facets present, and it would be worthwhile to consider the data obtained in ref 19 in terms of them.

Acknowledgment is made to the donors of the Petroleum Research fund, administered by the American Chemical Society, for support of this research through a Summer Research Fellowship for J.A.N. A.B.A. owes W. Keith Hall thanks for many stimulating discussions.

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Bonding in Transition-Metal Methylene Complexes. 3. Comparison of Cr and Ru Carbenes; Prediction of Stable $L_nM(CXY)$ Systems[1]

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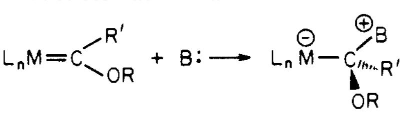
Abstract: The electronic structure of the lowest carbene state of a representative early-transition-metal complex, $CrCH_2^+$ ($^6A_1$ symmetry), has been examined by using ab initio techniques. Its properties reveal a complex with a single σ-donor bond from singlet CH_2 to high-spin (d^5) Cr^+ and no π-back-bond, resulting in a low bond energy (38.7 kcal/mol) and a large carbene–alkylidene state splitting (18.8 kcal/mol). These results are contrasted with Ru carbene (possessing both σ- and π-donor bonds) properties [D_e(Ru=C) = 65.8 kcal/mol and ΔE(carbene–alkylidene) = 12.9 kcal/mol]. This comparison enables, for the first time, a separation of σ-donor bond strengths from π-donor bond strengths. Finally, using only valence electron properties, we are able to predict stabilities of $L_nM(CXY)$ complexes (e.g., how substituents at carbon affect the preference for bridging vs. terminal CXY), discussing trends for the entire transition series.

1. Introduction

Terminal metal carbene and alkylidene complexes are ubiquitous throughout the transition elements.[2] The nomenclatural distinction between "carbene" and "alkylidene" represents a fundamental difference in reactivity.[3] Metal carbene complexes usually behave as electrophiles, with typical reactions including Lewis base adduct formation via attack at the carbon center[4]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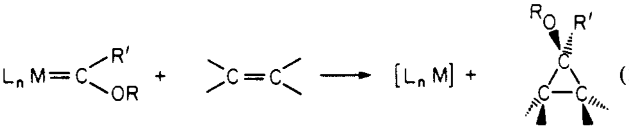
and stoichiometric cyclopropanation of olefins[5]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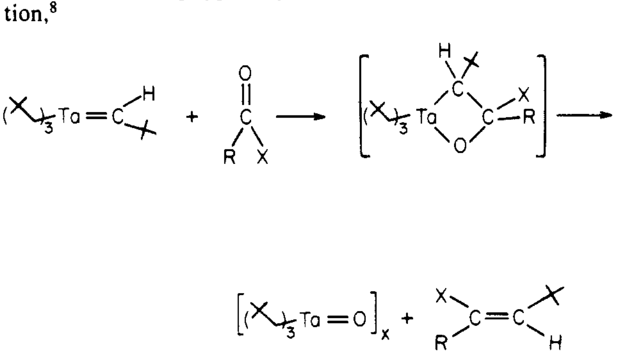
On the other hand, metal alkylidene complexes are nucleophilic, undergoing Wittig-type alkylations,[6,7] Lewis acid adduct formation,[8]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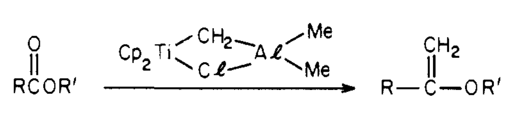
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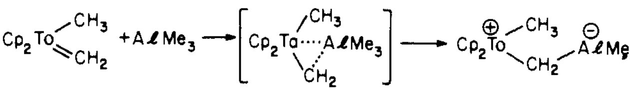
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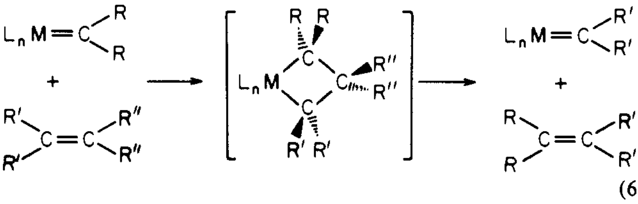
and olefin metathesis.[9]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These two greatly different modes of reactivity reflect a dra-

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† National Science Foundation Predoctoral Fellow, 1982–1985.

(1) (a) Paper 1 of this series: Carter, E. A.; Goddard, W. A., III *J. Phys. Chem.* **1984**, *88*, 1485. (b) Paper 2: Carter, E. A.; Goddard, W. A., III *J. Am. Chem. Soc.* **1986**, *108*, 2180. (c) Earlier work on high-valent alkylidene complexes includes: Rappé, A. K.; Goddard W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 297; **1982**, *104*, 448; **1980**, *102*, 5114.

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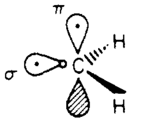
matic difference in the metal–carbon bonding. Conventional design prescriptions call for "low-valent" metal fragments [e.g., $W(CO)_5$] for carbenes and "high-valent" metal moieties (e.g., Cp_2TaR) for alkylidenes in order to maximize stability of the resultant complex. In addition, the presence of a heteroatom on the CXY ligand is known to stabilize carbenes, while alkyl or hydrogen groups are thought to stabilize alkylidene ligands. The combination of a "low-valent" metal fragment with a C(OR)R′ [or $C(NR_2)R'$, etc.] carbene ligand translates into the now-familiar σ-donor bond from the carbene and donor π-back-bond from the "low-valent" metal. As we have shown previously,[1] "high-valent" metals interacting with an alkyl-only-substituted CXY ligand results in an olefinic-type, *covalent* double bond.

These contrasting bonding structures (donor/acceptor for carbene and covalent for alkylidene) are given physical justification via the *valence bond view* of metal–carbene (alkylidene) bonds.

1. Metal Carbenes. The "low-valent" metal fragment is generally surrounded by closed-shell ligands (such as CO or PR_3). In this environment, the metal atom is forced into a *low-spin, d^n electronic state* to minimize Pauli repulsions (orthogonality) with ligand lone pairs. A low-spin, d^n metal atom has doubly occupied d-orbitals set up for π-back-bonding to a carbene (or other ancillary ligands with low-lying acceptor orbitals). The carbene fragment will be a σ-donor as desired, if the *singlet* state of the CXY ligand is the ground state. The purpose of the electronegative heteroatom linkage (e.g., X = OR, NR_2, F, Cl) is to stabilize the singlet (σ^2) state of CXY. The two lowest states of CXY are triplet ($\sigma\pi$) and singlet (σ^2).



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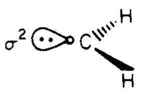

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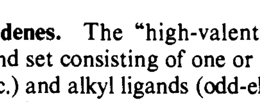
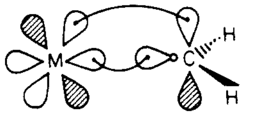
If either X or Y is electron-withdrawing, then the C–X and C–Y bonds will involve mostly p-character on carbon [lower ionization potential (IP) than s]. In addition, the $p\pi$ lone pairs on X (or Y) will donate electron density into the C $p\pi$-orbital. Both of these effects work to destabilize the carbon $p\pi$ and to stabilize the carbon σ-orbital, resulting in a σ^2 (singlet) ground state. Thus the requirement of "low-valent" metals and "heterocarbenes" for the formation of stable metal–carbenes physically means that doubly occupied metal d-orbitals and a ground-state singlet carbene will result in σ-donor/π-acceptor metal–carbene bonds.



2. Metal Alkylidenes. The "high-valent" metal fragment generally has a ligand set consisting of one or more ionic ligands (Cp, Cl, O(*t*-Bu), etc.) and alkyl ligands (odd-electron fragments). The ionic ligands prefer to bond to s-electrons (lower IP than d-electrons) on the metal, while the alkyl ligands require singly occupied metal d-orbitals to bond to. As described previously,[1b] the ionic ligands effectively oxidize the metal (e.g., $Cp_2Ta^{II}CH_3$, where "II" indicates Ta is oxidized by two units in essentially transferring the metal s-electrons to the Cp ligands), leaving a d^n metal ion. Without closed-shell ligands to force a low-spin metal configuration, the metal adopts the lowest energy configuration available, namely, the highest spin state allowed within the five d-orbitals. This metal atom (ion) is now set up to covalently bond to any ligand with unpaired electrons, be it alkyls or the triplet ($\sigma\pi$) state of the CXY ligand (two unpaired electrons). A triplet ground state of CXY will be favored when X and Y are not heteroatoms but rather are alkyl (or hydrogen) substituents. Hence, the statement that "high-valent" metal fragments and alkylcarbenes are necessary for stable metal–alkylidene formation translates physically to high-spin metal atoms (in which the s-electrons are utilized in ionic bonds), forming covalent metal–carbon double bonds to ground-state triplet CRR′ ligands.



In this paper we compare and contrast properties of simple metal carbenes, $(M{=}CH_2)^+$, involving an early, first-row transition metal (Cr) and a late, second-row transition metal (Ru). In particular, their relative stabilities and M–C bond strengths are examined, with the emphasis on how early transition metals are expected to differ from late transition metals in these unsaturated systems. Section II discusses new results of ab initio calculations on the lowest carbene state of $CrCH_2^+$ ($^6A_1$), while section III briefly reviews previous work on the lowest carbene state of $RuCH_2^+$ ($^4A_2$). The comparison of Cr and Ru carbenes allows, for the first time, donor/acceptor bond strengths to be separated into σ-donor and π-donor single bond strengths (section IV). Finally, using information gleaned from our present and previous work on both carbenes and alkylidenes, we predict stabilities of $L_nM(CXY)$ complexes, discussing trends for the entire transition series (section V). Section VI contains a summary, while section VII supplies calculational details.

II. Carbene Bonding for $CrCH_2^+$: The $^6A_1$ State

The lowest (two) states of $CrCH_2^+$ are formed by combining the ground state of CH_2 ($^3B_1$; see **1**) with the ground state of Cr^+ (^6S). This combination of spins ($S = 1$ with $S = ^5/_2$) leads to three possible values of total spin: $S = ^3/_2$ (with a double bond), $S = ^5/_2$ (with a single bond), and $S = ^7/_2$ (with no bond). Thus the ground state of $CrCH_2^+$ is $^4B_1$ with covalent σ and π bonds [leading to a total bond energy of $D_e(Cr{=}C,^4B_1) = 44.0$ kcal/mol (49.6 kcal/mol at the fully correlated limit)], leaving three unpaired d-electrons on the Cr center. The first excited state is $^6B_1$ with a covalent σ bond, leaving four unpaired d-electrons on Cr and the unpaired C $p\pi$-electron all coupled high spin to yield $S = ^5/_2$ [leading to a total bond energy of $D_e(Cr{-}C,^6B_1) = 25.0$ kcal/mol (30.6 kcal/mol at the fully correlated limit)]. The other combination of ground-state Cr^+ and CH_2 where $S = ^7/_2$ has no bond, leading to a repulsive potential curve.[1a]

A simple-minded interpretation of the above results would suggest a σ bond worth 30.6 kcal/mol and a π bond of 19 kcal/mol, both seemingly quite weak. In fact, the *inter*atomic spin pairing essential to covalent bond formation necessarily leads to a reduction in the *intra*atomic high-spin coupling favored for each atom (Hund's rule), so that the observed bond is much weaker than it would be if no extra unpaired orbitals were available. Indeed, the spin pairing for the double bond of $^4B_1$ leads to a loss of 57.8 kcal/mol in exchange energy. Thus, the *intrinsic* strength of the double bond is 107.4 kcal/mol even though the observed bond strength is only 49.6 kcal/mol. On the other hand, for the $^6B_1$ excited state, with only one covalent bond, the loss of intraatomic exchange is only 33 kcal/mol, so that the *intrinsic* strength of the σ bond is calculated to be 63.6 kcal/mol.

This enormous loss of intraatomic exchange energy engendered by covalent bond formation to ground state CH_2 (methylidene bonding) leads to the possibility that states involving the singlet excited state (**2**) of CH_2 might be low-lying. In this case, the bonding is dominated by overlap of the σ pair of CH_2 with Cr^+

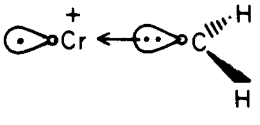


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Table I. $CrCH_2^+$ State Splittings[a] and Bond Dissociation Energies (kcal/mol) for the Carbene State of $CrCH_2^+$ ($^6A_1$)

calculational level	D_e(Cr–C)	$^6A_1$ $CrCH_2^+$ total energy, hartree[b]	$\Delta E(^6A_1-^6B_1)$[c]	$\Delta E(^6A_1-^4B_1)$[c]
HF	35.8	−1080.94226 (1/1)	−16.8	−70.5
GVB(1/2)PP	29.9	−1080.95362 (2/2)	−12.6	−23.9
GVB-RCI(2)	30.3	−1080.95427 (3/8)	−11.3	+1.2
RCI(2)*D_σ	33.4	−1080.97403 (184/759)		
RCI(2)*S_{val}	36.7	−1080.97048 (211/1184)	+0.8	+18.8
RCI(2)*D_σ + RCI(2)*S_{val}	38.7	−1080.98848 (366/1799)		

[a] The $^6B_1$ and $^4B_1$ $CrCH_2^+$ total energies are reported in ref 1a. [b] Total energy in hartrees where 1 hartree = 27.2116 eV = 627.5096 kcal/mol. The values in parentheses are (number of spatial configurations)/(number of spin eigenfunctions). [c] The values shown are at the correlationally consistent calculational levels for $^6A_1$, $^6B_1$, and $^4B_1$, as discussed in section VII.

with no loss of intraatomic exchange energy.[10] This requires the promotion of CH_2 from $^3B_1$ to $^1A_1$, at an energy cost of 9 kcal/mol,[11] followed by complexation via a σ-donor bond to ground-state, high-spin d^5 Cr^+ to form the $^6A_1$ (carbene) state. In contrast to the $^4B_1$ and $^6B_1$ states, no exchange terms are lost on Cr^+, since all five high-spin paired electrons on Cr^+ remain high spin. Since the C pπ-orbital is empty, this donor–acceptor state could be stabilized by dπ–pπ-back-bonding. However, we find that with only one electron in the Cr dπ-orbital, this back-bonding provides negligible stabilization.

The $^6A_1$(carbene)–$^4B_1$(methylidene) state splitting as a function of electron correlation is given in Table I. The three GVB calculational levels used here to obtain $\Delta E(^6A_1-^4B_1)$ are correlationally and orbitally consistent. That is, at each level, the same number of orbitals and the same types of excitations are included for both the $^6A_1$ and the $^4B_1$ states. [Other levels of calculation examined in evaluating the Cr–C bond energies (see Table I) do not treat these two states comparably and are not used in considering the state splitting.]

From Table I, we see that the state splitting is sensitive to the level of electron correlation. Notice the complete about-face of $\Delta E(^6A_1-^4B_1)$ upon relaxation of the perfect pairing restriction, as in the GVB-RCI wavefunction. At the best level of calculation, we find that the carbene state ($^6A_1$) lies 18.8 kcal/mol above the methylidene ($^4B_1$) ground state. Thus, $^6A_1$ is only 0.8 kcal/mol above the $^6B_1$ state at the same level of theory.[12]

Supporting evidence for the presence of *two* excited states of $CrCH_2^+$ lying about 18–19 kcal/mol above the ground state comes from recent experiments by Beauchamp and co-workers[13] in which translational energy loss spectroscopy was used to search for excited states of $CrCH_2^+$ formed from Cr^+ colliding with CH_4 in a molecular beam. The spectrum indicates a wide weak peak consistent with at least one spin-forbidden transition at an energy of ~24 kcal/mol less than the elastic peak. Given an energy resolution of 0.2 eV (~5 kcal/mol), our theoretical values for the sextet–quartet energy gaps are within the experimental error. The relative energies of the three low-lying states of $CrCH_2^+$ as well as their respective limits at infinite *R*(Cr–C) are displayed in Figure 1.

The optimum geometry of the single-bonded donor/acceptor $^6A_1$ state [see Figure 2a: *R*(Cr–C) = 2.32 Å, θ(HCH) = 108.9°] differs considerably from the covalently single-bonded $^6B_1$ state [*R*(Cr–C,$^6B_1$) = 2.07 Å, θ(HCH,$^6B_1$) = 118.3°], with a Cr–C bond length longer by 0.3 Å and a much smaller HCH bond angle, close to that in free singlet CH_2 (102°).[14,15a] The long Cr–C bond length and the small HCH angle are expected for a σ-donor bond with negligible dπ–pπ-back-bonding from the singly occupied Cr $d\pi_{xz}$-orbital, a description that is also indicated by Mulliken populations and orbital plots.

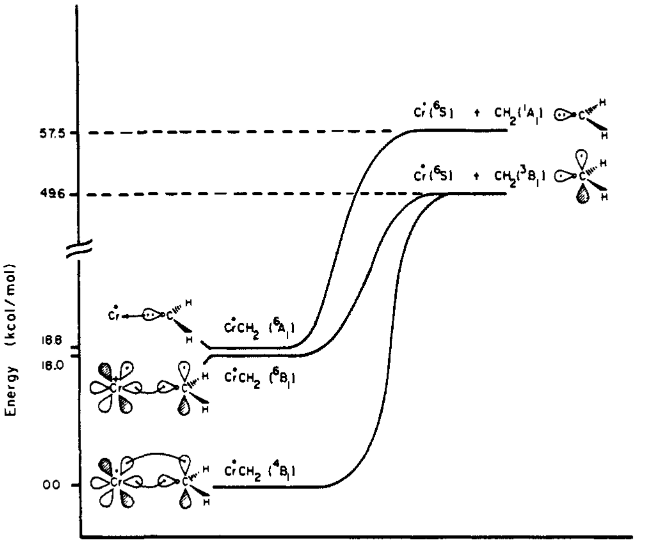

Figure 1. Electronic state correlation diagram for the three lowest states of $CrCH_2^+$: $^6A_1$, $^6B_1$, and $^4B_1$. The two B_1 states dissociate to ^6S Cr^+ and $^3B_1$ CH_2, while the $^6A_1$ state dissociates to ^6S Cr^+ and $^1A_1$ CH_2.

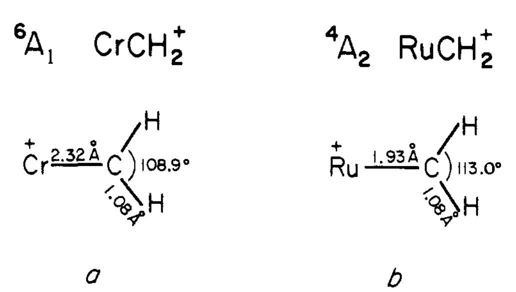

Figure 2. Optimum geometries for the carbene states of (a) $CrCH_2^+$ ($^6A_1$) and (b) $RuCH_2^+$ ($^4A_2$).

The orbitals for the carbene state, $CrCH_2^+$ ($^6A_1$), are shown in Figure 3a where we see a Cr–C σ bond consisting of an "in/out" correlated CH_2 σ pair (1.75 electrons on CH_2 with a high bond orbital overlap of 0.83) delocalizing toward the Cr cation (0.25 electrons transferred to Cr^+), similar in character to the σ-donor bond for the carbene state of $RuCH_2^+$ ($^4A_2$), as shown in Figure 3b.i. In contrast to the carbene state of $RuCH_2^+$, however, we find no dπ–pπ-back-bonding for the carbene state of $CrCH_2^+$. Thus, Mulliken populations indicate only 0.01 electrons donated from the Cr $3d\pi_{xz}$ singly occupied orbital to the CH_2 $2p_x$ orbital, and even at the much shorter Cr–C bond length of 2.07 Å, the dπ delocalization is only 0.05 electrons for $CrCH_2^+$ ($^6A_1$). In contrast, for the carbene state of $RuCH_2^+$, there are 0.43 electrons transferred from the Ru dπ *doubly occupied* orbital into the C

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[10] An exception to this statement exists if enough ligand donor bonds force the orbital into a lower spin state in order to allow more effective σ-donation. In this case, the spin coupling is indeed affected, and some exchange energy is lost. For $CrCH_2^+$, however, we need not force the metal into a lower spin state.

[11] Leopold, D. F.; Murray, K. K.; Lineberger, W. C. *J. Chem. Phys.* **1984**, *81*, 1048.

[12] There is no correlationally consistent calculational analogue for $^6A_1$ $CrCH_2^+$ at the RCI*S_{val} + [RCI$_\sigma$*D_π + RCI$_\pi$*D_σ] calculational level (see ref 1a) which yielded $\Delta E(^6B_1-^4B_1)$ = 19.0 kcal/mol. Therefore we compare excitation energies at the highest *correlation-consistent* level, RCI*$S_{valence}$.

[13] Hanratty, M. A.; Carter, E. A.; Beauchamp, J. L.; Goddard III, W. A.; Illies, A. J.; Bowers, M. T. *Chem. Phys. Lett.* **1986**, *123*, 239.

[14] The C–H bond length is insensitive to mode of bonding and was kept fixed at 1.078 Å. θ(H–C–H) for $^1A_1$ CH_2: Harding, L. B.; Goddard, W. A., III *Chem. Phys. Lett.* **1978**, *55*, 217.

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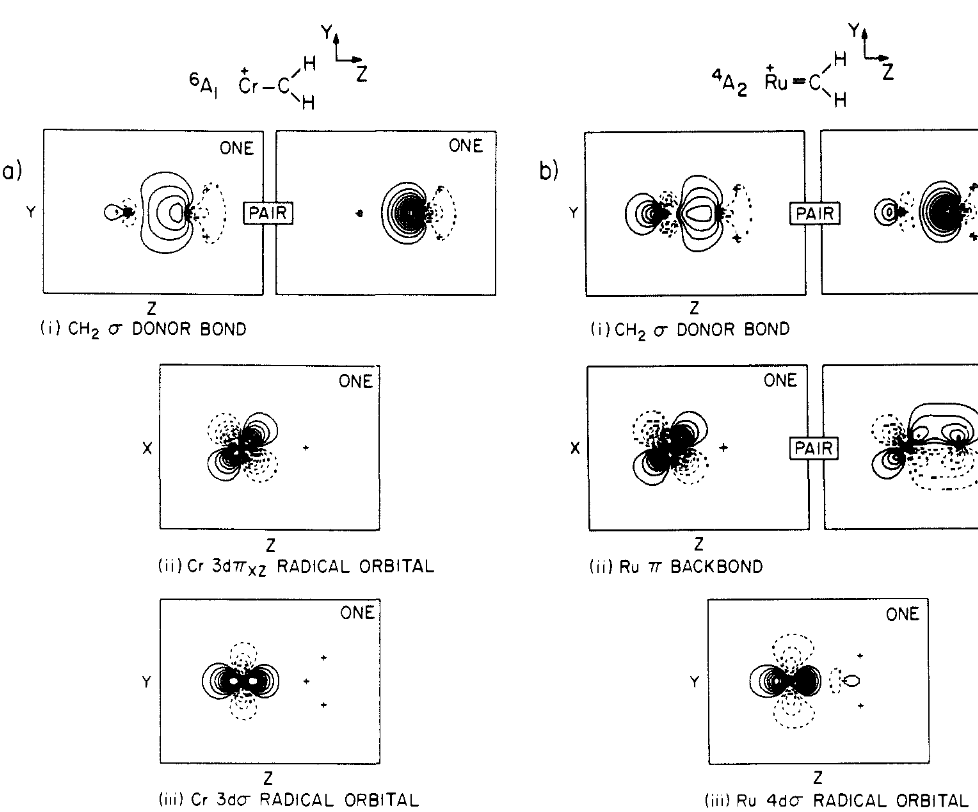

Figure 3. GVB one-electron orbitals for the carbene states of (a) $CrCH_2^+$ ($^6A_1$) [(i) CH_2 σ-donor bond; (ii) Cr 3dπ singly occupied orbital; (iii) Cr 3dσ singly occupied orbital] and (b) $RuCH_2^+$ ($^4A_2$) [(i) CH_2 σ donor bond; (ii) Ru 4dπ-back-bond; (iii) Ru 4dσ singly occupied orbital]. Contours represent regions of constant amplitude ranging from −0.5 to +0.5 au, with increments of 0.05 au.

pπ empty orbital. The difference here is that electron repulsion in the doubly occupied orbital drives one of the electrons toward delocalization, as displayed in Figure 3b.ii. The lack of a π-back-bond leads to the long bond length of 2.32 Å for Cr—carbene and a low Cr—C carbene stretching frequency of 295 cm^{-1} (in comparison with 464 cm^{-1} calculated for the doubly bonded Ru=C carbene stretching frequency).

Another difference between the bonding in the carbene states of $CrCH_2^+$ and $RuCH_2^+$ is in the behavior of the singly occupied metal dσ-orbital, illustrated in Figure 3, parts a.iii and b.iii. For $CrCH_2^+$ ($^6A_1$), there is minimal s–d mixing into the singly occupied Cr σ orbital (94.1% 3d/5.9% 4s) because the small size of the 3d orbital and the long Cr–C bond length leads to little overlap between Cr 3d and the σ pair of CH_2. However, for $RuCH_2^+$, the M–C bond length is much shorter (due to the π-back-bond) and the Ru^+ 4d-orbital is larger (than Cr 3d), leading to a high overlap with the σ pair of CH_2. As a result, the singly occupied Ru dσ-orbital must s–d hybridize in order to minimize repulsive interactions (the singly occupied Ru σ orbital has hybridization 72% 4d/28% 5s).

Summarizing, the various properties (orbital character, long bond length, small vibrational frequency, and small HCH bond angle) in the carbene state $CrCH_2^+$ ($^6A_1$) reveals a bond involving a donor σ bond from singlet CH_2 to high-spin, d^5 Cr^+. The carbene–methylidene state splitting ($^6A_1$–$^4B_1$) is larger for $CrCH_2^+$ than for $RuCH_2^+$ ($^4A_2$–$^2A_2$) due to the presence of a strong two-electron π back-bond for $RuCH_2^+$ ($^4A_2$) and no π-back-bond for $CrCH_2^+$ ($^6A_1$).

III. Carbene State of $RuCH_2^+$: A Review

Ground-state high-spin d^7 Ru^+ forms three degenerate carbene states upon interaction with CH_2 ($^1A_1$). These three states ($^4A_2$, $^4B_1$, $^4B_2$) arise from degenerate valence electron configurations[1b] on Ru^+ and differ in the CH_2 complex only in the occupation of the nonbonding d-orbitals. They have equivalent bonding descriptions, namely, that of a Ru–C σ-donor/π-acceptor double bond. We chose to examine the $^4A_2$ state in the most detail simply because it has the same spatial symmetry as the ground ($^2A_2$) alkylidene-type state.

The basic properties of the carbene state of $RuCH_2^+$ necessary for comparison with the Cr carbene system include the following:

(i) The carbene–alkylidene energy gap [$\Delta E(^4A_2–^2A_2)$] is 12.9 kcal/mol at our highest level of theory.

(ii) The optimum geometry at the GVB-RCI(2/4) level is shown in Figure 2b. The carbene nature of the Ru–C bond is supported by the small H–C–H bond angle of 113° and the longer bond length of 1.93 Å compared to that of the ground alkylidene state (1.88 Å).

(iii) The GVB orbitals are shown in Figure 3b where we see that the CH_2 forms a σ-donor bond to Ru^+ involving an in/out correlated, sp^2 hybrid, while the Ru^+ forms a π-back-bond to the empty C pπ orbital. The charge transfers involved in these bonds work in concert (electroneutrality principle). Thus, the Mulliken populations indicate 0.73 electrons donated to Ru^+ in the σ system and 0.43 electrons donated to CH_2 in the π system.

(iv) The Ru=C carbene bond energy is 65.8 kcal/mol in $RuCH_2^+$ ($^4A_2$), probably a representative bond energy for coordinatively saturated, low-valent metal heterocarbenes. The Ru=C alkylidene bond energy in $RuCH_2^+$ ($^2A_2$) is 68.0 kcal/mol, leading to an estimated[1b] Ru=CH_2 alkylidene bond energy of 83.0 kcal/mol for a saturated complex. (An independent, direct calculation on a model saturated system yielded 84.7 kcal/mol for the Ru=C bond strength.)

IV. Partitioning the Double Bond into σ- and π-Donor Contributions

π-Back-bonding is commonly involved in discussions of organometallic metal–ligand bonds having ligands with low-lying π-acceptor orbitals (e.g., CO or CXY, where X and/or Y are electron-withdrawing groups), but little quantative evidence is available regarding the strength of and the extent of charge transfer in such a π-bond. The only experimental verification of this effect is obtained indirectly by assigning changes in bond lengths and vibrational frequencies in M–CO or M=CXY systems as due to changes in the extent of back-bonding. The calculation outlined below provides a direct, quantitative assessment regarding such bonds.

From two independent analyses, we find that the π-back-bond in the carbene state of $RuCH_2^+$ ($^4A_2$) is worth approximately 30 kcal/mol. Our approach was to eliminate the C $2p_x$ and $3d_{xz}$ basis functions from the SCF calculation, thereby prohibiting π-back-bonding since no delocalization into the C π system is possible. This results in an energy destabilization of 27.4 kcal/mol. Since the rest of the bonding remains the same as in the full basis set description, this destabilization may be attributed solely to the strength of the π-back-bond. A more reliable estimate for the π bond strength is obtained by examining the $^4B_1$ carbene state of $RuCH_2^+$ which differs from $RuCH_2^+$ ($^4A_2$) only in having reversed $d\pi_{xz}$- and $d\delta_{xy}$-orbital occupations [$(d\pi_{xz})^1(d\delta_{xy})^2$ for $^4B_1$ and $(d\pi_{xz})^2(d\delta_{xy})^1$ for $^4A_2$].[16] Since the $^4B_1$ state has a negligible one-electron π-back-bond (vide infra) and the $^4A_2$ state has a significant two-electron π-back-bond, the $^4B_1$–$^4A_2$ splitting is a measure of the Ru–C π bond strength. This energy splitting was calculated to be 31.5 kcal/mol, in close agreement with the other π bond strength estimate of 27.4 kcal/mol. Thus, we conclude that the strength of the π-back-bond for $RuCH_2^+$ ($^4A_2$) is ~30 kcal/mol. For neutral, less electrophilic metal centers, we expect π-back-bond strengths to be higher than 30 kcal/mol, since delocalization into the carbene π system should be more facile.

Both the $RuCH_2^+$ ($^4B_1$) excited state with its singly occupied $d\pi$-orbital and the $CrCH_2^+$ ($^6A_1$) excited state (high-spin d^5 Cr^+) can only provide *one*-electron $d\pi$–$p\pi$-back-bonding to CH_2 ($^1A_1$). The extent of charge transfer is negligible in both cases, with 0.10 electrons transferred by Ru^+ and 0.01 electrons transferred by Cr^+. (We expect slightly more electron transfer for Ru^+ since 4d-orbitals are larger than 3d-orbitals and can thus delocalize more effectively.) Thus, for both first- and second-row transition-metal ions, the *one*-electron $d\pi$–$p\pi$-back-bond is negligible in comparison with a *two*-electron $d\pi$–$p\pi$-back-bond.

The bond energy of the $CrCH_2^+$ ($^6A_1$) is interesting because it provides quantitative determination of the strength of a single σ-donor bond, unlike the case of $RuCH_2^+$ ($^4A_2$), in which there is both a σ- and a π-donor bond, making it difficult to determine the energy partitioning in the Ru–C double bond. Table I contains an analysis of the Cr–C bond energy for $CrCH_2^+$ ($^6A_1$) as a function of electron correlation. [The Cr–C bond energy is for the symmetry-allowed process

$$(^6A_1)\ CrCH_2^+ \rightarrow (^6S)\ Cr^+ + (^1A_1)\ CH_2$$

yielding an intrinsic σ-donor bond strength.] At our highest calculational level, we find a bond energy of 38.7 kcal/mol. Hence, we estimate the strength of a C to Cr σ-donor bond with no π-back-bond to be worth ~39 kcal/mol.

Since the total bond energy for the carbene state of $RuCH_2^+$ ($^4A_2$) is $D_e = 65.8$ kcal/mol, then we estimate the σ-donor bond energy to be $D_e^\sigma = D_e - D_e^\pi = 65.8 - 31.5 = 34.3$ kcal/mol. This value is quite close to the value (39 kcal/mol) obtained for Cr-carbene. For systems with a singly occupied nonbonding $d\sigma$-orbital, we would expect the values for σ-donor bond strengths to *decrease* going from first row to second row due to the higher metal 4d/carbene σ overlap for the more diffuse 4d electrons. Our value of 30 kcal/mol for the two-electron π-back-bond of a second-row transition metal is probably a lower limit on the strength of such a bond in a neutral complex. However, the strength of such a two-electron π-back-bond for low-spin d^n first-row metals is probably less than 30 kcal/mol (due to the small radial extent of the 3d-orbitals).

V. Transition-Metal-Ligand Bonding Trends: Control of Reactivity

In the above sections, we found that, with proper choices of metal and ligands, one can obtain complexes in which the ground and excited states exhibit vastly different bonding character. Given the opportunity of added ligands to perturb the electronic state splittings at the metal center, we have the potential for designing complexes either with covalently bonded alkylidene ligands or with σ-donor/π-back-bonding carbene ligands depending upon the choice of metal and ligand environment.

The purpose of this section is to discuss how to use such valence bond ideas to control metal–ligand bond character, thus opening up the possibility for distinctive changes in chemical reactivity of organotransition-metal systems. Our premise is that control of the electronic configuration of the metal center—not merely oxidation state—is the key to controlling both the bond *type* and bond *strength* for a given metal–ligand system. For the sake of brevity we will illustrate such effects only for M–CXY systems, but the arguments expressed may be applied to any other metal-ligand system with overall covalent character.

First, we discuss how intraatomic exchange stabilization and promotional energies affect metal-orbital hybridization, bond character (covalent vs. donor/acceptor), and bond strengths in metal–carbon bonds. Second, we describe how ligand type affects the nature of the metal–carbon bond. Third, we conclude with a general prescription of how to bias the outcome in favor of alkylidene, carbene, or intermediate bonding in M–CXY complexes.

A. Metal Exchange and Promotional Effects on M–CXY Bonds. Due to the greater number and larger magnitude of favorable exchange interactions between valence electrons in a transition metal as compared with a main-group or nonmetal atom,[17] the loss of exchange energy upon forming covalent bonds with ligands (via spin pairing in the bonds) plays a much more significant role in determining bond properties for transition metals than for other atoms. If this exchange loss destabilization is large enough, promotion of the metal atom to an excited state may be favorable if it results in less exchange loss. These two effects are evidenced by changes in hybridization of metal bonding orbitals, bond character, and bond strength. Since these effects are most dramatic in bare metal systems, we will discuss only bare M–CXY systems.

1. Hybridization. Metal orbital hybridization in M–CXY bonds can be predicted qualitatively by comparing the relative metal destabilization upon bonding the ligand to an s- vs. a d-orbital. Valence s → p and d → p excitations for transition metals are sufficiently high in energy that valence p-orbitals make little contribution to bonding. Thus the hybridization changes are greatest in the M–C σ bond, with little d–p mixing in the π bond (>90% d). Therefore we will describe only hybridization effects in the σ bond.

For a ground-state metal atom or ion with an *occupied* valence s orbital (s^1d^{n-1} or s^2d^{n-2} state), the CXY covalent σ bond will have a large amount of s character in the metal-bonding orbital. This is due to spin pairing of the metal s-electron with the ligand electron in the bond, resulting in the loss of *only* s–d exchange terms (K_{sd}), each typically ~5 kcal/mol (10–15 kcal/mol smaller than d–d exchange terms). In cases where the metal has a choice between s and d, the s-orbital is preferred since it loses less exchange energy upon forming the metal–ligand bond. For example, binding Mn^+ (s^1d^5 ground state) to CH_2 ($^3B_1$) leads to a σ bond which has 87% s character.[18] This is due to the reluctance of Mn^+ to destroy the stabilization of the half-filled d-shell (i.e., a large loss in exchange energy).

If the metal has a d^n ground state, then to form a bond to a metal s-orbital will require the d → s promotional energy in addition to various s–d + d–d exchange losses ($E_p^{d\rightarrow s} + \Delta K_{sd+dd}$).[19] To decide whether bonding to an s orbital will occur, we must compare this sum with the d–d exchange loss incurred upon bonding to the d^n ground state (ΔK_{dd}). These relative energies will determine the dominant hybridization. In other words, for $E_p^{d\rightarrow s} + \Delta K_{sd+dd} > \Delta K_{dd}$, we expect >50% d-character in the M–C σ bond and vice versa. As the difference between these two values grows, so does the dominant orbital contribution to the metal σ-orbital.

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[16] The corresponding Ru^+ occupations are degenerate, leading to no added promotional effects. See Table I in ref 1b.

[17] Typical values: K_{dd} ~ 15–20 kcal/mol and K_{sd} ~ 5–8 kcal/mol for transition metals; K_{pp} ~ 10 kcal/mol for non-transition metals.

[18] Brusich, M. J.; Goddard, W. A., III, unpublished results.

[19] $E_p^{d\rightarrow s}$ designates the $d^n \rightarrow s^1d^{n-1}$ promotional energy. ΔK_{sd+dd} refers to a loss of both s–d and d–d exchange terms when forming both σ and π bonds.

As an illustration of this competition, consider that the σ bond in $CrCH_2^+$ is 53% d/47% sp on the metal, arising from $E_p^{d\rightarrow s} + \Delta K_{sd+dd} - \Delta K_{dd} = 13.7$ kcal/mol.[1a] The difference in destabilization energy suggests that metal d-character should dominate. However, the large difference in the size of the 3d and 4s orbitals favors s-bonding, leading to rather balanced d vs. s character. The case of covalently bonded $RuCH_2^+$ ($^2A_2$) provides an example at the opposite extreme. Forming two covalent bonds to d^7 Ru^+ costs $1.5K_{dd} = 22.5$ kcal/mol, while forming one s bond and one d bond to s^1d^6 Ru^+ costs $E_p^{d\rightarrow s} + 2K_{sd} + 1.5K_{dd} = 65.9$ kcal/mol.[1b] Thus a dσ bond is favored over an sσ bond by 43.4 kcal/mol. This is borne out convincingly in the actual Ru–C σ-bond hybridization of 88% 4d/12% 5s character on the metal.

Thus we see that knowledge of the ground-state configuration of the metal, coupled with values for promotional and exchange energies, allows qualitative prediction of the hybridization in metal–ligand covalent σ bonds for all ranges of cases: mostly s character ($MnCH_2^+$), a 50/50 mixture of s and d ($CrCH_2^+$), and mostly d character ($RuCH_2^+$).

2. Bond Character. The same analysis also yields predictions about donor/acceptor vs. covalent bond character. Donor/acceptor bonds will be favored when the exchange and promotional destabilizations for forming covalent bonds are prohibitively large and when two-electron π-back-bonds are achievable. Covalent bonds will be favored when little promotional or exchange energy is lost upon bonding or when a π-back-bond is not possible (reducing the prospective donor bond order from two to one). A competition between covalent and donor/acceptor bonding will be expected when the exchange loss is intermediate and π-back-bonds are possible.

We expect group 8–10 metals to be good candidates for carbene bonding, since two-electron π-back-bonds may be formed without requiring intermediate or low-spin metal centers. We expect those metals that can have a σ hole (allowing formation of a σ-donor bond from the ligand) to be even more likely to exhibit carbene bonding. In addition, carbene bonding is also favored for those systems where covalent bonding costs too much in exchange loss. For example, the loss of exchange and promotional energies for forming two covalent bonds in $FeCH_2^+$ is ~40 kcal/mol, bonding to either the s^1d^6 ground state of Fe^+ (^6D) or to the low-lying ($E_p^{s\rightarrow d} = 6.7$ kcal/mol)[20] d^7 excited state of Fe^+ (^4F).[21] Since ^6D and ^4F Fe^+ have both singly and doubly occupied d-orbitals, π-back-bonding from Fe^+ and σ-donation from CH_2 can both be achieved as in $RuCH_2^+$ ($^4A_2$). Since the loss of exchange and/or promotion is greater for Fe^+ than for Ru^+ [$\Delta K_{dd}(Ru^+, d^7) = 1.5K_{dd} = (1.5)(15) = 22.5$ kcal/mol], we expect carbene bonding to be favored for Fe^+. This is nicely illustrated by the experiments of Brandt and Helquist who isolated the dimethyl sulfide adduct of the $FeCH_2^+$ complex $[(Cp(CO)_2FeCH_2SMe_2]^+$. This complex, or perhaps the free $L_nFeCH_2^+$ species, was found to directly cyclopropanate olefins, as expected for the reaction chemistry of an electrophilic carbene.[5d] Gas-phase work of Stevens and Beauchamp[5k] also implies cyclopropanation chemistry by $CpFe(CO)_2CH_2^+$.

Covalently bonded metal alkylidenes are most favorable for early transition metals, since two-electron π-back-bonding is not possible (no doubly occupied valence d-orbitals in the ground state) and only a minor loss of exchange and promotional energy is incurred (due to the small number of valence electrons). A classic example of this is the first-isolated $M{=}CH_2$ complex, $Cp_2(CH_3)Ta{=}CH_2$, which exhibits nucleophilic alkylidene character.[8] This can be understood by an exchange energy analysis modified by the presence of other ligands. Ta has an s^2d^3 ground state in which the s electrons and one d electron are involved in bonding to the Cp and CH_3 ligands, leaving two high-spin d-electrons to bond to CH_2. Binding CH_2 to the 16-electron $Cp_2(CH_3)Ta$ fragment results in only $0.5K_{dd}$ loss (~7 kcal/mol). The small exchange loss coupled with no π-back-bonding possibilities leads to the formation of a covalent, nucleophilic metal–alkylidene bond.

Competitive carbene and alkylidene bonding should occur when π-back-bonding is possible and there is an intermediate loss of exchange in forming covalent bonds. We expect this behavior in second- and third-row group 8–10 metals, since π-back-bonding is possible and the exchange loss is not as large (the average K_{dd}'s for second- and third-row group 8–10 metals are ~5 kcal/mol smaller than for their first-row congeners[22]). $RuCH_2^+$ is one example of this, in which the dπ–pπ back-bonding is great enough (30 kcal/mol) and exchange loss is large enough (66 kcal/mol) to allow competitive carbene/alkylidene states. Binding CH_2 ($^3B_1$) to the ground-state d^7 Ru^+ leads directly to a stable alkylidene. Due to the lack of exchange loss and the strength of the donor/acceptor bond, a CH_2 ($^1A_1$) bound to d^7 Ru^+ results in a carbene of nearly the same stability as the alkylidene. Experimental examples from group 8–10 second- and third-row metals span the range of behavior from nucleophilic to electrophilic. Roper and co-workers[23] have shown that the complexes $Cl(NO)(PPh_3)_2M{=}CH_2$ (M = Ru, Os) are nucleophilic, reacting with acids not bases, while Thorn and Tulip[24] isolated the pyridine adduct of the electrophilic $Br(PMe_3)_3(CH_3)Ir^+{=}CH_2$.

3. Bond Strengths. Although conventional wisdom correlates bond strengths with orbital overlaps, other factors contribute significantly to bond energy trends. M–CXY bond strengths are weakened by both exchange loss and possible promotion of the metal and/or the ligand. In general, due to small exchange loss, early transition-metal alkylidenes are expected to have strong bonds, with the bond strengths *increasing* down a column due to the *decreasing* size of the exchange terms.[22] The bond strengths in metal–carbenes depend on the effectiveness of σ-donor/π-back-bonding, since the metal need not incur exchange loss. Promotional effects may sometimes be required for effective σ-donor/π-acceptor bonding. Hence the bond strengths in unsaturated late-transition-metal carbene systems are expected to be stronger than for early-transition-metal carbene systems due to more effective π-back-bonding. In addition, we expect these bond strengths to *increase* down a column since the *increasing size* of the d-orbitals may allow more effective delocalization for the π-back-bond. The intermediate cases suggest metal–carbene bond strengths can be as strong as the corresponding metal–alkylidene bond strengths (for the unsaturated systems).

The trends for saturated metal complexes are even simpler to analyze. For a given set of ligands, the valence electron configuration at the metal is expected to be *constant* for metals in the same column. Thus, there is no need to consider promotional energy (since the constant ligand set induces the same ground-state valence electron configuration for each metal) and the same *number* of exchange terms is lost as we go down a column. Since $\Delta E_p = 0$ and $\Delta K_{dd} = (\text{constant})K_{dd}$, then the only variable in determining the bond energies is the *magnitude* of the intraatomic exchange integral, which decreases as we go down a column.[22] This *decreases* the destabilization due to exchange loss and hence *increases* the bond energy as we go down a column. Conventional wisdom attributes this trend solely to the increasing size of the d orbitals inducing larger overlap and hence stronger bonds.

B. Effect of Ligand Type on the M–CXY Bond. Metal–carbon bond character is determined not only by electronic interactions on the metal but also by the nature of the CXY ligand. The substituents on the carbon ligand can greatly influence the stability of alkylidene vs. carbene bonding. We have shown that alkylidenes involve triplet CXY fragments forming *covalent* bonds, whereas carbenes involve singlet CXY fragments forming *donor/acceptor* bonds to a metal center. Therefore, if X and Y are chosen to stabilize the triplet, alkylidene bonding will be favored, while if

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(20) Moore, C. E. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1971**, *3*, (35).

(21) Since $K_{dd}(Fe^+) = 20.7$ kcal/mol and $K_{sd}(Fe^+) = 5.0$ kcal/mol, $\Delta K(Fe{=}CH_2^+, s^1d^6Fe^+) = 1.5\ K_{dd} + 2K_{sd} = 41$ kcal/mol. $\Delta K_{dd}(FeCH_2^+, d^7Fe^+) + E_p^{s\rightarrow d}(Fe^+) = 1.5K_{dd} + E_p = 31.05 + 6.7 = 37.75$ kcal/mol.

(22) Froese Fischer, C. *The Hartree-Fock Method for Atoms—A Numerical* Approach; Wiley-Interscience: New York, 1977.

(23) (a) Hill, A. F.; Roper, W. R.; Waters, J. M.; Wright, A. H. *J. Am. Chem. Soc.* **1983**, *105*, 5939. (b) Roper, W. R. *Group VIII Transition Metal Complexes of CH_2, CF_2, and Other Simple Carbenes*; Seminar at the California Institute of Technology, 23 July 1984.

(24) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984.

X and Y are chosen to stabilize the singlet, carbene bonding will be favored (ignoring the metal's electronic interaction already discussed in section V.A).

In general, electronegative substituents (e.g., F, Cl, OR) on the carbon ligand stabilize the singlet carbene state,[15] whereas electron-donating substituents favor the triplet alkylidene state of CXY.[25] For instance, while CH_2 has a *triplet* ground state (with $^1A_1$ lying ∼9 kcal/mol higher[11]), CF_2 has a *singlet* ground state with the triplet state lying ∼57 kcal/mol higher.[15c] Thus, replacing CH_2 with CF_2 will lead to a bias of ∼66 kcal/mol toward formation of a metal–carbene! If carbene bonding is desired, a CXY ligand (X,Y = F, Cl, OR, H; R = alkyl) in conjunction with a metal from groups 8–10 increases the driving force for formation of a terminal σ-donor/π-acceptor bond. Examples of such bonding in group 8–10 systems included CH_2 complexes of Fe[26] and Ir[24] and CF_2, CCl_2, C(F)(Cl), and C(F)(O-*t*-Bu) complexes of Fe, Ru, and Os, all of which exhibit the expected electrophilic, singlet carbene character (e.g., facile reactions with nucleophiles).[27] The only exception is found in CF_2 complexes of Ru(0) and Os(0) where the π-back-bonding is so effective as to inhibit the electrophilicity of these carbenes, rendering them slightly nucleophilic.[28]

It is well-known that group 6 metals readily form the so-called Fischer carbenes in which a low-valent metal, usually surrounded by five carbonyl ligands, is bonded to an alkoxycarbene ligand in a donor/acceptor fashion.[2] These systems are metal carbenes partly because the alkoxycarbene has a singlet ground state and partly because the closed-shell ancillary ligands (e.g., PR_3, CO) force the metal into a low-spin d^n configuration primed for forming donor/acceptor bonds (with doubly occupied $d\pi$-orbitals). A dramatic example of how the chemistry (and, we believe, the bond character) changes going from an unsaturated to a saturated metal complex (with closed-shell ligands) is found in the work of Stevens and Beauchamp[5c] who demonstrated that $MnCH_2^+$ undergoes metathesis reactions, while $(CO)_5MnCH_2^+$ yields only cyclopropanation products. The unsaturated system s^1d^5 Mn^+, being unable to form a π-back-bond, is forced to form a covalent alkylidene bond which, as such, undergoes metathesis. Attaching the CO's forces Mn^+ into a low-spin d^6 state which can now form π-back-bonds, leading to a donor/acceptor carbene bond that can undergo cyclopropanation.

In order to prepare stable alkylidenes, we require CXY to have a triplet ground state or a low-lying triplet excited state. This requirement is fulfilled by methylene and mono- or dialkyl or aryl carbenes. Examples are prevalent among the early transition metals, as evidenced by their nucleophilic chemistry. For instance, Ta neopentylidene complexes are catalysts for ethylene polymerization,[29] Ti alkylidene complexes are postulated intermediates in olefin metathesis,[9] and other early transition metals participate in the reactions shown in (3)–(5).[6-8] This predominance of alkylidenes in the early metals is due to small exchange losses, strong M–C π bonds (large d-orbitals for early metals), and the lack of doubly occupied d orbitals (disfavoring donor/acceptor bond formation). The late transition metals generally prefer not to form terminal alkylidene bonds in a mononuclear complex. Late transition metals form weak covalent π bonds since d-orbitals contract as we go across a row. Thus reactions which would form $M{=}CR_2$ complexes in early transition metals lead instead to dinuclear *bridging* CR_2 complexes in late transition metals.[30]

C. Design Prescription of Carbenes and Alkylidenes. From sections V.A and V.B, we see that the electronic state of a metal and its ligands greatly influences its bond character and reactivity. Using the ideas presented thus far, we can now predict, based solely on the electronic structure of the metal complex, what elements are necessary to form stable carbenes and alkylidenes.

To ensure the formation of a metal–alkylidene with nucleophilic character, we require the CXY ligand to be a triplet so that it can form two covalent bonds to a metal atom. This suggests CXY ligands where X and Y are σ-donating or electropositive. Then the C–X and C–Y bonds will use more C s character to lower the energy of the carbene, destabilizing the C σ nonbonding orbital. Second, use of substituents X and Y without $p\pi$ lone pairs will favor occupation of the C π nonbonding orbital. Third, use of bulky X and/or Y will force sp^2 hybridization on the C to obtain larger X–C–Y bond angles to relieve steric (Pauli) repulsion. The increased s character in the C–X/C–Y bonds results in increased p character in the nonbonding carbon σ-orbital. These three factors leading to the destabilization of the carbon σ-orbital and the stabilization of the carbon π-orbital favor $\sigma\pi$ (triplet) alkylidene (**1**) over σ^2 (singlet) carbene (**2**).

Indeed, the metal alkylidenes which have been synthesized to date contain hydrogen, alkyl, or aryl substituents on the carbon, which are σ-donating (H and R), do not possess $p\pi$ lone pairs (H, R, and Ar), and may be bulky (R and Ar). As a further synthetic extension, we suggest that X and/or Y = SiR_3, AlR_2, and BR_2 should be effective in stabilizing triplet CXY (and hence metal alkylidenes), since all three are electropositive, are σ-donating, lack $p\pi$ lone pairs, and are bulky. While a tungsten $C(H)(SiMe_3)$ alkylidene system has been synthesized,[31] $CX(AlR_2)$ and $CX(BR_2)$ alkylidenes are unknown. However, $M{-}C(X)(AlR_2)$ and $M{-}C(X)(BR_2)$ should exhibit unusual reactivity due to the presence of a Lewis acid adjacent to a nucleophilic carbon center. In particular, such systems may show enhanced reactivity as olefin polymerization or metathesis catalysts, since those reactions often require Lewis acid cocatalysts. The formation of a temporary olefin adduct at the Lewis acid site may promote reaction at the M=C bond.

To form a stable alkylidene, the metal center must incur little exchange loss upon bonding to the CXY ligand. This requirement is satisfied best by early transition metals, where the small number of valence d electrons results in small exchange losses. It is also important that these metals can form stable, coordinatively unsaturated complexes (e.g., 14- and 16-electron complexes) in which the metal has unpaired electrons set up for bonding to triplet CXY.[32] Thus stable terminal alkylidenes are expected (and found) for early-transition-metal mono- and dialkyl or aryl alkylidenes, with the most stable alkylidenes found among the third-row elements (due to a smaller K_{dd} and a stronger π bond). Terminal alkylidene complexes involving late transition metals will generally be less stable due to weaker covalent π bonds, and thus late transition metals will prefer to make two σ bonds to CXY, resulting in the formation of *bridging* alkylidenes (as is found experimentally).[30] Those few examples of terminal CR_2 complexes bound to group 8–10 metals all indicate *carbene* character (most of these examples involve CH_2, since the small $^1A_1$–$^3B_1$ splitting

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(25) (a) Ab initio theoretical calculations on CLiH and CLi_2 (extreme electron-donating substituents) yield triplet ground states. See: Harrison, J. F.; Liedtke, R. C.; Liebman, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 7162. (b) GVB-CI calculations yield a triplet ground state for $CH(SiH_3)$: Carter, E. A.; Goddard III, W. A., unpublished results.

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in CH_2 makes the carbene more accessible).[24,26]

For a strong metal–carbene bond, we require a singlet ground state (or low-lying singlet excited state) of the CXY ligand in order to form a σ-donor/π-acceptor bond to the metal center. When X or Y in the CXY ligand are electronegative, the C–X/C–Y bonds utilize C p-orbitals, since the lower ionization potential of the C 2p allows more charge transfer to the electronegative substituents. More p character in the C–X/C–Y bonds stabilizes the nonbonding C σ-orbital by introducing more s character into it. In addition, pπ lone pairs on X or Y may delocalize into the nonbonding C pπ, disfavoring pπ occupation by one of the carbon valence electrons. Both high electronegativity and the presence of pπ lone pairs act to stabilize the σ^2(carbene) state of CXY **2**.[15b,33]

To favor a stable metal–carbene, we would like either a late transition metal with doubly occupied d-orbitals to induce π-back-bonding [e.g., $Cp(dppe)Fe{=}CH_2^+$][26] or an early transition metal with ancillary closed-shell ligands that force the metal to be low-spin d^n [e.g., $(CO)_5Cr{=}C(OMe)(Me)$][2] such that dπ–pπ back-bonding is possible. Examples of such metal–carbene complexes include many group 6 carbonyl alkylalkoxy carbenes as well as late transition metal CH_2, CF_2, CCl_2, and CF(OtBu) complexes, all exhibiting varying degrees of electrophilic character.[27]

Strong preference for carbene bonding is expected in the first-row group 8–10 metals since the exchange loss incurred in forming covalent (alkylidene) bonds is particularly high (due to large K_{dd}). However, for second- and third-row late transition metals, the more moderate exchange losses lead to more *competitive* alkylidene and carbene bonding when the CXY ligand has a *small* $^1A_1$–$^3B_1$ splitting (namely, for CH_2), just as found for $RuCH_2^+$. Bridging carbenes with electronegative substituents at carbon should be (and are) rare, since donor/acceptor (terminal) bonding is preferred.[30a] Indeed, the M–C bonds in a μ-CF_2 complex should be weaker than those in a μ-CR_2 system by the singlet-triplet gap of CF_2 (57 kcal/mol), since excitation to $^3B_1$ CF_2 is necessary in order to form the bridged species.

In sum, a desired bonding/reactivity scenario, be it carbene, alkylidene, or an intermediate case, can be designed by appropriate choice of both metal and ligand to meet the electronic requirements dictated by the character of each mode of bonding.

VI. Summary

Ab initio electronic structure calculations on simple metal carbenes reveal the following conclusions:

(i) Relative stabilities of metal carbenes vs. metal alkylidenes are predicted to be most sensitive to choice of metal for the first-row transition-metal CH_2 complexes (alkylidene state lowest for the early metals and the carbene state more favored for the late metals).

(ii) Second- and third-row metals lead to situations where both states may be competetive and where the ground state may be determined by other factors (e.g., substituents on CXY and/or ancillary ligands).

(iii) M–CH_2 σ-donor bonds are calculated to be worth 35–40 kcal/mol while π-back-bonds are found to be ~30 kcal/mol. These values are expected to vary systematically depending on the electronegativity of the metal complex, with the σ bond becoming stronger and the π bond becoming weaker as the metal becomes more electrophilic.

(iv) The above ideas are utilized in formulating a general design prescription for the synthesis of $L_nM(CXY)$ complexes, based on quantitative electronic properties. For example, terminal CXY groups will be favored by electronegative substituents at carbon (X, Y = F, Cl, OR, NR_2), while bridging CXY will be favored when X and/or Y are electropositive (X, Y = R, H, SiR_3).

VII. Calculational Details

A. Basis Sets. All atoms were described with all-electron valence double-ζ (VDZ) basis sets. The Four's level VDZ basis sets[34] were used for Cr, contracted (10s8p5d/5s4p2d), and for Ru, contracted (16s13p7d/6s5p3d).[34b] The standard Huzinaga–Dunning VDZ bases[35] for C (9s5p/3s2p) and H (4s/2s) were used, with one set of d-polarization functions ($\zeta_d = 0.69$)[1a] added to the carbon basis set.

B. Wavefunctions. The generalized valence bond (GVB) method was used in all calculations. The GVB perfect pairing wavefunction is an MCSCF (multiconfigurational self-consistent field) wavefunction in which each bond pair is described with two GVB one-electron orbitals

$$\varphi(1)\varphi(2) \rightarrow \varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)$$

whose shapes are optimized. As a bond is broken, the overlap, S_{ab}, of the two GVB orbitals describing the bond goes to zero, but for a strong bond near R_e, or for a lone pair, the overlap is near unity. In the limit that $S_{ab} \rightarrow 1$, the GVB description degenerates to the HF description. Generally it is only necessary to use the GVB description for electron pairs where the overlap differs significantly from unity. This applies most strongly to M–X bonds in which the mismatch in orbital sizes results in overlaps ranging from 0.3 to 0.7 between metal and ligand orbitals, while the doubly occupied core orbitals and C–H bonds (each pair with nearly unit overlap) are treated at the Hartree–Fock level. Thus, the general wavefunction has the form

$$\mathcal{A}\{\Phi_{CORE}(\varphi_{1a}\varphi_{1b} + \varphi_{1b}\varphi_{1a})(\varphi_{2a}\varphi_{2b} + \varphi_{2b}\varphi_{2a})\cdots\chi_{SPIN}\} \tag{I}$$

where the doubly occupied orbitals are in Φ_{CORE} but calculated self-consistently with the GVB orbitals $(\varphi_{1a},\varphi_{1b})$, $(\varphi_{2a},\varphi_{2b})$, etc.

In order to indicate how many electrons are correlated, we denote the wavefunction as

$$GVB(n/m)$$

where n is the number of GVB electron pairs and m (usually $m = 2n$) is the total number of natural orbitals within the GVB space. The wavefunction (I) is denoted as PP (for perfect pairing) because the electrons in orbitals φ_{1a} and φ_{1b} have their spins coupled into a singlet, the electrons in orbitals φ_{2a} and φ_{2b} have their spins coupled into a singlet, etc.

C. Geometry Optimization. The geometry of the $^6A_1$ state of $CrCH_2^+$ was optimized at the GVB-RCI(1/2)*S_{val} level (generalized valence-bond-restricted configuration interaction times all single excitations from all valence orbitals to all virtual orbitals). The GVB-RCI(1/2) description allows a full CI within the pair of natural orbitals describing the Cr–C σ bond, resulting in three spatial configurations. For $^6A_1$ $CrCH_2^+$ these three configurations have eight associated spin eigenfunctions (SEF's), while for the $^4B_1$ state, the GVB(2/4)-RCI description (two bond pairs with four natural orbitals to describe both σ and π bonds) has nine configurations with 34 associated SEF's. The physical interpretation of the RCI wavefunction involves inclusion of interpair correlation and high-spin coupling on the metal atom. Single excitations from the valence orbitals to all virtuals allows orbital shapes to relax as the geometry is optimized. Note we kept the C–H bond distance fixed at 1.078 Å, while optimizing the H–C–H angle and the Cr–C distance.

D. Bond Energies. The bond energies for the $^6A_1$ state of $CrCH_2^+$ were calculated at the GVB(1/2)-PP, GVB-RCI(2), GVB-RCI(2)*D_σ, GVB-RCI*S_{val}, and GVB-RCI(2)*S_{val} + GVB-RCI(2)*D_σ levels. Since the PP, RCI, and RCI*S levels are explained above, we will now outline the two calculations which allow double excitations to the virtual space. While the GVB-RCI wavefunction generally leads to a good description of potential surfaces as bonds are formed and broken, we find that it is systematically low for bond energies. The reason is that at R_e there are a number of ways that the electrons correlate their motion, only part of which can be described with the two GVB orbitals (per bond pair). Thus, to obtain good bond energies, we must allow the two electrons of the bond pair to use any orbital of the basis (double excitations out of the bond pair are thus required). This CI, denoted as GVB-RCI(2)*D_σ, includes all single and double excitations from the Cr–C σ bond pair starting from the set of RCI configurations. The other (higher level) calculation is just a sum of the RCI*S and the RCI*D_σ calculations. We calculate the energy to dissociate to ground-state Cr^+ (^6S) and excited state CH_2 ($^1A_1$), since this process corresponds to the experimentally observable metal–carbene dissociation pathway in which no electronic relaxation from singlet fragments is expected (e.g., for low-valent $M(CO)_5$ and heterocarbene fragments). At infinite Cr–C separation, we allow the CH_2 σ pair to use a π-correlating orbital as a second natural orbital, since this

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provides the best correlation for singlet CH_2 described as a GVB(1/2) orbital pair. (The CH_2 σ pair at R_e(Cr–C) prefers a σ-correlating orbital.)

We now discuss the CI's in terms of their dissociation limits.

(1) GVB(1/2)-PP and GVB-RCI(2) both dissociate to Hartree–Fock (HF) Cr^+ (total energy = −1042.004 30 hartree) and GVB(1/2)CH_2 (total energy = −38.901 64 hartree). [We calculate an HF bond energy by dissociating to HF Cr^+ and HF CH_2 (total energy = −38.880 98 hartree).]

(2) RCI(2)*D_σ dissociates to HF Cr^+ and RCI(2)*D_σ CH_2 (total energy = −38.916 49 hartree; 45 spatial configurations/45 spin eigenfunctions).

(3) RCI(2)*S_{val} dissociates to HF*S_{val} Cr^+ (equivalent to HF here) and RCI(2)*S_{val} CH_2 (total energy= −38.907 64 hartree; 34 spatial configurations/37 spin eigenfunctions). The RCI*$S_{valence}$ CI in general not dissociation-consistent, but due to the equivalence of HF to HF*S for d^5 Cr^+, this CI, as are all the ones discussed here, is indeed dissociation-consistent.[1]

(4) RCI(2)*S_{val} + RCI(2)*D_σ dissociates to HF (or equivalently, HF*S_{val}) Cr^+ and {RCI(2)*S_{val} + RCI(2)*D_σ} CH_2 (total energy = −38.922 49 hartree; 69 spatial configurations/72 spin eigenfunctions), since the σ bond localizes back on CH_2 at $R = \infty$.

E. State Splittings. In order to preserve a balanced description of the $^6A_1$ and $^4B_1$ states of $CrCH_2^+$, we must allow the same degree of freedom for both states in order to ensure we are treating both states equivalently (no artificial biases). We can accomplish this by maintaining the same number of occupied orbitals included in the SCF description of both states. The $^6A_1$ state, with a GVB(1/2) description, has a valence space consisting of two C–H doubly occupied orbitals (treated as HF MO's), one Cr–C bond pair with two natural orbitals (NO's), and five singly occupied nonbonding 3d-orbitals, for a total of nine orbitals in the valence space. The $^4B_1$ state, with a GVB(2/4) description, has a valence space consisting of the two C–H HF MO's, two Cr–C bond pairs (four NO's), and three singly occupied 3d-orbitals, for a total of nine orbitals again. Therefore we have a balanced orbital description of the two states at the two levels described above.

F. Ru Carbene Calculations. All calculations on the various electronic states of $RuCH_2^+$ are described in paper 2 of this series.[1b]

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Electrochemically Catalyzed Aromatic Nucleophilic Substitution. Reactivity of Cyanide Ions toward Aryl Radicals in Liquid Ammonia

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Abstract: The mechanism of the substitution of a series of aromatic halides by cyanide ion under electrochemical induction is described as a function of the substrate. The rate constants of the addition of cyanide ion on eight aryl radicals have been determined by using either a direct or a competitive electrochemical method. The variation of the reactivity toward the CN^- ions with the structure of the aryl radicals is discussed.

Aromatic nucleophilic substitution occurring along a $S_{RN}1$ mechanism[2a] has been the object of active attention during the past 15 years.[2,3] It proceeds along the following reaction sequence:

$$ArX + e^- \rightleftarrows ArX^{\bullet-} \qquad (0)$$

$$ArX^{\bullet-} \xrightarrow{k_1} Ar^\bullet + X^- \qquad (1)$$

$$Ar^\bullet + Nu^- \xrightarrow{k_2} ArNu^{\bullet-} \qquad (2)$$

$$ArNu^{\bullet-} - e^- \rightleftarrows ArNu \qquad (3)$$

and/or

$$ArNu^{\bullet-} + ArX \rightleftarrows ArNu + ArX^{\bullet-} \qquad (4)$$

thus requiring an electron transfer reduction (the source of electron being an electrode,[3] solvated electrons,[2] or other redox reagents[4]) or a photoreduction[2] of the substrate ArX. Cleavage of the anion radical, $ArX^{\bullet-}$, thus generated produces the σ-aryl radical, $Ar^\bullet$, which is the actual electrophilic reactant in the reaction rather than the starting ArX. The key step of the reaction is then the coupling of the aryl radical and the nucleophile, leading to the

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