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Reactions of Transition Metal Carbonyls with Nucleophilic Reagents: Reactivity and Bonding[1]

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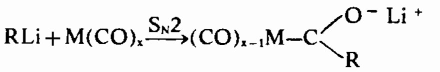
Initial investigations into the reaction of organomagnesium halide reagents with metal carbonyls indicate this reaction to be adaptable to relative rate studies of nucleophilic attack on the carbonyl carbon. New carbene type complexes as well as preliminary rate studies are presented.

Force constants and integrated infrared intensities of the CO stretching vibrations in $M(CO)_5L$ compounds suggest the carbene ligand to be bound to the metal in a manner similar to phosphines and phosphites and significantly different from purely sigma donating amine ligands. Dipole moment derivative calculations and band shape analyses of the CO vibrations in metal carbonyl carbene complexes are described.

Introduction

The laboratories of E. O. Fischer have produced an extensive study of the addition of organolithium reagents to metal carbonyls.[2] The presumed reaction pathway is



$$RLi + M(CO)_x \xrightarrow{S_N2} (CO)_{x-1}M{-}C\begin{cases} O^- \; Li^+ \\ R \end{cases}$$

The reactions are very fast and kinetic studies have not been attempted. Qualitatively, however, the reactions are dependent on the nature of $M(CO)_x$ and RLi.

Organomagnesium halides react with metal carbonyls apparently by a similar process as organolithium reagents, but the reactions proceed much more slowly. Therefore the Grignard systems appear to be more amenable to kinetic studies by conventional techniques.

The relationship of carbonyl stretching force constants to the charge on carbon in metal carbnyls is depicted in Figure 1 and is fully discussed in the literature.[3] This correlation has been used to predict nucleophilic attack and the site of nucleophilic attack if a choice of carbonyls with different force constants exists in the same molecule.

The initial results of relative rate studies using Grignard reagents as the nucleophilic attacking agents are reported herein. Force constants and integrated infrared intensities of the CO stretching vibrations are presented for metal carbonyl carbene compounds and the results are discussed in terms of the bonding in these compounds.

Experimental Section

Reagents and Solvents. The Grignard reagents were obtained from Alfa Inorganics and only freshly opened bottles were used for the kinetic studies. The active Grignard concentration was determined by the Gilman technique.[4]

$W(CO)_6$ was generously donated by the Climax Molybdenum Company and was sublimed before use.

$Cr(CO)_6$ was obtained from Strem Chemicals and was purified by sublimation.

Triethyloxonium fluoroborate was prepared as described in the literature.[5]

Tetrahydrofuran was purified by distillation under N_2 from freshly cut sodium, and was flushed with dried N_2 before use.

Preparation and Identification of new Compounds. Benzylethoxycarbenemetalpentacarbonyl (metal = chromium and tungsten) and benzylethoxycarbene (L) tungstentetracarbonyl ($L = (C_6H_5)_3P$ and $(C_6H_5)_3Sb$) were prepared by reacting the hexacarbonyl or substituted pentacarbonyl with benzyl magnesium chloride (in approximately 1 to 2 molar ratios) in THF at 0°C under N_2. Without exposure to air the solvent was removed at reduced pressures and the ethylation procedure carried out as previously described.[6]

$M(CO)_5C(OC_2H_5)CH_2C_6H_5$ ($M = Cr$ and W) are golden oils at room temperature and are extremely soluble in organic solvents. Recrystallization from methanol and filtration at −70°C can be effected but complete removal of solvent was impossible since the purified complexes decomposed to $M(CO)_6$ under vacuum. Consequently, an elemental analysis was not possible. The mass spectra of these complexes (direct probe introduction of compound at 200°) showed the parent ion ($M(CO)_5C(OC_2H_5)CH_2C_6H_5^+$) and subsequent peaks

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(1) Presented at the Third International Symposium of Inorganica Chimica Acta, Venice, Italy, September (1970) and in part at the 160tn Meeting of the American Chemical Society, September (1970), Chicago, Illinois.

(2) E.O. Fischer and A. Maasböl, *Angew. Chem. Internat. Ed.*, *3*, 580 (1964); E.O. Fischer and R. Aumann, *ibid.*, *6*, 879 (1967); E.O. Fischer and V. Kiener, *J. Organometal. Chem.*, *23*, 215 (1970).

(3) D.J. Darensbourg and M.Y. Darensbourg, *Inorg. Chem.*, *9*, 1691 (1970).

(4) H. Gilman, E.A. Zoellner, and J.B. Dickey, *J. Am. Chem. Soc.*, *51*, 1576 (1929).

(5) H. Meerwein, *Org. Syn.*, *46*, 113 (1966).

(6) M.Y. Darensbourg and D.J. Darensbourg, *Inorg. Chem.*, *9*, 32 (1970).

at 28 mass units lower; the $MC(OC_2H_5)CH_2C_6H_5^+$ ion was the metal species (other than M^+) present in greatest abundance.

$W(CO)_4P(C_6H_5)_3C(OC_2H_5)CH_2C_6H_5$ was prepared in an analagous manner. Golden orange crystals, m.p. 137-139°, are obtained pure with methanol recrystallizations. Elemental analysis (Schwarzkopf Microanalytical Laboratories): Calcd: %H, 3.85; %C, 54.40. Found: %H, 3.93; %C, 54.38. $W(CO)_4Sb(C_6H_5)_3C(OC_2H_5)CH_2C_6H_5$ was prepared and purified in a similar manner.

The infrared bands in the CO stretching region are as follows:

$Cr(CO)_5C(OC_2H_5)CH_2C_6H_5$: 2066 cm^{1-} (m), 1981 (vw), 1961(s), 1947(vs).

$W(CO)_5C(OC_2H_5)CH_2C_6H_5$: 2075 cm^{-1} (m), 1957 (s), 1945(vs).

$W(CO)_4P(C_6H_5)_3C(OC_2H_5)CH_2C_6H_5$: 2023 cm^{-1} (s), 1927.1(s), 1919.6(s), 1902.6(vs).

The ^1H magnetic resonances relative to TMS=O ppm are listed below. Assignments were made on the basis of integrated spectra and splitting patterns.[7]

$Cr(CO)_5C(OC_2H_5)CH_2C_6H_5$: 7.15 $(-C_6H_5)$, 4.99 $(C-CH_2CH_3)$, 4.50 $(-CH_2C_6H_5)$, 1.43 (OCH_2CH_3).

$W(CO)_5C(OC_2H_5)CH_2C_6H_5$: 7.14 $(-C_6H_5)$, 4.83 $(-O-CH_2CH_3)$, 4.37 $(-CH_2C_6H_5)$ and 1.52 $(-CH_2CH_3)$.

$W(CO)_4P(C_6H_5)_3C(OC_2H_5)CH_2C_6H_5$: 7.14 $(-C_6H_5)$, 4.35 $(-O-CH_2CH_3)$, 3.65 $(-CH_2C_6H_5)$, 1.30 (OCH_2-CH_3).

Kinetic Measurements. The solutions used for kinetic studies were kept under N_2 in a rubber serum capped flask which was partially immersed in a thermostatted bath (±0.2°C). At regular intervals samples were removed by syringe and spectra recorded. The infrared spectra were taken on Perkin-Elmer 521 or 21 instruments.

The reactions were followed by observing the disappearance of bands due to CO vibrations in the starting materials. Linear first-order plots of $\ln(A-A_\infty)$, where A is the absorbance at time t and A_∞ is the absorbance at infinite time, vs. t were obtained. These plots were linear for at least 75% reaction completion. All data were analyzed by the linear least-squares method.

^{13}CO Enrichment Experiment. $W(CO)_5C(OC_2H_5)C_6H_5$ in 20 ml of hexane contained in a quartz tube over an atmosphere of 55% ^{13}CO (ISOMETT, Palisades Park, New Jersey) was irradiated for approximately eight hours with a 550 watt Hanovia lamp. Samples were withdrawn at various times and their infrared spectra in the 2100-1850 cm^{-1} region recorded.

Infrared Measurements. Infrared spectral measurements were made on a Perkin-Elmer 521 Spectrophotometer equipped with a linear absorbance potentiometer. The spectrophotometer was calibrated in the CO stretching region with the spectrum of water vapor. The spectral slit width of the instrument was set at 1.5 cm^{-1}. Recordings were made on an expanded scale (2.5 cm^{-1}/cm) and areas under bands were determined by use of a planimeter. 1 mm sodium chloride cells calibrated by the interference fringes method were employed in the measurements. Intensities were determined at a number of concentrations and extrapolated to zero concentration. All data were analyzed by the linear least-squares method.

Calculations. Machine calculations were performed on a CDC 6400 at the State University of New York at Buffalo Computer Center.

The force constants and L matrix elements were calculated using ^{13}CO frequency data with an iterative computer program based on the work of Schachtschneider and Snyder.[8] The program adjusts a set of force constants common to a group of related molecules to give simultaneously a least-squares fit between observed and calculated frequencies for all molecules. Calculations were performed using an energy-factored block matrix for the carbonyl stretching vibrations, but without any other predetermined constraints on the force field.

Infrared band shape analyses were performed using a program based on the work of R. N. Jones and J. Pitha[9] of the Division of Pure Chemistry, National Research council of Canada. The program fits a Cauchy, Gauss, product, or sum function to an infrared absorption band envelope and will handle up to 20 bands.

Results and Discussion

Products. Phenyl- and methylmagnesium bromides react with $W(CO)_6$ and $Cr(CO)_6$ to produce, upon ethylation with triethyloxonium fluoroborate, phenyl- or methylethoxy-carbenemetalpentacarbonyl compounds which are identical with those obtained using phenyl- or methyllithium as the nucleophilic reagent.[6] Benzylmagnesium chloride reacts to produce analogous carbene type complexes.

Although the reaction of $W(CO)_6$ with phenylmagnesium bromide in diethylether occurred with good yield over a reaction period of 20 hours, no reaction

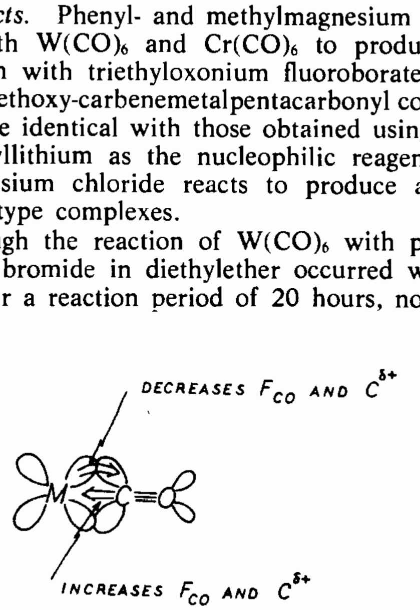

Figure 1. Relationship between CO force constant and the positive charge on the carbonyl carbon atom.

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[7] H.C. Clark and M.H. Chisholm (*Chem. Comm.*, 763 (1970)) have prepared a benzylmethoxycarbene ligand by reaction or, for example, *trans*-$[(CH_3)_3As]_2$ $H_3CPt(HC\equiv C(C_6H_5))+$ with methanol. The benzyl protons for this complex ion are assigned a resonance of 2.9 ppm. In some of the spectra for the compounds reported here resonance at 2.9 ppm were observed and were assigned to dibenzyl, an impurity in the Grignard reagent as well as seemingly produced in the decomposition of the ethyoxybenzylcarbene complexes. The dibenzyl ion was also observed in the mass spectra of previously purified complexes.

[8] J H. Schachtschneider and R.G. Snyder, *Spectrochim. Acta, 19,* 85, 117 (1963).

[9] R.N. Jones and J. Pitha, National Research Council Bulletin, No. 12, Ottawa, Canada (1968).

occurred with $Cr(CO)_6$ under the same conditions. Upon changing the solvent to anhydrous tetrahydrofuran (THF) however $Cr(CO)_5C(C_6H_5)(O)^- MgBr^+$ was formed in high yield. Therefore, THF was generally employed as the solvent in these reactions.

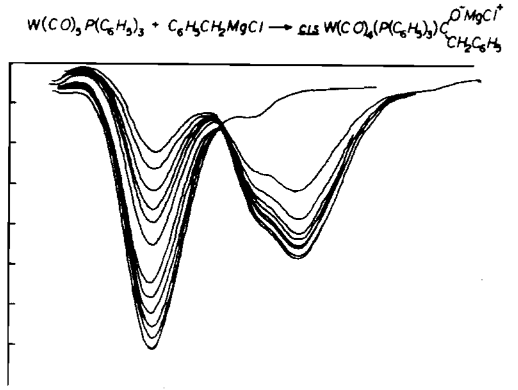

Figure 2. Infrared spectra of the reaction between $W(CO)_5P(C_6H_5)_3$ and benzylmagnesium chloride in THF as a function of time (peaks to the right are those of the product).

Kinetics. Kinetic studies of the reaction of benzylmagnesium chloride with $W(CO)_6$ and $W(CO)_5P(C_6H_5)_3$ have been initiated. The reactions were carried out in THF and at 27.9°C.

Examples of the infrared spectra in the carbonyl stretching region taken at time intervals are shown in Figure 2. The spectra obtained for the disappearance of $W(CO)_5P(C_6H_5)_3$ show one isosbestic point thus suggesting a clean, one-product reaction is occurring. The bands due to the product are actually three overlapping absorbances with a fourth at high energy not shown. Upon ethylation of this compound and dissolution into hydrocarbon solvent there appears four distinct bands, of intensity and frequency similar to, for example, *cis*–$W(CO)_4[P(C_6H_5)_3]_2$. It is concluded that the Grignard addition is thus *cis*.

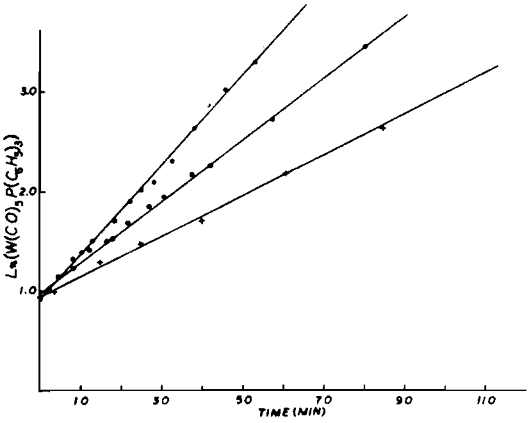

Figure 3. Plots of ln $[W(CO)_5P(C_6H_5)_3]$ versus time for benzylmagnesium chloride concentrations: ○, 0.120*M*; ●, 0.090*M*; +, 0.060*M*.

Plots of $\ln[W(CO)_5P(C_6H_5)_3]$ *vs.* time are linear (Figure 3) and, at high concentrations of Grignard, the observed rate constants thus obtained are dependent on the Grignard concentration. (See Figure 4 and Table I.)

Table I. Observed Rate Constants at 27.9°C in Tetrahydrofuran

$[W(CO)_6]$ (m/l)	$[C_6H_5CH_2MgCl]$ (m/l)	k_{obsd} [a] (sec^{-1})
5.54×10^{-3}	0.120	6.08×10^{-3}
5.55×10^{-3}	0.090	4.99×10^{-3}
5.46×10^{-3}	0.060	7.00×10^{-4}
$[W(CO)_5P(C_6H_5)_3]$ (m/l)	$[C_6H_5CH_2MgCl]$ (m/l)	k_{obsd} [a] (sec^{-1})
5.61×10^{-3}	0.120	7.52×10^{-4}
5.57×10^{-3}	0.090	5.16×10^{-4}
5.48×10^{-3}	0.060	3.38×10^{-4}

[a] The rate constants were reproducible to ± 10%.

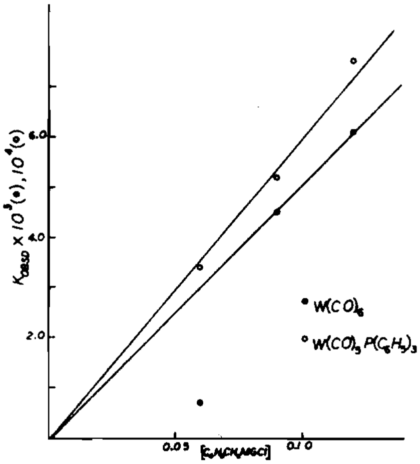

Figure 4. Plots of k_{obsd} versus benzylmagnesium chloride concentrations.

Plots of k_{obsd} *vs.* Grignard concentration (Figure 4) are linear and have an intercept of zero. The low point in the hexacarbonyl data illustrates the complexity that arises at low Grignard concentrations. This anomalously low rate constant is reproducible and is dependent on the metal carbonyl. Its origin is not quite understood at this time.

Although generalizations can hardly be made as yet, it is interesting to note that the relative rate of nucleophilic attack on the carbon of $W(CO)_5P(C_6H_5)_3$ is slower than that on the carbonyl carbon of $W(CO)_6$. This rate is much slower than would be predicted were statistical factors alone involved. Since the force constant of $W(CO)_6$ ($k = 16.41$) is larger than the equatorial force constant of $W(CO)_5P(C_6H_5)_3$ ($k_2 = 15.89$), this is in line with our earlier prediction.[3]

CO Force Constants. Simple force constant calculations on the Grignard addition compounds of C_{4v} symmetry (see Figure 5) show both the force constants of the axial (k_1) and the equatorial (k_2) carbonyls to be smaller than those of complexes for which neutral ligands are substituents. This is as expected for anionic or electron-rich metal carbonyls. Replace-

Table II. CO Force Constants, Calculated and Observed Frequencies in $M(CO)_5C(OC_2H_5)CH_2C_6H_5$ Compounds.

Compound	Vibrations	Calcd. (cm^{-1})	Obsd.[a] (cm^{-1})	Force Constants[b] k_1	k_2	k_t	$k_{c'}$	k_c
M=Cr	A_1	2066.0	2065.7	15.63	15.90	0.59	0.32	0.20
(All ^{12}CO molecule)	B_1	1980.9	1981.0					
	A_1	1961.0	1961.3					
	E	1947.7	1947.4					
		1947.7						
Mono-^{13}CO	A_1'	2058.0	2058.5					
(equatorial)	A_1'	1974.5						
	A_1'	1960.7						
	A_1''	1947.7	1947.4					
	A_1'	1918.2						
M=W	A_1	2073.9	2074.6	15.71	15.89	0.61	0.31	0.31
(All ^{12}CO molecule)	B_1	1983.4	1984.0					
	A_1	1957.7	1957.0					
	E	1945.2	1944.8					
		1945.2						
Mono-^{13}CO	A_1'	2066.3	2066.7					
(equatorial)	A_1'	1976.7						
	A_1'	1957.1						
	A_1''	1945.2	1944.8					
	A_1'	1916.0						

[a] Observed ^{13}CO frequencies obtained from natural abundance ^{13}CO. [b] k_1 and k_2 are the stretching force constants of the axial and equatorial CO groups respectively, and k_t, $k_{c'}$ and k_c refer to the interaction constants for *trans* CO_{eq}—CO_{eq}, *cis* CO_{eq}—CO_{eq} and CO_{eq}—CO_{ax} respectively. These are in units of mdynes/Å.

ment of the cation with an ethyl group however moves the force constants into the phosphine range.

The CO stretching force constants for $Cr(CO)_5C(OC_2H_5)CH_2C_6H_5$ and $W(CO)_5C(OC_2H_5)CH_2C_6H_5$ are contained in Table II along with the observed and calculated frequencies.

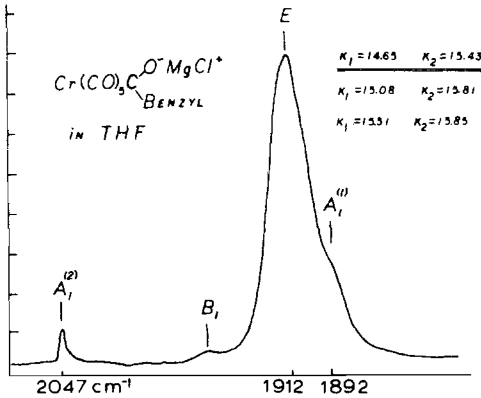

Figure 5. Infrared spectrum of $Cr(CO)_5C(CH_2C_6H_5)(O)^-MgCl^+$ in THF solution.

The corresponding data for the $W(CO)_5C(OC_2H_5)C_6H_5$ compound which was isotopically enriched with ^{13}CO is shown in Table III. The species possible as a result of ^{13}CO enrichment studies are depicted in Figure 6. ^{13}CO enrichment studies were performed using u.v. irradiation,

$$W(CO)_5C(OC_2H_5)C_6H_5 + {}^{13}CO \xrightarrow[\text{hexane}]{h\nu} W(CO)_{5-n}({}^{13}CO)_nC(OC_2H_5)C_6H_5 + CO.$$

Unambiguous bands could be assigned to the species with n=1, 2, and 3. Infrared spectra observed be-

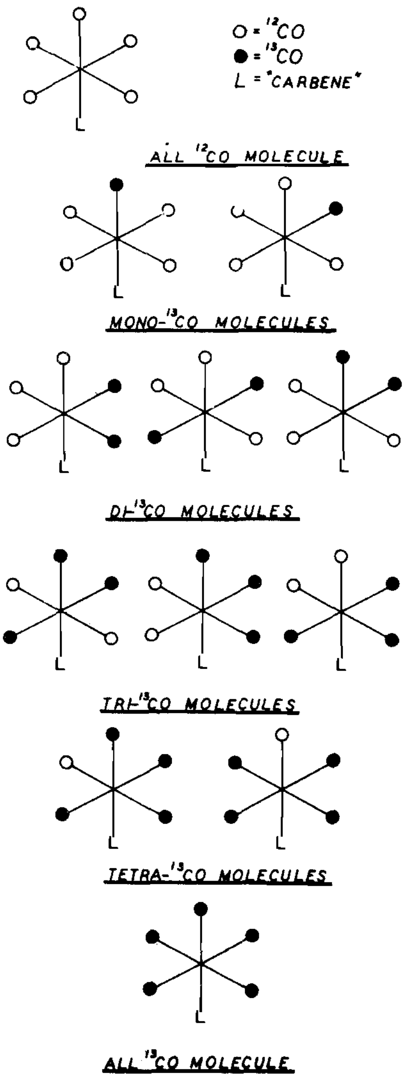

Figure 6. ^{13}CO substitution products in $M(CO)_5L$ species.

Table III. Calculated Frequencies and Force Constants for ^{13}CO Substituted $W(CO)_5C(OC_2H_5)C_6H_5$

Molecule	Observed Frequencies	Calculated Frequencies
All ^{12}CO molecule	2071.5	2071.1
	1983.1	1983.4
	0.0	1949.4
	1948.0	1949.4
	1958.0	1958.6
Mono-^{13}CO (equatorial)	2064.0	2063.5
	1978.3	1977.1
	1958.0	1958.2
	1948.0	1949.4
	1921.0	1919.6
Mono-^{13}CO (axial)	0.0	2067.2
	1983.1	1983.4
	0.0	1949.4
	1948.0	1949.4
	1921.0	1918.7
Di-^{13}CO (equatorial) *cis*	2055.0	2054.5
	0.0	1972.1
	0.0	1957.8
	0.0	1922.1
	1916.4	1917.0
Di-^{13}CO (equatorial) *trans*	2055.0	2055.8
	0.0	1965.0
	1906.2	1906.0
	1948.0	1949.4
	0.0	1947.4
Di-^{13}CO (equatorial and axial)	2058.7	2059.2
	1976.7	1976.9
	1924.4	1924.1
	1948.0	1949.4
	0.0	1914.4
tri-^{13}CO (equatorial)	2046.0	2045.1
	0.0	1962.1
	1906.2	1906.0
	0.0	1947.4
	0.0	1918.8
tri-^{13}CO (two equatorial *cis,* one axial)	2050.0	2049.6
	0.0	1972.1
	0.0	1927.5
	0.0	1917.0
	0.0	1913.6
tri-^{13}CO (two equatorial *trans,* one axial)	2050.0	2051.0
	0.0	1957.1
	1906.2	1906.0
	1948.0	1949.4
	0.0	1916.2

$k_1 = 15.70$, $k_2 = 15.92$, $k_{c'} = 0.306$, $k_c = 0.292$, $k_t = 0.576$.

fore and after several hours of exchange time are shown in Figure 7. The rate of equatorial carbonyl exchange appeared to be slightly faster than axial carbonyl exchange. However, due to the complexity in the region of the axial carbonyl absorbances, it is difficult to make an accurate comparison. No cleavage of the *carbene* ligand was observed during the irradiation. This is in agreement with mass spectral data which show the W-carbene$^+$ species as its major peak.

We have previously discussed the bonding in transition-metal carbene complexes based on inferences made from calculated carbonyl stretching force constants.[6] At that time quantitative σ and π Graham parameters were computed. Although we feel that the essential conclusions drawn on the basis of these parameters are correct, we can see no real advantage in their usage since some of the assumptions made in the calculation of these parameters appear to be suspect.[10]

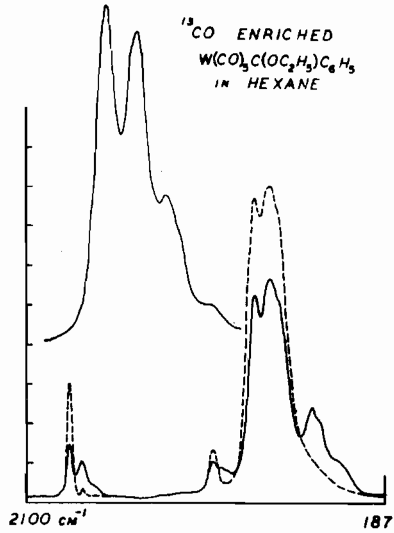

Figure 7. Infrared spectra of $W(CO)_5C(OC_2H_5)C_6H_5$ in hexane: - - - before exchange, — after 8 hours of ^{13}CO exchange. (Overlay is enlargement of high frequency portion of the spectrum).

Nevertheless, it is qualitatively possible to conclude that the force constants of the CO vibrations in metal carbonyl carbene complexes clearly place the carbene ligand in the π-acceptor class (CO, phosphines, phosphites, etc.), considerably different from those of purely σ donor ligands, such as amines.

Integrated Infrared Intensities. It has been demonstrated that it is possible to infer about the nature of the M–L bond in $M(CO)_5L$[13,14] and $M(CO)_4L$[15] compounds by infrared intensity measurements of the CO stretching vibrations. We therefore undertook a study of these CO vibrations in a typical metal carbonyl carbene complex, namely, $W(CO)_5C(OC_2H_5)C_6H_5$.

Unfortunately in $M(CO)_5$carbene complexes the $A_1^{(1)}$ CO stretching mode is extensively overlapped with the E mode, thereby making it impossible to accurately assess the areas under the respective bands visually It was therefore necessary to perform a band shape analysis before any meaningful information could be obtained from infrared intensity measurements in these complexes.

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(10) The calculations of Fenske and DeKock[11] have shown that in $Mn(CO)_5X$ molecules there is direct ligand (X) orbital overlap with one of the π^* orbitals of the equatorial carbonyl groups. Since a similar interaction does not occur with the axial CO ligand, the isotropic nature of the sigma effect which is assumed in Graham's method may be incorrect in these systems. Secondly, we find the σ parameters to be very insensitive to variations in the base strengths of amines in $M(CO)_5$amine complexes. For example, where pK_b varies by factors of as much as 10 there is little change in the σ parameter.[12] This is unreconcilable with the proposal that these parameters are indications of the donor ability of the substituted ligand.

(11) R.F. Fenske and R.L. DeKock, *Inorg. Chem.*, 9, 1053 (1970).

(12) R J. Dennenberg and D.J. Darensbourg, *ibid.*, In press.

(13) T.L. Brown and D.J. Darensbourg, *Inorg. Chem.*, 6, 971 (1967).

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

(15) D.J. Darensbourg, *Inorg. Chim. Acta, 4,* 597 (1970).

The experimental band envelope in $W(CO)_5C(OC_2H_5)C_6H_5$ in the carbonyl stretching region in solution was obtained using a Cauchy-Gauss product function, equation 1.[16]

$$(T/T_o)_{\nu(calcd)} = \exp -2.30258 \left\{ \alpha + \sum_{P=1}^{M} x_{1(P)} (1 + x_{3\,(P)}^{2} (\nu - x_{2(P)})^2)^{-1} \cdot \exp[-x_{4\,(P)}^{2} (\nu - x_{2\,(P)}^{2})] \right\} \quad (1)$$

α is the baseline; x_1 is the absorbance at the band's maximum; x_2 is the peak position in cm^{-1}; x_3 and x_4 jointly define the half-band width and the Cauchy-Gauss ratio; M is the number of constituent bands.

The quantities $(x_1, x_2, x_3, \text{and } x_4)_P$ and α are varied to minimize Φ where

$$\Phi = \Sigma[(T/T_o)_{\nu(obs)} - (T/T_o)_{\nu(calcd)}]^2.$$

The calculated and observed band envelopes are illustrated in Figure 8. The discrepance in the transmittance difference (root mean square of $(T/T_o)_{\nu(obs)} - (T/T_o)_{\nu(calcd)}$) was found to be less than 0.005. This procedure therefore allows for very accurate separation of the areas under the $A_1^{(1)}$ and E bands.

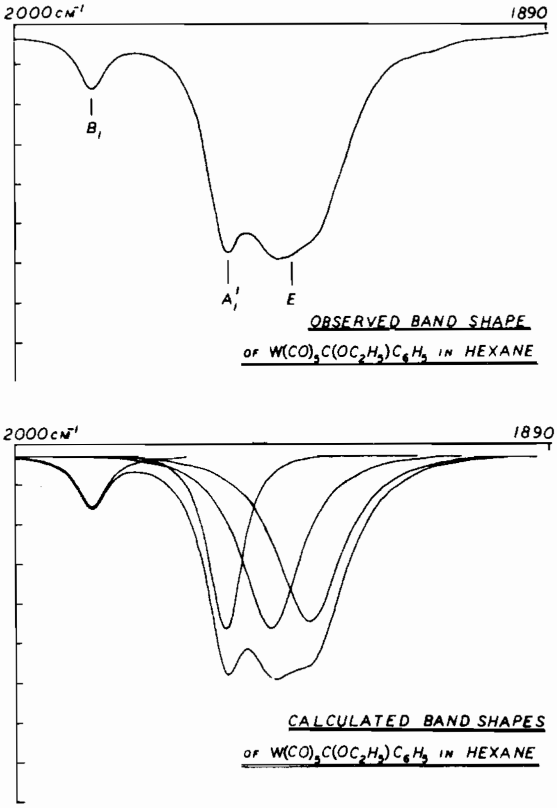

Figure 8. Observed and calculated band shapes for the CO vibrations in $W(CO)_5C(OC_2H_5)C_6H_5$ in hexane.

The integrated infrared intensities of the CO stretching modes in $W(CO)_5C(OC_2H_5)C_5H_5$ and $W(CO)_5HNC_5H_{10}$ are shown in Table IV. The L_{ij} matrix elements for the mixing of the two A_1 vibrations are expressed in terms of symmetry coordinates and found in Table V.

Table IV. Infrared Intensities of the Carbonyl Stretching Vibrations

Compound	Vibration,[a] (cm^{-1})	Intensity[b] $\times 10^{-4}(M^{-1}$—$cm^{-2})$
$W(CO)_5C(OC_2H_5)C_6H_5$	2071.5 (A_1)	4.00
	1948.0 (E)	52.5
	1958.0 (A_1)	14.5
$W(CO)_5HNC_5H_{10}$	2073.5 (A_1)	0.92
	1928.5 (E)	60.0
	1918.0 (A_1)	14.0

[a] All spectra were observed in hexane solution.

[b] Defined as $\frac{2.303}{c\,.\,l}\int_{band}\log\frac{I_o}{I}d\nu$, where c equals the concentration in moles/liter and l equals the cell path length in cm.

Table V. Calculated Values of the L_{ij} Matrix Elements[a]

Compound	L_{12}	L_{11}
$W(CO)_5C(OC_2H_5)C_6H_5$	0.12941	0.35930
$W(CO)_5HNC_5H_{10}$[b]	0.11200	0.36500

[a] $L_{12} = -L_{21}$ and $L_{11} = L_{22}$. [b] Reference 12.

We wish to calculate a characteristic MCO group dipole moment derivative for each of the three symmetry coordinates in the $W(CO)_5L$ species, $2A_1+E$.

Equations 2 and 3 are used to describe the two A_1 vibrations and are similar to those previously derived[14] with the added modification for electronic migration along the fourfold axis during the stretching of the four equatorial carbonyl groups. This is the same approach as that used for the $M(CO)_4L(C_{3v})$ molecules.[15]

$$I_1^{A_1^{(1)}} = (\mu'_{MCO}{}^{(1)} L_{11} + 2(\cos\theta + \rho)\mu'_{MCO}{}^{(2)} L_{21})^2 \quad (2)$$

$$I_2^{A_1^{(2)}} = (\mu'_{MCO}{}^{(1)} L_{12} + 2(\cos\theta + \rho)\mu'_{MCO}{}^{(2)} L_{22})^2 \quad (3)$$

I_1 and I_2; $\mu'_{MCO}{}^{(1)}$ and $\mu'_{MCO}{}^{(2)}$; and θ are defined as previously.[14,15] ρ is a parameter which allows for a contribution from electronic migration along the fourfold molecular axis during the equatorial carbonyls' symmetrical stretching motion. The analogous quantity for the axial CO group is built into the value of $\mu'_{MCO}{}^{(1)}$, the dipole moment derivative for this particular A_1 vibration.[17]

The dipole moment derivative for the E mode vibration is calculated from equation 4. $\mu'_{MCO}{}^{(3)}$ is quite insensitive to values of θ around 90°±10°.

$$I_3 = G_{11}\mu'_{MCO}{}^{(3)} 4\sin^2\theta \quad (4)$$

The calculated values for $\mu'_{MCO}{}^{(1)}$ and $\mu'_{MCO}{}^{(3)}$ in $W(CO)_5L$ compounds, where $L = C(OC_2H_5)C_6H_5$, HNC_5H_{10}, and CO, are found in Table VI. For comparison, several analogous $Mo(CO)_5L$ compound are included in Table VI.

The enhancement observed of the A_1 vibration moment derivative over that of the E vibration can be

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[16] Details of the calculation of CO band shapes in transition metal carbonyl species will be submitted for publication at a later date.

[17] The values of ρ will differ for the two A_1 vibrations since the demand made for π electrons during these respective CO vibrations is different. There is a greater demand made in the $A_1^{(2)}$ vibration since all the CO group are simultaneously withdrawing electron from the metal.

Table VI. Values of μ'_{MCO}, the MCO Group Dipole Moment Derivatives [a]

Compound	$\mu'_{MCO}{}^{(1)}$	$\mu'_{MCO}{}^{(3)\,b}$	$\mu'_{MCO}{}^{(1)}/\mu'_{MCO}{}^{(3)}$
$W(CO)_5C(OC_2H_5)C_6H_5$	11.2	9.49	1.18
$W(CO)_5HNC_5H_{10}$	10.1	10.2	0.996
$W(CO)_5CO$ [c]	—	9.35	—
$Mo(CO)_5P(OCH_3)_3$ [d]	10.5	9.01	1.17
$Mo(CO)_5PCl_3$ [d]	10.3	8.81	1.16
$Mo(CO)_5HNC_5H_{10}$ [d]	9.61	9.64	0.970
$Mo(CO)_5CO$ [d]	—	9.23	—

[a] The μ'_{MCO}'s are effective group dipole moment derivatives which involve both MC and CO stretching motions.[13] The units employed here are arbitrary; the intensities are expressed in units of 10^4 M^{-1}—cm^{-2}, and L and G terms are based on atomic mass units. [b] These are all calculated for a θ value of 90°. [c] Calculated from intensity value listed in Ref. 13. [d] Taken from Ref. 14.

thought to arise from a vibronic contribution.[14] This results from a transfer of π-electronic charge from the carbene ligand through the metal to the carbonyl groups as the CO groups stretch. This is not possible for saturated amine ligands as exemplified by a lack of enhancement of $\mu'_{MCO}{}^{(1)}$ over $\mu'_{MCO}{}^{(3)}$ in these cases. It is possible to conclude from the fact that $\mu'_{MCO}{}^{(1)} > \mu'_{MCO}{}^{(3)}$ in metal-carbene complexes that there is π-electronic charge in the metal-carbene bond.

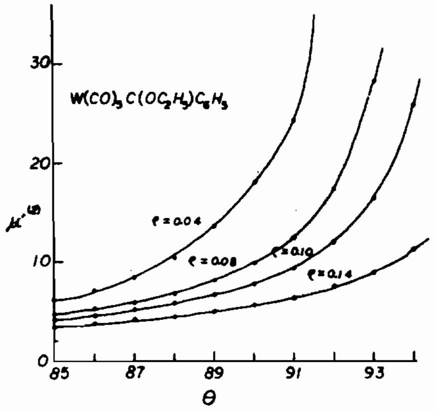

Figure 9. Plot of $\mu'_{MCO}{}^{(2)}$ versus θ and ρ for $W(CO)_5C(OC_2H_5)C_6H_5$.

The dipole moment derivative for the equatorial A_1 vibration in $W(CO)_5C(OC_2H_5)C_6H_5$ was calculated as a function of both θ and ρ and is shown in Figure 9. The value of θ is expected to be quite close to 90° since in the chromium analogue θ has been found to be 88° in the solid state.[18] Therefore, as is seen in Figure 9, in order for $\mu'_{MCO}{}^{(2)}$ to be similar to $\mu'_{MCO}{}^{(1)}$ ρ must be in the neighborhood of 0.04 to 0.08 or a vibronic contribution to the dipole moment derivative of 4 to 8%. This is approximately the order of magnitude observed for vibronic contributions in the molybdenum pentacarbonyl phosphine (phosphite) series.[14] The value of ρ is zero in the piperidine derivative since this electronic migration is associated with the π-electronic charge in the W–L bond. The dipole moment derivative for the $A_1{}^{(2)}$ vibration in $W(CO)_5HNC_5H_{10}$ was calculated to be ±14.1 and ±7.04 for values of θ of 90±1° and 90±2° respectively.

In conclusion, although there are difficulties in quantitatively comparing *carbene*, phosphine, and saturated amine ligands, the salient feature from all physical and chemical studies is that the carbene ligands behave in a similar manner to π-acceptor ligands (such as CO, phosphines, phosphites) as contrasted with exclusively σ-donor ligands (such as saturated amines).

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