

Competitive Ligand Substitution Reactions in the Gas Phase: Ion–Molecule Reactions of Ligand Molecules with Ions Derived from Nitrosyltricarboxylcobalt(0) and with Li^+ 1

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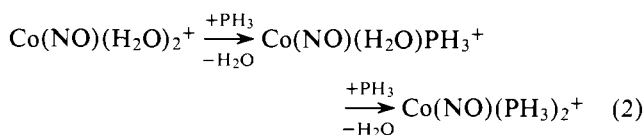
Abstract: Gas-phase ion–molecule reactions in mixtures containing $\text{Co}(\text{NO})(\text{CO})_3$ and one or two ligand species are described. The ligands examined are NO , NH_3 , PH_3 , AsH_3 , C_2D_4 , H_2O , CO , and O_2 . The carbonyls in $\text{Co}(\text{NO})(\text{CO})_n^+$ and $\text{Co}(\text{CO})_n^+$ are displaced by each of the ligands but O_2 . Several of the ligands will displace two carbonyls in a single bimolecular step. In the presence of two ligands, X and Y, species of the type $\text{Co}(\text{NO})(\text{X})(\text{Y})^+$ are formed. Examination of X for Y displacements in such species gives rise to an ordering of cobalt ligand bond strengths. The ligands are listed above in the deduced order of decreasing affinity for cobalt in the complexes studied, i.e., three- and four-coordinate unipositive ionic complexes containing the $\text{Co}(\text{NO})$ moiety and additional ligands from the above list. In the $\text{Co}(\text{NO})(\text{X})(\text{Y})^+$ species no evidence was found that the Co–X bond energy varies with the nature of Y. The same series of ligands was examined in the presence of Li^+ . The order of Li^+ affinities deduced from ligand substitutions is $\text{NH}_3 > \text{H}_2\text{O} > \text{PH}_3 > \text{AsH}_3, \text{C}_2\text{D}_4, \text{CO}, \text{O}_2$, and NO . $D(\text{Li}^+ - \text{PH}_3)$ is determined to be 28 ± 1 kcal/mol. The results are discussed in terms of simple bonding theory.

Most studies of metal–ligand interactions are done in the condensed phase, where the solvent may exert a controlling influence on the nature of interaction.^{2,3} In addition, conventional studies frequently rely on an indirect measure of the strength of metal–ligand bond, such as molecular vibrational frequencies.^{4,5} Recently, ligand substitution has been observed in ion–molecule reactions in the gas phase.^{6–8} This suggests the possibility of investigating metal–ligand interactions in the absence of solvent. Such gas-phase studies have the further advantage that relative metal–ligand bond strengths can be determined directly. That is, techniques such as ion cyclotron resonance⁹ make it possible to determine directly whether at equilibrium



favors products or reactants. In fact in the case of $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{NO})^+$, where the metal complex has only one replaceable ligand, it has been possible to measure equilibrium constants for eq 1.¹⁰

The present study involves the examination of the gaseous ion chemistry of mixtures containing a metal complex, $\text{Co}(\text{NO})(\text{CO})_3$, and one or more potential ligands. Ionization is induced by electron impact and the subsequent chemistry is followed using conventional ion cyclotron resonance techniques.⁹ Among the reactive species formed initially are $\text{Co}(\text{NO})(\text{CO})_3^+$ and $\text{Co}(\text{NO})(\text{CO})_2^+$. The carbonyls in these species are readily displaced by a number of ligands. If two potential ligands are present, species appear containing one or both of the ligands in place of the carbonyls. In a mixture of water, phosphine, and the complex, for example, $\text{Co}(\text{NO})(\text{H}_2\text{O})_2^+$, $\text{Co}(\text{NO})(\text{PH}_3)(\text{H}_2\text{O})^+$, and $\text{Co}(\text{NO})(\text{PH}_3)_2^+$ are formed from $\text{Co}(\text{NO})(\text{CO})_2^+$. Ion cyclotron double resonance⁹ provides positive evidence that



occurs. Moreover, since the total time available for reaction is at most an order of magnitude greater than the time between collisions,⁹ reactions observed by double resonance must proceed on nearly every collision. A reaction of such high efficiency must, of course, be exothermic or thermoneutral. Thus

we conclude from double resonance observations that in the complexes involved in eq 2 the cobalt–phosphine bond is both thermodynamically and kinetically more stable than the cobalt–water bond. A technique analogous to this has been successfully applied to the determination of relative proton affinities.¹¹

$\text{Co}(\text{NO})(\text{CO})_3$ was chosen for this study since it is volatile and its ligand substitution reactions have been studied by conventional techniques.^{12–19} The nitrosyl substituent provides an opportunity to examine the behavior of both NO and CO , two very important ligands in transition metal chemistry. The reagent ligands chosen for the study are NH_3 , PH_3 , AsH_3 , H_2O , C_2H_4 , NO , CO , and O_2 . These ligands are of general importance in transition metal chemistry and show characteristic affinities for different classes of metals.²⁰

To provide insight into the role of electrostatic interactions between metal ions and ligands we examined the chemistry of Li^+ with the same series of ligands. In solution Li^+ forms strong electrostatic bonds and should have different behavior toward ligands than does Co in its lower oxidation states.²⁰ Our results confirm that this is the case.

Below, following an account of experimental procedures, is a description of the gaseous ion chemistry observed in $\text{Co}(\text{NO})(\text{CO})_3$, in mixtures of the complex with one ligand, in mixtures of the complex with two ligands, and the results of the Li^+ studies. In conclusion, we deduce an order of relative metal–ligand bond strengths and discuss the results in terms of bonding theories.

Experimental Section

All experiments were performed on an ion cyclotron resonance spectrometer of conventional design built at Ford Scientific Research Laboratories and at the University of Delaware. The ICR cell is $1.1 \times 2.5 \times 11.5$ cm. The source region is 1-cm long and the resonance region is 10.5-cm long. Experiments were carried out in the normal drift mode using trapping voltage modulation coupled with phase-sensitive detection. The marginal oscillator detector was of solid-state design.^{21,22} Double resonance experiments were performed using a Wavetek Model 144 HF sweep generator as the secondary oscillator. The signal amplitude for irradiation was between 25 and 500 mV cm^{-1} .

The ICR instrument has two sample inlet systems controlled by two Model 951-5700 Varian leak valves. The cell region is pumped by both a 4-in. diffusion pump and a 20 l./s ion pump. Approximate pressures may be obtained using ion pump current readings. Above 2×10^{-5}

Table I. Carbonyls Displaced from Ions Containing NO

Ligand	Reactant ion		
	CoNO(CO) ⁺	CoNO(CO) ₂ ⁺	CoNO(CO) ₃ ⁺
NO	1	2	2
NH ₃	1	1, 2	1, 2
PH ₃	a	1, 2	1, 2
AsH ₃	1	1	1
C ₂ D ₄	1	1	1
H ₂ O	1	1	1
CO	1	1	1
O ₂	0	0	0

^a CoNO(PH₃)⁺ was observed, but it showed no response on irradiation of Co(NO)(CO)⁺.

Table II. Carbonyls Displayed from Ions Not Containing NO

Ligand	Reactant ion	
	Co(CO) ⁺	Co(CO) ₂ ⁺
NO	1	1, 2
NH ₃	1	1, 2
PH ₃	1	1
C ₂ D ₄	1	1
H ₂ O	1	1
AsH ₃	1	1
CO	1	1
O ₂	0	0

Torr pressure was determined accurately using an MKS baratron capacitance manometer.

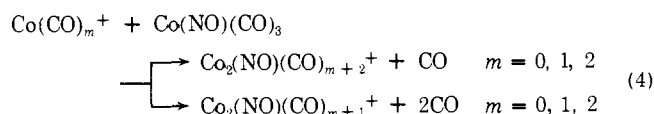
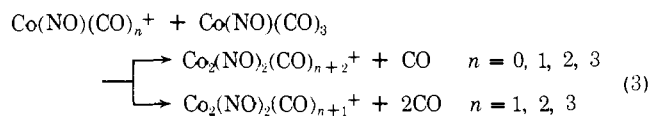
Nitrosyltricarboxylcobalt was obtained from Alpha Ventron. The liquid sample was purified by freezing it to -196 °C and pumping off the vapor. The sample was degassed using freeze-pump-thaw cycles. C₂D₄ was purchased from Stohler Isotope Chemicals, O₂ was provided by Linde, ¹⁵NH₃ was supplied by British Oxygen Co., Ltd. (96.6% pure), NO and NH₃ were procured from Matheson and H₂O was appropriated from a distillation tap at the University of Delaware. Both phosphine²³ and arsine²⁴ were made by well-known methods.

Co(NO)(CO)₃ alone and mixtures of Co(NO)(CO)₃ with one ligand were examined at an electron energy of 15 eV. In the mixtures the ratio of ligand pressure to metal complex pressure was maintained at 2:1 by adjusting leak ratios from the two inlets. Total pressure in the cell was controlled by adjusting the valves between the pumps and the cell. Double resonance experiments were performed at total pressures of ~10⁻⁵ Torr where product ion concentrations are significant.

Mixtures of two ligands were admitted through one inlet and Co(NO)(CO)₃ through the other to obtain the three component mixtures.

Results

Co(NO)(CO)₃. At 15 eV electron impact on Co(NO)(CO)₃ produces significant relative abundances of Co(NO)(CO)_n⁺ and Co(CO)_m⁺ where *n* = 0, 1, 2, and 3, and *m* = 1 and 2. These ions react as indicated in eq 3 and 4. The formation of



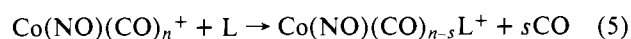
polynuclear complexes in the ion chemistry of metal carbonyls seems to be a general phenomenon.^{6,7,25} No evidence for loss of more than two carbonyls or loss of a nitrosyl was obtained. In each case, loss of two carbonyls is favored by an increase in the kinetic energy of the reactant ion. If Co(CO)₂⁺ is accelerated with the irradiating oscillator, for example, the

Table III. Maximum Number of Ligands Included in Species of the Type CoNO(CO)_{3-n}L_n

L	Max <i>n</i>	L	Max <i>n</i>
NO	1	AsH ₃	2
NH ₃	1	H ₂ O	3
PH ₃	3	C ₂ D ₄	1

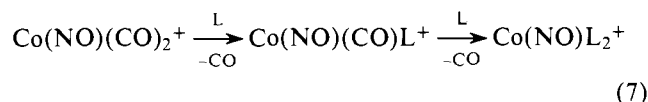
Co₂(NO)(CO)₃⁺ signal increases and the Co₂(NO)(CO)₄⁺ signal decreases. Ejecting Co(CO)₂⁺ from the cell before it can react decreases both Co₂(NO)(CO)₃⁺ and Co₂(NO)(CO)₄⁺ signals indicating both products are formed by the thermalized reactant ion.²⁶

Co(NO)(CO)₃ + Ligand. Bimolecular reactions between ligand L and electron impact products of Co(NO)(CO)₃ result in ions of the type Co(NO)(CO)_nL⁺ and Co(CO)_nL⁺. Reactions 5 and 6 represent the processes generally observed.



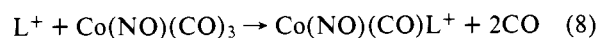
Either one or two (*s* = 1, 2) carbonyls may be displaced from ions with two or more carbonyls. As indicated in Tables I and II, the number of carbonyls displaced varies with the identity of the ligand. Since the energy to displace carbonyls comes from the new metal-ligand bond, the number of carbonyls displaced is a rough indication of metal-ligand bond strengths.

Products of reactions 5 and 6 react further with ligand L to produce ions containing two and three L molecules as indicated in the equation



Each ligand that displaces one CO from Co(NO)(CO)₂⁺ and Co(CO)₂⁺ goes on to displace a second in this way. The maximum number of carbonyls displaced from Co(NO)(CO)₃⁺ in steps analogous to eq 7 by each ligand is given in Table III. These numbers should not be confused with those in Tables I and II, which correspond to carbonyls displaced in a single biomolecular process (reactions 5 and 6). Since the predominant products of the first reaction between NH₃ and Co(NO)(CO)₃⁺ correspond to loss of two and three carbonyls, very little Co(NO)(CO)₂(NH₃)⁺ is available for further reaction. Hence further reaction is not observed. The relatively high mass of Co(NO)(AsH₃)₃⁺ requires operating the oscillator detector at low frequency, which may account for our failure to observe Co(NO)(AsH₃)₃⁺. Co(NO)₂(CO)₂⁺ and Co(NO)(C₂D₄)(CO)₂⁺, on the other hand, are readily observed and seem to be inert to further substitution even at relatively high partial pressure of the ligand (~3 × 10⁻⁴ Torr).

The parent ions of the ligands C₂D₄ and NO react according to



displacing two carbonyls. H₂O⁺, NH₃⁺, and PH₃⁺ displace three carbonyls and O₂⁺ reacts by charge exchange to form Co(NO)(CO)₃⁺.

The parent ions and parent neutrals of H₂O, NH₃, PH₃, and AsH₃ react to form the protonated parents which then react with the metal complex. H₃O⁺, AsH₄⁺, and PH₄⁺ transfer a proton to Co(NO)(CO)₃, while NH₄⁺ does not, indicating the proton affinity of Co(NO)(CO)₃ to be between that of PH₃ (175 kcal/mol²⁷) and that of NH₃ (207 kcal/mol²⁸).

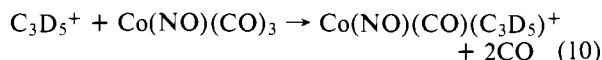
One additional reaction of interest occurs in the presence of ethylene. C₃D₅⁺, probably an allyl cation, is formed by re-

Table IV. Reactions of $\text{CoNO}(\text{CO})_2^+$ in Mixtures of Ligand Molecules X and Y

X	Reaction scheme ^a	Y
NO	<pre> CO,CO / \ / \ / \ / \ / \ / \ / \ / \ / \ NO,NO NO,NH3 \ / \ / \ / \ / \ / \ / \ / \ / \ / CO,NO </pre>	NH_3
NH_3	<pre> CO,CO / \ / \ / \ / \ / \ / \ / \ / \ / \ NH3,NH3 NH3,PH3 \ / \ / \ / \ / \ / \ / \ / \ / \ / CO,CO </pre>	PH_3
PH_3	<pre> CO,CO / \ / \ / \ / \ / \ / \ / \ / \ / \ PH3,PH3 PH3,H2O \ / \ / \ / \ / \ / \ / \ / \ / \ / CO,CO </pre>	H_2O
PH_3	<pre> CO,CO / \ / \ / \ / \ / \ / \ / \ / \ / \ PH3,PH3 PH3,AsH3 \ / \ / \ / \ / \ / \ / \ / \ / \ / CO,CO </pre>	AsH_3
AsH_3	<pre> CO,CO / \ / \ / \ / \ / \ / \ / \ / \ / \ CO,AsH3 CO,C2D4 \ / \ / \ / \ / \ / \ / \ / \ / \ / CO,CO </pre>	C_2D_4
C_2D_4	<pre> CO,CO / \ / \ / \ / \ / \ / \ / \ / \ / \ CO,C2D4 CO,H2O \ / \ / \ / \ / \ / \ / \ / \ / \ / CO,CO </pre>	H_2O

^a Ligands in addition to one nitrosyl included in the ionic Co complexes are indicated. Diagonal arrows represent substitution of X or Y for CO. Horizontal arrows indicate substitution of X for Y. All arrows represent reactions identified by double resonance.

action 9²⁹ and goes on to react according to eq 10. This is typical of metal carbonyls



and is discussed elsewhere.⁸

$\text{Co}(\text{NO})(\text{CO})_3 + 2$ Ligands. The chemistry of the three-component mixtures is exceedingly complex at an electron energy of 15 eV, so the present studies were conducted with an electron energy of 8.9 eV (nominal). At this energy the ligands are not ionized and only $\text{Co}(\text{NO})(\text{CO})_3^+$ and $\text{Co}(\text{NO})(\text{CO})_2^+$ are formed from the metal complex. In the presence of two ligands, X and Y, species of the type $\text{Co}(\text{NO})(\text{X})(\text{Y})^+$ are formed by successive carbonyl displacements as described above. In general, CO is lost in preference to X or Y, so that X and Y displace each other only from ions with no carbonyls to be displaced. Thus the reactions which bear on relative metal-ligand bond strengths involve ions which are products of a sequence of two or three reactions. Such reactions are observed only at relatively high pressures, where the resonances are broadened and sensitivity is decreased. As a result it is generally possible to observe displacement of X for Y in three-coordinate ions but only in two cases in four-coordinate ions.

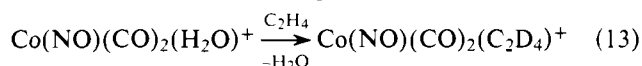
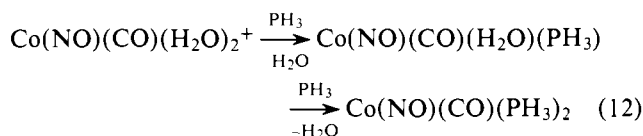
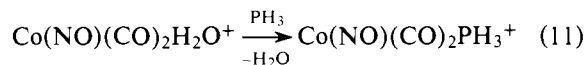
The ligand substitutions involving three-coordinate ions observed in three-component mixtures are represented in Table IV. Since NO is never displaced only the remaining two ligands in each ion are indicated. The diagonal arrows represent carbonyl displacements. The horizontal arrows indicate displacement of X by Y. All the arrows indicate reactions unambiguously identified by double resonance.

In two cases substitutions of X for Y were observed in ions

Table V. Relative Reaction Rates of $\text{CoNO}(\text{CO})_3^+$ and $\text{CoNO}(\text{CO})_2^+$

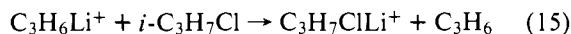
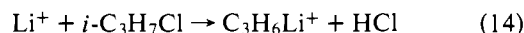
Ligand	$k(\text{CoNO}(\text{CO})_3^+)/k(\text{CoNO}(\text{CO})_2^+)$
NO	0.3
NH_3	0.8
PH_3	0.8
AsH_3	0.5
C_2D_4	0.2
H_2O	0.6

derived from $\text{Co}(\text{NO})(\text{CO})_3^+$. In the mixture containing water and phosphine reactions 11 and 12 occur, and reaction 13 occurs in the water-ethylene mixture.

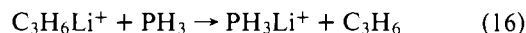


Reaction Rates. The complexity of the chemistry in these systems prevented more than very rough estimates of reaction rates. Most of the ligand displacements proceeded with rate constants in the range between $\sim 2 \times 10^{-10}$ and 10^{-9} cm^3 molecule⁻¹ s⁻¹. It was possible to determine the ratio of the rate of disappearance of $\text{Co}(\text{NO})(\text{CO})_3^+$ to that of $\text{Co}(\text{NO})(\text{CO})_2^+$ in several of the ligands. These ratios are reported in Table V.

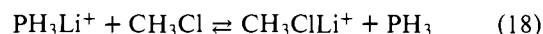
Li^+ Reactions. Li^+ ions were generated by thermionic emission by the method of Blewett and Jones.^{30,31} If $i\text{-C}_3\text{H}_7\text{Cl}$ is exposed to Li^+ ions, then the reactions



occur.^{8,32} Species which bind Li^+ more strongly than does propylene rapidly displace C_3H_6 from $\text{C}_3\text{H}_6\text{Li}^+$ as exemplified by eq 15.³² If the $i\text{-C}_3\text{H}_7\text{Cl}$ pressure is held constant and AsH_3 , NO , O_2 , or CO admitted, no ions other than the products of eq 14 and 15 are observed even at additive partial pressures in excess of 10^{-4} Torr. This indicates that AsH_3 , NO , O_2 , and CO bind Li^+ less strongly than does propylene. If PH_3 is added to the $i\text{-C}_3\text{H}_7\text{Cl}$ then PH_3Li^+ is formed by



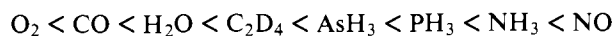
which may be confirmed by double resonance. Other reactions identified in the appropriate mixtures are



The latter reaction seems to be approximately thermoneutral, since both forward and backward reactions give a "negative" double resonance response. That is, accelerating either ion decreases the concentration of the other. Furthermore, if the pressure of a 1:1 mixture of CH_3Cl and PH_3 is increased the ratio of the concentrations of the two ions reaches a steady state. If this is interpreted as approach to equilibrium, then we can estimate $K_{\text{eq}} = 2$ for eq 18.

Relative Metal-Ligand Bond Strengths. The chemistry described above provides three criteria for relative strength of ligand to cobalt bonds: (1) the number of carbonyls the neutral ligand displaces from ions produced by electron impact on $\text{Co}(\text{NO})(\text{CO})_3$ (Tables I and II); (2) the number of carbonyls

the ligand parent ion displaces from neutral Co(NO)(CO)_3 (Table III); and (3) the results of the competitive ligand substitution reactions (Table IV). As mentioned above, the only energy available to break metal carbonyl bonds in reactions 5 and 6 is that released by formation of the new metal ligand bond, hence criterion 1. Phosphine, for example, reacts with Co(NO)(CO)_3^+ to displace two carbonyls, forming $\text{Co(NO)(PH}_3\text{)(CO)}^+$. Water, on the other hand, displaces only one carbonyl forming $\text{Co(NO)(H}_2\text{O)(CO)}_2^+$, indicating water to be a weaker ligand than phosphine. The second criterion resembles the first except that reaction 4 involves charge transfer to the metal as well as ligand substitution. The energy released by the charge transfer as well as that released by forming the new metal–ligand bond is available to break metal carbonyl bonds. Hence the ligand ionization potential as well as the strength of the metal–ligand bond may affect the number of carbonyls displaced. Nevertheless, criterion 2 places some restrictions on the metal–ligand bond strengths. The third criterion is, of course, the most direct and the most informative. The order of relative bond strengths consistent with all three criteria is unique. This order, which applies specifically to three- and four-coordinate unipositive ionic complexes containing the Co(NO) moiety and additional ligands from the list, is:



A study of ligand substitution reactions of electron impact products of Fe(CO)_5 suggests a criterion for metal–ligand bond strengths other than those listed above.⁶ Only bidentate ligands displace more than one carbonyl in a single reaction step in that system. Furthermore, successive displacements analogous to reaction 7 do not generally lead to complete displacement of all the carbonyls in Fe(CO)_n^+ ($n = 1-5$). Sequential displacements in general produce species of the type $\text{Fe(CO)}_{n-r}\text{L}_r^+$ ($r < n$), which are inert to further ligand substitution. The number of ligand molecules in the inert complex tends to increase with the proton affinity of the ligand. This suggests a correlation between the strength of the metal–ligand interaction and the maximum number of ligand molecules that will displace carbonyls from the various ionic complexes. This correlation does not apply to the present case, since the ligands examined, with exceptions discussed below, displace all of the carbonyls in the electron impact fragments of Co(NO)(CO)_3 . The above three criteria provide a more direct measure of metal to ligand bond strength.

Interpretation of the Li^+ reactions is straightforward. The bond strengths between Li^+ and the ligands unreactive with $\text{C}_3\text{H}_6\text{Li}^+$ are evidently less than that between Li^+ and propylene. The Li^+ –propylene bond energy is known to be 23 kcal/mol,³² which is thus an upper limit on $D(\text{Li}^+-\text{L})$ for $\text{L} = \text{AsH}_3, \text{NO}_2,$ and CO as indicated in Table VI. The reported values of $D(\text{Li}^+-i-\text{C}_4\text{H}_8)$ and $D(\text{Li}^+-\text{CH}_3\text{Cl})$ are 25.0 and 28.0 kcal/mol, respectively. The present results thus correspond to a value of 28.0 ± 1.0 kcal for $D(\text{PH}_3-\text{Li}^+)$. The error limits include an allowance for a nonzero entropy change for reaction 18 and for an order of magnitude error in the measured equilibrium constant.

Discussion

A number of factors affect the strength of the interaction between a metal ion and a neutral ligand. These include: (1) electrostatic interactions between the charge on the metal and the dipole moment and induced dipole moment of the ligand; (2) covalent bonding resulting from donation of electrons from the ligand to vacant orbitals on the metal; (3) π bonding resulting from back-donation of electrons from the metal to vacant π orbitals on the ligand; and (4) the nature of other ligands attached to the metal. Solvation effects which are often crucial

Table VI. Properties of the Ligands

Ligand ^a	Proton affinity, kcal/mol ^b	Ionization potential, eV ^c	Electrostatic energy, kcal/mol ^d	$D(\text{Li}^+-\text{L}),$ kcal/mol ^e
NO	120	9.26	12	<23
NH ₃	207	10.16	26	39 ^h
PH ₃	185	9.96 ^f	10	28
AsH ₃	175	10.03 ^g	8	<23
C ₂ D ₄	160	10.51	7	<23
H ₂ O	165	12.61	29	34 ^h
CO	140	14.01	11	<23
O ₂	100	12.06	9	<23

^aLigands listed in order of their affinity for Co^+ complexes as determined in the present study. ^bReference 9. ^cExcept as noted from D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley, New York, N. Y., 1970. ^dCalculated as described in the text. ^eExcept as noted, determined in the present study. ^fJ. P. Maier and D. W. Turner, *J. Chem. Soc., Faraday Trans. 2*, 68, 711 (1972). ^gG. R. Branton, D. C. Frost, C. A. McDowell, and I. A. Stenhouse, *Chem. Phys. Lett.*, 5, 1 (1970). ^hReference 32.

in solution are, of course, absent in the gas phase. Table VI lists the ligands in order of decreasing affinity for cobalt in the complexes studied. Table VI also lists data pertinent to an evaluation of the importance of the factors enumerated above which contribute to bond strengths.

Estimates of the electrostatic energy of interaction between cobalt and the various ligands are obtained from

$$E = (-\alpha e^2/2r^4) - (\mu e/r^2) \quad (19)$$

where μ and α are the dipole moment and polarizability of the neutral ligand and r is estimated from known cobalt–ligand bond distances. It is evident from these electrostatic energies (Table VI) that electrostatic interactions are not dominant in determining relative cobalt–ligand bond strengths in these systems. Li^+ , on the other hand, binds the small, polar H_2O and NH_3 much more strongly than the other ligands. This is just what is expected when electrostatic interactions dominate in bond formation. Hence, Li^+ behaves in the gas phase much as it does in solution.²⁰

In general, covalent bonding between an electron donor and an electron acceptor requires that the energy of the highest occupied orbital for the donor be close to the energy of the highest unoccupied orbital of the acceptor. The closer the energies, the stronger the bond. Ionization potentials provide the most convenient measure of the energies of the highest occupied orbitals of the ligands. These are listed in Table VI. Since ionization potentials of the various Co(NO)(X)(Y) neutrals are not available, the vertical ionization potential of Co(NO)(CO)_3 , 8.90 eV,³³ provides the most convenient measure of the energy of the highest unoccupied orbital of the metal ion complexes. Hence, the closer the ligand ionization potential to 8.90 eV, the stronger the expected covalent metal–ligand bond. It is evident from Table VI that the observed order of cobalt–ligand bond strengths follows the expected order of covalent bond strengths with two exceptions. The two exceptions are NH_3 , which forms bonds somewhat stronger than expected, and O_2 , which forms bonds weaker than expected. It may be that the cobalt– NH_3 bond is strengthened by electrostatic interactions, and that the cobalt– O_2 bond is weak because the symmetry of the triplet ground state of O_2 prevents favorable interaction with the metal. This comparison of ionization potentials, while it neglects a number of undoubtedly important effects, at least indicates that covalent interactions play an important role in ligand–cobalt bonding in the unipositive ionic complexes studied.

It is of interest to note that the proton affinities of the ligands tend to increase with the strength of the bonds the ligands form with cobalt in these ionic complexes. The most marked exception to this trend is NO, which has a very low proton affinity but forms the strongest bonds with cobalt of all the ligands studied. The relationship between nucleophilicity of a ligand towards a metal or other Lewis acid and that towards a proton has been extensively studied over the years. Of particular relevance to the present results are the linear free energy relationships of the rates of ligand substitution reactions of neutral $\text{Co}(\text{NO})(\text{CO})_3$ with the basicities of the ligands.¹⁴ For a homologous series of ligands, the rate constants for the ligand substitution reactions of neutral $\text{Co}(\text{NO})(\text{CO})_3$ increase logarithmically with the ligand basicity. These results might reasonably be interpreted as indicating that ligand bonding interactions toward $\text{Co}(\text{NO})(\text{CO})_3$ increase with ligand basicity. This is, of course, analogous to the conclusion suggested by the present study with regard to species of the type $\text{Co}(\text{NO})(\text{X})(\text{Y})^+$ and $\text{Co}(\text{NO})(\text{X})^+$. The kinetics of the ligand substitution reactions of neutral $\text{Co}(\text{NO})(\text{CO})_3$ further suggest that ligands with π -bonding properties are better nucleophiles than would be expected from their basicities.¹⁴ This is analogous to the behavior of NO in the present study. The nitrosyl ligand forms stronger bonds with cobalt in the ionic complexes than expected from its basicity, and ab initio calculations on $\text{Co}(\text{NO})(\text{CO})_3^+$ indicate extensive bonding interaction between the NO π^* orbital and d orbitals on the metal.³⁴ Similar conclusions regarding the relationship between proton affinity and metal–ligand bond strengths have been inferred from a study of equilibria in gas-phase ligand substitution reactions of $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{NO})^+$.¹⁰ Some care must be taken in drawing conclusions from comparison of proton affinities and strengths of other types of donor–acceptor interactions. Since proton affinities have a tendency to follow ionization potentials,³⁵ correlations with proton affinity may be a reflection of correlations with ionization potential. In the present case, both parameters are of some use. One provides an indication of the importance of covalent bonding and the other an indication of the importance of π bonding.

The reactions of species of the type $\text{Co}(\text{NO})(\text{X})(\text{Y})^+$ provide no indication that the strength of the Co–X interaction depends on the identity of Y. In two instances, however, four-coordinate complexes are inert to further reaction. This suggests that the combinations of ligands in these two complexes, $\text{Co}(\text{NO})_2(\text{CO})_2^+$ and $\text{Co}(\text{NO})(\text{C}_2\text{D}_4)(\text{CO})_2^+$, are particularly stable. It may be in these cases that the NO and C_2D_4 ligands contribute electron density to metal orbitals involved in back-donation from the metal to the carbonyls. This would stabilize the metal carbonyl bonds and perhaps render the complexes inert to further substitution.

As pointed out above, ligand substitution reactions of the neutral molecule $\text{Co}(\text{NO})(\text{CO})_3$ provide an interesting comparison to the present results. It is clear from studies of these neutral $\text{Co}(\text{NO})(\text{CO})_3$ reactions that the cobalt–phosphorus bond is considerably more stable than the cobalt–nitrogen bonds in species derived from $\text{Co}(\text{NO})(\text{CO})_3$ by ligand substitution. Ligands with both phosphorus and nitrogen donor sites, for example, displace only one carbonyl to form exclu-

sively cobalt–phosphorus bonds.¹⁶ The present study shows that removing an electron from the complex reverses the relative phosphorus and nitrogen bond stabilities. As argued above, this may be the result of electrostatic interactions between the small polar ammonia molecule and the charge on the complex. Another effect observed in ligand substitution reactions of neutral $\text{Co}(\text{NO})(\text{CO})_3$ in solution is that the first CO is more readily displaced than the second, and the third is not displaced at all by phosphine ligands.^{12,13} An explanation proposed for this effect is that the first phosphine ligand contributes electron density to the metal, which is back-donated to the remaining carbonyl ligands, bonding them more strongly to the metal.^{12,13} As noted above, a similar effect is observed only for NO and C_2D_4 ligands with the ionized metal complex.

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