

means that the reaction is simple and does not involve a rearrangement. The energy of the benzyl ion, listed in Table II, is reasonably well known from both recent PEPICO studies²⁴ as well as from the measured ionization energy of the benzyl radical.²⁵

Over the energy range in which the $C_7H_7^+$ ion is observed, the reaction is already rapid. Thus, we were not able to determine the absolute rate of dissociation. On the other hand, we can determine the relative rates of $C_7H_8^+$ and $C_7H_7^+$ formation. These are given in the breakdown diagram in Figure 4. Furthermore, we can extrapolate the measured rates for m/z 92 formation at low energies into the high-energy region by assuming that the reaction mechanism remains the same over this energy range. The smooth change in the breakdown diagram, in fact, supports a constant reaction mechanism.

In Figure 8 we show the calculated rate of $C_7H_8^+$ formation up to 16 eV. By combining these calculated rates with the formation from the breakdown diagram, we can determine the rate of $C_7H_7^+$ ion formation. These rates, given as points in Figure 8, are thus obtained by a combination of experimental and calculated information. We can now attempt to fit the rate for $C_7H_7^+$ production with the RRKM/QET calculation. Two $C_3H_7^*$ radicals can accompany the production of the benzyl (m/z 91) ion, $n-C_3H_7^*$ or $i-C_3H_7^*$, which are associated with activation energies of 1.61 and 1.48 eV, respectively. In view of the high ion internal energies and therefore high dissociation rates involved in this reaction, it seems most likely that the direct bond cleavage produces the higher energy $n-C_3H_7^*$ radical. With this assumption, the transition-state frequencies were varied until the "measured" m/z 91 rates in Figure 8 were matched. The best fit was obtained when the transition-state frequencies were lower than those of the molecular ion (see Table I). This is consistent with a simple bond-breaking mechanism and leads to a ΔS^\ddagger of + 3.5 cal/K. Considering the many assumptions involved in both the "experimental" and calculated rates, the fit is quite satisfactory.

V. Conclusions

The rate measurements and the breakdown diagram for the dissociation of the *n*-butylbenzene ion have shown that, at low energies, the reaction proceeds via a tight transition state to produce the methylene-1,3-cyclohexadiene ion and propene. The analysis of the small kinetic energy release reported by Holmes and Osborne²⁹ indicates that this reaction proceeds with no reverse activation energy. This is somewhat odd, given the very negative entropy of activation associated with this reaction. Normally, very negative activation entropies (tight transition states) are accompanied by large reverse activation energies.³¹ These facts suggest that the rate-determining step is an isomerization to a structure that is more stable than the dissociation products, so that the final dissociation proceeds with no reverse activation energy.

The threshold for the m/z 91 product ion lies at 0.6 eV above the m/z 92 onset, which agrees with the conclusion of Chen et al.⁹ Both energetic and mechanistic considerations are consistent with the production of the benzyl ion and $n-C_3H_7^*$ via a direct bond cleavage reaction.

The accurate branching ratio for the m/z 92 and 91 ions has been measured from 11 to 16 eV. These results improve upon earlier ICR photodissociation and charge-exchange measurements for this ratio and allow for a more accurate use of this branching ratio as a thermometer for measuring the internal energy content of the *n*-butylbenzene ion in chemical reactions.

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Relationships between Bond Energies in Coordinatively Unsaturated and Coordinatively Saturated Transition-Metal Complexes: A Quantitative Guide for Single, Double, and Triple Bonds[†]

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A prescription is presented for converting M^+-X bond energies (from experiment or theory) in *unsaturated* complexes to M^+-X bond energies appropriate for coordinatively *saturated* organometallic compounds. The theoretical basis for the predicted conversion factors originates from quantitatively evaluating the consequences of (i) the loss of high-spin coupling (exchange energy) between valence electrons on the unsaturated transition-metal ion subsequent to the formation of covalent metal-ligand bonds, (ii) the cost (promotional energy) of bonding to a low-lying excited state of the metal ion (either s^1d^{n-1} or d^n) instead of to the ground electronic state, and (iii) the loss of high-spin coupling in coordinatively saturated transition-metal complexes upon bond formation (assuming a d^n valence electron configuration). These predictions should be most useful for *covalent* metal-ligand bonds in complexes where the metal has at least a +1 oxidation state and where the ligands of interest have electronegativities comparable to carbon or hydrogen. This method is *not* appropriate for prediction of bond strengths where the bonds are primarily of ionic or donor-acceptor character.

I. Introduction

Thermochemical data for organotransition-metal compounds are sparse, especially for the coordinatively saturated complexes which are often the important players in transition-metal-catalyzed reaction chemistry. However, a growing list of metal-ligand bond

energies is becoming available for gas-phase metal ions with one ligand attached (M^+-X).¹⁻⁴ The bond energies have been de-

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terminated in a variety of ways, including (i) the translational energy dependence of endothermic reactions in ion beam experiments,¹ (ii) ion cyclotron resonance (ICR) measurements of proton affinities to derive metal-hydrogen bond strengths,² (iii) bracketing bond energies by using Fourier transform mass spectrometry (FTMS) to study chemical reactions,³ and (iv) photodissociation studies which yield bond energies from photoappearance thresholds.⁴

While bond energies derived from the above techniques are useful for interpreting the chemistry of gas-phase, highly unsaturated, metal ion complexes, it is unclear how these values can be used for predicting the thermochemistry of the majority of organometallic species, namely, for coordinatively saturated, "18-electron" complexes. In order to clarify this relationship, we present a prescription for the conversion of the experimentally observed or theoretically calculated values for coordinatively unsaturated transition-metal-ligand bond energies to those appropriate for coordinatively saturated transition-metal-ligand bond strengths, based on examining the differential exchange and promotional costs (vide infra) inherent to bond breaking/making events. For main-group X-H bond energies, Goddard and Harding⁵ showed that a similar approach using only differential exchange leads to excellent quantitative predictions of trends in the bond strengths of XH_n as a function of n .

We commence with some background on the energetics of bonding to high-spin metal ions, concentrating on the costs due to loss of high-spin coupling between valence electrons on the metal center. We also consider whether it is energetically feasible to form bonds to low-lying excited states of the metal ions (either s^1d^{n-1} or d^n). The energetics involved in forming single, double, and triple bonds to first- and second-row transition metals (Sc-Ni and Y-Pd) are computed from ab initio calculations of intraatomic exchange integrals and from experimental excitation energies for both the s^1d^{n-1} and d^n states of M^+ . We then predict, taking the lowest cost for a given metal and a given bond multiplicity, the quantity ΔK which must be added to bond energies found for the completely unsaturated M^+-X species

$$D_{M-X}^{\text{sat}} = D_{M-X}^{\text{unsat}} + \Delta K \quad (1)$$

in order to obtain estimates for the corresponding bond energies in coordinatively saturated organometallic complexes. Finally, we conclude by comparing our predictions from this method with some of the few metal-ligand bond energies available for 18-electron complexes.

II. Description of the Method

In a recent paper, Carter and Goddard⁶ compared the $M=CH_2$ bond energy found for a completely unsaturated molecule, $RuCH_2^+$, with that of a (model) coordinatively saturated complex, $(Cl)(H)Ru^+CH_2$. As discussed in ref 6, the *valence bond* (VB) view of oxidation states assigns an oxidation state to the metal of 0, +1, or +2, corresponding to removal of only s-electrons (which have a much lower ionization potential than the d-electrons). Each ligand is initially considered neutral with electronegative ligands, such as Cp ($\eta^5-C_5H_5$) or Cl, allowed to ionize the metal up to M(II), while less electronegative groups such as alkyl or hydrogen form covalent bonds to unpaired d-electrons on the metal. Closed-shell ligands such as CO or PR_3 donate into empty s and p metal orbitals to reach coordinative saturation. The method presented here will apply to either coordinatively saturated, 18-electron complexes or to less saturated complexes with a singlet ground state.

Thus, for the two molecules mentioned above, Ru is in the +1 oxidation state, with $Ru^+=CH_2$ having a 2A_2 ground state, while we model a coordinatively saturated complex with a less saturated complex in a singlet electronic state: $(Cl)(H)Ru=CH_2$. While the metal-carbon bond character is essentially identical in both complexes, the bond energies for the unsaturated and saturated complexes are predicted to differ by 16 kcal/mol, essentially the differential intraatomic exchange loss. This is typical; as discussed below, the correction term ΔK can be as large as 60 kcal/mol, yet we find that changes in metal valence electron spin coupling and (possible) promotional energies adequately account for the trends in transition-metal-ligand bond energies.

For isolated metal ions (or atoms), the ground electronic state always has the singly occupied valence orbitals coupled to form the highest spin state, as predicted by Hund's rule (e.g., Ru^+ in its ground-state configuration of $4d^7$ has $S = 3/2$). The quantitative basis for Hund's rule is the energy lowering contributed by exchange interactions in the electronic energy expression:⁷

$$E_{\text{ex}} = -\sum_{i>j} K_{i\alpha,j\alpha} - \sum_{i>j} K_{i\beta,j\beta} \quad (2)$$

These exchange terms are only nonzero between electrons of the same spin. Therefore, the lowest energy state of M^+ , whether it be s^1d^{n-1} or d^n , is always high spin.

For m high-spin-coupled electrons, there are $m(m-1)/2$ exchange terms, each leading to a lowering of the electronic energy. However, upon covalent bond formation, some of this exchange energy is lost, weakening the intrinsic metal-ligand bond. This loss of exchange energy results from necessarily singlet coupling the electrons in each metal-ligand bond pair. On average, then, the metal electrons involved in covalent bonding have α (up) spin half of the time and β (down) spin half of the time. This results in partial quenching of intraatomic exchange stabilization. The magnitude of this effect depends on the number of other (non-bonding) singly occupied orbitals on the metal (as well as on the magnitude of each exchange term), and therefore it depends on the degree of saturation at the metal center.

For example, a two-electron triplet ($\chi_{\text{spin}} = \alpha\alpha$) has one exchange term ($-K$) in its energy expression. Making a single bond to one of these electrons changes the spin coupling between the two formerly high-spin electrons to

$$\chi_{\text{spin}} = \frac{1}{2}[\alpha\alpha + \alpha\beta] \quad (3)$$

due to the averaged spin of the bonding electron. This spin function results in an exchange contribution of only $-1/2K$ and a net energy destabilization of $+1/2K$. A three-electron quartet ($\chi_{\text{spin}} = \alpha\alpha\alpha$) has a $-3K$ exchange energy. Forming a single covalent bond to the quartet results in the spin function

$$\chi_{\text{spin}} = \frac{1}{2}[\alpha\alpha\alpha + \alpha\alpha\beta] \quad (4)$$

with an exchange energy now of only $-2K$, a destabilization of $+1K$. Thus, we see that the exchange loss grows as the number of unpaired electrons grows (or as the degree of unsaturation grows).

In this manner, it is easy to compute the loss of exchange energy upon covalent bond formation for single, double, and triple bonds by merely considering the effect of averaged spin coupling for bonding electrons. In the case of transition metals, d-d exchange terms are nearly always much larger than s-d exchange terms. Thus, for metals with a high-spin d^n ground state, it may be advantageous to promote an electron from a valence d-orbital to the valence s-orbital (forming the s^1d^{n-1} state), since bonding to an s-electron will result in less exchange loss. Therefore, we shall

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(7) The changes in electrostatic energy from configuration to configuration involve changes in both Coulomb and exchange integrals, and hence it is not strictly correct to imply that only exchange interactions are responsible for high-spin ground states. However, use of averaged exchange terms (weighted by the number of terms of a given type, e.g., one $\delta\delta$ versus four $\pi\delta$) from averaged-field orbitals (see ref 11 below), leads to sufficiently accurate results for our considerations and keeps the method simple enough to apply easily (accuracy of $\sim 1-2$ kcal/mol).

TABLE I: Symbolic Exchange and Promotional Costs for the Formation of Single, Double, and Triple Covalent Bonds to s^1d^{n-1} and d^n Metal Ions^a

| M ⁺ | ground state | E_{lost} (single bond) | | E_{lost} (double bond) | | E_{lost} (triple bond) | |
|-----------------------------------|--------------|---------------------------------|--------------------|---------------------------------|--------------------|---------------------------------|---------------|
| | | s^1d^{n-1} | d^n | s^1d^{n-1} | d^n | s^1d^{n-1} | d^n |
| Sc ⁺ | s^1d^1 | $1/2sd$ | $E_p + 1/2dd$ | $1/2sd$ | $E_p + 1/2dd$ | | |
| Y ⁺ | s^2 | $E_p(s^1d^1) + 1/2sd$ | $E_p(d^2) + 1/2dd$ | $F_p(s^1d^1) + 1/2sd$ | $E_p(d^2) + 1/2dd$ | | |
| Ti ⁺ , Zr ⁺ | s^1d^2 | $1sd$ | $E_p + 1dd$ | $1sd + 1/2dd$ | $E_p + 3/2dd$ | $1sd + 1/2dd$ | $E_p + 3/2dd$ |
| V ⁺ , Nb ⁺ | d^4 | $E_p + 3/2sd$ | $3/2dd$ | $E_p + 3/2sd + 1dd$ | $5/2dd$ | $E_p + 3/2sd + 3/2dd$ | $3dd$ |
| Cr ⁺ , Mo ⁺ | d^5 | $E_p + 2sd$ | $2dd$ | $E_p + 2sd + 3/2dd$ | $7/2dd$ | $E_p + 2sd + 5/2dd$ | $9/2dd$ |
| Mn ⁺ , Tc ⁺ | s^1d^5 | $5/2sd$ | $E_p + 3/2dd$ | $5/2sd + 2dd$ | $E_p + 5/2dd$ | $5/2sd + 7/2dd$ | $E_p + 3dd$ |
| Fe ⁺ | s^1d^6 | $2sd$ | $E_p + 1dd$ | $2sd + 3/2dd$ | $E_p + 3/2dd$ | $2sd + 5/2dd$ | $E_p + 3/2dd$ |
| Ru ⁺ | d^7 | $E_p + 2sd$ | $1dd$ | $E_p + 2sd + 3/2dd$ | $3/2dd$ | $E_p + 2sd + 5/2dd$ | $3/2dd$ |
| Co ⁺ , Rh ⁺ | d^8 | $E_p + 3/2sd$ | $1/2dd$ | $E_p + 3/2sd + 1dd$ | $1/2dd$ | $E_p + 3/2sd + 3/2dd$ | |
| Ni ⁺ , Pd ⁺ | d^9 | $E_p + 1sd$ | $0dd$ | $E_p + 1sd + 1/2dd$ | | $E_p + 1sd + 1/2dd$ | |

^a E_{lost} = total energy lost upon forming single, double, or triple bonds to the high spin valence states of M⁺, in the form of promotional energy (E_p) and exchange energy $K_{sd} \equiv sd$ and $K_{dd} \equiv dd$.

consider the costs for forming single, double, and triple covalent bonds to the first- and second-row metal ions in both the high-spin s^1d^{n-1} and d^n electronic states.

Table I symbolically displays the cost of covalent bond formation in these cases, where E_{lost} is the sum of the exchange and any promotional (excitation) energy destabilization. Exchange loss peaks in the middle of each row, and hence we expect the Cr and Mn triads to have the weakest bonds (in completely unsaturated metal ion complexes), consistent with many experimental¹⁻⁴ and theoretical⁸⁻¹⁰ observations. Table II provides ab initio values of $sd \equiv K_{sd}^{\text{av}}$ and $dd \equiv K_{dd}^{\text{av}}$ from averaged-field Hartree-Fock calculations on each ion ($\text{Sc}^+ - \text{Ni}^+$ and $\text{Y}^+ - \text{Pd}^+$)¹¹ and excitation energies, $E_p(s^1d^{n-1} \rightarrow d^n$ and $d^n \rightarrow s^1d^{n-1}$).¹² These numbers are used to evaluate each entry in Table I, with the results displayed in Table III. For the remaining discussion, we will utilize the values in boldface, which represent the lowest energy cost to form a particular bond to a particular metal ion.

In order to predict metal-ligand bond strengths for saturated systems, we first must define an *intrinsic* (exchangeless) bond energy

$$D_{\text{int}} = D^{\text{unsat}} + E_{\text{lost}}^{\text{unsat}} \quad (5)$$

where D^{unsat} is the observed bond strength of the unsaturated complex and E_{lost} is taken from Table III. D_{int} is the bond energy one would observe if no promotional or exchange losses were incurred. To obtain the bond energy of a corresponding saturated complex, D^{sat} , we must subtract from D_{int} the exchange and/or promotional costs associated with forming covalent bonds in the *saturated system*. Therefore, we obtain

$$\begin{aligned} D^{\text{sat}} &= D_{\text{int}} - E_{\text{lost}}^{\text{sat}} \\ &= D^{\text{unsat}} + (E_{\text{lost}}^{\text{unsat}} - E_{\text{lost}}^{\text{sat}}) \\ &= D^{\text{unsat}} + \Delta K \end{aligned} \quad (6)$$

In order to calculate $E_{\text{lost}}^{\text{sat}}$, we assume that the metal prefers a d^n configuration in a saturated complex, since repulsive interactions between the metal and its ligands should disfavor occupation of the valence s-orbital. The spin state associated with the metal electrons in the coordinatively saturated complex is consistent with the number of covalent bonds formed, e.g., one unpaired d-electron for a single bond, two unpaired d-electrons for a double bond, and three unpaired d-electrons for a triple bond. Bonding to this d^n configuration in the saturated complex leads

TABLE II: Exchange (K_{sd}^{av} and K_{dd}^{av}) and Promotional (E_p) Energies in s^1d^{n-1} and d^n Metal Ions (kcal/mol)^a

| M ⁺ | state | valence | | E_p |
|-----------------|----------------|------------------|--------------------------------|-------|
| | | electron confign | $K_{sd}^{\text{av}} \equiv sd$ | |
| Sc ⁺ | ³ D | s^1d^1 | 7.3 | 0.0 |
| | ³ F | d^2 | | 13.8 |
| Ti ⁺ | ⁴ F | s^1d^2 | 5.7 | 0.0 |
| | ⁴ F | d^3 | | 2.5 |
| V ⁺ | ⁵ D | d^4 | | 0.0 |
| | ⁵ F | s^1d^3 | 5.5 | 7.8 |
| Cr ⁺ | ⁶ S | d^5 | | 0.0 |
| | ⁶ D | s^1d^4 | 5.0 | 35.1 |
| Mn ⁺ | ⁷ S | s^1d^5 | 4.8 | 0.0 |
| | ⁵ D | d^6 | | 41.7 |
| Fe ⁺ | ⁶ D | s^1d^6 | 5.0 | 0.0 |
| | ⁴ F | d^7 | | 5.8 |
| Co ⁺ | ³ F | d^8 | | 0.0 |
| | ⁵ F | s^1d^7 | 4.8 | 9.9 |
| Ni ⁺ | ² D | d^9 | | 0.0 |
| | ⁴ F | s^1d^8 | 4.8 | 25.1 |
| Y ⁺ | ³ D | s^1d^1 | 9.9 | 3.7 |
| | ³ F | d^2 | | 24.0 |
| Zr ⁺ | ⁴ F | s^1d^2 | 9.2 | 0.0 |
| | ⁴ F | d^3 | | 7.1 |
| Nb ⁺ | ⁵ D | d^4 | | 0.0 |
| | ⁵ F | s^1d^3 | 8.9 | 7.6 |
| Mo ⁺ | ⁶ S | d^5 | | 0.0 |
| | ⁶ D | s^1d^4 | 8.5 | 36.7 |
| Tc ⁺ | ⁷ S | s^1d^5 | 8.3 | 0.0 |
| | ⁵ D | d^6 | | 11.8 |
| Ru ⁺ | ⁴ F | d^7 | | 0.0 |
| | ⁶ D | s^1d^6 | 7.5 | 25.1 |
| Rh ⁺ | ³ F | d^8 | | 0.0 |
| | ⁵ F | s^1d^7 | 7.5 | 49.1 |
| Pd ⁺ | ² D | d^9 | | 0.0 |
| | ⁴ F | s^1d^8 | 7.3 | 73.6 |

^a K_{sd}^{av} and K_{dd}^{av} are ab initio values for the sd and dd exchange integrals from averaged-field Hartree-Fock calculations (ref 11). The dd exchange terms have been averaged over the five types of interactions (i.e., $\sigma\delta$, $\sigma\pi$, $\delta\pi$, $\pi\bar{\pi}$, and $\delta\delta$). E_p is the (J -weighted) relative energy of the M⁺ excited state (ref 12).

to the following exchange losses (and no promotional costs since we assume a d^n ground state):

$$E_{\text{lost}}^{\text{sat}} = K_{\text{lost}}^{\text{sat}} = \begin{cases} 0K_{dd}, & \text{single bond} \\ 0.5K_{dd}, & \text{double bond} \\ 1.5K_{dd}, & \text{triple bond} \end{cases} \quad (7)$$

Using (7) and the values listed in Table III, we can calculate ΔK of (6) to determine the conversion factors which transform unsaturated bond energies into saturated bond energies, for each bond multiplicity and for each first- and second-row transition metal. These differential exchange energies are listed in Table IV. Adding these values to gas-phase M⁺-X bond energies allows one to estimate metal-ligand bond strengths in 18-electron, coordinatively saturated complexes (or in singlet states of unsaturated complexes). To this end, Table V lists observed unsaturated bond strengths and predicted saturated bond strengths for a number

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(12) Excitation energies (weighted over J -values) are taken from Moore, C. E. *Atomic Energy Levels*, NSRDS-NBS-35, 1971.

TABLE III: Exchange and Promotional Costs (kcal/mol) for the Formation of Single, Double, and Triple Covalent Bonds to s^1d^{n-1} and d^n Metal Ions^a

| M ⁺ | ground state | $E_{\text{lost}}(\text{single})$ | | $E_{\text{lost}}(\text{double})$ | | $E_{\text{lost}}(\text{triple})$ | |
|-----------------|--------------|----------------------------------|-------------|----------------------------------|-------------|----------------------------------|-------------|
| | | s^1d^{n-1} | d^n | s^1d^{n-1} | d^n | s^1d^{n-1} | d^n |
| Sc ⁺ | s^1d^1 | 3.7 | 19.5 | 3.7 | 19.5 | | |
| Ti ⁺ | s^1d^2 | 5.7 | 17.8 | 13.3 | 22.5 | 13.3 | 22.5 |
| V ⁺ | d^3 | 16.1 | 22.5 | 32.9 | 37.5 | 41.3 | 45.0 |
| Cr ⁺ | d^4 | 45.1 | 33.0 | 72.7 | 57.8 | 91.1 | 74.3 |
| Mn ⁺ | s^1d^5 | 12.0 | 68.1 | 51.6 | 85.7 | 81.3 | 94.5 |
| Fe ⁺ | s^1d^6 | 10.0 | 24.6 | 41.4 | 34.0 | 62.3 | 34.0 |
| Co ⁺ | d^7 | 17.1 | 10.0 | 39.2 | 10.0 | 50.3 | |
| Ni ⁺ | d^8 | 29.9 | 0.0 | 41.6 | | 41.6 | |
| Y ⁺ | s^2 | 8.7 | 28.7 | 8.7 | 28.7 | | |
| Zr ⁺ | s^1d^2 | 9.2 | 17.9 | 15.0 | 23.3 | 15.0 | 23.3 |
| Nb ⁺ | d^4 | 21.0 | 18.3 | 34.0 | 30.5 | 40.5 | 36.6 |
| Mo ⁺ | d^5 | 53.7 | 26.8 | 75.0 | 46.9 | 89.2 | 60.3 |
| Tc ⁺ | s^1d^5 | 20.8 | 33.3 | 51.4 | 47.6 | 74.4 | 54.7 |
| Ru ⁺ | d^7 | 40.1 | 14.6 | 63.5 | 21.9 | 79.1 | 21.9 |
| Rh ⁺ | d^8 | 60.4 | 8.1 | 77.5 | 8.1 | 86.1 | |
| Pd ⁺ | d^9 | 80.9 | 0.0 | 89.9 | | 89.9 | |

^a E_{lost} = total energy lost upon forming single, double, or triple bonds to the high spin valence states of $M^+ = E_p + K_{\text{lost}}$ (promotional energy and exchange energy losses). The values in boldface correspond to the least energy cost for M^+ to form a given type of covalent bond.

TABLE IV: Predicted Differential Exchange Energies in kcal/mol ($\Delta K = E_{\text{lost}}^{\text{unsat}} - K_{\text{lost}}^{\text{sat}}$) for the Formation of Single, Double, and Triple Covalent Bonds in Coordinatively Saturated Metal Complexes^a

| M ⁺ | $\Delta K = E_{\text{lost}}^{\text{unsat}} - K_{\text{lost}}^{\text{sat}}$ | | |
|-----------------|--|-------------|-------------|
| | single bond | double bond | triple bond |
| Sc ⁺ | 3.7 | -2.0 | |
| Ti ⁺ | 5.7 | 6.7 | -6.7 |
| V ⁺ | 16.1 | 25.4 | 18.8 |
| Cr ⁺ | 33.0 | 49.6 | 49.6 |
| Mn ⁺ | 12.0 | 42.8 | 54.9 |
| Fe ⁺ | 10.0 | 24.6 | 5.8 |
| Co ⁺ | 10.0 | 0.0 | 20.3 |
| Ni ⁺ | 0.0 | 31.0 | 9.8 |
| Y ⁺ | 8.7 | 4.1 | |
| Zr ⁺ | 9.2 | 9.6 | -1.2 |
| Nb ⁺ | 18.3 | 24.4 | 18.3 |
| Mo ⁺ | 26.8 | 40.2 | 40.2 |
| Tc ⁺ | 20.8 | 40.5 | 33.3 |
| Ru ⁺ | 14.6 | 14.6 | 0.0 |
| Rh ⁺ | 8.1 | 0.0 | 62.0 |
| Pd ⁺ | 0.0 | 81.4 | 64.3 |

^a Adding ΔK to unsaturated $D(M^+-X)$ gives estimates for saturated $D(M^+-X)$. $E_{\text{lost}}^{\text{unsat}}$ values are taken from Table III. $K_{\text{lost}}^{\text{sat}} = 0K_{\text{dd}}$ for a single bond, $1/2K_{\text{dd}}$ for a double bond, and $3/2K_{\text{dd}}$ for a triple bond (assuming the saturated complex has a local metal electron configuration of d^n). K_{dd} values (for $d^n M^+$) are taken from Table II.

of M^+-H , $M^+=CH_2$, and $M^+\equiv CH$ bonds. We have not included values for gas-phase M^+-CH_3 bond energies, which are much

larger than those expected for saturated $M-CH_3$ bond strengths. This result has been attributed by Mandich et al.^{1d} to the anomalously large stabilization of the metal methyl cation due to the high polarizability of the (approximately spherical) methyl group. In contrast, we believe that the *planar* CH_2 and CH ligands are not as easily polarizable and no extra stabilization is expected in the bare metal cation complexes. The gross trends in Table V are correct for the saturated systems, with the bond energies decreasing as we go across a row and increasing as we go down a column. Some exceptions exist, but given current experimental uncertainties, we believe that these discrepancies tag systems worthy of additional experimental study.

The predictions for saturated bond energies mostly await experimental verification. However, a few bond energies have been measured, and these are compared to our predicted values in Table VI. The agreement is generally quite good, but as this model does *not* account for changes at the metal center due to the electron-withdrawing or electron-donating character of the ancillary ligands, we see variations in the experimentally observed bond strengths as the ligand set is altered.

The largest discrepancies occur for $(CO)_5Fe^+-H$ and $(CO)_4Ni^+-H$, where the most recent experiments yield 72.4 ± 3.6 and 52.8 ± 2.2 kcal/mol, respectively, whereas the theory yields 57.0 ± 4 and 38.5 ± 1.4 kcal/mol. On the other hand, the binary carbonyl hydride bond energies for Cr and Mo agree well with our predictions (55.9 ± 2.4 versus 60.7 ± 2 kcal/mol for Cr and 63.1 ± 2.2 versus 67.8 ± 3 kcal/mol for Mo). Experimental bond energy determinations in these cationic systems rely on the ac-

TABLE V: Predicted Coordinatively Saturated M-X Bond Energies from Coordinatively Unsaturated M-X Bond Energies [$D_{\text{pred}}^{\text{sat}}(M^+-X) = D_{\text{unsat}}^{\text{sat}}(M^+-X) + \Delta K$] in kcal/mol

| M ⁺ | $D_{\text{unsat}}^{\text{sat}}(M^+-H)$ | $D_{\text{pred}}^{\text{sat}}(M^+-H)$ | $D_{\text{unsat}}^{\text{sat}}(M^+=CH_2)$ | $D_{\text{pred}}^{\text{sat}}(M^+=CH_2)$ | $D_{\text{unsat}}^{\text{sat}}(M^+\equiv CH)$ | $D_{\text{pred}}^{\text{sat}}(M^+\equiv CH)$ |
|-----------------|--|---------------------------------------|---|--|---|--|
| Sc ⁺ | 55.3 ± 2^a | 59.0 ± 2 | 97 ± 6^d | 95 ± 6 | | |
| Ti ⁺ | 55.1 ± 2^a | 60.8 ± 2 | 85 ± 6^d | 91.7 ± 6 | | |
| V ⁺ | 47.3 ± 1.4^a | 63.4 ± 1.4 | 76 ± 2^d | 101.4 ± 2 | 114 ± 2^d | 132.8 ± 2 |
| Cr ⁺ | 27.7 ± 2^a | 60.7 ± 2 | $49.6,^e 52 \pm 3^d$ | $99.2, 101.6 \pm 3$ | | |
| Mn ⁺ | 47.5 ± 3.4^a | 59.5 ± 3.4 | 58.4^f | 101.2 | | |
| Fe ⁺ | 47.0 ± 4^a | 57.0 ± 4 | $69.2,^g 82 \pm 5^g$ | $93.8, 106.6 \pm 5$ | 101 ± 7^g | 106.8 ± 7 |
| Co ⁺ | 45.5 ± 2.3^a | 55.5 ± 2.3 | 84 ± 5^g | 84 ± 5 | 100 ± 7^g | 120.3 ± 7 |
| Ni ⁺ | 38.5 ± 1.4^a | 38.5 ± 1.4 | $(86 \pm 6)^h$ | (117 ± 6) | | |
| Y ⁺ | 58 ± 3^a | 66.7 ± 3 | | | | |
| Zr ⁺ | 54 ± 3^a | 63.2 ± 3 | | | | |
| Nb ⁺ | 53 ± 3^a | 71.3 ± 3 | | | | |
| Mo ⁺ | 41 ± 3^a | 67.8 ± 3 | | | | |
| Tc ⁺ | 46.3^b | 67.1 | | | | |
| Ru ⁺ | 41 ± 3^c | 55.6 ± 3 | 73.6^i | 88.2 | | |
| Rh ⁺ | 42 ± 3^c | 50.1 ± 3 | 94 ± 5^j | 94 ± 5 | | |
| Pd ⁺ | 45 ± 3^c | 45 ± 3 | | | | |

^a Reference 1g. ^b Reference 10b. ^c Reference 1d. ^d Reference 1f. ^e Reference 8. ^f Reference 9. ^g Reference 4b. ^h Reference 1b. The value is placed in parentheses to emphasize its uncertainty. ⁱ Reference 6. ^j Reference 3.

TABLE VI: Comparison of Observed and Predicted Coordinatively Saturated (18-Electron) Metal-Ligand Bond Energies (kcal/mol)

| complex | $D_{\text{obsd}}^{\text{sat}}(\text{L}_n\text{M}^+-\text{X})^a$ | $D_{\text{unssd}}^{\text{sat}}(\text{M}^+-\text{X}) = D_{\text{unssd}}^{\text{sat}}(\text{M}^+-\text{X})^b + \Delta K^c$ |
|--|---|--|
| (CO) ₆ Cr ⁺ -H | 55.9 ± 2.4, ^d 58 ± 3 ^e | 60.7 ± 2 |
| (CO) ₆ Mo ⁺ -H | 63.1 ± 2.2, ^d 65 ± 3 ^e | 67.8 ± 3 |
| (CO) ₅ (CH ₃)Mn ⁺ -H | 64.8 ± 2.6, ^d 67 ± 3 ^e | 59.5 ± 3.4 |
| (CH ₃ C ₂ H ₄)(CO) ₃ Mn ⁺ -H | 68.6 ± 3.1, ^d 71 ± 3 ^e | 59.5 ± 3.4 |
| (CO) ₅ (CH ₃)Re ⁺ -H | 71.2 ± 3.1, ^d 73 ± 3 ^e | 67.1 ^f |
| (CO) ₅ Fe ⁺ -H | 72.4 ± 3.6, ^d 74 ± 5 ^e | 57.0 ± 4 |
| Cp(CO) ₂ (CH ₃)Fe ⁺ -H | 51.2 ± 3.3, ^d 53 ± 3 ^e | 57.0 ± 4 |
| Cp ₂ Fe ⁺ -H | 52.4 ± 5, ^d 54 ± 5, ^e 56 ± 5 ^g | 57.0 ± 4 |
| Cp ₂ Ru ⁺ -H | 65.7 ± 3.6, ^d 68 ± 5, ^h 79 ± 5 ^e | 55.6 ± 3 |
| Cl(CH ₂)Ru-H | 54.1 ⁱ | 55.6 ± 3 |
| Cp(CO) ₂ Co ⁺ -H | 57 ± 5, ^h 59.5 ± 2.9, ^d 73 ± 5 ^e | 55.5 ± 2.3 |
| [(CN) ₅ Co-H] ³⁻ ^{aq} | 58 ^j | 55.5 ± 2.3 |
| Cp(CO) ₂ Rh ⁺ -H | 55 ± 5, ^h 69.6 ± 2.9, ^d 80 ± 5 ^e | 50.1 ± 3 |
| (CO) ₄ Ni ⁺ -H | 52.8 ± 2.2, ^k 60.2 ± 2.2, ^d 62 ± 3 ^e | 38.5 ± 1.4 |
| (CO) ₅ Mn ⁺ =CH ₂ | 104 ± 3 ^l | 101.2 |
| (Cl)(H)Ru=CH ₂ | 90.3 ⁱ | 88.2 |

^a Observed M⁺-X bond energy in coordinatively saturated complexes (cs). ^b Observed M⁺-X bond energy in coordinatively unsaturated complexes (cu). ^c ΔK = the differential cost in exchange and promotional energies between cs and cu. ^d Simões, J. A. M.; Beauchamp, J. L., unpublished results. ^e Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 190. ^f Value for $D_{\text{pred}}^{\text{sat}}(\text{Tc}^+-\text{H})$ which should be comparable to $D_{\text{pred}}^{\text{sat}}(\text{Re}^+-\text{H})$. ^g Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4814. ^h Revised version (Beauchamp, J. L., private communication) of footnote e. ⁱ Theoretical value: Carter, E. A.; Goddard, W. A., *Organometallics* **1988**, *7*, 675. ^j de Vries, B. *J. Catal.* **1962**, *1*, 484. ^k Revised according to new value of the adiabatic IP for Ni(CO)₄ from PES spectra (Reutt, J. E.; Wang, L. S.; Lee, Y. T.; Shirley, D. A. *Chem. Phys. Lett.* **1986**, *126*, 399). ^l Stevens, A. E. Ph.D. Thesis, California Institute of Technology, 1981.

curacy of the ionization potentials (IP's) of the neutral carbonyls. Experimental IP data always provide upper bounds to the true adiabatic IP's, since structural relaxation of the resultant cations is not always observed on the time scale of the experiments. (If vibrational fine structure is observed, it is still difficult to determine the 0-0 transition.) Thus, for those cations that have the ability to relax geometrically, the observed IP's of the corresponding neutrals are upper bounds, leading to upper bounds on the bond energies. Since Cr(CO)₆ and Mo(CO)₆ are low-spin octahedral with (t_{2g})⁶ configurations, they are unlikely to change geometries upon ionization. Hence, the measured IP's are close to the adiabatic IP's, leading to adiabatic bond energies. For Fe(CO)₅ and Ni(CO)₄, however, structural relaxation upon ionization is likely, due to the change in occupation of d-orbitals overlapping the ligands [in contrast to Cr(CO)₆ and Mo(CO)₆]. Indeed, recent analysis of the photoelectron spectrum of Ni(CO)₄ led to a decrease in the experimental (CO)₄Ni⁺-H bond energy by 7.4 kcal/mol (due to the decrease in the measured IP) and revealed a distortion from T_d to D_{2d} symmetry upon ionization.¹³ With such structural relaxation occurring, the observed IP's are upper bounds, leading to bond energies that are also upper bounds for Fe and Ni carbonyl hydride cations. To bring the experimental values in line with the theoretically predicted bond energies would require decreasing the observed IP's of Fe(CO)₅ and Ni(CO)₄ by 0.67 and 0.62 eV, respectively.

Finally, another possible explanation for the discrepancies in bond strengths may be due to structural isomerism in which the H is not bound to the metal but rather is protonating a ligand. In this case, the measured bond strength does not reflect a metal-H bond strength at all. This situation provides an alternative reason for the discrepancies found for Fe(CO)₅ and Ni(CO)₄.

III. Summary

A simple method has been derived which accurately predicts bond strengths in *coordinatively saturated* organotransition-metal

complexes from values currently available for coordinatively unsaturated M⁺-X bond strengths. The analysis is based on calculating the differential exchange and promotional losses which necessarily accompany covalent bond formation. The assumptions made in the derivation are (i) that exchange and promotional energy effects dominate orbital hybridization and overlap contributions to the determination of bond strength conversion factors (inaccuracies in the method are no doubt due to this simplifying assumption)¹⁴ and (ii) that metal centers in coordinatively saturated complexes have (low or intermediate spin) dⁿ electronic ground states.

The prescription as outlined above should be appropriate for 18-electron (or singlet states of even electron) metal complexes with oxidation states of at least +1, since zerovalent metal complexes will contain ionic character in the alkyl and H bonds (introducing complications of ionization potentials and electron affinities into the bond strength analysis). The approach is designed for predicting metal-ligand bond energies where the ligand is either a hydrocarbon moiety or hydrogen (i.e., where covalent bonding prevails). It is *not* designed to predict bond strengths for ionic (e.g., cyclopentadienyl, oxo, halide) or donor-acceptor (e.g., CO or Fischer carbene) metal-ligand interactions.

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(13) Reutt, J. R.; Wang, L. S.; Lee, Y. T.; Shirley, D. A. *Chem. Phys. Lett.* **1986**, *126*, 399.

(14) A possible improvement to this method would involve a quantitative assessment of the relative preference for d versus s bonding to each metal, based on the intrinsic (exchangeless) bond strengths. However, such intrinsic bond strengths for s versus d are difficult to extract accurately (see ref 10), and application of the method would be considerably more complicated.