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Bis[tris(*m*-(sodium sulfonato)phenyl)phosphine] hexacarbonyl dicobalt, $Co_2(CO)_6(P(m\text{-}C_6H_4SO_3Na)_3)_2$, in a supported aqueous phase for the hydroformylation of 1-hexene

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Abstract

The synthesis of the cobalt carbonyl phosphine complex, $Co_2(CO)_6(P(m\text{-}C_6H_4SO_3Na)_3)_2$, is described and the complex is used as a catalyst for the hydroformylation of 1-hexene under two-phase and supported aqueous phase reaction conditions. Under two-phase reaction conditions both with and without excess phosphine substantial quantities of cobalt are leached into the organic phase and the observed activity is consistent with catalysis from $HCo(CO)_4$ in the organic phase. When the complex is supported onto the controlled pore glass CPG-340 in a supported aqueous phase configuration the amount of cobalt lost into the organic phase is minimized and the observed activity appears to come from the complex on the glass. When excess phosphine as well as the complex are supported on the glass cobalt leaching is further reduced under batch reaction conditions.

Introduction

Recently we reported on a novel supported water-soluble catalyst for the hydroformylation of liquid olefins [1,2]. This system is based on the now well known water-soluble rhodium complex, $HRh(CO)(P(m\text{-}C_6H_4SO_3Na)_3)_3$ [3–5]. The key features of the supported aqueous phase (SAP) catalyst include no observable loss of rhodium to the substrate phase and enhanced activity towards high molecular weight olefins compared to a simple two-phase catalytic system [2,6,7]. The enhanced activity is expected from the increase in surface area between the supported phase containing the catalyst and the organic substrate phase that results upon immobilization of the aqueous phase on a hydrophilic support. One major advantage of the SAP catalysts is that the supported water layer is immiscible with hydrocarbons. This allows the SAP catalysts to be used with liquid hydrocarbon substrates in contrast with other supported liquid phase catalysts which can be used only with gas phase reactants [8].

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In practice cobalt is often preferable to rhodium as a hydroformylation catalyst for liquid olefin substrates [9]. With higher molecular weight substrates the separation of catalyst and products is a difficult operation and the potential cost due to loss of rhodium in a liquid phase reaction is prohibitively high. Thus cobalt has an economic advantage over rhodium due to its lower cost. Rhodium, however, is orders of magnitude more active than cobalt, which gives incentive to the development of immobilized rhodium catalysts such as the SAP catalysts mentioned above [1,2,6]. Another advantage of cobalt carbonyl and its derivatives in the hydroformylation reaction is the high rate of isomerization that is achieved [9,10]. Thus internal olefins can be used as the substrate and still yield a relatively high degree of linear aldehyde, or alcohol, as product. Although the recycling of phosphine-modified cobalt carbonyls appears straightforward [11] the process could be simplified with a heterogeneous catalyst. For this reason immobilized cobalt catalysts are also of interest. Cobalt carbonyls have previously been immobilized on diphenylphosphine-modified polystyrene [12] and on poly(vinyl pyridine) [13,14] and used as hydroformylation catalysts. In both cases significant quantities of cobalt are lost from the support.

Here we show that the concept of SAP catalysis can be applied to a phosphine-modified cobalt carbonyl for the hydroformylation of 1-hexene. Cobalt loss is significantly reduced compared to two-phase reaction conditions and the catalytic activity can be mostly attributed to the supported cobalt complex rather than the cobalt that has leached. The water-soluble cobalt complex chosen for the study is the new compound, $Co_2(CO)_6(P(m\text{-}C_6H_4SO_3Na)_3)_2$, **1**. The details of the preparation of this compound are also reported.

Figure 1 shows a schematic representation of the cobalt SAP catalyst. Although the exact nature of the interface requires further investigation the scheme represents

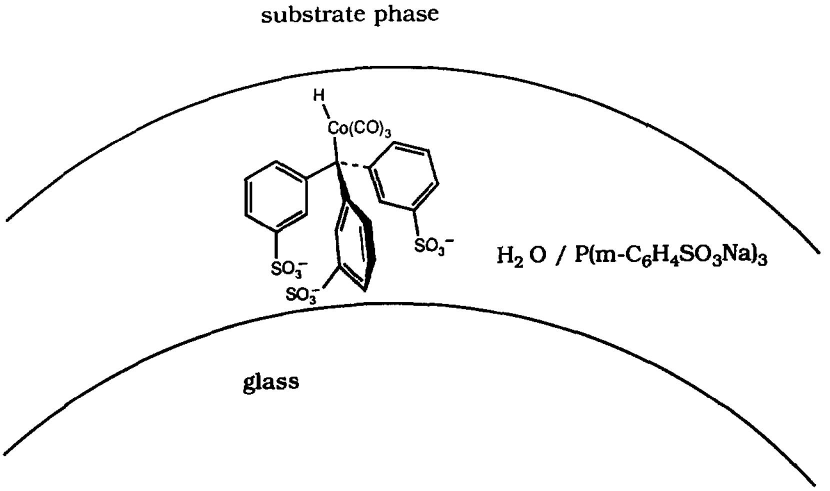


Fig. 1. Schematic representation of the glass/catalyst/substrate interface. The hydrido complex shown above is the expected form of the catalyst under reaction conditions (see Scheme 1). In the catalysts prepared from CPG-340, surface area 68 m^2 g^{-1}, with 11 wt.% water, approximately 5.4 monolayers of water are expected in the as-prepared catalyst if the water is perfectly distributed.

a reasonable working model for the function of the catalysts. In particular it is suggested that the cobalt complex, **1**, or any reaction intermediate that contains trisulfonated triphenylphosphine will remain strongly associated with the water layer on the glass.

Experimental section

All synthetic operations were performed under nitrogen. Toluene was distilled under nitrogen prior to use. Distilled deionized water was degassed by three cycles of vacuum boiling and readmission of nitrogen. The controlled pore glass CPG-340 was obtained from Electronucleonics Corporation. 1-Hexene was purchased from Aldrich and used without further purification. Dicobaltoctacarbonyl (Pressure Chemical Co.) was sublimed and stored in sealed glass ampoules at 4° C. Trisulfonate triphenylphosphine, $P(m\text{-}C_6H_4SO_3Na)_3$, was prepared by literature methods [3] or obtained as a gift from Dr. Istvan Horvath. All NMR spectra were recorded on an IBM WP200 spectrometer; infrared spectra were recorded on a Nicolet 5DXB spectrometer.

Hydroformylation reactions were performed in a 300 mL Parr stirred reactor at the conditions shown in the accompanying tables. Reaction products were determined by GC on a 25 m 1.0 μm SPB-5 capillary column in a Varian 3300 GC.

Cobalt leaching was determined by first separating the substrate and catalytic phases and then removing solvent and products from the substrate phase under vacuum. The residue was extracted with aqueous HCl and cobalt was determined by atomic absorption spectroscopy. Elemental analyses are from Galbraith Labs.

Preparation of $Co_2(CO)_6(P(m\text{-}C_6H_4SO_3Na)_3)_2$

In a typical reaction $Co_2(CO)_8$ (210 mg, 0.61 mmol) was dissolved in 10 mL toluene. Solid $P(m\text{-}C_6H_4SO_3Na)_3$ as the trihydrate (760 mg, 1.22 mmol) was added directly to the toluene solution above followed by the addition of 10 mL water. The mixture was stirred vigorously for 30 h at room temperature. During this time the aqueous phase gradually became red brown in color. The aqueous phase was collected and the water removed under vacuum. The solid was washed with methanol followed by diethylether and vacuum dried. Yield 570 mg (68%). The product was recrystallized from aqueous methanol. Analysis based on $Co_2P_2C_{42}H_{24}O_{24}S_6Na_6$; calc. C 35.46, H 1.70%; found C 35.70, H 1.76%. Infrared, ν(CO) 1964, 1942 cm^{-1} (KBr). ^{31}P NMR (H_2O) 66.8 ppm relative to 85% H_3PO_4.

Preparation of the supported aqueous phase catalyst

The controlled pore glass, CPG-340, was degassed by stirring in degassed deionized water for several hours. The water was removed by syringe and the glass vacuum dried at room temperature. Sufficient water to dissolve 100 mg of **1** was used to prepare a solution of **1**. For those catalysts with excess phosphine 80 mg $P(m\text{-}C_6H_4SO_3Na)_3$ trihydrate was dissolved together with **1**. The solution was then added to 3 g of degassed CPG-340 by the incipient wetness technique. Excess water was removed under vacuum at room temperature to yield a "dry" catalyst. Thermogravimetric analysis showed that the dry catalysts contained 3% water by weight. The catalysts were then hydrated by addition of 0.27 mL water. The total water in the hydrated catalysts was 11 wt.%. The magic angle spinning phosphorus-31 NMR spectrum of a sample which contained less than 4% water shows two phosphorus signals, one at 67 ppm which corresponds to complex **1** and one at 29 ppm which corresponds to phosphine oxide on the surface. The phosphine oxide must be generated from the decomposition of some of **1** on the surface.

Results and discussion

Bis[tris(*m*-(sodium sulfonato)phenyl)phosphine] hexacarbonyl dicobalt was prepared in a toluene/water slurry and recrystallized from aqueous methanol. As a result of the substitution the product, **1**, is extracted into the water layer. This compound, and many other trisulphonated triphenylphosphine derivatives, have recently been reported by Herrmann et al. [15].

Unlike many metal carbonyl derivatives of sulfonated phosphines [16,17], **1** is crystalline and an X-ray structure determination is underway. Elemental analysis, infrared spectroscopy, and ^{31}P NMR are consistent with **1** being isostructural with $Co_2(CO)_6(P(n\text{-}Bu)_3)_2$ [18], with all terminal carbonyls and phosphines in axial positions *trans* to the cobalt–cobalt bond.

Impregnation of **1** onto a controlled pore glass, CPG 340, was accomplished either by stirring an aqueous solution of **1** with 3 g of glass or, preferably, by the incipient wetness technique described in the Experimental Section. After removal of water under vacuum the catalysts were rehydrated by adding a quantity of water by microliter syringe.

Results for the hydroformylation of 1-hexene by **1** under "two-phase" reaction conditions are shown in Table 1. The normal to branched (n/b) ratios under these conditions are low and the degree of cobalt leaching to the organic phase is high. In examples 5 and 6 a liquid water phase is not present at the reaction temperature and pressure used. Not surprisingly the activity of the solid in the absence of a suitable solvent is virtually nil.

The corresponding results for the supported complex are given in Table 2. The water contents listed in Table 2 represent the total water present in the reactor during the catalytic reaction. Cobalt leaching is reported as the percent of total cobalt originally in the reactor which is present in the organic phase after catalysis.

Table 1

Two-phase hydroformylation of 1-hexene by $Co_2(CO)_2(CO)_6(P(m\text{-}C_6H_4SO_3Na)_3$ [a]

Entry	**1** (mg)/H_2O (mL)/toluene (mL)	P/Co [b]	Conversion to aldehydes (%)	n/b of aldehydes	Conversion to alcohols (%)	n/b of alcohols	tof (h^{-1})	Co leached (% of total cobalt)
1	100/50/20	1	26.7	1.25	0	–	19.0	10.9
2	100/50/20	2	27.1	1.85	4.8	1.46	19.3	5.7
3	100/5/5	1	32.6	1.33	3.0	0.99	25.4	3.6
4	100/2/5	1	19.0	1.37	1.4	0.91	14.5	3.1
5	100/0.5/5	1	3.96	1.07	0.2	1.14	3.0	1.7
6	100/0/5	1	0.73	1.48	0	–	0.5	0.5

[a] Reactor charged with 800 psi, $H_2/CO = 1:1$ at room temperature; reaction temperature 190 °C; reaction time 8 h; 10 mL 1-hexene. [b] Moles phosphorus per mole cobalt.

Table 2

Hydroformylation of 1-hexene by $Co_2(CO)_6(P(m\text{-}C_6H_4SO_3Na)_3)_2$/glass [a]

Entry	loading (mg 1)/ total water (mL)	P/Co	Conversion to C-7 aldehydes (%)	n/b of aldehydes	Conversion to C-7 alcohols (%)	n/b of alcohols	tof (h^{-1}) [b]	Co leached (% of total cobalt)
7	200/5.0 [c]	1	50.6	2.02	20.4	1.39	25.3	1.1
8	200/5.0 [c]	2	59.4	2.28	16.9	1.33	27.2	0.8
9	200/0.5 [c]	2	66.3	2.2	5.6	1.12	25.6	0.4
10	200/0 [c]	2	68.2	2.12	5.8	0.95	26.1	0.4
11	100/0.2 [d]	1	34.0	2.06	10.3	1.20	31.6	0.5
12	50/0.27 [d]	1	30.4	2.12	9.6	1.05	57.0	0.2
13	50/0.5 [c]	2	32.0	2.37	4.2	1.36	51.4	0.1
14	30/0.27 [d]	1	22.4	2.32	1.2	1.51	55.9	0.1
15	10/0.27 [d]	1	5.9	2.50	2.9	1.73	59.7	0.1

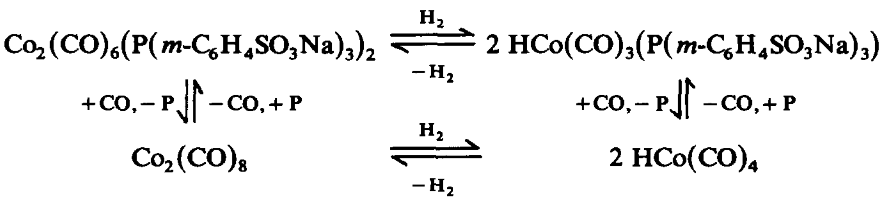
[a] Reactions conditions: 190 °C, reactor charged with 800 psi, $H_2/CO = 1:1$ at room temperature; reaction time 8 h, 10 mL 1-hexene, 3.0 g glass. [b] Turnover frequencies are per mole cobalt, not per mole 1. [c] 50 mL toluene. [d] 10 mL toluene.

At high pressures of CO and H_2 the equilibria shown in Scheme 1 are likely for cobalt carbonyl phosphine complexes [19].

Dicobaltoctacarbonyl and hydridotetracarbonylcobalt are both more soluble in organic solvents than in water. Thus if these complexes are formed they are likely to be extracted into the organic phase under two-phase reaction conditions. The low n/b ratios are consistent with cobalt carbonyl in the organic phase as the dominant active species for the hydroformylation. As the amount of water in the system is decreased the total amount of cobalt lost decreases. Also the activity as expressed by turnover frequency (tof) decreases. This suggests that less of the cobalt is active when the total water in the system is decreased. Given the large reactor volume and the high temperatures it is likely that much of **1** precipitates during the reaction as water enters the gas phase and is thus unavailable for either decomposition to cobalt carbonyl or catalytic activity. The pure solid, entry 6, is virtually inactive for hydroformylation and also loses very little cobalt to the organic phase. The n/b ratios appear to be independent of water content.

More of the cobalt is kept in the water phase upon addition of excess phosphine (compare results from runs 1 and 2). However, significant quantities of cobalt are still leached into the organic phase. The relatively low n/b ratios are consistent with leached cobalt carbonyl as the dominant catalyst in the system.

The results shown in Table 2 demonstrate that immobilization of **1** has a significant effect on its activity. Most noticeable are the improvement in n/b ratios



Scheme 1

and the decreased level of cobalt leaching. Because of the reactor volume and temperature only in examples 7 and 8 is a liquid water phase expected under reaction conditions. The total water content in the reactor does not significantly affect the activity of the supported catalyst; all catalysts behave similarly to the catalyst to which no water was added (entry 10, 3 wt.% water). This is opposite to what was observed with rhodium SAP catalysts with octene and other high molecular weight substrates in cyclohexane solvent [2]. For the rhodium catalysts activity was maximized at about 8 wt.% water and decreased rapidly as the water content increased. At elevated temperatures 1-hexene has appreciable water solubility which may account for the catalytic activity even in the presence of excess water, which is expected to fill the pores of the glass (examples 7 and 8). Water, in turn, has an appreciable solubility in toluene; the substrate phase may in fact be homogeneous at these high temperatures. These aspects of the cobalt catalysts suggest that the surface composition has very little water content under reaction conditions. The surface water content is more readily controlled in a small volume reactor [1,2]; experiments are underway to explore more fully the effects of water on the catalyst activity.

Importantly, the activity of the supported catalysts does not correlate with cobalt leached to the organic phase. Both in absolute terms and when expressed as a percent of total cobalt the amount of cobalt leached is much less when **1** is supported on CPG-340 compared to the two-phase reaction. This suggests that the activity observed for the supported catalysts is due to the cobalt on the glass and not to the small quantities that have leached from the glass. Further evidence for this conclusion comes from the observed n/b ratios which are higher for the supported catalysts than for **1** at similar levels of conversion under two-phase conditions. The n/b ratios are similar to those obtained with triphenylphosphine-modified cobalt carbonyl catalysts at similar temperatures and pressures [9,19]. Reaction selectivity is also a function of temperature and pressure and may be improved through modification of the reaction conditions. The major side reaction was hydrogenation of the olefin. Conversion to hexane was in the range 13 to 27%.

The reaction rates, as expressed by the average turnover frequency per cobalt, improve as the cobalt loading of the catalysts is decreased. This suggests that at high cobalt loading much of the cobalt is not available for catalytic activity in the SAP catalysts.

The addition of excess phosphine to the cobalt SAP catalysts has little effect on the reaction selectivity and activity at 190 °C and 800 psig. However, cobalt loss from catalysts with P/Co molar ratios of 2 is further reduced under batch conditions, compare runs 7 and 8. Also a comparison of reactions 12 and 13 shows that even with an increase in the toluene volume less cobalt is leached in the presence of excess phosphine.

From studies of homogeneous phosphine modified cobalt catalysts it is well known that phosphine ligand dissociation is significant for triphenylphosphine and that the equilibria represented in Scheme 1 are shifted in favor of the phosphine-substituted complexes in the presence of excess phosphine [19]. This is particularly true for large, less basic, phosphines such as triphenylphosphine. The role of excess phosphine in keeping the cobalt on the glass is most likely to lower the equilibrium concentration of $HCo(CO)_4$. Thus, the ultimate stability and lifetime of the cobalt SAP catalysts with $P(m\text{-}C_6H_4SO_3Na)_3$ as the water solubilizing ligand is limited by this equilibrium. Also the catalysts darken with use, which may indicate decomposition of some of the complex to cobalt metal on the glass.

The degree of alcohol formation for the cobalt SAP catalysts is less than expected from the results reported with $Co_2(CO)_6(PPh_3)_2$ as a homogeneous catalyst in organic solvents [18]. The difference in the activity towards alcohol formation is not understood at this time.

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