Bond Strengths in First-Row-Metal Carbonyl Anions

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Abstract: Energy-resolved collision-induced dissociation of metal carbonyl anions $M(CO)_n^-$ (M = V, Cr, Mn, and Co) is used to determine sequential metal–carbonyl bond energies. The derived thermochemistry can be used in conjunction with literature measurements of neutral chromium carbonyl electron affinities to provide $(CO)_nCr–CO$ bond strengths, which are compared to previous experimental determinations. Literature observations of ligand exchange reactions are used to derive other metal–ligand bond strengths. Analysis of the present data and previous values for the iron and nickel carbonyl anions shows that most metal–carbonyl ligand bond strengths are *ca.* 40 kcal/mol, which is apparently the intrinsic metal–carbonyl bond strength in anions. Several of the values for $D[M^-–2CO]$ are significantly lower than average; these bond strengths correlate with the energy needed to promote the metal anion into a state suitable for bonding. The electronic promotion is apparently complete after the addition of two carbonyl ligands. Comparisons of isoelectronic species confirm the general order of metal–carbonyl bond strengths, anion ≥ neutral ≥ cation.

Introduction

The sequence of bond dissociation energies involved in the hypothetical stepwise decomposition of a molecule into its constituent parts can provide important insights into the interplay of electronic structure and thermochemistry. However, complete sets of accurate sequential bond energies are known for only the simplest (one and two carbon) organic compounds[1,2] and for only a handful of inorganic species such as homoleptic hydrides, halides, and metal oxides.[1] Consequently, our intuition about bond energy trends in polyatomic molecules is largely guided by the more easily determined and more commonly known *average* bond strengths. For coordinatively saturated transition metal carbonyl complexes, the average M–CO bond strengths have been known for some time from calorimetric measurements, and numerous accounts of the periodic trends in these properties have appeared.[3-5] However, measurements of individual bond strengths in metal carbonyls indicate that they often vary greatly from the average,[6-12] calling into question the significance of the average values. For example, from the well-known gas-phase heats of formation of $Fe(CO)_5$, Fe, and CO, the average Fe–CO bond strength is determined to be 28 kcal/mol. In contrast, the first Fe–CO bond strength, $D[(CO)_4Fe–CO]$, is 41 kcal/mol,[6] and the last, $D[Fe–CO]$, is only 10 kcal/mol,[12,13] quite different values from the average.

We recently described measurements of collision-induced dissociation (CID) threshold energies for $Fe(CO)_n^-$ and $Ni(CO)_n^-$ ions using a flowing afterglow–triple quadrupole apparatus and the use of the data in deriving sequential M–CO bond strengths for these anions and the corresponding neutrals.[12] In this study, we present our measurements of the bond strengths in $V(CO)_n^-$, $Cr(CO)_n^-$, $Mn(CO)_5^-$, and $Co(CO)_n^-$ ($n \geq 3$). Along with the previous data for iron and nickel, these data provide a relatively complete and precise set of M–CO bond strengths for the first transition series metal carbonyl anions. Comparisons with currently available measurements and theoretical predictions of the sequential and average bond strengths in the anionic metal carbonyls are also made, and the trends in the data are examined.

A brief survey of experimental methods used to determine metal–carbonyl bond strengths was given in a previous paper,[12] along with a discussion of the available information from experiment and theory for the iron and nickel carbonyls. Remarkably little thermochemical information is available for the carbonyl anions of V, Cr, Mn, and Co. $D[(CO)_5V^-–CO]$ has been calculated to be 40.3 kcal/mol by density functional theory.[14] For the $Cr(CO)_n^-$ ions, a relatively complete set of appearance energies from electron impact on $Cr(CO)_6$ has been measured.[15] $D[(CO)_4Cr^-–CO] = 44.7 \pm 3.5$ kcal/mol has been determined through measurement of the threshold for CID in an ion cyclotron resonance (ICR) mass spectrometer.[16] Although photodissociation cross sections for some metal carbonyl anions have been obtained, the observed onsets are considered to correspond to absorption profiles rather than thermodynamic thresholds for dissociation[17] and therefore do not yield reliable M–CO bond strengths. Thus, with the exception of the chromium carbonyls, there are no previous experimental measurements for the metal–carbonyl bond strengths given in this paper.

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Experimental Section

All experiments were performed with a flowing afterglow–triple quadrupole apparatus described previously.[18] The operating conditions in the 7.3 cm i.d. × 100 cm flow tube were $P = 0.40$ Torr, flow(He) = 190 STP cm^3/s, and $T = 298$ K. The reactant metal carbonyl anions were formed by dissociative ionization of $V(CO)_6$, $Cr(CO)_6$, $Mn_2(CO)_{10}$, or $Co_2(CO)_8$ using an electron impact (EI) source or a DC discharge source.[12] Pure He buffer gas is used with the EI source and a *ca.* 5:1 He:Ar mixture with the DC discharge source. Ions are thermalized by *ca.* 10^5 collisions with the bath gas. For the metals discussed in this paper, it was possible to form sufficient amounts of $M(CO)_n^-$ ions with $n \geq 4$ to measure thresholds for loss of one or two carbonyl ligands. For $M(CO)_3^-$ ions, it was possible to form sufficient quantities of ions to measure thresholds only for loss of one carbonyl ligand; insufficient quantities of $M(CO)_2^-$ and $M(CO)^-$ ions were generated to perform any CID threshold measurements.

Ions in the flow tube are gently extracted through a 1-mm orifice into a region of differential pumping and then focused into an EXTREL triple quadrupole mass analyzer. The desired reactant ion is selected with the first quadrupole and injected into the rf-only, gas-tight central quadrupole (Q2) with an axial kinetic energy determined by the Q2 rod offset voltage. Argon is maintained in Q2 at a pressure of ≤0.04 mTorr. Use of Ar as the CID target gas for metal carbonyl anions has been tested previously.[12] Fragment ions resulting from single or multiple ligand loss upon collision with Ar are efficiently contained in Q2 and extracted by a low-voltage exit lens into the third quadrupole, which is maintained at a constant attractive voltage (5–10 V) with respect to the variable Q2 rod voltage. Ion detection is carried out with a conversion dynode and an electron multiplier operating in pulse-counting mode.

Detailed accounts of the data collection procedures and analysis method for CID threshold energy measurements have been provided recently.[12,19] Briefly, the axial kinetic energy of the mass-selected reactant ion is scanned while monitoring the intensity of the CID fragment ion formed in Q2 under single-collision conditions. The center-of-mass (CM) collision energy E_{CM} for the system is given by $E_{CM} = E_{lab}[m/(M + m)]$, where E_{lab} is the nominal lab energy and M and m represent the masses of the reactant ion and neutral target, respectively. The energy axis origin is verified by retarding potential analysis, and the reactant ion kinetic energy distribution is found to have a near-Gaussian shape with a full width at half-maximum (fwhm) of 0.5–2 eV (lab). An uncertainty of ±0.15 eV in the lab frame energy scale is included in the uncertainty of the derived thresholds.

The neutral target gas pressure in Q2 (≤0.04 mTorr) is low enough to ensure predominantly single-collision conditions. Under these conditions, less than *ca.* 4% of ions react. Absolute cross sections (σ_p) are calculated by use of $\sigma_p = I_p/INl$, where I_p and I are the measured intensities for the product and reactant ion beams, respectively, N is the number density of the neutral target, and l is the effective path length for reaction (24 ± 4 cm).[12]

Phase incoherence between the quadrupoles of the triple quadrupole mass analyzer causes oscillations in the apparent intensity of the reactant ion, but not the CID product ions, as the Q2 pole offset voltage is scanned.[20] For this reason, the intensity of the reactant ion beam is estimated to be equal to the maximum transmitted intensity in the region of the thresholds for dissociation. The absolute cross sections may also be in error because of different collection or detection efficiencies for the reactant and product ions. These two factors lead to inaccuracies in the absolute cross sections, which have an estimated uncertainty of a factor of 2. Relative cross sections should be more reliable (*ca.* ±50%).

Reagents were obtained from commercial sources: $V(CO)_6$, $Cr(CO)_6$, and $Co_2(CO)_8$ (all 98%) from Alfa, and $Mn_2(CO)_{10}$ from Pressure Chemical.

CID Threshold Measurement and Analysis. In our previous study of the energy-resolved CID of iron and nickel carbonyl anions, it was assumed that the measured dissociation thresholds were equivalent to the bond dissociation energies at the ambient temperature of 298 K. A more complete analysis of the reaction thresholds would include the internal energy of the reactants and would account for the possibility of "kinetic shifts" in the apparent thresholds, which occur if some ions with sufficient energy to dissociate have such long lifetimes that they fail to decompose within the experimental time window.[21] These factors can be significant, particularly for the larger metal carbonyls studied in this work. In the following analyses, the data are first fit in the manner previously described, where internal energy effects and kinetic shifts are neglected. The more complete analysis is then carried out to derive the final thermochemistry.

In the simplest form of the CID threshold analysis, the activation energy for the dissociation is derived from the ion appearance curve by means of a fitting procedure based on the assumed model function given by eq 1a,[12,19,22-24] where $I(E)$ is the intensity of the product ion signal at center-of-mass collision energy E, E_T is the desired threshold energy, I_0 is a scaling factor, and n is an adjustable parameter. Optimization is

$$I(E) = I_0[(E - E_T)^n/E] \tag{1a}$$

carried out by an iterative procedure in which n, I_0, and E_T are varied so as to minimize the deviations between the calculated trial function and the experimental appearance curve in the steeply rising portion of the threshold region. The region very near and below the threshold is not usually fit because of tailing in the data that is attributed to translational excitation of the ions in the first quadrupole or to internal excitation due to collisions outside the interaction region. This limitation on the fitting range significantly contributes to the relative uncertainty of the derived thresholds.

Convoluted into the fit are the reactant ion kinetic energy distribution approximated by a Gaussian function with a 2-eV (lab) fwhm, and a Doppler broadening function developed by Chantry to account for the random thermal motion of the neutral target.[25] The fits of the steeply rising portion of the data are insensitive to the assigned width of the ion beam energy distribution, and this does not contribute significantly to the final uncertainty (typically ≤0.03 eV). Bond strengths derived in this manner are assumed to correspond to 298 K reactants and products. In order to convert E_T to a bond dissociation enthalpy term for use in deriving heats of formation, an expansion work factor ΔnRT is added, where Δn is the change in the number of molecules for the reaction (at 298 K, RT = 0.6 kcal/mol).

Kinetic Shifts and Internal Energy. A more complete model of the reaction threshold including reactant internal energy and kinetic shifts has been derived recently[11] and is given in eq 1b, where i denotes vibrational

$$I(E) = I_0\sum_i [g_i P_D(E,E_i,\tau)(E + E_i - E_T)^n/E] \tag{1b}$$

states having energy E_i and population g_i ($\sum g_i = 1$), and P_D is the probability that metastable ions formed at particular values of E and E_i will in fact dissociate within the time τ, the average time between excitation in the second quadrupole and mass analysis in the third quadrupole (*ca.* 30 μs). This probability can be determined by performing RRKM calculations[21] of the decay rate as a function of reactant internal energy.[26-29] These calculations require several assumptions concerning the reaction. In the present calculations, the well-known vibrational frequencies of $Cr(CO)_6$,[30] $Fe(CO)_5$,[31] and $Ni(CO)_4$[31] are used as models

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Table I. Optimized Fitting Parameters for the CID Reaction $M(CO)_x^- \rightarrow M(CO)_y^- + (x - y)CO$

reaction	M	x	y	$E_T{}^a$ (eV)	$E_T{}^b$ (eV)	n^a	σ_{max}
2a	V	6	5	1.47 ± 0.16	1.32 ± 0.15	1.77 ± 0.07	19
2b	V	6	4	2.75 ± 0.15		1.74 ± 0.15	9.3
3a	V	5	4	1.31 ± 0.09	1.29 ± 0.11	1.66 ± 0.11	14
3b	V	5	3	3.31 ± 0.13		1.66 ± 0.10	4.1
4a	V	4	3	1.59 ± 0.10	1.53 ± 0.12	1.77 ± 0.14	9.5
4b	V	4	2	3.55 ± 0.09		1.76 ± 0.12	2.9
5	V	3	2	1.55 ± 0.16	1.53 ± 0.19	1.72 ± 0.17	6.4
6a	Cr	5	4	1.88 ± 0.11	1.70 ± 0.15	1.56 ± 0.11	19
6b	Cr	5	3	3.72 ± 0.16		1.59 ± 0.19	4.4
7a	Cr	4	3	1.84 ± 0.14	1.70 ± 0.17	1.70 ± 0.20	12
7b	Cr	4	2	3.85 ± 0.14		1.45 ± 0.22	3.4
8	Cr	3	2	1.94 ± 0.12	1.88 ± 0.17	1.70 ± 0.17	6.1
9a	Mn	5	4	2.00 ± 0.09	1.70 ± 0.17	1.70 ± 0.19	16
9b	Mn	5	3	3.76 ± 0.13		1.84 ± 0.10	1.9
10a	Mn	4	3	1.86 ± 0.14	1.76 ± 0.13	1.79 ± 0.11	8.8
10b	Mn	4	2	3.12 ± 0.13		1.63 ± 0.07	5.9
11	Mn	3	2	1.18 ± 0.08	1.21 ± 0.09	1.79 ± 0.10	15
12a	Co	4	3	1.74 ± 0.13	1.70 ± 0.16	1.73 ± 0.12	12
12b	Co	4	2				1.5
13	Co	3	2	1.66 ± 0.15	1.63 ± 0.17	1.75 ± 0.14	8.3

[a] Derived using eq 1a. [b] Derived using eq 1b.

for the frequencies in the hexa-, penta-, and tetracarbonyl anions. For the tricarbonyl anions, two of the MCO bending frequencies, two of the CMC bending frequencies, one of the M–CO stretching frequencies, and one of the CO stretching frequencies are removed from the set for $Ni(CO)_4$. The RRKM results are not very sensitive to the details of these frequency assignments.[11] One of the M–CO stretch frequencies is taken to be the reaction coordinate.

A more critical decision involves the assignment of frequencies for the dissociation transition state. Most of the frequencies should be nearly the same as those of the reactant ion. However, two of the MCO bending modes in the reactant eventually become CO rotations in the separated products, and two of the CMC bending modes become translational degrees of freedom. It is likely that some or all of these frequencies are considerably lower in the transition state than in the excited parent ion. Lower frequencies in the transition state lead to a higher density of states and thus a higher decomposition rate. For the present work, it is assumed that the four frequencies identified above are reduced by a factor of 2 in the transition state compared to those in the reactant ion. The relative loosening of the transition state adopted here is similar to past assumptions used in RRKM calculations for the dissociation of neutral metal carbonyls[6,8,37,69] and chromium carbonyl cations,[11] although Dearden *et. al.*[29] assumed a somewhat tighter transition state for dissociation of manganese carbonyl cations. The resulting uncertainty in the threshold analysis is estimated by calculating the onsets assuming that the four frequencies are not lowered at all, or that they are all lowered by a factor of 4. Although this covers the range of values that we feel are most reasonable, it is conceivable that the transition-state frequencies are in fact lower by more than a factor of 4, which would result in the reported bond strengths being too low. Dearden *et al.* used a similar range in the transition-state parameters to derive error limits in their calculations.[29] The uncertainty is included with the imprecision of the energy scale and the standard deviation of the thresholds to derive the final error limits for the bond strengths obtained using eq 1b. For the larger metal carbonyls examined in this study, the uncertainty due to the unknown RRKM parameters is as important as the imprecision in the measured thresholds, but for smaller systems, the RRKM uncertainty is relatively minor. A minimum uncertainty of ±3 kcal/mol is given to all final bond strengths.

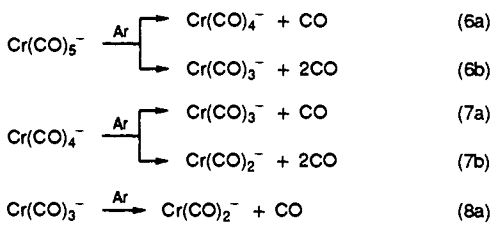
The rotational energy content of the reactant is assumed to be conserved on average during the collision with the target gas. Rotational energy of an activated complex is generally not available to drive the dissociation reaction, but rather must be approximately conserved in order to conserve angular momentum. Thus, no corrections to the derived thresholds are made for rotational energy effects.

Since internal energy is explicitly taken into account in this method of threshold determination, bond strengths derived in this manner correspond to 0 K reactants and products. Adjustments to 298 K values[1] can be made using the heat capacities of CO and the metal carbonyls, along with the vibrational energy content of the metal carbonyls calculated using the estimated vibrational frequencies.

Results

Energy-resolved collision-induced dissociation is, in principle, well suited for determining sequential M–CO bond energies in metal carbonyl ions. A large variety of different metal carbonyl anions can be made by (usually dissociative) electron capture by stable, volatile metal carbonyl precursors. The simple elemental compositions of mononuclear metal carbonyl anions make selection of the desired reactant ion unambiguous, and all ions of this type examined to date undergo low-energy (<50 eV, lab) CID exclusively by loss of one or more CO ligands. The reactions examined in this work are examined in Table I. Losses of one and two carbonyl ligands are always the dominant processes observed in the energy range covered, *ca.* 0–8 eV, although small amounts of further CO loss are observed at sufficiently high energies. In this section we first present the appearance curves for CID of the chromium carbonyl anions to illustrate the measurements. The analysis of the CID thresholds is discussed, and metal–carbonyl bond strengths are then derived from these results.

The main products observed from CID of $Cr(CO)_n^-$ with argon correspond to loss of one or two carbonyl ligands, reactions 6–8. The appearance curves for reactions 6, 7, and 8 are shown in Figures 1, 2, and 3, respectively. CID threshold plots for $V(CO)_n^-$ (n = 6, 5, 4, and 3), $Mn(CO)_n^-$ (n = 5, 4, and 3), and $Co(CO)_n^-$ (n = 4 and 3) are similar in appearance and are available as supplemental material.



The respective maximum cross sections for reactions 2–13 in the 0–8 eV energy range are included in Table I. The maximum total cross sections for all of the reactions examined in this work are in the range 6–28 Å². For comparison, maximum total cross sections for the corresponding $Fe(CO)_n^-$ and $Ni(CO)_n^-$ ions are 4–17 Å²,[12] and total cross sections for CID of $Fe(CO)_n^+$ (n =

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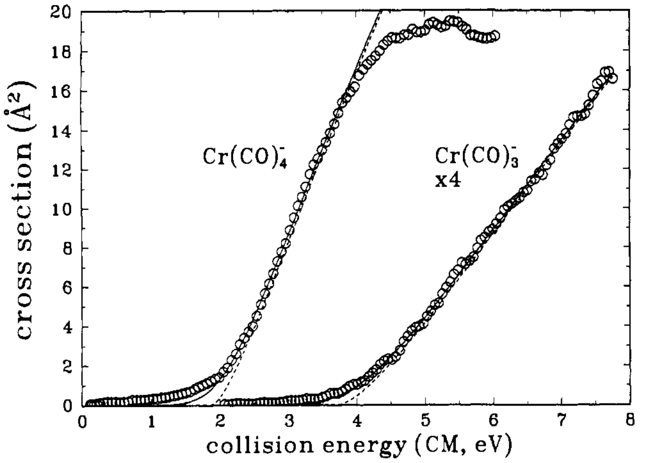

Figure 1. Appearance curves for products from CID of $Cr(CO)_5^-$ as a function of kinetic energy. The solid lines are model appearance curves calculated using eq 1a and convoluted as discussed in the text, and the dashed lines are unconvoluted fits. The eq 1a parameters are $n = 1.56$, $E_T = 1.88$ eV for $Cr(CO)_4^-$ and $n = 1.59$, $E_T = 3.72$ eV for $Cr(CO)_3^-$.

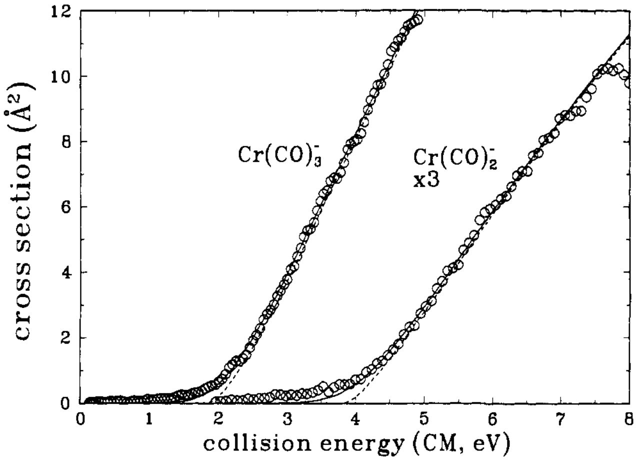

Figure 2. Appearance curves for products from CID of $Cr(CO)_4^-$ as a function of kinetic energy. The solid lines are model appearance curves calculated using eq 1a and convoluted as discussed in the text, and the dashed lines are unconvoluted fits. The eq 1a parameters are $n = 1.70$, $E_T = 1.84$ eV for $Cr(CO)_3^-$ and $n = 1.45$, $E_T = 3.85$ eV for $Cr(CO)_2^-$.

2–4) with Xe are in the 13–35-Å^2 range. The CID cross sections listed in Table I indicate that loss of two carbonyl ligands is a factor of 2–8 less efficient than loss of one carbonyl ligand for all systems where multiple ligand dissociation cross sections were determined. Similar effects are also generally evident in the CID results for $Fe(CO)_n^-$, $Ni(CO)_n^-$,[12] and $Fe(CO)_n^+$.[10] Equal or greater falloffs are apparent in the electron impact AE measurements for the iron and nickel carbonyl anions.[32]

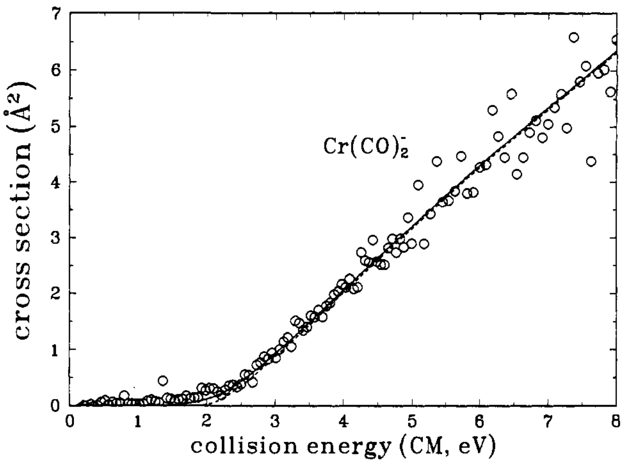

Figure 3. Appearance curve for CID of $Cr(CO)_3^-$ to form $Cr(CO)_2^-$ as a function of kinetic energy. The solid line is a model appearance curve calculated using eq 1a and convoluted as discussed in the text, and the dashed line is the unconvoluted fit. The eq 1a parameters are $n = 1.70$, $E_T = 1.94$ eV.

Table II. Metal–Carbonyl Bond Strengths (298 K)

bond	bond strength (kcal/mol) lit.	bond strength (kcal/mol) this work
$(CO)_5V^-$–CO	40.3[a]	30.8 ± 3.5
$(CO)_4V^-$–CO		31.1 ± 3.0
$(CO)_3V^-$–CO		40.4 ± 5.8
$(CO)_2V^-$–CO		35.8 ± 4.4
$(CO)_4Cr^-$–CO	≥12[b], 44.7 ± 3.5[c]	40.6 ± 3.5
$(CO)_3Cr^-$–CO	55[b]	39.7 ± 3.9
$(CO)_2Cr^-$–CO	35[b]	43.9 ± 3.9
$(CO)Cr^-$–CO	35[b]	
Cr^-–CO	20[b]	
$(CO)_4Mn^-$–CO		40.6 ± 3.9
$(CO)_3Mn^-$–CO		41.1 ± 3.0
$(CO)_2Mn^-$–CO		28.4 ± 3.0
$(CO)_3Co^-$–CO		39.7 ± 3.7
$(CO)_2Co^-$–CO		38.1 ± 3.9

[a] Reference 14. [b] Reference 15. [c] Reference 16.

CID Threshold and Bond Strength Determinations. The optimized fitting parameters using both eq 1a and eq 1b are listed in Table I, and a sample of the corresponding fits using eq 1a are shown in Figures 1–3. Fits using eq 1b are always essentially identical in appearance. The error limits listed are standard deviations for the parameters optimized for the individual data sets. Optimized fits for the reactions studied have average values of *n* ranging from 1.45 to 1.84, and the *n* value for any given data set is typically 0.01 lower when using eq 1b than when using eq 1a. Similar parameters were obtained for CID of the iron and nickel carbonyls.[12] This is consistent with the usual CID mechanism[33] wherein collision of the ion with the neutral target results in efficient conversion of kinetic energy into internal energy in the anion. If sufficient energy is deposited, then dissociation occurs. Since the energy deposition should be relatively insensitive to the exact nature of the carbonyl complex, it is not surprising that the appearance curves display similar functional forms.

The average vibrational energy of the metal carbonyls varies from 4.3 kcal/mol for the tricarbonyl anions to 7.3 kcal/mol for $V(CO)_6^-$. This internal energy lowers the observed dissociation thresholds. The magnitude of the kinetic shift rises rapidly with increasing threshold energy and with increasing size of the reactant ion.[34] The calculated kinetic shifts raise the observed thresholds by amounts ranging from 3.7 to 10.7 kcal/mol for the largest system, $V(CO)_6^-$. Thus, the internal energy effects and the kinetic shifts both increase with molecular size, but they work in opposite directions. Overall, the inclusion of internal energy and RRKM effects changes the calculated thresholds by amounts ranging from +1.2 to −3.4 kcal/mol after correcting the values derived with eq 1b to 298 K. The bond energies derived from these thresholds are given in Table II.

In our previous work on the iron and nickel carbonyl anions, it was assumed that the reaction products are formed at the same temperature as the reactants.[12] This is essentially the same as assuming that the kinetic shift exactly cancels the internal energy effect.[35] For the smaller metal carbonyls studied previously, this approximation gives the same results as the present analysis to within 2 kcal/mol. Therefore, we do not reanalyze the iron and nickel data with the more complete model.

Finally, the analysis assumes that the dissociations occur at the statistical rate. This has been found to be true for neutral metal carbonyls if spin multiplicity is conserved in the reaction.[6,8,36,37] In the Discussion section we identify those systems in which dissociation is likely to be accompanied by a spin multiplicity change between the products and reactants and estimate the effect that spin conservation may have on the derived thermochemistry.

Multiple CO Loss. Threshold measurements for the loss of one carbonyl ligand give the most reliable results because of the larger cross sections and because competing reactions that might affect the measured thresholds are minimized. Appearance curves for loss of more than two ligands are generally characterized by a low signal-to-noise ratio and a slow rise from base line, making threshold analysis difficult. Furthermore, measured thresholds for loss of more than two ligands may be affected by competing electron detachment,[12,38] as discussed below. However, the thresholds for loss of two ligands can be used as a check on the derived thermochemical information. Ideally, internal energy effects and lifetime effects should be included in this analysis. Although the internal energy effects can be handled in the same manner as for loss of one ligand, correctly accounting for the energy disposal in multiple dissociations is problematic.[29] If the metal carbonyl ions examined in these experiments have sufficient energy to lose two ligands, then the first ligand loss will be rapid compared to the instrumental time scale. Therefore, the kinetic shift for loss of two carbonyl ligands from $M(CO)_n^-$ should be similar to that for loss of one carbonyl ligand from $M(CO)_{n-1}^-$. Unfortunately, the first carbonyl ligand lost can carry away an unknown but possibly large amount of energy, leaving an unknown amount of excess internal energy to fuel the second ligand loss. Therefore, the results from analysis of the double ligand loss channels using eq 1b are not of sufficient reliability to be included in the derived thermochemistry, although the errors should not be too large. Thus, in the following section the thresholds for loss of two ligands are determined using eq 1a and are used only as a check on the derived bond strengths.

In five out of the eight cases where loss of two ligands was studied, the thresholds derived are in very good agreement with the sums of the thresholds for single ligand loss. For example, the threshold for reaction 2b, 2.75 ± 0.15 eV, is quite close to the sum of the thresholds for reactions 2a and 3a, 2.78 ± 0.18 eV. The appearance curve for reaction 12b is consistent with the sum of the two single CO loss thresholds, reactions 12a and 13, but the data cannot be analyzed with sufficient precision to be useful. A notable deviation from additivity is the threshold for reaction 3b, 3.31 ± 0.13 eV, which is higher by 0.41 ± 0.18 eV than the sum of the thresholds for reactions 3a and 4a, 2.90 ± 0.13 eV. Similarly, the threshold for reaction 4b, 3.55 ± 0.09 eV, is higher by 0.41 ± 0.21 eV than the sum of the thresholds for reactions 4a and 5, 3.14 ± 0.19 eV. These results suggest that the measured threshold for reaction 4a is too low by *ca.* 0.4 eV. In order to accommodate this discrepancy, the value for $D[(CO)_3V^-{-}CO]$ derived above using eq 1b is raised by 0.2 eV, and the uncertainty is increased to 0.25 eV.

Discussion

In this section we first consider three possible sources of experimental error: electron detachment upon collisional activation of the reactant metal carbonyl ion, diabatic dissociation to form excited-state products, and kinetic shifts in the observed reaction onsets. We then compare the bond energies derived in this work to previous determinations in the literature and use the recently measured electron affinities for $Cr(CO)_n$ fragments to derive neutral $Cr(CO)_n$ bond strengths. The homologous and periodic trends in metal carbonyl anion bond strengths are described, and comparisons are made with isoelectronic[39] neutral and cationic metal carbonyls. Finally, thermochemistry for other metal–ligand bonds are inferred from the present results.

Table III. Literature Thermochemistry

species	ΔH_f (kcal/mol)[a]	EA (eV)
CO	−26.42	
$V(CO)_6$	−204 ± 7	≥0.53 ± 0.01[g]; 2.4[h]
V	123.2 ± 2[b]	0.53 ± 0.01[i]
$Cr(CO)_6$	−217.1 ± 0.5[c]	
$Cr(CO)_5$	−153.9 ± 2.1[d]	>2.3[g]
$Cr(CO)_4$		≈1.9[j]
$Cr(CO)_3$		1.349 ± 0.006[k]
$Cr(CO)_2$		≤0.96[l]
Cr	95.0 ± 1.0[b]	0.675 ± 0.004[k]
$Mn(CO)_5$	−170.4 ± 2.6[e]	2.43 ± 0.21[m]
Mn	67.7 ± 1.0[b]	≤0[i]
$Fe(CO)_4$	−104.5 ± 2.8[f]	2.4 ± 0.3[n]
Fe	99.0 ± 0.2[b]	0.151 ± 0.003[i]
$Co(CO)_4$	−134.1 ± 2.9[c]	≥2.35[e]
Co	102.0 ± 1.0[b]	0.66 ± 0.01[i]
$Ni(CO)_3$	−94.5 ± 1.1[f]	1.077 ± 0.013[o]
Ni	102.7 ± 0.7[b]	1.157 ± 0.010[i]
H_2S	−4.9 ± 0.2	
S	66.2 ± 0.1	

[a] Data from ref 1 unless otherwise noted. Heats of formation are in the gas phase at 298 K. [b] Reference 31. [c] Reference 3. [d] Calculated using $DH[(CO)_5Cr{-}CO]$ = 36.8 ± 2 kcal/mol from ref 6. [e] Reference 71. [f] Derived in ref 12. [g] Reference 41. [h] Estimated; see text. [i] Reference 42. [j] Lineberger, W. C. Reported at the NSF Workshop on Gas Phase Ion Chemistry, Boulder, CO, 1985. [k] Reference 65. [l] Reference 66. [m] Reference 70. [n] Reference 61. [o] Reference 58.

Electron Detachment. A potential difficulty in the analysis of CID thresholds with negative ions is the possibility that electron detachment might compete effectively with dissociation. This could cause a competitive shift[40] in the derived CID thresholds by suppressing the cross sections for CO loss. This possibility has been discussed previously for the case of iron and nickel carbonyl anions.[12] Wysocki *et al.* have previously noted that CID of $Cr(CO)_5^-$ and $Fe(CO)_4^-$ results in lower yields for loss of more than two CO ligands compared to CID of the corresponding cations.[38] This suggests that significant electron detachment can occur at energies near the threshold for loss of *three* carbonyl ligands from these ions, but generally does not affect the cross sections (and therefore the threshold determinations) for the first one or two carbonyl losses. Collisional activation experiments under multiple-collision conditions in an FTICR apparatus with various metal carbonyl anions, including $M(CO)_5^-$ (M = V, Cr, and Mn) and $M(CO)_4^-$ (M = Fe and Co), also suggest that electron detachment does not compete with dissociation until enough energy is deposited in the metal carbonyl to dissociate multiple ligands.[41]

The one probable exception to this behavior is the loss of two carbonyls from $Fe(CO)_2^-$ to form Fe^-, a reaction that has an unusually low cross section.[12] Fe has a low electron affinity (EA) of only 0.15 eV, so loss of an electron from Fe competes more effectively than that for species with higher electron affinities.[42] Even in this case, the measured reaction threshold is not apparently affected by competition from electron detachment.[12] The CID reactions discussed in this paper involve the formation of fragment ions with at least two carbonyl ligands. The thermochemical data in Table III and ref 12 suggest that none of the $M(CO)_n^-$ ($n \geq 2$) ions formed as products in this work have very low electron binding energies. We therefore believe that the dissociation thresholds measured in this work are unaffected by electron detachment.

Dissociation Barriers. The usefulness of a measured M–CO dissociation threshold depends on whether it corresponds to the true thermochemical bond energy or to a dissociation barrier, *i.e.*, whether the dissociation has a reverse activation energy. The

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(39) In this work, "isoelectronic" denotes "having the same number of valence electrons and ligands, but not necessarily the same electronic state".

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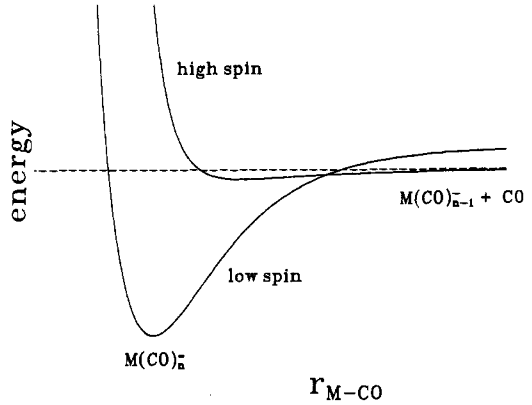

Figure 4. Potential energy surface illustrating possible interaction between an attractive (low-spin) surface and a primarily repulsive (high-spin) surface with an ion-induced dipole attraction at large radii.

two plausible causes for a barrier to dissociation are geometric reorganization and changes in electron configuration between ground-state reactants and products. The discussion below of the preferred structures of the metal carbonyl fragments examined in this work suggests that the geometric reorganization accompanying loss of a carbonyl ligand is relatively minor. Since the bending potentials in metal carbonyl complexes are generally quite flat,[43-45] any structural rearrangements accompanying CO dissociation are unlikely to lead to a substantial barrier. Moreover, for ion dissociations, the relatively long-range ion-induced dipole attraction can dominate repulsive interactions along the dissociation pathway.[46]

Since orbital occupation is not conserved in these systems, the only component of the change in electron configuration that might lead to a barrier is the spin multiplicity. For example, the ground-state reactants and products could have different spin multiplicities, as shown in Figure 4. An "excess" dissociation barrier could occur if the crossing between the potential energy surfaces for the two spin states was higher in energy than the ground-state products. There are several examples where this is known not to be the case. Although the spin-forbidden addition of CO to triplet $Fe(CO)_4$ is nearly 3 orders of magnitude slower than the allowed addition of CO to $Fe(CO)_2$ and $Fe(CO)_3$,[47] the activation energy for the reverse reaction is apparently ≤ 2.5 kcal/mol,[47] and Daniel *et al.* calculate that the singlet–triplet crossing is "allowed with a very low barrier"[48] when spin–orbit coupling is included. Addition of CO to $Mn(CO)_4^-$ (which is presumed to have a triplet ground state)[49,50] to form singlet $Mn(CO)_5^-$ is a factor of 69 less efficient than the apparently spin-allowed reaction of CO with $Fe(CO)_3^-$.[49] This is consistent with either a small barrier of *ca.* 2.5 kcal/mol or (more likely) a kinetic bottleneck due to the spin change.[49] The measured rates of $^{13}CO/^{12}CO$ exchange by $Mn(CO)_n^+$ (n = 1–5) ions in an FTICR indicate that each exchange proceeds efficiently.[29] Kinetic energy release measurements for metastable dissociations of these ions also show that there is no excess energy barrier for CO loss for n = 2–6, even though these dissociations almost certainly involve at least two changes in spin multiplicity.[29] Thus, carbonyl addition reactions can occur with $Mn(CO)_n^+$ ions without a barrier despite changes in multiplicity.

Rapid addition of CO to a metal carbonyl anion indicates that there is no significant barrier to addition and therefore no barrier in excess of the endothermicity to ligand loss. McDonald *et al.* have observed that CO adds rapidly to $V(CO)_{4,5}^-$,[51] $Cr(CO)_{3,4}^-$,[51] $Mn(CO)_3^-$,[49] and $Fe(CO)_{2,3}^-$ [51,52] in a flowing afterglow apparatus. This indicates that there are no barriers to dissociation in excess of the endothermicity for $V(CO)_{5,6}^-$, $Cr(CO)_{4,5}^-$, $Mn(CO)_4^-$, and $Fe(CO)_{3,4}^-$. In the present experiments, the reaction of $Co(CO)_3^-$ with ^{13}CO was monitored in Q2 at low collisional energies ($\sim$0.02 eV CM). Exchange and addition of ^{13}CO were observed with a collision energy dependence characteristic of barrierless reactions, indicating that there is no significant barrier to addition of CO to $Co(CO)_3^-$ and no significant excess barrier for loss of CO from $Co(CO)_4^-$. The flowing afterglow results of McDonald *et al.* for $Cr(CO)_4^-$ and $Fe(CO)_3^-$ were also confirmed in this way. These results directly indicate that at least six out of the twelve CO dissociation reactions studied in this work do not have excess energy barriers. The evidence obtained in this work and in the earlier studies of other metal carbonyl systems strongly suggests that CO dissociations from metal carbonyl ions are not significantly influenced by reverse activation energies.

Metal Carbonyl Spin States and Geometries. In this section, we discuss the available information concerning the electronic and geometric structures of first-row-metal carbonyl anions. Bauschlicher and co-workers have given a detailed discussion of the electronic structures of neutral transition metal mono- and dicarbonyls based on *ab initio* calculations.[53,54] Extended Hückel calculations provide predictions of the geometries and spin multiplicities of larger $M(CO)_n$ (n = 3, 4, and 5) species.[43,55,56] These results and the available experimental data on the anions or isoelectronic species are the major sources of information for the present discussion.

The ground states of the first-row atomic metal anions from V^- to Ni^- are all s^2d^{n-2}.[42] Addition of one CO to M^- results in a repulsive interaction between the electrons in the filled 4s orbital of M^- and the σ-donor orbital of CO, which can be relieved by promoting the 4s electrons to a hybrid of the 4s and 4pσ orbitals that has less overlap with the CO σ orbital. If a second carbonyl ligand is added, the sp hybridization will not reduce repulsion with both σ donors, and hybridization of the 4s and 3dσ orbitals is usually favored. The 3dσ orbital is much smaller than the 4s and 4p orbitals and therefore has a less repulsive interaction with the CO ligands. This rehybridization should result in a reduction in spin multiplicity for metal anions that have five to eight d electrons (Cr^-–Co^-), since one orbital is left vacant (five rather than six orbitals are energetically accessible). Thus, there is an energetic trade-off between occupying the high-energy 4s orbital and maintaining high spin. The loss of exchange energy accompanying the reduction of spin multiplicity will be greatest for species with the highest spin. Further addition of CO ligands should continue to raise the energy of the 4s orbital and reduce its occupation until it is essentially unoccupied by the metal electrons and a "d^n" configuration[43] is achieved. Further CO saturation may also reduce the spin multiplicity; the 17-electron species $Ni(CO)_3^-$, $Fe(CO)_4^-$, and $Cr(CO)_5^-$ have doublet ground states, while the 18-electron species $Co(CO)_4^-$, $Mn(CO)_5^-$, and $V(CO)_6^-$ are singlets.

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$Ni(CO)_n^-$. $Ni(CO)_3^-$ is a 17-electron doublet with a trigonal planar D_{3h} geometry,[57] while Ni^- is an s^2d^9 doublet.[42] Photoelectron spectroscopy (PES) measurements suggest that $Ni(CO)^-$ and $Ni(CO)_2^-$ are also doublets.[58] Theoretical calculations confirm the assignment for $Ni(CO)^-$ and indicate that the open-shell electron is in an sp-hybridized orbital.[59] Therefore, there are no spin changes in the $Ni(CO)_n^-$ system.

$Co(CO)_n^-$. $Co(CO)_4^-$ is a tetrahedral[43] 18-electron singlet, while Co^- is an s^2d^8 triplet.[42] MO calculations on the relative energetics of $M(CO)_3$ systems suggest that the ground state of $Co(CO)_3^-$ is a d^{10} singlet of planar (D_{3h}) or near-planar (C_{3v}) geometry.[43,55] $Co(CO)^-$ could be an $(sp)^2d^8$ triplet or hybridization of the 4s electrons with the 3dσ orbital could result in a singlet configuration for $Co(CO)^-$ that is analogous to the singlet ground state of Ni(CO).[60] According to the model described above, $Co(CO)_2^-$ should be a singlet with sd hybridization. Thus, the change from singlet to triplet multiplicity most likely occurs between Co^- and $Co(CO)_2^-$ and therefore should not affect the reaction thresholds measured in this study.

$Fe(CO)_n^-$. $Fe(CO)_4^-$ is a 17-electron doublet with a near-tetrahedral (C_{3v}) structure,[57] and Fe^- is an s^2d^7 quartet.[42] MO calculations suggest that $Fe(CO)_3^-$ is a d^9 doublet with a C_{2v} geometry.[55] Earlier PES data for $Fe(CO)^-$ suggested that this species is a doublet.[61] However, higher resolution PES data recently obtained by Leopold and co-workers suggest that the ground state of $Fe(CO)^-$ is in fact a $(3d\pi)^4(3d\delta)^2(4s3d\sigma)^2(4sp\sigma)^1$ quartet.[13] As discussed above, it is most likely that the one spin change (doublet–quartet) occurs upon addition of the second CO to Fe^-. Results reported previously for CID of $Fe(CO)_n^-$ (n = 1–4) showed that the sum of the derived $Fe(CO)_n^-$ ($n \leq 4$) bond energies was somewhat less than, but within error of, the known total bond energy, $D[Fe^-–4CO]$.[12] Thus, it appears that even though one of the Fe^-–CO dissociation reactions involves a change in spin, this does not lead to a significant excess energy barrier.

$Mn(CO)_n^-$. $Mn(CO)_5^-$ is an 18-electron singlet with a trigonal bipyramidal D_{3h} geometry.[62] Mn^- is not bound;[42] since Mn is an s^2d^5 sextet, $[Mn + e^-]$ can have quintet multiplicity. Thus, there are at least two spin changes involved in the $Mn(CO)_n^-$ series. MO calculations suggest that the lowest energy structure for $Mn(CO)_4^-$ is a D_{2d} singlet.[43,56] However, slow rates for addition of ligands to $Mn(CO)_4^-$ suggest that this 16-electron species is a triplet,[49,50] like the isoelectronic $Fe(CO)_4$.[63] $Mn(CO)_3^-$ should be a C_{2v} triplet,[43,55] like the isoelectronic $Fe(CO)_3$.[36,64] $Mn(CO)_2^-$ is likely to have a triplet ground state, with eight metal electrons in the five available orbitals, as detailed above. Thus, there is probably one spin change (singlet to triplet) in the $Mn(CO)_n^-$ dissociation reactions studied in this work, occurring in the first CO dissociation from $Mn(CO)_5^-$. It is possible that the observed threshold for reaction 9a is too high because slow dissociation arising from the necessity for a singlet–triplet surface crossing causes the kinetic shift to be larger than that calculated above. Since addition of CO to $Mn(CO)_4^-$ is a factor of 69 less efficient than the apparently spin-allowed reaction of CO with $Fe(CO)_3^-$,[49] the appearance curve for reaction 9a was refit assuming the dissociation rate is a factor of 70 lower than the RRKM calculations would otherwise indicate. The derived threshold of 1.60 eV is lower than the value derived assuming statistical dissociation by 0.19 eV. Since it is possible that either threshold is correct, an intermediate value of 1.70 ± 0.17 eV is assigned for this dissociation threshold.

$Cr(CO)_n^-$. $Cr(CO)_5^-$ is a 17-electron doublet with a C_{4v} (square pyramidal) geometry,[43,55–57] whereas Cr^- is an s^2d^5 sextet.[42] There are therefore two spin changes to consider as the CO ligands are removed from $Cr(CO)_5^-$. Calculations suggest that $Cr(CO)_4^-$ is a doublet[43,55,56] with either a C_{2v}[43,56] or a D_{4h}[55] structure. Photoelectron spectra of $Cr(CO)_3^-$ [65] and $Cr(CO)_2^-$ [66] suggest that these species are $(sp\sigma)^1d^6$ doublets. Therefore, it is likely that there are no spin changes involved in the dissociation reactions studied in this work, and the changes from doublet to sextet spin needed to produce the s^2d^5 Cr^- ground state occur as the last two CO ligands are removed. The energetic cost of the changes in spin should cause the two Cr–CO bond strengths in $Cr(CO)_2^-$ to be unusually weak (*vide infra*).

$V(CO)_n^-$. $V(CO)_6^-$ is an octahedral[57] 18-electron singlet, while V^- is an s^2d^4 quintet.[42] Thus, there are again at least two spin changes as the six CO ligands are removed from $V(CO)_6^-$. MO calculations suggest that the ground state of $V(CO)_5^-$ is a d^6 C_{4v} singlet, as is the isoelectronic $Cr(CO)_5$.[43,55,56] Buckner and co-workers[67] suggest that $V(CO)_5^-$ is a 16-electron triplet on the basis of the observation of low reactivity with certain two-electron-donor ligands other than CO, although observation of rapid addition of CO to $V(CO)_5^-$ at higher pressures leads to the opposite conclusion.[51] In the present work we assume that $V(CO)_5^-$ is a ground-state singlet. It is also unclear whether $V(CO)_4^-$ is a singlet or a triplet.[43] $V(CO)_3^-$ is a C_{3v} singlet,[43,55] like the isoelectronic $Cr(CO)_3$.[65] $V(CO)_2^-$ should be a quintet, in contrast to the more general behavior of $M(CO)_2^-$ having lower spin than M^- and $M(CO)^-$. This is due to the 3d shell in V^- being less than half full, as mentioned above. Thus, the two spin multiplicity changes in the $V(CO)_n^-$ system apparently occur between n = 3 and n = 2. It is conceivable, but unlikely, that the ground-state multiplicity changes to triplet upon addition of one or two CO ligands to $V(CO)_3^-$ before singlet spin pairing is again achieved in $V(CO)_6^-$. In any case, it is likely that some of the $V(CO)_n^-$ CID reactions studied involve changes in spin. The measured bond strengths are not unusually high, so there is no indication of any excess energy barriers accompanying these changes in spin. CO adds rapidly to neutral $V(CO)_n$ (n = 3–5), indicating that $V(CO)_n$ (n = 3–6) all have doublet spin or that spin is not well conserved in that system.[68] In the absence of any evidence for spin effects on dissociation (or addition) rates in the vanadium system, the kinetic shifts are not recalculated.

Comparisons to Literature. Only for the chromium carbonyl anions are any previous experimental data available for comparison to the present results (Table II). The value $D[(CO)_4Cr^-–CO]$ = 44.7 ± 3.5 kcal/mol derived from the threshold for CID of $Cr(CO)_5^-$ in an FTICR spectrometer[16] is somewhat higher than the bond strength obtained in the present work, 40.6 ± 3.5 kcal/mol, although the discrepancy of 4.1 ± 4.9 kcal/mol is within the combined error limits. $Cr(CO)_5^-$ has one of the largest kinetic shifts studied here because of its large size and high bond strength. The FTICR experiments allow at least 10 ms for dissociation to occur following collisional activation, 3 orders of magnitude more than in the present experiments. It is therefore surprising that the FTICR value is in fact higher than the present value.

The values for $D[(CO)_3Cr^-–CO]$ and $D[(CO)_2Cr^-–CO]$ derived from electron impact appearance potential measure-

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Table IV. Periodic Trends in Metal–Carbonyl Bond Strengths

metal	n	D(M–nCO)	$\bar{D}$(M–CO)	D(M$^-$–nCO)	$\bar{D}$(M$^-$–CO)	D(M$^-$–2CO)
V	6	165.1 ± 7.3	27.5 ± 1.2	≈208	≈35	≈70
Cr	5	113.8 ± 2.3	22.8 ± 0.5	≥151 ± 3	≥30.2 ± 0.6	≥27 ± 7
Mn	5	103.0 ± 2.8	20.6 ± 0.6	159.0 ± 5.6	31.8 ± 1.1	49 ± 8
Fe	4	95.4 ± 2.8	23.9 ± 0.7	147.2 ± 7.6	36.8 ± 1.9	69 ± 5
Co	4	128.0 ± 3.1	32.0 ± 0.8	≥167.0 ± 3.1	≥41.8 ± 0.8	≥89 ± 6
Ni	3	116.1 ± 1.3	38.7 ± 0.4	114.3 ± 1.3	38.1 ± 0.4	76 ± 3

ments[15] are 15 kcal/mol higher and 9 kcal/mol lower, respectively, than the values obtained in the present work. These discrepancies could be due to the appearance potential for $Cr(CO)_3^-$ being too high by 9–15 kcal/mol (0.4–0.6 eV). The reproducibility of the appearance potentials is stated to be 0.1–0.5 eV.

Only one prior theoretical calculation is available that gives thermochemical data for the metal carbonyl anions discussed in this paper. Ziegler *et al.* performed molecular orbital calculations using density functional theory on several 18-electron metal carbonyl species, including $V(CO)_6^-$.[14] They derived $D[(CO)_5V^-–CO]$ = 40.3 kcal/mol, a value that exceeds the experimental bond energy by 9.5 kcal/mol. In contrast, the calculated values for the isoelectronic $M(CO)_6$ neutrals (M = Cr, Mo, and W) are somewhat lower than the experimental values. Further density functional calculations on metal carbonyl ions are needed in order to evaluate the performance and reliability of this method.

Neutral Chromium Carbonyl Bond Strengths. In the previous study of iron and nickel carbonyl anions, the measured bond strengths could be combined with the known electron affinities of the neutral metal carbonyls to derive neutral metal carbonyl bond strengths using eq 15.[12] For the vanadium, manganese, and cobalt carbonyls, the relevant electron affinities are not known. However, some electron affinity measurements have been reported recently for a few of the chromium carbonyl anions;[13,65] these data are summarized in Table III. The data indicate that the electron affinities increase with increasing number of attached carbonyl ligands. As a result, the neutral metal carbonyl bond strengths are consistently lower than those in the corresponding anions. Electron affinities for $Cr(CO)_n$ (n = 3–5) can be combined with results from the present work to give $D[(CO)_4Cr–CO] \leq 32 \pm 4$ kcal/mol, $D[(CO)_3Cr–CO] \approx 27$ kcal/mol, and $D[(CO)_3Cr–2CO] \leq 59 \pm 5$ kcal/mol. The derived limit for $D[(CO)_4Cr–CO]$ is consistent with the two previous values reported in the literature: 25 ± 5 kcal/mol[37] (derived from modeling the recombination kinetics of $Cr(CO)_4$ with CO) and 33 kcal/mol (estimated from modeling the competition between dissociation and collisional stabilization in photoexcited $Cr(CO)_6$).[8] The bond strength $D[(CO)_3Cr–CO] \approx 27$ kcal/mol is distinctly lower than the value of 39 kcal/mol estimated by Rayner *et al.*,[8] while the limit $D[(CO)_3Cr–2CO] \leq 59 \pm 5$ kcal/mol obtained in this work is consistent with the value 60 ± 10 kcal/mol derived from modeling the translational energy distribution of fragments of photodissociated $Cr(CO)_6$.[69] Electron affinities for $Cr(CO)_2$ and $Cr(CO)_3$ can be used to derive $D[(CO)_2Cr–CO] \leq 35 \pm 4$ kcal/mol; no literature values for this bond strength are available for comparison. Additional measurements of electron affinities for metal carbonyls are highly desirable since they could be combined with the anion thermochemistry reported here to establish a large number of currently unknown bond energies for neutral metal carbonyls.

$$D[M(CO)_n–mCO] = D[M(CO)_n^-–mCO] + EA[M(CO)_n] - EA[M(CO)_{n+m}] \quad (15)$$

Periodic Trends. Equation 16 can be used with data in Table III to compute the sum of the neutral metal–carbonyl bond strengths. The sum of the anionic metal–carbonyl bond strengths can then be computed with use of eq 15. Since Mn^- is unbound, EA(Mn) is taken to be 0. Unfortunately, a reliable value for EA[$V(CO)_6$] is unavailable. However, EA[$Mn(CO)_5$] = 2.43 ± 0.21 eV,[70] EA[$Fe(CO)_4$] = 2.4 ± 0.3 eV,[61] and EA[$Co(CO)_4$][71] and EA[$Cr(CO)_5$][41] are both ≥2.3 eV. Given the apparent consistency in the electron affinities of the 17- and 18-electron carbonyls, we estimate EA[$V(CO)_6$] ≈ 2.4 eV for use in deriving the bond strength sum. Both sets of numbers can then be divided by the number of ligands n to give the average metal–carbonyl bond strengths shown in Table IV. Similar quantities have been derived for neutral metal carbonyls previously;[3,4] the values derived here for chromium, iron, and nickel are somewhat different because they are the average bond strengths in the 16-electron species $Cr(CO)_5$, $Fe(CO)_4$, and $Ni(CO)_3$ rather than in the saturated 18-electron carbonyls. This allows direct comparison to the 17-electron anionic metal carbonyls with the same number of ligands.

$$D[M–nCO] = \Delta H_f^\circ(M) + n\Delta H_f^\circ(CO) - \Delta H_f^\circ[M(CO)_n] - nRT \quad (16)$$

The average bond strengths display a trend of weak bonds to seven-electron metals (Mn and Cr^-) to stronger bonds for ten-electron metals (Ni and Co^-), as shown in Figure 5. It has been noted previously that the average neutral bond strengths correlate with the "valence-state excitation energy",[7] *i.e.*, the $s^2d^{n-2} \rightarrow d^n$ promotion energy of the metal atoms. This excitation enery was chosen because the valence state of the metal in the saturated metal carbonyl is considered to derive from the d^n states.[7] This issue will be discussed in more detail below.

Four values for $\bar{D}[M^-–2CO]$ can be derived from the present data and the bond strength sums for the metal carbonyl anions. These values and previous results for iron and nickel are given in the last column of Table IV, as well as in Figure 5. The lower limits are probably not very far from the actual values, since the limits on the electron affinities should be close to the true values. A clear trend is evident from the extremely low value of $D[Cr^-–2CO] \geq 27 \pm 7$ kcal/mol to the much higher value for cobalt, $D[Co^-–2CO] \geq 89 \pm 6$ kcal/mol. $Cr^-(s^2d^5)$ should have a very stable electronic structure with a half-filled d shell. The promotion energy necessary to hybridize electrons out of the 4s orbital should be large, thus leading to weak bonds. Co^- should have relatively strong bonds to the first two CO ligands since a 10-electron singlet configuration is particularly stable, and thus the promotion energy from the ground s^2d^8 state of Co^- to a state suitable for bonding two carbonyl ligands should be relatively low. The manganese and iron values are between these two. $D[Ni^-–2CO]$ is nearly as large as $D[Co^-–2CO]$, indicating that the extra electron in $Ni(CO)_2^-$ is not forced into a particularly high-lying orbital. $D[V^-–2CO]$ is significantly higher than $D[Cr^-–2CO]$, indicating that the seventh metal electron in $Cr(CO)_2^-$ is forced to occupy a very high-lying orbital by the two carbonyl ligands.

Electronic promotion energies are typically unavailable for the atomic metal anions, since few of them have stable electronically excited states.[42] However, the promotion energies in the isoelectronic neutral metal atoms can be used to indicate the overall trends expected for the atomic anions. The $D[M^-–2CO]$

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(69) Venkataraman, B.; Hou, H.; Zhang, Z.; Chen, S.; Bandukwalla, G.; Vernon, M. *J. Chem. Phys.* **1990**, *92*, 5338–5362.

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(71) Simões, J. A. M.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629–688.

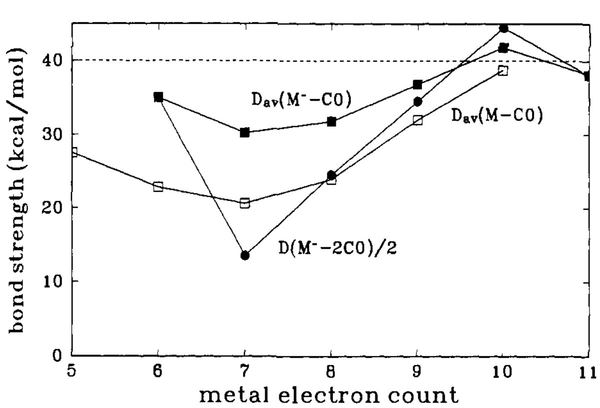

Figure 5. Periodic trends in metal–carbonyl bond strengths. The dashed line represents the "intrinsic" metal–carbonyl bond strength for the anions (see text).

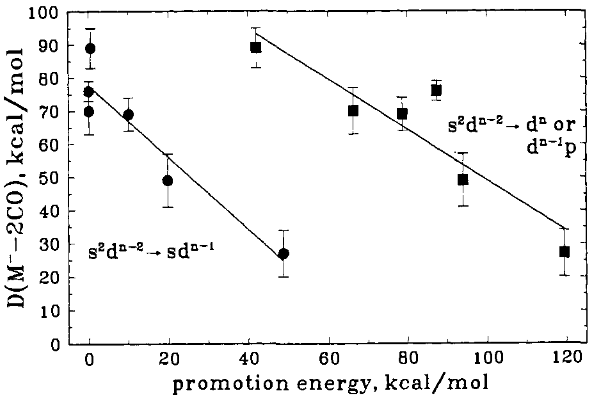

Figure 6. Metal–dicarbonyl anion bond strengths *vs* metal atom promotion energy (see text).

bond strengths are plotted in Figure 6 against the promotion energy from the ground state of the metal atom to the lowest sd^{n-1} state and to the lowest state with the 4s orbital unoccupied (d^n or pd^{n-1}).[72] Although there is a reasonable correlation between the M^-–2CO bond strength and both promotion energies, the correlation to the sd^{n-1} state is somewhat better. The slopes of the best fit to the two promotion energies are -1.2 ± 0.2 (sd^{n-1} state) and -0.9 ± 0.2 (d^n or pd^{n-1} state). The expected slope would be -1 if the promotion energy were directly subtracted from the bond energy, in reasonable agreement with both of the derived values. However, the zero promotion energy intercepts of the fits are 79 kcal/mol for the sd^{n-1} state and 139 kcal/mol for the $s^0(dp)^n$ state. The former value corresponds to an average M^-–CO bond strength of 40 kcal/mol, which can be taken as an "intrinsic" bond strength (*i.e.*, the bond strength that would be expected if no promotion is needed). The latter number corresponds to an unrealistically high average M^-–CO bond energy of 70 kcal/mol. The good correlation with the sd^{n-1} state can be interpreted as indicating that the electrons are partially but not completely removed from the metal 4s orbital after bonding by two carbonyl ligands.[53,73]

The trend outlined above has been foreshadowed in the literature. A noticeably lower efficiency for formation of $Cr(CO)^-$ from $Cr(CO)_5^-$ by CID in an FTICR was previously observed and attributed to the high lability of $CrCO^-$ caused by the stability of the s^2d^5 Cr^- configuration.[41] A correlation between carbonyl stretching frequencies in MCO and the $s^2d^{n-2} \rightarrow sd^{n-1}$ promotion energy has been discussed by Weltner and co-workers.[60] A similar correlation exists between the bond strengths in the homonuclear metal dimers Mn_2–Ni_2 and the atomic $s^2d^{n-2} \rightarrow sd^{n-1}$ promotion energy,[7,74,75] although the uncertainties in some of the data obscures this relationship to some degree.

Given the rather large promotion energies that must be counterbalanced by the addition of the first one or two carbonyl ligands to certain metals, it is not entirely clear whether all metal monocarbonyl anions and neutrals can exist as stable species. This is most questionable for M–CO systems involving seven- and eight-electron metal centers. $Mn(CO)^-$ is observed in this work as a reasonably abundant product from the CID of $Mn(CO)_4^-$. This demonstrates that $Mn(CO)^-$ is a bound species (barring the highly unlikely formation of a stable electronically excited state of $Mn(CO)^-$). $Cr(CO)^-$ has also been observed as a CID product.[41] FeCO is weakly bound, as mentioned above. However, Mn(CO) is probably only bound by van der Waals forces.[60]

A striking feature of the accumulated data in Table II is that of the 15 individual bond strengths in $M(CO)_n^-$ ($n \geq 3$) listed, 12 are within their error limits of 40 kcal/mol (the average of these values is 40.2 kcal/mol). This value is the same as the "intrinsic" M^-–CO bond strength derived from the intercept of the fit in Figure 6 and supports the notion that a metal anion–carbonyl bond should be about 40 kcal/mol if no promotion energy is required. Bond strengths in $M(CO)^-$ and $M(CO)_2^-$ are often smaller because of the promotion energy effects discussed above, although $D[Co^-–2CO] \geq 89 \pm 6$ kcal/mol suggests that both Co^-–CO bond strengths are around 40–50 kcal/mol as well. Apparently, most of the energetic effects of electronic promotions are complete after addition of the first two ligands. However, three bonds in the larger metal carbonyls are noticeably weaker than the rest, falling in the range 28–31 kcal/mol. $D[(CO)_nV^-–CO]$ for $n = 4$ and 5 may be somewhat low because there are too few metal electrons available to back-bond effectively to more than four carbonyl ligands. The origin of the exceptionally weak M–CO bond in $Mn(CO)_3^-$, $D[(CO)_2Mn^-–CO] = 28.4 \pm 3.0$ kcal/mol, remains a puzzle.

It is now clear why the average M^-–CO bond strengths shown in Figure 5 follow the same trend as the dicarbonyls. The strong trend for the dicarbonyls is dampened by averaging in the bond strengths for the larger carbonyls, which are in general nearly the same. The similar shape of the average M–CO bond strength plot indicates that the same general trend holds for the neutral metal carbonyls as well. Even though the data for the neutral carbonyls are incomplete, the known bond strengths for individual iron and nickel carbonyls are consistent with the conclusion that the first *two* M–CO bond strengths determine the overall trend illustrated in Figure 5. For instance, $D[Fe–CO] = 10.5 \pm 3.7$ kcal/mol[12,13] brings the average Fe–CO bond strength down dramatically. It therefore appears that the sum of the first two carbonyl bonds to *seven*-electron neutral or anionic metal centers are weak, while the corresponding bonds to *eleven*-electron metal centers are strong. The present results do not in general provide a means to determine what proportions of the energetic costs of the electronic promotion are paid upon addition of the first and second carbonyl ligands.

Comparisons with Isoelectronic Species. A complete set of thermochemical data for individual neutral $M(CO)_n$ fragments would provide additional useful information for understanding metal–carbonyl bonding. Unfortunately, sequential M–CO bond energies in neutral metal carbonyl complexes are exceedingly difficult to measure directly because of the inherent difficulties in forming highly unsaturated $M(CO)_n$ fragments under conditions where their physical properties can be examined. In Table V, the bond energy measurements for first-row $M(CO)_n^-$ ions are given along with the available literature data for the corresponding isoelectronic neutral and cationic metal carbonyls. Allowing for

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[72] Moore, C. E. NSRDS-NBS 35 Vol. II, 1971. Sugar, J.; Corliss, C. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 2. In all cases the energies chosen are for the lowest J level of a given electronic state.

[73] A more detailed discussion of the orbital occupations in $FeCO^-$ and FeCO is given in ref 13.

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Table V. M–CO Bond Energies for Isoelectronic $M(CO)_n^-$, $M(CO)_n$, and $M(CO)_n^+$ Species, (kcal/mol)[a]

$V(CO)_6^-$	30.8(3.5)	$Cr(CO)_5^-$	40.6(3.5)	$Mn(CO)_5^-$	40.6(3.9)	$Fe(CO)_4^-$	41.7(2.1)	$Co(CO)_4^-$	39.7(3.7)
$Cr(CO)_6$	36(5)[b]	$Mn(CO)_5$		$Fe(CO)_5$	41.5(2.0)[e]	$Co(CO)_4$		$Ni(CO)_4$	21.5(0.4)[g]
$Mn(CO)_6^+$	32(5)[c]	$Fe(CO)_5^+$	26.8(0.9)[d]	$Co(CO)_5^+$		$Ni(CO)_4^+$	17.3(1.2)[f]	$Cu(CO)_4^+$	
$V(CO)_5^-$	31.1(3.0)	$Cr(CO)_4^-$	39.7(3.9)	$Mn(CO)_4^-$	41.1(3.0)	$Fe(CO)_3^-$	42.4(3.5)	$Co(CO)_3^-$	38.1(3.9)
$Cr(CO)_5$	25(5)[b]	$Mn(CO)_4$		$Fe(CO)_4$	27.9(8.8)	$Co(CO)_3$		$Ni(CO)_3$	28.3(2.3)
$Mn(CO)_5^+$	16(3)[c]	$Fe(CO)_4^+$	24.7(1.4)[d]	$Co(CO)_4^+$		$Ni(CO)_3^+$	22.6(0.9)[f]	$Cu(CO)_3^+$	
$V(CO)_4^-$	40.4(5.8)	$Cr(CO)_3^-$	43.9(3.9)	$Mn(CO)_3^-$	28.4(3.0)	$Fe(CO)_2^-$	35.7(3.5)	$Co(CO)_2^-$	
$Cr(CO)_4$	30(6)	$Mn(CO)_3$		$Fe(CO)_3$	29.1(5.8)	$Co(CO)_2$		$Ni(CO)_2$	47.1(5.8)
$Mn(CO)_4^+$	20(3)[c]	$Fe(CO)_3^+$	15.9(1.2)[d]	$Co(CO)_3^+$		$Ni(CO)_2^+$	40.4(2.1)[f]	$Cu(CO)_2^+$	
$V(CO)_3^-$	35.8(4.4)	$Cr(CO)_2^-$		$Mn(CO)_2^-$		$Fe(CO)^-$	33.7(3.5)	$Co(CO)^-$	
$Cr(CO)_3$	<36(3)	$Mn(CO)_2$		$Fe(CO)_2$	36.7(3.5)	$Co(CO)$		$Ni(CO)$	40.5(5.8)
$Mn(CO)_3^+$	31(6)[c]	$Fe(CO)_2^+$	36.1(1.8)[d]	$Co(CO)_2^+$		$Ni(CO)^+$	42.7(2.1)[f]	$Cu(CO)^+$	

[a] Bond energies from this work or ref 12 unless otherwise noted. [b] Reference 37. [c] Reference 29. [d] Reference 10. [e] Reference 6. [f] Khan, F. A.; Steele, D. L.; Armentrout, P. B. *J. Phys. Chem.*, submitted for publication. [g] Day, J. P.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc* **1968**, *90*, 6927–6933.

the error limits on the measured bond strengths, the consistent ordering $D[(CO)_nM^-–CO] \geq D[(CO)_nM–CO] \geq D[(CO)_nM^+–CO]$ holds in nearly every case. The origin of this trend is easily understood in terms of the expected differences in π back-bonding ability among isoconfigurational complexes with differing metal nuclear charges. For metal carbonyl complexes in which all s → d transitions have been made, the isoelectronic $M(CO)_n^{-/0/+}$ species should share a common electronic configuration. Since the general ordering of $d\pi$ orbital energies is $E_{d\pi}[M(CO)_n^-] > E_{d\pi}[M(CO)_n] > E_{d\pi}[M(CO)_n^+]$, then the degree of $(d\pi - \pi^*)$ back-bonding will be greatest for the anions and least for the cations. This is, of course, the familiar argument commonly given to explain the decreasing ν_{CO} stretching frequencies observed for the isoelectronic complexes $V(CO)_6^- > Cr(CO)_6 > Mn(CO)_6^+$.[76] That it also pertains to M–CO bond energies is a reflection of the importance of $d\pi - \pi^*$ back-bonding in determining the overall strength of the interaction.[14,53,77,78]

We can understand the failure of this simple trend with the $Fe(CO)^-/Ni(CO)^+$ pair in terms of the differing atomic ion asymptotes to which the iron carbonyl anions and nickel carbonyl cations dissociate. Although the ions have the same number of valence electrons, an Fe^- ion has a d^7s^2 configuration that must undergo electronic hybridization in order to bind a CO ligand, while d^9 Ni^+ need not undergo any electronic promotion to form $Ni(CO)^+$ and therefore bonds to CO more strongly. This promotion energy argument may also explain why the bond strength in $Ni(CO)_2^+$ is similar to or slightly higher than the bond strength in $Fe(CO)_2^-$. Since the effects of electronic promotions on the metal carbonyl bond strengths appear to be absent in the larger metal carbonyl anions, the relative M–CO bond strength ordering (anion ≥ neutral ≥ cation) should prevail for the $M(CO)_n^{+/0/-}$ ($n \geq 3$) systems.

The existence of this trend suggests that it is possible to estimate M–CO bond energies in neutral $M(CO)_n$ fragments by *interpolation* between the more easily measured bond energies in the corresponding isoelectronic $M(CO)_n^-$ and $M(CO)_n^+$ ions. Such predictions give $D[(CO)Co–CO] = 38 \pm 4$ kcal/mol, $D[(CO)_2Co–CO] = 32 \pm 11$ kcal/mol, $D[(CO)_3Co–CO] = 30 \pm 12$ kcal/mol, $D[(CO)_2Mn–CO] = 30 \pm 15$ kcal/mol, $D[(CO)_3Mn–CO] = 32 \pm 9$ kcal/mol, and $D[(CO)_4Mn–CO] = 34 \pm 8$ kcal/mol. Unfortunately, the magnitude of the difference in M–CO bond strengths between isoelectronic anions and cations can be as high as 28 kcal/mol, and systems with such a large difference lead to predictions of limited utility. Measurements of the electron affinities for the cobalt and manganese carbonyls, when combined with the anion bond strengths reported in this work, would provide an interesting test of the above predictions.

Related Metal–Ligand Bond Strengths. The relative ordering of metal–ligand bond strengths can be determined from ligand exchange reactions, since for gas-phase ligand substitution to be efficient, the reaction must be exothermic or thermoneutral.[79] In other words, $D[(CO)_{n-m}M^-–L] \geq D[(CO)_{n-m}CO]$ if reaction 17 is efficient for room-temperature reactants. Lower limits on

$$(CO)_nM^- + L \rightarrow (CO)_{n-m}ML^- + mCO \qquad (17)$$

metal–ligand bond strengths for various compounds containing vanadium,[67] chromium,[80,81] and manganese[50,82,83] can be derived in this manner. For example, the reaction of $Mn(CO)_3^-$ with H_2S gives $[(CO)_2MnS^- + CO + H_2]$ as products,[83] leading to the remarkably high bond strength $D[(CO)_2Mn^-–S] \geq 99 \pm 3$ kcal/mol. VanOrden *et al.* reported that $V(CO)_5^-$ reacts with NO with 16% efficiency in an FTICR to displace primarily two carbonyl ligands, with a small amount of three ligands displaced as well.[67] Displacement of two ligands would require that $D[(CO)_3V^-–NO] \geq 71 \pm 7$ kcal/mol, an extraordinarily high value for a single metal–ligand bond energy, even for a potential three-electron donor ligand. In the flowing afterglow, displacement of only a single CO ligand by NO occurs, indicating that $D[(CO)_4V^-–NO] \geq 31 \pm 3$ kcal/mol. This suggests that the $V(CO)_5^-$ ions formed in the earlier FTICR experiments were probably kinetically or internally excited or that the reaction product distribution was complicated by CID. We also observe that $V(CO)_4NO^-$ reacts with NO by a further single ligand displacement to form $V(CO)_3(NO)_2^-$, but no further displacement of CO by NO is observed. This is consistent with NO acting as a three-electron donor, forming a stronger bond to V^- than CO until an electron count of 18 is reached in $V(CO)_3(NO)_2^-$. $V(CO)_6^-$ is unreactive with NO.

Gregor has observed ligand exchange reactions in an FTICR instrument for several of the species studied in this work. These experiments are of limited utility for deriving relative metal–ligand bond strengths because the internal energy content of the reactant ions was not well characterized and because absolute reaction rates were not measured. The observed substitutions for CO in $Cr(CO)_3^-$ suggest $D[(CO)_2Cr^-–L] \geq 44 \pm 4$ kcal/mol for $L = NH_3$,[84] CH_3CHO,[85] and various amines,[84] ketones,[85] and alkenes.[86] This is an unusual result in that metal–alkene bonds are generally weaker than metal–carbonyl bonds.[3,4] $D[(CO)_2Cr^-–1,3\text{-butadiene}] \geq 73 \pm 4$ kcal/mol[86] and $D[(CO)Cr^-–CS_2]$

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$\geq$ 84 ± 6 kcal/mol[87] can also be derived from this FTICR study. The bond to CS_2 is high enough to suggest that the metal has in fact *inserted* into a C–S bond to form $(CO)(CS)Cr^-–S$. Similarly, the reported[87] displacement of all four CO ligands in $Mn(CO)_4^-$ and all three CO ligands in $Fe(CO)_3^-$ by CS_2 would require $D[Mn^-–CS_2] \geq 118 \pm 9$ kcal/mol and $D[Fe^-–CS_2] \geq 112 \pm 8$ kcal/mol.[12] Thus, insertion into a C–S bond by the metal is probable for these unsaturated metal ions as well. For comparison, the reaction of $Mn(CO)_4^-$ with CS_2 in the flowing afterglow results in the displacement of only one CO ligand by CS_2. The differing behavior indicates that either the helium buffer gas in the flowing afterglow experiments cools the nascent collision complex and prevents further ligand loss or the ions in the FTICR experiment had significant amounts of excess internal energy. Repetition of these experiments with special care devoted to cooling the reactant ions would be worthwhile in order to confirm the thermochemical conclusions noted above.

Nibbering and co-workers[88] have also performed ligand exchange studies using an FTICR instrument for several of the species examined in the present work. The ions were thermalized prior to reaction, and approximate absolute reaction rate coefficients were determined. Thus, these results can be reliably used for determining thermochemistry. The observed ligand exchange reactions indicate $D[Cr^-–L] \geq 27 \pm 7$ kcal/mol and $D[(CO)_2Cr^-–L] \geq 44 \pm 4$ kcal/mol for L = methanol and water. Structures involving metal insertion into O–H bonds were proposed for the products of these reactions.

Summary. Energy-resolved collision-induced dissociation has been used to determine the metal–carbonyl bond energies in $V(CO)_n^-$ (n = 3–6), $Cr(CO)_n^-$ (n = 3–5), $Mn(CO)_n^-$ (n = 3–5), and $Co(CO)_n^-$ (n = 3–4). These can be combined with earlier measurements for $Fe(CO)_n^-$ and $Ni(CO)_n^-$ to obtain a nearly complete set of metal carbonyl anion bond strengths. Almost all of the M–CO bond strengths in $M(CO)_n^-$ ($n \geq 3$) are in the range 36–44 kcal/mol, which can be taken as the "intrinsic" bond strength in these systems. The dicarbonyl bond strengths $D[M^-–2CO]$ show a distinct periodic dependence on the $s^2d^{n-2} \rightarrow sd^{n-1}$ promotion energy, consistent with promotion from the atomic ground states to a hybridized state suitable for bonding carbonyl ligands. The measured bond strengths for $Cr(CO)_n^-$ ions are combined with other data in the literature to derive bond strengths for the neutral chromium carbonyls. Comparison of bond energies in isoelectronic metal carbonyls indicates that for anionic, neutral, and cationic species with the same electron count, the bond strengths are in the order anion ≥ neutral ≥ cation, consistent with known trends in the degree of $d\pi - \pi^*$ back-bonding. Combining the present data with results from ligand exchange reactions gives an extensive set of lower limits on other metal–ligand bond strengths, although there are some questions as to whether these results correspond to thermal reactions.

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Supplementary Material Available: Figures showing appearance curves for CID of $M(CO)_n^-$ (M = V, Mn, and Co) (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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