Czechoslovak Academy of Sciences.) A quartz beamsplitter was used to reflect about 10% of the monochromatic light which then passed through a cell containing pure solvent and onto a reference photodetector. The remaining 90% of the beam (10^{-8}–10^{-9} einstein·s^{-1}) passed through the sample solution (volume $V = 3$ mL, optical length $l = 1$ cm) and onto the sample photodetector. Model 6220 integrating photodetectors using a Si-diode and a Rhodamine B quantum counter were used. To achieve high precision, the detectors were calibrated at each individual irradiating wavelength using Aberchrome 540P (400 nm < λ_{exc} < 550 nm), 540 (λ_{exc} = 362 nm) or 999P (λ_{exc} > 550 nm) reversible actinometers[53] supplied by Aberchromics, Ltd., Wales, U.K. Absorption spectra were monitored after each irradiation interval of known duration (Δt). Quantum yields were evaluated by two different procedures which afforded, within the experimental error, identical results. Both procedures took into account the decrease of the light absorbance by the photoactive compound due to both its depletion and the increasing inner-filter effect exerted by the photoproduct. The first procedure used only the value of the incident light intensity I_0 as measured by the reference photodetector. The quantum yields were calculated according to the equation[26]

$$\ln \frac{A - A_\infty}{A_0 - A_\infty} = \frac{\phi I_0 \epsilon l}{V} \int_0^t \frac{1 - 10^{-A}}{A}\, dt \qquad (2)$$

where A, A_0, and A_∞ are the values of the absorbance at λ_{exc} of the sample solution at time t, before the irradiation, and after the completion of the reaction. ϵ is the extinction coefficient of the starting compound at λ_{exc}. Values of A_∞ were calculated as $\epsilon_p A_0/\epsilon$ where ϵ_p is an extinction coefficient of the $[Cr(CO)_3(PPh)_3bpy]$ photoproduct measured at λ_{exc}. The ϵ_p values were determined from the spectra of authentic samples of $[Cr(CO)_3(PPh)_3bpy]$. Alternatively, the number of photons absorbed in each irradiating interval, N, was calculated by subtracting the light intensity passed through the sample (measured by the sample photodetector) from I_0. The quantum yields can than be evaluated according to the equation

$$\phi = \frac{V}{\epsilon N}\left[(A_0 - A) + A_\infty \ln\left(\frac{A_0 - A_\infty}{A - A_\infty}\right)\right] \qquad (3)$$

where A is the absorbance at the irradiating wavelength measured after the absorption of N moles of photons. In the case of excitation into the isosbestic point, eq 4[54] was used:

$$\ln \frac{c_0}{c_p} = \frac{\phi I_0}{c_0 V}(1 - 10^{-A_0})\Delta t \qquad (4)$$

where c_0 and c_p are the initial concentration of the photoreactive species and the photoproduct concentration after irradiating interval Δt. These values were determined spectroscopically. Quantum yields were always measured for several irradiating intervals at the beginning of the irradiation when reaction 1 occurred completely isosbestically. All measurements were repeated at least three times.

Picosecond absorption spectra were obtained using a system[55] based on a mode-locked Nd/YAG laser and OMA for data collection. The samples were excited either at 355 or 532 nm using 30-ps laser pulses of an average energy of 2.5 mJ per pulse. The spectra were monitored with a 425–675 nm probe pulse. Larger volumes (5–10 mL) of sample solutions were placed in a Schlenk tube with an attached 2 mm spectral cell under nitrogen atmosphere and thoroughly mixed between the measurements. Absorbance at the excitation wavelength was kept within the 0.35–0.55 range. When experiments were performed in pyridine, fresh solutions of identical concentration were used for the measurement of the spectra at each time delay.

Acknowledgment. Picosecond spectra were measured using the facilities of the Canadian Picosecond Laser Center at Concordia University, Montreal. Dr. D. K. Sharma is thanked for his technical assistance. Laser experiments, as well as the stay of one of the authors (A.V.) at Concordia, were financially supported by NSERC. A.V. gratefully acknowledges Prof. C. H. Langford for his great hospitality and for many stimulating discussions. Prof. D. J. Stufkens (Universiteit van Amsterdam) is thanked for his valuable comments. We also acknowledge the generous loan of Aberchrome actinometers from Prof. H. G. Heller, University of Wales, Aberystwyth.

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Metal Carbonyl Complexes with Xenon and Krypton: IR Spectra, CO Substitution Kinetics, and Bond Energies[1]

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Abstract: IR spectra for complexes between Xe and Kr and $M(CO)_5$ (M = Cr, W) have been obtained using laser photolysis of $M(CO)_6$ and rapid-scan FTIR spectroscopy of liquid rare-gas solutions. The Kr complexes have lifetimes of ~0.1 s at 150 K in liquid Kr while $W(CO)_5Xe$ has a lifetime of ~1.5 min at 170.0 K in liquid Xe. $W(CO)_5Xe$ reacts with CO to form $W(CO)_6$ and the CO substitution kinetics were investigated in liquid Xe over a range of temperatures (173.0–198.0 K) and CO concentrations. The kinetics are consistent with a dissociative substitution mechanism in which $W(CO)_5Xe$ is in equilibrium with $W(CO)_5$. From the temperature dependence of the equilibrium constant, the Xe–W bond energy in $W(CO)_5Xe$ is obtained, $\Delta H = 8.4 \pm 0.2$ kcal/mol in good agreement with a recent gas-phase value.

Introduction

The coordinatively-unsaturated, pentacarbonyl fragments, $M(CO)_5$ (M = Cr, Mo, and W), are extremely reactive and form complexes with species normally considered inert such as CF_4, SF_6, CH_4, Ar, Kr, and Xe.[2] Recent work has focussed on the complexes with alkanes due to their importance in catalysis and in solution reaction mechanisms.[3] However, the ability to form complexes with rare-gas atoms is intriguing and further inves-

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tigation is required in order to discern the nature of this bonding interaction.

Rare-gas complexes with metal carbonyls were first discovered in early matrix isolation studies of the d^6 pentacarbonyl fragments, $M(CO)_5$ (M = Cr, Mo, and W).[2] This work showed that the visible absorption band of the fragment is strongly dependent on the identity of the matrix host and indicated the formation of complexes with species including Ar, Kr, and Xe. Subsequently, these same authors were able to observe FTIR spectra of $Cr(CO)_5Xe$ in liquid Xe and Kr,[4] providing further evidence for the formation of rare-gas complexes with significant stability. EPR spectra of the complexes $KrMn(CO)_5$ and $KrFe(CO)_5^+$ have been observed[5] and recent work using time-resolved IR spectroscopy implicated the formation of Cp*Rh(CO)Q (Cp* = η^5-$C_5(CH_3)_5$, Q = Kr, Xe) from photolysis of $Cp^*Rh(CO)_2$ in liquid rare-gas solvents.[6,7]

In this work we have used rapid-scan FTIR spectroscopy of liquid rare-gas solvents to characterize the complexes $M(CO)_5Q$ (M = Cr, W; Q = Kr, Xe). Using a commercial FTIR spectrometer synchronized with a pulsed laser, we have obtained IR spectra of the complexes in liquid rare-gas solvents with 0.09 s time resolution and 8 cm^{-1} frequency resolution. This is the first observation of $Cr(CO)_5Kr$, $W(CO)_5Kr$, and $W(CO)_5Xe$ in fluid solution. In addition, we have investigated the CO substitution kinetics of $W(CO)_5Xe$ to reform $W(CO)_6$ under a range of temperatures and CO concentrations. The kinetics are consistent with a dissociative substitution mechanism in which $W(CO)_5Xe$ is in equilibrium with $W(CO)_5$. From the temperature dependence of the equilibrium constant, we have determined the bond energy of Xe to $W(CO)_5$ to be $\Delta H = 8.4 \pm 0.2$ kcal/mol. This result is in excellent agreement with a recent value from gas-phase studies[8] and demonstrates the utility of this approach for determining the bond energies of weakly-bound ligands to coordinatively-unsaturated metal centers.

Experimental Section

A full description of the experimental details is in preparation.[9,10] Briefly, liquid rare-gas solutions were formed in a special high-pressure, low-temperature cell. The cell, consisting of a copper block with two perpendicular optical axes 1.43 and 5.0 cm in length and 0.375 in. in diameter, was enclosed in an evacuated dewar. It was cooled with liquid nitrogen and the temperature was measured with silicon diodes (±0.1 K) and controlled via heaters. The cell windows (BaF_2) were sealed onto the copper block using indium metal gaskets, threaded mounts, and spring washers to achieve pressures as high as 1000 psia. The cell was equipped with magnetic stirring and was mounted in the sample compartment of a commercial FTIR spectrometer (Nicolet 800). Samples containing metal carbonyls, CO, and rare gases were prepared on a stainless steel vacuum line.

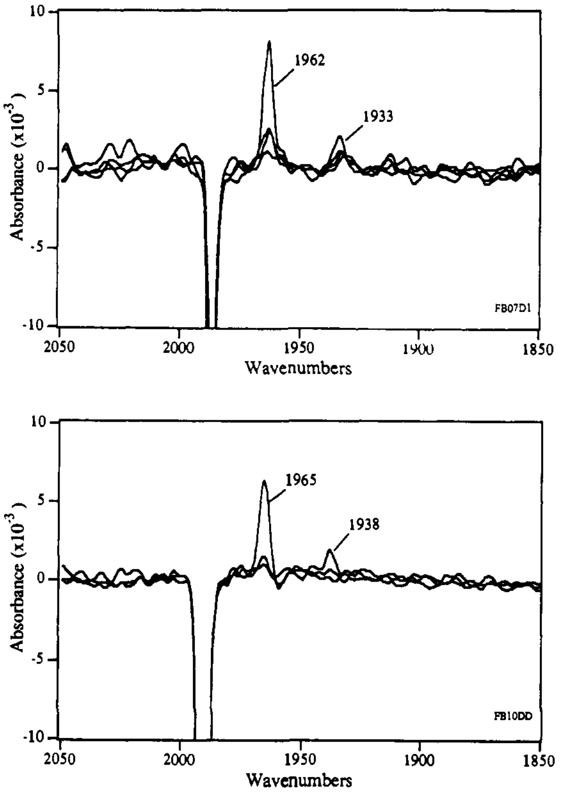

Figure 1. Rapid-scan FTIR spectra of $M(CO)_5Kr$ in liquid Kr at 150 K: (a, top) M = W, (b, bottom) M = Cr. Both spectra are the difference between spectra taken before and after photolysis and the large negative peak is due to photolysis of $M(CO)_6$. The time between spectra is 0.09 s.

Table I. IR Frequencies for $M(CO)_5(Q)$ Complexes

$M(CO)_5Q$	frequencies (cm^{-1})			conditions	ref
$W(CO)_5(Ar)$		1969	1935	Ar (s), 10 K	18
$W(CO)_5(Kr)$		1962[a]	1933[a]	Kr (l), 150 K	this work
$W(CO)_5(Xe)$	2090	1958	1930	Xe (l), 170 K	this work
		1963	1936	Kr (l), 183 K	this work
$W(CO)_5(CO_2)$		1956	1926	Ar (s), 10 K	18
		1957[a]	1930[a]	Kr (l), 180 K	9
$W(CO)_5(CyH)$[b]		1959	1935	Kr (l), 180 K	19
$W(CO)_5(H_2)$	2098	1972	1970	Xe (l), 193 K	16a
$Cr(CO)_5(Ar)$		1973	1936	Ar (s), 10 K	18
$Cr(CO)_5(Kr)$		1965[a]	1938[a]	Kr (l), 150 K	this work
		1961[c]	1933[c]	Ar (s), 10 K	2
$Cr(CO)_5(Xe)$	2087	1960	1934	Xe (l), 163 K	this work
		1960.3	1934	Xe (l), 175 K	4
		1956	1929	Xe (s), 20 K	2
$Cr(CO)_5(CO_2)$		1952	1925	Ar (s), 10 K	18
$Cr(CO)_5(CyH)$		1961	1939	Kr (l), 140 K	19
$Cr(CO)_5(N_2)$	2086	1974	1964	Xe (l), 183 K	15
$Cr(CO)_5(H_2)$	2094	1974	1972	Xe (l), 200 K	16b
$Cr(CO)_5(H_2O)$		1946	1916	CyH (l), 298 K	17

[a] Spectral resolution was 8 cm^{-1} but the peak positions are accurate to ~±2 cm^{-1}. [b] CyH = cyclohexane. [c] Estimated frequencies from ref 2.

For time-resolved IR spectra, an Excimer laser (Questek) was synchronized with the moving mirror of the spectrometer. With the mirror modulated at the maximum velocity, it was possible to collect a full interferogram in ~45 ms at 8 cm^{-1} frequency resolution. The laser was aligned along the long axis of the cell while the IR beam passed through the short axis. A shutter (Uniblitz) served to block the laser until the start command was given at the keyboard of the computer. A TTL pulse then opened the shutter to let a single laser pulse irradiate the sample and interferograms were collected at equal time intervals after the laser pulse for the desired time period. The laser wavelength was 248 nm and typical laser pulse energies were ~40 mJ in a 0.71 cm^2 beam. The laser was synchronized to fire 2 ms prior to start of data collection and data were collected in the forward direction only to give a 90 ms time interval between spectra. After data collection, the interferograms were transformed and converted to absorbance and the difference was taken with reference spectra. For kinetic measurements, peak areas were used in order to avoid complications from potential distortions in peak widths.[11] CO concentrations were determined from the integrated absorbance of the CO band using the gas-phase band strength[12] corrected for the index of refraction of the solvent.[13] Chemicals were obtained from the following suppliers: $Cr(CO)_6$ and $W(CO)_6$ (Alfa), Xe and Kr (Spectra

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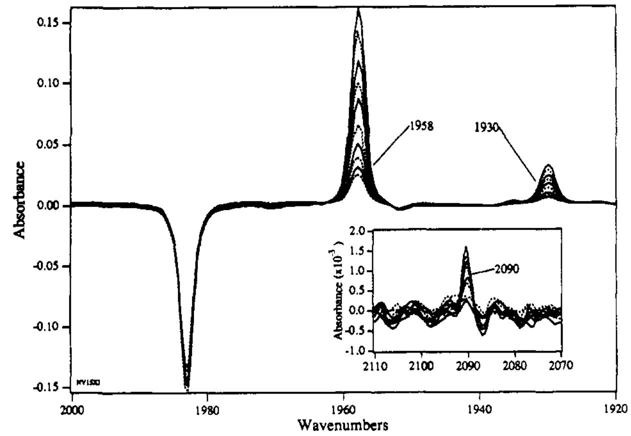

Figure 2. Spectra of $W(CO)_5Xe$ in liquid Xe at 170.0 K. The times of the spectra after photolysis are 0.00, 0.17, 0.33, 0.50, 0.65, 1.00, 1.33, 1.67, 2.00, and 2.32 min.

Gases, research grade), and CO (Matheson, research grade). CO was purified with a liquid-N_2 cooled trap and the other chemicals were used without further purification.

Results and Discussion

$W(CO)_5Kr$ and $Cr(CO)_5Kr$. Figure 1 shows the IR spectra obtained after photolysis of $W(CO)_6$ (top) and $Cr(CO)_6$ (bottom), both obtained in liquid Kr at ~150 K using a single laser pulse. In each case two IR bands could be observed and are listed in Table I along with literature data for complexes of $Cr(CO)_5$ and $W(CO)_5$ with Ar, Kr, and Xe. In both cases, the transient decays after the first scan of the interferometer at this temperature. At lower temperatures the transients are longer lived but solubility is a problem. The bands in Figure 1 could not be observed at temperatures above 160 K or when the Kr was doped with added reagents such as CO_2 at ~0.05 M concentrations. The metal carbonyls are not soluble in liquid Ar and it was not possible to examine solutions of Ar doped with Kr. As shown in Table I, the IR bands that we observe are in agreement with matrix isolation observations for $M(CO)_5Kr$. In addition, the band positions are consistent with the expected trend with polarizability of the rare-gas atom. Therefore we assign these bands to $M(CO)_5Kr$.

It is unlikely that impurities in the Kr are responsible for the spectra in Figure 1. We have observed the same features using three separate bottles of Kr from two manufacturers including one which was specially purified.[14] The IR spectra for the complexes with the potential impurities N_2,[15] H_2,[16] H_2O,[17] Xe,[4] CO_2,[18] and cyclohexane[19] have been observed previously and are presented in Table I. In addition to having the wrong frequencies, the N_2, H_2, H_2O, and Xe complexes are all too stable to account for the short lifetimes observed at 150 K. Experiments using CF_4 or CH_4 dissolved in the Kr gave no new bands but the transient decays faster with added O_2. O_2 has been observed to photooxidize $M(CO)_6$ in matrix isolation studies.[17] The stability of alkane complexes varies widely[3a] and alkanes such as cyclohexane form long-lived (minutes) complexes with $W(CO)_5$ and $Cr(CO)_5$ at these temperatures[18] whereas the CH_4 complex is not observable. Given the similarity in IR frequencies for the hydrocarbon and Kr complexes, a possibility that we cannot rule out conclusively is a hydrocarbon impurity that forms a complex of moderate stability. However, assignment to the Kr complexes is the simplest and most likely explanation that is consistent with other spectroscopic observations.

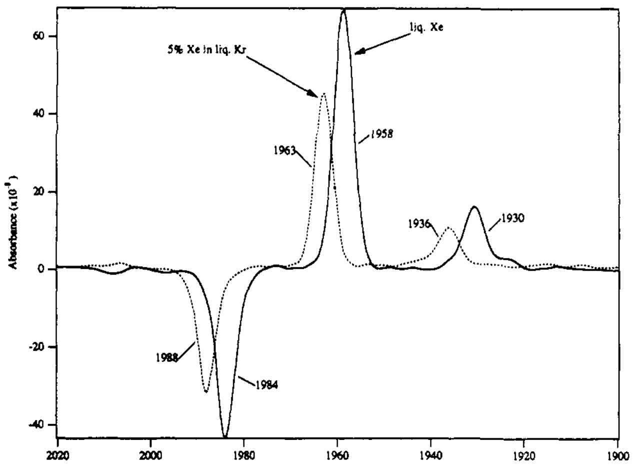

Figure 3. Spectra of $W(CO)_5Xe$ in liquid Xe and liquid Kr. The liquid Xe spectrum is at 198 K and the liquid Kr spectrum is from a 5% mixture of Xe in Kr at 183 K.

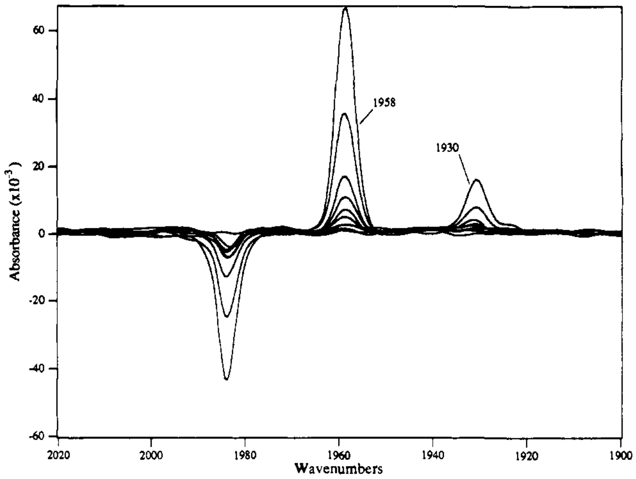

Figure 4. Rapid-scan FTIR spectra of $W(CO)_5Xe$. The temperature is 198.0 K and the CO concentration is 0.011 M.

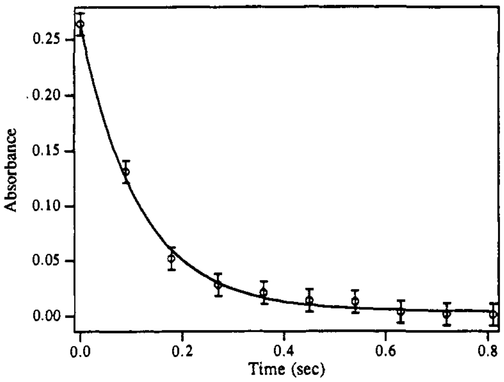

Figure 5. Time dependence of $W(CO)_5Xe$. The integrated absorbance of the peak at 1958 cm^{-1} is plotted versus time. The solid line is an exponential fit with a decay constant (k_{obs}) of 8.6 ± 0.4 s^{-1}.

$W(CO)_5$ and $Cr(CO)_5Xe$. Figure 2 shows the IR spectrum observed when $W(CO)_6$ is photolyzed in liquid Xe at 170.0 K with no added reagents. At this temperature the lifetime is ~1.5 min. Similar results have been obtained for $Cr(CO)_6$ and are shown in Table I. As Table I shows, the bands that we observe from photolysis of $Cr(CO)_6$ in liquid Xe are in excellent agreement with

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[14] Ar, CO_2, CF_4, H_2, and N_2 < 0.5 ppm each, total hydrocarbons, O_2, and H_2O < 0.25 ppm each, and Xe < 1 ppm. Analysis supplied by Spectra Gases, Inc., Irvington, NJ.

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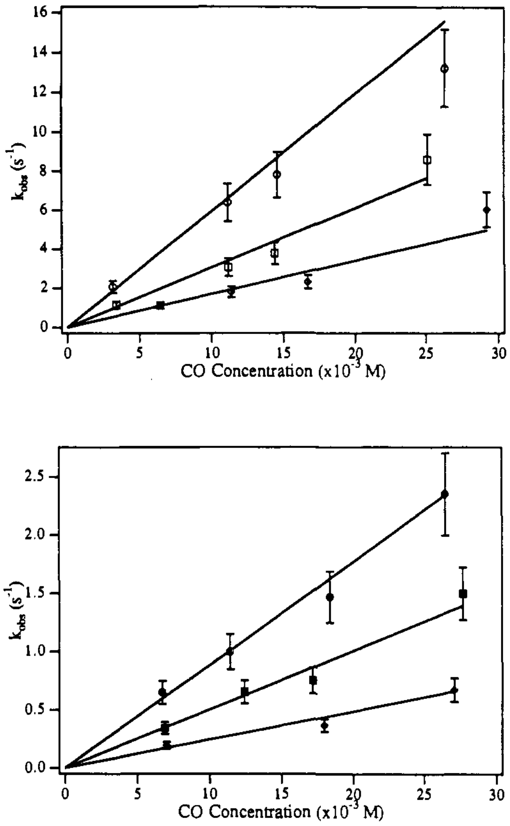

Figure 6. CO concentration dependence of k_{obs}: (a) 198.0 (○), 193.0 (□), and 188.0 K (◇); (b) 183.0 (●), 178.0 (■), and 173.0 K (◆). The slopes of these lines are termed k_{CO} and are shown in Table II. The last data point in the 198.0 K set is not included in the fit (see text).

Table II. Comparison of Calculated and Observed Rate Constants

T (K)	[Xe] (M)	10^7K_1 (M)	K_1k_2/[Xe] (s^{-1})^a	k_{CO} (s^{-1})
198.0	20.60	22.8	554	592 ± 69
193.0	20.89	13.1	314	304 ± 42
188.0	21.18	7.35	174	169 ± 28
183.0	21.45	3.98	93	88 ± 7
178.0	21.72	2.09	48	50 ± 5
173.0	21.98	1.05	24	24 ± 3

^{a}Calculated using $k_2 = 5 \times 10^9$ M^{-1} s^{-1}, see text.

previous studies in liquid Xe that showed the product to be $Cr(CO)_5Xe$.[4] We are also able to observe the weak a_1 band at higher frequency expected for C_{4v} symmetry. The decay rates we observe are much slower than previously reported.[4]

In order to confirm the assignment to $W(CO)_5Xe$, we have obtained IR spectra using a mixture of ~5% Xe in Kr as shown in Figure 3 along with the spectrum in pure Xe. In liquid Kr, all of the bands, including that for $W(CO)_6$, display the same shift (4 cm^{-1}) from liquid Xe. Furthermore, the lifetime of the complex in liquid Kr is approximately the same as in liquid Xe. Given these observations and the agreement with previous studies in rare-gas solvents and matrices, we assign the bands in Figures 2 and 3 to $W(CO)_5Xe$.

CO Substitution Kinetics. Figure 4 shows the time-resolved IR spectra obtained after photolysis of $W(CO)_6$ in liquid Xe at 198.0 K with a CO concentration of 0.011 M. $W(CO)_5Xe$ decays and $W(CO)_6$ recovers with the same time constant within experimental error. Figure 5 shows that the integrated absorbance of the peak at 1958 cm^{-1} is well characterized by a simple exponential decay. Figure 6 shows the CO dependence of the observed decay constants at various temperatures from 173.0 to 198.0 K. At all temperatures the decay constants show a linear dependence on CO concentration; the slopes are termed k_{CO} and are listed in Table II. The last data point in the 198.0 K set is too fast for the spectrometer and is not included in the fit. The slopes are observed to increase approximately 2-fold for every 5 °K increase.

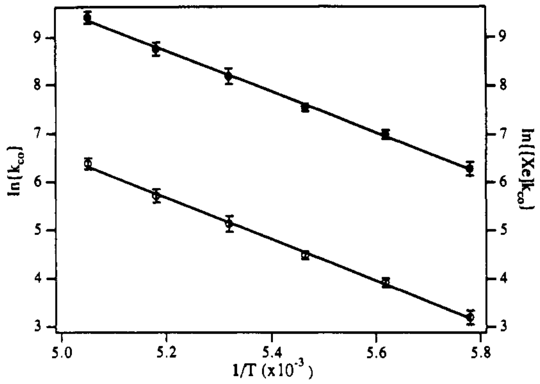

Figure 7. Arrhenius plots: ln $\{k_{CO}\}$, log (A) = 12.2 ± 0.2, E_a = 8.5 ± 0.2 kcal/mol (○); ln $\{[Xe]k_{CO}\}$, log (A) = 13.3 ± 0.2, E_a = 8.4 ± 0.2 kcal/mol (●).

A probable mechanism for the reaction of $W(CO)_5Xe$ with CO is dissociative substitution in which loss of Xe from $W(CO)_5Xe$ forms $W(CO)_5$ which can react with Xe or CO:

$$W(CO)_5Xe \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} W(CO)_5 + Xe \tag{1}$$

$$W(CO)_5 + CO \xrightarrow{k_2} W(CO)_6 \tag{2}$$

Using the steady state approximation on the intermediate, $W(CO)_5$, results in the following expression for the observed decay constant (k_{obs})

$$k_{obs} = \frac{k_1k_2[CO]}{k_1[Xe] + k_2[CO]} \sim \frac{K_1k_2[CO]}{[Xe]} \tag{3}$$

where $K_1 = k_1/k_{-1}$, and we have reduced the expression for k_{obs} using the following approximation: $k_{-1}[Xe] \gg k_2[CO]$. The room-temperature gas-phase values for k_{-1} and k_2 have been determined[8b] to be $k_{-1} = 2.6 \pm 0.2 \times 10^{-10}$ cm^3 s^{-1} and $k_2 = 1.4 \pm 0.1 \times 10^{-10}$ cm^3 s^{-1} and are close to the gas kinetic values. Therefore in solution, both k_{-1} and k_2 will be close to the diffusion-controlled value, $k_{-1} \sim k_2 \sim 5 \times 10^9$ M^{-1} s^{-1},[20] and this approximation depends mainly on the relative concentrations of Xe and CO, here [Xe] ~ 20 M, [CO] < 0.05 M and [Xe]/[CO] > 400. Therefore, eq 3 predicts a linear dependence on CO concentration as is observed.

Under these conditions, the mechanism is indistinguishable from an associative substitution process in which CO attacks the metal center and displaces Xe in one step:

$$W(CO)_5Xe + CO \xrightarrow{k_a} W(CO)_6 + CO \tag{4}$$

Under the pseudo-first-order conditions of this experiment, the observed rate constant for this process would be a simple function of [CO]: $k_{obs} = k_a[CO]$ where $k_a = k_{CO}$. The dissociative process should be dependent on the concentration of leaving ligand (Xe) and this is one method to distinguish between these two mechanisms. However, since the leaving ligand is also the solvent in this case, it is not possible to vary its concentration in a controlled way.[21] Therefore we must use other means to identify the mechanism.

The pre-exponential factors derived from Arrhenius plots can be used to distinguish between these two mechanisms. If an associative mechanism is operative, then the slopes of the lines (k_{CO}) in Figure 6 are equal to k_a and the preexponential factor we derive from plot of ln (k_{CO}) versus $1/T$ should be appropriate

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(20) Estimated using the following approximate expression: $k_d = 8RT/3\eta$, where η is the viscosity of the solvent. Atkins, P. W. *Physical Chemistry*; W. H. Freeman and Co.: San Francisco, 1978. The viscosity of liquid Xe is 0.53 cP at 290 K. Braker, W.; Mossman, A. L. *Matheson Gas Data Book*; Matheson: Lyndhurst, NJ, 1980.

(21) If the concentration of Xe could be determined in mixtures of Xe in liquid Kr, this would be a good approach. While it is possible to prepare accurate gas phase mixtures, the solution concentrations may not be the same and are difficult to measure directly.

for a bimolecular reaction. Figure 7 shows that a straight line is observed for such a plot and gives a pre-exponential factor of log (A) = 12.2 ± 0.2 and an activation energy of 8.5 ± 0.2 kcal/mol. The pre-exponential factors for similar bimolecular organometallic reactions in solution are typically in the range of 10^8 to 10^9 M^{-1} s^{-1}.[22] A good reference system for this work is the reaction of Cp*Rh(CO)Xe with CO, which was studied using fast time-resolved IR spectroscopy of liquid Xe solutions.[7] The ligand substitution kinetics for this and related complexes generally proceed by associative substitution,[23] and the pre-exponential factor derived for this system is log (A) = 8.8 ± 0.1. Given these observations we rule out an associative mechanism for the reaction of $W(CO)_5Xe$ with CO.

The Arrhenius parameters we derive here are more consistent with a dissociative substitution process as expected for the group VI carbonyls.[24] Equation 3 for k_{obs} from the dissociative mechanism shows that $k_{obs}[Xe]/[CO] = k_{CO}[Xe] = k_1k_2/k_{-1}$. As mentioned earlier, k_{-1} and k_2 are nearly equal in magnitude, and to a first-order approximation, k_{-1} and k_2 cancel each other and $k_{CO}[Xe] \sim k_1$, the elementary rate constant for dissociation of Xe from $W(CO)_5Xe$. Therefore, a plot of ln $\{k_{CO}[Xe]\}$ versus $1/T$ should yield Arrhenius parameters appropriate for a unimolecular rate constant. Figure 7 also shows that when the data are plotted this way a straight line is observed with Arrhenius parameters of log (A) = 13.3 ± 0.2 and E_a = 8.4 ± 0.2 kcal/mol.[25] The pre-exponential factor is in good agreement with the expected range for unimolecular dissociation reactions, 10^{13} to 10^{14} s^{-1}.[26] The dissociative substitution mechanism is confirmed by our derivation of the same bond energy for Xe–$W(CO)_5$ as in the gas phase (see below).

An interpretation of the Arrhenius parameters that provides more information about reaction 1 uses the equilibrium constant K_1, $k_{CO}[Xe] = K_1k_2$. The temperature dependence of ln $\{K_1k_2\}$ is given by

$$\ln\{K_1k_2\} = \frac{\Delta S_1}{R} + \ln(A_2) + \frac{-(\Delta H_1 + E_2)}{RT} \qquad (5)$$

The slope of a plot of ln $\{K_1k_2\}$ versus $1/T$ is equal to $-(\Delta H_1 + E_2)/R$ where ΔH_1 is the enthalpy for reaction 1 and E_2 is the activation energy for reaction 2. The intercept is equal to $\{\Delta S_1/R + \ln(A_2)\}$ where ΔS_1 is the entropy change for reaction 1 and A_2 is the pre-exponential factor for the rate constant for reaction 2. The room temperature gas-phase value for k_2 approaches the gas kinetic value,[8b] therefore $E_2 \sim 0$ and we obtain the Xe–W-$(CO)_5$ bond energy: ΔH_1 = 8.4 ± 0.2 kcal/mol. Since $E_2 \sim 0$, we can estimate A_2 in solution; a reasonable value for this reaction is $A_2 = 5 \times 10^9$ M^{-1} s^{-1} giving ΔS_1 = +(16 ± 5) cal/(mol K). The error is derived assuming an estimated error in A_2 of a factor of 10.

As a consistency check of the kinetics, it is useful to compare the experimental observable k_{CO} with values calculated from ΔS_1, ΔH_1, k_2, and [Xe]. Table II shows the results of such a calculation using $K_1 = \exp(\Delta S_1/R)\exp(-\Delta H_1/RT)$ and $k_{CO} = K_1k_2/[Xe]$. The experimental values of k_{CO} are in good agreement with the calculated values, demonstrating that the derived parameters are representative of the data.

Analysis of ΔH_1 and ΔS_1. The value of ΔS_1 = +(16 ± 5) cal/(mol K) can be compared with expectations from statistical mechanics for the analogous gas-phase reaction.[27] The calculated value for the translational entropy change in reaction 1 is ΔS_{trans} = +37 cal/(mol K) and an estimate for the rotational entropy change is ΔS_{rot} = −2 cal/(mol K) assuming 2 Å bond lengths. A similar system for which vibrational frequencies are available is the complex Xe–Zn.[28] The excited state Xe–Zn($C^1\Pi_1$) has a vibrational frequency of 117 cm^{-1} and a well depth (D_0 = 3183 cm^{-1}) that is similar to that for $W(CO)_5Xe$. Therefore we use 100 cm^{-1} as an estimate for the stretching frequency and 20 cm^{-1} for each of the degenerate bending vibrations to give $\Delta S_{vib} \sim -12$ cal/(mol K). These values give an estimate of ΔS_1 = +23 cal/(mol K) at 185 K. While this is somewhat larger than the observed value in liquid Xe, solvent effects undoubtedly play a role and this level of agreement is not unreasonable.

The Xe–$W(CO)_5$ bond energy determined here, ΔH_1 = 8.4 ± 0.2 kcal/mol, is in excellent agreement with a recently published gas-phase value of 8.2 ± 1.0 kcal/mol.[8] The gas-phase value was determined from the temperature dependence of the unimolecular rate constant for dissociation of Xe from $W(CO)_5$. This gives E_a which was converted to ΔH_1 based on the observation that the reverse reaction is not activated to within experimental error. An advantage of our low-temperature method is a significantly more precise value for ΔH_1 that results from measurements carried out over a wide range in $1/T$.

The magnitude of ΔH_1 is significant but is consistent with expectations for Xe bonding to the group VI pentacarbonyls. Veillard et al.[29] have calculated the dispersion energy in KrMo-$(CO)_5$ and found a stabilization of 5.3 kcal/mol which is consistent with the upper bound on the $KrW(CO)_5$ bond energy of 6 kcal/mol from the gas-phase work.[8b] Given that Xe is more polarizable than Kr, one would expect a larger dispersion energy for $XeW(CO)_5$. A preliminary estimate for the bond energy in $XeCr(CO)_5$ was presented as 3.5 kcal/mol based on kinetic assumptions about the decay mechanism in liquid Xe,[4] but the gas-phase value is 9.0 ± 0.9 kcal/mol.[8] The larger is more consistent with the long lifetime (minutes) we observe for Xe-$Cr(CO)_5$ in liquid Xe.

Desorption energy measurements of Xe on metal surfaces correspond closely with the bond energy for $XeW(CO)_5$. The desorption energy of Xe on W(111) has been measured from thermal desorption data to be 9.3 ± 1.3 kcal/mol[30] and is similar to the value for Xe on Pt(111), 9.2 ± 0.9 kcal/mol.[31] If the primary interaction between Xe and $W(CO)_5$ and metal surfaces is due to dispersion forces, then it is reasonable to expect similarities in the binding energies. Additional bond energy data for related systems would help develop a unified picture of the bonding between rare gases and metal atoms in organometallic compounds and metal surfaces.

Conclusions

We have observed IR spectra for the complexes $W(CO)_5Kr$, $Cr(CO)_5Kr$, and $W(CO)_5Xe$ for the first time in fluid solution. The substitution kinetics of the reaction of $W(CO)_5Xe$ with CO were investigated and found to proceed by dissociative subtitution with no apparent associative pathway. Under the conditions of the experiment, the approximation that $W(CO)_5Xe$ is in equilibrium with $W(CO)_5$ is valid and allows us to measure the temperature dependence of the equilibrium constant and to determine the Xe–$W(CO)_5$ bond energy. Our value for the bond energy, ΔH = 8.4 ± 0.2 kcal/mol, is in excellent agreement with a recent gas-phase value confirming that the mechanism is dissociative. This also demonstrates the value of the technique for determining the bond energies of weak ligands to electron-deficient metal centers in cases where the mechanism proceeds by dissociative substitution. We are currently pursuing the binding energies of other weak ligands such as CO_2 with our current apparatus and,

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with improved time resolution, we hope to determine the bond energies for very weak ligands such as Kr.

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Note Added in Proof. The author would like to point out that Turner and co-workers[32] have previously used CO substitution kinetics in liquid Kr to determine the N_2–Ni bond energy in $Ni(CO)_3(N_2)$. In this system, the kinetics are complicated by the existence of parallel associative and dissociative pathways. Nevertheless, the authors were able to extract a bond energy and the reader is referred to their paper for a thorough discussion of the kinetics.

Picosecond Radical Kinetics. Ring Openings of Phenyl Substituted Cyclopropylcarbinyl Radicals

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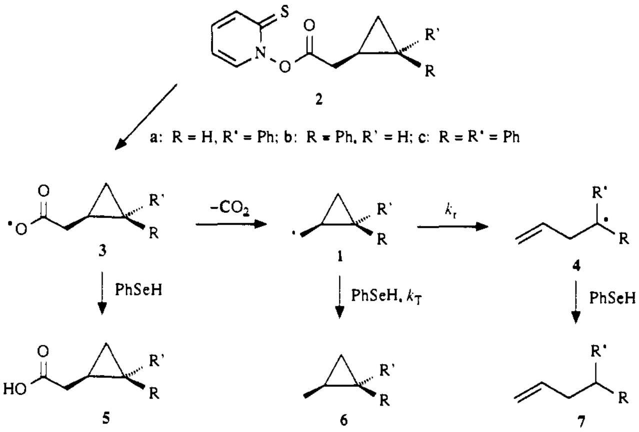
Abstract: Rate constants for ring openings of the *trans*-(2-phenylcyclopropyl)carbinyl radical (**1a**), the *cis*-(2-phenylcyclopropyl)carbinyl radical (**1b**), and the (2,2-diphenylcyclopropyl)carbinyl radical (**1c**) were studied by competition kinetics using PTOC esters as radical precursors and hydrogen atom transfer trapping from benzeneselenol as the basis reaction. Radical **1a** was studied in two solvents, toluene and THF; the experimental Arrhenius function for ring opening of **1a** was $\log (k_r \cdot s) = 13.9 - 3.3/2.3RT$ (R in kcal/mol). It is possible that the immediate precursor to **1a**, acyloxy radical **3a**, suffers a concomitant decarboxylation–ring opening process that competes with simple decarboxylation leading to **1a**. The experimental rate constant for ring opening of **1a** at 25 °C is 3×10^{11} s^{-1}. Preliminary kinetic studies of radicals **1b** and **1c** gave Arrhenius functions of $\log (k_r \cdot s) = 13.9 - 3.1/2.3RT$ and $\log (k_r \cdot s) = 13.1 - 2.0/2.3RT$, respectively, and the respective rate constants for ring openings at 25 °C are 4 and 5×10^{11} s^{-1}. Rate constants for ring openings of substituted cyclopropylcarbinyl radicals were estimated by Marcus theory using the known rate constants and equilibrium constant for the parent system and expected $\Delta G°$ values for the substituted systems. From these results, the estimated rate constants at 25 °C for ring opening of **1a** and **1b** were 1×10^{11} s^{-1} and that for **1c** was 4×10^{11} s^{-1}. Precursors to radicals **1**, such as the corresponding hydrocarbons, represent hypersensitive radical probes that, in principle, can provide unequivocal conclusions regarding the intermediacy of a radical in a reaction.

Radical rearrangements are useful both for mechanistic probe studies in which one attempts to determine whether or not a radical intermediate is formed during a particular reaction and for radical clock[1] applications wherein one wishes to measure the kinetics of competing radical reactions. The archetypal radical rearrangements are cyclization of the 5-hexenyl radical ($k = 2 \times 10^5$ s^{-1} at 25 °C)[2] and ring opening of the cyclopropylcarbinyl radical ($k = 1.0 \times 10^8$ s^{-1} at 25 °C),[3] the most precisely calibrated radical reaction. Despite the relatively large rate constant of the cyclopropylcarbinyl ring opening, this reaction is considerably slower than the fastest possible unimolecular reactions, and the failure to detect rearranged products in a mechanistic study employing this ring opening as a probe reaction does not provide unequivocal evidence that radical intermediates were not formed. Radical rearrangements faster than that of cyclopropylcarbinyl are desired for this reason and for radical clock applications involving very fast first-order or pseudo-first-order competitions.

Scheme I



Over the past few years, the kinetics of several fast radical rearrangements have been characterized. These include ring openings of a series of (poly)methyl-substituted cyclopropylcarbinyl radicals ($k = 1 \times 10^8$–4×10^9 s^{-1} at 25 °C),[3,4] the bicyclo[2.1.0]pent-2-yl radical ($k = 2 \times 10^9$ s^{-1} at 25 °C),[4b,5] spirocyclic cyclopropylcarbinyl radicals ($k = 2$–9×10^9 s^{-1} at 75 °C),[6] and the cubylcarbinyl radical ($k = 3 \times 10^{10}$ s^{-1} at 25 °C).[7] In developing radical probes for enzyme mechanistic studies, Castellino and Bruice estimated a lower limit for ring opening of *trans,trans*-(2,3-diphenylcyclopropyl)carbinyl radical at 25 °C of $k = 2 \times 10^{10}$ s^{-1};[8] this result prompted us to investigate ring openings of phenyl-substituted cyclopropylcarbinyl radicals. In

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