of benzene and petroleum ether), and 50 mg (17%) of benzamide (10), mp 128-129 °C (mixture mp) (elution with a mixture (9:1) of benzene and ethyl acetate).

In repeat runs, irradiations of 1a in methanol (1.5 h) and acetonitrile (2.5 h) under analogous conditions gave a mixture of 11a (35%, 26%), 8a (25%, 51%), and 10 (36%, 27%).

1b. Irradiation of 1b (299 mg, 1 mmol) in benzene (200 mL) for 3 h and workup as in the earlier cases gave a mixture of 11a (32 mg, 16%), 8a (150 mg, 50%), and 10 (55 mg, 18%). In a repeat run, irradiation of 1b in methanol (1.5 h) gave a similar mixture of 11a (37%), 8a (22%), and 10 (38%).

1c. Irradiation of 1c (313 mg, 1 mmol) in benzene (200 mL) for 1.5 h and workup as in the earlier cases gave 38 mg (18%) of dibenzylketone (11c), mp 31-32 °C (mixture mp) (elution with a mixture (1:9) of benzene and petroleum ether), 165 mg (53%) of *erythro-N*-(1-benzyl-2-hydroxy-2-phenylethyl)benzamide (5c), mp 137-138 °C (lit.^{29,30} mp 138 °C) (elution with a mixture (1:1) of benzene and petroleum ether and recrystallization from a mixture (1:9) of benzene and petroleum ether), and 25 mg (21%) of benzamide (10), mp 128-129 °C (mixture mp) (elution with a mixture (9:1) of benzene and ethyl acetate).

In a separate run, a solution of 1c (100 mg, 0.32 mmol) in methylene chloride (15 mL) was treated with silica gel (3.0 g, 60-120 mesh) and maintained at 25 °C for 12 h. Workup by removal of the silica gel (filtration) and solvent and chromatographing the residual solid over silica gel gave 95 mg (91%) of 5c, mp 137-138 °C (mixture mp) (elution with a mixture (1:1) of benzene and petroleum ether).

Irradiation of a Mixture of 1b and DMAD. A mixture of 1b (449 mg, 1.5 mmol) and DMAD (426 mg, 3 mmol) in acetonitrile (200 mL) was irradiated for 2.5 h and worked up by removal of the solvent under vacuum and chromatographing the residual mass over silica gel. Elution with petroleum ether gave 110 mg (38%) of 11a, mp 52-53 °C (mixture mp). Further elution with a mixture (1:1) of benzene and petroleum ether gave 280 mg (65%) of unchanged DMAD. Continued elution with a mixture (3:7) of benzene and petroleum ether gave 50 mg (12%) of 8a, mp 169-170 °C (mixture mp). Further elution with a mixture (9:1) of benzene and ethyl acetate gave 150 mg (23%) of dimethyl

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cis-1-benzoyl-2,5-diphenyl-3-pyrroline-3,4-dicarboxylate (**3b**) as a viscous liquid: IR (ν_{max} , KBr) 3060, 3040, 2960, 2940, 2840, (CH), 1720 and 1650 (C—C), 1580 (C—C) cm⁻¹; UV (CH₃OH) λ_{max} (ϵ) 213 (ϵ 19 200), 234 (13 500), 280 (5000) nm; ¹H NMR (CDCl₃) δ 3.60 (1 H, d, J = 3.5 Hz), 3.72 (1 H, d, J = 3.5 Hz), 3.85 (6 H, s, OCH₃), 7.08–7.75 (15 H, m, aromatic).

Subsequent elution of the column with a mixture (4:1) of benzene and ethyl acetate gave 80 mg (42%) of 10, mp 128-129 (mixture mp).

Conversion of 3b to 4b. To a solution of **3b** (50 mg, 0.1 mmol) in benzene (3 mL) was added nickel peroxide³¹ (50 mg), and the reaction mixture was stirred at 25 °C for 3 h. Removal of the inorganic material and the solvent gave a product mixture, which was chromatographed over neutral alumina. Elution with benzene gave 25 mg (65%) of **4b**, mp 145–146 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether (lit.³² mp 146–148 °C).

Laser Flash Photolysis. Details of absorption-emission spectral measurements and laser flash photolysis are given in previous papers.³³ For laser pulse excitation, outputs were used from a Lambda Physik EMG MSC 101 excimer laser source (308 nm, ≤ 20 mJ, ~ 20 ns, Xe-HCl) and a Molectron UV-400 nitrogen laser system (337.1 nm, 2-3 mJ, ~ 8 ns). Unless oxygen effects were under examination, the solutions were deoxygenated by purging with high-purity argon.

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UV Laser Photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$: Time-Resolved Infrared Studies of Gas-Phase $(\eta^6-C_6H_6)Cr(CO)_x$ (x = 2 and 1)

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The time-resolved infrared absorption spectra of the coordinatively unsaturated $(\eta^6-C_6H_6)Cr(CO)_x$ (x = 2 and 1) species generated via UV laser photolysis of the gas-phase $(\eta^6-C_6H_6)Cr(CO)_3$ are presented and discussed. The photofragments produced upon 355- and 266-nm photolysis are identified. $(\eta^6-C_6H_6)Cr(CO)_2$ is the predominant product upon 355-nm photolysis, while both $(\eta^6-C_6H_6)Cr(CO)_2$ and $(\eta^6-C_6H_6)Cr(CO)$ are produced upon 266-nm photolysis with a ratio of $(\eta^6-C_6H_6)Cr(CO)_2$: $(\eta^6-C_6H_6)Cr(CO)_2$ and $(\eta^6-C_6H_6)Cr(CO)$ are produced upon 266-nm photolysis with a ratio of $(\eta^6-C_6H_6)Cr(CO)_2$ in the rate constants for reactions of $(\eta^6-C_6H_6)Cr(CO)_2$ and $(\eta^6-C_6H_6)Cr(CO)$ with CO are measured and found to be $(6.3 \pm 0.3) \times 10^{12}$ and $(1.4 \pm 0.2) \times 10^{12}$ cm³ mol⁻¹ s⁻¹, respectively. The rate constant for reaction of $(\eta^6-C_6H_6)Cr(CO)_2$ with CO lies between the corresponding values for spin-allowed and spin-disallowed reactions of other coordinatively unsaturated metal carbonyl species with CO.

Introduction

Transition metal carbonyl photochemistry continues to be of major interest due to the application of metal carbonyl compounds in photocatalyzing or photoassisting the transformation of organic substrates.¹⁻³ The dominant photochemical process for metal carbonyls is ligand dissociation, which provides open, highly re-

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Figure 1. Schematic diagram of the time-resolved infrared absorption spectroscopy apparatus used for monitoring photolytically generated coordinatively unsaturated organometallic species. Abbreviations: AM, amplifier; BS, beam splitter; C, chopper; D1, HgCdTe detector; D2, InSb detector; DM, dichroic mirror; F, IR filter; HG, harmonic generator; I, iris; M, monochromator; OSC, oscilloscope; PC, personal computer; TD, transient digitizer; TO, telescoping optics.

active, coordination sites at the metal center. Details of the nature of these coordinatively unsaturated species are thus central in developing a complete understanding of the mechanisms of transition metal carbonyl-photocatalyzed or photoassisted processes. Recent time-resolved infrared spectroscopic studies of gas-phase unsaturated metal carbonyl photofragments have provided us with a large amount of information on the structure and reactivity of these highly reactive species free from disturbance of host matrix or solvent molecules.4-7 Some propensity rules followed by gas-phase coordinatively unsaturated metal carbonyl species have been summarized by Weitz.⁸ Detailed studies to date, however, have been effectively restricted to the coordinatively unsaturated metal carbonyls with only carbonyl ligand except $(\eta^5-C_5H_5)Co(CO)$.⁷ It is obviously very important to determine whether the conclusions reached for these species can be generalized to the larger class of coordinatively unsaturated metal carbonyl complexes with non-carbonyl ligands.

The condensed-phase photochemistry of $(\eta^6-C_6H_6)Cr(CO)_3$ has been the subject of many studies⁹⁻¹⁶ due in large part to the expected dissimilarity between the Cr to CO bonding and η^6 Cr to C_6H_6 bonding and the dramatic differences in the thermal and photochemical reactivity of this species.¹ In condensed media, the one-photon-induced chemistry of $(\eta^6-C_6H_6)Cr(CO)_3$ is known to be dominated by the formation of $(\eta^6-C_6H_6)Cr(CO)_2$ via

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Figure 2. Infrared absorption spectra obtained (a) 1.4 μ s following 355-nm photolysis of 12 mTorr of $(\eta^6-C_6H_6)Cr(CO)_3$ in the presence of 15 Torr of Ar and (b) 2.0 µs following 266-nm photolysis of 14 mTorr of $(\eta^6-C_6H_6)Cr(CO)_3$ in 7 Torr of Ar.

light-induced CO dissociation. The photochemical loss of the six-electron π -donor ligand C₆H₆ is thought to be very inefficient if it obtains at all, although it is implied by the early work of Strohmeier and Von Hobe⁹ and the identification of C_6H_6 and $Cr(CO)_6$ as the products of photodecay of $(\eta^6-C_6H_6)Cr(CO)_3$.¹⁵ The coordinatively unsaturated species $(\eta^6-C_6H_6)Cr(CO)_2$ has been characterized in Ar and CH₄ matrix at 12 K.¹³ However, very few works are reported regarding the reaction kinetics of this species.17 In this paper, time-resolved infrared absorption spectroscopy is used to study the photochemistry of $(\eta^6-C_6H_6)$ - $Cr(CO)_3$ in the gas phase and infrared spectra and reactivity of coordinatively unsaturated species $(\eta^6-C_6H_6)Cr(CO)_2$ as well as $(\eta^6-C_6H_6)Cr(CO)$ produced upon 355- and 266-nm laser photolysis of $(\eta^{6}-C_{6}H_{6})Cr(CO)_{3}$.

Experimental Section

The time-resolved infrared absorption apparatus used for monitoring photolytically generated coordinatively unsaturated metal carbonyl species is depicted schematically in Figure 1.18 The output of a frequency tripled (355 nm) or quadrupled (266 nm) Nd:YAG (Quanta Ray) laser operating at ca. 3 Hz was used as a photolysis source. The laser pulse width is about 5 ns, and fluences of 2-5 mJ/cm² were typically employed. The transient species produced upon UV photolysis of metal carbonyl complexes were monitored via the output of a liquid nitrogen-cooled linetunable CW CO laser. In its present configuration the CO laser can span the spectral range 2055-1650 cm⁻¹ at a spectral resolution, determined by the spacing of available vibration-rotation lines, of ca. 4 cm⁻¹. The CO laser beam, after passing through the gas cell coaxially with respect to the UV laser beam, was directed to a liquid nitrogen-cooled InSb detector. For wavelength determination a portion of the CO laser beam was split by a Ge splitter and passed through a 0.5-m monochromator previously calibrated by the eighth order of the output of a 632.8 nm He-Ne laser. The output of the InSb detector was amplified and fed to a transient digitizer, and the average of 30-50 traces was stored in an IBM/XT personal computer. Time-resolved infrared absorption spectra were generated by connecting points at common delay times from signals at different IR frequencies. The measured risetime of the whole detection system is about 100 ns.

Two different types of gas cells were available for each experiment. For generating time-resolved spectra a flow cell was used. The flow cell has, in addition to a central gas inlet, two

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Ar purge gas inlets near the ends of the cell that allow Ar to flow over the windows of the cell to prevent buildup of polynuclear species on the windows. In the studies involving detailed kinetics a static cell was employed. The static cell has two cool water jackets near the ends of the cell to avoid deposition of the parent molecules on the windows. The static cell allows more accurate determination of pressure-dependent rate constants by avoiding uncertainties in the flow rates of the sample gas and possible thermal nonequilibration in the flow cell. Controlled and variable amounts of Ar and/or CO were added to the flow cell by means of needle valves. Determination of the partial pressure of CO in the flow cell, when necessary, was indirectly obtained via comparison of decay or growth rate of a particular absorption with CO pressure-dependent kinetics measured in the static cell, while gas mixtures in the static cell were prepared according to a standard method. A constant steady-state pressure ($\sim 10 \text{ mTorr}$) of $(\eta^6-C_6H_6)Cr(CO)_3$ was achieved by placing a small amount of the solid into the cells and warming the cells to about 350 K. Measurement of the partial pressure of $(\eta^6-C_6H_6)Cr(CO)_3$ was made by monitoring the attenuation of the 355-nm laser beam and applying Beer's law, with the absorption cross section of $\sim 6600 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1} \text{ at } 355 \text{ nm}.^{19}$

 $(\eta^6-C_6H_6)Cr(CO)_3$ was obtained from Strem Chemical Co. and used without further purification since it was sublimed in situ. Ar (99.999+% purity) and CO (99.98% purity) were obtained from Beijing Oxygen Co. and Beijing Analytical Instrument Co., respectively, and used without further purification.

Results and Discussion

It is now well established that UV photolysis of gas-phase metal carbonyl complexes can lead to the loss of more than one ligand. Further, production of the more highly unsaturated species is favored upon photolysis with higher energy photons. Figure 2 shows the infrared spectra recorded following the photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$ in the gas phase with 355- and 266-nm laser radiation. The spectra were taken at times following photolysis indicated in the figure caption. The times were selected to maximize the extent of rovibration relaxation of the hot nascent fragments and to minimize the extent of secondary, bimolecular reactions of the fragments. In the following sections, the spectra are assigned to particular $(\eta^6-C_6H_6)Cr(CO)_x$ (x = 1, 2) species on the basis of comparison with the available data of matrix isolation studies and examination of the temporal behavior of the absorptions observed.

355-nm Photolysis. The infrared spectra obtained 1.4 μ s following 355-nm laser photolysis of ~12 mTorr of $(\eta^6-C_6H_6)Cr$ - $(CO)_3$ in 15 Torr of Ar buffer gas is shown in Figure 2a. The two negative peaks at 1939 and 1999 cm⁻¹ represent photolytical depletion and are clearly the E and A_1 carbonyl-stretching modes of the local $C_{3\nu}$ (η^6 -C₆H₆)Cr(CO)₃.¹³ In an Ar matrix, the bands observed at 1937.5 and 1985.0 cm^{-1} have been attributed to B_1 and A₁ carbonyl-stretching modes of the local $C_{2\nu}$ (η^6 -C₆H₆)-Cr(CO)2.13 Since the absorption frequency of Ar matrix-isolated species are in general shifted to lower frequency relative to that of gas-phase species, we assign the two positive bands centered at ~1917 and ~1981 cm⁻¹ as the B₁ and A₁ modes of local $C_{2\nu}$ $(\eta^6-C_6H_6)Cr(CO)_2$, respectively. The larger shift of the positions of the absorption bands of $(\eta^6-C_6H_6)Cr(CO)_2$ in the gas phase vs in low-temperature matrix (the B_1 and A_1 bands of (η^6 - $C_6H_6)Cr(CO)_2$ shift 32 (47) and 43.5 (46) cm⁻¹ in the gas phase vs in $Ar(CH_4)$ matrix, respectively, while the E and A_1 bands of $(\eta^{6}-C_{6}H_{6})Cr(CO)_{3}$ shift only 16 (26) and 9 (16.5) cm⁻¹, respectively) (Table I) is presumably due to the stronger stereospecific interaction²⁰ between $(\eta^6 - C_6 H_6) Cr(CO)_2$ and the matrix species.

Convincing kinetic evidence supporting assignment of the 1917and 1981-cm⁻¹ bands to $(\eta^6-C_6H_6)Cr(CO)_2$ can be obtained via

TABLE I: CO-Stretching Frequencies (cm⁻¹) of Matrix-Isolated and Gas-Phase (η^6 -C₆H₆)Cr(CO)_x Species

	assign	Ar matrix ^a	CH ₄ matrix ^a	gas phase ^b
$\overline{(\eta^6 - C_6 H_6) Cr(CO)_3}$	A ₁	1990.0	1982.5	1999
	E	1923.0	1913.0	1939
$(\eta^6 - C_6 H_6) Cr(CO)_2$	A ₁	1937.5	1925.0	1981
	Β	1885.0	1870.0	1917
(η ⁶ -C ₆ H ₆)Cr(CO)				1985

.

^aReference 13. ^bThis work.



Figure 3. CO pressure dependence of the pseudo-first-order decay rate of $(\eta^6-C_6H_6)Cr(CO)_2$ species and reproduction rate of $(\eta^6-C_6H_6)Cr(CO)_3$ observed upon 355-nm photolysis of about 10 mTorr of $(\eta^6-C_6H_6)Cr(CO)_2$ was monitored at 1914 (\bullet) and 10 Torr of Ar. $(\eta^6-C_6H_6)Cr(CO)_2$ was monitored at 1914 (\bullet) and 1981 cm⁻¹ (Δ) and $(\eta^6-C_6H_6)Cr(CO)_3$ at 1939 cm⁻¹ (\Box).

observation of the temporal behavior of these bands, as well as those of the parent, in the presence of added CO. In the addition of sufficient CO, all bands observed return to the baseline almost completely and no new strong absorption appears (see below). These observations exclude the possibility that the loss of C_6H_6 ligand upon 355-nm photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$ takes place at high efficiency since C₆H₆-lost products would undergo consecutive CO addition to form $Cr(CO)_6$ and as a result the strong absorptions of $Cr(CO)_6$ and incomplete recovery of the parent would be observed. Further, as is expected on the basis of our assignment, the 1917- and 1981-cm⁻¹ bands return to the baseline at the same rate as do the parent absorptions over a range of added CO pressure of 0.2-1.2 Torr (Figure 3). We thus conclude that $(\eta^{6}-C_{6}H_{6})Cr(CO)_{2}$ strongly dominates the distribution of fragments generated upon 355-nm photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$. The dominant process in addition of CO is

$$(\eta^{6}-C_{6}H_{6})Cr(CO)_{2} + CO \xrightarrow{k_{23}} (\eta^{6}-C_{6}H_{6})Cr(CO)_{3} \quad (1)$$

From the slope of the line in Figure 3, the rate constant for reaction of $(\eta^6 \cdot C_6 H_6) Cr(CO)_2$ with CO is calculated to be $(6.3 \pm 0.3) \times 10^{12}$ cm³ mol⁻¹ s⁻¹. This value remains constant within experimental error at Ar pressure in the range 5–70 Torr, indicating that it is a high pressure limited rate constant. This rate constant, only slightly slower than that for spin-allowed reactions of other coordinatively unsaturated metal carbonyls with CO,^{4–7} is on the order of 1/10 gas kinetics, reflecting negligible barrier for reaction 1.

Previous workers^{21,22} have recognized that an estimate of the OC-Cr-CO bond angle in $(\eta^6-C_6H_6)Cr(CO)_2$ can be obtained from the relative intensities of the two infrared bands of $(\eta^6-C_6H_6)Cr(CO)_2$ via

$$[\tan \left(\frac{\theta}{2}\right)]^2 = I_a/I_s \tag{2}$$

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Figure 4. Time-resolved infrared spectra following 355-nm photolysis of 13 mTorr of $(\eta^6-C_6H_6)Cr(CO)_3$ in the presence of 0.6 Torr of CO and 6.4 Torr of Ar. The spectra were shown at 1.0-µs intervals in the range 2.0-6.0 μ s. An up arrow indicates absorption increasing with time, and a down arrow shows absorption decreasing. The × donotes an absorption that has not been positively assigned (see text).

where θ is the bond angle, I, is the intensity of the symmetric band (A_1) , and I_2 is the intensity of the antisymmetric band (B_1) . Although the band intensities can only be roughly compared due to the relatively low resolution of the spectra, the ratio I_{a}/I_{c} is determined to be ~ 1.5 , giving a bond angle of $\sim 101^{\circ}$. This angle is close to that found for $(\eta^6-C_6H_6)Cr(CO)_2$ in a CH₄ matrix (102.4°).²² We thus believe that no significant difference in the OC-Cr-CO bond angle of $(\eta^6-C_6H_6)Cr(CO)_2$ occurs in a lowtemperature matrix vs in the gas phase.

It is possible that some $(\eta^6 - C_6 H_6)Cr(CO)$ is formed upon 355-nm photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$ since the carbonylstretching band of $(\eta^6-C_6H_6)Cr(CO)$ almost overlaps the 1981 cm^{-1} band of $(\eta^6 - C_6H_6)Cr(CO)_2$ (see 266-nm Photolysis). However, on the basis of the bond energy and kinetic arguments, we consider that no significant amount of $(\eta^6-C_6H_6)Cr(CO)$ is formed. The thermochemical studies suggest that the average bond energy E(Cr-CO) in $(\eta^6-C_6H_6)Cr(CO)_3$ is 27 kcal mol⁻¹, on the same order as that in $Cr(CO)_6$ (26 kcal mol⁻¹).²³ In addition, the extended Hückle MO calculations indicate that the average Cr–CO bond strength for $(\eta^6-C_6H_6)Cr(CO)_3$ is about 8 kcal mol⁻¹ stronger than that for $Cr(CO)_6$.²⁴ From above arguments and in view of the fact that the distribution of fragments generated upon 351-nm (81 kcal mol⁻¹) photolysis of Cr(CO)₆ is strongly dominated by Cr(CO)₅,^{4b} we expect that 355-nm (80 kcal mol⁻¹) photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$ leads to the predominant formation of $(\eta^6-C_6H_6)Cr(CO)_2$. This prediction is supported by the kinetic observation that the decay of both 1917and 1981-cm⁻¹ bands can exactly be fit to a single exponential function with a rate corresponding to the recovery of the parent at CO pressure in a range 0.2-1.2 Torr. We therefore infer that no significant amount of $(\eta^6-C_6H_6)Cr(CO)$ is formed upon 355-nm photolysis of $(\eta^6 - C_6 H_6) Cr(CO)_3$.

In condensed phase the ejection of C₆H₆ ligand from photo excited $(\eta^6 - C_6 H_6) Cr(CO)_3$ is thought to be very inefficient, if it obtains at all. Nevertheless, it still remains a concern whether a pathway exists involving the loss of C_6H_6 when $(\eta^6-C_6H_6)Cr$ -(CO), is photoexcited to a particular excited electronic state.¹⁹ The bond energy $E(Cr-\eta^6-C_6H_6)$ in $(\eta^6-C_6H_6)Cr(CO)_3$ is estimated to be on the order of 43 kcal mol^{-1,23} Thus, in 355-nm (80 kcal mol⁻¹) photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$, the available energy is likely sufficient that the formation of $Cr(CO)_3$ via light-induced C_6H_6 ligand dissociation is energetically possible. We observe no strong absorption features in the region about 1885 cm⁻¹ that can be assigned to $Cr(CO)_{3}$,^{4b,6d} although it is possible that such features, if present, would be obscured by the nearby B₁ band of $(\eta^6 - C_6 H_6) Cr(CO)_2$. In addition, as mentioned above, in the presence of sufficient CO almost complete recovery of the parent



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Figure 5. Time-resolved infrared spectra following 355-nm photolysis of 12 mTorr of $(\eta^6 - C_6 H_6)Cr(CO)_3$ in the presence of 15 Torr of Ar. The spectra were shown at 100- μ s intervals in the range 2-402 μ s. An up arrow indicates absorption increasing with time, and a down arrow indicates absorption decreasing.

is observed. These observations indicate that the loss of C_6H_6 ligand does not occur to any significant extent. However, we note that a weak absorption at ~1999 cm⁻¹ is formed following 355-nm photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$ in the addition of CO. Figure 4 displays the spectra obtained 2.0-6.0 μ s following 355-nm photolysis of ~13 mTorr of $(\eta^6 - C_6 H_6)Cr(CO)_3$ in the presence of 6.4 Torr of Ar and 0.6 Torr of CO. The subtle absorption at \sim 1999 cm⁻¹ is denoted by \times in this figure. The fact that this absorption occurs only in the later time following photolysis and in the presence of CO suggests that this absorption is due to the secondary products formed via the reaction of primary fragments with CO. It is likely that this absorption is due to the T_{1u} band $(\sim 2000 \text{ cm}^{-1})$ of $Cr(CO)_6^{4b,5a,6d}$ formed via the consecutive addition of CO to the primary Cr(CO)₃ fragment. However, such an assignment remains a speculation before convincing evidence is obtained since alternative assignments may exist.

 $(\eta^6-C_6H_6)Cr(CO)_2$ formed upon 355-nm photolysis of $(\eta^6 C_6H_6$)Cr(CO)₃ is initially found to be rovibrationally excited. It undergoes vibrational relaxation upon collisions with Ar, as is evidenced by the absorption bands assigned to $(\eta^6-C_6H_6)Cr(CO)_2$ which narrow and blue shift with a rate dependent on Ar pressure. Also, the absence of an absorption in the region which would correspond to CO ($\nu = 2$) \rightarrow CO ($\nu = 3$) ($\sim 2050 \text{ cm}^{-1}$) signified that the vibrational-state distribution of CO generated upon 355-nm photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$ is strongly dominated by CO (v = 0, 1).

It is now well recognized that coordinatively unsaturated metal carbonyl species react with parents in the gas phase to form binuclear complexes having high rate constants. Some evidence for the existence of secondary, binuclear formation reactions upon 355-nm photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$ is displayed in the time-resolved spectra in the absence of CO (Figure 5). These spectra illustrate that, while the bands of $(\eta^6-C_6H_6)Cr(CO)_2$ have nearly returned to the baseline, the recovery of the parent is incomplete. Note the distortion of the B₁ band of $(\eta^6-C_6H_6)$ - $Cr(CO)_2$ as it returns to the baseline. Although it is not conveniently shown for the time scale of traces in Figure 5, $(\eta^6$ - C_6H_6)Cr(CO)₃ is slightly further depleted on a time scale well beyond that expected if photolysis were the only mechanism responsible for $(\eta^6-C_6H_6)Cr(CO)_3$ depletion. These observations, as well as the fact that a long-lived (~ 1 ms) absorption at 1914 cm⁻¹ is observed, indicate the presence of the reaction

$$(\eta^{6}-C_{6}H_{6})Cr(CO)_{2} + (\eta^{6}-C_{6}H_{6})Cr(CO)_{3} \rightarrow (C_{6}H_{6})_{2}Cr_{2}(CO)_{5}$$
(3)

The absorption at 1914 cm⁻¹ can be attributed to $(C_6H_6)_2Cr_2$ -(CO)₅. This assignment is based on the implicit assumption of retention of all CO ligands in the binuclear products. Although the rate constants for reaction 3 cannot be determined exactly on our experiment due to the uncertainty of the $(\eta^6-C_6H_6)Cr(CO)_3$ concentration, it is estimated to be of the order of 1×10^{13} cm³



Figure 6. CO pressure dependence of the pseudo-first-order decay rate of $(\eta^6-C_6H_6)Cr(CO)$ and reproduction rate of $(\eta^6-C_6H_6)Cr(CO)_3$ observed upon 266-nm photolysis of about 10 mTorr of $(\eta^6-C_6H_6)Cr(CO)_3$ in the addition of CO and 30 Torr of Ar. $(\eta^6-C_6H_6)Cr(CO)$ was monitored at 1984 cm⁻¹ (**m**). The reproduction rate of $(\eta^6-C_6H_6)Cr(CO)_3$ (O) was obtained via fitting the tails of time-dependent absorption signals at 1939 cm⁻¹ to single exponentials.

mol⁻¹ s⁻¹. This rate constant is about an order of magnitude lower than the reported rate constant for other metal carbonyl binuclear-forming reactions,⁴⁻⁷ except that for Fe(CO)₄ with Fe(C-O)₅.²⁵ The rate constant for reaction of Fe(CO)₄ with Fe(CO)₅ was found to be 3×10^{11} cm³ mol⁻¹ s⁻¹,²⁵ over 30 times lower than the corresponding value for the reaction of $(\eta^6-C_6H_6)Cr(CO)_2$ with $(\eta^6-C_6H_6)Cr(CO)_3$.

266-nm Photolysis. The spectra obtained 2.0 μ s following 266-nm photolysis of ~14 mTorr of $(\eta^6-C_6H_6)Cr(CO)_3$ in the presence of 7 Torr of Ar is shown in Figure 2b. It is clear from Figure 2 that the distribution of fragments generated upon 266-nm photolysis is different from that upon 355-nm photolysis. On the basis of the temporal behavior of the bands observed (see below), the band at 1917 cm⁻¹ is assigned to the B₁ mode of $(\eta^6 - C_6 H_6)$ - $Cr(CO)_2$, while the new band at ~1984 cm⁻¹, overlapping partially with the A_1 band of $(\eta^6-C_6H_6)Cr(CO)_2$ and the A_1 band of the parent, is attributed to the carbonyl-stretching band of $(\eta^6$ - C_6H_6)Cr(CO). Although the related species (η^5 -C₅H₅)Mn(CO) was identified in hydrocarbon glasses at 77 K,¹⁴ (η^6 -C₆H₆)Cr(CO) has not been characterized previously. We assign the new band observed to $(\eta^6 - C_6 H_6) Cr(CO)$ on the basis of the simple observation that the almost complete parent recovery is obtained when $(\eta^6-C_6H_6)Cr(CO)_3$ is photolyzed in the presence of sufficient CO. This observation, as in the case of 355-nm photolysis, eliminates the possibility that the loss of C_6H_6 upon 266-nm photolysis obtains at high efficiency. In addition, $(C_6H_6)Cr$, another possible fragment, is not expected to exhibit a strong absorption at ~ 1984 cm⁻¹. Therefore, the band at \sim 1984 cm⁻¹ generated upon 266-nm photolysis of $(\eta^6 - C_6 H_6) Cr(CO)_3$ is attributed to $(\eta^6 - C_6 H_6) Cr(CO)$. This assignment is also consistent with the fact that UV photolysis of gas-phase metal carbonyl species can lead to the loss of more than one ligand and the production of more highly unsaturated species is favored upon photolysis with shorter wavelength light.⁸

A detailed examination of the temporal evolution of these bands supports the above assignments. The evolution of the time-resolved spectra obtained upon 266-nm photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$ with added CO is anticipated to be described by the kinetic scheme

$$(\eta^6 - C_6 H_6) Cr(CO) + CO \xrightarrow{k_{12}} (\eta^6 - C_6 H_6) Cr(CO)_2$$
 (4)

$$(\eta^{6}-C_{6}H_{6})Cr(CO)_{2} + CO \xrightarrow{\kappa_{23}} (\eta^{6}-C_{6}H_{6})Cr(CO)_{3} \quad (5)$$

Under pseudo-first-order conditions, $[(\eta^6-C_6H_6)Cr(CO)]$ is predicted to decay single exponentially with a rate of $k_{12}[CO]$. Since upon 266-nm photolysis the absorption intensity of $(\eta^6-C_6H_6)$ - $Cr(CO)_2$ at 1984 cm⁻¹ is rather low compared with that of $(\eta^6-C_6H_6)Cr(CO)$ at 1984 cm⁻¹ (see Figure 2), single exponential

decay of the absorption at 1984 cm⁻¹ with a rate of k_{12} [CO] is expected and observed. Figure 6 shows the decay rate of the absorption at 1984 cm⁻¹ in the presence of a series of CO pressures. The slope of the line gives a value for k_{12} , the rate constant for reaction of $(\eta^{6}-C_{6}H_{6})Cr(CO)$ with CO, of $(1.4 \pm 0.2) \times 10^{12} \text{ cm}^{3}$ mol⁻¹ s⁻¹. This value remains constant within experimental error at Ar pressure over 10 Torr, indicating that it is a high pressure limited rate constant. This rate constant is over an order of magnitude lower than the corresponding values for spin-allowed reactions of other coordinatively unsaturated metal carbonyl species with CO^{4-7} and is almost 50 times higher than the rate constant for reaction of $Fe(CO)_4$ with $CO, 4^{a}$ which is believed to be a spin-disallowed reaction. This rate constant is even lower than $k_{23}(k_{12} \simeq 1/5 k_{23})$, the rate constant for reaction of $(\eta^6 - C_6H_6)Cr(CO)_2$ with CO. This is interesting since it is in contrast with the hypothesis that 14-electron systems are usually more reactive than 16-electron systems.^{1b} The predicted time dependences of $[(\eta^6-C_6H_6)Cr(CO)_2]$ and $[(\eta^6-C_6H_6)Cr(CO)_3]$ are given by

$$\frac{[(\eta^{6}-C_{6}H_{6})Cr(CO)_{2}]}{k'_{23}-k'_{12}} = \frac{k'_{12}[A]_{0}}{k'_{23}-k'_{12}} \exp(-k'_{12}t) + \left([B]_{0} - \frac{k'_{12}[A]_{0}}{k'_{23}-k'_{12}} \right) \exp(-k'_{23}t)$$
(6)

$$\begin{bmatrix} (\eta^{6} - C_{6}H_{6})Cr(CO)_{3} \end{bmatrix} = \begin{bmatrix} A \end{bmatrix}_{0} + \begin{bmatrix} B \end{bmatrix}_{0} + \begin{bmatrix} C \end{bmatrix}_{0} - \frac{k'_{23}[A]_{0}}{k'_{23} - k'_{12}} \exp(-k'_{12}t) - \left(\begin{bmatrix} B \end{bmatrix}_{0} - \frac{k'_{12}[A]_{0}}{k'_{23} - k'_{12}} \right) \exp(-k'_{23}t)$$
(7)

where $k'_{12} = k_{12}[CO]$, $k'_{23} = k_{23}[CO]$, and $[A]_0$, $[B]_0$, and $[C]_0$ are the initial concentrations of $(\eta^6-C_6H_6)Cr(CO)$, $(\eta^6-C_6H_6)$ - $Cr(CO)_2$, and $(\eta^6-C_6H_6)Cr(CO)_3$, respectively. Since $k'_{12} \simeq$ $1/5k'_{23}$ and $[A]_0 \simeq 5/2[B]_0$ (see below), it is obvious that two preexponential factors in the right side of eq 6 have the same sign (+). Thus, the double exponentially monotonic decay of $[(\eta^6 C_6H_6)Cr(CO)_2$ is expected and observed. However, at long time the decay of $[(\eta^6-C_6H_6)Cr(CO)_2]$, as well as the regrowth of $[(\eta^6-C_6H_6)Cr(CO)_3]$, approaches single exponential with a rate of k'_{12} . Single-exponential fits were made to the tails of $(\eta^6$ - $C_6H_6)Cr(CO)_2$, 1917-cm⁻¹ decays, and to the tails of the parent absorption recoveries at a series of CO pressures. A set of data, measured at the parent 1939-cm⁻¹ band, is shown in Figure 6. Both sets of observed data follow the same linear dependence on [CO] and lead to the same rate constant, within experimental error, as that obtained from the measurements on the CO dependence of $(\eta^6-C_6H_6)Cr(CO)$ decay at the 1984-cm⁻¹ band. The reaction of $(\eta^6-C_6H_6)Cr(CO)$ with CO appears virtually temperature independent. Values for the rate constant at temperatures in the range 340-380 K are the same within experimental error.

We cannot eliminate the possibility that some $(C_6H_6)Cr$ is formed upon 266-nm photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$, since this fragment is not detectable with our technique. If $(C_6H_6)Cr$ is formed in significant amount, it will react with CO to produce $(\eta^6-C_6H_6)Cr(CO)$, which then will react with CO to generate $(\eta^{\circ}-C_{6}H_{6})Cr(CO)_{2}$. As a result, the slower rate constant observed for reaction of $(\eta^6-C_6H_6)Cr(CO)$ with CO would be an "effective" rate constant. However, we note that the decay of the $(\eta^6$ - C_6H_6)Cr(CO) absorption is fit by single exponential very well. This observation suggests that the amount of $(\eta^6-C_6H_6)Cr(CO)$ derived from the reaction of $(C_6H_6)Cr$ with CO is negligible. In addition, the bond energy arguments (see above section), as well as the fact that upon 248-nm (115 kcal mol⁻¹) photolysis of $Cr(CO)_6$ only a slight amount of $Cr(CO)_3$ was formed,^{4b,5a} imply that no appreciable amount of $(C_6H_6)Cr$ would be formed upon 266-nm (107 kcal mol⁻¹) photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$. Further argument, although circumstantial, can be obtained via observation of the reaction kinetics of $(\eta^6-C_6H_6)Cr(CO)$ with other ligands, such as H₂ and N₂, since in those cases the decay of $(\eta^6 - C_6 H_6)$ -Cr(CO) can be monitored free from disturbance of $(C_6H_6)Cr$. We find that the rate constants for reactions of $(\eta^6-C_6H_6)Cr(CO)$ with H_2 and N_2 are an order of magnitude slower than corresponding values for $(\eta^6-C_6H_6)Cr(CO)_2$.²⁶ We thus believe that

⁽²⁵⁾ Ryther, R.; Weitz, E. Unpublished results, cited in ref 4e.



Figure 7. Time-resolved infrared spectra following 266-nm photolysis of 14 mTorr of $(\eta^6-C_6H_6)Cr(CO)_3$ in the presence of 7 Torr of Ar. The spectra were shown at 25- μ s intervals in the range 2-102 μ s. An up arrow indicates absorption increasing with time, and a down arrow indicates absorption decreasing.

the existence of $(C_6H_6)Cr$, if any, has no significant contribution to the slower rate constant for reaction of $(\eta^6-C_6H_6)Cr(CO)$ with CO. A subtle absorption at ~1999 cm⁻¹ is also observed following 266-nm photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$ in the presence of CO and, as in the case of 355-nm photolysis, is not positively identified.

The ratio of $(\eta^6 - C_6 H_6) Cr(CO)_2$: $(\eta^6 - C_6 H_6) Cr(CO)$ generated via 266-nm photolysis of $(\eta^6 - C_6 H_6)Cr(CO)_3$ can be estimated from the relative intensities of the absorption bands observed upon 355and 266-nm photolysis. Since the distribution of fragments is strongly dominated by $(\eta^6-C_6H_6)Cr(CO)_2$ and $(\eta^6-C_6H_6)Cr(CO)$ plus (n⁶-C₆H₆)Cr(CO)₂ upon 355- and 266-nm photolysis, respectively, we assume that upon 355-nm photolysis the number of $(\eta^6 - C_6 H_6)Cr(CO)_2$ formed is equal to that of $(\eta^6 - C_6 H_6)Cr(CO)_3$ depleted and that upon 266-nm photolysis the number of $(\eta^6$ - $C_6H_6)Cr(CO)$ plus $(\eta^6-C_6H_6)Cr(CO)_2$ is equal to that of $(\eta^6-C_6H_6)Cr(CO)_2$ C_6H_6)Cr(CO)₃ depleted. On the basis of the above assumption, the ratio of the absorption coefficients between the 1917-cm⁻¹ band of $(\eta^6-C_6H_6)Cr(CO)_2$ and the 1939-cm⁻¹ band of $(\eta^6-C_6H_6)Cr$ -(CO), can be estimated from Figure 2a to be $\sim 1/2$. From Figure 2b, the ratio of absorption *intensities* between these two bands upon 266-nm photolysis is determined to be $\sim 1/7$. As a result, the ratio of the molecular numbers between $(\eta^6 \cdot C_6 H_6) Cr(CO)_2$ formed and $(\eta^6 - C_6 H_6) Cr(CO)_3$ depleted upon 266-nm photolysis is calculated as (1/7)/(1/2) = 2/7. Therefore, the ratio $(\eta^6 - \eta^6)$ $C_6H_6)Cr(CO)_2$; $(\eta^6-C_6H_6)Cr(CO)$ generated upon 266-nm photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$ is determined as 2/7:(1-2/7) = 2:5. The Ar buffer gas pressure should in principle effect this ratio if photodissociation of $(\eta^6-C_6H_6)Cr(CO)_3$ proceeds via the sequential loss of CO,^{6d} yet such an effect was not observed in the present experimental conditions at Ar pressure in the range 5-30 Torr.

Both $(\eta^6-C_6H_6)Cr(CO)_2$ and $(\eta^6-C_6H_6)Cr(CO)$ formed upon 266-nm photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$ are initially rovibrationally excited. They undergo vibrational relaxation upon collisions with Ar. Also, CO ejected upon 266-nm photolysis is found to be vibrationally excited ($\nu = 2, 3$), as evidenced by the growth of a strong absorption over 2020 cm⁻¹ (CO ($\nu = 3$) \rightarrow (CO ($\nu = 4$)) (Figure 2b) which remains almost unchanged during the observation over 20 μ s even in the presence of excess CO. The primary production of hot CO ($\nu = 2$ or 3) has also been observed in the KrF, KrCl, or ArF laser photolysis of M(CO)_n (M = Cr,^{4b,5a,6d} Mo^{6d}, W,^{6c,6d} and Fe^{4a}) and Mn₂(CO)₁₀.^{4c}

TABLE II:	Rate C	onstants f	or Reac	tions of	Some	Coordinatively
Unsaturated	Metal	Carbonyl	Species	with C	0	-

	spin allowed	rate constant, 10^{13} cm ³ mol ⁻¹ s ⁻¹
$(\eta^6 - C_6 H_6) Cr(CO)_2 + CO$		0.634
$(\eta^6 - C_c H_c) Cr(CO) + CO$?	0.14 ^a
$Cr(CO)_{\epsilon} + CO$	Y	1.5 ^b , 2.2, ^c 2.4 ^d
$Cr(CO)_{4} + CO$	Y	2.4, ^b 2.6, ^c 2.2 ^d
$Fe(CO)_4 + CO$	N	0.003e
$Fe(CO)_1 + CO$	Y	1.2*

^aThis work. ^bReference 4b. ^cReference 5a. ^dReference 6d. ^cReference 4a.

Since the photofragments formed upon 266-nm photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$ are dominated by $(\eta^6-C_6H_6)Cr(CO)$, the formation of $(C_6H_6)_2Cr_2(CO)_4$ via reaction 8 is also anticipated. $(\eta^6-C_6H_6)Cr(CO) + (\eta^6-C_6H_6)Cr(CO)_3 \rightarrow (C_6H_6)_2Cr_2(CO)_4$ (8)

Figure 7 shows the time-resolved spectra obtained 2–102 μ s following 266-nm photolysis of ~10 mTorr of (η^6 -C₆H₆)Cr(CO)₃ in 7 Torr of Ar. The band at 1984 cm⁻¹ decreases accompanied by the growth of a long-lived (~1 ms) new band at ~1910 cm⁻¹ and the second decrease of the parent bands. Both reactions 3 and 8 may be responsible for the formation of the band at 1910 cm⁻¹. However, we consider that upon 266-nm photolysis reaction 8 is the most important process since (η^6 -C₆H₆)Cr(CO) is the most abundant fragment and the time-resolved spectra exhibit different temporal behavior from that upon 355-nm photolysis. Thus, the band at 1910 cm⁻¹ is assigned to (C₆H₆)₂Cr₂(CO)₄. The rate constant for reaction 8 is estimated to be on the order of 1 × 10¹³ cm³ mol⁻¹ s⁻¹, again about an order of magnitude lower than corresponding values for other metal carbonyls,⁴⁻⁷ except Fe(CO)₄.²⁵

Conclusions

Time-resolved infrared laser absorption spectra have been obtained for the coordinatively unsaturated metal carbonyl species, $(\eta^6-C_6H_6)Cr(CO)_2$ and $(\eta^6-C_6H_6)Cr(CO)$. These reactive intermediates were generated via UV laser photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$ in the gas phase. We found that the distribution of fragments generated upon 3⁵5-nm photolysis of $(\eta^6-C_6H_6)-Cr(CO)_3$ is strongly dominated by $(\eta^6-C_6H_6)Cr(CO)_2$, whereas the distribution of fragments generated upon 266-nm photolysis is strongly dominated by $(\eta^6-C_6H_6)Cr(CO)_2$ and $(\eta^6-C_6H_6)Cr(CO)$ with a ratio of $(\eta^6-C_6H_6)Cr(CO)_2:(\eta^6-C_6H_6)Cr(CO)$ of about 2:5.

The kinetics of reaction of unsaturated species $(\eta^6-C_6H_6)Cr$ -(CO)_x (x = 1, 2) with CO have been determined and are shown in Table II. For comparison, the rate constants for reaction of some Cr(CO)_x and Fe(CO)_x fragments with CO are also displayed. It is interesting to note that the rate constant for reaction of $(\eta^6-C_6H_6)Cr(CO)$ with CO lies between the corresponding values for the spin-allowed and the spin-disallowed reactions. We have also reported evidence that $(\eta^6-C_6H_6)Cr(CO)_x$ reacts with the parent to form binuclear species. The rate constants for these binuclear-forming reactions are also found to be lower than corresponding values for the reaction of other coordinatively unsaturated metal carbonyl species, except Fe(CO)₄, with their parents. Further studies to understand the lower reactivity of $(\eta^6-C_6H_6)Cr(CO)_x$ species are in progress.

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⁽²⁶⁾ Zheng, Y., et al. Unpublished results.