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Homologation of methanol with a new cobalt phosphine carbonyl complex catalyst

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Abstract

A new cobalt phosphine carbonyl complex has been prepared by treating a mixture of $Co_2(CO)_8$ and tri-n-butylphosphine with synthesis gas. The structure of the complex was shown to be $Co(CO)_3PBu_3PBu_2(O)$ on the basis of ^1H, ^{13}C and ^{31}P NMR, IR, and mass spectral data, molecular weight determination and elemental analysis. The complex was found to be a very effective catalyst for the homologation of methanol, exhibiting high activity and high ethanol selectivity.

Introduction

Reaction for the synthesis of ethanol from methanol and synthesis gas (homologation of methanol) has been examined in the presence of various catalytic systems since the initial report by Wender et al. [1]. Most of the catalysts contain cobalt and iodine as their basic ingredients [2]. The catalysts have been improved by the addition of a third of fourth ingredient such as a phosphine or ruthenium [3].

We have studied extensively the homologation of methanol in order to find a more efficient catalyst system [4]. In our studies, we have found a cobalt/tri-n-butylphosphine/chlorine catalyst system without iodine which has exhibited high ethanol selectivity [5]. In the course of the development of a new catalyst system, we have found that high activity and high ethanol selectivity can be attained by prior treatment of the cobalt/tri-n-butylphosphine catalyst system with synthesis gas (designated "activation"). In addition, we have detected a new cobalt complex, which exhibits high activity and high ethanol selectivity, in the pretreated catalyst solution [6]. The structural analysis of the complex (**1**) is reported here.

Experimental

The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Hitachi R-90H spectrometer. The ^1H and ^{13}C NMR chemical shifts are relative to Me_4Si. ^{31}P NMR chemical shifts are relative to external 85% H_3PO_4. IR spectra were recorded on a

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Shimadzu IR-440 spectrometer. Mass spectra were recorded on a Shimadzu GCMS-QP1000 spectrometer.

The commercial reagents were used as received.

The reaction products were identified and determined by gas chromatography. Using Chromosolbu-101 as a column, the temperature-gradient analysis was carried out from 60 to 230 ° C at 4 ° C/min.

Preparation and isolation of complex 1

A 500-ml Hastelloy-C autoclave was charged under N_2 with $Co_2(CO)_8$ (20.0 g, 58.5 mmol), tri-n-butylphosphine (PBu_3, 47.3 g, 234 mmol) and benzene (100 g, 1.28 mol). The autoclave was twice sealed, pressurized and vented with a synthesis gas (1 : 1 H_2/CO), then pressurized to 200 kg/cm^2 and heated to 230 ° C. After 2 h, the vessel was cooled to 0 ° C, the pressure was released, and the solvent was removed.

To isolate complex **1**, the column was charged with styrene-divinylbenzene porous synthetic resin HP-20 (manufactured by Mitubishi Kasei), followed by development with hydrous methanol–anhydrous methanol and fractionation. After removal of the solvent by distillation, the solid obtained was recrystallized from n-heptane, to give complex **1** as pale yellow-green crystals: 13.0 g (22%); mp 95–96 ° C. ^1H NMR($CDCl_3$)δ(ppm) 2.13(m), 1.50(m) and 0.96(m). ^{13}C NMR($CDCl_3$)δ(ppm) 196.9(t, J 22.1 Hz), 40.7(d, J 37.3 Hz), 27.1(d, J 26.3 Hz), 24.6, 23.0(d, J 13.8 Hz) and 12.4. ^{31}P NMR($CDCl_3$)δ(ppm) 101.0(d, J 74.5 Hz) and 39.5(d, J 74.5 Hz). IR(CCl_4): ν(CO) 2046, 1972, 1952 cm^{-1} ν(PO) 1125 cm^{-1}. MS: 422, 450 and 478 (EI mass); 423, 451, 479 and 507 (CI mass). Molecular weight by freezing point depression: 510. Anal. Found: C, 54.46; H, 9.14; Co, 11.58; P, 12.19. $C_{23}H_{45}CoO_4P_2$ calcd.: C, 54.54; H, 8.96; Co, 11.64; P, 12.23%.

Homologation of methanol

A 100-ml Hastelloy-C autoclave was charged under N_2 with catalyst (11.7 mmol), methanol (10.0 g, 312 mmol) and benzene (10.0 g, 128 mmol). The autoclave was twice sealed, pressurized and vented with synthesis gas (1 : 1 H_2/CO), then pressurized to 200 kg/cm^2 and heated to 230 ° C. After 0.25–1.5 h, the vessel was cooled to 0 ° C and the pressure was released. The products were then analysed by gas chromatography.

Results and discussion

Isolation and structural characterization of the cobalt phosphine carbonyl complex

When a reaction product solution of the homologation reaction of methanol with the 'activated' Co/Cl/P catalyst [5] system was developed by thin layer chromatography, many differently-coloured spots were observed. Under suitable chromatography conditions, we succeeded in isolating complex **1** as crystals from the solution.

The structure of complex **1** was determined by ^1H, ^{13}C and ^{31}P NMR, IR, mass spectroscopy, molecular weight determination, carbon monoxide determination, elemental analysis, and from its reactions with acids.

^1H, ^{13}C and ^{31}P NMR spectra

The ^{31}P NMR spectrum exhibits two doublets at 39.5 and 101.0 ppm. This shows two cobalt-bonded phosphorus atoms in different environments. The peaks at 39.5 and 101.0 ppm appear to be due to PBu_3 and $PBu_2(O)^-$ respectively.

The peak at 196.9 ppm in the ^{13}C NMR is attributable to the carbon of the coordinated carbonyl group, and the other peaks are due to the carbons of the butyl group bonded to phosphorus. The triplet at 196.9 ppm and the doublets at 40.7, 27.1 and 23.0 ppm are all attributed to coupling with phosphorus.

The peak at 40.7 ppm, which has a large coupling constant of 37.3 Hz, suggests direct carbon-to-phosphorus bonding. The chemical shift of this carbon, however, is more downfield than that of C_1 carbon ($P-C_1-C_2-C_3-C_4$) of ordinary PBu_3. Gated Decoupling J-Splitting method, which retains coupling with hydrogen, two hydrogens are bonded to the carbon. The anomalous downfield shift of the carbon, probably the C_1 carbon of P-Bu, should be vitally important in analysing the structure of the complex. The downfield shift is assumed to be caused by the structure of $PBu_2(O)^-$.

In the ^1H NMR spectrum, the peak observed is due to the butyl group only.

IR spectra

The C–H stretching vibration was observed at 2870 to 2960 cm^{-1}, and the CO stretching vibration at 2046, 1951 and 1972 cm^{-1}. An intense absorption, observed at 1125 cm^{-1} is noteworthy. It has been reported [7], that the PO bond of the $PR_2(O)^-$ ligand has some double bond character, and so the stretching vibration of the bond should be observed at 1100 to 1200 cm^{-1}. Therefore, we suggest that the absorption is due to the PO stretching vibration of $PBu_2(O)^-$.

Mass spectra

In the EI (electron-impact ionization) mass spectrum peaks were observed at 422, 450 and 478, and in the CI (chemical ionization) mass spectrum, peaks were observed at 423, 451, 479 and 507, the difference between the values of each successive member of each series is 28 which indicates the loss of CO. When the EI mass spectrum is compared with the CI mass spectrum, the figures of the latter are all larger by 1 than those of the former, although peaks that appear are due to the same fragments. This is because $(n+1)$ ions are generated in the case of the CI mass spectrum. In this way, it is known that in CO-coordinated complexes, CO is eliminated first [8]. The molecular weight of complex **1** is 506 if three CO's are coordinated.

Molecular weight determination

The molecular weight of complex **1** was determined by cryoscopy in benzene.

An approximately linear relationship exists between the weight of complex **1** and its freezing point depression. The value of 510 was obtained as the molecular weight of complex **1**. This value agrees well with the molecular weight of 506, deduced from the mass spectra.

Determination of CO

The number of CO ligands coordinated with complex **1** was determined in benzene by reaction with I_2. For comparison, an additional investigation was carried out using $[Co(CO)_3PBu_3]_2$. The theoretical value of CO/Co for $[Co(CO)_3PBu_3]_2$ is 3.0, which is consistent with the experimental value of 2.94. In the case of the complex **1**, the CO/Co was 2.86–2.91, from which it can be deduced that three CO ligands are coordinated with Co.

Decomposition of complex 1

On addition of 6 *N* nitric acid at room temperature, both the complex **1** and $[Co(CO)_3PBu_3]_2$ decomposed immediately, and the resultant oil layer was separated from the nitric acid layer. The oil layer was extracted with chloroform, and decomposition products were studied by ^1H, ^{13}C and ^{31}P NMR spectroscopy and gas chromatography.

One of the decomposition products from $[Co(CO)_3PBu_3]_2$ was identified as tri-n-butylphosphine oxide. Two kinds of the decomposition products from complex **1** were identified as tri-n-butylphosphine oxide and dibutylphosphinic acid.

Comparison of the decomposition products of the two complexes suggests that a phosphine having the PBu_2 unit, other than PBu_3, is bonded to complex **1**. In addition, since no carbon compound could be found from the results of the ^{13}C NMR spectroscopy and gas chromatography, there is little likelihood that other carbon compounds are bonded to the PBu_2 unit.

Elemental analysis and determination of the structure of complex 1

The structure of complex **1** has been inferred to be as follows:

Two phosphorus compounds and three CO's coordinate with the metal center. The two phosphorus compounds have PBu_3 and PBu_2 units. Since no carbon compound is bonded to the PBu_2, this is probably bonded to the O, OH, H or two cobalts (phosphide). However the hypothesis that OH, H or Co is bonded to the PBu_2 unit is not possible since such bonding by any of the three is not consistent with the set of results obtained, viz. elemental analysis, molecular weight determination, IR spectrum, etc.

If the PBu_2 unit is bonded to oxygen, the elemental analysis is satisfactory, but then the oxygen is in the form O^-; cobalt is expected to be univalant in a pentacoordinated cobalt complex.

Up to now the existence of complexes having ligands such as $PR_2(O)^-$ had not been confirmed and, only a limited number of such complexes have been reported. For example, $BupyCo(DH)_2PPh_2(O)$ (Bupy = 4-t-butylpyridine, DH = dimethylglycoxymato) [7], $Et_3NH[Mo(CO)_5PPh_2(O)]$ [9], $Fe(C_5H_5)(CO)_2PPh_2(O)$ [10], and $AuP(t\text{-}Bu)_3P(t\text{-}Bu_2)(O)$ [11] are known.

Complex **1** is thus considered to have a structure as similar to that of $Co(CO)_3PBu_3PBu_2(O)$ in which PBu_3, $PBu_2(O)^-$ and three CO's are coordinated. Complex **1** is a novel compound having a unique $PBu_2(O)^-$ ligand. In general, compounds having a $PR_2(O)^-$ ligand are rare and no reports on their catalytic activity have appeared.

A single-crystal X-ray diffraction study should fully elucidate the structure of complex **1**.

Reactions of complex 1 with HCl and HBr

A similar complex $Fe(C_5H_5)(CO)_2PPh_2(O)$, has been previously described [10]. This complex reacts with HBr to form $[Fe(C_5H_5)(CO)_2(PPh_2OH)]Br$. The reaction was monitored by IR spectroscopy, which showed that the absorption of P=O double bond character due to the $P\text{–}O^-$ of the initial complex disappeared, and the absorption of P–OH grew up as a broad peak near 2520 cm^{-1}. Such behavior can be expected for complex **1** if it has the inferred structure. Accordingly, reaction of

Table 1

IR and ^{31}P NMR data for the complex **1** and reaction products of the complex **1** with HCl and HBr

	IR spectrum (cm^{-1})			^{31}P NMR spectrum
	CO	P–OH	P–O$^-$	Chemical shifts (ppm)
Complex 1	2046, 1972, 1951	–	1125	94.2(d, 73.4Hz), 39.2(d, 73.4Hz)
Complex 1 + HCl	2065, 1998, 1978	2500–2600	–	142.0(d, 81.2Hz), 48.4(d, 81.2Hz)
Complex 1 + HBr	2067, 1998, 1979	2500–2600	–	142.2(d, 81.2Hz), 48.7(d, 81.2Hz)

Reaction conditions: room temperature, 20 min, CCl_4. Reaction products were not isolated and their spectra were measured in solution.

complex **1** with HCl and HBr was investigated. The IR and ^{31}P NMR spectra of reaction products are shown in Table 1 and Fig. 1.

As is clear from the IR data, on addition of HCl and HBr the P–O$^-$ absorption with some double bond character disappeared, and the broad absorption of P–OH near 2500 to 2600 cm^{-1} appeared. The absorption of CO is shifted to the high frequency side by about 20 cm^{-1}.

The ^{31}P NMR data listed in Table 1, indicate that the spectra of the addition products of HCl and HBr are almost the same. The peak at 39.2 ppm, due to PBu_3, is shifted downfield by about 10 ppm, and the peak at 94.2 ppm, due to $PBu_2(O)^-$, is shifted downfield by about 50 ppm. The extent of shift is more prominent in the peak of $PBu_2(O)^-$. This suggests that there is a change in the neighborhood of $PBu_2(O)^-$. Since the spectra are almost the same for the addition of HCl and HBr, the Cl^- and the Br^- are probably not bonded to cobalt or phosphine. Thus the complex formed is concluded to be $[Co(CO)_3PBu_3(PBu_2OH)]X$ (X = Cl, Br), the same type as the iron complex. The behavior of complex **1** as described above confirms that the inferred structure of complex **1** is correct.

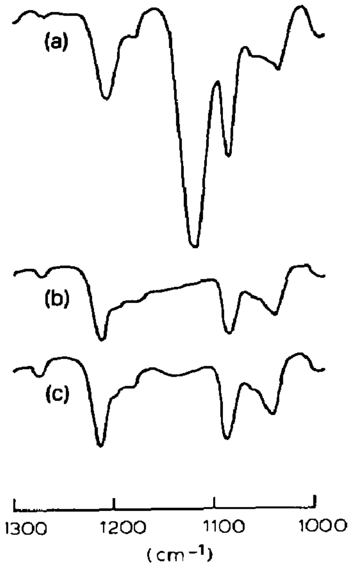

Fig. 1. IR spectra of the complex **1** and reaction products: a) complex **1**, b) complex **1** + HCl, c) complex **1** + HBr, (solvent; CCl_4).

Table 2

Homologation of methanol [a]

		$[Co(CO)_3PBu_3]_2$	$[Co(CO)_3PBu_3]_2 + PBu_3$			Complex **1**
			Without activation	Activation [b]		
P/Co		1.0	2.0	2.0	2.0	2.0
Activation time, h		–	–	1.5	3.0	–
Reaction time, h		1.5	1.5	1.5	1.5	0.25
MeOH	conversion, %	28.7	4.7	12.9	37.1	28.7
HCO_2Me	selectivity, %	1.5	14.7	8.3	0.9	1.4
MeOEt	selectivity, %	1.9	6.7	–	0.9	0.5
EtOH	selectivity, %	61.9	59.1	74.7	77.6	89.2
PrOH	selectivity, %	1.8	–	2.5	3.4	2.0
EtOH [c]	selectivity, %	64.8	76.8	81.5	79.2	91.0

[a] Conditions: 11.7 mmol Co complex, 312 mmol methanol, 128 mmol benzene, $H_2/CO = 1$, 200 kg/cm^2, 230 °C. [b] Activation conditions: 11.7 mmol Co complex, 128 mmol benzene, $H_2/CO = 1$, 200 kg/cm^2, 230 °C. [c] Convertible ethanol selectivity $= \frac{\text{convertible ethanol, mol}}{\text{(charged} - \text{unreacted} - \text{converted) methanol, mol}} \times 100(\%)$. Converted methanol; methanol and methanol content recoverable by hydrolysis as follows: MeOEt, $HCO_2Me \rightarrow$ MeOH. Convertible ethanol; ethanol and the ethanol content convertible by hydrogenation and hydrolysis by: MeOEt → EtOH.

Homologation of methanol

The homologation was carried out with complex **1** as the catalyst. For a comparison of catalytic activity, the reactions were also carried out with the complex, $[Co(CO)_3PBu_3]_2$ ($P/Co = 1.0$) and the catalytic system $[Co(CO)_3PBu_3]_2/PBu_3$ ($P/Co = 2.0$). The results, listed in Table 2, shows that the activity and ethanol selectivity of the $[Co(CO)_3PBu_3]_2$ catalyst are low, and the activity is further lowered when the turns into catalyst P/Co ratio becomes 2.0 by the addition of PBu_3. The activity and ethanol selectivity, however, were improved by the pretreatment (activation) of the catalytic system with synthesis gas. This is probably because complex **1** is formed. When complex **1** was used separately as a catalyst, very high activity and high ethanol selectivity were obtained.

Thus, complex **1** is a very effective catalyst for the homologation of methanol.

In summary, we have prepared a new cobalt phosphine carbonyl complex by treatment of $Co_2(CO)_8$/tri-n-butylphosphine catalyst with synthesis gas, and have clarified the structure of the new complex. It is very effective for the homologation of methanol with high activity and high ethanol selectivity.

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