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Review

Hydroformylation studies using high pressure NMR spectroscopy

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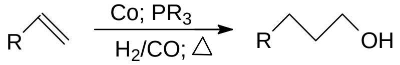
Contents

Abstract

High pressure nuclear magnetic resonance (HP-NMR) spectroscopy has become a useful tool for homogeneous catalysis research, both in industry and academia. It is a "window" on catalysis at variable temperatures and elevated pressures, and allows the researcher unprecented access to information on catalyst behaviour under process conditions. HP-NMR studies carried out on modified cobalt hydroformylation catalysts are presented from an industrial perspective. The ligands of interest are bridged bicyclic phosphines derived from phobane and (*R*)-(+)-limonene. Integration of HP-NMR with HP-IR, molecular modelling and bench experiments is also discussed.



Keywords: Hydroformylation; High pressure NMR; Cobalt; Phosphabicyclononane

1. Introduction to HP-NMR spectroscopy

Understanding the mechanism of chemical reactions is essential for the advancement of chemistry. This field was traditionally the domain of academic researchers owing to the significant time and effort required to gain this un-

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derstanding. At the same time, the chemical industry was progressing by a laborious process of empirical testing of catalysts, often with little understanding of the results generated. This "black box" approach to chemistry is no longer sufficient to meet the needs of a highly competitive chemical industry. The development of various in situ spectroscopic and spectrometric techniques which allow one to observe the behaviour of catalysts under process conditions has revolutionised the way in which industrial catalysis research is carried out [1]. Such techniques, in combination with bench work, molecular modelling and other tools now available to R&D chemists, allow rapid access to a more fundamental understanding of a particular catalytic system. This shortens the time required for development of a process, by providing direct access to information on catalyst behaviour and stability under process conditions.

High pressure nuclear magnetic resonance (HP-NMR) spectroscopy is a particularly useful technique for homogeneous catalysis research [2,3]. Although NMR has a rather low sensitivity, the ability to focus on a specific nucleus allows one to generate information on very particular species, while eliminating complications arising from the abundance of other species in solution. In particular, by focussing on an element present in the catalyst alone (either the metal itself or an element of the ligand), one can observe the catalyst species quite clearly despite the huge excess of reagent and product. This enables researchers to generate much data on structures of and relationships between different catalytic species.

The first high pressure NMR studies were carried out in the 1950s by Benedek and Purcell in a pressurisable NMR probe [4]. Since then, several systems have been developed for carrying out HP-NMR studies, including various high pressure NMR probes [5–7] and sapphire NMR cells [8,9]. In the case of modified NMR probes, excellent results can be obtained, however costly and specialised equipment, a wide bore NMR magnet, and a dedicated NMR are often required. The sapphire cells (known as "Roe" cells, after their inventor) are relatively simple to manufacture and may be used in any commercially available spectrometer with a suitably sized probe. A typical Roe cell and shield are shown in Fig. 1.[1]

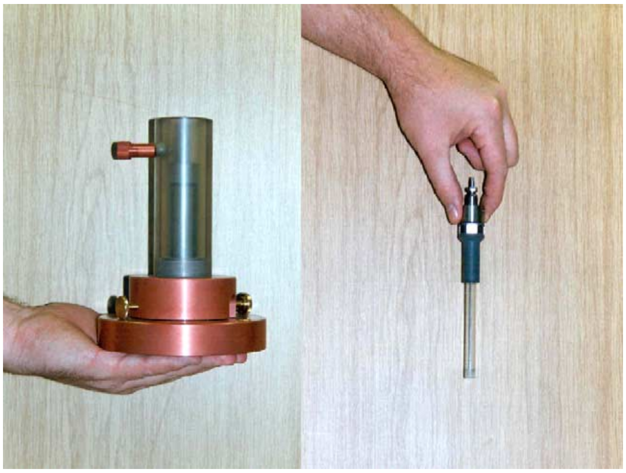

Fig. 1. Typical Roe high pressure NMR cell and shield.

The Roe cells are made from a single sapphire crystal capped with a titanium alloy head, and can sustain pressures of at least 200 bar. The titanium head is glued in place with an epoxy adhesive which is resistant to temperature, pressure and chemicals. Regular pressure testing is recommended to ensure the integrity of the cell when in frequent use, particularly at high temperatures and pressures. For safety reasons, the pressurised cells should always be handled in a shield. The major limitation of the sapphire tubes is that they are a closed system, and thus where gas is consumed in a reaction, constant pressure cannot be maintained. In addition, as there is no stirring mechanism, mass transfer limitations may come into play. However, provided the researcher takes cogniscence of these limitations when drawing conclusions from results, the ease of use of these tubes generally outweighs the drawbacks. In particular, when used in conjunction with other high pressure techniques where gas can be fed on demand and mixtures can be stirred (such as HP-IR), these limitations can be quantified and can actually yield very useful information.

Many applications of HP-NMR studies in homogeneous catalysis have been reported, although it is surprising that there is not more work of this nature in the open literature. Areas of interest include detection of intermediates in catalytic cycles and investigations of equilibria between metals and their ligands [10,11]. In recent years, the groups of Millar et al. [12], Iggo [13], and Roe [14] have generated much practical information on various homogeneous catalyst systems of interest to industry. Roe has described an elegant ^{13}C HP-NMR study of CO exchange reactions of various cobalt carbonyl complexes which are catalytic intermediates or precursors in unmodified cobalt catalysed hydroformylation [14]. This gives some insights into the inherent reactivity and stability of these complexes in the pressure and temperature ranges of the study. The group of Rathke at the Argonne National Laboratory have carried out extensive HP-NMR studies looking at various nuclei including ^{1}H, ^{13}C, ^{31}P and ^{59}Co. These studies include several supercritical fluid systems [15,16] including cobalt carbonyl catalysts in supercritical CO_2 [17–19]. The latter include calculations of the energetics of $HCo(CO)_4$ formation from $Co_2(CO)_8$ under hydrogen pressure, as well as in situ measurement of steady state concentrations of catalytic species and reaction rate. Intriguing evidence for formation of the $Co(CO)_4$ radical is also presented. Significant studies of homogeneous phosphine modified and unmodified cobalt carbonyl hydroformylation catalysts were reported by the same group in the 1990s [20,21]. The interconversion of var-

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[1] The Roe cells used in Sasol Technology were purchased from the University of Amsterdam, who constructed the titanium heads and affixed them to single crystal sapphire tubes sourced from Saphikon (USA).

ious tri-*n*-butylphosphine substituted cobalt carbonyls was investigated in detail at different temperatures and CO pressures and in various solvents [21]. Strategies to maximise formation of $HCo(CO)_3(PBu_3)$ are highlighted, as this is the key precatalyst which enters the hydroformylation cycle by loss of CO.

2. Hydroformylation with cobalt carbonyl-phosphine complexes

Phosphine modified cobalt carbonyl catalysts for hydroformylation were developed extensively by Shell in the 1960s and 1970s, and are being used in large scale production of detergent alcohols from linear alkenes [22–24]. While the well-studied rhodium phosphine and phosphite catalysts have the advantage of mild operating conditions and generally high selectivities to linear aldehyde products, phosphine modified cobalt catalysts can also give good selectivities to linear products and have several other advantages:

- Alcohols are formed from alkenes in a single reactor, as the hydroformylation catalyst also hydrogenates the aldehyde intermediates.
- The catalysts are more robust towards feedstock impurities than rhodium.
- Cobalt is less expensive than rhodium.
- Apart from Sasol's Secunda-based Safol plant, to date there are no other rhodium-based hydroformylation processes for longer chain alkenes ($>C_{10}$) as the rhodium catalysts are generally temperature sensitive and cannot survive the high temperatures required for distillation of the hydroformylation products.

For these reasons, Sasol Technology is investigating phosphine modified cobalt hydroformylation technology. As part of this study, HP-NMR and HP-IR competencies were established in order to gain a more fundamental unsterstanding of the catalyst systems and how they behave.

The accepted hydroformylation reaction mechanism of Heck and Breslow [25] with phosphine modified cobalt catalysts is depicted in Fig. 2 (where P = any phosphine ligand). Loss of a CO ligand from $HCo(CO)_3P$ creates a vacant site allowing the coordination of an alkene. Insertion of the alkene into the Co–H bond results in formation of an alkylcobalt intermediate. This insertion can occur at either the α- or β-carbon, giving rise to the linear (*n*) or 2-methyl branched (*iso*) isomers typical of hydroformylation reaction products. In the presence of syngas, hydrogenation of the alkylcobalt intermediates may also occur, to afford paraffins as byproducts. Hydride migration along the alkyl chain can also lead to isomerisation of the starting olefin. Insertion of CO into the metal–alkyl bond results in the formation of an acylcobalt intermediate. This may be cleaved with hydrogen to afford the aldehyde hydroformylation product.

The highly reactive aldehydes may react further to form "heavies" such as aldol products, but owing to the high hydrogenation activity of the cobalt catalyst, the aldehydes are primarily hydrogenated in situ to the alcohol. A second pathway may exist for direct formation of alcohols from the acyl cobalt carbonyl intermediate, without formation of the intermediate aldehyde. This pathway has been confirmed for phosphine-modified rhodium catalysts [26] but no evidence exists in the case of cobalt catalysts. The route involves coordination of molecular hydrogen to the coordinatively unsaturated acyl cobalt species, followed by hydrogenation of the C=O double bond. Further reaction with hydrogen would

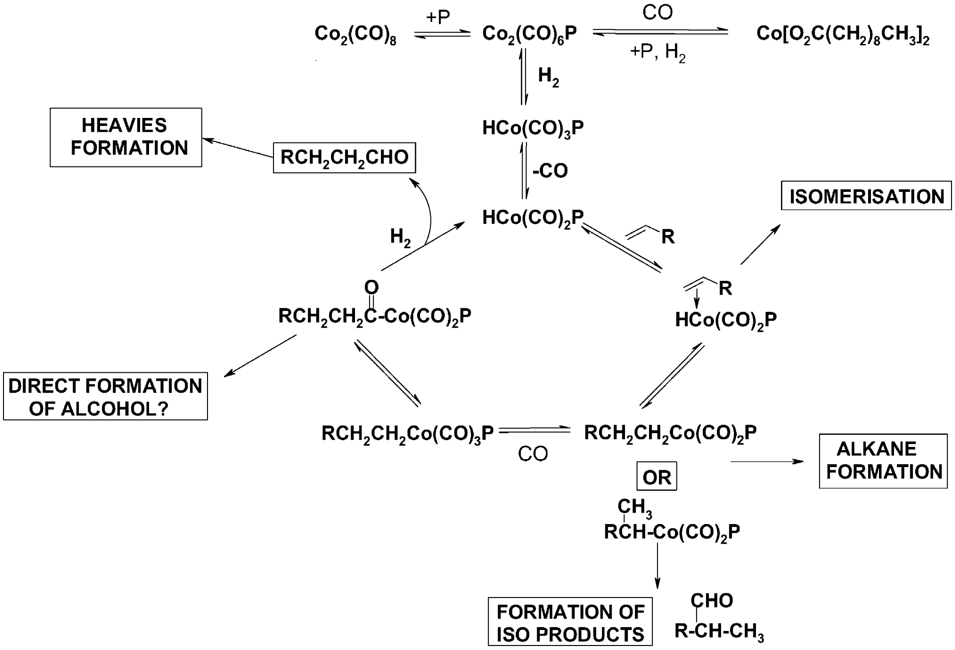


Fig. 2. Catalytic cycle for hydroformylation with phosphine-modified cobalt carbonyl catalysts.

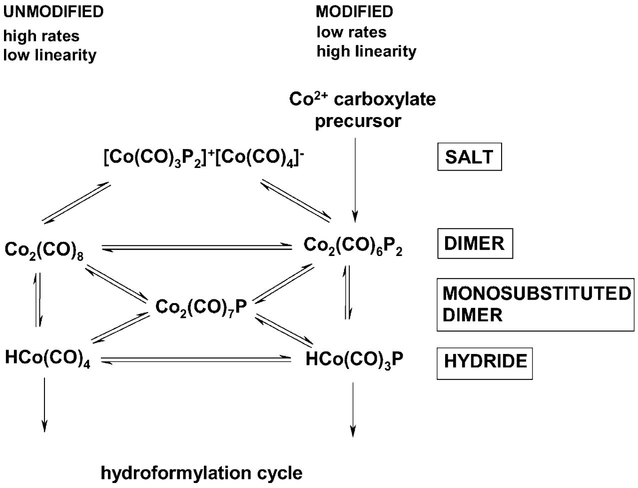


Fig. 3. Precatalyst equilibria.

release the alcohol and regenerate $HCo(CO)_2P$. Molecular modelling studies on unmodified cobalt catalysts have indicated that the activation energy for this pathway is considerably higher than that for hydrogenation of the aldehyde, suggesting that the direct route to alcohols is not significant for cobalt carbonyl catalysts [27].

HP-NMR may be employed to identify intermediates or resting states within a catalytic cycle, and from that the rate determining step of the mechanism. In unmodified cobalt catalysis the long-lived acylcobalt species can be observed by HP-IR during reaction with simple olefins, indicating that hydrogenolysis to the aldehyde is rate determining [28]. However in the same study with phosphine modified catalysts, no species within the catalytic cycle were seen. This indicates that the rate determining step for the overall process is likely to be the initial interaction of the olefin with the coordinatively unsaturated $HCo(CO)_2P$. It also means that HP-NMR studies of such systems are by default restricted to observations of the precatalyst behaviour and equilibria.

It is important to note that there are two main routes to enter the modified hydroformylation cycle, one via a cobalt(II) carboxylate precursor, and the other via cobalt octacarbonyl. The route from cobalt octacarbonyl proceeds via a dicobalt bis(phosphine) salt $[Co(CO)_3P_2]^+[Co(CO)_4]^-$, while that from Co^{2+} proceeds directly to the dimer $[Co_2(CO)_6P_2]$ and hydride $[HCo(CO)_3P]$ (Fig. 3) under syngas pressure. These cobalt carbonyl species have an inherent instability in the absence of CO pressure, thus several decomposition pathways to cobalt metal are possible. The unmodified hydrido species $HCo(CO)_4$ is particularly unstable and requires a certain minimum ρCO at a particular temperature and cobalt concentration to prevent metal plating. In the presence of excess ligand, equilibria may shift to di- and trisubstituted cobalt species (e.g. $HCo(CO)_2P_2$), while “ligand starved” species such as $Co_2(CO)_7P$ may form where there is less than stoichiometric ligand present. As these are equilibrium reactions, even in the presence of a large ligand excess small amounts of unmodified cobalt may be present leading to some “unmodified catalysis”.

Even though the amount of unmodified catalysis may be very small, reaction rates for unmodified catalysis are so much higher that significant effects may be observed. Unmodified cobalt catalysts typically afford very high reaction rates and low product linearities. The hydridocobalt carbonyl catalyst $[HCo(CO)_4]$ has low hydrogenation activity, and thus affords aldehydes as the main product, with low paraffin formation. High heavies formation is typical due to high concentrations of aldehyde in the presence of a very acidic catalyst. Phosphine-modified cobalt catalysts afford lower rates, but far higher selectivity to linear products. The catalyst is more hydridic in nature, hence results in more paraffin and less heavies formation.

The following sections will describe HP-NMR studies towards:

1. Identification of key catalytic species.
2. The effect of reaction parameters such as temperature on catalyst behaviour.
3. Catalyst stability and the effect of poisons.
4. Comparison of ligands: investigation of the properties of modified cobalt carbonyl species with different ligands in an attempt to explain the observed differences in reaction rate and selectivity.

3. Experimental procedures

As the species of interest are phosphine-modified cobalt carbonyls, ^{31}P NMR spectra were used almost exclusively in the work that is reported. ^{1}H NMR spectra were acquired where necessary in order to observe hydride resonances. The difficulty of obtaining good, quantifiable ^{13}C NMR spectra of carbonyls, particularly at low concentrations, precluded this nucleus from being used. A Roe cell with a 10 mm diameter was used, and spectra were acquired on a 400 MHz Varian and a 500 MHz Bruker spectrometer.

In all HP-NMR experiments cobalt octacarbonyl [$Co_2(CO)_8$, purchased from Fluka] was employed as the cobalt source, rather than the cobalt(II) carboxylate precursors employed in HP-IR and autoclave work. This is because facile reduction of the Co^{2+} precursors to the required cobalt carbonyls was not possible under the conditions employed in most of the experiments (maximum temperature of 150 °C). The reduction is highly dependent on temperature and mass transfer and generally requires good stirring and temperatures of at least 170 °C to occur within a reasonable time. It has been shown that the catalyst species and equilibria formed via both types of precursor are the same [29].

The syngas employed was a 2:1 H_2:CO mixture purchased from Fedgas. Operating conditions for the modified cobalt process are typically 50–100 bar and 150–200 °C. As the sapphire NMR cell is a closed system, pressure inside the cell will increase with temperature. As per the variation of the ideal gas law with constant n and V, the cell was therefore pressurised at room temperature (25 °C) to a pressure corresponding to the desired reaction pressure at the end temperature. In most cases, the cell was pressurised to 65 bar at 25 °C to afford a pressure of ~85 bar at 150 °C.

A typical experiment was carried out as follows: $Co_2(CO)_8$ was weighed into an argon-filled sample tube, and dissolved in 1.5 ml of solvent (usually toluene) and 0.5 ml of d_8-toluene. An appropriate amount of ligand (usually 2–3 eq. with respect to cobalt) was then transferred under argon to the sample tube. This addition was accompanied by visible evolution of CO. The HP-NMR cell was flushed with argon, and the reaction solution was transferred via syringe to the cell. The cell was closed and purged by pressurising to the appropriate pressure (usually 60 bar) with syngas and releasing pressure several times. Once pressurised to the desired operating pressure, the cell was left overnight at room temperature (at least 15 h) to allow proper gas dissolution before acquisition of spectra. In recent months a vortex shaker has been employed to effect far quicker dissolution of syngas (15 min).

4. Studies with limonene derived ligands

In recent years, Sasol has investigated the use of (*R*)-(+)-limonene derived ligands for modified cobalt hydroformylation [30,31]. These “Lim” ligands are formed by radical addition of PH_3 to limonene, followed by a further radical addition of the resultant R_2PH (or Lim-H) species to an appropriate alkene [32]. Lim-18 is therefore the ligand derived from addition of octadecene to Lim-H (Fig. 4, RI: radical initiator). The resultant bridged bicyclic phosphines contain two methyl groups on the bicycle and are formed as a mixture of two diastereomers. Nomenclature and assignment of the diastereomers is described elsewhere [31,33].

4.1. Reactivity of diastereomers

To investigate whether the diastereomers behave similarly in their reactivity towards cobalt, an experiment was carried out where $Co_2(CO)_8$ and 2 eq. of Lim-18 (with respect to Co) were mixed in the HP-NMR cell, with resultant evolution of CO. ^{31}P NMR spectra were taken at different temperatures. The reaction is given below:

$$\begin{aligned}&Co_2(CO)_8 + 4\,\text{eq Lim-18}\\&\quad\rightarrow Co_2(CO)_6(\text{Lim-18})_2 + 2\text{Lim-18} + 2CO\end{aligned}$$

Fig. 5 shows the free ligand region of the ^{31}P NMR spectrum before and after the addition of $Co_2(CO)_8$. The free ligand consists of two diastereomers in a 1:1 ratio as indicated by the two resonances at −45.2 ppm and −51.7 ppm. After the addition of $Co_2(CO)_8$ at 30 °C, the resonance at −45.2 ppm (the (4*R*)-diastereomer) decreased considerably relative to that at −51.7 ppm. As the temperature increased, more ligand reacted with the $Co_2(CO)_8$ resulting in a further decrease of the −45.2 ppm resonance relative to that at −51.7 ppm. Although one isomer clearly coordinates more readily to cobalt, resonances corresponding to complexes from both diastereomers were observed. Furthermore, if only one equivalent of Lim-18 is added to $Co_2(CO)_8$ all the free ligand (i.e. both diastereomers) complexes to cobalt. Thus, the (4*S*)-diastereomer is not inactive, which is important in terms of process development, as separation of the diastereomers would not be economical on a large scale. These differences in reactivity have since been confirmed by molecular modelling calculations at Sasol Technology and by elegant studies at the University of St Andrews, where cobalt complexes corresponding to a single diastereomer were isolated and tested for catalytic activity [31,33].

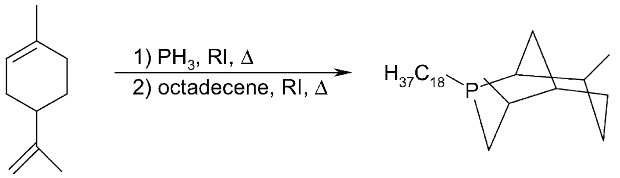


Fig. 4. Synthetic route to Lim-18.

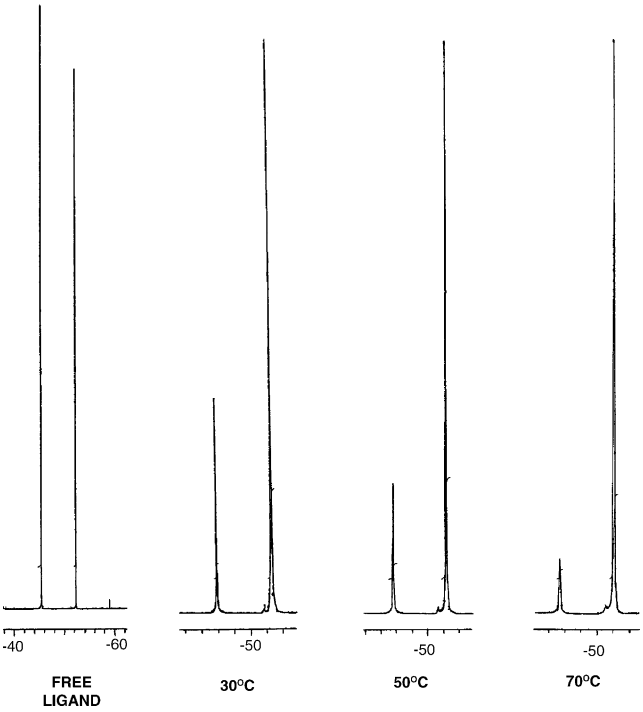


Fig. 5. Reactivity of Lim-18 diastereomers.

4.2. Catalyst preforming

Conversion of the cobalt precursor to an active catalyst is an important part of the hydroformylation process. In an attempt to build up a knowledge base and characterise certain key species, initial studies focussed on synthesis and interconversions of cobalt carbonyl species in the absence of syngas. Phosphine ligands P react with $Co_2(CO)_8$ by displacement of CO to form a salt $[Co(CO)_3P_2]^+[Co(CO)_4]^-$. This salt is converted rapidly at higher temperatures to a bis(phosphine) dimer $Co_2(CO)_6P_2$ by further displacement of CO [34].

$$\begin{tikzcd}
Co_2(CO)_8 + 2P \arrow[r] & \underset{\textbf{salt}}{[Co(CO)_4]^+[Co(CO)_3P_2]^- + CO} \arrow[d] \\
 & \underset{\textbf{dimer}}{Co_2(CO)_6P_2 + CO}
\end{tikzcd}$$

Synthesis and characterisation of the tri-*n*-butylphosphine substituted salt and dimer was achieved using literature procedures [21]. However, when Lim-18 was employed as ligand, the salt could not be isolated cleanly at room temperature. NMR studies showed that even at room temperature, the conversion of salt to dimer was so rapid that the salt was not obtained in reasonable yields. The studies were, however, sufficient to identify the characteristic resonances of the species for further reference. Thus in d_8-toluene using 2 eq Lim-18 with respect to cobalt, two sets of resonances for salt and dimer were observed to resonate at 38 and 41 ppm in the ^{31}P NMR spectrum (Fig. 6). The two sets of signals correspond to the bis[(4*R*)-Lim-18] complex and a mixed (4*R*), (4*S*) complex [33] in a ratio of about 2:1. Small amounts of the bis(4*S*) complex are also observed. At higher temperatures (above 70 °C) complete conversion of salt to dimer was observed.

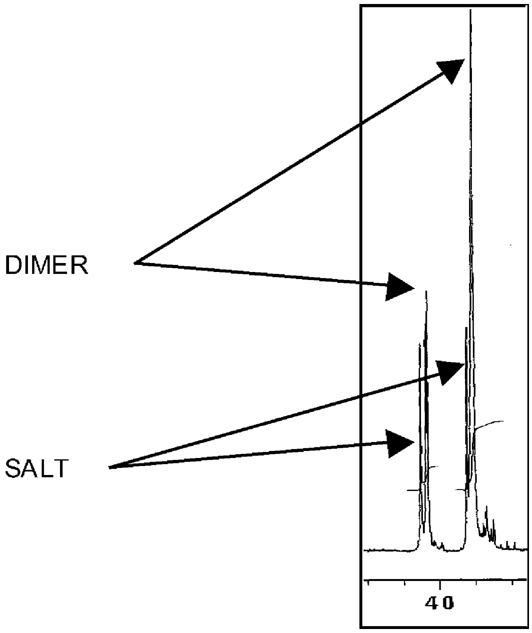


Fig. 6. Salt and dimer resonances with Lim-18 as ligand.

Once an understanding of this simple interconversion had been obtained, investigations in the presence of syngas were initiated. Upon heating under a positive hydrogen pressure, the dimer can be converted to a mononuclear hydrido species as follows:

$$\underset{\text{dimer}}{Co_2(CO)_6P_2} + H_2 \overset{\Delta}{\rightarrow} \underset{\text{hydride}}{2HCo(CO)3P}$$

This hydride is the precursor to the hydroformylation cycle, as discussed in Section 2. Thus, it is important to study the formation, stability and equilibria of this species. Preforming experiments were carried out to observe the formation of the Lim-substituted hydride under 85 bar of 2:1 syngas. A typical sequence of ^{31}P NMR spectra obtained at different temperatures is shown in Fig. 7. For simplicity, only the region between 18 and 44 ppm is shown—this is the region where phosphine-cobalt species resonate (the free ligand resonances are not shown).

At 30 °C, only salt and dimer resonances were evident in the spectrum. Upon heating to 90 °C, the salt resonances slowly decreased in intensity relative to dimer, and a small amount of a new species (resonating as a broad peak at 28 ppm) started to form. This species was assigned as the monosubstituted hydride $HCo(CO)_3$(Lim-18). At 120 °C, the salt had disappeared completely, and the new resonance increased in intensity with a further increase in temperature. After 2 h at 150 °C, the amount of this species reached a maximum. Upon cooling, the broad 27 ppm resonance was observed to sharpen and split into two peaks, corresponding to the hydride complex for each Lim-18 diastereomer. To confirm this, ^{1}H NMR of the sample was run to see if the hydrides could be detected. Two doublets were detected at −11 ppm, with a coupling constant of 48 Hz. This correlates well with coupling constants reported for other hydrides of this nature, e.g. 47 Hz for $HCo(CO)_3(PBu_3)$ [21]. Fig. 8 shows the full ^{31}P NMR spectrum of a typical cobalt-Lim-18 system at room temperature under 65 bar of syngas pressure. The insert shows the hydride resonance in the ^{1}H NMR spectrum.

4.3. Effect of reaction parameters

Experiments were carried out to investigate the effect of typical reaction parameters such as temperature, pressure and solvent on the formation of the hydride, $HCo(CO)_3P$. It appears that temperature is the most critical parameter determining formation of the hydride. For example, little or no difference in hydride formation was observed when carrying out preforming experiments at 40 bar, with 1:1 syngas, in a paraffinic, alcoholic or aromatic solvent.

With regard to temperature, hydride formation was generally not observed below 90 °C, explaining why

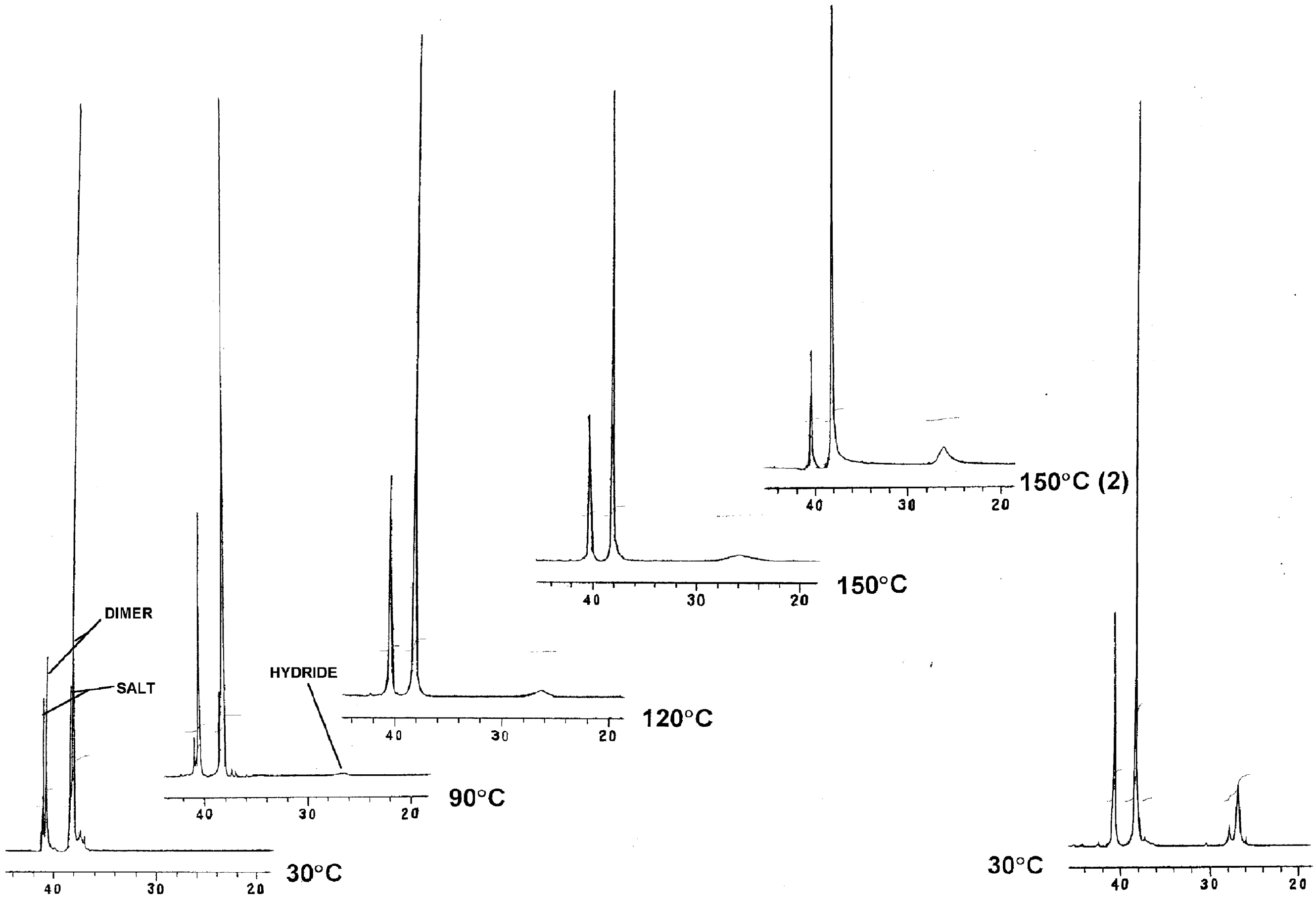


Fig. 7. ^{31}P NMR spectra of the Co/Lim-18 system at various temperatures (85 bar syngas).

hydroformylation activity of these catalysts is negligible at lower temperatures. Only at and above 150 °C were significant amounts of hydride formed. Changes in the distribution of Lim-18 with time and temperature for a typical run (65 bar starting pressure of 2:1 H_2:CO) are shown in Fig. 9. Spectra were taken at half hour intervals. Upon heating from 30 to 120 °C, a drop in free ligand concentration and an increase in the amount of complexed cobalt were observed. However, with time and above 120 °C the amount of complexed cobalt remained more or less constant through the run. This confirms that elevated temperature is required to effect the full conversion of $Co_2(CO)_8$ to $Co_2(CO)_6$(Lim-18)$_2$. The amount of free ligand remaining corresponds to the excess of ligand used in the experiment, and this can always be used as a crude cross-check to see if any cobalt (as unmodified cobalt complexes) is "missing" from the ^{31}P NMR. Over time at 120 °C, the hydride concentration slowly increased and then levelled off as equilibrium was reached. Upon heating to 150 °C the equilibrium was shifted and hydride formation again increased, reaching a maximum after 2 h. The slow equilibrium likely reflects the slow dissolution of syngas into solution. Coinciding with the increasing hydride formation was a decrease in the amount of dimer. As no other species were observed, this suggests that hydride formation occurs via the interaction of hydrogen with the dimer in a concerted process with no discrete intermediates.

4.4. Ligand starvation

Another potentially significant species in the modified cobalt catalyst system is the monosubstituted dimer, $Co_2(CO)_7P$. Formation of this species will be favoured when the system is starved of ligand. Reaction of $Co_2(CO)_7P$ with hydrogen will result in the formation of one molecule of modified hydride and one molecule of unmodified hydride as shown below:

$$Co_2(CO)_7P + H_2 \rightarrow HCo(CO)_3P + HCo(CO)_4$$

It is therefore important that formation of this species is minimised under process conditions as it will lead to a faster but less selective reaction. Using 0.5 eq. of Lim-18 relative to cobalt, the monosubstituted dimer was observed at elevated temperatures and 65–85 bar of syngas pressure (Fig. 10). At 30 °C at the start of the experiment $Co_2(CO)_6$(Lim-18)$_2$ was the predominant species, although $Co_2(CO)_7$(Lim-18) and $[Co(CO)_3(\text{Lim-18})_2]^+[Co(CO)_4]^-$ were also present. Upon heating to 100 °C, the concentration of $Co_2(CO)_6$(Lim-18)$_2$ decreased and that of $Co_2(CO)_7$(Lim-18) increased,

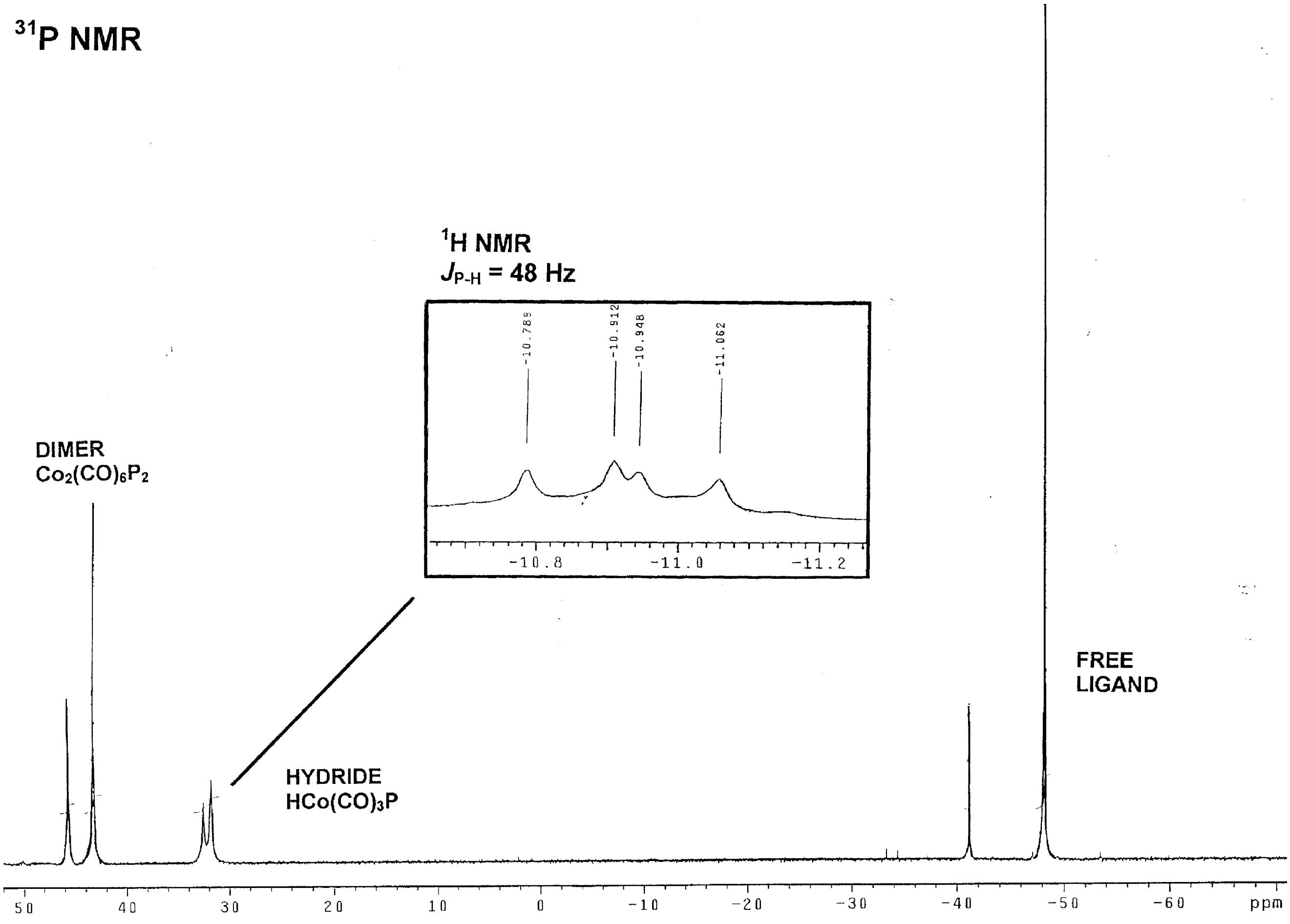


Fig. 8. ^{31}P and ^{1}H (hydride region) NMR of Co/Lim-18 system (85 bar syngas).

presumably by equilibration of $Co_2(CO)_6$(Lim-18)$_2$ with unsubstituted $Co_2(CO)_8$. $Co_2(CO)_6$(Lim-18)$_2$ concentration then remained relatively constant, while $HCo(CO)_3$(Lim-18) concentration increased to a maximum at 170 °C at the expense of $Co_2(CO)_7$(Lim-18). As described above, it was postulated that the amount of unmodified hydride, $HCo(CO)_4$ also increased. This was later confirmed by similar HP-IR studies. While unmodified cobalt species such

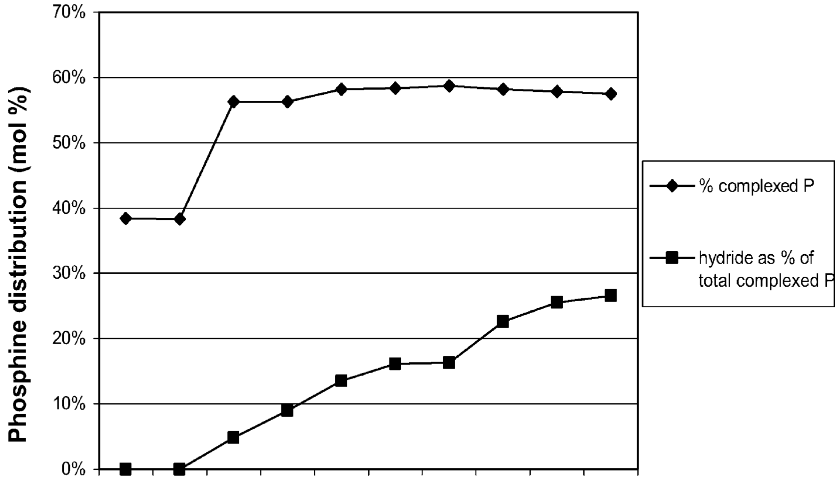


Fig. 9. Phosphine distribution at different temperatures (85 bar syngas; 30 min intervals).

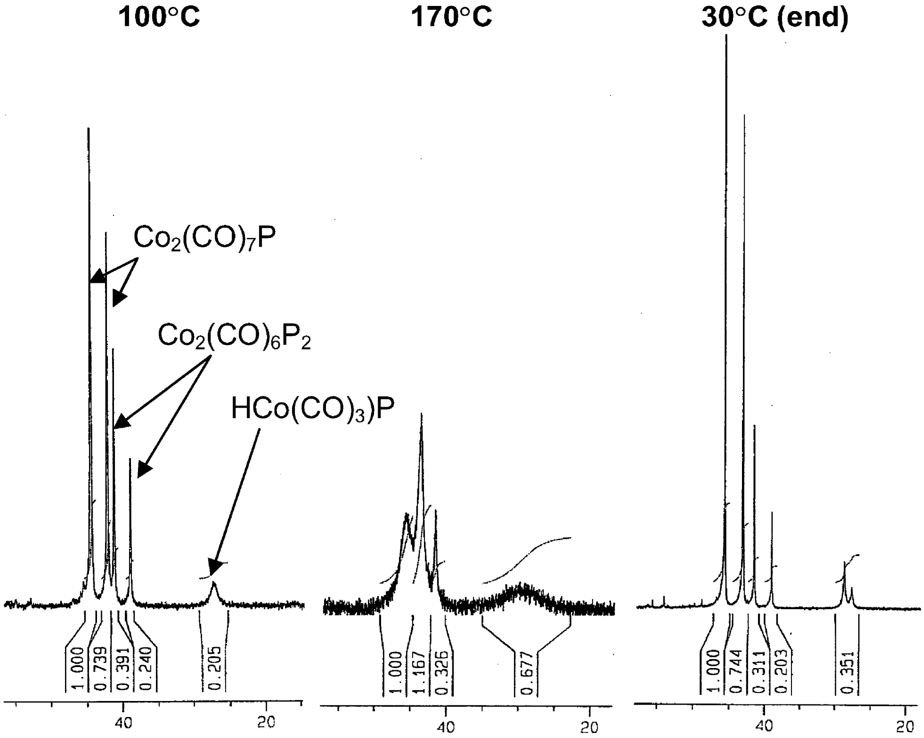
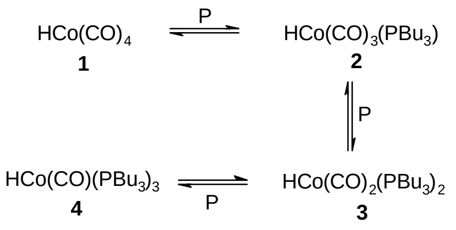


Fig. 10. ^{31}P NMR of ligand-starved Co/Lim-18 system (85 bar syngas).

as $HCo(CO)_4$ cannot be observed using ^{31}P NMR, HP-IR can be used as a complementary technique to identify them. At 170 °C extreme broadening of all peaks was observed, indicating extensive ligand exchange between species (there is no free ligand). Upon cooling, the peaks sharpened again and the monosubstituted dimer was the predominant species.

4.5. Formation of a disubsituted hydride

In the presence of excess ligand, there is a possibility of forming a bis phosphine hydride species, $HCo(CO)_2P_2$. The equilibria between such species is discussed in an article by Pregaglia et al. [35]. In various experiments with $HCo(CO)_4$ and PBu_3, the authors reported the formation of three modified hydrides:



In the presence of phosphine ligand, the first equilibrium is shifted totally to the monosubstituted hydride **2**. If CO is present, the equilibrium between **2** and **3** is largely shifted to the left hand side, but under a hydrogen atmosphere in the presence of excess ligand, the equilibrium will shift towards **3**. Trisubstituted hydride **4** could only be prepared by stoichiometric hydroformylation using $HCo(CO)_2(PBu_3)_2$ [35]. The trisubstituted species was not observed under any other conditions. In Rathke's study [21] no disubstituted hydride was reported, but this is presumably because they were working with preformed complexes and no ligand excess. Disubstituted hydridocobalt carbonyls of this nature are very effective hydrogenation catalysts: for hydrogenation of alkene feed to paraffin (undesired) or of aldehyde to alcohol (desired). It is therefore important to identify such complexes and be able to identify conditions under which they might form, as they could have a significant impact on reaction selectivities.

It was decided to investigate the behaviour of tri-*n*-butylphosphine under typical operating conditions by means of a preforming experiment using 4 eq PBu_3 with respect to cobalt. Spectra acquired at 30 and 120 °C are shown in Fig. 11.

At 30 °C, free PBu_3, tributylphosphine oxide, and three small impurities in the commercially available ligand (marked with '∗') were seen, along with two resonances corresponding to the salt $[Co(CO)_3P_2]^+[Co(CO)_4]^-$ and dimer $Co_2(CO)_6P_2$. Above 120 °C, two broad hydride resonances appeared at 46 ppm and 52 ppm. These were assigned as the monosubstituted $[HCo(CO)_3P]$ and disubstituted $[HCo(CO)_2P_2]$ hydrides, respectively [35].

Formation of the disubstituted hydride was also attempted with the sterically demanding Lim-18 ligand. Initial experiments with excess ligand under syngas pressure showed no trace of a second hydride species so a high pressure experiment was carried out with $Co_2(CO)_8$ and 4 eq. of

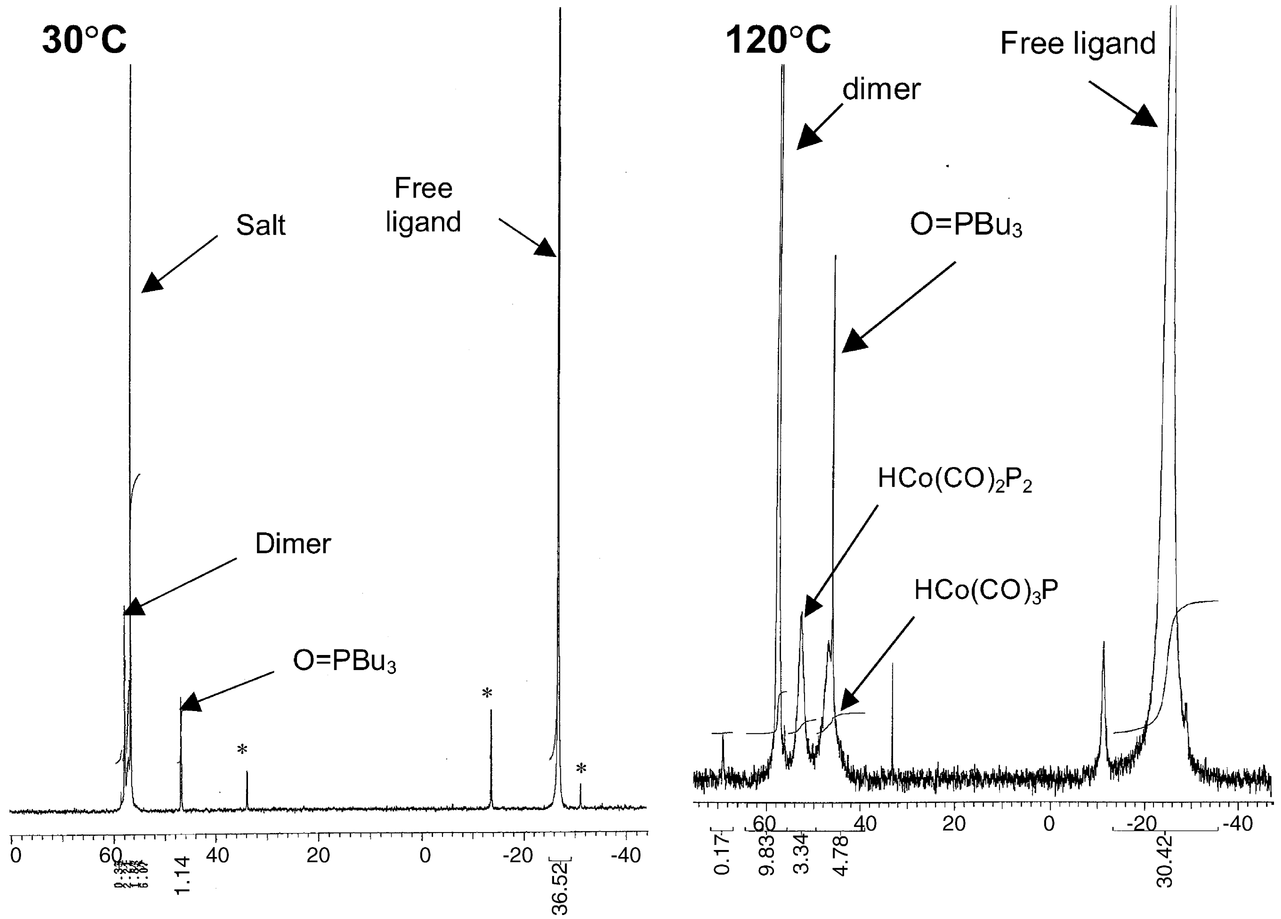


Fig. 11. ^{31}P NMR of Co/PBu_3 system (85 bar syngas).

Lim-18 under 40 bar of pure hydrogen as suggested by Pregaglia et al. With increasing temperature, the broad $HCo(CO)_3$(Lim-18) resonance at 27 ppm increased. However, at 150 °C a small amount of a second species began forming at around 33 ppm in the ^{31}P NMR spectrum. The peak was also very broad, suggesting considerable exchange between bound and free ligand. The concentration of this species increased slowly over 2 h at 150 °C, and disappeared again upon cooling to 30 °C. The species was not observed in any other runs and is believed to be the disubstituted hydride $HCo(CO)_2(\text{Lim-18})_2$. The compound appears to be thermodynamically unfavourable, probably owing to the great steric bulk of the Lim-18 ligand around the relatively small cobalt centre. In contrast, the smaller tri-*n*-butylphosphine ligand allows formation of a bisphosphine. $HCo(CO)_2(PBu_3)_2$ is a very effective hydrogenation catalyst as the second phosphine increases the hydridic nature of H. This was confirmed by batch autoclave studies where paraffin formation in the order of 10–20% was obtained for PBu_3, compared to 5–6% for Lim-18.

4.6. *Effect of iron carbonyls*

Iron carbonyls are a potential contaminant in the hydroformylation process. Syngas which passes through steel tubes can become contaminated with iron carbonyls, and corrosion within the process loops can lead to the formation of soluble iron corrosion products which may be converted to iron carbonyls at high temperatures and syngas pressures. Two HP-NMR experiments were carried out at different ligand concentrations.

The first run was carried out with $Co_2(CO)_8$, $Fe(CO)_5$ and Lim-18 in a ratio of 1:1:2 Co:Fe:Lim-18. At 30 °C, the only species observed was the dicobalt diphosphine dimer, $Co_2(CO)_6P_2$ (Fig. 12). Upon heating to 100 and 120 °C, the dimer concentration decreased as hydride increased. At 170 °C, two new resonances appeared at 42.0 and 44.8 ppm. Based on similar experiments in the HP-IR and correlation with literature values [36,37], this species was assigned as $Fe(CO)_4$(Lim-18). The formation of $Fe(CO)_4$(Lim-18) was accompanied by a decrease in the free ligand concentration, while the dimer and hydride concentrations remained relatively constant. This suggests that in a regime where there is excess ligand, $Fe(CO)_5$ will scavenge free ligand rather than interacting with the cobalt species.

Although the species only forms at 170 °C, upon cooling the concentration of $Fe(CO)_4$(Lim-18) persists. This suggests that it is thermodynamically favoured relative to the corresponding Co species, but that kinetically, it is difficult to form except at high temperatures. This has further

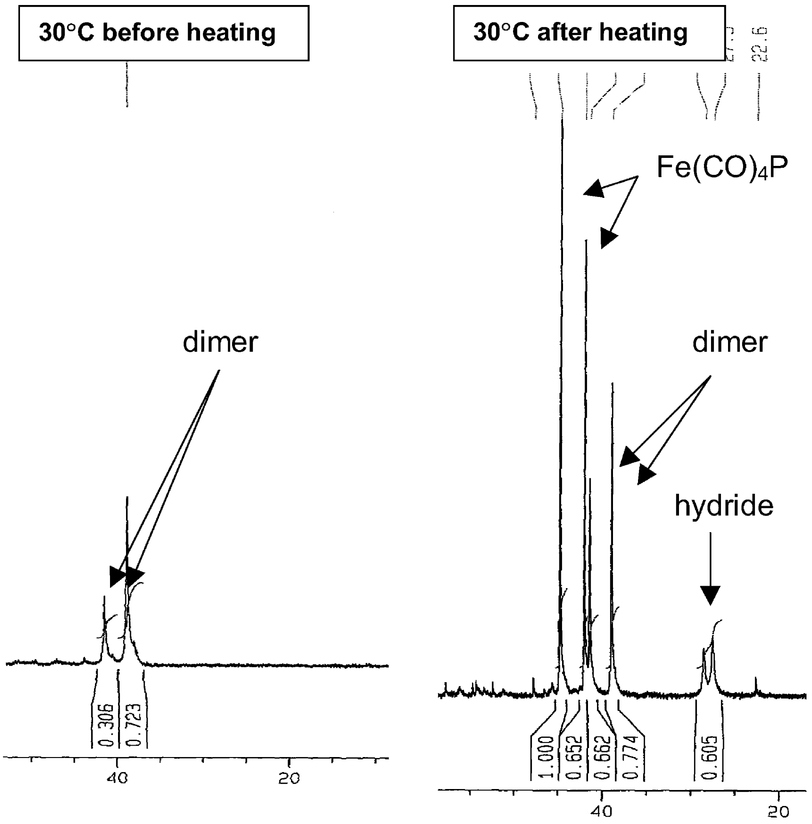


Fig. 12. ^{31}P NMR of $Co_2(CO)_8$:$Fe(CO)_5$:Lim-18 (1:1:2) system.

implications as the scavenged ligand will be irreversibly lost from the process loop via such a reaction.

As an excess of ligand was present in the above experiment, no interaction between iron and cobalt carbonyl complexes was observed, as the $Fe(CO)_5$ “mopped up” free Lim-18 to form a phosphine-modified iron tetracarbonyl compound. It was therefore decided to carry out a follow-up experiment using a 1:1:1 mixture of Co:Fe:Lim-18, in order to determine whether iron would scavenge ligand from a discrete cobalt complex. The spectra shown in Fig. 13 vividly depict the adverse effect of $Fe(CO)_5$ on the Lim-18 modified cobalt dimer and hydride. At 30 °C at the start of the experiment there was no free ligand, and cobalt dimer, salt and a small amount of Lim-18 oxide were observed. Upon heating $HCo(CO)_3$(Lim-18) began to form, as seen in typical preforming runs. At 170 °C the two $Fe(CO)_4$(Lim-18) resonances appeared, as before, at 42.0 ppm and 44.8 ppm. As no free ligand was present, the formation of this species must have occurred via loss of ligand from the corresponding cobalt species. This was supported by the appearance of $Co_2(CO)_7$(Lim-18) which is typical of a ligand starved system. Within 2 h at 170 °C, almost all the cobalt-phosphine species had vanished and $Fe(CO)_4$(Lim-18) was the predominant species, persisting on cooling to room temperature.

If one considers the plot of ligand distribution with temperature and time (Fig. 14), it can be seen that over time at 170 °C, $Fe(CO)_5$ gradually scavenges all the Lim-18 from the cobalt species—at the end of the experiment virtually all the ligand is complexed to iron instead of cobalt. Furthermore, it appears as if this transfer of ligand between metal centres is occurring via the hydride $HCo(CO)_3$(Lim-18), as hydride concentration drops rapidly over the first hour at 170 °C as $Fe(CO)_4$(Lim-18) forms. Eventual decrease in dimer concentration over 2 h at 170 °C may be ascribed to a gradual shift from dimer to hydride to reestablish equilibrium as hydride is consumed.

Although it is possible that this transfer of ligand to iron might be occurring via formation of a discrete bimetallic Fe-Co intermediate, it seems likely that iron pentacarbonyl is scavenging Lim-18 as it dissociates from the hydride $HCo(CO)_3$(Lim-18). This is supported by the knowledge that ligand exchange is a significant process at high temperatures, as well as by the suggestion that it is the modified hydride (and not dimer) which is consumed by reaction with $Fe(CO)_5$. Furthermore it has been shown that reaction of $Rh(PPh_3)_3Cl$ with $Fe(CO)_5$ yields $Fe(CO)_4(PPh_3)$, $Fe(CO)_3(PPh_3)_2$ and $Rh(CO)(PPh_3)_2Cl$, and that this reaction is retarded by addition of excess phosphine [38]. This indicates that ligand dissociation from the rhodium centre is required for the reaction to proceed.

These studies show a fascinating interaction between metal species competing for phosphine ligands. In modified cobalt hydroformylation an excess of ligand is always employed and any iron entering the system would be at very

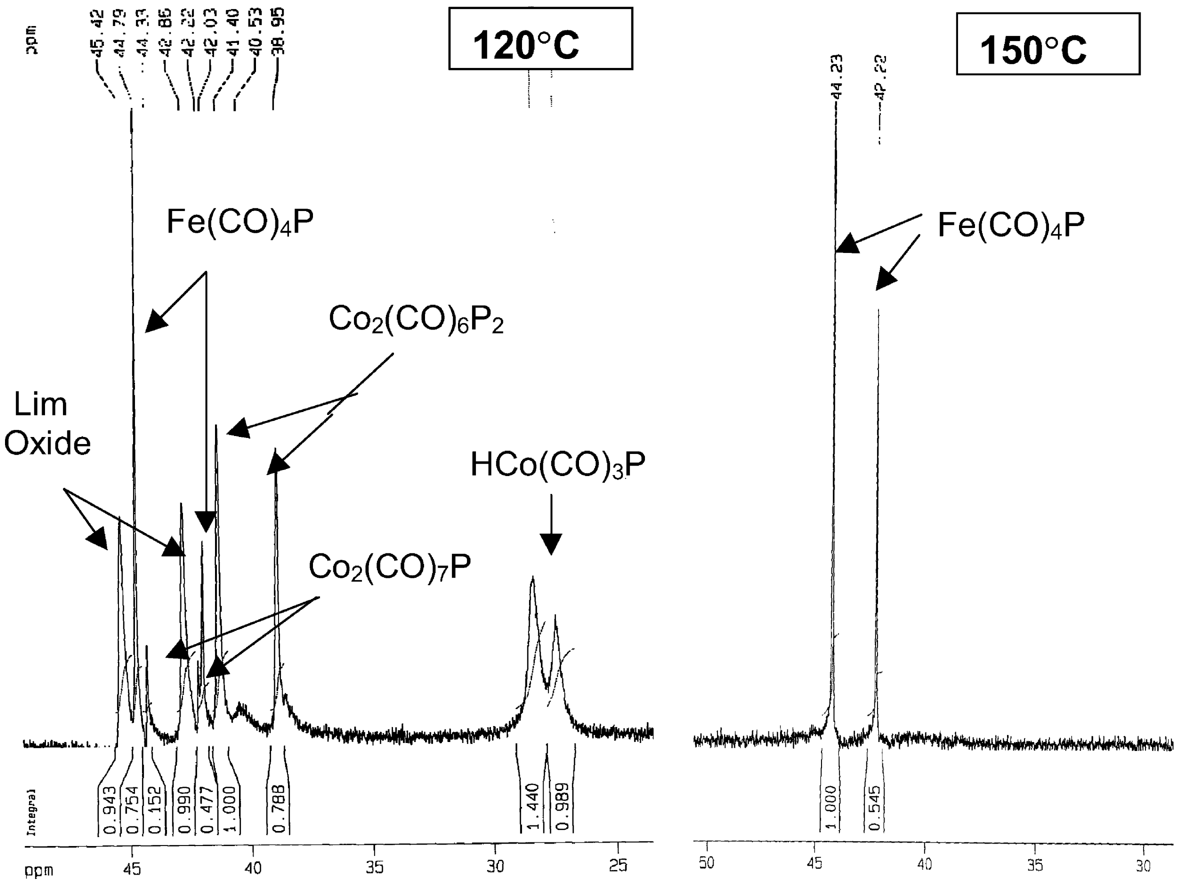


Fig. 13. ^{31}P NMR of $Co_2(CO)_8$:$Fe(CO)_5$:Lim-18 (1:1:1) system.

low levels. Thus, it is not anticipated that the presence of iron carbonyls would immediately affect the catalyst performance. However, trace amounts of $Fe(CO)_5$ fed constantly into a process loop would, with time, slowly scavenge phosphine ligand. It is therefore important to constantly monitor both the reactor product and incoming syngas for traces of iron and to keep a close watch on the ligand to metal ratio in the reactor.

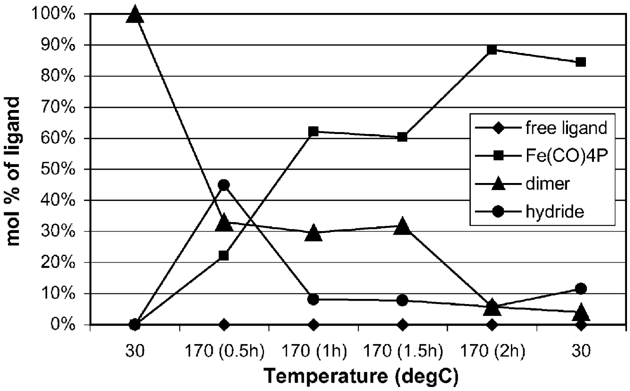


Fig. 14. Phosphine distribution at different temperatures (1:1:1 Co:Fe:Lim-18; 85 bar syngas).

4.7. Hydroformylation of 1-dodecene

An interesting aspect of homogeneous catalysis research is identifying the key species in the catalytic cycle, the rate determining step, and the resting state of the catalyst. This is a difficult task as most catalytic intermediates are very short-lived. Literature reports indicate that the rate-determining step for unmodified cobalt systems is cleavage of the acyl intermediate to release the aldehyde product. Little information is available on the corresponding phosphine-modified systems, although Whyman has reported that only hydride $HCo(CO)_3P$ and dimer are observed during HP-IR studies of a Co-PBu_3 system [28]. In-house HP-IR studies have confirmed that under hydroformylation conditions in the presence of an alkene, no intermediates within the proposed cycle are observed.

Although the HP-NMR cell is a closed system and constant pressure cannot be maintained during a hydroformylation experiment, the hydroformylation of 1-dodecene was investigated. Surprisingly, in the presence of olefin a new catalyst species was observed (resonances at 20.6 and 18.5 ppm; Fig. 15). While the hydride peak is always broad at high temperature, the peaks arising from the new species were very sharp. Comparison with chemical shifts of

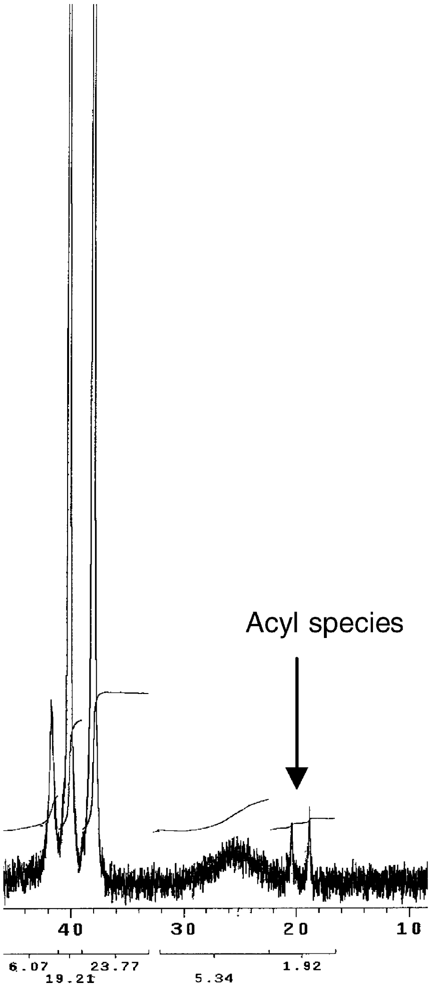


Fig. 15. ^{31}P NMR of Co/Lim-18 system in the presence of 1-dodecene.

prepared Lim-18 hexanoyl complexes suggests that this may be the acyl species RC(O)Co(CO)$_3$(Lim-18) [33].

The observation of a new catalyst species under hydroformylation conditions was unexpected as no such species has been observed in in-house HP-IR work to date. As mentioned previously, this is supported by literature: Whyman has reported that under hydroformylation conditions using the corresponding PBu$_3$ complex only the hydride species is observed in solution. It is likely that conditions in the HP-NMR cell are more prone to mass transfer limitation. The artificially low ρCO may facilitate initial loss of CO from HCo(CO)$_3$P to form HCo(CO)$_2$P which initiates the catalytic cycle. In contrast, the low ρH$_2$ would lead to slower hydrogenolysis of the aldehyde. The results indicate that where the reaction is mass transfer limited cleavage of the acyl species may be the rate determining step in the cycle, as is the case for unmodified catalysis. Although slow mass transfer is generally undesireable, it has the overall effect of slowing down the reactions and “trapping out” reactive intermediates which would not normally be seen.

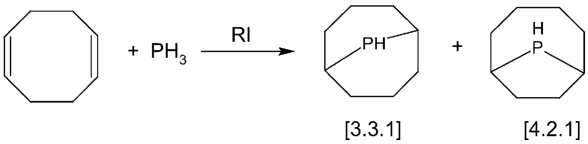


Fig. 16. Formation of phobane skeleton.

5. Studies with eicosyl phobane

Eicosyl phobane (EP) is the ligand patented extensively by Shell in the 1960’s for modified cobalt hydroformylation [39,40]. This technology is currently being employed on large scale for the production of detergent alcohols [41]. The ligand is a bridged bicyclic phosphine bearing a C$_{20}$ linear alkyl chain. It is prepared from 1,5-cyclooctadiene (COD) by radical addition with PH$_3$ to afford phobane as a mixture of structural isomers (the [3.3.1] or [4.2.1] phosphabicyclononanes, Fig. 16; RI: radical initiator). Separation of these isomers is possible [42] but for industrial purposes the isomers are usually employed as a mixture. Further radical addition of phoban to eicosene allows attachment of the alkyl side chain.

5.1. Catalyst preforming

A typical preforming run was carried out using three equivalents of EP with respect to cobalt. Fig. 17 shows the ^{31}P NMR spectra obtained at the start and end of the run under 65–85 bar of 2:1 syngas. The most obvious difference with EP as ligand is that only one resonance was observed for each catalyst species, although the ligand is a 1:1 mixture of structural isomers. This suggests that only one of the two structural isomers is reacting with cobalt, and that the difference in reactivity between the two EP isomers is therefore far greater than observed for the two Lim-18 diastereomers. At 30 °C, both salt and dimer were present, as expected. Unlike Lim-18, the Co-EP salt (47.1 ppm) was the major species at room temperature, although it was fully converted to dimer (43.5 ppm) upon increasing the temperature to 100 °C. At 100 °C and higher, hydride formed at 34.5 ppm as dimer was consumed. At 150 °C, the amount of hydride formed was around 60% of the complexed cobalt species, compared to 30% seen under similar conditions with Lim-18. This reflects a lower barrier to hydride formation. However, HP-IR experiments have shown that at preferred operating conditions of 170 °C and higher the hydride conversions for both ligands are similar.

5.2. Ligand starvation

In order to characterise the monosubstituted dimer, as well as to investigate the reactivity of the less reactive EP isomer, a preforming experiment was carried out with a less than stoichiometric amount of EP at 65–85 bar syngas (0.5 eq. EP:Co). Fig. 18 shows ^{31}P NMR spectra at the start

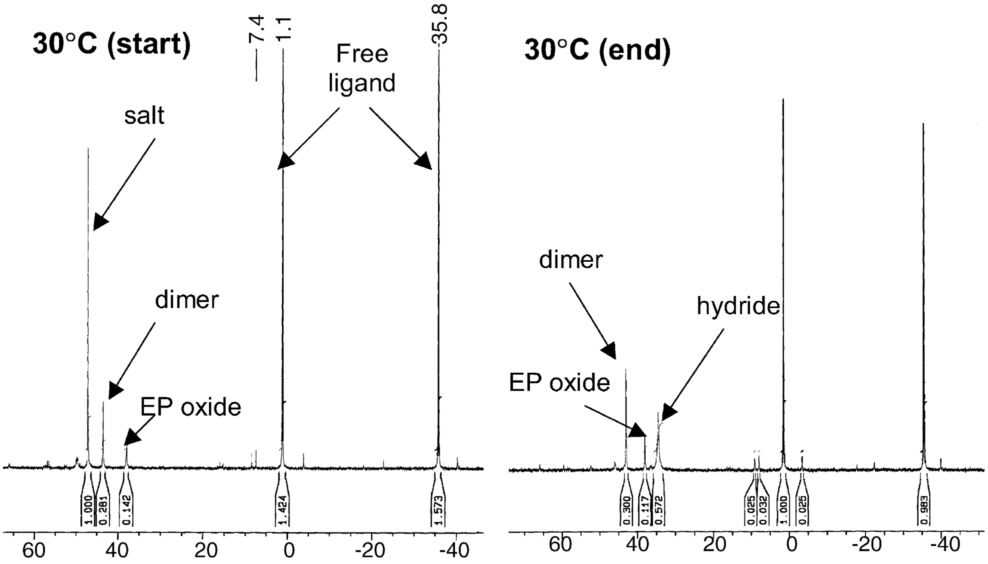


Fig. 17. ^{31}P NMR of Co/EP system (85 bar syngas).

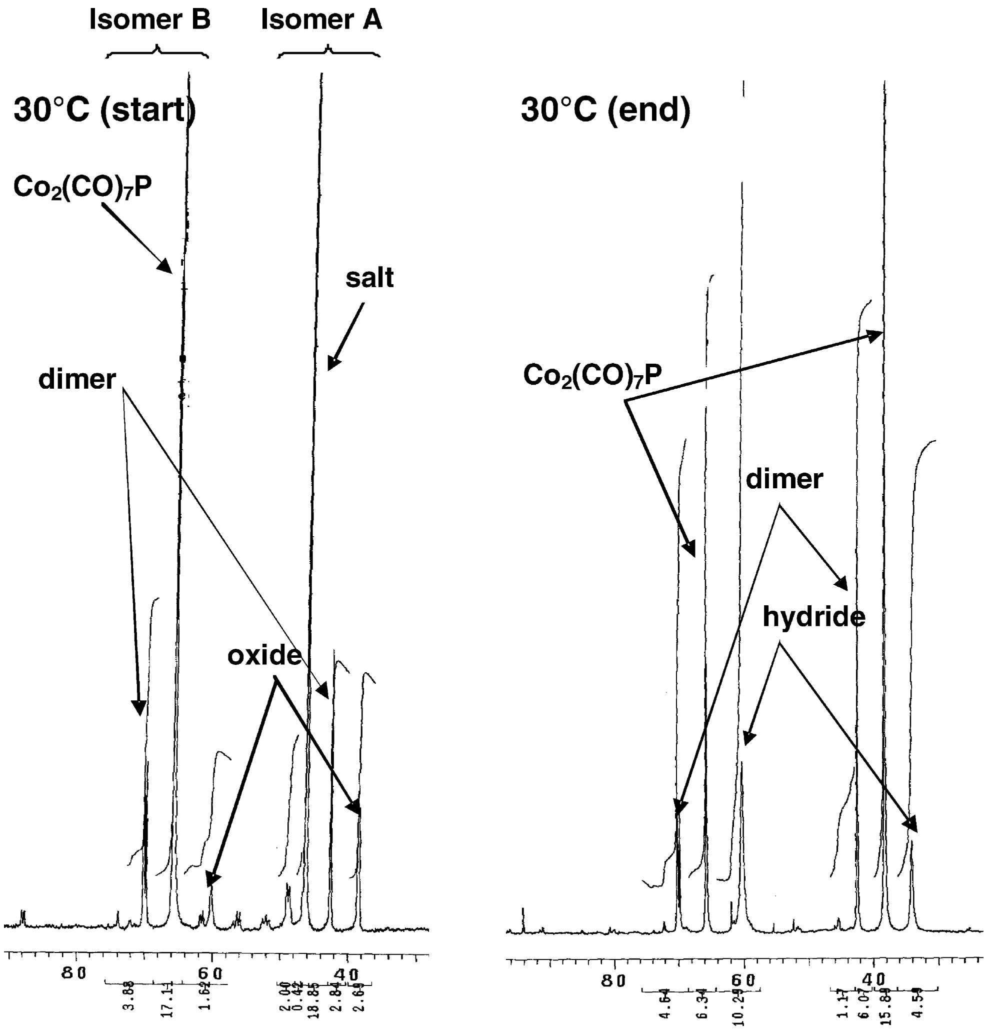


Fig. 18. ^{31}P NMR of ligand-starved Co/EP system (85 bar syngas).

and end of the run. A and B denote complexes formed from the two EP isomers. No free ligand was observed at any time during the run. From the observed two sets of resonances it was immediately evident that both EP isomers had reacted with $Co_2(CO)_8$. This indicates that in the case of EP, isomer A (−35 ppm) dominates completely if an excess of ligand is used, while isomer B (1 ppm) will only complex once the −35 ppm isomer has been consumed. However this experiment clearly shows that the second isomer is still reactive, which is important from a catalysis perspective. The resonances for the complexes are well separated, and thus differences in terms of complex formation can be readily quantified. It should be remembered that unmodified hydride may form in significant amounts, but cannot be seen in the ^{31}P NMR spectra.

At 30 °C isomer A formed significant quantities of the salt but no monosubstituted dimer $Co_2(CO)_7(EP)$, while isomer B (1.7 ppm) formed significant amounts of $Co_2(CO)_7P$ at 30 °C but no salt. Overall hydride formation increased steadily from 100 to 150 °C. However under these conditions isomer B formed significantly more modified hydride than isomer A.

The distribution of EP isomers between the possible Co complexes at different temperatures is depicted in Fig. 19. The two EP isomers behave quite differently, in contrast to the two Lim isomers which show fairly similar trends. In the presence of more than 2:1 EP:Co, only isomer A appears to complex, and is therefore the species which gives rise to catalysis in batch autoclave studies. However, hydride formation appears more facile with isomer B under the conditions in this experiment. This indicates the complexity of catalysis using mixed ligand systems, where the isomer which complexes preferentially may not necessarily lead to improved catalysis.

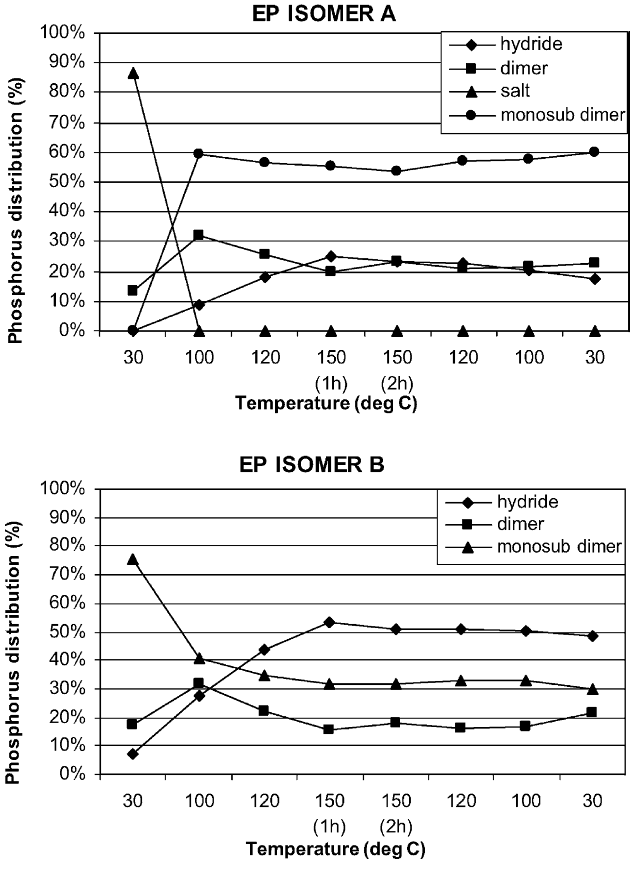


Fig. 19. Phosphine distribution of EP isomers at different temperatures (85 bar syngas).

6. Integration with other techniques

As mentioned in the introduction, HP-NMR has its limitations, most notably poor sensitivity, poor mass transfer and in hydroformylation research, difficulty in observing the unmodified cobalt species. For this reason, within Sasol Technology HP-NMR is always used in conjunction with other techniques such as HP-IR and molecular modelling to rationalise the results which are obtained.

HP-IR is carried out in a modified autoclave fitted with an efficient stirrer, and therefore mass transfer is not problematic. In addition, reactions can be studied at very low catalyst concentrations. However HP-IR spectra are often quite complex to interpret, with many bands arising from a single species. Unlike NMR where quantification via integrals is relatively straightforward, quantification using IR is very difficult. While the HP-IR can be used to observe unmodified cobalt species, free ligand cannot be seen and information on ligand exchange processes cannot be obtained. Thus, the two techniques are distinct but complementary. All absorbances were assigned by comparison or extrapolation to literature values of known compounds [21,28,35,43].

Figs. 20 and 21 show the HP-IR of a typical preforming experiment using Lim-18. Referring back to the HP-NMR spectra of Figs. 7 and 8, the same species are evident in the HP-IR spectra, allowing direct correlation of results. However, the pattern of absorbance bands for each cobalt species is a lot more complex. As seen in the HP-NMR, at room temperature salt and dimer were present, but on increasing the temperature to 80 °C the salt was replaced by dimer. Fig. 21 shows the IR spectrum obtained at 170 °C for the same experiment. Hydride formation predominated at higher temperatures, and a small amount of the unmodified hydride and monosubstituted dimer were observed. Thus, good a correlation with NMR results was obtained.

Molecular modelling has also been used as a valuable tool to predict and rationalise the obtained experimental results. It can also provide a wealth of information regarding steric and electronic properties of ligands and their complexes. The different reactivities of ligand isomers has been discussed in Sections 4 and 5. Molecular modelling can “quantify” this difference by estimating the reaction

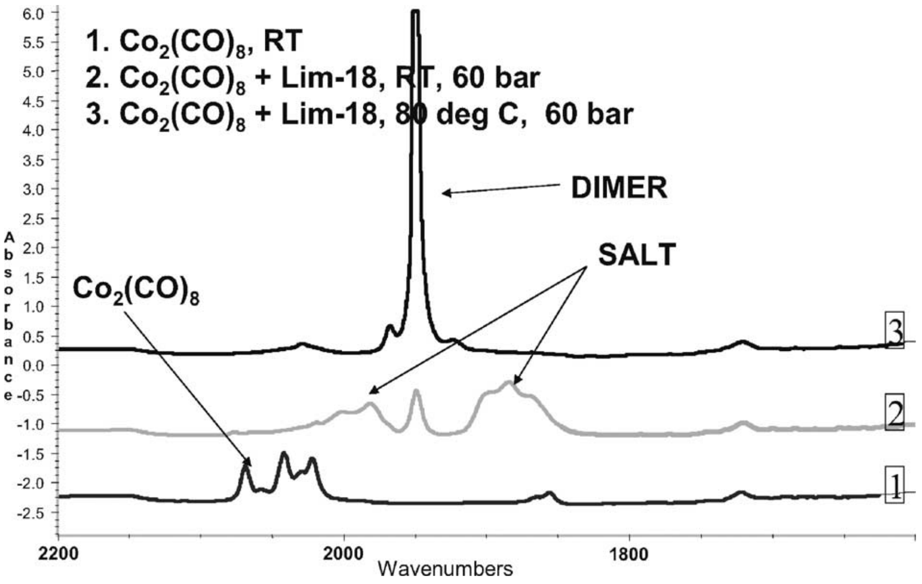


Fig. 20. IR spectra of catalyst preforming with Co/Lim-18.

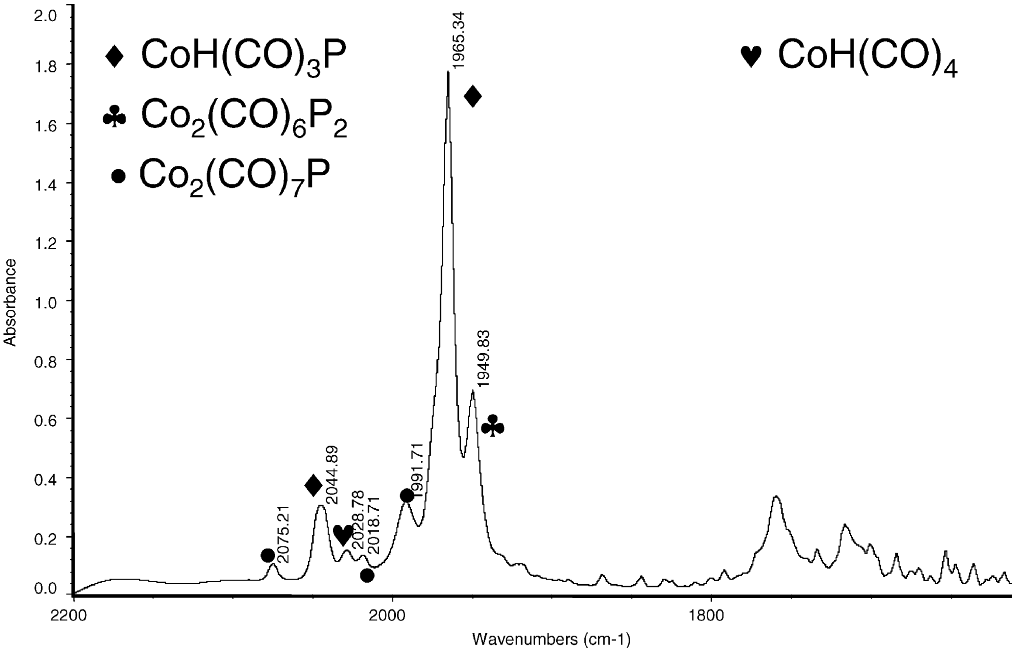
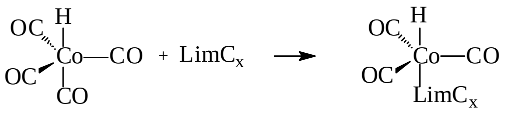


Fig. 21. IR spectrum of Co/Lim-18 system (170 °C; 85 bar syngas).

energy of the coordination to cobalt for each isomer as follows:



For instance, modelling predicts that (4*R*)-Lim-18 has a reaction energy of −0.82 kcal mol^{-1}, while (4*S*)-Lim-18 has a reaction energy of 2.24 kcal mol^{-1} [31]. This confirms the observed preference of the (4*R*) diastereomer to react with $Co_2(CO)_8$, and allows us to rank ligands in terms of their coordination ability. This has been very useful for further catalyst development and allowed us to predict ligands with improved properties.

7. Conclusions

HP-NMR spectroscopy is becoming a popular tool, both in industry and academia, as it has tremendous potential to provide both practical and fundamental information. Details of intricate mechanistic cycles and effects of changing reaction conditions on the catalytic species can be observed directly, allowing better understanding and hence more effective control of process parameters. With an integrated approach, catalyst design and prediction are now well within the grasp of any researcher.

The use of HP-NMR spectroscopy has contributed greatly to development of a modified cobalt hydroformylation technology. As is often the case, experimental results can be difficult to interpret and apply in isolation. Thus, the ongoing hydroformylation research within Sasol Technology relies on close interaction between HP-IR, HP-NMR, batch autoclave work and molecular modelling studies in an iterative process.

Acknowledgements

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References

[1] W.B. Holzapfel, N.S. Isaacs, High Pressure Techniques in Chemistry and Physics: A Practical Approach, Oxford Press, Oxford, 1997.
[2] L. Helm, A.E. Merbach, D.H. Powell, in: W.B. Holzapfel, N.S. Isaacs (Eds.), High Pressure Techniques in Chemistry and Physics: A Practical Approach, Oxford Press, Oxford, 1997, Chapter 4, p. 187.
[3] I.T. Horvath, J.M. Millar, Chem. Rev. 91 (1991) 1339.
[4] G.B. Benedek, E.M. Purcell, J. Chem. Phys. 22 (1954) 2003.
[5] J. Jonas, Rev. Sci. Instrum. 43 (1972) 643.
[6] J.W. Rathke, J. Magn. Res. 85 (1989) 150.
[7] J. Jonas, D.L. Hasha, W.J. Lamb, G.A. Hoffman, T. Eguchi, J. Magn. Res. 42 (1981) 169.
[8] D.C. Roe, J. Magn. Res. 63 (1985) 388.
[9] I.T. Horvath, E.C. Ponce, Rev. Sci. Instrum. 62 (1991) 1104.
[10] M. Brookhart, A.F. Volpe Jr., D.M. Lincoln, I.T. Horvath, J.M. Millar, J. Am. Chem. Soc. 112 (1990) 5634.
[11] T.B. Marder, D.C. Roe, D. Milstein, Organometallics 7 (1988) 1451.
[12] J.M. Millar, R.J. Kastrup, M.T. Melchior, I.T. Horvath, C.D. Hoff, R.H. Crabtree, J. Am. Chem. Soc. 112 (1990) 9643.
[13] J.A. Iggo, D. Shirley, N.C. Tong, New J. Chem. (1998) 1043.
[14] D.C. Roe, Organometallics 6 (1987) 942.
[15] J.W. Rathke, L.M. Wojcinski, R.J. Klingler, M.J. Chen, R.E. Gerald Jr., Chemist 78 (2001) 7–10.
[16] D.E. Fremgen, E.S. Smotkin, R.E. Gerald, R.J. Klingler, J.W. Rathke, J. Supercrit. Fluids 19 (2001) 287–298.
[17] J.W. Rathke, R.J. Klingler, T.R. Krause, Organometallics 10 (1991) 1350.
[18] J.W. Rathke, R.J. Klingler, T.R. Krause, Organometallics 11 (1992) 535.
[19] R.J. Klinger, J.W. Rathke, J. Am. Chem. Soc. 116 (1994) 4772.
[20] J.W. Rathke, K.W. Kramarz, R.J. Klingler, M.J. Chen, D.E. Fremgen, R.E. Gerald Jr., Trends Organomet. Chem. 3 (1999) 201.
[21] K.W. Kramarz, R.J. Klingler, D.E. Fremgen, J.W. Rathke, Catal. Today 49 (1999) 339.
[22] L.H. Slaugh, R.D. Mullineaux, US 3,239,569 (1966).
[23] L.H. Slaugh, R.D. Mullineaux, US 3,448,157 (1969).
[24] R.F. Mason, J.L. van Winkle, US 3,527,818 (1970).
[25] R.F. Heck, D.S. Breslow, JACS 83 (1961) 4023.
[26] J.K. MacDougall, M.C. Simpson, M.J. Green, D.J. Cole-Hamilton, J. Chem. Soc., Dalton Trans. (1996) 1161.
[27] M. Torrent, M. Sola, G. Frenking, Chem. Rev. 100 (2000) 439.
[28] R. Whyman, J. Organomet. Chem. 81 (1974) 97.
[29] C. Dwyer, L. Damoense, unpublished results.
[30] J.P. Steynberg, K. Govender, P.J. Steynberg, WO 014248 (2002).
[31] C. Crause, L. Bennie, L. Damoense, C.L. Dwyer, C. Grove, N. Grimmer, W. Janse van Rensburg, M.M. Kirk, K.M. Mokheseng, S. Otto, P.J. Steynberg, J. Chem. Soc., Dalton Trans. (2003) 2036.
[32] A. Robertson, C. Bradaric, C.S. Frampton, J. McNulty, A. Capretta, Tetrahedron Lett. 42 (2001) 2609.
[33] A. Polas, J.D.E.T. Wilton-Ely, A.M.Z. Slawin, D.F. Foster, P.J. Steynberg, M.J. Green, D.J. Cole-Hamilton, J. Chem. Soc., Dalton Trans. (2003) 4669.
[34] M. Absi-Halabi, J.D. Atwood, N.P. Forbus, T.L. Brown, J. Am. Chem. Soc. 102 (1980) 6248.
[35] G.F. Pregaglia, A. Andreeta, G.F. Ferrari, R. Ugo, J. Organomet. Chem. 30 (1971) 387.
[36] F.A. Cotton, R.V. Parrish, J. Chem. Soc. (1960) 1440.
[37] M. Bigorgne, J. Organomet. Chem. 24 (1970) 211.
[38] Y.S. Varshavsky, E.P. Shestakova, N.V. Kiseleva, T.G. Cherkasova, N.A. Buzina, L.S. Bresler, V.A. Kormer, J. Organomet. Chem. 170 (1979) 81.
[39] R.F. Mason, J.L. van Winkle, US 3,400,163 (1968).
[40] J.L. van Winkle, S. Lorenzo, R.C. Morris, R.F. Mason, US 3,420,898 (1969).
[41] K. Weisselmel, H.-J. Arpe, Industrial Organic Chemistry, VCH, New York, 1993.
[42] J.H. Downing, V. Gee, P.G. Pringle, Chem. Commun. (1997) 1527.
[43] L. Rosi, A. Salvini, M. Bianchi, P. Frediani, F. Piacenti, J. Organomet. Chem. 535 (1997) 143.