Synthesis and Characterization of Dihydrogen Complexes of Tetracarbonylbromomanganese(I) and Tetracarbonylchloromanganese(I) in Argon Matrices

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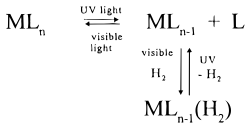
When argon matrices of $MnX(CO)_5$, X = Br and Cl, containing dihydrogen are photolyzed with either visible light or light of 254 nm, a new species is formed which is $MnX(\eta^2\text{-}H_2)(CO)_4$. The compounds have been characterized by infrared and Raman spectroscopies, and an energy-factored force field has been fit to the carbonyl modes. The structures can be thought of as arising from an octahedron with no halide and dihydrogen occupying cis-positions. While the H−H stretching vibration was not observed, the symmetric metal−hydrogen stretches have been observed at 788.6, 665.2, and 588.5 cm^{-1} for the adducts of H_2, HD, and D_2 and $MnBr(CO)_4$, respectively. The same mode occurs at 764 cm^{-1} for $MnCl(H_2)(CO)_4$; hence, H_2 is not strongly bound to the metal. An analysis of the carbonyl stretching force constants supports the view that H_2 is not as strong of a π-acid as CO. The spectra of $MnX(CO)_4$ have been re-examined, and it is clear that the features that had been previously assigned to $MnX(CO)_4$ of C_{2v} symmetry actually belong to two different species. The spectra are consistent with one isomer of low symmetry, presumably due to the loss of an equatorial CO from $MnX(CO)_5$. The other isomer gives only a single strong infrared absorption and could be the isomer formed with the loss of an axial CO from $MnX(CO)_5$.

Introduction

Over the last decade, there has been a great deal of interest in the coordination chemistry of molecular hydrogen.[1] Transition metal dihydrogen complexes are conveniently synthesized in inert gas matrices by photolyzing an organometallic precursor in the presence of dihydrogen.[2] Light absorption frequently expels a ligand, thus, opening a site for hydrogen to coordinate. By this technique, complexes of a variety of transition metals have been synthesized. The advantage of the technique is that vibrationally simple complexes can be synthesized, which might allow the unambiguous assignments of the hydrogen-containing vibrational coordinates. What has limited the utility of this approach is the photosensitivity of the resulting dihydrogen complex. The light used to vacate a coordination site is also capable of ejecting dihydrogen, as shown in Scheme 1. As a result, insufficient quantities have usually been synthesized to allow the observation of the weak hydrogen modes in the infrared spectrum.

Scheme 1



In one instance, the yellow $M(CO)_5(NMe_3)$, M = Cr and W, allowed the use of photons from the visible spectrum for opening up a coordination site.[3] $M(\eta^2\text{-}H_2)(CO)_5$ was synthesized in large yields because the product is not as photosensitive in the visible region of the spectrum as it is to UV photons. With large quantities of $M(\eta^2\text{-}H_2)(CO)_5$ available, it was possible to observe the hydrogen-containing vibrational coordinates. Both the H−H and the symmetric $M{-}H_2$ stretching vibrations of $Cr(\eta^2\text{-}H_2)(CO)_5$ were complicated by the ease of rotation about the $H_2{-}Cr$ vector and matrix site effects.

$MnX(CO)_5$ complexes, X = Br and Cl, are also yellow, and it has been possible to synthesize large quantities of the adduct $MnX(H_2)(CO)_4$ by using visible photons. Some of the hydrogen-containing vibrational features have been observed, and it is now possible to make comparisons between the spectra of $MnX(H_2)(CO)_4$ and $Cr(H_2)(CO)_5$. The intermediate in these syntheses $MnX(CO)_4$, had previously been observed in matrices and was reported to be of C_{2v} symmetry.[4] Herein, we also report a re-examination of the spectrum of $MnX(CO)_4$ and the presumption that there is a single isomer of $MnX(CO)_4$.

Experimental Section

$MnX(CO)_5$ was synthesized from $Mn_2(CO)_{10}$ (Pressure Chemical), using the corresponding halogen in CCl_4.[5] The crude product was sublimed once and then again as the matrix was prepared. Argon (99.999% pure), N_2 (99.99%), and H_2 (99.9% pure) were obtained from Lincoln Big Three and passed through tubes of Ascarite and molecular sieves before use. CH_4 (99.996% pure, Matheson), D_2 (99.9% pure, Air Products), and HD (99% pure, MSD Isotopes) were used without further

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[2] Sweany, R. L. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH Publishers: New York, 1992; pp 65−101.

[3] Sweany, R. L.; Moroz, A. *J. Am. Chem. Soc.* **1989**, *111*, 3577.

[4] McHugh, T. M.; Rest, A. J.; Taylor, D. J. *J. Chem. Soc., Dalton Trans.* **1980**, 1803.

[5] King, R. B. In *Organometallic Synthesis*; Eisch, J. J., King, R. B., Eds.; Academic Press: New York, 1986; pp 174−175.

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purification. Gas mixtures were prepared manometrically, with H_2 ranging between 1−20 mol %.

Matrices were produced by slow deposition onto either 2.54 cm in diameter KBr or CsI disks that were held in an oxygen-free hard copper holder that masked over half of the surface. Indium was used to facilitate the heat transfer between the holder and the crystals. The crystal was cooled by an Air Products Displex closed-cycle helium refrigerator, which was operated at 10 K during deposition and most irradiations. $MnX(CO)_5$ was sublimed from a container at the same time matrix gases were being admitted to the cryostat at ca. 1 mmol/h. The rate of sublimation was controlled by adjusting the temperature of the solid from 0−25 °C. For infrared experiments, temperatures were maintained between 0−10 °C. Similar conditions were used in the earlier study.[4] The faster deposit rates were used to prepare samples for a Raman investigation. Infrared spectra were obtained by using either a Perkin-Elmer 1760 or 2000 FTIR from 250−4300 cm^{-1}, with 1 cm^{-1} resolution. Typically, each spectrum was the result of signal-averaging 50 spectra. Raman spectra were obtained by exciting samples with 1064 nm light from a YAG laser on the Perkin-Elmer 2000 operated at power levels up to 800 mW. The 180° back-scattered radiation was collected through a quartz window on the cryostat. The spectral resolution was usually opened to 8 cm^{-1} in order to obtain acceptable signal-to-noise levels over as many as 200 acquisitions. The Raman spectrum was sensitive to oxygen impurities in the matrix gases. Its narrow fluorescence appeared at a Raman shift of 1510 cm^{-1} or at 1269 nm. After irradiation, the band is joined by a much more intense and more broad fluorescence centered at a Raman shift of 1361 cm^{-1} (1244 nm). In addition to this alteration, matrices develop broad fluorescence in the region of the D−D stretch at 3235 cm^{-1} (1620 nm) and 2910 cm^{-1} (1538 nm). The response of the fluorescence to increased laser power was similar to that of the Raman bands. This suggests that access to the fluorescent states is obtained by multiphoton excitation. These features were obtained with both $MnCl(CO)_5$ and $MnBr(CO)_5$ with or without hydrogen, suggesting the source of the fluorescence is impurities. Photolyses were conducted by using unfiltered mercury penlamps, phosphor-coated penlamps (Hammatsu), or an unfiltered 400 W tungsten projector lamp.

Curve fitting was accomplished by an program written by J. Pitha and R. N. Jones of the National Research Council of Canada. The digitized spectrum was fit to a product function of Lorentzian and Gaussian band shapes. The factored force fields were calculated using a program by K. Purcell of the University of Illinois.

Results

When argon matrices containing $MnX(CO)_5$, X = Br or Cl, and H_2 are photolyzed by a 400 W tungsten lamp, new bands appear in the infrared spectrum which are not observed in the absence of H_2. Bands appear at 2127.7, 2055.2, 2050.1, and 1992.4 cm^{-1} for X = Cl. For X = Br, the bands appear at 2123.3, 2050.8, and 1994.9 cm^{-1}. In Figure 1, the bands are designated by the number 1. The species responsible for these bands will also be referred to by **1** or **1Br** and **1Cl** when there is a need for differentiation. At the same time as these bands appear, a band due to uncoordinated CO at 2138.5 cm^{-1} also grows in. The positions of all the bands in the carbonyl region are unaffected by the mass of the hydrogen.

In addition to the bands of **1**, which require the presence of dihydrogen, other features appear, the most intense of which have been assigned to $MnX(CO)_4$.[4] Using the 254 nm irradiance of low-pressure mercury lamps, the bands assigned to $MnX(CO)_4$ are much more intense relative to the bands due to **1** than when visible light is used for photolysis. These bands are labeled by a 2 in Figure 1. Other bands labeled by a 3, which are presumably due to $MnBr(CO)_x$, $x < 4$, can be seen in the absence of H_2. On subsequent irradiation with visible light, these bands become less intense while bands due to **1** become more intense, as do those of the starting material. A single band at 2037.4 cm^{-1} and possibly a second band at 1970.3 cm^{-1} for X = Br are labeled by a 4. They grow as a result of visible and UV photolysis of both argon and argon/H_2 matrices; they do not become attenuated under conditions that ordinarily cause the depletion of coordinatively unsaturated species. The analogous positions occur at 2039.3 and 1969.9 cm^{-1} for X = Cl. The growth of bands belonging to 4 lags those of 1 and never achieve the intensity of bands belonging to 1. No other bands grow in as a result of visible irradiation other than what has been described with H_2 concentrations ranging from 1 mol % to nearly 20 mol %.

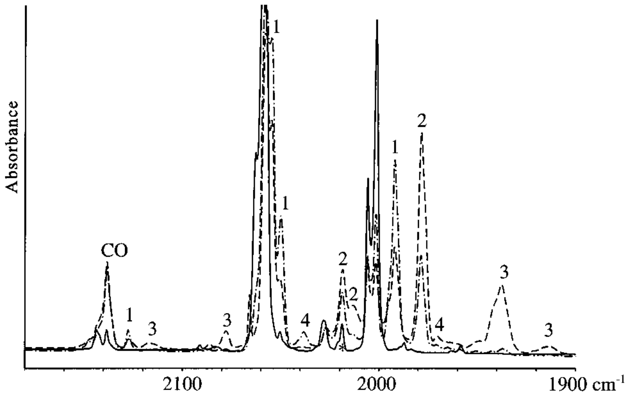

Figure 1. Infrared spectra of $MnCl(CO)_5$ (solid line) after sublimation at 16 °C for 70 min in 17.5 mol % H_2 in Ar, (dashed line) after 180 min irradiation with low-pressure Hg lamps; (dash−dotted line) after 10 min irradiation with 400 W tungsten lamp. Asterisk marks the principal absorption of $Mn_2(CO)_{10}$. Bands marked by 1 are assigned to $MnCl(H_2)(CO)_4$; by 2 are assigned to $MnCl(CO)_4$, by 3 are assigned to $MnCl(CO)_x$, $x < 4$. Those marked by 4 have not been assigned.

FT-Raman spectra were obtained from concentrated matrices of $MnBr(CO)_5$ containing either H_2 or D_2 at about 10 mol %. Deposits were collected over as long as 3 h. The unphotolyzed matrix gives scattering peaks at 2138, 2084, and 2004 cm^{-1} in the carbonyl region. Upon irradiation with visible light, new bands were observed at 2122, 2047, and 1994 cm^{-1} in the carbonyl region.[6] The band at 2047 cm^{-1} is actually present in the infrared spectrum at 2048.0 cm^{-1} as an unresolved shoulder on the band at 2050.8 cm^{-1} which is itself a shoulder on the parent band at 2054.7 cm^{-1}. Its presence was confirmed by curve resolving that indicated that it was somewhat more intense and just as wide (3.2 cm^{-1} at half-maximum) as the band at 2050.8 cm^{-1}.

Concomitant with the growth of new bands in the carbonyl region, new infrared bands are also observed in the region of 650 cm^{-1}, where the carbonyl deforma-

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[6] The usual accuracy of FT-IR is not retained in the FT-Raman experiment because the light source is not held in a precisely fixed location. Calibration is accomplished by bands in the spectrum the positions of which are known.

Table 1. Positions of Absorptions Arising from the Photolysis of $MnX(CO)_5$ in Argon

	$MnBr(H_2)(CO)_4$				$MnCl(H_2)(CO)_4$		
	H_2	HD	D_2	N_2	H_2	D_2	N_2
ν(NN)				2287.8			2291.5
ν(CO)	2123.3	2123.0	2123.5	2120.8	2127.7	2128.2	2125.0
ν(CO)	2050.8	2050.5	2050.9	2051.8	2055.2	2056	2054
ν(CO)[a]	2047		2047	2045.2	2050.1	2050.1	2046.5
ν(CO)	1994.9	1994.9	1995	1990.6	1992.4	1992.2	1988.6
$\nu_a(MnH_2)$	1392, 1369	1230.5	1019.5		1357, 1322	995.3	
$\nu_s(MnH_2)$	788.6	665.2	588.5		764		
δ(MnCO)	651.8	638.7	658.1	656.6	653.5	659.4	658.0
δ(MnCO)	647.7	623.4, 621.1	635.9	635.3	651	635.7	634.0
δ(MnCO)	631.6	615.1, 611.5	620.1	614.4	626.2	618.6	613.0
?			473.0				
ν(MnC)	410.9	410.9	410.4	404.0			
ν(MnC)	420.0	419.6	418.4	414[a]			

[a] Seen by spectral subtraction or by Raman.

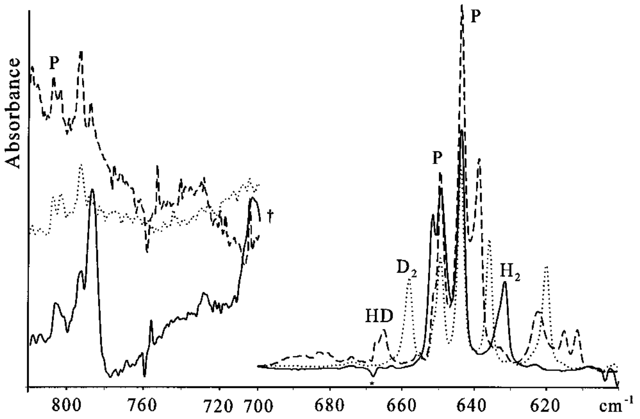

Figure 2. Infrared spectra of $MnBr(XY)(CO)_4$. Bands marked by P belong to $MnBr(CO)_5$. Dagger marks band that cannot be assigned to $MnBr(H_2)(CO)_4$. Solid spectrum, XY = H_2; dashed spectrum, XY = HD; dotted spectrum XY = D_2. Asterisk marks the position of CO_2. The shoulder on the band at 665.2 cm^{-1} is probably due to the incomplete removal of intensity due to CO_2.

tion modes are found.[7] With X = Br and D_2, the new bands appear at 658.1, 635.9, and 620.1 cm^{-1}. With X = Br and H_2 or HD, the spectrum is completely altered. With H_2, new bands appear at 631.6, 651.8, and 648 cm^{-1}, the latter two growing in as shoulders on a band at 649 cm^{-1} of $MnBr(CO)_5$. The band at 648 cm^{-1} is never resolved from the band at 649 cm^{-1}. Its existence was first noticed because intensity at 649 cm^{-1} survived photolysis more than at other positions of parent absorption. Spectral subtraction showed the band at 648 cm^{-1} to be nearly as intense as the band at 652 cm^{-1}. The spectrum that results from the photolysis of $MnBr(CO)_5$ in HD-containing matrices is less well-studied but clearly differs from the other two, being bands at 611.5, 615.1, 621.1, 623.4, 638.7, and 665.2 cm^{-1} in the region. The spectra are shown in Figure 2. The positions are tabulated in Table 1. The Raman spectrum of the visible photolysis products of $MnBr(CO)_5$ shows only a single band in the region at 634 cm^{-1} for H_2-containing matrices and 636 cm^{-1} for D_2-containing matrices.

When matrices of $MnX(CO)_5$ were irradiated in N_2-containing matrices, new bands were observed which were nearly coincident with those formed in D_2-containing matrices. They are listed in Table 1. In addition to these bands, a band at 2288 cm^{-1} is observed. With higher concentrations of N_2 and prolonged irradiations, bands at 2075.2 and 1915.4 cm^{-1} grow in. They never obtained a large intensity and are not accompanied by new bands in the region of the N−N stretch.

McHugh et al. reported absorptions for $MnCl(CO)_4$ at 2126.0, 2055.3, 2051.0, 2018.9, and 1977.4 cm^{-1}.[4] While these observations are largely replicated in Ar, the pattern is altered in argon matrices doped with H_2. In general, site splittings are less severe with H_2 present. In this, the matrices resemble what is seen in methane. Features that can be correlated to $MnCl(CO)_4$ in argon occur at 2125.1, 2018.6, and 1978.7 cm^{-1}. The band at 2125.1 cm^{-1} appears as a shoulder on a band due to **1**. The absorptions at 2055 and 2051 cm^{-1} reported by McHugh et al. for argon matrices occur in the same region as bands assigned to **1**, and it is difficult to identify them in this busy region of the spectrum.

The bands at 2018.6 and 1978.7 cm^{-1} belong to different species because there is no clear correlation between the intensities. The analysis is made more difficult by the presence of small amounts of $Mn_2(CO)_{10}$ which gives intensity at 2019 cm^{-1} as well. The behavior of the band due to $Mn_2(CO)_{10}$ has been independently characterized under similar conditions. In the experiment shown in Figure 1, the band at 1979 cm^{-1} loses over half of its intensity with 10 min of projector illumination. The intensity of the band at 2019 cm^{-1} is retained to a much larger degree. The same behavior was noted for matrices that were 17 mol % and 6 mol % in H_2. The band due to $Mn_2(CO)_{10}$ should have lost over half its intensity in 180 min of irradiation with the low-pressure mercury lamps. With visible illumination, the doubling time for recovery is more than 100 min. Thus, there probably is very little intensity due to $Mn_2(CO)_{10}$ after the 10 min of visible irradiation.

A similar lack of correlation between the bands was also noted in argon matrices. Shown in Figure 3 are the spectra taken from a matrix which was contaminated very little by $Mn_2(CO)_{10}$. In this experiment, the band at 2019 cm^{-1} grew to its maximum intensity after 10 min of 254 nm irradiation while the band at 1978 cm^{-1} continued to grow. Of the bands originally assigned to $MnCl(CO)_4$, the intensity at 2124.0 correlates well with the intensity of 1978 cm^{-1}. A weaker band at 2117.9 cm^{-1} correlates with the band at 2019 cm^{-1}. The band at 1978 cm^{-1} comes closest to correlating with the band at 2052 cm^{-1}, but the latter band cannot be

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[7] Ottesen, D. K.; Gray, H. B.; Jones, L. H.; Goldblatt, M. *Inorg. Chem.* **1973**, *12*, 1051.

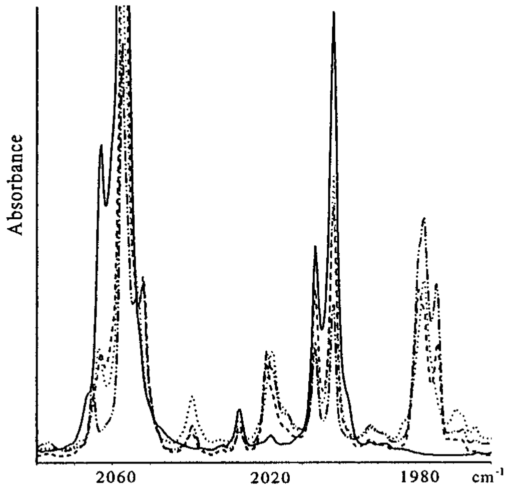

Figure 3. Infrared spectra of MnCl(CO)$_5$ in Ar matrix (solid line) initial spectrum; (dashed spectrum) after 10 min low-pressure mercury lamp photolysis; (dash–dotted spectrum) after 58 min additional UV irradiation; (dotted spectrum) after 5 min irradiation with tungsten lamp.

well characterized because it is a shoulder on the principal absorption of MnCl(CO)$_5$. Although we assume a similar lack of correlation in the set assigned to MnBr(CO)$_4$, the lack of correlation between the bands was never so clear.

Discussion

A number of issues must be addressed in order to rationalize the spectrum of **1**. It must be established what is the number of CO ligands remaining on manganese and what is the number of H$_2$ molecules involved. It must also be established what is the mode of attachment of H$_2$ and what is the gross structure at manganese.

Four bands are assigned to **1**, three of which are easily observed by infrared spectroscopy and one was derived from Raman spectroscopy. For **1Br**, they appear at 2123.3, 2050.8, 2047, and 1994.9 cm^{-1}. That there are four bands is consistent with there being at least four carbonyl ligands, if one presumes that the bands at 2051 and 2047 cm^{-1} are due to different fundamentals rather than a single mode perturbed by different sites. If they were due to site splittings, then one would expect both components to be observed in the Raman spectrum and the infrared spectra with the same relative intensities. From the infrared spectrum, both are present with nearly equal areas. In the Raman spectrum, the band at 2051 cm^{-1} is absent. Although the spectral resolution for the Raman experiment was 8 cm^{-1}, the band at 2047 cm^{-1} shows no asymmetry nor is the band maximum displaced toward 2051 cm^{-1}. Thus, the two bands are of different origins, and there must be at least four carbonyl ligands.

It is clear that H$_2$ is required for the formation of **1**, and nothing else in the spectrum can be assigned to a H$_2$-containing species. **1** has been observed to form with very low concentrations of H$_2$ when it is unlikely that there is more than one H$_2$ in the vicinity of a manganese complex. At higher concentrations of H$_2$, no new features appear that could be assigned to a bis(dihydrogen) complex. At this stage, we have argued that **1** has four carbonyl ligands and is formed from one H$_2$ molecule.

It is unlikely that the halide is lost upon photolysis. When MnBr(CO)$_5$ is photolyzed in CO-containing matrices, no Mn(CO)$_5$ or Mn(CO)$_6^+$ is detected by infrared methods.[8] Even if the Mn–Br bond were to be cleaved, the cage effect would undoubtedly cause the process to be reversed.

Three observations suggest that the hydrogen does not oxidatively add. First, the carbonyl modes do not shift markedly to the blue, as would be expected with the loss of electron density at the metal as H$_2$ oxidatively adds. By contrast, when H$_2$ oxidatively adds to Fe(CO)$_4$, the totally symmetric CO stretch shifts by 42 cm^{-1} whereas the position of the analogous modes of MnBr(CO)$_4$ and MnBr(H$_2$)(CO)$_4$ are nearly superimposed.[9] Second, there is no band in the region of 1800 cm^{-1} in the Raman spectrum that can be assigned to a Mn–H stretch. Such a mode can be very strong in the Raman spectrum, relative to even the carbonyl modes.[10] Its absence can be used as a form of proof. Finally, the bands that are strongly mass dependent at low wavenumbers include a band which must be assigned to the Mn–H$_2$ stretching mode. The position of the band in diprotium matrices is at 789 cm^{-1}, which is admittedly close to the position of the Mn–H deformation mode at 729 cm^{-1} of MnH(CO)$_5$.[11] The claim of a nonclassical H$_2$ ligand rests on the absence of any band in this region when HD is used. In fact, a band is assigned to the HD–Mn stretching mode at 665 cm^{-1}. Had HD oxidatively added, one would expect two bands, one in the Mn–H deformation region near 790 cm^{-1} and the other in the region of the Mn–D deformation region at 550 cm^{-1}. Regardless of the exact assignment of the HD–Mn stretch (vide infra), the absence of any infrared activity in the regions of the Mn–H deformation modes is compelling.

Having established that the H$_2$ is coordinated, then it is proper to view **1** as a six-coordinate complex of manganese. It can be considered a derivative of MnX(CO)$_5$ in which an equatorial CO is replaced by H$_2$. Such a species is of C_s symmetry, for which four carbonyl modes are expected. The other isomer results from the substitution of the CO trans to halide and is of C_{4v} symmetry. Such a moiety will produce two infrared-active carbonyl stretching vibrations, only one of which will be readily observed. Certainly, **1** cannot be this isomer. Moreover, there is no evidence for such a species.

With the inclusion of the Raman band and several ^{13}CO infrared bands in the region of the totally symmetric CO stretching mode, it is possible to fit the observed spectra to an energy-factored force field consisting of seven force constants, which presumes C_s symmetry at manganese. The observed spectrum was fit with the minimum number of 7 frequencies with an average error of 0.2 cm^{-1}. The results are shown in Table 2. The large error in $k_{11'}$ is due to the high level of correlation.

Morris has claimed that H$_2$ might be a better π-acid than CO.[12] The site-preference of dihydrogen cannot

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[8] Church, S. P.; Poliakoff, M.; Timney, J. A.; Turner, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7515. Beach, N. A.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 5713.

[9] Sweany, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 2410.

[10] Kristjánsdóttir, S. S.; Norton, J. R.; Moroz, A.; Sweany, R. L.; Whittenburg, S. L. *Organometallics* **1991**, *10*, 2357.

[11] Cotton, F. A.; Down, J. L.; Wilkinson, G. *J. Chem. Soc.* **1959**, 833.

Table 2. Fitted Force Constants for $MnBr(H_2)(CO)_4$ and $MnBr(CO)_5$[a]

force constant (N m^{-1})	$MnBr(H_2)(CO)_4$	$MnBr(CO)_5$
k_1	1739.2 ± 7.4	1751.0 ± 0.4
k_2	1620.0 ± 8.8	1631.1 ± 1.2
k_3	1715.1 ± 7.9	
k_{11}	41.7 ± 7.3	44.3 ± 0.3
$k_{11'}$	23.1 ± 31.9	20.9 ± 0.4
k_{12}	35.1 ± 8.2	22.6 ± 1.5
k_{32}	37.2 ± 8.7	

[a] k_1 refers to the force constants of carbonyls in the equatorial plane of $MnBr(CO)_5$ or the carbonyls of $MnBr(H_2)(CO)_4$ that are trans to each other. k_2 refers to the carbonyl ligand trans to bromide. k_3 belongs to the CO trans to H_2 of $MnBr(H_2)(CO)_4$. k_{11} and $k_{11'}$ are interaction force constants that link equatorial carbonyls which are trans and cis to each other, respectively. k_{12} and k_{32} refer to off diagonal elements that link equatorial carbonyls to the axial carbonyl.

shed light on this claim. The placement of the H_2 ligand in an equatorial site can indicate that CO is a better π-acid, thus preferring the axial site.[13] Alternatively, the bromine may interact attractively with H_2, forcing it into a proximal position.[14] We note that H_2 prefers equatorial coordination in $CoH(H_2)(CO)_3$ and $Co(CH_3)(H_2)(CO)_3$.[15] In these latter examples, the site of H_2 binding is one associated with greater π-participation.[16] Again, interactions between H_2 and hydride or methide might also stabilize the H_2 in the equatorial position. In this regard, it is unlikely that the cis interaction could exceed 8 kJ/mol, the size of the barrier to rotation of H_2 when it is cis to either halide or hydride.[17]

The carbonyl force constants may offer some assistance in addressing the relative acid strengths of CO and H_2. McHugh et al. have fit the carbonyl stretching frequencies of $MnCl(CO)_5$ with an energy-factored force field.[4] We have fit the spectrum of $MnBr(CO)_5$ (see Table 2) using their fit as a guide and data obtained from natural abundance carbon isotopomers. The fit of $MnBr(CO)_5$ matched seven frequencies with an average error of 0.1 cm^{-1}; the force field for $MnBr(CO)_5$ does not differ from that of $MnCl(CO)_5$ by more than 2%. In the complex $MnBr(H_2)(CO)_4$, the energy-factored force field yields two unique diagonal force constants, one of which belongs to the carbonyl trans to bromine and the other is trans to dihydrogen (Table 2). The force constant, 1620.0 N m^{-1}, is nearly equal to that which was obtained for the carbonyl mode trans to the bromide in $MnBr(CO)_5$, and we assign it to the carbonyl trans to bromide in **1**. Therefore, the force constant, 1715.1 N m^{-1}, is assigned to the carbonyl trans to dihydrogen. It is lower than the force constants for carbonyls which are trans to each other. By contrast, the force constant for the equatorial carbonyls of $MnBr(CO)_5$ is 1751.0 ± 0.4 N m^{-1}. If geometry changes were not a factor, then the remaining equatorial carbonyls would experience an increase in the metal basicity as a CO is replaced by H_2. This would argue for H_2 being less acidic than CO. If force constants depended only on electronic factors, then it would be apparent that H_2 is not as good of a π-acid as CO. In fact, other factors play a role, making a rigorous analysis impossible. Still, the basis is as firm as that of Morris.[12]

The spectra are lacking the H−H stretching vibration. The mode was observed for $Cr(H_2)(CO)_5$, however, it was broad and split into components, depending on the mass of hydrogen.[3] The spectrum of $W(H_2)(CO)_5$ was less complex. The complexity of the spectrum was ascribed to the nearly free rotation of H_2 in a 4-fold potential created by the equatorial carbonyl ligands.[18] It was hoped that the presence of a halide might inhibit the motion of the hydrogen so that the complexity of the spectrum would be reduced. Presumably, the H−H stretch would be more readily observed. The totally symmetric stretching vibration of **1Br** has been observed as great as 0.8 OD and more routinely at 0.4 OD. These would have been adequate intensities to observe the H−H stretch had the molecule been $Cr(H_2)(CO)_5$.[3] It is particularly disappointing that the band and the Mn-(H_2) stretching modes could not be identified in the Raman spectrum. It appears, therefore, that the hydrogen-containing modes of $MnBr(H_2)(CO)_4$ are not among the most intense Raman scatterers.[19]

The position of the H_2−Mn stretch is 80 cm^{-1} to the red of the analogous mode of $Cr(H_2)(CO)_5$, itself one of the lowest wavenumber positions of the mode in dihydrogen complexes.[20] This suggests a weaker binding between H_2 and manganese than what is found in the others. This is not totally surprising because the metal is relatively electron poor, a conclusion based on the position of the totally symmetric breathing mode and the associated force constants. The position of the mode due to $MnCl(H_2)(CO)_4$ is still to smaller wavenumbers than that of $MnBr(H_2)(CO)_4$, which may reflect less electron density on the metal which can be used in π-bonding with H_2. Eckert has discouraged a reliance on infrared frequencies as a basis of judgment of the extent of interaction between the metal and H_2.[20] The comparison between that of $MnBr(H_2)(CO)_4$ and $MnCl(H_2)(CO)_4$ is probably valid because the two molecules are so similar. Moreover, the vibrational interactions that have been characterized actually lead to the mode being shifted to higher energy (vide infra). Consistent with there being a very weak interaction between H_2 and $MnX(CO)_4$ is the very high wavenumber for the N−N stretch of the associated $MnX(N_2)(CO)_4$.[21]

The assignment of the spectrum in the region of 600 cm^{-1} is not easy. The region is shown in Figure 2. The bands are due to three sources: the metal carbonyl deformation modes are most intense, the position of the Mn−H_2 stretch is most mass dependent, and overtones and combination bands are weak.[7] The spectrum of **1**

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(12) Morris, R. H.; Schlaf, M. *Inorg. Chem.* **1994**, *33*, 1725.

(13) The degree of π-bonding in $MnBr(CO)_5$ is greatest in the axial position. Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366. Fenske, R. F.; DeKock, R. L. *Inorg. Chem.* **1970**, *9*, 1053.

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(18) See: also Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 3645. Turner, J. J.; Poliakoff, M.; Howdle, S. M.; Jackson, S. A.; McLaughlin, J. G. *Faraday Discuss. Chem. Soc.* **1988**, 271.

(19) The Raman spectrum of $[Ru(C_5H_5)(Ph_2PCH_2PPh_2)(H_2)]BF_4$ yields a low frequency, intense feature at 2082 cm^{-1}, which is assigned to the H−H stretch. Chopra, M.; Wong, K. F.; Jia, G.; Yu, N.-T. *J. Mol. Struct.* **1996**, *379*, 93.

(20) Eckert, J. *Spectrochim. Acta* **1992**, *48A*, 363.

(21) Morris, R. H.; Earl, K. A.; Luck, R. L.; Lazarowych, N. J.; Sella, A. *Inorg. Chem.* **1987**, *26*, 2674.

differs considerably depending on the mass of the hydrogen. The differences are due to Fermi resonance interactions between H-containing modes and carbonyl deformation modes. The spectrum of $MnX(N_2)(CO)_4$ shows that three strong bands are expected in the region of the carbonyl deformation modes in the absence of mixing with H-containing modes. The spectrum of $MnX(D_2)(CO)_4$ comes closest to matching that of $MnX(N_2)(CO)_4$ both in the number of bands and their position. (The expectation that the number of bands should be the same hinges on the two complexes being isostructural. The expectation that the frequencies should be similar is based on the match of frequencies in the C−O stretching region.) The band at 620 cm^{-1} of **1Br** is blue-shifted, suggesting that there is a D-containing mode to somewhat lower frequency. Such a band is found at 588.5 cm^{-1}. If this band is a deuterium-containing mode, one expects a correlated band at 818.5 cm^{-1} in the H_2-containing isomer. Nothing is seen in this region, but a band is found at 788.6 cm^{-1}. This band is pushed to higher wavenumbers by mixing with the carbonyl deformation modes, just as the band at 588.5 cm^{-1} is pushed to lower wavenumbers. Evidence for this mixing is a red shift in the Mn-CO deformation mode by 6 cm^{-1}.

One expects a HD−Mn stretch at 688 cm^{-1} to correlate with the H_2−Mn stretch. A broad complex feature is observed in the region in HD-containing matrices, with peak maxima at 682 and 687 cm^{-1} as shown in Figure 2. No intensity is found in this region for either D_2- or H_2-containing matrices. The complexity in the region is surprising in light of the simplicity of the band at 788.6 cm^{-1} of the diprotium isomer.[22] We are reluctant to assign the broad feature in the spectrum of $MnBr(HD)(CO)_4$ to the same mode and have, therefore, assigned a feature at 665 cm^{-1} to the HD−Mn stretch, the contour of which is similar to what is observed at 788 cm^{-1}. The presence of the Mn−HD stretch so near to the region of the deformation modes causes major perturbations on the spectrum of the latter. There is nothing in the region of 655 cm^{-1}, the mode of which has undoubtedly been displaced far to the red. There are four distinct bands in the deformation region rather than the expected three. The pair of bands at 615 and 611 cm^{-1} are so matched in intensity and shape that it is tempting to claim that they arise from the loss of symmetry inherent in HD.

We point out two other anomalies for which we can offer no explanations. The band at 631 cm^{-1} of the diprotium isomer is at higher frequency than that expected based on either the N_2 or D_2 complex. One might suppose a hydrogen-containing mode at lower frequency has caused it to shift to the blue, yet none is evident. Also, a rather prominent band at 473 cm^{-1} in the spectrum of $MnBr(D_2)(CO)_4$ cannot be assigned. If it is a deuterium-containing mode, then either the correlated features of the H_2 and HD isomers are unobserved or the band is due to a Mn-C stretching vibration which has been blue-shifted by Fermi resonance.

The bands assigned to 4 behave in a fashion that suggests that they belong to a species which is coordinatively saturated. The bands cannot be attributed to dimanganese features formed by near-neighbor $MnX(CO)_5$ nor are they due to interactions of $MnX(CO)_4$ with common impurities in the matrices. Since the bands occur regardless of whether H_2 is present, we are intrigued by the possibility that the species contains an isocarbonyl ligand. Prolonged photolyses can result in the production of coordinatively unsaturated fragments that are well-isolated from the CO that was ejected.[23] This type of fragment would survive irradiation by visible radiation, a procedure which usually differentiates between coordinatively saturated and unsaturated species. Because the positions of the bands of 4 are so different from $MnX(CO)_4$, such an explanation cannot be credited.

The spectrum of $MnCl(H_2)(CO)_4$ can assist in the interpretation of the spectrum of $MnCl(CO)_4$. The lack of correlation between the bands at 2019 and 1977 cm^{-1} suggests that the bands reported by McHugh et al. belong to two different species, presumably isomers of $MnCl(CO)_4$.[4] Were there to be two isomers, then the pattern of behavior is completely analogous to what is observed for $MnH(CO)_4$ and $Mn(CH_3)(CO)_4$, for which isomers of C_{4v} and C_s symmetry have been characterized.[24,25] The bands at 2118 and 2019 cm^{-1} can be assigned to the isomer of C_{4v} symmetry. The bands at 2124, 2052, and 1978 cm^{-1} can be assigned to the isomer of C_s symmetry. The fourth expected band of such a species may be buried amongst the intensity due to $MnCl(CO)_5$.

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[22] The shoulder at 794 cm^{-1} is probably an overtone of **1Br**; it is observed in HD- and D_2-containing matrices as well. Thus, a single band results from the symmetric Mn−H_2 stretch. The simplicity in the Mn−H_2 stretch is in contrast to what was observed for $Cr(H_2)(CO)_5$.[3] This may indicate that H_2 is less free to rotate in **1Br**.

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