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ARTICLE

Valorisation of Mixtures of Linear Alkenes using Cobalt-Mediated Isomerisation and Hydroformylation Chemistries

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Active catalysts derived from cobalt and the Xantphos ligand were synthesised, characterised and tested in the hydroformylation of pure linear alkenes or their mixtures. The preformed complex [$Co_2(CO)_6$(Xantphos)] showed similar reactivity and selectivity towards aldehydes as the active catalyst formed *in situ* from equimolar amounts of [$Co_2(CO)_8$] and Xantphos. In the case of oct-1-ene, the linear aldehyde was obtained with good chemo- and regio-selectivity (linear to branched ratio was up to 75:25). For all octene isomers, tandem isomerisation-hydroformylation processes took place. Regioselectivities for all the studied octene isomers remained practically constant, independently of the position or geometry of the C=C double bond in the starting material. Moreover, by-products were formed in similarly small amounts for all the octene isomers. We also demonstrated that this chemistry is an interesting strategy for valorising mixtures of linear hexenes, heptenes or octenes by transforming the initial mixture into one major aldehyde (addition of a CHO group to the C_1 carbon of the alkene skeleton, up to 73% selectivity). Moreover, these mixtures of alkenes were hydroformylated with low final amounts of non-hydroformylated alkenes, hydrogenated alkenes and alcohols.

Introduction

Cobalt-catalysed hydroformylations were discovered by Otto Roelen in 1938.[1] First reports of cobalt-catalysed hydroformylations avoided the use of ligands and operated at high temperatures and pressures.[2] The introduction of ligands produced important milestones in this chemistry, such as catalyst stabilisation,[3] increased activity of the catalyst[4] and/or smoothing of the reaction conditions,[5] and improved chemo- and/or regio-selectivities.[6]

Alkenes, under cobalt-catalysed hydroformylation reaction conditions, can undergo several transformations in addition to hydroformylation (mainly C=C isomerisation and hydrogenation).[4,7,8] Moreover, depending on the reaction conditions and the catalyst employed, the hydroformylation products are unstable and evolve into corresponding alcohols through the hydrogenation of the C=O double bond.[4,7,8] Up to a certain extent, the complexity of the outcome of cobalt-catalysed hydroformylations can be reduced by tuning the reaction conditions (mainly H_2 and CO partial pressures and the temperature, but also the catalyst concentration, the choice of solvent or the use of additives).[4,6b,9] The use of organic ligands in cobalt-catalysed hydroformylations simplifies the complexity of the reaction mixtures, shifting the outcome of the reaction towards the products of interest. For instance, tertiary trialkyl monophosphines have been exploited in hydroformylations as useful ligands for increasing the regioselectivity towards linear products (Shell process).[6a,10]

Diphosphine ligands (for instance, $Ph_2P(CH_2)_nPPh_2$, with n = 2, 4 or 5) were introduced to cobalt-catalysed hydroformylations at the early stages of the application of this chemistry.[6a] Regioselectivity towards *n*-hexanal in the hydroformylation of pent-1-ene drops with the size of the cobalt chelate (regioselectivity towards the linear aldehyde for $n = 5 \approx n = 4 > n = 2$).[5,6a,11] The use of diphosphine ligands with a well-defined rigid backbone improves the catalytic results in the hydroformylation of terminal alkenes to aldehydes.[12,13] Most remarkably, Stanley and co-workers[13] recently reported highly active cationic cobalt(II) catalysts for hydroformylation. These authors noted that the activity of the monometallic catalyst precursor [Co(acac)(DPEBz)]BF_4 (DPEBz = 1,2-bis(diethylphosphaneyl)benzene) approached that of rhodium[14] catalysts.

The isomerisation of C=C double bonds and the hydroformylation reaction itself are competing processes under cobalt-catalysed hydroformylation reaction conditions.

The formation of a complex mixture of aldehydes is the main consequence of the isomerisation processes under hydroformylation conditions. Interestingly, if the C=C isomerisations are faster than the hydroformylations, the net addition of the H and CHO groups will take place, irrespective of the position and geometry of the C=C bond in the starting

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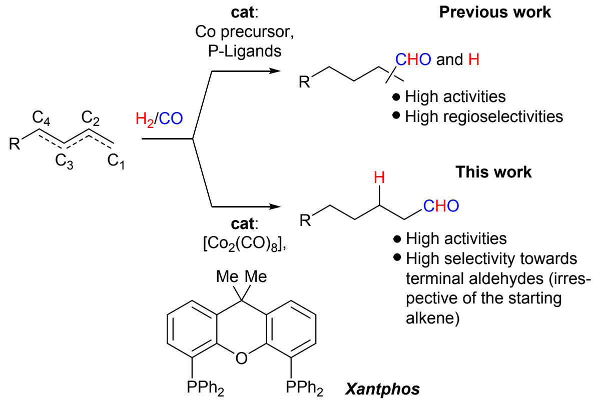
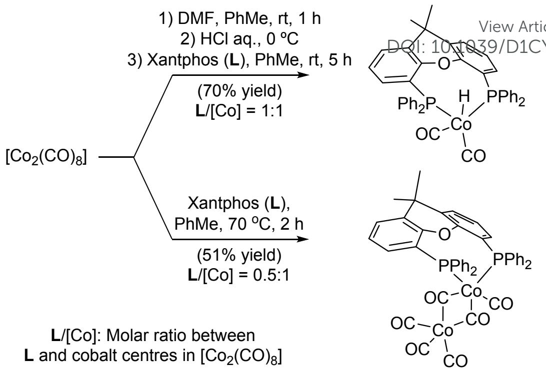


Scheme 1 Overview of the hydroformylation process.



Scheme 2 Synthesis of cobalt-Xantphos complexes.

material, at the most reactive and/or favourable position of the C=C double bond after isomerisation. Although it has been reported that unmodified hydrido carbonyl cobalt complexes such as $[Co(H)(CO)_4]$ play an important role in C=C isomerisations,[8,15] examples of cobalt-based hydroformylations of long chain internal alkenes are scarce in the literature.[6b,16]

The main objective of this work was to develop cobalt-based catalysts for the selective production of C_1-aldehydes irrespective of the position and geometry of the C=C bond in a given hydrocarbon skeleton. In terms of the ligand to be used, we hypothesised that cobalt catalysts incorporating the Xantphos ligand[17] (Xantphos = (9,9-dimethyl-9*H*-xanthene-4,5-diyl)bis(diphenylphosphane); **L**) could be appropriate given its wide bite angle[17] that could favour the preferential formation of C_1-aldehydes. While rhodium-catalysed hydroformylations using Xantphos-type ligands[17,18] have been well studied, their use in cobalt-catalysed hydroformylation remains unexplored. We also hypothesised that the use of an excess of cobalt centres (as a tool to mediate C=C bond isomerisation) with respect to the ligand could lead to the discovery of selective catalysts for the addition of a CHO group to the C_1 carbon of the alkene skeleton (Scheme 1).

Herein, we describe the results obtained in the tandem isomerisation/hydroformylation reactions of linear alkenes employing cobalt catalysts. We also demonstrate that mixtures of alkenes differing in the position and geometry of the C=C double bond can be transformed into one major aldehyde.

Results and discussion

Synthesis of Xantphos-cobalt complexes

Our investigations began with the synthesis and characterisation of suitable cobalt complexes derived from the Xantphos ligand for the hydroformylation reactions. The line of reasoning behind the ligand design included standard cobalt complexes in hydroformylation[4,7,8] (for instance, the hydrido dicarbonyl complex of cobalt(I) (**C1**); Scheme 2) and other complexes with different ratios of the number of Xantphos units to the number of cobalt centres. For instance, we hypothesised that in complexes with **L**/[Co] ratios lower than 1:1 (such as **C2**), one cobalt centre could be responsible for the hydroformylation and the other for the C=C isomerisation.

We envisaged that **C1** could be prepared from $[Co(H)(CO)_4]$ and Xantphos through the displacement of two CO ligands. The $[Co(H)(CO)_4]$ complex was prepared following the methodology developed by Roodt[19] and Kluwer[12] *et al.* which consisted of disproportionating $[Co_2(CO)_8]$ into $[Co(DMF)_6]^{2+}$ and $[Co(CO)_4]^-$ species. **C1** was isolated in a 70% yield after acidification of $[Co(CO)_4]^-$ with the formation of $[Co(H)(CO)_4]$ followed by the reaction with Xantphos (Scheme 2). As expected, the IR spectra showed two strong C≡O bands at 1910 and 1971 cm^{-1}. ^{1}H NMR spectroscopy showed a triplet signal at −11.23 ppm, corresponding to the hydrido ligand coupled to two equivalent phosphorus nuclei from the ligand ($^2J_{P-H}$ = 23.3 Hz). The multiplicity of the signal and the magnitude of the coupling constants suggested that both P–groups were coordinated in equatorial positions and the hydrido ligand in an axial position in a trigonal-bipyramidal cobalt geometry.[14a] The structure of **C1** was confirmed by single-crystal X-ray diffraction analysis,[20] which confirmed the axial position of the hydrido ligand at a distorted trigonal-bipyramidal cobalt centre. The equatorial position of the two phosphino groups at the trigonal-bipyramidal metal centre with a P–Co–P bond angle of 110.2º was also demonstrated.

The cobalt(0) complex **C2** was prepared by reacting equimolar amounts of $[Co_2(CO)_8]$ with Xantphos. The complex crystallised out from the reaction mixture, which allowed for a practical preparation protocol. Complex **C2** was characterised with standard spectroscopic techniques and X-ray analysis unequivocally confirmed the structure of **C2** as $[Co_2(CO)_6(Xantphos)]$[20] (Scheme 2 shows the synthesis and Figure 1 shows the X-ray structure of **C2**). Interestingly, the Xantphos ligand was coordinated with the same cobalt atom (d_{Co-Co} = 2.51 Å; d_{P-Co} = 2.258 and 2.308 Å), with the other cobalt atom being coordinated only with CO ligands.[21]

Development of optimal hydroformylation reaction conditions for oct-1-ene as a model substrate

We envisioned that the combination of a metal centre, such as cobalt, with a wide bite angle diphosphine, such as Xantphos,

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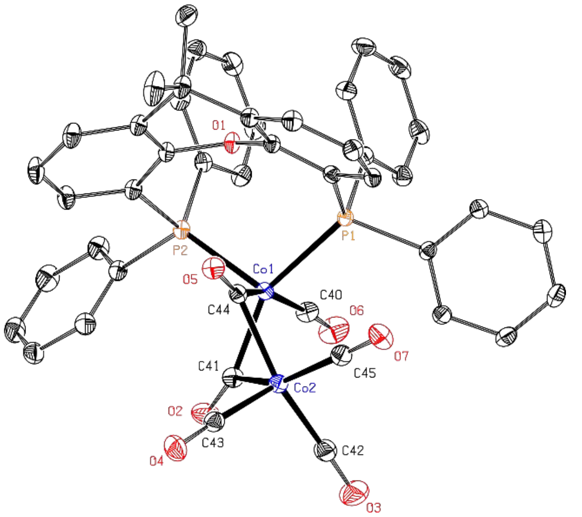
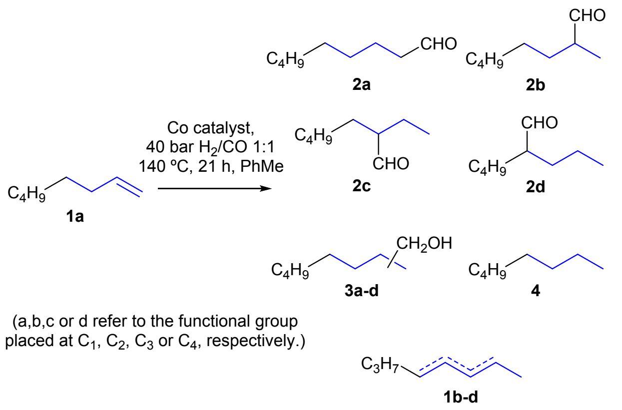


Fig. 1 ORTEP drawing of the crystal structure of **C2**. Hydrogen atoms have been omitted for clarity. Colour Scheme: C: black, Co: blue, O: red, P: orange.

would be a suitable starting point in developing efficient hydroformylation reaction conditions for oct-1-ene (**1a**).[22] The hydroformylation of oct-1-ene can potentially lead to a mixture of different products. The main aldehydes nonanal (**2a**) and 2-methyloctanal (**2b**) are obtained by direct hydroformylation, while 2-ethylheptanal (**2c**) and 2-propylhexanal (**2d**) can only be derived from a C=C bond isomerisation process followed by hydroformylation. The corresponding alcohols nonan-1-ol (**3a**), 2-methyloctan-1-ol (**3b**), 2-ethylheptan-1-ol (**3c**) and 2-propylhexan-1-ol (**3d**) are obtained after the hydrogenation of the aldehydes **2a-d**. Other potential products are the hydrogenation product **4** (octane) and non-hydroformylated octenes **1b-d** arising from the isomerisation of **1a**.

Initial studies focussed on the identification of active and selective cobalt catalysts derived from Xantphos. The activity of the cobalt complexes **C1** and **C2** in the hydroformylation of **1a** was initially studied (Table 1, entries 1 and 2). With the aim of following a rational process to discover catalysts for hydroformylation and to minimise the number of experiments, typical temperatures (140 °C) and partial H_2 and CO pressures (40 bar H_2/CO at a ratio of 1:1) were used throughout the catalyst discovery process. **C1** provided high selectivity towards aldehydes (abbreviated as "HF selectivity" in the discussion that follows; 73%, Table 1, entry 1), although there were considerable amounts of **4** formed (10%) as well as non-hydroformylated octenes (**1b-d**, 15%). **C2** proved to be a more selective catalyst than **C1** (HF selectivity of 89%; Table 1, entry 2). To increase the practicality of the hydroformylation by avoiding the necessity of synthesising the cobalt catalyst, we also studied the *in situ* generation of catalysts using different **L**/[Co] ratios (Scheme 2) by varying the relative molar amounts of the ligand and cobalt precursor. **L**/[Co] ratios ranging from 0:1 (*i.e.* absence of ligand) to 2:1 were studied. The results are indicated in Table 1 (entries 3-7). As previously observed for other diphosphine ligands and substrates,[5] changes in the **L**/[Co] ratio led to different outcomes in the hydroformylation of oct-1-ene. The conversion decreased with the **L**/[Co] ratio, with a 51% conversion at an **L**/[Co] ratio of 2:1 (Table 1, entry 7). The regioselectivity towards the linear aldehyde **2a** was not appreciably affected by the different *in situ* generated catalysts studied (Table 1). The amounts of **2a** with respect to all the aldehydes ranged from 62% to 70% throughout the whole study. Interestingly, the **L**/[Co] ratio of 0.5:1 (*i.e.* equimolar amounts of ligand **L** and $[Co_2(CO)_8]$) led to high HF selectivities (85%). It is interesting to highlight that the relative ratio of **L** units to Co centres in **C2** was the same as that in the complex generated *in situ* with an **L**/[Co] ratio of 0.5:1, leading to similar results in the hydroformylation of oct-1-ene (compare entries 2 and 5 in Table 1). As indicated in Table 3, **C1**, **C2** and the ligand-free system are equally active (conversions are in all cases ≥ 99%). In terms of selectivity towards aldehydes, **C2** provides a higher selectivity than **C1** or the ligand-free system (89% *vs.* 73% or 71%, respectively). The main difference in the reactivity between **C2** and **C1**/ligand-free system is that **C1** provides much

Table 1 Hydroformylation[a] of oct-1-ene (**1a**).



Entry	Co complex or L/[Co] ratio[b]	Conv.[c] (%)	Selectivity (%)[c]				
			2	3	4	1b-d	Ratio *2a:2b:2c:2d*
1	**C1** (1 mol%)	99	73	2	10	15	*64:22:8:6*
2	**C2** (1 mol%)	> 99	89	2	4	5	*69:19:7:5*
3	0:1[d]	> 99	71	25	2	2	*66:19:8:7*
4	0.25:1	98	80	17	0	3	*70:19:6:5*
5	0.5:1	> 99	85	11	2	2	*65:21:8:6*
6	1:1	> 99	79	13	4	4	*62:23:8:7*
7	2:1	51	37	1	13	49	*64:26:6:4*

[a]Reaction conditions: [alkene] = 0.26 M; reaction time = 21 h; stirring rate = 800 rpm. [b]**L**/[Co] ratio refers to the molar ratio between **L** and cobalt centres from $[Co_2(CO)_8]$, with [Co centres] = 5.2 mM (2 mol% with respect to oct-1-ene) unless otherwise indicated. [c]Conversion and product distribution were determined and quantified by GC analysis with dodecane as internal standard. [d]*In situ* generated $[Co(H)(CO)_4]$.

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higher amounts of *n*-octane and non-hydroformylated octenes (10% and 15%, respectively) than **C2**, whilst the ligand-free system leads to much higher amounts of alcohols **3a-d** (25%, Table 1, entry 3) than **C2**. Overall, **C2** and the catalyst generated *in situ* with an **L**/[Co] ratio of 0.5:1 were the best performing catalysts, with the selectivities towards 1-nonanal being amongst the highest reported in the literature.[22]

Hydroformylation is highly influenced by the reaction conditions.[4,8] A temperature screening study (90-160 °C) was also performed with oct-1-ene and *in situ* generated cobalt catalysts incorporating Xantphos. That study[23] revealed that 140 °C was the temperature of choice for obtaining a high HF selectivity. As expected, low conversions were observed at 90 °C and 110 °C (< 50%), although the selectivity towards **2a** was slightly higher at 90 °C (ratio **2a**/(**2b** + **2c** + **2d**) = 75:25) than at 140 °C (ratio **2a**/(**2b** + **2c** + **2d**) = 62:38; Table 1, entry 6). Temperatures above 140 °C (*e.g.* 160 °C) did not confer any advantage to the previously studied reaction conditions, as the amounts of **3a-d** surpassed the 12% yield. The catalyst screening study (Table 1) was performed with an H_2/CO ratio of 1:1 and H_2 and CO partial pressures of 20 bar. To study the effects of an excess of H_2 or CO on the outcome of the hydroformylation reactions, two experiments were conducted with H_2/CO ratios of 1:3 and 3:1, with the overall pressure maintained at 40 bar. In both cases, the cobalt catalysts were generated *in situ*.[23] An excess of CO (H_2/CO ratio = 1:3) led to a decrease in the conversion (52% with respect to > 99% for the H_2/CO ratio of 1:1) and in the HF selectivity (59% with respect to 79%).[23] Much higher amounts of non-hydroformylated octenes were generated from the isomerisation of **1a** with an excess of CO (33% with respect to 2%). When an excess of H_2 with respect to CO was used (H_2/CO ratio = 3:1), increased amounts of non-hydroformylated octenes arising from the isomerisation of **1a** (29% with respect to 2%) were observed.[23] The fact that significant amounts of non-hydroformylated octenes arising from the isomerisation of **1a** remained unreacted towards hydroformylation for both the 1:3 and 3:1 H_2/CO ratios indicated that the hydroformylations did not proceed as efficiently at these H_2/CO ratios when compared to the H_2/CO ratio of 1:1. Overall, these optimisation studies confirmed that 40 bar of H_2/CO at a ratio of 1:1 at 140 °C were the optimal hydroformylation conditions for achieving high HF selectivities.

The practicality of the method was demonstrated by performing the hydroformylation of **1a** at the gram scale using **C2** as catalyst, with a 1.8 M concentration of alkene (*i.e.* 7-fold increase in the concentration with respect to standard experiments) and at a S/C ratio of 1000 (*i.e.* 10-fold reduction in the amount of catalyst with respect to standard experiments in Table 1, entry 2). Under these new reaction conditions, the hydroformylation showed a conversion of 99% and led to the target aldehydes in a 51% isolated yield after distillation. The regioselectivity of the hydroformylation (50% of nonanal) was lower than that obtained under more diluted reaction conditions and employing higher amounts of catalyst (61% of nonanal; Table 1, entry 2).

Cobalt-catalysed hydroformylation of oct-1-ene isomers

Having demonstrated that Xantphos-based cobalt catalysts were active and selective in the hydroformylation of **1a**, we then broadened the substrate scope to its isomers with the C=C double bond at different positions and with different geometries. These substrates are inherently less reactive than the terminal isomer **1a** and studies of their cobalt-catalysed hydroformylation are scarce.[24] The results of the hydroformylation of the octenes (*Z*)-**1b**, (*E*)-**1b**, (*E*)-**1c**, (*Z*)-**1d** and (*E*)-**1d** are summarised in Table 2.

Hydroformylation of oct-1-ene isomers was performed under optimised catalytic conditions, forming the active catalyst *in situ*. In all cases, full conversion and high selectivities towards the aldehydes **2a-d** were observed, producing better results than those for **1a**. For (*Z*)-**1b** and (*E*)-**1b**, the aldehydes **2a-d** were formed with an 89 and 86% selectivity, respectively. By-products such as **3a-d**, **4** and non-hydroformylated octenes were obtained in low amounts (selectivities of 3-4%, 4-5% and 3-6%, respectively; Table 2, entries 2 and 3). In the case of (*E*)-oct-3-ene ((*E*)-**1c**), the corresponding aldehydes were obtained with a 91% selectivity, whilst the sum of all the by-products amounted to 9%. For (*Z*)-**1d** and (*E*)-**1d** (Table 2, entry 5 and 6), the results were similar, with a slightly higher HF selectivity for (*Z*)-**1d** (91%) than for (*E*)-**1d** (89%). Interestingly, for all the octene isomers studied (Table 2), a similar product distribution of **2a-d** was observed, with the hydroformylation of **1a** leading to the highest regioselectivity towards the linear aldehyde **2a** (Table 2, entry 1).

In general terms, very high aldehyde selectivities (from 85% to 91%) and low selectivities towards by-products were observed independently of the position or geometry of the C=C double bond (Figure 2). The selectivity towards **2a-d** was slightly higher for the internal alkenes, with the highest HF selectivity being obtained for (*E*)-**1c** and (*Z*)-**1d**. This behaviour is remarkable as the hydroformylation selectivities of internal alkenes are generally lower than those of the terminal analogues.[16f]

Table 2 Hydroformylation[a] of a series of octenes employing catalysts generated *in situ* with an **L**/[Co] ratio of 0.5:1.

Entry	Alkene	Conv.[b] (%)	Selectivity (%)[b]			
			2	**3**	**4**	**1b-d**
			Ratio ***2a:2b:2c:2d***			
1	**1a**[c]	> 99	85	11	2	2
			65:21:8:6			
2	**(*Z*)-1b**	99	89	4	4	3
			62:22:9:7			
3	**(*E*)-1b**	> 99	86	3	5	6
			62:22:9:7			
4	**(*E*)-1c**	99	91	4	3	2
			60:21:10:9			
5	**(*Z*)-1d**	> 99	91	3	4	2
			59:21:10:10			
6	**(*E*)-1d**	99	89	3	5	3
			60:21:9:10			

[a,b] For details, see Table 1. [c] These results are already shown in Table 1, but are included here for comparison.

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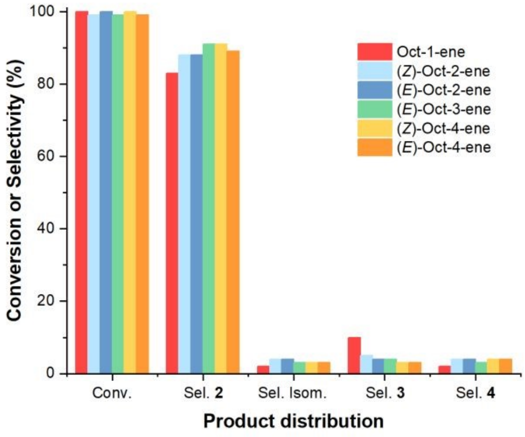

Fig. 2 Cobalt-catalysed hydroformylation of octenes with Xantphos as the ligand.

Valorisation of mixtures of alkenes by cobalt-catalysed hydroformylations

In recent years, the valorisation of petrochemical feedstocks (generally available as non-separable mixtures of hydrocarbons) has emerged as a driving force in fundamental research to produce high value-added products derived from petrochemicals rather than higher performing fuels.[25] Researchers have found that hydroformylation is useful in transforming mixtures of unsaturated hydrocarbons into value-added products such as aldehydes. The valorisation of mixtures of alkenes into the corresponding aldehydes by cobalt-catalysed hydroformylations is a well-established process, both in academia and industry.[25] However, the hydroformylation of mixtures of isomeric C_6-, C_7- and C_8-olefins retaining the same carbon connectivity but varying the position of the unsaturation has received less attention.[7,8a,26] Taking into account the similar regioselectivities observed in the hydroformylation of terminal and internal octenes with our cobalt-Xantphos catalysts, we turned our attention to mixtures of linear alkenes in cobalt-catalysed hydroformylation. For practical reasons, we prepared equimolar mixtures of all available linear hexene, heptene and octene isomers. These mixtures were subjected to our optimised hydroformylation conditions (140 °C, 40 bar H_2/CO at a 1:1 ratio, preformed catalyst **C2** or catalyst generated *in situ* with an **L**/[Co] ratio of 0.5:1).

Mixtures of linear hexenes, heptenes and octenes (see Table 3 for the components of the alkene mixtures) were successfully hydroformylated to the corresponding aldehydes, with low final amounts of by-products. The mixtures of linear hexenes, heptenes or octenes were hydroformylated with HF selectivities ranging from 82% to 91%, depending on the alkene mixture and the catalyst used (Table 3). In general, slightly higher HF selectivities were obtained with the *in situ* generated catalysts (85% *vs.* 82%, 87% *vs.* 85%, and 91% *vs.* 83% for the mixtures of linear hexenes, heptenes and octenes, respectively; Table 3, entries 1, 3 and 5). By contrast, the regioselectivity towards the hydroformylation at the terminal carbon C_1 was slightly higher for **C2** (up to a 4% increase in the regioselectivity towards the hydroformylation product at C_1 (*i.e.* the terminal aldehyde; Table 3, entry 6). For each alkene mixture, selective hydroformylation conditions were discovered, with low amounts of alkanes or alcohols produced.

These results illustrate that cobalt-catalysed hydroformylation could be a useful valorisation tool for mixtures of alkenes with the same carbon connectivity given the high regioselectivities towards addition of a CHO group to the C_1 carbon of the alkene skeleton (up to 73%) under the specific reaction conditions optimised for each mixture of alkenes.

Table 3 Hydroformylation[a] of mixtures of alkenes employing the cobalt complex **C2** or catalysts generated *in situ* with an **L**/[Co] ratio of 0.5:1.

Entry	Alkene mixture	Co complex or **L**/[Co] ratio	Selectivity (%)[b] Aldehydes	Alcohols	Alkanes	Alkenes	*Hydroformylation at C_1:C_2:C_3:C_4*
1	Hexenes[c]	**L**/[Co] = 0.5:1	85	1	2	12	*72:20:8*
2	Hexenes[c]	**C2**	82	3	2	13	*73:19:8*
3	Heptenes[d]	**L**/[Co] = 0.5:1	87	1	1	11	*69:20:8:3*
4	Heptenes[d]	**C2**	85	2	1	12	*70:19:8:3*
5	Octenes[e]	**L**/[Co] = 0.5:1	91	3	3	3	*62:21:9:8*
6	Octenes[e]	**C2**	83	1	7	9	*66:19:8:7*

[a,b] For details, see Table 1. Product distribution was determined by GC analysis (area % results). [c] Mixture of hexenes contained equimolar amounts of hex-1-ene, (*E*)-hex-2-ene, (*Z*)-hex-2-ene, (*E*)-hex-3-ene and (*Z*)-hex-3-ene. [d] Mixture of heptenes contained equimolar amounts of hept-1-ene, (*E*)-hept-2-ene, (*E*)-hept-3-ene and (*Z*)-hept-3-ene. [e] Mixture of octenes contained equimolar amounts of oct-1-ene, (*E*)-oct-2-ene, (*Z*)-oct-2-ene, (*E*)-oct-3-ene, (*E*)-oct-4-ene and (*Z*)-oct-4-ene.

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Rationalisation of the hydroformylation results

As described in the previous sections, the ratios of terminal aldehydes (*i.e.* hydroformylation at C_1) with respect to their branched isomers (*i.e.* hydroformylation at C_2 and C_3 and also at C_4 for heptenes and octenes) remained practically constant. These results led us to hypothesise that under the effects of the Xantphos-based cobalt catalysts, a tandem isomerisation-hydroformylation process could be taking place, with the isomerisation process being faster than the hydroformylation reaction. The isomerisation of C=C bonds through the formation of cobalt-alkyl or cobalt-π-allyl complexes has been reported in the literature.[27] The final regioselectivity would correspond to the product distribution obtained after the isomerisation processes, with the hydroformylation products of the terminal alkene being the major aldehyde isomers obtained.

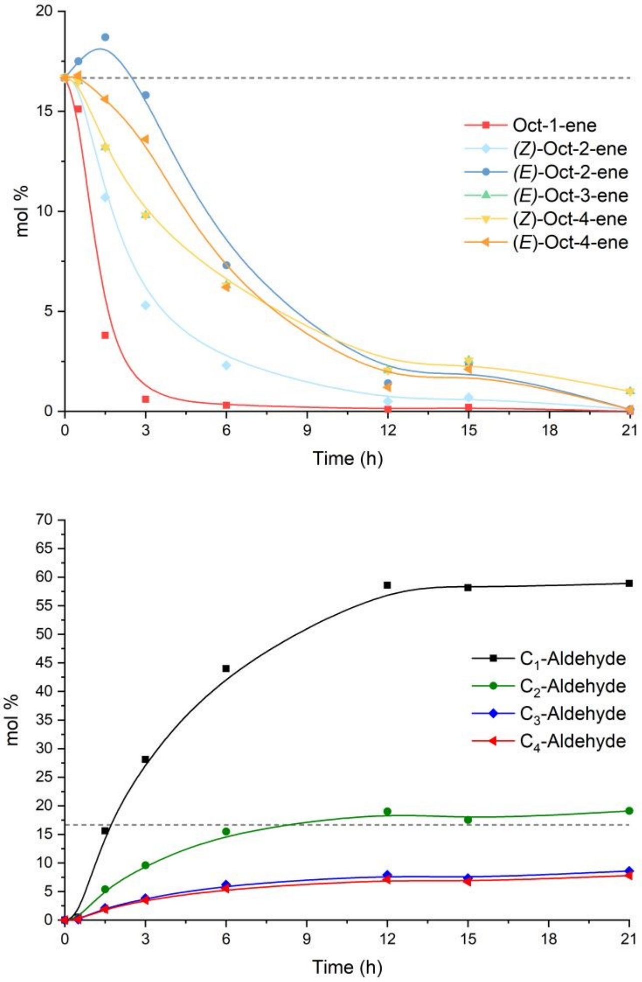
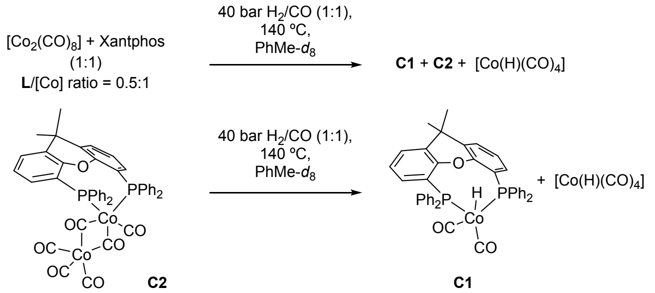


Fig. 3 Reaction progress monitoring of the hydroformylation of a mixture of octenes (1 mol% **C2**, 140 ºC, 40 bar H_2/CO 1:1, toluene, 43.3 mM in oct-1-ene, (*E*)-oct-2-ene, (*Z*)-oct-2-ene, (*E*)-oct-3-ene, (*E*)-oct-4-ene and (*Z*)-oct-4-ene); top: consumption of each octene isomer with time (GC peaks of 3-*E*- and 4-*Z*-octene coelute); bottom: formation of the four possible aldehydes with time; grey dotted line indicates initial mol% amount of each octene isomer; solid lines correspond to eye guidelines.

To confirm these observations, the progress of the hydroformylation of an equimolar mixture of linear octenes (for details, see caption to Fig. 3) was monitored by running independent hydroformylations at different reactions times and analysing the composition of the resulting reaction mixtures. Changes in the concentration of all starting octene isomers and final aldehydes against time are shown in Fig. 3. An analysis of the concentration of 1-octene at short reaction times confirms that isomerization is faster than hydroformylation: whilst *ca.* 9% of the initial amounts of 1-octene were consumed after 30 minutes, only 3% of the final amounts of the terminal hydroformylation product were formed. It is also interesting to note that the concentration of 2-*E*-octene in the reaction mixture at short reaction times was higher than the initial one (*ca.* 5% and 12% increase in the concentration after 30 and 90 min, respectively, with respect to the initial concentration of 2-*E*-octene). As for the formation of aldehydes, the reaction rate slopes for hydroformylation at C_1 in the first 90 minutes (mmol L^{-1} min^{-1}) are 2.9, 7.4 and 8.2 times higher than for hydroformylation at C_2, C_3 and C_4, respectively, which is in agreement with the experimental results.

To identify catalytically active cobalt complexes in this chemistry, *in situ* generated cobalt complexes (**L**/[Co] ratio 0.5:1) and **C2** were reacted with 40 bar H_2/CO at a ratio of 1:1 at 140 °C in the absence of alkene. Analysis of the mixture by ^1H and $^{31}P\{^1H\}$ NMR and ESI-MS indicated that **C1** was formed in both cases (Scheme 3). In addition to the formation of **C1** (Scheme 3), NMR and ESI-MS indicated that $[Co(H)(CO)_4]$ was also formed (hydride signal in ^1H NMR for $[Co(H)(CO)_4]$ in PhMe-d_8: $\delta_{exp} = -11.58$ ppm; $\delta_{lit} = -11.55$ ppm;[28] HRMS ESI-MS *m/z*: $[M-H]^-$ calcd. for $C_4O_4Co^-$ 170.9129, found 170.9298). It is reported in the literature that $[Co(H)(CO)_4]$ plays an important role in C=C double bond isomerisation.[15]

These results demonstrated that **C2** and the cobalt complexes generated *in situ* with an **L**/[Co] ratio of 0.5:1 evolve into the same cobalt complexes (**C1** and $[Co(H)(CO)_4]$) under the hydroformylation reaction conditions. Whilst it is reasonable to assume that $[Co(H)(CO)_4]$ plays a major role in the C=C isomerisation processes, **C1** is associated with the addition of a CHO group to the C_1 carbon of the alkene skeleton, irrespective of the position and geometry of the C=C bond in the starting material.



Scheme 3 Cobalt complexes generated under hydroformylation reaction conditions.

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In terms of the stability of **C1** under hydroformylation reaction conditions (toluene, 140 ^oC, 40 bar H_2/CO 1:1, 21 h), $^{31}P\{^1H\}$ NMR analysis revealed that complex **C1** remains unchanged in solution (*ca.* 90%; Figure SI7) under the above-mentioned reaction conditions, with free ligand not being detected (see ESI for details). The role of **C1** in this chemistry is important (either because it is directly used or it is formed *in situ* from **C2** in the presence of syngas as previously discussed) and this stability test confirms its catalytic role in hydroformylation as it remains mostly unchanged.

Conclusions

Cobalt complexes $[Co(H)(CO)_2(Xantphos)]$ (**C1**) and $[Co_2(CO)_6(Xantphos)]$ (**C2**) were efficiently synthesised and characterised for their application in the hydroformylation of an array of structurally diverse alkenes differing in the position of the unsaturation and the geometry of the C=C double bond. **C1** and **C2** showed high performance as catalysts in terms of conversion and selectivity towards aldehydes in the hydroformylation of alkenes. Comparative studies employing the preformed **C2** or complexes formed *in situ* from Xantphos and $[Co_2(CO)_8]$ indicated that the results obtained in the hydroformylation reactions were comparable, therefore demonstrating that the two strategies for the preparation of the catalysts were equally valid (*i.e.* synthesis of cobalt catalysts in advance or *in situ* generation).

The cobalt-catalysed hydroformylation of oct-1-ene employing Xantphos as a ligand was highly selective towards aldehydes under the optimised catalytic reaction conditions (**C2** or *in situ* generated catalyst with an **L**/[Co] ratio of 0.5:1, 140 °C and 40 bar of H_2/CO at a 1:1 ratio). Furthermore, the formation of hydrogenated products, non-hydroformylated alkenes arising from the C=C isomerisation processes in the starting material and alcohol derivatives was minimised. Hydroformylations of other octenes were successfully carried out. High aldehyde selectivities were observed in all the cases. Regioselectivities for all the studied linear octene isomers remained practically constant, irrespective of the position and geometry of the double bond. These results lead us to suggest that under the effects of our Xantphos-cobalt-based catalyst, a tandem isomerisation-hydroformylation process takes place, with the isomerisation mediator $[Co(H)(CO)_4]$ being formed in the reaction mixture from **C2** or Xantphos/$[Co_2(CO)_8]$. We also demonstrated that this chemistry is an interesting strategy for valorising mixtures of linear hexenes, heptenes or octenes by transforming the initial mixture into one major aldehyde (addition of a CHO group to the C_1 carbon of the alkene skeleton, up to 73% selectivity.

Experimental part

Essays for screening catalysts: Xantphos (*ca.* 2.3 μmol in 360 μL of toluene) and $[Co_2(CO)_8]$ (*ca.* 2.3 μmol in 360 μL of toluene) or, alternatively, $[Co_2(CO)_6(Xantphos)]$ (**C2**) (*ca.* 2.3 μmol in 65 μL of toluene) were added under N_2 to a 2-mL vial equipped with a magnetic stirrer. The alkene or mixture of alkenes (*ca.* 230 μmol) and additional toluene were added to the vial to provide the desired final solution (0.26 M respect to the substrate). The vial was transferred to an autoclave. The autoclave was purged three times with syngas (1:1 H_2/CO ratio, at a pressure not higher than 10 bar) and, finally, the autoclave was pressurised with syngas to 40 bar. The reaction mixture was stirred at 140 °C for 21 h. The reaction was cooled down to room temperature (ice bath) and the pressure was carefully released in a well-ventilated hood. Conversion as well as the chemo- and regio-selectivities of the products arising from the hydroformylation reaction were determined by GC analysis and/or quantitative NMR.

Hydroformylation at the preparative scale: The complex **C2** (21.8 mg, 0.025 mmol; S/C ratio = 1000) was placed under N_2 in a 25 mL autoclave with a magnetic stirrer. Compound **1a** (4.0 mL, 25.2 mmol) and toluene (10.4 mL) were added to provide the desired final solution, giving a 1.75 M concentration of **1a**. The autoclave was purged three times with syngas (1:1 H_2/CO ratio, at a pressure not higher than 10 bar) and, finally, the autoclave was pressurised with syngas to 40 bar. The autoclave was connected to a five-litre steel reservoir filled with syngas to ensure that pressure was high enough during the whole hydroformylation process. The reservoir was isolated from the reactor by a valve, and the pressure inside the autoclave was restored to 40 bar by opening the valve, when the pressure inside the autoclave dropped by 10%, and closing it afterwards. The reaction was cooled down to room temperature (ice bath) and the pressure was carefully released in a well-ventilated hood. The reaction mixture was distilled under vacuum to obtain the aldehydes (fraction 1, b.p. = 40-45 °C, 25-30 mbar, 8.40 g, 1.72 mmol of aldehydes; fraction 2, b.p. = 75-80 °C, 25 mbar, 2.16 g, 11.0 mmol of aldehydes; 51% overall yield).

Conflicts of interest

There are no conflicts of interest to declare.

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