

Absence of Hydrogen Bonding between $\text{HCo}(\text{CO})_4$ and Nitrogen or Oxygen Bases. IR and Raman Study

S. Sóley Kristjánssdóttir and Jack R. Norton*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Antoni Moroz, Ray L. Sweany,* and Scott L. Whittenburg

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

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$\text{HCo}(\text{CO})_4$ has been observed by Raman spectroscopy in acetonitrile at -26°C in the presence and absence of 2,4-dichloroaniline. Although $\text{HCo}(\text{CO})_4$ is substantially deprotonated by the aniline, there is no evidence of a hydrogen bond between the excess aniline and the remaining hydride. Matrices containing $\text{HCo}(\text{CO})_4$ and a polar molecule such as acetonitrile, water, ammonia, or trimethylamine have also been examined by infrared and Raman spectroscopy. Prior to proton transfer, which occurs on heating, there is little interaction between the base and the hydride ligand. The only observed perturbation of a vibrational mode was that of the H-Co deformation when the strongest base examined, Me_3N , was present. This evidence, along with the large infrared intensity of the deformation mode, suggests that the deformation coordinate may play a large role in the transfer of a proton from $\text{HCo}(\text{CO})_4$.

$\text{HCo}(\text{CO})_4$ is a strong acid in water¹ and has a $\text{p}K_a$ in CH_3CN about equal to that of HCl .² However, like transition-metal hydrides of lower thermodynamic acidity, it offers a large kinetic barrier to deprotonation in solution. The intrinsic barrier, i.e., ΔG^\ddagger at thermoneutrality, when $\text{HCo}(\text{CO})_4$ is deprotonated in CH_3CN by a series of substituted anilines is 10.7 kcal/mol, whereas the intrinsic barrier when $\text{HW}(\text{CO})_3\text{Cp}$ is similarly deprotonated is 9.3 kcal/mol.³

A plausible explanation of the size of these barriers is that they arise from the need to repolarize the H-M bond in the transition state. In the gas phase $\text{HCo}(\text{CO})_4$ remains more acidic than other carbonyl hydrides,⁴ but (despite a suggestion to the contrary⁵) there is a good evidence that its H-M bond is polarized $\text{H}^\delta-\text{M}^{\delta+}$. Ab initio Hartree Fock calculations in a Gaussian basis set^{6,7} show a substantial negative charge on the hydride ligand of $\text{HCo}(\text{CO})_4$. Experimentally, (1) the carbonyl stretching frequency differences between hydrides and the corresponding metalloradicals⁸ and (2) the core binding energies measured by X-ray photoelectron spectroscopy⁹ imply that the hy-

dride ligands of carbonyl hydride complexes such as $\text{H}_2\text{Fe}(\text{CO})_4$, $\text{HMn}(\text{CO})_5$, and $\text{HCo}(\text{CO})_4$ are negatively charged. Charge densities determined by comparing X-ray and neutron diffraction data show a partial negative charge on the hydride ligand of $\text{HMo}(\text{CO})_3\text{Cp}$ in the crystal.¹⁰

If this $\text{H}^\delta-\text{H}^{\delta+}$ polarization is to be responsible for the kinetic barrier to solution deprotonation, it must remain unchanged in solution. It has, however, not been clear whether the H-Co bond retains the $\text{H}^\delta-\text{Co}^{\delta+}$ polarization in a polar environment or whether such an environment can induce hydrogen bond formation. As vibrational spectroscopy is the most powerful tool for identifying weak hydrogen bonding, we have examined, by Raman and infrared spectroscopy, the behavior of $\text{HCo}(\text{CO})_4$ in the presence of bases in acetonitrile solution and in matrices containing polar molecules.

Results

We have obtained the first Raman spectra of $\text{HCo}(\text{CO})_4$. A concentrated CH_3CN solution of this unstable hydride remained stable under 647.1-nm irradiation for over 24 h when spun at -26°C . The resulting Raman spectrum (Figure 1) showed a strong band at 1931 cm^{-1} , which was clearly the H-Co stretching vibration. The peak positions are listed in Table I.

The Raman spectrum of $\text{HCo}(\text{CO})_4$ was also obtained when the molecules of this volatile hydride were isolated in CO, Ar, and acetonitrile matrices. The results were compared with the known IR spectra of $\text{HCo}(\text{CO})_4$ in CO^{11} and Ar matrices.¹² For comparison the IR spectrum of $\text{HCo}(\text{CO})_4$ was also obtained in an acetonitrile matrix. These peak positions are also listed in Table I.

The positions of the Raman bands of $\text{HCo}(\text{CO})_4$ in CH_3CN at -26°C agree well with other values in the literature. In particular the H-Co stretching frequency of 1931 cm^{-1} in Table I agrees well with the value of 1934 cm^{-1} measured by IR in the gas phase,¹³ and the deformation

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(5) Labinger and Bercaw (Labinger, J. A.; Bercaw, J. E. *Organometallics* 1988, 7, 926) have said that the electronegativity inferred for $\text{Co}(\text{CO})_4$ from the $\text{H-Co}(\text{CO})_4/\text{CH}_3\text{-Co}(\text{CO})_4$ BDE difference "suggests that $[\text{Co}(\text{CO})_4]$ resemble[s] fluorine". However, this inference rests on the assumption that the relation between the electronegativity of a group A and the $\text{H-A}/\text{CH}_3\text{-A}$ BDE difference is the same as that found for main-group elements A; this assumption implies an unrealistically high electronegativity for metal fragments such as $(\eta^5\text{-C}_5\text{Me}_5)_2(\text{R})\text{W}$ that are obviously quite electropositive.

(6) Antolovic, D.; Davidson, E. R. *J. Am. Chem. Soc.* 1987, 109, 977.

(7) Other calculations also indicate a partial negative charge on the hydride ligand: (a) Boudreaux, E. A. *Inorg. Chim. Acta* 1984, 82, 183. (b) Grima, J. P.; Chaplin, F.; Kaufman, G. *J. Organomet. Chem.* 1977, 129, 221. (c) Fønnesbech, N.; Hjortkjaer, J.; Johansen, H. *Int. J. Quantum Chem.* 1977, 12 (Suppl. 2), 95-104.

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

(9) Chen, H.; Jolly, W. L.; Kopf, J.; Lee, T. H. *J. Am. Chem. Soc.* 1979, 101, 2607.

(10) Cameron, R. P., Jr. Ph.D. Dissertation, University of New Orleans, New Orleans, LA, 1990. Cameron, R. P., Jr.; Sweany, R. L.; Stevens, E. D.; Koetzle, T. F. Manuscript in preparation.

(11) Sweany, R. L. *Inorg. Chem.* 1982, 21, 752.

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(13) Edgell, W. F.; Summitt, R. *J. Am. Chem. Soc.* 1961, 83, 1772.

Table I. Positions of Carbonyl and Co-H Vibrational Modes (cm^{-1}) of $\text{HCo}(\text{CO})_4^a$

Ar	CO ^b	matrix material				fluid media		
		H ₂ O	(CH ₃) ₃ N/Ar	NH ₃ /Ar	CH ₃ CN	CH ₃ CN ^c	gas ^d	
2121	2119	2118	2120	2120	2118	2119 (R)	2118 (R)	2123
2058	2055	2056	2057	2058	2056	2059 (R)	2056 (R)	2062
2034	2028	2027	2032	2034	2023	2022 (R)	2025 (R)	2043
				2025 (sh)	2015			
1966	1946 (R)		1965 ^e	1965	1942 (br)	1942 (R)	1931 (R)	1934 ^f
1964 (R)						1935 (R)		
			736					
			721					
708		702 (br)	706	708	703		702 (R)	703
		697 (sh)						

^a Matrix frequencies obtained at 10 K from FTIR spectra with either 1- or 2- cm^{-1} resolution. Raman shifts (marked by R) were obtained by using the 488-nm line of an argon ion laser. Positions are accurate to $\pm 2 \text{ cm}^{-1}$. ^b Reference 11. ^c Observed at $-26 \text{ }^\circ\text{C}$ with 1- cm^{-1} resolution by using the 647-nm line of a krypton ion laser. ^d Edgell, W. F.; Magee, C.; Gallup, G. *J. Am. Chem. Soc.* 1956, 78, 4185. ^e Only observed in very dilute matrices. ^f Reference 13.

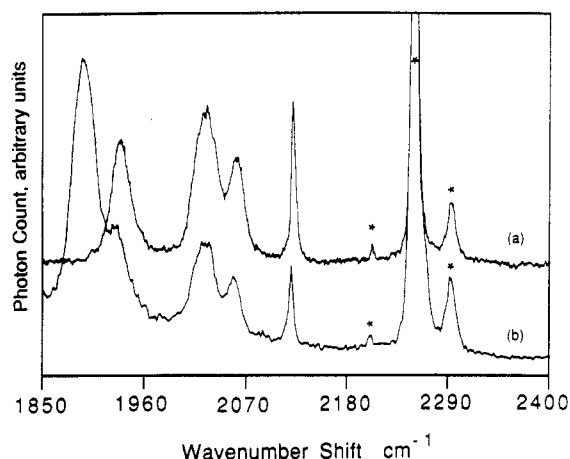


Figure 1. Raman spectra at $-26 \text{ }^\circ\text{C}$ in CH_3CN of (a) $\text{HCo}(\text{CO})_4$ and (b) $\text{HCo}(\text{CO})_4$ and an excess of 2,4-dichloroaniline. Peaks due to CH_3CN are marked with an asterisk.

frequency of 702 cm^{-1} in Table I agrees well with the gas-phase IR value of 703 cm^{-1} and with the frequency (696 cm^{-1}) observed by inelastic neutron scattering in solid $\text{HCo}(\text{CO})_4$ at 90 K .¹⁴

The Raman H-Co stretching frequencies showed thermochromic behavior. A substantial blue shift was observed on going from acetonitrile solution to an acetonitrile matrix at 10 K . In an argon matrix the H-Co stretch reversibly blue-shifted by 2 cm^{-1} when the temperature was lowered from 35 to 10 K ; there was, however, no accompanying change in intensity.

In the presence of 2 equiv of 2,4-dichloroaniline ($\text{p}K_a$ 8.0 in CH_3CN), $\text{HCo}(\text{CO})_4$ ($\text{p}K_a$ 8.3 in CH_3CN) underwent substantial but not complete deprotonation. However, the Raman spectrum of $\text{HCo}(\text{CO})_4$ could still be observed, and the Co-H stretch was unaffected by the presence of a substantial amount of the free nitrogen base (Figure 1).

In contrast to the Raman spectrum, where the H-Co stretch is one of the more intense features, the most intense infrared absorptions of $\text{HCo}(\text{CO})_4$ are the three carbonyl modes and the H-Co deformation mode. Observing the very weak H-Co stretching vibration in the IR spectrum is possible but usually requires the improved signal-to-noise of FTIR spectroscopy.

The H-Co stretching band of $\text{HCo}(\text{CO})_4$ was observed by IR spectroscopy in an argon matrix and did not shift (Table I) when the matrix was doped with Me_3N or NH_3 . However, upon warming to temperatures as low as 30 K ,

Table II. Positions of Carbonyl Vibrational Modes (cm^{-1}) of $[\text{baseH}][\text{Co}(\text{CO})_4]^a$

base/matrix material			
(C ₂ H ₅) ₃ N/toluene ^b	(CH ₃) ₃ N/Ar		
	NH ₃ /Ar	H ₂ O	
2015	2024	2015 br	
1931	1938	1935	1926 (br)
1895	1905	1903	
	1897 (sh)	1887 (sh)	

^a Obtained from FTIR spectra by using 1- and 2- cm^{-1} resolution. ^b Reference 16.

these matrices showed attenuation of all of the $\text{HCo}(\text{CO})_4$ bands and new absorptions between 1950 and 1850 cm^{-1} (Table II). These changes are best explained as the result of proton transfer between $\text{HCo}(\text{CO})_4$ and a nearby base. (The new absorptions have frequencies similar to those assigned to photoproducted $\text{Co}(\text{CO})_4^-$ in a CO-doped Ar matrix.¹⁵) In solution free $\text{Co}(\text{CO})_4^-$ is tetrahedral and has a single carbonyl region IR absorption, at 1892 cm^{-1} .² In a matrix $\text{Co}(\text{CO})_4^-$ will be close to the cation formed by the proton transfer; the resulting ion pair will presumably have a structure like that of $[\text{Et}_3\text{NH}][\text{Co}(\text{CO})_4]^-$,¹⁶ with the acidic hydrogen lying directly between the nitrogen and cobalt. The symmetry of $\text{Co}(\text{CO})_4^-$ will thus be reduced to C_{3v} , and the number of expected IR absorptions will increase to three, with the highest frequency A_1 absorption being weak unless the distortion away from tetrahedral geometry is severe.

No ion pairs were observed when weaker bases such as water, acetonitrile, or methanol were codeposited with $\text{HCo}(\text{CO})_4$ in an argon matrix, but warming these matrices always caused proton transfer. In the presence of these weak bases the true proton acceptor may have been water, a ubiquitous impurity in matrices. Proton transfer was even observed in a wet heptane matrix that had been warmed to 90 K and in an argon matrix warmed to 35 K . The amount of water present was minimized by passing both the acetonitrile and the $\text{HCo}(\text{CO})_4$ through bead-packed tubes containing P_4O_{10} ; a band due to water in the O-H stretching region then showed an optical density of only 0.03 units. On warming to 120 K , some proton transfer was still observed but in low yield.

The presence of water impurities will render the interpretation of behavior in polar matrices ambiguous, but need not cause concern when water itself is the matrix. We therefore recorded the IR spectrum of $\text{HCo}(\text{CO})_4$ in a water

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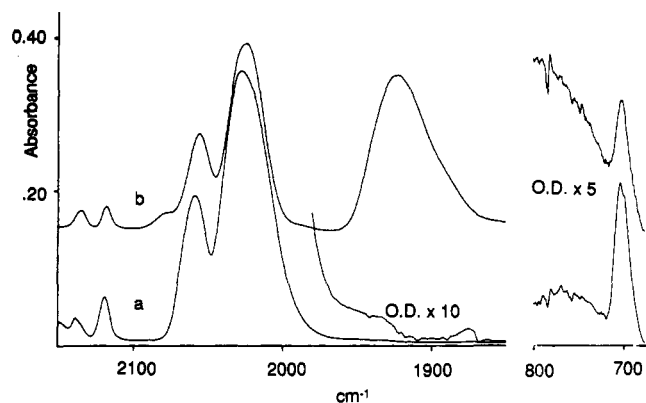


Figure 2. Infrared spectra of a 30-min deposit of $\text{HCo}(\text{CO})_4$ in water at 20 K (a) initially and (b) after a brief period of heating at 120 K.

matrix (Figure 2 and Table I).

Although the *positions* of none of the easily observed IR absorptions shifted appreciably in any of the media studied, the *widths* of these absorptions increased considerably in the more polar environments. As the polarizability of the host has a small effect on the positions of the vibrational bands of nonpolar guest molecules, the guests in the anisotropic environment produced by a polar host need not have identical vibrational frequencies and considerable broadening can result.

The broadest spectra for $\text{Co}(\text{CO})_4^-$ were obtained for those polar hosts (e.g., H_2O) that possessed acidic hydrogens themselves. The cations resulting from the protonation of these hosts may associate with $\text{Co}(\text{CO})_4^-$ via more than one hydrogen and thus lower its symmetry even below C_{3v} .

Another cause of broadness in the present study was the use of host/guest ratios that may have allowed some interaction among the guest molecules. The speed with which the gaseous mixtures were quenched increased the variation among the matrix sites. In fact, the matrices were often flawed by a high degree of scattering, which led to low-energy throughput and gave a derivative appearance to the spectra (a phenomenon known as the Christiansen effect).¹⁷ Some improvement in the quality of the deposits was achieved by doping the polar molecule and $\text{HCo}(\text{CO})_4$ into an argon host or, alternatively, by quenching the matrix gas mixture at temperatures in excess of 20 K.

The IR spectrum of $\text{HCo}(\text{CO})_4$ in a water environment showed that it was still in its molecular form, although proton transfer did occur when the matrix was heated to 90 K (see Figure 2).¹⁸ As the temperature was raised, an increasing fraction of the $\text{HCo}(\text{CO})_4$ became deprotonated; at any given temperature a plot of the log of the absorbance of the E mode of $\text{HCo}(\text{CO})_4$ vs time was convex, indicating that the reaction did not approach complete proton transfer in a first-order fashion and that its instantaneous rate constant was decreasing. As the process continued, the IR bands of the remaining $\text{HCo}(\text{CO})_4$ became narrower. To explain these observations we must presume that the activation energy for proton transfer from $\text{HCo}(\text{CO})_4$ to the host depends on the orientation of the host molecules in the vicinity of the hydride molecule. Those assemblies that are most favorably arranged will undergo proton transfer at lower temperatures; other as-

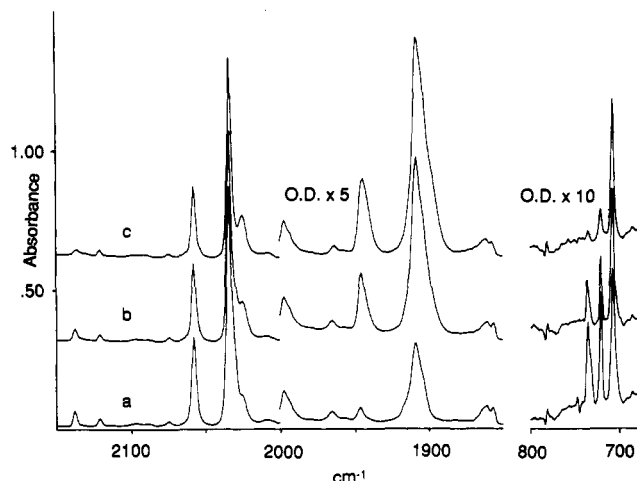


Figure 3. Infrared spectra of a 30-min deposit of $\text{HCo}(\text{CO})_4$ in an argon matrix containing 2.6 mol % of Me_3N (a) at 10 K initially, (b) at 10 K after a brief period of heating at 30 K, and (c) after heating briefly at 35 K.

semblies will face larger activation barriers and undergo proton transfer at higher temperatures. Similar behavior has been noted in other matrix studies.¹⁹

The influence of the host on the rate of proton transfer was demonstrated in water matrices. When these matrices were slowly heated, proton transfer in H_2O occurred at 96 K, whereas in D_2O temperatures higher than 125 K were required. (The carbonyl region and the H-Co deformation region of the initial spectrum of $\text{HCo}(\text{CO})_4$ in a D_2 matrix showed that little H/D exchange had taken place during the formation of the matrix.)

The absorptions of $\text{Co}(\text{CO})_4^-$ in the ion pairs shifted slightly to lower frequencies as the matrix was heated. (The change can easily be discerned in the $\text{Me}_3\text{N}/\text{Ar}$ matrix spectra in Figure 3 as well as in the H_2O matrix spectra in the Figure 2.) This shift may have resulted from the reorganization of the host molecules around the nascent ion pairs.

It was not always possible to deposit $\text{HCo}(\text{CO})_4$ in a polar host matrix without proton transfer. The extent of deprotonation during deposition seemed to correlate with the basicity of the host. For example, in contrast to the spectra in a water matrix (Figure 2), little or no $\text{HCo}(\text{CO})_4$ was observed when $\text{HCo}(\text{CO})_4$ was codeposited with undiluted Me_3N or NH_3 .

Although the position of the H-Co deformation of $\text{HCo}(\text{CO})_4$ remained fairly constant in all the media studied, two new features at 736 and 721 cm^{-1} were noted in argon matrices containing Me_3N (Figure 3). These features were most evident when the concentration of Me_3N was lowest. Further experiments showed that these two bands belonged to molecules that were especially prone to proton transfer. When a matrix containing 2.6 mol % of Me_3N was heated to 30 K, the bands at 736 and 721 cm^{-1} lost 45% and 37% of their intensity, respectively, as the $\text{Co}(\text{CO})_4^-$ bands arising from proton transfer grew. The unperturbed $\text{HCo}(\text{CO})_4$ deformation mode at 708 cm^{-1} and the H-Co stretching vibration at 1964 cm^{-1} lost insignificant intensity (1%), while the carbonyl bands uniformly lost 11% of their original intensity; only upon heating to 35 K, when the band at 736 cm^{-1} had nearly vanished, did the H-Co stretch begin to lose intensity. The molecules with perturbed deformation modes were thus the most prone to undergo proton transfer; these molecules must

(17) Rao, C. N. R. *Chemical Applications of Infrared Spectroscopy*; Academic: New York, 1963; pp 586-591.

(18) Proton transfer occurred at lower temperature in argon-diluted water than in water itself, presumably because the dilution reduced self-association of the water and made it more basic.

(19) Sponsler, M. B.; Jain, R.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* 1989, 111, 2240.

have had carbonyl bands like those of unperturbed $\text{HCo}(\text{CO})_4$ but no significant H-Co stretching band. The perturbed deformation modes were not observed in matrices containing 10 mol % of Me_3N , presumably because the high concentration of Me_3N reduced the quenching efficiency and allowed the $\text{HCo}(\text{CO})_4$ molecules that would have given rise to these perturbed modes to undergo proton transfer instead.

In argon matrices with high concentrations of Me_3N , the H-Co stretch became less intense relative to the carbonyl bands; this band could not be observed with 10 mol % Me_3N or in pure water matrices. Apparently, the H-Co stretch cannot be observed when a base is positioned in the immediate vicinity of the H-Co bond. There are more molecules absorbing at 1964 cm^{-1} when the concentration of base is low because there is not enough base to populate all the cages in the vicinity of the Co-H bond.

Discussion

Hydrogen bonding between AH and B causes the A-H stretch to shift to lower frequency and to gain IR intensity and the A-H deformation to shift to higher frequency.²⁰ The size of the shift in the frequency of the A-H stretch correlates well with the strength of the hydrogen bond. For example, the O-H stretching vibration of *tert*-butyl alcohol shifts between 73 and 344 cm^{-1} , with a series of bases which form hydrogen bonds varying in strength from 2.4 to 5.2 kcal/mol;²¹ the shift is 77 cm^{-1} with acetonitrile. Although an H-Co stretch need not be as sensitive to hydrogen bonding as an O-H stretch, the fact that the frequencies of the H-Co stretches only vary by 3 cm^{-1} between the gas phase and CH_3CN solution suggests that there is no hydrogen bonding between $\text{HCo}(\text{CO})_4$ and CH_3CN ; the small red shift in CH_3CN is induced by its polarizability. Even the decrease of 24 cm^{-1} between the position of the H-Co stretch in argon and acetonitrile matrices can hardly be attributed to hydrogen bonding, since a similar shift is observed in CO matrices. (Although CO can serve as a hydrogen bond acceptor for phenols, the strength of the interaction is much weaker than that with acetonitrile.^{20b})

The 2,4-dichloroaniline used in the CH_3CN solution Raman experiments should have been an ideal hydrogen bond acceptor for $\text{HCo}(\text{CO})_4$, as the similarity of their pK_a values means that 2,4-dichloroaniline is a base strong enough to partially deprotonate $\text{HCo}(\text{CO})_4$ but weak enough to coexist with it in solution. However, the fact that the H-Co stretch of $\text{HCo}(\text{CO})_4$ in CH_3CN solution remains unaffected by the presence of excess 2,4-dichloroaniline²² implies that these two species do not form a hydrogen bond.

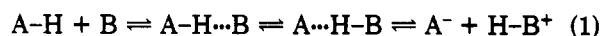
The fact that we have not observed the H-Co stretch in a water matrix also argues against hydrogen bond formation, since hydrogen bonding should increase the IR intensity of this band. Because the H-Co stretch is strongly coupled to the low frequency A_1 carbonyl vibration,²³ a hydrogen-bond-induced decrease in the frequency

of the H-Co stretching mode should cause that carbonyl mode to shift to lower frequency. However, the decrease in the frequency of that mode between an argon matrix (2058 cm^{-1}) and a water matrix (2056 cm^{-1}) is negligible. To summarize, the observed H-Co stretches offer no evidence for hydrogen bond formation between $\text{HCo}(\text{CO})_4$ and acetonitrile, 2,4-dichloroaniline, or water. The hydride ligand probably remains as negatively charged in a water matrix as it is in less polar environments.

The small variation in the position of the H-Co deformation mode of $\text{HCo}(\text{CO})_4$ (it appears within 3 cm^{-1} of 705 cm^{-1} in a variety of environments) must be attributed to polarizability differences. Only with dilute trimethylamine in argon matrices are there significant shifts (28 cm^{-1} , or 4.0%, and 13 cm^{-1} , or 1.8%) in the deformation mode. Similar shifts are observed in strongly interacting systems, e.g., 55 cm^{-1} , or 3.4%, and 31 cm^{-1} , or 1.9%, in the deformation mode of water when it hydrogen bonds to pyridine or acetonitrile respectively.²⁴

The appearance of the new deformation bands and the observation that they belong to molecules with relatively low barriers to proton transfer initially seemed to imply that there was $\text{Me}_3\text{N}/\text{HCo}(\text{CO})_4$ hydrogen bonding in these matrices. However, the fact that no H-Co stretch was observed for the molecules with perturbed deformation modes argues otherwise, since hydrogen bonding should have significantly shifted the frequency of the stretching vibration and increased its IR intensity.¹⁹ The absence of the stretch must result from broadening rather than a shift with loss of intensity because no change is observed in the A_1 carbonyl band (which is coupled to the H-Co stretch) when the deformation mode is perturbed.

Thus, prior to proton transfer, there are no strong interactions between $\text{HCo}(\text{CO})_4$ and the solvent or host that might presage it. We must conclude that the negative charge that the hydrogen atom of $\text{HCo}(\text{CO})_4$ bears in nonpolar environments is preserved in polar ones. The fact that $\text{HCo}(\text{CO})_4$ does not form hydrogen bonds means that its proton-transfer reactions cannot proceed through the hydrogen-bonded intermediates found in the proton-transfer reactions of other types of acids.²⁵ For example, proton transfers among oxygen and nitrogen bases proceed by mechanisms like that in eq 1. Even carbon acids can



form strong hydrogen bonds to oxygen and nitrogen bases: in matrix studies similar to this one Ault and co-workers have shown that the C-H stretching modes of terminal alkynes are perturbed from 131 to 64 cm^{-1} by acetone and ether,^{26a} from 170 to 125 cm^{-1} by NH_3 ,^{26b} and from 288 to 188 cm^{-1} by Me_3N .^{25b}

Thus the $\text{H}^{\delta-}\text{-Co}^{\delta+}$ polarization of the electrons in the H-Co bond remains unchanged until proton transfer occurs, and the need to repolarize this bond during the removal of H^+ from $\text{HCo}(\text{CO})_4$ contributes to the large intrinsic barrier associated with this reaction.²⁷ At least as

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(21) (a) Drago, R. S.; O'Bryan, N.; Vogel, G. C. *J. Am. Chem. Soc.* **1970**, *92*, 3924. (b) The phenol-CO interaction results in a shift of 37.5 cm^{-1} in the O-H stretch of phenol: Gebicki, J.; Krantz, A. *J. Am. Chem. Soc.* **1984**, *106*, 8093 and 8097.

(22) Since the Raman intensity ratios of the $\text{HCo}(\text{CO})_4$ and $[\text{Co}(\text{CO})_4]^-$ bands are not known, the extent of deprotonation in these solutions cannot be determined from the spectra in Figure 1. However, if the equilibrium constant (0.5) calculated for the equilibrium between $\text{HCo}(\text{CO})_4$ and 2,4-dichloroaniline from our dilute solution pK_a values² is assumed applicable to the concentrated solutions of this study, approximately half of the $\text{HCo}(\text{CO})_4$ is deprotonated and free 2,4-dichloroaniline is 1 M (a 3.7-fold excess).

(23) In a water matrix this band is 5 cm^{-1} lower for $\text{DCo}(\text{CO})_4$ than for $\text{HCo}(\text{CO})_4$.

(24) Greinacher, E.; Lüttke, W.; Mecke, R. Z. *Elektrochem.* **1955**, *59*, 23.

(25) (a) Bell, R. P. *The Proton in Chemistry*; Cornell University Press: Ithaca, NY, 1973. (b) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1. (c) Reutov, O. A.; Beletskaya, I. P.; Butin, K. P. *CH-Acids*; Pergamon Press: New York, 1978.

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(27) An extensive discussion of the origins of the barriers to proton transfer from transition-metal hydrides can be found in: Kristjánssdóttir, S. S.; Norton, J. R., In *Acidity of Hydrido Transition Metal Complexes in Solution*; Dedieu, A., Ed.; Transition Metal Hydrides: Recent Advances in Theory and Experiment; VCH: New York, in press.

extensive a repolarization is probably associated with the deprotonation of all transition-metal hydrides.²⁸

The low IR intensity of the $\text{HCo}(\text{CO})_4$ H-Co stretch suggests that the polarity of the H-Co bond is not substantially altered by stretching.²⁹ The relatively high IR intensity of the H-Co deformation mode suggests that deformation does change the H-Co bond polarity.³⁰ If the hydride ligand becomes more positively charged as it moves off the 3-fold axis, it is conceivable that proton transfer from $\text{HCo}(\text{CO})_4$ involves the deformation coordinate to a larger extent than for ordinary acids.

Experimental Section

General Considerations. Ammonia and trimethylamine were obtained from Matheson and used without further purification. Argon was obtained from Air Products and was 99.99% pure. Acetonitrile was purified by a series of steps previously shown to be effective;² it was distilled from CuSO_4 and then from alkaline KMnO_4 , passed through a column of Woelm N-Super 1 Alumina, and finally vacuum-transferred from P_2O_5 . Commercial 2,4-dichloroaniline was recrystallized twice from EtOH, then from THF, and finally from CH_3CN in order to remove traces of a fluorescent impurity; it was dried in vacuo after each recrystallization.

All manipulations were performed under an inert atmosphere (N_2 or Ar) using high-vacuum line, Schlenk or inert-atmosphere box techniques.

$\text{HCo}(\text{CO})_4$ in CH_3CN Solution. The reddish brown solution of $[\text{Co}(\text{CH}_3\text{CN})_6][\text{Co}(\text{CO})_4]_2$ obtained by mixing 0.208 g (0.608 mmol) of $\text{Co}_2(\text{CO})_8$ and 1.60 g of CH_3CN was frozen, and 1 mL of degassed concentrated H_2SO_4 was added under a flow of Ar. The mixture was quickly frozen and degassed. The mixture was then thawed and the volatiles transferred into a 5-mm NMR tube ($\text{HCo}(\text{CO})_4$ transfers faster than CH_3CN). The tube was flame-sealed, and the resulting yellow solution of $\text{HCo}(\text{CO})_4$ in acetonitrile was kept frozen until use; its volume was 0.35 mL. The concentration of $\text{HCo}(\text{CO})_4$, 1.5 M, was determined by allowing the solution to decompose and determining the concentration of $\text{Co}(\text{CO})_4^-$ from its measured absorbance and known absorptivity.²

$\text{HCo}(\text{CO})_4$ and 2,4-Dichloroaniline in CH_3CN Solution. The sample was prepared in the same way as the one above except that 0.061 g (0.38 mmol) of 2,4-dichloroaniline was placed in the NMR tube prior to the addition of the $\text{HCo}(\text{CO})_4$ (0.18 mmol).

(28) No interaction other than deprotonation is observed when the H-Re stretch of $\text{HRe}(\text{CO})_5$ (observable by Raman) is treated with an excess of Et_3N , pyrrolidine, or tetramethylguanidine or when the H-Mn stretch of $\text{HMn}(\text{CO})_5$ (observable as a weak band in the IR spectrum) is treated with an excess of aniline or pyridine.

(29) Although the intensity of the H-Co stretch is modified by coupling with the low frequency A_1 mode of the carbonyl groups, it is doubtful that the isolated H-Co stretch would exhibit much intensity; the H-M stretches of most carbonyl hydrides have low IR intensities, although some of them exhibit very little coupling between the carbonyl and hydride vibrational coordinates.

(30) In principle an intense deformation mode could arise from the back and forth motion of a hydride ligand if the latter had a substantial negative charge, but such intensity is not observed for the deformation modes of hydrides more likely to bear negative charge than the one in $\text{HCo}(\text{CO})_4$. For example, the deformation mode of $\text{HM}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3$ has not been found: Sweany, R. L. *J. Am. Chem. Soc.* 1986, 108, 3577 and references cited therein.

The formal concentrations (i.e., the total concentrations before proton transfer) were 1.4 M (2,4-dichloroaniline) and 0.64 M ($\text{HCo}(\text{CO})_4$).

Solution Raman Spectra. The sample tube was placed in an NMR spinner and cooled with the boiloff from a tank of liquid N_2 . The rate of boiloff was regulated so that the temperature, as measured by a thermocouple at the sample, stayed about -26°C . Raman spectra were obtained with excitation by the red line (647.1 nm) of a Kr laser (Ionpure Plasma tube, Innova 70*Coherent). The laser power at the sample was 40 mW, and the beam angle was 45° . The radiation was passed through a SPEX 1401 monochromator and analyzed with a SPEX Digital photometer.

Matrix Isolation Spectra. Mixtures of gases were made manometrically and admitted to the cryostat through a metering valve at a rate of approximately 1 mmol/h. Water matrices were made by admitting water vapors through the same valve, albeit nearly fully open. Acetonitrile was dried over CaH_2 and then distilled prior to its use as a matrix gas; it was introduced into the cryostat in a fashion similar to that of water. The flow rate of water or acetonitrile through the valve was set in order to achieve maximum transparency. Several experiments were made with varying flow rates of water to determine any unusual concentration-dependent behavior. Heating the sample plate to 20 K during the deposit helped achieve maximum transparency.

$\text{HCo}(\text{CO})_4$ for these experiments was synthesized by the addition of commercial H_3PO_4 to solid $\text{NaCo}(\text{CO})_4$ that had been generated by the reduction of $\text{Co}_2(\text{CO})_8$ with Na/Hg in THF. The product removed from this mixture by vacuum stripping was contaminated with both water and CO_2 . The latter was removed by warming the frozen product to -100°C under dynamic vacuum. Water was less successfully removed by either condensing the $\text{HCo}(\text{CO})_4$ onto P_4O_{10} or by passing the vapor of $\text{HCo}(\text{CO})_4$ over P_4O_{10} just as it was being introduced to the cryostat. The rate of deposit of $\text{HCo}(\text{CO})_4$ was controlled by subliming it from a cold source container. To achieve adequate isolation, temperatures between -120 and -90°C were required. Water was sufficiently volatile under these conditions to contaminate the matrix.

Infrared spectra were obtained with either a Beckman 4260 infrared spectrophotometer or a Perkin-Elmer 1760 Fourier Transform spectrometer. Matrix Raman spectra were obtained by a recently published procedure;³¹ a diode array detector was used in place of a photomultiplier tube.

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(31) Moroz, A.; Sweany, R. L.; Whittenburg, S. L. *J. Phys. Chem.* 1990, 94, 1352.