Strengthening of N−H···Co Hydrogen Bonds upon Increasing the Basicity of the Hydrogen Bond Acceptor (Co)

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Low temperature crystal structures of (DABCO)$H^+Co(CO)_4^-$ (**1**) and (DABCO)$H^+Co(CO)_3PPh_3^-$ (**2**) (DABCO = 1,4-diazabicyclooctane) indicate that both salts exhibit N−H···Co hydrogen bonding. IR and NMR data indicate that these hydrogen bonded species persist in nonpolar solvents such as toluene, but exist as solvent separated ions in more polar solvents. Replacement of the axial CO ligand by PPh_3 leads to a shortening of the N···Co separation in the solid state from 3.437(3) to 3.294(6) Å. This change is accompanied by an increase in the angle between the equatorial carbonyl ligands. Thus, the crystallographic results suggest a strengthening of the N−H···Co hydrogen bond upon increasing the basicity of the metal center, the first observation of this type in the solid state. This assertion is supported by variable-temperature ^1H and ^{13}C NMR data in toluene-d_8 solution which, discussed in the light of ab initio calculations, indicate that the barrier to a fluxional process involving cleavage of the N−H···Co hydrogen bond is greater in **2** than in **1**. The crystal structures of **1** and **2** have been determined by X-ray diffraction at 135(5) and 123(5) K, respectively [**1** monoclinic, $P2_1/n$ (No. 14), $a = 8.728(2)$, $b = 23.333(5)$, $c = 12.146(2)$ Å, $\beta = 95.74(2)°$, $V = 2461.1(9)$ Å^3, $Z = 8$, $R(F) = 0.043$, $R_w(F) = 0.043$, $S(F) = 1.21$; **2** orthorhombic, $Pca2_1$ (No. 29), $a = 16.084(8)$, $b = 8.874(3)$, $c = 17.312(3)$ Å, $V = 2471(1)$ Å^3, $Z = 4$, $R(F) = 0.065$, $R_w(F) = 0.060$, $S(F) = 1.16$].

Introduction

In recent years there has been considerable interest in hydrogen bonding in which transition metal centers are involved. A number of groups have described examples of hydrogen bonding in which an electron-rich transition metal center acts as the hydrogen bond acceptor, i.e., X−H···M.[1−6] Work to date in this area has been summarized in two very recent reviews.[1d,7] Recent work has also demonstrated that transition metal hydride moieties can also serve as hydrogen bond acceptors, i.e. X−H···H−M.[8] In both cases N−H or O−H groups typically function as the hydrogen bond donor.

A hydrogen bond, X−H···Y, can in effect be considered as a competition for a proton between two bases, X and Y. When one base (X) is substantially stronger than the other, the proton will be bonded to that base via a σ-bond, X−H, while forming a weaker, often largely electrostatic, interaction with the other base. If the strength of the weaker base (Y) is increased, the hydrogen bond becomes stronger and shorter. Thus, the distances H···Y and X···Y should decrease. A concomitant weakening and lengthening of the covalent interaction X−H is also anticipated. Increasing the basicity of Y ultimately leads to proton transfer to give an H−Y covalent bond. The extent to which a (reversed) X···H−Y hydrogen bond is then formed depends upon the polarity

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of the H−Y bond and upon the basicity of X. Often dissociation to yield X + H−Y will occur.

Solution IR studies by Poliakoff and Kazarian,[3] and by Epstein and co-workers,[5] on hydrogen bonds from alcohols to d^8 Co, Rh, and Ir centers, and to d^6 Fe, Ru, and Os centers, respectively, indicate that O−H···M hydrogen bonds are strengthened by increasing the basicity at the metal center. Protonation of the most basic metal centers was observed, but there was no evidence for (reverse) M−H···O hydrogen bond formation. Indeed, observations of M−H···O hydrogen bonds have been rare to date. Epstein and co-workers[9] first suggested, in 1993, that such an interaction is present in the system $(\eta^5\text{-}C_5Me_5)_2Os{-}H^+\cdots O{=}PPh_3$, i.e. an Os−H···O hydrogen bond. Their conclusion was based upon solution IR data which indicate diminished ν(Os−H) and ν(P=O) stretching frequencies. This assertion is supported in recent studies by Peris and Crabtree of a number of cationic iridium hydrides that show the same IR behavior indicative of $L_nIr{-}H^+\cdots O{=}PPh_3$ hydrogen bond formation.[10] Pickett and co-workers[11] have also demonstrated the existence of M−H···O hydrogen bonds by obtaining crystallographic and NMR evidence for a W−H···O hydrogen bond in the compound $[WH_3(\eta^1\text{-}OCOMe)(dppe)_2]$ (dppe = 1,2-bis(diphenylphosphinoethane)).

We have previously described salts of the form $R_3NH^+Co(CO)_4^-$ that exhibit N−H···Co hydrogen bonds[1b,c] and sought to examine the similarities, and differences, between such hydrogen bonds and (conventional) hydrogen bonds which do not involve metal atoms. In furthering these studies we have investigated the effect of changing the basicity of the hydrogen bond acceptor, Co, in salts of the type $R_3NH^+Co(CO)_3L^-$ (L = CO, PR_3) by changing its ligand environment. Structural and spectroscopic studies of the salts $(DABCO)H^+Co(CO)_3L^-$ (DABCO = 1,4-diazabicyclooctane; L = CO, PPh_3) were initiated. These studies are presented together with ab initio calculations on the model complexes $Me_3NH^+Co(CO)_3L^-$ (L = CO, PH_3) and permit the examination of the effect of increasing the basicity at the metal center by replacing a CO ligand by a phosphine ligand.

Experimental Section

General Procedures. All manipulations of oxygen- or water-sensitive materials were carried out under an atmosphere of argon either using Schlenk-line techniques or in a Vacuum Atmospheres drybox. NMR spectra were recorded on either a Varian XL-300 or Bruker ARX-500 spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrometer. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

$(DABCO)H^+Co(CO)_4^-$ (1) was prepared by methods similar to those described for other $R_3NH^+Co(CO)_4^-$ salts.[1b,c,6] $HCo(CO)_4$ was prepared in situ and added by vacuum transfer directly to a toluene solution of DABCO to give **1** as a colorless powder, which was recrystallized under argon from THF solution at 20 °C to yield crystals suitable for X-ray diffraction. Maximum yield obtained, 79%. ^1H NMR (300 MHz, $C_6D_5CD_3$, 298 K) δ 2.18 (s, CH_2); (300 MHz, $C_6D_5CD_3$, 193 K) δ 1.74 (s, CH_2); 10.1 (s, NH). ^{13}C NMR (75.3 MHz, $C_6D_5CD_3$, 298 K) δ 47.2 (s, CH_2), no signal observed for CO ligands; (75.3 MHz, $C_6D_5CD_3$, 188 K) δ 43.9 (s, CH_2) no signal observed for CO ligands. IR (CH_3CN) ν CO 1892 (s) cm^{-1}; IR (C_6H_5Me) ν CO 2020 (w), 1935 (w), 1898 (s) cm^{-1}. Anal. Calcd. for $C_{10}H_{13}CoN_2O_4$: C, 42.27; H, 4.61; N, 9.86. Found C, 39.85; H, 4.93; N, 9.88. Better elemental analysis for this compound could not be obtained.

$(DABCO)H^+Co(CO)_3PPh_3^-$ (2) was prepared by a modification of the procedure for **1**. $HCo(CO)_4$ prepared in situ was first vacuum transferred to a toluene solution containing ca. 1 equiv of the phosphine ligand and stirred for 1 h prior to introduction of the diamine. Typical byproducts in this reaction include $[HCo(CO)_2(PPh_3)_2]$[12] and $[Co_2(CO)_6(PPh_3)_2]$. Compound **2** was originally isolated as a yellow crystalline product by direct crystallization at −23 °C from an acetonitrile solution of the crude mixture of products. Subsequently, efforts to minimize byproducts included the use of less than 1 equiv of PPh_3 (to prevent $HCo(CO)_2(PPh_3)_2$ formation) and reducing the amount DABCO present in the toluene solution into which the initial $HCo(CO)_3PPh_3$ product is transferred. Recrystallization from acetonitrile was then used to purify material subsequently used in the NMR experiments. ^1H NMR (500 MHz, $C_6D_5CD_3$, 298 K) δ 2.42 (s, CH_2), δ 7.55 (t, C_6H_5); (500 MHz, $C_6D_5CD_3$, 183 K) δ 2.24, 1.66 (s, CH_2), δ 8.06 (t, C_6H_5), 13.1 (s, NH). ^{13}C NMR (125.5 MHz, $C_6D_5CD_3$, 298 K) δ 46.9 (s, CH_2), no signal observed for CO ligands; (125.5 MHz, $C_6D_5CD_3$, 188 K) δ 43.4, 43.3 (s, CH_2), no signal observed for CO ligands. ^{31}P NMR (202.5 MHz, $C_6D_5CD_3$, 223 K) δ 63.7 ppm (s, PPh_3) weak signal presumably due to quadrupole broadening of ^{59}Co; no signal observed at higher temperatures. IR (CH_3CN) ν CO 1928 (w), 1839 (s) cm^{-1}; IR (C_6H_5Me) ν CO 1955 (w), 1857 (s) cm^{-1} (often additional bands at 2050 (w) and 1972 (s), probably due to the presence of $HCo(CO)_3PPh_3$, were also observed). Anal. Calcd for $C_{28}H_{28}CoN_2O_3P$: C, 62.55; H, 5.44; N, 5.40. Found C, 61.79; H, 5.66; N, 5.25.

X-ray Crystal Structure Determinations of 1 and 2. Both crystal structures were solved by direct methods and refined to convergence using the SHELXTL suite of programs.[13] Data were corrected for absorption by semiempirical methods.[13] For **1** all non-hydrogen atoms were refined anisotropically, ammonium hydrogens H(11) and H(21) were refined isotropically, and all methylene hydrogens were refined using a riding model with fixed isotropic displacement parameters. For **2** the DABCO moiety exhibited orientational disorder about the N···N axis (staggered with respect to the carbonyl groups, 67%; eclipsed with respect to the carbonyl groups, 33%). Non-hydrogen atoms were refined anisotropically, except for carbon atoms of the minor orientation of DABCO. Ammonium hydrogen H(1) was refined isotropically, and all phenyl hydrogens were refined using a riding model with fixed isotropic displacement parameters. The contributions of the disordered methylene hydrogens were not included in the model. Experimental data pertinent to both structure determinations is given in Table 1.

Results and Discussion

The structures of **1** and **2** have been determined by low temperature X-ray diffraction and are depicted in Figure 1. Selected interatomic distances and angles are listed in Table 2. **1** and **2** have structures similar to that reported for $Et_3NH^+Co(CO)_4^-$,[1b,6] with an approximately linear N−H···Co hydrogen bond (N−H···Co 173(3)° for **1**; N−H···Co 175(10)° for **2**). The DABCO methylene groups in **1** are staggered with respect to the carbonyl groups. In compound **2** the phenyl groups of

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Table 1. Data Collection, Structure Solution, and Refinement Parameters for 1 and 2

	1	2
crystal color, habit	colorless prisms	yellow prisms
crystal size (mm)	0.50 × 0.30 × 0.28	0.50 × 0.25 × 0.20
crystal system	monoclinic	orthorhombic
space group, *Z*	$P2_1/n$, $Z = 8$	$Pca2_1$,[a] $Z = 4$
a (Å)	8.728(2)	16.084(8)
b (Å)	23.333(5)	8.874(3)
c (Å)	12.146(2)	17.312(3)
β (deg)	95.74(2)	−
V (Å^3)	2461.1(9)	2471(1)
density (g/cm^{-3})	1.534	1.394
temperature (K)	135(5)	123(5)
X-ray wavelength[b] (Å)	0.71073	0.71073
$\mu_{(\mathrm{Mo\ K}\alpha)}$ (mm^{-1})	1.398	0.791
2θ range (deg)	4.0−55.0	4.0−55.0
reflections collected	6195	5039
independent reflections (R_{int})	5580 (0.025)	4636
observed ($F > 3.0\ \sigma(F)$) (n)	4269	3257
L.S. parameter (p)	315	335
$R(F)$,[c] $R_w(F)$[c]	0.043, 0.043	0.065, 0.060
$S(F)$[c]	1.21	1.16

[a] Absolute structure: Rodgers η-parameter = 0.82(13). [b] Graphite monochromated. [c] $R(F) = \sum|F_o - F_c|/\sum F_o$; $R_w(F) = [\sum w|F_o - F_c|^2/\sum wF_o^2]^{1/2}$; $S(F) = [\sum w|F_o - F_c|/(n - p)]^{1/2}$.

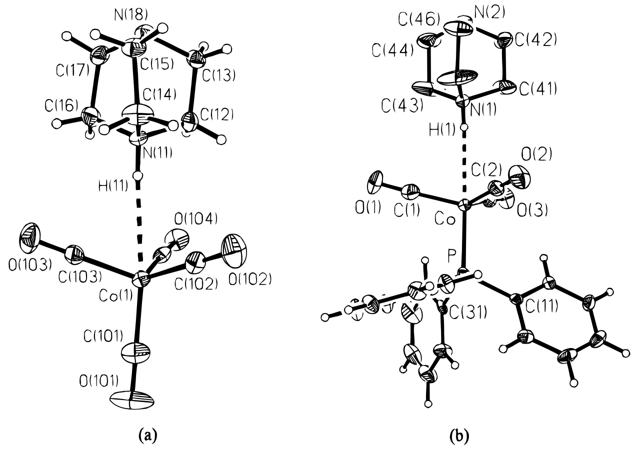

Figure 1. (a) Structure of one independent "molecule" of **1**. (b) Structure of **2**, shown with the major (staggered) orientation of the diamine unit. Each structure is shown with 50% probability ellipsoids for non-hydrogen atoms.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 1 and 2

	1[a]	2	
Co(1)−C(101)	1.777(4), 1.781(3)	2.172(2)	Co−P
Co(1)−C(102)	1.760(3), 1.760(3)	1.752(7)	Co−C(1)
Co(1)−C(103)	1.763(3), 1.771(3)	1.751(7)	Co−C(2)
Co(1)−C(104)	1.781(3), 1.769(3)	1.744(6)	Co−C(3)
C(101)−O(101)	1.149(5), 1.146(4)	−	−
C(102)−O(102)	1.151(4), 1.156(4)	1.155(9)	C(1)−O(1)
C(103)−O(103)	1.151(4), 1.155(4)	1.170(9)	C(2)−O(2)
C(104)−O(104)	1.144(4), 1.148(4)	1.159(9)	C(3)−O(3)
		1.827(6)	P−C(11)
		1.829(6)	P−C(21)
		1.824(6)	P−C(31)
N(11)−H(11)[14]	0.91(4), 0.97(4)	0.83(8)	N(1)−H(1)[14]
C(101)−Co(1)−C(102)	109.0(2), 106.5(1)	103.0(2)	P−Co−C(1)
C(101)−Co(1)−C(103)	106.8(2), 107.6(1)	98.8(2)	P−Co−C(2)
C(101)−Co(1)−C(104)	107.4(1), 104.9(1)	105.2(2)	P−Co−C(3)
C(102)−Co(1)−C(103)	112.0(2), 111.2(2)	118.3(3)	C(1)−Co−C(2)
C(102)−Co(1)−C(104)	107.6(1), 110.5(1)	113.8(3)	C(1)−Co−C(3)
C(103)−Co(1)−C(104)	113.9(1), 115.4(1)	114.6(3)	C(2)−Co−C(3)

[a] Values for both independent "molecules" are listed.

the phosphine are staggered with respect to the carbonyl ligands, but disorder of the DABCO moiety about the approximate molecular 3-fold axis results in the presence of both staggered and eclipsed conformations of the methylene groups in a 67:33 ratio. The key structural parameter from the X-ray diffraction studies is the N··· Co separation. This separation is substantially reduced in **1** (3.437(3) Å) relative to Et$_3$NH$^+$Co(CO)$_4^-$ (3.684(2) Å at 123 K)[1e] and is further reduced in **2** (3.294(6) Å) relative to **1**. Thus, replacement of Et$_3$N by the less sterically demanding base DABCO results in a strengthening of the N−H···Co hydrogen bond. Furthermore, increasing the basicity of the metal center also strengthens the hydrogen bond. Necessarily the bridging hydrogen more closely approaches the metal center,[14] and we presume that a concomitant lengthening of the N−H bond should take place. As the N−H···Co hydrogen bond is strengthened upon traversing this series of compounds, there is also an accompanying structural trend associated with geometry about the metal center; the equatorial carbonyl groups bend back away from the N−H group to yield geometries closer to that adopted by HCo(CO)$_3$L (L = CO, PR$_3$) (Table 3), the product of proton transfer to the metal. Thus, taken in sequence, this series of structures serves as a model for progression along the pathway of electrophilic addition at a tetrahedral center to yield a trigonal bipyramidal product.

In Table 4, IR stretching frequencies for the CO ligands of **1** and **2** are compared with those for related salts and for the corresponding cobalt hydride species. Clear trends emerge. As anticipated, substitution of CO ligands by P(OPh)$_3$ and PPh$_3$ ligands decreases the stretching frequencies for the remaining CO ligands. This conclusion, based primarily on the IR data of Norton and co-workers,[17] is reached both the for cobalt hydride species and for the salts when measured in acetonitrile solution. In such solutions, the latter are present as solvent-separated ions, as is apparent from the data for R$_3$NH$^+$Co(CO)$_4^-$ salts, which exhibit only the T$_2$ ν(CO) band characteristic of an anion of T_d symmetry. However, in toluene (or indeed benzene) solution the corresponding IR data are consistent with the salts adopting the associated form present in the solid state, i.e. in which N−H···Co hydrogen bonding is present. This is particularly evident in the R$_3$N-H$^+$Co(CO)$_4^-$ salts which now exhibit three bands (2A$_1$ + E) consistent with C_{3v} symmetry, the new bands appearing at higher frequencies. Such a change in symmetry cannot occur for **2**. However, it is noted that

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[14] Assuming a N−H separation of 1.05 Å, as determined by neutron diffraction for Et$_3$NH$^+$Co(CO)$_4^-$,[1b] the H···Co separations in **1** and **2** are 2.39 Å (mean) and 2.25 Å, respectively. Observed separations based on refined hydrogen positions are necessarily longer at 2.48(4) and 2.52(4) Å for **1** and 2.47(7) Å for **2**.

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[16] Preliminary NMR and crystallographic data for the salt (DABCO)H$^+$Co(CO)$_3$PPh$_2$(*p*-tol)$^-$ also support the observations made for **2**. Variable-temperature NMR data for (DABCO)H$^+$Co(CO)$_3$PPh$_2$(*p*-tol)$^-$ suggest that the coalescence point for the fluxional process lies in the range 215−240 K, but the exact temperature has not yet been resolved due to overlapping peaks in this region of the spectrum. Preliminary analysis of single crystal X-ray diffraction data from a weakly diffracting crystal of (DABCO)H$^+$Co(CO)$_3$PPh$_2$(*p*-tol)$^-$ as its acetonitrile solvate confirms that the connectivity of this salt is analogous to that of **2**. However, disorder of both the DABCO and PPh$_2$(*p*-tol) units have prevented an accurate analysis.

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Table 3. Comparison of the Geometries of Salts with N−H···Co Hydrogen Bonds with That of $HCo(CO)_3L$ (L = CO, PR_3)

compound	N···Co, Å	C_{eq}−Co−C_{eq}, deg	L_{ax}−Co−C_{eq}, deg	temp (K)	X/N/E[a]	ref
$Et_3NH^+Co(CO)_4^-$	3.684(2)	112.4(1)	106.3(1)	123.0(5)	N	1e
$[(NMP)_3H_2][Co(CO)_4]_2$[b]	3.639(1)	112.1(9)	106.7(7)	135(5)	X[c]	1c
$(DABCO)H^+Co(CO)_4^-$ (**1**)	3.437(3)	111.2(2)	107.2(2)	135(5)	X[c]	d
$Me_3NH^+Co(CO)_4^-$	3.402(4)	113(1)	106(1)	295	X[c]	6
$(DABCO)H^+Co(CO)_3PPh_3^-$ (**2**)	3.294(6)	115(3)	103(3)	123(5)	X[c]	d
$HCo(CO)_4$	na	117.3	99.7(6)	238	E	15a
$HCo(CO)_3PCy_3$[e]	na	118(2)	99(2)	296	X[c]	15b

[a] X = X-ray diffraction, N = neutron diffraction, E = electron diffraction. [b] NMP = *N*-methylpiperazine. [c] Averaged dimensions, with esds (in parentheses) calculated according to $[\sum(d_i - d)^2/n(n-1)]^{1/2}$ which thus reflect the scatter in the (three) observed values, rather than esds of the individual values. [d] This work. [e] Cy = cyclohexyl.

Table 4. Infrared Carbonyl Stretching Frequencies (cm^{-1}) of $HCo(CO)_3L$ and $A^+Co(CO)_3L^-$ Compounds (L = CO, $P(OPh)_3$, PPh_3; A^+ = Na^+, R_3NH^+)

compound	ν(CO), cm^{-1}	solvent	anion symmetry	symmetry of bands	hydrogen bond
$HCo(CO)_4$[17]	2117, 2054, 2023	CH_3CN	C_{3v}	$2A_1 + E$	na
$HCo(CO)_3P(OPh)_3$[17]	2075, 1996	CH_3CN	C_{3v}	$A_1 + E$	na
$HCo(CO)_3PPh_3$[17]	2050, 1971	CH_3CN	C_{3v}	$A_1 + E$	na
$Me_3NH^+Co(CO)_4^-$	2015, 1934, 1895	C_6H_5Me	C_{3v}	$2A_1 + E$	N−H···Co
$Et_3NH^+Co(CO)_4^-$	2015, 1931, 1895	C_6H_5Me	C_{3v}	$2A_1 + E$	N−H···Co
$Et_3NH^+Co(CO)_4^-$	1892	CH_3CN	T_d	T_2	none
$(DABCO)H^+Co(CO)_4^-$ (**1**)	2020, 1935, 1898	C_6H_5Me	C_{3v}	$2A_1 + E$	N−H···Co
$(DABCO)H^+Co(CO)_4^-$ (**1**)	1892	CH_3CN	T_d	T_2	none
$Na^+Co(CO)_3P(OPh)_3^-$[17]	1961, 1872	CH_3CN	C_{3v}	$A_1 + E$	none
$(DABCO)H^+Co(CO)_3(PPh_3)^-$ (**2**)	1955, 1857	C_6H_5Me	C_{3v}	$A_1 + E$	N−H···Co
$(DABCO)H^+Co(CO)_3(PPh_3)^-$ (**2**)	1928, 1839	CH_3CN	C_{3v}	$A_1 + E$	none
$Et_3NH^+Co(CO)_3(PPh_3)^-$[17]	1927, 1838	CH_3CN	C_{3v}	$A_1 + E$	none

Table 5. Chemical Shifts (ppm) of the Methylene Groups of DABCO for 1 and 2 in Toluene-d_8 Solution

temp (K)	^1H NMR for **1**	^{13}C NMR for **1**	^1H NMR for **2**	^{13}C NMR for **2**	^1H NMR for DABCO
298	2.18	47.2	2.42	46.9	2.40
253	−	−	2.16	−	2.40
233	2.05	−	2.22, 1.84	44.2[a]	2.40
213	1.87	−	2.26, 1.70	−	2.40
193	1.74	−	2.26, 1.67	−	2.40
188	−	43.9	2.24,[b] 1.66[b]	43.4, 43.3	−

[a] At 235 K. [b] At 183 K.

an increase in the carbonyl stretching frequencies does occur upon formation of the N−H···Co hydrogen bond, i.e. on going from acetonitrile solution to toluene solution. Such a change in the frequencies of the ν(CO) bands is consistent with the role of the metal center as a Lewis base in forming the N−H···Co hydrogen bond.

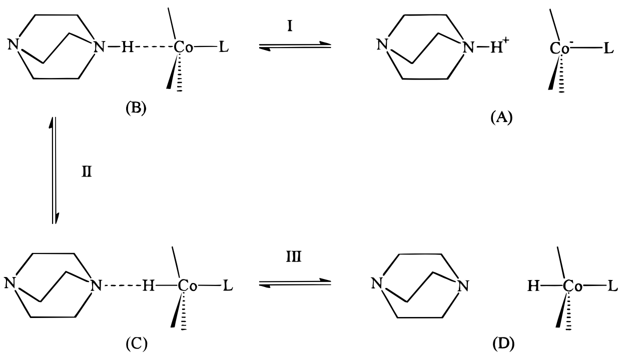
^1H NMR spectra for **1** and **2** in toluene-d_8 solution at 298 K show only a singlet for the methylene hydrogens of the DABCO. The N−*H* proton is not observed. Upon lowering the temperature the methylene signal moves upfield and the N−*H* signal is observed at low field (**1** δ 10.1, **2** δ 13.1). In addition, for **2** the methylene signal broadens and separates into two signals at temperatures below ca. 235 K.[16] The methylene signal for **1** remains a singlet down to a temperature of 193 K (Table 5). Other ^1H NMR data show no apparent temperature dependence. These data suggest a fluxional process in which the hydrogen bond is broken and the diamine can either undergo “intermolecular” interchange with other diamines prior to reformation of the hydrogen-bonded salt, or reform the hydrogen bond using the nitrogen atom at the opposite end of the same molecule, i.e. “intramolecular” interchange. This fluxional process necessarily involves proton transfer between nitrogen sites.

On the basis of the observed crystal structures, the IR data (Table 4), and the fact that a N−*H* signal but no Co−*H* signal is observed in the ^1H NMR spectrum, we assume that, in toluene solution, the N−H···Co hydrogen bonded species (B, *vide infra*) is the resting state of the fluxional system. We therefore infer from the temperature-dependent NMR data that a process which interconverts the methylene protons of DABCO by separation of the DABCO-containing species from the cobalt-containing species occurs, and that this process is retarded when PPh_3 is substituted for CO. The shortening of the N···Co separation indicated by the crystallographic studies suggest a possible explanation, namely that an increased N−H···Co hydrogen bond strength in the phosphine-substituted system decreases the tendency of the zwitterionic complex to separate into the component ions. While we will suggest that this is indeed the case, such an effect cannot be inferred from the NMR data alone as there remains some ambiguity over the pathway for the fluxional process. We will not focus here on the intra- *versus* intermolecular nature of the process; the key issue is that the fluxional process could conceivably involve one of two pathways for dissociation/reassociation (Scheme 1).

The simplest process (I) mentioned above is the cleavage of the N−H···Co hydrogen bond in the suggested resting state (B) to yield the two ions (A). Alternatively, transfer of a proton (II) could yield another hydrogen-bonded complex (C) incorporating neutral DABCO and cobalt-hydride moieties. Cleavage of this hydrogen bond (III) would allow the interchange of the DABCO coordination site via free DABCO (D).

To investigate the expected effects of PPh_3 substitution on the second pathway we have performed a series of ab initio SCF calculations on the model complexes

Scheme 1. Possible Dissociation/Reassociation Paths[18] for $(DABCO)H^+\cdots Co(CO)_3L^-$ (L = CO, PPh$_3$)



($Me_3NH^+\cdots Co(CO)_3L^-$, L = CO and PH$_3$).[19] We adopted the same skeletal geometry for the two complexes, and computed the energy profile as the proton migrates from N to Co, shown in Figure 2. In both cases, the potential energy surface shows two distinct minima corresponding to species of type (B) (N−H ca 1.05 Å) and (C) (N−H ca. 1.80 Å). From the energy curves it is clear that the calculations predict that the most stable conformation considered is the cobalt hydride (C in Scheme 1). The discrepancy between this result and that observed experimentally (B) can be attributed to the fact that the computations were performed in vacuo, where there is no dielectric medium to stabilize the separation of charge characteristic of the zwitterionic system (B).

We might anticipate that if the species were soluble in nonpolar media the resting state would be of type (C), and pathway III would be the preferred dissociation route.

Of more relevance to the current discussion is the change in the energy profile produced by phosphine substitution. As expected from considerations of the charge density at Co the stability of the cobalt hydride complex with respect to the zwitterionic species is found to increase by 6 kcal/mol on replacement of CO by PH$_3$. Clearly this also has the effect of lowering the barrier to the conversion B → C. Turning now to step III, we would anticipate that phosphine substitution at Co would increase the charge density at the hydride ligand and thereby weaken its potential as a hydrogen bond donor. Therefore, both processes II and III would be expected to become more facile on phosphine substitution. Taken together with the NMR evidence that the observed process shows the opposite behavior, we infer that our original supposition of an ionic pathway (I) is correct. The NMR evidence thus provides support for the crystallographic evidence presented herein, that the N−H···Co hydrogen-bonding interaction is strengthened when the basicity of the metal-containing fragment is increased.

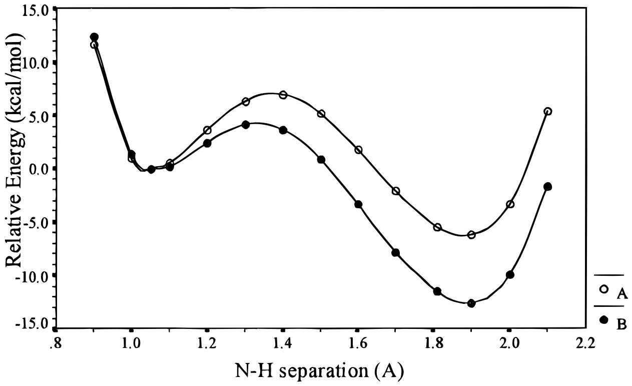


Figure 2. Plot of relative energy vs N−H separation from ab initio SCF calculations. Curve A is for $Me_3NH^+\cdots Co(CO)_4$ and curve B for $Me_3NH^+\cdots Co(CO)_3PH_3^-$.

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Supporting Information Available: Tables of crystallographic data, positional and displacement parameters, interatomic distances and angles for **1** and **2**; figures showing the other independent "molecule" of **1** and disorder model for **2** (18 pages). Ordering information is given on any current masthead page

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[18] Only illustration of the possible "intramolecular" processes are shown in the scheme. From the present data, it is not possible to distinguish between these and related "intermolecular" processes which may occur.

[19] (a) All calculations were with the GAMESS-UK[19b] package. DZ quality basis sets were used for all atoms[19c,d] and augmented with polarization functions on the heavy atoms of the NMe$_3$ group (C d exponent 0.75, N d exponent 0.80) and the hydrogen-bonded H (p exponent 1.0). Additional diffuse p (exponent 0.0525) and d (0.0783) functions were added to the Co basis. The model heavy-atom geometries were based on the X-ray results with Co···N set to 3.36 Å. (b) GAMESS-UK is a package of ab initio programs written by M. F. Guest, J. H. van Lenthe, J. Kendrick, K. Schoffel, P. Sherwood, and R. J. Harrison, with contributions from R. D. Amos, R. J. Buenker, M. Dupuis, N. C. Handy, I. H. Hillier, P. J. Knowles, V. Bonacic-Koutecky, W. von Niessen, V. R. Saunders, and A. J. Stone. The package is derived from the original GAMESS code due to M. Dupuis, D. Spangler, and J. Wendoloski, NRCC Software Catalog, Vol. 1, Program No. QG01 (GAMESS), 1980. (c) For C, H, O, N: Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823. (d) For Co, P: Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatewaki, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984. The basis was contracted to (8s,6p,2d) as suggested by Dunning and Hay (Dunning, T. H., Jr.; Hay, P. J. *Methods of Electronic Structure Theory*; Shaefer, H. F., III, Ed.; Plenum Press: 1977; p 1.)