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Homogeneous Hydroformylation with CO and H₂O Catalysed by an Octacarbonyl-dicobalt-1,2-Bis(diphenylphosphino)ethane Complex

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Summary A novel catalyst system has been found that causes the hydroformylation of propene with CO and H₂O.

We have found that Co₂(CO)₈ modified by 1,2-bis(diphenylphosphino)ethane (diphos) is an effective catalyst for hydroformylation with CO and H₂O, especially in polar ether solvents, providing the first example of the use of a cobalt carbonyl for this reaction.

Anionic metal hydrides have been proposed as intermediates in the homogeneous water gas shift reaction catalysed by transition metal carbonyl complexes.¹ Also, metal hydrides are well known to be active catalysts for hydroformylation, hydrogenation, and isomerization of olefins.² We have previously reported that Co₂(CO)₈ modified by diphos is a very active catalyst for this shift reaction with organic tertiary amines as solvent.³ These findings prompted us to study the interaction of olefins with solutions that are active for this shift reaction.

Typically, the catalytic solution prepared from Co₂(CO)₈ (2 mmol), diphos (2 mmol), and H₂O (1 ml) in an aprotic solvent (50 ml) was placed in a stainless steel bomb (100 ml) which was subsequently charged with both propene (9 kg/cm²) and CO (12 kg/cm²). After reaction at 135 °C for 17 ± 1 h, the reaction vessel was cooled to room temperature and the gases above the solution and the solution itself were both analysed by g.l.c. The water gas shift reaction was carried out under identical conditions,

except that the propene was omitted. As shown in Table 1, pronounced solvent effects were observed. Unexpectedly, in triethylamine solution, which was very effective for the shift reaction, hydroformylation of propene with CO and H₂O occurred to only a slight extent. At most, 1.7 mmol in total of hydroformylation products, accompanied by undefined yellow precipitates,† were formed which is less than the molar amounts of Co₂(CO)₈ initially added (run 1). However, polar ethers such as tetrahydrofuran (THF), dioxan, and diglyme were relatively effective and suitable solvents for this hydroformylation. For example, in diglyme no precipitates were formed and the total amounts of the products were 5–6 times the amounts in triethylamine (run 5). Moreover, since only a little hydrogen as co-product was detected, hydroformylation predominates over the evolution of H₂ in the presence of propene (Table 1 column C). In conformity with this finding the rate of the shift reaction is fairly slow in diglyme (column D). THF and dioxan showed similar results to those with diglyme (runs 2 and 4). The cobalt carbonyl cluster MeCCo₃(CO)₆⁴ [1.33 mmol under standard conditions, equivalent in cobalt content to 2 mmol of Co₂(CO)₈] as catalyst precursor showed identical activity to that of Co₂(CO)₈ (run 3).

For comparison, a further three aprotic solvents as well as the protic acetic acid were tested in both the hydroformylation and the shift reaction. However, they were hardly effective for either reaction (runs 6–9).‡

† When precipitates were recharged with CO (12 kg/cm²), H₂O (1 ml), and triethylamine (50 ml) they were found to be active for the shift reaction.

‡ I.r. data relevant to the interpretation of these solvent effects are as follows (Hitachi-215 spectrometer; metal carbonyl region of the catalyst solutions after the formylation) Et₃N solvent: ν_{CO} 1930m and 1985m cm⁻¹; THF: ν_{CO} 1890ms, 1955m, 1990s, 2055m, and 2080m cm⁻¹; spectra in diglyme and dioxan were analogous to that in THF; Me₂CO: ν_{CO} 1890vs, 1960w, 1990w, 2020s, 2030s,sh, and 2090s cm⁻¹; analogous spectra were obtained for acetonitrile and γ-butyrolactone except for the absence of the band at 1990 cm⁻¹.

TABLE 1. Hydroformylation of propene with CO and H₂O in various solvents.^a

Run	Solvent	Total mmol ^b (A)	% Aldehyde (B)	Gaseous hydrogen (mmol) (C)	Water gas shift reaction (mmol of H ₂) (D)
1	Et ₃ N	1.7	60.1	27.8	31.0
2	THF	7.1	100	<0.1	1.9
3	THF ^d	6.8	98.9	0.1	1.6
4	Dioxan	9.2	99.2	<0.1	1.0
5	Diglyme	9.5	100	<0.1	0.9
6	Me ₂ CO	0.5	— ^e	0.2	0.6
7	MeCN	0.2	—	0.4	0.6
8	γ-Butyrolactone	<0.1	—	0.3	0.4
9	AcOH	0.1	—	0.3	— ^f

^a Conditions are as in the text. In Runs 2–5, small amounts of three unknown products as well as propane were generated. Further work is in progress to identify these products and to obtain them in higher yields. ^b Total amounts of C₄-aldehyde and -alcohol formed. ^c Percentage of C₄-aldehydes relative to total amounts in (A). In Runs 2 and 5, C₄-alcohols were not detected under the conditions employed. ^d The cobalt carbonyl cluster MeCCo₃(CO)₉ was used as catalyst precursor. ^e A dash indicates that the calculation was not carried out because the amount of products formed was too small. ^f Not determined.

The hydroformylation is inhibited by increase in initial CO pressure, which is analogous to observations in normal hydroformylations using CO–H₂.² The effect of the diphos:Co₂(CO)₈ ratio on the activity was also examined using THF as solvent. As shown in Table 2, the most active catalyst appears to be formed with a *ca.* 0.75:1 ratio. However, for ratios < 1:1, the catalyst partially decomposes to metallic cobalt during the reaction. With ratios > 1:1, the activity decreases, with increased formation of hydrogen as co-product.

TABLE 2. Effect of diphos:Co₂(CO)₈ ratio

diphos/Co ₂ (CO) ₈ (mmol/mmol)	Total mmol ^a	%Aldehyde ^a	Gaseous H ₂ (mmol)
0	2.1	55.5	0.1
0.5	7.3	98.1	0.1
0.75	9.5	98.1	0.16
1.0	7.1	100	<0.1
1.5	4.7	93.9	2.3
2.0	2.7	87.6	2.4

^a See Table 1.

The activity and catalytic nature of the Co₂(CO)₈-diphos-polar ether solvent for hydroformylation with CO and H₂O was confirmed by the following control experiments with

THF as solvent. (i) The identity of the C₄-aldehydes was verified by mass spectrometry. (ii) The amount of CO₂ formed, determined by titration, was in good accordance with the amount of C₄-aldehydes. (iii) The use of mono-, di-, or tri-phosphines other than diphos was examined. The order of reactivity is: diphos (7.1) > Ph₂PC≡CPh (3.5) > PPh₃ (2.1) > Ph₂P[CH₂]₃PPh₂ (1.8) > Ph₂P[CH₂]₄PPh₂ (0.5) > Ph₂PCH₂PPh₂ (0.1) > PhP(CH₂CH₂PPh₂)₂ (0.04) (numerical values refer to column A in Table 1). (iv) In the absence of diphos, C₄-aldehydes were produced only in molar amounts comparable to the amount of Co₂(CO)₈ with complete decomposition of Co₂(CO)₈ to metallic cobalt (see Table 2). (v) The absence of H₂O led to formation of < 0.1 mmol of C₄-aldehydes. Also the use of D₂O instead of H₂O yielded > 91% deuteriated C₄-aldehydes, as shown by g.l.c.-mass spectrometry. This indicates that the presence of H₂O is essential for the formation of C₄-aldehydes. (vi) The true catalytic nature of this system was shown by the fact that the reaction solution, when recharged with both propene (9 kg/cm²) and CO (12 kg/cm²) after run 2 in Table 1 exhibited entirely the same activity as in run 2.

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