Influence of an Additional Gas on the Hydroformylation and Related Reactions

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The initial rate of the catalytic carbonylations reported in this paper [the hydroformylation of olefins in the presence of $Co_2(CO)_8$, the carbonylation of orthoesters catalyzed by $Co_2(CO)_8$], and the formation of tetracarbonylhydridocobalt(I) from octacarbonyldicobalt and dihydrogen] was reduced by the addition of dinitrogen, argon, or xenon. The influence of xenon on the rate of hydroformylation was greater than that of dinitrogen or argon. Helium and neon, on the other hand, did not show any influence, as expected, in view of their chemical-physical features. The experimental data may be explained assuming that the additional gas competes with one or more reactants for a coordinatively unsaturated site responsible for their activation, thus affecting the reaction rate.

Introduction

In the mechanism for the hydroformylation reaction, Heck and Breslow proposed (Scheme 1)[1] that molecular hydrogen was involved in two steps of the catalytic cycle. In a first step (Scheme 1, step A) dihydrogen reacts with $Co_2(CO)_8$ to give $CoH(CO)_4$, while in a subsequent step (Step F) hydrogenolysis of an acylcarbonylcobalt intermediate gives the aldehyde, thus restoring the carbonylhydridocobalt. In an intermediate step (C) the olefin is activated by reaction with $CoH(CO)_3$. In this paper we report the results of some experiments aimed to collect evidence on the intermediates connected with the activation step of dihydrogen in the hydroformylation reaction. Taking into account the literature data, a dihydrogen metal complex should precede the oxidative addition of dihydrogen to the cobalt(0) complex (step A in Scheme 1).

Dihydrogen[2] and dinitrogen complexes[3] are well documented in the literature, the first dihydrogen complex $[W(\eta^2\text{-}H_2)(CO)_3(P\mathit{i}Pr_3)_2]$ being reported by Kubas et al.[2a] Preliminary data on xenon containing transition metal complexes have also been reported in a solid matrix, in liquid xenon, in supercritical fluids, and in gas phase.[4] Very recently, the first stable xenon complex $[AuXe_2^{2+}][Sb_2F_{11}^{-}]_2$ was characterized by X-ray crystal structure analysis.[5] The interactions in these non-classical complexes are relatively weak (between 1 and 10 kcal mol^{-1}).[4a,4g,6] Nevertheless, coordination may be considered as the initial step of an activation process by a metal-containing catalyst. For instance, dihydrogen complexes may be intermediates in the oxidative addition leading to a metal dihydride (Scheme 2).

Other weak interactions such as those between a transition metal and an alkyl group (agostic interactions $[M\cdots H{-}C]$)[7] play an important role in catalytic processes, such as the polymerization of olefins.[8]

The identification of a dihydrogen-cobalt interaction in the photolysis of $CoH(CO)_4$ and in a solid H_2/Ar matrix[9] supports the suggestion that a dihydrogen cobalt complex may be the precursor of dihydrogen activation in the hydroformylation reaction. Dinitrogen was found to displace dihydrogen from the coordination of a cobalt(I) complex, as reported by Sacco and Rossi[3a] in the $CoH(H_2)(PR_3)_3$/$CoH(N_2)(PR_3)_3$ system and analogous equilibria are reported for Ru^{II} and Fe^{II} complexes.[3c,10] Taking into account these results we have investigated the influence of an appropriate "additional" gas, dinitrogen and others, on the rate of hydroformylation (and related reactions) and this paper reports new data on this subject.

Results and Discussion

The first additional gas employed in our experiments was dinitrogen and the investigation was then extended to rare gases such as helium, neon, argon, and xenon.[11] The initial rate for the hydroformylation of cyclohexene in the presence of an "additional gas" was established by determining the conversion of the substrate in isochronous experiments. An analogous methodology has been employed to study the carbonylation of orthoesters and the formation of $CoH(CO)_4$ from $Co_2(CO)_8$ and H_2.

Cyclohexene Hydroformylation

The influence of an additional gas on the rate of hydroformylation was determined by converting cyclohexene to the corresponding aldehyde (Scheme 3) in a set of experi-

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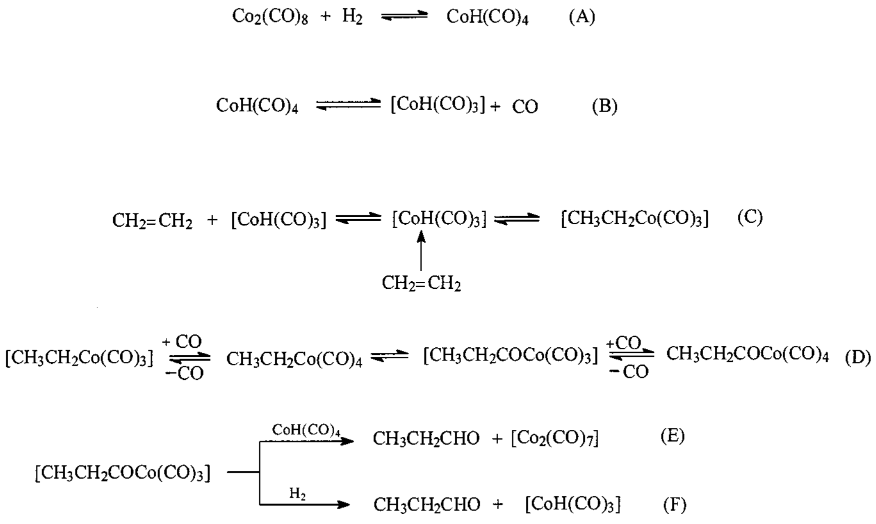
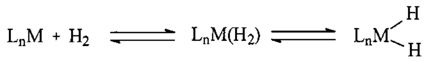
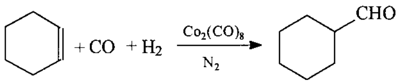


Scheme 1



Scheme 2

ments carried out under the same reaction conditions [100 °C, p(CO) 85 bar, p(H_2) 85 bar, reaction time 3 h], but under different pressures of dinitrogen (0−1000 bar).



Scheme 3

Preliminary results on this reaction have been reported,[11] and the data obtained are summarized in Table 1. A relevant amount of dinitrogen in the reaction medium due to a dinitrogen pressure of 1000 bar, reduced the initial rate of the reaction from 627 to 250 μmol h^{-1}. A reduction of the rate might also be due to a decrease in concentration of the catalyst and substrate resulting from the volume increase of the solution caused by the dissolution of the additional gas. It has been experimentally determined that the amount of dinitrogen dissolved in 7 mL of toluene at 100 °C under 1000 bar produce a volume increase of 1.4 mL. If the volume additivity holds, the molar fraction of dinitrogen[12] is 0.381, the total volume of the solution becomes 8.4 mL. The effect of the dilution on the initial rate of the hydroformylation has been determined by a reference test using 8.5 mL of solvent. As shown in Table 2, the initial rate of the hydroformylation is almost unchanged (595 μmol h^{-1}) (Table 2). By doubling the volume of the solution to 14 mL, the initial rate was reduced to 474 μmol h^{-1}. These data clearly show that although dilution reduces the conversion at a given time, the rate reduction observed in the hydroformylation test carried out under the high pressure of dinitrogen adopted is significantly greater. The hydroformylation of cyclohexene carried out in the presence of argon as additional gas shows a behavior analogous to that observed in the presence of dinitrogen, see Table 1. A specific chemical effect must therefore operate. A purely physical effect due to the increase of dinitrogen pressure should also be excluded since the same reaction carried out in the presence of helium under the same pressure does not show any significant change in the initial rate.

Table 1. Influence of additional gases on the initial rate of cyclohexene hydroformylation[11a]; reaction conditions: toluene 7 mL; $Co_2(CO)_8$ 0.149 mmol (51 mg); cyclohexene 6.15 mmol (500 mg); p_{CO} 70 ± 1 bar at 100 °C; p_{H2} 85 ± 2 bar at 100 °C; reaction time 3 h; T = 100 °C

Gas	Additional gas pressure [bar]	Initial rate [μmol h^{-1}]	Initial rate reduction[a] [%]
N$_2$	0	627	0.0
	500	449	28.4
	800	353	43.7
	1000	250	60.1
He	0	627	0.0
	500	595	5.1
	800	554	11.6
Ne	0	627	0.0
	500	595	5.1
Ar	0	627	0.0
	500	373	40.5
	800	207	67.0
	1000	191	69.5

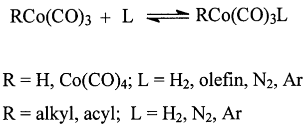
[a] Initial rate reduction: [(Initial rate)$_{0\ bar}$ − (Initial rate)$_{observed}$]/(Initial rate)$_{0\ bar}$.

The observed reduction of the rate of hydroformylation may be ascribed to the formation of a cobalt complex containing dinitrogen (or argon). The formation of a similar complex does in fact reduce the concentration of the catalytically-active cobalt complex and consequently the initial rate of the reaction, see Scheme 4.

Table 2. Hydroformylation of cyclohexene to $C_6H_{11}CHO$; influence of dilution on the rate; solvent: toluene; $Co_2(CO)_8$ 0.149 mmol (51 mg); cyclohexene 6.15 mmol (500 mg); $p_{CO} = 70 \pm 1$ bar at 100 °C; $p_{H2} = 85 \pm 2$ bar at 100 °C; reaction time 3 h; $T = 100$ °C

Solvent [mL]	Dilution [%]	Initial rate [μmol h^{-1}]	Initial rate reduction[a] [%]
7	0	627	0
8.5	20	595	5.1
14	100	472	24.7

[a] Initial rate reduction: [(Initial rate)$_{0\ bar}$ − (Initial rate)$_{observed}$]/(Initial rate)$_{0\ bar}$



Scheme 4

In other words, the reduced hydroformylation rate may be attributed to a lower concentration of the available active intermediate due to a competition between dinitrogen (or argon) and dihydrogen (or olefin) for the same vacant coordination site within the catalytically active species.

The ability of an electron-deficient cobalt complex to coordinate dinitrogen (or rare gases) may be related to the availability of outer shell electrons of this gas that is connected with the first ionization potential (IP).[13] Within rare gases, the IP decreases from helium to xenon. The large rare gases have been reported to coordinate a transition metal.[14,15]

The estimated bond dissociation enthalpy (BDE) for W−Xe in $W(CO)_5Xe$[16] is 35.1 ± 0.8 *k*J mol^{-1}. Furthermore, the estimated BDE's of the metal(0) pentacarbonyl derivatives[17] decrease from xenon (34.3 ± 4.2 *k*J mol^{-1}), to krypton (ca. 25 *k*J mol^{-1}), to argon (ca. 12 *k*J mol^{-1}).

In the hydroformylation of cyclohexene the initial rate was affected by the presence of xenon more than by argon or dinitrogen, while neon or helium had no effect, see Table 1, Table 3 and Table 4. The small difference in the observed rates when working in the presence of helium and neon may be attributed to their different solubility in toluene and therefore to the different volume increase. The concentration of N_2, Ar, Xe in toluene has been experimentally detected and the data are reported in the supplementary materials. The initial rate reduction evaluated for the same concentration of the additional gas in solution (Table 4), is 31.3 for Xe, 16.8 for N_2, and 8.2 [mM]$^{-1}$ for Ar.

Table 3. Influence of xenon on the initial rate of cyclohexene hydroformylation; toluene 7 mL; $Co_2(CO)_8$ 0.149 mmol (51 mg); cyclohexene 6.15 mmol (500 mg); reaction time 3 h; $T = 100$ °C

Xenon [g]	Initial rate [mmol h^{-1}]	Initial rate reduction[a] [%]
0	627	0.0
2.5[b][c]	513	18.2
3.8[b][d]	431	31.3

[a] Initial rate reduction: [(Initial rate)$_{0\ bar}$ − (Initial rate)$_{observed}$]/(Initial rate)$_{0\ bar}$. [b] Gases were introduced in the sequence: CO (1 bar), xenon, CO (53 bar a room temp., 70 ± 1 bar a 100 °C), p_{H2} 85 ± 2 bar at 100 °C. [c] Xenon pressure at 100 °C: 18.5 bar. [d] Xenon pressure at 100 °C: 23.5 bar.

Table 4. Hydroformylation of cyclohexene; initial rate reduction; data from Tables 1 and 3, solvent: toluene

	Ar	N_2	Xe
Additional gas [A. G.] (bar)	1000	1000	23.5[a]
A. G. in solution (mol/L)[b]	0.085	0.036	0.010
Initial rate reduction (%)	69.5	60.1	31.2
Initial rate reduction/ additional gas dissolved [mM]$^{-1}$	8.2	16.8	31.3

[a] Xenon 3.8 g. [b] The additional gas in solution was measured: see the supplementary materials.

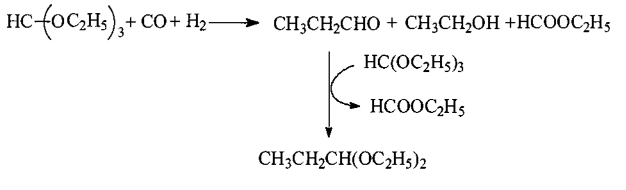
The inhibiting effect of these additional gases (nitrogen, argon, or xenon) on the rate of hydroformylation may be considered as an indirect evidence of an interaction between these additional gases and a catalytically active cobalt complex. These interactions are presumably weak, and carrying out the hydroformylation of cyclohexene in heptane or toluene (Table 5) the initial rate is almost unaffected by the solvent although the solubilities of CO and H_2 differ significantly between heptane and toluene.[12]

Table 5. Hydroformylation of cyclohexene in different solvent; solvent 7 mL; $Co_2(CO)_8$ 0.149 mmol (51 mg); cyclohexene 6.15 mmol (500 mg); p_{CO} 70 bar at 100 °C; p_{H2} 85 bar at 100 °C; reaction time 3 h; *T* 100 °C

Solvent	Additional gas	Amount of additional gas	Initial rate [μmol h^{-1}]
Toluene	Argon	0	627
Heptane	Argon	650 bar	350
Toluene	Argon	500 bar	373
Toluene	Xenon	0	627
Heptane	Xenon	3.1 g	478
Toluene	Xenon	3.8 g	431

Carbonylation of Triethyl Orthoformate

The synthesis of aldehydes by carbonylation of orthoformic esters (Scheme 5) in the presence of $Co_2(CO)_8$ has the same kinetic dependence on CO and H_2 pressure, cata-



Scheme 5

lyst and substrate concentration as the hydroformylation of olefins.

The reaction proceeds through the protonation of one of the oxygen atoms of the ester,[18,19] followed by $RCo(CO)_4$ formation and collapse of the organic residue into ROH and HCOOR. Only one aldehyde is formed, due to the insertion of the formyl group onto the carbon atom of the alkyl group initially bound to the oxygen in the ester.

The aldehyde formed usually reacts through a fast reaction, with the orthoformic ester still present to provide the corresponding dialkyl acetal. The overall reaction is the formation of the acetal of the aldehyde (Scheme 5).

In this reaction no olefin is involved and there is no activation of the substrate by coordination to the metal atom of the catalyst. Coordination vacancies on the catalytically active intermediate should therefore be involved only for the activation of molecular hydrogen. The effect, if any, of the presence of the "additional gas" on the rate of this reaction, which uses the same catalyst as the hydroformylation, should therefore reveal the intervention of these gases on the specific activation steps of dihydrogen.

We have therefore tested the effect of the presence of "additional gases" on the carbonylation of orthoformic esters. The initial rate of the reaction was determined in isochronous (3 h) experiments carried out at 90 °C in the presence of an additional gas (pressure range: 0−1500 bar) through the conversion of triethyl orthoformate to 1,1-diethoxypropane, (see Scheme 5 and Table 6).

Table 6. Carbonylation of triethyl orthoformate: influence of additional gas on the initial rate; ethanol 8 mL; $Co_2(CO)_8$ 0.0789 mmol (27.0 mg); triethyl orthoformate 7.5 mmol (1.110 g); p_{CO} 50 ± 1 bar at 40 °C; p_{H2} 95 ± 2 bar at 90 °C; reaction time 3 h; $T = 90$ °C

Additional gas	Pressure [bar]	Initial rate [μmol h^{-1}]	Initial rate reduction[a] [%]
N_2	0	540	0.0
	1000	343	36.5
	1500	313	42.0
Ar	0	540	0.0
	500	400	25.9
	1000	233	56.9
	1500	100	81.5

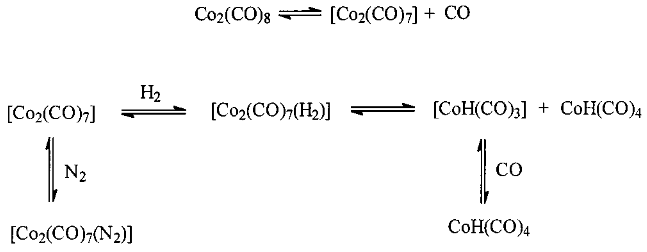
[a] Initial rate reduction: [(Initial rate)$_{0\ bar}$ − (Initial rate)$_{observed}$]/(Initial rate)$_{0\ bar}$.

The additional gas remarkably affects the rate of carbonylation of orthoesters as in the case of cyclohexene hydroformylation. Argon apparently has an even higher influence than dinitrogen.

These data suggest that the steps responsible for the activation of dihydrogen (Scheme 1, steps A, F) are involved in the competition between dihydrogen and the additional gas for the coordinatively unsaturated site.

Formation of $CoH(CO)_4$ from $Co_2(CO)_8$ and Dihydrogen

During the carbonylation of organic substrates in the presence of $Co_2(CO)_8$ as a catalytic precursor, the first reaction is the formation of the catalytically active tetracarbonylhydridocobalt(I). Its kinetic[20] and general considerations, however, on the necessary activation of dihydrogen suggest the following steps (Scheme 6).



Scheme 6

In order to get further evidence, although indirect, on the presence of a coordinatively unsaturated intermediate responsible for the activation of dihydrogen, we tested the effect of the presence of an additional gas on the rate of formation of $CoH(CO)_4$.

A solution of $Co_2(CO)_8$ in hexadeuterobenzene was heated at 50 °C under carbon monoxide (1 bar) to stabilize the carbonyl complex which, even in the absence of O_2 would decompose to $Co_4(CO)_{12}$.[21] The CO was also used to reduce the reaction rate, which in its absence is fast.[22] Dihydrogen and the additional gas were then added. The results are reported in Table 7. Dinitrogen shows a marked influence on the initial rate of the reaction. The conversion of $Co_2(CO)_8$ was almost suppressed in the presence of 1000 bar of dinitrogen: only a trace of $CoH(CO)_4$ was found to be present in solution. The presence of helium (1070 bar) did not affect the rate of this reaction: a conversion of 14−15% was observed under the same conditions. We assume that dinitrogen and dihydrogen compete for a coordinatively unsaturated site of an intermediate, tentatively indicated as $Co_2(CO)_7$ in Scheme 6.

Table 7. Formation of $CoH(CO)_4$ from $Co_2(CO)_8$ and dihydrogen; influence of the additional gas on the initial rate; hexadeuteriobenzene 4 mL; $Co_2(CO)_8$ 0.2339 mmol (80.0 mg); $T = 50$ °C; $p_{CO} = 1$ bar at room temp.; $p_{H2} = 50$ bar at 50 °C; reaction time 3 h

Additional gas	Additional gas pressure at 50 °C [bar]	Initial rate [μmol h^{-1}]	Initial rate reduction[a] [%]
He	0	11.8	0.0
He	1070	5.6	52.6
N_2	0	11.8	0.0
N_2	1025	< 0.1	> 99.2

[a] Initial rate reduction: [(Initial rate)$_{0\ bar}$ − (Initial rate)$_{observed}$]/(Initial rate)$_{0\ bar}$

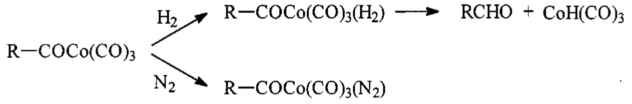
Conclusion

Several authors discussing the mechanism of the hydroformylation of olefins have indicated the reduction of an acylcarbonylcobalt intermediate as the rate determining step.[23,24] The negative influence of the pressure of carbon monoxide on the reaction rate[25] may be explained in terms of the shift of equilibrium D (Scheme 1) to the acyltricarbonylcobalt that was found to be more easily reducible than acyltetracarbonylcobalt.

The higher rate of hydroformylation under a low pressure of carbon monoxide may be attributed to the higher concentration in solution of the coordinatively unsaturated acyltricarbonylcobalt, necessary to activate dihydrogen, which is the predominant reducing agent in the system (Step F, Scheme 1).

Dihydrogen was suggested as the reducing agent[23,24] in consideration of its high concentration in solution when compared with that of the alternative reducing agent: tetracarbonylhydridocobalt(I).

Such an explanation is confirmed by the detected influence of the “additional gases” on the rate of hydroformylation. These gases do not take part in the formation of the product but compete with both dihydrogen and carbon monoxide for the coordinatively unsaturated site in the acyltricarbonylcobalt (Scheme 7). These interactions decrease the concentration of the intermediate available for the activation of dihydrogen and therefore retard its reaction with the acylcobalt complex that leads to the formation of the aldehyde.



Scheme 7

Experimental Section

General Methods: Quantitative GC analyses were performed with a Shimadzu mod. GC-14A instrument equipped with a PPG column (“Polypropylenglicol” LB-550-X on Chromosorb W at 15%, 1/8” i.d., 2 m) and a Shimadzu mod. C-R4A integrator. Unless otherwise stated, no correction factors were introduced, in consideration of the analogy of the products examined. Products were identified by GC-MS using a Shimadzu apparatus having a GC14A chromatograph equipped with a CP-Sil8 (50 m) capillary column and a QP2000 mass detector. Elemental analyses were performed using a Perkin−Elmer mod. 2400 Series II elemental analyzer. IR spectra were recorded with a Perkin−Elmer mod. 1760-X FT-IR spectrophotometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded using a Varian VXR300 spectrometer operating at 299.987 MHz for ^{1}H, and at 75.429 MHz for ^{13}C, using $SiMe_4$ as external standard.

$Co_2(CO)_8$ (m.p. 56 °C) was prepared according to Natta and Ercoli,[26] and recrystallized from hexane; cyclohexene (Fluka) was purified (99.9% purity by GC) through elution on an Al_2O_3 column and then distilled (b.p. 83 °C) under dinitrogen; triethyl orthoformate: (Fluka) was distilled under dinitrogen (b.p. 146 °C); toluene was heated under reflux over sodium for 5 h, then distilled under dinitrogen (b.p. 110 °C).[27] Heptane was dried by heating under reflux over $LiAlH_4$. Dinitrogen (Sol Centro, 99.996% purity), argon (Sol Centro, 99.998% purity), neon, (Rivoira, 99.997% purity), xenon (Rivoira, 99.997% purity), and helium (Sol Centro, 99.998% purity) were used as received.

The experiments were carried out in a stainless-steel rocking reactor, inner volume 24.5 mL, tested to a total pressure of 4000 bar. The vessel was equipped with a high-pressure Nova Swiss valve used for the introduction of gases and liquids. The temperature was measured using a Pt100 indicator and regulated with an accuracy of ±1 °C. The pressure was measured through a transducer (Sensotec, model Z Absolute) with an accuracy of ±1 bar. The experimental conditions are reported in Table 1−3 and Table 5−7. The amount of reagents were chosen to avoid relevant pressure drops during each experiment.

Hydroformylation of Cyclohexene: The same procedure was adopted for the hydroformylation of cyclohexene in the presence of dinitrogen, argon, or helium. The catalyst was placed in the stainless-steel autoclave under dinitrogen the vessel was sealed and the gas evacuated. A solution of the olefin was prepared in a Schlenk tube and introduced into the autoclave by suction. CO of up to 5 bar was then added. The reactor was rocked and heated at 100 °C. When the solution reached the predetermined temperature, further CO up to 75 bar was added, followed by dihydrogen up to a total pressure of 160 bar (partial pressure of H_2, 85 ± 2 bar). The additional gas was then rapidly introduced up to the required pressure. Only a few minutes were necessary to perform these operations. The reactor was rocked for 3 h, then rapidly cooled to room temperature. The gases were vented and the pale yellow solution analyzed by GC to evaluate the conversion of cyclohexene to the aldehyde. GC conditions adopted when the experiments were carried out in toluene were the following: 50 °C for 5 min than up to 110 °C at a rate of 4 °C/min and kept at this temperature for 50 min. When heptane was the solvent, GC conditions were the following: 35 °C for 20 min then up to 110 °C at a rate of 4 °C/min and keeping this temperature for 60 min. Cyclohexane, cyclohexene, toluene or heptane, and cyclohexanecarboxyaldehyde were determined by gas-chromatography. The amount of cyclohexane present was less than 1% of the starting cyclohexene in all experiments.

The experiments with xenon were carried out using a different procedure. After the introduction of both catalyst and solvent, CO up to 1 bar was added. Liquid xenon was introduced at room temperature from a pressure cylinder, followed by CO up to 53 bar at room temperature. The amount of xenon introduced was evaluated by weight difference. The reactor was heated at 100 °C and then pressurized with hydrogen. The subsequent procedures were identical to those reported above. The data in the presence of xenon were compared with a reference test performed, with the same procedure, in the presence of helium.

The results of the hydroformylation tests on cyclohexene are reported in Table 1−5.

Carbonylation of Triethyl Orthoformate: All conditions employed are reported in Table 6. The catalyst was placed in the autoclave under dinitrogen. The vessel was sealed and the gas evacuated. A solution of triethyl orthoformate in anhydrous ethanol was prepared in a Schlenk tube and introduced into the autoclave by suction. CO up to 50 bar was then added and the vessel heated at 90 °C. When the selected temperature was reached, hydrogen up to a total pressure of 145 bar was introduced (hydrogen partial pressure 95 ± 2 bar) followed rapidly by the additional gas. The reactor was rocked for 3 h, and then rapidly cooled to room temperature. The gases were vented and the pale yellow solution analyzed by GC using heptanol as internal standard, to evaluate the conversion of triethyl orthoformate into 1,1-diethoxypropane. The following GC conditions were adopted: 50 °C for 5 min, then heated up to 70 °C at a rate of 5 °C/min and kept at this temperature for 15 min, then heated up to 120 °C at a rate of 5 °C/min and kept at this temperature for 20 min. Ethanol, ethyl formate, 1,1-diethoxypropane, and heptanol were separated and quantified by GC. The results are reported in Table 6.

Synthesis of $CoH(CO)_4$ from $Co_2(CO)_8$ and Hydrogen: The experimental conditions used are listed in Table 7. Under CO, a solution of octacarbonyldicobalt in [D$_6$]benzene was introduced into the autoclave, which was then sealed and heated up to 50 °C. Dihydrogen and the additional gas (helium or dinitrogen) were then introduced and the autoclave rocked for 3 h. The vessel was cooled at 0 °C, the gases were slowly vented (about 20 min) and the autoclave opened under dihydrogen. An aliquot of the solution (1 mL, 0 °C) was examined by ^{1}H NMR after addition of 21.0 mg (0.0146 mmol) of $Ru_4H_4(CO)_8(PBu_3)_4$ as internal standard [$CoH(CO)_4$, $\delta = -11.6$; $Ru_4H_4(CO)_8(PBu_3)_4$, $\delta = -16.7$] and the conversion of $Co_2(CO)_8$ into $CoH(CO)_4$ was detected (Table 7).

The loss of $CoH(CO)_4$ was estimated by carrying out an experiment in the absence of an additional gas under the conditions reported in Table 7. At the end of the reaction, helium was introduced up to a pressure of 930 bar, the gases were vented and the amount of $CoH(CO)_4$ evaluated as previously described. The initial rate of the transformation of $Co_2(CO)_8$ into $CoH(CO)_4$ is 5.6 μmol h^{-1}: 50% of the hydride present in the solution was lost.

Supporting information available (see footnote on the first page of this article): Table with the data of the additional gas employed. Solubilities of dinitrogen in toluene, Method 1 and Method 2. Solubility of argon in toluene. Solubility of xenon in toluene. Relation between theoretical and effective pressure of dinitrogen at 10 °C. Relation between theoretical and effective pressure of dinitrogen at 100 °C. Fugacity coefficient of dinitrogen as a function of the pressure at 10 °C. Fugacity coefficient of dinitrogen as a function of the pressure at 100 °C.

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