

Infrared Spectroscopic Evidence for New Metal Carbonyl Complexes with Aromatic Ligands

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A new kind of complex with the formula $W(CO)_5L$, with aromatic molecules as monodentate ligands, is formed photochemically. A variety of substituted arenes and polycyclic and heterocyclic systems were studied. Owing to the thermal instability of the complexes, they could not be isolated, but infrared spectra in the $C=O$ stretching region indicate that bonding is to the ring center and not to a fixed double bond. The mechanism of bonding in the new complexes is discussed.

Introduction

Many complexes of metal carbonyls with aromatic ligands are known.¹ In general the number of double bonds in the simple forms of the ligands determines the number of coordination sites they utilize; the sandwich complexes $Cr(C_6H_6)_2$ and $Fe(C_5H_5)_2$ ² are examples of this rule.

The photochemical preparation³ of the reactive species $W(CO)_5$ which is capable of reacting with simple olefins⁴ to yield the relatively stable monosubstituted carbonyl $W(CO)_5L$ suggests the employment of substituted arenes or other aromatic systems as the ligands. The nature of the bonding in these systems would be of considerable interest.

It is found that the reaction products of $W(CO)_5$ with aromatic ligands are all quite unstable. Infrared spectra, mainly in the $C=O$ stretching region, have therefore been employed in their characterization. Brief ultraviolet irradiations produce only lower substituted products, so that no polysubstituted compounds are formed, thus facilitating interpretation of the infrared spectra.⁴ Since the infrared spectra in the $C=O$ stretching region of octahedral derivatives of known structure are well understood, detailed structural assignments can be made.

Increases in $C=O$ frequency with an increasing number of rings for condensed polycyclic ligands and the decreases in frequency with increasing number of methyl substituents on the arenes may be interpreted.

Experimental

Infrared spectra calibrated against the known peaks of polystyrene were taken with the Perkin-Elmer Model 221 spectrometer. Solutions of *n*-hexane or a 1:4 mixture of isopentane and methylcyclohexane were generally made 0.005 *M* in $W(CO)_6$ and 0.2 *M* in ligands. Owing to the low solubility of anthracene, pyrene, and phenanthrene, solutions saturated with respect to these

ligands were used. *n*-Hexane was employed for work at room temperature and -80° , while at -180° a 1:4 mixture of isopentane and methylcyclohexane was used. The experimental procedure has been previously described.³ When solutions in sealed NaCl cells (path length 0.1 mm.) were irradiated with an A-H6 lamp for 3, 10, 30, 60, 120, and 300 sec., the yellow color became progressively more intense; infrared spectra were taken immediately. This procedure allows the separation of the bands of unchanged, monosubstituted, and disubstituted metal carbonyls. Irradiation of a solution of 10 mg. of $W(CO)_6$ and 50 mg. of naphthalene in 100 ml. of *n*-hexane at -30° for 5 min. and evaporation at -40° gave a yellow complex mixed with an excess of colorless starting material. The product decomposes at -10° into $W(CO)_3C_{10}H_8$ (identified by infrared). All operations were performed under carefully purified nitrogen.

Discussion

Three different types of ligands were used to study the bonding in these compounds: arenes and condensed polycyclic and heterocyclic systems. Tables I-III show the $C=O$ stretching frequencies ($1800-2200\text{ cm.}^{-1}$ of the infrared) of complexes with each type of ligand. Each type will be discussed in turn.

It is first important to point out that all the compounds studied showed an infrared pattern in the terminal $C=O$ stretching region characteristic of a square-pyramidal arrangement of the $C=O$ groups. This is strong evidence that all the ligands studied formed complexes with the formula $W(CO)_5L$, where *L* = benzene, naphthalene, anthracene, phenanthrene, pyrene, toluene, *p*-xylene, mesitylene, 1,2,3-trimethylbenzene, hexamethylbenzene, biphenyl, furan, thiophene, and pyridine.

A. Polycyclic Systems. If the idea of stabilization of metal carbonyl complexes by back donation of charge from filled metal *d*-orbitals into unfilled ligand orbitals is correct, complexes with aromatic systems acting as monodentate ligands will be more stable when the ligand has energetically low-lying antibonding orbitals. Since the polycyclic ligands have lower-lying antibonding orbitals than benzene, it is not surprising that complexes with condensed polycyclic systems are much more stable than are those of arenes. All compounds with condensed polycyclic systems can be formed in solution at room temperature, but attempts to isolate the naphthalene complex (which seems to decompose most slowly) were only partially successful.

If the changes (in the infrared frequencies) of the effects of the polycyclic ligands in Table I are due only to the stronger back bonding in the higher conjugated systems, the increase in frequency of the $A_1^{(1)}$ vibration should be twice that of the *E* vibration. This is to be expected because the effect of back donation on a *trans*

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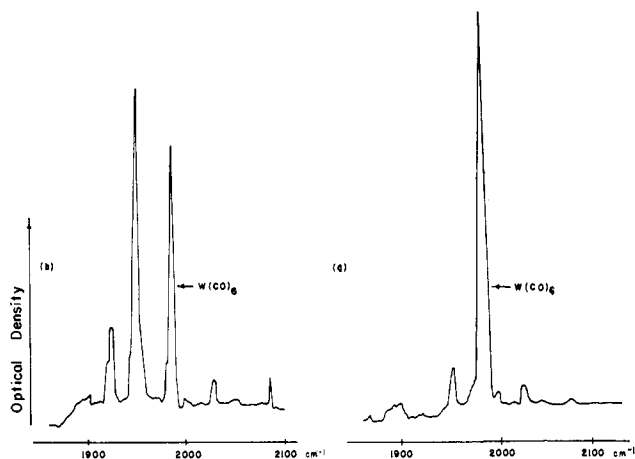


Figure 1. Infrared spectrum (C=O stretching region) in *n*-hexane at -80° : (a) $W(CO)_6 + C_6H_6$ before irradiation; (b) $W(CO)_6 + C_6H_6$ after irradiation.

C=O is roughly twice as great as on a C=O *cis* to the substituent. The similarity of the frequencies in Table I suggests the same kind of bonding in all of these compounds.

Table I. Infrared Frequencies of Metal Carbonyl Complexes with Benzene and the Polycyclic Ligands (cm^{-1})

Ligand	W(CO) ₆ L			<i>trans</i> -W(CO) ₄ L ₂	Temp., °C.
	A ₁ ⁽²⁾	E	A ₁ ⁽¹⁾		
Benzene	2083 (w)	1948 (s)	1921 (ms)		-80
Naphthalene	2081 (w)	1950 (s)	1930 (ms)	1942	20
Anthracene	2082 (w)	1951 (s)	1932 (ms)	1942	20
Phenanthrene	2082 (w)	1952 (s)	1934 (ms)	1945	20
Pyrene	2083 (w)	1954 (s)	1936 (ms)	1948	20

The fact that the infrared spectrum of the phenanthrene complex is so different from that of *cis*-stilbene (see Table III) suggests very different kinds of bonding in the two complexes. If the bonding were between the nearly pure double bond in the 9,10-position in phenanthrene and the metal carbonyl, frequencies and bonding should be similar to those in the *cis*-stilbene complex. This indicates that the bonding in the aromatic systems is not through a fixed double bond of the ligand as in the ligands of the ethylene series.

If mixtures of polycyclic ligands and $W(CO)_6$ in hexane were irradiated for a longer time, a new infrared band appeared, the frequency of which showed that it did not belong to the known compounds $W(CO)_6L$. It has tentatively been assigned to complexes of the formula *trans*- $W(CO)_4L_2$. The frequencies of this band showed the same trend as did those of the mono-substituted complexes.

B. Substituted Benzenes. The C=O stretching frequencies for substituted arene complexes are compared with those of the benzene complex in Table II. A typical spectrum is shown in Figure 1. It was expected that methyl substitution would destabilize the complex through an inductive effect, while an electron-withdrawing ligand like phenyl in biphenyl should enhance stability. This general trend is observed. All complexes could be observed at -80° , except hexamethyl-

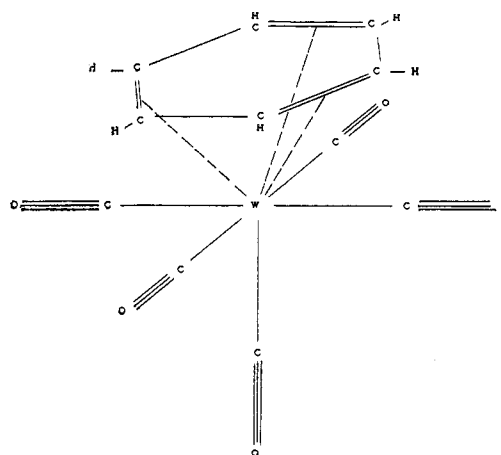


Figure 2. Probable structure of the observed complexes.

benzene- $W(CO)_6$, which formed at -180° . Unfortunately, the species $W(CO)_6$ is also stable at this temperature and this complicates the infrared interpretation. For this reason, only the strongest E band for the hexamethylbenzene complex could be assigned.

Table II. Infrared Frequencies of Complexes $W(CO)_6L$ with Substituted Benzenes (cm^{-1})

Ligand	A ₁ ⁽²⁾	E	A ₁ ⁽¹⁾	Temp., °C.
Biphenyl	2083 (w)	1949 (s)	1922 (ms)	-80
Benzene	2083 (w)	1948 (s)	1921 (ms)	-80
Toluene	2083 (w)	1947 (s)	1921 (ms)	-80
<i>p</i> -Xylene	2082 (w)	1945 (s)	1920 (ms)	-80
Mesitylene	2082 (w)	1943 (s)	1915 (ms)	-80
1,2,3-Trimethylbenzene	2081 (w)	1944 (s)	1915 (ms)	-80
Hexamethylbenzene		1939		-180

The shifts of the A₁⁽¹⁾ and E frequencies produced by methyl groups are about equal, as one would expect, since their only effect is to increase charge donation. In going from benzene to hexamethylbenzene, the total shift is about 10 cm^{-1} . This corresponds to a similar shift of 10 cm^{-1} in going from ethylene to *trans*-butene.⁴

This regularity in the decrease of the frequency is a strong argument that bonding involves the whole ring (Figure 2) rather than one fixed double bond. If bonding occurred through one double bond, it is most reasonable to believe that it should occur through the double bond with the smallest number of attached methyl groups. Thus one would expect, for example, that the A₁⁽¹⁾ and E frequencies of the 1,2,3-trimethylbenzene complex would be about 4 cm^{-1} higher than those of the mesitylene derivative. That this is not observed is a further indication that bonding is to the ring center (Figure 1).

The slightly higher frequencies of the biphenyl complex when compared to the benzene complex may be due to increased backbonding.

C. Heterocyclic Systems. Table III shows the infrared frequencies for the pentacarbonyltungsten complexes of pyridine, furan, and thiophene. The infrared frequencies for other complexes are also

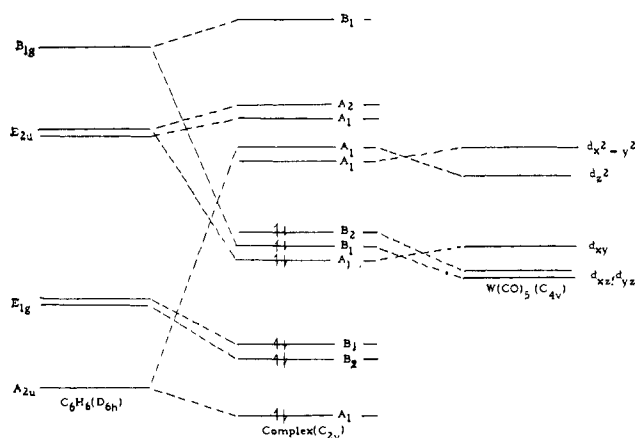


Figure 3. Schematic diagram of the molecular orbital levels for the proposed bonding mechanism (level spacing only qualitative).

shown for comparison. Only the well-known $\text{py-W}(\text{CO})_5$ ⁵ was observed with pyridine, while with furan and thiophene different products were formed at low temperatures and at room temperature.

Table III. Infrared Frequencies of Complexes $\text{W}(\text{CO})_5\text{L}$ with Heterocyclic Ligands and Other Ligands of Interest (cm.^{-1})

Ligand	$A_1^{(2)}$	E	$A_1^{(1)}$	Temp., °C.
Pyridine	2074 (w)	1932 (s)	1919 (ms)	-180
Furan	2090 (w)	1949 (s)	1919 (ms)	-180
	2083 (w)	1950 (s)	1935 (ms)	20
Thiophene	2092 (w)	1952 (s)	1921 (ms)	-180
	2085 (w)	1953 (s)	1937 (ms)	20
Tetrahydrofuran	2077 (w)	1934 (s)	1912 (ms)	20
cis-Stilbene	2084 (w)	1952 (s)	1967 (ms)	20

The low-temperature forms were converted into the high-temperature forms at about -110° . However, repeated coolings indicate that the conversion is irreversible. The configurations of the two "isomers" remain uncertain. However, bonding through a fixed double bond can probably be ruled out from the infrared frequencies. Since the frequencies of the low-temperature forms are similar to those of the benzene complex, the bond again seems to be to the ring center. The

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frequencies of the high-temperature form of the furan complex are much higher than those of the tetrahydrofuran complex, but this behavior is expected if bonding is through the free electron pair at the oxygen, since the aromatic ring strongly decreases the electron density at the heteroatom.

D. Bonding. The spectroscopic evidence outlined in sections A and B under Discussion strongly indicates that bonding in complexes of the type $\text{W}(\text{CO})_5\text{-C}_6\text{H}_6$ involves the whole aromatic ring. The structure shown in Figure 2 seems the most probable. This kind of complex has not been observed previously; all complexes of metal atoms with benzene as monodentate ligand are formed through a fixed double bond in the ring⁶; in fact, a molecular orbital argument has been given that the type of bond we propose should not exist.⁷

In view of the experimental evidence given for its existence, an attempt to explain the bonding seems justified. Since the observed complexes are not very stable, it may be possible to explain the bond in terms of benzene molecular orbitals not commonly used for bonding. It is proposed that electron-pair donation comes from the ring orbital of (hexagonal) symmetry A_{2u} , while the back donation is to the B_{1g} ring orbital (Figure 3). Calculations indicate⁸ that donation from the A_{2u} benzene orbital is present even in the normal sandwich complex. Overlap integrals for $\text{W}(\text{CO})_5\text{C}_6\text{H}_6$ with the proposed geometry have been computed using Slater orbitals: $(d_{z^2}/A_{2u}) = 0.20$, $(d_{xy}/E_{2u}) = 0.10$, $(d_{xz}/E_{1g}) = 0.35$; therefore, the mechanism for back donation could also involve the interaction of the E_{2u} benzene orbital with the d_{xy} metal orbital forming a δ -bond.

The interaction of the filled E_{1g} benzene orbitals and the filled d_{xz} and d_{yz} metal orbitals seems unimportant, since the latter is nonbonding, not antibonding to first order.

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