

THE GAS PHASE CHEMISTRY OF BARE AND LIGATED TRANSITION METAL IONS: CORRELATIONS OF REACTIVITY WITH ELECTRONIC STRUCTURE—I. M^+ AND MCO^+

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Abstract—In the gas phase, univalent cations such as Cr^+ , $CrCO^+$, $Cr(CO)_2^+$, etc. have been generated, and their chemistry with neutral molecules characterized, using a number of mass spectrometric techniques. Presented here are results of *ab initio* calculations on two transition metal ion-monocarbonyl molecules, $ScCO^+$ and $CrCO^+$. These calculations suggest that the bonding in such systems is predominantly electrostatic in nature; this information is used to evaluate existing data on the gas phase chemistry of a variety of bare and ligated first-row transition metal ions.

Since the early 1970s, a substantial number of publications on the gas phase chemistry of transition metal and metal-containing ions with organic molecules have appeared.¹ Using a variety of mass spectrometric techniques, bare metal ions such as Fe^+ , Co^+ and Ni^+ as well as ligated metal ions such as $CrCO^+$, $Co(CO)_2^+$, $Ni(PF_3)_3^+$, CoO^+ , etc. can be generated, manipulated, and their chemistry studied. The chemistry of these 'exotic' gas phase species has the potential for providing insights into the fundamental aspects of organometallic chemistry and catalysis.

Currently, there are a number of experimental techniques used to generate gas phase metal and metal-containing ions such as surface ionization and laser ionization. However, early work in this area utilized electron impact ionization (EI) on volatile species (ML_n) such as $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$ and $Co(CO)_3NO$ to generate various atomic metal ions, M^+ . Also formed are the various ML_n^+ ions that are seen in the mass spectra of these compounds. Thus, there is a considerable amount of information available on how M^+ and ML^+ ions react with organic molecules. We will focus our discussion here on the monoligated metal ions, to determine how and why their chemistry varies when compared to the free M^+ species.

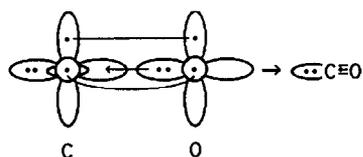
Historically, this area of research was largely descriptive in nature.¹ Most of the work was

directed towards understanding the mechanisms through which reaction products are formed. Recently, these systems have received attention from electronic structure theorists.² The experimental and theoretical methods each have strengths and limitations. Gas phase experiments can be used to identify both exothermic and endothermic reactions, and cross sections/rate constants can be determined for bimolecular reactions. However, only the m/z values of the reactants and products are determined in mass spectrometric experiments. No direct information is available on the states of reactants and products, their vibrational and rotational temperatures, and geometrical structures. In contrast, high level *ab initio* calculations can be used to accurately determine geometries and electron distributions in species such as CrO^+ . Such calculations yield bond dissociation energies, although the substantial contribution from the electron correlation to these bond energies precludes them being calculated as reliably as other features, such as geometries. The combination of experimental and theoretical efforts is required in this area of research, to identify the structure/function relationships that cannot be realized by experimental data alone.

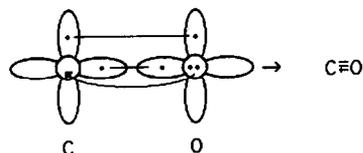
Discussed here are data that address the question: how does the chemistry of a bare, first row transition metal ion (M^+) change when a ligand (L) is added? The focus is mainly on the carbonyl ligand, CO. Correlations between the observed chemistry and theoretical descriptions of various M^+ and ML^+ ions will be presented.

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Scheme 1.



Scheme 2.

Classical description of the metal–CO bond

Consider first the CO molecule, which we may imagine as being formed in one of two ways. In the first, the C and O are asymptotically both in $^3P_{m=0}$ states, see Scheme 1. A dative bond is formed in the σ system with O contributing two electrons from its $2p_\sigma$ orbital to the empty C $2p_\sigma$ orbital. As the electrons flow into the carbon orbital the C $2s$ electrons hybridize away from the O atom and form the characteristic lone pair on the C. The second possibility has both the carbon and oxygen approach in their $^3P_{\pm 1}$ states, see Scheme 2. In this representation the dative bond is in the π system and the σ bond has much more carbon $2p_\sigma$ character to it than in the previous ($m = 0$) structure, and the C lone pair is essentially a $2s^2$ electron pair. These two localized views of the CO bonding have the same overall $^1\Sigma^+$ symmetry and of course both contribute to the CO wave function, see Scheme 3.

The more donor ability (Lewis basicity) as represented by

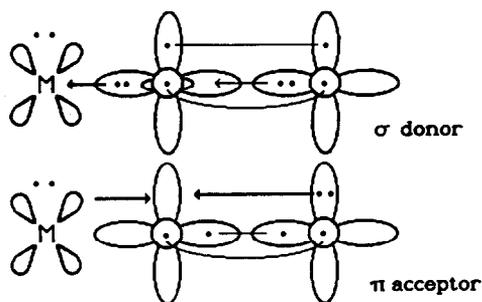


the less π acceptor ability the CO will have. The classic Dewar–Chatt³ mechanism for the interaction of a transition metal with CO is shown in Scheme 4.

This coupling of the σ donor/ π acceptor character allows a synergism which can increase the M–CO bond strength substantially. Note that if the metal is able to donate d_π electrons to CO they will contribute to the anionic character which will decrease

$$\begin{aligned} |^1\Sigma^+\rangle &\equiv \cos \theta |\llcorner\text{C}\equiv\text{O}\rangle + \sin \theta |\text{C}\equiv\text{O}\rangle \\ &\equiv \cos \theta |\sigma \text{ donor}\rangle \\ &\quad + \sin \theta |\pi \text{ acceptor}\rangle \end{aligned}$$

Scheme 3.



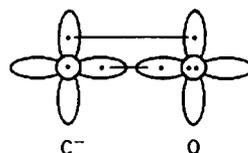
Scheme 4.

the π acceptor ability and therefore increase the σ donor ability (see Scheme 5). If the metal has no σ valence electrons to repel the CO σ electrons, a significant donation can occur, resulting in a large metal–CO bond energy. The strength of this bond will be decreased if the metal has σ valence electrons or does not have d_π electrons available for back donation. With this analysis in mind it would seem that the bonding in MCO^+ could be very similar to that in the neutral MCO if the electron which is removed on ionization is not critical to the σ – π synergism. In the subsequent discussion we will argue that this is not the case, i.e. the bonding in MCO^+ is essentially different from that in the neutral MCO .

Recently, Bauschlicher *et al.*^{4,5} have explored the Dewar–Chatt mechanism for the bonding of a single CO to a transition metal atom. In a series of *ab initio* calculations on various metal–carbonyl systems they have used the Constrained Space Orbital Variation technique to analyse the energetic consequences of the σ donation– π acceptor steps in the M–CO bonding. In all cases studied, it was found that the metal-to-CO π back donation is more important than the donation of CO σ electron density to the metal when the $3d_\sigma$ and $4s$ shells are empty, and becomes increasingly weaker as the $3d_\sigma$ and $4s$ shells are filled.

Experimental data on the M^+ –CO bond

Prior to this work, little was known of the bonding in such ionic complexes, or of the strength of the M^+ –CO bond. Using appearance potential measurements,⁶ heats of formation for a variety of



Scheme 5.

ionic species have been determined successfully; thus one might expect that data from EI or photoionization studies of compounds such as $Ni(CO)_4$ could be used to determine values such as $\Delta H_f(NiCO^+)$. From this, the bond energy $D(Ni^+-CO)$ could be calculated. Unfortunately, this is not the case. For example, the appearance potential of the $CrCO^+$ ion from EI on $Cr(CO)_6$ is 14.9 eV.⁷ From this, $\Delta H_f(CrCO^+) = 235$ kcal mol⁻¹ is calculated. Using $\Delta H_f(Cr^+) = 250.3$ kcal mol⁻¹ and $\Delta H_f(CO) = -26.4$ kcal mol⁻¹,⁸ this would suggest that $D(Cr^+-CO) = -11.1$ kcal mol⁻¹, i.e. that the bond has a negative bond energy. In such experiments, the appearance potential for the bare metal ion does not give the correct $\Delta H_f(M^+)$. It has been suggested that what is being measured is the energy required to form the metal ion in some excited state, M^{+*} , that reflects the electronic configuration of the metal in the neutral compound. Thus, appearance energy data from mass spectrometric experiments did not provide useful information on the M^+-CO bond.

Some of the earliest experiments involving gas phase species such as MCO^+ were studies of ligand displacement reactions.^{9,10} The results suggested that M^+-L interactions in the gas phase did not necessarily parallel $M-L$ interactions in condensed phases—that is, a strongly bound ligand in an organometallic compound may not be strongly bound to M^+ in the gas phase. (For example, in the gas phase hexane appears to be more strongly bound to a transition metal ion than does CO .¹¹)

A variety of ligand displacement reactions were studied in the 1970s. Reactions such as eq. (1)



were observed⁹ for a number of π and n donor bases (L). If reaction (1) occurs in the gas phase, the reaction is assumed to be exothermic or thermoneutral, implying that $D(Fe^+-CO) < D(Fe^+-L)$. Ligands such as CH_3F , CH_3Cl , H_2O , HCN , NH_3 , NO and C_2H_4 were observed to displace CO from Fe^+ . HCl , however, did not. It was noted that all of these 'ligands' were better Lewis acids than CO , except for HCl . Thus, there appeared to be a correlation between M^+ -affinity and H^+ -affinity. The exception was NO , $P.A.(NO) = 127$ kcal mol⁻¹ $<$ $P.A.(CO) = 143$ kcal mol⁻¹, which is also unique in that it was the only ligand studied that had an unpaired electron.

Results similar to those for $FeCO^+$ were also reported for $CoCO^+$. $CoCO^+$ was generated by EI on $Co(CO)_3NO$, thus a variety of $Co(CO)_n^+$ and $CoNO(CO)_n^+$ species were generated and studied.¹⁰ In addition to ligand displacement studies, that

allowed for an ordering of ligands in terms of their relative M^+ -affinities, the number of CO s displaced by a ligand could be used as a measure of relative $D(M^+-L)$ s. For example, in the reaction



C_2H_4 will displace one CO from $Co(CO)_3NO^+$, AsH_3 will displace two and PH_3 will displace three. The implication is that $D(Co^+-L)$ increases for the series $C_2H_4 < AsH_3 < PH_3$. Again, this correlates with the proton affinities—the ligand with the greatest gas phase basicity displacing the most CO s in reaction (2).

Thus, while CO is considered to be a 'strong' ligand in organometallic chemistry, this does not seem to be the case in these gas phase ionic species. This early work suggested that M^+-L bonding may have a substantial electrostatic component, although this would contradict the more conventional descriptions of metal-ligand bonding common to organometallic chemistry.¹²

In addition to the unusual behaviour displayed by NO in deviating from the proton affinity correlation of relative $D(M^+-L)$ values, it was observed that NO could not be displaced by ligands that displaced CO from a metal centre.¹⁰ Thus, reactions such as (3)



were not observed. Also, in reactions such as (2), while one or more CO could be displaced, the NO could not. Thus, the behaviour of NO as a ligand in these gas phase studies was very different from that observed for the variety of other ligands studied. Similar studies showed that 'Li⁺ affinities'¹⁰ paralleled proton affinities, with NO not being an exception in terms of its relative bond energy to Li^+ .

Theoretical description of the M^+-CO bond (M = 1st row transition metal)

Although there have been several theoretical studies^{4,5} of the interaction of a transition metal and a carbonyl there have been very few studies of the corresponding ions.⁵ Accordingly we have recently embarked upon a systematic theoretical study of the positive ions of the transition metal mon-carbonyls. Presented here are our results for $ScCO^+$ and $CrCO^+$. We chose to begin with Sc^+ because there are two electrons in the valence shell ($4s^1 3d^1$) allowing extensive *ab initio* calculations of the interaction between Sc^+ and CO with a modest computational effort. In addition, the low-lying

electronic states of Sc^+ , corresponding to the configuration $3d^2$, allow us to explore the effect of the $4s$ occupancy. Cr^+ is a d^5 ion and has the advantage of being spherically symmetric (6S ground state) and therefore, when it interacts with CO, only one low-lying molecular electronic state is formed.

THE FRAGMENTS

The transition metal ions

The electronic configuration of the Sc^+ ion is [argon core] $4s^13d^1$ or simply $4s^13d^1$. This gives rise to 3D and 1D states with the triplet being the ground state.¹³ The lowest state of the $3d^2$ configuration is of 3F symmetry and lies 0.596 eV above the ground 3D state. The electronic configuration of Cr^+ is $3d^5$ and results in a ground state of 6S symmetry and the lowest state of the first excited configuration $4s^13d^4$ is of 6D symmetry and lies 1.5 eV above the 6S . The relative energies of these states as well as the corresponding states in Ti^+ and V^+ are shown in Fig. 1. The metal basis set used in these calculations is described in ref. 14. There are three sets of data shown; the experimental separation, the separations calculated at an SCF level and the separations calculated using an MCSCF theory that allows a limited (radial) correlation among the

valence orbitals. This shows that the splittings calculated at the MCSCF level are in reasonable agreement with experimental data.

The CO molecule

The SCF description of CO (${}^1\Sigma^+$) results in the electronic configuration

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4$$

with an approximate description being that 1σ is the O $1s$ orbital; 2σ , the C $1s$; 3σ , the O $2s$; 4σ , the C—O sigma bond and 5σ the lone pair on the carbon. The 1π is a mixture of C and O p_π orbitals polarized toward the O atom. The GVB description used in this study keeps the 1σ , 2σ and 3σ orbitals at the SCF level and correlates the 4σ , 5σ and $1\pi^4$, e.g.

$$(4\sigma^2 - \lambda 6\sigma^2)(5\sigma^2 - \mu 7\sigma^2)(1\pi_x^2 - \gamma 2\pi_x^2)(1\pi_y^2 - \gamma 2\pi_y^2).$$

For internal calibration purposes we also constructed an MCSCF wavefunction for CO in which all spin couplings between the 4σ , 5σ , 6σ and 7σ orbitals were included. In C_{2v} symmetry the function contains 306 configuration state functions. The basis set used for both C and O is the Duijneveldt¹⁵ $11s, 7p$ set, augmented with an additional s and p selected in an even tempered way, and two single-component d functions on C and O. The resulting $12s, 8p, 2d$ basis was contracted to $4s, 4p, 2d$ following Rafenetti's¹⁶ recommendations. The potential energy curves for the SCF, GVB and MCSCF¹⁷ functions are shown in Fig. 2. Table 1 compares the calculated spectroscopic parameters with experiment. Figure 3 shows the variation of the dipole moment with internuclear separation for the three wavefunctions. Note that the SCF solution predicts the wrong sign for the dipole but that both the GVB and the MCSCF descriptions predict a sign in agreement with experiment, i.e. $\text{C}^{\delta-}\text{O}^{\delta+}$.

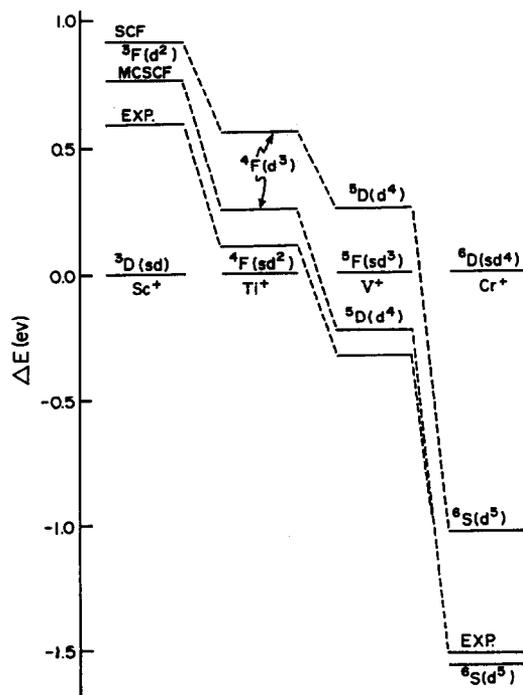


Fig. 1. The relative energies of the $4s3d^n$ and $3d^{n+1}$ configurations of the first four transition metal ions.

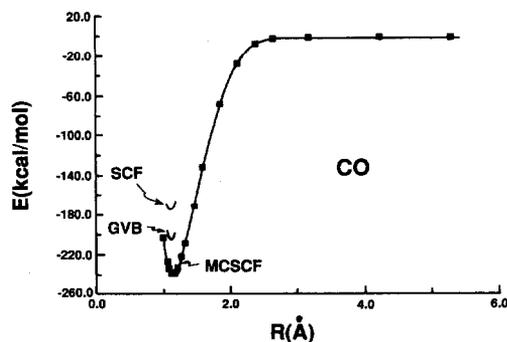


Fig. 2. Potential energy curves for CO at the SCF, GVB and MCSCF level.

Table 1. Comparison of calculated and experimentally-determined spectroscopic constants for CO

Variable	SCF	GVB	MCSCF	Experimental ^a
R _e (Å)	1.1129	1.1245	1.1414	1.1283
D ₀ (kcal mol ⁻¹)	174.7	204.8	236.0	255.8
ω _e (cm ⁻¹)	2409	2304	2169	2169.81
χ _e ω _e (cm ⁻¹)	11.6	12.3	13.1	13.288
E _{min} (au) ^b	-112.777071	-112.843864	-112.911329	

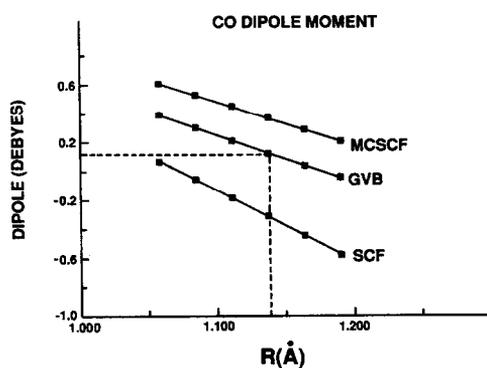
^a Taken from ref. 26.^b Electronic energy at the minimum of the calculated potential curve.

Fig. 3. Variation of the dipole moment of CO with internuclear separation. A positive dipole moment corresponds to C^{δ-}—O^{δ+}. The horizontal dotted line indicates the experimental dipole moment of 0.12 Debyes, which is also the value predicted by the GVB wavefunction at the C—O bond length (1.138 Å) used in the M⁺CO calculations.

THE MOLECULES

ScCO⁺

When Sc⁺ in its ground ³D state approaches the C end of CO colinearly, three molecular states are possible according to whether the 3d electron is in a d_σ(³Σ⁺), d_π(³Π) or d_Δ(³Δ) orbital. The GVB wavefunction for these states has the schematic form

$$\sim 4s^1 3d^1 (4\sigma^2 - \lambda 6\sigma^2) (5\sigma^2 - \mu 7\sigma^2) (1\pi_x^2 - \gamma 2\pi_x^2) (1\pi_y^2 - \gamma 2\pi_y^2) \quad (4)$$

where the 4s and 3d electrons are triplet-coupled. The interaction energy as a function of the Sc—C separation (the CO separation is fixed at 1.138 Å) is shown in Fig. 4; also included are the curves for the singlet states arising from the ¹D state of Sc⁺. The equilibrium bond lengths and bond energies for these and other calculations are collected in

Table 2. Analysis of the GVB wavefunction suggests that very little electron density has been interchanged between the metal ion and the CO ligand. The relative bond energies of the triplets follow the order Δ > Π > Σ⁺, while the singlet states vary as Π > Δ > Σ⁺. Recent studies^{4,5} on the neutral transition metal monocarbonyls suggest that, if the metal has an occupied 4s orbital, the initial M—CO interaction will be repulsive. The fact that the calculated interactions for Sc⁺ and CO are attractive at long distances, even though Sc⁺ has an occupied 4s orbital, suggests that the electrostatic interaction between Sc⁺ and CO is important. If μ, Θ and Ω are the dipole, quadrupole and octapole moment tensor elements along the internuclear axis of CO, relative to the centre of mass, and α is the corresponding dipole polarizability, the interaction energy can be written as

$$\Delta E = -\mu/R^2 + \Theta/R^3 - \Omega/R^4 - \alpha/2R^4. \quad (5)$$

The fourth order term involving the quadrupole moment of Sc⁺ and the dipole moment of CO is negligible and not shown above. Using μ = +0.04885, Θ = -1.6019, Ω = +3.9577 and α = 16.06 [all values are in atomic units (au)], all

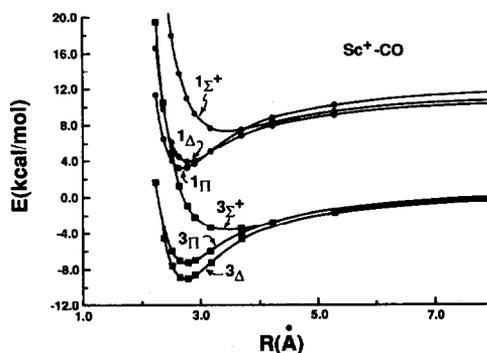


Fig. 4. Interaction energies for the low-lying triplet and singlet states of ScCO⁺ calculated with the GVB technique. Zero energy corresponds to Sc⁺(³D) + CO(¹Σ⁺).

Table 2. Equilibrium bond lengths and bond energies for various ScCO⁺, CrCO⁺ and LiCO⁺ electronic states^a

Molecule	State	R _e (Å)	ΔE (kcal mol ⁻¹)
ScCO ⁺	³ Δ	2.739	9.1
	³ Δ (CI)	2.697	10.2
	³ Π	2.755	7.3
	³ Σ ⁺	3.385	3.4
	¹ Δ	2.804	6.9
	¹ Π	2.711	7.6
	¹ Σ ⁺	3.504	3.2
	³ Σ ⁻	2.471	13.5
ScOC ⁺	³ Δ	2.469	5.5
CrCO ⁺	⁶ Σ ⁺	2.479	13.5
	⁶ Σ ⁺ (CI)	2.335	14.9
LiCO ⁺	⁴ Π	2.250	21.5
	¹ Σ ⁺	2.259	16.5 ^b

^a All results refer to GVB calculations, except where noted.

^b A. Mavridis and J. F. Harrison, unpublished results.

calculated from the CO GVB wavefunction, we calculated ΔE as a function of the Sc—C distance. The results of this calculation are shown as the solid curve on Fig. 5. The *ab initio* electrostatic expression given above tracks the energy variation rather well and suggests that the dominant interaction between CO and Sc⁺ is electrostatic, and that the bond energies are determined by that separation at which the electrostatic attraction gives way to the Pauli repulsion between the Sc 4s, 3d electrons and the CO lone pair. This apparently happens first when the 3d electron is in the 3d_σ orbital, second for the 3d_π and last for the 3d_Δ orbital—consistent with their spatial extension along the internuclear axis.

If CO approaches Sc⁺ (³F) and the two d electrons on Sc⁺ are in the d¹_{πx}d¹_{xy} configuration, the resulting electronic state of ScCO⁺ has ³Σ⁻ sym-

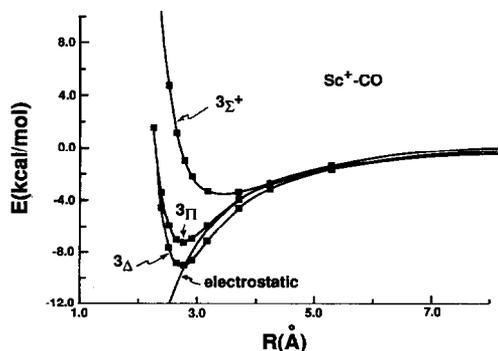


Fig. 5. Comparison of the electrostatic interaction between a point charge and CO with the *ab initio* GVB interaction energies for the ³Δ, ³Π and ³Σ⁺ states.

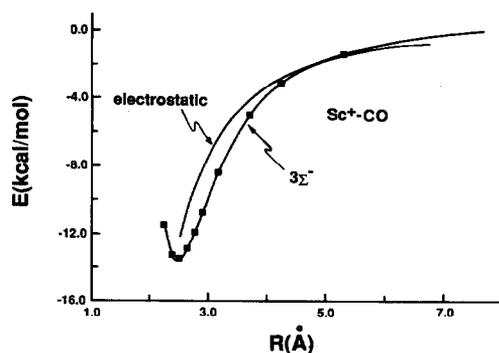


Fig. 6. Comparison of the *ab initio* interaction energy in the lowest ³Σ⁻ state of ScCO⁺ with the calculated electrostatic energy.

metry. The interaction energy in the 4-pair GVB model is plotted in Fig. 6. Note that the interaction energy is well represented at large distances by the electrostatic multipole expansion. The absence of a d_σ or 4s electron on Sc⁺ allows the CO to approach closer than in those states that correlate with a 4s¹3d¹ configuration. While the electrostatic representation for the energy fails at short Sc—C separations, this could be due to the importance of terms omitted from eq. (5), or simply due to the penetration of the electron densities of the two fragments. These two are, of course, not independent.

To assess the effect of configuration interaction (CI) on these systems we constructed the SCF + 1 + 2 function for the ³Δ state using the GVB orbitals. While the absolute energies dropped by 81 kcal mol⁻¹, the interaction energy remained essentially the same as the GVB calculation. The GVB and CI results are plotted in Fig. 7.

In Fig. 8 we show the GVB ³Δ interaction energy for the colinear approach of Sc⁺ from the O end of CO. Note that while the Sc⁺—O bond length (in Sc⁺—OC) of 2.47 Å is significantly shorter than the

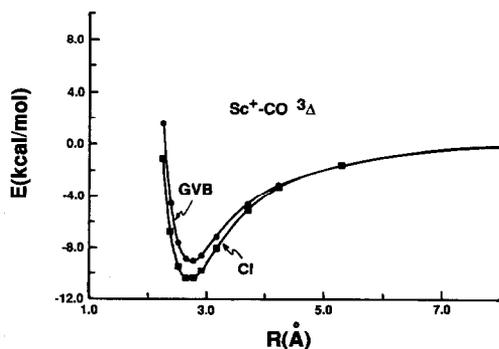


Fig. 7. Comparison of the GVB and SCF + 1 + 2 potential curves for ScCO⁺(³Δ).

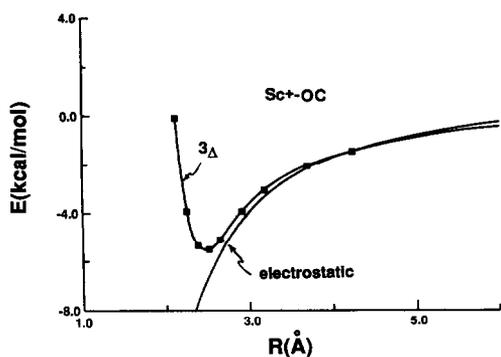


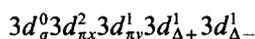
Fig. 8. Comparison of the GVB and electrostatic interactions for $Sc^+—OC(^3\Delta)$.

$Sc^+—C$ bond length (in $Sc^+—CO$) of 2.74 Å, the bond energies (5.5 and 9.1 kcal mol⁻¹, respectively) favour approach at the C end. The interaction energy for $Sc^+—OC$ is well represented by an electrostatic calculation, using the same CO parameters as in the C-side approach (Fig. 8).

$CrCO^+$

When the ground state of Cr^+ ($d^5, ^6S$) approaches CO, the resultant electronic state has $^6\Sigma^+$ symmetry. The interaction energy calculated with the GVB function equivalent to eq. (4) is shown in Fig. 9. Also plotted on Fig. 9 is the interaction energy curve for the $^3\Sigma^-$ state of $ScCO^+$. The resemblance is striking and suggests that the fundamental mechanism which leads to bonding in both molecules is very similar and largely electrostatic.

Interestingly, if one promotes the $3d_\sigma$ electron of Cr^+ to a $3d_\pi$ orbital, and allows the resulting configuration



to interact with CO, a much shorter and a much stronger $Cr^+—C$ bond is formed. Our preliminary

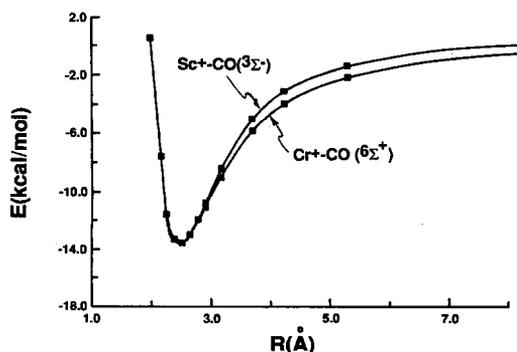


Fig. 9. Comparison of the $Sc^+—CO$ and $Cr^+—CO$ interaction energies at the GVB level.

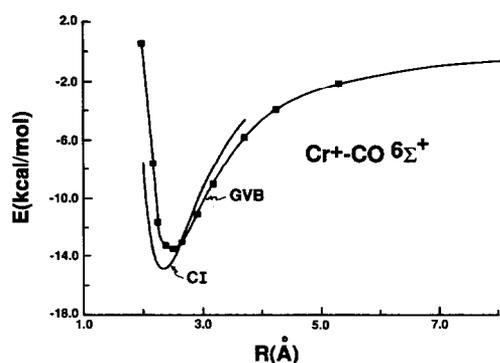


Fig. 10. Comparison of the GVB and SCF+1+2 potential curves for $CrCO^+(^6\Sigma^+)$.

GVB results suggest that, upon this excitation of the Cr^+ , the bond length in the $CrCO^+$ thus formed is reduced to 2.25 Å, and the bond strength is increased to 21.5 kcal mol⁻¹. The increase in bond energy observed on promotion of the d_σ electron appears to reflect the fact that this promotion allows the Cr^+ and CO to move closer to each other. Thus, the shortened bond results in an increased electrostatic interaction.

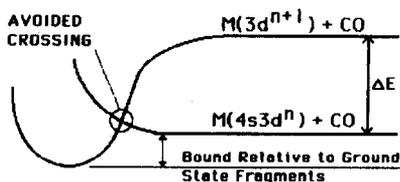
A comparison of the GVB result with an SCF+1+2 result for $CrCO^+$ is shown in Fig. 10. As in $ScCO^+$ the CI increases the bond energy by approximately 1 kcal mol⁻¹ but, unlike the $ScCO^+$ result, the CI predicts a significantly shorter bond length than the GVB calculation.

Relationship to previous calculations

In a recent publication, Bauschlicher⁵ reports the results of calculations on $NiCO$ and $NiCO^+$. Both have bond energies of ~ 1.1 eV, but rather different bonding characteristics. The neutral $NiCO$ has the Ni atom in the $3d^{10}$ configuration and correlates with the Ni 1S excited state, while the positive ion has a hole in the d_σ orbital and correlates with the 2D ground state of Ni^+ . The Ni—C bond length is 1.70 Å in the neutral and 2.10 Å in the ion. Bauschlicher notes that while the neutral metal contributes a significant number of electrons via its d_π orbitals to the CO fragment the positive ion contributes virtually none. He suggests that Ni^+ binds electrostatically to the CO, as we have found for Sc^+ and Cr^+ . It has also been suggested, by Orti *et al.*,²⁸ that Cu^+ binds electrostatically to CO.

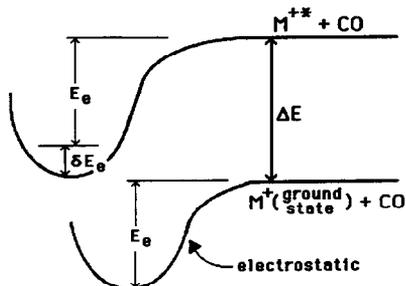
Implications and consequences of the calculated structure of MCO^+

Why do the first row transition metal positive ions bond differently from the neutrals to CO?

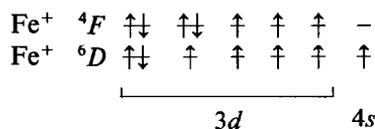


When CO approaches a neutral transition metal atom with an electronic configuration $4s^1 3d^n$, there is an initial repulsion¹¹ due to the $5\sigma(\text{CO})-4s(\text{M})$ interaction (a Pauli principle effect). If the $4s$ electron is singlet coupled to one of the $3d$ electrons, electronic states belonging to the excited configuration $4s^0 3d^{n+1}$ with a d_{π}^2 occupancy have the same spin symmetry as the $4s^1 3d^n$ states and can 'mix' in a Valence Bond sense, one has the situation shown in Scheme 6. Whether or not the upper state is bound, relative to the ground state fragments, depends on ΔE and the intrinsic M—CO bond strength. For a transition metal cation, the long range interaction with CO is electrostatic and therefore always bonding, whether the metal is in a ground or excited state (M^{+*}).

In the diagram shown in Scheme 7, the quantity E_e denotes the electrostatic interaction energy between the ground state M^+ and CO; the bond energy for the excited state is equal to $\{E_e + \delta E_e\}$. Does the ground state of the molecule MCO^+ always correlate with the ground state fragments? That is, under what circumstances could the additional binding energy (δE_e) of the metal in the excited state be greater than the excitation energy (ΔE)? There seems to be at least two extreme possibilities that could lead to positive values of δE_e : (a) when the electrostatic interaction is greater for M^{+*} than for M^+ and (b) when M^{+*} corresponds to an electronic configuration that favours the σ donation/ π acceptor mechanism. (Of course, some combination of these two extremes could also be realized.) For example, consider Fe^+ . The ground state ion has a $4s^1 3d^6$ configuration (6D), and there



are low lying states of the $3d^7$ configuration (4F state, $\Delta E = 5.4 \text{ kcal mol}^{-1}$). A closer approach (shorter bond length), and thus a larger electrostatic interaction energy would be expected for $\text{Fe}^+({}^4F)\text{—CO}$ relative to $\text{Fe}^+({}^6D)\text{—CO}$. The $\text{Fe}^+({}^4F)$ would also have an increased opportunity for backbonding, i.e. for the d_{π}^2 electrons to back donate into the CO $2\pi^*$ orbitals. For $\text{Fe}^+({}^4F)$, the ideal state would correspond to the configuration $3d_{\sigma}^1 3d_{\pi x}^2 3d_{\pi y}^2 3d_{\Delta+}^1 3d_{\Delta-}^1$, i.e.



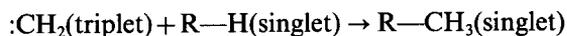
Although the opportunity exists here for increasing δE_e as a result of backbonding for this state, would it occur? In response to this question, consider the following: the ${}^3\Sigma^-$ state of ScCO^+ correlates with the 3F state of Sc^+ ($d_{xx}^1 d_{yy}^1$) and has a calculated equilibrium $\text{Sc}^+\text{—C}$ bond length of 2.47 Å, with a bond energy of 13.6 kcal mol⁻¹. The electrostatic energy, calculated using eq. (5) for this $\text{Sc}^+\text{—C}$ separation, is approximately 12.8 kcal mol⁻¹. For the ${}^4\Pi$ state of CrCO^+ , which correlates with the Cr^+ configuration $3d_{\sigma}^0 3d_{\pi x}^2 3d_{\pi y}^1 3d_{\Delta+}^1 3d_{\Delta-}^1$, the calculated bond length is 2.25 Å, the calculated bond energy is 21.5 kcal mol⁻¹, and the electrostatic energy from eq. (5) is approximately 16 kcal mol⁻¹. For NiCO^+ , the calculated ${}^5\text{Ni}^+\text{—C}$ bond length is 2.10 Å, the calculated bond energy is 25.3 kcal mol⁻¹, and the estimate from eq. (5) is 20.1 kcal mol⁻¹. The increasing importance of terms of order $1/R^5$, of course, results in the rapidly deteriorating ability of eq. (5) to accurately represent the electrostatic interaction energy at small separations. However, the correlation of the *ab initio* results with electrostatics suggests that little dative bonding/backbonding takes place in these ionic species, and that the bond energies for both $M^+\text{—CO}$ and $M^{+*}\text{—CO}$ species are dominated by electrostatics. (Note that the ground state of Li^+ cannot bond to CO by a Dewar—Chatt mechanism; even so, the data in Table 2 for LiCO^+ correlate with the ScCO^+ and CrCO^+ results listed, further supporting the dominance of the electrostatic mechanism for these ions.) It follows, then, that the bond energies are determined by how close the M^+ and CO can approach before repulsive terms become significant. This would predict that bond lengths will decrease, and $D(M^+\text{—CO})$ s increase, as the ionic radii of the various M^+ ions decrease. In the case of Fe^+ , the 4D excited state would then form a stronger bond to CO than would its 6D ground state, because the excited state atomic ion is smaller (the $3d$ orbitals

are more compact than the $4s$ orbital). An example of the opposite situation would be Co^+ , with a $3d^8$ (3F) ground state configuration, and a low-lying 5F excited state ($3d^74s^1$). In this case, the excited state would be more weakly bound than the ground state, i.e. δE_e will be negative.

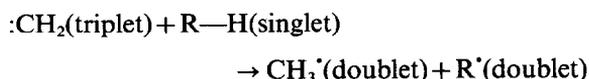
In response to the question of whether the global MCO^+ ground states correlate to the ground state fragments, in light of the above discussion, we have considered the ground and low-lying configurations of the various metal ions of the first transition series. $TiCO^+$ and $FeCO^+$ appear to be the only candidates for a situation where δE_e could be both positive, and greater than ΔE . Thus, these two MCO^+ species may indeed correlate with excited states of the corresponding metal ions. This question is being explored computationally in this laboratory.

The possibility that the cations of the transition metal elements could bond electrostatically to CO molecules has some intriguing consequences. First of all, in such a molecule the CO group would not modify the electronic structure of the transition metal ion. An ion with a $4s3d^n$ configuration would remain an *in situ* $4s3d^n$ in the monocarbonyl. To the extent that the chemistry of the ion is determined by its electronic configuration one would anticipate similar chemistry for M^+ and MCO^+ .

Not only would the electronic configuration of M^+ and MCO^+ remain the same but so would the spin. Is the spin relevant to the chemistry of M^+ , MCO^+ or any transition metal-containing ion? This question has been recently discussed by Armentrout *et al.*¹⁸ One knows from carbene chemistry¹⁹ that singlet carbenes insert into C—H bonds while triplet carbenes abstract. These processes conserve the electronic spin in the reaction for if a triplet carbene were to insert into a C—H bond the spin multiplicity would change. For example

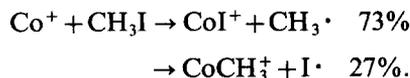


would be spin forbidden, while

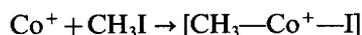


is allowed, provided the products are coupled into a triplet state. While electronic spin is a much better quantum number for carbon than for the transition metal cations, an examination of the atomic spectra¹³ of the bare transition metal ions suggests that spin might be a good quantum number, at least when the energy spacing between the LS coupling terms is larger than the energy spacing within the terms; this situation is often obtained for the low-lying electronic states.

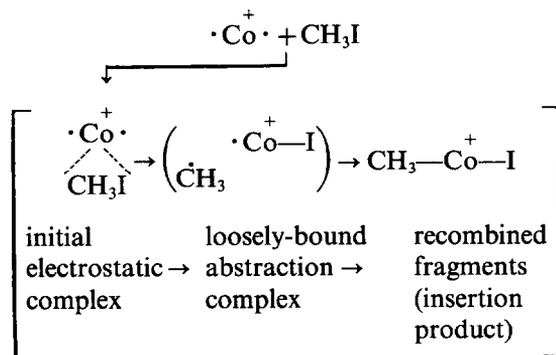
Thus, in the chemistry of transition metal ions, there are at least two options: (a) the electronic spin is a good quantum number and must be conserved in the reaction; or (b) the spin can easily change and is not a factor in the reactivity. While option (b) is uninteresting in that it yields no predictive capabilities, there are some consequences of option (a). Consider, for example the reaction of Co^+ with CH_3I .²⁰ Two products are observed:



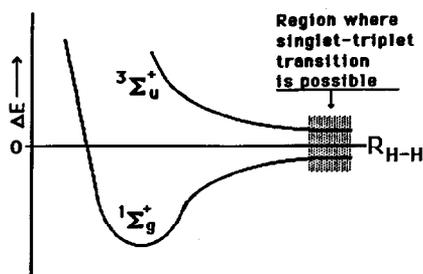
The ground state of Co^+ is a triplet d^8 configuration with two singly occupied orbitals and could react to form the products shown here and conserve spin. However, it has been proposed that this reaction (and others which follow) occurs by an insertion mechanism.²⁰ If, in the initial insertion reaction



spin was conserved, the Co^+ would have to uncouple a singlet-coupled d^2 electron pair and use these electrons to bond to the CH_3 and I fragments. This it could do by *in situ* promotion of a d electron to an s orbital, and mixing a triplet state of the $4s^13d^7$ configuration into the evolving wavefunction. The product would then be a triplet which might indeed be the ground state for CH_3-Co^+-I . While this is possible it presumably would result in an activation barrier which could make it problematic as to whether it is energetically possible for the triplet to react. If this direct insertion channel is precluded by a large activation barrier, perhaps the insertion process takes place in "two steps", as shown here:



First a spin-allowed abstraction occurs, followed by the recombination of the two radicals. This mechanism allows a triplet Co^+ to form a singlet insertion product, provided the products of the abstraction are able to recombine on a lower spin



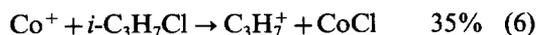
Scheme 8.

surface. For this to happen the products would have to be separated to the extent that a "small" spin-orbit interaction would allow the required surface change. This is similar to the reaction of two H atoms to form H₂. While the ground state in this case is the $^1\Sigma_g^+$, at large separations the energy difference between this singlet and the $^3\Sigma_u^+$ is very small, and a small spin-orbit interaction could take one from the triplet to the singlet surface, see Scheme 8.

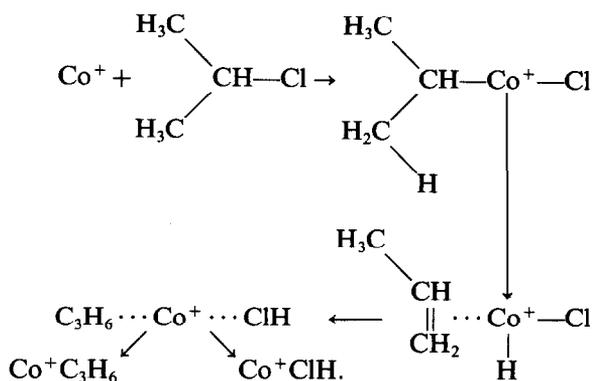
This mechanism, where one substitutes an abstraction and subsequent recombination for a concerted insertion is sensible only if the fragments involved in the abstraction reaction remain sufficiently close (loosely-bound abstraction complex) so that the recombination is efficient and yet are separated sufficiently to permit a small spin-orbit interaction to induce the required surface change. One way for this to happen is if the neutral abstraction fragments are from a large, easily polarizable molecule. Thus, spin considerations may require these details as part of the overall 'insertion' mechanism.

Experimental observations: the gas phase chemistry of M^+ vs MCO^+

The ion/molecule reaction products shown here for Co^+ have been observed for a number of other first row transition metal ions.²⁰

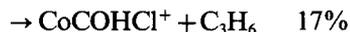


Reaction (6) is a halide abstraction, that is frequently observed when the ionization energy of the alkyl radical involved is sufficiently low. The products in (7) and (8) are proposed to be formed as follows:



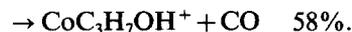
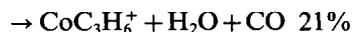
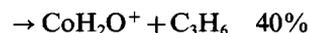
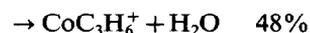
The metal ion first forms a complex with the polar neutral molecule. Following this, the metal inserts into the polar C—Cl bond. If the alkyl group is an ethyl group or larger, and possesses a H atom on a C atom that is β to the metal, this H will shift onto the metal, then onto the Cl. The result is that the metal has choreographed the degradation of propyl chloride to propene and HCl. These two ligands thus formed compete for a site on the metal²¹ and, as the distribution of products shows, the retention of propene is favoured [consistent with the observation that $P.A.(HCl) < P.A.(C_3H_6)$].

The two possible scenarios for insertion presented above would lead to different consequences in terms of the final products. If, on insertion, the overall spin of the system changes, the products may be formed in excited states. That is, products such as $CoC_3H_6^+$ may be singlets, although the ground state of this species (if electrostatically bound) would be a triplet. When a CO is attached to Co^+ , the following products are formed from iso-propyl chloride:



The same reaction occurs, with retention of propene favoured over that of HCl. While $CoCO^+$ does react with propyl chloride, $CoNO^+$ does not, suggesting that NO is covalently bonded to Co^+ .

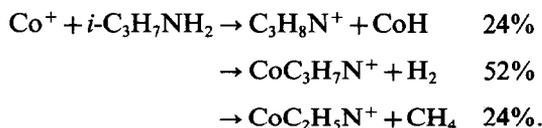
As a second example,²⁰ the reaction products of Co^+ and $CoCO^+$ with isopropanol are given below.



Again, both Co⁺ and CoCO⁺ induce the dehydration of propanol. In comparing the distribution of products from propanol and propyl chloride, retention of H₂O occurs more frequently than retention of HCl, with retention of propene favoured over both, consistent with the proton affinity ordering PA(C₃H₆) > PA(H₂O) > PA(HCl). It can be difficult to compare reaction products of M⁺ and MCO⁺ to determine if the chemistry of the metal changes due to the presence of the ligand because the ligand appears to reside on the metal as the reaction proceeds. Thus, when CoCO⁺ reacts with e.g. propanol, the complex that dissociates to give the observed products is Co⁺(CO)(H₂O)(C₃H₆). It is the relative metal-ligand binding energies that determine which of these ligands will be lost, and the distribution of products. This also suggests that the CoC₃H₇OH⁺ products in the CoCO⁺ reaction above exist, at least in part, as Co⁺(H₂O)(C₃H₆). Similar reactions are also observed in comparing the chemistry²⁰ of Fe⁺ with FeCO⁺, and the reactions of Ni⁺ with NiCO⁺. Thus, the Co appears to be a 'spectator' in such reactions. Its presence does not appear to alter the chemistry of the metal ion, consistent with the electrostatic bonding scheme suggested by the earlier experimental results and the *ab initio* calculations presented here.

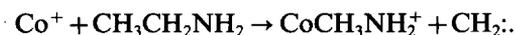
The reactions of M⁺ and MCO⁺ are not *always* the same. We have noted that the order in which metal insertion occurs into the various skeletal bonds of larger molecules such as octane appears to be different when a CO is attached to the metal.²² This may reflect a steric effect which affects the relative stabilities of the various M⁺(CO)(R₁)(R₂) insertion intermediates that may be formed upon insertion into various (R₁—R₂) skeletal bonds.

There are also cases reported in which the MCO⁺ group appears to insert into a bond, although these are not commonly evident. One system in which this was reported is in the reactions of Co⁺ with amines. While Co⁺ has been observed to insert into a variety of polar bonds¹ such as C—Cl, C—OH, C—SH, C—NO₂, etc., it does not appear to insert into the C—NH₂ bond of primary amines. Reaction products reflecting the insertion into C—C and C—H bonds are observed,²³ e.g.

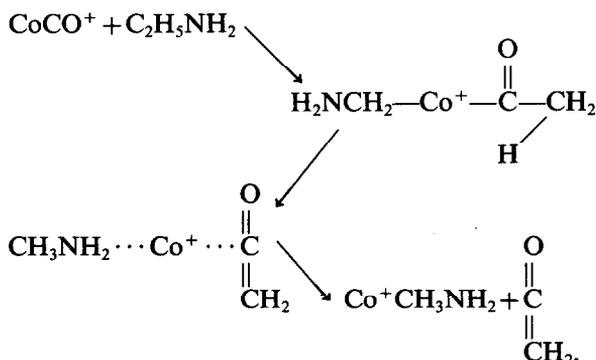


When a mixture of Co(CO)₃NO and a primary amine are subjected to EI, and the resulting ions allowed to react in an ICR experiment, one product that is frequently formed is CoCH₃NH₂⁺. This ion

is a reaction product of Co⁺, for amines larger than ethylamine, formed via insertion into the R—CH₂NH₂ bond. However, CoCH₃NH₂⁺ is also formed when the amine is ethylamine. If Co⁺ was the precursor, this would suggest an unusual reaction in which CH₂ would be lost:

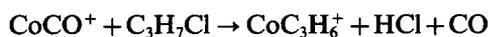


However, double resonance experiments²³ show that the ionic precursor is *not* Co⁺, but instead CoCO⁺, suggesting the following mechanistic sequence:



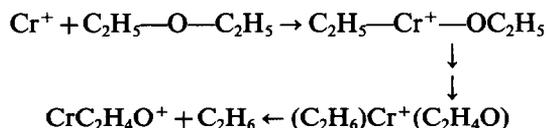
Thus, the Co⁺ and the CO appear to insert into the C—C bond, with the CH₃ group being bound to the CO, forming an acetyl-metal complex. These are now Hs that are β to the metal that can shift, resulting not in the loss of CH₂, but ketene.

Such reactions may be common, but difficult to detect. For example, in the reaction

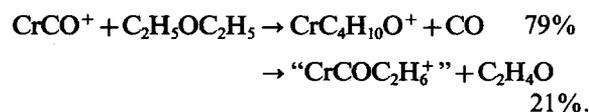


the neutral(s) lost may be HCOCl, formed by active participation of the CO, however this cannot be determined in these experiments.

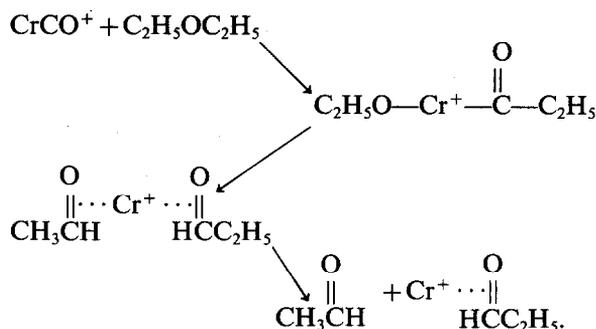
Another example of a reaction in which the CO is actively involved is in the chemistry of CrCO⁺ with diethyl ether.²⁴ Cr⁺ reacts by the insertion/H-shift/competitive ligand loss mechanism, inserting into a C—O bond:



This reaction is reasonable, since the poorer ligand, ethane, is lost exclusively, with the ligand retained being presumably acetaldehyde. However, when CrCO⁺ reacts, the observed products are

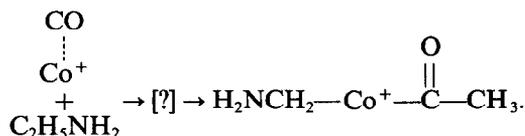


Loss of C_2H_4O would reflect *retention* of ethane over acetaldehyde when the CO is attached, which would violate the proton affinity rule. However, the reaction product could be explained by invoking insertion of the $CrCO^+$ moiety intact:

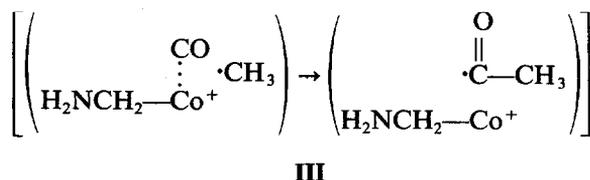


By this mechanism, acetaldehyde and propionaldehyde would be competing as ligands on Cr^+ , with the ligand characterized by the lower PA being lost. Therefore the " $Cr(CO)(C_2H_5)^+$ " ion should actually be a Cr^+ -propionaldehyde structure.

Thus, there are cases in which the CO is involved in the chemistry of the metal ion to which it is attached. The question arises as to how the apparent " MCO^+ " insertion occurs. Consider the reaction discussed above for $CoCO^+$ with ethylamine. How is the " MCO^+ " insertion intermediate formed?



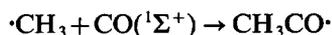
There are a number of possible mechanisms. Three are suggested by the structures shown here.



Intermediate I suggests the possibility of the direct interaction of the metal with one C and the CO with the second C of the C—C bond in a concerted

manner. Intermediate II suggests a scenario in which the metal first inserts into the C—C bond. The CH_3 and CO groups are next converted into a CH_3CO group. (It should be noted that reactions involving the process $R-M-CO \rightarrow M-C(O)-R$ have received considerable attention in the literature recently,²⁵ to determine whether this rearrangement is more accurately described as an R-migration to the CO, or as a CO insertion into the R—M bond.) In III, the mechanism discussed previously for the insertion process is utilized. The Co^+ forms a bond to the CH_2NH_2 fragment, and a loosely-bound electrostatic complex with the CH_3 fragment. The CH_3 then has the option of approaching the metal, or the CO, to form a bond. If the CH_3 attacks the CO, the resulting $CH_3CO\cdot$ radical can then bond to the metal.

These various mechanisms can be evaluated by considering information such as the energy that must be supplied to break the C—C bond and the Co^+-CO bond, and the energy released when the Co^+-C bonds and the CH_3-CO bond are formed. The C—C bond energy in ethylamine is 82 kcal mol⁻¹.⁸ The presence of the amino group weakens this bond slightly, when compared to a C—C bond energy of 87 kcal mol⁻¹ in ethane.⁸ The singlet-triplet spacing in CO ($X^1\Sigma^+ - a^3\Pi$) is large, 139 kcal mol⁻¹.²⁶ Based on the calculations presented here, we estimate the Co^+-CO bond energy to be approximately 10 kcal mol⁻¹. With these numbers, reaction via intermediate I would seem unlikely. If the CO remains a singlet, direct interaction with the methyl group could not occur, and the energy produced upon formation of the initial electrostatic complex would not be sufficient to induce conversion of the CO to a higher spin state. Intermediate II can be formed, i.e. Co^+ can insert into the C—C bond in an exothermic process. If the sum of the two Co^+-C bonds formed is approximately 100 kcal mol⁻¹, the insertion would be exothermic by 20 kcal mol⁻¹. It has been suggested that $(CO)Co^+CH_3$ is more stable than $CoC(O)CH_3^+$ by approximately 20 kcal mol⁻¹.²⁷ However, this was an estimate made using thermochemical approximations²⁷ such as: $D(RCo^+-CO) = 35$ kcal mol⁻¹; $D[Co^+-C(O)R] = 60$ kcal mol⁻¹; and $D(Co^+-CO) = D[(H_3C)Co^+-C(O)R] = 40$ kcal mol⁻¹. If, as suggested in this work, the Co^+-CO binding energy is considerably weaker than 40 kcal mol⁻¹, CH_3 'migration' onto the CO could occur exothermically. The mechanism suggested by III is attractive. The reaction



is *exothermic* by 21.4 kcal mol⁻¹.⁸ Thus, CH_3 can react with the CO, and the resulting radical can

bond to the metal ion. The mechanism for insertion proposed here would allow for ligands such as CO to become actively involved in the chemistry, even though the ligand itself is not 'activated' by the metal, but only electrostatically bound.

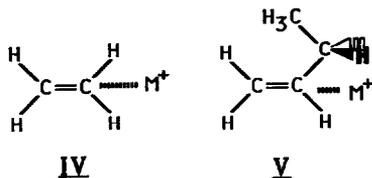
CONCLUSIONS

Theoretical attention to these ionic organometallic systems is allowing us to go back to early data of this area of research, and begin to understand in much greater detail how observed reactions occur. Thus, we are beginning to understand some of the relationships between electronic structure and reactivity for these gas phase systems.

The possibility that $M^+—CO$ bonding is dominated by an electrostatic, rather than the traditional Dewar–Chatt scheme may explain why attempts to model systems such as the water–gas shift reaction via gas phase ionic studies have not been successful,²⁸ since the CO is not 'activated' by the metal ion.

The system discussed here shows that the opportunity to form a dative bond is overshadowed by electrostatic interactions at these M^+ –ligand separations for first row transition metal ions. One may expect other ligands such as water, ammonia, polar organic compounds, etc. to be bound in this way as well. The strength of the metal–ligand interaction would then be reflected in the ligand's multipole moments and polarizability.

There could be some interesting geometrical implications that result from an electrostatic bonding description. For example, suppose that olefins are only bound electrostatically to univalent transition metal ions in the gas phase. Since the $C=C$ double bond in, e.g. ethylene, appears to be more polarizable along the bond axis, than perpendicular to the axis,²⁹ an electrostatic M^+ –(ethylene) complex may take the geometry shown in IV. For a M^+ –(1-butene) complex, consideration of interactions of the M^+ with not only the polarizable double bond, but the polarizable ethyl group, leads one to envisage the geometry as shown in V.



It is interesting to note that M^+ –olefin reactions frequently proceed via M^+ insertion into the allyl $C—H$ bond;³⁰ the description in V places the M^+ in close proximity to this bond.

The exception to this bonding scheme would be, of course, ligands such as NO that could form covalent bonds. Publications which follow from this group will focus on those ligands/fragments that have the option of bonding as CO (i.e. approaching M^+ with its lone pair), or bonding through a single electron (covalently), or through bonding schemes in which three electrons on the ligand are involved. These ligands include NO, Cl, OH and NH_2 .

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