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Thermodynamic Parameters for the Formation of Cobalt–Rhodium Heptacarbonyl and Cobalt–Rhodium Octacarbonyl

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The thermodynamic parameters for the chemical equilibrium $Co_2Rh_2(CO)_{12} + 2CO \rightleftarrows 2CoRh(CO)_7$ in n-hexane as solvent have been experimentally determined: $\Delta_r H^\circ_x = -29 \pm 3$ kJ/mol (-6.9 ± 0.6 kcal/mol) and $\Delta_r S^\circ_x = -38 \pm 8$ J/(mol K) (-9.1 ± 2.0 cal/(mol K)). The Gibbs free energy of reaction is approximately $\Delta_r G^\circ_x$(293 K, 0.1 MPa) = −16.8 kJ/mol (−4.0 kcal/mol). These parameters were determined by regression of experimental data obtained for the temperature interval T = 268–288 K and the pressure interval P_{CO} = 0.002–0.04 MPa. Under these experimental conditions, conversions of $Co_2Rh_2(CO)_{12}$ to $CoRh(CO)_7$ greater than 95% were observed. Further, the thermodynamic parameters for the chemical equilibrium $CoRh(CO)_7 + CO \rightleftarrows CoRh(CO)_8$ in n-hexane as solvent have been experimentally determined: $\Delta_r H^\circ_x = -23.5 \pm 3.4$ kJ/mol (-5.7 ± 0.8 kcal/mol), $\Delta_r S^\circ_x = -71 \pm 12$ J/(mol K) (-17 ± 2.8 cal/mol K), and $\Delta_r V^\infty_x$(288 K) = -48 ± 21 ml/mol. The Gibbs free energy of reaction is approximately $\Delta_r G^\circ_x$(293 K, 0.1 MPa) = −2.0 J/mol (−0.5 kcal/mol). These parameters for the chemical equilibrium were determined by regression of experimental data obtained for the temperature interval T = 258–288 K and the pressure interval P_{CO} = 1.0–10 MPa. Under the experimental conditions used, conversions of $CoRh(CO)_8$ up to 75% were observed. Hence, the coordinatively unsaturated species $CoRh(CO)_7$ was the predominant mixed-metal species in the present thermodynamic study. The entire system defined as dissolved $Co_2Rh_2(CO)_{12}$, $CoRh(CO)_7$, $CoRh(CO)_8$, and CO in n-hexane represents only a metastable equilibrium. The homometallic metal carbonyls $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ form upon decomposition of the above system, to reach finally an equilibrium mixture between homo- and heterometallic carbonyls; however, this rate of decomposition at these temperatures is negligibly slow. The thermodynamics of the cobalt, rhodium, and cobalt–rhodium tetranuclear metal carbonyl systems are compared. The results of the equilibrium $CoRh(CO)_7 + CO \rightleftarrows CoRh(CO)_8$, together with considerations of the partial molar volume of CO, suggest an unusually large reaction volume $|\Delta_r V^\infty_x|$ for the transformation of metal carbonyls under CO. It is shown that reaction volumes on the order of 10^2 mL/mol are realistic for the fragmentation of many metal carbonyl clusters and that there is an associated nonnegligible contribution to the molar Gibbs free energy under typically encountered reaction conditions.

Introduction

The coordinatively unsaturated species $CoRh(CO)_7$ (**3**) was first proposed, on infrared evidence, upon reaction of $Co_2(CO)_8$ (**1**) with $Rh_4(CO)_{12}$ (**2**) in n-hexane.[1] In fact, reaction 1 was shown to be reversible.

$$\underset{\mathbf{1}}{2Co_2(CO)_8} + \underset{\mathbf{2}}{Rh_4(CO)_{12}} \rightleftarrows \underset{\mathbf{3}}{4CoRh(CO)_7} \qquad (1)$$

Subsequent to this initial study, three additional syntheses of $CoRh(CO)_7$ (**3**) were developed. In the first, $CoRh(CO)_7$ (**3**) could be quantitatively formed at −70 °C in n-hexane by the reaction of $NaCo(CO)_4 + [Rh(CO)_2Cl]_2$ under 0.1 MPa of CO.[2] In the second synthesis, which is central to the present study, $Co_2Rh_2(CO)_{12}$ (**4**), a compound first reported by Chini,[3] was shown to react with dissolved CO in n-hexane at temperatures T = 253–293 K.[2] Finally, in the third synthesis, $CoRh(CO)_7$ (**3**) formed on addition of $HCo(CO)_4$ to a n-hexane solution of $Rh_4(CO)_{12}$ (**2**).[4]

In the present study, reaction 2 is examined. Under P_{CO} = 0.002–0.04 MPa, measurable quantities of both the metal carbonyls $Co_2Rh_2(CO)_{12}$ (**4**) and $CoRh(CO)_7$ (**3**) can be identified in solution. The equilibrium in this system is established relatively quickly. That is, 10–60 min is needed under P_{CO} = 0.002–0.04 MPa and T = 258–288 K in order to obtain reproducible measurements for the concentrations in solution.

$$\underset{\mathbf{4}}{Co_2Rh_2(CO)_{12}} + 2CO \rightleftarrows \underset{\mathbf{3}}{2CoRh(CO)_7} \qquad (2)$$

System 2 is particularly interesting since the reversible cluster transformation occurs under such facile conditions. Of course there are other metal carbonyl clusters that show reversible transformations under CO; however, in general these transformations occur under more severe conditions.[5,6]

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In our paper[2] dealing with the preparation and characterization of the coordinatively unsaturated $\mathrm{CoRh(CO)_7}$ (**3**), it was tentatively suggested that the compound $\mathrm{CoRh(CO)_8}$ (**5**) was reversibly formed from the mixed heptacarbonyl under high carbon monoxide pressure ($13.0 < P_{CO} < 16.0$ MPa). This suggestion was based on the perfect analogy of the infrared spectra, mainly in the bridging ν(C–O) region, of the analogous compounds $\mathrm{Co_2(CO)_8}$ (**1**),[7,8] the supposed $\mathrm{CoRh(CO)_8}$ (**5**), and $\mathrm{Rh_2(CO)_8}$[5b] (cf. Figure 4). Also, the satisfactory correspondence between the approximate concentration of the new species (as checked by the intensities of its infrared absorption bands) and the carbon monoxide pressure seemed to confirm the hypothetical formula of a mixed octacarbonyl, i.e. $\mathrm{CoRh(CO)_8}$ (**5**).

$$\underset{\mathbf{3}}{\mathrm{CoRh(CO)_7}} + \mathrm{CO} \rightleftarrows \underset{\mathbf{5}}{\mathrm{CoRh(CO)_8}} \qquad (3)$$

A preparative approach to a more exact characterization of this compound had to be excluded because of the high carbon monoxide pressure required for its formation and because of its fast decomposition back to $\mathrm{CoRh(CO)_7}$ (**3**). Therefore, an exact study of the equilibrium (3) was also carried out. The results presented here confirm unequivocally the stoichiometry of reaction 3 and thus the formula $\mathrm{CoRh(CO)_8}$ (**5**).

Evidence at the time of the first observation of $\mathrm{CoRh(CO)_8}$ (**5**), i.e. the spontaneous decomposition into $\mathrm{CoRh(CO)_7}$ (**3**) upon a decrease in the CO partial pressure, suggested that reaction 3 was reversible. The high partial pressures of carbon monoxide needed for this transformation simply indicated the unusually small and negative free energy $\Delta_r G^\circ_x$ of reaction.

Equation 4 presents the equilibria for the formation of both $\mathrm{CoRh(CO)_7}$ (**3**) and $\mathrm{CoRh(CO)_8}$ (**5**) in a manner that emphasizes the partial pressure intervals, and hence the experimental range, in which each equilibrium can be, for all practical purposes, independently studied (T = 258–288 K). This independence arises due to the limited number of species observable in each pressure range and hence a simplification of the corresponding mass balances.

$$\underset{\mathbf{4}}{\mathrm{Co_2Rh(CO)_{12}}} \underset{P_{CO} = 0.002\text{–}0.04\ \mathrm{MPa}}{\overset{\mathrm{2CO}}{\rightleftarrows}} \underset{\mathbf{3}}{\mathrm{2CoRh(CO)_7}} \underset{P_{CO} > 1.0\ \mathrm{MPa}}{\overset{\mathrm{2CO}}{\rightleftarrows}} \underset{\mathbf{5}}{\mathrm{2CoRh(CO)_8}} \qquad (4)$$

It should be noted that experimentally, one is restricted to temperatures below 293 K in order to study the equilibria in (4). At higher temperatures, the species in eq 4 decompose (at a nonnegligible rate) to $\mathrm{Co_2(CO)_8}$ (**1**) and $\mathrm{Rh_4(CO)_{12}}$ (**2**) according to the reverse of eq 1. Equilibrium measurements are made possible simply because, at temperatures between 258 and 288 K, the equilibria in eq 4 can be established in a matter of minutes, whereas the formation of homometallic species, i.e. $\mathrm{Co_2(CO)_8}$ (**1**) and $\mathrm{Rh_4(CO)_{12}}$ (**2**), in spectroscopically significant quantities requires days. In this paper we present the thermodynamic parameters for both equilibria 2 and 3 in the pressure range P_T = 0.002–10.0 MPa and temperature range T = 258–288 K.

Experimental Section

General Information. All solution preparations and transfers were carried out under a nitrogen (99.995%, Pan Gas, Luzern, Switzerland) or argon (99.998%, Pan Gas, Luzern, Switzerland) atmosphere with use of standard Schlenk techniques.[9] The mixed cluster $\mathrm{Co_2Rh_2(CO)_{12}}$ (**4**) was prepared from $\mathrm{NaCo(CO)_4}$ and $\mathrm{Rh_2(CO)_4Cl_2}$ in *n*-hexane.[2] Anal. Calcd for **4**: C, 21.8; Rh, 31.2. Found: C, 21.7; Rh, 31.1 (courtesy Ciba-Geigy AG, Basel, Switzerland). *n*-Hexane (Purissimum quality, Fluka AG, Buchs) was refluxed from sodium–potassium alloy under nitrogen. The carbon monoxide used for reactions 2 and 3 was produced at the ETH-Zürich (and stored in aluminum cylinders).

Kinetic studies were performed in a 1.5-L stainless steel (SS316) autoclave (Büchi-Uster, Switzerland) which 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 Engineers, Erie, PA) and was constructed with a heating/cooling mantle. A high-pressure membrane pump (Model DMK30, Orlita AG, Geissen, Germany) 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, PA). The entire system autoclave, transfer lines, and infrared cell, was cooled with a Lauda RX20 (Königshofen, Germany) cryostat and could be maintained isothermal (ΔT = 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). Both 0.2000- and 1.000-MPa piezocrystals (Keller AG, Winterthur, Switzerland) were used for pressure measurements during the low-pressure measurements involving equilibrium 2, and both 5.00- and 10.00-MPa piezocrystals (Keller AG, Winterthur, Switzerland) were used during the high-pressure measurements involving equilibrium 3. The entire system was gastight under vacuum as well as at 20.0 MPa, the maximum operating pressure.

The high-pressure infrared cell (SS316) was constructed at the ETH-Zürich and could be heated or cooled. The NaCl (Korth, Kiel, GFR), KBr (Korth, Kiel, GFR), and silicon (ETH-Zürich) 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[5l] is a variation of a cell first constructed by Noack[10a] and differs in some respects from other high-pressure infrared cells described in the literature (for a review see ref 10f). 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.[11]

Extinction Coefficient for $\mathrm{Co_2Rh_2(CO)_{12}}$. The absorption at 1871 cm^{-1} in the infrared spectrum of dicobalt dirhodium dodecacarbonyl was chosen for calibration. Dicobalt dirhodium dodecacarbonyl has strong absorptions at 2074, 2064, 2059, 2038, 2030, 1920, 1910, 1885, 1871, and 1858 cm^{-1};[3] however, only the absorptions at 1885 and 1871 cm^{-1} were considered, since certain overlap with other metal carbonyl absorptions would occur at

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higher wavenumbers. Further, the band at 1885 cm^{-1} overlaps with absorptions from tetrarhodium dodecacarbonyl (1885 cm^{-1})[12] and $Co_3Rh(CO)_{12}$ (1882 cm^{-1}),[3] and therefore, it was also discarded.

Experimental data were taken from 12 measurements, and the standard Lambert–Beer law was used as $A = \epsilon cd$, where A is the absorbance, ϵ is the extinction coefficient, c is the concentration (mol/L), and d is the cell thickness. The standard solutions were prepared from the recrystallized complex and *n*-hexane under nitrogen. The experimentally determined extinction coefficient for dicobalt dirhodium dodecacarbonyl was 3640 ± 200 L mol^{-1} cm^{-1} at 1871 cm^{-1} (all errors are reported as standard deviations).[11]

Equilibrium Measurements for the Formation of $CoRh(CO)_7$. Typically, 66 mg of $Co_2Rh_2(CO)_{12}$ (4) was dissolved in 400 mL of *n*-hexane (0.25 mM solution, 3.25×10^{-5} mole fraction) in a Schlenk tube under a nitrogen atmosphere and the solution was transferred to the evacuated and thermostated batch reactor. Stirring was maintained at 200 rpm. Nitrogen was added to a partial pressure of about 0.1 MPa. This partial pressure was sufficient to stop most, if not all, the cavitation phenomena that were observed when pumping *n*-hexane at pressures near its vapor pressure. Then, small partial pressure increases in carbon monoxide were made to the system and the solution was circulated (pumped) through the infrared cell. The two-phase system was allowed to equilibrate. That is, the solution became saturated with carbon monoxide in less than about 60 s;[13] however, an additional 10–60 min was needed before the new chemical equilibrium was established between complexes in solution. After spectra were taken at 2200–1800 cm^{-1} for the metal carbonyl region and 1300–1100 cm^{-1} for the *n*-hexane reference of the equilibrated system, the partial pressure of carbon monoxide was increased.

Equilibrium Measurements for the Formation of $CoRh(CO)_8$. $Co_2Rh_2(CO)_{12}$ (4; 66 mg) was dissolved in 400 mL of *n*-hexane (0.25 mM solution, 3.25×10^{-5} mole 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 (T = 258–288 K), the total pressure in the autoclave, i.e. the vapor pressure of *n*-hexane plus a low partial pressure of nitrogen, was P_T = 0.01–0.03 MPa. At this point, 0.2 MPa of carbon monoxide was added to the system in order to quantitatively transform the $Co_2Rh_2(CO)_{12}$ to $CoRh(CO)_7$ (3). The stirring speed was kept constant at 200 rpm. During this time, the high-pressure membrane pump continuously circulated the *n*-hexane solution from the high-pressure infrared cell and back to the autoclave. In situ infrared spectra were taken from 2200 to 1800 cm^{-1} and from 1300 to 1100 cm^{-1} of this $CoRh(CO)_7$ (3) and *n*-hexane solution. 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. At this point, the partial pressure of CO was raised in intervals to 10.0 MPa. After each partial pressure increase, 5–15 min was required before constant infrared spectra were obtained.

Solubility of CO. The temperature-dependent "Henry constant" $H(T)$ for dissolved CO in *n*-hexane as $P \rightarrow 0$ was calculated by using eq 5,[11] where P_{sat} is the vapor pressure of the pure solvent *n*-hexane[14] and T is expressed in degress Kelvin.[15] This Henry constant was used for the study of the low-pressure chemical equilibrium (2) at T = 258–288 K and at $P_{CO} < 0.04$ MPa.

$$\ln\,[H(P = 0.1\ \mathrm{MPa})/P_{sat}] = -1.46 + 2840/T \qquad (5)$$

However, since the Henry constant is known to be pressure-dependent, eq 5 could not be used directly for the study of the high-pressure chemical equilibrium (3) over the interval P = 1.0–10 MPa. The Krichevsky–Kasarnovsky equation[16] gives a theoretical basis for the evaluation of Henry constants for binary gas–liquid systems when a nonnegligible total pressure exists in the system. The Krichevsky–Kasarnovsky equation takes the well-known form (6), where $H(P_{ref})$ is the Henry constant evaluated at the reference pressure P_{ref}, $H(P)$ is the Henry constant to be determined at the pressure P, and v^{∞}_i is the partial molar volume of the dissolved species i in the binary system at infinite dilution.

$$\ln\,[H(P)/H(P_{ref})] = v^{\infty}_i(P - P_{ref})/RT \qquad (6)$$

The partial molar volume of dissolved carbon monoxide has been determined by Connolly in both *n*-octane and benzene.[17] In both cases, the measured partial molar volume for carbon monoxide evaluated at infinite dilution was v^{∞}_{CO} = 52 mL/mol at 308 K. Further, this value for the partial molar volume was not strongly temperature-dependent in the vicinity of 300 K (less than 0.2 mL/(mol deg)). Therefore, as a first approximation, this value v^{∞}_{CO} = 52 mL/mol would appear to be valid for many hydrocarbon solvents, including *n*-hexane, in the present study.

Combining the expression for the Henry constant (eq 5) with the Krichevsky–Kasarnovsky equation (eq 6) and the data of Connolly results in an expression for the Henry constant for CO in *n*-hexane at elevated pressures (eq 7). This equation was used

$$\ln\,[H(P)/P_{sat}(-1.49 + 2890/T)] = 0.052(P - 0.1)/RT \qquad (7)$$

for calculations involving the high-pressure chemical equilibrium (3) at T = 258–288 K and at P = 1.0–10 MPa. As an example, for the pressure dependence involved, the Henry constant at 288 K and $P \rightarrow 0$ is $H(288\ \mathrm{K}, P \rightarrow 0)$ = 55.5 MPa, and that at 288 K and 100 bar is 69.0 MPa.

Concerning the accuracy of the equation used for the Henry constants, eq 7 gives the Henry constant, evaluated at 0.1 MPa of carbon monoxide, *H293* K, 0.1 MPa) = 56.6 MPa. The corresponding solubility in mole fraction is $x_{CO} = 1.76 \times 10^{-3}$. This is in very good agreement with the few available reports on the solubility of carbon monoxide in *n*-hexane at 0.1 MPa: Patyi et al.,[18] $x_{CO} = 1.7 \times 10^{-3}$; Gjaldbaek,[19] $x_{CO} = 1.74 \times 10^{-3}$; Oldani,[20] $x_{CO} = 1.6 \times 10^{-3}$; Koelliker,[61] $x_{CO} = 1.75 \times 10^{-3}$; Makranczy,[21] $x_{CO} = 1.85 \times 10^{-3}$.

Results

Extinction Coefficient for $CoRh(CO)_7$. The extinction coefficient for cobalt rhodium heptacarbonyl was determined at 1955 cm^{-1} from the in situ infrared spectra of seven equilibrated solutions containing both dicobalt dirhodium dodecacarbonyl and cobalt rhodium heptcarbonyl. The complex $CoRh(CO)_7$ (3) itself has absorbance maxima at 2134, 2064, 2058, 2049, 2006, 1977, and 1955 cm^{-1}.[2] A *n*-hexane solution containing dicobalt dirhodium dodecacarbonyl with an initial concentration of approximately 2.5×10^{-4} M (3.25×10^{-4} mole fraction) was transferred to the batch reactor. The system was allowed to equilibrate with various partial pressures of carbon monoxide. A typical in situ spectrum of an equilibrated $Co_2Rh_2(CO)_{12}$ (4) and $CORh(CO)_7$ (3) solution with dissolved CO is shown in Figure 1. No $CoRh(CO)_8$ (5) was observed in these spectra.

Since the path length in a high-pressure IR cell is, in general, a function of pressure, a dimensionless Lambert–Beer expression (eq 8) was used to obtain the extinction coefficient of cobalt rhodium heptacarbonyl at 1955 cm^{-1}. In expression 8 the terms A, c, and ϵ represent

$$A_{tet}/A_{hept} = (c_{tet}/c_{hept})(\epsilon_{tet}/\epsilon_{hept}) \qquad (8)$$

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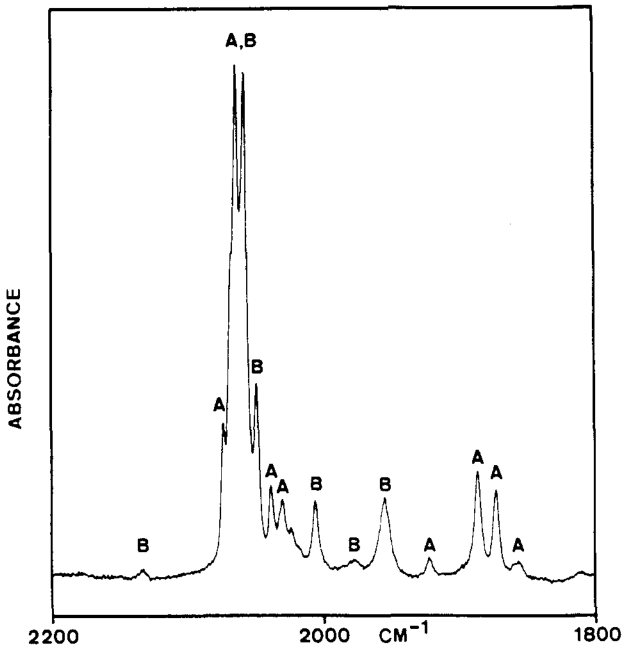

Figure 1. In situ spectrum of an equilibrated solution in the mixed-metal system at low pressure (P_{CO} = 0.005 MPa): (A) $Co_2Rh_2(CO)_{12}$; (B) $CoRh(CO)_7$.

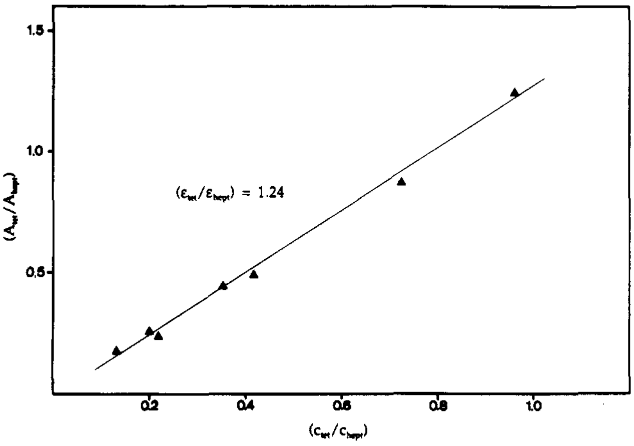

Figure 2. Determination of the extinction coefficient of cobalt rhodium heptacarbonyl at 1955 cm^{-1}.

absorbance, concentration (mol/L), and extinction coefficient, respectively. The subscripts tet and hept refer to the tetranuclear complex $Co_2Rh_2(CO)_{12}$ and the heptacarbonyl $CoRh(CO)_7$.

A least-squares regression analysis of the data for the $Co_2Rh_2(CO)_{12}$ (4) and $CoRh(CO)_7$ (3) solutions gave a slope of $\epsilon_{tet}/\epsilon_{hept}$ = 1.24. Given that the extinction coefficient at 1871 cm^{-1} for dicobalt dirhodium dodecacarbonyl is 3640 L mol^{-1} cm^{-1}, then the extinction coefficient of cobalt rhodium heptacarbonyl at 1955 cm^{-1} is 2950 ± 170 L mol^{-1} cm^{-1}. The results are graphically presented in Figure 2.

Equilibrium Constants $K_x(T)$ for the Formation of $CoRh(CO)_7$. Six series of experiments were made in the presence of nitrogen when determining the equilibrium compositions between cobalt rhodium heptacarbonyl and dicobalt dirhodium dodecacarbonyl at various temperatures and partial pressures of carbon monoxide. These experiments were made by starting with two different $Co_2Rh_2(CO)_{12}$ (4) solutions, referred to in the figures and tables as RX and RY.

The data for three series of equilibrium experiments (RY) are presented in Figure 3 and are in the form suggested for the equilibrium constant $K_x(T)$ (see Appendix I).

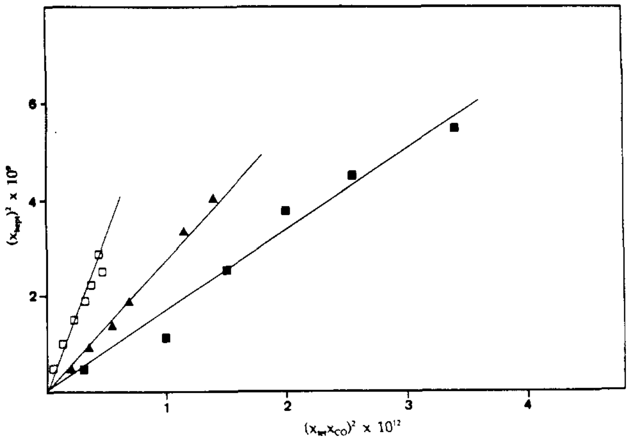

Figure 3. Equilibrium constant $K_x(T)$ for RY Experiments: (■) 288 K; (▲) 278 K; (□) 268 K.

Table I. Equilibrium Constants for the Formation of Cobalt Rhodium Heptacarbonyl in *n*-Hexane

series	temp/K	$K_x(T)$	series	temp/K	$K_x(T)$
RX000	288	1800 ± 210	RY000	288	1710 ± 170
RX006	278	2890 ± 380	RY050	278	2680 ± 300
RX013	268	4710 ± 810	RY100	268	3930 ± 480

A regression analysis of the data for both RX experiments and RY experiments (Figure 3) yields the equilibrium constants for reaction 2. The equilibrium constants are listed in Table I.

Values of $\Delta_rG°_x$, $\Delta_rH°_x$, and $\Delta_rS°_x$ for the Formation of $CoRh(CO)_7$. A linear regression analysis of the results in Table I was made to obtain the values of the thermodynamic parameters $\Delta_rH°_x$ and $\Delta_rS°_x$. Since the integral $\int \Delta_rV^\infty_x \, dP$ at these low pressures can definitely be neglected in the calculation of the total free energy of reaction, the expression for the Gibbs free energy is simply

$$-RT \ln K_x(T,P_0) = \Delta_rG°_x = \Delta_rH°_x - \Delta_rS°_xT \quad (9)$$

Since these data were collected in the vicinity of "standard" conditions, 298 K and 0.1 MPa, and in a very small region, i.e. 268–288 K, a simple linear regression analysis of the data was made. The regression analysis of the data sets in Table I gave $\Delta_rH°_x$ = −29 ± 3 kJ/mol (−6.9 ± 0.6 kcal/mol) and $\Delta_rS°_x$ = −38 ± 8 J/(mol K) (−9.1 ± 2.0 cal/(mol K)).

The negative value of the enthalpy is consistent with the observation of higher conversions to the complex $CoRh(CO)_7$ (3) at lower temperatures. Furthermore, the negative sign for the entropy of reaction is consistent with the stoichiometric equation for this reaction, i.e. 3 mol of reactants going to 2 mol of products.

It should be stressed that the conversion to cobalt rhodium heptacarbonyl is increased at lower temperatures by *both* the negative value of the enthalpy of reaction and the increased solubility of carbon monoxide in *n*-hexane at low temperatures.

Evaluation of the Extinction Coefficient for $CoRh(CO)_8$. Although $CoRh(CO)_8$ (5) cannot be isolated and, hence, its extinction coefficient ϵ_{oct} cannot be independently measured, an extinction coefficient can nevertheless be evaluated from solutions containing simultaneously $CoRh(CO)_7$ (3) and $CoRh(CO)_8$ (5). This can be done by using a mass balance and by using the standard Lambert–Beer law as shown below. Considering an experiment with n_c moles of cobalt (or rhodium), n_{hept} moles

Table II. Data for Evaluation of the Extinction Coefficient for Cobalt Rhodium Octacarbonyl

expt no.	abs[a] (1955 cm^{-1})	abs[b] (1851 cm^{-1})	abs[c] (1138 cm^{-1})
RZ140	0.367		1.02
RZ141	0.296	0.062	1.02
RZ142	0.236	0.131	1.06
RZ143	0.153	0.217	1.14
RZ144	0.117	0.241	1.15
RZ145	0.100	0.249	1.11

[a] Absorbance from $CoRh(CO)_7$. [b] Absorbance from $CoRh(CO)_8$. [c] Absorbance from *n*-hexane.

of $CoRh(CO)_7$ (**3**), and n_{oct} moles of $CoRh(CO)_8$ (**5**), one can write

$$n_c = n_{hept} + n_{oct} \qquad (10)$$

Equation 10 is valid if (i) there is no loss of cobalt (or rhodium) from solution and (ii) if $CoRh(CO)_7$ (**3**) and $CoRh(CO)_8$ (**5**) are the only observable cobalt and rhodium species during the measurements.

Equation 10 can be divided by any constant (in the system); for example, with the total moles of *n*-hexane n_h as a convenient constant

$$n_c/n_h = n_{hept}/n_h + n_{oct}/n_h \qquad (11)$$

Further, it can be shown that use of the Lambert–Beer law in the mass balance equation (11) results in an expression which relates the measured in situ infrared absorptions A_i with the ratio of concentrations. In eq 11, it is not necessary to explicitly consider the expansion of the optical path length in the infrared cell due to increases in the operating pressure. Thus, a plot of the measured A_{oct}/A_{hept} versus the calculated n_{oct}/n_{hept} provides the unknown extinction coefficient.

$$A_{oct}/A_{hept} = (\epsilon_{oct}/\epsilon_{hept})(n_{oct}/n_{hept}) \qquad (12)$$

The absorption data presented in Table II, for the determination of the extinction coefficient of $CoRh(CO)_8$ (**5**), were obtained from a 400-mL solution of $CoRh(CO)_7$ (**3**) in *n*-hexane ($n_c/n_h = 3.04 \times 10^{-4}$). The carbon monoxide partial pressure was systematically increased and the new chemical equilibria between the two dinuclear carbonyls were established. The maxima in the infrared spectra at 1955 cm^{-1} ($CoRh(CO)_7$ (**3**)), 1851 cm^{-1} ($CoRh(CO)_8$ (**5**)), and 1138 cm^{-1} (*n*-hexane) are reported in Table II. Noteworthy is the expansion of the high-pressure cell as a function of pressure as indicated by the increase of the absorbance of *n*-hexane (A_h).

The previously determined extinction coefficients for $CoRh(CO)_7$ (**3**) and *n*-hexane were $\epsilon(1955\ cm^{-1}) = 2940 \pm 170$ L mol^{-1} cm^{-1},[7] and $\epsilon(1138\ cm^{-1}) = 2.35 \pm 0.04$ L mol^{-1} cm^{-1}, respectively.[11] A regression analysis of the data in Table II according to eq 2 gave a slope of 0.95 (similar to that in Figure 2) and an extinction coefficient for $CoRh(CO)_8$ (**5**) of $\epsilon(1851\ cm^{-1}) = 2800 \pm 200$ L mol^{-1} cm^{-1}. An infrared spectrum of the bridging region of $CoRh(CO)_8$ (**5**), including the band at 1851 cm^{-1}, and a comparison with the bridging region of $Co_2(CO)_8$ (**1**)[6,7] and $Rh_2(CO)_8$[8] are given in Figure 4.

Equilibrium Constants $K_x(P,T)$ for the Formation of $CoRh(CO)_8$. Four different series of experiments were made to determine the thermodynamic parameters $\Delta_r H°_x$, $\Delta_r S°_x$, and $\Delta_r V^\infty_x$, which fully describe the chemical equilibria in the system cobalt rhodium heptacarbonyl plus dissolved carbon monoxide to give cobalt rhodium octacarbonyl in the limit of infinite dilution. Each series represented a different temperature at which experiments were made. The temperatures used in this study were 258, 268, 278, and 288 K. Further, within each series of experiments, the partial pressure of carbon monoxide was varied between 0.2 and 10.0 MPa.

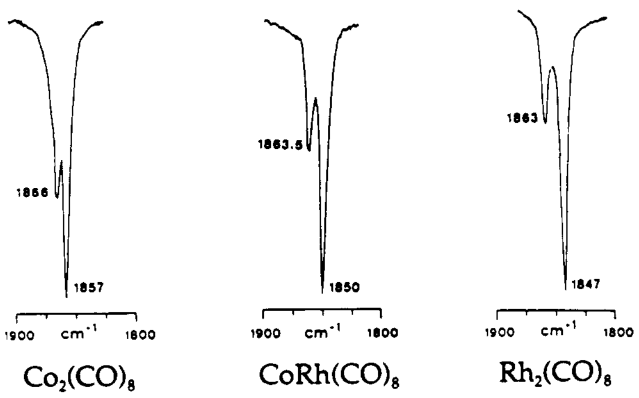

Figure 4. Comparison of the bridged-carbonyl region of the IR spectra of $Co_2(CO)_8$, $CoRh(CO)_8$, and $Rh_2(CO)_8$.

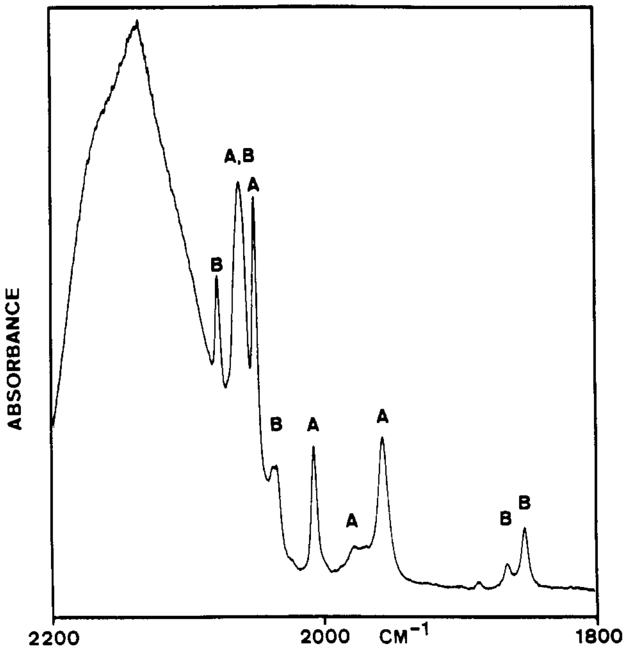

Figure 5. In situ infrared spectrum of an equilibrated solution of (A) $CoRh(CO)_7$ and (B) $CoRh(CO)_8$ at 258 K under high pressure (5.0 MPa carbon monoxide) with *n*-hexane substraction.

In spectra of equilibrium mixtures of the mixed-metal carbonyls in this study, $CoRh(CO)_7$ (**3**) can be identified by its characteristic absorbances at 2134, 2064, 2058, 2049, 2006, 1977, and 1955 cm^{-1}, and $CoRh(CO)_8$ (**5**) can be identified at 2077, 2064, 2060, 2034, 1969, 1864, and 1851 cm^{-1}. A typical spectrum is shown in Figure 5.

The results of experiments at 258, 268, 278, and 288 K for the determination of the pressure as well as the temperature-dependent equilibrium constant $K_x(T,P)$ (see Appendix II) between $CoRh(CO)_7$ (**3**) and $CoRh(CO)_8$ (**5**) are summarized in Table III.

Equations for $\Delta_r G°_x$, $\Delta_r H°_x$, $\Delta_r S°_x$, and $\Delta_r V^\infty_x$ for the Formation of $CoRh(CO)_8$. The data in Table III, for the chemical equilibrium between cobalt rhodium heptacarbonyl and cobalt rhodium octacarbonyl indicate that, indeed, there is a measurable pressure dependence for the equilibrium constant $K_x(P,T)$. The value of $K_x(P,T)$ in each series of experiments shows an increase with increasing total pressure. From a linear regression analysis of the values of ln $K_x(P,T)$ in Table III versus pressure, one obtains the values for $\Delta_r V^\infty_x(T)$[22] and $\Delta_r G°_x(T,P_0)$

Table III. In Situ Infrared Data for the Chemical Equilibria between Cobalt Rhodium Heptacarbonyl and Cobalt Rhodium Octacarbonyl in *n*-Hexane at High Partial Pressures of Carbon Monoxide and between 258 and 288 K

expt no.	abs[a] (1955 cm^{-1})	abs[b] (1851 cm^{-1})	pressure of CO, MPa	$K_x(P,T)$
RZ130 (288.2 K)	0.367	0.0	0.2	
RZ131	0.353	0.015	1.0	2.62
RZ132	0.318	0.040	2.5	3.16
RZ133	0.286	0.073	5.0	3.26
RZ134	0.257	0.091	7.5	3.21
RZ135	0.230	0.104	10.0	3.32
RZ100 (278.2 K)	0.367	0.0	0.2	
RZ101	0.354	0.029	1.0	4.19
RZ102	0.301	0.064	2.5	4.60
RZ103	0.261	0.107	5.0	4.61
RZ104	0.237	0.133	7.5	4.50
RZ105	0.186	0.153	10.0	5.27
RZ110 (268.2 K)	0.376	0.0	0.2	
RZ111	0.332	0.038	1.0	5.28
RZ112	0.274	0.082	2.5	5.78
RZ113	0.224	0.149	5.0	6.68
RZ114	0.179	0.173	7.5	6.90
RZ115	0.149	0.204	10.0	7.86
RZ140 (258.2 K)	0.367	0.170	0.2	
RZ141	0.296	0.062	1.0	8.85
RZ142	0.236	0.131	2.5	9.94
RZ143	0.153	0.217	5.0	13.1
RZ144	0.117	0.241	7.5	13.5
RZ145	0.100	0.249	10.0	13.3

[a] In situ absorbance from $CoRh(CO)_7$. [b] In situ absorbance from $CoRh(CO)_8$.

Table IV. Molar Gibbs Free Energies of Reaction and Volumes of Reaction for the Formation of Cobalt Rhodium Octacarbonyl

series	$\Delta_rG°_x(T,P_0)$, cal/(g mol)	$\Delta_rV^\infty_x$, mL/mol
RX130 (288 K)	-585 ± 57	-48 ± 21
RX100 (278 K)	-791 ± 61	-43 ± 17
RX110 (268 K)	-875 ± 55	-92 ± 12
RX140 (258 K)	-1127 ± 62	-101 ± 31

(refer to Appendix III). The results of this analysis are presented in Table IV.

The negative values for the molar volume of reaction for the reaction between cobalt rhodium heptacarbonyl and dissolved carbon monoxide and cobalt rhodium octacarbonyl presented in Table IV indicate that the partial molar volume of the product $CoRh(CO)_8$ (**5**) is measurably less than the sum of the partial molar volumes of the reactants. This result is not surprising, considering that dissolved gases have relatively large partial molar volumes.[23,24]

The experimental values of $\Delta_rV^\infty_x$ of approximately −45 mL/mol at 288 and 278 K are realistic. Indeed, a significant reaction volume should be expected when dissolved CO with a partial molar volume of 52 mL/mol[17] loses its translational degrees of freedom and coordinates to a metal center. As a comparison for $CoRh(CO)_7$ (**3**), the molar volume of $Co_2(CO)_8$ (**5**), having eight carbonyl ligands, is only 175.3 mL/mol as calculated from its solid-state structure.[25]

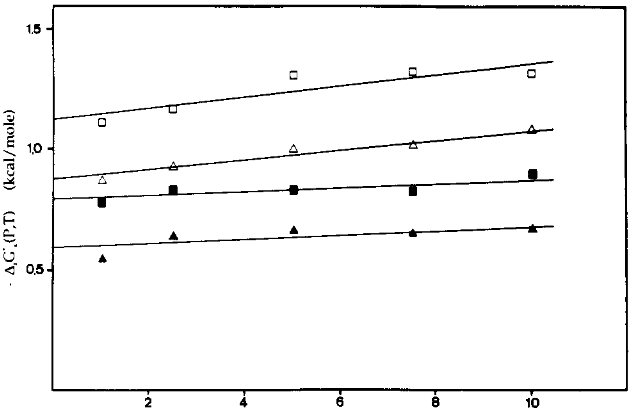

Figure 6. Free energy of reaction $\Delta_rG°_x(T,P_0)$ versus total pressure for the formation of cobalt rhodium octacarbonyl: (▲) 288 K; (■) 278 K; (▲) 269 K; (□) 258 K.

At 10.0 MPa, the reaction volume of approximately −45 mL/mol implies a 0.1 kcal/mol (0.4 kJ/mol) free energy difference from the standard state at 0.1 MPa. The larger $\Delta_rV^\infty_x$ values at 268 and 258 K probably reflect the fact that some calibrations may not entirely hold at the lower temperatures. The data in terms of $\Delta_rG°_x(T,P)$ and total pressure are shown in Figure 6.

A linear regression analysis of $\Delta_rG°_x(T,P_0)$ versus $1/T$ yields the remaining two thermodynamic parameters $\Delta_rH°_x$ = −23.5 ± 3.4 kJ/mol (−5.7 ± 0.8 kcal/mol) and $\Delta_rS°_x$ = −71 ± 12 J/(mol K) (−17 ± 2.8 cal/(mol K)) for the formation of $CoRh(CO)_8$ (**5**). The negative signs in both terms are consistent with the increased conversion at lower temperatures and the decrease in the number of moles in the stoichiometric reaction, respectively.

Discussion

The methods applied to the experimental study of the discussed reversible reactions (reactions 2 and 3) as well as to the quantitative evaluation of the observations have been substantially improved upon in this study as compared with those in the previous studies on fundamental metal carbonyl equilibria performed in this laboratory.[5h–m] For example, changes were made concerning experimental aspects: (i) a dimensionless Lambert–Beer equation was used to evaluate the concentrations in order to eliminate problems associated with the cell thickness and volumetric properties of the *n*-hexane solution and (ii) a temperature- and pressure-dependent Henry constant was used for the solubility of dissolved carbon monoxide in *n*-hexane. Also, in terms of the evaluation of the results, liquid-phase concentrations in mole fractions and pressure-dependent equilibrium constants $K(T,P)$ have been introduced. The pressure dependence of the equilibrium constant was accounted for through inclusion of the term $\int \Delta_rV^\infty_x\, dP$.

There are a number of interesting and interrelated observations concerning the measured reaction volume $\Delta_rV^\infty_x$ for reaction 3: (i) the reaction volume of approximately $\Delta_rV^\infty_x$ = −45 mL/mol is unusually large for an inorganic reaction,[23ab] (ii) the magnitude of $\Delta_rV^\infty_x$ is very similar to the partial molar volume of many dissolved gases in gen-

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[22] The volume of reaction Δ_rV_x is defined in terms of stoichiometries ν_i and partial molar volumes v_i as

$$\Delta_rV_x = \sum \nu_i v_i$$

or experimentally by the pressure dependence of the equilibrium constant K_x

$$\Delta_rV_x = -RT(\partial \ln K_x/\partial P)_T$$

[23] (a) van Eldik, R.; Asano, T.; le Noble, W. J. *Chem. Rev.* **1989**, *89*, 549. (b) Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407. (c) In many inorganic reactions, total pressure differences on the order of 50 MPa are needed to measure typical volumes of reaction $|\Delta_rV^\infty_x|$ of 5 cm^3/mol or less. In the present case, $|\Delta_rV^\infty_x|$ is 1 order of magnitude larger and experimentally a correspondingly lower pressure difference is sufficient for measurements.

[24] (a) Cysenski, G. R.; Prausnitz, J. M. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 304. (b) Handa, Y. P.; Benson, G. C. *Fluid Phase Equilib.* **1982**, *8*, 161.

[25] Sumner, G. G.; Klug, H. P.; Alexander, L. E. *Acta Crystallogr.* **1964**, *17*, 732.

Table V. Calculated Volumes of Reaction for Metal Carbonyl Cluster Fragmentations

cluster fragmentation reacn	$\Delta_r V^\infty_x$, mL/mol[a]
$Co_4(CO)_{12} + 4CO \rightleftharpoons 2Co_2(CO)_8$	-116
$4Rh_6(CO)_{16} + 8CO \rightleftharpoons 6Rh_4(CO)_{12}$	-126
$4Ir_6(CO)_{16} + 8CO \rightleftharpoons 6Ir_4(CO)_{12}$	-212
$3Os_4(CO)_{14} + 6CO \rightleftharpoons 4Os_3(CO)_{12}$	-143
$3Os_5(CO)_{16} + 12CO \rightleftharpoons 5Os_3(CO)_{12}$	-566

[a] Calculated as $\sum \nu_i v_i$.

eral[24] and dissolved CO in particular,[17] (iii) there is an enormous discrepancy between the partial molar volume of CO (v^∞_{CO} = 52 mL/mol) and the solid-state molar volumes of many metal carbonyl clusters such as $Co_2(CO)_8$ (175.3 mL/mol),[25] and (iv) it is recognized that the partial molar volumes of dissolved gases at ambient temperatures are considerably larger than their corresponding molar volumes in a pure condensed state and, further, these partial molar volumes are in many ways atypical for common organic and inorganic solutes.[26] When they are taken together, the above observations argue that there is a severe reduction in the effective volume of CO on going from dissolved CO to a coordinated carbonyl ligand.

If the solid-state molar volumes of metal carbonyl clusters are assumed to be a good first approximation to their corresponding partial molar volumes in apolar solvents,[27] then crystallographic data from the literature can be used to quantify the volume loss associated with many metal carbonyl cluster fragmentations. In this regard, the solid-state molar volumes of the following metal carbonyl clusters are known: $Co_2(CO)_8$ (175.3 mL/mol),[25] $Co_4(CO)_{12}$ (273.6 mL/mol),[28] $Rh_4(CO)_{12}$ (296.7 mL/mol),[28] $Rh_6(CO)_{16}$ (372.5 mL/mol),[29] $Ir_4(CO)_{12}$ (275.5 mL/mol),[30] $Ir_6(CO)_{16}$ (362.3 mL/mol),[31] $Os_3(CO)_{12}$ (257.5 mL/mol),[32] $Os_4(CO)_{14}$ (301.9 mL/mol),[33] and $Os_5(CO)_{16}$ (315.3 mL/mol).[34] These were used to help clarify the problem concerning $\Delta_r V^\infty_x$. The calculated volumes of reaction for a number of metal carbonyl cluster fragmentations are presented in Table V. The calculated reaction volumes clearly reflect the importance of the unusually large partial molar volume of dissolved CO.

After it is recognized that the reduction in the effective volume of CO is the primary component of $\Delta_r V^\infty_x$, the results presented in Table V can be organized into a useful and meaningful form. It is found that a rough approximation of both the magnitude and sign of $\Delta_r V^\infty_x$ for a cluster fragmentation can be predicted by using eq 13,

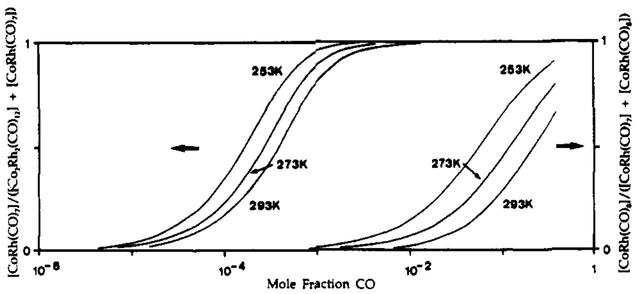

Figure 7. Relative concentrations of the dinuclear mixed-metal carbonyls in the cobalt–rhodium system as a function of the mole fraction of dissolved carbon monoxide in *n*-hexane as solvent. The initial concentration of $Co_2Rh_2(CO)_{12}$ is 1 mM in *n*-hexane as solvent (at 273 K, $x_{CO} = 10^{-1}$ corresponds to approximately 4.9 MPa and $x_{CO} = 10^{-4}$ corresponds to approximately 4.4 × 10^{-3} MPa).

$$\Delta_r V^\infty_x = \phi \nu_{CO} v^\infty_{CO} \qquad (13)$$

$$\phi = (\textstyle\sum \nu_i v^\infty_i)/\nu_{CO} v^\infty_{CO} \qquad (14)$$

where ν_{CO} is the stoichiometry of CO in the cluster fragmentation, v^∞_{CO} is the partial molar volume of CO at infinite dilution, and ϕ is an empirically determined constant with the value $\phi \approx 0.5$. Indeed, for the reactions $Co_4(CO)_{12} \rightarrow Co_2(CO)_8$, $Rh_6(CO)_{16} \rightarrow Rh_4(CO)_{12}$, $Ir_6(CO)_{16} \rightarrow Ir_4(CO)_{12}$, $Os_4(CO)_{14} \rightarrow Os_3(CO)_{12}$, and $Os_5(CO)_{16} \rightarrow Os_3(CO)_{12}$, the numerical values of ϕ were found to be 0.56, 0.3, 0.5, 0.46, and 0.69, respectively, as determined with use of eq 14, where the summation *i* extends over all species in the stoichiometric equation for the cluster fragmentation. The value $\phi \approx 0.8$ for reaction 3 may be due to very similar values of the partial molar volume for the two dinuclear carbonyls $CoRh(CO)_7$ (**3**) and $CoRh(CO)_8$ (**5**).

A check of some of the previous results concerning metal carbonyl equilibria shows that the *upper limit* of the error for these calculated Gibbs free energies due to the previous omission of the pressure-dependent term $\int \Delta_r V^\infty_x \, dP$ seems to be about 2.0 kJ/mol; e.g., in the reversible reaction of $Rh_4(CO)_{12}$ to yield $Rh_2(CO)_8$ at 20.0 MPa carbon monoxide pressure the influence of pressure is 2 kJ/mol ($\Delta_r V^\infty_x \approx -4 \times 0.5 \times 52$ mL/mol). This is to be compared with the reported value $\Delta_r G^\circ_c$ of 32 kJ/mol[5j,k] ($\Delta_r G^\circ_x$ = 18 kJ/mol).[35]

Previous to the present study and on the basis of preliminary data, carbonyl concentration versus P_{CO} curves were presented to visualize the concentration regimes for reactions 2 and 3.[5m] Now on the basis more extensive measurements, we present temperature-dependent carbonyl concentration versus x_{CO} curves for reactions 2 and 3 as shown in Figure 7. These curves clearly indicate the two different x_{CO} regions where the two equilibria (eqs 2 and 3) could be conveniently and separately measured.

For a qualitative comparison between the related Co–Co, Rh–Rh, and Co–Rh systems, let us consider the corresponding metal carbonyl systems at 273 K, in the presence of carbon monoxide. Thus, starting with solutions of $Co_2(CO)_{12}$, $Rh_4(CO)_{12}$, and $Co_2Rh_2(CO)_{12}$ in *n*-hexane (x_{tot}

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(26) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid Phase Equilibrium*; Prentice-Hall: Englewood Cliffs, NJ, 1986; p 457.

(27) (a) The partial molar volume of a dissolved species, i.e. a metal complex in solution at infinite dilution, can be conveniently partitioned into intrinsic (int) and solvation (solv) parts; see: Hammann, S. D. *Rev. Phys. Chem. Jpn.* **1980**, *50*, 147.

$$v^\infty_i = v_{int} + v_{solv}$$

(b) The first term, v_{int}, is determined by the van der Waals radius of the species. The second term, v_{solv}, becomes particularly important when the solute is ionic. In the present study we are considering a neutral species in a noncoordinating solvent. Therefore, the contribution of v_{solv} can be neglected, and since no further data are available, v_{int} can be approximated by the corresponding solid-state crystallographic data. It is recognized that variations in crystal packing and solvent-dependent variations in partial molar volumes do in fact exist, but these effects will have a limited influence on the present conclusions.

(28) Wei, C. H. *Inorg. Chem.* **1969**, *8*, 2384.

(29) Corey, E. R.; Dahl, L. F.; Beck, W. *J. Am. Chem. Soc.* **1963**, *85*, 1202.

(30) Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1978**, *17*, 3528.

(31) Garlaschelli, L.; Martinengo, S.; Bellon, P. L.; Demartin, F.; Manassero, M.; Chiang, M. Y.; Wei, C. Y.; Bau, R. *J. Am. Chem. Soc.* **1984**, *106*, 6664.

(32) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

(33) Johnston, V. J.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* **1988**, *7*, 1867.

(34) Reichert, B. E.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1977**, *33*, 173.

(35) For dilute solutions, a simple dimensional analysis shows that the difference between the Gibbs free energy of reaction in molar concentrations and mole fractions is related to the molar density of the pure solvent (ρ_m) by

$$\Delta_r G^\circ_x - \Delta_r G^\circ_c = \textstyle\sum \nu RT \ln \rho_m$$

$= 1 \times 10^{-5}$), the following carbon monoxide dependences arise. At $x_{CO} = 0.1$ (4.9 MPa) the equilibrium in the cobalt carbonyl system is entirely shifted in favor of $Co_2(CO)_8$ ($[Co_2(CO)_8]/[Co_4(CO)_{12}] \approx 10^{11}$, $\Delta_r G^\circ_x = -56$ kJ/mol).[5i] Further, at $x_{CO} = 0.1$ in the rhodium carbonyl system, $Rh_4(CO)_{12}$ effectively resists fragmentation and the equilibrium does not go appreciably toward $Rh_2(CO)_8$ ($[Rh_2(CO)_8]/[Rh_4(CO)_{12}] \approx 10^{-1}$ $\Delta_r G^\circ_x = 18$ kJ/mol).[5j,k] Of course, in the two above homometallic systems, only the dinuclear octacarbonyl species have been observed as reaction products.

The behavior of the mixed system starting with $Co_2Rh_2(CO)_{12}$ is entirely different in more than one respect. At $x_{CO} = 0.1$, $Co_2Rh_2(CO)_{12}$ is essentially absent from solution ($[CoRh(CO)_8]/[Co_2Rh_2(CO)_{12}] \approx 10^6$, $\Delta_r G^\circ_x = -28$ kJ/mol). Thus, in the mixed-metal system, the relative concentration of dinuclear octacarbonyl to tetranuclear dodecacarbonyl assumes a value intermediate between the pure cobalt and rhodium cases. But most importantly, we see that the "intermediate" formation of another dinuclear mixed-metal carbonyl, namely $CoRh(CO)_7$, occurs in significant quantities ($[CoRh(CO)_8]/[CoRh(CO)_7] \approx 1$, $\Delta_r G^\circ_x = -4.8$ kJ/mol) ($[CoRh(CO)_7]/[Co_2Rh_2(CO)_{12}] \approx 10^6$, $\Delta_r G^\circ_x = -19$ kJ/mol). Finally, the unsaturated complex is formed in essentially quantitative yield ($[CoRh(CO)_7]/[Co_2Rh_2(CO)_{12}] \approx 10^3$) under a low partial pressure of carbon monoxide (0.1 MPa).

The saturation of the vacant coordination site in $CoRh(CO)_7$ (**3**) with an eighth CO ligand to yield $CoRh(CO)_8$ (**5**) requires high carbon monoxide pressures and is fully reversible. The loss of the eighth ligand, which occurs when the carbon monoxide pressure is reduced, is also kinetically fast (on the order of several minutes).

It would be challenging to try to explain theoretically the peculiarities of the mixed cobalt–rhodium system, especially the high selectivity of the cluster fragmentation; i.e., when $Co_2Rh_2(CO)_{12}$ is treated with carbon monoxide, only the homometallic Co–Co and Rh–Rh bonds are split (selectively >98%). Unfortunately, the present experimental data do not suffice for a detailed theoretical discussion, and for the time being we are forced to restrict the explanation of the unique stability of the Co–Rh bonds to a combination of a slight polar component of them in the $Co^{\delta-}$–$Rh^{\delta+}$ sense. The intermediate occurrence of the coordinately unsaturated $CoRh(CO)_7$ in the transformation of $Co_2Rh_2(CO)_{12}$ to $CoRh(CO)_8$ is unprecedented in metal carbonyl chemistry, and its domination over a wide concentration range of carbon monoxide, as shown in Figure 7, is probably related to the partial saturation of the additional coordination sites at the rhodium center by the semibridging CO ligands. These, in turn, may have their origin again in the polarity, or at least a charge asymmetry, of the Co–Rh bond.[2]

Appendix I

Equations for $K_x(T)$ for the Formation of $CoRh(CO)_7$. At equilibrium, one can define an appropriate dimensionless equilibrium constant $K_x(T)$ for reaction 2 as in (15), where all solution activity coefficients have been set to unity. Indeed, all the species in this study are nonelectrolytes at essentially infinite dilution, necessary and sufficient conditions for setting the activity coefficient to unity.

$$K_x(T) = x_{hept}^2 / x_{tet} x_{CO}^2 \tag{15}$$

Since the absolute moles of the complexes and carbon monoxide in solution are extremely low under the experimental conditions in this study (i.e. 0.5 mM initial complex concentration and ≤0.8 mM in dissolved CO), there is the condition that $n_{tet}, n_{hept}, n_{CO} <<< n_h$. Therefore, eq 16 and 17 are valid and can be substituted directly into

$$x_{tet} \approx n_{tet}/n_h \tag{16}$$

$$x_{hept} \approx n_{hept}/n_h \tag{17}$$

eq 15 for the determination of the equilibrium constant K_x. The mole fraction of CO is calculated by using eq 5.

Appendix II

Equations for $K_x(P,T)$ for the Formation of $CoRh(CO)_8$. To define the system, let the standard conditions for the high-pressure chemical equilibrium in eq 3 be the dissolved components $CoRh(CO)_7$ (**3**), $CoRh(CO)_8$ (**5**) and CO at infinite dilution in *n*-hexane as solvent. A dimensionless equilibrium constant $K_\alpha(P,T)$ based on activities for the high-pressure reaction (3) can then be written as

$$K_\alpha(P,T) = \gamma_{oct} x_{oct} / \gamma_{hept} x_{hept} \gamma_{CO} x_{CO} \tag{18}$$

where the γ_i values are the liquid-phase activity coefficients (observing the proper standard conditions) and x_i values are the liquid-phase mole fractions. Then, since the concentration of the organometallic species is very low (nearly infinite dilution) and since at these temperatures and pressures dissolved CO behaves ideally,[17] all three activity coefficients will be set to unity, $\gamma_i = 1$.

Upon substitution of the pressure-dependent Henry law expression $x_{CO} = f_{CO}/H_{CO}(P,T)$, where f_{CO} is the fugacity of carbon monoxide in the gas phase, the simplified equilibrium constant $K_x(P,T)$ takes the form

$$K_x(P,T) = x_{oct} / (x_{hept} f_{CO} / H_{CO}(P,T)) \tag{19}$$

Further, the liquid-phase mole fractions x_{hept} and x_{oct} of cobalt rhodium heptacarbonyl and cobalt rhodium octacarbonyl respectively are related to the in situ infrared absorptions A_i by

$$x_{oct}/x_{hept} = (n_{oct}/n_h)/(n_{hept}/n_h) \tag{20}$$

$$x_{oct}/x_{hept} = (A_{oct}/\epsilon_{oct})/(A_{hept}/\epsilon_{hept}) \tag{21}$$

Thus, the final expression for the equilibrium constant $K_x(P,T)$ for the chemical equilibrium between cobalt rhodium heptacarbonyl and cobalt rhodium octacarbonyl in terms of the measured in situ absorptions and the pressure dependent Henry constant is

$$K_x(P,T) = [(A_{oct}/\epsilon_{oct})/(A_{hept}/\epsilon_{hept})](H_{CO}(P,T)/f_{CO}) \tag{22}$$

Equation 22 can be used directly to determine the numerical value of the equilibrium constant $K_x(P,T)$ from in situ spectroscopic data, given absorptions A_i, extinction coefficients ϵ_i, and the Henry constant.

Appendix III

Calculation of $\Delta_r G^\circ_x$, $\Delta_r H^\circ_x$, $\Delta_r S^\circ_x$, and $\Delta_r V^\infty_x$ for the Formation of $CoRh(CO)_8$. The equilibrium constant $K_x(P,T)$ is related to the free energy of reaction $\Delta_r G^\circ_x$, the enthalpy of reaction $\Delta_r H^\circ_x$, the entropy of reaction $\Delta_r S^\circ_x$, and the volume of reaction $\Delta_r V^\infty_x$ by eqs 23–25. Following the recommended notation,[36] we have

$$-\ln K_x(P,T) = \Delta_r G^\circ_x(P,T)/RT \tag{23}$$

$$-\ln K_x(P,T) = \Delta_r G^\circ_x(P_{ref},T)/RT + \Delta_r V^\infty_x(P - P_{ref})/RT \tag{24}$$

$$-\ln K_x(P,T) = \Delta_r H^\circ_x/RT - \Delta_r S^\circ_x/R + \Delta_r V^\infty_x(P - P_{ref})/RT \tag{25}$$

Implicit in eqs 24 and 25 is the assumption that the volume of reaction $\Delta_r V^{\infty}_x$ can be approximated as a constant (for equilibrium 3) and that the reference state shall be taken to be standard conditions, specifically $P = 0.1$ MPa. It is known that the partial molar volume of dissolved CO becomes strongly pressure-dependent at temperatures in excess of approximately 400 K. Therefore, the assumption that the volume of reaction (under the present conditions) can be treated as a constant, and not a function of pressure, is not a trivial and automatic condition. A discussion of the theory regarding the reaction volume $\Delta_r V^{\infty}_x$ and its inclusion into the general expression for the equilibrium constant $K_x(P,T)$ determined at varying total pressures can be found in the literature.[37]

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Preparation of d^4 Molybdenum–Olefin Complexes $[Cp(diphos)Mo(CO)(ethylene)]^+PF_6^-$ and $[Cp(Pom\text{-}Pom)Mo(CO)(ethylene)]^+PF_6^-$ (Pom-Pom = 1,2-Bis(dimethoxyphosphino)ethane) and Reactivity Studies with Carbanion Nucleophiles

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The preparation and characterization of several novel bis phosphine-substituted d^4 molybdenum-olefin complexes $[Cp(diphos)Mo(CO)(ethylene)]^+PF_6^-$ (**3**) and $[Cp(Pom\text{-}Pom)Mo(CO)(ethylene)]^+PF_6^-$ (**4**) (Pom-Pom = 1,2-bis(dimethoxyphosphino)ethane) have been carried out. Complex **3** was found to lose ethylene readily at room temperature in solution; however, complex **4** was stable for days under the same conditions. Complex **4** was further characterized by crystallographic studies. Crystal data for **4**: $P2_1/c$, $a = 10.543$ (3) Å, $b = 12.055$ (2) Å, $c = 17.372$ (5) Å, $\beta = 90.54$ (3)°, $V = 2207.7$ (11) Å^3, $Z = 4$, $R(F) = 4.95\%$. The ethylene ligand is contained in the plane defined by the metal, the center of the Cp ligand, and the *trans*-phosphorus atom. The reactivity of a simple d^4 molybdenum-olefin system toward nucleophilic attack was studied as a model for the phosphine-substituted systems. Thus, reaction of $[CpMo(CO)_3(ethylene)]^+BF_4^-$ (**1**) with the carbanion nucleophiles $Na^+[CH(COOEt)_2]^-$ and $Na^+[CH(COOEt)(COMe)]^-$ at −80 °C gives the σ-alkyl products $Cp(CO)_3MoCH_2CH_2CH(COOEt)_2$ and $Cp(CO)_3MoCH_2CH_2CH(COOEt)(COMe)$ in good yields. The phosphine-substituted ethylene complexes **3** and **4** also react with $Na^+[CH(COOEt)_2]^-$ at −78 °C to give the σ-alkyl products $Cp(P\text{-}P)(CO)Mo(CH_2CH_2CH(COOEt)_2)$, **10a** (P-P = diphos) and **10b** (P-P = Pom-Pom).

Transition-metal–olefin complexes have been utilized extensively as reagents for organic synthesis;[1] however, only a few of the presently known systems are able to transform prochiral olefins into *chiral* organic molecules. Examples of these transformations include the Monsanto process to make L-Dopa via catalytic hydrogenation using a chiral rhodium catalyst[2] and the Sharpless epoxidation of allylic alcohols in the presence of $Ti(O\text{-}i\text{-}Pr)_4$ and a chiral auxiliary.[3] These are important reactions that have enhanced the ability of chemists to pursue the synthesis of analogues of naturally occurring compounds that rely on chirality for their biological activity. In all of these systems, a heteroatom on the olefin is essential for bringing the olefin into the coordination sphere of the metal. An area of research that has yet to be successfully addressed is the design of transition-metal complexes that will facilitate the functionalization of prochiral olefins not necessarily containing heteroatoms.

The binding of an olefin to a transition metal has the effect of removing electron density from the bond between the unsaturated carbon atom. As a result, the ligand becomes susceptible to attack by nucleophilic reagents, including carbanion nucleophiles. This reactivity has been exploited most extensively by Hegedus with a palladium–

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