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Speciation and Kinetics Related to Catalytic Carbonylation in the Presence of *cis*-$[Ir(CO)_2I_2]P(C_6H_5)_4$ under CO and H_2 Pressures

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The differences in the reactivities of the square-planar complexes *cis*-$[Rh(CO)_2I_2]^-$ (**1**) and *cis*-$[Ir(CO)_2I_2]^-$ (**2**), involved in the catalytic carbonylation of olefins, are investigated, with $P(C_6H_5)_4^+$ as the counterion, by ambient- and high-pressure NMR and IR spectroscopy. Under an elevated pressure of CO, **1** and **2** form the $[M(CO)_3I]$ complexes with the equilibrium constants $K_{Ir} \approx 1.8 \times 10^{-3}$ and $K_{Rh} \approx 4 \times 10^{-5}$. The ratio K_{Ir}/K_{Rh} close to 50 shows that, under catalytic conditions (a few megapascals), only complex **1** remains in the anionic form, while a major amount of the iridium analogue **2** is converted to a neutral species. The oxidative addition reactions of HI with **1** and **2** give two monohydrides of different geometries, *mer,trans*-$[HRh(CO)_2I_3]^-$ (**3**) and *fac,cis*-$[HIr(CO)_2I_3]^-$ (**4**), respectively. Both hydrides are unstable at ambient temperature and form, within minutes for Rh and within hours for Ir, the corresponding *cis*-$[M(CO)_2I_2]^-$ (**1** or **2**) and $[M(CO)_2I_4]^-$ (**5** or **6**) species and H_2. When an H_2 pressure of 5.5 MPa is applied to a nitromethane solution of complex **2**, ca. 50% of **2** is transformed to *cis*-dihydride complexes. The formation of *cis,cis,cis*-$[IrH_2(CO)_2I_2]^-$ (**8a**) is followed by intermolecular rearrangements to form *cis,trans,cis*-$[IrH_2(CO)_2I_2]^-$ (**8b**) and *cis,cis,trans*-$[IrH_2(CO)_2I_2]^-$ (**8c**). A small amount of a dinuclear species, $[Ir_2H(CO)_4I_4]^{x-}$ (**9**), is also observed. The formation rate constants for **8a** and **8b** at 262 K are $k_1^{262} = (4.42 \pm 0.18) \times 10^{-4}\ M^{-1}\ s^{-1}$, $k_{-1}^{262} = (1.49 \pm 0.07) \times 10^{-4}\ s^{-1}$, $k_2^{262} = (2.81 \pm 0.04) \times 10^{-5}\ s^{-1}$, and $k_{-2}^{262} = (5.47 \pm 0.16) \times 10^{-6}\ s^{-1}$. The two equilibrium constants $K_1^{262} = [\mathbf{8a}]/([\mathbf{2}][H_2]) = 2.97 \pm 0.03\ M^{-1}$ and $K_2^{262} = [\mathbf{8b}]/[\mathbf{8a}] = 5.13 \pm 0.10$ show that complex **8b** is the thermodynamically stable addition product. However, no similar H_2 addition products of the rhodium analogue **1** are observed. The pressurization with H_2 of a solution containing **2** and **6** give the monohydride **4**, the dihydrides **8a** and **8b**, the dinuclear complex **9**, and the two new complexes $[Ir(CO)_2I_3]$ (**10**) and $[HIr(CO)_2I_2]$ (**11**). The reactions of the iridium complexes with H_2 and HI are summarized in a single scheme.

Introduction

The square-planar complexes *cis*-$[Rh(CO)_2I_2]^-$ (**1**) and *cis*-$[Ir(CO)_2I_2]^-$ (**2**) are important intermediates in catalytic cycles for industrial carbonylations of alcohols to form carboxylic acids.[1−7] Carbonylations of alcohols higher than ethanol produce mixtures of linear- and branched-chain carboxylic acid isomers for both rhodium and iridium systems. The isomerizations occur through hydride−olefin species.[3,5,6] Under the catalytic conditions used for alcohol carbonylations, the alkenes also transform into carboxylic acids.[5,8] A recent study, by Roe et al., on the carbonylation of ethene using rhodium as the catalyst under mild conditions in CD_2Cl_2 (Scheme 1) shows the presence of the hydride complex *mer,trans*-$[HRh(CO)_2I_3]^-$ (**3**), formed by the oxidative addition of HI to **1**.[9] The nonsaturated hydride $[HRh(CO)_2I_2]$ (**3a**), in equilibrium with **3**, is proposed to react with ethene to form an acyl species, which will form the propanoic acid. Olefin carbonylation reactions have not received as much attention as alcohol carbonylation reactions, especially in the presence of iridium catalysts.[8−12]

The goal of this work is to understand the speciation and the kinetics of olefin carbonylation in the presence of the iridium complex **2** and to compare these with the behavior of the rhodium analogue **1** in the absence and presence of different components (CO, olefins, and HI) that participate in the catalytic cycle.[9] We have chosen $P(C_6H_5)_4^+$ as the counterion, but it should be stressed that the equilibria and kinetic behaviors of our model systems depend also on the nature of the counterion (e.g., Na^+ or PPN^+). This study, followed by NMR and IR spectroscopy, is performed under a high pressure of CO to increase the dissolved gas concentrations and to displace the

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(1) Forster, D. *J. Chem. Soc., Dalton Trans*. **1979**, 1639.
(2) Haynes, A.; Mann, B. E.; Morris, G. E.; Maitlis, P. M. *J. Am. Chem. Soc*. **1993**, *115*, 4093.
(3) Forster, D.; Dekleva, T. W. *J. Chem. Educ*. **1986**, *63*, 204.
(4) Fulford, A.; Hickey, C. E.; Maitlis, P. M. *J. Organomet. Chem*. **1990**, *398*, 311.
(5) Ellis, P. R.; Pearson, J. M.; Haynes, A.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *Organometallics* **1994**, *13*, 3215.
(6) Maitlis, P. M.; Haynes, A.; Sunley, G. J.; Howard, M. J. *J. Chem. Soc., Dalton Trans*. **1996**, 2187.
(7) Paulik, F. E.; Hershman, A.; Knox, W. R.; Roth, J. E.; Monti, D. (Monsanto Co.) U.S. Patent 3,769,329, 1973.
(8) Mizoroki, M.; Matsumoto, T.; Ozaki, A. *Bull. Chem. Soc. Jpn*. **1979**, *52*, 479.
(9) Roe, D. C.; Sheridan, R. E.; Bunel, E. E. *J. Am. Chem. Soc*. **1994**, *116*, 1163.
(10) Hershman, A.; Morris, D. E.; Forster, D. (Monsanto Co.). French Patent 2,280,622, 1975.
(11) Forster, D.; Hershman, A.; Morris, D. E. French Patent 2,280,586, 1975.
(12) Forster, D.; Hershman, A.; Morris, D. E. *Catal. Rev.*—*Sci. Eng*. **1981**, *23*, 89.

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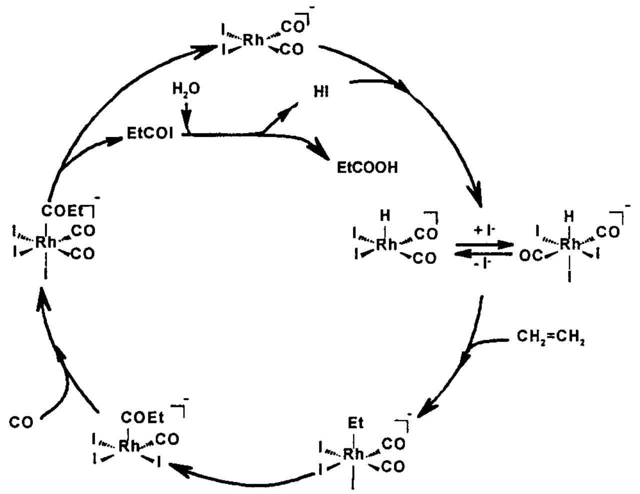
Scheme 1. Proposed Rhodium Catalytic Cycle for Ethylene Carbonylation[5,9]



equilibria to favor the observation of possible intermediates. The study is extended to high pressure of dihydrogen not because H_2 enters into the reaction equations but rather because it is a byproduct of the carbonylation process, produced through the water-gas shift reaction from H_2O and CO.

Experimental Section

Chemicals and Solutions. Methanol (Fluka, >99.8%), *n*-hexane (Merck, >95%), $[Rh(CO)_2Cl]_2$ (Strem Chemical, >95%), $[Ir(CO)_3Cl]_n$ (Strem Chemical, >95%), $P(C_6H_5)_4I$ (Fluka, >95%), chloroform-*d* ($CDCl_3$, Armar, 99.8 atom % D), methylene-d_2 chloride (CD_2Cl_2, Armar, 99.6 atom % D), nitromethane-d_3 (CD_3NO_2, Armar, 99.5 atom % D), CO (Carbagaz, 99.997%), and carbon-13-enriched carbon monoxide (Cambridge Isotope Laboratories, 99 atom % ^{13}C) were used without further purification. HI was purified before use by distillation according to a literature procedure, but without adding hypophosphorous acid as a stabilizer.[4]

The complexes *cis*-$[Rh(CO)_2I_2]P(C_6H_5)_4$,[4,13] *cis*-$[Ir(CO)_2I_2]P(C_6H_5)_4$,[14] and *cis*-$[Ir(CO)_2I_4]P(C_6H_5)_4$[15,16] were synthesized according to methods described in the literature. The purities of the three complexes were checked by IR and NMR comparison to literature data.[2,15,17] The ^{13}C-enriched square-planar complexes of rhodium(I) and iridium(I) were each obtained by pressurizing a solution of the complex in a sapphire tube[18] twice with 1.0 MPa of ^{13}CO, shaking the tube for 1 min to solubilize the gas more rapidly in solution, then removing the CO pressure, and, finally, removing free CO by pressurizing twice with 1.0 MPa of N_2. The ^{13}C enrichment of the two square-planar complexes could be performed according to this procedure because, as we have shown in a preceding study, the exchange of CO between free CO and **1** (or **2**) is fast.[19]

NMR Measurements. The ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 spectrometer with a narrow-bore cryomagnet (9.4 T; 400.18 and 100.63 MHz, respectively). The ^1H and ^{13}C NMR chemical shifts, $\delta(^1H)$ and $\delta(^{13}C)$, were referenced to TMS and measured with respect to the solvent (^1H and ^{13}C shifts: $CDCl_3$, 7.24 and 77.0 ppm; CD_2Cl_2, 5.32 and 53.8 ppm; CD_3NO_2, 4.33 and 62.8 ppm) at all temperatures. The temperature was controlled to within ±0.2 K using a Bruker B-VT 2000 unit and was measured (±1 K) before and after each spectral acquisition by a substitution technique with a platinum resistor.[20] For the medium gas pressure work (up to 2.0 MPa of ^{13}CO and 5.5 MPa of H_2), 10 mm (outer diameter) NMR sapphire tubes were used.[18] The parameters for the acquisition of ^{13}C (^1H) NMR spectra were as follows: spectral width 21 (4−15) kHz; 32−128 K (32−128 K) data points; pulse length 10 (7) μs; exponential line broadening 1 (0) Hz; 0.5−2 K (0.5−2 K) scans. All ^{13}C NMR spectra were obtained with ^{13}C-enriched carbon monoxide, except where stated.

IR Measurements. The IR spectra were recorded on a Perkin-Elmer FTIR 2000 spectrometer using a high-pressure cell.[21] Due to an intense absorption of free CO under pressure, no signals could be detected between 2100 and 2200 cm^{-1}.

Data Treatment. The analysis of data using the appropriate equations was accomplished with the nonlinear least-squares-fitting program Scientist.[22] The reported errors correspond to one standard deviation.

Results and Discussions

Reactivities of *cis*-$[M(CO)_2I_2]P(C_6H_5)_4$ (M = Rh, Ir) with CO, Olefins, and HI. In solution, under a nitrogen atmosphere, the iridium(I) complex **2** is quite stable and decomposes only at temperatures higher than 340 K in $CDCl_3$ or 380 K in CD_2Cl_2 or CD_3NO_2. Under the same conditions, the rhodium(I) complex **1** is unstable, showing partial decomposition at room temperature after several hours. Olefins, CO, and HI are reactants in olefin carbonylation processes catalyzed by *cis*-$[Rh(CO)_2I_2]^-$. Therefore, the interactions of these reactants with **2** were studied.

Previously, we investigated the exchange between free and coordinated CO in complexes **1** and **2** by high pressure ^{13}C NMR spectroscopy in dichloromethane. The study pointed to a limiting associative, A, mechanism with second-order CO exchange rate constants of 850×10^3 and 99×10^3 L mol^{-1} s^{-1} at 298 K, respectively.[19] In this previous study, a color change from yellow to red was observed when a CH_2Cl_2 solution of **2** was pressurized with CO up to 1.5 MPa. We could estimate the formation constant of the red species, $[Ir(CO)_3I]$, formed by iodide substitution, using UV−visible spectroscopy. In the present study, we investigated the effect of higher CO pressures (up to 28 MPa) by IR spectroscopy in $CHCl_3$. The low-pressure spectra confirmed the formation of $[Ir(CO)_3I]$, which had already been identified by its two characteristic CO stretches at 2046 and 2073 cm^{-1}.[1,23] This allowed the determination of its formation constant, $K_{Ir} \approx 1.8 \times 10^{-3}$ ($K_{Ir} = [Ir(CO)_3I][I^-]/[cis\text{-}Ir(CO)_2I_2^-][CO]$), in $CHCl_3$. A further increase of the pressure caused the appearance of two new CO stretches at 2010 and 2090 cm^{-1} due to an unknown species. Simultaneously, there was a strong decrease of the two bands of **2** at 1970 and 2048 cm^{-1}: 35% of complex **2** was converted at 15 MPa. Under the same pressure, less than 4% of **1** (CO stretches at 1988 and 2059 cm^{-1}) was converted into $[Rh(CO)_3I]$ (one CO stretch at 2087 cm^{-1}, the second one at 2061 cm^{-1} being obscured by the CO stretch of **1**).[24] We then estimated the formation constant, $K_{Rh} \approx 4 \times 10^{-5}$, of this species in $CHCl_3$. This result shows a difference in CO affinity for complexes **1** and **2** by a factor of $K_{Ir}/K_{Rh} \approx 50$.

The reactivity of **2** toward olefins (either substitution or oxidative addition) was also checked. In the absence or presence of a CO pressure, no reactions with ethylene, hexene, butadiene,

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(13) Vallarino, L. M. *Inorg. Chem.* **1965**, *4*, 161.
(14) Piraino, P.; Faraone, F.; Pietropaolo, R. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 1237.
(15) Forster, D. *Synth. Inorg. Met.-Org. Chem.* **1971**, *1*, 221.
(16) Forster, D. *Inorg. Chem.* **1972**, *11*, 473.
(17) Forster, D. *Inorg. Chem.* **1969**, *8*, 2556.
(18) Cusanelli, A.; Frey, U.; Richens, D. T.; Merbach, A. E. *J. Am. Chem. Soc.* **1996**, *118*, 5265.
(19) Churlaud, R.; Frey, U.; Metz, F.; Merbach, A. E. *Inorg. Chem.* **2000**, *39*, 304.
(20) Ammann, C.; Meier, P.; Merbach, A. E. *J. Magn. Res.* **1982**, *46*, 319.
(21) Laurenczy, G.; Lukacs, F.; Roulet, R. *Anal. Chim. Acta* **1998**, *359*, 275.
(22) *Scientist*, Version 2.0; MicroMath, Inc.: Salt Lake City, UT, 1995.
(23) Schrod, M.; Luft, G.; Grobe, J. *J. Mol. Catal.* **1983**, *22*, 169.
(24) Morris, D. E.; Tinker, H. B. *J. Organomet. Chem.* **1973**, *49*, C53.

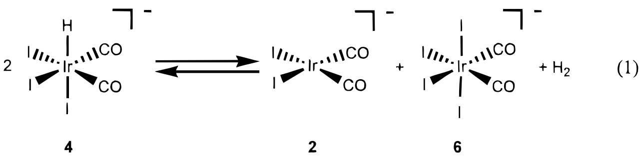
Table 1. Chemical Shifts, δ, Coupling Constants, ^2J, and IR Data for All Complexes of This Study

complex	δ_H (ppm)	δ_{CO} (ppm)	$^2J_{^1H-^1H}$ (Hz)	$^2J_{^{13}C-^{13}C}$ (Hz)	$^2J_{^1H-^{13}C}$ (Hz)	ν(CO) (cm^{-1})	ν(Ir−H) (cm^{-1})
1[a]		183.8				1988, as 2059, s	
2		171.4				1970, as 2048, s	
3[9,b,c]	−10.4	177.9			3.8	2080	n.d.[k]
4[d]	−11.7	156.0			2.3	2107[e] 2051[e]	2160[e]
5[f]		169.7				2084	
6		150.6				2065 2110	
8a[g]	−10.1 (a) −14.3 (b)	161.1 (b) 164.7 (a)	4.6	1.8	57.9 (a−a) 6.2 (a−b) 3.1 (b−a) 4.0 (b−b)	2015 n.d.[k]	2164 2135
8b[g]	−16.4	171.2	0.9[h]		5.5	2033	2119 2139
8c[g]	−11.3	164.7	5 or 7	5 or 7	41.9, 5, or 7		
9[g]	−15.6	161.3[i] 162.3[j]		1.3	23.5, n.d.[k]		
10[g]		157.2					
11[g]	−16.8	163.7			5.1		

[a] $^2J_{^{13}C-^{103}Rh} = 72.3$ Hz. [b] In CD_2Cl_2. [c] $^2J_{^1H-^{103}Rh} = 3.8$ Hz; $^2J_{^{13}C-^{103}Rh} = 50.5$ Hz. [d] In $CDCl_3$. [e] In $CHCl_3$. [f] $^2J_{^{13}C-^{103}Rh} = 53.4$ Hz. [g] In CD_3NO_2. [h] $^2J_{H-D} = 0.9$ Hz. [i] Terminal. [j] Bridged. [k] n.d. = not determined.

and $CF_2{=}CH_2$ were observed for **2** in CD_2Cl_2 and $CDCl_3$. Similarly, no reaction with hexene was observed for **1** in $CDCl_3$.

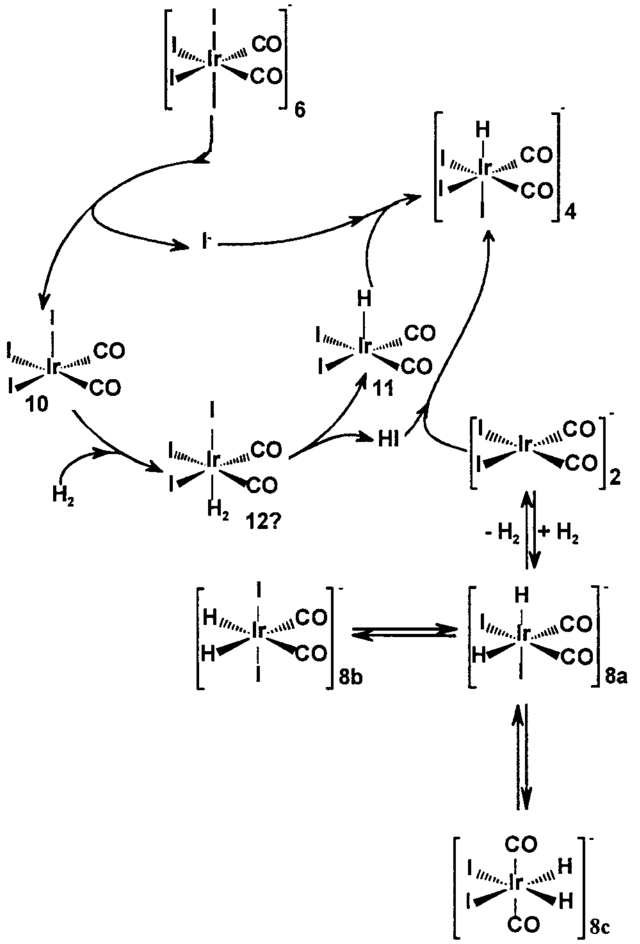
The olefin fixation on the rhodium complex **1** (Scheme 1) is known to proceed through the hydride species **3** formed by the oxidative addition of HI. When 1 equiv of HI is added to a solution of ^{13}C-enriched iridium analogue **2** in $CDCl_3$ at ambient temperature, we observe the formation of the monohydride *fac,cis*-$[HIr(CO)_2I_3]^-$ (**4**). The ^1H NMR spectrum shows a triplet at −11.7 ppm ($^2J_{^1H-^{13}C} = 2.3$ Hz) which is characteristic of a hydride ligand coupled to two equivalent CO ligands (Table 1). In the ^{13}C NMR spectrum, a doublet due to the presence of one hydride is present at 156 ppm. The IR spectrum in $CHCl_3$ shows three vibrational bands at 2158 (br, ν(Ir−H)), 2113 (i, ν(CO)), and 2058 (i, ν(CO)) cm^{-1} in agreement with the literature.[1,10,11] Roe et al. showed that HI reacted with the rhodium analogue, **1**, to form the hydride *mer,trans*-$[HRh(CO)_2I_3]^-$ (**3**) at 253 K.[9] The geometries of the two hydrides **3** and **4** are different: the two CO ligands are in trans and cis positions, respectively. Roe et al. found that when a solution of **3** was cooled to 193 K, a new hydride, $[HRh(CO)_2I_2]$ (**3a**), formed upon the elimination of an iodide.[9] Under these conditions, we found no iridium hydride analogue. However, the possible iridium analogue $[HIr(CO)_2I_2]$ (**11**) could be assigned as one of the minor products in the reaction of a mixture of *cis*-$[Ir(CO)_2I_2]^-$ and *cis*-$[Ir(CO)_2I_4]^-$ with H_2 (see Scheme 2). Moreover, Forster et al. found that this hydride, $[HIr(CO)_2I_2]$, is formed from $[HIr(CO)_3I_2]$ upon removal of a CO in CH_2Cl_2 by flushing N_2.[11] The fully NMR-characterized iridium hydride **4** is stable for hours at room temperature but rapidly reacts according to eq 1 when the temperature is raised.



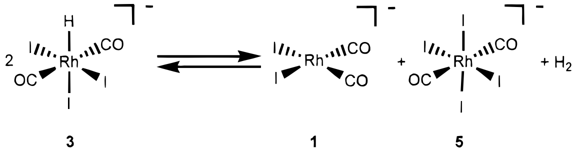
(1)

The mixture of the resulting products **2** and **6**, obtained by evaporation from CD_2Cl_2, can reversibly give **4** after addition of solvent and pressurization with H_2. A more detailed study of this back-reaction will be discussed below. Roe et al. found

Scheme 2. Reactions among Different Iridium Complexes in the Presence of HI and H_2



that the rhodium hydride **3** reacts already at 273 K (eq 2).[9] The

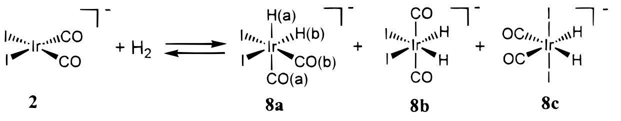


(2)

structures of the $[M(CO)_2I_4]^-$ complexes, **5** and **6**, are also different for rhodium and iridium. For the iridium complex **6**, the cis geometry is the thermodynamically stable form; the trans isomer can be synthesized, but under a CO atmosphere, an isomerization to the cis configuration was observed.[5,25,26] The rhodium compound **5** was found to have a trans geometry,[3,5,26] but a cis geometry could also be found in solids, depending on the counterion.

We have shown that the square-planar complexes **1** and **2** react differently toward some of the entering components (CO and HI) of the catalytic cycle proposed by Roe et al. for rhodium.[9] Indeed, under 15 MPa of CO, while 35% of complex **2** is transformed into the $[Ir(CO)_3I]$ species, less than 4% of **1** forms the analogous $[Rh(CO)_3I]$ species. The reactivities with HI are also different, oxidative additions of HI to **1** and **2** producing two structurally different hydrides: *fac,cis*-$[HIr(CO)_2I_3]^-$ and *mer,trans*-$[HRh(CO)_2I_3]^-$. A further difference is found in the reactivities of these two hydrides with olefins. While the rhodium hydride complex **3** reacts with ethylene to form an acyl complex,[9] the iridium hydride **4** is unreactive.

Reactivities of *cis*-$[M(CO)_2I_2]P(C_6H_5)_4$ (M = Rh, Ir) and *cis*-$[Ir(CO)_2I_4]P(C_6H_5)_4$ with H_2. H_2 does not explicitly appear in the rhodium catalytic cycle (Scheme 1); in other words, it is not an entering or leaving constituent. Nevertheless, H_2 can play an important role, as it is produced either by hydride decomposition (eq 1) or by a water-gas shift reaction in the presence of complex **6**.[1] We first investigated the reactions of H_2 with **2** and **6** independently. The addition reaction of H_2 with **2** was performed in CD_3NO_2 using a high pressure of H_2. The ^1H and ^{13}C NMR spectra (Figure 1) recorded after applying 5.5 MPa of H_2 ($[H_2] = 0.12$ M) to a solution of **2** at room temperature indicate that around 50% of the starting complex is converted into different hydride complexes (eq 3). If H_2 is added from



(3)

one side of the square plane of **2**, the first dihydride complex that is formed must be **8a** (two enantiomers) and all other isomers are formed through either inter- or intramolecular rearrangements. Compound **8a** was only formed as a minor product of the observed new dihydride complexes (Figure 1). The addition reaction of H_2 with **2** was also followed by high-pressure (14.5 MPa of H_2) IR spectroscopy at ambient temperature (Figure 2). As soon as H_2 is present in the solution, the two CO stretching bands of **2** (1970 (ν_{as}) and 2048 (ν_s) cm^{-1}) decrease with time and some other signals appear, in both the carbonyl and the hydride regions. The first three appearing new vibration bands ν(CO), ν(Ir–H), and ν(Ir–H), at 2015, 2135, and 2164 cm^{-1}, respectively, are attributed to **8a** in agreement with the order of appearance of the signals of the species in the NMR study. The second ν(CO) stretching band of **8a** should be superposed on the ν_{as}(CO) band of **2**. The NMR chemical shifts, coupling constants, and IR data for **8a** are given in Table 1.

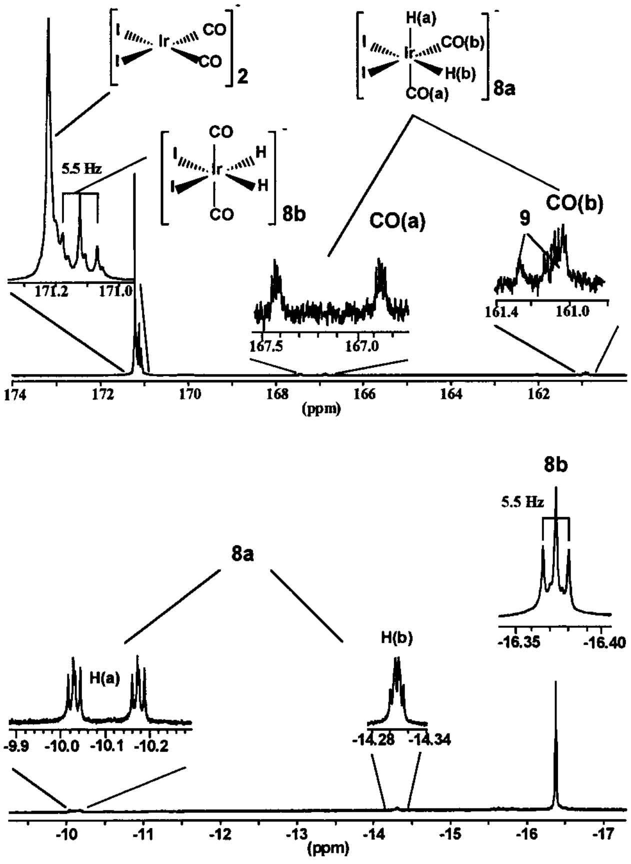


Figure 1. ^{13}C (top) and ^1H (bottom) NMR spectra of a solution of *cis*-$[Ir(^{13}CO)_2I_2]^-$ solution (3.2×10^{-2} M) in CD_3NO_2 under 5.5 MPa of H_2 at 298 K: major complex **8b** and minor complexes **8a** and **9**.

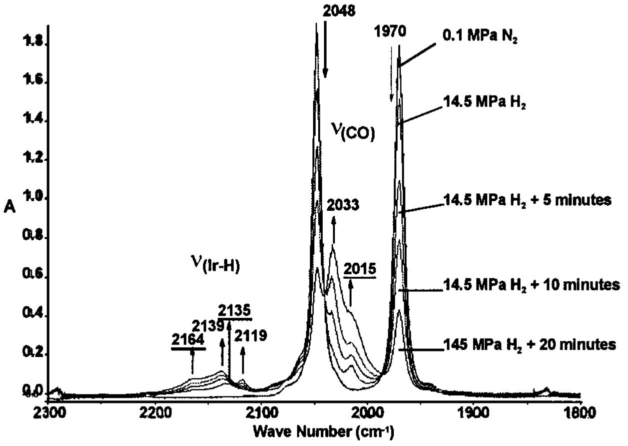


Figure 2. IR spectra of a 1.1×10^{-2} M solution of **2** in CH_3NO_2 under an N_2 atmosphere and 14.5 MPa of H_2 (after 0, 5, 10, and 20 min) at 298 K.

The chemical shifts, coupling constants (Figure 1), and IR data (Figure 2, IR time-dependent spectra) for the major product **8b**, appearing after 5 min, are also reported in Table 1. The determination of the structure of **8b**, using the NMR data, was not straightforward. Even if the value of the $^2J_{^1H-^{13}C}$ coupling constant indicated that the hydride and the carbonyl ligands are cis to each other, three structures are still possible: **8b** (H cis

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(25) Kumbhar, A. S.; Padhye, S. B.; Kelkar, A. A.; Patil, R. P.; Chaudhari, R. V.; Puranik, V. G.; Dhaneshwar, N. N.; Tavale, S. S. *Polyhedron* **1996**, *15*, 1931.

(26) Haynes, A.; McNish, J.; Pearson, J. M. *J. Organomet. Chem.* **1998**, *551*, 339.

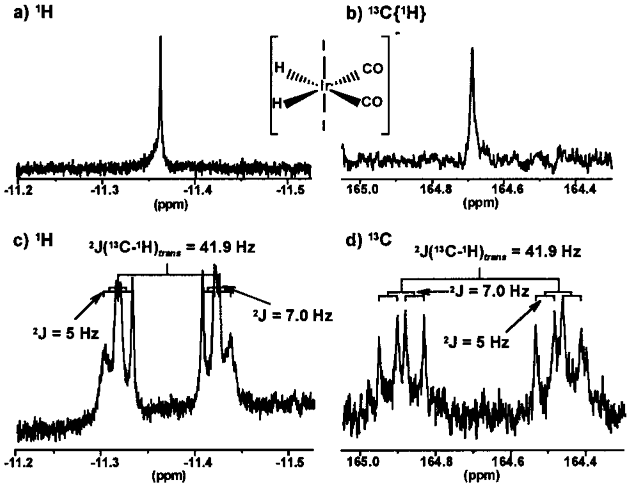


Figure 3. ^1H and ^{13}C NMR spectra of **8c** obtained from a ≈ 3.5×10^{-2} M solution of **2** in CD_3NO_2 under 5.0 MPa of H_2 at 253 K: spectrum a, natural-abundance ^{13}C; spectra b−d, 99%-enriched ^{13}C.

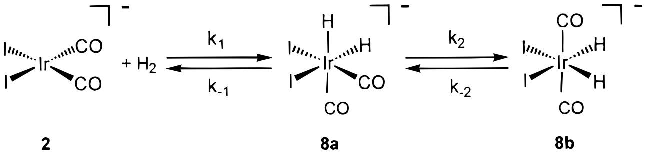
and CO trans) and two complexes with the hydrogens trans and with the carbonyls cis or trans to each other. Two NMR techniques were used to distinguish if the hydrogens were cis or trans: $^2J_{H-D}$ coupling constant[27−29] and longitudinal relaxation time T_1 measurements.[30] For a *cis*-dihydride, the values of $^2J_{H-D}$ are between 2 and 3 Hz, and for a *trans*-dihydride, this value is near 0 Hz. The measured value of 0.9 Hz for **8b** does not permit a clear assignment. The T_1 temperature dependence of the hydride signal of **8b** fitted to the relaxation equations yielded a d_{H-H} value of 2.18 ± 0.01 Å. This value is close to the calculated value of 2.26 Å (based on an average d_{Ir-H} value of 1.60 Å from crystal data) for two cis hydrides. These T_1 NMR data together with the two observed IR ν(Ir−H) stretches confirm the structure of **8b** given in eq 3. We should note that, during the $^2J_{H-D}$ measurement, HD slowly converted to H_2 and D_2. Therefore, it was not necessary in this case to use HD pressure to obtain the $^2J_{H-D}$ value but was sufficient just to pressurize with a mixture of H_2 and D_2. To explain this reaction, we propose that the rearrangement from **8a** to **8b** proceeds via an intermolecular exchange of the hydrides.

At low temperature (253 K), we observed a new H_2 addition complex, **8c** (Figure 3), which disappeared with time at 269 K. The structure of **8c** could be determined in nitromethane using ^1H and ^{13}C NMR spectroscopy. The NMR data are given in Table 1. The $^2J_{^1H-^{13}C_{trans}}$ value of 41.9 Hz indicates the presence of a CO trans to H. Three other coupling constants of 5, 5, and 7 (or 5, 7, and 7) Hz were observed, but as the two homonuclear coupling constants were identical, no assignments could be made. The three dihydride complexes (**8a**−**c**) observed in this study and formed by addition of H_2 to the square-planar complex **2** and further isomerizations all have a cis geometry for their hydride ligands. No dihydrides with a trans geometry could be detected.

A small amount of a new dinuclear compound $[I_2(OC)Ir(\mu_2\text{-}CO)_2(\mu_2\text{-}H)Ir(CO)I_2]^{x-}$ (**9**), was also detected. The values of the chemical shifts and the coupling constants are given in Table 1. The $^2J_{^1H-^{13}C_{trans}}$ value of 23.5 Hz is between the values of the coupling constants found for CO trans to H (42−58 Hz for **8a** and **8c**) and for CO cis to H (4−6 Hz for **4**, **8a**, **8b**, and **8c**). These NMR data are compatible with the structure suggested, having one hydride and two CO bridging ligands.

Very recently, parahydrogen enhanced NMR spectroscopy at low pressure (P = 0.3 MPa, in benzene-d_6) has enabled Hasnip et al. to detect isomers **8a** and **8b** of the *cis*-dihydride $[IrH_2(CO)_2I_2]^-$; however, the third isomer **8c** and the dinuclear species **9** were not observed.[31] Furthermore, in the parahydrogen study, the monohydride complex $[IrH(CO)_2I_3]^-$, which may have formed according to eq 1 in the presence of a small amount of **6**, was observed and a trans CO structure was assigned, different from the cis CO structure of **4** found in nitromethane.

To obtain quantitative kinetic and thermodynamic information about the formation and rearrangement of **8a** and **8b**, we performed a high-pressure (5.5 MPa of H_2) ^1H NMR study at 262 K. The model used to adjust the experimental data is presented in eq 4. The reversibility of these reactions is easily observed by the disappearance of complexes **8a** and **8b** after flushing of the solution with N_2. Equations 5−7 were fitted to



(4)

$$d[\mathbf{2}]/dt = d[H_2]/dt = -k_1[\mathbf{2}][H_2] + k_{-1}[\mathbf{8a}] \quad (5)$$

$$d[\mathbf{8a}]/dt = -k_{-1}[\mathbf{8a}] - k_2[\mathbf{8a}] + k_1[\mathbf{2}][H_2] + k_{-2}[\mathbf{8b}] \quad (6)$$

$$d[\mathbf{8b}]/dt = -k_{-2}[\mathbf{8b}] + k_2[\mathbf{8a}] \quad (7)$$

the time-dependent concentrations of complexes **8a** and **8b**, and the obtained rate constants are $k_1^{262} = (4.42 \pm 0.18) \times 10^{-4}$ $M^{-1}\ s^{-1}$, and $k_{-1}^{262} = (1.49 \pm 0.07) \times 10^{-4}\ s^{-1}$, $k_2^{262} = (2.81 \pm 0.04) \times 10^{-5}\ s^{-1}$, and $k_{-2}^{262} = (5.47 \pm 0.16) \times 10^{-6}\ s^{-1}$. This allows one to determine the two equilibrium constants $K_1^{262} = [\mathbf{8a}]/([\mathbf{2}][H_2]) = 2.97 \pm 0.03\ M^{-1}$ and $K_2^{262} = [\mathbf{8b}]/[\mathbf{8a}] = 5.13 \pm 0.10$, which show that complex **8b** is effectively the more stable of the *cis*-dihydrides $[IrH_2(CO)_2I_2]^-$.

The rhodium(I) square-planar analogue **1** shows no reaction with H_2 at ambient temperature, but modest reactivity could be observed at 350 K using the parahydrogen technique.[31] The higher extent of formation of dihydrides from iridium(I) than from rhodium(I) should favor olefin hydrogenation reactions. We therefore reacted dihydrogen (5.5 MPa) at 327 K with hexene in the presence of small amounts of *cis*-$[Ir(CO)_2I_2]^-$ (10:1 ratio). The reaction was followed by $^{13}C\{^1H\}$ NMR spectroscopy, which revealed that, after 3 days, hexene was quantitatively converted to hexane. During this reaction, no species with bound olefin were detected in either aliphatic or carbonyl ^{13}C-enriched regions. This reaction can compete with olefin carbonylation when **2** is used as the catalyst.

To complete the study of the back-reaction of eq 1, we pressurized the octahedral iridium(III) complex **6** with H_2 and could detect no reaction.

Reactivity of a Mixture of *cis*-$[Ir(CO)_2I_2]P(C_6H_5)_4$ and *cis*-$[Ir(CO)_2I_4]P(C_6H_5)_4$ with H_2. We have shown that Ir(III) monohydride **4** reacts according to eq 1 to form **2** and **6** and that this reaction can be made fully reversible by pressurizing with H_2. We now present the results of a study of the back-

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[27] Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913.
[28] Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.
[29] Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.
[30] Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126.
[31] Hasnip, S.; Duckett, S. B.; Taylor, D. R.; Barlow, G. K.; Taylor, M. J. *Chem. Commun.* **1999**, 889.

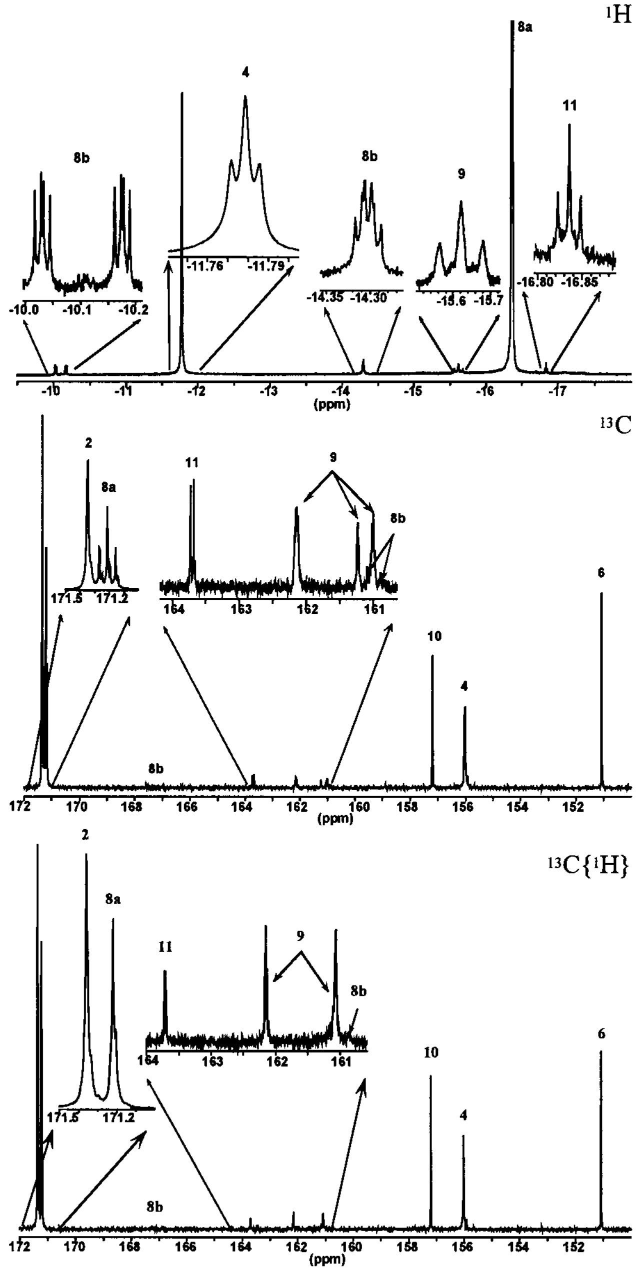

Figure 4. ^{1}H (top), ^{13}C (middle), and ^{13}C{^{1}H} (bottom) NMR spectra of a solution of **2** (2.5×10^{-2} M) and **6** (7.9×10^{-3} M) in CD_3NO_2 under 5.5 MPa of H_2 at 298 K after 29 h.

reaction of eq 1, but with an excess of **2** under the following conditions: a solution containing 2.50×10^{-2} mol L^{-1} of **2** and 7.90×10^{-3} mol L^{-1} of **6** with 5.5 MPa of H_2 in CD_3NO_2. After more than 1 day, the ^{1}H, ^{13}C, and ^{13}C{^{1}H} spectra (Figure 4) show as products the expected hydride **4**, the starting complexes (**2** and **6**), the previously observed complexes (**8a**, **8b**, and **9**) due to the excess of **2** and the two new complexes **10** and **11**. Complex **10** shows one ^{13}C NMR signal at 157.2 ppm and has no hydride ligand, since no $^2J_{^1H-^{13}C}$ coupling constant and no corresponding ^{1}H NMR signal are observed. This complex should contain only two magnetically equivalent CO moieties, and therefore we suggest the formula $[Ir(CO)_2I_3]$. The ^{1}H NMR spectrum of the minor product **11** shows a triplet at -16.8 ppm ($^2J_{^1H-^{13}C} = 5.1$ Hz) and the ^{13}C NMR spectrum a doublet at 163.7 ppm, indicating two equivalent CO ligands and a unique hydride ligand, compatible with the formula $[HIr(CO)_2I_2]$, already suggested for a compound formed under different conditions.[11]

The reactions of the iridium complexes with H_2 and HI are summarized in Scheme 2.

The proposed intermediate **12** was not observed but should be involved in the formation of *fac,cis*-$[HIr(CO)_2I_3]^-$ from *cis*-$[Ir(CO)_2I_2]^-$, *cis*-$[Ir(CO)_2I_4]^-$, and H_2.

Conclusions

With the use of ambient- and high-pressure NMR and IR spectroscopy, the main differences in the catalytic cycles of the carbonylation of olefins in the presence of the iridium complex **2** and in the presence of the rhodium analogue **1** have been presented. Under elevated pressures of CO, **1** and **2** form the corresponding tricarbonyl halides $M(CO)_3I$ by substitution of an iodide by CO, with the equilibrium constants $K_{Ir} \approx 1.8 \times 10^{-3}$ and $K_{Rh} \approx 4 \times 10^{-5}$. The ratio K_{Ir}/K_{Rh} close to 50 shows that, under catalytic conditions (a few megapascals), only complex **1** remains in the anionic form, while a major amount of the iridium analogue **2** is converted to a neutral species.

The oxidative addition reactions of HI with **1** and **2** give two monohydrides of different geometries, *mer,trans*-$[HRh(CO)_2I_3]^-$ (**3**) and *fac,cis*-$[HIr(CO)_2I_3]^-$ (**4**), respectively. Both hydrides are unstable at ambient temperature and form, within minutes for Rh and within hours for Ir, the corresponding *cis*-$[M(CO)_2I_2]^-$ (**1** or **2**) and $[M(CO)_2I_4]^-$ (**5** or **6**) species and H_2.

Applying a high pressure of H_2 (H_2 is produced in situ during the carbonylation reaction) at ambient temperature to a nitromethane solution containing complex **2** first formed the *cis*-dihydride **8a**, followed by intermolecular isomeration to form **8b** and the newly observed complex **8c**. However, no similar H_2 addition products of the rhodium analogue were observed. Very small quantities of H_2 addition products were previously observed by Hasnip et al. in benzene at 350 K. These major differences between rhodium and iridium help to explain their different activities in the olefin carbonylation catalytic cycle. Applying a pressure of H_2 to a solution containing **6** and an excess of **2** forms, in addition to the already described complexes **4**, **8a**, **8b**, and **9**, the two new complexes **10** and **11**. All these observations are summarized in Scheme 2.

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Supporting Information Available: Experimental concentrations of complexes **8a** and **8b** as functions of time, obtained from a solution of **2** under 5.5 MPa of H_2 at 262 K (Table S1), IR spectra of solutions of *cis*-$[Ir(CO)_2I_2]^-$ and *cis*-$[Rh(CO)_2I_2]^-$ in $CHCl_3$ under different CO pressures at ambient temperature (Figure S1),^{1}H NMR spectra of **8b** (H_2 addition product) and **8b*** (HD addition product), obtained from a solution of **2** in CD_3NO_2 under 3.2 MPa of HD at 298 K, showing the $^2J_{H-D}$ coupling constant of **8b*** (Figure S2, top), ^{1}H NMR T_1 of the hydride **8b** as a function of temperature, obtained from a solution of **2** in CD_2Cl_2 under 5.0 MPa of H_2 (Figure S2, bottom), experimental and adjusted concentrations of complexes **8a** and **8b** as functions of time, obtained from a solution of **2** under 5.5 MPa of H_2 at 262 K (Figure S3), NMR spectra of **9**, obtained from a solution of *cis*-$[Ir(^{13}CO)_2I_2]^-$ in CD_3NO_2 under 5.5 MPa of H_2 at 298 K (Figure S4), and NMR spectra of a *cis*-$[Ir(^{13}CO)_2I_2]^-$/hexene solution in CD_3NO_2 under 5.5 MPa of H_2 at 327 K after 5 min, 5 h, and 3 days (Figure S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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