of this reaction with temperature and ionic strength, the numbers are generally within experimental error. The reaction rates observed here are also comparable with those measured for the rate of unimolecular electron self-exchange within oligomers of cytochrome *c*.[14b] It is perhaps useful to compare the estimated first-order electron-transfer rates with the bimolecular rate for electron transfer from ferrocytochrome b_5 to ferricytochrome *c*.[14c,15] At 298 K, this rate is $\sim 3 \times 10^7$ M^{-1} s^{-1} (100 mM phosphate, pH 7.0), which, assuming a 200-mV driving force, leads to a hypothetical reverse electron-transfer rate of approximately 10^3 M^{-1} s^{-1}. If the concentration of ferricytochrome b_5 is 1 mM, this would give a notional "lifetime" for ferrocytochrome *c* of 1 s under these solution conditions. The notional lifetime is similar to the actual lifetime measured at low ionic strength, implying that complex formation may not promote electron transfer. One explanation for this would be that, in the ground state of the binary complex formed at low ionic strength, cytochrome *c* and cytochrome b_5 are locked in a geometry that requires a form of configurational rearrangement prior to electron transfer.[14c] The replacement of Phe-82 with Gly in yeast iso-1-ferrocytochrome *c* has no effect on the lifetime of the protein in the presence of ferricytochrome b_5, indicating that the presence of an aromatic group at position 82 is not essential for electron transfer from ferrocytochrome *c* to ferricytochrome b_5. Taken together with the electron self-exchange data, the results argue strongly against the direct involvement of the aromatic group in physiological electron-transfer reactions whose driving forces are relatively low. In conclusion, we have measured the reverse rate of electron transfer within a preformed binary complex of cytochrome *c* and cytochrome b_5 by NMR methods. This rate is not accessible to measurement using many prevailing methods and has given insight into the possible role of phenylalanine-82 of cytochrome *c* in biological electron transfer.

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Reactions of Co_{1-4}^+ and $Co_4(CO)_n^+$ with Cyclohexane: C–H Activation as a Function of Cluster Size and Ligand Substitution

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Abstract: Rate constants and product distributions for the bimolecular gas-phase reaction of cyclohexane with Co^+, Co_2^+, Co_3^+, $Co_4(CO)_n^+$ (n = 0–12), Ir_2^+, and Ir_3^+ are reported. All of the ions except Co_2^+ and $Co_4(CO)_n^+$ (n = 2–4, 8–12) react with observable rates. In most cases the predominant product is C_6H_6 bound to the metal cluster. Observed products of the Co^+ reaction and the failure of Co_2^+ to react agree with previously reported results. The results for $Co_4(CO)_n^+$ are compared with previously reported results for $Ir_4(CO)_n^+$ and $Re_4(CO)_n^+$. Like the third-row clusters, the reactivity of the Co tetramer diminishes and disappears as ligands are added to increase the number of cluster valence electrons to more than 48. $Co_4(CO)_7^+$ reacts slowly and the $Co_4(CO)_{8-12}^+$ do not react at an observable rate. This can be rationalized on the basis of frontier orbital theory. It is found on examining the cluster molecular orbitals with extended Hückel calculations that the failure of Co_2^+ and $Co_4(CO)_{2-4}^+$ to react can also be rationalized on the basis of frontier orbital theory. The contrast between the failure of $Co_4(CO)_4^+$ to react and the reactivity of $Co_4(CO)_5^+$ is attributed to a change from a high-spin electronic configuration of the former to a low-spin configuration for the latter.

Introduction

The activation of C–H bonds by gas-phase metal clusters has been the subject of a number of recent studies[1-6] which raise a variety of interesting questions. The Mn_2^+ and Co_2^+ dimer ions are unreactive with alkanes,[1a] but $Co_2(CO)^+$ reacts with butane to form $Co_2(CO)C_4H_8^+$.[1b] $Re_3(CO)_n^+$,[1c] $Re_4(CO)_n^+$,[1c] and $Ir_4(CO)_n^+$[1d] all dehydrogenate cyclohexane provided n is not too large. The critical value of n for each case can be rationalized in terms of frontier orbital theory.[1d] Several MFe^+ species (M = Co,[2b] V,[2c] Cu[2d]) do not react with alkanes, but $LaFe^+$ and Co_2Fe^+ do.[2e,a] Neutral Pt_n (n = 2–8) clusters dehydrogenate small alkanes in a fast flow reactor.[3a] In this case both the extent of dehydrogenation and the number of molecules absorbed increase with cluster size. Neutral Nb_n (n = 4–13) clusters dehydrogenate benzene.[3b,6] The reactivity of the Nb clusters varies with cluster size in the same way that ionization potential varies with cluster

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size. This correlation with ionization potential emphasizes the sensitivity of reactivity to cluster electronic structure suggested by all of the studies. Sputtered ionic (and perhaps energetic) clusters of Cu,[4] Ni,[5] Pd,[5] and Pt[5] also dehydrogenate small alkanes. From these studies it appears that Cu clusters are more reactive than Ag clusters,[4] but Pt clusters are more reactive than Pd clusters which are more reactive than Ni clusters.[5]

We recently described the chemistry of tetrameric iridium (group 9) and rhenium (group 7) carbonyl cluster ions with cyclohexane.[1d] As noted above the $M_4(CO)_n^+$ clusters dehydrogenate cyclohexane unless n is too large. Specifically, if n is small enough that the number of cluster valence electrons is less than 48, the cluster reacts. Clusters with more CO ligands than this tend to be unreactive. Since a cluster of four transition-metal atoms can accommodate 48 electrons in orbitals derived from metal s and d orbitals, this reactivity pattern suggests that a cluster LUMO derived from atomic s or d orbitals facilitates reaction. Molecular orbital theory suggests that the d orbitals will fill first so that empty s band orbitals may be the key to reaction. Furthermore the failure of negative ions to react suggests that the LUMO must have sufficiently low energy to be a good acceptor of the electrons in the σ C–H bond under attack.

The reactivity of iron clusters with hydrogen also provides evidence of the correlation between the ability of small metal clusters to accept electron density and their reactivity toward σ bonds.[7] For clusters with fewer than 8 Fe atoms the reactivity of the clusters increases systematically with cluster electron binding energy (ionization potential of the neutral). This can be interpreted in terms of frontier orbital arguments analogous to those applied to the Re and Ir carbonyl cluster ions discussed above.

We describe here the chemistry of tetrameric cobalt carbonyl cluster ions with cyclohexane. Cobalt is the first row group 9 congener of the third-row iridium, and the pattern of reactivity shows interesting similarities and distinctions from that of iridium. They are similar in that the iridium tetrameric cationic clusters with 7 or more carbonyl ligands are unreactive, and the cobalt tetrameric clusters with 8 or more carbonyl ligands are unreactive. In contrast to the iridium clusters, the cobalt clusters with 2, 3, and 4 carbonyls are unreactive. The M_2^+ and M_3^+ species also show interesting contrasts for the two metals. We discuss similarities and distinctions in terms of a simple molecular orbital model for the electronic structures of the clusters.

Experimental Section

Reactant ions were formed by 70 eV electron impact on commercially obtained $Co_4(CO)_{12}$ or $Ir_4(CO)_{12}$. The ions formed were initially trapped in the source cell and then moved to the differentially pumped analyzer cell of an FTMS-2000 ion cyclotron resonance spectrometer[8,9] (Extrel, Madison, WI). All of the ions but the one of interest were then ejected from the analyzer trap by accelerating their cyclotron motion.[10] Cyclohexane was then injected into the analyzer region through a computer-controlled valve.[11] The cyclohexane pressure rose to the 10^{-7}-Torr range and then fell back to the 10^{-9}-Torr range in less than 1 s. A Fourier transform ion cyclotron resonance mass spectrum[12] taken after the pressure burst contains peaks corresponding to products of reaction between the cluster ion and cyclohexane. These experiments identify unambiguously the products originating with each reactant ion. Rate constant measurements were done by introducing both the metal carbonyl and cyclohexane into the source region and obtaining mass spectra at various delay times after the ionizing electron beam pulse. Rate constants for the reactions were deduced from these constant pressure spectra. Product and reactant ion intensities were fit to functions appropriate for pseudo-first-order kinetics. This procedure provided absolute rate constants. Accuracy of the determinations was estimated at ±30% from the internal consistency of rate constants from product and reactant data and from the estimated accuracy of the pressure determination.

Table I. Reactions of $M_n(CO)_m^+$ with Cyclohexane

reactant ion	neutral products	total rate constant,[a] 10^{-10} cm^3 s^{-1}
$M_n(CO)_m^+$	$3H_2$, $2H_2$, H_2	
Ir_2^+	1.0, 0.0, 0.0	7.2
Ir_3^+	1.0, 0.0, 0.0	10.1
Ir_4^+	1.0, 0.0, 0.0	11.8
Co^+	0.1, 0.3, 0.3[b]	8.0
Co_2^+	products not observed	<0.08
Co_3^+	0.5, 0.4, 0.0	6.0
Co_4^+	0.9, 0.1, 0.0	9.2
$Co_4(CO)^+$	0.4, 0.6, 0.0	13.8
$Co_4(CO)_{2,3,4}^+$	products not observed	<0.2
$Co_4(CO)_5^+$	1.0, 0.0, 0.0	8.4
$Co_4(CO)_6^+$	1.0, 0.0, 0.0	8.4
$Co_4(CO)_7^+$	1.0, 0.0, 0.0	3.3
$Co_4(CO)_{8-12}^+$	products not observed	<1.0

[a] The rate constants are estimated to be accurate to ±30%. [b] An additional product, $Co(C_3H_6)^+$, is observed with branching ratio 0.2. Previously reported values[13] are 0.07, 0.37, 0.33 for the tabulated product branching ratios and 0.20 for the $Co(C_3H_6)^+$ product. Kinetic energy dependent branching ratios reported in the first observation of this reaction[14] are discussed in the text.

Results

Bare Clusters. The reactions of the bare cobalt clusters Co_n^+ with cyclohexane are summarized in eqs 1 and 2. An additional

$$Co_n^+ + c\text{-}C_6H_{12} \rightarrow Co_n(C_6H_{12-2m})^+ + mH_2 \quad (1)$$

$$(n = 1,\ m = 1\text{–}3;\ n = 2,\ \text{no products};\ n = 3\text{–}4,\ m = 2\text{–}3)$$

$$Co_4(C_6H_8)^+ + c\text{-}C_6H_{12} \rightarrow Co_n(C_6H_6)(C_6H_8)^+ + 3H_2 \quad (2)$$

product, $Co(C_3H_6)^+$, is observed in the case of the Co^+ reaction. The total rate constants for reaction of the clusters with cyclohexane and the branching ratios for the various products are listed in Table I. Note particularly the failure of Co_2^+ to react at an observable rate.

The branching ratios for products of the reactions of Co^+ are in good agreement with those reported for laser produced ions[13] as noted in Table I. The same Co^+ reactions were first observed when a beam of Co^+ ions produced by thermionic emission reacting with cyclohexane vapor was used.[14] The relative kinetic energy of the beam was varied from 0.5 eV upward, and the product distributions observed were somewhat different from those reported here, the $Co(C_6H_{10})^+$ product being strongly dominant at low kinetic energies. The total cross section observed in the beam study is large (>100 Å^2) and decreases with ion kinetic energy—a behavior characteristic of efficient exothermic reactions. There is ample evidence that a substantial portion of the Co^+ produced by electron impact on Co compounds is in metastable excited states[15,16] but ions produced therionically are predominantly in the ground state.[15] We conclude that while the Co^+ product branching ratios observed in the present experiment could be affected by electronically excited Co^+, the overall rate constant is probably not substantially affected. We note that the facility of the thermal reaction of Co^+ with cyclohexane is also supported by collision-induced decomposition and metastable kinetic energy release studies of $CoC_6H_{12}^+$.[17] The present study provided no

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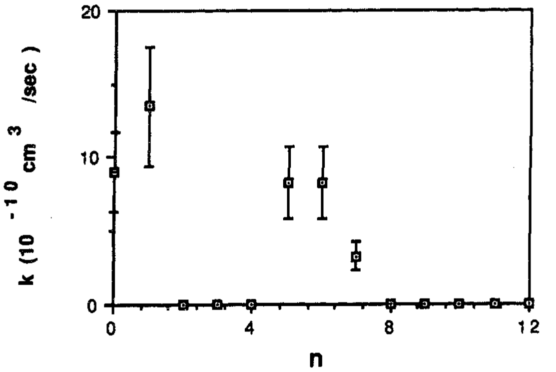

Figure 1. Rate constants for reaction of $Co_4(CO)_n^+$ with cyclohexane vs *n*, the number of CO ligands in the cluster.

kinetic evidence for excited states that reacted at different rates than ground states.

The reactions of the Ir_n^+ clusters with cyclohexane are summarized in eqs 3, 4, and 5. The total relative rate constants for

$$Ir_n^+ + c\text{-}C_6H_{12} \rightarrow Ir_n(C_6H_6)^+ + 3H_2 \quad (n = 2\text{–}4) \tag{3}$$

$$Ir_n(C_6H_6)^+ + c\text{-}C_6H_{12} \rightarrow Ir_n(C_6H_6)_2^+ + 3H_2 \quad (n = 2\text{–}4) \tag{4}$$

$$Ir_n(C_6H_6)_2^+ + c\text{-}C_6H_{12} \rightarrow Ir_n(C_6H_6)_3^+ + 3H_2 \quad (n = 4) \tag{5}$$

the reaction of Ir_n^+ with cyclohexane are listed in Table I. Note that in contrast to cobalt dimer Ir_2^+ is reactive. In agreement with a previous report[18] no Ir^+ was observed in the mass spectrum of $Ir_4(CO)_{12}$.

Metal–Carbonyl Clusters. The reactions of $Co_4(CO)_n^+$ with cyclohexane are summarized in eqs 6 and 7. Note that Co_4-

$$Co_4(CO)_n^+ + c\text{-}C_6H_{12} \rightarrow Co_4(CO)_n(C_6H_6)^+ + 3H_2 \quad (n = 0\text{–}1,\ 5\text{–}7) \tag{6}$$

$$Co_4(CO)_n^+ + c\text{-}C_6H_{12} \rightarrow Co_4(CO)_n(C_6H_8)^+ + 2H_2 \quad (n = 0\text{–}1) \tag{7}$$

$(C_6H_8)^+$ undergoes subsequent reaction 2. $Co_n(CO)_m^-$ species were observed for (n,m) = (2,5), (3,1–7), (4,0–11), (5,13), (7,15), and (8,15–17). None of these anions were observed to react with cyclohexane ($k <$ ca. 10^{-11} cm^3 s^{-1}). The total relative rate constants for reactions of $Co_4(CO)_n^+$ with cyclohexane are plotted in Figure 1 and listed in Table I.

Discussion

The dehydrogenation chemistry requires an initial oxidative addition of the C–H bond to a metal center. In atomic metal ions an empty, low-energy s orbital facilitates oxidative addition because of its ability to accept electron density from the σ C–H bond.[19,20] Molecular orbitals derived from atomic s orbitals play a similar role in ionic clusters. This is supported by the fact that rhenium and iridium four-atom ionic clusters with 48 or fewer electrons react at an observable rate while clusters with more electrons do not.[1d] A cluster of four metal atoms will have 20 molecular orbitals derived from d atomic orbitals and 4 molecular orbitals derived from metal s orbitals. Hence it takes 48 electrons to fill the s and d "bands" of molecular orbitals. The onset of reactivity for clusters with fewer than 48 electrons suggests the importance of s band vacancies in the chemistry.

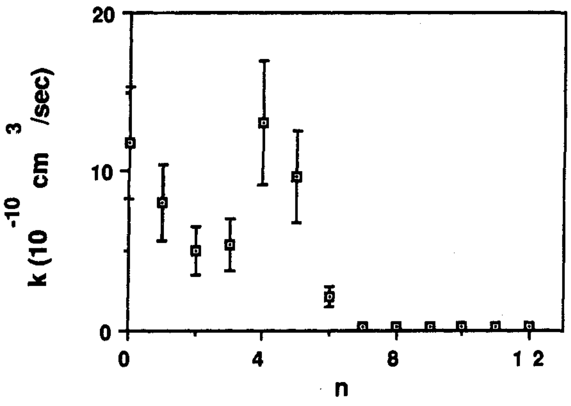

Figure 2. Rate constants from ref 1d for reaction of $Ir_4(CO)_n^+$ with cyclohexane vs *n*, the number of CO ligands in the cluster.

Cobalt is similar to rhenium and iridium in that if there are too many CO ligands in $Co_4(CO)_n^+$ no reaction occurs. This is evident from the present results for cobalt plotted in Figure 1 and from previous results for Ir[1d] plotted in Figure 2. The most substituted reactive $Co_4(CO)_n^+$ cluster has 7 CO ligands corresponding to 49 valence electrons. The most substituted reactive $Ir_4(CO)_n^+$ cluster has 6 CO ligands corresponding to 47 valence electrons. The most dramatic difference between iridium and cobalt is the lack of reactivity of $Co_4(CO)_n^+$ for n = 2, 3, and 4.

Frontier MO Model. This apparently idiosyncratic reactivity of the substituted cobalt tetramers with n = 2, 3, and 4 can be rationalized in terms of arguments analogous to those used to rationalize the reactivity of the rhenium- and iridium-substituted tetramers. The treatment used here was suggested by Lauher's cluster valence molecular orbital treatment of metal carbonyl clusters,[21] by the frontier orbital interpretation of atomic transition metal ion reactivity first discussed by Armentrout et al.,[20] and by the frontier orbital interpretation of metal cluster reactivity discussed by Zakin et al.[7] The critical factor for reactivity can be taken as the presence or absence of a vacant s-band orbital with sufficient orbital electron affinity to act as a good acceptor. Simple molecular orbital calculations provide a basis for asserting that the unreactive species may lack such an orbital. The extended Hückel calculations provide a very approximate but easily interpreted picture of the orbital interactions involved in the reactivity of the clusters. The calculations involve, of course, a number of empirical parameters, but the important features of the results are not very sensitive to the choice of parameters.

The specific model has the following features: (1) Only the "s-band" orbitals, the orbitals derived from metal s orbitals, will be considered explicitly. (2) Those s-band orbitals with metal–metal bonding character will be assumed to be doubly occupied. Those s-band orbitals with metal–metal nonbonding and antibonding character will be assumed to be available for ligand bonding. (3) Since s-band orbitals are used for both metal–metal bonding and metal–ligand bonding, it will be assumed that a metal atom bound to a ligand is weakly bound to its neighboring metal atoms. (4) The d-band orbitals are assumed to be occupied in a high-spin sense when there are few CO ligands. If there are too few s-band orbitals to bind all the CO ligands, it will be assumed that the configuration of the d-band orbitals switches to low spin. The resulting vacant d-band orbitals are assumed to be available to bind CO ligands. (5) The s-band orbitals not involved in metal–metal or metal–CO bonding under the preceding assumptions will be assumed to be the lowest unoccupied orbitals (LUMOs) in the cluster.

These features and assumptions are consistent in a general way with known properties of transition metals and with principles of MO theory. In particular the predominance of 4s orbitals in the bonding of late-first-row transition elements is well-established

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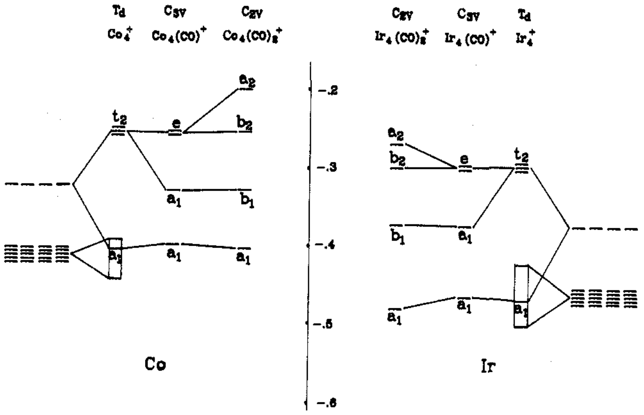

Figure 3. Molecular orbital energy level diagrams for Co_4^+ and Ir_4^+. Shown are energy levels of metal cluster orbitals derived from d and s metal atom orbitals. The energy scale is in atomic units (hartrees). The energy levels were calculated by using the extended Hückel method as described in the text. The orbital energies correspond to the energy of adding an electron to the ion.

by a number of ab initio calculations.[22] For second- and third-row elements and for early transition elements d orbitals are more significant in bonding.

Figure 3 shows the results of extended Hückel MO calculations on Co_4^+ and Ir_4^+. The bulk metal bond lengths (2.50 and 2.71 Å) were used for the metal–metal bond lengths. Other parameter choices are described in the Appendix. The valence orbital ionization energies of neutral metal atoms were used in the calculations which means that the orbital energies obtained correspond to the orbital electron affinities of the ion. Calculations were done for three geometries, T_d, C_{3v}, and C_{2v}. The lower symmetries were treated as limiting cases. For C_{3v} the interaction between the unique Co atom and the remaining three was considered to be negligible. For C_{2v} the interaction between the atoms at the ends of the unique edge was considered to be negligible.

The important features of the results of the calculations are evident in Figure 3. These results support the emphasis on s orbital interactions in our model. The interactions between the d orbitals are relatively weak, particularly in the case of Co. The relatively small range of energies of the d-band orbitals is indicated on Figure 3 for T_d symmetry. The energy range of the d-band orbitals for other symmetries is essentially the same as for T_d and are omitted from Figure 3 for simplicity. The s–d interactions are also weak. Setting the s–d overlaps to zero changes the energies of the s-band orbitals so slightly as to be almost indiscernible on a diagram such as Figure 3. On the other hand, the s orbitals interact strongly with one another producing bonding and antibonding orbitals whose energies vary significantly with geometry. The difference between the strength of the s–s and d–d interactions is less pronounced in Ir than in Co. The Ir orbitals are also lower in energy than the Co orbitals. As noted above these features of the calculations are not very sensitive to the parameters used. They are also consistent in a general way with the results of higher level calculations on transition-metal systems.[22]

The tendency of the more extensive s orbitals to interact more strongly than the more compact d orbitals is an important feature of the behavior of late-first-row transition-metal atoms in M–M, M–H, and M–C bonds.[22] In second- and third-row transition metals d orbitals are more important in bonding, hence the variation of reactivity of Ir_4^+ with the addition of CO ligands shown in Figure 2, while qualitatively similar to that of Co_4^+ (Figure 1), is not as dramatic.

Our procedure will be to determine whether the clusters of interest have low-lying unoccupied s-band frontier orbitals (LUMOs). We will make this determination on the basis of the MO calculations and assumptions described above. Our expectation is that clusters with such a LUMO should be significantly more reactive than clusters lacking such a LUMO.

Reactivity of M_4^+ and $M_4(CO)^+$. Since the precursor neutrals have tetrahedral metal cores we assume that Co_4^+ and Ir_4^+ have T_d symmetry. In this case the metal s orbitals give one bonding orbital (a_1) and three antibonding orbitals (t_2). If two electrons occupy the a_1 orbital and the remaining 33 electrons occupy the d-band orbitals in a high-spin configuration, then the t_2 orbitals will be vacant. The t_2 orbitals have significant orbital electron affinities and should be good acceptors, consistent with the reactivity of the tetramers.

If the $Co_4(CO)^+$ and $Ir_4(CO)^+$ clusters have C_{3v} symmetry as expected for a terminally bound CO, then the calculation suggests that the metal s orbitals give two a_1 orbitals, one nonbonding and one bonding, and two degenerate e antibonding orbitals. The 35 metal valence electrons would occupy the bonding a_1 orbital and the d-band orbitals. The nonbonding a_1 orbital interacts with the CO ligand, and the e orbitals would be vacant. These orbitals have orbital electron affinities identical with the t_2 orbitals in tetrahedral Co_4^+ or Ir_4^+ and should be good acceptors, consistent with the observed reactivity of the clusters.

Reactivity of $M_4(CO)_{2,3}^+$. If the $Co_2(CO)_2^+$ cluster has C_{2v} symmetry as expected for two terminally bound CO ligands then the metal s orbitals give one bonding (a_1), one nonbonding (b_2), and two antibonding orbitals. One orbital (b_1) is only slightly antibonding, but the other (a_2) is strongly antibonding. The metal valence electrons occupy the a_1 orbital and the d-band orbitals. The b_1 and b_2 orbitals are involved in bonding to the two CO ligands leaving only the a_2 orbital vacant. This orbital has a relatively small orbital electron affinity and is therefore a relatively poor acceptor. This rationalizes the failure of $Co_4(CO)_2^+$ to react. $Ir_4(CO)_2^+$ has an analogous a_2 LUMO, but this orbital is slightly lower in energy than in the $Co_4(CO)_2^+$ case. Evidently the Ir orbital is a sufficiently good acceptor to initiate reaction. Note in Figure 2, however, that $Ir_4(CO)_2^+$ is significantly less reactive than Ir_4^+ and $Ir_4(CO)^+$.

If $Co_4(CO)_3^+$ is assumed to have an occupied bonding s-band orbital and the d-band orbitals are occupied in a high-spin sense, then each of the remaining three s-band orbitals will form bonding orbitals with the ligands. There are then no remaining unoccupied s orbitals to act as acceptors consistent with the failure of this cluster to react. $Ir_4(CO)_3^+$ reacts, but relatively slowly. It may be that the iridium complex has a vacancy in the d shell by virtue of a lower spin state as discussed below. That vacant orbital could interact with the ligands leaving an s-band orbital free for reaction.

Reactivity of $M_4(CO)_{4-12}^+$. If it is assumed that $Co_4(CO)_4^+$ is tetrahedral the MO scheme suggested in Figure 3 can be used. The 35 metal electrons occupy the bonding 4s a_1 orbital and the 3d orbitals. The spin state must be such that at least one of the d-band orbitals is vacant (no more than 5 unpaired spins) along with the 4s t_2 orbitals to interact with the ligands. All the s-band orbitals are then occupied consistent with the failure of the cluster to react.

The $Ir_4(CO)_4^+$ cluster, however, reacts more rapidly than $Ir_4(CO)_3^+$, constrasting sharply with the behavior of the analogous cobalt cluster ions. As in the case of $Ir_4(CO)_3^+$ the effects of a lower spin state could help account for the greater reactivity of the iridium ion. The lower spin state would have vacant d-band orbitals which could be used to bind the ligands leaving s orbitals vacant for reaction. The presence of spin-coupled electrons in relatively high lying d-band orbitals could also enhance reactivity. Donation of electrons from such a highest occupied orbital (HOMO) into the vacant σ^* orbital of the C–H bond can enhance the rate of oxidative addition. It is not unreasonable that iridium species would tend to have lower spin than analogous cobalt species. Exchange interactions generally tend to be stronger in first-row transition metals than they are in second- and third-row metals. In the bulk, for example, cobalt is ferromagnetic and iridium is not.

With the addition of a fifth CO ligand, however, the cobalt tetramer evidently adopts a low-spin configuration vacating d-band orbitals to interact with the ligands leaving an s-band LUMO available for reaction. Thus a dimunition of spin with addition

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[22] Langhoff, S. R.; Bauschlicher, C. W., Jr. *Annu. Rev. Phys. Chem.* **1988**, *39*, 181.

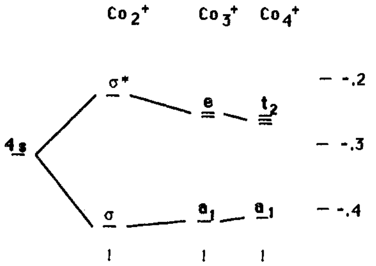

Figure 4. Molecular orbital energy level diagram for Co_n^+. Shown are energy levels for orbitals derived from metal s orbitals calculated by the extended Hückel method as described in the text. The energy scale is in atomic units (hartrees). The trimer is assumed to have C_{3v} symmetry and the tetramer is assumed to have T_d symmetry.

of CO ligands to the clusters is essential to the rationalization of the observed reactivity patterns in terms of our simple MO model. The fact that $Co_4(CO)_6^+$ and $Co_4(CO)_7^+$ are reactive suggests that both d and p orbitals are used in the CO bonding. Otherwise there would be no possibility of s-band orbital vacancies. Finally as enough ligands are added, s-band orbital vacancies become impossible and reactivity disappears. This occurs after 6 and 7 CO ligands for iridium and cobalt respectively.

Reactivity of Co_n^+. Application of this simple MO model to the reactivity of the dimer and trimer Co ions is illustrated in Figure 4. Shown is the splitting between the bonding and antibonding molecular orbitals derived from metal s orbitals as calculated with the extended Hückel method. The parameters given in the Appendix were used except for the bond length. The dimer, trimer, and tetramer have one, two, and three antibonding s-band orbitals, respectively. Extended Hückel theory would give all of these orbitals the same energy if the three clusters all had the same metal–metal bond length. Since the dimer, trimer, and tetramer each have only one bonding s-band orbital we will consider the bond order to be different for the three clusters. We will assume the bonding is predominantly s-band bonding and that the bonding s orbital in each cluster is doubly occupied. We take the dimer as having a bond order of 1 since it has one doubly occupied orbital binding the two atoms. Taking the bond order to be the number of doubly occupied bonding orbitals divided by the number of edges ("bonds") gives $^1/_3$ and $^1/_6$ for the bond orders for the trimer and the tetramer. Taking the bond order to be the number of bonding electrons divided by the number of atoms bound gives $^2/_3$ and $^1/_2$ for the bond orders for the trimer and tetramer. Our conclusion is not sensitive to which of these sets of bond orders we choose. Lacking a criterion for choosing between them we average the "edge number" and "atom number" bond orders to get $^1/_2$ and $^1/_3$ for bond orders for the trimer and tetramer. Pauling's bond order–bond length relation[23] then gives 2.21, 2.39, and 2.50 Å for the dimer, trimer, and tetramer bond lengths. These bond lengths give the relative energies of the s-band orbitals shown in Figure 4.

The important feature in Figure 4 is the relatively high energy of the σ* antibonding orbital in Co_2^+, which should consequently be a relatively poor acceptor. It is thus consistent with the model that Co_2^+ would be less reactive than the other clusters as experimentally observed. Co_2^+ does not react at an observable rate while Co^+, Co_3^+, and Co_4^+ all react efficiently (Table I). A similar effect should be present in the iridium cluster ions, but it should be less pronounced because of the importance of the d orbitals in iridium bonding and because all of the iridium cluster orbitals are lower in energy than the corresponding cobalt cluster orbitals. In fact, the Ir_2^+ rate constant is only slightly less than the Ir_3^+ and Ir_4^+ rate constants (Table I).

The photoelectron spectrum of Co_2^- suggests a $(3d)^{15}(4s\sigma_g)^2(4s\sigma_u{}^*)^1$ configuration for Co_2.[24] This, of course, supports the picture of bonding in Co_2^+ discussed above. In particular it supports a $4s\sigma_u{}^*$ LUMO for Co_2^+.

This rationale for the inertness of Co_2^+ toward alkanes in thermal bimolecular encounters is not inconsistent with the observed reactivity of Co_2^+ toward H_2 in translationally driven processes.[25] The Co_2H^+ product appears at its thermochemical threshold and increases in intensity with increasing energy. At the thermochemical threshold for the Co_2H^+ product there is of necessity enough energy in the collision complex to form the oxidative addition transition state (assuming that $Co_2H_2^+$ is no higher in energy than $Co_2H^+ + H$). There is an empty $\sigma^*Co_2^+$ antibonding orbital which correlates with the filled σ H_2 orbital and hence with the oxidative addition transition state. Thus the model does not imply that energy in excess of the thermochemical threshold is required to drive the reaction to Co_2H^+ and H. The model does imply that the Co_2^+ LUMO is too high in energy to render the oxidative addition transition state accessible to *thermal* reactants.

Reactivity of $Co_2(CO)^+$. While Co_2^+ is unreactive toward alkanes, $Co_2(CO)^+$ reacts efficiently.[1b] This effect can also be simply rationalized in terms of the model. We postulate that the CO ligand is attached to one end of the Co_2^+ and has the effect of weakening the metal–metal interaction. The antibonding $\sigma^*Co_2^+$ orbital consequently drops in energy becoming a suitable acceptor for oxidative addition to a C–H bond. According to this view $Co_2(CO)^+$ correlates with ground states of Co^+ ($3d^8$ ^3F) and Co(CO), and the metal–metal bond is primarily electrostatic while the Co–CO bond is primarily π back-donation.

Reactivity of Other Dimer and Trimer Ions. The failure of $FeCo^+$,[2b] FeV^+,[2c] and $FeCu^+$[2d] to react with alkanes may similarly result from a 4sσ* LUMO that is too high in energy to initiate reaction. Co^+, V^+, and Cu^+ have (3d),[8] (3d),[4] and $(3d)^{10}$ ground states. Correlating those with the $(3d)^6(4s)^2$ ground state of Fe gives $(3d)^{14}(4s\sigma)^2$, $(3d)^{10}(4s\sigma)^2$, and $(3d)^{16}(4s\sigma)^2$ configurations for $FeCo^+$, FeV^+, and $FeCu^+$, respectively. Thus they all are expected to have a 4sσ* LUMO, and similar to the Co_2^+ case this antibonding orbital may not be a sufficiently good acceptor to initiate reaction with alkanes. The reactivity of $FeCo_2^+$[2a] with alkanes may then be rationalized by bond order arguments analogous to those applied to Co_3^+ above.

$FeCo^+$,[2b] FeV^+,[2c] and $FeCu^+$[2d] each react to dehydrogenate olefins, which are more energetic reagents than alkanes. Olefins have relatively weak allylic C–H bonds which may provide sufficiently good donor HOMOs that they can interact with the high-energy LUMOs of the metal dimers. This reactivity with olefins is thus consistent with our frontier orbital model.

The failure of Mn_2^+ to react[1a] can be rationalized in terms of similar arguments. Correlating the $(3d)^5(4s)^1$ and $(3d)^5(4s)^2$ ground-state configurations of Mn^+ and Mn gives a $(3d)^{10}(4s\sigma)^2(4s\sigma^*)^1$ configuration for Mn_2^+. A partially occupied 4sσ* orbital will not be a good acceptor even if it is at low energy. Hence the failure of Mn_2^+ to react. Furthermore, Mn_2^+ reacts with alcohols to form $Mn(ROH)^+$, breaking the metal-to-metal bond.[26] This behavior is consistent with a singly occupied antibonding orbital which both reduces reactivity and weakens the metal-to-metal bond. Co_2^+, on the other hand, reacts with alcohols to form olefin complexes with the dimer ion,[27] emphasizing the difference in the bonding of Mn_2^+ and Co_2^+.

The reactivity of $FeLa^+$ with alkanes[2e] emphasizes the limitations of the generalizations we have been making. Correlating the $(3d)^6(4s)^2$ ground state of Fe with the $(5d)^2$ ground state of La^+ gives a ground state of the dimer with eight "d" electrons and two "s" electrons. It might be expected that a high-energy antibonding σ* LUMO would result as in the first-row dimers. There are only eight "d" electrons, however, and even if they are not spin paired there will be at least one vacant d orbital. The d orbitals are more important in bonding in early transition metal

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and in second- and third-row transition metals. In fact the d and s orbitals in La^+ are very close in energy (two $(5d)^1(6s)^1$ states are lower than the $J = 4$ state of the $(5d)^2\ {}^3F$ ground state). The La^+ could use one vacant s–d hybrid to bond to Fe and the other vacant s–d hydrid would be only slightly perturbed from the energy of the LUMO in the free ion. Hence the dimer is reactive with alkanes, as is the free ion. It is probably the case that dimer ions with fewer than ten d electrons will in general behave differently than dimers with more than ten d electrons just as atomic ions with fewer than five d electrons behave differently than those with more than five d electrons.[28]

Summary and Conclusions

The cobalt and iridium tetrameric cluster ions are similar in that addition of 7 or more CO ligands in the Ir case and 8 or more CO ligands in the Co case prevents reaction with cyclohexane. The tetrameric clusters differ in that the Co clusters with 2, 3, and 4 CO ligands are unreactive while the corresponding Ir clusters react at an observable but, in the case of two and three CO ligands, reduced rate. The two metals also differ in that the Co dimer ion is unreactive while $Co_{1,3,4}^+$ and Ir_{2-4}^+ are all reactive.

A simple frontier MO model can rationalize the differences in the behavior of the clusters of the two metals. The MO model assumes that reactivity requires an acceptor LUMO derived from metal s orbitals in the cluster. A cluster will not react if all the s-band orbitals are occupied or if the LUMO has a low orbital electron affinity. Relative energies of the s-band orbitals are estimated by using extended Hückel theory. Some features of the model and assumptions made consistent with generally accepted notions about transition metals are as follows: (1) In oxidative addition a critical interaction is that between an empty metal s orbital and the filled σ bonding orbital of the species to which addition occurs. (2) Bonding in late-first-row transition elements derives more form s–s interactions than from d–d or s–d interactions. For third-row transition elements interactions with both s and d orbitals are important. (3) Coordinatively unsaturated transition-metal species are high spin, and low spin becomes more probable with additional CO ligands.

The model gives filled or high-energy s-band orbitals for the species that are observed to be unreactive and low-energy unfilled s-band orbitals for species that are observed to be reactive. In particular the failure of $Co_2(CO)_{2-4}^+$ to react with cyclohexane is rationalized in terms of high-energy or filled s-band orbitals. The contrasting reactivity of $Co_4(CO)_5^+$ is attributed to a low-spin state stabilized by the CO ligands.

The previously reported failure of Co_2^+ [1a] to react and the reactivity of $Co_2(CO)^+$ [1b] can be rationalized in terms of the ability of their s-band LUMOs to accept electron density. The previously reported failure of FeM^+ (M = Co,[2b] V,[2c] and Cu[2d]) to react with alkanes and the reactivity of Co_2Fe^+ [2a] can be similarly rationalized. The reactivity of $laFe^+$ [2e] suggests limitations on our model when applied to early and third-row transition elements.

Appendix

The Co 4s and 3d valence orbital ionization energies used (8.94 and 11.26 eV, respectively) are statistically weighted averages of the ionization energies for a 4s or 3d electron from all the states derived from the $3d^74s^2$ ground configuration of a Co atom.[29] Finding very limited data in the literature on the orbital ionization potentials of Ir we used values (10.18 ev and 12.5 eV for 6s and 5d respectively) obtained by subtracting from the Co orbital ionization energies the difference between the Ir and Co atomic ionization potentials. Overlap integrals were calculated numerically using orbital exponents recommend by Summerville and Hoffmann[30] for Co and those recommended by Basch and Gray[31] for Ir. The overlaps were calculated by direct numerical integration. The Wolfsberg Helmholtz constant was taken as 1.75.

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