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Olefin Hydroformylation Catalyzed by a Cobalt Carbonyl Complex Containing a Water-soluble Phosphine

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Abstract

The water-soluble complex $[Co(CO)_3(amphos)]_2(PF_6)_2$ (I) (amphos = $Ph_2PCH_2CH_2NMe_3)^+$ has been synthesized and characterized by spectroscopic techniques and elemental analyses. The properties of I as an olefin hydroformylation catalyst under homogeneous conditions, in aqueous–organic solvent two phase systems and when adsorbed onto strong acid cation exchange resins are studied, but it is found that the amphos–cobalt system is less effective than a similar rhodium system because of the lighter metal's greater proclivity to oxidation and phosphine dissociation.

Introduction

The 'heterogenization' of homogenous catalysts, via either the attachment of normally soluble catalysts on insoluble supports [1, 2] or via phase-transfer systems [3, 4], has been a subject of intense study in recent years and a number of comparisons have been made between heterogenized catalysts and their homogeneous precursors, We have recently reported the synthesis of the tertiary phosphine $[Ph_2CH_2CH_2NMe_3]^+$ (amphos), as the iodide and nitrate salts [5, 6], and have shown that this cationic ligand imparts unusually high solubilities in polar solvents to its coordination compounds. Interestingly, it was found that aqueous solutions of amphos–rhodium(I) complexes constitute very effective catalysts for both the hydrogenation of water-soluble olefins and for the hydrogenation and hydroformylation of water-immiscible olefins, either neat or dissolved in water-immiscible solvents [7]. Furthermore, it was found that adsorption of a cationic amphos–rhodium(I) complex on a strong acid, cation exchange resin resulted in the formation of a very novel supported catalyst for the hydrogenation and hydroformylation of olefins. Virtually no leaching of rhodium into the olefin-containing phase occurred in either type of two-phase system, although the rhodium could be readily recovered from the resin by elution with acid [7].

The use of ion-exchange resins for the support of a variety of homogeneous catalysts has also been reported by others [8–11], and it is clear that this approach to novel catalyst systems has great potential. In an effort to both extend our earlier work and to better assess the potential usefulness and limitations of heterogenized amphos complexes, we have therefore prepared and characterized a cationic amphos complex of a third row transition metal, specifically $[Co(CO)_3(amphos)]_2[PF_6]_2$ (I). The properties of I as an olefin hydroformylation catalyst, both in aqueous–organic solution and when adsorbed on cation exchange resins, are studied and compared with the catalytic properties of complexes of the type $[Co(CO)_3(tertiaryphosphine)]_2$, which are known to be excellent hydroformylation catalysts [12, 13]. Unfortunately, catalytic systems containing I are not as robust as those containing the previously studied rhodium system [7].

Experimental

Instrumentation and Materials

Proton (^1H) NMR spectra were run on Bruker HX 60, CXP 200 and AM 400 NMR spectrometers, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra on the latter two instruments. Infrared (IR) spectra were run on Beckman IR 4240 and Bruker IFS 85 FTIR spectrometers, while gas–liquid chromatography was carried out on a Hewlett Packard 5880A gas chromatograph with FI detector and either methyl silicone or carbowax columns. A 300 ml Parr 4561 Mini Reactor equipped with automatic temperature control and variable speed stirring was used for catalytic runs. Elemental analyses of I were performed by Canadian Microanalytical Services Ltd., Vancouver, B.C.

Acetonitrile and methylene chloride were distilled from P_2O_5 prior to use, ethyl ether and benzene from sodium ribbon, and tetrahydrofuran from

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TABLE I. Spectroscopic Data for **I, II** and **III**

Compound	ν(CO) (cm^{-1})	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$	$\delta(^{31}P\{^1H\})^a$
I	1958(s), 1980(sh)^b	3.07(m, Me), 3.39 (m, NCH_2), 2.6(m, PCH_2)^c	26.52(P*C*, J_{PC} = 24 Hz), 63.23(N*C*), 53.75(Me), 202.6(CO)^c	58.9 (Δ = 79.2), −143(PF_6^-)^c
II	1953(s), 1980(sh)^b	3.03(m, Me), 3.34(m, NCH_2), 3.49(m, PCH_2)^d	26.64(P*C*, J_{PC} = 24 Hz), 63.50(N*C*, J_{PC} = 22 Hz), 54.0(Me), 202.7(CO)^d	58.2 (Δ = 79.0)^d
III	1958(s), 1979(w)^e		201.4(CO)^d	50.4 (Δ = 78.1)^d

[a]Coordination shifts (ppm) in parentheses. [b]Acetonitrile. [c]Acetonitrile-d_3. [d]Chloroform-d_1. [e]Toluene.

potassium. Methanol was distilled from magnesium methoxide and stored over 3A molecular sieves, while acetone was distilled from 4A molecular sieves. All solvents were purged with nitrogen prior to use. The cation ion exchange resins Amberlyst 15 (20–50 mesh, macroreticular, strong acid, Na^+ form) and Ion Exchange Resin CGC-240 (100–200 mesh, microreticular, strong acid, Na^+ form) were purchased from BDH Chemicals Ltd and Canlab, respectively.

$[Co(CO)_3(Ph_2PCH_2CH_2NMe_3)]_2[PF_6]_2$ (I)

To 3.6 g of $Co_2(CO)_8$ (10.5 mmol) in 100 ml benzene was added dropwise a stoichiometric amount of 1-dimethylamino-2-diphenylphosphinoethane [6] (5.5 g, 21.0 mmol) dissolved in 20 ml benzene. The mixture was stirred at room temperature for one hour under nitrogen, the solvent was removed under reduced pressure, and the dark, reddish brown residue was recrystallized from methylene chloride/hexane to give brown crystals of $[Co(CO)_3(Ph_2CH_2CH_2NMe_2)]_2$ (**II**) (yield 73%). Spectroscopic properties of this intermediate are listed in Table I.

A five-fold excess of methyl iodide (6.5 ml) was added to 1.0 g of **II** (1.25 mmol) dissolved in 100 ml ethyl ether, and the mixture was stirred for eight hours under nitrogen. At this point, 1.0 g $NaPF_6$ (5 mmol) dissolved in 50 ml methanol was added dropwise over 30 min with stirring to the cooled (0 °C) ether solution. Fine, orange–brown crystals of **I** precipitated and were collected after 30 min (yield 78%). *Anal.* Calc: C, 42.86, H, 4.11. Found: C, 41.99, H, 4.03%. Spectroscopic properties are listed in Table I.

Compound **I** was also prepared by adding $Co_2(CO)_8$ (0.75 g, 2.19 mmol) dissolved in benzene dropwise to a suspension of amphos iodide (1.8 g, 4.40 mmol) in 100 ml benzene. The mixture was refluxed under nitrogen for one hour, the solvent was removed under reduced pressure, and the residue was dissolved in acetonitrile and filtered through celite to remove a fine black precipitate. Metathesis was accomplished by adding 1.5 g (7.5 mmol) $NaPF_6$ dissolved in 50 ml methanol to the acetonitrile solution. The resulting orange, crystalline material (30% yield) was identical to the sample of **I** obtained above, confirming the formulation suggested. The former route to **I** is to be preferred, however, as it avoids two tedious steps in the synthesis of amphos iodide [6], and results in higher yields.

Catalytic Studies

The hydroformylation of 1-hexene was carried out in two types of heterogenized systems. The first, a liquid–liquid two-phase system, involved a solution of **I** (0.11 g) in 20 ml water buffered to the pH range 5–7 (NaH_2PO_4/Na_2HPO_4) and a water-immiscible solution of about 3 ml of the olefin in 20 ml of an organic solvent. The solutions were transferred under nitrogen to the Parr Mini Reactor, and reactions were run for 24 h at 100 °C and at a total pressure of 80 atm of 1.5:1 H_2/CO. The reactor was then cooled to −78 °C in a dry ice/acetone bath, vented, and opened, and the organic layer was separated and analyzed by gas chromatography. The results are shown in Table II.

Hydroformylation reactions were also carried out using **I** adsorbed onto 10 g of each of the cation exchange resins. The resins were prepared by washing with deionized water, methanol and ethyl ether, followed by drying for one hour at reduced pressure. Catalysts were prepared by stirring 0.11 g of **I** dissolved in 50 ml acetone with 10 g of resin. After about one hour, the deep red colour of the cobalt compound had disappeared, and the resin was washed with acetone and ethyl ether, and dried. The resin was transferred to the Mini Reactor under nitrogen, 1-hexene (3 ml) in 30 ml of solvent was added, and the reaction was carried out under the same conditions of temperature and pressure outlined above (Table II).

For purposes of comparison, some homogeneous experiments were carried out by adding 3 ml of 1-hexene to the catalyst dissolved in 30 ml solvent,

TABLE II. Heterogenized Catalysts (100 °C)[a]

Catalyst	Co-solvent	TON	% Linear aldehyde	% Branched aldehyde	% Linear alcohol	% Branched alcohol	Overall n/iso ratio	% 2-Hexenes
I in H_2O	None	151[b]	35	33	32	0	2.0	0
I in H_2O	Ether	16[c]	40	14	46	0	6.1	0
I on R_M[d]	Benzene	79[c]	70	30	0	0	2.3	0
I on R_G[d]	Ether	106[c]	15	36	28	13	0.9	0[e]
I on R_G[d]	Ether		0	0	0	0	0	100
I on R_G[d]	Acetone		0	0	0	0		77[e]
I on R_G[d]	CH_2Cl_2		0	0	0	0		100

[a] Yields based on amount of 1-hexene which reacted. [b] Maximum TON = 560. [c] Maximum TON = 120. [d] R_M = macroreticular resin; R_G = microreticular (gel) resin. [e] Considerable 1-hexene converted to unidentified products.

TABLE III. Homogeneous Catalysts (100 °C)[a]

Catalyst	Solvent	TON[b]	% Linear aldehyde	% Branched aldehyde	% Linear alcohol	Overall n/iso ratio	% 2-Hexenes
$Co_2(CO)_8$	Benzene	⩾120	82	18	0	4.6	0
I	Benzene	67	82	18	0	4.6	0
III	Benzene	107	82	18	0	4.6	0
$Co_2(CO)_8$	Acetone	77	35	24	6	1.7	0[c]
I	Acetone	49	21	45	0	0.5	0[c]
II	Acetone	48	19	21	13	1.5	38[c]
III	Acetone	76	39	28	0	1.4	27[c]

[a] Yields based on amount of 1-hexene which reacted. [b] Maximum TON = 120. [c] Considerable 1-hexene converted to unidentified products.

and proceding as for the two-phase systems. The results of these experiments are shown in Table III.

Results and Discussion

Catalyst Synthesis and Characterization

As described under 'Experimental', **I** could be prepared either by direct substitution of CO on $Co_2(CO)_8$ or, preferably, via the intermediate aminophosphine complex **II**. The new compound **I** was characterized by elemental analyses and by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. Compound **II** was not obtained analytically pure but, on the basis of its spectroscopic properties and facile conversion to **I**, there can be no doubt as to its identity. The spectroscopic properties of both compounds, with data for a similar compound, $[Co(CO)_3PMePh_2]_2$ (**III**) [14, 15], are listed in Table I.

As can be seen, the IR spectra of **I** and **II** in the carbonyl stretching region both exhibit two bands at characteristic frequencies of about 1955(s) and 1980(sh) cm^{-1}, thus confirming the expected similarity in structure to **III** and other known compounds [14, 15]. The very minor variations in the CO stretching frequencies suggest that amphos and the aminophosphine have essentially normal σ-donor strengths, as has been noted previously [5, 6].

The ^1H and ^{13}C NMR data are very similar to data reported previously for similar amphos complexes [5–7], and do not merit further discussion here except to point out that they are entirely consistent with the suggested formulation of the compounds. However, the ^{31}P chemical shift data are of significant interest because of the striking similarity in the coordination shifts (the change in chemical shift on coordination), 79.2, 79.0 and 78.1 ppm for **I**, **II** and the complex of $PMePh_2$, respectively. It is anticipated that similar compounds of the three tertiary phosphines will exhibit similar coordination shifts [7].

Catalytic Studies

The activities of **I** and, for purposes of comparison, of $Co_2(CO)_8$ and the complexes of the aminophosphine (**II**) and of $PMePh_2$ (**III**) as catalysts for the hydroformylation of 1-hexene were studied under homogeneous conditions (solutions in acetone, benzene), in aqueous–organic solvent (benzene, ethyl ether) two phase systems, and supported on cation exchange resins. The experimental details are described in the 'Experimental', and the results are shown in Tables II and III. In the Tables, the turnover numbers (TON) are defined as the total number of moles of hydroformylation products (aldehydes + alcohols) formed per mole of cobalt catalyst used.

In Table III are shown data for **I** in acetone, in which the compound was soluble, and in benzene, in which it had limited solubility. For comparison, data are also presented for runs in which **II**, $Co_2(CO)_8$ and $[Co(CO)_3PMePh_2]_2$ (**III**) were also used. As can be seen, **I** and **II** exhibit relatively low activities in benzene, although the low activity of **I** may be attributed in part to its low solubility. The product distributions for the three catalysts are strikingly similar, however, suggesting that the active catalyst in all three systems may be the same, *i.e.* $HCo(CO)_4$. Displacement of the tertiary phosphines of **I** and **III** by CO would appear to have precedent in the literature [16], but we do not have the means to study the systems spectroscopically *in situ*. All the catalysts exhibited relatively poor activity, selectivity and n/iso ratios in acetone, and the systems were not studied in detail. Other products, probably resulting from condensation reactions, were formed, but their identities were not determined. It was established, however, that they did not include isopropanol, the compound expected from hydrogenation of the solvent.

As we have previously demonstrated [6, 7], the tetra-alkylammonium functionality of amphos often imparts useful water solubility to its complexes. The cobalt compound described here was no exception, and the water solubility of **I** permitted its use as a phase transfer catalyst. Its aqueous solutions, buffered to the pH range 5–7, formed very effective catalysts for the hydroformylation of 1-hexene, either neat or in ethyl ether solution, as shown in Table II. Thus the products could be readily separated from the aqueous solution of catalyst by decantation. Unfortunately, either the n/iso (neat 1-hexene) of the activity (ether solution) was low; the latter problem was undoubtedly in part a result of partial oxidation of the cobalt catalyst to cobalt(II), which was detected by pink colouration of the aqueous phase.

The supported catalysts described here undoubtedly involve ionic interactions of the tetra-alkylammonium groups of the amphos ligands with the sulfonate groups of the strong acid cation exchange resins, as has been postulated previously for a rather similar rhodium system [7]. The resins chosen here were of two types, microreticular and macroreticular. The former is characterized by its swellable, gel-type structure, the latter by its dimensionally stable, porous structure [17, 18].

Interestingly, as shown in Table II, the catalysts based on the microreticular resin catalyzed the isomerization of 1-hexene to 2-hexene almost exclusively, no aldehyde or alcohol hydroformylation products being detected. A similar attempt to hydroformylate styrene, which cannot isomerize, resulted only in the formation of ethylbenzene, the product of hydrogenation. The total lack of products of hydroformylation, coupled with the observation that no metal carbonyl stretching vibrations could be detected in the IR spectra of the organic phases of these reactions, suggest a lack of significant leaching of cobalt from the support. Possibly the gel structure restricts the mobility of the cobalt, thus preventing its dissociation. Olefin isomerization is, of course, rarely observed with cobalt hydroformylation catalysts [13], and we do not known the reason(s) for the very unusual behaviour of the 1-hexene in these systems. Again the gel structure of the support may play a role.

Better hydroformylation results were obtained with the macroreticular resin which, because of its porous structure, was expected to be the better support. In these cases, no olefin isomerization was observed, but the hydroformylation products exhibited rather low n/iso ratios. Somewhat similar results with other macroreticular ion exchange-supported cobalt catalysts have been reported elsewhere [8]. Unfortunately, cobalt carbonyl peaks at 2050 and 1893 cm^{-1} were observed in the IR spectra of the solutions after the reactions, indicative of severe leaching of the catalyst from the support. In this sense, the amphos–cobalt catalyst system is decidedly inferior to the analogous rhodium system [7].

The present study shows that amphos complexes of the third row transition metals may be expected to exhibit unexpected catalytic properties, but that they may also be rather unstable with respect to replacement of the amphos by other ligands. While no new and interesting catalyst systems have been discovered in this work, it is clear that the use of amphos to 'heterogenize' otherwise homogeneous catalysts can lead to unexpected catalytic properties, but that care must be taken to choose metals which are relatively stable to both oxidation and to phosphine dissociation. Research continues with amphos complexes of the platinum metals.

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