

# Photolysis of Hexacarbonylchromium in Hydrogen-Containing Matrices: Evidence of Simple Adducts of Molecular Hydrogen

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**Abstract:** When dihydrogen-containing matrices of  $\text{Cr}(\text{CO})_6$  are photolyzed, the infrared spectrum gives evidence of three species, the spectra of which correlate with the amount of hydrogen in the matrix and duration of the photolysis. The formulations of these species which are most in accord with the data has the hydrogen molecule coordinated on the metal as a simple ligand. The species are  $\text{Cr}(\text{CO})_5\text{H}_2$ ,  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$ , and  $\text{Cr}(\text{CO})_4\text{H}_2$ . The hydrogen is successfully removed from  $\text{Cr}(\text{CO})_5\text{H}_2$  by irradiation at 364 nm. There is no evidence that CO is ever lost from  $\text{Cr}(\text{CO})_5\text{H}_2$  with 364 nm or longer wavelength radiation. Thus,  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$  probably forms from the reaction of  $\text{Cr}(\text{CO})_4$  and two hydrogen molecules.

The reactions of hydrogen with metal-containing complexes require that the complexes be coordinatively unsaturated at the metal. Except for the  $d^8$  transition-metal complexes, these coordinatively unsaturated complexes are usually very short lived in fluid media.<sup>1</sup> Many of them have been well characterized in inert gas matrices because of their increased lifetimes.<sup>2</sup> When hydrogen is doped into these otherwise inert environments, it has been observed to oxidatively add to a variety of metals, both naked and complexed.<sup>3,4</sup> A photon is frequently required for reaction, although there is some evidence for thermal reactions as well.<sup>4</sup> It should not be surprising that activation energies of oxidative addition are frequently low, because reaction with hydrogen is often observed even for very short lived species in fluid media.<sup>5</sup> Also, the reaction is analogous to the rapid chemisorption of hydrogen on metal surfaces.<sup>6</sup> The oxidative addition of hydrogen to metals has been treated by numerous theoretical investigations, the conclusions of which are in general accord.<sup>7,8</sup> The hydrogen acts as a  $\sigma$  donor using its bonding electrons at the same time as it accepts metal electron density back into the  $\sigma^*$  orbital. These interactions are usually involved in a process which leads to the disruption of the H-H bond as two new M-H bonds are formed. These same interactions can also lead to the formation of a complex in which the hydrogen acts as a  $\pi$ -acid ligand in the same fashion as ethylene or CO.<sup>8,9</sup> The existence of such a mode of bonding has only recently been reported. In addition to the work that appears herein,<sup>10</sup> Kubas et al. have reported the existence

of dihydrogen complexes of bis(phosphine)tungsten and -molybdenum  $16 e^-$  systems.<sup>11</sup>

Dihydrogen can be thought of as a prototypical  $\sigma$ -bonded species and thus serves, in a very restricted sense, as a model for the interaction of a metal with other fairly nonpolar  $\sigma$  bonds. The analogy between C-H bonds and the H-H bond has been developed by several theoretical studies.<sup>8</sup> Oxidative addition of C-H bonds to metals has been frequently reported<sup>12</sup> while the existence of coordinated C-H has only recently been realized.<sup>13</sup> Because hydrogen is free of the steric restraints of many other oxidatively adding molecules, hydrogen is uniquely reactive.

## Experimental Section

$\text{Cr}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_6$ , and  $\text{W}(\text{CO})_6$  were obtained from several vendors, stored cold, and used without further purification. Because they were added to the matrix by a low-temperature sublimation, they are undoubtedly purified in the process of forming a matrix. Argon and hydrogen were obtained from Airco and were greater than 99.99% and 99.5% pure, respectively.  $\text{D}_2$  was obtained from Matheson and was 99.5% free of impurities. HD was obtained from Merck or synthesized by the reaction of  $\text{CaH}_2$  and dilute  $\text{D}_3\text{PO}_4$ . The latter preparation gave mixtures of  $\text{D}_2$  and HD which were characterized by mass spectrometry.

Spectra were taken of deposits of  $\text{H}_2$ , HD, or  $\text{D}_2/\text{Ar}$  (up to 30 mol %) which were cocondensed with  $\text{M}(\text{CO})_6$  from an evaporation source which has been previously described.<sup>14</sup> The  $\text{M}(\text{CO})_6$  was introduced into the gas mixture by slow sublimation at approximately  $-35^\circ\text{C}$ . The gas mixture was introduced through a needle valve which was calibrated with pure argon at approximately 3 mmol/h. The flow rate was not calibrated for the  $\text{H}_2$  mixture. The matrices were deposited on KBr or NaCl plates which were held in an OFHC holder that was machined from a single piece which maximizes the contact between the crystal and metal surfaces. The holder was cooled with either an Air Products LT-3-110 liquid helium cooled refrigerator or a Displex closed cycle refrigerator. While the deposits were being made the cryostat was usually isolated from the vacuum pumps to guarantee that none of the hydrogen was pumped out of the system. In order to successfully trap such large concentrations of  $\text{H}_2$  in the matrix, the liquid helium flow rate was set to between 1.5 and 2 L/h. The temperature was constantly monitored at a point just above where the sample was mounted. If the temperature rose to 10 K due to thermal grounding, the system was temporarily opened to a diffusion pump to prevent thermal grounding. Once the  $\text{H}_2$  pressure was adequately reduced, the system could again be sealed. When the cold end is not thermally loaded by a depositing matrix, the hydrogen remains trapped in the matrix until the temperature exceeds approximately 20 K. More recent experiments made use of a Displex refrigerator which, surprisingly, were rarely troubled by thermal grounding due to hydrogen pressure.

In order to conserve time, photolyses were occasionally begun while a new matrix was still being formed. Usually, the deposit was begun

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without photolysis until it was certain that an adequate rate of sublimation had been achieved. The bath temperature which controls the rate of sublimation was monitored during the formation of a deposit with a thermocouple and was kept within 5 °C of the desired temperature. Photolyses were effected by using either a low-pressure mercury pen lamp (Hammamatsu Corp.) or a 175-W medium-pressure mercury lamp adapted from an overhead light. The ultraviolet absorbing shroud was cut away to expose the 4 cm long lamp. Its irradiance was focused by using a large parabolic mirror of approximately 30 cm focal length. The silver surface absorbs some ultraviolet radiation in the region of 300 nm.<sup>15</sup> The output of the lamp was occasionally filtered through 5 cm of chlorine, glass, or cobalt glass. The latter filter is opaque in the blue portion of the visible spectrum but becomes transmitting at 350 nm.

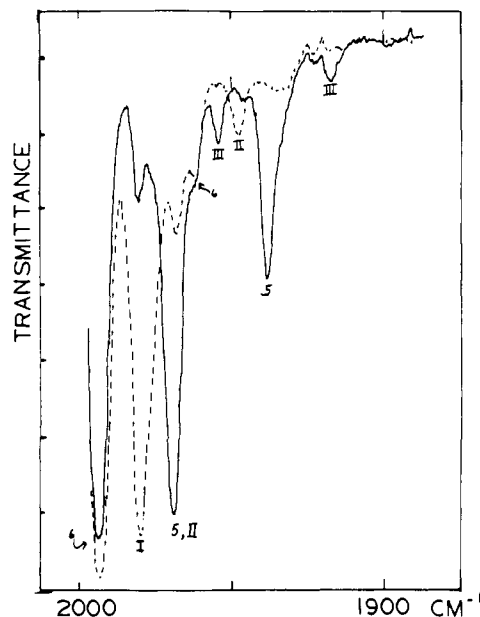
Infrared spectra were measured on a Beckman 4260 infrared spectrometer from 4000 to 400  $\text{cm}^{-1}$ . An argon-filled gas cell of nearly the same path length as the cryostat was placed in the reference beam for most spectra so that the reference beam would not traverse more atmosphere than the sample beam. This technique proved to be only marginally successful. A more elaborate purge system was installed for some of the last experiments which are herein reported. Ultraviolet, visible, and near-infrared spectra were obtained with a Cary 17. ESR spectra were obtained with a Varian E3 spectrometer, using the Displex refrigerator configured as previously described.<sup>14</sup>

Energy factored force fields were calculated<sup>16</sup> by using the carbonyl modes of adducts formed from natural abundance  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_6$  that had 6, 13, and 26%  $^{13}\text{C}$  incorporation, as determined by mass spectrometry. Frequencies are accurate to  $\pm 1 \text{ cm}^{-1}$ , except for bands which are not clearly resolved of other features. These latter bands were not treated with the same weight in the calculation of a force field.

## Results and Discussion

Upon ultraviolet photolysis, matrices of  $\text{Cr}(\text{CO})_6$  yield a variety of coordinatively unsaturated chromium species.<sup>17–20</sup> The fragments are never far removed from the ejected CO molecules, and recombination is usually effected by irradiation in the absorption spectrum of the metal-containing fragment.<sup>20</sup> When molecular hydrogen is doped into an argon matrix, the photolysis of  $\text{Cr}(\text{CO})_6$  yields new bands. The most prominent band appears at 1978  $\text{cm}^{-1}$ , the intensity of which correlates with weaker bands at 2096  $\text{cm}^{-1}$  and 364 nm (see Table I). The species which is associated with these bands is designated species I and is believed to be  $\text{Cr}(\text{CO})_5\text{H}_2$  in which the hydrogen molecule is coordinated as a unit. In addition, a species is formed which gives infrared bands at 2068, 1965, and 1945  $\text{cm}^{-1}$  which is designated species II. This species is assigned the formula *cis*- $\text{Cr}(\text{CO})_4(\text{H}_2)_2$ . Finally, weak features of a third species (species III) are observed at 1914 and 1951  $\text{cm}^{-1}$ . This species may well be the coordinatively unsaturated  $\text{Cr}(\text{CO})_4\text{H}_2$ .

The most prominent bands of all sets are the bands at 1978 and 1945  $\text{cm}^{-1}$ . These bands correlate with the amount of hydrogen in a manner that suggests that they are due to species which involve hydrogen in some fashion. Unique to this sort of matrix isolation study, a matrix can be constructed with hydrogen and then warmed so that the hydrogen evaporates out. If an impurity were causing intensity at 1978 and 1945  $\text{cm}^{-1}$ , then the impurity would undoubtedly remain while the hydrogen was evaporated out. Little to no intensity was noted at those positions of the spectrum when  $\text{Cr}(\text{CO})_6$  was photolyzed in a matrix out of which the hydrogen had been evaporated prior to photolysis. Also, the spectra assigned to the three species do not correspond to the spectrum of other well-characterized adducts of  $\text{Cr}(\text{CO})_x$  or to the homoleptic carbonyl species themselves. In this list of failed comparisons are  $\text{Cr}(\text{CO})_5$ ,<sup>18</sup>  $\text{Cr}(\text{CO})_4$ ,  $\text{Cr}(\text{CO})_3$ ,<sup>19</sup>  $\text{Cr}(\text{CO})_5\text{N}_2$ ,<sup>21</sup>



**Figure 1.** (a, solid line) Spectrum of an argon matrix of  $\text{Cr}(\text{CO})_6$  and  $\text{H}_2$  after irradiation with an unfiltered medium-pressure lamp followed by irradiation by the same lamp through a cobalt glass filter. The labels refer to bands assigned to the following: I,  $\text{Cr}(\text{CO})_5\text{H}_2$ ; II,  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$ ; III,  $\text{Cr}(\text{CO})_4\text{H}_2$ ; 6,  $\text{Cr}(\text{CO})_6$ ; 5,  $\text{Cr}(\text{CO})_5$ . These data were taken with use of a Displex refrigerator. (b, dashed line) Spectrum after the same matrix was irradiated with the visible light of the Nernst glower for 90 min.

and  $\text{Cr}(\text{CO})_5\text{H}_2\text{O}$ .<sup>22</sup> Although there are no reports of matrix  $\text{CO}_2$ -chromium carbonyl adducts, the new sets of bands do not correlate with the small impurity band due to atmospheric  $\text{CO}_2$ . The species are thus formulated as  $\text{Cr}(\text{CO})_n\text{H}_m$ . Consistent with this formulation, the extent of growth and the rapidity of growth of the bands at 1978 and 1945  $\text{cm}^{-1}$  increases as the proportion of hydrogen is increased in the gas mixture.

**The Stoichiometry of Species I, II, and III.** Species I appears to arise from the interaction of  $\text{Cr}(\text{CO})_5$  and  $\text{H}_2$ . This is best illustrated by referring to Figure 1. The solid-lined spectrum is of a matrix which had been prepared by irradiating first with broad-band ultraviolet radiation followed by irradiation into the absorption feature of species I at 364 nm. The result of the first unfiltered irradiation is the appearance of bands assigned to species I, II, and III as well as bands due to  $\text{Cr}(\text{CO})_5$  and  $\text{Cr}(\text{CO})_4$ . The cobalt glass filtered photolysis causes the spectrum to be dominated by the features due to  $\text{Cr}(\text{CO})_5$  (Figure 1a). The matrix was then exposed to the unfiltered output of the Nernst glower for 90 min. The spectrum of  $\text{Cr}(\text{CO})_5$  nearly vanishes (Figure 1b). Concomitantly, there is dramatic growth of bands assigned to species I. The much weaker bands of species III are also lost, and there is growth in bands of species II and  $\text{Cr}(\text{CO})_6$ . The action of visible radiation on  $\text{Cr}(\text{CO})_5$  is thought to cause disruption of weak interactions with a coordinated matrix molecule and pseudorotation of  $\text{Cr}(\text{CO})_5$ .<sup>20</sup> This results in reaction with a dopant of the matrix cage whenever the rotation leaves the vacant coordination site of  $\text{Cr}(\text{CO})_5$  adjacent to the dopant. Thereby,  $\text{Cr}(\text{CO})_5$  is thought to form  $\text{Cr}(\text{CO})_6$ , and species I may form by an analogous process. It is interesting to note that warming a matrix containing hydrogen and large quantities of  $\text{Cr}(\text{CO})_5$  does not result in the formation of species I even though the hydrogen has become sufficiently mobile as to evaporate out of the matrix. The photobleaching must both disrupt the Ar-Cr interaction as well as rotate the  $\text{Cr}(\text{CO})_5$ . Although the photon energy which  $\text{Cr}(\text{CO})_5$  absorbs is sufficient to break a M-CO bond of at least 37 kcal/mol,<sup>23</sup> it appears that CO loss does not result from visible irradiation of

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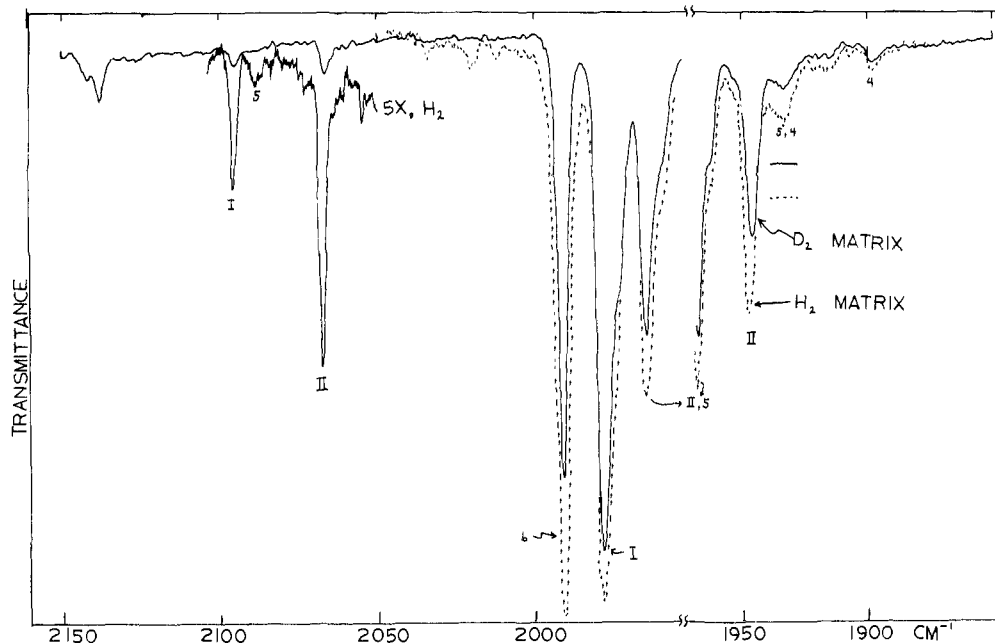
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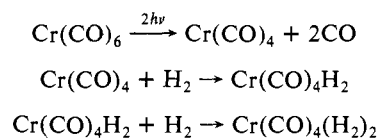
**Figure 2.** The spectrum of an argon matrix of  $\text{Cr}(\text{CO})_6$  with  $\text{D}_2$  (solid line spectrum) and  $\text{H}_2$  (dashed line spectrum plus inset) after photolysis with a medium pressure mercury lamp and the visible light of the Nernst glower of the spectrometer. These data were taken with liquid helium cooling. The prominence of the bands due to species II should be compared with those of Figure 1. Horizontal lines at  $1935\text{ cm}^{-1}$  mark the expected intensity if the band at  $1965\text{ cm}^{-1}$  were due to  $\text{Cr}(\text{CO})_5$ , alone. The band at  $1965\text{ cm}^{-1}$  was scanned with both grating orders and appears duplicated in the tracing. The features at  $2140\text{ cm}^{-1}$  are due to CO.

$\text{Cr}(\text{CO})_5$ . Thus, species I forms from the association of hydrogen with  $\text{Cr}(\text{CO})_5$ .

It is attractive to formulate species I as  $\text{Cr}(\text{CO})_5\text{H}_2$  from the evidence of the aforementioned experiment. Other data are also consistent with such a formulation. The band at  $1978\text{ cm}^{-1}$  appears early during the photolysis of  $\text{Cr}(\text{CO})_6$  as one would expect from a process that proceeds stepwise in the removal of CO from the hexacarbonyl.<sup>24</sup> Species I behaves as if it is coordinatively saturated because the spectrum of species I is quite prominent even when 5% of the matrix is CO. If species I were coordinatively unsaturated, the excess CO should cause such a species to add CO and become saturated. Also, the visible and ultraviolet spectrum of species I is clear of absorptions to the red of the band at  $364\text{ nm}$ . This is clear both from an analysis of the actual spectrum as well as from the absence of any photochemistry leading to the destruction of species I due to chlorine/soda-lime glass filtered irradiation by a medium pressure mercury lamp or by prolonged irradiation by the Nernst glower of the infrared spectrometer. Perutz and Turner have characterized  $\text{Cr}(\text{CO})_5$  in a number of environments. When the sixth coordination site is occupied by a group which might be expected to be bonded, the optical transition of  $\text{Cr}(\text{CO})_5$  is shifted toward the ultraviolet. Thus,  $\text{H}_3\text{NCr}(\text{CO})_5$  absorbs at  $420\text{ nm}$  in argon matrices<sup>18</sup> and  $\text{N}_2\text{Cr}(\text{CO})_5$  absorbs at  $364\text{ nm}$ ,<sup>21</sup> whereas  $\text{ArCr}(\text{CO})_5$  absorbs at  $533\text{ nm}$ .<sup>18</sup> To summarize, species I is thought to be  $\text{H}_2\text{Cr}(\text{CO})_5$  because it forms early in the photolysis of  $\text{Cr}(\text{CO})_6$ , its appearance correlates with the decline of  $\text{Cr}(\text{CO})_5$ , and it does not appear to be coordinatively unsaturated.

The bands assigned to species II behave very similarly to those of species I. For example, they are first noted on ultraviolet photolysis of  $\text{Cr}(\text{CO})_6$ . They too grow in as the ultraviolet photolyzed matrix is irradiated with visible light. They become attenuated as a result of cobalt glass filtered irradiation by a medium-pressure mercury lamp and are not photobleached by visible radiation. Their behavior is differentiated from those of species I in the following manner. Their intensity becomes more pronounced relative to those of species I as a function of ultraviolet irradiation time. Also, they become more pronounced, relative to those of species I, as the amount of hydrogen in a matrix is

increased. These observations are consistent with a species that requires the loss of more than one carbonyl and the uptake of at least two hydrogen molecules. The behavior of the bands is best described by assuming that species II is  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$  and is formed by the following sequence.



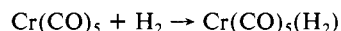
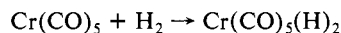
Although I claim that the relative yield of species II is sensitive to the amount of hydrogen in the matrix, the observations made with use of the two refrigeration systems show apparent contradictions of these assertions. Matrices cooled by liquid helium with 10 mol % of hydrogen produce as much as or more of species II as matrices containing 20 mol % of hydrogen that are cooled by the Displex refrigerator. This contradiction is resolved if one assumes that the matrix does not contain the same mixing ratio of hydrogen and argon as are present in the gases used to form the matrix. Because hydrogen is such a volatile molecule, it can preferentially seek out the coldest surface. The Displex was capable of achieving 8 K at the site to which the sample holder was attached. With use of liquid helium and the same sample holder, temperatures approaching 4.2 K were attainable. The high thermal conductivity of the OFHC sample holder guarantees that it will be colder than the crystal substrate of the matrix, especially under the conditions of high thermal loads when a matrix is being deposited. Thus, if hydrogen does not stick on its first impact, there is a good chance that it will redeposit on the sample holder or other cold metal surfaces. The probability of this increases as the temperature increases. When liquid was used as a coolant, it was noted that a slight increase in temperature caused a rapid increase of pressure in the refrigerator which occasionally aborted an experiment. It was surprising that the warmer Displex system was not similarly affected. This suggests that the excess hydrogen which was so easily vented during a liquid helium cooled deposit was being volatilized on a continuing basis at the higher temperatures of the Displex. Thus, the experiments using the two cooling methods are not directly comparable because the mixing ratio of hydrogen in the matrix may be quite different even with similar starting gas mixtures.

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Figure 2 shows the spectra of two matrices which were formed with liquid helium cooling. The spectrum of species II is prominent. The spectra of Figure 1 were of a matrix which was cooled by the Displex refrigerator. The spectrum of the matrix showed far less intensity for the bands of species II just prior to the cobalt-glass filtered photolysis than what is exhibited in Figure 2. With use of the Displex refrigerator, matrices with from 5 to as much as 27 mol % H<sub>2</sub> have been studied. Those matrices with the highest nominal hydrogen concentration show the largest amounts of species II, relative to the amounts of species I. These data by themselves suggest that species II forms with more than one hydrogen molecule. To summarize, the data obtained with liquid helium need not be taken as contradictory, even though a great deal of species II forms for there being only 10 mol % hydrogen present. Species II is probably coordinatively saturated because it does not absorb in the visible. It does not form in the presence of 5% CO, but this inability probably only reflects the difficulty in producing Cr(CO)<sub>4</sub> in such an environment.

The bands of species III have never been observed to be very intense. The species behaves as if it is coordinatively unsaturated because the bands become attenuated as the matrix is irradiated by the full output of the glower or visible radiation from the medium-pressure mercury lamp. Because the bands do not belong to any known species of the formula Cr(CO)<sub>x</sub>, they probably belong to a species which has incorporated H<sub>2</sub>. The loss of hydrogen from species II is presumed to be the source of species III. When there is no detectable species II present, cobalt glass filtered photolysis yields no species III. If species II is correctly formulated, then a species of Cr(CO)<sub>4</sub>H<sub>2</sub> stoichiometry makes intuitive sense.<sup>25</sup> The yield of Cr(CO)<sub>4</sub> is increased in photolyses in xenon and methane matrices.<sup>19</sup> In the presence of H<sub>2</sub>, photolysis in these matrices gave smaller amounts of Cr(CO)<sub>5</sub>H<sub>2</sub>. In xenon, bands due to Cr(CO)<sub>5</sub> and Cr(CO)<sub>4</sub> were not resolved from the most intense band of Cr(CO)<sub>4</sub>(H<sub>2</sub>)<sub>2</sub>. In methane, the conversion of Cr(CO)<sub>5</sub> to either Cr(CO)<sub>5</sub>H<sub>2</sub> or Cr(CO)<sub>4</sub>(H<sub>2</sub>)<sub>x</sub>, x = 1 or 2, was very inefficient, so those experiments were not developed past the exploratory stages. These experiments also imply that no photon of >360 nm causes CO loss from H<sub>2</sub>Cr(CO)<sub>5</sub>. At 360 nm H<sub>2</sub> is lost instead. At still shorter wavelengths species II is observed to form, but such processes can undoubtedly occur via CO loss from Cr(CO)<sub>5</sub>.

**Structure and Bonding.** The following equations summarize how the reaction of H<sub>2</sub> and Cr(CO)<sub>5</sub> might be described.



In the first instance, hydrogen is oxidatively added to chromium, forming a legitimate dihydride. In the second instance, hydrogen is coordinated with its H-H bond intact, perhaps in an η<sup>2</sup> fashion similar to the well-characterized H<sub>2</sub>W(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>.<sup>11</sup> Finally, an oxidative addition reaction is postulated in which the H-H bond is cleaved, yielding a hydrogen atom.<sup>26</sup> The second formulation is preferred for the following reasons.

(1) No ESR signal is detected for the hydrogen atom which results from the third process.

(2) A hydride product would presumably give fairly intense M-H bending modes between 900 and 700 cm<sup>-1</sup>.<sup>27</sup> No such absorption is observed. The M-H stretching vibrations are fre-

quently quite weak, and their absence cannot be treated as negative evidence.

(3) Were oxidative addition to occur, the hydrogen would withdraw electron density from the chromium and this should result in a blue shift of the carbonyl modes.<sup>28</sup> The behavior of Fe(CO)<sub>4</sub> is instructive in this regard; a shift of 42 cm<sup>-1</sup> is noted between the totally symmetric breathing modes as H<sub>2</sub> is added.<sup>4,29</sup> To be compared with a shift of 3 cm<sup>-1</sup> measured between the totally symmetric A<sub>1</sub> mode of Cr(CO)<sub>5</sub> and the same mode of H<sub>2</sub>Cr(CO)<sub>5</sub>. If electronegativities can serve as a guide, the hydrogen should withdraw even more electron density from chromium and result in a larger shift in the carbonyl modes than is observed for the iron of Fe(CO)<sub>4</sub>.

(4) Finally, the dihydride of Cr(CO)<sub>5</sub> should be of low symmetry which might be expected to yield a richer carbonyl spectrum.<sup>30</sup>

If species I is a molecular adduct, then the carbonyl arrangement is of nominal C<sub>4v</sub> symmetry. Three carbonyl modes are anticipated, two of A<sub>1</sub> symmetry and one of E symmetry. Poliakoff et al. have observed a species in liquid xenon which corresponds to species I, the third band of which is nearly coincident with the band which correlates with 1977 cm<sup>-1</sup> in argon matrices.<sup>31</sup> The third band, the low-frequency A<sub>1</sub> mode, is observed to move out from behind the band at 1977 cm<sup>-1</sup> for the deuterium isotopomer. Similar observations were made in matrices, but the appearance of a shoulder for the deuterium isotopomer could not be differentiated from solid-state effects (see Figure 2).

Observations of the hydrogen coordinates would yield evidence of the manner of coordination. Numerous attempts have been made to locate those modes with only one success. The M-C stretching region at about 660 cm<sup>-1</sup> shows dramatic differences between the several isotopomers (see Figure 3). A band at 657 cm<sup>-1</sup> for D<sub>2</sub>-containing matrices correlates with a band at 660 cm<sup>-1</sup> with HD, which, in turn, correlates with a shoulder at 665 cm<sup>-1</sup> for H<sub>2</sub>. The latter band is difficult to resolve from the intense T<sub>1u</sub> mode of Cr(CO)<sub>6</sub>. It appears to be split into a pair of bands although part of the band contour is due to atmospheric CO<sub>2</sub> in the spectrometer. In addition to the above, the spectrum of the D<sub>2</sub> isotopomer also exhibits an unsymmetrical band at 679 cm<sup>-1</sup> which correlates with a band of D<sub>2</sub>:W(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub> at 703 cm<sup>-1</sup> that was assigned to a metal-D<sub>2</sub> stretching coordinate.<sup>11</sup> No analogous features have been detected for the H<sub>2</sub> or HD isotopomers of Cr(CO)<sub>5</sub>. The band is tentatively assigned to a deuterium-containing coordinate which has become intensified by Fermi resonance with the nearby M-C stretching modes. Mixing of the coordinates would account for the fairly dramatic shift to lower frequencies of the M-C stretching modes as a function of the increased mass of the hydrogen isotopomer. Only a single M-C stretching frequency has been positively assigned to species I. It must be of A<sub>1</sub> symmetry because of the observed shift. The E mode may be coincident with the intense band of Cr(CO)<sub>6</sub>. The other hydrogen modes must be very weak. The E mode of species I at 1978 cm<sup>-1</sup> has been observed to be ca. 1.5 optical density units; the other hydrogen features must be less than approximately 1% as intense. With the present data the orientation of the hydrogen cannot be deduced.

Species II is formally a complex of Cr(CO)<sub>4</sub>, a species of C<sub>2v</sub> symmetry.<sup>19</sup> If the carbonyls maintain the same geometry, then four bands are expected. In addition to the two clearly defined bands, intensity due to species II is also located at 1965 cm<sup>-1</sup>,

(28) Sweany, R. L.; Owens, J. W. *J. Organomet. Chem.* **1983**, *255*, 327-334.

(29) Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2276-2285.

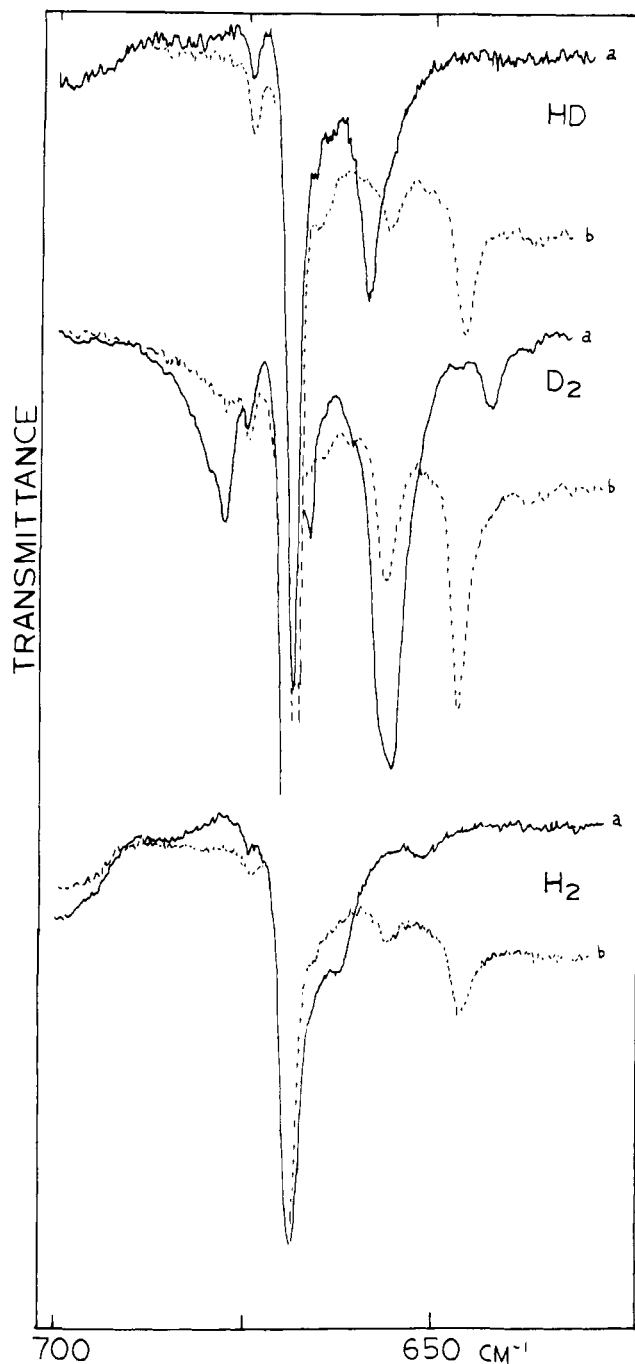
(30) H<sub>2</sub>Cr(P(OMe)<sub>2</sub>)<sub>3</sub> is taken to be pentagonal bipyramidal from NMR evidence with the two hydrogens cis and in the equatorial plane. Van-Catledge, F. A.; Ittel, C. A.; Tolman, C. A.; Jesson, I. P. *J. Chem. Soc., Chem. Commun.* **1980**, 254-255. H<sub>2</sub>Mo(PMe<sub>3</sub>)<sub>3</sub> is also pentagonal bipyramidal with the two hydrogens in the equatorial plane but separated by a phosphine. Lyons, D.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 695-700.

(31) Upmacis, R. K.; Gadd, G. E.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; Whyman, R.; Simpson, A. F. *J. Chem. Soc., Chem. Commun.*, submitted.

(25) The correlation of the band at 2062 with those at lower frequency may be erroneous because the two regions of the spectrum were seldom observed under conditions of no visible irradiation. When a matrix is exposed to the full output of the glower, the bands of species III change too rapidly for observations to be made over the entire carbonyl region.

(26) The synthesis of the dihydride, H<sub>2</sub>Cr(CO)<sub>5</sub>, has been claimed by Behrens and Weber [Behrens, H.; Weber, R. Z. *Anorg. Allg. Chem.* **1957**, *241*, 122] but disputed by King et al. [King, A. D., Jr.; King, R. B.; Yang, D. B. *J. Am. Chem. Soc.* **1981**, *103*, 2699-2704]. My own attempts have also failed.

(27) Jesson, J. P. In "Transition Metal Hydrides"; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; pp 75-201.



**Figure 3.** Spectra of argon matrices of  $\text{Cr}(\text{CO})_6$  with HD,  $\text{D}_2$ , and  $\text{H}_2$  in the region of the metal-carbon stretching vibrations. In each case the solid-line spectrum is of matrices which contain large amounts of species I with little of species II or III present (Displex cooling). The dashed-line spectrum is that made following photolysis with a cobalt glass filter and a medium-pressure mercury lamp. The spectra were recorded so that the top 50% of the transmittance scale was spread over the full width of the 10 in. recorder paper. The drift of the base line in the long-wavelength region of the dashed-line spectrum is due to the increasing absorbance of the coated germanium filter which is used to shield the matrix from the visible irradiance of the Nernst glower.

coincident with the E mode of  $\text{Cr}(\text{CO})_5$ . That this is so is shown on Figure 2. The ratios of intensities of the E and low-frequency  $A_1$  mode of  $\text{Cr}(\text{CO})_5$  have been published and also independently measured in this lab. Assigning the entire intensity of the band at  $1965\text{ cm}^{-1}$  to  $\text{Cr}(\text{CO})_5$  requires that a band at  $1934\text{ cm}^{-1}$  be approximately no more intense as marked by the horizontal lines at the latter position in the figure. The band at that position falls far short of the mark which suggests intensity at  $1965\text{ cm}^{-1}$  is due to a species other than  $\text{Cr}(\text{CO})_5$ . The additional intensity roughly

**Table I.** Absorption Maxima ( $\text{cm}^{-1}$ ) for  $\text{Cr}(\text{CO})_x(\text{H}_2)_y$  in Argon<sup>a</sup>

species I	2096.3 <sup>b</sup>
$\text{Cr}(\text{CO})_5(\text{H}_2)$	1978.5
	679 ( $\text{D}_2$ )
	657.1 ( $\text{D}_2$ )
	660.3 (HD)
	666 ( $\text{H}_2$ )
species II	2067.8
$\text{Cr}(\text{CO})_4(\text{H}_2)_2$	1965.
	1943.7 ( $\text{D}_2$ )
	1944.6 (HD)
	1945.4 ( $\text{H}_2$ )
	653.0
	643.5
species III	2062
$\text{Cr}(\text{CO})_4(\text{H}_2)$	1951
	1914

<sup>a</sup> Bands assigned to  $\text{Mo}(\text{CO})_5\text{H}_2$  appear at  $2101.3$  and  $1974.1\text{ cm}^{-1}$ . Bands assigned to  $\text{W}(\text{CO})_5\text{H}_2$  appear at  $2102.1$  and  $1975.7\text{ cm}^{-1}$ .

<sup>b</sup> Band positions are corrected to vacuum conditions with IUPAC calibration data with DCl and  $\text{CO}_2$ . Frequencies are accurate to  $\pm 1\text{ cm}^{-1}$  except where neighboring absorptions cause perturbations in the apparent band maximum.

correlates with the amount of intensity at  $1945\text{ cm}^{-1}$ . Other regions of the spectrum appear to be clear of major absorptions due to species II. To determine whether any part of the intensity at  $1977\text{ cm}^{-1}$  might be due to species II, an attempt to fit the equation  $A_{1977} = k_1(A_{2096}) + k_2(A_{1945})$  was made. Here,  $A_x$  is the absorbance at position  $x$  in the spectrum and  $k_1$  and  $k_2$  are proportionality constants. The solution cannot be very precise because of the large intensity differences of the three bands. The value of  $k_2$  was indistinguishable from zero. There is no easy means to check whether intensity due to species II is buried under the band due to  $\text{Cr}(\text{CO})_6$ . The spectrum below  $1945\text{ cm}^{-1}$  and above  $2000\text{ cm}^{-1}$  is quite clear of complications, and no band has been noted in these regions which correlates to the other bands of species II.

The appearance of the spectrum of species II resembles those of  $\text{M}(\text{CO})_4$  stoichiometry of  $\text{C}_{2v}$  point group.<sup>19,29</sup> The spectrum of matrices formed from the photolysis of carbon-13 labeled  $\text{Cr}(\text{CO})_6$  yields bands which are reasonably assigned to species II which allow a solution of energy factored force field force constants, which are tabulated in Table II. As can be noted from Figure 2, the band at  $1945\text{ cm}^{-1}$  shifts slightly for the isotopomers of hydrogen. The force field calculation shows this mode to be of  $b_1$  symmetry which involves the carbonyl ligands that are trans to the hydrogen molecules. Treating the hydrogen molecules as point ligands, this is the same symmetry vibration as the unsymmetric combination of  $\text{M}-(\text{H}_2)$  stretches. Being of the same symmetry, they mix and one observes the isotope effect in the carbonyl modes. This behavior is often noted for legitimate hydrides, although the degree of mixing follows no simple logic.<sup>32</sup> There is no evidence for a trans isomer of the same stoichiometry of species II.

It is interesting to note the degree of perturbation of the hydrogen on the spectrum of the carbonyl bands of  $\text{Cr}(\text{CO})_5$  and  $\text{Cr}(\text{CO})_4$ . The presence of hydrogen on  $\text{Cr}(\text{CO})_5$  causes little change in the carbonyl frequencies, as judged by the totally symmetric breathing mode. The force constants reported by Poliakov et al.<sup>31</sup> also are very similar to those of  $\text{Cr}(\text{CO})_5\text{Ar}$ .<sup>18</sup> We have argued that this change in the force constants of the equatorial carbonyl is diagnostic of the degree of charge transfer from metal to hydrogen in several carbonyl hydrides.<sup>28</sup> With the possibility of  $\pi$  bonding by hydrogen, this system becomes dissimilar to the simple dihydride,  $\text{H}_2\text{Fe}(\text{CO})_4$ . Recognizing the limitations in the comparison, these data would argue for little charge transfer. At the same time the interaction of hydrogen with chromium must not be considered trivial. The presence of hydrogen causes a dramatic increase in the frequency of the d-d

(32) See, for example: Braterman, P. S.; Harrill, R. W.; Kaesz, H. D. *J. Am. Chem. Soc.* **1967**, *89*, 2851-2859.

Table II. Energy Factored Force Field Fit ( $\text{cm}^{-1}$ ) for  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$ 

Molecule	obsd	calcd
$\text{Cr}(\text{CO})_4(\text{H}_2)_2$	2067.8	2067.8
	<i>a</i>	1970.3
	1965.1	1965.1
	1945.4	1945.8
$\text{Cr}(\text{CO})_3(*\text{CO})(\text{H}_2)_2$ label is trans to $\text{H}_2$	2062.4	2062.4
	1913.8 <sup>e</sup>	1914.1
	<i>b, c</i>	1963.3
	<i>b, c</i>	1965.1
$\text{Cr}(\text{CO})_3(*\text{CO})(\text{H}_2)_2$ label is trans to CO	2056.3	2055.8
	<i>b, c</i>	1969.2
	<i>b</i>	1945.8
	<i>a</i>	1933.6
$\text{Cr}(\text{CO})_2(*\text{CO})_2(\text{H}_2)_2$ labels are trans to label	2041.0	2041.2
	<i>d</i>	1951.5
	1920.8	1921.3
	<i>b</i>	1945.8
$\text{Cr}(\text{CO})_2(*\text{CO})_2(\text{H}_2)_2$ label is trans to CO label is trans to $\text{H}_2$	2048.9	2049.2
	<i>b, c</i>	1963.7
	<i>a</i>	1934.6
	1913.8	1912.9
$\text{Cr}(\text{CO})_2(*\text{CO})_2(\text{H}_2)_2$ labels are trans to $\text{H}_2$	<i>b?</i>	2057.1
	<i>a</i>	1936.4
	<i>b</i>	1965.1
	1900 <sup>e</sup>	1902.4
	$k_1 = 15.727 \pm 0.034$	
	$k_2 = 16.178 \pm 0.038$	
	$k_3 = 0.368 \pm 0.032$	
	$k_4 = 0.588 \pm 0.038$	
	$k_5 = 0.442 \pm 0.048$	



<sup>a</sup> Position is obscured by band of species I. <sup>b</sup> Position is obscured by band of species II. <sup>c</sup> Position is obscured by band of  $\text{Cr}(\text{CO})_5$ . <sup>d</sup> Position is obscured by band of  $\text{Cr}(\text{CO})_6$ . <sup>e</sup> Band is broad.

transition, the character of which is  $d_\pi \rightarrow d_\sigma$ , as compared to the argon complex.<sup>20</sup> The energy of the transition becomes similar to that of  $\text{Cr}(\text{CO})_5\text{N}_2$ .  $\sigma$  donation from hydrogen to metal and  $\pi$  back-bonding from metal to hydrogen account for the increase in the transition energy. Hay has calculated the Kubas complex and found there to be very little charge transfer from metal to hydrogen.<sup>9</sup> He has concluded that hydrogen acts mostly as a  $\sigma$  donor. Were this the case for species I, one would expect an optical

transition similar to that of  $\text{NH}_3$  at 420 nm. The observed transition at 364 nm suggests more  $\pi$  interaction than is exhibited by  $\text{NH}_3$ . The frequency is identical with the transition energy of the  $\text{N}_2$  complex of  $\text{Cr}(\text{CO})_5$ , in which  $\text{N}_2$  undoubtedly also accepts metal  $\pi$  electron density.

The bis(dihydrogen)chromium tetracarbonyl spectrum is much more perturbed (see Table II). There is a significant blue shift in the infrared frequencies as the hydrogen coordinates to  $\text{Cr}(\text{CO})_4$ , which is reflected in increases in the force constants. An energy factored force field was calculated by using the Cotton-Kraihanzel assumption on frequencies reported by Poliakoff and Turner for  $\text{Cr}(\text{CO})_4$  in argon. The resulting force constants were  $k_1 = 15.40$  and  $k_2 = 15.53$  mdyne/Å, nearly 0.4 mdyne/Å smaller than those calculated for species II. Taken at face value, the data suggest increased charge transfer from metal to hydrogen. Charge transfer ought to become more facile as electron withdrawing carbonyl groups are removed. Perhaps with phosphine coordination the hydrogen would more nearly oxidatively add. Dihydrides of pentakisphosphines are reported for chromium triad metals; they are normal hydrides.<sup>30</sup>

Little can be claimed for the limited observations of species III. If the stoichiometry is correctly assigned, the spectrum also shows significant blue shifts compared to the correlated features of  $\text{Cr}(\text{CO})_4$ .

Finally, a limited number of observations of the other group 16 metal hexacarbonyls in hydrogen-containing matrices show similar behavior as  $\text{Cr}(\text{CO})_6$ . Species corresponding to  $\text{Cr}(\text{CO})_5\text{H}_2$  have been identified, the carbonyl frequencies for which are included in Table II. The carbonyl E modes are no better resolved from the low-frequency  $A_1$  modes than those of  $\text{Cr}(\text{CO})_5\text{H}_2$ . The experiments were performed with use of the Displex refrigerator; hence, very small amounts of species corresponding to  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$  have been observed.

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**Registry No.**  $\text{Cr}(\text{CO})_6$ , 13007-92-6;  $\text{H}_2$ , 1333-74-0;  $\text{Cr}(\text{CO})_5\text{H}_2$ , 95313-93-2;  $\text{Cr}(\text{CO})_4(\text{H}_2)_2$ , 95313-94-3;  $\text{Cr}(\text{CO})_4\text{H}_2$ , 95313-95-4.