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Photolysis of Tetracarbonylmethylcobalt(I) and Tetracarbonylhydridocobalt(I) in Inert-Gas and Hydrogen-Containing Matrices: The Reaction of 16-Electron, Coordinatively Unsaturated Complexes with Dihydrogen

Ray L. Sweany* and Franklin N. Russell

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

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The photolysis of $CH_3Co(CO)_4$ in inert-gas matrices yields two isomers of $CH_3Co(CO)_3$, I(Ar) and II(Ar). The spectrum of I(Ar) is consistent with a molecule of C_{3v} symmetry and corresponds to the structure of the parent molecule that has lost the axial carbonyl ligand. The other isomer gives a spectrum consistent with a molecule of lower symmetry, an isomer which is formed from $CH_3Co(CO)_4$ by the loss of an equatorial CO. Both isomers recombine with CO readily to give the parent $CH_3Co(CO)_4$. In the presence of H_2, the spectrum of irradiated $CH_3Co(CO)_4$ is grossly similar to what is observed in argon matrices. The species that correlates with I(Ar) is unaffected by the presence of H_2. On the other hand, the species that corresponds to II(Ar) does not recombine with CO. Rather, it (II(H_2)) is converted into CH_4, $HCo(CO)_4$, and $H_3Co(CO)_3$ when irradiated by a medium-pressure mercury lamp filtered by cobalt glass. Dihydrogen is presumed to be coordinated to cobalt in II(H_2) because of the lack of reactivity with CO and because of similarities between spectra of II(Ar), II(H_2), and $CH_3Co(CO)_3N_2$. The surprising similarities between the spectrum of II(Ar) and II(H_2) can be ascribed to interactions between the vacant coordination site of II(Ar) and the methyl group. The interaction of H_2 and coordinatively unsaturated cobalt complexes formed from $HCo(CO)_4$ was reinvestigated. In an earlier investigation, spectral changes were interpreted as evidence of the formation of a trihydride, $H_3Co(CO)_3$ (III). At the time of this hypothesis, little was known about the existence of dihydrogen adducts. The spectrum of III is very similar to that of II(H_2). This similarity has led us to reformulate the species as $H(H_2)Co(CO)_3$. A detailed energy factored force field that includes some of the hydrogen-containing vibrational coordinates has been determined. A fit of the observed intensities suggests that the environment about cobalt is nearly square-pyramidal, with the hydrogen molecule occupying the axial position. More detailed studies of the reactions of $HCo(CO)_4$ and H_2 in matrices have also led to the identification of another product that is the product of a reaction with two molecules of H_2, both presumably coordinated.

Introduction

Matrix-isolation techniques have proven ideal for the study of reactive organometallic complexes that result from the photolysis of stable 18-electron precursors.[1] One of the most extensively utilized processes involves the removal of a carbonyl ligand, the reversal of which can usually be prevented. Less successful have been studies of homolytic processes that result in the formation of a radical pair; this failure is due to facile recombination of the radical products that are generated in a cage with little propensity for escape at such low temperatures. Thus, the cleavage of metal–metal bonds are usually not observed in matrices.[2,3] Observations of the homolysis of M–H bonds in CO matrices have been reported, however. The success in these instances is due to the mobility of hydrogen and its ability to form formyl radicals in CO matrices.[4–7] In particular, when $HCo(CO)_4$ is irradiated with 254-nm light, the homolytic cleavage of Co–H bonds competes especially well with CO dissociation.[5]

The electronic structures of methyl–metal complexes are very similar to hydridometal complexes so that one might expect to observe homolysis of the metal–methyl bond.[8,9] Recognizing that the quantum yield of H–Co homolysis is probably larger than the yields for homolysis which are exhibited by any of the other hydrides which have been studied to date, we undertook a study of the photochemistry of $CH_3Co(CO)_4$. We have found little evidence to suggest that homolysis occurs. Rather, the principal products of ultraviolet irradiation of $CH_3Co(CO)_4$ are formed by CO loss. This behavior is analogous to what has been observed in matrices for several other organometallic alkyl complexes.[10–13] We report here two isomers of the coordinatively unsaturated $CH_3Co(CO)_3$, their reactivity with dihydrogen, and some related studies of $HCo(CO)_4$.

Experimental Section

$CH_3Co(CO)_4$ was synthesized by syringing freshly distilled dimethyl sulfate into an evacuated flask containing solid $NaCo(CO)_4$ to which was attached a trap cooled to −196 °C. The contents of the trap were either resublimed at 0 °C to remove small amounts of dimethyl sulfate or used without further purification. Matrices were formed by subliming the contents of the trap at −90 °C into a flow of matrix gases just prior to deposit.

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Dimethyl sulfate, the principal impurity, it not very volatile under such conditions and was present to a very small extent in the matrices. The most intense infrared absorptions of dimethyl sulfate were observed in matrices but underwent no significant changes as a result of photolysis. Even small amounts of dimethyl sulfate interfered with ESR studies. Resublimed $CH_3Co(CO)_4$ were not so affected.

Although the concentration of the organometallic species in the matrix is not known, we argue that the analyte is well-isolated for the following reasons: bandwidths of nondegenerate modes were on the order of 2–4 cm^{-1} in argon, these bands were symmetric, and the appearance of the spectrum did not change appreciably with deposition rates varying over a factor of 2. Further, the products of irradiation either are known mononuclear complexes or can be converted into known mononuclear complexes. In studies of $CH_3Co(CO)_4$, the only feature that might be ascribed to near-neighbor interactions is one appearing at 1963.9 cm^{-1} (Ar), the origin of which is not understood at present. The broad absorption grew as a result of ultraviolet irradiation but did not then lose intensity when the matrix was subsequently exposed to a strong visible light source. Thus, it did not behave typically for bands due to coordinatively unsaturated complexes.

Some elaboration is necessary on why the widths of carbonyl modes are sensitive to the homogeneity of the immediate environment. If a molecule that is more polarizable than a typical matrix molecule were present in the vicinity of an oscillating C–O group, the interaction would perturb the vibration and shift the energy of the transition to lower energy.[14] In poorly isolated samples, that fraction of molecules so affected will absorb on the low-energy side of the absorption envelope of those molecules that are well-isolated. This behavior makes the use of spectral subtraction in hydrogen-containing matrices problematic. The bands do not lose intensity uniformly across their width when a species is being converted into a product by reaction with hydrogen. This is because the molecules that are most reactive will have at least one molecule of hydrogen as a near neighbor. The spectra of these molecules will not be uniformly distributed across the absorption envelope because of the unique polarizability of dihydrogen. Thus, only that part of the envelope that results from the molecules with nearby hydrogen will be readily attenuated.

The synthesis of $HCo(CO)_4$ for matrix use has been described elsewhere.[4] Isotopically labeled $HCo(CO)_4$ was obtained by exposing $HCo(CO)_4$ to ^{13}CO for about 15 min at room temperature. The enriched gas (ICN Biomedicals) was found to contain 10% $^{13}C^{18}O$ by mass spectral analysis. Enrichment levels were estimated from the ratio of absorptions of CO that were present in the unphotolyzed matrices. The enriched samples were not homogeneous because the hydride was not stirred as it was being exposed to the ^{13}CO atmosphere. Thus, the enrichment level decreased as a function of how much of the sample had been used. In one particular experiment, a nonstatistical distribution of isotopomers was assumed to fit the spectrum of $HCo(CO)_4$ and the ensuing $H(H_2)Co(CO)_3$.

The argon and hydrogen were supplied by Airco. The argon was of 99.99% purity, and the hydrogen was of 99.5%. D_2 of 99.5% purity was obtained from Matheson. The cold temperature equipment has been described elsewhere.[29,30] Irradiation of matrices was affected by the use of 1-in. long, low-pressure mercury lamps that are manufactured by Hammamatsu Corp. They were mounted adjacent to the window of the cryostat. Alternatively, matrices were irradiated by a medium-pressure mercury lamp (H39KC-175/DX supplied by Norelco) which was focused through quartz lenses from approximately 18 in. The glass shroud of the lamp was cut away in order to transmit ultraviolet radiation. Several filters were used to selectively irradiate in particular regions of the spectrum. A piece of cobalt glass transmitted light with $\lambda > 690$ nm (at which wavelength the optical density was 1.0) and between 480 and 320 nm. A piece of ordinary crown glass became opaque at 315 nm. A 10-cm path through Cl_2 is opaque from 370 nm out to 295 nm.

Infrared spectra were recorded on a Beckman 4260 infrared spectrophotometer which was, in latter studies, coupled to a Zenith 100 microcomputer. Analog signals were digitized by a Dual Systems 12-bit A-to-D converter at intervals determined by the spectrometer at a rate of one point every 0.2 cm^{-1}. The computer and spectrometer were set up so that signal averaging could be accomplished by multiple scanning. The wavelength marker signal of the spectrometer was also received by the computer, and the data set was marked every 50 cm^{-1} for absolute frequency calibration. The spectrometer was calibrated by using DCl and ^{13}CO in the region of the carbonyl absorptions. Wavenumber data are corrected to vacuum conditions and are accurate to ±1 cm^{-1} in regions of the spectrum where bands are reasonably well-resolved. In order to obtain accurate peak areas of unresolved peaks, data were subjected on several occasions to curve resolution using a program adapted from one written by J. Pitha and R. N. Jones of the National Research Council of Canada. The force field for $HCo(CO)_3H_2$ was fit by using a program written by K. Purcell of the University of Illinois. The **G** matrix was constructed by using reciprocal atomic masses, and no attempt was made to adjust those values to optimize the fit.[15] The force field of $DCo(CO)_3D_2$ was first fit by using only carbonyl force constants. The set of observed frequencies was then augmented by those of $HCo(CO)_3H_2$. The force field was expanded to include the metal–hydrogen stretching force constant and those interaction force constants that link the M–H stretch to the stretching vibration to both types of carbonyl group.[16] Initially, only the force constants involving the hydrogen were allowed to vary in order to accommodate the frequency shifts caused by the coupling to the M–H stretching mode. Finally, the entire force field was allowed to adjust to give a best fit. Although no band was assigned to the M–H stretch of $HCo(CO)_3H_2$, it is interesting to note that the solution of the force field assigned a value of the stretching force constant for the hydride ligand that was nearly the same as was found for $HCo(CO)_4$. Having obtained a best fit of the frequencies, the eigenvectors expressed in terms of the valence coordinates were used to estimate the intensities of the bands. In this endeavor, the dipole moment derivatives of each of the carbonyl groups were treated as the same in each of the normal modes. Calculated intensities were compared to the ratios of intensities of the ^{12}C isotopomer in order to determine the most probable bond angles. Spectra were then calculated and plotted of mixtures of isotopomers for comparison with observed spectra. The bond angle for the dicarbonyl species IV could be obtained by an analytical expression.[17] Integrated intensities of the resolved absorptions were used in this calculation.

ESR spectra were recorded at 9 GHz by using a Varian E3 spectrometer. Samples were deposited on an OFHC rod cooled by a Displex refrigerator. Typically, spectra were recorded by using 1 mW of irradiating power with a modulation amplitude of 6.3 G at 100 kHz. Visible and ultraviolet spectra were recorded on a Cary 17 spectrometer. Samples that were analyzed in this fashion were also observed in the infrared so that bands could be correlated. Thus, the cryostat windows and the matrix support were made of infrared transmitting materials, either NaCl or KBr.

Results and Discussion

$CH_3Co(CO)_4$ in Ar and Ar/H_2 Matrices. $CH_3Co(CO)_4$ is a molecule of C_{3v} symmetry;[18] the environment at cobalt is that of a trigonal bipyramid with a methyl group in one of the axial positions. One expects three infrared-allowed transitions in the carbonyl region of the infrared spectrum, two of A_1 symmetry and one of E symmetry. These bands are tabulated in Table I for a variety of matrices. Argon matrices of $CH_3Co(CO)_4$ show considerable perturbation of the carbonyl bands. In particular, the E mode is split into three components at 2025.7, 2022.7 and 2016.7 cm^{-1}. The magnitude of the splitting is larger than any that we have encountered for carbonyl groups of well-isolated molecules and may reflect the difficulty

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Table I. Position of Infrared Absorptions of $CH_3Co(CO)_4$ (I and II) in the Carbonyl Region

assignt	Ar	Xe	Ar/H_2	CH_4
$CH_3Co(CO)_4$	2108.8	2103.7	2109.9	2106.2
II	2087.4	2083.0 br	2088.7	2086.4
	2084.6^b			
$CH_3Co(CO)_2$?				2071.9
$CH_3Co(CO)_4$	2039.2	2034.2	2040.2	2036.5
$CH_3Co(CO)_4$ + II	2025.7^b			
$CH_3Co(CO)_4$	2022.5	2014.5	2023 br	2019.1
$CH_3Co(CO)_4$	2016.7^b			
?				2014.9 sh
II	2006.5	2001.3	2008.8	2005.1
$CH_3Co(CO)_2$?				1992.4
$CH_3Co(CO)_4$ ^{13}C	1985.8		1986.8	
$CH_3Co(CO)_4$ ^{13}C	1981.5^b			
I	1990.4	1981.1 br	1992.4 br	1986.0
I	1985.6^b			
I	1983.4^b			
?	1963.9	1955.2		1962.7

[a] Band positions are accurate to ±1.0 cm^{-1} for bands that are well-resolved. Positions are corrected to vacuum conditions. [b] Bands in argon are believed to be of the same origin but split by the site.

of packing argon atoms around the vicinity of the methyl and equatorial carbonyl groups. The analogous E mode of $HCo(CO)_4$ is not so affected in argon matrices. Also, the spectrum of $CH_3Co(CO)_4$ is less severely perturbed in CH_4, Xe, and Ar–H_2 mixtures.

Irradiation of $CH_3Co(CO)_4$ at 254 nm produces new infrared absorptions in all matrices except CO; these data are recorded in Table I. Accompanying the other changes in the spectrum is the growth of a band at 2138.9 cm^{-1} which is undoubtedly due to free CO. Figure 1 shows the spectrum of $CH_3Co(CO)_4$ in argon both before and after photolysis. A complex of bands at about 1990 cm^{-1} is attributed to a single vibrational mode of one species, I(Ar). This assignment is justified because the bands grow and decline in the same proportion throughout the course of an experiment and because they correlate with single broad bands in the other matrices. The complexity of the spectrum in argon is attributed to site splitting; this pattern of splitting resembles the pattern displayed by the E mode of $CH_3Co(CO)_4$ in argon. Another band that grows in as a result of ultraviolet irradiation also appears to be split in argon matrices. The pair of bands at 2087.4 and 2084.6 cm^{-1} appears as a single, sometimes broad band in the other matrices. This pair is also presumed to be a single vibrational mode of a single species, split by differing trapping sites.

With the exception of the band at 1963.9 cm^{-1}, most of the new bands that result from ultraviolet irradiation of $CH_3Co(CO)_4$ must be assigned to coordinatively unsaturated species rather than to radical species. There are several observations that support such a claim. The growth and decline of the band due to free CO correlate with the growth and decline of the other new bands. This behavior is consistent with the reversible loss of CO. Except when hydrogen is present, the reversal of the changes caused by ultraviolet irradiation is best accomplished by exposing the matrix to a strong source of visible radiation. Argon matrices that have been irradiated with ultraviolet light show an absorption at 468 nm. It is the presence of such absorptions at long wavelength that permits coordinatively unsaturated species to become activated in matrix experiments, with recombination with CO a frequent outcome.[1]

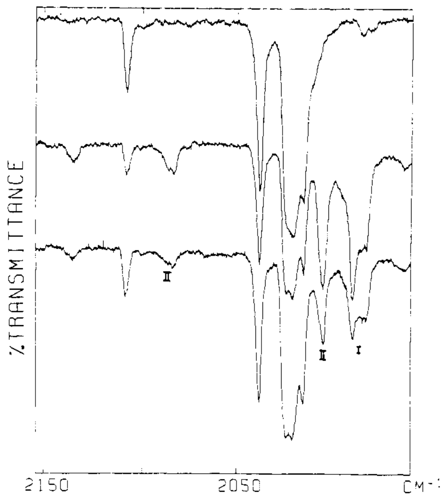

Figure 1. The spectra are the average of three scans, one point being taken every 0.2 cm^{-1}. Uper plot: computer-drawn spectrum of $CH_3Co(CO)_4$ in an argon matrix. The matrix was deposited over 52 min with a sublimation temperature of −90 °C. Middle plot: spectrum of the matrix after 18 min of irradiation with a low-pressure mercury lamp. Lower plot: spectrum of the photolyzed matrix after approximately 15-min exposure to the full irradiance of the Nernst glower. The behavior exhibited in these three spectra contrast with what is observed in a hydrogen-containing matrix as shown in Figure 2.

The behavior just described is not what one would expect if these new bands were due to radical products. The two most likely radical products, CH_3 and $Co(CO)_4$, probably cannot coexist in the same argon cage because of their recombination efficiency. To be observed, the radical pair would have to become separated, presumably by making use of the excess energy of the photon. If they did become so separated, it is unlikely that absorption of a photon from the visible portion of the spectrum would cause sufficient mobility so as to allow recombination. Thus, the reversibility of the damage caused by ultraviolet irradiation argues for the product having been formed via CO loss processes. There is no infrared evidence for the homolysis of the CH_3–Co bond. In CO matrices, homolysis of M–H bonds is readily detected because CO loss processes are quenched.[4-7] Irradiation of $CH_3Co(CO)_4$ in CO leads to no detectable changes. In argon, one expects $Co(CO)_4$ absorptions at 2022.9 and 2016.2 cm^{-1}.[4] These are within experimental error of the positions of two of the components of the E mode of $CH_3Co(CO)_4$. Thus, detection of $Co(CO)_4$ is difficult. The ESR of photolyzed $CH_3Co(CO)_4$ in argon shows growth of methyl and $Co(CO)_4$ signals.[4,19] Although the methyl signal is ubiquitous, the concomitant growth of both signals suggests that homolysis does occur to a small extent. No attempt was made to integrate the signals in order to determine if the amount of growth in both was the same. Because ESR spectroscopy is a very sensitive technique, these results need not be viewed as contradicting the infrared results. The quantum yield for homolysis must be very small. The larger yields of homolysis products from metal hydrides in CO matrices may be due to two factors. The stability of CH_3CO is not as great as that of HCO,[20] and one expects a more dominate cage effect in the homolysis of CH_3–M bonds. Thus, it is unlikely that matrix studies will lead to a determination of the yields of carbonyl loss and CH_3–M homolysis.

Granting that most of the absorptions caused by ultraviolet irradiation are due to CO loss, it is difficult to ascribe

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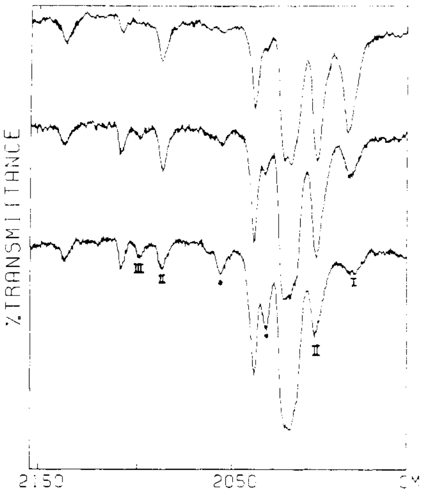

Figure 2. These spectra were taken of $CH_3Co(CO)_4$ in an argon matrix containing 24 mol % H_2. The deposition conditions were similar to those used to obtain the spectra shown in Figure 1. The asterisk identifies bands due to $HCo(CO)_4$. The roman numerals represent species that are defined in the text. Upper plot: the result of irradiating $CH_3Co(CO)_4$ for 26 min with a low-pressure mercury lamp. Middle plot: after additional irradiation with a medium-pressure mercury lamp filtered by Cl_2 (5-cm path cell) and crown glass. The spectrum shows the attenuation of bands due to I(H_2) as bands due to $CH_3Co(CO)_4$ grow in. Lower plot: after additional irradiation with the medium-pressure lamp filtered by cobalt glass for 50 min. One can see by this spectrum the attenuation of bands due to II(H_2) along with major gains in intensity of bands due to $HCo(CO)_4$ and III.

a stoichiometry or geometry to the species that are observed. Upon irradiation with visible light, the bands at 2071.9 and 1992.4 cm^{-1} in methane attenuate more rapidly than the other new bands; thus they may be due to a doubly unsaturated complex, $CH_3Co(CO)_2$. Because no corresponding bands were observed in other matrices, we will not attempt to develop this hypothesis. In argon, methane, and xenon, the bands that correlate with 2086, 2005, and 1986 cm^{-1} (methane) become attenuated by visible light at the same rate as if they belong to the same species. At the same time, bands due to $CH_3Co(CO)_4$ grow in. This inverse correlation suggests that these three bands are due to $CH_3Co(CO)_3$. In spite of the apparent correlation of intensities, these bands actually belong to two species.

It was not clear that these new bands belonged to two species, I(Ar) and II(Ar), until hydrogen was doped into the matrix. (We will append (Ar) and (H_2) to the Roman numeral designations to indicate the matrix in which I and II are found. It will become clear later that I(Ar) and I(H_2) are indistinguishable, whereas II(Ar) and II(H_2) are two different species, albeit closely related.) In hydrogen-containing matrices, the bands that are assigned to $CH_3Co(CO)_3$ do not all photobleach under the same conditions. When a photolyzed matrix is exposed to the visible irradiance of the Nernst glower or a chlorine-filtered, medium-pressure mercury lamp, the band at 1992.4 cm^{-1} becomes attenuated while the other bands that are assigned to $CH_3Co(CO)_3$ are little affected (see Figure 2). As the band at 1992 cm^{-1} becomes attenuated, the amount of free CO also becomes reduced and the bands due to $CH_3Co(CO)_4$ exhibit growth. From this and the observations made in argon, it is clear that the band at 1992.4 cm^{-1} is due to $CH_3Co(CO)_3$ (I) and that another species, II, is also present that is characterized by bands at 2088.7 and 2008.8 cm^{-1}. I (I(Ar) or I(H_2)) is assigned to $CH_3Co(CO)_3$, a molecule of C_{3v} symmetry for which two infrared-active carbonyl bands are expected. No absorption has been assigned to I in the region of 2100 cm^{-1} where one would expect to find the totally symmetric breathing mode of the three carbonyls. Depending on the planarity of the three carbonyls, this mode can be quite weak. What makes the assignment more convincing is the similarity of the splitting patterns of the band at 1992 cm^{-1} in argon with that of the E mode of $CH_3Co(CO)_4$. If the symmetry of I is C_{3v}, then the band at 1992 cm^{-1} is an E mode. The similar appearances of the two bands may reflect the fact that the normal modes are nearly identical in composition, and, hence, they are similarly affected by the site.

II(Ar) is certainly $CH_3Co(CO)_3$ as well[21] but must be a lower symmetry because of the relatively intense band that can be assigned to the totally symmetric breathing mode at 2088.4 cm^{-1}. It is attractive to view it as a derivative of the parent molecule with a vacancy in the equatorial plane, just as the other isomer can be viewed as a derivative of the parent molecule with an axial vacancy. Three bands are expected for such a molecule of C_s symmetry. The third band appears as a shoulder on bands due to the parent at 2025.7 cm^{-1} in argon. It is unlikely that II(Ar) can be ascribed to a stoichiometry other than $CH_3Co(CO)_3$. When II(Ar) is irradiated with visible light in the absence of H_2, only bands assigned to $CH_3Co(CO)_4$ grow in. II is distinct from anything that is formed from $CH_3COCo(CO)_4$ by photolysis, and in particular, II is not $CH_3COCo(CO)_3$.[22] A reviewer has suggested the possibility that II(Ar) might be formulated as a coordinatively saturated species, $CH_2CoH(CO)_3$. Observations of $CH_2CrCp(CO)_2H$ are precedent for such an expectation.[13] Such a formulation is unlikely for several reasons. The carbonyl bands of II(Ar) are in the region where one might expect a coordinatively unsaturated species. Also, bands are identified in the region of 1100 cm^{-1} that can be assigned to the C–H deformation modes of a methyl group on I(Ar) and II(Ar)[23] (vide infra). Finally, no absorption is noted for an M–H deformation mode in the region of 950–700 cm^{-1}.[24] It should be noted that calculations have been reported for the isoelectronic isomers of $HCo(CO)_3$.[25] Hydride isomers that are isostructural to what has been proposed for I(Ar) and II(Ar) are nearly isoenergetic. The theoretical treatment suggests that other isomers in which the hydride ligand occupies the equatorial site should not be ruled out. The experimental evidence does not differentiate between the various low-symmetry forms of $CH_3Co(CO)_3$. It is clear, however, that several isomers of $CH_3Co(CO)_3$ are not unexpected.

What differentiates II(H_2) from II(Ar) is the insensitivity of II(H_2) to visible irradiation, conditions under which II(Ar) reacts with CO to form $CH_3Co(CO)_4$. Moreover, when II(H_2) is irradiated with ultraviolet radiation, rather than combining with CO, methane is lost as evidenced by the growth of a band at 1304 cm^{-1}[26] and bands assigned to hydride containing species. These include $HCo(CO)_4$ and $H(H_2)Co(CO)_3$ about which more will be described below. The observed chemistry can be rationalized by eq 1–6; it requires that the hydrogen molecule be attached to II(H_2) in some fashion. (Reaction 1 reverses with visible

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photons when no hydrogen is present.)

$$CH_3Co(CO)_4 \xrightarrow{254\ \mathrm{nm}} CH_3Co(CO)_3 + CO \tag{1}$$

$$I(H_2) + CO \xrightarrow{\text{visible light}} CH_3Co(CO)_4 \tag{2}$$

$$II(H_2) + CO \xrightarrow{\text{visible light}} \text{little or no reaction} \tag{3}$$

$$II(H_2) \xrightarrow{\text{ultraviolet}} HCo(CO)_3 + CH_4 \tag{4}$$

$$HCo(CO)_3 + CO \rightarrow HCo(CO)_4 \tag{5}$$

$$HCo(CO)_3 + H_2 \rightarrow H(H_2)Co(CO)_3 \tag{6}$$

$II(H_2)$ must interact with hydrogen in some fashion so as to prevent its reaction with CO, and, eventually, the hydrogen is used to convert the complex to a hydride with the extrusion of methane. The interaction causes very little perturbation of the spectrum of II, however. Thus, it is unreasonable to claim that the hydrogen has oxidatively added to cobalt.[27] As an alternative, we propose that hydrogen is coordinated in a fashion similar to what has been observed in a variety of transition-metal complexes.[28-34] Large amounts of $II(H_2)$ have not been observed because the photolytic conditions that are necessary for the formation of II also result in the loss of II as $HCo(CO)_3$ is formed. It should be noted that nothing was observed in the region of the spectrum of $II(H_2)$ which is characteristic of the M–H deformation modes except the band at 708 cm^{-1} which can be attributed to $HCo(CO)_4$. This also argues against the hydrogen having oxidatively added. Since the elimination of methane placed a limit on how much $II(H_2)$ could be formed, attention was directed at the isoelectronic $H(H_2)Co(CO)_3$ for which the analogous elimination process yields no new species. The results of those experiments appear in the next section.

It is bothersome that the carbonyl regions of the spectra of II(Ar) and $II(H_2)$ are so similar since the two molecules differ by the coordination of H_2. The reason for the similarity may have more to do with unique properties of the methyl group than any peculiarities in the interaction of H_2 with cobalt. Although we have argued that the methyl group has not undergone α-elimination, the evidence points to some form of interaction between the methyl group and the vacant coordination site. In irradiated argon matrices, two new weak absorptions are noted at 1154 and 1146 cm^{-1}. The intensity of these bands correlates with the intensities of carbonyl bands due to I(Ar) and II(Ar), respectively. The bands are located at somewhat lower energy than the symmetric deformation mode of the parent molecule at 1181 cm^{-1}.[35] As they are not observed in the spectrum of $CD_3Co(CO)_4$, they are assigned to C–H deformation modes of I(Ar) and II(Ar). In the presence of H_2, the absorption at 1154 cm^{-1} is still observed, but the absorption at 1146 cm^{-1} is not observed. Instead, an absorption is observed at 1176 cm^{-1} that is nearly coincident with the band at 1183 cm^{-1} of $CH_3Co(CO)_4$. These data suggest that the methyl group is perturbed in II(Ar) in a manner that is not evident in $II(H_2)$. It is impossible to derive a structural model of the methyl interaction from the data in hand. Theoreticians have explored how methyl groups could stabilize a coordinatively unsaturated metal either by establishing an agostic interaction or by becoming canted in the coordination site.[36] Either possibility must be entertained at this point. Also, it should be noted that the structure of methylene can be greatly perturbed when coordinated to an electron-deficient metal.[37]

In further efforts to document the interaction of H_2 with cobalt, argon matrices containing N_2 were deposited with $CH_3Co(CO)_4$, hoping that the nitrogen would mimic hydrogen. After photolysis, new bands were observed at 2090.4, 2078.6, 2071.2, 2007.5, 1997.5, 1989.8, and 1961.2 cm^{-1} in the carbonyl region. After a period of exposure to the Nernst glower, only the bands at 2079, 1998, and 1961 cm^{-1} remained. The band at 1961 cm^{-1} has not been assigned to any particular species; it corresponds to bands observed in other matrices. The intensities of the bands at 2079 and 1998 cm^{-1} do correlate with each other and therefore belong to the same species. It is reasonable to claim that the bands are due to a coordinatively saturated moiety involving N_2 because they are not further attenuated by further irradiation by visible light. We assign the bands to an adduct of $CH_3Co(CO)_3$ and N_2 which we will refer to as $II(N_2)$ because the appearance of the spectrum resembles that of II(Ar) and $II(H_2)$. A band at 2257 cm^{-1} also belongs to the same species and is assigned to the N–N stretch. The similarity between the spectra of $II(H_2)$ and $II(N_2)$ suggests the the two species are isomorphic. In a later section, we will show the spectrum of III, $HCo(CO)_3H_2$, which also mimics the spectrum of $II(H_2)$. Two points are worth noting. First, H_2 and N_2 do not coordinate to an axial position in an isomer analogous to I(Ar). σ-Bonding ligands usually are found in the axial positions. Carbon monoxide bound in this position does not act so much as a π acceptor as a σ donor.[9] The absence of any evidence of coordinated H_2 or N_2 in the axial position may reflect the weaker σ-bonding capabilities of these two ligands as compared to CO. If hydrogen is found in the equatorial plane, then it implies it is bound as a π-bonding ligand, and, therefore, it should be viewed as an η^2 ligand. The second point that we note concerns the positions of the carbonyl bands. The spectra of II(Ar) and $II(H_2)$ in the carbonyl region are both displaced to higher energy relative to the nitrogen adduct. The position of II(Ar) is unexpected in this ordering. In other instances, the π-accepting, N_2 group causes the carbonyl spectrum of the coordinatively unsaturated complex to shift to higher energy.[38] As in the preceding paragraph, this evidence

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[27] The carbonyl modes have been used to estimate the amount of electron density residing on the metal. In oxidatively adding, hydrogen is expected to withdraw a significant amount of charge off the metal. See ref 29, 30, and Sweany, R. L.; Owens, J. W. *J. Organomet. Chem.* **1983**, *255*, 327–334.

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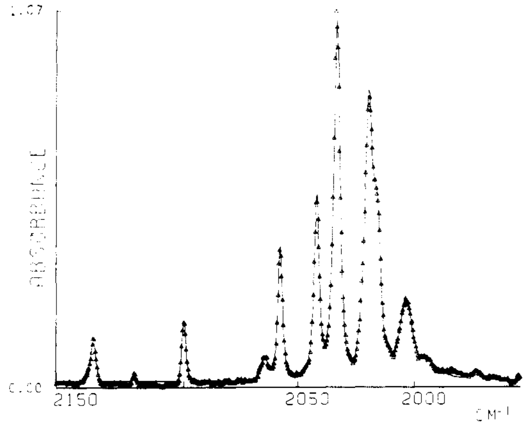

Figure 3. Spectrum of $HCo(CO)_4$ in a hydrogen-containing matrix after irradiation with a low-pressure mercury lamp. The triangles represent every other point of the actual spectrum. The solid line is of the fitted spectrum from which peak areas were calculated. Because of the sloping base line, a second fit was obtained for the region from 2155 to 2080 cm^{-1} to calculate more accurate areas of the peaks in that region.

suggests an unusual interaction of the methyl group with the vacant coordination site. To summarize the above three paragraphs, the evidence for H_2 occupation of the vacant coordination site is compelling. Carbon monoxide is prevented from reacting with II(H_2), and the photodecomposition products of II(H_2) make use of the hydrogen. What is disturbing is the similarity of the spectra in the carbonyl region between II(Ar) and II(H_2). It is not unreasonable to expect some interaction between a methyl group and a vacant coordination site, and the observations of the C–H deformation region and of $CH_3Co(CO)_3$ in N_2-containing matrices support the existence of such an interaction.

$HCo(CO)_4$ in H_2/Ar Matrices. Previously, it was reported that $HCo(CO)_4$ produced a trihydride, $H_3Co(CO)_3$, in hydrogen-containing matrices.[39] The assertion that the hydrogen had oxidatively added was based on observations of isotope exchange and on the relatively high carbonyl frequencies. Comparisons of the spectrum of $H_3Co(CO)_3$ with that of $HCo(CO)_3$ could not be made because $HCo(CO)_3$ has not been well-characterized.[4,5,40]

The observation of coordinatively unsaturated forms of $CH_3Co(CO)_3$ makes the prediction of the spectrum of $HCo(CO)_3$ somewhat less speculative. The features of $CH_3Co(CO)_4$ are found approximately 10 cm^{-1} to smaller wavenumbers as those of $HCo(CO)_4$. The features of II(H_2) are also located about 10 cm^{-1} to smaller wavenumber as those of the analogous $H(H_2)Co(CO)_3$ (vide infra). These differences may be attributed to differences in the electron-withdrawing capabilities of the hydride and CH_3 groups and to structural differences, to the extent that they occur. With the expectation of a 10 cm^{-1} shift on trading methyl for hydrogen, we can attempt to interpret the spectrum of $HCo(CO)_3$. One band has been assigned to $HCo(CO)_3$ at 1997 cm^{-1}.[4,40] The band at 1997 cm^{-1} reasonably correlates to a band at 1987 cm^{-1} of an analogous methyl complex. This latter band belongs to I(Ar), a molecule of C_{3v} symmetry. Hence, the band observed in matrices of photolyzed $HCo(CO)_4$ can be assigned to $HCo(CO)_3$ of the same symmetry. A tricarbonylhydridocobalt of the same structure as II might absorb in the region of 2018 cm^{-1}, a region which is dominated by the spectrum of $Co(CO)_4$ in argon matrices of $HCo(CO)_4$. It was noted that the intensity ratio of the bands of $Co(CO)_4$ did vary, which suggests that another species like $HCo(CO)_3$ might be absorbing at the same energy.[4] Other bands due to this species might occur at 2098 and 2036 cm^{-1}. These bands are expected to be weaker than a band at 2018 cm^{-1}, and nothing in those regions have been re-

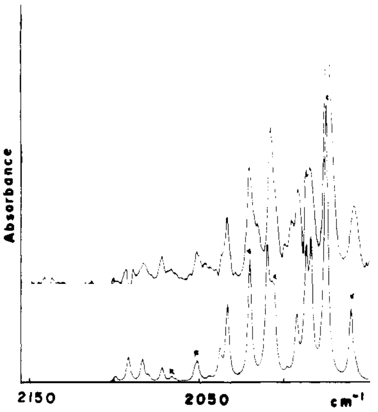

Figure 4. The upper spectrum is a difference spectrum, showing the positions of bands assigned to isotopomers of $DCo(CO)_3D_2$ and IV without interferences due to starting material. The difference spectrum was calculated from spectra from two different experiments. There are two reasons for choosing an initial spectrum from another experiment. In the spectrum that was chosen the optical densities of even the most intense bands of the unphotolyzed matrix were less than 1.0. Thus, Beer's law is more likely to be obeyed. Second, this preparation of $DCo(CO)_4$ showed a smaller amount of contamination by $HCo(CO)_4$ as judged by the Co–D and Co–H deformation modes. The bottom spectrum is a calculated spectrum using the force field of Table III and the following assumptions: $\theta = 105°$, $\Phi = 170°$, and an abundance of 54% ^{13}CO in addition to those assumptions that are mentioned in the text. Additionally, bands due to IV were added to the calculated spectrum by assuming a carbonyl bond angle of 136°. The positions of those bands are marked by an asterisk. All bands are assumed to be Lorentzian with a width of 2.5 cm^{-1} at half-height.

Table II. Position of Infrared Absorptions of $HCo(CO)_4$ (III and IV) in the Carbonyl Region

assignt	$HCo(CO)_4/H_2$[b]	$DCo(CO)_4/D_2$
$HCo(CO)_4$	2121.0 (1.00)[c]	2121.1
$HCo(CO)_4$	2058.6 (23.4)	2052.9
$HCo(CO)_4$	2034.4 (79.4)	2034.2
III	2100.2 (1.00)	2100.2
III	2042.5 (4.51)	2038 sh[a]
III	2020.8 unsym[d] (9.35)	2020.8
IV	2066.5 (1.00)	2064.2
IV	2006.2 (6.04)	2004.5
$HCo(CO)_3$	1994.9	1995.8

[a] The band is a shoulder on the low-energy side of another band. The measurement of its position is less accurate than it would be if it were well-resolved. [b] Numbers in parentheses are relative areas based on the curve resolution of the spectrum shown in Figure 3. [c] Area is flawed somewhat because the fit of the spectrum requires a flat base line. A segment of the spectrum was fit so that the base line could be more appropriately fit. [d] Curve resolution shows a band at 2016 cm^{-1} that is assignable to $Co(CO)_4$, a known product of irradiated $HCo(CO)_4$.

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(38) To substantiate this claim, we cite the ligand effect constants that have been calculated by Timney. A N_2 molecule either cis or trans to a CO will cause the associated stretching force constant to increase. Thus, the spectrum of $M(CO)_5N_2$ is expected to be at higher frequency than a $M(CO)_5$ fragment of the same symmetry. Timney, J. A. *Inorg. Chem.* **1979**, *18*, 2502–2506. The difference is less pronounced in $CH_3MoCp(CO)_2$ which may indicate some CH_3Mo interaction in this molecule. Rest notes that $CH_3MoCp(CO)_2$ is observed even in a pure N_2 matrix. See ref 10. We have failed to obtain an H_2 adduct of the molecule. In tetrahedral symmetry, the same ordering is observed for $Ni(CO)_3$ and $Ni(CO)_3N_2$ as for octahedral complexes. Rest, A. J. *J. Organomet. Chem.* **1972**, *40*, C76–C78. DeKock, R. L. *Inorg. Chem.* **1971**, *10*, 1205–1212.

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ported although the latter position is obscured by the parent, $HCo(CO)_4$. We infer from this analysis that the photolysis of $HCo(CO)_4$ does yield two isomers of $HCo(CO)_3$, the one of C_{3v} symmetry being more prominent in the spectrum.[25,41]

Noting a strong resemblance between the spectrum of $CH_3Co(CO)_3(H_2)$ and what is formed by the photolysis of $HCo(CO)_4$ in the presence of hydrogen, the latter system was reexamined. Far greater quantities of the new species have now been obtained in recent matrix studies than were observed in the previous study.[39] (See Figure 3). Two products have been characterized by absorptions in the carbonyl region of the infrared spectrum. The band positions are noted in Table II. The new species shall be referred to as III and IV. There are two bands associated with the spectrum of IV in the carbonyl region. Both sets of bands grow as a result of irradiation with 254-nm light. The sets are differentiated by two procedures. The spectrum of III becomes more intense when a matrix containing III and IV is exposed to ultraviolet radiation filtered by cobalt glass while the bands due to IV are attenuated. Also, the prominence that is attained by the bands of IV is greatest in matrices with high H_2/Ar mixing ratios. This suggests that the formation of IV requires more H_2 than that of III. III is characterized by three bands at 2100.2, 2042.5, and 2020.8 cm^{-1}. Starting with $DCo(CO)_4$ in D_2-containing matrices, the band at 2043 cm^{-1} is found at about 2039 cm^{-1}, a region in which $HCo(CO)_4$ also adsorbs. Such a large shift is associated with a carbonyl mode with a large contribution from the CO that is trans to a hydride ligand. The bands due to IV do not exhibit a measurable shift. Thus, we infer there is no hydride ligand trans to a CO ligand in IV. As reported earlier, continued photolysis of $HCo(CO)_4$ in a D_2-containing matrix results in the formation of $DCo(CO)_4$[39] in a process which may be viewed as exactly analogous to the loss of CH_4 from $CH_3Co(CO)_3(H_2)$. When the isotope exchange was first noted in experiments with $HCo(CO)_4$ and H_2, no examples of coordinated dihydrogen had been reported. It was presumed that oxidative addition was a necessary precondition for exchange. In light of recent evidence for coordinated dihydrogen, the formulation of III as a trihydride must be reexamined. As a result of this reexamination, $H_3Co(CO)_3$ is reformulated as $H(H_2)Co(CO)_3$.

A number of characteristics have been used to differentiate hydrogen that has oxidatively added from hydrogen which is merely coordinated. These include NMR,[28,32,33] infrared,[28-31] and X-ray[28,32] methods. The most convincing infrared evidence for coordinated dihydrogen is the observation of the H–H stretching vibration. This mode is weak, though, and requires either long paths or high concentrations.[31] The mode is broadened by rapid rotation,[31] and recent matrix studies suggest it is still further broadened in low-temperature matrices.[42] Other indirect evidence has been used to ascertain the mode of coordination. Infrared absorptions due to the M–H deformation modes are frequently fairly intense.[24] A single band at 721 cm^{-1} is assignable to III in the region of 950–700 cm^{-1}. This is consistent with at least one normal hydride but does not preclude III from being a trihydride. A trihydrido species is analogous to CH_3 that is characterized by two bands, only one of which is characterized as strong. Thus, the observation of a single mode for III in the region of 950–700 cm^{-1} does not preclude III from being a trihydride. The carbonyl modes can give evidence of the charge on the metal.[27] Oxidative addition of hydrogen will presumably draw charge off the metal leading to carbonyl force constants which are larger than those exhibited if the hydrogen were merely coordinated.[29,30,43] Thus, we have undertaken a force constant determination.

Table III. Force Constants Calculated for $H(H_2)Co(CO)_3$ Compared to Those of $HCo(CO)_4$

	$H(H_2)Co(CO)_3$	$HCo(CO)_4$	$HCo(CO)_4$[a]
k_1[b]	1726.4 ± 2.3	1734.2 ± 2.6	1751
k_2	1688.6 ± 1.7	1706.4 ± 1.1	1696
k_{12}	36.4 ± 0.6	30.0 ± 0.7	30
k_{22}	40.9 ± 1.4	37.2 ± 0.9	35
k_H	224.8 ± 4.4	223.5 ± 0.3	
k_{1H}	7.6 ± 4.1	11.1 ± 3.0	
k_{2H}	−4.1 ± 3.0	−3.7 ± 2.7	

[a] Data taken from ref 5. Fit was without regard to the Co–H vibrational coordinates. [b] Units are nm^{-1}. The subscript 1 refers to the carbonyl ligand trans to a hydride; the subscript 2 refers to the carbonyl ligands that are nominally in the equatorial plane; the subscript H refers to the hydride. The use of two subscripts denotes an off-diagonal force constant.

The force field determination is made more difficult by the mixing of the M–H stretching symmetry coordinate with those carbonyl modes of A_1 symmetry.[16,44] We are aware of only one other instance in which the explicit mixing of the M–H coordinates with the carbonyl modes was included in a force field calculation.[16] The mixing will be pronounced to the extent that the frequency of the Co–H stretch is near the carbonyl modes. The assignment of the Co–H stretch of $HCo(CO)_4$ at approximately 1956 cm^{-1} was aided by observations of $^{13}C^{16}O$- and $^{13}C^{18}O$-substituted molecules. The carbonyl modes of these molecules are nearly coincident with the Co–H stretching vibration. As a result of the extensive mixing, the Co–H stretching vibrations attain uncharacteristically large intensities. Because each isotopomer has its own unique Co–H stretching vibration, a sample having a mixture of ^{13}C-enriched molecules gives a broad infrared absorption which peaks at 1956 cm^{-1}. The assignment of the band is unambiguous. Not only is the band not observed in matrices of $DCo(CO)_4$, but also the behavior of the carbonyl modes that occur at energies below 1956 cm^{-1} is just the opposite of those above 1956 cm^{-1} upon substitution of deuterium for hydrogen. Because of the mixing of the carbonyl modes with the Co–H stretch, the carbonyl bands of A_1 symmetry that are found to higher energy than the Co–H stretch are found at still higher energy for the hydride as compared to the deuteride. On the other hand, the $^{13}C^{18}O$ ligands vibrate at lower energy than the Co–H stretch. The interaction with the Co–H stretching vibration forces these carbonyl modes to still lower energy, again compared to the deuteride. The Co–H stretching vibration of III has not been observed. As the Co–H deformation coordinate is not greatly perturbed in the conversion of $HCo(CO)_4$ into III, it is assumed that the Co–H stretch is not much different for $HCo(CO)_4$ and III.

The energy-factored force field for III was solved making use of additional frequencies obtained from the irradiation of isotopically labeled $HCo(CO)_4$ and $DCo(CO)_4$. A structure of C_s symmetry, analogous to that of II, was assumed. The energy-factored force field consisted of the usual carbonyl force constants as well as a force constant

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(41) The energies of these two isomers has been calculated; the isomer of C_{3v} was found to be more stable. Bellagamba, V.; Ercoli, R.; Gamba, A.; Suffriti, G. B. *J. Organomet. Chem.* **1980**, *190*, 381–392. Similar results were obtained by: Grima, J. Ph.; Choplin, F.; Kaufmann, G. *J. Organomet. Chem.* **1977**, *129*, 221–237.

(42) Unpublished observations of $H_2Cr(CO)_5$.

(43) Sweany, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 2410–2412.

(44) Darensbourg, M. Y.; Darensbourg, D. J.; Barros, H. L. C. *Inorg. Chem.* **1978**, *17*, 297–301.

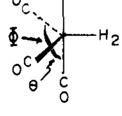
Table IV. Observed and Calculated Positions[a] of Carbonyl Bands of $DCo(CO)_3D_2$ and $HCo(CO)_3H_2$ (cm^{-1})

	$DCo(CO)_3D_2$		$HCo(CO)_3H_2$	
	obsd	calcd	obsd	calcd
isotopomer I	2100.2	2099.4	2100.2	2099.4
$^{12}C_3$	2039.4	2037.9	2042.5	2040.7
C_s	2020.8	2020.2	2020.8	2020.2
isotopomer II	*b*	2091.5	*b*	2091.6
$^{12}C_2{}^{13}C$	2033.3	2033.5	2034.1	2035.9
C_1	*d*	1986.9	*d*	1988.1
isotopomer III	*c*	2084.3	*c*	2084.3
$^{12}C_2{}^{13}C$	2006.5	2007.0	*d*	2011.4
C_s	2020.7	2020.2	2020.7	2020.2
isotopomer IV	2082.5	2083.2	2083.2	2083.5
$^{12}C^{13}C_2$	*d*	2008.0	*d*	2011.7
C_s	1974.7	1975.2	1974.1	1975.2
isotopomer V	2071.6	2071.8	2071.1	2071.8
$^{12}C^{13}C_2$	*d*	2009.9	2012.7	2012.9
C_1	1983.8	1984.2	1987.4	1986.8
isotopomer VI	*e*	2052.6	*e*	1952.6
$^{13}C_3$	1991.4	1992.5	1998.5	1998.7
C_s	1974.7	1975.2	1974.1	1975.2

[a] The force field found in Table III was used in the calculation. [b] Band obscurred by ^{13}CO. [c] Too weak to be observed. [d] Band is unresolved. [e] Band is obscurred by $H_2Co(CO)_2(H_2)_2$

for the metal–hydrogen stretch and the interaction constants between the stretching vibration and the carbonyl stretching vibrations. A force field was also constructed for $HCo(CO)_4$ which hitherto has not been modeled by a force field which includes any of the hydrogen vibrational coordinates. The results of the calculations are summarized in Tables III and IV and in the supplementary material. It is conceivable that the D–D stretch of $DCo(CO)_3D_2$ mixes with the carbonyl modes; a slight shift in the carbonyl modes has been noted in the spectrum of $H_2Cr(CO)_5$ as compared to that of $D_2Cr(CO)_5$.[31] This possibility has had to be ignored because $DCo(CO)_3H_2$ cannot be reliably characterized due to facile isotopic exchange. The effect is not expected to be large. The Co–H stretch of $HCo(CO)_3H_2$ does interact with the carbonyl modes, but it was not observed. It is noteworthy that the force constant for the Co–H stretch was determined to be nearly the same as that determined for $HCo(CO)_4$ even though no frequency had been assigned to a Co–H stretching vibration. An absorption appears at 1960 cm^{-1} that may in fact result from the Co–H stretch. The assignment is difficult because an isotopomer of IV absorbs in the same region. The results of the calculation are shown in Tables III and IV. The calculated carbonyl frequencies for $HCo(CO)_4$ and $DCo(CO)_3D_2$ were within experimental error of the observed frequencies in most instances. In some cases the experimental frequencies are not well-determined because of problems incurred in subtraction or because of overlapping absorptions. The lack of agreement in the totally symmetric combination of the carbonyl valence coordinates is real, however. A similar lack of agreement was reported by Burdett.[17] Presumably a complete normal coordinate analysis would have to be used to obtain a better fit. The off-diagonal force constants coupling the carbonyl vibrations to the Co–H stretch for both $HCo(CO)_4$ and III are much smaller in magnitude than those found for $HRe(CO)_5$.[16] This is expected because the M–H stretching frequencies of $HCo(CO)_4$ and presumably $HCo(CO)_3H_2$ are much closer to the carbonyl region, yet the spectrum is not much more perturbed than is observed for $HRe(CO)_5$. It may be that the coupling through a first-row transition element is not as great as for a heavier congener. We note that there are no observable differences in the spectrum of $HMn(CO)_5$ and $DMn(CO)_5$.[16] Not enough is known about this sort of interaction constant to merit a detailed analysis at this point. The carbonyl force constants should not be considered to be any less accurate than other force constants derived from factored force fields because the carbonyl force constants fit the spectrum of the deuterium isotopomers in which coupling to the deuteride is not significant. The carbonyl force constants for $HCo(CO)_3H_2$ were found to be somewhat less than those of $HCo(CO)_4$. This observation is consistent with a model in which the hydrogen molecule has not oxidatively added. This ordering is similar to what has been found for $H_2Cr(CO)_5$ and $H(H_2)MoCp(CO)_2$.[30,31] By contrast, the carbonyl force constants have been found to be greater when oxidative addition has occurred as evidenced by $H_2Fe(CO)_4$[43] and H_3WCpCO.[30]

With encouragement from a reviewer the force field was used to calculate infrared intensities. The approximations inherent in this exercise are numerous,[17,44] although it should be noted that the spectrum of $HCo(CO)_4$ was fit by using a bond angle of 98° between the axial and equatorial carbonyl groups. This is within 2° of what has been determined by electron diffraction.[45] The results of that calculation are included with the supplementary material. Three parameters were fit for III by successive approximation: two angles and the isotopic enrichment of the sample. The angles were determined from fits of intensities at natural isotopic abundance. Relative intensities were determined from a best fit of the observed spectrum by a product function of Gaussian and Lorentzian line shapes. The areas of the deconvoluted peaks were used for comparisons with calculated intensities. We have assumed the same intensity per unit extension for all CO groups. The dipole moment derivative for the Co–H stretch of the hydride ligand has been set at zero, so that only the carbonyl groups contribute to the intensity of the Co–H stretch. The line shape of the band at 2021 cm^{-1} was fit to two peaks, one of which was found to be at 2016.8 cm^{-1}. If the band at 2017 cm^{-1} is presumed to be due to $HCo(CO)_3H_2$, then the combined intensity of both peaks cannot be fit with any selection of bond angles. A band at 2016.2 cm^{-1} is observed in hydrogen-free matrices and is assigned to $Co(CO)_4$.[4] Therefore, we have assumed that the band at 2017 cm^{-1} is due to $Co(CO)_4$ and have used the intensity of only the band at 2020.8 cm^{-1} in determining the bond angles. We have used the fit of the spectrum of the all-protium isotopomer. The mixing of the carbonyl modes with the nearby M–H stretch adds little uncertainty in the analysis; the composition of the eigenvector for the most perturbed vibration is altered by less than 3% by the Co–H vibration as compared to the fit of the deuterium isotopomer. Also, it is clear from the intensity of the Co–H stretch that little carbonyl intensity has been robbed. The best fit of the structure is shown.



The angle between the cisoid carbonyl groups is $\theta = 105 \pm 2°$, somewhat larger than the analogous angle in $HCo(CO)_4$ of 100°. It is conceivable that the hydride ligand is bent out of the plane to accommodate the distortion, but the strong coupling between a carbonyl group and the hydride argues for an essentially trans relationship. Most dramatically, the two carbonyls that were formerly in the

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(45) McNeill, E. A.; Scholer, F. R. *J. Am. Chem. Soc.* 1977, *99*, 6243–6249.

equatorial plane have become nearly trans with an angle of $\Phi = 168 \pm 10°$. The errors have been estimated on the basis of uncertainties in the areas. There are two reasons for the latter estimate being so much larger. The sensitivity of the relative intensities to changes in Φ is less than for θ, and second, the two independent measurements of relative intensity did not point to the same angle. $HCo(CO)_3$ is a d^8, 16-electron complex for which square-planar geometry is expected. The isoelectronic $HRh(PR_3)_3$ is roughly square planar.[46] Saillard and Hoffman computed the structure of the transition state of the reaction of hydrogen with $Rh(CO)_4^+$. The approach of the hydrogen along the molecular fourfold axis was facilitated by two trans ligands bending away from the incoming hydrogen in much the same fashion as evidenced in III.[47] This distortion allowed the hydrogen to approach side-on. It is conceivable that the hydrogen of III is thus bound in an η^2 fashion. Although the bond angles of III are not well-determined, it is clear that the structure is dramatically perturbed from what it would be if hydrogen had simply replaced a carbonyl group in $HCo(CO)_4$. Burdett and Pourian have used extended Hückel-type calculations to explore the species $(H_3)Co(CO)_3$.[48] They found an energy minimum for a structure of C_{3v} symmetry in which the three hydrogen atoms were arranged in a tight cluster analogous to H_3^+. Such a species would yield only two infrared bands in the carbonyl region. Although it is clear that III is not the species described by Burdett and Pourian, the process that results in isotope exchange in $H(D_2)Co(CO)_3$ may be related to the trihydrogen adduct. It must also be pointed out that the Hückel-type calculation cannot assess the energy difference between $(H_3)Co(CO)_3$ and $H(H_2)Co(CO)_3$.

The behavior of the spectrum of IV is consistent with its involving two molecules of dihydrogen. The spectrum of IV only becomes prominent with extended periods of photolysis. The extent to which it grows, relative to the spectrum of III, varies and is least for low mixing ratios of H_2/Ar. The observation of two carbonyl bands requires that IV also include at least two carbonyl groups. It is tempting to formulate IV as $HCo(CO)_2(H_2)_2$. There is no evidence, however, to support the presence of the hydride ligand. It is noteworthy that none of the carbonyl bands are shifted in the deuterium isotopomer. This can be explained by postulating that no carbonyl group is trans to the hydride or by claiming that no hydride is present. Although no ESR evidence for $Co(CO)_2(H_2)_2$ was obtained, we consider the result equivocal. We do not have enough confidence in our ability to trap large quantities of H_2 in a matrix for ESR work in order to claim that IV is diamagnetic. The question of whether the dihydrogen is oxidatively added or not is largely unresolved. It is interesting that the spectrum of IV is similar to what may be $CH_3Co(CO)_2$ that was observed in methane, displaced by the approximate 10 cm^{-1} that has been noted in other comparisons. The absence of an even larger blue shift suggests that the hydrogen is not oxidatively added. An energy factored force field was calculated by assuming that the carbonyl ligands were equivalent. This allowed the assignment of bands due to IV in isotopically labeled samples. In most instances, the positions were superimposed on positions already occupied by other absorptions. The bond angle between two equivalent CO ligands can be estimated without regard to a force field.[17] The ratio of intensities of the bands at 2066 and 2006 cm^{-1} leads to a prediction of a $134 \pm 4°$ bond angle. If a hydride ligand were present, this angle would imply a structure in which both CO ligands occupy the trigonal plane of a molecule that is nominally trigonal-bipyramidal. However, it unclear why the carbonyl ligands would now be less spread out than what was found for III. If the hydride were absent, then the structure could be viewed as a derivative of a trigonally distorted $Co(CO)_4$.[19] Obviously, the structure of IV can only be resolved with information regarding the presence of the hydride ligand.

Summary

Both $HCo(CO)_4$ and $CH_3Co(CO)_4$ form complexes of molecular hydrogen with the dihydrogen occupying an equatorial coordination site of a distorted trigonal bipyramid. The distortion of the hydride complex is such as to expand the angle between the two equatorial carbonyl groups so that the structure might as well be viewed as a distorted square pyramid. In either complex, the dihydrogen undergoes an exchange reaction with the methyl or hydride group.

Registry No. I, 112172-97-1; II (N_2), 112172-99-3; II (H_2), 112173-01-0; III, 112172-98-2; IV, 112318-72-6; $CH_3Co(CO)_4$, 14709-64-9; $NaCo(CO)_4$, 14878-28-5; $HCo(CO)_4$, 16842-03-8; H_2, 1333-74-0; $HCo(CO)_3$, 60105-25-1; $DCo(CO)_4$, 62342-66-9; $H_3Co(CO)_3$, 81875-87-8; $DCo(CO)_3D_2$, 112173-00-9; N_2, 7727-37-9.

Supplementary Material Available: A listing of the results of a factored force field calculation of $HCo(CO)_4$ and $H_?Co(CO)_2(H_2)_2$ and spectra of the deformation region (12 pages). Ordering information is given on any current masthead page.

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[46] R = isopropyl. Yoshida, T.; Thorn, D. L.; Okano, T.; Otsuka, S.; Ibers, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 6451–6457.

[47] Saillard, J. Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006–2026.

[48] Burdett, J. K.; Pourian, M. R. *Organometallics* **1987**, *6*, 1684–1691.