Cobalt-Catalyzed Hydroformylation of Alkenes: Generation and Recycling of the Carbonyl Species, and Catalytic Cycle

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Contents

1. Introduction 4272
2. Generation of the [Co(H)(CO)$_4$] Key Species 4273
  2.1. General Mechanism of the Hydroformylation Reaction 4273
  2.2. Preparative Modes of [Co(H)(CO)$_4$] 4273
  2.3. [Co(H)(CO)$_4$] in the Oxo Process 4274
  2.4. Characterization and Structure of [Co(H)(CO)$_4$] 4275
3. Preparation and Behavior of the Substituted [Co(H)(CO)$_{4-x}$L$_x$] Complexes 4275
4. Mechanism of the Catalysis 4277
5. Recycling 4278
  5.1. Industrial Recycling 4278
  5.2. Use of Hard Lewis Bases 4279
  5.3. Biphasic Systems 4279
6. Conclusion 4280
7. References 4280

1. Introduction

In 1938, while Otto Roelen was studying the Fischer−Tropsch reaction, which converts H_2/CO into alkanes and alkenes, and was trying to improve the yields by recycling ethylene, the cobalt catalyst deposited on a ThO_2/SiO_2 support produced some propanal. Fortunately, Roelen focused on this unexpected reaction and discovered that cobalt was able to catalyze specifically the hydrocarbonylation of ethylene.[1−3] It was rapidly established that this reaction, which has been extended to various alkenes, was occurring in the organic phase: homogeneous catalysis was born.

Despite delays caused by World War II, the hydroformylation, also known as the “oxo” reaction, was developed to produce long chain aldehydes on an industrial scale (and detergent alcohols by subsequent hydrogenation), and before 1945 the first plant of ca. 10 000 ton/year capacity was ready to operate.[4] Since this period, the aldehyde production increased constantly, and, more especially, since the 1970s, when rhodium-based processes were developed to carbonylate light alkenes. Nowadays, the world production approaches 10.10^6 ton/year.[5]

Concerning the mechanism, as early as 1953, a short communication by Wender, Sternberg, and Orchin appeared and confirmed the initial Roelen’s postulate: the involvement of [Co(H)(CO)$_4$] in the catalytic cycle.[6] Although many kinetic, spectroscopic, and more recently theoretical investigations have continuously been carried out, studies related to the intimate mechanism are still regularly reported.

Frédéric Hébrard was born in Montauban, South-Western France, in 1978. He chose to study chemistry in Toulouse in 1993. For studies, he moved to IUT de Castres (France), then the University of Northumbria at Newcastle (U.K.), and back to Toulouse, where he graduated in the Chemistry and Physicochemistry of Transition Elements in 2001. After a training period in Professor Philippe Kalck’s laboratory, working on palladium catalyzed carbonylation reactions, he remained in Toulouse for his doctoral research under the direct supervision of Pr. Kalck. He worked on cobalt catalyzed hydroformylation in the presence on ionic liquids, observed high pressure IR, and completed his Ph.D. in 2006. He then went on to work as a postdoctoral fellow with Pr. Cornelius J. Elsevier in Amsterdam, again working on palladium catalyzed carbonylation reactions. He is currently a temporary teacher at the University of Reims and deals with palladium catalyzed coupling reactions.

Concurrently, new industrial units have been established with various improvements in the cobalt recycling and its modifications by phosphine ligands.[7,8] However, through the years, this process has progressively appeared as obsolete. Indeed, when compared to rhodium performances, especially for propene, cobalt catalyzed hydroformylation chemoselectivity toward aldehydes is poor and its regioselectivity for linear aldehydes is reduced to 66%. Moreover, this process operates at 200 bar and the separation of cobalt is tedious and requires separate treatments. Nevertheless, it is still operated for $C_{10}−C_{16}$ aldehydes. Nowadays, promising solutions have been reported concerning the catalyst management using $scCO_2$ or ionic liquids, and the catalytic conditions can be milder.

Due to the emergence of recent mechanistic studies and to innovative solvents/separation systems, it seemed to us interesting to analyze the chemistry of cobalt carbonyl complexes, their generation, and their involvement in the hydroformylation reaction.

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Philippe Kalck was born near Besançon, France, in 1944. He studied in Toulouse and received his Diplôme d'Ingénieur Chimiste from the Ecole Nationale Supérieure de Chimie de Toulouse (ENSCT) in 1967. He remained in Toulouse for his doctoral research under the supervision of Professor René Poilblanc, completing his Doctorat d'Etat in 1975. Up until 1980, he combined research at the Laboratoire de Chimie de Coordination (CNRS) with teaching at the ENSCT. At that point, he was appointed Professor at the Institut National Polytechnique de Toulouse (of which the ENSCT formed part) and started a research group devoted to the catalysis of carbonylation reactions that has become the "Laboratoire de Catalyse et Chimie Fine" in the Ecole Nationale Supérieure des Ingénieurs en Arts Chimiques et Technologiques, and since 2007 a team belonging to the Laboratoire de Chimie de Coordination. He is particularly attached to promoting links between industry and academia, and he spent two years on secondment to Rhône-Poulenc Chimie between 1986 and 1988. His research interests include the design of highly selective catalysts and the molecular understanding of catalytic processes, fields in which he has published over 195 papers and supervised 53 Ph.D. students. A part of his research activity is devoted to the preparation of heterogeneous catalysts by decomposition under mild conditions in a fluidized bed of coordination compounds. An application of these studies is the selective process for producing multiwalled carbon nanotubes. He is also the author of 25 patents; among them, two are under predevelopment phase in the industry.

2. Generation of the [Co(H)(CO)$_4$] Key Species

2.1. General Mechanism of the Hydroformylation Reaction

As early as 1953, Wender et al. demonstrated that [Co(H)(CO)$_4$] was the oxo cobalt catalyst, after the first intuition of Roelen and indirect evidence provided by Adkins and Krsek and by Wender's and Orchin's groups.[6,9−14] Indeed, [Co(H)(CO)$_4$] reacts with pyridine to provide [C_5H_5NH]$^+$[Co(CO)$_4$]$^-$, which is the product formed when [$Co_2(CO)_8$] is heated under H_2/CO pressure (120 °C, 233 bar) in pure pyridine as solvent. Moreover, both [Co(H)(CO)$_4$] at atmospheric pressure or [$Co_2(CO)_8$] under oxo conditions transform an alkene into the corresponding aldehyde(s). After various studies staggered over a decade, Heck and Breslow published the whole series of equations accounting for the reactivity of cobalt under oxo conditions.[15] Subsequently, many papers and textbooks have adapted the initial set of equations into a more illustrative representation, as displayed in Figure 1.

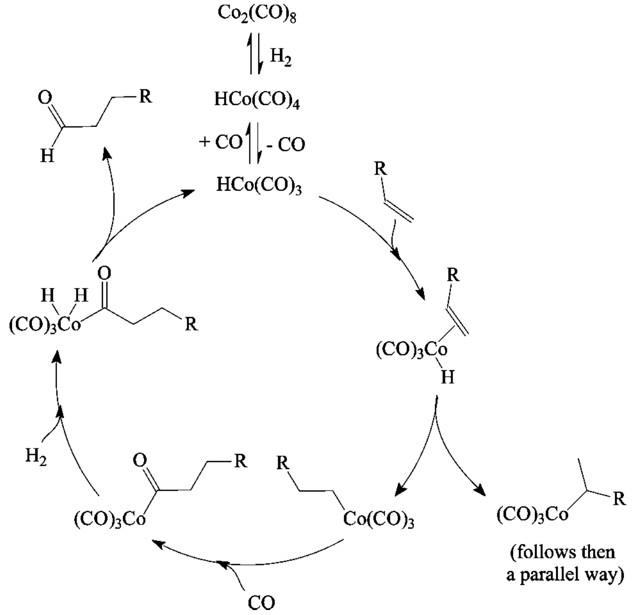

Figure 1. Mechanism of the cobalt catalyzed hydroformylation of alkenes.

The 16e active species [Co(H)(CO)$_3$] is generated by loss of a CO ligand from the [Co(H)(CO)$_4$] resting state. The inhibiting effect of the CO partial pressure, which was evidenced by the kinetic studies, appears in this pre-equilibrium.[16] The first clear identification of [Co(H)CO)$_3$] was reported by Wermer et al., who performed matrix infrared observations, only in 1978.[17]

The catalytic cycle involves successively the coordination of the alkene, the hydride transfer to provide the linear alkyl species (and the isomeric branched one), CO coordination and migratory CO insertion, and then oxidative addition of H_2 followed by the reductive elimination of the aldehyde which regenerates the active species.

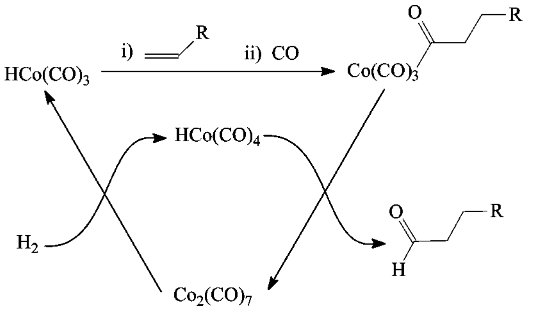

Figure 2. Alternate (dinuclear) mechanism for hydroformylation: [Co(H)(CO)$_4$] reacts with [Co{C(O)CH_2CH_2R}(CO)$_3$] to release the aldehyde. The resulting dimer reacts with H_2 to generate both [Co(H)(CO)$_3$] and [Co(H)(CO)$_4$].

A second possibility exists, when reactions are carried out under stoichiometric conditions, in which [Co(H)(CO)$_4$] reacts directly with the acyl species [Co($COCH_2CH_2R$)(CO)$_3$] to give the aldehyde and [$Co_2(CO)_7$].[18,19] This latter unsaturated dimer can coordinate H_2 and regenerate both hydrides, [Co(H)(CO)$_4$] and [Co(H)(CO)$_3$] (Figure 2). This parallel pathway, already considered by Heck and Breslow, should only occur when catalytic solutions contain high concentrations of cobalt.

2.2. Preparative Modes of [Co(H)(CO)$_4$][20]

On the bench scale, the easiest way to produce [Co(H)(CO)$_4$] is to protonate a salt of the [Co(CO)$_4$]$^-$ anion. Stable complexes of [Co(CO)$_4$]$^-$ can be generated from a cobalt(II) salt or from [$Co_2(CO)_8$]. In an approach similar to iron and nickel carbonyls, K[Co(CO)$_4$] has been prepared as early as 1934 by treating aqueous cobalt(II) nitrate solutions, and more recently $CoCl_2$, under one atmosphere of CO in the presence of potassium cyanide and potassium hydroxide.[21−28] The reaction proceeds through the oxidation of three CO equivalents per two cobalt atoms into carbonates, as shown in eq 1:

$$2Co^{2+} + 12OH^- + 11CO \xrightarrow{CN^-} 3CO_3^{2-} + 6H_2O + 2[Co(CO)_4]^- \qquad (1)$$

In this reaction, the promoting role of the CN^- ions is the most efficient among various tested additives, such as cysteine, amino acids, tartrates, etc.

To obtain anhydrous $[Co(CO)_4]^-$ solutions, a convenient method is to reduce a Co(II) salt, $CoCl_2$ or $CoBr_2$, by sodium naphtalenide under CO.[29]

Another way to generate $[Co(CO)_4]^-$ is to react $[Co_2(CO)_8]$ with a Lewis base (OH^-, ROH, NR_3, PR_3, among others), which leads to a disproportionation reaction.[30,31] According to the base strength, Co^I/Co^{-I} or Co^{II}/Co^{-I} ionic couples are produced, as shown for instance in eqs 2, 3, and 4:

$$\underset{2Co^0}{[Co_2(CO)_8]} + 2PR_3 \xrightarrow{-CO} \underset{Co^I}{[Co(CO)_3(PR_3)_2]}\underset{Co^{-I}}{[Co(CO)_4]} \qquad (2)$$

$$\underset{2Co^0}{3[Co_2(CO)_8]} + 12py \xrightarrow{-16CO} \underset{Co^{II}}{2[Co(py)_6]}\underset{Co^{-I}}{[Co(CO)_4]_2} \qquad (3)$$

$$\underset{2Co^0}{11[Co_2(CO)_8]} + 32OH^- \rightarrow \underset{Co^{II}}{2Co^{2+}} + \underset{Co^{-I}}{20[Co(CO)_4]^-} + 8CO_3^{2-} + 16H_2O \qquad (4)$$

The general scheme of disproportionation can then be written

$$\underset{\text{for soft Lewis bases}}{2Co^0 \rightarrow Co^I + Co^{-I}} \quad \text{and} \quad \underset{\text{for hard Lewis bases}}{3Co^0 \rightarrow Co^{II} + 2Co^{-I}}$$

As can be seen, using hard bases provides higher quantities of $[Co(CO)_4]^-$ per mole of dimer.

Moreover, reducing agents can fully transform $[Co_2(CO)_8]$ into $[Co(CO)_4]^-$. For instance, the reaction of $[Co_2(CO)_8]$ with KH or $NaK_{2.8}$ produces $K[Co(CO)_4]$; tin provides the Sn(IV) complex $Sn[Co(CO)_4]_4$, and the thallium salt Tl^I-$[Co(CO)_4]$ reacts with $[Co_2(CO)_8]$ to give $Tl^{III}[Co(CO)_4]_3$.[32−34]

Once obtained, protonation of $[Co(CO)_4]^-$ by strong Brönsted acids gives rise to the $[Co(H)(CO)_4]$ neutral hydride in which cobalt is formally in the +I oxidation state and we can see that most preparations of $[Co(H)(CO)_4]$ from Co^{II} salts actually proceed through the intermediate formation of $[Co(CO)_4]^-$.

A very convenient method, for the generation of $[Co(H)(CO)_4]$ on a laboratory scale, is to start from $[Co_2(CO)_8]$, dissolved in an alkane, and then to add large quantities of dimethylformamide to produce $[Co(DMF)_6][Co(CO)_4]_2$. At low temperature, ca. 0 °C, hydrochloric acid is added to this DMF solution to generate $[Co(H)(CO)_4]$, which moves to the alkane phase, whereas $[Co(DMF)_6]Cl_2$ remains in the DMF/water phase.[35]

2.3. $[Co(H)(CO)_4]$ in the Oxo Process

On an industrial scale, $[Co(H)(CO)_4]$ is prepared under pressure of syngas (H_2/CO) in an appropriate generator before being introduced in the hydroformylation reactor. Various sources of cobalt can be used, including metallic cobalt, obtained by reduction of cobalt oxalate, and generally cobalt(II) salts such as carbonate, hydroxide, carboxylate, etc.[36−38] Actually, $[Co_2(CO)_8]$ is systematically generated as an intermediate, since it is in equilibrium with $[Co(H)(CO)_4]$ as a function of temperature and pressure.

In the industrial process, cobalt separation from the organic products is mainly achieved by two methods:[8,39] (i) addition of an aqueous basic solution to form $[Co(CO)_4]^-$, which is evolved in the aqueous phase, or (ii) oxidation to Co(II) in an acidic aqueous solution by oxygen, air, or hydrogen peroxide. Phase separation is followed by (i) acidification in the presence of H_2/CO or (ii) treatment of the cobalt(II) solution in the carbonyl generator, with both methods giving rise to the regeneration of the $[Co_2(CO)_8]/[Co(H)(CO)_4]$ mixture.

An interesting (but unsolved) question arises from the dynamic relationship between $[Co_2(CO)_8]$ and $[Co(H)(CO)_4]$ under the hydroformylation conditions and more especially how the activation of H_2 occurs on $[Co_2(CO)_8]$ (eq 5).[18,19,40−54]

$$[Co_2(CO)_8] + H_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2[Co(H)(CO)_4] \qquad (5)$$

Two mechanisms have been considered in the literature. The first one is related to the dissociation of a CO ligand to form the transient species $[Co_2(CO)_7]$, which can coordinate H_2 and produce $[Co(H)(CO)_4]$ and $[Co(H)(CO)_3]$. At low pressure, the reaction rate is inversely proportional to the CO partial pressure and, for instance, when $P_{CO} = 11$ bar the k_1 rate constant is 8.5×10^{-3} min^{-1} (80 °C, $P_{H_2} = 46$ bar), whereas $k_1 = 4.5 \times 10^{-3}$ min^{-1} when $P_{CO} = 22$ bar.[46]

The second mechanism, which prevails at higher CO partial pressures and which is more likely to occur under the hydroformylation conditions, involves an associative pathway between H_2 and $[Co_2(CO)_8]$, giving directly 2 equiv of $[Co(H)(CO)_4]$. Proofs have been accumulated progressively that the reaction proceeds through a radical species, namely $^{\bullet}Co(CO)_4$, arising from the homolytic cleavage of the metal−metal bond of $[Co_2(CO)_8]$, for which the activation energy is $\Delta H° = 19 \pm 2$ kcal·mol^{-1}.[49−54] This associative process was shown to be independent of the CO partial pressure above $P_{CO} \sim 25$ bar ($P_{H_2} = 45$ bar). As the CO dissociation energy and the Co−Co bond dissociation energy have been calculated to be approximately the same, it can be anticipated that a range should exist where both processes compete. Moreover, in our opinion, we cannot exclude a four centers intermediate in which the two H−H and Co−Co bonds lengthen while the two Co−H bonds are formed.

The $[Co_4(CO)_{12}]$ cluster can also be a convenient source of $[Co(H)(CO)_4]$. In the generation of cobalt carbonyl species, infrared and UV observations have shown that, under syngas pressure (H_2/CO = 1), $[Co_2(CO)_8]$ is formed prior to $[Co(H)(CO)_4]$. However, some authors have reported the higher rate of hydroformylation when starting from $[Co_4(CO)_{12}]$ versus $[Co_2(CO)_8]$, which should mean that the "$Co(CO)_3$" fragments arising from the tetramer generate more easily the $[Co(H)(CO)_3]$ active species.[55]

It is worth underlining that $[Co(H)(CO)_4]$ very easily gives the dimer $[Co_2(CO)_8]$, according to reaction conditions and particularly when the CO partial pressure is too low. This equilibrium between $[Co(H)(CO)_4]$ and $[Co_2(CO)_8]$, corresponding roughly to 66% of $[Co(H)(CO)_4]$ and 34% of $[Co_2(CO)_8]$, exists in a large range of temperature and

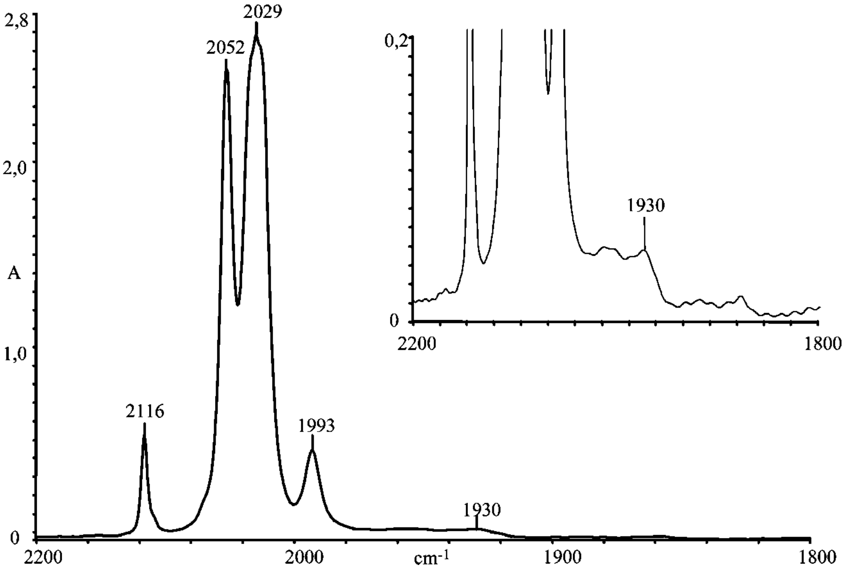

Figure 3. Infrared spectrum of $[Co(H)(CO)_4]$ in heptane under ambient conditions.

Table 1. Stretching Bands of $[Co(H)(CO)_4]$

assignment	frequency (cm^{-1})	intensity	symmetry
ν_{CO}	2116	w	A_1
	2052	s	A_1
	2029	vs	E
$\nu_{^{13}CO}$	1993	w	E
ν_{Co-H}	1930	vw	(A_1)

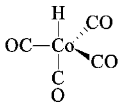

Figure 4. Geometry of $[Co(H)(CO)_4]$ (C_{3v} symmetry).

pressure beyond which the stability of the system is lost, with precipitation of metallic cobalt.

2.4. Characterization and Structure of $[Co(H)(CO)_4]$

Complex $[Co(H)(CO)_4]$ has been characterized very early by infrared, and recent studies, involving observations of $[Co(D)(CO)_4]$ and $[Co(H)(CO)_x(^{13}CO)_{4-x}]$ labeled species, permit the accurate assignment of the whole of its stretching frequencies.[31,56−66] As shown in Figure 3 and Table 1, infrared spectra present one strong band and one very strong ν_{CO} band, at 2052.40 and 2029.80 cm^{-1}, respectively, and two weak ν_{CO} bands at 2116.00 and 1992.85 cm^{-1}, with this latter arising from natural ^{13}CO in the nonenriched complex.[66]

The cobalt−hydride bond gives rise to a very weak ν_{Co-H} band at 1930 cm^{-1}. The complex $[Co(H)(CO)_4]$ adopts a trigonal bipyramidal geometry with the hydride ligand lying in the axial position (Figure 4), and this TBP geometry is not affected by pressure or temperature. From the force constants used in this study,[66] we can conclude that the retrodonation from cobalt to a CO ligand is more important for an equatorial than for an axial CO.

NMR experiments have been performed, in supercritical CO_2, under various conditions.[52,67,68] In ^1H NMR, the H ligand clearly shows a hydridic character with $\delta = -11.7$ ppm. In ^{59}Co NMR, the cobalt chemical shift is $\delta = -3055$ ppm and invariant between 60 and 190 °C. This value differs significantly from that of $[Co_2(CO)_8]$, $\delta = -2200$ ppm, while the studied complex $[Co(H)(CO)_4]$ has been generated from $[Co_2(CO)_8]$. However, in this case, the spectrum shows that a reversible exchange phenomenon involving the cobalt centers occurs between $[Co(H)(CO)_4]$ and $[Co_2(CO)_8]$, presumably through a radical process (as shown by mixing $[Co(H)(CO)_4]$ and $[Mn(H)(CO)_4]$).

On one hand, in organic media, complex $[Co(H)(CO)_4]$ is a hydride species that is capable of reacting through radical pathways. On the other hand, in water, it has a strong acidic character, with its pK_a being comprised between those of HNO_3 and HCl, although it presents a relatively low solubility, which probably explains why we did not detect in the literature any catalytic use of complex $[Co(H)(CO)_4]$ in water.

3. Preparation and Behavior of the Substituted $[Co(H)(CO)_{4-x}L_x]$ Complexes

At approximately the same time Heck and Breslow reported on the catalytic cycle of $[Co(H)(CO)_4]$, Slaugh and Mullineaux from the Shell Development Company patented the use of a $\{[Co_2(CO)_8]/PBu_3\}$ system to obtain higher selectivities toward linear aldehydes.[69,70] The total syngas pressure could be reduced to 50−150 bar, and the required temperature was slightly higher (160−200 °C), but the hydrogenative activity was so important that the process was focused on the production of alcohols, mainly *n*-butanol from propene.

Very rapidly, these authors proposed the $[Co(H)(CO)_3(PBu_3)]$ active species arising from $[Co_2(CO)_6(PBu_3)_2]$ under the hydroformylation conditions, and they interpreted the higher *l*/*b* ratio as resulting from the stronger hydridic character of the hydride ligand with regard to $[Co(H)(CO)_4]$. This discovery initiated many studies on the effects of various phosphorus-containing ligands and even arsines or stibines, and it has been shown, from infrared analyses of the monosubstituted complexes, that the $\nu_{CO}(A_1)$ band correlates well with the basicity of the ligands.[34,35,71−85]

Several preparations of these phosphine substituted complexes involve the addition of a given stoichiometry of ligand to $[Co_2(CO)_8]$ and either the further pressurization under H_2/CO or acidification. However, under ambient conditions, the direct substitution of $[Co(H)(CO)_4]$ appears to be a more elegant way. Several mono- and disubstituted cobalt hydride complexes have been prepared by this method.

Recently, a convenient method has been published describing the direct preparation of substituted cobalt hydrides by addition of the appropriate stoichiometry of a phosphine ligand to $[Co(H)(CO)_4]$.[35] By this method, the mono- and disubstituted complexes have been easily prepared and the X-ray crystal structure of $[Co(H)(CO)_2\{P(OPh)_3\}_2]$ has been determined. Its geometry is a significantly distorted trigonal bipyramide with the hydride ligand in one axial position, with the other one being occupied by a CO ligand.

The complex $[Co(H)(CO)L_3]$, in which L = $P(OCH_2)_3CC_2H_5$, has been prepared starting from $[Co(H)(CO)L_2]$ by heating the solution at 80 °C and adding an excess of the phosphine ligand.[76]

Presumably, it should be the case for the less basic phosphorus containing ligands, since addition of PF_3 to $[Co(H)(CO)_4]$ provides $[Co(H)(CO)(PF_3)_3]$ at room temperature and even $[Co(H)(PF_3)_4]$ for higher PF_3/CO ratios.[77,78] For more basic ligands, other strategies have been adopted such as the protonation of $Na[Co(CO)_2L_2]$ (L = $P(OPh)_3$ and PPh_3), the addition of ligand under a CO atmosphere to $[Co(C_8H_{13})(C_8H_{12})]$ to produce $[Co(H)(CO)L_3]$ (L = PPh_3 and $PMePh_2$), or the carbonylation of $[Co(H)(CO)(PPh_3)_3]$.[34] This latter complex presents a trigonal bipyramidal structure in which the three phosphine ligands lie in the equatorial plane.

High pressure infrared observations of the phosphine substituted cobalt hydridocarbonyls under H_2/CO atmosphere have shown that increasing the temperature can lead to the formation of $[Co(H)(CO)_4]$. For instance, substitution of a triphenylphosphite ligand with CO in $[Co(H)(CO)_3\{P(OPh)_3\}]$ occurs very easily above 120 °C and ca. 50 bar.[35] However, addition of 4 equiv of phosphite per cobalt atom is sufficient to maintain the existence of both mono- and disubstituted complexes.

As the synthesis of the hydrides is most often performed from the substituted dimeric complexes, we will briefly describe the reactivity of the dimer $[Co_2(CO)_8]$ vis-a-vis various equivalents of phosphorus-containing ligands.

According to the basicity of the ligand and the polarity of the solvent, a dismutation equilibrium can occur which provides an ionic complex associating a substituted cationic cobalt(I) species $[Co(CO)_{5-x}L_x]^+$ and the unmodified cobalt(−I) carbonyl anion $[Co(CO)_4]^-$, as shown in eq 6.

$$[Co_2(CO)_8] + xL \rightarrow [Co_2(CO)_{8-x}L_x] \rightleftharpoons [Co(CO)_{5-x}L_x][Co(CO)_4] \quad (6)$$

A very detailed analysis has been reported by Poilblanc et al.[79] If we include more recent results, the major tendency is that soft ligands, such as phosphites, give rise to the highest x values, mainly $x = 3$, with, in some cases, x reaching the value of 5. For trialkyl- and triarylphosphine, usually $x = 2$, which is the case for PBu_3, for which the equilibrium in *n*-hexane involves $[Co_2(CO)_6(PBu_3)_2]$ and $[Co(CO)_3(PBu_3)_2][Co(CO)_4]$, with this latter complex being largely converted into the former under hydroformylation conditions. Lee and Kochi have particularly focused on the mechanisms by which the $[Co(CO)_3(PR_3)_2]^+$ cation and the $[Co(CO)_3(PR_3)]^-$ anion react to produce the neutral dinuclear complex $[Co_2(CO)_6(PR_3)_2]$.[86] To evidence that a radical mechanism is occurring between the two ionic fragments, cyclic voltammetry measurements have confirmed that electroreduction of $[Co(CO)_3(PR_3)_2]^+$ or electrooxidation of $[Co(CO)_3(PR_3)]^-$ both provide the neutral dimer through the rapid coupling of carbonyl-cobalt radicals (eq 7).

$$2^\bullet Co(CO)_3(PR_3) \rightarrow [Co_2(CO)_6(PR_3)_2] \quad (7)$$

Their studies show that polar solvents induce a strong retardation of such a process, as well as neutral salts. In nonpolar solvents, the two ions exist as contact ion pairs whose formation is inhibited once again by added neutral salts.

It is necessary to underline the great facility by which the anion $[Co(CO)_4]^-$ and the radical species $^\bullet Co(CO)_4$ can be formed one from the other, as E_{red} is ca. 0.2 V vs NHE for $^\bullet Co(CO)_4$. Then, a charge transfer can easily occur between $[Co(CO)_4]^-$ and various cations, provided their proximity is ensured by contact ion-pairing. This one-electron transfer can also be induced by a low energy irradiation ranging from 440 to 560 nm. Concerning the substitution of a CO ligand in $[Co(CO)_4]^-$, the scavenging role of PPh_3 on $^\bullet Co(CO)_4$ has been proposed so that $^\bullet Co(CO)_3(PPh_3)$ thus formed very easily produces $[Co_2(CO)_6(PPh_3)_2]$. Presumably, substitution of $[Co(CO)_4]^-$ proceeds through a radical intermediate.

Moreover, photochemical studies have shown that the ionic complex $[Co(CO)_3(PBu_3)_2][Co(CO)_4]$, inactive at 80 °C and 80 bar in the hydroformylation of oct-1-ene, is converted under UV irradiation into $[Co(H)(CO)_3(PBu_3)]$ and becomes an active catalyst.[87]

Noteworthy, direct substitution of a CO ligand can occur in $[Co(CO)_4]^-$ to give $[Co(CO)_3(PR_3)]^-$, but indirect methods are interesting, since, for instance, treating $[Co_2(CO)_6\{(P(OPh)_3\}_2]$ with sodium amalgam affords $Na[Co(CO)_3\{(P(OPh)_3\}]$, from which $[Co(H)(CO)_3\{P(OPh)_3\}]$ is obtained by addition of HCl at 0 °C. Further treatment of the sodium salt by $POCl_3$ and $P(OPh)_3$ produces $[Co(CO)_2\{P(OPh)_3\}_2]Cl$, which, by successive reactions of Na/Hg and HCl, gives rise to $[Co(H)(CO)_2\{P(OPh)_3\}_2]$.

Various ligands have been considered, either for the synthesis of substituted precursors or directly engaged with $[Co_2(CO)_8]$ to analyze the catalytic activity of the resulting system. For example, the two tetrametallic clusters $[Co_4(\mu_4\text{-}PPh)_2(CO)_{10}]$ and $[Co_4(\mu_4\text{-}PPh)_2(CO)_8(PPh_3)_2]$ have been prepared and isolated, and proved to be active hydroformylation catalysts for pent-1- and pent-2-ene under mild syngas pressures (lower than 80 bar).[88,89] Depending on reaction conditions, linear hexanal selectivity could reach 4.7 and turnover frequencies ca. 16 h^{-1}. At the end of the reaction, the former unsubstituted cluster could be recovered almost quantitatively while the latter looses the two PPh_3 ligands leading to the unsubstituted cluster. The contrasting reactivity of both cluster precursors with regard to the $[Co_2(CO)_8]$ systems, as well as the presence of two stable PPh bridging entities, allowed the authors to rule out the involvement of mononuclear fragments and to propose dinuclear intermediates.

Similarly, mild conditions can be maintained by using the bis(diphenylphosphino)ethane ligand with $[Co_2(CO)_8]$: the catalytic activity at 50 bar and 90 °C can be more than 7-fold that of single $[Co_2(CO)_8]$.[90] However, the molar P/Co ratio has to be maintained close to 1, and it is confirmed that monophosphine ligands cannot allow such mild conditions. More recently, a hindered monophosphine based on a limonene framework has been introduced in the coordination sphere of cobalt, starting from $[Co_2(CO)_8]$.[81] The system shows a lower catalytic activity than the unmodified one, and due to the ligand steric hindrance, significant amounts of $[Co(H)(CO)_4]$ are formed when raising the temperature.

However, interesting selectivities, near 70% linear aldehyde, are reached.

Due to the successful results obtained in the rhodium chemistry with the water-soluble $P(m\text{-}C_6H_5SO_3Na)_3$ ligand (or TPPTS), the $[Co(H)(CO)_3(TPPTS)]$ complex has been engaged in the hydroformylation reaction. The most attractive results concern a reaction carried out for hex-1-ene at 140 °C, 130 bar, $H_2/CO = 2/1$, TPPTS/Co = 4, since the selectivity in aldehydes reaches 89%, with ca. 8% heptanol and 1% hexane as the main byproduct. Twenty years after the patent in which the TPPTS ligand has been added to $[Co_2(CO)_8]$,[91] new investigations have been done so that internal alkenes are shown to be transformed at 190 °C and 100 bar of $H_2/CO = 1/1$ into 75% of aldehydes with a linear to branched ratio of 3/1.[92]

In a similar approach, functionalities have been introduced on the phosphine ligands, giving them some hydrophilic character. Although phosphorus remains the only coordinating atom, the performances given by $P(CH_2CH_2CN)_3$, $P(CH_2CH_2COOMe)_3$, $P(CH_2CH_2OMe)_3$, or $P(CH_2CH_2OEt)_3$ are rather deceiving, since they reach, for instance, 5% yield in a dioxane/water mixture but 88% in pure dioxane.[93]

Additionally, arsine and stibine ligands have been tested in place of phosphines. They contain substituted arene or plain phenyl groups. Generally, the stibine allows a noticeable increase of the selectivity toward aldehyde, but as compared to PPh_3, the l/*b* selectivity is rather modest.[94,95]

Concerning the analogous nitrogen-containing Lewis bases, such as pyridines, the behavior is completely different and systematically ionic complexes are produced. As previously described in section 2.2, devoted to the $[Co(H)(CO)_4]$ preparation, the $[Co^{II}(pyridine)_6][Co^{-I}(CO)_4]_2$ type complexes are formed when pyridine is added to $[Co_2(CO)_8]$. These complexes are able to generate $[Co(H)(CO)_4]$ under hydroformylation conditions and have been involved in several carbonylation reactions.[96-99]

To prepare a CO free cobalt hydride complex, a recent study reports the reduction of the Co^{II} salt $[Co(dppe)_2(CH_3CN)][BF_4]_2$ in ethanol by $NaBH_4$.[100,101] The resulting hydride is $[Co(H)(dppe)_2]$ (dppe = bis(diphenylphosphino)ethane), and the X-ray crystal structure shows the geometry being a distorted trigonal bipyramide with the hydride ligand in the apical position ($d_{Co-H} = 1.46$ Å). Analyses of this complex reveal an infrared signal at 1882 cm^{-1} for the ν_{Co-H} and a ^1H NMR signal at −14.9 ppm for the hydride. These values clearly show that the phosphine ligands induce a more hydridic character of the Co−H bond since for $[Co(H)(CO)_4]$ the corresponding values are $\nu_{Co-H} = 1934$ cm^{-1} and $\delta_H = -11.7$ ppm. In addition to their steric hindrance, phosphine ligands exert electronic effects so that, in the hydroformylation reaction, the hydride ligand is transferred more selectively on the more electrophilic carbon atom of the alkene, resulting in a higher selectivity toward linear aldehyde (Figure 5). Conversely, if R is an electron withdrawing group, the terminal carbon atom of the C=C double bond is then the more electrophilic center so that the branched aldehyde is preferentially formed. Concerning the industrial process, it is necessary to adjust the coordination sphere in order to maintain a high activity and to promote the desired selectivity. For the PBu_3 ligand, the active substituted complex, $[Co(H)(CO)_3(PBu_3)]$, is less reactive than $[Co(H)(CO)_4]$ but allows a significant increase of selectivity toward linear aldehyde, reaching 86% instead of 66%.

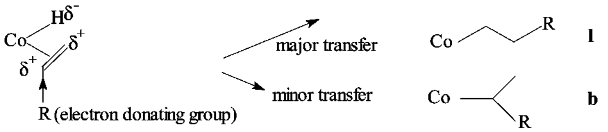

Figure 5. Differentiation between electrophilic centers during the formation of the alkyl species.

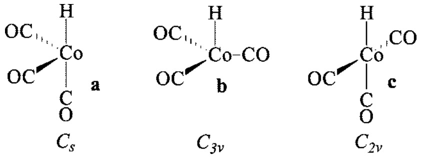

Figure 6. Possible geometries for $[Co(H)(CO)_3]$.

4. Mechanism of the Catalysis

The first catalytic cycle (vide supra), proposed nearly 50 years ago, is still valid nowadays, although precise features have been given on some steps all along this period. We can be impressed that, with a few pieces of spectroscopic information and indirect evidence only, the early research groups were able to assemble so fertile a concept. At the present time, operando infrared and UV−visible studies, multinuclear NMR studies,[102-106] and theoretical calculations provide a realistic view of the various steps constituting this catalytic cycle.[107-115]

The generation of the 16e active species $[Co(H)(CO)_3]$ from the 18e resting state $[Co(H)(CO)_4]$ involves the dissociation of a CO ligand in a pre-equilibrium step. Calculations undertaken at several levels of theory have tried to determine the correct geometry for $[Co(H)(CO)_3]$ (Figure 6).

For Versluis et al., the most stable form is a C_s, butterfly shaped, singlet state complex (Figure 6a) resulting from the dissociation of CO at an equatorial position, 38 $kJ\cdot mol^{-1}$ lower in energy than the C_{3v} geometry (Figure 6b), resulting from a CO loss at the apical position.[108,109]

More recently, further optimization calculations, at the B3LYP density functional level of theory (DFT), have estimated the dissociation energy of an equatorial CO ligand to be 108 $kJ\cdot mol^{-1}$, whereas it is 152 $kJ\cdot mol^{-1}$ for an axial one.[112] This work has also shown that the lowest potential energy for $[Co(H)(CO)_3]$ can be found for a C_{2v} square planar geometry (Figure 6c), also in the singlet state.

However, this latter geometry is energetically close to the butterfly shape, and these two C_s and C_{2v} conformers cannot be differentiated by infrared, since each of them has three ν_{CO} active bands, and it appears that both could be observed experimentally.[17,107]

Thus, it is admitted that $[Co(H)(CO)_3]$ is formed by dissociation of a CO ligand in the equatorial plane of $[Co(H)(CO)_4]$ of C_{3v} symmetry, which is also favorable for subsequent olefin coordination, and the production of the $[Co(H)(CO)_3]$ active species from the $[Co(H)(CO)_4]$ resting state is governed by the equilibrium shown in eq 8.

$$[Co(H)(CO)_4] \rightleftharpoons [Co(H)(CO)_3] + CO \qquad (8)$$

In a detailed catalytic cycle, adapted from Huo et al.[113] and displayed in Figure 7 for the linear aldehyde, the first step is the coordination of the alkene $CH_2{=}CHR$ to $[Co(H)(CO)_3]$. From either of the two isomers, calculations show that propene occupies an equatorial position of a trigonal bipyramide (**a** and **a′**) and the most stable structure has the C=C double bond perpendicular to the apical Co−H bond.

The methyl group can be in either a syn (**a**) or an anti position (**a′**) with regard to the hydride ligand, with the energy difference between both situations being less than 0.2 kJ·mol^{-1}.

The second step is the hydride transfer to the double bond to produce the alkyl species. This step requires a 90° rotation of the propene, with the methyl group being syn to the H ligand to obtain the linear alkyl group (and anti for the branched one). In the 16e [$Co(CH_2CH_2CH_3)(CO)_3$] intermediate **b**, a stabilizing agostic interaction is shown to be present between the metal center and a C_β−H bond. In the presence of carbon monoxide, this agostic interaction is shifted by the approach of a CO ligand in the equatorial plane. This transition state involves simultaneously the rotation of the propyl ligand and leads to the 18e tetracarbonyl intermediate **c**.

The third step of the catalytic cycle consists of the cis-migration of the apical *n*-propyl group on one equatorial CO ligand. This step involves the breaking of the Co−C_α bond and the concomitant C(O)−C_α carbon−carbon coupling. The resulting acyl species **d** presents an agostic interaction between cobalt and one C_β−H bond in the equatorial plane, and one possibility is it evolves toward a more stable species in which the C=O bond is interacting with the cobalt center in a η^2-manner (**d′**).

At this point, dihydrogen reacts either with **d′** or directly with **d** to produce first the η^2-H_2 species **e**, in which the H_2 ligand is in the equatorial plane, and the acyl group of this [$Co\{C(O)CH_2CH_2CH_3\}(\eta^2\text{-}H_2)(CO)_3$] intermediate occupies the axial position of a trigonal bipyramide. This H_2 coordination to the acyl species appears to be the rate determining step, rather than the subsequent H_2 oxidative addition. Photolysis of [$Co(H)(CO)_4$] and [$Co(CH_3)(CO)_4$] in hydrogen-containing argon matrices has shown the presence of the two species [$Co(H)(\eta^2\text{-}H_2)(CO)_3$] and [$Co(CH_3)(\eta^2\text{-}H_2)(CO)_3$], indicating the hypothesis of intermediate **e** is reasonable.[116] Similarly, when argon matrices of [$Co\{C(O)CH_3\}(CO)_4$] were irradiated under UV, a decrease in the infrared spectra of the intensity of the acetyl ν_{CO} band has been interpreted as being due to a η^2-C=O(acyl) interaction with the cobalt metal center.[117]

One can expect, from **d** or **d′**, that CO instead of H_2 could coordinate, leading to a saturated 18e acyl complex. It would then compete directly with the rate determining step, which is the H_2 coordination leading to **e**, and the reaction velocity for the hydroformylation process clearly shows an inhibiting effect of CO partial pressure. This coordination appears to be highly exothermic (−66.0 kJ·mol^{-1} for **d**, −55.2 kJ·mol^{-1} for **d′**),[113] which should not be favored under the reaction conditions, and it is admitted that the preformation step to produce [$Co(H)(CO)_3$] from [$Co(H)(CO)_4$] supports the −1 order with regard to CO. However, it should be interesting to evaluate the inhibiting CO contribution in this step.

Species **e** evolves with a low activation barrier toward the dihydride complex [$Co\{C(O)CH_2CH_2CH_3\}(H)_2(CO)_3$] **f** in a pseudo-octahedral fac-geometry. The last step of the catalytic cycle is the reductive elimination of the aldehyde with the simultaneous reformation of [$Co(H)(CO)_3$]. The transition state of this step involves the bending of the two Co−H and Co acyl bonds toward each other. A stable intermediate **g** can be described as a [$Co(H)(CO)_3$] entity, close to a square planar geometry, weakly interacting with the aldehydic hydrogen atom (with the calculated Co···$H_{aldehyde}$ distance being 2.006 Å).

In Figure 7, all the **a**−**g** intermediates are the stable calculated species, and most of the transition states are represented between them. It is noteworthy that a similar catalytic cycle could be displayed for the branched aldehyde.

As we already mentioned, it has been proposed early on that, when stoichiometric conditions are applied, [$Co(H)(CO)_4$] reacts with the acyl species [$Co\{C(O)CH_2CH_2CH_3\}(CO)_3$] to provide the hydrogen atom and thus produce the aldehyde and [$Co_2(CO)_7$], which rapidly gives [$Co_2(CO)_8$] even at 1 bar of CO. Recently, this proposal has been re-evaluated and the authors have used stoichiometric quantities of [$Co(H)(CO)_4$] under a CO atmosphere, i.e. 2 mol of [$Co(H)(CO)_4$] per alkene (type I) or 1 equiv of [$Co_2(CO)_8$] under a H_2 pressure (type II).[118] It is clearly confirmed that, in type I experiments, hydrogen is provided by [$Co(H)(CO)_4$], which represents the only source. However, in type II reactions, labeling studies evidence that the aldehydic hydrogen atom arises from the gas phase even in the presence of [$Co(D)(CO)_4$].

Thus, under catalytic conditions, in which low concentrations of [$Co(H)(CO)_4$] are involved and high pressures of H_2 are required, the oxidative addition of H_2 onto the acyl species is the only mechanism which occurs, and it is the rate determining step.

5. Recycling

5.1. Industrial Recycling

For economical and environmental reasons, in an industrial process, it is necessary to efficiently recycle the catalyst. As the two main species [$Co(H)(CO)_4$] and [$Co_2(CO)_8$] are soluble in the organic phase and sublime or decompose under reduced pressure, it is impossible to separate directly the homogeneous catalyst from the reaction mixture. Two solutions have been developed on an industrial scale.[7,8,39] The first one, due to BASF, consists in decobalting the crude mixture, after depressurizing, by addition of oxygen and formic or acetic acid.[119] A mixture of two phases results, in which the aqueous phase contains the cobalt(II) carboxylate. After decantation in a phase separator, this acidic Co^{II} solution is concentrated and sent to a carbonylation reactor where a high H_2/CO pressure regenerates the active species, which are again introduced in the hydroformylation reactor. In the second industrial approach, due to Produits Chimiques Ugine Kuhlmann (now Exxon process), a diluted aqueous soda solution is introduced on the crude mixture to convert [$Co(H)(CO)_4$] into Na[$Co(CO)_4$].[120,121] After scrubbing with water and a phase separation step, the aqueous solution is treated with sulfuric acid under syngas pressure to regenerate the hydride, whereas an olefin stream ensures feeding of the hydroformylation reactor with the most active species [$Co(H)(CO)_4$] dissolved in an organic medium.

Even if quite efficient, both approaches use corrosive media at one point, precipitation of cobalt can occur and obstruct the proper flow of the unit, and they both generate substantial quantities of mineral and aqueous effluents. Other possibilities have then been investigated to ease the separation of the catalyst from the products and to minimize the loss of cobalt. A very recent example taken from the patent literature shows that this recycling problem is still the subject of improvement: thus, a multistage process has been described in which the sulfuric acid dilution is carefully

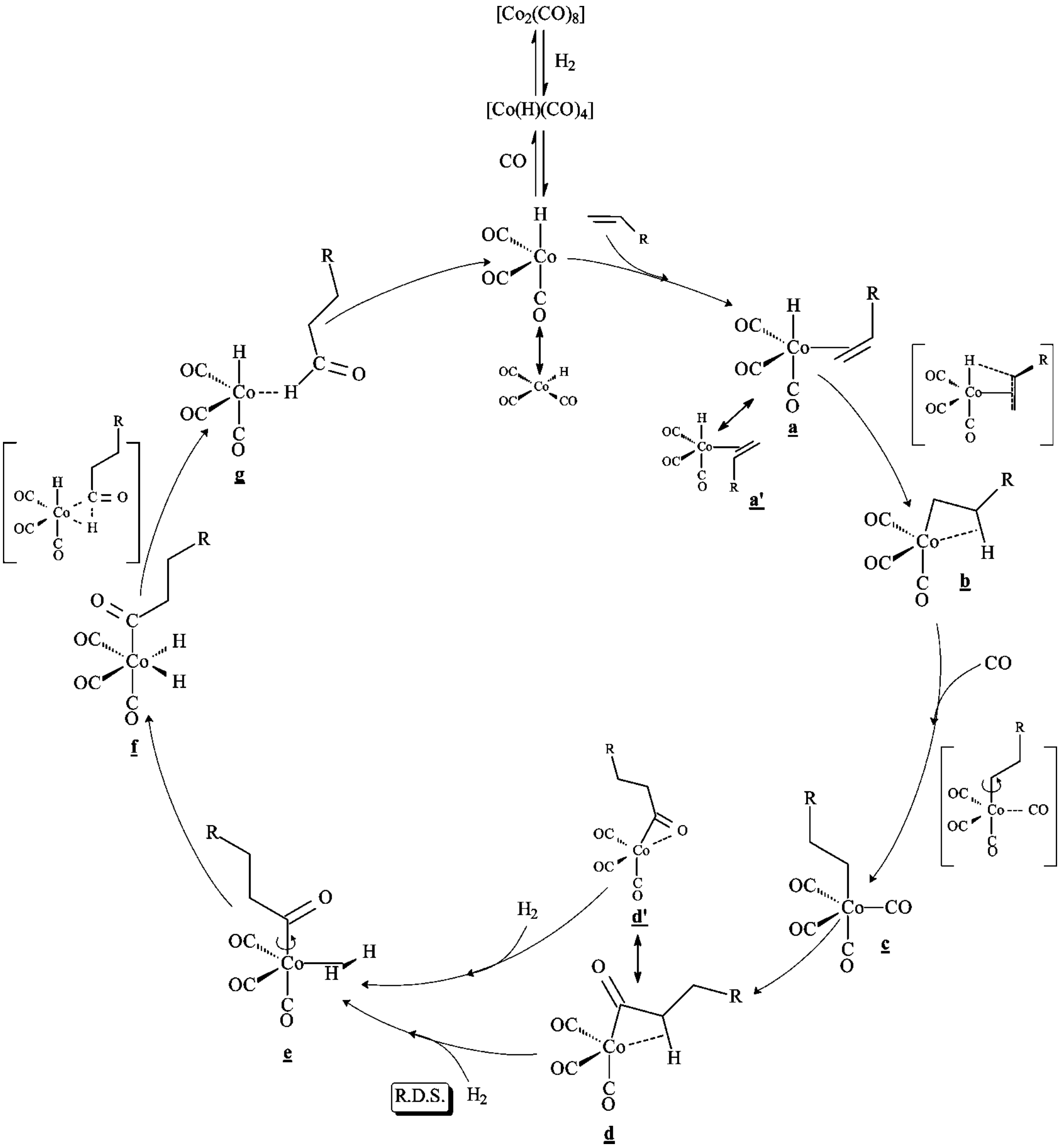

Figure 7. Calculated intermediates and transition states for the catalytic hydroformylation of propene into *n*-butanal.

controlled to protonate $[Co(CO)_4]^-$ and produce the hydride.[122] However, the most important reports for the recycling of cobalt are related to the use of biphasic systems where functionalized ligands can be introduced or disproportionation methods are applied. These various strategies are described hereafter.

5.2. Use of Hard Lewis Bases

The use of pyridine-type additives, even if not always fully understood, is not new in cobalt-catalyzed carbonylation reactions, and for example, Iwanaga has shown in 1962 that the hydroformylation reaction can be performed in the presence of several equivalents per cobalt of a hard Lewis base, which can even increase the rate of reaction.[123] On the other hand, the disproportionation behavior induced by these bases on neutral cobalt carbonyl species is reversible according to the operating conditions. Based on this behavior, Moffat proposed the use of a poly(2-vinylpyridine) solid polymer for the immobilization of cobalt, directly in the hydroformylation reactor.[124] While $[Co(H)(CO)_4]$ is fully transformed into the pyridinium salt of $[Co(CO)_4]^-$ and simply regenerated due to the absence of H_2, $[Co_2(CO)_8]$ is inefficiently complexed by the polymer, leading to a substantial loss of metal. Similarly, a bipyridine ligand based on an ethylene glycol backbone (EBP, ethyl bis(3-(2-pyridyl))propanoate, $py(CH_2)_2C(O)O(CH_2)_2OC(O)(CH_2)_2py$) was interestingly used to separate cobalt carbonyl species from the reaction mixture.[125] Precipitation of a polynuclear ion pair ($[H_2Co_3(CO)_9(EBP)_4]$) occurs at room temperature, while it is soluble in the medium under the operating conditions (50−60 °C, 20−50 bar) and regenerates neutral cobalt species which perform the hydroformylation reaction. However, the major drawback of this technique is the high solubility of this ion pair in polar media, and particularly the produced aldehydes, leading to a 1% loss of cobalt for each recycling.

5.3. Biphasic Systems

As we already mentioned in section 3, the benefits of aqueous biphasic catalysis developed in the 1970s for rhodium, thanks to water-soluble ligands such as TPPTS, were extended to cobalt a few years later.[91,92,126] As rhodium-based systems remained globally more efficient for low-boiling alkenes, cobalt has been applied to heavier ends as for purely homogeneous systems.[126] Even when supporting these hydrosoluble complexes onto a hydrophilic support, a major limitation appears, as increasing the chain length rapidly decreases the substrate solubility in water and thus the transfers between reactants. Due to the high performances shown by the rhodium/TPPTS system which is mainly operated for the hydroformylation of propene, Beller et al. used cobalt to investigate the hydroformylation of internal pentenes to linear aldehydes, using the ability of cobalt to isomerize internal olefins to terminal positions. Under their optimal conditions for the production of aldehydes (190 °C, 100 bar), the authors noticed less than 2% leaching of cobalt in the organic phase, and the catalytic system could be reused 4 times without noticeable loss of activity.[92] More recently, Haumann et al. tried to overcome miscibility issues by adding a surfactant to a Co/TPPTS/H_2O system for the hydroformylation of 7-tetradecene.[127] While the system affords more than 50% selectivity toward linear aldehydes, it shows particularly efficient retention of cobalt, with less than 1 ppm leaching in the organic phase, after an ultrafiltration step. Lately, Parmar and co-workers performed the aqueous biphasic hydroformylation of hex-1-ene, oct-1-ene, and dec-1-ene with an aqueous Co^{II}/TPPTS system.[128,129] Interestingly, the system is active under milder conditions (100 °C, 90 bar) than usual oxo ones, and the reaction can be performed starting directly from a cobalt(II) salt in the presence of TPPTS ligand. With the miscibility of hex-1-ene with water being reasonable, a purely biphasic medium is used in this case, leading to about 2% leaching of cobalt while, for oct- and dec-1-ene, it is necessary to add a surfactant to increase the conversion and dramatically lower the amount of cobalt solubilized in the organic phase.

As another alternative medium for catalytic reactions, the growing use of supercritical fluids has been recently applied to cobalt catalyzed hydroformylation, although supercritical carbon dioxide ($scCO_2$) was already used in the early 1990s for NMR studies of the cobalt carbonyl complexes.[52,67,68] Indeed, $scCO_2$ is an ideal medium due to its high diffusivity and low viscosity, allowing gaslike mass transport properties, so that high pressure and high temperature catalytic processes can be studied by NMR, such as, for example, the relationship between $[Co_2(CO)_8]$ and $[Co(H)(CO)_4]$ or the involvement of radical species, which have been developed in section 2.4. Such studies have been extended to fluorophosphines containing cobalt complexes.[82,130] The most interesting point is that $[Co_2(CO)_6\{P(m\text{-}FC_6H_4)_3\}_2]$, engaged in the hydroformylation of oct-1-ene, is insoluble in the cold reaction mixture whereas it is entirely soluble in $scCO_2$, which allows easy separation and recycling of the catalyst after reaction.

Chauvin and Olivier-Bourbigou have taken advantage of this property of maintaining cobalt in one phase, whereas the reactants and the reaction products are mainly present in a second phase, by using nonaqueous ionic liquids to retain the catalyst.[131,132] Cobalt and rhodium catalysts have been later claimed by Olivier-Bourbigou and co-workers to improve the performances, provided a nitrogen-containing ligand is added.[133] In the most efficient application, pyridine ligands are introduced into the system to produce, by disproportionation, the ionic complex $[Co(py)_6][Co(CO)_4]_2$, which is maintained in the ionic liquid. Interestingly, the reaction can be efficiently carried out under milder conditions than the oxo process, i.e. 100 bar and 130 °C, and turnover frequencies as high as 110 h^{-1} can be reached for hex-1-ene.[134−136] High pressure infrared studies have shown that, for this system, the hydroformylation reaction involves $[Co(H)(CO)_4]$ and occurs in the organic phase.[137] The main role of pyridine is to convert the neutral cobalt carbonyl species into the ionic species $[pyH][Co(CO)_4]$ and $[Co(py)_6][Co(CO)_4]_2$, which are fully maintained in the ionic liquid phase. As for the aqueous biphasic system, a simple decantation allows us to separate efficiently the catalyst from the organic phase.

Figure 8. Photograph of Otto Roelen on "official" duty, in September 1976 on the occasion of the 100th birthday of Franz Fischer (Fischer−Tropsch process) at the Mülheim Max-Planck Institute (courtesy of Boy Cornils).

6. Conclusion

The cobalt-catalyzed hydroformylation of alkenes, which converts alkenes into the corresponding aldehydes, appeared during many years as an old reaction, having mainly a historical importance. This reaction, discovered in 1938, was only recognized several years later, presumably due to World War II, as the first case of a homogeneous process, and all the details of this story can be found elsewhere.[4] Thus, the name of Otto Roelen (Figure 8) is clearly associated with the first homogeneously catalyzed process.

At the present time, all the details on the catalytic steps are clearly established including intermediates whose geometries, calculated by DFT methods, reveal new concepts of coordination chemistry, like η^2-H_2−Co species or agostic interactions. Not only cobalt is still operating in industrial units to produce aldehydes from heavy alkenes, but the new biphasic processes recently described open the way to operate under milder conditions with an elegant recycling step. As cobalt is a cheap transition metal, especially with regard to rhodium, we can consider that its use in this carbonylation reaction will be further developed. This field is still active and alive, so that it is not excluded that its use, with adapted ligands, even including stereogenic centers, could open the way to various synthetic pathways.

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