenylphosphine sulfide, is not an effective promoter for the homologation reaction.

The role of the phosphorus compound for promotion of methyl formate homologation is presumed to be either (a) as a ligand to the active Ru catalyst, (b) as a phosphonium cation to the anionic Ru catalyst, or (c) as a methylating agent through methylphosphonium salts. Role (c) has recently been suggested for promotion by the tetramethylammonium cation in Fe(CO)$_5$ catalysis of methanol homologation in the absence of iodide [23]; however, this role is not likely in the presence of iodide because of the greater reactivity of methyl iodide toward nucleophiles, and benzyltrimethylammonium bromide was not a promoter for our system. Role (b) might be suggested by promotion by methyltriphenylphosphonium salts. However, since decomposition of these salts was demonstrated by the ^{31}P NMR spectra of the catalyst residues, the possibility of the presence of small amounts of trivalent phosphorus species under the reaction conditions cannot be discounted. Although no conclusive evidence for phosphine complexes was obtained, a number of compounds, including Ru(PPh$_3$)(CO)$_3$I$_2$, have infrared spectra which would be masked in the catalyst solution. Furthermore, the fact that triphenylarsine is ineffective as a promoter, even though the methyltriphenylarsonium cation should give the same cation effects as phosphonium cations, suggests an explanation other than a simple cation effect. On the other hand, ligand effects upon reactions of transition metals are commonly observed in the order N << P > As > Sb [24]. Additional support for role (a) comes from the isolation of a complex of trimethylantimony, $Ru(CO)_2(Sb(CH_3)_3)_2I_2$ from a catalyst run with triphenylantimony as an added ligand; this result suggests that methylated phosphine complexes could be formed in situ, even when triphenylphosphine is the added ligand, although the primary species under reaction conditions is the $Ru(CO)_3I_3^-$.

For Ru-catalyzed homologation of methyl formate the primary homologated products are ethyl derivatives — ethanol, ethyl formate or dimethyl acetal. Methane and carbon dioxide are also major products. Unlike Co- and Rh-catalyzed homologations, only small amounts of acetates are formed. The homologation of methyl formate is quite complex, but a likely reaction sequence based upon individual steps demonstrated in other systems can be proposed:

$$HCO_2CH_3 + HI \rightarrow CH_3I + HCO_2H \tag{4}$$

$$HCO_2H \rightarrow H_2 + CO_2 \tag{5}$$

$$CH_3I + [Ru^0] \rightarrow [CH_3Ru^{II}I] \tag{6}$$

$$[CH_3Ru^{II}I] + CO \rightarrow [CH_3CORu^{II}I] \tag{7}$$

$$[CH_3CORu^{II}I] + H_2 \rightarrow CH_3CHO + [HRu^{II}I] \tag{8}$$

$$[HRu^{II}I] \rightarrow [Ru^0] + HI \tag{9}$$

$$CH_3CHO + H_2 + [Ru] \rightarrow C_2H_5OH + [Ru] \tag{10}$$

$$C_2H_5OH + HCO_2CH_3 \rightarrow HCO_2C_2H_5 + CH_3OH \tag{11}$$

$$HCO_2H \rightarrow H_2O + CO \tag{12}$$

$$H_2O + HCO_2CH_3 \rightarrow HCO_2H + CH_3OH \tag{13}$$

$$CH_3CHO + 2\ CH_3OH \rightarrow CH_3CH(OCH_3)_2 + H_2O \tag{14}$$

$$CH_3I + H_2 + [Ru] \rightarrow CH_4 + HI + [Ru] \tag{15}$$

Methyl iodide is the presumed organic intermediate in iodide-promoted homologations of methyl alcohol, esters, or ethers. This has been substantiated for Rh-catalyzed methanol carbonylation [25]. Methyl iodide and formic acid can be produced from the reaction of HI with methyl formate (eq. 4). Decomposition of formic acid proceeds by eq. 5 and 12. The latter reaction is probably thermal, rather than metal-catalyzed [26], and is highly undesirable since it provides a path for catalytic decarbonylation of methyl formate (eq. 13). The other major side reaction, given by eq. 15, has been demonstrated by the direct reaction of methyl iodide with hydrogen using Ru catalysts under homologation conditions [7,8]. The high selectivity to ethyl derivatives is due to facile hydrogenation of the $[CH_3CORu^{II}I]$ intermediate to acetaldehyde and further, rapid hydrogenation of acetaldehyde to ethanol by Ru species (eq. 10) [27].

Promotion of homologation by phosphorus compounds is presumably due to modification of the active Ru catalyst in one or more of eqs. 6—9. At this time the identity of the catalyst is unknown, and the role of the promoter may be either a cation effect or as a ligand to the Rh catalyst. The degree of enhancement of yield could be consistent with a cation effect, but no enhancement was observed for triphenylarsine or benzyltrimethylammonium bromide, both of which should show similar cation effects under reaction conditions. On the other hand, ligand effects upon the rates of oxidative addition of methyl iodide can be quite dramatic. Oxidative addition of methyl iodide by $Ru(CO)_3(PPh_3)_2$ has been reported to be much more facile than by $Ru(CO)_5$ [24]. Equation 7 represents methyl migration to a coordinated carbonyl ligand. Particularly relevant to this process is the facile equilibrium between $Ru(\eta^2\text{-}C(O)CH_3)I(CO)(PPh_3)_2$ and $Ru(CH_3)I(CO)_2(PPh_3)_2$, reported by Roper and Wright [28]. The former species was shown by X-ray crystallography to display dihapto coordination of the acyl. A reasonable candidate for the catalyst species for methyl formate homologation in our system is $RuI(CO)_3(PR_3)^-$. Under synthesis gas, $Ru(acac)_3$ and other Ru compounds give $Ru(CO)_5$ or $Ru(CO)_4(PR_3)$ in the presence of phosphines [10a]. Iodide substitution would generate a more reactive Ru^0 anion. We have shown that phosphine-substituted Ru^{II} complexes can be isolated from the reaction of $Ru(acac)_3$ with triphenylphosphine and lithium iodide under homologation conditions in tetrahydrofuran, and trimethylantimony, formed by methylation of triphenylantimony, gives an isolable complex even in the presence of methyl iodide. A Ru^0 complex would be in equilibrium under hydrogen.

Even though a substantial increase in activity for homologation can be achieved with phosphine promoters, the activities and stabilities of these systems are still too low to be practical for industrial production. Additionally, the large amount of methanation observed under our conditions is a very substantial liability. Highly corrosive iodide-promoted catalysts must show high activity and selectivity for economical operation and further substantial improvements are required. Our work shows that under the vigorous conditions used for many of these systems, modification of the catalyst with Lewis bases is limited by ligand instability.

Experimental section

Chemicals

Ruthenium(III) acetylacetonate was supplied by Strem Chemical. Methyl iodide, methyl formate, and triphenylphosphine were obtained from Aldrich. Triphenylantimony was purchased from Alfa. Other ligands were purchased from Strem Chemical. Literature methods were used for the syntheses of $Ru(CO)_3(PPh_3)_2$ [30] and $Ru(CO)_2(PPh_3)_2I_2$ [31].

Methods of characterization

Infrared spectra were recorded using a Beckman 4250 spectrophotometer and were referenced to cyclohexane (2138.5 cm^{-1}) and polystyrene. ^{31}P NMR spectra were recorded on a Jeol FX-90Q spectrometer in deuterochloroform solution; chemical shifts are downfield from the calculated position of 1 *M* phosphoric acid. ^1H NMR spectra were recorded on a Varian EM-360 instrument. Gas chromatographic analyses of liquid products were performed on an HP 5840A instrument with a thermal conductivity detector using both 0.2%

Carbowax 1500 on 60/80 Carbopack C (6′) and 5% SE-30 on 80/100 Chromosorb W (10′) columns supplied by Supelco. Gas analyses were done by mass spctrometry. Elemental analyses were performed by Galbraith Laboratories.

Batch autoclave runs

Catalytic reactions were carried out in a 300-cc, Hastalloy C, stirred autoclave (Autoclave Engineers Magnadrive) equipped with a liquid sampling system and a catalyst injection bomb. In a typical run methyl formate (100 ml) and methyl iodide (usually 0.78 g, 5.4 mmol) were placed in the autoclave with hexane (17.0 g) as an internal standard. The unit was then pressurized to 12 MPa with 1/1 CO/H_2 and the internal temperature was brought to 220°C. Upon reaching the desired temperature the Ru catalyst (usually 0.55 mmol) and promoter (usually 2.2 mmol) were injected as a solution in methyl formate (75 ml) and then the pressure was raised to 28 MPa. After injection of the catalyst the reaction was allowed to proceed for 4 h and then the unit was cooled via internal cooling coils. A gas sample was taken and gas chromatographic analysis was performed on the final solution. Molar quantities of liquid products were determined relative to the known quantity of hexane. Definitive identification of products was achieved by GC-MS. Finally, a portion of the liquid was evaporated to dryness and the infrared spectrum of the residue in dichloromethane was recorded. Samples taken during runs were treated in the same manner.

$Ru(CO)_2(Sb(CH_3)_3)_2I_2$

A batch run as described above was performed using $Ru(acac)_3$ (0.44 g, 1.1 mmol), triphenylantimony (1.56 g, 4.4 mmol), and methyl iodide (1.56 g, 11 mmol). At the end of the run the pale yellow solution was filtered and evaporated to dryness. The residue was dissolved in dichloromethane and applied to a preparative TLC silica gel plate. Elution with dichloromethane yielded only one significant product, which had an infrared spectrum identical to that of the solution prior to chromatography. The pale yellow product was recrystallized from dichloromethane to give 617 mg (75%) of $Ru(CO)_2(Sb(CH_3)_3)_2I_2$.

IR(CH_2Cl_2): 2036s, 1979s cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.57 ppm (s). Anal. Found: C, 13.04; H, 2.30; I, 33.10; Ru, 13.56; Sb, 31.70. Calcd. for $C_8H_{18}O_2I_2$-$RuSb_2$: C, 12.90; H, 2.44; I, 34.08; Ru, 13.57; Sb, 32.70%. *m/e* 750 (^{104}Ru-$^{123}Sb_2$, rel. int. 320), 748 ($^{104}Ru^{121}Sb^{123}Sb$, $^{102}Ru^{123}Sb_2$, rel. int. 1517), 747 ($^{101}Ru^{123}Sb_2$, rel. int. 564), 746 ($^{104}Ru^{121}Sb_2$, $^{102}Ru^{121}Sb^{123}Sb$, $^{100}Ru^{121}Sb_2$, rel. int. 2490), 744 ($^{102}Ru^{121}Sb_2$, $^{100}Ru^{121}Sb^{123}Sb$, rel. int. 1875).

Acknowledgements

We thank Drs. Gerald Doyle and Roy L. Pruett for helpful discussions and Exxon Research and Engineering Company for support of this work.

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