are significantly smaller than observed with the other more bulky amines where steric factors were of predominant importance.

Equilibrium constants for the reactions of a given $M(CO)_4L_2^+$ complex with different amines depend on at least two factors: the bulkiness of the amine and the basicity of the amine, since one of the products is RNH_3^+ (eq 2). In water, all of the amines have essentially the same pK_a values (10.6-10.7). If this were also true in CH_2Cl_2 solvent, steric effects should then establish the observed trend. In fact, except for $Mn(CO)_4[P(C_6H_5)(CH_3)_2]_2^+$, all other $M(CO)_4L_2^+$ complexes follow the trend *n*-butylamine > isopropylamine > cyclohexylamine > *sec*-butylamine, expected from steric arguments. In this trend, isopropylamine is believed to be slightly less bulky than cyclohexylamine, where the 3-, 4-, and 5-CH_2 groups in the cyclohexyl ring are also repelled by the L groups. It should be added that in several instances the differences in K values for different amines are very small, and it is difficult to rationalize some cases where there are large differences. In general, however, the results are very similar to equilibrium constants for the related reaction[11]

$$Re(CO)_5CO_2CH_3 + RNH_2 \rightarrow Re(CO)_5CONHR + CH_3OH \qquad (5)$$

where the K value order was as follows: *n*-butylamine (1.2) > isopropylamine (1.0) ~ cyclohexylamine (1.0) ~ *sec*-butylamine (1.0).

Registry No. $Mn(CO)_5Cl$, 14100-30-2; $P(C_6H_5)_2(CH_3)$, 1486-28-8; CO, 630-08-0; NH_2CH_3, 74-89-5; $NH_2(CH_2)_3CH_3$, 109-73-9; $NH_2CH(CH_3)_2$, 75-31-0; $NH_2C_6H_{11}$, 108-91-8; $NH_2CH(CH_3)(C_2H_5)$, 13952-84-6; $Mn(CO)_3[P(C_6H_5)_3]_2Cl$, 29961-98-6; $Mn(CO)_3[P(C_6H_5)_2(CH_3)]_2Cl$, 38496-58-1; $Mn(CO)_3[P(C_6H_5)(CH_3)_2]_2Cl$, 33988-79-3; $Re(CO)_3[P(C_6H_5)_3]_2Cl$, 19394-85-5; $Mn(CO)_4[P(C_6H_5)_3]_2PF_6$, 38426-96-9; $Mn(CO)_4[P(C_6H_5)_2(CH_3)]_2PF_6$, 38496-52-5; $Mn(CO)_4[P(C_6H_5)(CH_3)_2]_2PF_6$, 38496-53-6; $Re(CO)_4[P(C_6H_5)_3]_2PF_6$, 38496-54-7; $Mn(CO)_3[P(C_6H_5)_3]_2CONHCH_3$, 38466-94-3; $Mn(CO)_3[P(C_6H_5)_3]_2CONHCH(CH_3)_2$, 38466-95-4; $Mn(CO)_3[P(C_6H_5)_3]_2CONH(CH_2)_3CH_3$, 38466-96-5; $Mn(CO)_3[P(C_6H_5)_3]_2CONHC_6H_{11}$, 38466-97-6; $Mn(CO)_3[P(C_6H_5)_3]_2CONHCH(CH_3)(C_2H_5)$, 38466-98-7; $Mn(CO)_3[P(C_6H_5)_2(CH_3)]_2CONHCH_3$, 38466-99-8; $Mn(CO)_3[P(C_6H_5)(CH_3)_2]_2CONHCH_3$, 38599-47-2; $Re(CO)_3[P(C_6H_5)_3]_2CONHCH_3$, 38467-00-4; $Re(CO)_3[P(C_6H_5)_3]_2CONHCH(CH_3)_2$, 38467-01-5; $Re(CO)_3[P(C_6H_5)_3]_2CONH(CH_2)_3CH_3$, 38467-02-6; $Re(CO)_3[P(C_6H_5)_3]_2CONHC_6H_{11}$, 38467-03-7; $Re(CO)_3[P(C_6H_5)_3]_2CONHCH(CH_3)(C_2H_5)$, 38467-04-8; $Mn(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$, 38496-55-8; $Re(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$, 38496-56-9.

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A Carbon-13 Nuclear Magnetic Resonance Study of Carbene-Pentacarbonyl Complexes of Chromium(0) and Tungsten(0)

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The ^{13}C nmr spectra of a variety of complexes of the type $(CO)_5MC(X)R'$ ($M = Cr, W$; $X = NH_2, OR$; $R' = CH_3$, Ph, and meta- and para-substituted phenyl) have been studied. The extremely low-field position of the carbene carbon resonance together with the strong interaction of this carbon atom with the X and R′ groups (when R′ = phenyl) suggests that this carbon atom be considered as a transition metal stabilized carbonium ion center. In tetrahydrofuran solvent, a 6-7-ppm upfield shift of the carbene carbon resonance relative to the shift found in $CHCl_3$ or CH_2Cl_2 was observed. This result is interpreted as due to Lewis acid-base complexation of the ether with the carbene carbon. Better electron-donating carbene groups cause the cis carbonyl carbon resonance to move to lower field. It is suggested that variations in the metal-to-carbonyl π bond are chiefly responsible for the observed trend.

Introduction

Stable group VIb transition metal complexes containing apparent "carbene" ligands were first reported in 1964.[2] These compounds are of considerable interest because of their synthetic possibilities and the unusual bonding that occurs between the metal atom and the carbene carbon. We have undertaken an investigation of the bonding in this type of compound by analyzing the ^{13}C nmr spectra of a variety of complexes of the general type $(CO)_5MC(X)R'$ ($M = Cr, W$; $X = NH_2, OR$; $R' = CH_3$, Ph, and meta- and para-substituted phenyl). During the course of our investigation a brief note appeared on this subject from another laboratory.[3] Our study is in excellent agreement with that reported by Kreiter and Formacek. We wish to report here additional results which were obtained from our more extensive investigation.

Experimental Section

Materials. Trimethyloxonium[4] and triethyloxonium[5] tetrafluoroborate were prepared by the methods of Meerwein and stored under argon in a sealed container at −20°. Butyllithium in hexane and phenyllithium in 20% ether-80% benzene were obtained from the Foote Chemical Co. Chromium and tungsten hexacarbonyls were obtained from Pressure Chemical Co. Complexes of the type $(CO)_5MC(OR)R'$ ($M = Cr, W$) were prepared by the method of Aumann and Fischer.[6] The modification suggested by Darensbourg and Darensbourg[7] for removing unreacted metal hexacarbonyl was

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(1) (a) NASA Predoctoral Fellow, 1969-1972. (b) NSF Undergraduate Research Participant, 1971.

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used. This involved filtering the aqueous solution of the lithio salt of the transition metal-carbene complex prior to the addition of the trialkyloxonium tetrafluoroborate. The complexes were purified by crystallization in a minimum amount of pentane at −20° and subsequent filtration and drying on a Schlenk filter. The complexes were characterized by melting points and infrared spectra which were compared with literature data. Complexes of the type $(CO)_5MC(OCH_2CH_3)Ph$ and $(CO)_5MC(OCH_2CH_3)CH_3$ (M = Cr, W) were prepared by the method of Darensbourg and Darensbourg.[7] Complexes of the type $(CO)_5MC(OCH_3)Ph$ and $(CO)_5MC(OCH_3)CH_3$ (M = Cr, W) were synthesized by the procedure of Fischer and Maasbol.[8] The phenyl-substituted complexes of the type $(CO)_5CrC(OCH_3)C_6H_4X$ were prepared by the method of Fischer and coworkers.[9] Some of the tungsten complexes were previously unreported. They were prepared by the method used for the corresponding chromium complex and characterized by elemental analysis (see Table I) and carbon-13 nmr spectroscopy. Complexes of the type $(CO)_5MC(NH_2)R$ (M = Cr, W; R = CH_3, Ph) were prepared by the method of Fischer and Kollmeier.[10] In this procedure ammonia was bubbled through a toluene solution of the corresponding methoxycarbene complex until color changes ceased and the product recrystallized from ether-pentane. In most cases the ^{13}C nmr spectra were obtained within 2 days after preparation of the complexes. Infrared spectra and melting points were measured before and after obtaining the ^{13}C nmr spectra in order to demonstrate that the compounds had not decomposed during the 1-4 hr required to achieve sufficient signal to noise.

Instrumentation. The infrared spectra were measured on a Perkin-Elmer 621 spectrometer using a linear scale with a 10-fold expanded abscissa and a scan speed of less than 20 cm^{-1}/min. The infrared spectra were obtained in hexane solution in a 1-mm cell. The spectrometer was calibrated in the 2150-2000-cm^{-1} region with CO gas and in the 2000-1900-cm^{-1} region with water vapor.[11] The carbon-13 nmr spectra were obtained in chloroform or methylene chloride solution with a Fourier transform pulsed nmr spectrometer operating at 15.08 MHz as described previously.[12] The ^{13}C chemical shifts were measured relative to an internal solvent reference and then reported relative to a tetramethylsilane (TMS) standard. The chemical shift conversion factors used in this study are $\delta_{TMS} = \delta_{CHCl_3} - 77.18$ ppm and $\delta_{TMS} = \delta_{CH_2Cl_2} - 53.89$ ppm. Chemical shifts are reproducible to within ±0.06 ppm.

Table I. Analytical Data for Complexes of the Type $(CO)_5WC(OCH_3)R$

		% calcd			% found[a]		
R	Mp, °C	C	H	Halogen	C	H	Halogen
p-BrC_6H_4	131-132	29.84	1.15	15.29	29.93	1.37	15.60
p-ClC_6H_4	124-125	32.61	1.46	7.42	32.94	1.43	7.45
p-FC_6H_4	81-82	33.78	1.52	4.11	33.82	1.62	3.82
p-$CF_3C_6H_4$	77-78	32.82	1.37	11.14	32.58	1.51	11.40
p-$CH_3OC_6H_4$	113-114.	35.45	2.11		36.01	2.20	
p-$CH_3C_6H_4$	102-103	36.69	2.18		36.82	2.07	

[a] Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Table II. ^{13}C Nmr Chemical Shift Data (Ppm) of the Carbene and Carbonyl Resonances in $(CO)_5MC(OR)R'$ and $(CO)_5MC(NH_2)R$

Complex	C	Trans CO	Cis CO
$(CO)_5CrC(OCH_3)CH_3$	−360.38[a]	−223.29	−216.34
$(CO)_5CrC(OCH_2CH_3)CH_3$	−357.27	−223.35	−216.34
$(CO)_5CrC(OCH_3)Ph$	−350.93	−224.15	−216.11
$(CO)_5CrC(OCH_2CH_3)Ph$	−349.02	−224.15	−216.10
$(CO)_5CrC(NH_2)CH_3$	−289.83	−223.12	−217.38
$(CO)_5CrC(NH_2)Ph$	−289.55	−223.55	−217.08
$(CO)_5WC(OCH_3)CH_3$	−333.04	−203.40	−197.17
$(CO)_5WC(OCH_2CH_3)CH_3$	−330.11	−203.43	−197.17
$(CO)_5WC(OCH_3)Ph$	−321.82	−203.60	−197.22
$(CO)_5WC(OCH_2CH_3)Ph$	−319.97	−203.52	−197.29
$(CO)_5WC(NH_2)CH_3$	−266.57	−203.83	−198.45
$(CO)_5WC(NH_2)Ph$	−264.99	−203.83	−198.21

[a] Chemical shifts were measured in chloroform solution relative to the internal $CHCl_3$ resonance and are reported relative to an internal TMS standard.

Results and Discussion

The ^{13}C nmr spectrum of a transition metal-carbene complex of the type $(CO)_5MC(X)R'$ (M = Cr, W) exhibits a large range of chemical shifts. The low-field portion of the spectrum consists of three distinct carbon resonances, with a relative intensity, reading upfield, of 1:1:4, which are due to the carbene carbon, the trans carbonyl, and the four cis carbonyls, respectively. The ^{13}C nmr spectrum of $(CO)_5CrC(OCH_3)Ph$ is presented in Figure 1 to illustrate the chemical shift pattern. The most striking feature in this spectrum is the extremely low-field position of the carbene carbon resonance. In fact it may be best to consider this type of carbon atom as a "transition metal stabilized carbonium ion."[13]

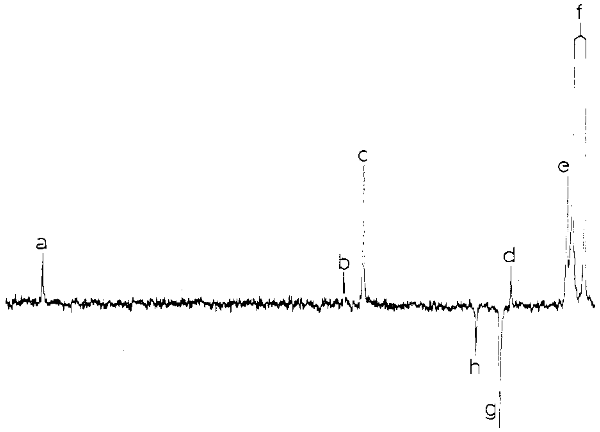

Figure 1. The ^1H decoupled Fourier transform ^{13}C nmr spectrum of $(CO)_5CrC(OCH_3)Ph$ in chloroform; 1024 scans, 10-sec pulse delay, 250-ppm window. The two negative peaks are reflected peaks which occur upfield of the 250-ppm region under investigation. Resonance assignments (chemical shifts in ppm relative to TMS) are (a) carbene carbon (−350.93), (b) trans CO (−224.15), (c) cis CO (−216.11), (d) substituted-phenyl carbon (−153.50), (e) para phenyl carbon (−130.16), (f) ortho and meta phenyl carbons (−128.09 and −122.84), (g) chloroform (−77.18), and (h) methyl carbon (−66.93).

As is seen in Table II, the carbene carbon atom resonance shifts to higher field (50-70 ppm) if an alkoxy function is replaced by a better electron donor such as the amino group. Replacement of a methyl group for a phenyl group in complexes of the type $(CO)_5MC(OCH_3)R$ (M = Cr, W; R = CH_3, Ph) causes a 8-11-ppm downfield shift in the carbene carbon resonance while that same variation with the aminocarbene complexes causes only a 0.5-1.5-ppm downfield shift in the carbene carbon resonance. The amino group appears to have a much more dominant shielding effect on the carbene carbon resonance than the alkoxy group. In agreement with the observations above, comparison of the chemical shifts of the methyl resonances of $(CO)_5CrC(OR)CH_3{}^*$ and $(CO)_5CrC(NH_2)CH_3{}^*$ (Table III) or of the analogous tungsten complexes indicates that the amino group is better than the alkoxy group at shielding the methyl carbon resonance.

The nmr spectra of all these carbene compounds were run in chloroform or methylene chloride solvent. In one preliminary set of experiments, when tetrahydrofuran was used as solvent, a 6-7-ppm upfield shift of the carbene carbon resonance was observed relative to the shift found in chloroform. These data are presented in Table IV. The carbene

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Table III. ^{13}C Nmr Chemical Shift Data (Ppm) of the OR and R′ Resonances of $(CO)_5MC(OR)R'$ and $(CO)_5MC(NH_2)R'$

Complex	OCH_3	$OC^*H_2CH_3$	$OCH_2C^*H_3$	CH_3
$(CO)_5CrC(OCH_3)CH_3$	−66.68[a]			−48.85
$(CO)_5CrC(OCH_2CH_3)CH_3$		−77.14	−14.75	−48.86
$(CO)_5CrC(NH_2)CH_3$				−43.62
$(CO)_5CrC(OCH_3)Ph$	−66.93			
$(CO)_5CrC(OCH_2CH_3)Ph$		−78[b]	−14.92	
$(CO)_5WC(OCH_3)CH_3$	−69.98			−51.79
$(CO)_5WC(OCH_2CH_3)CH_3$		−80.36	−14.56	−51.89
$(CO)_5WC(NH_2)CH_3$				−45.62
$(CO)_5WC(OCH_3)Ph$	−69.86			
$(CO)_5WC(OCH_2CH_3)Ph$		−79.98	−14.67	

[a] Chemical shifts were measured in chloroform solution relative to the internal $CHCl_3$ solvent resonance and are reported relative to an internal TMS standard. [b] Shoulder on the chloroform solvent resonance.

Table IV. ^{13}C Nmr Chemical Shift Values of $p\text{-}XC_6H_4(NH_2)CCr(CO)_5$ in Chloroform and in Tetrahydrofuran

	^{13}C chemical shift values, ppm			
X	Carbene carbon	Trans CO	Cis CO	Solvent
H	−282.89	−224.42	−218.51	THF
CH_3	−282.35	−224.42	−218.63	THF
Br	−281.79	−224.00	−218.07	THF
H	−289.71	−223.71	−217.24	$CHCl_3$
CH_3	−288.28	−223.65	−217.48	$CHCl_3$
Br	−289.38	−223.19	−216.88	$CHCl_3$

Table V. ^{13}C Nmr Chemical Shift Data of $(CO)_5CrC(OCH_3)C_6H_4X$ in Chloroform Solution

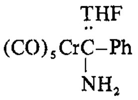
Para substituent on phenyl ring	Chemical shift values relative to TMS, ppm		
	Carbene carbon	Trans carbonyl	Cis carbonyl
CF_3	−350.18	−223.71	−215.54
H	−350.93	−224.09	−216.09
CH_3	−347.97	−223.82	−216.25
Br	−348.18	−223.67	−215.85
Cl	−347.93	−223.66	−215.87
F	−346.84	−223.55	−216.10
OCH_3	−340.49	−223.72	−216.83

Meta substituent on phenyl ring	Chemical shift values relative to TMS, ppm		
	Carbene carbon	Trans carbonyl	Cis carbonyl
CF_3	−348.79	−223.60	−215.61
Cl	−348.72	−223.61	−215.67
OCH_3	−350.48	−223.89	−215.83

Table VI. ^{13}C Nmr Chemical Shift Data of $(CO)_5WC(OCH_3)C_6H_4X$ in Dichloromethane Solution

Para substituent on phenyl ring	Chemical shift values relative to TMS, ppm		
	Carbene carbon	Trans carbonyl	Cis carbonyl
CF_3	−322.20	−203.92	−197.08
H	−322.07	−204.16	−197.81
CH_3	−319.82	−203.80	−197.82
Br	−319.64	−203.67	−197.32
Cl	−319.39	−203.67	−197.32
F	−318.48	−203.49	−197.38
OCH_3	−313.29	−203.43	−197.93

carbon resonance is affected most by the solvent change. This may be due to the formation of the following type of complex



$$(CO)_5Cr\overset{\overset{\text{THF}}{\cdot\cdot}}{C}\text{–Ph} \quad \underset{NH_2}{\mid}$$

This type of complex has been postulated to be a stable intermediate at low temperatures of dimethylphosphine with $(CO)_5CrC(OCH_3)C_6H_5$.[14]

We have studied the variation of the carbene carbon resonance of a series of compounds of the type $(CO)_5MC(OCH_3)C_6H_4X$ (M = Cr, W; X = meta or para OCH_3, Cl, CF_3, etc.). The chemical shift data are presented in Tables V and VI. The general trend observed is that δ_c of the carbene carbon is found at higher field with increasing π-donor ability of the substituent. This relationship is supported by the finding that when X = meta OCH_3, the carbene carbon shift is at much lower field than when X = para OCH_3 because the π donation is absent in the meta derivative. These results are in agreement with a variable-temperature pmr study of these compounds by Fischer and coworkers.[9] Their data indicate that as the carbene carbon becomes more electron rich (*via* π donation from the substituted phenyl group), the temperature decreases at which the pmr resonances of the cis and trans forms of the methoxy function coalesce.

The trend in the cis carbonyl carbon resonances of the alkoxy- and aminocarbene complexes (see Table II) is apparently not in accord with the observations given above. The better electron-donating amino group causes the cis carbonyl resonance to move to lower field relative to the analogous alkoxyl derivative. The trends in the trans carbonyl resonance were found to have a smaller and less regular variation. A plot of the infrared stretching force constants for the cis carbonyls *vs.* the cis carbonyl carbon ^{13}C chemical shifts for $(CO)_5CrC(X)R'$ derivatives is given in Figure 2. The force constant data were calculated using the Cotton-Kraihanzel approximation and are given in Table VII.[15] It is found that the cis carbonyl stretching force constant (K_2) increases as the ^{13}C chemical shift of the cis carbonyl carbon goes to higher field. Similar correlations between ^{13}C chemical shifts of carbonyl carbon atoms and their infrared stretching force constants have been found for $LW(CO)_5$ and π-$CpFe(CO)_2X$ derivatives by Gansow and coworkers,[16,17] for $LM(CO)_5$, M-Cr, and Mo, and $(C_6H_5X)Cr(CO)_3$ in our studies,[18] and for a series of derivatives of the type $Rh(CO)(ligand)_2Cl$.[19] It has been postulated that increases in carbonyl force constants resulting from either increased CO-to-metal σ bonding or decreased metal-to-CO π bonding will lead to decreases in electron density at carbon.[20] A study of the reaction rates of methyllithium with a series of $(ligand)W(CO)_5$ derivatives has recently been reported.[21] The product, illustrated in the following equation, is known to have cis geometry.[22] The carbonyl complex with the largest cis carbonyl force constant appears to have the smallest electron density at carbon since the rate of

$$CH_3Li + (ligand)W(CO)_5 \rightarrow cis\text{-}Li[(ligand)WC(CH_3)O(CO)_4]$$

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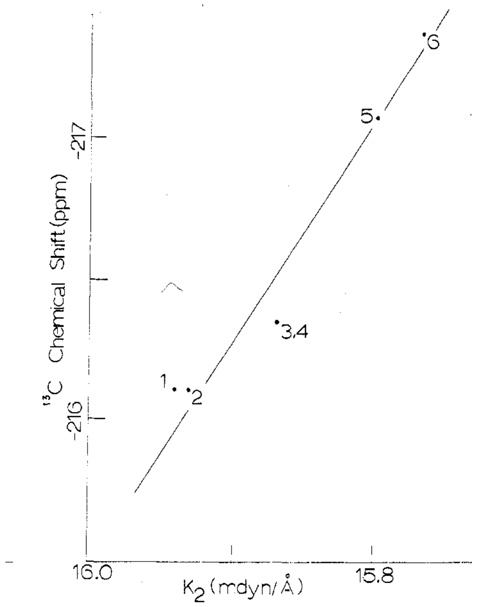

Figure 2. Plot of the ^{13}C nmr chemical shift values of the cis carbonyls of $(CO)_5CrC(X)R'$ *vs.* the respective K_2 stretching force constants. X, R′ groups respectively for the various points: (1) OCH_2CH_3, Ph; (2) OCH_3, Ph; (3) OCH_3, CH_3; (4) OCH_2CH_3, CH_3; (5) NH_2, Ph; (6) NH_2, CH_3.

Table VII. Carbonyl Ir Stretching Force Constants (mdyn/Å) for Derivatives of the Type $(CO)_5CrC(X)R$

Complex	K_1	K_2
$(CO)_5CrC(OCH_2CH_3)Ph^a$	15.75	15.94
$(CO)_5CrC(OCH_3)Ph^b$	15.76	15.93
$(CO)_5CrC(OCH_2CH_3)CH_3{}^a$	15.76	15.87
$(CO)_5CrC(OCH_3)CH_3$	15.78	15.87
$(CO)_5CrC(NH_2)Ph^b$	15.13	15.80
$(CO)_5CrC(NH_2)CH_3{}^c$	15.54	15.77

[a] Calculated from data reported in ref 7. [b] Calculated from data reported in ref 10. [c] Calculated from data reported by U. Klabunde and E. O. Fischer, *J. Amer. Chem. Soc.*, 89, 7141 (1967).

methyllithium attack on this complex is most rapid. Apparently the most electron-deficient carbonyl carbon has the highest field ^{13}C chemical shift. Assuming that large anisotropic effects are absent, the difference in carbonyl shieldings is mainly due to the local paramagnetic screening constant which has been approximated[23] as

$$(\sigma_p{}^{AA})_{ZZ} = -\frac{e^2\hbar^2}{2m^2c^2(\Delta E)}\langle r^{-3}\rangle_{2p}\{(Q_{AA})_{ZZ} + \sum_{B\neq A}(Q_{AB})_{ZZ}\}$$

The Q_{AB} term reflects changes in the M–C and C≡O π-bond orders. As the metal-to-CO π back-bonding decreases, Q_{AB} (for the M–C part) should decrease which would result in a smaller (negative) value and therefore a higher field chemical shift for the carbonyl carbon. We suggest that the variations in the M–CO π back-bonding are chiefly responsible for the observed changes in the carbonyl chemical shifts for the specific cases mentioned above.

The chemical shifts of the carbene and carbonyl carbon resonances of $(CO)_5MC(X)R$ are found at higher field as the metal is changed from chromium to tungsten (see Table II).[24] This same trend has been observed for the carbonyl carbon resonance of other classes of complexes such as the group VI hexacarbonyls,[16] $LM(CO)_5$ (M = Cr, MO),[18] (mestiylene)-$M(CO)_3$ (M = Cr, Mo, W),[18] and $(PPh_3)_2M(CO)Cl$ (M = Rh, Ir).[19,24] Within each of these classes of compounds, as the metal is changed (*e.g.*, Cr → Mo → W) with a constant array of ligands, there is no apparent correlation between the ^{13}C chemical shift and the stretching force constant for the carbonyl groups. The chemical shifts of the two methyl group carbon resonances of $(CO)_5MC(OCH_3)CH_3$ (see Table III) are found at lower field as the metal is changed from chromium to tungsten. This suggests that the metal center is more electron withdrawing for the higher atomic weight elements. This is supported by the finding that the coalescence temperature of the cis and trans forms of the methoxy function is higher for the tungsten complex.[25] In addition, the rate of reaction of methyllithium on the group VIb hexacarbonyls[21] increases in the order Cr < Mo < W. These lines of evidence again suggest that the most electron-deficient carbonyl carbon has the highest ^{13}C nmr chemical shift. The factors influencing this chemical shift trend are not now clear.

Both the cis and trans carbonyl resonances of $(CO)_5CrC(X)R$ derivatives are found at lower field than the chemical shift value of $Cr(CO)_6$.[16] A similar relationship is observed in the tungsten series also. The trend we have seen throughout this discussion is that the most electron-deficient carbonyl carbon has its nmr chemical shift at highest field. These nmr data therefore suggest that the carbene group has a smaller acceptor-to-donor ratio than the carbonyl group. The same conclusion was reached by Mills[26] from comparison of X-ray crystallographic Cr–CO distances of carbene-metal carbonyls and other metal carbonyl derivatives.

Registry No. $(CO)_5CrC(OCH_3)CH_3$, 20540-69-6; $(CO)_5CrC(OCH_2CH_3)CH_3$, 25879-46-3; $(CO)_5CrC(OCH_3)Ph$, 15809-68-4; $(CO)_5CrC(OCH_3)C_6H_4CF_3$-*p*, 27637-27-0; $(CO)_5CrC(OCH_3)C_6H_4CH_3$-*p*, 29160-36-9; $(CO)_5CrC(OCH_3)C_6H_4Br$-*p*, 32011-03-3; $(CO)_5CrC(OCH_3)C_6H_4Cl$-*p*, 29160-37-0; $(CO)_5CrC(OCH_3)C_6H_4F$-*p*, 32011-01-1; $(CO)_5CrC(OCH_3)C_6H_4OCH_3$-*p*, 27437-03-2; $(CO)_5CrC(OCH_3)C_6H_4CF_3$-*m*, 32011-08-8; $(CO)_5CrC(OCH_3)C_6H_4Cl$-*m*, 32011-07-7; $(CO)_5CrC(OCH_3)C_6H_4OCH_3$-*m*, 28549-63-5; $(CO)_5CrC(OCH_2CH_3)Ph$, 38669-66-8; $(CO)_5CrC(NH_2)CH_3$, 22852-50-2; $(CO)_5CrC(NH_2)Ph$, 32370-44-8; $(CO)_5CrC(NH_2)C_6H_4CH_3$-*p*, 32370-47-1; $(CO)_5CrC(NH_2)C_6H_4Br$-*p*, 32370-49-3; $(CO)_5WC(OCH_3)CH_3$, 20540-70-9; $(CO)_5WC(OCH_2CH_3)CH_3$, 38669-69-1; $(CO)_5WC(OCH_3)Ph$, 37823-96-4; $(CO)_5WC(OCH_3)C_6H_4CF_3$-*p*, 38669-71-5; $(CO)_5WC(OCH_3)C_6H_4CH_3$-*p*, 38669-72-6; $(CO)_5WC(OCH_3)C_6H_4Br$-*p*, 38669-73-7; $(CO)_5WC(OCH_3)C_6H_4Cl$-*p*, 38669-74-8; $(CO)_5WC(OCH_3)C_6H_4F$-*p*, 38669-75-9; $(CO)_5WC(OCH_3)C_6H_4OCH_3$-*p*, 38744-28-4; $(CO)_5WC(OCH_2CH_3)Ph$, 36834-98-7; $(CO)_5WC(NH_2)CH_3$, 38669-77-1; $(CO)_5WC(NH_2)Ph$, 38669-78-2.

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(24) In contrast we have observed that π-bonded aromatic ligands in classes of compounds such as $(C_5H_5)_2M$ (M = Fe, Ru, Os) and (mesitylene)$M(CO)_3$ (M = Cr, Mo, W) do not follow the chemical shift trend with change in metal that is found for carbene and carbonyl ligands.

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