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Kinetics of Molecular Hydrogen Activation by Cobaltrhodium Heptacarbonyl

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The kinetics of the activation of molecular hydrogen by the coordinatively unsaturated mixed-metal carbonyl $CoRh(CO)_7$ (1) were studied at temperatures between 276 and 294 K, hydrogen pressures between 0.05 and 0.20 MPa, and carbon monoxide pressures between 0.20 and 0.80 MPa in *n*-hexane as solvent. The reactions were run under isothermal and isobaric conditions, and the extent of the reaction was followed by high-pressure in situ infrared spectroscopy. The immediately observable products of the activation of molecular hydrogen were $HCo(CO)_4$ (2) and $Rh_4(CO)_{12}$ (4), but eventually the dinuclear carbonyl $Co_2(CO)_8$ (5) began to form via recombination of cobalt carbonyl hydrides. Under these conditions, the reaction was found to be first order in 1, first order in hydrogen, and zero order in carbon monoxide. The experimentally determined parameters of activation are $E_a = 23 \pm 2$ kJ/mol (5.6 ± 0.5 kcal/mol), $\Delta S^{\ddagger} = -169 \pm 13$ J/(mol K) (-40 ± 3 cal/(mol K)), and $\Delta H^{\ddagger} = 21 \pm 2$ kJ/mol (5.0 ± 0.5 kcal/mol). It is concluded on the basis of the orders of reaction that activation occurred through the bimolecular reaction of molecular hydrogen with $CoRh(CO)_7$ without the prior dissociation of a carbonyl ligand. Further, the magnitude of the activation parameters, particularly the low enthalpy of activation, suggests that this activation occurred via oxidative addition at a single metal site, in all probability at the rhodium, generating a transient rhodium dihydride species $\{(CO)_4CoRhH_2(CO)_3\}$, followed by elimination of $HCo(CO)_4$ (2). The observed $Rh_4(CO)_{12}$ (4) then arises via the rapid recombination of the rhodium carbonyl species $\{HRh(CO)_3\}$ (3).

Introduction

The activation of molecular hydrogen[2] by soluble mononuclear metal complexes, via the oxidative addition at a single metal center,[3] has been the subject of intensive study.[4] An important characteristic of hydrogen activation, evident in many cases, is the prior dissociation of a coordinated ligand. The dissociation of a ligand is necessary to generate a coordinatively unsaturated metal center (often in extremely low concentrations) at which the oxidative addition of hydrogen can occur. Representative examples of the prior dissociation of a ligand before addition of hydrogen include $Ru(CO)_2(PPh_3)_3$,[5a] $IrCl(CO)(PMe_2Ph)_3$,[5b] and $Os(CO)_3(PPh_3)_2$.[5c] The generation of a coordinatively unsaturated complex is a general phenomenon and central to many organometallic reaction schemes:[6]

$$ML_n \rightleftharpoons ML_{n-1} + L \tag{1}$$

Of course, the activation of molecular hydrogen is not restricted to mononuclear metal complexes alone. Higher nuclearity complexes, in particular homometallic dinuclear carbonyls,[7] homometallic dinuclear complexes,[8] and heterobimetallic dinuclear complexes[9] but also clusters,[10] have been shown to readily dissociate molecular hydrogen. In the slightly more well-defined case of activation by dinuclear complexes, the activation has been formally classified as an oxidative addition to a dinuclear center.[4b] A relevant example, in the context of the present problem with $CoRh(CO)_7$ (1), would be hydrogen activation by $Co_2(CO)_8$. Once again, a prerequisite for such activation is the dissociation of a ligand (eq 2). In the case of activation by

$$M_1M_2L_n \rightleftharpoons M_1M_2L_{n-1} + L \tag{2}$$

$Co_2(CO)_8$, the formation of a transient species $\{Co_2(CO)_7\}$ has been proposed primarily on the basis of kinetic arguments.[7d] Evidence for the formation of $\{Co_2(CO)_7\}$ is also available from argon matrix studies.[7e]

For activation of hydrogen in the presence of coordinatively saturated complexes, the implications of the formation of a coordinatively unsaturated species such as

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shown in eqs 1 and 2 cannot be over emphasized. If the activation of molecular hydrogen proceeds through an intermediate in equilibrium with the starting coordinatively saturated species, which often is the case, then it can be shown[11] that the experimentally measured apparent activation energies E_{app} are larger than the true activation energies E_a (eq 3) by a term $\Delta_r H°$ where the latter is the enthalpy of reaction for the formation of the (usually) unobserved coordinately unsaturated complex.

$$E_{\text{app}} = E_a + \Delta_r H° \qquad (3)$$

The coordinately unsaturated heterometallic dinuclear carbonyl $CoRh(CO)_7$ (1) has previously been shown to activate molecular hydrogen under mild conditions, i.e., 293 K, 0.2 MPa hydrogen, and 0.2 MPa carbon monoxide in *n*-hexane as solvent.[12] The reaction was tentatively believed to produce $HCo(CO)_4$ (3) as the immediate products (eq 4). Then, after the initial activation of

$$\underset{1}{CoRh(CO)_7} + H_2 \rightleftharpoons \underset{2}{HCo(CO)_4} + \underset{3}{\{HRh(CO)_3\}} \qquad (4)$$

$$\underset{1}{CoRh(CO)_7} + \tfrac{1}{2}H_2 \rightleftharpoons \underset{2}{HCo(CO)_4} + \underset{4}{\tfrac{1}{4}Rh_4(CO)_{12}} \qquad (5)$$

molecular hydrogen, the species $\{HRh(CO)_3\}$ (3) was assumed to rapidly undergo recombination to form the initial observable products 2 and 4 according to the reaction shown in eq 5. This reaction is reversible as has been shown by mixing 2 and 4.[14]

Depending on both the concentrations of hydrogen and carbon monoxide present in the system, $Co_2(CO)_8$ is readily formed from $HCo(CO)_4$, and the kinetics of this reaction have been well documented.[15] Furthermore, the reaction shown in eq 6 represents a readily attained and measurable equilibrium system.

$$\underset{2}{2HCo(CO)_4} \rightleftharpoons \underset{5}{Co_2(CO)_8} + H_2 \qquad (6)$$

Due to the coordinative unsaturation of the complex 1, the activation of molecular hydrogen was tentatively believed to proceed without the prior dissociation of a carbonyl ligand. To test this hypothesis and to strengthen the arguments for the existence of $\{HRh(CO)_3\}$, appropriate well-defined kinetic experiments were performed. This paper examines the 1, hydrogen, carbon monoxide, and temperature dependencies of the forward rate of the hydrogen reaction shown in eq 5.

Experimental Section

General Information. All solution preparations and transfers were carried out under a nitrogen (99.995%, Pan Gas, Luzern) or argon (99.998%, Pan Gas, Luzern) atmosphere using standard schlenk techniques.[16] $Co_2Rh_2(CO)_{12}$ (6) was prepared from $NaCo(CO)_4$ and $[Rh(CO)_2Cl]_2$ in *n*-hexane.[17] Elemental analysis of recrystallized 6 gave 21.7% carbon and 31.1% rhodium (courtesy Ciba-Geigy AG, Basel). The calculated values are 21.8% carbon and 31.2% rhodium. $CoRh(CO)_7$ (1) was prepared from 6 in *n*-hexane under at least 0.2 MPa carbon monoxide.[17] Puriss quality *n*-hexane (Fluka AG, Buchs) was refluxed from sodium potassium alloy under nitrogen. Reactions were carried out with carbon monoxide produced at the ETH-Z (and stored in aluminum cylinders) and 99.999% hydrogen (Pan Gas, Luzern).

Kinetic studies were performed in a 1.5-L stainless steel (SS316) autoclave (Büchi-Uster, Switzerland) that was connected to a high-pressure infrared cell. The autoclave (to 22.5 MPa) was equipped with a packed magnetic stirrer with six-bladed turbines in both the gas and liquid phases (Autoclave Engineer, Erie) and was constructed with a heating/cooling mantel. A high-pressure membrane pump (Model DMK30, Orlita AG, BRD) with a maximum rating of 32.5 MPa and 3 L/h flow rate was used to circulate the *n*-hexane solutions from the autoclave to the high-pressure IR cell and back to the autoclave via jacketed $^1/_8$-in. (SS316) high-pressure tubing (Autoclave Engineers, Erie). The entire system (autoclave, transfer lines, and infrared cell) was cooled by using a Lauda RX20 (Austria) cryostat and could be maintained isothermal ($\Delta T \pm 0.5$ °C) in the range −20 to 40 °C. Temperature measurements were made at the cryostat, autoclave, and IR cell with Pt-100 thermoresistors. The necessary connections to vacuum and gases were made with $^1/_4$-in. (SS316) high pressure tubing (Autoclave Engineers), and both 0.3000-MPa (accuracy to 0.1%) and 1.000-MPa piezocrystals were used for pressure measurements (Keller AG, Wintertur). The entire system was gastight under vacuum as well as at 20.0 MPa, the maximum operating pressure.

The high-pressure infrared cell was constructed at the ETH-Z of SS316 steel and could be heated or cooled. The NaCl (Korth, BRD), KBr (Korth, BRD), and silicon (ETH-Z) windows used had dimensions of 40-mm diameter by 15-mm thickness. Two sets of viton and silicone gaskets provided sealing, and Teflon spacers were used between the windows. The construction of the flow-through cell[18a] is a variation on a design due to Noack[18b] and differs in some respects from other high-pressure infrared cells described in the literature (for a review see Whyman[18g]). The high-pressure cell was situated in a Perkin-Elmer PE983 infrared spectrophotometer equipped with a Model 3600G data station. Spectra were recorded with a 0.22-mm slit width. Details of the equipment and IR cell can be found elsewhere.[19]

The tetranuclear carbonyl 6 has absorbances at 2074, 2064, 2059, 2038, 2030, 1910, 1885, 1871, and 1858 cm^{-1} in the infrared region,[20] and the dinuclear carbonyl 1 has absorbances[17] at 2134, 2064, 2058, 2049, 2006, 1977, and 1955 cm^{-1}. The determined extinction coefficient at 1955 cm^{-1} for 1 is $\epsilon(1955) = 2950\ l$/mol cm with use of a slit width of 0.22 mm. The extinction coefficient of *n*-hexane at 1138 cm^{-1} is $\epsilon(1138) = 2.353$ L/mol cm, also at a slit width of 0.22 mm. With the Lambert–Beer law, the in situ concentration of 1 in units of mole fractions were directly measured in the low-pressure kinetic experiments with a high degree of accuracy (eq 7), where A is the absorbance. When eq 7 was applied, the mole fractions of dissolved gases were understood to approach zero.[21]

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[11] If we substitute $[ML_{n-1}] = [ML_n]K_x/[L]$ for the equilibrium concentration of the unsaturated species into the bimolecular rate expression for hydrogen activation, rate $= k[ML_{n-1}][H_2]$, and take the partial derivative $(\partial \ln k_{\text{obs}}/\partial(1/T))$, eq 3 results.

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[21] (a) In general, concentrations in moles/liter are not directly measurable quantities in most high-pressure IR cells due to cell expansion and since the volumetric properties of most hydrocarbon solvents under finite dissolved gas concentrations are rarely known. (b) Further, we recognize that the use of mole fractions in kinetics studies is absolutely acceptable, and is in fact that norm in high-pressure solution kinetics.

$$x(\mathrm{CoRh(CO)_7}) = A(1955)\,\epsilon(1138)/A(1138)\,\epsilon(1955) \qquad (7)$$

Kinetic Studies. General Procedures. $Co_2Rh_2(CO)_{12}$ (**6**, 33 mg) was dissolved in 200 mL of *n*-hexane (0.25 mM or 3.25 × 10^{-5} mol fraction) in a Schlenk tube under a nitrogen atmosphere, and the solution was transferred via a $^1/_8$-in. inlet line into the evacuated and thermostated autoclave. Depending on the system temperature, the total pressure in the autoclave was P_T = 0.01–0.03 MPa, the vapor pressure of *n*-hexane plus a low partial pressure of nitrogen. During stirring (200 rpm), a partial pressure (P_{CO} = 0.20 MPa) of carbon monoxide was added to the system, and the reaction of **6** with carbon monoxide to $CoRh(CO)_7$ (**1**, eq 8) was allowed to go to completion (≥97%) over the next

$$\underset{\mathbf{6}}{\mathrm{Co_2Rh_2(CO)_{12}}} + 2\mathrm{CO} \rightleftharpoons 2\underset{\mathbf{1}}{\mathrm{CoRh(CO)_7}} \qquad (8)$$

30–60 min.[22,23] During this time, the high-pressure membrane pump continuously circulated the *n*-hexane solution from the autoclave to the high-pressure infrared cell and back to the autoclave. Full in situ infrared spectra were taken from 2200 to 1800 cm^{-1} and from 1300 to 1100 cm^{-1} at the end of reaction. Little to no additional noise could be identified in the in situ spectra as the solution was pumped (10 cm/s) through the high-pressure infrared cell.

Kinetics. Variation of CO. Experiments with four different carbon monoxide partial pressures, P_{CO}, were made to determine the effect of CO on the kinetics of the forward reaction (eq 5). These partial pressures were P_{CO} = 0.20, 0.40, 0.60, and 0.80 MPa. At a time t = 0, with the membrane pump running and with a CO partial pressure above the $CoRh(CO)_7$/*n*-hexane solution, hydrogen to a partial pressure P_{H_2} = 0.20 MPa was added to the system. The in situ measured absorbance at 1955 cm^{-1} was then measured every 10 s for 60 min. At the end of the 60 min, full in situ spectra were recorded from 2200 to 1800 cm^{-1} and from 1300 to 1100 cm^{-1}. The temperature of the system in each experiment was 276.0 K.

Kinetics. Variation in Hydrogen. Experiments at four different hydrogen partial pressures, P_{H_2}, were performed to determine the reaction order of dissolved hydrogen in the kinetics of reaction (eq 5). The partial pressure of carbon monoxide in each experiment was the same; P_{CO} = 0.20 MPa. At a time t = 0, with the membrane pump running and with a partial pressure P_{CO} = 0.20 MPa in the system, hydrogen to a pressure P_{H_2} = 0.05, 0.10, 0.15 or 0.20 MPa was added. The in situ measured absorbance at 1955 cm^{-1} was then measured every 10 s for 60 min. At the end of the 60 min, full in situ spectra were recorded from 2200 to 1800 cm^{-1} and from 1300 to 1100 cm^{-1}. The temperature of the system in each experiment was 276.0 K. Literature data[24] for the solubility of hydrogen in *n*-hexane were analyzed for the temperature dependence according to Jonah.[25] The necessary physical properties of *n*-hexane, including the saturated vapor pressure of *n*-hexane, can be found in the literature.[26] The final form of the temperature dependent Henry constant is eq 9, where H is the Henry constant at low pressures, and P_{sat} is the saturated vapor pressure of *n*-hexane.

$$\ln (H/P_{sat}) = -4.96 + 4050/T \qquad (9)$$

Kinetics. Variation of Temperature. To determine the activation energy E_a for reaction (eq 5), experiments were conducted at four different temperatures. These temperatures were T = 293.8, 289.6, 282.1, and 276.0 K. At the beginning of each experiment, the carbon monoxide partial pressure was P_{CO} = 0.20 MPa above the $CoRh(CO)_7$ (**1**)/*n*-hexane solution. At a time t = 0, with the solution circulating through the high pressure infrared cell, P_{H_2} = 0.20 MPa was added to the system. The in situ measured absorbance at 1955 cm^{-1} was then measured every 10 s for 60 min. At the end of the 60 min, full in situ spectra were recorded from 2200 to 1800 cm^{-1} and from 1300 to 1100 cm^{-1}.

In terms of short-term transient effects, (a) approximately 15 s was required to achieve the pressure jump ΔP ($\Delta P = P_i$) in the stirred autoclave, (b) approximately 30 s was required before the solution was essentially saturated with dissolved gas, and (c) a 30–40-s delay existed between the time at which events in the stirred autoclave occurred and the time at which the corresponding event could be measured at the spectrophotometer. The experimentally measured overall mass-transfer coefficient, K_La, for hydrogen into *n*-hexane in the present apparatus at 200 rpm was K_La = 0.1/s. This was determined by using the method of Deimling.[27] The effect of the transient effects on the quality of the kinetic data obtained for pseudo-first-order reactions with half-lives $\tau \geq 4$ min was considered negligible. This question of transient effects as well as the residence time distributions in the stirred autoclave with a recycle loop have been considered in detail elsewhere.[19]

Results

Effect of Carbon Monoxide. The concentration of $CoRh(CO)_7$ (**1**) as a function of the partial pressure of carbon monoxide in the system and as a function of time for the first 8 min of reaction is shown in Figure 1.

During these first 8 min, 40–50% conversion of **1** has occurred in all experiments. The variation in carbon monoxide partial pressure used, 0.20–0.80 MPa, had little or no measurable effect on the initial rate of disappearance of **1**, certainly not in the first 4 min of reaction. Hence, dissolved carbon monoxide was not involved in a preequilibrium with **1** before hydrogen activation and therefore a zero-order carbon monoxide dependence can be deduced (eq 10).

$$\mathrm{d[CoRh(CO)_7]}/\mathrm{d}t \propto [\mathrm{CO}]^0 \qquad (10)$$

At longer reaction times a measurable inverse carbon monoxide rate dependence for the disappearance of **1** arises. Higher carbon monoxide partial pressures lower the net disappearance of **1**. Also, at these longer reaction times, the slow formation of $Co_2(CO)_8$ (**5**) can be identified in the in situ spectra. The higher partial pressures of carbon monoxide decrease the rate of formation of **5**.

These results can be explained in terms of product inhibition. If the slow formation of $Co_2(CO)_8$ did not occur (i.e., if a higher hydrogen pressure were used), then a stable and measurable equilibrium between the carbonyl species in eq 5 should develop. Indeed, in these carbon monoxide experiments at a fixed 0.2 MPa of hydrogen, only 55–70% conversion had occurred after 60 min. As already mentioned the reaction is reversible.[13] Therefore, at high conversions of **1**, the measured net rate of disappearance of **1** becomes controlled by the successful recombination rate of $HCo(CO)_4$ (**2**) to form **5**, which is carbon monoxide dependent.[15]

Effect of Hydrogen. The concentrations of **1** as a function of the partial pressure of hydrogen and as a function of time for the first 8 min of reaction are shown in Figure 2. During these first 8 min, under 0.2 MPa of carbon monoxide and at 276 K, 23–50% conversion of **1** has occurred. The variation in hydrogen partial pressure used, from 0.05 to 0.20 MPa, has a pronounced effect on the rate of disappearance of $CoRh(CO)_7$. It should be noted that 43, 52, 55, and 55% conversion has occurred in these experiments at 0.05, 0.10, 0.15, and 0.20 MPa of hydrogen, respectively, after 60 min of reaction.

The data presented in Figure 2 for the overall reaction (eq 5) were analyzed by assuming that the measured rate of hydrogen activation is first order in the concentration

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(22) The kinetics of the forward reaction have been studied.[19]

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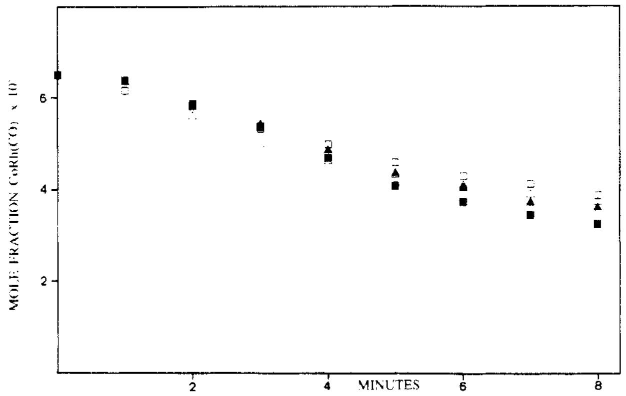

Figure 1. Effect of carbon monoxide on the conversion of $CoRh(CO)_7$ at 276.0 K with 0.20 MPa of hydrogen: ■, 0.20 MPa of CO; ▲, 0.40 MPa of CO; △, 0.60 MPa of CO; □ 0.80 MPa of CO.

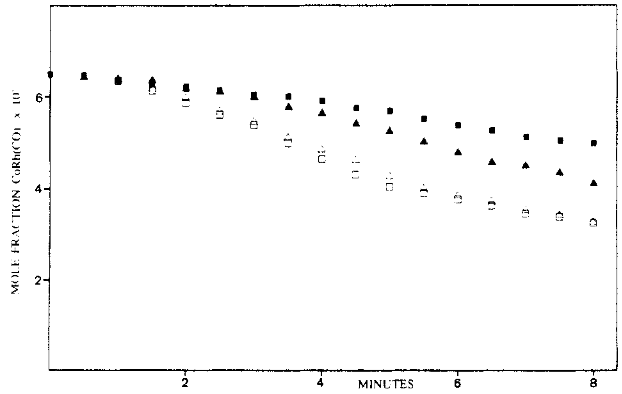

Figure 2. Effect of hydrogen on the conversion of $CoRh(CO)_7$ at 276.0 K with 0.20 MPa of carbon monoxide: ■, 0.05 MPa of H_2; ▲, 0.10 MPa of H_2; △, 0.15 MPa of H_2; □, 0.20 MPa of H_2.

of the coordinatively unsaturated complex 1, and *n*th order in the concentration of hydrogen. The concentration of carbon monoxide need not be included in any overall rate expression since the reaction order n_{CO} was shown to be zero in the previous section. Further, total pressure effects can be neglected.[28] With the above conditions, rate expressions can be written where the concentration of dissolved hydrogen remains a constant for the duration of each reaction:

$$d[CoRh(CO)_7]/dt = -k[CoRh(CO)_7][H_2]^n \quad (11)$$

$$\ln([CoRh(CO)_7]_t/[CoRh(CO)_7]_0) = -k[H_2]^n t \quad (12)$$

$$\ln(k_{obs}(T)) = \ln k(T) + n \ln [H_2] \quad (13)$$

Transforming the data presented in Figure 2 according to eq 12 results in the data presented in Figure 3. The transformed data, specifically the linear slopes shown in Figure 3, confirm that the overall reaction (eq 4) is indeed first order in the concentration of the dinuclear carbonyl 1.[29] The experimentally determined rate constants k_{obs} for the overall reaction are $(5.9 \pm 0.4) \times 10^{-4}$, $(1.08 \pm 0.07) \times 10^{-3}$, $(1.67 \pm 0.11) \times 10^{-3}$, and $(1.87 \pm 0.16) \times 10^{-3}$ s^{-1} at 0.05, 0.10, 0.15, and 0.20 MPa of hydrogen, respectively.

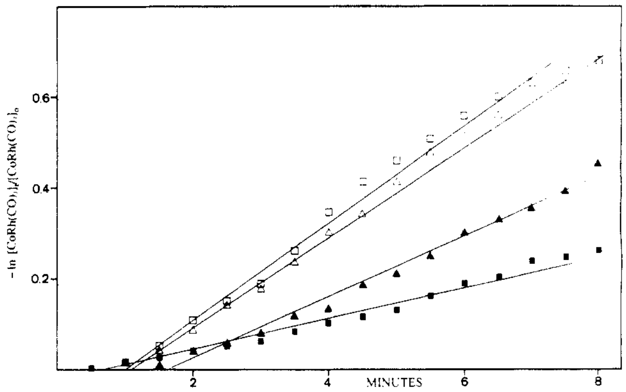

Figure 3. Effect of hydrogen on the rate constant k_{obs} for the reaction of hydrogen with $CoRh(CO)_7$ at 276.0 K with 0.20 MPa of carbon monoxide: ■, 0.05 MPa of H_2; ▲, 0.10 MPa of H_2; △, 0.15 MPa of H_2; □, 0.20 MPa of H_2.

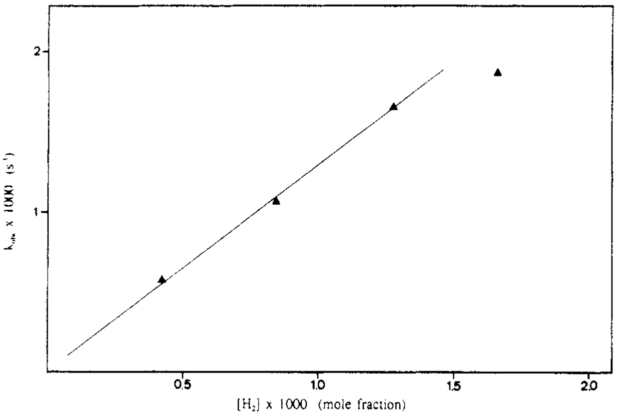

Figure 4. Observed rate constant k_{obs} as a function of the hydrogen concentration at 276.0 K under 0.20 MPa of carbon monoxide.

The mole fractions of dissolved hydrogen at 0.05, 0.10, 0.15, and 0.20 MPa are 4.25×10^{-4}, 8.49×10^{-4}, 1.27×10^{-3}, and 1.74×10^{-3}, respectively. A plot of the observed rate constant k_{obs} versus the liquid-phase concentration of dissolved hydrogen is presented in Figure 4. It is important to observe that to rather good accuracy, the extrapolated data proceed through the origin. The rate constant is $k(276.0\,K) = 1.11 \pm 0.09$ s^{-1} mole fraction^{-1}. The experimentally determined order in hydrogen taken from the four data sets is $n_{H_2} = 0.87$.

Effect of Temperature. The measured concentration of 1 as a function of the reaction temperature and as a function of time for the first 4 min of reaction is shown in Figure 5. During these first 4 min, under 0.2 MPa of carbon monoxide and 0.2 MPa of hydrogen, approximately 40–50% conversion of $CoRh(CO)_7$ occurred. The variation in the reaction temperature, 276.0–293.8 K, has only a small effect on the rate of disappearance of 1, indicating a low activation energy. Under these reaction conditions, specifically under a hydrogen partial pressure of 0.20 MPa, quantitative reaction of $CoRh(CO)_7$ was not observed in any of these reactions at the end of 60 min.

Again, the rate data (i.e., Figure 5) for the overall reaction can be analyzed according to eq 12. The trans-

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[28] Two parameters, the mole fraction dissolved hydrogen x_{H_2} and the total system pressure P_T are being varied simultaneously in these experiments. However, the term $\int \Delta V^{\ddagger}\, dP$ will be justifiably neglected in these experiments over the very limited pressure range P = 0–1.0 MPa. It should be recognized that a large activation volume $\Delta V^{\ddagger} = -20$ mL/mol for the oxidative addition of molecular hydrogen in solution to *trans*-$IrCl(CO)(PPh_3)_2$ has been measured: Schmidt, R.; Geis, M.; Kelm, H. *Z. Phys. Chem. (Munich)* **1974**, *92*, 223.

[29] A first-order rate dependence due to homolysis of the Co–Rh bond as the initial step in these rapid hydrogen activation experiments can be discounted. Indeed hours, or even days and not minutes are required before spectroscopically significant quantitites of the thermodynamically favored homometallic species $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ rise in solutions of $CoRh(CO)_7$ and CO alone at $T \leq 293$ K.

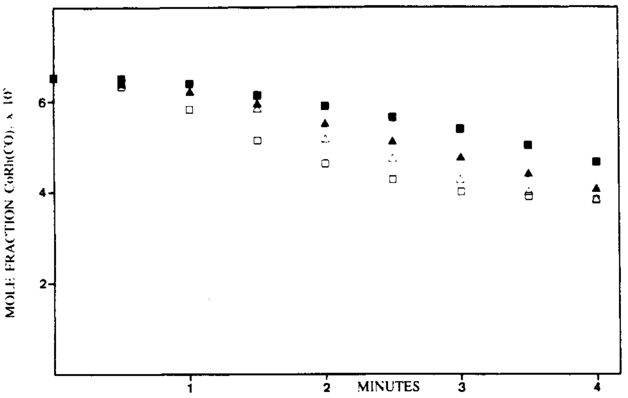

Figure 5. Effect of temperature on the conversion of $CoRh(CO)_7$ under 0.20 MPa of carbon monoxide and 0.20 MPa hydrogen: ■, 276 K; ▲, 282.1 K; △, 289.6 K; □, 293.8 K.

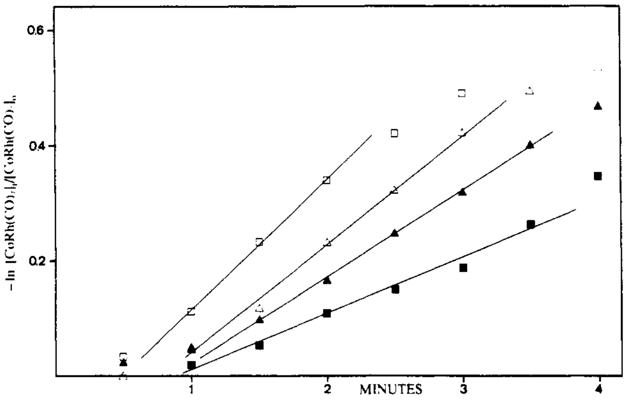

Figure 6. Effect of temperature on the rate constant k_{obs} for the reaction of hydrogen with $CoRh(CO)_7$ under 0.20 MPa of carbon monoxide: ■, 276 K; ▲, 282.1 K; △, 289.6 K; □, 293.8 K.

formed rate data are presented in Figure 6. The resulting numerical values of the rate constants k_{obs} are (3.77 ± 0.25) × 10^{-3}, (3.10 ± 0.21) × 10^{-3}, (2.49 ± 0.15) × 10^{-3}, and (1.87 ± 0.16) × 10^{-3} s^{-1} at 293.8, 289.6, 282.1, and 276.0 K, respectively. In Figure 6 the delay time of 40 s between events in the reactor and the time at which this event arrives at the spectrophotometer is clearly seen. No attempt has been made to compensate for this effect.

The solubility of hydrogen in *n*-hexane in these experiments was 1.86 × 10^{-3}, 1.82 × 10^{-3}, 1.78 × 10^{-3}, and 1.74 × 10^{-3} mole fraction at 293.8, 289.6, 282.1, and 276.0 K. The resulting numerical values of the rate constants k are 2.03, 1.70, 1.40, and 1.07 s^{-1} mole $fraction^{-1}$. Figure 7 shows the natural logarithm of the rate constants k versus reciprocal temperature, i.e., an Arrhenius plot. The apparent activation energy is $E_{app} = 23 \pm 2$ kJ/mol. The determined enthalpy of activation and entropy of activation were $\Delta H^{\ddagger} = 21 \pm 2$ kJ/mol and $\Delta S^{\ddagger} = -169 \pm 13$ J/(mol K), respectively.

Spectra. A typical in situ spectrum of the reaction solution, containing the starting complex 1 (2134, 2064, 2058, 2049, 2006, 1977, 1955 cm^{-1}) as well as the products 2 (2116, 2070, 2053, 2030, 1996, 1957, 1934 cm^{-1}[30]) and $Rh_4(CO)_{12}$ (4; 2074, 2068, 2043, 1885 cm^{-1}[31]) is shown in Figure 8. This spectrum was taken after approximately 15 min of reaction under 0.20 MPa of carbon monoxide and 0.20 MPa of hydrogen.

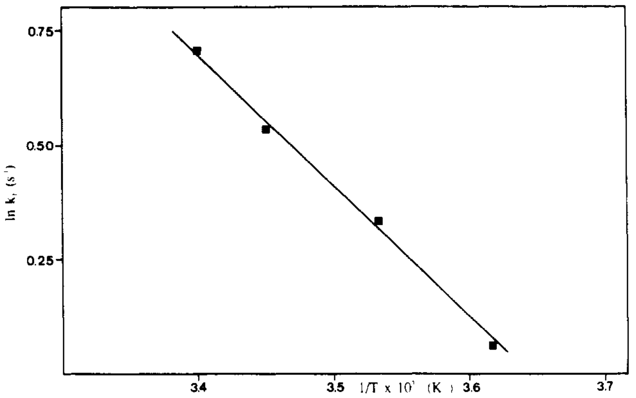

Figure 7. Arrhenius plot and activation energy for the reaction of hydrogen with $CoRh(CO)_7$ under 0.20 MPa of carbon monoxide.

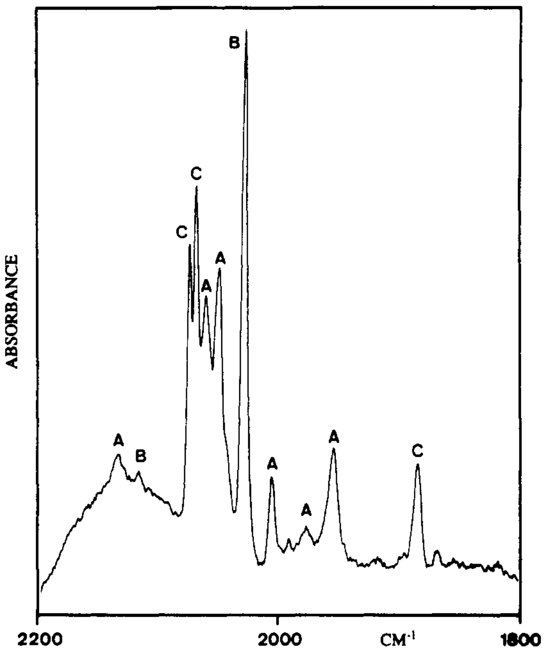

Figure 8. In situ infrared spectrum of reaction products after 15 min of reaction: A, $CoRh(CO)_7$; B, $HCo(CO)_4$; C, $Rh_4(CO)_{12}$.

Discussion

Experimentally, during the initial phase of the reaction (eq 5), the overall rate of disappearance of $CoRh(CO)_7$ (1) was found to be first order in the concentration of 1, first order in the concentration H_2, and zero order in the dissolved concentration of carbon monoxide. These orders of reaction are consistent with the bimolecular reaction of molecular hydrogen with 1 without the prior dissociation of a carbonyl ligand. Hence, the measured activation energy probably represents the true E_a for hydrogen activation and is not an activation energy masked by a preequilibrium.[32]

Concerning the experimentally determined entropy and enthalpy of activation, it is first meaningful to consider

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[30] Noack, K. *Helv. Chim. Acta* **1964**, *47*, 1555.

[31] Beck, W.; Lottes, K. *Chem. Ber.* **1961**, *94*, 2578.

[32] It is not clear if an activated process involving the *semibridged* carbonyls might be required if hydrogen activation occurs on the square-planar rhodium, i.e., semibridge carbonyl to terminal carbonyl. If such a process were required, it would not be rate limiting since the ^{13}C NMR shows only one signal and thus total fluxionality above −80 °C.[17] The other possibility is an effect on the measured activation energy through a contribution from $\Delta H°$ (semibridge → terminal); however, this difference is probably negligible. Indeed, for the *bridged* and terminal forms of $Co_2(CO)_8$, a free energy difference of less than 0.3 kcal/mol was found. (a) Noack, K.; *Spectrochim. Acta* **1963**, *19*, 1925. (b) Bor, G. *Spectrochim. Acta* **1963**, *19*, 2065.

the two realistic mechanisms for hydrogen activation that could arise with $CoRh(CO)_7$. These mechanisms are (a) the oxidative addition of hydrogen to the square-planar rhodium, generating a rhodium dihydride intermediate $\{(CO)_4CoRhH_2(CO)_3\}$, followed by reductive elimination of $HCo(CO)_4$, and (b) a concerted four-center addition at both rhodium and cobalt. Indeed, in principle more than one mechanism exists for addition to a dinuclear complex.[33] It can be shown that both of these models (a and b) are consistent with the experimentally determined reaction orders.[34]

The entropy of activation $\Delta S^{\ddagger} = -169$ J/(mol K) (−150 J/(mol K) if molar units are used instead of mole fractions) is as large as those values experimentally determined for the oxidative addition of hydrogen to some mononuclear rhodium and iridium complexes having bulky bidentate phosphine ligands.[35] An example is hydrogen activation on $[Ir(diphos)_2]^+$, where an entropy of activation of $\Delta S^{\ddagger} = -155$ J/(mol K) (molar units) has been observed.[35b] The magnitude of the entropy of activation in the present case suggests severe translational and rotational restrictions in the transition state. Indeed, calculations support an upper limit of $\Delta S^{\ddagger} = -125$ J/(mol K) for bimolecular reactions in which all translational and rotational degrees of freedom have been lost for the incoming ligand[36] and for which there are no other secondary effects such as solvent effects. In the present case, the large entropy of activation could be due to the stearic interference of the two semibridging carbonyls[17] if mechanism (a) is valid or due to the intrinsic requirements of a four-center mechanism (b).

However, the measured enthalpy of activation $\Delta H^{\ddagger} = 21$ kJ/mol is typical for hydrogen addition at a single coordinatively unsaturated mononuclear metal center where values of 10–45 kJ/mol can be anticipated.[37] In contrast, enthalpies of activation between 50 and 70 kJ/mol are observed for 2M or M_2 transition states where a concerted four-center mechanism is often suggested.[38] One would expect a higher enthalpy of activation for a concerted four-center dinuclear transition state since a large number of bonds are being formed and broken simultaneously.[39]

Therefore, on the basis of the above activation parameter arguments, we tentatively assign the present case of hydrogen activation to mechanism (a), i.e., the oxidative addition of hydrogen to rhodium thus generating a transient rhodium dihydride $\{(CO)_4CoRhH_2(CO)_3\}$, followed by elimination of $HCo(CO)_4$. A further relevant nonkinetic argument in favor of mechanism (a) concerns the known heterosite reactivity of mixed cobalt–rhodium carbonyls in general and $CoRh(CO)_7$ in specific. Indeed, Horváth[40] has shown that numerous nucleophiles react preferentially at the rhodium site. Heterosite reactivity has been shown in numerous other higher nuclearity metal complexes.[41]

It is instructive to compare the present case of hydrogen activation by $CoRh(CO)_7$ and the formation of $\{(CO)_4CoRhH_2(CO)_3\}$, with hydrogen activation by the iridium complexes $Ir(CO)(PPh_3)_2X$ ($X = GeR_3, SiR_3$) where the iridium dihydride intermediates $IrH_2(CO)(PPh_3)_2X$ have been observed. In the latter, the oxidative addition of hydrogen has been shown to occur on the coordinatively unsaturated iridium atom followed by cleavage of the metal–metalloid bond, yielding the corresponding germanium and silicon hydrides.[42]

This kinetic study provides further convincing arguments in favor of the transient species $\{HRh(CO)_3\}$. Since the rhodium site in $CoRh(CO)_7$ is coordinately unsaturated and since the reaction has simple bimolecular kinetics, the generation of $\{HRh(CO)_3\}$ by elimination of $HCo(CO)_4$ appears certain (the generation of $HRh(CO)_4$ by the elimination of $\{HCo(CO)_3\}$ seems highly improbable). The observed product $Rh_4(CO)_{12}$ is then the result of the recombination of transient metal carbonyl species, particularly the recombination of hydrido species. The kinetics and chemistry of the recombination of metal hydride species have received rather continued examination.[43] Finally, the facile generation of $\{HRh(CO)_3\}$ from $CoRh(CO)_7$ in the presence of alkenes explains to a large degree the formation of the observed species $RCORh(CO)_4$[44] and the reasons low-temperature and low-pressure hydroformylation can be initiated starting with $CoRh(CO)_7$.[45]

The present experimental results have broader implications for hydrogen activation in cobalt–rhodium systems under very high carbon monoxide partial pressures at ambient temperatures. Since $CoRh(CO)_7$ (1) is the predominant cobalt–rhodium mixed-metal species in the system of $Co_2Rh_2(CO)_{12}$ (6), 1, and $CoRh(CO)_8$ (7) plus carbon monoxide in n-hexane at 293 K and up to 10 MPa of carbon monoxide[22] (eq 14), hydrogen can be readily dissociated under equally high carbon monoxide partial pressures in this mixed-metal system.

$$\underset{6}{Co_2Rh_2(CO)_{12}} \overset{K_1}{\rightleftharpoons} \underset{1}{2CoRh(CO)_7} \overset{K_2}{\rightleftharpoons} \underset{7}{2CoRh(CO)_8} \qquad (14)$$

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(33) Balch, A. L. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum: New York, 1983.

(34) In mechanism (a), two consecutive transition states must be successfully crossed. First, the oxidative addition of molecular hydrogen occurs at the square-planar rhodium, and then this is followed by reductive elimination. These two seperate elementary steps can be represented

$$(CO)_4CoRh(CO)_3 + H_2 \overset{k_1}{\rightleftharpoons} \{(CO)_4CoRhH_2(CO)_3\} \overset{k_2}{\rightleftharpoons} HCo(CO)_4 + \{HRh(CO)_3\}$$

where $\{(CO)_4CoRhH_2(CO)_3\}$ is a distinct intermediate, the product of the oxidative addition at rhodium, and is not a transition state. If $k_1[H_2][CoRh(CO)_7] \ll k_2[\{(CO)_4CoRhH_2(CO)_3\}]$, then

$$\text{rate} = k_1[H_2][CoRh(CO)_7]$$

or if $k_1[H_2][CoRh(CO)_7] \gg k_2[\{(CO)_4CoRhH_2(CO)_3\}]$, then

$$\text{rate} = k_2K_{eq}[H_2][CoRh(CO)_7]$$

In both cases there is a first-order dependence on hydrogen and $CoRh(CO)_7$. In mechanism (b), the concerted dinuclear activation of molecular hydrogen can be represented

$$CoRh(CO)_7 + H_2 \overset{k_3}{\rightleftharpoons} HCo(CO)_4 + \{HRh(CO)_3\}$$

where only one transition state (a four-center transition state) is encountered in the transformation. The rate expression is

$$\text{rate} = k_3[H_2][CoRh(CO)_7]$$

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(44) Garland, M.; Bor, G. *Inorg. Chem.* **1989**, *28*, 410.

(45) Garland, M. Manuscript in preparation.

In the experiments performed in the present paper, the possibility that the rapid activation of molecular hydrogen occurs via the small quantity of **6** in the system (which is in equilibrium with **1**) can be discounted. It is known[19] that **6** reacts with hydrogen in the absence of dissolved carbon monoxide; however, the rate per mole of complex under otherwise identical conditions is more than 1 order of magnitude slower. Further, it has been shown that, in the presence of carbon monoxide, **6** transforms to **1** before H_2 activation in the system occurs.[12,19]

A truly elegant, but technically difficult experiment, for the reaction of hydrogen in the **6**, **1**, and **7** system remains to be performed, e.g., the determination of the apparent activation energy E_{app} for the activation of molecular hydrogen in the presence of **7**. Given a sufficiently high partial pressure of carbon monoxide (i.e., $P_{CO} \geq 20$ MPa) and a low enough reaction temperature (i.e., $T \leq 258$ K), nearly quantitative conversion of **1** to **7** (>97%) will occur. Reaction of hydrogen under these conditions could be anticipated to give a measured apparent activation energy E_{app} equal to approximately 50 kJ/mol, that is, the enthalpy of reaction for the formation of **1** from **7** (24 kJ/mol) plus the actual activation energy E_a for hydrogen dissociation on **1**.

Acknowledgment. This work was supported by the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forchung. The starting material $Co_2Rh_2(CO)_{12}$ used in this study was synthesized by Dr. I. T. Horvâth. Discussions with Professors L. Venanzi and G. Consiglio are greatly appreciated.

Registry No. $CoRh(CO)_7$, 78714-10-0; H_2, 1333-74-0; CO, 630-08-0.

Conversion of Metallacyclic Zirconoxycarbene Complexes Yielding Conventional Fischer-Type Carbene Complexes or Metal-Free Organic Products

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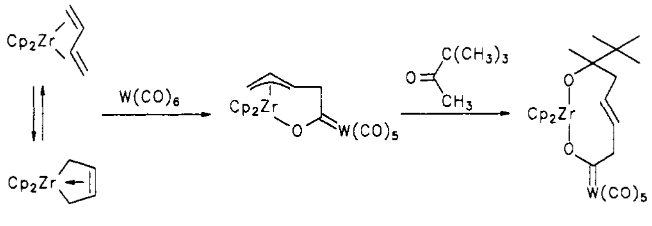
Reaction of (butadiene)zirconocene with hexacarbonyltungsten yields the metallacyclic (π-allyl)zirconoxycarbene complex $Cp_2\overline{ZrOC[{=}W(CO)_5]C}_4H_6$ (**2**). Subsequent coupling with pinacolone gives the nine-membered metallacycle *trans*-$Cp_2\overline{ZrOC[{=}W(CO)_5]CH_2CH{=}CHCH_2CMe(CMe_3)O}$ (**3**). Both compounds **2** and **3** show a very low Fischer carbene complex reactivity. Hydrolytic removal of the zirconocene moiety transforms the rather unreactive zirconoxycarbene complexes into conventional heteroatom-stabilized transition-metal carbene complexes. Thus, treatment of **3** with water in tetrahydrofuran generates a hydroxycarbene tungsten complex in situ, which is efficiently trapped by added excess diazomethane to yield the enol ether $H_2C{=}C(OCH_3)CH_2CH{=}CHCH_2CMe(CMe_3)OH$ as the major reaction product. Similarly, controlled hydrolysis of **3** in the presence of pyridine *N*-oxide gives $HOOCCH_2CH{=}CHCH_2CMe(CMe_3)OH$. The reaction of **3** with tetra-*n*-butylammonium fluoride trihydrate in tetrahydrofuran cleaves the metallacycle to give a zirconium-free acylmetallate anion (Bu_4N^+ counterion) which is readily O-alkylated by using Meerwein's reagent to produce $H_5C_2OC[{=}W(CO)_5]CH_2CH{=}CHCH_2CMe(CMe_3)OH$ (**11**, ca. 70% overall yield). Similarly, the zirconoxycarbene complex **2** yields $H_5C_2OC[{=}W(CO)_5]CH_2CH{=}CHCH_3$ upon treatment with $Bu_4NF(H_2O)_3$ followed by alkylation with $(H_5C_2)_3OBF_4$.

Introduction

Many metal carbonyl complexes can readily be converted to heteroatom-stabilized carbene complexes by reacting them with a variety of (olefin)group 4 metallocene type reagents.[1] This essentially nonnucleophilic alternative to the conventional Fischer synthesis[2] often gives high yields of the corresponding metallacyclic titano-, hafnio-, or zirconoxycarbene complexes. The reaction of the (*s-cis/s-trans*-η^4-butadiene)zirconocene system with hexacarbonyltungsten is a typical example, cleanly giving the carbene complex **2**[3] (Scheme I). Subsequent addition of an organic carbonyl compound (here pinacolone) to the (π-allyl)zirconocene unit selectively converts **2** to the nine-membered metallacyclic zirconoxycarbene complex

Scheme I



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