

Discussion

The dissociation of NiDPA proceeds through reaction pathways similar to those observed with NiNTA.^{2,8} Both systems include terms for Cu^{2+} and H^+ attack—rate constants $k_{\text{Cu}}^{\text{NiDPA}}$, $k_{\text{Cu}}^{\text{NiNTA}}$ and $k_{\text{H}}^{\text{NiDPA}}$, $k_{\text{H}}^{\text{NiNTA}}$, respectively. Some minor differences are observed. The simple dissociation path (k^{NiNTA}) of NiNTA is not observed with NiDPA and the NiDPA system shows a squared H^+ -dependent term ($k_{\text{H}}^{\text{NiDPA}}$) that is not observed in the NiNTA system. The NiDPA system was studied at somewhat higher acidities and this can account for these differences.

The rate constants for the two systems are of the same order of magnitude and initially suggest that steric factors are small. Considering the H^+ and Cu^{2+} paths for the two systems, the ratios $k_{\text{H}}^{\text{NiNTA}}/k_{\text{H}}^{\text{NiDPA}}$ and $k_{\text{Cu}}^{\text{NiNTA}}/k_{\text{Cu}}^{\text{NiDPA}}$ can be predicted in a manner analogous to the comparison made between the NiNTA and NiEDTA systems.² In this comparison, it must be assumed that the same rate-determining step is involved and that steric hindrance is not important. The predicted values of $k_{\text{H}}^{\text{NiNTA}}/k_{\text{H}}^{\text{NiDPA}}$ and of $k_{\text{Cu}}^{\text{NiNTA}}/k_{\text{Cu}}^{\text{NiDPA}}$ are identical, 0.41, and reflect the difference in the stability constants^{1,9} of NiNTA ($10^{11.26}$) and NiDPA ($10^{10.87}$). Any statistical effects are not included in the predicted value. The observed ratios are 0.54 and 0.46, respectively. The agreement is good but probably fortuitous when the energy and entropy of activation are considered. The values of E_a for the NiNTA system are approximately 18 kcal/mol for all paths, whereas they are considerably lower (12–14 kcal/

(8) Values² of $k_{\text{Cu}}^{\text{NiNTA}}$, $k_{\text{H}}^{\text{NiNTA}}$, and k^{NiNTA} are $1.39 \times 10^{-8} M^{-1} \text{sec}^{-1}$, $4.34 \times 10^{-1} M^{-1} \text{sec}^{-1}$, and $3.5 \times 10^{-8} \text{sec}^{-1}$, respectively.

(9) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964.

mol) for the NiDPA system. This suggests a weaker nickel–nitrogen bond in the nickel complex, as a result of strain due to the ring structure in the ligand. However, this lower energy of activation is offset by the entropies of activation, which are more negative in the NiDPA system. The values of ΔS^\ddagger associated with $k_{\text{H}}^{\text{NiNTA}}$ and $k_{\text{Cu}}^{\text{NiNTA}}$ are -1 and -13 eu compared to -13 and -31 eu for the similar NiDPA paths. The large changes in ΔS^\ddagger suggest that ring orientation has a significant effect on the formation of the intermediates. Similarly the values of the frequency factor, A , are much lower for the NiDPA pathways.

No attempt was made to determine E_a , ΔH^\ddagger , and ΔS^\ddagger for the CdDPA system since the experimental method employed gives rate constants good to only $\pm 10\%$ and leads to large errors in these values. Even though the cadmium(II) reactions are approximately five orders of magnitude faster than the nickel(II) reactions, similarities suggest that the reactions proceed through closely related intermediates. The ratio¹⁰ $k_{\text{H}}^{\text{CdDPA}}/k_{\text{H}}^{\text{CdDPA}}$ (6.7×10^4) is in agreement with similar ratios for CdNTA and NiNTA, 1.9×10^5 and 1.2×10^5 , respectively. Like the NiNTA and NiDPA systems, the ratio $k_{\text{H}}^{\text{CdNTA}}/k_{\text{H}}^{\text{CdDPA}}$ (0.9) reflects the difference in stability constants^{1,9} of CdNTA ($10^{9.80}$) and CdDPA ($10^{8.81}$). It is therefore not unreasonable to assume that the ring structure in the DPA ligand shows similar effects in the dissociation of the cadmium(II) complex, lowering the energy of activation and the frequency factor.

Acknowledgment.—This work was supported by the National Science Foundation, Grant GP-7319.

(10) Values of k^{CdNTA} (1.6 sec^{-1}) and $k_{\text{H}}^{\text{CdNTA}}$ ($3.0 \times 10^5 M^{-1} \text{sec}^{-1}$) are taken from ref 5.

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Spectroscopic Studies of Some Carbene Pentacarbonyl Complexes of Chromium(0) and Tungsten(0)

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Infrared, nuclear magnetic resonance, and electronic spectral studies of several $\text{M}(\text{CO})_5\text{C}(\text{OC}_2\text{H}_5)_2\text{R}$ compounds have been carried out, where $\text{M} = \text{Cr}$ and W and $\text{R} = \text{CH}_3$, $n\text{-C}_4\text{H}_9$, and C_6H_5 . σ - and π -bonding properties of the carbene ligands are interpreted using Graham's approach. These results indicate the carbene ligands to be comparable to phosphines in σ -donor strengths and much better σ donors than a carbonyl ligand. At the same time the carbene groups behave as strong π acceptors.

Introduction

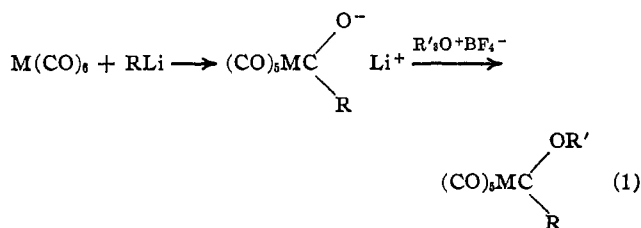
The reaction of organolithium compounds with carbon monoxide and with metal carbonyls has been reported as a new method for synthesis of ketones and

aldehydes.² The discovery that alkylation of lithium salts of the organolithium–metal carbonyl addition product leads to a carbene-type ligand (eq 1) has raised considerable interest in organometallic chemistry.³

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(2) M. Ryang and S. Tsutsumi, *Trans. N. Y. Acad. Sci.*, **27**, 724 (1965).

(3) E. O. Fischer and A. Maasbol, *Angew. Chem. Intern. Ed. Engl.*, **3**, 580 (1964).



Complexes previously prepared are those with $\text{M} = \text{Cr}$ and W , $\text{R}' = \text{CH}_3$, and $\text{R} = \text{CH}_3$ and C_6H_5 , as well as carbene ligands with the methoxy group replaced by various amines.³⁻⁶

In our inquiry into the nature of the metal-carbene bond we have analyzed the infrared, nmr, and electronic spectra of $\text{M}(\text{CO})_5\text{C}(\text{OC}_2\text{H}_5)\text{R}$ complexes ($\text{M} = \text{Cr}$, W ; $\text{R} = \text{CH}_3$, $n\text{-C}_4\text{H}_9$, C_6H_5). The reaction of $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ with n -butyllithium and subsequent alkylation is reported here for the first time.

Experimental Section

Materials.—The complexes were prepared according to the method of Aumann and Fischer⁷ with a slight modification: upon dissolving the lithium salt in water, the solution was then filtered, thus removing most of the unreacted hexacarbonyl.

Triethylxonium fluoroborate, the ethylating agent, was prepared as described in the literature.⁸

$\text{W}(\text{CO})_6$ was the generous gift of Climax Molybdenum Co. and was used without further purification. $\text{Cr}(\text{CO})_6$ was purchased from Strem Chemicals Inc.

The crystalline carbene complexes were purified by recrystallization from pentane; the liquids, by vacuum distillation or column chromatography (silica gel, pentane as eluent, short path with suction). The purified complexes were stored over desiccant at -5° with some decomposition.

Chemical analysis on the tungsten complexes were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. *Anal.* Calcd for $\text{CH}_3(\text{C}_2\text{H}_5\text{O})\text{CW}(\text{CO})_5$: W, 46.43; C, 27.30; H, 2.04. Found: W, 45.63; C, 27.42; H, 2.12. Calcd for $\text{C}_6\text{H}_5(\text{C}_2\text{H}_5\text{O})\text{CW}(\text{CO})_5$: W, 40.13; C, 36.71; H, 2.20. Found: W, 39.94; C, 36.84; H, 2.46. Calcd for $n\text{-C}_4\text{H}_9(\text{C}_2\text{H}_5\text{O})\text{CW}(\text{CO})_5$: mol wt, 438.09; W, 41.97; C, 32.90; H, 3.22. Found: mol wt, 435.7 (osmometric in benzene); W, 41.50; C, 33.02; H, 3.31.

Nuclear Magnetic Resonance Spectra.—The proton magnetic resonance spectra were obtained at instrument temperature in deuteriochloroform with tetramethylsilane as internal reference. A Varian HA-100 spectrometer operating at 100 MHz was used for $(\text{CH}_3, \text{C}_6\text{H}_5, \text{and } n\text{-C}_4\text{H}_9)(\text{C}_2\text{H}_5\text{O})\text{CW}(\text{CO})_5$ complexes, $\text{C}_6\text{H}_5(\text{C}_2\text{H}_5\text{O})\text{CCr}(\text{CO})_5$, and valeraldehyde. Other and duplicate spectra were taken on a Varian T-60 spectrometer operating at 60 MHz.

Infrared Spectra.—Ir spectra in the CO stretching region were measured on a Perkin-Elmer 521 spectrophotometer in pentane or hexane solution. Far-ir spectra were taken as a neat film between two polyethylene sheets. The instrument was calibrated against the spectrum of water vapor. The spectral slit width in the 21–1900- cm^{-1} region was between 1.8 and 1.5 cm^{-1} and in the 700–350 cm^{-1} region between 2.0 and 3.0 cm^{-1} . The spectra were measured on an expanded abscissa scale (1 $\text{cm} = 10 \text{ cm}^{-1}$) with a scan speed of 10–15 $\text{cm}^{-1}/\text{min}$.

Electronic Spectra.—The spectra were recorded in the visible and uv regions on a Cary 14 spectrophotometer in 1.0-cm cells using the pure solvent in the reference beam. Samples were

weighed out to 0.01-mg accuracy and dissolved in Spectrograde cyclohexane or methanol and the spectra were recorded immediately.

Calculations.—The vibrational frequencies and mixing parameters were computed using the familiar $GFL = LA$ method.⁹ In these calculations internal coordinates were employed for the CO stretches and the desired L_{ij} matrix elements were calculated by hand using the relationship $L = Ul$, where U is the transformation matrix between internal and symmetry coordinates and l is the machine calculated matrix elements. Machine calculations were performed on the IBM 360-30 at the Vassar College Computer Center.

Results and Discussion

The complexes were identified by their infrared and nmr spectra and chemical analyses. All are extremely soluble in organic solvents and exhibit only slight, if any, decomposition in both polar and nonpolar solvents for periods of 1 hr or more. In general the tungsten complexes are more stable to oxidation by air, but all complexes slowly decompose upon storage yielding the parent hexacarbonyl and unidentified products. Although CH_3Li , $n\text{-C}_4\text{H}_9\text{Li}$, and $\text{C}_6\text{H}_5\text{Li}$ were very reactive toward $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$, no reaction occurred upon addition of propynyllithium to $\text{W}(\text{CO})_6$.

$\text{C}_6\text{H}_5(\text{C}_2\text{H}_5\text{O})\text{CCr}(\text{CO})_5$ is an orange-red solid at room temperature, mp $29 \pm 1^\circ$, without decomposition. The analogous tungsten complex was obtained as deep red crystals, mp 54° and, unlike the Cr complex, was quite stable to air oxidation.

$n\text{-C}_4\text{H}_9(\text{C}_2\text{H}_5\text{O})\text{CM}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{W}$) complexes are yellow-orange liquids. Distillation of $n\text{-C}_4\text{H}_9(\text{C}_2\text{H}_5\text{O})\text{CW}(\text{CO})_5$ in a microdistillation apparatus at 65° (0.05 mm) yielded the complex in an essentially pure form (<1% of $\text{W}(\text{CO})_6$). However upon sealing and storing overnight at -5° , some $\text{W}(\text{CO})_6$ was produced.

$\text{CH}_3(\text{C}_2\text{H}_5\text{O})\text{CM}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{W}$) complexes were obtained as yellow liquids. Attempted purification of the W compound by vacuum distillation (45–50° (0.05 mm)) led to rapid decomposition to $\text{W}(\text{CO})_6$ and the aforementioned unidentified products. Furthermore it was found that the methyl(ethoxy)carbene complexes were unstable at low pressures (~ 1 mm) at room temperature.

Methyl(methoxy)carbenetungsten pentacarbonyl is crystalline (mp 52°).³ The added bulkiness of the ethoxy group undoubtedly hinders crystal formation in both the n -butyl and methyl derivatives prepared here.

The mode of decomposition of these compounds and the type of products produced is a very interesting and complex problem.¹⁰

Nmr Spectra.—Peak positions, splitting patterns, and assignments are tabulated in Table I.

In all spectra the methylene quartet and the methyl triplet of the ethoxy group, with relative intensities of 2:3, were clearly evident and at the same approximate chemical shifts (4.9 and 1.6 ppm, respectively). Since ordinary $-\text{CH}_2\text{OR}$ protons absorb near 3.6 ppm, the

(4) U. Klabunde, *Dissertation Abstracts*, **28B**, 2321 (1967).

(5) U. Klabunde and E. O. Fischer, *J. Am. Chem. Soc.*, **89**, 7141 (1967).

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(9) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(10) E. O. Fischer, B. Heckl, K. H. Dotz, J. Muller, and H. Werner, *J. Organometal. Chem. (Amsterdam)*, **16**, P29 (1969).

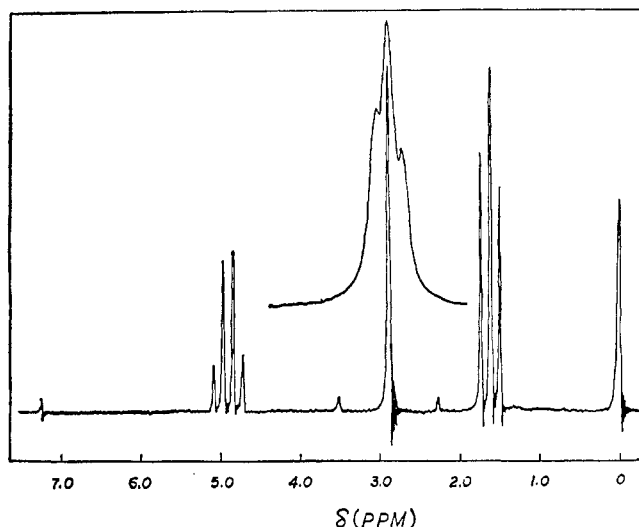


Figure 1.—The 60-MHz proton nmr spectrum of methyl(ethoxy)carbenetungsten pentacarbonyl in DCCl_3 . Overlay expanded 20 times.

TABLE I
 ^1H NMR RESULTS OF $\text{R}(\text{C}_2\text{H}_5\text{O})\text{CM}(\text{CO})_5$ COMPLEXES
IN DEUTERIOCHLOROFORM

R	Chemical shift ^a — δ , ppm—		Multiplicity	Assignment ^b
CH_3	4.90	4.98	Q	OCH_2CH_3
	2.90	2.93	S	$\text{O}-\text{C}-\text{CH}_3$
	1.64	1.61	T	OCH_2CH_3
C_6H_5	7.52	7.28	M	$\text{C}-\text{C}_6\text{H}_5$
	5.09	4.90	Q	OCH_2CH_3
	1.75	1.62	T	OCH_2CH_3
$n\text{-C}_4\text{H}_9$	4.90	5.11	Q	OCH_2CH_3
	3.12	3.30	T	$\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
	1.62	1.65	T	OCH_2CH_3
	1.41	1.40	M	$\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
	0.92	0.93	T	$\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

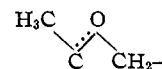
^a Chemical shifts (δ) relative to TMS = 0.0 ppm. ^b Assignments made on the basis of the splitting pattern and relative intensities.

downfield shift is indicative of the electron-withdrawing character of the carbene carbon. Indeed the absorption of methylene protons in an ester ($-\text{CH}_2\text{OOCCH}_3$) is near 4.1 ppm, a situation more comparable to the protons on a carbene ligand.

The spectra of the methyl(ethoxy)carbene complexes are quite simple (Figure 1). The methyl absorption at 2.9 ppm is at somewhat lower field than methyl protons attached to an ester group ($\text{CH}_3\text{COOR} \approx 2.0$ ppm). Upon abscissa expansion it was found that the methyl singlet in the tungsten complex was actually a triplet, as is shown by the overlay in Figure 1. This is attributed to coupling with the methylene protons on the ethoxy group, $J_{\text{CH}_2-\text{O}-\text{C}-\text{CH}_3} = 0.45 \pm 0.1$ Hz. The high-resolution spectrum of the methylene quartet on the ethoxy group did not afford accurate estimates of the reciprocal methyl to methylene proton coupling constants. The peaks were broadened compared to the ethoxy methyl triplet peaks, and unsymmetrical but complete resolution into quartets separated by 0.45 Hz was not observed.

Although the magnitude of J is generally negligible

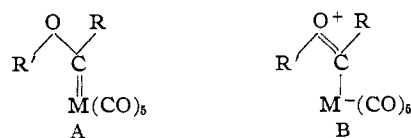
for coupling of nuclei separated by more than three bonds, long-range coupling is often observed in unsaturated molecules. The presence of this coupling over a five-bond range is therefore indicative of a π -electron system within the oxycarbene ligand



This homoallylic coupling has been previously observed by Moser and Fischer in the case of methyl(methoxy)carbenetungsten pentacarbonyl in which the methyl singlet was found to be a quartet under conditions of high resolution.¹¹ The coupling constant, $J_{\text{CH}_3-\text{O}-\text{C}-\text{CH}_3} = 0.4 \pm 0.1$ Hz, is in line with our observations.

Fischer and Moser observed only line broadening in the high-resolution spectrum of *cis*-methyl(methoxy)carbenetriphenylphosphinetungsten tetracarbonyl.¹¹ The carbene ligand in this complex has been shown to be in a *cis* configuration by crystal structure analysis.¹² Since generally $J_{\text{H}-\text{H}, \text{cis}} < J_{\text{H}-\text{H}, \text{trans}}$, the existence of the *cis* isomer in solution is indicated by the lack of resolution of the methyl protons. From this we conclude the methyl(ethoxy)carbene ligand bonded to $\text{W}(\text{CO})_5$ to be in a *trans* configuration, as Fischer asserts the methyl(methoxy)carbene ligand to be in the case of $\text{CH}_3(\text{CH}_3\text{O})\text{CW}(\text{CO})_5$.

This long-range coupling of methyl carbene protons with methylene ethoxy protons was not observed in the analogous Cr complex. The methyl singlet remained unresolved and symmetrical although somewhat broadened under high-resolution conditions. Low-temperature studies by Moser and Fischer revealed no splittings in the methyl(methoxy)carbenechromium pentacarbonyl signals at -50° .¹¹ This might indicate the presence of the *cis* isomer or it could mean a possible decrease of long-range coupling due to less C-O-R π bonding. In other words, resonance structure A might predominate for $\text{M} = \text{Cr}$. There is no real



supporting evidence for this since ir results indicate similar M-carbene bonding for both W and Cr.¹³

The spectrum of valeraldehyde ($n\text{-C}_4\text{H}_9\text{CHO}$) aided in the assignment of the *n*-butyl(ethoxy)carbene complexes. The chemical shifts, assignments, and splitting patterns of $n\text{-C}_4\text{H}_9\text{CHO}$ are as follows: 9.72 ppm, aldehyde proton, triplet; 2.41 ppm, α -methylene protons, triplet of doublets; 1.46 ppm, β - and γ -methylene protons, complex multiplet; 0.90 ppm, methyl protons, triplet of triplets.

(11) E. Moser and E. O. Fischer, *J. Organometal. Chem.* (Amsterdam), **13**, 209 (1968).

(12) O. S. Mills and A. D. Redhouse, *Chem. Commun.*, 814 (1966).

(13) For methyl(amino)carbenechromium pentacarbonyl Fischer reported long-range coupling between the methyl group and the amino group hydrogens with $J_{\text{aminocarbene}} > J_{\text{oxycarbene}}$. It is interesting to compare this with ir results to be discussed later which suggest an increase in nitrogen-carbene double-bond character as compared to that in the oxygen-carbene bond.

The spectra of the *n*-butyl(ethoxy)carbene complexes were very similar to that of valeraldehyde excepting the superposition of the ethoxy protons. The α -methylene protons (3.3 ppm) of the carbene are downfield from those of the aldehyde (2.41 ppm) or those of esters in general ($R'CH_2COOR = 2.1$ ppm). Again the electron-withdrawing character of the carbene carbon is illustrated.

High-resolution conditions did not yield observation of long-range coupling in the *n*-butyl(ethoxy)carbene-tungsten pentacarbonyl complex.

Infrared Spectra.— $M(CO)_5L$ molecules are ideally of C_{4v} symmetry resulting in three infrared-allowed CO stretching modes, two of symmetry A_1 and one of E symmetry. Generally it is found however that the infrared-inactive B_1 vibration gains some intensity due to perturbation of the C_{4v} symmetry by the L group.¹⁴ Occasionally this perturbation may even lead to a splitting of the degenerate (E) mode. In this study we have observed the weak B_1 vibrations, and in the case of the phenyl(ethoxy)carbene derivatives of both chromium and tungsten a splitting of the E mode was also observed (Figure 2). This splitting is comparable to that found in the structurally similar $Mn(CO)_5C(O)-C_6H_5$ and $Re(CO)_5C(O)C_6H_5$ complexes where the E mode was observed to be split by 11 and 3 cm^{-1} , respectively.^{15,16} In the phenyl(ethoxy)carbene complexes the B_1 band was not distinguishable from the T_{1u} band present from trace quantities of the respective hexacarbonyls.

In this work energy factoring of the carbonyl stretching vibrations was used to calculate the CO force constants. The commonly employed restriction on the interaction constants was also made, *i.e.*, $k_o(CO^{eq}, CO^{eq}) = k_o(CO^{eq}, CO^{ax}) = \frac{1}{2}k_t(CO^{eq}, CO^{eq})$.¹⁷ The observed and calculated CO stretching frequencies and force constants are shown in Table II. The agreement between observed and calculated frequencies is generally within ± 1.0 cm^{-1} . Although some improvement in the interaction constants can be obtained by lifting the restrictions placed on these values and using ¹³CO frequency data, this has little effect on the stretching force constants k_1 and k_2 .¹⁸⁻²¹ It has recently been pointed out by Gay and Graham²² that the Cotton-Kraihanzel method, which requires $k_1 < k_2$, can break down in certain cases to give inconsistent results with

(14) Recently it has been suggested (J. R. Miller, *Inorg. Chim. Acta*, **2**, 421 (1968)) that this band can also gain intensity from a cubic term in the dipole moment series expansion and by borrowing intensity from another hot band involving the A_1 CO stretching vibration. However these effects are believed to be of less importance than the effects caused by distortion due to the presence of unsymmetrical ligands.

(15) J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965).

(16) P. W. Jolly, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.*, 5830 (1965).

(17) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

(18) H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *ibid.*, **89**, 2844 (1967).

(19) P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *ibid.*, **89**, 2851 (1967).

(20) F. A. Cotton, A. Musco, and G. Yagupsky, *Inorg. Chem.*, **6**, 1357 (1967).

(21) D. J. Darensbourg, Ph.D. Dissertation, University of Illinois, 1968, p 39; University Microfilms, Ann Arbor, Mich., No. 69-1328.

(22) R. S. Gay and W. A. G. Graham, *Inorg. Chem.*, **8**, 1561 (1969).

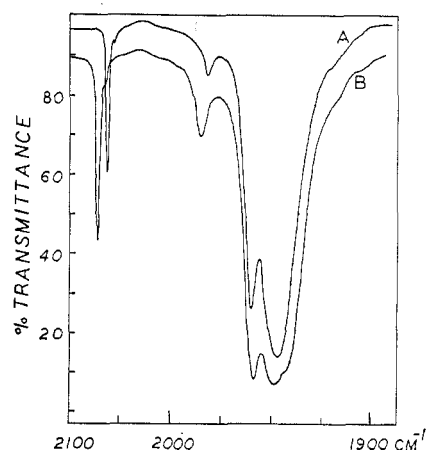


Figure 2.—Infrared spectra in the CO stretching region in pentane: A, $n-C_4H_9(C_2H_5O)CCr(CO)_5$; B, $C_6H_5(C_2H_5O)CW(CO)_5$.

more precisely calculated force constants. They found $k_1 > k_2$ for $Mn(CO)_5M(C_6H_5)_3$ ($M = Ge$ and Sn) when ¹³CO frequency data were employed in the force constant calculations. However in our studies if we assume $k_1 > k_2$ the agreement between observed and calculated B_1 frequencies is very poor.

It can be seen from the magnitude of the L_{12} matrix elements listed in Table II that there is considerable coupling between the two modes of A_1 symmetry. This coupling largely accounts for the intensity of the highest frequency A_1 vibration.²³

Initially all changes in CO stretching force constants, when CO was substituted by other ligands (L) to form $M(CO)_5L$ compounds, were ascribed to changes in the extent of back-donation in the M-CO and M-L bonds.²⁴ Since that time it has been fairly well established that inductive effects operating through the metal-ligand σ bond as well as metal-ligand π bonding are important in determining the CO stretching frequencies or force constants.²⁵

Graham has proposed a semiquantitative method for separating these two effects.²⁶ He has defined the σ and π effects of a ligand in $M(CO)_5L$ compounds ($M = Mn$ and Mo) in terms of the effect of L on the CO force constants. The equations used to compute these parameters are eq 2 and 3 where Δk_1 and Δk_2 are the differences between the force constants in $M(CO)_5L$ and a reference compound. In the $Mo(CO)_5L$ series

$$\Delta k_1 = \sigma + 2\pi \quad (2)$$

$$\Delta k_2 = \sigma + \pi \quad (3)$$

$C_6H_{11}NH_2Mo(CO)_5$ was taken as the reference compound since cyclohexylamine has no capacity for accepting π electrons from the metal. A positive value of σ or π parameters implies that L is acting as a σ or π acceptor, whereas a negative value of σ or π parameters implies L

(23) Detailed measurements of the integrated intensities of the CO vibrations in these and related molecules are presently underway in our laboratory and results will be submitted for publication at a later date.

(24) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

(25) D. J. Darensbourg and T. L. Brown, *ibid.*, **7**, 959 (1968).

(26) W. A. G. Graham, *ibid.*, **7**, 315 (1968).

TABLE II
 OBSERVED AND CALCULATED STRETCHING FREQUENCIES, FORCE CONSTANTS,
 AND VIBRATIONAL MIXING PARAMETERS FOR SOME $M(\text{CO})_5\text{C}(\text{OC}_2\text{H}_5)\text{R}$ COMPOUNDS

Compound		Obsd bands, cm^{-1} ^a	Calcd freq, cm^{-1}	Symmetry	Force constants, $\text{mdyn}/\text{\AA}^d$				Mixing parameters ^e	
M	R				k_1	k_2	k_t	$k_o' = k_o$	L_{11}	L_{21}
Cr	CH_3	2064.1	2063.8	$A_1^{(2)}$	15.76	15.87	0.56	0.28	0.3560	0.1378
		1982.8	1982.0	B_1						
		1961.4	1961.5	$A_1^{(1)}$						
		1946.9	1946.7	E						
		2062.8	2065.9	$A_1^{(2)}$						
Cr	$n\text{-C}_4\text{H}_9$	1981.8	1981.4	B_1	15.73	15.87	0.57	0.29	0.3565	0.1367
		1959.7	1959.2	$A_1^{(1)}$						
		1946.5	1946.5	E						
		2062.0	2062.2	$A_1^{(2)}$						
Cr	C_6H_5	<i>b</i>	1987.0	B_1	15.76	15.95	0.52	0.26	0.3585	0.1313
		1963.0	1963.2	$A_1^{(1)}$						
		1954.0, ^e 1942.0	1954.3	E						
		2071.5	2072.6	$A_1^{(2)}$						
		1980.0	1982.6	B_1						
W	CH_3	1957.8	1957.3	$A_1^{(1)}$	15.71	15.89	0.61	0.31	0.3572	0.1348
		1944.8	1944.8	E						
		2072.9	2072.4	$A_1^{(2)}$						
		1980.6	1982.6	B_1						
W	$n\text{-C}_4\text{H}_9$	1956.5	1956.2	$A_1^{(1)}$	15.69	15.89	0.61	0.31	0.3577	0.1335
		1944.5	1944.8	E						
		2070.5	2071.2	$A_1^{(2)}$						
		<i>b</i>	1984.5	B_1						
W	C_6H_5	1958.0	1957.4	$A_1^{(1)}$	15.70	15.92	0.59	0.30	0.3583	0.1318
		1948.0, ^e 1941.0	1948.0	E						

^a All spectra were observed in pentane solution and are accurate to $\pm 0.5 \text{ cm}^{-1}$. ^b It was impossible to observe this band due to the presence of a trace of the hexacarbonyls which have their maximum absorptions at 1988 and 1984 cm^{-1} for $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$, respectively. ^c In calculating the force constants the highest frequency vibration for the E mode was employed. ^d Force constant designations are as given in ref 18. k_1 is the stretching force constant of the CO group *trans* to the carbene ligand, while k_2 is the stretching force constant for CO groups *cis* to the carbene ligand. Interaction force constants are as defined in the text. ^e These indicate the mixing between the two A_1 modes, where $L_{11} = L_{22}$ and $L_{21} = -L_{12}$.

TABLE III

GRAHAM σ AND π PARAMETERS FOR SOME $\text{LCr}(\text{CO})_5$ COMPLEXES^a

L	k_1	k_2	Δk_1	Δk_2	σ^b	π^c
$(\text{C}_6\text{H}_5)_3\text{P}^d$	15.51	15.85	0.43	0.08	-0.27	0.35
CO^e	16.49	16.49	1.41	0.72	0.03	0.69
$\text{C}(\text{OC}_2\text{H}_5)(\text{CH}_3)$	15.76	15.87	0.68	0.10	-0.48	0.58
$\text{C}(\text{OC}_2\text{H}_5)(\text{C}_6\text{H}_5)$	15.73	15.87	0.65	0.10	-0.45	0.55
$\text{C}(\text{OC}_2\text{H}_5)(\text{C}_6\text{H}_5)_2$	15.76	15.95	0.68	0.18	-0.32	0.50
$\text{C}(\text{CH}_3)\text{N}(\text{C}_6\text{H}_5)_2^f$	15.25	15.04	0.17	-0.13	-0.43	0.30
$\text{C}(\text{CH}_3)\text{NH}(\text{C}_6\text{H}_5)^f$	15.36	15.74	0.28	-0.03	-0.34	0.31

^a Symbols are as explained in the text. All data were taken from spectra measured in saturated hydrocarbon solution. The reference compound is cyclohexylaminechromium pentacarbonyl which has force constants of $k_1 = 15.08$ and $k_2 = 15.77$. (Force constants are in $\text{mdyn}/\text{\AA}$.) ^b Estimated experimental uncertainty is ± 0.12 . ^c Estimated experimental uncertainty is ± 0.08 . ^d Calculated from published frequencies of 2065 ($A_1^{(2)}$), 1947 ($A_1^{(2)}$), and 1944 (E) cm^{-1} : T. L. Brown and D. J. Darensbourg, *Inorg. Chem.*, **6**, 971 (1967). ^e Force constants were taken from F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962). ^f Force constants were taken from J. A. Connor and E. O. Fischer, *J. Chem. Soc.*, **A**, 578 (1969).

is a σ or π donor as compared to the reference ligand where σ and π are equal to zero. This approach has also been extended to the $\text{W}(\text{CO})_5\text{L}$ series by Stewart and Treichel.²⁷

Table III contains similar data for $\text{Cr}(\text{CO})_5\text{L}$ compounds, for which we employed the analogous reference compound, $\text{C}_6\text{H}_{11}\text{NH}_2\text{Cr}(\text{CO})_5$. The large negative values of the σ parameters are indicative of the strong σ -donor properties of the ethoxycarbene ligands in

(27) R. P. Stewart and P. M. Treichel, *Inorg. Chem.*, **7**, 1942 (1968).

these complexes. This is also true for the aminocarbene ligands which have very similar σ values. It appears that the donor strengths of the ethoxy- and aminocarbene ligands are comparable to that of the triphenylphosphine ligand and much greater than that of the carbonyl group. At the same time the carbene ligands are behaving as strong π acceptors from the metal, with the oxycarbene being more strongly π accepting than the aminocarbene. This difference in acceptor ability can be understood if we consider the nitrogen group to be a better electron donor into the carbene p_z acceptor orbital. This would in turn decrease the carbene π -acceptor capacity from the $\text{Cr}(\text{CO})_5$ moiety. A similar conclusion has been reached by Connor and Fischer based on X-ray diffraction results and chemical reactivity.⁶

Therefore it is likely that the π -acceptor properties of the aminocarbene and triphenylphosphine ligands are very similar, whereas the oxycarbene is much better π acceptor and is only slightly less π accepting than a carbonyl ligand. Initial intensity measurements of the CO stretching modes support this description of the metal-carbene bond.²⁸ A large enhancement of the A_1 dipole moment derivative over that of the E mode is observed. This may be taken as evidence for extensive π bonding in the metal-ligand bond.²⁵

(28) The fact that Graham's σ and π parameters correlate so well with data obtained from other sources is not assumed here to be proof of this approach but is meant to offer support for such an approach.

TABLE IV

GRAHAM σ AND π PARAMETERS FOR SOME LW(CO)₅ COMPLEXES^a

L	k_1	k_2	Δk_1	Δk_2	σ^b	π^c
CO	16.41	16.41	1.34	0.66	-0.02	0.68
C(OC ₂ H ₅)(CH ₃)	15.71	15.89	0.64	0.14	-0.36	0.50
C(OC ₂ H ₅)(C ₆ H ₅)	15.69	15.89	0.62	0.14	-0.34	0.48
C(OC ₂ H ₅)(C ₆ H ₅)	15.70	15.92	0.63	0.17	-0.29	0.46
(<i>n</i> -C ₄ H ₉) ₃ P ^d	15.47	15.78	0.40	0.03	-0.34	0.37
(C ₆ H ₅) ₃ P ^d	15.57	15.89	0.50	0.14	-0.22	0.36

^a Symbols are as explained in the text. All data were taken from spectra measured in saturated hydrocarbon solutions. The reference compound is cyclohexylamino tungsten pentacarbonyl which has force constants of $k_1 = 15.07$ and $k_2 = 15.75$. (Force constants are in mdyne/Å.) ^b Estimated experimental uncertainty is ± 0.12 . ^c Estimated experimental uncertainty is ± 0.08 . ^d Values taken from R. P. Stewart and P. M. Treichel, *Inorg. Chem.*, **7**, 1942 (1968).

In conclusion this method of analysis suggests the bonding in pentacarbonylchromium carbene complexes to be similar to that proposed²⁵ for the analogous phosphine- and phosphite-substituted metal carbonyls. That is, these ligands all have the effect of increasing the negative charge on the metal through the inductive effect thereby slightly weakening the remaining metal-carbonyl σ bonds. However these ligands also are acting as strong π acceptors which causes a lowering of the metal π orbitals resulting in little, if any, net increase in metal-CO π bonding.²⁹

σ and π parameters obtained for tungsten carbene complexes are found in Table IV. In this case the carbene ligands may be slightly weaker σ donors and π acceptors as compared with their chromium analogs, but general conclusions are the same as expressed above.

In M(CO)₅L molecules 4 δ (MCO) ($A_1 + 3 E$) and 3 ν (MC) ($2 A_1 + E$) infrared-active vibrations occur. The M-C-O bending and M-C stretching modes of vibration were assigned by analogy with the reported spectra for the parent hexacarbonyls. For Cr(CO)₆ and W(CO)₆ the deformation modes occur at 668 and 585 cm⁻¹ and the stretching vibrations occur at 441 and 374 cm⁻¹ in the vapor state.³⁰ Table V

TABLE V

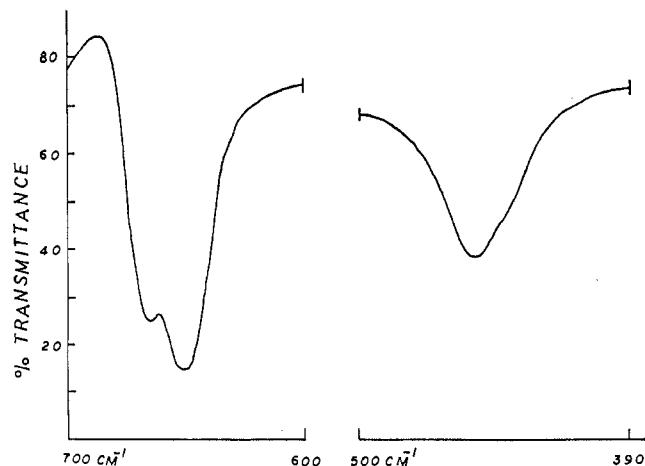
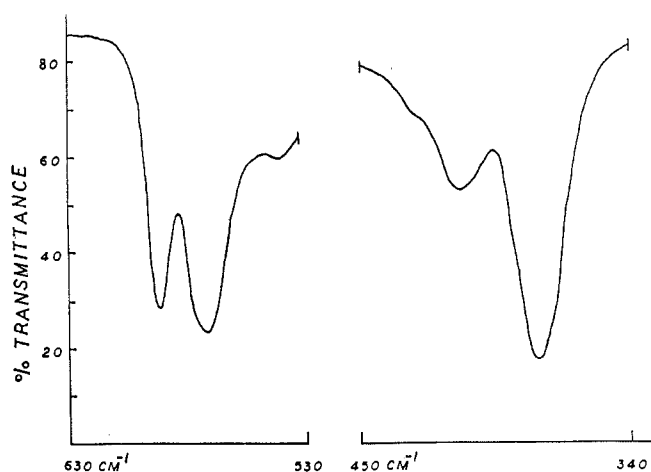
 δ (MCO) AND ν (MC) ABSORPTION FREQUENCIES (CM⁻¹) OF M(CO)₅C(OC₂H₅)R COMPOUNDS^a

R	δ (MCO)		ν (MC)	
	Cr	W	Cr	W
CH ₃	667 vs	593 vs	453 s	425 sh
	652 vs	573 vs	440 sh	409 m
		544 vw		375 vs
<i>n</i> -C ₄ H ₉	666 vs	593 s	454 s	406 m, br
	653 vs	573 sh	441 sh	377 vs
		559 s		

^a Bands were measured on neat liquids. Frequencies are accurate to ± 1.0 cm⁻¹. Abbreviations: m, medium; s, strong; sh, shoulder; br, broad; v, very; w, weak.

(29) Here we have assumed that there is no mixing of the σ and π electrons in the M(CO)₅L compounds. This appears to be a valid assumption since fairly thorough semiempirical calculations indicate this to be true in Cr(CO)₆. See A. F. Schreiner and T. L. Brown, *J. Am. Chem. Soc.*, **90**, 3366 (1968); K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, **7**, 1273 (1968).

(30) L. H. Jones, *Spectrochim. Acta*, **19**, 329 (1963). R. L. Amster, R. B. Hannan, and M. C. Tobin, *ibid.*, **19**, 1489 (1963), reported δ (MCO) at 664 and 584 cm⁻¹ and ν (MC) at 449 and 376 cm⁻¹ in the solid state for Cr(CO)₅ and W(CO)₅, respectively.

Figure 3.—Far-infrared spectrum of CH₃(C₂H₅O)CCr(CO)₅ as a neat liquid in the δ (MCO) and ν (MC) regions.Figure 4.—Far-infrared spectrum of CH₃(C₂H₅O)CW(CO)₅ as a neat liquid in the δ (MCO) and ν (MC) regions.

contains the δ (M-C-O) and ν (M-C) for several of the carbene complexes studied. Figures 3 and 4 show representative spectra of chromium and tungsten carbene complexes. The intense bands at 453 (Cr) and 375 cm⁻¹ (W) in methyl(ethoxy)carbene derivatives and at 454 (Cr) and 377 cm⁻¹ (W) in *n*-butyl(ethoxy)carbene derivatives are undoubtedly the degenerate E vibrations.

Since the E mode in the M(CO)₅ carbene compounds correlates with the T_{1u} mode in the hexacarbonyls, both involving antisymmetric stretching of *trans* CO groups, it is of interest to compare their ν (MC) values. ν (CrC) is 12–13 cm⁻¹ higher in the carbene complexes than in Cr(CO)₆.³¹ This is however still 9 cm⁻¹ lower than the corresponding ν (CrC) in Cr(CO)₅P(C₆H₅)₃.³² The tungsten-carbon stretching vibrations are about the same in the carbene complexes as that in the hexacarbonyl.

The far-infrared spectral results therefore strongly suggest a close similarity between the metal-carbonyl bond strength in the carbene compounds and the hexa-

(31) The effect of the difference in media would be to lower this difference. See R. J. Clark and B. Crociani, *Inorg. Chim. Acta*, **1**, 12 (1967).

(32) A. A. Chalmers, J. Lewis, and R. Whyman, *J. Chem. Soc.*, **A**, 1817 (1967).

TABLE VI
 ELECTRONIC SPECTRA OF $M(\text{CO})_5\text{C}(\text{OC}_2\text{H}_5)\text{R}$

Compound		Solvent ^a	Energy, cm^{-1} ^b	$10^{-3}\epsilon$, M^{-1} cm^{-1} ^c	f , M^{-1} cm^{-2} ^d	
R	M					
CH_3	Cr	CH	26,525	5.4	0.084	
			(31,095)	0.6	...	
			41,102	26.7	...	
	M	CH	26,831	5.2	0.087	
			(30,931)	0.4	...	
			41,254	21.6	0.614	
$n\text{-C}_4\text{H}_9$	Cr	CH	26,525	4.9	0.059	
			(30,441)	0.7	...	
			41,051	18.2	0.492	
	M	CH	26,903	6.2	0.095	
			(30,276)	0.7	...	
			41,442	23.7	0.697	
C_6H_5	Cr	CH	24,504	6.5	0.131	
			41,085	26.9	0.962	
			25,050	7.5	0.142	
	W	CH	41,929	26.7	1.170	
			26,961	7.3	0.061	
			28,629	7.3	0.118	
$n\text{-C}_4\text{H}_9$	M	CH	35,162	2.0	...	
			41,528	56.7	0.906	
			27,405	7.2	0.072	
			28,977	7.8	0.129	
			35,932	2.0	...	
			41,964	68.7	1.231	
	W	CH	26,853	5.3	0.060	
			28,458	5.1	0.115	
			35,063	1.6	...	
		M	CH	41,391	45.3	0.705
				27,337	5.5	0.062
				28,860	5.6	0.118
C_6H_5	W	CH	35,174	1.6	...	
			41,719	46.1	0.801	
			24,832	8.4	0.168	
			28,106	1.8	...	
			(29,851)	1.2	...	
			(35,570)	3.0	...	
	M	CH	41,085	53.1	1.019	
			(43,234)	
			25,329	8.2	0.156	
			28,161	2.6	...	
			(35,224)	2.0	...	
			41,135	50.7	0.932	
(43,234)				

^a CH = cyclohexane; M = methanol. ^b Energy values are accurate to $\pm 120 \text{ cm}^{-1}$, except for shoulders which are listed in parentheses and are accurate to $\pm 300 \text{ cm}^{-1}$. ^c The extinction coefficients for the shoulders are only approximate values and are believed accurate to $\pm 25\%$. ^d These were calculated from the equation $f = (4.6 \times 10^{-9})(\epsilon \Delta\nu_{1/2})$, where $\Delta\nu_{1/2}$ is the band width at half-intensity in cm^{-1} .

carbonyls. This adds further support to the conclusions drawn from the CO stretching frequencies and force constants.

Electronic Spectra.—It has been shown that an estimate of the extent of metal-carbonyl π bonding can be obtained from molecular orbital calculations.³³⁻³⁶ Results from these calculations may then be correlated with ionization potentials and infrared and electronic spectral data. At the present time electronic spectral data on metal carbonyls, especially substituted metal carbonyls, are scarce.

(33) K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, **7**, 1273 (1968).

(34) D. G. Carroll and S. P. McGlynn, *ibid.*, **7**, 1285 (1968).

(35) A. F. Schreiner and T. L. Brown, *J. Am. Chem. Soc.*, **90**, 3366 (1968).

(36) N. A. Beach and H. B. Gray, *ibid.*, **90**, 5713 (1968).

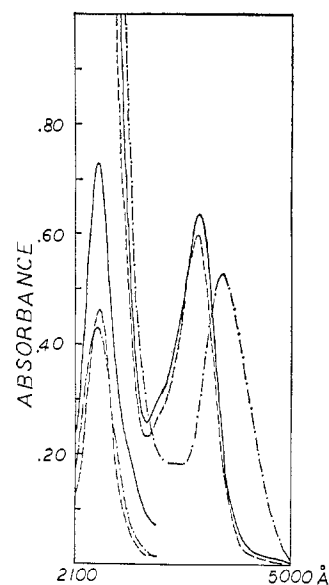


Figure 5.—Electronic spectra in cyclohexane: —, $\text{CH}_3(\text{C}_2\text{H}_5\text{O})\text{CCr}(\text{CO})_5$; ---, $n\text{-C}_4\text{H}_9(\text{C}_2\text{H}_5\text{O})\text{CCr}(\text{CO})_5$; - · - · -, $\text{C}_6\text{H}_5(\text{C}_2\text{H}_5\text{O})\text{CCr}(\text{CO})_5$.

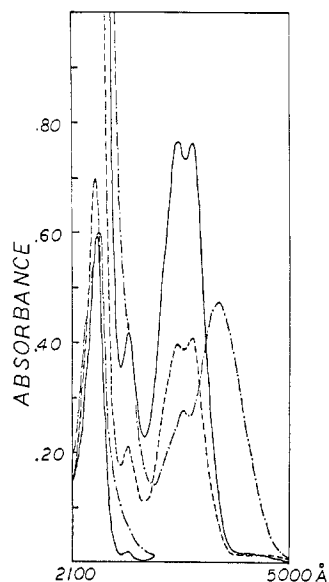


Figure 6.—Electronic spectra in cyclohexane: —, $\text{CH}_3(\text{C}_2\text{H}_5\text{O})\text{CW}(\text{CO})_5$; ---, $n\text{-C}_4\text{H}_9(\text{C}_2\text{H}_5\text{O})\text{CW}(\text{CO})_5$; - · - · -, $\text{C}_6\text{H}_5(\text{C}_2\text{H}_5\text{O})\text{CW}(\text{CO})_5$.

In our efforts to understand further the bonding in substituted octahedral metal carbonyls we have observed the electronic spectra of chromium and tungsten carbene complexes. These spectra were studied in the visible and ultraviolet regions in both cyclohexane and methanol solutions. Table VI contains the transitional energies, extinction coefficients, and oscillator strengths. The spectra obtained in cyclohexane solution are depicted in Figures 5 and 6 at room temperature for the chromium and tungsten carbene series, respectively. Owing to the broadness and extensive overlapping of bands it is difficult to assign accurately all of the shoulders observed with respect to energy and intensity. This will have to await low-temperature measurements along with Gaussian analysis of the spectra.

A blue shift of approximately $150\text{--}900 \text{ cm}^{-1}$ was

observed for most of the bands in going from cyclohexane to methanol. This is possibly due to increased dipole-dipole or hydrogen-bonding interactions of the ground-state molecules with the solvent. Although there are some changes in extinction coefficients and oscillator strengths in the two solvents, no trends are apparent.

The spectra of the chromium-carbene complexes consist essentially of two intense bands with quite different oscillator strengths. The low-energy bands have oscillator strengths of ~ 0.1 ; the high-energy bands, ~ 1.0 . The spectra of the tungsten complexes are very similar to their chromium analogs except that the low-energy bands are split into two bands of comparable intensity. It is noteworthy that in both series the high-energy absorption bands at approximately $41,000 \text{ cm}^{-1}$ are unaffected by changes in the carbene groups. At the same time the low-energy transitions are very sensitive to changes in the carbene ligand. When R goes from CH_3 or $n\text{-C}_4\text{H}_9$ to C_6H_5 , a shift to lower energy of about 2000 cm^{-1} occurs.

In spite of the fact that a firm assignment of these transitions is not possible at this time, from the magnitude of the oscillator strengths they are all probably charge transfer in nature.

The spectra of $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ in solution are very similar to those reported here.³⁷ Although there are some discrepancies in the assignment of the electronic transitions in these cases, it is generally felt that the low-energy transition is primarily metal to ligand in character, whereas the high-energy transition is ligand to metal and/or metal to ligand.

A similar assignment of transitions in the carbene complexes is expected. However presently detailed MO calculations and spectral assignments in $\text{M}(\text{CO})_5\text{L}$ compounds are not available.

Acknowledgments.—The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this research.

(37) H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, **85**, 2922 (1963).

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Rates and Mechanism of Formation of Mono(acetylacetonato)copper(II) Ion in Water and Methanol¹

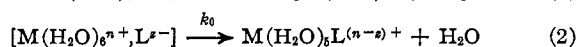
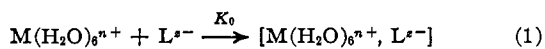
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Stopped-flow kinetic studies of the reaction between acetylacetonone (2,4-pentanedione) and cupric ion to form the mono complex in water and in methanol show two separable reactions. Both reactions are much slower than the normal substitution kinetics of the Cu(II) ion. The concentration dependence of the observed rate constants agrees with a mechanism involving direct, reversible reaction between the solvated Cu(II) ion and both the keto and enol tautomers of acetylacetonone, the enol tautomer reacting much faster. The second-order rate constants at 25° for the reaction between the enol form and the Cu(II) ion are the same in water and in methanol ($2 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$), in agreement with a mechanism due to Kustin in which the rate-controlling process is the sterically difficult closure of the six-membered ring. For the reaction between the Cu(II) ion and the keto form, the rate-limiting step is metal ion catalyzed proton transfer from the weakly bound keto tautomer. This is supported by the increase in rate constant of two orders of magnitude on changing from water ($12 \text{ M}^{-1} \text{ sec}^{-1}$) to methanol ($1300 \text{ M}^{-1} \text{ sec}^{-1}$) and the results of deuterium isotope substitution studies.

Introduction

In the usual mechanism of complex formation for the six-coordinate transition metal ions, the first step is the reversible, diffusion-controlled formation of an ion pair between the solvated metal ion and the potential ligand.² If the metal ion then loses a water molecule, the complex may be formed. This scheme is outlined in eq 1 and 2. The loss of water from the metal ion in



the ion pair is thought to be the rate-controlling step in this process. In agreement with this interpretation, the rates of formation of transition metal complexes have normally been found to parallel the rates of water exchange for the metal ions. In the terminology of Langford and Gray, (2) is a dissociative interchange mechanism.

Most previous studies of the rates of formation of complexes of the cupric ion in aqueous solution agree on the extreme rapidity of these reactions. Measured values of formation constants for Cu(II) complexes are in the range 10^7 to $4 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$.^{2,3} Exchange reactions of complexes of the cupric ion have also been found to be very fast.⁴ This behavior is consistent

(1) Abstracted from the Ph.D. Thesis of O. P. Anderson, Northwestern University, 1969.

(2) M. Eigen and R. G. Wilkins in "Inorganic Reaction Mechanisms," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 55.

(3) A. F. Pearlmutter and J. Stuehr, *J. Am. Chem. Soc.*, **90**, 858 (1968).

(4) R. G. Pearson and R. D. Lanier, *ibid.*, **86**, 765 (1964).