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Review

Recent advances in high-pressure infrared and NMR techniques for the determination of catalytically active species in rhodium- and cobalt-catalysed hydroformylation reactions

Llewellyn Damoense, Michael Datt, Mike Green*, Casper Steenkamp

Sasol Technology Research and Development, P.O. Box 1, Sasolburg 1947, South Africa

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Contents

Abstract

The nature of the organometallic species in solution is critical to defining whether or not an active catalyst is present. Much of traditional thinking for homogeneously catalysed reactions is based on proposals as to the nature of such species, however, in most cases there is limited concrete evidence for such proposals and the systems in reality remain a black box. Certainly there have been a large number of elegant studies where specific complexes within a proposed catalytic cycle have been synthesised and 'in vitro' reactions carried out, but questions always remain as to the validity of such experiments. More recently, the latest modelling techniques have been brought to bear on the issue, but these are at best correlative tools supporting other theoretical evidence.

As long ago as the early 1970s, a small number of gifted individuals embarked along the path of using high-pressure infrared and more recently NMR spectroscopy, to observe species under reaction conditions. Much of this work has gone unnoticed and has never really been embraced by the community as a whole. In this review, we seek to put the record straight and to summarise the insights that have been gained by using these tools in the hope that their worth will be recognised and their use expanded in the future.

Keywords: Hydroformylation; High-pressure NMR and IR; Rhodium; Cobalt

1. Introduction

The effect of ligands on the structure and reactivity of transition metal complexes are important topics of research in coordination and organometallic chemistry as well as homogeneous catalysis [1]. In organometallic and coordination

* Corresponding author. Tel.: +27-16-9602906; fax: +27-11-5223713.
E-mail address: mike.green@sasol.com (M. Green).

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chemistry the problem is particularly complex due to the large variety of metal centres (and oxidation states) and their corresponding coordinating properties as well as the large variety of possible ligands and their corresponding binding properties [2–4]. Phosphine ligands are probably the most widely used ligands in catalysis today. They stabilize low oxidation states of metal centres (due to π-properties) and their electronic and steric properties can be readily modified which will govern the reactivity of their corresponding metal complexes [5–8]. Metal-phosphine-catalysed reactions encompass a wide range of chemical processes [9–18], for example, hydrogenation, hydroformylation and carbonylation to name but a few [5,19–28]. A great challenge in homogeneous catalysis lies in the prediction of catalytic activity and selectivity. A tremendous amount of research has focused on the quantification of ligand effects (QALE), particularly those of phosphorus(III) ligands. The effect of the ligands is typically described in terms of steric and electronic properties and correlations are established between the molecular property under consideration and these properties. Giering and Prock have recently collected all the available material in a web site (http://www.bu.edu/qale/) describing each set of data analysis with commentary on how each analysis is done and how successful it is. Detailed discussions of these effects are beyond the scope of this review and will not be discussed further [29–43].

To improve the selectivity and activity of catalytic reactions, it is important to have a detailed knowledge of the nature of the catalytic intermediates and if possible the rates of the individual steps involved in the catalytic cycle. Since many important reactions involve the use of liquids under high gas pressure, high-pressure spectroscopic techniques were developed to facilitate mechanistic investigations of these systems [44]. The two most frequently used high-pressure spectroscopic techniques in use today are high-pressure infrared (HP-IR) and high-pressure nuclear magnetic resonance (HP-NMR) spectroscopy. This review will highlight the use of HP-NMR and HP-IR spectroscopy as a tool for the identification of catalytic intermediates and resting states with particular emphasis on phosphine-modified rhodium- and cobalt-catalysed hydroformylation reactions.

2. Types of HP-NMR and HP-IR cells

Most high-pressure infrared cells are modified autoclaves equipped with infrared transmittance windows (transmission cell). The limits of operation of the cells depend on the material used for the windows [45–53].

A cylindrical internal reflectance (CIR) cell was developed by Moser and Slocum (see, for example [54]) and comprises a modified reactor fitted with a CIR crystal consisting of silicon, ZnSe or any infrared transmittance material. The infrared spectrum obtained for both transmission and reflectance cells are similar, with the sensitivity of the CIR cell less compared to transmission cells, due to a shorter effective path length.

Poliakoff and co-workers [55] recently reported the use of a miniature high-pressure low-temperature copper cell which allows the use of polyethylene (PE) matrixes in combination with high-pressure gases, where the catalyst and substrates are dissolving in the matrix. An advantage of this technique is that only micrograms of chemicals are required and that gaseous reactants can be easily removed or replaced.

Ford and co-workers [56–59] developed a nanosecond flash-photolysis apparatus in combination with an IR detection technique. This technique has been proven to be very useful in the study of reactive intermediates. It is often difficult to detect organometallic species found at low concentrations or in mixtures. Garland and co-workers [60,61] recently reported a band-target entropy minimization (BTEM) algorithm which can be used to identify species in low concentrations from mixtures. The BTEM algorithm also produces spectra with reduced noise and eliminates spectral features due to suspended solids.

Several high-pressure NMR systems are currently known, e.g. various high-pressure NMR probes [62–66] and sapphire NMR cells [67,68]. Modified NMR probes are costly and often require specialised equipment, such as a wide bore NMR magnet, and a dedicated NMR. Vander Velde and Jonas reported a modified hydrostatic probe of high sensitivity capable of operating from −50 to 150 °C and pressures up to 5000 atm with internal stirring [69].

Toroidal detection probes designed by Rathke [63] were shown to have improved sensitivity and resolution relative to traditional probes. Sealed glass ampoules have been used at high temperatures by a number of groups. Gordon and Dailey [70] reported pyrex tubes with various pressure limits depending on the thickness of the tubes.

The sapphire cells [67] (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. Pressures of about 130 atm and a temperature range of 100–150 °C can be attained. A limitation of the Roe cell is that it is a closed system and constant gas pressure cannot be maintained for reactions where gas is consumed. More detailed information on the advantages and disadvantages of various NMR cells have been reported by Horváth and Millar [44].

3. Transition metal chemical shifts and metal-phosphorus coupling

Several features of metal shielding are of particular importance when using multinuclear NMR spectroscopy to identify catalytic intermediates and to correlate chemical shifts and coupling constants with observed selectivities and rates [71–74]. Transition metal nuclei may exhibit very large chemical shift ranges and thus this parameter is very sensitive to small changes in the electronic and stereochem-

ical environment of the metal centre in question. Changes in chemical shift for a given transition metal are largely governed by the paramagnetic shielding term σ_{para}. This paramagnetic term is not only dependant on the electron density at the nucleus but is also related to the electronic excitation energy, ΔE^{-1}, non-s-orbital expansion terms, $\langle r^{-3} \rangle$, and p- and d-orbital population terms P_u and D_u, respectively [72,75]. Therefore, it is difficult to separate, identify and quantify a change in chemical shift with a particular electronic or steric parameter with a change in ligands as the steric and electronic effects are interdependent.

The use of multinuclear NMR spectroscopy has become routine for the identification and characterisation of compounds containing NMR active nuclei. For example, the ^{1}H and ^{13}C NMR spectra of mixtures of complexes tend to be complicated, while the corresponding ^{103}Rh and ^{31}P NMR spectra are relatively simple and easier to interpret. The ^{103}Rh chemical shift is very sensitive to the coordination sphere around the metal centre and small changes in the molecular structure or geometry of the complex generally result in significantly different chemical shifts for the different species [76,77]. Several papers have described correlations of the ^{103}Rh chemical shift with various rate data, stability constants, catalytic activity, and the steric and electronic parameters of phosphine ligands [78–82]. Care should be taken in the interpretation of NMR data under different conditions as both solvent, temperature and concentration can affect the chemical shifts, therefore, conclusions based on small differences in the chemical shifts, must be drawn from measurements made in the same solvent and at the same temperature and concentration.First order coupling constants in general are governed by the Fermi contact term, shown below:

$$J(A, B) = (\text{constant})\gamma_A\gamma_B|\Psi(0)|^2_A|\Psi(0)|^2_B\pi_{AB}$$

where γ is the gyromagnetic ratio, $|\Psi(0)|^2$ describes the valence s-electron densities at the nuclei A and B and π_{AB} is the mutual polarisability of nuclei A and B. Nuclei with small γ and $|\Psi(0)|^2$ values have smaller ^{1}J(MP) coupling constants than nuclei with larger γ values. For example, ^{1}J(PtP) coupling constants are an order of magnitude larger than ^{1}J(PtN) coupling constants. The ^{1}J(MP) coupling constants are sensitive to changes in the ligand *trans* to the phosphorus atom and are hardly affected by a change in the nature of the *cis* neighbour and therefore have been used to determine the *trans*-influence of various groups *trans* to the phosphines [83]. The *trans*-influence of a ligand *Y* in a metal complex is defined as the extent that *Y* weakens the bond *trans* to itself in the ground state [84]. Therefore, the coupling constants can give structural information of the composition of the coordination sphere of a metal centre. The ^{1}J(MP) coupling constants provide information on the s-orbital contribution and therefore extreme care must be taken in extrapolating to other types of metal-ligand bonding, for example, dπ–dπ backbonding.

4. Rhodium-catalysed hydroformylation

4.1. Diphosphine-based catalysts

In the generally accepted mechanism for the rhodium-catalysed hydroformylation reaction as proposed by Wilkinson and co-workers in 1968 [85], the active catalyst is thought to be a trigonal–bipyramidal hydridorhodium(I) complex, usually containing two phosphorus ligands. According to this mechanism, the selectivity is determined in the step that converts a five-coordinate [HRh(alkene)(CO)P_2] complex into a four-coordinate [Rh(alkyl)(CO)P_2] complex, with either a branched or linear alkyl chain. For the linear alkyl chain this step is virtually irreversible at moderate temperatures and sufficiently high pressures of carbon monoxide [86,87]. Therefore, the structure of the five-coordinate alkene complex is thought to play a crucial role in controlling the regioselectivity of the reaction. Bianchini et al. recently used high-pressure NMR spectroscopy, to evaluate the influence of CO/H_2 pressure on the equilibria of all the rhodium-triphenylphosphine species that are visible on the NMR time scale during the hydroformylation of 1-hexene by [$HRh(CO)(PPh_3)_3$] [88]. As many as four rhodium resting states were identified and some of the factors controlling their formation/interconversion/inhibition were determined. Upon the introduction of CO/H_2 gas to the reaction mixture, several new signals were observed in the NMR spectrum. The [$HRh(CO)(PPh_3)_3$] complex was converted into the five-coordinate [$HRh(PPh_3)_2(CO)_2$] complex and a signal corresponding to the [Rh(acyl)$(CO)_2(PPh_3)_2$] complex was also assigned. The stability and composition of the rhodium-hydride complexes was also found to be dependent on the CO/H_2 pressure. Upon venting the NMR cell, several resting states (rhodium dimeric species) were formed whose equilibrium concentrations were found to be dependent on the pressure of carbon monoxide and hydrogen. Previous to this study only the [$HRh(PPh_3)_2(CO)_2$] complex had been characterised spectroscopically [89]. Brown and Kent showed that the [$HRh(PPh_3)_2(CO)_2$] complex consists of two rapidly equilibrating isomeric structures in which the phosphine ligands were coordinated either in an equatorial–equatorial (ee) or an equatorial–apical (ea) fashion [89]. Studies on electronically modified diphosphine ligands have demonstrated that similar dynamic equilibria between equatorial–equatorial and equatorial–apical complex isomers also exist for these ligand systems [78,90–96].

Casey and co-workers developed a molecular mechanics method to estimate the natural bite angle of bidentate phosphines and their flexibility. They defined the natural bite angle as the preferred chelation angle determined only by ligand backbone constraints and not by metal valence angles. Very importantly, this definition is independent of any electronic preference for a specific bite angle that is imposed by the metal centre and is based solely on steric considerations [97]. The authors reported that the regioselectivity of the rhodium-catalysed hydroformylation of

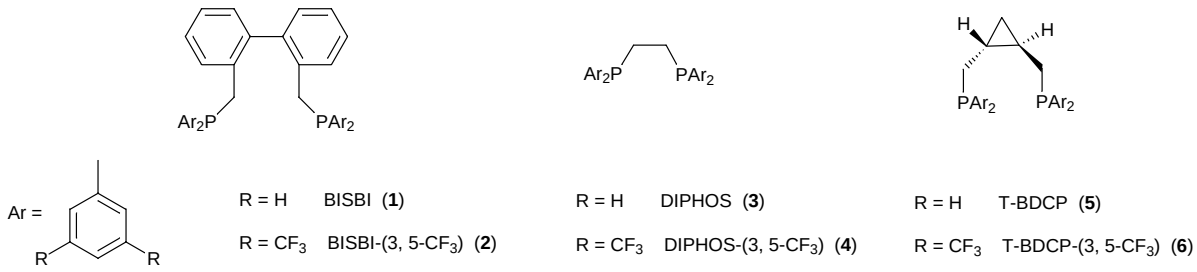


Fig. 1. Diphosphine ligands.

1-alkenes was dramatically affected by the bite angle of bidentate diphosphines ligands [86,90,93,96]. Hydroformylation of 1-hexene using BISBI gives a linear to branched aldehyde ratio (*n*:*i*) as high as 66:1, while under the same conditions the equatorial–apical coordinated dppe gave a *n*:*i* ratio of only 2:1 (see Fig. 1). The correlation between regioselectivity and coordination mode of the phosphine ligands suggests that equatorial–equatorial coordinated diphosphines such as BISBI and equatorial–apical coordinated diphosphines like DIPHOS have either significantly different steric or electronic properties. Molecular mechanics calculations were therefore employed to determine whether the selectivity arose from steric differences between the two transition states leading to the linear and branched rhodium-alkyl intermediates. The steric difference between the transition state models leading to [Rh(*n*-propyl)(BISBI)(CO)] and [Rh(*i*-propyl)(BISBI)(CO)] was calculated to be 1.9 kcal/mol favouring the *n*-propyl transition state. This energy difference corresponds to a 25:1 partitioning between *n*- and *i*-propyl rhodium intermediates, which is in reasonable agreement with the 66:1 *n*:*i* aldehyde selectivity obtained for the hydroformylation with BISBI which corresponds to 2.5 kcal/mol. However, the steric energy difference between the transition state models leading to [Rh(*n*-propyl)(DIPHOS)(CO)] and [Rh(*i*-propyl)(DIPHOS)(CO)] was even larger at 2.1 kcal/mol also favouring the *n*-propyl transition state. This energy difference corresponds to a 35:1 *n*:*i* aldehyde selectivity, which is significantly higher than the 2.6:1 observed for DIPHOS. The estimates of the steric effects incorrectly suggested that DIPHOS should be more selective than BISBI, which is opposite to the trend observed. Thus, these studies indicated that the steric differences between the equatorial–equatorial and equatorial–apical isomers were not solely responsible for the observed increase in selectivity with increasing natural bite angle [86]. The electronic properties of these ligands (**1**–**6**) (see Fig. 1) were therefore varied by substituting the phenyl groups with strongly electron-withdrawing groups such as trifluoromethyl groups. A five-fold increase in rate and an increase in the *n*:*i* ratio was observed. In contrast introduction of trifluoromethyl groups on the phenyl rings of DIPHOS resulted in a decrease in linear aldehyde selectivity when compared to the unsubstituted DIPHOS. The ratio of the equatorial–equatorial and equatorial–apical isomers of the corresponding [HIr(diphosphine)$(CO)_2$] complexes were determined by NMR spectroscopy (see Table 1). Introduction of electron-withdrawing groups lead to an increase of the equatorial–equatorial isomer of T-BDCP complex. It was also noted that electron-withdrawing groups in equatorial positions give raise to faster rates and increased *n*:*i* ratios. Unfortunately no conclusive results could be obtained from this study due to the steric differences between the BISBI and DIPHOS complexes. Casey concluded that the "regioselectivity of hydroformylation is governed by a complex web of electronic and steric effects that have so far defied unraveling" [93].

Table 1
Selected regioselectivity data for the hydroformylation of 1-hexene with diphosphine ligands [93]

Ligand	Ligand	ee:ea[a]	*n*:*i*
1	BISBI	100:0	66.5
2	BISBI-(3,5-CF_3)	100:0	123
3	DIPHOS	0:100	2.6
4	DIPHOS-(3,5-CF_3)	0:100	1.3
5	T-BDCP	37:63	12.1
6	T-BDCP-(3,5-CF_3)	90:10	17.7

[a] Ratio of ee:ea chelates of [HIr(diphosphine)$(CO)_2$] at room temperature.

To further investigate the influence of the natural bite angle and electronic effect of diphosphine ligands on catalytic activity and selectivity in hydroformylation reactions van Leeuwen et al. developed a series of diphosphine ligands based on a xanthene-type backbone [78,91,92,95,98,99]. The bite angle effect on the rhodium diphosphine catalysed hydroformylation was evaluated using an extensive series of ligands (**7**–**15**) (see Fig. 2) [91,98]. Variation of the substituent at position-9 of the generic backbone structure enabled the construction of a series of diphosphine ligands having a wide range of natural bite angles. The mutual backbone within the series ensures that variation in electronic properties and in steric size were kept to a minimum [91,98].

Hydroformylation of 1-octene with this series of ligands showed a correlation between the bite angle and regioselectivity. The regioselectivity increased regularly with increasing natural bite angle. Spectroscopic studies showed that all the [HRh(diphosphine)$(CO)_2$] complexes

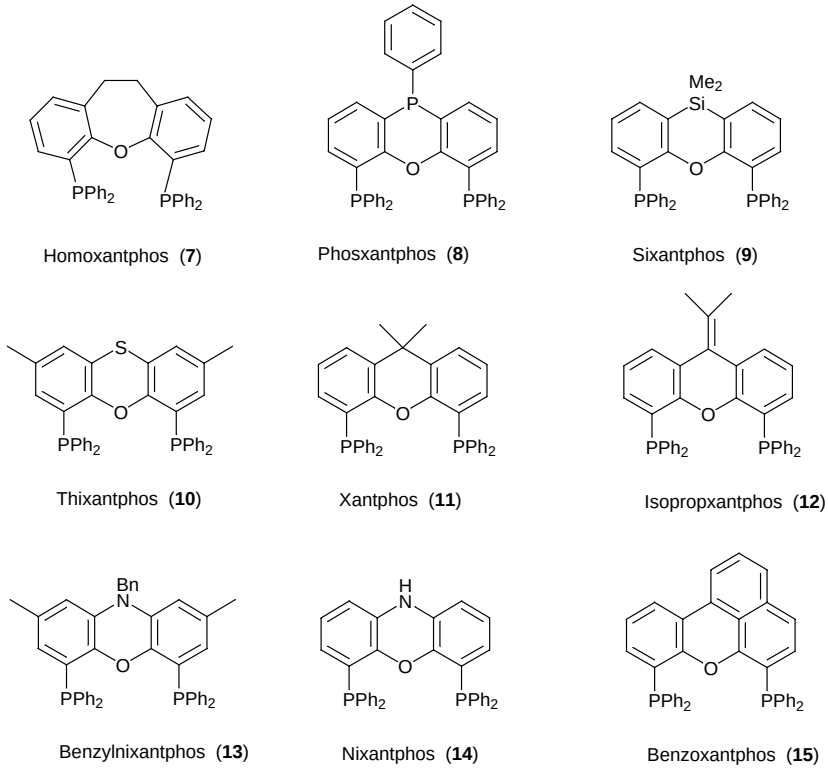


Fig. 2. Diphosphine ligands based on a xanthene backbone.

exhibited dynamic equilibria between equatorial–equatorial and equatorial–apical isomers [93]. No clear correlation between the ee:ea ratio and the natural bite angle could be found as the ee:ea ratios of the complexes containing sixantphos ($\beta_n = 108.5°$) and benzoxantphos ($\beta_n = 120.6°$) are approximately the same (6:4) (see Table 2). These results are in direct contradiction with those reported by Casey, in which diphosphines with wide bite angles have a preference for equatorial–equatorial coordination. It appears that the correlation between bite angle and diphosphine coordination geometry is only valid for flexible diphosphines having either relatively narrow bite angles (dppe) or a relatively wide bite angle such as with BISBI. The more rigid rhodium xantphos-derivatives have an intermediate natural bite angle appeared to be sensitive to small changes in the electronic properties and the rigidity of the ligand backbone. In these cases the diphosphine coordination mode is only partially governed by the natural bite angle. These results unambiguously prove that the ee:ea isomer ratio in the [HRh(diphosphine)$(CO)_2$] catalyst resting state is not a key parameter controlling regioselectivity in hydroformylation reactions as was previously believed to be the case.

Table 2
Selected regioselectivity data for the hydroformylation of 1-octene by [HRh(diphosphine)$(CO)_2$] complexes [91,98]

Ligand	Common name	β_n (°)	Flexibility (°)	*n*:*i*	ee:ea ratio
7	Homoxantphos	102.0	92–120	8.50	3:7
8	Phosxantphos	107.9	96–127	14.6	7:3
9	Sixantphos	108.7	93–132	34.3	–
10	Thixantphos	109.4	94–130	56.6	–
11	Xantphos	111.7	97–135	52.2	–
12	Isopropxantphos	113.2	98–139	49.8	8:2
13	Benzylnixantphos	114.1	99–139	50.6	7:3
14	Nixantphos	114.2	99–141	69.4	8:2
15	Benzoxantphos	120.6	102–146	50.2	6:4

Due to the dependence of the regioselectivity on subtle electronic changes a new series of ligands with different electronic properties were prepared based on the thixantphos backbone (**16**–**21**) (see Fig. 3) [78,92]. The phosphine basicity was varied by varying the electronic nature of the arylphosphine moiety. Selected spectroscopic and selectivity data for these complexes are given in Table 3.

The equilibrium between the equatorial–equatorial and equatorial–apical isomers was found to be dependent on the phosphine basicity as is reflected in the NMR coupling constants. Decreasing phosphine basicity gives decreasing ^1J(RhH) and ^2J(PH) coupling constants, but increasing

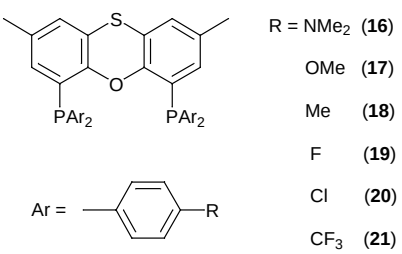
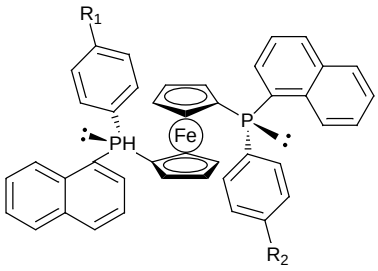


Fig. 3. Diphosphine ligands based on a thixanthphos backbone.

Table 3
Selected regioselectivity and spectroscopic data for the hydroformylation of 1-octene by [HRh(diphosphine)$(CO)_2$] complexes [78,92]

Ligand	^1J(RhH) (Hz)	^1J(RhP) (Hz)	^2J(PH) (Hz)	Percent ee	$\delta(^{103}Rh)$ (ppm)	*n*:*i*
16	8.7	121	27.9	44–50	−814.2	44.6
17	7.5	124	21.6	56–62	−825.4	36.9
18	7.2	126	17.6	63–69	−831.6	44.4
10	6.6	128	14.7	69–75	−840.1	50.0
19	6.3	130	11.0	76–83	−835.7	51.5
20	6.0	132	8.4	81–88	−840.7	67.5
21	4.5	134	3.6	89–96	−851.0	86.5

^1J(RhP) coupling constants [92,100]. For strongly electron-donating substituents the equatorial–apical isomer is slightly favoured, while for strongly electron-withdrawing substituents the equilibrium is shifted almost completely to the equatorial–equatorial isomer. Interestingly the authors noted that the basicity of the substituted-thixantphos complexes had no influence on the selectivity for linear aldehydes for the hydroformylation of 1-octene. This again suggested that the mode of diphosphine binding to the rhodium metal centre in [HRh(diphosphine)$(CO)_2$] complexes does not govern the regioselectivity in hydroformylation reactions. Electronic effects were also evaluated on a series of ferrocene-based ligands (**22**–**25**) (see Fig. 4). Electronically modified 1,1'-bis(1-naphthylphenylphosphino)ferrocenyl ligands were prepared bearing methoxy- and trifluoromethyl-groups in *para* positions of the phenyl rings, thus minimizing possible steric variations within the series of ligands [94]. The ee:ea ratio for the corresponding [HRh(diphosphine)$(CO)_2$] complexes showed a strong dependence on the basicity of the phosphine ligand. In agreement with the work discussed above, an increase in the electron-donating capacity within the ligand series was accompanied by a decrease in the ee:ea ratio. In the hydroformylation of 1-octene the electronic properties of the ligands had no effect on selectivity and were found to only affect the rate of the reaction (see Table 4).

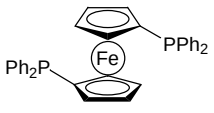


$R_1 = R_2 = H$ (**22**)

$R_1 = R_2 = OMe$ (**23**)

$R_1 = R_2 = CF_3$ (**24**)

$R_1 = OMe$ $R_2 = CF_3$ (**25**)



DPPF (**26**)

Fig. 4. Examples of bidentate ferrocene based phosphine ligands.

Table 4
Selected regioselectivity and spectroscopic data for the hydroformylation of 1-octene by [HRh(diphosphine)$(CO)_2$] complexes [94]

Ligand	ee:ea	*n*:*i*	TOF	^1J(RhH) (Hz)	^1J(RhP) (Hz)	^2J(PH) (Hz)
22	84:16	7.3	370	5.2	135.4	6.9
23	84:16	7.4	224	5.4	134.6	7.2
24	88:12	7.3	606	5.1	137.7	5.0
25	71:20:9	7.2	650	4.0	136.1	3.4, 9.3
26	22:78	5.4	87	9.5	121.9	41.5

Due to the strong relationship observed between the electronic and steric properties of the diphosphine ligands on the selectivity a detailed QM/MM study was initiated to try and determine the major factors governing the regioselectivity in the xantphos-type catalytic systems [101]. Diphosphine ligands generate two kinds of steric effects: those originated by ligand–ligand or ligand–substrate nonbonding interactions (nonbonding effects) and those directly related to the bite angle (orbital effects). The bite angle determines metal hybridization and this in turn the metal orbital energies. Therefore steric effects may to some extent also be considered an electronic effect. The roles of the diphosphine bite angle and the nonbonding interactions were analysed in detail. The authors were able to separate, identify and evaluate the different contributions to regioselectivity. The calculated structures of the [HRh(alkene)(diphosphine)(CO)] complexes showed that the nonbonding interactions of the phenyl groups with coordinated ligands are crucial in controlling the regioselectivity, whereas the effects directly associated with the bite angle (orbital effects) had a smaller influence.

van Leeuwen et al. also prepared a series of phosphacyclic diphosphine ligands based on the xanthene backbone (see Fig. 5). Spectroscopic studies of the corresponding [HRh(diphosphine)$(CO)_2$] complexes indicated that the phosphacyclic ligands exhibited a preference for equatorial–equatorial coordination compared to the diphenyl-substituted compounds, except POP-xantphos which formed an equatorial–apical complex. These ligands in the hydroformylation of 1-octene showed greater activity than the noncyclic ligands and very importantly, DBP-xantphos (**27**) and POP-xantphos (**30**) were found to be very active and selective catalysts for the hydroformylation of internal octenes to linear nonanal. Complexes **27**

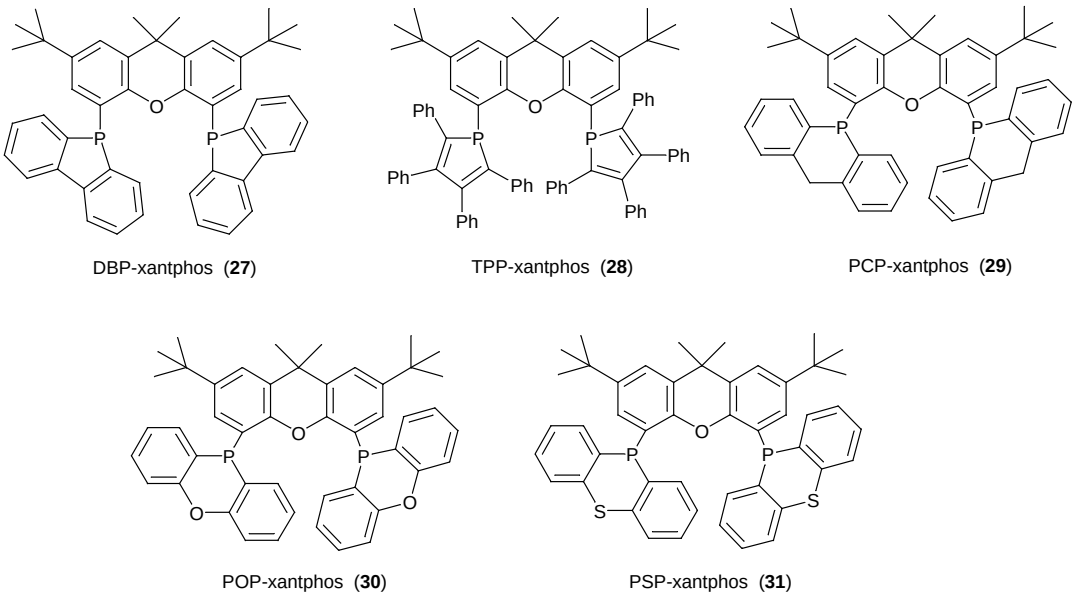


Fig. 5. Examples of phosphacyclic diphosphine ligands based on the xanthene backbone.

and **30** constitute the first rhodium diphosphine catalysts for the selective hydroformylation of internal alkenes to linear aldehydes. The very high hydroformylation and isomerisation activity of **30** was shown to be the direct result of an enhanced rate of carbon monoxide dissociation from the [HRh(diphosphine)$(CO)_2$] complex, which was measured using rapid-scanning IR spectroscopy [95]. These results are consistent with the QM/MM study that the ligand backbone determines the regioselectivity of the reaction by controlling the orientation of the phenyl substituents.

Stanley et al. prepared a tetradentate phosphine ligand, which could simultaneously coordinate two metal centres. The dinuclear complex showed high activity and selectivity in the hydroformylation of 1-hexene, with the racemic bimetallic rhodium complex giving both high rates and selectivities, whereas the *meso* complex was found to be considerably slower and less selective. This catalytic system represents the first example of bimetallic cooperativity in homogeneous catalysis. Spectroscopic data gave evidence for the existence of unusual dicationic rhodium(II) complexes. The bimetallic cooperativity was thought to originate from the intramolecular hydride transfer from the rhodium hydride to the rhodium acyl species, enhancing the elimination of the aldehyde from the acyl intermediate [102–105].

4.2. Phosphite-based catalysts

Pruett and Smith [106] of Union Carbide Corporation (UCC) were among the first to report the beneficial effects of phosphites as ligands for rhodium-catalysed hydroformylation reactions. The first reports of bulky monophosphites giving high rates for internal and terminal alkenes were reported by van Leeuwen and Roobeek [107]. These ligands did however not give good selectivities. Bryant and co-workers at UCC reported high selectivities for the rhodium-catalysed hydroformylation of internal and terminal alkenes using bulky diphosphites [108].

Facile CO dissociation and stronger alkene association causes reaction rates to increase when electron-withdrawing substituents on ligands are used. This comes as no surprise, because π-backbonding contributes significantly to the strength of the metal-to-ligand bond, especially in the case of carbonyl ligand. Phosphites are better π-acceptors than phosphines and therefore have significant potential as ligands in rhodium-catalysed hydroformylation. An additional advantage of phosphites is their relative ease of synthesis and the fact that they are less prone to oxidation and reactions with sulphur compounds. Disadvantages of phosphites include side reactions such as hydrolysis, alcoholysis, transesterification, Arbusov rearangement (restricted to alkyl phosphites, hence the predominant use of aryl phosphites) and O–C or P–O bond cleavage [109].

4.2.1. Monophosphites

Although the use of phosphite ligands and especially bulky phosphites give significantly higher reaction rates than phosphines in rhodium-catalysed hydroformylation, the loss of selectivity associated with these ligands, remains a concern. For this reason only a selected example is given to illustrate the use of in situ spectroscopy in the study of these ligands is included and more focus will be given to the use of diphosphites. The bulky tris(ortho-*tert*-butylphenyl)phosphite gives unexpectedly high reaction rates for the hydroformylation of unreactive alkenes like 2-methyl-1-hexene [110]. This high reactivity is thought to be due to the formation of a monoligated rhodium phosphite complex, which was characterised by the use of in situ NMR and IR techniques [111].

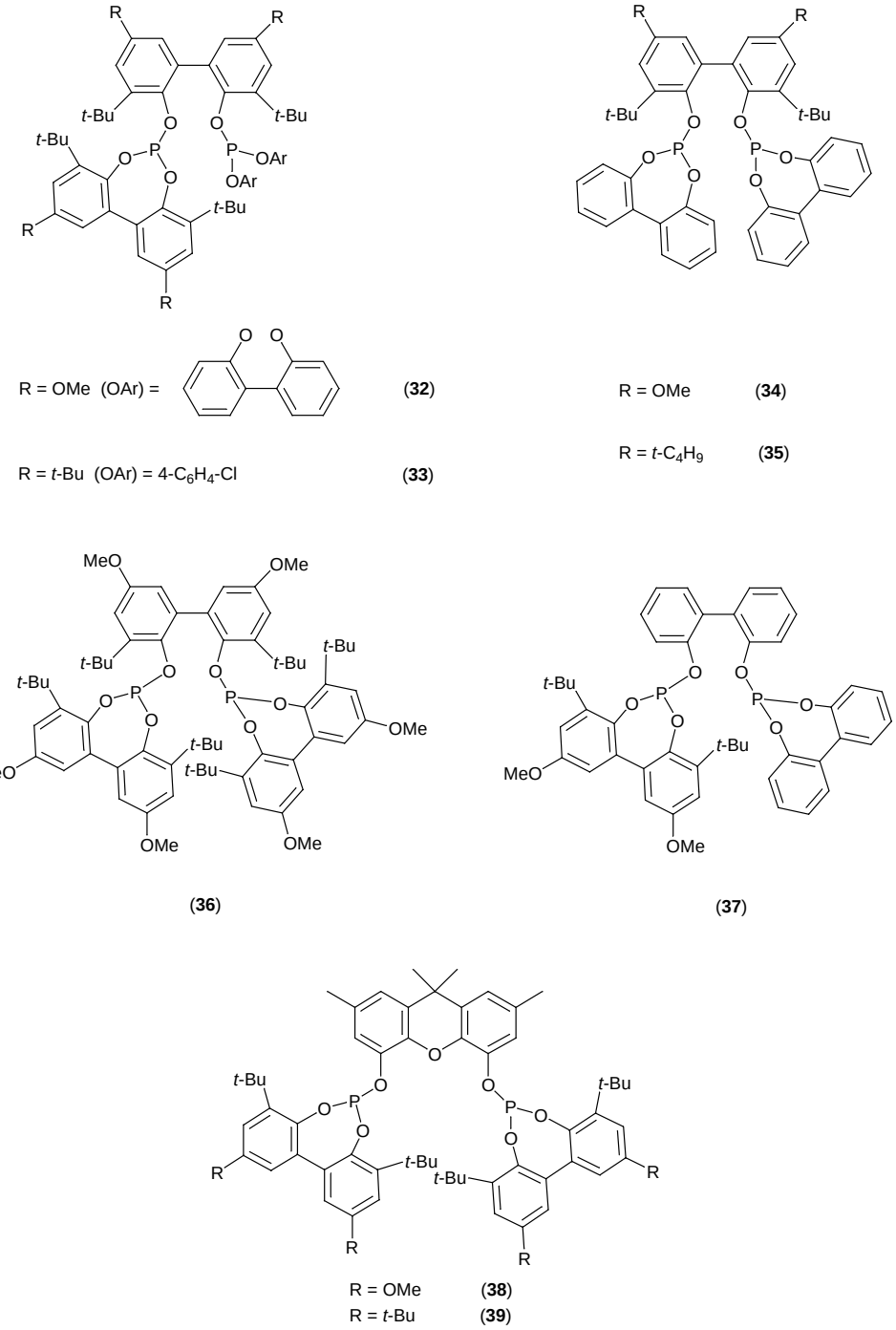


Fig. 6. Examples of diphosphite ligands.

4.2.2. Diphosphites

Changing the ligand system to a diphosphite represents an important trade-off between the low selectivities obtainable with bulky monophosphites and the poor reaction rates generally observed when using phosphines as ligands. As might be expected, reaction rates are much lower when diphosphites are used instead of bulky monophosphites [112]. The reason for this is that bulky monophosphites form mono-ligand complexes with rhodium hydride carbonyls, which are more reactive catalysts both for electronic and steric reasons. The development of the ligands (**32**–**37**) (see Fig. 6) led to a widespread interest in diphosphites from both the industrial and academic sector. A complete patent search covering the multitude of available ligands is beyond the scope of this work. The reader is directed to some representative examples [108,113,114].

Considering the performance of the diphosphite examples taken from the early UCC patents [108], it is clear that

the type of bridge in the ligand as well as the bulkiness of the substituents play a role, but that there is no evidence of what governs the linearity of the formed products. Studies by van Leeuwen et al. [115,116] described the performance of a few of the ligands or slight variations of the ligands first reported by Bryant and co-workers [108]. NMR and IR data of the [HRh(diphosphite)$(CO)_2$] complexes were also obtained using high-pressure techniques [115,116]. The active catalysts were prepared from [Rh(acac)$(CO)_2$] in the presence of excess phosphite. Under CO/H_2 pressure the rhodium precursor is converted to the active hydride complex [$HRh(CO)_2$(diphosphite)], which is generally assumed to have a trigonal bipyramidal structure. This structure lends itself to the formation of two isomers, with the diphosphite coordinated either in an equatorial–equatorial (ee) or an equatorial–apical (ea) manner. The complex structures were determined using both NMR and infrared data. Typical carbonyl absorptions for the ee complexes arise around 2015 and 2075 cm^{-1} [115–117], whereas the absorptions for ea complexes can be found at 1990 and 2030 cm^{-1} [116,117]. Care must be taken not to assign extra carbonyl signals originating from the formation of mixtures of complexes to the rhodium hydride species, as these also appear in the carbonyl region. The rhodium hydride signals are mostly very weak and disappear upon deuteration of the complex (rhodium-deuteride vibration appears in the fingerprint region).

The above authors also prepared ligands (**38**, **39**) based on the 9H-xanthene skeleton as a backbone and showed by high-pressure NMR and IR spectroscopy that the bidentate ligands only form catalysts where one of the phosphite donor atoms occupies the apical position and the other one the equatorial position. These ligands resulted in very active and selective hydroformylation catalysts for both terminal and internal alkenes [118]. The catalyst precursors were prepared in situ by reacting a slight excess of the diphosphite with [Rh(acac)$(CO)_2$] at 80 °C under 20 bar of synthesis gas. They found ^1J(RhP) coupling constants of 206 and 211 Hz for [$HRh(CO)_2$(diphosphite)] using **38** and **39**, respectively. These are in the typical range for rhodium hydride complexes with a trigonal–bipyramidal structure. It was previously shown that a *trans* relationship between the hydride and the phosphorous atom in such a structure causes a large ^2J(PH) coupling constant, in the range of 160–200 Hz, while values of less than 3 Hz are reported for *cis* arrangements [115,116,119]. The intermediate values found for [$HRh(CO)_2$(**38**)] and [$HRh(CO)_2$(**39**)] complexes (^2J(PH) = 100 and 99 Hz, respectively) suggests a fluxional process which is responsible for the average coupling constants. Coupling constants for an equatorially coordinated phosphite in a trigonal–bipyramidal structure are in the range of 220-246 Hz and they concluded that the ^1J(RhP) of 241 Hz found for [$HRh(CO)_2$(**39**)] corresponds to an equatorially coordinated phosphorus atom. These findings therefore dismiss the assumption that the regioselectivity of the reaction is solely dependent on the bisequatorial coordination of the phosphite in the active rhodium catalyst.

The rhodium-catalysed hydroformylation of 1-octene using the bis(phosphite) ligand **32** was studied by in situ, high-pressure ^1H and ^{31}P NMR and Fourier transform infrared (FTIR) spectroscopy. Four species, [Rh(acac)(**32**)], [$HRh(CO)_2$(**32**)] and two dimeric complexes appeared sequentially during different stages of the catalysis when [Rh(acac)$(CO)_2$] was used as the catalyst precursor. These complexes were independently synthesised and their stoichiometric and catalytic reactivity was evaluated. The major species present during catalysis is [$HRh(CO)_2$(**32**)]. They could not observe any ligand degradation via hydrolysis or reaction with the aldehyde by means of ^{31}P NMR spectroscopy. Furthermore, they also concluded that poor mass transfer of reactive gases from the headspace of the NMR tube could have lead to rapid depletion of CO and H_2 from the solution, therefore resulting in alkene isomerisation to be favoured. In the HP-IR cell, where no mass transfer limitations exist due to the possibility of rapid stirring, it is difficult to determine the degree of isomerisation due to the overlapping of multiple C=C stretching bands [120]. The bridge length of the diphosphites seem to have an effect on the selectivity for linear aldehyde, as does the presence of a bisphenol bridge, although the latter does not always hold true, as seen from the low linearities afforded with **36** and **37**. The bite angle of the diphosphite ligands (which may be equivalent to the bridge length) is most likely a parameter that influences the selectivity of the hydroformylation reaction, the same observation that was made for diphosphine ligands [90,91,98]. The large number of conformations with similar calculated energies complicates the calculation of bite angles of diphosphites. It can be noted in summary that NMR and FTIR, especially the complimentary high pressure additions to these powerful techniques have led to a better understanding of rhodium-catalysed hydroformylation reactions using phosphite ligands. An increasing collection of spectroscopic data (both NMR and FTIR) can be found in the literature and we have selected a number of representative examples (see Table 5).

5. Cobalt-catalysed hydroformylation

Cobalt-catalysed hydroformylation (also known as the oxo process) was discovered by Roelen [121,122] in 1938. Initial catalyst systems were unmodified with [$HCo(CO)_4$] derived from either cobalt(0) or from cobalt(II) via treatment with a 1:1 mixture of CO/H_2 (syngas) at high pressures (>200 bar) and temperatures. Later developments [123] showed that the addition of a tertiary phosphine could stabilise the catalyst to such an extent that reaction pressures below 100 atm were feasible. Although the phosphine-modified cobalt catalyst systems are less reactive than the unmodified catalyst, they were found to be more effective hydrogenation catalysts to the primary alcohols and better selectivities towards linear products were obtained. On the other hand, for modified catalysis,

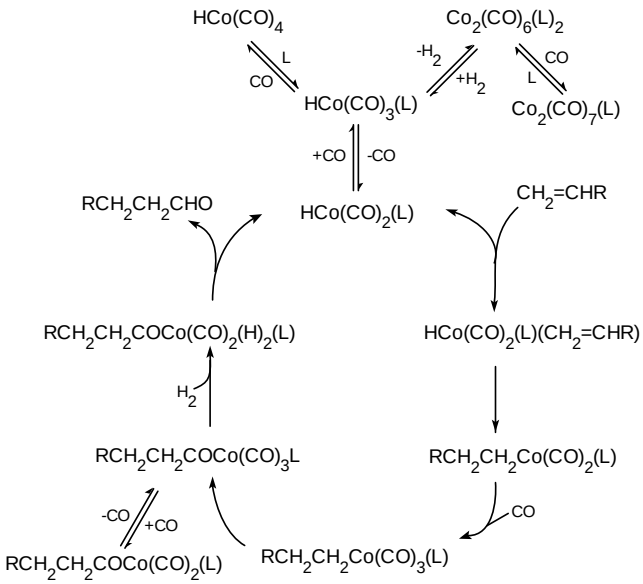
Table 5
Selected spectroscopic data for [HRh(diphosphite)$(CO)_2$] complexes [115,118,120]

Ligand	^1J(RhH) (Hz)	^1J(RhP) (Hz)	^1J(PH) (Hz)	^1J(PP) (Hz)	ν(CO) (cm^{-1})
32	–	235	3.5	–	2074, 2016
33	3.5	237, 226	–19.7	170	2049, 1996
33 (^{13}CO)	–	–	–	–	1994, 1957
32 (deuteride)	–	–	–	–	2058, 2012
34	3.5	239	4	–	2074, 2013
35	3	234	9	–	
38	8	206	–	–	1990, 2029
39	8	211	–	–	1990, 2029

more hydrogenation of the olefin feed to paraffins was observed.

An ongoing challenge in hydroformylation technology is a fundamental understanding of the catalytic cycle, thereby pursuing improvements to obtain a highly selective catalyst. The general mechanistic scheme for unmodified hydroformylation was first proposed by Heck and co-workers [124,125] which has also been broadly accepted to apply to modified cobalt catalysis.

The active species is an 16-electron hydride complex, $[HCo(CO)_2L]$ (L = CO or phosphine), in equilibrium with the 18-electron tricarbonyl $[HCo(CO)_3L]$ complex. Coordination of alkene and insertion into the Co–H bond generates a cobalt–alkyl complex which is followed by CO-insertion to give an acyl species. Hydrogenation of the acyl liberates the aldehyde and regenerates the active hydride species. This mechanism is depicted in Scheme 1. For the sake of simplicity, the hydrogenation step of the alkyl, $[RCH_2CH_2Co(CO)_2(L)]$, complex to paraffins and isomerisation by H-elimination to give internal alkenes and therefore internal aldehyde and alcohol products, have been omitted.



Scheme 1. Cobalt modified hydroformylation cycle.

The development of HP-IR cells during the late sixties and early seventies [126–128], allowed for the study of catalyst species at conditions close to or at hydroformylation conditions. The majority of HP-IR spectroscopic studies were performed on the unmodified catalyst systems and this will be discussed in conjunction with modified hydroformylation studies.

HP-IR spectroscopic studies carried out by Whyman [129–132] during the early 1970s identified the principal species, $[HCo(CO)_3(PBu_3)]$ and $[Co_2(CO)_6(PBu_3)_2]$, existing under catalytic conditions for a PBu_3 modified cobalt catalyst. The initial disproportionation reaction between $[Co_2(CO)_8]$ and PBu_3 results in the formation of the salt, $[Co(CO)_3(PBu_3)_2][Co(CO)_4]$, which is converted to the dimer, $[Co_2(CO)_6(PBu_3)_2]$, at elevated temperatures. At high temperatures in the presence of H_2, the hydride, $[HCo(CO)_3(PBu_3)]$ is formed. In the presence of excess phosphine $[HCo(CO)_2(PBu_3)_2]$ was observed whilst $[Co_2(CO)_7(PBu_3)]$ was observed at low phosphine concentrations. In contrast to the unmodified cobalt catalyst, no acyl species was observed. On this basis it was suggested that displacement of CO in $[HCo(CO)_3(PBu_3)]$ by the alkene was rate limiting for the catalytic process, whereas in the absence of phosphine, hydrogenation of the acyl intermediate contributed to the rate law.

Penninger and co-workers [133] also determined equilibrium constants and thermodynamic data for the reactions of cobalt complexes (in heptane) over the range 100–150 °C (Scheme 2).

HP-IR studies were also undertaken by Penninger and co-workers [134] on unmodified hydroformylation. In contrast to previous observations by Whyman [131], they concluded that no evidence for the presence of the acyl complex could be found.

Conflicting reports have appeared regarding the relative importance of reactions (1) and (2) under catalytic conditions (>100 °C, >100 bar H_2 + CO).

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2HCo(CO)_4$$
$$Co_2(CO)_8 + PBu_3 \rightleftharpoons Co_2(CO)_7(PBu_3) + CO$$
$$Co_2(CO)_7(PBu_3) + H_2 \rightleftharpoons HCo(CO)_4 + HCo(CO)_3(PBu_3)$$
$$HCo(CO)_4 + PBu_3 \rightleftharpoons HCo(CO)_3(PBu_3) + CO$$

Scheme 2. Reactions of cobalt complexes.

$$RC(O)Co(CO)_4 + HCo(CO)4 \rightarrow RCHO + Co_2(CO)_8 \quad (1)$$

$$RC(O)Co(CO)4 + H_2 \rightarrow RCHO + HCo(CO)_4 \quad (2)$$

On the basis of HP-IR studies Alemdaroğlu and co-workers claimed reaction (1) (bimolecular catalysis) to be the principal route to aldehyde formation [134], whereas Mirbach provided evidence for the predominant role of reaction (2) [135]. The acylcobalt hydrogenation is about one order of magnitude faster for 1-octene compared to cyclohexene at 80 °C and 95 bar $CO/H_2 = 1$ in methylcyclohexane. The alternative reaction of $[RC(O)Co(CO)_4]$ with $[HCo(CO)_4]$ was found to be only a minor pathway. The activation of the catalyst precursor $[Co_2(CO)_8]$ is the slowest step of the reaction.

Pino et al. studied [136] the mechanism of the activation of molecular hydrogen in cobalt-catalysed hydroformylation of olefins by HP-IR at room temperature. These studies showed that the mechanism of H_2 activation in the presence of $[HCo(CO)_4]$ is highly dependent on the reaction conditions. Under H_2 pressure (100 bar) at room temperature the activation of molecular hydrogen starts at a coordinatively unsaturated acyl cobalt carbonyl, yielding an aldehyde and an unknown cobalt species. This species is believed to be a coordinatively unsaturated hydrido carbonyl, which in turn, is able to activate and catalytically hydroformylate the olefin. It was also suggested that at higher temperatures and partial pressures of CO, the hydrido species $[HCo(CO)_4]$ and/or $[HCo(CO)_y$ ($y = 3$, 4)] are probably involved in the catalytic hydroformylation of olefins, as was suggested by Kovács et al. [137].

Ford and co-workers [138,139] elegantly showed how reactive intermediates can be formed from modified cobalt acyls by laser flash photolysis. The decay of this intermediate was shown by two different pathways, alkyl migration to the cobalt to give $[RCo(CO)_3PR_3']$ (R′ = Ph or Bu) and reaction with CO to reform the acyl at elevated temperatures and pressures. Activation parameters and rate constants for the two pathways were calculated using time-resolved infrared studies. Ligand effects were observed for the migration step ($k_M(PBu_3) \gg k_M(PPh_3)$), while small differences were observed for the rates of CO-insertion.

Most high-pressure spectroscopic work up to date gave important information on the nature of the metal carbonyl species under hydroformylation conditions and very little on direct application regarding rates and selectivities. Whyman [132] demonstrated that mainly the pre-catalyst, $[HCo(CO)_3(PBu_3)]$, was observed by HP-IR during hydroformylation reactions. Crause et al. [140] from Sasol Technology in South Africa combined HP-IR, HP-NMR, kinetic and modelling data to demonstrate that the activity and selectivity for a modified catalyst is, to a large extent, governed by the equilibria between the modified and unmodified cobalt catalysts in solution (see reaction below).

$$HCo(CO)_4 \underset{-L}{\overset{L}{\rightleftharpoons}} HCo(CO)_3L$$

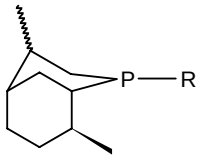


Fig. 7. Tertiary phosphine ligands derived from (*R*)-(+)-limonene.

For modified catalysis, $[HCo(CO)_3L]$ is accepted as the desired form of the pre-catalyst and optimisation of the catalysts in this form is thus important. Limonene derived bicyclic phosphines (Fig. 7) with different carbon length on the alkyl chain were first studied by HP-IR at conditions where both modified and unmodified hydride exist.

The modified hydride peaks assigned at around 2045 and 1966 cm^{-1} are well separated from the unmodified hydride at 2029 cm^{-1} and from peak heights the ratio of modified to unmodified hydride was obtained. In situ high pressure studies on the formation of phosphine modified cobalt carbonyl species were conducted using ^{31}P NMR spectroscopy in a sapphire NMR tube. Experiments were designed specifically to determine the extent of modified hydride $[HCo(CO)_3L]$ formation for different phosphines under standard catalyst pre-forming conditions.

The modified/unmodified ratio for the catalyst resting state, $[HCo(CO)_3L]$ (L: bicyclic phosphine) was correlated by HP-IR with the amount of hydride formation by ^{31}P NMR. The modified/unmodified ratio for $[HCo(CO)_3L]$ is dependent on the nature of the bicyclic phosphine side chain. For the ligands containing functionalised alkyl chains the effects induced are believed to be mainly electronic in nature with the more electron-deficient ligands giving lower modified:unmodified ratios. The spectroscopic data were then correlated with kinetic (rates and selectivities toward linear products) and modelling data (reaction energies for coordination of different phosphines to $[HCo(CO)_4]$). It was clearly demonstrated that the modified cobalt catalyst is less reactive than the unmodified catalyst, but exhibits significantly improved regioselectivity towards the desired linear products. This study illustrated that spectroscopic data can give useful information regarding catalyst performance towards selectivities and rates. This approach could be useful to obtain qualitative information with regards to new ligands.

Dagang et al. [141] used HP-IR spectroscopy to correlate electronic properties of various phosphine ligands to the stability and activity of the catalyst. The experimental results indicated that the stability of the active species, $[HCo(CO)_3PR_3]$, and the hydroformylation activity of the cobalt phosphine catalysts increase with increasing electron-donating ability of the ligands.

^{13}C NMR CO-exchange reactions of various cobalt carbonyl complexes which are catalytic intermediates or precursors in unmodified cobalt-catalysed hydroformylation were described by Roe [142]. This gave some insights into the inherent reactivity and stability of these complexes in the pressure and temperature ranges of the study.

Rathke et al. reported pre-equilibrium studies of cobalt phosphine catalysts [143]. Upon reaction of $[Co_2(CO)_6(PBu_3)_2]$ with H_2, $[HCo(CO)_3(PBu_3)]$ was observed and characterised by ^{31}P and ^{1}H NMR. Under CO pressure, the dimer was shown to form the salt, $[Co(CO)_3(PBu_3)_2][Co(CO)_4]$. The formation of salt is reversible and favoured by high CO pressures and polar solvents, e.g. dioxane and *i*-butanol. This observation is important since during hydroformylation when alcohols are formed, salt formation would be enhanced at the expense of the hydride. The interconversion of various tri-*n*-butylphosphine substituted cobalt carbonyls was also investigated in detail at different temperatures [144].

6. Alternate solvents

Supercritical fluids (SFCs) are attractive alternatives to organic solvents as reaction media for a number of reasons. The reasons include their pressure tunable properties, physical properties and solvent powers as well as the high miscibility of the reactant gases, efficient mass transfer, local clustering, and possible weakening of the solvation of the reactants [145–147].

Rathke carried out in situ high-pressure studies on the unmodified cobalt-catalysed hydroformylation of propylene in supercritical carbon dioxide ($scCO_2$) employing ^{59}Co, ^{13}C and ^{1}H NMR spectroscopy [148–150]. These studies have shown that under actual catalytic conditions cobalt is present in the form $[Co_2(CO)_8]$, $[HCo(CO)_4]$, and the aldehyde precursor, an acylcobalt tetracarbonyl, $[RC(O)CoCO_4]$. The rate of hydroformylation and in situ measurements of the steady-state concentrations of catalytic intermediates were determined and found to be comparable to similar reactions in non-polar solvents. For the hydrogenation of $[Co_2(CO)_8]$ at 80 °C in $scCO_2$, the equilibrium and rate constants for the forward and reverse reactions were calculated and found to be comparable to similar reactions in methylcyclohexane. The possible presence of the tetracarbonylcobalt radical was also proposed from broadening and ultimately merging of the two ^{59}Co NMR signals for $[HCo(CO)_4]$ and $[Co_2(CO)_8]$ during equilibrium studies at 200 °C in $scCO_2$ under H_2 pressure.

Haji and Erkey [151] studied reactions of $[HRh(CO)L_3]$ (L = P(3,5-$(CF_3)_2C_6H_3)_3$) with CO, H_2, C_2H_4 and mixtures of these in $scCO_2$ using high-pressure FTIR spectroscopy. The results were compared to the behaviour of the conventional catalyst, $[HRh(CO)(PPh_3)_3]$, in organic solvents. $[HRh(CO)L_3]$ does not dissociate in $scCO_2$ and it is converted to $[HRh(CO)_2L_2]$ and $[Rh(CO)_2L_2]_2$ in the presence of CO and mainly to $[HRh(CO)L_2]$ in the presence of an equimolar mixture of CO and H_2. In the presence of CO and C_2H_4, the peaks observed in the acyl region and the terminal metal carbonyl region indicate the formation of three different acylrhodium complexes, $[Rh(CO)L_2(COEt)]$, $[Rh(CO)_2L_2(COEt)]$ and $[Rh(CO)_3L(COEt)]$. Similar species were also observed during the hydroformylation reaction. This first ever detection of the presence of the $[Rh(CO)L_2(COEt)]$ acyl species under hydroformylation conditions provides direct evidence for the mechanism originally proposed by Wilkinson and co-workers.

Yonker and Linehan [152] monitored the rhodium-catalysed hydroformylation of C_2H_4 in $scCO_2$ using tris(*p*-trifluoromethylphenyl)phosphine as a ligand by high-pressure NMR spectroscopy. The proposed $[HRh(CO)(P_2)(\eta^2\text{-}C_2H_4)]$ intermediate, where (P = $(p{-}CF_3C_6H_4)_3$), was identified directly in situ for the first time. The kinetics of the reaction were also determined.

Ionic liquids [153–155] have become an attractive option for the possible replacement of conventional molecular solvents. Features that make ionic liquids attractive include their lack of vapour pressure and the great versatility of their chemical and physical properties. A further advantage is the possibility of biphasic catalysis. This can be achieved where the catalyst and reactants are miscible in the ionic liquid and the products are insoluble. The rhodium-sulfoxantphos catalysed hydroformylation of 1-octene in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($BMI{\cdot}PF_6$) was monitored in situ by high-pressure IR and NMR by van Leeuwen and co-workers [156]. Similar equatorial–equatorial and equatorial–apical $[HRh(CO)_2(diphosphine)]$ catalytic species, as observed in organic solvents, are formed in the ionic liquid. The reaction was found to be independent of hydrogen partial pressure, unlike some hydroformylation systems using xanthene backbone ligands in conventional organic solvents.

Reaction of $[Rh(acac)(CO)_2]$ with (m-$NaO_3SC_6H_4)_3P(H_2O)_3$ (Rh:P = 3.5) in water under CO pressure results in the formation of a $[HRh(CO)(m\text{-}NaO_3SC_6H_4)_3P)_3]$ complex [157]. High-pressure NMR studies of an aqueous solution of $[HRh(CO)(m\text{-}NaO_3SC_6H_4)_3P)_3]$ and 3 M excess $(C_6H_4SO_3Na)_3P$ did not show the formation of new species at <200 atm 1:1 CO/H_2. This is in contrast to the reaction of $[HRh(CO)(PPh_3)_3]$ and 3 M PPh_3 in toluene which was completely converted to $[HRh(CO)_2(PPh_3)_2]$, the desirable form of the catalyst pre-cursor, under 30 atm 1:1 CO/H_2.

Aghmiz et al. [158] investigated the rhodium-catalysed hydroformylation of *p*-methoxystyrene and *p*-fluorostyrene with sulfonated 1,3-diarylphosphines ligands, tetrasulfonated 1,3-bis(diphenylphosphino)propane (dpppts) and (*S*,*S*)-2,4-bis(diphenylphosphino)pentane ((*S*,*S*)-bdppts)) in a water/methanol mixture. High-pressure NMR and IR spectroscopy was used to analyse the rhodium-sulphonated-phosphine species present in solution under carbon monoxide and hydrogen pressure as a function of pH. The pH of the reaction medium was found to control the species formed and hence the activity and selectivity. In basic media the major species was found to be $[HRh(CO)_2(dpppts)]$, whereas at neutral pH the main species observed was $[Rh(bdppts)_2]^+$. The low reaction rate in the neutral medium compared to the basic medium for the hydroformylation of

vinyl arenes could be accounted for by the formation of the cationic inactive bischelated $[Rh(bdppts)_2]^+$.

7. Parahydrogen-induced polarization (PHIP)

The use of parahydrogen as a high-sensitivity spin label for NMR was first proposed by Bowers and Weitekamp from Caltech during the 1980s [159]. Parahydrogen and orthohydrogen are the two nuclear spin isomers of dihydrogen, representing its nuclear singlet and triplet state, respectively. Parahydrogen, the singlet spin state, is magnetically inactive and is therefore not observed in the NMR spectrum, meaning that any observed ^1H NMR resonance of dihydrogen is exclusively due to orthohydrogen. PHIP is based on the PASADENA [160] (parahydrogen and synthesis allow dramatically enhanced nuclear alignment) effect and originates from the breakdown of the initially high symmetry of parahydrogen as the consequence of a chemical reaction. The two formerly equivalent protons are transferred into either chemically or magnetically inequivalent positions because of this reaction. It is important to note that the transformation of the two hydrogen atoms has to occur pairwise during the hydrogenation. This means that the initial A_2 spin system of parahydrogen becomes converted into a transient AB or AX spin system in the hydrogenation products and only those energy levels become selectively populated, which have some degree of singlet character. The details thereof depend on the conditions under which the hydrogenations are carried out, i.e. whether the reaction occurs only within the high magnetic field of the NMR spectrometer [161], or outside the spectrometer in the Earth's low magnetic field [162], followed by transfer into the NMR spectrometer for immediate analysis. Because of the considerable signal enhancement associated with PHIP (proportional to the reciprocal Boltzmann factor, typically a few orders of magnitude), detection of reaction intermediates and products at lower concentrations not attainable with conventional NMR spectroscopy becomes possible. *para*-Enriched hydrogen can be prepared by passing hydrogen through activated carbon at 77 K at a pressure of 3 bar [163], or by cooling hydrogen over $FeCl_3$ adsorbed on silica at 77 K [164].

Oxidative addition of hydrogen to chlorocarbonylbis(triphenylphosphine)rhodium(I) [165], iodocarbonylbis (triphenylphosphine)rhodium(I) [166] and identification of new intermediates in hydrogenation catalysed by Wilkinson's catalyst [167] using PHIP have been reported. Brown and co-workers reported the characterisation of the elusive rhodium-dihydride catalyst derived from the PHANEPHOS ligand [168]. Hydrogen addition to iridium tribromostannyl carbonylate anions [169], iridium carbonyl complexes and platinum-tin carbonyl complexes have been reported by Eisenberg and Permin [170]. Addition of dihydrogen to complexes of other metals such as tantalum [171], ruthenium [172], osmium [173] and platinum [174] have also been studied using *para*-hydrogen induced polarization.

8. Conclusion

An understanding of the how the electronic (σ and π) and steric properties of ligands govern the coordination chemistry of the resulting metal complexes is of fundamental importance in catalysis and coordination chemistry as a whole. This understanding will enable chemists to design more efficient catalytic systems with predictable selectivities and rates. A variety of tools are available to chemists to probe and quantify these effects. As we have demonstrated for the above for hydroformylation reaction, HP-NMR and HP-IR spectroscopy and quantum mechanic/molecular mechanic calculations are proving to be a useful and generally available tool to further our understanding of metal–ligand interactions.

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