Cr(III) centers show more tendency toward associative reactions, but no definitive evidence for a seven-coordinate intermediate exists.[2] Nucleophilic attack at the chloride seems unlikely and would probably lead to the chloro carbonyl complex as the initial product. Nucleophilic attack on the coordinated *o*-phenanthroline was not observed in reactions of the metal carbonyl anions with $Co(o\text{-phen})_3^{3+}$.[4c] Thus, an outer-sphere mechanism is most likely for reaction of metal carbonyl anions with $Co(o\text{-phen})_2Cl_2^+$ and $CrCl_3{\cdot}3S$.

$$M^- + Co(o\text{-phen})_2Cl_2^+ \rightarrow [M^\bullet, Co(o\text{-phen})_2Cl_2] \qquad (10)$$

$$2M^\bullet \rightarrow M_2$$

The good (0.98 correlation coefficient) correlation of the ln *k* versus driving force is consistent with an outer-sphere process.

Reactions of $Co(o\text{-phen})_2Cl_2^+$ with $Mn(CO)_5^-$ and $Re(CO)_5^-$ occur more readily than reactions of $Co(o\text{-phen})_3^{3+}$. Although the reduction of $Co(o\text{-phen})_2Cl_2^+$ is not reversible, the peak potential for reduction is ~0.3 V more positive than that for $Co(o\text{-phen})_3^{3+}$.[21] The greater potential for reactions of the metal carbonyl anions with $Co(o\text{-phen})_2Cl_2^+$ in comparison to $Co(o\text{-phen})_3^{3+}$ leading to more rapid reactions are consistent with an outer-sphere process for both reaction types. Thus, all data currently available are consistent with an outer-sphere electron-transfer process for reaction of metal carbonyl anions with $Co(o\text{-phen})_2Cl_2^+$ and with $CrCl_3{\cdot}3S$.

Acknowledgment. We are grateful to the Department of Energy (Grant ER 13775) for support of this research. Jerry Keister performed the electrochemistry and provided useful comments.

Supplementary Material Available: Tables of microanalytical data and IR spectral data of the complexes and figures showing rate–concentration plots (6 pages). Ordering information is given on any current masthead page.

(21) Cyclic voltammetry was performed on CH_3CN solutions (~1 × 10^{-3} M) at a Pt working electrode and referenced to Ag/Ag^+. Peak potentials $E_{p,a}$ were determined at a scan rate of 100 mV/s.[3a]

Thermodynamics for the Hydrogenation of Dicobalt Octacarbonyl in Supercritical Carbon Dioxide†

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Received July 30, 1991

Some thermodynamic parameters relevant to hydroformylation catalysis in supercritical media are reported. Equilibrium constants for the hydrogenation of $Co_2(CO)_8$ to produce $HCo(CO)_4$ in supercritical CO_2 at a gas density of 0.5 g/mL were determined using in situ high-pressure ^1H and ^{59}Co NMR spectral measurements. van't Hoff plots for temperatures between 60 and 180 °C yielded the enthalpy and entropy changes for the reaction, 4.7 ± 0.2 kcal/mol and 4.4 ± 0.5 cal/(mol·K), respectively. The results for the CO_2 medium are close to reported values for liquid *n*-heptane solutions. The enthalpy and entropy of dissolution of $Co_2(CO)_8$ in CO_2, 4.9 ± 0.4 kcal/mol and 8 ± 1 cal/(mol·K), respectively, are also reported. Solubility measurements were facilitated with use of a novel toroid NMR detector, which differs from conventional detectors in its internally confined magnetic flux. This feature allowed selective measurement of gaseous or dissolved species within the detector coil while minimizing interference from undissolved solids or liquids exterior to it.

I. Introduction

Because of their gaslike transport properties, complete miscibilities with gases, and sharp changes in dissolving power with fluid density, supercritical fluids[1] offer the possibilities both of accelerating diffusion-controlled reactions of gases with liquid or solid substrates and of separating catalysts or products by energy-efficient pressure (and thereby, fluid density) alterations. These features would seem to be particularly beneficial in homogenous catalysis, where diffusion across the gas–liquid interface and catalyst separation are typical problems.

As part of a study of the oxo reaction in supercritical CO_2,[2] we report here the enthalpy and entropy changes for dissolution of $Co_2(CO)_8$ in CO_2 at a gas density of 0.5 g/mL and for the reaction of $Co_2(CO)_8$ with hydrogen (eq 1) in this medium.

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2HCo(CO)_4 \qquad (1)$$

II. Experimental Section

Solubility and equilibrium constant measurements were conducted in the in situ mode using a General Electric GN 300/89 NMR spectrometer equipped with a home-built pressure probe (Be-Cu, Brush-Wellman alloy 25 pressure vessel). The design and several variations of it are more fully described elsewhere.[2,3] The probe uses a novel toroid detector (elongated in the *z* direction of the magnetic field) which differs from the usual Helmholtz or solenoid detectors in its internally confined magnetic flux. The toroid detector (inner radius, 1.2 mm; outer radius, 7.1 mm; height, 16 mm) consisted of 4 turns of 20-gauge Teflon-coated (0.004 in.) copper magnet wire (Phoenix Wire, Inc.) and was double-tuned

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to observe both ^{1}H and ^{59}Co at 300.5 and 71.1 MHz, respectively. Probe heating was accomplished by means of an outer-jacketed electrical furnace that fit snugly around the pressure vessel and was powered from the spectrometer's temperature controller. Temperature control was constant to within ±0.1 °C using a copper–constantan thermocouple built into the furnace. Measured temperatures agreed to within ±1.0 °C with independent chromel–alumel thermocouple measurements inside the pressure vessel covering the range 25–175 °C.

Since $Co_2(CO)_8$ is difficult to maintain in pure form, and even freshly prepared samples are often only 90% pure, a strategy was devised for the equilibrium and solubility measurements that did not depend on the rigorous purity of the carbonyl and allowed the use of fresh samples, purchased from Alfa and stored under refrigeration, without further purification. Thus, the ratio of $[Co_2(CO)_8]$ to $[HCo(CO)_4]$ was determined by integration of the respective ^{59}Co resonances at δ −2200 and −3000 ppm (saturated aqueous $K_3Co(CN)_6$ at 0 ppm). To complete the analysis, the concentration of $HCo(CO)_4$ was determined by integration of its ^{1}H NMR signal (δ −11.7 ppm, TMS at 0 ppm) relative to that for a known concentration of H_2 at δ 4.45 ppm. In this approach, absolute concentrations of each of the species involved in the equilibrium of eq 1 were determined on the basis of the known concentration of hydrogen (high purity, Matheson), which was calculated from its pressure using the ideal gas law. ^{1}H spectra were obtained using 500 (15°) pulses with a 2.2-s recycle time. ^{59}Co spectra were obtained using 1000 (30°) pulses with a 28-ms recycle time. Tests with longer recycle times and smaller tip angles indicated the absence of saturation effects with the acquisition parameters used. In order to minimize transmitter offset effects potentially stemming from the large ^{59}Co chemical shift differences, quadrature phase detection was used, with placement of the transmitter frequency precisely between the $HCo(CO)_4$ and $Co_2(CO)_8$ resonances. This optimized equal irradiation of the two resonances by the transmitter and equal attenuation by the spectrometer's audio filters. Because of the large temperature dependence of ^{59}Co shieldings, ~100 Hz/K,[4] the transmitter and spectral window settings were recentered and the probe was returned for each temperature used in the measurements. Ratios of signal integrals obtained in this fashion agreed closely with values obtained in tests where the two peaks were irradiated separately when centered in a much smaller spectral window. The large chemical shift difference prevented significant contribution from foldovers in the test spectra.

Equilibrium constant measurements were initiated by admitting the required pressures of reactive gases, H_2 (34.0 atm) and CO (68.0 atm), into the pressure vessel containing $Co_2(CO)_8$ under 1 atm of N_2. Pressures were measured to within ±0.07 atm using a strain-gauge pressure transducer (Omega, Model PX302-5KGV). The vessel was then heated to 34 °C, and liquid CO_2 was added by means of a high-pressure syringe pump until the measured pressure increase was 82 atm, thereby achieving a fluid density of approximately 0.5 g/mL.[1] A temperature slightly above its critical value of 31.2 °C was used for the addition to ensure complete vaporization of CO_2 to avoid a potentially hazardous pressure surge which could be generated by the syringe pump were the vessel to inadvertently fill with liquid. Automated magnet shimming, on the ^{1}H signal of H_2, and spectral observations, alternating between ^{1}H and ^{59}Co, were commenced shortly after heating the closed system to the desired reaction temperature. The progress of the equilibrium was followed for ≥5 half-lives of reaction, 4 days at 60 °C, and equilibrium constants were calculated by averaging the results from five spectra on each nucleus at each temperature.

Solubility measurements for $Co_2(CO)_8$ in the gas mixture (H_2 34.0 atm, CO 68.0 atm, CO_2 81.6 atm) were conducted in the same manner as the equilibrium constant measurements except that the pressure vessel was initially charged with an excess of solid $Co_2(CO)_8$, 1.0 g, situated below the toroid detector coil. Gas-phase concentrations of $Co_2(CO)_8$ within the detector coil were calculated from the measured H_2 pressure and the integrated intensities of the H_2, $HCo(CO)_4$, and $Co_2(CO)_8$ resonances in the ^{1}H and ^{59}Co spectra. Data acquisition parameters were the same, and equilibrium times were similar to those used in the equilibrium constant measurements.

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III. Results and Discussion

A. Related Chemistry in Supercritical CO_2. In an earlier study of the hydroformylation reaction[2] we had found that carbon dioxide is remarkably free of ancillary chemical reactions that could interfere with the measurements described here. Thus, at least at the high CO pressures used in our experiments, CO_2 participation in the type of exchange processes that occur with the metal carbonyls and H_2 and CO appears to be negligible. For example, the normally separate ^{13}C resonances measured at 34 °C for free CO (1.4 M, δ 185 ppm) and coordinated CO in $Co_2(CO)_8$ (0.03 M, δ 201 ppm) coalesce at 145 °C to form a broad singlet near 186 ppm in supercritical CO_2 solution. Under these conditions where CO exchange is rapid, the CO_2 resonance (11 M, δ 125 ppm) remains sharp, indicating that CO_2 exchange is slower or, at least, less extensive. Indeed, we have not observed significant broadening of the CO_2 resonance even at temperatures above 200 °C. In another test, ^{1}H spectra also did not reveal dynamic or equilibrium processes involving CO_2 or other species that might interfere with the measurements. The ^{1}H spectra of a supercritical CO_2 solution containing $Co_2(CO)_8$, H_2, and CO (4.4×10^{-3}, 0.28, and 2.8 M, respectively) were recorded at intervals of 10–25 °C for temperatures between 34 and 205 °C. The proton resonances for H_2 and $HCo(CO)_4$ showed no significant change in width or in relative chemical shift values even at 205 °C. Apparently, reversible processes that would lead to chemical shift changes or line broadening, such as formation of $HCO_2Co(CO)_4$, $HC(O)Co(CO)_4$,[5-7] or $H_3Co(CO)_3$,[8] are not rapid and extensive enough to observe by this means under the conditions tested. The proton spectra revealed the presence of a small amount of water, δ = ~0.9 ppm, apparently produced by reverse water-gas shifting. The reverse water-gas shift can yield only trace amounts of water due to both an unfavorable enthalpy change and the high pressures of carbon monoxide present. It is noteworthy that although $HCo(CO)_4$ behaves as a strong acid in polar solvents including H_2O,[9] CH_3OH,[10] and CH_3CH[11] the proton signals for H_2O and $HCo(CO)_4$ in the low dielectric supercritical CO_2 medium do not show evidence for exchange broadening even at 205 °C.

In addition to resonances for $HCo(CO)_4$ and $Co_2(CO)_8$, the ^{59}Co spectra showed the presence of an unidentified sharp peak (HHW = 660 Hz; HHW = half-height width) at δ −1370 ppm. Although this resonance might be due to $HCO_2Co(CO)_4$ or one of the other aforementioned cobalt species, its low concentration, less than 1% of the total cobalt present, has so far prevented observation of related ^{1}H signals which might lead to its identification. We are currently exploring reaction conditions that might be more conducive to its formation with the aim of determining its identity.

The fate of $Co_4(CO)_{12}$ has also been investigated in supercritical CO_2 solution. Although not present under

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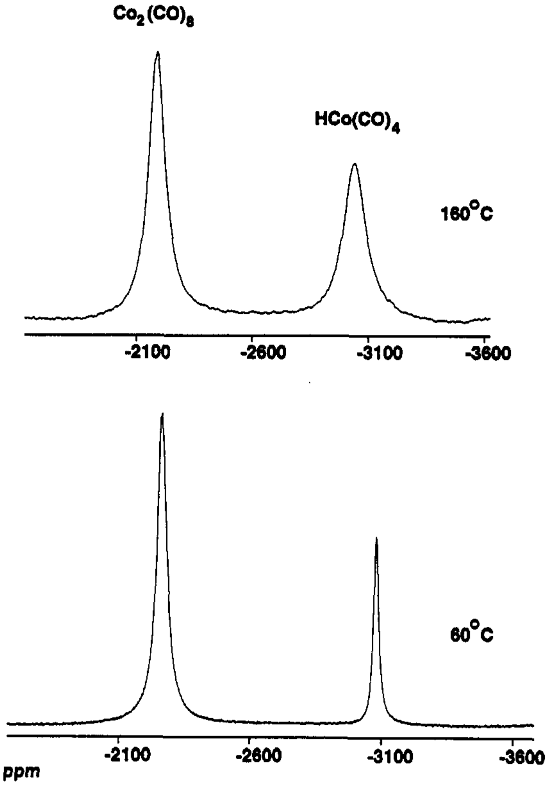

Figure 1. Representative ^{59}Co spectra used in the equilibrium constant measurements for the hydrogenation of dicobalt octacarbonyl in supercritical CO_2.

conditions used in the equilibrium constant measurements, at higher temperatures or lower CO pressures $Co_4(CO)_{12}$ is formed and can be observed as a well-separated single ^{59}Co resonance at −1660 ppm. This resonance stems from interconversion of the apical and basal cobalt in $Co_4(CO)_{12}$ which is rapid on the NMR time scale above 70 °C.[2] Significantly, the resonance for $Co_4(CO)_{12}$ does not show evidence for fast exchange with either $Co_2(CO)_8$ or HCo-$(CO)_4$ at 200 °C in supercritical CO_2.

Other than those for the cobalt species already discussed, no additional ^{59}Co signals were observed, even though the entire range of chemical shift values (18 000 ppm)[12] was searched. However, it should be noted that even if a significant cobalt species were overlooked, the accuracy of the method chosen for the equilibrium constant and solubility measurements would not be affected so long as accidental chemical shift overlaps with the species of eq 1 do not occur.

A typical ^{59}Co spectrum used in the equilibrium constant determinations is shown in Figure 1. The spectral measurements benefited from substantial line narrowing that occurs for quadrupolar nuclei,[13] stemming from the lower viscosities of supercritical fluids when compared with those of normal liquids. The ^{59}Co resonance of $Co_2(CO)_8$ is approximately a factor of 6 narrower in supercritical CO_2 at a density of 0.5 g/mL than in liquid benzene-d_6.[2] Signals for $HCo(CO)_4$ and $Co_2(CO)_8$ existed as well-separated resonances up to 180 °C. However, equilibrium measurements above this temperature were prevented by a dyanamic process that caused broadening, and, ultimately, merging of the two ^{59}Co signals. Although other possibilities exist,[14] this process is suspected to result from fast

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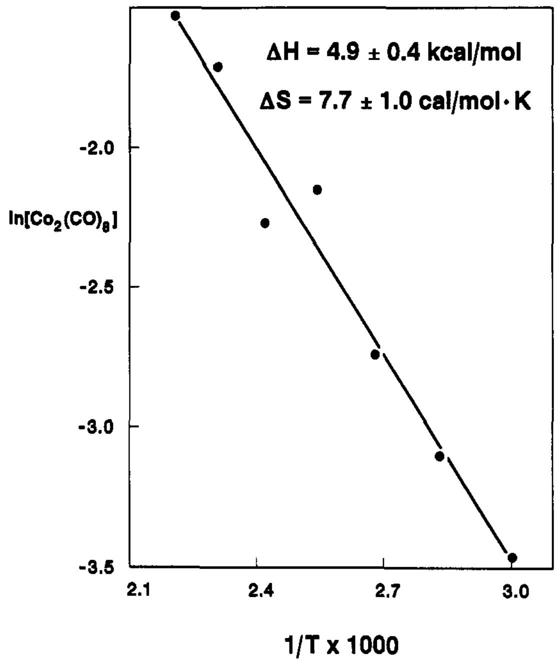

Figure 2. Solubility of $Co_2(CO)_8$ in supercritical CO_2.

hydrogen atom transfers involving the species of HCo(C-O)$_4$, $Co_2(CO)_8$, and $^{\bullet}Co(CO)_4$ and will be described more fully in a future publication.

B. Thermochemical Parameters. Solubilities of metal carbonyls in CO_2 are reasonably high. For the several carbonyls that we have tested, solubilities are suffient to allow NMR spectral measurements on many nuclei, even of ^{13}C at natural abundance. The results of measurements for $Co_2(CO)_8$ are shown in Figure 2. The plot of ln $[Co_2(CO)_8]$ vs $1/T$ is linear and yielded the values 4.9 ± 0.4 kcal/mol and 8 ± 1 cal/(mol·K) for the enthalpy and entropy of dissolution, respectively. It should be noted that the method for solubility determinations used here, which depends on the ability of a toroid coil to effectively exclude signals from undissolved solids or liquids near its exterior, differs from that used by Jonas et al.[15] to measure the solubility of naphthalene in supercritical CO_2. The latter method used a spin echo pulse sequence to separate signal contributions from solid and dissolved species both present within the confines of a solenoid detector. In our experience the toroid method appears to work well when the solubility of the measured material is reasonable high, and where line widths for the undissolved solid or liquid are much larger than those in the supercritical phase, as is usually the case for quadrupolar nuclei. Both of these features would tend to minimize signal contributions from undissolved species near (or that might condense onto) the detector. For example, with the acquisition parameters used in the experiments, no ^{59}Co signal for $Co_2(CO)_8$ could be detected prior to addition of CO_2. For cases less favorable than that measured here, use of a combination of the two methods just described would seem to be ideal. Toroid detectors with reasonably accurate π-nulls required for the spin echo pulse sequence have been described elsewhere.[3,16,17]

Equilibrium constants for the hydrogenation of dicobalt octacarbonyl (eq 1) were measured at two different initial

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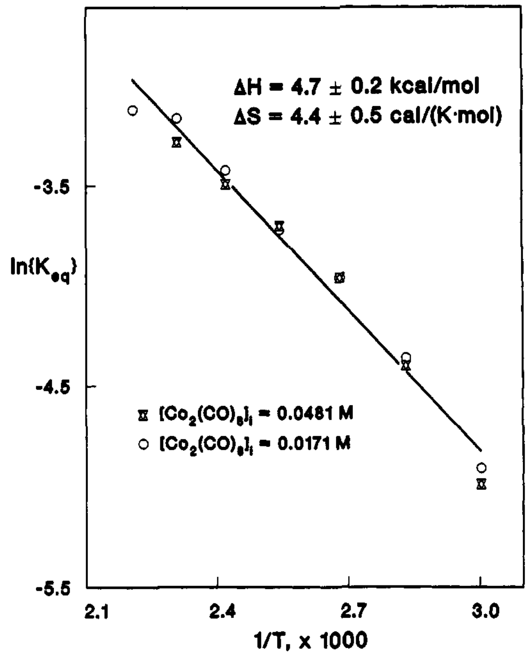

Figure 3. van't Hoff plot for the hydrogenation of dicobalt octacarbonyl in supercritical CO_2.

Table I. Thermochemical Parameters for the Hydrogenation of $Co_2(CO)_8$[a]

param	*n*-heptane(l)[b]	CO_2(g)
K(80 °C)	0.096 (5.9 × 10^{-4})	0.011 (3.9 × 10^{-4})
$\Delta H°$, kcal/mol	3.2 (4.3)	4.7 (4.0)
$\Delta S°$, cal/(mol·K)	4.4 (-2.6)	4.4 (-4.2)

[a] Standard states for H_2 in eq 1 are 1.0 M and 1.0 atm (in parentheses). [b] Data from Ungvâry.[18] [c] Equilibrium constants in parentheses are K_p values and have units of M/atm.

concentrations of $Co_2(CO)_8$ (0.0171 and 0.0481 M) at intervals of 20 °C for temperatures in the range 60–180 °C. Equilibrium constants measured at the two concentrations agreed closely, the largest discrepency being 11% for the two values at 160 °C. The van't Hoff plot (Figure 3) yielded the enthalpy and entropy changes for the reaction, 4.7 ± 0.2 kcal/mol and 4.4 ± 0.5 cal/(mol·K), respectively. Table I compares thermochemical results for the hydrogenation inCO_2 with Ungvâry's values for liquid *n*-heptane solutions.[18] Because the activities of gases are more closely related to their pressures than to their concentrations, the most meaningful comparison of the results in the supercritical fluid with the liquid medium is for data which use hydrogen pressure (1.0 atm) for the standard state of H_2 in eq 1. To obtain these parameters, solubilities of H_2 in *n*-heptane[19] were used to convert Ungvâry's results to the pressure data shown in the table. For parameters using the hydrogen pressure standard state, results for CO_2 (K_p(80 °C) = 3.9 × 10^{-4} M/atm, $\Delta H°$ = 4.0 kcal/mol, and $\Delta S°$ = -4.2 cal/(mol·K)) agree closely with Ungvâry's results for *n*-heptane solutions (K_p(80 °C) = 5.9 × 10^{-4} M/atm, $\Delta H°$ = 4.3 kcal/mol, and $\Delta S°$ = -2.6 cal/(mol·K)). The K_p values for the two media differ by only 34% and the enthalpy and entropy changes by 0.3 kcal/mol and 1.6 cal/(mol·K), respectively. The close correspondence of these values would be expected for the reaction in the relatively nonpolar liquid and supercritical media. The necessity for converting to a hydrogen pressure standard state to compare the data for the *n*-heptane and CO_2 solutions is most evident in the equilibrium constant measurements that use H_2 concentrations. As shown in Table I, the equilibrium constants in CO_2 (0.011) and in *n*-heptane (0.096) differ by nearly 1 order of magnitude when compared in this way.

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IV. Conclusions

Equilibrium constants for the hydrogenation of $Co_2(CO)_8$ in supercritical carbon dioxide were measured throughout the temperature range 60–180 °C, commonly employed for the catalyzed hydroformylation of olefins. No irreversible reactions with CO_2 were uncovered by the high-pressure NMR techniques used in the measurements, whereas the measured thermochemical parameters were determined to be close to those for a nonpolar liquid medium of the type prevalent in hydroformylation chemistry.

Enthalpy changes for the hydrogenation of complexes containing metal to metal bonds relate metal to hydrogen and metal to metal bond energies, parameters which are of central importance to many catalytic processes. The supercritical fluid/toroid probe technique employed here appears to be ideally suited for the requisite enthalpy determinations. Since only one phase is present, corrections for liquid expansion/compression or separate determinations of gas/liquid partitioning, often necessary for measurements in liquid media, are obviated in the supercritical system. ^1H NMR signals for dihydrogen and metal hydrides are generally intense and are well separated, while the aforementioned line-narrowing effect on the quadrupolar nuclei commonly present in the metal species facilitates their determination. Maximum sensitivity is often required in studies of organometallic systems, and toroid detectors achieve it through their superior coil efficiencies, optimal filling of the cylindrical space within the pressure vessel, and minimization of magnetic coupling losses.[3]

The observation of the dynamic process that causes coalescence of the ^{59}Co signals for $HCo(CO)_4$ and $Co_2(CO)_8$ near 200 °C indicates the possible presence of the tetracarbonylcobalt radical. In future studies, we aim to quantitate$^{\bullet}Co(CO)_4$ in this system while providing an independent determination of the Co–Co and Co–H bond energies in $Co_2(CO)_8$ and $HCo(CO)_4$, through high-pressure NMR magnetic susceptibility measurements and lineshape analysis.

Acknowledgment. We thank Professors J. Halpern and J. Norton for helpful discussions. Support for this work was provided by the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy.

Registry No. $Co_2(CO)_8$, 10210-68-1; $HCo(CO)_4$, 16842-03-8; *n*-heptane, 142-82-5.