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Photolysis of (Cyclopentadienyl)- and (Pentamethylcyclopentadienyl)tricarbonylhydridometal Complexes of Tungsten and Molybdenum in Dihydrogen-Containing Matrices: Evidence for Adducts of Molecular Hydrogen

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Abstract: When $HMCp(CO)_3$ and $HMCp'(CO)_3$ (M = Mo and W; Cp = η^5-C_5H_5; and Cp′ = η^5-$C_5(CH_3)_5$) are photolyzed with a low-pressure mercury lamp in dihydrogen-containing matrices, new bands appear in the carbonyl region of the infrared spectrum which are assignable to simple adducts of molecular hydrogen. These bands have been assigned to cisoid and transoid isomers of $HM(H_2)Cp(CO)_2$ and $HM(H_2)Cp'(CO)_2$. The molybdenum complexes can be shown to form from $HMoCp(CO)_2$ or $HMoCp'(CO)_2$ with radiation of $\lambda > 400$ nm. The dihydrogen complex is destroyed by using radiation of $\lambda < 400$ nm. The principal product of this latter process is $HMoCp(CO)_2$ or $HMoCp'(CO)_2$. Thus, all the steps leading to the formation of the adducts from the parent $HMoCp(CO)_3$ are reversible. The tungsten dihydrogen adducts form from $HWCp(CO)_3$ in an analogous fashion via the intermediacy of $HWCp(CO)_2$. However, the two isomers of $HW(H_2)Cp(CO)_2$ do not form $HWCp(CO)_2$ upon subsequent photolysis. Rather, a new species is formed which gives spectral data consistent with H_3WCpCO, in which the hydrogen is oxidatively added.

Recently, a great deal of attention has been paid to stable complexes of a metal and a ligand in which the ligand acts as a donor with use of electron pair that populated a ligand σ bond. The resultant three-center interaction has been labeled agostic when a carbon–hydrogen bond forms an adduct with a metal.[1] More recently, similar interactions have been characterized for dihydrogen.[2-6] Presumably, similarly configured complexes are intermediates during oxidative addition to a metal of a variety of substrates.[7] Whether a system will undergo oxidative addition depends on the energies of the newly created bonds to the metal relative to the strength of the σ bond that is broken in the ligand.[8] Thus, it is expected that a third row transition metal is more likely to oxidatively add a ligand because the new metal–ligand bond energies are almost always greater for such a metal as compared to the lighter congeners.[9] When oxidative addition is not favored, there still exists the potential for complexation. This latter type of interaction will be sensitive to crowding caused by the other ligands on the metal and by groups which are bonded to the ligating atoms.[10] Dihydrogen would appear to be ideally suited for such an arrangement, being free of additional atoms which might cause crowding. It is surprising therefore that the first complexes of this sort that were characterized were of the more encumbered carbon–hydrogen bonds. The scarcity of similar complexes of dihydrogen is due, in part, to the strengths of metal–hydrogen bonds; many attempts at forming dihydrogen adducts will result in dihydrides. Second, it is experimentally more difficult to maintain high concentrations of hydrogen to assure that a complex having temporarily lost dihydrogen will reform an adduct before the coordinatively unsaturated intermediate is scavenged.

The matrix isolation technique offers several advantages for the study of complexes of dihydrogen. Large concentrations of dihydrogen can be doped into a matrix so that every metal complex is entrapped with at least one molecule of hydrogen. Usually, the metal complex can be activated by photodissociation of a ligand. This forms an intermediate which can undergo very few types of reactions. It can react with hydrogen and with the ligand which was expelled or undergo an intramolecular transformation, leading perhaps to an unreactive product. Several complexes of hydrogen and the group 6 metal pentacarbonyls have been isolated.[2] Presuming that oxidative addition might occur for a more electron rich group 6 metal, several complexes of the general formula of $HMCp(CO)_2$ have been formed in matrices which contain dihydrogen. A portion of this work has been reported in a recent communication.[11]

Experimental Details

Matrices were formed on the cold-end of a Displex refrigerator; descriptions of the apparatus and procedures have already been published.[12] $HMoCp(CO)_3$ was prepared from $Mo(CO)_6$[13] or, alternatively, $[MoCp(CO)_3]_2$ was cracked with a sodium amalgum to give $NaMoCp(CO)_3$ which was then treated according to the former procedure. Matrices were formed by subliming the hydride at 0 °C into the flowing matrix gas mixture. Similar conditions were used by Rest to obtain good isolation as judged by the widths of infrared absorptions of the carbonyl ligands.[14] $HMoCp'(CO)_3$ was prepared from $C_7H_8Mo(CO)_3$ and $HC_5(CH_3)_5$.[15] The molecule was enriched with ^{13}CO by dissolving the

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carbon-12 isotopomer in hexane. The solution was photolyzed in a quartz vessel with a medium-pressure mercury lamp under an atmosphere of ^{13}CO. Matrices were formed by direct sublimation from the solvent-free residue. The product was also analyzed by mass spectroscopy. From this analysis, it was shown that other materials formed by the photolysis were probably not volatilized under the conditions of the matrix experiment. The most reliable measure of the extent of enrichment comes from a comparison of the relative intensity of the infrared absorptions of free carbon monoxide which was produced by photolyzing the enriched sample. $HMoCp'(CO)_3$ was sublimed at room temperature into flowing argon/hydrogen in order to form matrices with adequate isolation.

$HWCp(CO)_3$ was produced in the same manner as $HMoCp(CO)_3$.[13] A sublimation temperature of 10 °C gave matrices which appeared to be adequately dilute. $HWCp'(CO)_3$ was produced[16] from $W(CH_3CN)_3(CO)_3$[17] and $HC_5(CH_3)_5$. The complex was sublimed at 35 °C.

Infrared spectra were obtained on a Beckman 4260 infrared spectrometer. In the later phases of this research, the spectra were digitized by a Dual Systems 12-bit analog-to-digital converter and collected by a Zenith Z-100 computer. The data rate was synchronized with the spectrometer drive and, most frequently, data were obtained every 0.2 cm^{-1}. Data obtained in this fashion were summed over replicate scans in order to enhance the signal to noise. In one instance, the resultant spectrum was fit to a simulated spectrum with a curve fitting routine written by Pitha and Jones of the National Research Council of Canada. In another instance, spectra which had been converted to absorbance units were subtracted from each other. Because the spectra were taken at quite different times, the spectrometer wavelength marker was included in the data set so that absolute frequency position of the data could be ascertained.

Infrared frequencies in the carbonyl region were corrected to vacuum conditions with spectra of DCl and DBr.[18] Frequencies in that region are accurate to ± 1.0 cm^{-1}. Absorptions in other regions of the spectrum are accurate to ± 3.0 cm^{-1}.

Results and Discussion

When inert gas matrices of $HMCp(CO)_3$ are irradiated with ultraviolet light, two processes are observed, CO loss and H–M homolysis.[14] The dominant process yields $HMCp(CO)_2$ and free CO. They usually fail to recombine as long as the matrix is protected from visible or ultraviolet photons. Upon irradiation the 16 electron fragment becomes reactive, either recombining with the nearby CO or combining with nearby donor molecules such as N_2 or ethylene. Also, ultraviolet irradiation of $HMCp(CO)_3$ yields the radical products, H and $MCp(CO)_3$. These products have only been observed in CO matrices in which the CO loss process is surpressed and the reactive hydrogen atom is scavenged by CO to form HCO. The products of this latter process recombine much less efficiently than those formed by the CO loss process, presumably because the hydrogen atom is propelled out of the immediate vicinity of $MCp(CO)_3$. When $HMCp(CO)_3$ is irradiated in the presence of H_2, new bands are observed which are assigned to adducts of molecular hydrogen. The chemistry of the tungsten complexes is sufficiently different from that of molybdenum that the discussion will be broken into two parts.

$HMoCp(CO)_3$. The infrared spectra of $HMoCp(CO)_3$ (Ia) or $HMoCp'(CO)_3$ (Ib) in hydrogen-containing matrices are quite similar. For a molecule of C_s symmetry one expects three infrared allowed transitions involving the carbonyls. Two of the modes are nearly coincident; the pair appears at 1951 and 1939 cm^{-1} for $HMoCp(CO)_3$ and $HMoCp'(CO)_3$, respectively. The bands are not symmetric, suggesting that the absorption profile is the envelope of two modes. However, one cannot unambiguously assign the splitting to the presence of two fundamentals because of the possibility of site splitting in the solid state. Rest and co-workers have successfully fit the carbonyl spectrum of $HMCp(CO)_3$ in matrices using carbon-13 data, assuming the band at 1951 cm^{-1} was in fact the envelope of two fundamentals.[14] A similar result attains for the spectrum of Ib, the results of which are summarized in Table III.

Table I. Positions of the Carbonyl Bands of $HMoCp(CO)_3$ and Its Derivatives in Ar/H_2 and Ar/D_2 Matrices (in cm^{-1})

	$HMoCp(CO)_3$	$DMoCp(CO)_3$	$HMoCp'(CO)_3$	$DMoCp'(CO)_3$
I	2034.4	2033.4	2021.2	2020.6
	1950.0	1949.6	1938.7	1938.6
II (H_2)	2000.6	2000.4	1984.1	1983.9
	1930.6	1930.2	1913.2	1913.3
II (D_2)	2000.2	2000.4	1983.6	1984.4
	1928.8	1929.3	1912.0	1912.2
III (H_2)	1988.9	1988.6	1973.8	1973.6
	1921.4	1920.7	1904.2	1905.4
III (D_2)	1987.1	1988.1	1972.8	1973.3
	1919.2	1918.7	1903.7	1903.1
IV	1975.0	1973.6	1956.8	1957.4
	1895.8	1894.8	1876.3	1876.2

Table II. Positions of the Carbonyl Bands of $HWCp(CO_3)$ and Its Derivatives in Ar/H_2 and Ar/D_2 Matrices (in cm^{-1})

	$HWCp(CO)_3$	$DWCp(CO)_3$	$HWCp'(CO)_3$
V	2032.0	2032.0	2019.0
	1943.0	1943.2	1930.8
VI (H_2)	2016.7	2016.3	2003.1
	1947[a]	1947[a]	1931[a]
VI (D_2)	2016.0	2016.9	2003.4
	1947[a]	1947[a]	1931[a]
VII (H_2)	2034[a]	2034[a]	2019[a]
	1975.7	1974.8	1959.7
VII (D_2)	2032[a]	2032[a]	2019[a]
	1973.6	1972.6	1957.7
VIII (H_2)	2055.2	2054.2	2045.1
VIII (D_2)	2055.6	2055.5	2046.3
IX	1968	1967.0	1949.6
	1884.6	1884.0	1865.8

[a] Approximate position, due to near superposition of band with that of parent.

When $HMoCp(CO)_3$ or $HMoCp'(CO)_3$ is photolyzed with a low-pressure mercury lamp in the presence of H_2, two sets of new bands appear in the carbonyl region which correlate with the presence of hydrogen in the matrix. Each set consists of two bands. The frequencies are tabulated in Table I. The species which are responsible for these new absorptions shall be referred to as IIa and IIb, and IIIa and IIIb.[19] The bands due to II and III grow at approximately the same rate as a function of photolysis time and hydrogen abundance in the matrix, suggesting that they have similar compositions. When the bands due to $HMoCp(CO)_2$ become attenuated in response to exposure to the full irradiance of the Nernst glower, bands due to II and III grow in. This suggests that II and III are formed from $HMoCp(CO)_2$ and H_2. The parent molecule (I) has been referred to as a piano stool molecule; the cyclopentadienyl ring functions as the seat while the hydride and three carbonyl ligands splay out in the opposite direction as if they were legs. One can view II and III as simple substitution products of the parent, with H_2 functioning as a two-electron donor analogous to what is observed in $H_2W(CO)_3(PR_3)_2$.[4] There is the possibility of two isomers of such a compound, one with its two remaining CO ligands in a transoid orientation and the other with its ligands in a cisoid orientation. Although the bands of II and III are not completely resolved from each other, it is clear that the intensities of the two bands of II are fairly dissimilar, whereas the intensities of the two bands of III are nearly the same. Fitting the spectra with a product function of Lorentzian and Gaussian line shapes yields an estimate of the relative intensities of the two features. The ratio of intensities

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(19) Throughout this report, the species which arise from $HMCp(CO)_3$ shall be referred to with an a, whereas those species which arise from $HMCp'(CO)_3$ will be referred to with a b. The letter will be dropped when the two types of species are being referred to collectively.

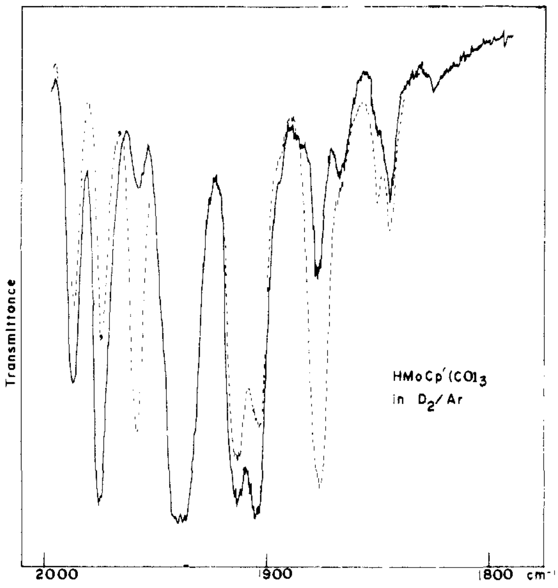

Figure 1. The solid line is the spectrum of Ib in a D_2/Ar matrix, having been photolyzed for a considerable time by a low-pressure mercury lamp. It shows considerable quantities of both IIb and IIIb. The dashed line shows the spectrum of the same matrix after 3 h of photolysis by a cobalt-glass-filtered, medium-pressure mercury lamp. The growth of bands which are due to IVb is very pronounced as is the decline of bands due to IIb and IIIb. Subsequent to the recording of the dashed spectrum, the matrix was exposed to the visible wavelengths of the medium-pressure mercury lamp. The spectrum which resulted was nearly identical with that shown with the solid line.

at maximum absorbance of the two bands of II is 1:3.0, while the ratio of the analogous features of III is 1:1.1. If the complexes are indeed $(H_2)MoHCp(CO)_2$, then one expects the carbonyl modes to result from the in-phase and out-of-phase combinations of the carbonyl stretching vibrations. The intensities of the two modes will be more nearly equal in the cisoid isomer, hence the structure of III is more likely to be cisoid. The assignment of II to a transoid geometry follows similar arguments.[20]

The assignment of the new bands which are observed in hydrogen-containing matrices to two sets was aided by observations of their behavior when the matrix was exposed to a medium-pressure mercury lamp filtered by cobalt glass. (See Figure 1.) The glass passes a broad band of ultraviolet radiation between 340 and 500 nm. The bands of both sets become attenuated, but those due to II are much more drastically affected. The principal product of this manner of photolysis is $HMoCp(CO)_2$ (IV). When the matrix is exposed to a medium-pressure mercury lamp filtered by Cl_2 and Pyrex glass, the bands of II and III are restored while the bands due to IV become attenuated. Thus, the chemistry which has been observed is consistent with the following scheme:

$$HMoCp(CO)_3 \xrightarrow{254\text{ nm}} HMoCp(CO)_2 + CO$$

$$HMoCp(CO)_2 + H_2 \xrightarrow{\text{visible light}} \textit{cis-}\text{ and }\textit{trans-}(H_2)HMoCp(CO)_2$$

$$HMoCp(CO)_2 + CO \xrightarrow{\text{visible light}} HMoCp(CO)_3$$

$$\textit{cis-}\text{ and }\textit{trans-}(H_2)HMoCp(CO)_2 \xrightarrow{350\text{ nm}} HMoCp(CO)_2 + H_2$$

Isotopically labeled $HMoCp'(CO)_3$ was used to collect additional data on the spectra of IIb and IIIb so that factored force fields could be calculated. The results of those calculations are summarized in Table III. The spectra of IIb and IIIb were chosen for fitting because there are fewer secondary photolysis products than for the simple cyclopentadienyl complexes.

Table III. Force Constants of $HMCp(CO)_3$ and Its Derivatives (mdyn/A)

	k_1[a]	k_2[b]	k_c[c]	k_t[d]
$HMoCp'(CO)_3$				
Ib	15.601	15.615	0.437	0.440
IIb	15.306			0.548
IIIb		15.169, 15.175	0.539	
IVb[e]		14.771, 14.900	0.620	
$HWCp(CO)_3$				
Va[f]	15.593	15.741	0.439	0.519
VIa	15.864			0.560
VIIa		16.279, 16.194	0.459	
VIIIa	17.062			
IXa[f]	14.945			0.670

[a] Force constant of a carbonyl group which is related to another by symmetry. [b] Force constant of the unique carbonyl group in molecules of three carbonyls. [c] Interaction force constant relating a unique carbonyl to another in the same molecule. [d] Interaction force constant relating carbonyl groups which are related by symmetry. [e] The molecule was not constrained to be of C_s symmetry. [f] Taken from ref 14.

The claim that the hydrogen is coordinated to the metal rests on indirect evidence. An analysis of the carbonyl modes of the infrared spectrum suggests that there is a more extensive interaction between the metal and dihydrogen than is the case for $H_2Cr(CO)_5$. The oxidative addition of hydrogen to molybdenum should result in considerable electron density being lost from the metal, and the positions of the carbonyl modes should shift to greater energies or, alternatively, the associated force constants should become greater.[21] There are two types of carbonyl groups in the parent molecule, Ib. The average of their associated force constant is 15.61 mdyn/A. The spectrum of the coordinatively unsaturated moiety, IVb, yields an average force constant of 14.83 mdyn/A; the smaller magnitude reflects, in part, the presence of fewer π acceptor ligands among which the metal π electrons are shared. Reaction with hydrogen yields either IIb or IIIb, the average force constants for which are 15.31 and 15.17, respectively. The force constant will reflect the charge density of the metal but will also be affected by the nature of the ligand trans to the CO. For IIb, the carbonyls are trans to each other whereas the carbonyls of IIIb are cis. Thus, one must resist claiming the interaction of II with hydrogen is stronger than the interaction of III with hydrogen. Still, the force constant of IIb for carbonyls which are approximately trans is less than those observed for Ib and, in particular, less than the force constant of Ib which is assigned to the carbonyls which are also approximately trans to each other. Also, the force constants of the carbonyls of IIIb are less than that of the unique carbonyl ligand of Ib. This evidence supports the hypothesis that hydrogen has not oxidatively added in either IIb or IIIb. The same is undoubtedly the case for IIa and IIIa. Two molecules serve to calibrate this analysis. The force constant for the carbonyls of $Fe(CO)_4$ which are approximately trans to other carbonyls is 16.15 mdyn/A;[22] when hydrogen is oxidatively added the force constants for transoid carbonyls is 17.11 mdyn/A[21] whereas the corresponding force constants for $Fe(CO)_5$ are 16.95 mdyn/A.[23] This example shows that as hydrogen oxidatively adds to iron the effect on the metal is about the same as adding CO. On the other hand, the force constant of the equatorial carbonyls of $Cr(CO)_5$ (16.21 mdyn/A)[24] is little different from the 16.32 mdyn/A[3] which attains when hydrogen is coordinated. For comparison, the carbonyl force constant of $Cr(CO)_6$ is 16.51 mdyn/A.[24]

Infrared observations have been made over the entire spectrum from 4000 to 400 cm^{-1}. (See Table 7 of supplementary material.)

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(20) If the two carbonyl modes were not interacting with other modes of the molecule, then the ratio of intensities would lead to estimates of the bond angle between the carbonyls of 120° and 93° for II and III, respectively. Such estimates are called into question when the normal modes are more complicated due to mixing of the other modes of the molecule. See, for example: Burdett, J. K. *Inorg. Chem.* **1981**, *20*, 2607–2615.

(21) Sweany, R. L.; Owens, J. W. *J. Organomet. Chem.* **1983**, *255*, 327.

(22) Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2276.

(23) Bor, G. *Inorg. Chim. Acta* **1969**, *3*, 191–195.

(24) Perutz, R. N.; Turner, J. J. *Inorg. Chem.* **1975**, *14*, 262–270.

The spectra of II and III have been incompletely characterized because large concentrations have not been obtained. This is due to inner filter effects and to the photosensitivity of II and III to the frequency of radiation being used to remove CO from the parent molecule. Detailed studies have been attempted with computer averaging in order to identify modes which derive from vibrations involving the hydrogen atoms that might support a hypothesis that hydrogen has either oxidatively added or coordinated. In particular, no bands have been identified which might be assigned to the H–H stretch of coordinated H_2, D_2, or HD.[3,4] As a measure of the quantity of material that has been observed, the totally symmetric carbonyl vibration of IIIb has reached as high as 1.4 absorbance units and the intensity of the ejected CO reached 0.4 absorbance units. Other observations of the H–H stretching mode have shown that it is weak and broad, making its observation less probable in a matrix limited by quantity. Very few of the other modes of coordinated dihydrogen have been observed except for those reported by Kubas et al.[4] They, too, are undoubtedly quite weak.

If II and III were not complexes of molecular hydrogen, then it is necessary to consider whether H_2 has oxidatively added. The most intense mode of a normal hydride is usually due to M–H deformations. These modes typically appear between 700 and 950 cm^{-1}.[25] There were no absorptions which could be assigned to either II or III which could be assigned to M–H deformation modes. By contrast, several bands of this origin have been observed for one of the tungsten complexes, VIII, with little difficulty (vide infra). The absence of any band in the region of the deformation modes and the evidence derived from the carbonyl force constants serve as a basis for the claim that dihydrogen is coordinated. To further buttress this claim, note that a band in the spectrum of $H_2Fe(CO)_4$ at 794 cm^{-1} is on the order of 10% of the most intense feature in the carbonyl region. Also, a band at 695 cm^{-1} is easily observed in the spectrum of $HCo(CO)_4$.[26] M–H stretching modes can be very weak by comparison. Not surprisingly, no bands in the positions in the vicinity of 1800 cm^{-1} could be assigned to either II or III.

If the spectral evidence for oxidative addition or complexation is incomplete then it is all the more important to assess whether the changes that are observed can be assigned to processes that involve the cyclopentadienyl rings. The fact that both cyclopentadienyl and pentamethylcyclopentadienyl complexes behave so similarly argues against extensive ring involvement in the reaction that forms II and III. Also, the fact that II and III can reversibly form IV so readily argues against the cyclopentadienyl ring playing a role. Were the ring to have become reduced, the presence of excess CO in the matrix would presumably lead to the formation of a variety of new products that could be identified by their carbonyl spectrum. The carbonyl region gives no evidence of this occurring.[27] Also, the absorptions due to ring modes of I do not undergo substantial perturbation when considerable changes are evidenced in the carbonyl region of the spectrum, and the bands become broadened. This would suggest that the spectra of the ring modes of II and III are essentially the same as for the parent. It can be argued that the ring has not been reduced or is otherwise involved in the chemistry that results in the formation of II and III.

The ability to descriminate between hydride- and deuteride-containing Ia allows the characterization of H, D_2 exchange process. The spectrum of the parent molecules have been observed in adequate concentrations so that most of its infrared spectrum has been observed. There are profound differences in the region of the spectrum from 700 to 400 cm^{-1} depending on the mass of the hydride. The affected bands are not assigned to the metal–hydrogen deformation mode which is apparently too weak to be observed even under the most favorable circumstances;[28] rather they belong to metal–carbon stretching and deformation modes which are mixed with the unobserved hydrogen coordinates. The experiment was least ambiguous when $HMoCp(CO)_3$ was photolyzed in a matrix containing 7 mol% of CO in addition to 20 mol% of D_2 and argon. After prolonged periods of photolysis, bands appear in positions expected for $DMoCp(CO)_3$. The CO was added to increase the probability that an adduct could be photochemically converted back to starting material. With larger amounts of CO present, very little adduct formation was noted and no H–D exchange was noted in Ia. With less CO present, the amount of Ia remaining in the matrix after prolonged photolysis did not allow easy analysis of the spectrum. It did appear that the bands which show substantial shifts upon deuteration were attenuated at a faster rate than bands that are unshifted by the mass of the hydrogen.

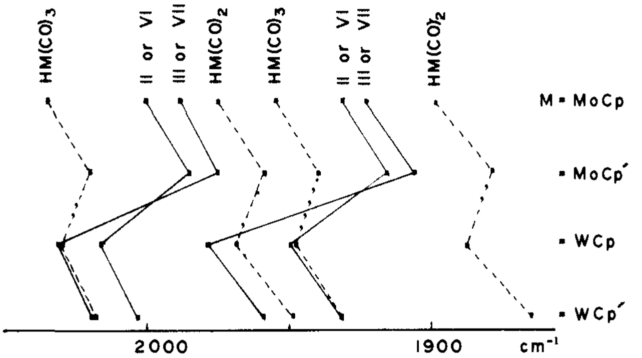

Figure 2. Plot showing the positions of the carbonyl modes of the molecules under study. Those points connected by dashed lines are of species that do not have coordinated hydrogen. II and VI are assigned to the transoid isomer of $H(H_2)MCp(CO)_2$; III and VII are assigned to the cisoid isomer. Of particular note is the dramatic blue shift exhibited by the adducts of tungsten as compared to the trends that are exhibited by the carbonyl modes of $HMCp(CO)_3$ and $HMCp(CO)_2$.

Prolonged irradiation of deposits of I gives rise to several bands in the carbonyl region which do not correlate with bands assigned to either II or III. The prolonged photolysis of Ia gives bands at 2015, 1905, 1873, and 1808 cm^{-1}. The photolysis of Ib leads to a simpler result with a principal absorption at 2000.6 and 1875.4 cm^{-1}. These modes do not appear to be M–H stretching modes because they are not drastically affected by the mass of the hydrogen. They do not become attenuated with prolonged irradiation with the Nernst glower of the spectrometer which suggests that they may belong to coordinatively saturated species. These bands may be assignable to dimers, $MoCp(CO)_3$,[14] HCO,[29] or a species like $HMoCp(H_2)_2(CO)$.

$HWCp(CO)_3$. The spectra of $HWCp(CO)_3$ (Va) and $HWCp'(CO)_3$ (Vb) are very similar to the spectra of the analogous molybdenum complexes; the bands are shifted to lower energy but the spacings and relative intensities are nearly identical. The spectra of the coordinatively unsaturated complexes $HWCp(CO)_2$, IXa and IXb, are also very similar to the analogous molybdenum species except for a red shift of the entire spectrum which is very similar in magnitude to the differences exhibited by the spectra of the molybdenum complexes I and V. The new bands which are observed as a result of interactions with hydrogen are divided into three sets. Two sets (due to species VI and VII) which are most similar to the bands due to II and III are found at higher energy than where one would expect them to occur if the product spectra were displaced from the spectra of V and IX by the same amount as the spectra of II and III are displaced from the bands of I or IV. This correlation of frequencies is diagrammed in Figure 2. The third set belonging to VIII has no obvious molybdenum analogue. Sets VI and VII both contain two bands. Fortuitous

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[25] "Stereochemistry and Steriochemical Nonrigidity in Transition Metal Hydrides": Jessen, J. P. in *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; pp 87–89.

[26] Sweany, R. L., unpublished data.

[27] As the concentration of CO is increased in the matrix, bands associated with the homolysis of the M–H bond become more prominent as might be expected.[14]

[28] Davidson, G.; Duce, D. A. *J. Organomet. Chem.* **1976**, *120*, 229–237.

[29] The position at which HCO absorbs in CO matrices is at 1860 cm^{-1}.[14] One expects a blue shift in matrices which are predominately Ar due to the lower polarizability of Ar.

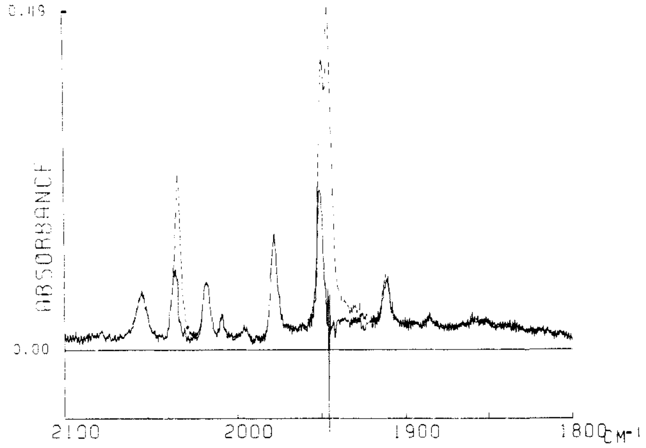

Figure 3. The dashed line spectrum shows the spectrum of Va in a H_2/Ar matrix after 1 h of photolysis by two low-pressure mercury pen lamps. The solid line spectrum shows the resultant spectrum after the spectrum of the unphotolyzed matrix was subtracted from the dashed line spectrum. This spectrum shows very clearly the band at 1947 cm^{-1} which is assigned to VIa and the band at 2034 cm^{-1} which is assigned to VIIa. The noise at 1945 cm^{-1} results from the spectrum of the unphotolyzed matrix; the band at 1945 cm^{-1} was too intense for accurate intensity measurements at its peak. The markers along the abscissa are generated by the spectrometer approximately every 50 cm^{-1} and must be corrected in order to read accurate wavenumbers off the axis.

overlapping of one band of each set with bands of the parent, V, make the gross appearance of the photolyzed matrix much simpler than that of the molybdenum complexes. Set VIII contains a single band found at 2055.2 cm^{-1}. A variety of matrices were utilized and the behavior of $HWCp'(CO)_3$ was studied in an effort to obtain well-resolved spectra of VI and VII, to no avail. Figure 3 shows an attempt at subtracting the spectrum of Va from a spectrum which resulted from the photolysis of Va. Uncharacteristically the low-frequency band of VIa is already somewhat resolved from that of the parent. The high-frequency band of VIIa has never been resolved from the spectrum of Va; its existence was first appreciated by anomolous behavior of the intensity of the envelope and when tracings were made which showed that the parent band had become wider upon photolysis with most of the additional intensity on the high energy side of the band. The computer subtractions consistently show a band has grown in on the high energy side which can be assigned to VIIa by the correlation of the envelope intensity with that of the band at 1976 cm^{-1}.

The behavior of the tungsten complexes differs considerably from that of the analogous molybdenum complexes. All three sets of bands appear in response to the ultraviolet irradiation of V. The coordinatively unsaturated complex, IX, forms as well. As with IV, exposure of the matrix to the full irradiance of the glower or to a medium-pressure mercury lamp filtered by Cl_2 and Pyrex causes an attenuation of the bands due to IX and a concomitant growth in the bands due to VI and VII. There is no evidence of the growth of the one band of VIII under these conditions. VIII has usually been noted after considerable amounts of VI and VII have formed and requires the use of photons with $\lambda < 400$ nm. This suggests that VIII is a secondary photolysis product. The use of a cobalt-glass filter with a medium-pressure lamp results in the attenuation of bands due to VII and a concomitant growth in the bands due to VI. Very little of the coordinatively unsaturated IX is formed under these conditions, which is contrary to the experience with the analogous molybdenum complexes as shown in Figure 1. In addition to the bands of VI, the band of VIII also becomes more intense as a result of this cobalt-filtered irradiation. The bands of the parent are not much affected, although precise measurements are impossible because of the superposition of both bands of the parent with bands of VI and VII. Thus, it appears that all the changes which are observed in the matrix are essentially irreversible as summarized in the following scheme:

$$HWCp(CO)_3 \xrightarrow{254\ \text{nm}} HWCp(CO)_2 + CO$$

$$HWCp(CO)_2 + H_2 \xrightarrow{\text{visible light}} cis\text{-and } trans\text{-}(H_2)HWCp(CO)_2$$

$$HWCp(CO)_2 + CO \xrightarrow{\text{visible light}} HWCp(CO)_3$$

$$cis\text{- and } trans\text{-}(H_2)HWCp(CO)_2 \xrightarrow{350\ \text{nm}} H_3WCpCO + CO$$

A sample of Va was enriched with ^{13}CO to approximately 50% as determined by the intensities of the photodissociated CO in the matrix. Although superposition continued to be a problem, several bands could be assigned to VIa and VIIa which allowed a factored force field fit of the spectrum. Because VI grew in response to the cobalt-glass-filtered irradiation, it was presumed that VI was a substitution product of overall trans configuration, by analogy with the molybdenum complex. The calculation successfully fit all the assigned bands and predicted no absorptions in positions where observations of bands assignable to VI ought to be possible. A similar calculation was attempted for the spectrum of VII, assuming an overall cisoid geometry. Again, a successful fit was obtained as judged by the goodness of fit of those bands which were assigned to VII and by the absence of bands which were predicted but not observed. The degree to which the band at 2032 cm^{-1} overlaps an absorption of the parent makes it nearly impossible to estimate the intensity ratio of the two bands which are observed for the all ^{12}C isotopomer. The bands of VIa show considerable differences in their intensity in the computer-generated spectrum of Figure 3, supportive of an assignment of an overall transoid geometry. The bands due to VIIa were more dissimilar, as was the case for III.

The spectrum of VIII contains a single absorption. A species with a single CO ligand is consistent with this observation. The ^{13}C-enriched isotopomer also contains a single band at 2008.1 cm^{-1}. This observation was made following extensive photolysis during which the spectra of V, VI, VII, and IX were substantially attenuated, so that there is little likelihood that other absorptions of VIII were hidden from view by other species. The position of the isotopomer band and the fact that only one band was observed suggest that VIII contains only one molecule of CO. A number of filters were used in attempting to convert VIII into another species to aid in its identification. Photolyses of Va gave rise to an absorption at still higher energy, at 2105 cm^{-1}. This species may originate from transformations of VIIIa because it, too, becomes most pronounced after prolonged photolyses of Va. However, no corresponding behavior was noted for Vb. It is unlikely that VIII requires more than one H_2. The yield of VIII relative to the yield of either VI or VII was not grossly changed as a function of the concentrations of H_2. Attempts to form VIII with only 10 mol% of H_2 produced very little VIII, but very little of VI or VII was produced either. Thus, it is attractive to claim that VIII results from the interaction of only one H_2 molecule and VIII would be H_3WCpCO. If the cyclopentadienyl ring is unaffected, then the complex is coordinatively unsaturated, in spite of its being trapped in a cage which undoubtedly still contains CO. The band at 2105 cm^{-1} might then be $H_3WCp(CO)_2$ which forms reluctantly because of crowding and electronic changes caused by the hydrogen having oxidatively added (vide infra).

The carbonyl force constant derived from the spectrum of VIIIa is 17.06 mdyn/A, which is considerably larger than any of those of Va or of any other of the derivatives that have been observed in this study. This complex must be considered a normal hydride. The additional evidence which makes this claim reasonable is the observation of several reasonably intense bands assignable to M–H deformation modes. In contrast to VI and VII, bands are observed at 905, 863, and 738 cm^{-1} which are assignable to VIII. The most intense of these bands is approximately 10% of the intensity of the band at 2055 cm^{-1}. These bands are not observed for the isotopomer, $D_3WCp(CO)$. Rather a band at 554 cm^{-1} is clearly evident among the bands that are normally found in that region. Because of its intensity it is presumed to correlate with the band at 738 cm^{-1}. Because of mixing with other modes of the deuterated molecule, it is not surprising that the isotopic shift does not conform to a simple prediction of 539 cm^{-1}.

Since bands of both VI and VII grow in when bands of IX decline, it is reasonable to assign stoichiometries of $H_3WCp(CO)_2$ to both. The force constants of both isomers are larger than the force constants of the carbonyls of the parent molecule which are approximately trans and considerably larger than the force constant for the coordinatively unsaturated IX. Taken by themselves, this evidence might argue for the dihydrogen of both VI and VII as having oxidatively added. Yet, no features have been observed that can be assigned to the metal–hydrogen deformation coordinates. If the absence of bands in the region of 950–700 cm^{-1} can be the basis for a claim of coordination, then VI and VII as well as II and III must be claimed to be complexes of hydrogen in spite of the considerable perturbation in the carbonyl region. It must be added in the context of this argument that the parent molecules, I and V, do not give evidence of a band in this region which is thought to give such good evidence of a normal hydride. The reason for this is not well understood. The presence of three hydride atoms will give rise to a number of combinations of M–H wagging valence coordinates, one of which ought to show the intensity which is more normal. Yet, not one band in that region is assigned to II, III, VI, or VII.

What has been shown in these experiments is that the interaction of hydrogen with both tungsten and molybdenum is stronger than that for the corresponding interactions of the pentacarbonyls, based on the carbonyl modes. This may indeed be due to the increased electron richness of the metal in the cyclopentadienyl derivatives. A similar conclusion is supported by a comparison of the H–H stretch of $(H_2)W(CO)_5$[30] and its bisphosphine derivative.[4] The more electron donating pentamethylcyclopentadienyl group did not result in observable changes in the observed chemistry, however. Consistent with these ideas is the observation that VI and VII must loose an electron-withdrawing carbonyl group before hydrogen oxidatively adds. That molybdenum should fail to oxidatively add hydrogen while tungsten eventually succeeds can be rationalized by realizing that W–H bonds are likely to be stronger than Mo–H bonds. The observation of H–D exchange between D_2 and Ia might suggest that deuterium actually becomes oxidatively added during the various photoexcitations, which affords an adduct and then ejects coordinated HD. However, the possibility that coordinated H_2 and the normal hydride form a three-center transition state, coordinated H_3^-, cannot be excluded. The same ambiguity remains in the exchange reactions which have been observed by NMR.[5,6]

Research is being initiated to determine the stability of these new adducts of hydrogen under ambient conditions. Although it might be argued that they represent metastable states which are prevented from exhibiting oxidative addition due to the very cold temperatures, one must bear in mind that adducts are formed via photoexcitation with photon energies of considerable magnitude. Because the activation barriers of many oxidative addition reactions of hydrogen have been found to be quite small, it is also reasonable to expect that oxidative addition would have occurred once hydrogen was present at the metal which was also photoexcited. This has been the experience with $Fe(CO)_4$[31] as well as several well documented reactions of metal atoms with hydrogen.[32] The synthesis of several complexes of molecular hydrogen which are stable at room temperature by other workers makes the expectation that these complexes are thermodynamically more stable than the oxidized isomers more plausible.

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Registry No. Ia, 12176-06-6; Ib, 78003-92-6; IIa, 104293-14-3; IIb, 104293-15-4; IIIa, 104371-28-0; IIIb, 104371-29-1; IVa, 85150-17-0; IVb, 104293-16-5; Va, 12128-26-6; Vb, 32839-62-6; VIa, 104293-17-6; VIb, 104293-18-7; VIIa, 104371-30-4; VIIb, 104371-31-5; VIIIa, 104293-19-8; VIIIb, 104322-97-6; IXa, 85150-18-1; IXb, 104293-20-1; $DMoCp(CO)_3$, 79359-05-0; $DMoCp'(CO)_3$, 104293-21-2; $DWCp(CO)_3$, 65915-50-6.

Supplementary Material Available: A listing of band positions of the parent molecules in the region of 1600–400 cm^{-1} and a comparison of observed and calculated positions of the carbonyl modes of Ib, IIb, IIIb, IVb, VIa, and VIIa (5 pages). Ordering information is given on any current masthead page.

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