Kinetics and mechanisms of homogeneous catalytic reactions
Part 7. Hydroformylation of 1-hexene catalyzed by cationic complexes of rhodium and iridium containing PPh$_3$

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Abstract

Cationic rhodium and iridium complexes of the type [M(COD)(PPh$_3$)$_2$]PF$_6$ (M = Rh, **1a**; Ir, **1b**) are efficient precatalysts for the hydroformylation of 1-hexene to its corresponding aldehydes (heptanal and 2-methylhexanal), under mild pressures (2–5 bar) and temperatures (60 °C for Rh and 100 °C for Ir) in toluene solution; the linear to branched ratio (*l*/*b*) of the aldehydes in the hydroformylation reaction varies slightly (between 3.0 and 3.7 for Rh and close to 2 for Ir). Kinetic and mechanistic studies have been carried out using these cationic complexes as catalyst precursors. For both complexes, the reaction proceeds according to the rate law $r_i = K_1K_2K_3k_4[M][olef][H_2][CO]/([CO]^2 + K_1[H_2][CO] + K_1K_2K_3[olef][H_2])$. Both complexes react rapidly with CO to produce the corresponding tricarbonyl species [M(CO)$_3$(PPh$_3$)$_2$]PF$_6$, M = Rh, **2a**; Ir, **2b**, and with syn-gas to yield [MH$_2$(CO)$_2$(PPh$_3$)$_2$]PF$_6$, M = Rh, **3a**; Ir, **3b**, which originate by CO dissociation the species [MH$_2$(CO)(PPh$_3$)$_2$]PF$_6$ entering the corresponding catalytic cycle. All the experimental data are consistent with a general mechanism in which the transfer of the hydride to a coordinated olefin promoted by an entering CO molecule is the rate-determining step of the catalytic cycle.
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1. Introduction

The hydroformylation of alkenes is one of the most important applications of transition metal based homogeneous catalysis [1–3]. The kinetics of olefin hydroformylation are generally complex and despite the wealth of mechanistic information available for this reaction catalyzed by rhodium complexes [1–3], detailed kinetic studies have been performed for relatively few catalysts: RhH(CO)(PPh$_3$)$_3$ [4–9], rhodium systems with bulky phosphites [10], phosphine-phosphite and diphosphite [11], and diphosphine [12] systems, a rhodium precatalyst with 1,2,5-triphenyl-1*H*-phosphole [13] and a rhodium-triphenylarsine precatalyst [14]. In the accompanying preceding paper of this series we reported a kinetic and

mechanistic study of the hydroformylation of 1-hexene using as precatalyst the system Rh(acac)(CO)$_2$/dppe [15]. Continuing our work on the kinetics and mechanisms of homogeneous catalytic reactions, we now present a study of the hydroformylation of 1-hexene catalyzed by the cationic rhodium and iridium complexes [M(COD)(PPh$_3$)$_2$]PF$_6$. On the basis of the kinetic evidence and some related preparative chemistry we propose a catalytic cycle and discuss it in the light of the extensive prior knowledge on rhodium hydroformylation catalysis [1–15]. Early reports by Oro et al. [16a] and by Crabtree and Felkin [16b] described the hydroformylation activity of cationic complexes of the type [Rh(COD)(PPh$_3$)$_2$]$^+$ first synthesized and used as hydrogenation catalysts by Schrock and Osborn [16c]. A great deal of information on the chemistry of these complexes and their application to hydrogenation catalysis has accumulated over the years [17] and much of that knowledge can be extended to hydroformylation mechanisms. Reports of catalytic hydroformylation by iridium complexes are scarce and generally deal with neutral

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monohydride catalysts [1–3]. Whyman applied high-pressure IR spectroscopy to the study of hydroformylation intermediates or model complexes using Ir-hydrido-triphenylhosphine complexes [18]. More recently, Godard et al. [19] have reported NMR studies on the reaction of $Ir(CO)(PPh_3)_2(\eta^3-C_3H_5)$ with hydrogen and CO, which produces a interesting series of complexes including acyl and alkyl dihydride intermediates that nicely model the hydroformylation mechanism for an iridium monohydride catalyst. Eisenberg and coworkers studied Ir–Xantphos complexes that catalyze alkene hydroformylation and used NMR studies with p-H_2 to identify a series of monohydride and trihydride complexes implicated in the catalytic cycle [20]. Haukka and coworkers reported the use of $Ir_4(CO)_{12}$, $IrCl_3$, and $[IrCl(CO)_3]n$ in the presence of inorganic salts in the hydroformylation of 1-hexene [21]. To the best of our knowledge, there are no prior reports in the open literature of the kinetics of hydroformylation by cationic dihydrido complexes of rhodium and iridium.

2. Experimental

2.1. Instruments and materials

All manipulations were conducted with rigorous exclusion of air using Schlenck techniques. The substrate (1-hexene) was purified by distillation under reduced pressure, solvents were purified by standard methods, and complexes $[M(COD)(PPh_3)_2]PF_6$ (M = Rh, Ir) were prepared by published procedures [16c]. NMR and IR spectra were recorded on a Bruker AM-300 spectrometer and Shimadzu 8300 FT-IR instrument, respectively.

2.2. Procedure for kinetic measurements

Kinetic experiments were carried out in a high-pressure reactor, supplied by Parr Instruments, which was provided with arrangements for sampling of liquid contents, automatic temperature and pressure control and variable stirrer speed. In a typical experiment, a solution containing the catalyst, 1-hexene, n-heptane (as internal standard) and the solvent (toluene, to 30 mL total volume) was placed in the reactor. The solution was carefully deoxygenated by flushing with argon, stirring was commenced and the reactor was heated to the desired temperature. When the reaction temperature was reached, a mixture of CO and H_2 in the required ratio was introduced into the autoclave; this moment was taken as the zero time of the reaction. Each reaction was followed by taking liquid samples at regular intervals of time, which were analyzed by using gas chromatography. Since, the major products formed were isomeric aldehydes, the CO/H_2 mixture was supplied in the appropriate ratio to maintain the same composition of the gases in the autoclave introduced at the beginning of the reaction.

Each reaction was repeated at least twice in order to ensure reproducibility of the results. All the reactions were carried out at low conversion (close to 10%) in order to perform a kinetic analysis based on the initial rate method [22]. The data for the hydroformylation of 1-hexene were plotted as molar con-

centration of the corresponding products versus time yielding straight lines, which were fitted by conventional linear regression programs. Initial rates of the reaction were obtained from the corresponding slopes. The H_2 and CO concentrations in toluene under the reaction conditions were calculated from solubility data reported in the literature [23,24].

The composition of the reaction mixture was analyzed by means of a 610 Series UNICAM gas chromatograph fitted with a thermal conductivity detector and a 3 m 10% SE-30 on Supelcoport glass column using helium as carrier gas; the chromatograph was coupled to a UNICAM 4815 data system.

2.3. Coordination chemistry related to hydroformylation of 1-hexene

*Reaction of $[M(COD)(PPh_3)_2]PF_6$, M = Rh (**1a**), Ir (**1b**), with carbon monoxide*: Carbon monoxide was bubbled through a solution of **1a** or **1b** (1.0 mmol) in benzene (10 mL) while the mixture was vigorously stirred under gentle reflux for 3 h. The solution was evaporated to dryness under a CO atmosphere to produce $[Rh(CO)_3(PPh_3)_2]PF_6$, (**2a**)—IR (KBr): 2090 (m), 2025 (vs), 1965 (vs) or $[Ir(CO)_3(PPh_3)_2]PF_6$, (**2b**)—IR (KBr): 2070 (m), 2001 (vs), 1983 (vs).

*Reaction of **1b** with syn-gas*: This reaction was carried out as described before but using a 1:1 mixture of CO and H_2 instead of carbon monoxide, to yield the known compounds $[IrH_2(CO)_2(PPh_3)_2]PF_6$ (**3b**)—IR (KBr): 2212, 2162, 2088, 2044 cm^{-1}; ^1H RMN (CDCl$_3$, 300 MHz): 7.3–7.6 (m, 30H, PPh$_3$), −9.90 ppm (t, J_{HP} = 8.7 Hz, 2H); $^{31}P\{^1H\}$RMN (CDCl$_3$, 121 MHz): 4.1 (s, 2PPh$_3$), 143.0 ppm (hept, PF$_6$).

*Interaction of **3b** with 1-hexene under CO*: A mixture of complex **3b** (92 mg, 0.1 mmol), 1-hexene (13 μL, 0.1 mmol) and benzene (10 mL) was placed under a CO atmosphere at 100 °C for 1 h. The liquid components were analyzed by GC; the solution was evaporated to dryness under a CO atmosphere, and the solid was analyzed by IR spectroscopy.

3. Results and discussion

3.1. Catalytic hydroformylation of 1-hexene

The complexes $[M(COD)(PPh_3)_2]PF_6$, M = Rh (**1a**), Ir (**1b**) are efficient catalyst precursors for the homogeneous hydroformylation of 1-hexene in toluene solution to give exclusively the corresponding aldehydes (heptanal and 2-methyl-hexanal), under mild conditions of temperature and pressure. Rhodium complexes of this type [16a,b] and neutral iridium complexes [2a,b,18–21] have been previously reported to hydroformylate alkenes. We now provide a direct comparison of the kinetics of these cationic systems for both metals under similar reaction conditions. The rhodium precatalyst was very active at 60 °C and 3 bar of syn-gas, while for Ir the catalysis was carried out at 100 °C; the lower hydroformylation activity of iridium as compared to rhodium has been previously documented [2a,b]. The variation of the linear to branched ratio (*l*/*b*) of aldehydes was small (between 3.0 and 3.7 for Rh and close to 2 for Ir) and did depend very slightly on the reaction conditions. Although these

complexes are known to be very active for the hydrogenation of alkenes [17], no hydrogenation products were detected under hydroformylation conditions, something that can be accounted for by the proposed mechanism (*vide infra*). The initial rates of hydroformylation of 1-hexene catalyzed by complexes **1a** and **1b** were practically independent of the speed of stirring, showing that the data obtained correspond to a kinetic regime and mass transfer effects were negligible.

3.2. Kinetic investigation for the hydroformylation of 1-hexene

The kinetics of the hydroformylation of 1-hexene catalyzed by the cationic Rh- and Ir-complexes in toluene were studied by carrying out runs at different catalyst, substrate, dissolved hydrogen and dissolved carbon monoxide concentrations, and at constant temperature for each precatalyst. The data for the hydroformylation reaction catalyzed by the rhodium complex are collected in Table 1, and the results indicate that:

(1) The initial rate of 1-hexene hydroformylation shows a direct dependence on the rhodium concentration ($\log r_i = -1.64 + 0.93 \log [Rh]$, $r^2 = 0.95$).
(2) The initial rate of 1-hexene hydroformylation is first order with respect to the concentration of substrate ($\log r_i = -4.19 + 1.02 \log [1\text{-hexene}]$, $r^2 = 0.97$).
(3) The reaction is of fractional order with respect to dissolved hydrogen concentration ($\log r_i = -3.04 + 0.65 \log [H_2]$, $r^2 = 0.96$) in the concentration range studied for this reaction.
(4) The dependence of the initial rate with respect to the dissolved carbon monoxide concentration was of fractional order ($\log r_i = -3.46 + 0.47 \log [CO]$, $r^2 = 0.95$) at low CO

pressure, but it becomes of inverse order at high CO pressure ($\log r_i = -6.74 - 1.05 \log [CO]$, $r^2 = 0.98$).

The linear to branched ratio (*l/b*) of the aldehydes formed by use of the rhodium precursor varied only slightly (between 3.0 and 3.7), decreasing when the concentrations of precatalyst, hydrogen and CO dissolved were higher and increasing with the substrate concentration.

Similarly, the kinetics of 1-hexene hydroformylation catalyzed by the iridium precursor (Table 2) are near first order on catalyst concentration ($\log r_i = -1.61 + 0.92 \log [Ir]$, $r^2 = 0.97$), near first order on substrate concentration ($\log r_i = -4.09 + 0.93 \log [1\text{-hexene}]$, $r^2 = 0.99$), and fractional order with respect to dissolved CO concentration ($\log r_i = -3.01 + 0.55 \log [CO]$, $r^2 = 0.98$), which tends to a highly negative order at high CO pressure ($\log r_i = -10.19 - 2.23 \log [CO]$, $r^2 = 0.96$). However, in contrast to the Rh precatalyst, in the case of the iridium complex the reaction rate varies in accord with a saturation curve with respect to hydrogen concentration, that is, a first order kinetics at low hydrogen concentration ($\log r_i = -2.42 + 0.92 \log [H_2]$, $r^2 = 0.99$), which tends to zero order at high H_2 concentration ($P > 3$ bar) ($\log r_i = -4.06 + 0.16 \log [H_2]$, $r^2 = 0.99$).

The linear to branched ratio (*l/b*) of the aldehydes formed was practically constant (between 1.6 and 2.0) and independent of the reaction conditions, except when increasing the syn gas and CO pressure, when a slight reduction of *l/b* ratio was observed.

3.3. Coordination chemistry related with the catalytic 1-hexene hydroformylation

In order to gain further understanding of the mechanisms of 1-hexene hydroformylation by the cationic systems, the reaction

Table 1
Kinetic data for the hydroformylation of 1-hexene catalyzed by [Rh(COD)(PPh₃)₂]PF₆

10^4 [Rh] (M)	10 [olefin] (M)	$p(H_2)$ (atm)	10^3 [H₂] (M)	$p(CO)$ (atm)	10^3 [CO]	$10^5 r_i$ (M s⁻¹)
6.44	5.08	1.3	5.7	1.3	7.1	2.40
8.33	5.08	1.3	5.7	1.3	7.1	3.42
11.00	5.08	1.3	5.7	1.3	7.1	4.62
16.70	5.08	1.3	5.7	1.3	7.1	5.29
20.88	5.08	1.3	5.7	1.3	7.1	8.13
8.33	2.16	1.3	5.7	1.3	7.1	1.44
8.33	3.18	1.3	5.7	1.3	7.1	1.88
8.33	3.96	1.3	5.7	1.3	7.1	2.23
8.33	5.84	1.3	5.7	1.3	7.1	3.51
8.33	6.57	1.3	5.7	1.3	7.1	4.51
8.33	5.08	0.7	3.4	1.3	7.1	2.31
8.33	5.08	1.0	4.8	1.3	7.1	2.63
8.33	5.08	2.0	8.0	1.3	7.1	3.91
8.33	5.08	2.7	9.9	1.3	7.1	4.57
8.33	5.08	1.3	5.7	0.3	1.3	1.44
8.33	5.08	1.3	5.7	0.6	2.8	2.15
8.33	5.08	1.3	5.7	1.0	4.2	2.25
8.33	5.08	1.3	5.7	1.1	6.2	3.16
8.33	5.08	1.3	5.7	2.4	12.9	1.64
8.33	5.08	1.3	5.7	2.9	15.8	1.42
8.33	5.08	1.3	5.7	3.4	18.8	1.35
8.33	5.08	1.3	5.7	4.5	24.7	0.85

Conditions: $T = 60\,°C$; solvent: toluene; r_i: initial; *l/b* ratio = 3.0–3.7.

Table 2
Kinetic data for the hydroformylation of 1-hexene catalyzed by [Ir(COD)(PPh$_3$)$_2$]PF$_6$

10^4 [Ir] (M)	10 [olefin] (M)	$p(H_2)$ (atm)	10^3 [H$_2$] (M)	$p(CO)$ (atm)	10^2 [CO] (M)	$10^5 r_i$ (M s^{-1})
6.43	4.96	2.0	6.9	2.0	2.7	2.71
8.36	4.96	2.0	6.9	2.0	2.7	3.96
11.00	4.96	2.0	6.9	2.0	2.7	4.65
13.80	4.96	2.0	6.9	2.0	2.7	5.97
16.60	4.96	2.0	6.9	2.0	2.7	6.59
8.36	1.30	2.0	6.9	2.0	2.7	1.32
8.36	2.08	2.0	6.9	2.0	2.7	1.81
8.36	2.99	2.0	6.9	2.0	2.7	2.83
8.36	5.79	2.0	6.9	2.0	2.7	4.99
8.36	4.96	1.3	4.1	2.0	2.7	2.44
8.36	4.96	1.6	5.5	2.0	2.7	3.26
8.36	4.96	3.0	9.8	2.0	2.7	4.15
8.36	4.96	3.8	12.6	2.0	2.7	4.36
8.36	4.96	2.0	6.9	0.3	0.5	1.47
8.36	4.96	2.0	6.9	0.6	1.2	2.47
8.36	4.96	2.0	6.9	1.0	1.6	2.24
8.36	4.96	2.0	6.9	1.3	2.0	2.85
8.36	4.96	2.0	6.9	1.6	2.3	3.32
8.36	4.96	2.0	6.9	2.3	3.1	2.35
8.36	4.96	2.0	6.9	2.7	3.4	2.04
8.36	4.96	2.0	6.9	3.0	3.8	1.79
8.36	4.96	2.0	6.9	3.3	4.2	1.37

Conditions: $T = 100\,^\circ$C; solvent: toluene; r_i: initial; l/b ratio = 1.6–2.0.

of complexes **1a** and **1b** with each component of the catalytic mixture was carried out, with the aim of isolating or detecting some intermediates of the reaction; the results are summarized in Fig. 1. When solutions of [M(COD)(PPh$_3$)$_2$]PF$_6$, M = Rh (**1a**), Ir (**1b**), in benzene are treated with carbon monoxide (1 atm, 60 °C), rapid displacement of COD occurs and the tricarbonyl species [M(CO)$_3$(PPh$_3$)$_2$]PF$_6$, M = Rh (**2a**), Ir (**2b**) can be isolated from the CO saturated solutions. The rhodium tricarbonyl complex loses CO only slowly in the solid state but when dissolved in benzene in the presence of acetonitrile, CO is rapidly evolved and [Rh(CO)(NCMe)(PPh$_3$)$_2$]PF$_6$ can be isolated as a crystalline solid. The reaction of complexes **1** with syn-gas in benzene generates [M(H)$_2$(CO)$_2$(PPh$_3$)$_2$]PF$_6$,

M = Rh (**3a**), Ir (**3b**). Complexes **3** also can be obtained by hydrogenation of the corresponding complex **2a** or **2b**. Complexes **2a**, **2b**, [Rh(CO)(NCMe)(PPh$_3$)$_2$]PF$_6$ and **3b**, have been isolated and characterized before by James and coworkers [25] and thus we have identified them by comparison of their spectroscopic properties with published data. It is important to note that **2a**, **2b** and **3b** displayed similar catalytic activities for the hydroformylation of 1-hexene to those of **1a** or **1b**, respectively, under the corresponding reaction conditions [(m.s.d. ± 0.5) × 10^{-5}, $P = 0.05$]. Finally, the interaction of complex **3b** with 1 eq. of 1-hexene under a CO atmosphere quantitatively yields the corresponding C$_7$ aldehydes ($l/b \approx 2$) and complex **2b**.
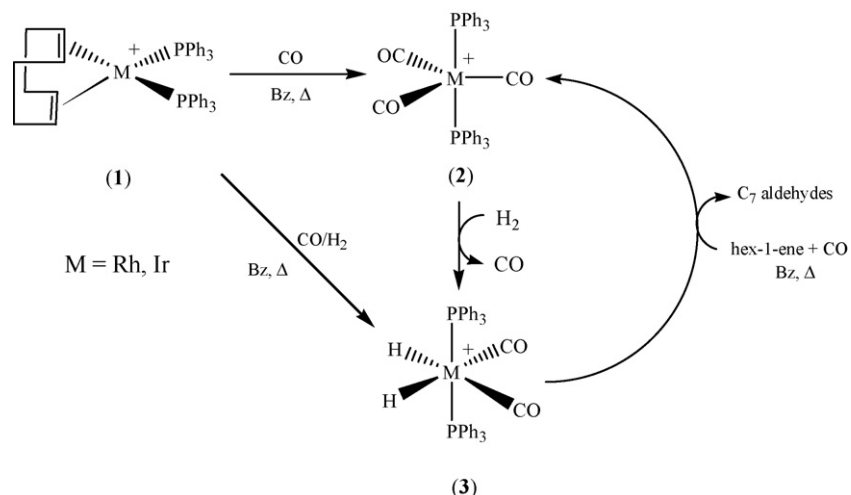

Fig. 1. Stoichiometric reactions related with the hydroformylation of 1-hexene catalyzed by [M(COD)(PPh$_3$)$_2$]PF$_6$ (M = Rh, Ir).
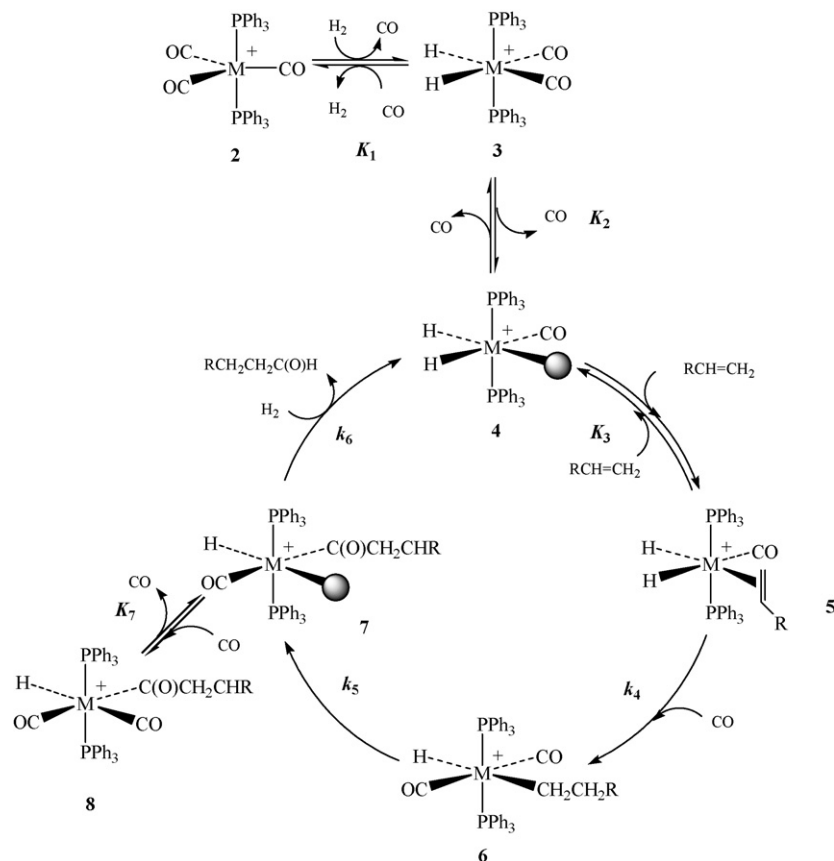
Fig. 2. Catalytic cycle for the hydroformylation of 1-hexene catalyzed by [M(COD)(PPh$_3$)$_2$]PF$_6$ (M = Rh, Ir).

3.4. Mechanistic aspects of the 1-hexene hydroformylation

On the basis of the experimental findings presented above and the extensive previous knowledge on hydroformylation mechanisms [1–15], the catalytic cycles depicted in Fig. 2 are proposed for the hydroformylation of 1-hexene catalyzed by complexes [M(COD)(PPh$_3$)$_2$]PF$_6$, M = Rh (**1a**), Ir (**1b**). Although similar in the main features, the two systems display notable differences in the values of the constants of the equilibria involved (*vide infra*). Complexes **1** react with syn-gas to yield [M(CO)$_3$(PPh$_3$)$_2$]PF$_6$ (**2**) with concomitant hydrogenation and/or hydroformylation of the COD ligand; species **2** are in equilibrium with [M(H)$_2$(CO)$_2$(PPh$_3$)$_2$]PF$_6$ (**3**) through oxidative addition of dihydrogen accompanied by dissociation of one CO ligand (K_1). Complexes **3** can reversibly dissociate a carbonyl ligand (K_2) to form the unsaturated reactive intermediates [M(H)$_2$(CO)(PPh$_3$)$_2$]PF$_6$ (**4**), which are believed to be the active species initiating the catalytic cycle. Complexes **4** can coordinate the olefin through the equilibrium K_3, to produce [M(H)$_2$(CO)(olefin)(PPh$_3$)$_2$]PF$_6$ (**5**). The hydride ligand of **5** is then thought to migrate to the olefin (k_4) with simultaneous coordination of a CO molecule, to yield [M(H)(CO)$_2$(alkyl)(PPh$_3$)$_2$]PF$_6$ (**6**); this is suggested as the rate-determining step of the catalytic cycle. With the data available it is impossible to ascertain whether this is a single concerted elementary step or a rapid succession of two independent events, but for our treatment of the kinetic data we assume the hydride

migration and CO coordination as a single step. Insertion of one of the CO ligands into the metal–alkyl bond of **6** (k_5) generates [M(H)(CO)(acyl)(PPh$_3$)$_2$]PF$_6$ (**7**). Finally, elimination of the aldehyde and addition of H$_2$ regenerates the catalytic species **4** and restarts the cycle (k_6). At high CO pressure, species **7** can coordinate CO to generate the peripheral coordinatively saturated [M(H)(CO)$_2$(acyl)(PPh$_3$)$_2$]PF$_6$ (**8**), through K_7. Although the intimate details of the product elimination step have not been investigated, it is interesting to speculate that this as might arise from coordination of a dihydrogen molecule to **7** to form an 18-electron species [M(H)(H$_2$)(CO)(acyl)(PPh$_3$)$_2$]PF$_6$, followed by a rapid elimination of the aldehyde through coupling of the acyl group with a proton originating from coordinated H$_2$. Alternatively, reductive elimination of the aldehyde from **7** to yield [M(CO)(solv)(PPh$_3$)$_2$]PF$_6$ followed by rapid oxidative addition of H could also be envisaged. Any of these sequences of events would be very fast and therefore do not affect our kinetic analysis.

In conclusion, the [M(COD)(PPh$_3$)$_2$]PF$_6$-catalyzed olefin hydroformylation seems to operate through a mechanism involving dihydrido intermediates, clearly related to well-understood hydrogenation mechanisms for these complexes [17]. The fact that no hydrogenation products were observed indicates that CO insertion into the metal–alkyl bond (k_4) proceeds much faster than reductive elimination of the corresponding alkanes from **5**, in line with other mechanisms for the Rh-catalyzed hydroformylation of alkenes [1,2].

In the cycle described in Fig. 2, if the CO-promoted migration of the hydride to the olefin is assumed to be the rds, a rate-law can be derived by applying the equilibrium approximation. Taking into account that the overall hydroformylation rate is given by the rate of this step, the rate equation may be expressed as:

$$r_i = k_4[\mathbf{5}][CO] \tag{1}$$

Considering the equilibria K_1, K_2 and K_3, $[\mathbf{3}] = K_1[\mathbf{2}][H_2]/[CO]$, $[\mathbf{4}] = K_1 K_2[\mathbf{2}][H_2]/[CO]^2$, and $[\mathbf{5}] = K_1 K_2 K_3[\mathbf{2}][olef][H_2]/[CO]^2$, we have:

$$r_i = \frac{K_1 K_2 K_3 k_4[\mathbf{2}][olef][H_2]}{[CO]} \tag{2}$$

Assuming that **6** and **7** are rapidly transformed to **4**, the mass balance for the metal is $[M]_o = [\mathbf{2}] + [\mathbf{3}] + [\mathbf{5}]$ and therefore, the concentration of **2** may be expressed as:

$$[\mathbf{2}] = \frac{[M]_o[CO]^2}{[CO]^2 + K_1[H_2][CO] + K_1 K_2 K_3[olef][H_2]} \tag{3}$$

Substituting [**2**] in Eq. (2) allows us to rewrite the rate expression as:

$$r_i = \frac{K_1 K_2 K_3 k_4}{[CO]^2 K_1[H_2][CO] + K_1 K_2 K_3[olef][H_2]} \\ \times [M]_o[olef][H_2][CO] \tag{4}$$

This equation explains the kinetic behavior for both precatalysts. For rhodium the equilibrium constant K_1 is smaller than for iridium, which explains why complex **3b** could be isolated whereas **2b** could not; this is in agreement with the fact that 18-electron Ir complexes are less prone to dissociate a ligand to form an active unsaturated species than the Rh counterparts [**2a**]. This also explains the [H$_2$] saturation curve observed for Ir. It seems that constants K_2 and K_3 for Rh are also smaller than the Ir ones. When the CO concentration is higher, the rate expression is transformed to:

$$r_i = \frac{K_1 K_2 K_3 k_4}{[CO] + K_1[H_2]}[M]_o[olef][H_2] \tag{5}$$

Eq. (5) explains the inverse order dependence of the reaction rate on dissolved carbon monoxide concentration at high CO pressure.

4. Conclusions

The results presented here show that cationic rhodium and iridium complexes are efficient precatalysts for the selective homogeneous hydroformylation of 1-hexene under mild reaction conditions; the linear to branched ratio (*l/b*) of the aldehydes in the hydroformylation reaction varies slightly (between 3.0 and 3.7) for Rh and close to 2 for Ir. Despite the fact that these complexes are known to be very active in alkene hydrogenation, no alkanes were formed under hydroformylation conditions because CO insertion is faster than alkane elimination. This reaction was found to be extremely sensitive to experimental conditions, due to the existence of various equilibria mainly controlled by concentrations of gaseous reactants that influence the reaction rates. On the basis of these results, a catalytic cycle is proposed for this reaction, in which $[M(H)_2(CO)(PPh_3)_2]PF_6$ is considered the active species, and the migration of the hydride ligand to the olefin is the rate determining step.

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