observed some variation in line widths of both the parent and satellite peaks from sample to sample which

could be interpreted as arising from mercury exchange. This possibility is being studied further.

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Infrared Spectra and Structures of Metal Carbonyl Derivatives. III.[1] Acetylene and Olefin Derivatives of Group VI Metal Carbonyls

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Several new molybdenum and tungsten π-complexes in which carbonyl groups have been replaced by alkene and alkyne ligands have been synthesized through ultraviolet irradiation. Their infrared spectra in the carbonyl stretching region are reported. The stereochemistry and the nature of bonding in such complexes is briefly discussed.

Introduction

There has been reported recently a considerable amount of work in which group VI metal hexacarbonyls have undergone replacement reactions with various nonaromatic ligands under the influence of ultraviolet radiation or heat. The resulting substitution products include those formed utilizing ligands which function primarily as electron donors[1,2] and those produced through replacement of carbonyl groups with cyclic olefins which function as chelating groups.[3]

This paper reports the investigation of some group VI carbonyl complexes $M(CO)_{6-x}(L)_x$ (M = Mo, W) in which L is an alkene or alkyne which replaces a carbonyl group through formation of a single π-bond. Their spectra in the carbonyl stretching region of the infrared are used as the basis of a discussion of the structures and type of bonding which may be expected in such complexes.

Experimental

The complexes investigated were somewhat unstable and their isolation was made difficult because of a tendency toward reversal of the reaction once irradiation was stopped. Therefore the work was limited primarily to an investigation of the changes observed in the carbonyl stretching region of the infrared as the length of irradiation was varied. Because the complexity of the spectra of solutions which contain derivatives in which more than two carbonyls have been replaced makes interpretation difficult and because many such complexes are insoluble in n-hexane, the solvent used in this study, assignments have been limited to those for mono and disubstituted complexes only.

Experimental methods differed only slightly from those used in previous work.[1b] The solubilities of the π-complexes in nonpolar solvents were, as one might expect, greater than those observed for complexes containing electron-donating ligands. It was therefore feasible to employ n-hexane as a common solvent for the photoproduction of the complexes investigated. In addition to being inert to substitution, this solvent permitted the resolu-

tion of close-lying infrared bands. For diethylacetylene, which unlike the other ligands is a liquid at room temperature, 1 ml. was dissolved in 40 ml. of n-hexane and the irradiation was carried out under a nitrogen atmosphere.

As a check on the assignments the complexes $W(CO)_5$(propylene), $W(CO)_4$(propylene)$_2$, $W(CO)_5$(butadiene), and $W(CO)_4$-(butadiene)$_2$ were isolated and purified.

Propylenetungstenpentacarbonyl and Butadienetungstenpentacarbonyl.—$W(CO)_6$ (200 mg.) was dissolved in 40 ml. of n-hexane and pure propylene or butadiene was bubbled through the solution for 15 min. before the irradiation was begun. The solution was then exposed to ultraviolet radiation from a G.E. A-H6 mercury arc lamp for 10 min., during which time propylene or butadiene was continuously bubbled through the solution. The reaction mixture was then frozen and the solvent removed by vacuum distillation. Purification was effected by twice vacuum-subliming the residue from an ice bath. The two complexes were volatile, difficult-to-crystallize solids which decomposed rapidly in air and slightly even under nitrogen. Propylenetungstenpentacarbonyl is whitish in color, while the corresponding butadiene complex is pale yellow.

Anal. Calcd. for propylenetungstenpentacarbonyl: C, 26.25; H, 1.65. Found: C, 25.64; H, 1.47. Calcd. for butadienetungstenpentacarbonyl: C, 28.59; H, 1.60. Found: C, 28.40; H, 1.51.

Di-(propylene)-tungstentetracarbonyl and Di-(butadiene)-tungstentetracarbonyl.—A fresh solution of $W(CO)_6$ and propylene or butadiene in n-hexane (as described above) was irradiated for 150 min., during which time propylene or butadiene was continuously bubbled through the solution. After the irradiation was completed and the solvent removed by vacuum distillation, the impure product was vacuum-sublimed at 35°. The sublimate was then allowed to stand on the cold finger for about 2 hr.; the complex, being more volatile than the $W(CO)_6$, sublimed on the upper of the cold finger while $W(CO)_6$ remained on the bottom. The two complexes are pale yellow, oily substances and are quite unstable. This instability made analysis impractical, but solutions of the products in n-hexane showed the single sharp carbonyl stretching peak to be expected for *trans*-disubstituted complexes.

Figure 1 illustrates typical spectra observed when a solution of $W(CO)_6$ and acetylene in n-hexane is irradiated for successively longer periods of time. Panel 1 shows the spectrum of the solution before irradiation; the weaker of the two bands is probably the C^{13} analog of the more intense band, the CO stretch for $W(CO)_6$. After a short period of irradiation (panel 2) three new peaks are observed, corresponding to those predicted for the monosubstituted carbonyl. Panel 3, which illustrates a spectrum taken after further irradiation, shows a decreased $W(CO)_6$ intensity, an increase in the intensities of the peaks assigned for

(1) The first two papers in this series: (a) G. R. Dobson, M. A. El Sayed, I. W. Stolz, and R. K. Sheline, *Inorg. Chem.*, **1**, 526 (1962); (b) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *ibid.*, **2**, 323 (1963).

(2) H. C. E. Mannerskantz and G. Wilkinson, *J. Chem. Soc.*, 4455 (1962). This paper lists references to such work.

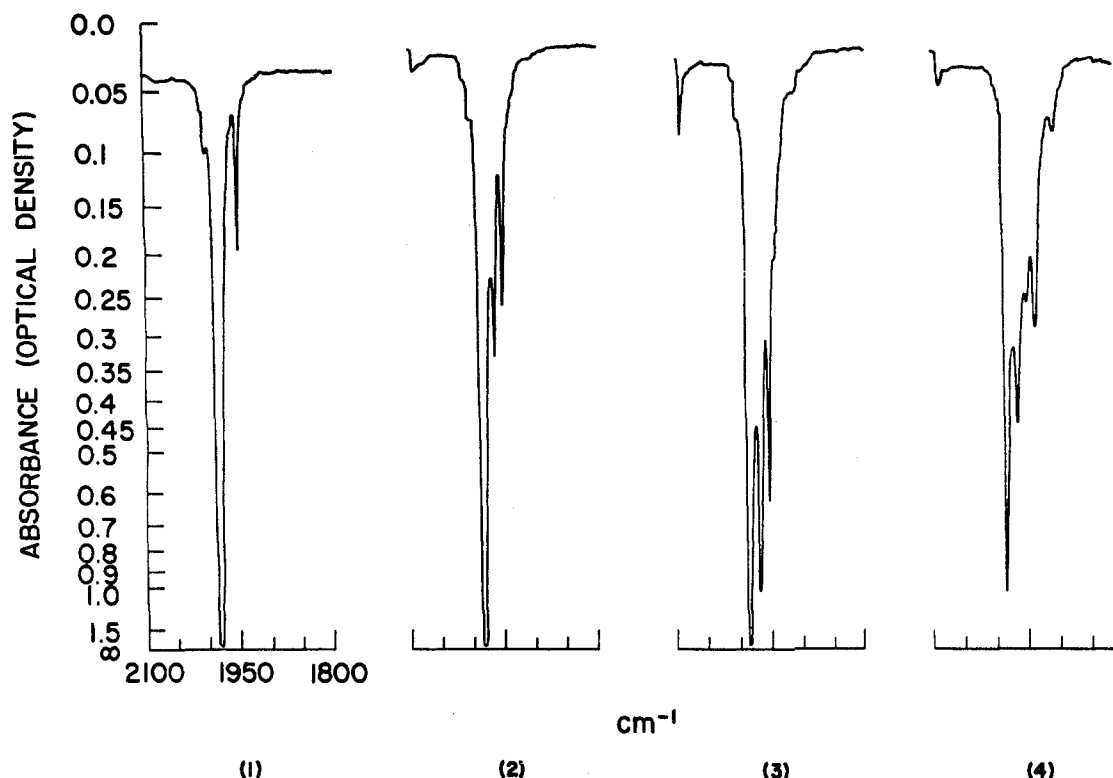(3) M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962).

Fig. 1.—Changes in the carbonyl stretching region of the infrared for $W(CO)_6$ and acetylene in *n*-hexane with different lengths of exposure to an ultraviolet source.

$W(CO)_5$(acetylene), and the presence of an unresolved shoulder at about 1930 cm.$^{-1}$. Still further irradiation (panel 4) shows the resolution of this shoulder as its intensity increases. This single peak corresponds to that predicted for the *trans* isomer of $W(CO)_4$(acetylene)$_2$. The concentrations of $W(CO)_6$ and $W(CO)_5$-(acetylene) as measured by band intensities are seen to decrease. The slight peak observed in panels 3 and 4 is of undetermined origin. Its intensity has been found, however, to be independent of the intensity of the band assigned as $W(CO)_4$(acetylene)$_2$.

Table I shows the carbonyl stretching frequencies and assignments for the various π-bonded complexes investigated by this method. The monosubstituted complexes have been arranged in order of the decreasing frequency of the A_1 band produced by the vibration of the carbonyl group *trans* to the substituent. Three additional monosubstituted complexes, with acetonitrile,[1a] ethyl ether, and acetone[1b] and for which evidence indicates that bonding is coordinate covalent, have been included for comparison. The disubstituted complexes have also been arranged in order of decreasing carbonyl stretching frequency.

The frequency of the remaining uncoordinated olefinic link in $W(CO)_5$(butadiene) was determined in a Nujol mull and was found to be at 1622 cm.$^{-1}$.

Discussion

It is generally accepted that the stability of zerovalent hexacarbonyl derivatives of alkenes and alkynes is the result of the removal from the metal atom of the negative charge supplied through interaction of the filled π-orbital of the ligand with an empty metallic d^2sp^3 hybrid orbital. This charge removal is effected through the back-donation of charge from a filled metallic d-orbital into vacant antibonding π-orbitals of the ligands. Such a mechanism produces more extensive bonding than would be expected through σ-bonding alone and results in carbonyl stretching frequencies only slightly lower than those of the parent carbonyls.

TABLE I

Complex	Carbonyl stretching frequencies, cm.$^{-1a}$		
$W(CO)_5$(butadiene)	2087 (s),	1955 (s),	1975 (ms)
$W(CO)_5$(ethylene)	2088 (w),	1953 (s),	1973 (ms)
$W(CO)_5$(propylene)	2085 (w),	1951 (s),	1966 (ms)
$W(CO)_5$(*trans*-2-butene)	2084 (w),	1947 (s),	1962 (ms)
$W(CO)_5$(*cis*-2-butene)	2083 (w),	1946 (s),	1960 (ms)
$W(CO)_5$(acetylene)	2095 (w),	1967 (s),	1952 (ms)
$W(CO)_5$(methylacetylene)	2088 (w),	1960 (s),	1944 (ms)
$W(CO)_5$(diethylacetylene)	2086 (w),	1953 (s),	1938 (ms)
$W(CO)_5$(acetonitrile)[1a]	2085 (w),	1948 (s),	1931 (ms)
$W(CO)_5$(ethyl ether)[1b]	2074 (w),	1931 (s),	1908 (ms)
$W(CO)_5$(acetone)[1b]	2067 (w),	1920 (s),	1847 (ms)
$W(CO)_4$(butadiene)$_2$		1966	
$W(CO)_4$(ethylene)$_2$		1964	
$W(CO)_4$(propylene)$_2$		1955	
$W(CO)_4$(*cis*-2-butene)$_2$		1943	
$W(CO)_4$(acetylene)$_2$		1939	
$Mo(CO)_5$(butadiene)	2087 (w),	1961 (s),	1977 (ms)
$Mo(CO)_5$(ethylene)	2087 (w),	1960 (s),	1976 (ms)
$Mo(CO)_5$(propylene)	2085 (w),	1959 (s),	1969 (ms)
$Mo(CO)_5$(acetylene)	2092 (w),	1974 (s),	1950 (ms)
$Mo(CO)_5$(methylacetylene)	2085 (w),	1963 (s),	1940 (ms)
$Mo(CO)_5$(diethylacetylene)	2079 (w),	1959 (s),	1939 (ms)
$Mo(CO)_4$(butadiene)$_2$		1965	
$Mo(CO)_4$(ethylene)$_2$		1964	
$Mo(CO)_4$(propylene)$_2$		1952	

^{a} Band intensities: w, weak; m, medium; s, strong.

These π-bonded complexes are similar in properties to the carbonyls from which they are derived; they are essentially nonpolar, volatile, and soluble in many common organic solvents.

The spectra in the carbonyl stretching region of the infrared for this type of monosubstituted complex are characteristic of the replacement of one CO group of an
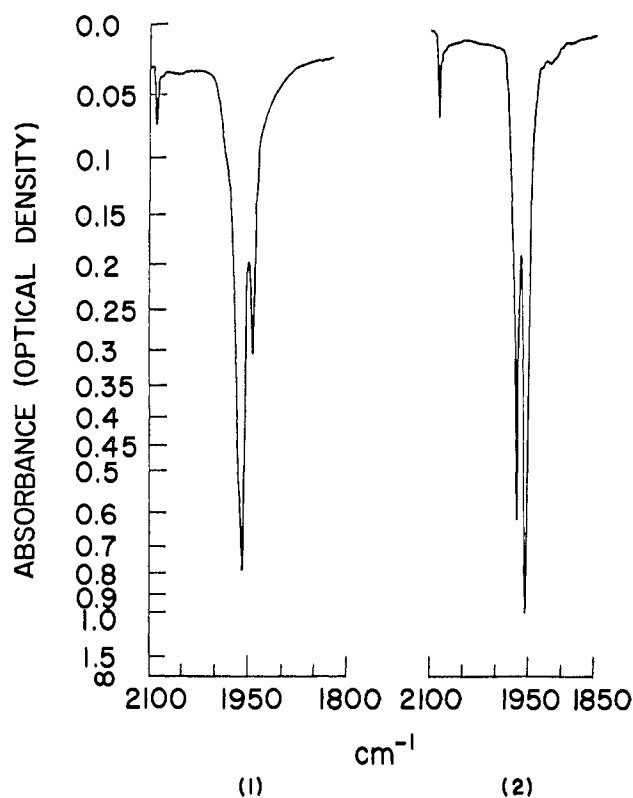
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Fig. 2.—Carbonyl stretching region of the infrared for (a) W(CO)₅(methylacetylene); (b) W(CO)₅(propylene).

octahedral complex leaving a square pyramid of carbonyls about the metal and producing a molecule of C_{4v} symmetry. Such spectra contain three carbonyl stretching bands, a strong E band, and two less intense A_1 vibrations.[4] The stronger of the two A_1 bands (A_{1a}) is produced by the vibration of the unique carbonyl group, the one *trans* to the substituent. Table I shows that this band undergoes a decrease in frequency along the series of ligands butadiene, ethylene, propylene, 2-butene, acetylene, methylacetylene, and diethylacetylene.

Such a trend may be explained in terms of the relative charge-donating power of the ligands. A ligand which possesses greater charge-donating power should, by increasing the electron density in the antibonding orbital of the *trans* carbonyl, lower the carbon–oxygen bond order and, therefore, the frequency of this vibration. A more thorough explanation is given in an earlier paper.[1b]

When a butadiene ligand replaces a carbonyl group in the metal hexacarbonyl only one site of unsaturation is involved in the bonding. It is noted, however, that the unbonded C═C stretching frequency (1622 cm.⁻¹) is intermediate to that in free butadiene (1597 cm.⁻¹) and 1-butene (1645 cm.⁻¹), implying that the conjugation is not completely destroyed upon coordination at a single site. It may be inferred, therefore, that the electron density about the metal–butadiene bond is less than that about a similar bond involving a nonconjugated ligand.

(4) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

Acetylenes should be better charge-donors than olefins because of the higher charge density about the acetylenic bond than about the olefinic link. Furthermore, inductive effects should render propylene and 2-butene better charge donors than ethylene, and methylacetylene and diethylacetylene better than acetylene itself. The stretching frequencies for the A_{1a} bands (listed in Table I) are in agreement with this order.

A further observation which tends to confirm the general order of charge-donating ability for these complexes is the increasingly polar nature of the higher complexes as one goes down the series from butadiene to diethylacetylene. The solubilities in *n*-hexane of the more highly substituted complexes regularly decrease along the series. Tetrasubstituted butadiene complexes appear to be appreciably soluble in *n*-hexane, but only the mono- and disubstituted carbonyl-containing complexes of acetylene and the mono complexes alone of methylacetylene and diethylacetylene are soluble enough in this solvent to permit observation of their infrared spectra in the carbonyl stretching region.

The A_{1b} and E bands in monosubstituted complexes are produced by the vibration of the equivalent planar carbonyl groups and are therefore affected to a different extent than is the A_{1a} band. This is illustrated in Fig. 2. Panel 1 shows the spectrum for W(CO)₅(methylacetylene) in which the A_{1a} band, of intermediate intensity, is at lower frequency than is the strongest band, E. Such a spectrum is characteristic of mono complexes in which the substituent is coordinately bonded[1b] as well as of the acetylene complexes. Panel 2 shows the spectrum of W(CO)₅(propylene) in which the two bands are reversed, with the A_{1a} band now at a higher frequency than the E band. This spectrum is characteristic of the olefin complexes which we have investigated. In going from the ethylene to the acetylene mono complex one notes a decrease in the A_{1a} frequency but increases in the frequencies of the A_{1b} and E bands. These divergent changes in frequencies result in the observed reversal of the E and A_{1a} band positions. Because of the directional nature of the hybrid metallic bonding orbital the carbonyl group *trans* to the substituent should receive the largest part of the charge donated to the metal through bond formation. Such an accumulation of charge on the *trans* CO can produce a greater mixing of this group's bonding and antibonding π-orbitals than for those of the four planar CO groups, which receive relatively little of the charge. The result of such a situation can be to lower the A_{1a} (*trans* carbonyl) stretching frequency much more than the A_{1b} and E (planar carbonyl) frequencies. Such an effect can be seen through the comparison of spectra for ligands which form coordinate covalent bonds with the metal. Acetone is presumed to be a better charge-donor than is the less polar ethyl ether, and one notes decreases of only 7 and 11 cm.⁻¹ in the A_{1b} and E bands in going from the complex W(CO)₅(ethyl ether) to W(CO)₅-(acetone) while the A_{1a} band decreases 61 cm.⁻¹ (Table I).

The acetylene ligand, as has been noted, probably

donates a greater amount of charge to the metal through the same mechanism as does ethylene. Spectroscopic data[5] show, however, that the difference in energy between the bonding and antibonding π-orbital in acetylene can be less than is this difference in ethylene. One might therefore expect greater mixing of the π-orbitals in acetylene, resulting in a greater tendency for acetylene to accept back metallic charge. Consequently, there exists the possibility that more charge may be withdrawn from about the planar carbonyls of the acetylene than was donated through bond formation while at the same time the reverse could be true with respect to the unique carbonyl. Such a hypothesis could account for the spectral changes noted in going from olefinic to acetylenic ligands.

For *trans*-disubstituted complexes one would expect a molecule of D_{4h} symmetry with one infrared-active carbonyl stretching fundamental, E_u, while *cis*-disubstitution should produce a molecule of C_{2v} symmetry with four infrared-active carbonyl stretching fundamentals.[4] Since only one band is observed for the disubstituted complexes we have investigated in this work, the *trans* configuration is highly probable. The frequencies for the single carbonyl bands decrease in order of the increased charge-donating power of the substituents in a manner similar to that observed for the A_{1a} band for the monosubstituted complexes.

Orgel[4] has pointed out that the T_{1u} band in the hexacarbonyl corresponds roughly to the E_u band for *trans*-disubstituted complexes. The frequencies observed for this latter vibration in the complexes studied are somewhat lower than that observed for the hexacarbonyl band and the ability of an olefinic or acetylenic ligand to stabilize the zero oxidation state is therefore seen to be inferior to that of the carbonyl group. This property of a ligand consequently does not appear to be the only factor directing the stereochemistry of disubstituted complexes, although it seems to be of primary importance.

The stereochemistry of complexes with ligands which can act as bidentate groups is also of interest. In the

case of butadiene the tendency of olefins to form *trans*-disubstitution complexes essentially eliminates the possibility of chelation by the first group in preference to replacement of the second carbonyl by a second ligand, but after the formation of the *trans*-$W(CO)_4$-(butadiene)$_2$ complex, each of the four remaining positions for possible substitution is equivalent, and one might expect chelation as a result of the preference for bond formation with partially conjugated bonded butadiene ligands rather than with a conjugated free ligand, the close proximity of the free ends of the bonded ligands to available substitution sites, and the entropy effect expected upon chelation. Although either chelation or attachment of a third butadiene ligand should lead to unsymmetrical trisubstitution, we cannot infer from infrared data whether the bonding involves three ligands, or two with one group chelated and one attached at one position only. However, Fischer[6] has shown that for the complex $Mo(CO)_2$-(butadiene)$_2$, both ligands are chelated. Upon lengthy irradiation, the infrared spectrum of butadiene and $Mo(CO)_6$ in *n*-hexane exhibits the bands characteristic of the $Mo(CO)_2$(butadiene)$_2$ reported by Fischer. We therefore conclude that after two butadiene ligands attach themselves *trans*, the next two replacements of carbonyl groups involve chelation of the two attached ligands at two of the remaining equivalent sites.

The spectrum in the carbonyl stretching region for the $Mo(CO)_2$(butadiene)$_2$ complex consists of two bands and is characteristic of *cis* carbonyl groups. At first glance this does not seem reasonable in light of our previous arguments and in view of the fact that the $Mo(CO)_4$(butadiene)$_2$ complex is in the *trans* form. It is not unreasonable to expect, however, that the cumulative charge-donating effect of four olefinic bonds, each slightly inferior to CO in its ability to stabilize the zero oxidation state, can produce the asymmetrical complex.

(5) F. A. Matsen in "Techniques of Organic Chemistry," W. West, Ed., Vol. IX, Interscience Publishers, Inc., New York, N. Y., 1956, p. 657.

(6) E. O. Fischer, H. P. Kogler, and P. Kuzel, *Chem. Ber.*, **93**, 3006 (1960).