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Energy Partitioning Analysis of the Bonding in Ethylene and Acetylene Complexes of Group 6, 8, and 11 Metals: $(CO)_5TM-C_2H_x$ and $Cl_4TM-C_2H_x$ (TM = Cr, Mo, W), $(CO)_4TM-C_2H_x$ (TM = Fe, Ru, Os), and $TM^+-C_2H_x$ (TM = Cu, Ag, Au)[†,§,⊥]

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Quantum chemical calculations at the DFT level have been carried out for the title compounds. The equilibrium geometries and bond dissociation energies are reported. The nature of the bonding between the metal and the π ligands ethylene and acetylene has been investigated by means of an energy partitioning analysis. The nature of the metal−ligand interactions is not very different from each other in the donor−acceptor complexes $(CO)_5TM-C_2H_x$ (TM = Cr, Mo, W), $(CO)_4TM-C_2H_x$ (TM = Fe, Ru, Os), and $TM^+-C_2H_x$ (TM = Cu, Ag, Au). The metal−C_2H_x bonds have a slightly more electrostatic than covalent character. The covalent bonding comes mainly from the metal ← ligand σ donation and the metal → ligand $\pi_{\|}$ in-plane back-donation. The contributions from the out-of-plane $\pi_{\perp}$ and δ orbitals are negligible. The main difference of the bonding interactions in the metallacyclic compounds $Cl_4TM-C_2H_x$ (TM = Cr, Mo, W) is that they are clearly more covalent than electrostatic. The covalent interactions come also mainly from $a_1(\sigma)$ and $b_2(\pi_{\|})$ interactions. The $a_2(\delta)$ orbital interactions are negligible but the interactions of the out-of-plane π orbitals in the acetylene complexes $Cl_4TM-C_2H_2$ contribute ∼11% to the total orbital term.

Introduction

The bonding situation in transition metal (TM) complexes with alkenes or alkynes as π-bonded ligands is usually discussed within the framework of the Dewar−Chatt−Duncanson (DCD) model.[1,2] The DCD model considers the metal−ligand bond as a donor−acceptor interaction between two closed-shell fragments. The bonding arises through a synergistic metal ← ligand σ-donation from the occupied in-plane π-orbital[3] of the alkene/alkyne into the empty d(σ) AO of the metal, and metal → ligand π-back-donation from the occupied d(π) orbital of the metal into the empty π^* orbital of the ligand. An alternative bonding model which is important for transition metals in high oxidation states considers the alkene/alkyne complex as a metallacyclic compound in which the metal−ligand interactions are described in terms of two electron sharing σ-bonds between the metal and the carbon atoms. This dual classification of the bonding situation in terms of covalent interactions in metallacycles and donor−acceptor bonds in complexes has been shown to be helpful for the understanding of experimental as well as theoretical results both in main group[4] and transition-metal compounds.[5,6]

In a recent paper, we reported about quantum chemical calculations of ethylene and acetylene complexes of the group 10 elements nickel, palladium, and platinum.[7] The nature of the metal−ligand bond was analyzed by means of an energy decomposition analysis. As an extension of this study, we report here the results of the bonding analysis of the ethylene and acetylene complexes of group 11 cations $TM-C_2H_x^+$ (TM = Cu, Ag, Au) as well as the ethylene and acetylene carbonyl complexes of the metals of group 8 $(CO)_4TM-C_2H_x$ (TM = Fe, Ru, Os) and group 6 $(CO)_5TM-C_2H_x$ (TM = Cr, Mo, W). One question we will address in this paper concerns the differences in the bonding situation between high-valent and low-valent compounds. We therefore include in this study the complexes of the group 6 elements $Cl_4TM-C_2H_x$.

The nature of the chemical bonding in high-valent and low-valent tungsten complexes with side-on bound π ligands has already been investigated by Pidun and Frenking.[5] From the analysis of the electronic charge distribution, the authors concluded that the bonding situation in the two classes of compounds is qualitatively different from each other. A very helpful tool in their study was the charge decomposition analysis (CDA).[8] The CDA is a partitioning scheme of the Hilbert (orbital) space which considers the bonding in a complex in terms of fragment molecular orbital interactions. Another method that also provides a quantitative analysis of the chemical bond is the energy decomposition analysis (EDA), developed by Morokuma[9] and by Ziegler,[10] which is based on energy terms rather than on an orbital-based population analysis. Its current implementation in the ADF program package[11] allows one to analyze both donor−acceptor interactions as well as electron-pairing covalent bonds. The advantage of the EDA method is that it gives also information about the electrostatic contributions and the Pauli repulsion to the metal−ligand interactions. The EDA results will thus complement the CDA investigation which considers only orbital interactions.

The nature of the metal−ligand bonding in some compounds of our work have already been studied with theoretical methods in earlier works.[5,12−26] The ethylene complexes of group 11 cations were investigated in an early study by Ziegler et al.[12] and more recently by Hertwig et al.[13a] with the same energy

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decomposition scheme we used in the present work. The EDA method has also been used previously to analyze the bonding situation in ethylene complexes of group 8 elements $(CO)_4FeC_2H_4$ by Weitz and co-workers[24a] and in $(CO)_4OsC_2H_4$ by Ziegler and co-workers.[19] In the latter two studies and in the earlier work by Ziegler et al., the authors interpreted the energy terms after adding up the Pauli repulsion and electrostatic attraction into a term called steric energy. This has been criticized by several authors, because the steric term has no real physical meaning, and it should not be confused with the loosely defined concept of steric interaction between substituents.[11,27] Also, electrostatic attraction and Pauli repulsion have usually opposite signs and sometimes nearly cancel each other numerically which leads to the deceptive impression that the metal−ligand bonding comes only from orbital interactions. We think that the electrostatic attraction and the Pauli repulsion, two well-defined terms with a clear physical meaning, have to be considered separately so that the bonding contributions of the electrostatic and orbital interactions can be properly compared to estimate the ratio of electrostatic and covalent bonding. An EDA analysis of the bonding situation in the group 6 complex $(CO)_5CrC_2H_4$ has been presented by Cedeno and Weitz.[24b]

This study extends a research program we started 3 years ago whose main goal is to quantitatively analyze the chemical bond in terms of contributions with a straightforward physical meaning. Previous results of this project have been summarized in a recent review.[27]

Methods

The geometries, harmonic frequencies, bond dissociation energies and the bonding analysis have been calculated at the nonlocal DFT level of theory using the exchange functional of Becke[28] and the correlation functional of Perdew[29] (BP86). Uncontracted Slater-type orbitals (STOs) were used as basis functions for the SCF calculations.[30] The basis sets for all atoms have a triple-ζ quality augmented with one set of polarization functions, i.e., p functions on hydrogen, d functions on carbon, oxygen, and chlorine, and f functions on the metals. The $(1s2s2p)^{10}$ core electrons of the transition metals and the chlorine atoms and the $1s^2$ core electrons of carbon and oxygen were treated by the frozen core approximation.[31] An auxiliary set of s, p, d, f, and g STOs were used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.[32] Scalar relativistic effects have been considered for the transition metals using the zero-order regular approximation (ZORA).[33,34] This level of theory is denoted BP86/TZP. The calculations have been performed with the program package ADF 2000.01.[11] All structures reported here have been checked to be energy minima on the potential energy surface.

The nature of the metal−ligand bond has been analyzed by means of the energy decomposition analysis implemented in the program package ADF, which is based on the methods of Morokuma[9] and Ziegler.[10] The bond dissociation energy D_e between two fragments A and B is partitioned into several contributions which can be associated with physically meaningful entities. In the present case, one fragment is the ligand ethylene or acetylene and the other the metal moiety TM^+, $(CO)_{4,5}TM$ or Cl_4TM. In the EDA method, the dissociation energy D_e is first separated into two major components ΔE_{prep} and ΔE_{int}:

$$-D_e = \Delta E_{prep} + \Delta E_{int} \quad (1)$$

ΔE_{prep} is the energy required to promote the fragments from their equilibrium geometry and electronic ground state to the geometry and electronic state they have in the complex. ΔE_{int} is then the instantaneous interaction energy between the two "prepared" fragments. The interaction term ΔE_{int} is partitioned into three components:

$$\Delta E_{int} = \Delta E_{Pauli} + \Delta E_{elstat} + \Delta E_{orb} \quad (2)$$

ΔE_{elstat} gives the classical electrostatic interaction energy between the fragments with frozen electron density when they are brought from infinite distance to the position they have in the complex. The second term ΔE_{Pauli} gives the repulsive four-electron interactions between occupied orbitals. It is calculated by enforcing the Kohn−Sham determinant of the molecule which results from superimposing the fragments to be orthonormal through antisymmetrization and renormalization. The stabilizing orbital interaction term ΔE_{orb} is calculated in the final step of the analysis when the Kohn−Sham orbitals are allowed to relax to their final form. The orbital term ΔE_{orb} can be identified as the covalent contributions to the attractive interactions. Thus, the ratio $\Delta E_{eltat}/\Delta E_{orb}$ indicates the electrostatic/covalent character of the bond. ΔE_{orb} can be further partitioned into different contributions according to the irreducible representations of the interacting system point group. This makes it possible to calculate the contributions of σ and π bonding to a covalent multiple bond. More details about the method can be found elsewhere.[11b]

Geometries

Figure 1 shows the BP86/TZP optimized geometries for the complexes studied in this work. All structures were optimized under C_{2v} symmetry constraint.

Previous theoretical investigations have already addressed a comparison of theoretically optimized geometries of the present complexes obtained at different levels of theory with experimental data.[5,13,17−26,35] We will therefore not discuss the geometrical data in detail. Our calculated geometries shown in Figure 1 are generally in good agreement with earlier theoretical work and with experimental data. We rather comment briefly on the trends observed when the geometries of the ethylene and acetylene complexes within the same group are compared.

Two geometrical aspects are relevant for us: the metal−ligand bond distances and the deformation of the C_2H_x ligand by complexation at the metal. With respect to the former, two points deserve to be commented. First, the calculated $TM-C_2H_x$ distances as one moves down the group have in all cases a V-shape trend with a maximum in the complex of the second-row transition metal. It is well-known that relativity causes a radial contraction of the atomic s-orbitals as well as a radial expansion of the d-orbitals.[36] This usually leads to a shortening in the metal−ligand bond distance in the complexes of the third-row TM when compared to the second-row ones. The relativistic effects in the complexes studied in this work have been analyzed in detail elsewhere.[13,19] The second point we want to point out is the fact that for all the systems collected in Figure 1 the TM−C(ethylene) bond distances are longer than the TM−C(acetylene) ones for the same metal. This can be explained with the hybridization at the carbon atoms. The orbitals of the TM−C(ethylene) bond have less s-character than the TM−C(acetylene) bond.

As a consequence of the metal−ligand interactions the structures of both the metal fragment and the ligand are affected. Within the framework of the DCD model one predicts an

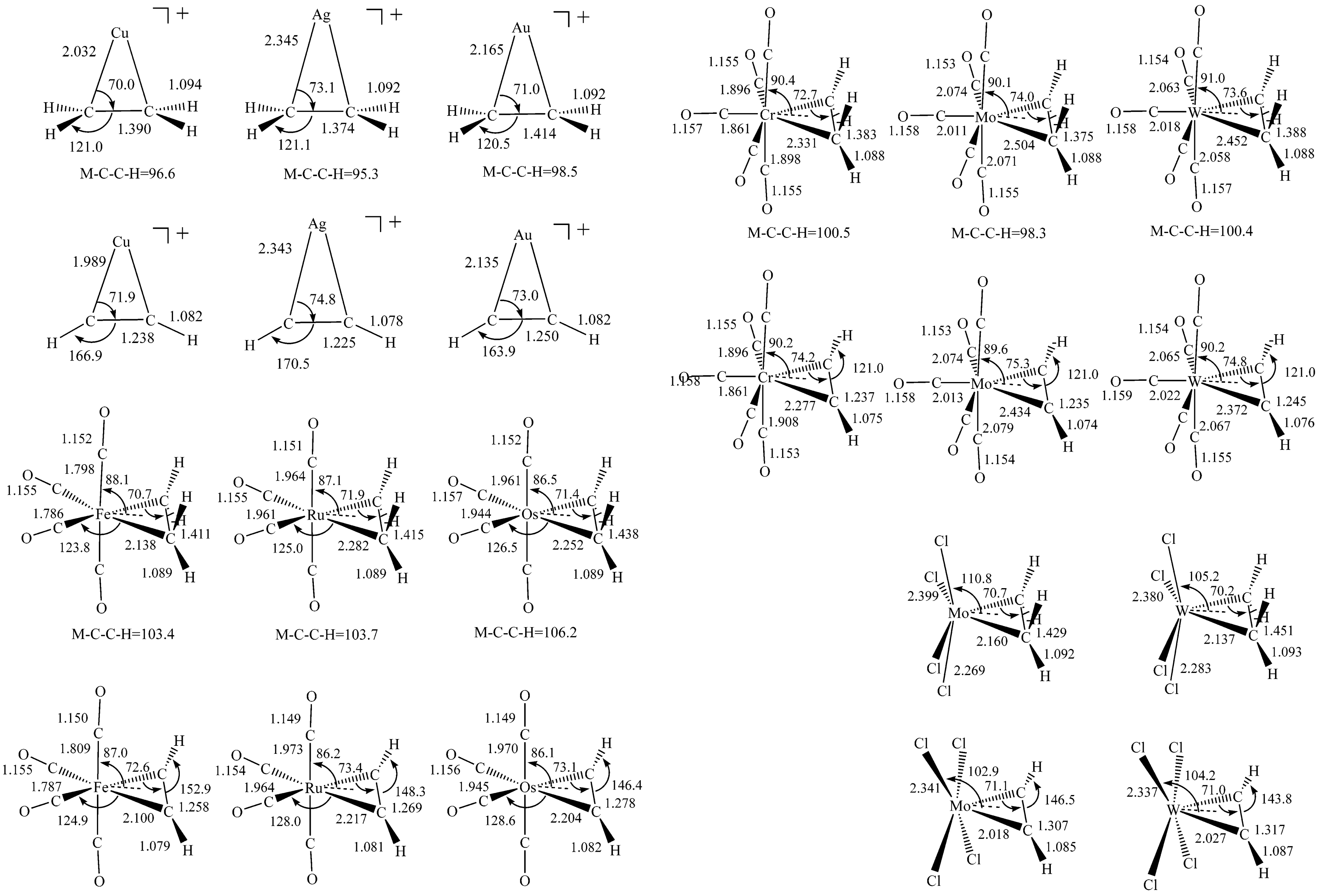

Figure 1. Optimized geometries of the complexes studied in this work. Bond lengths are given in angstoms and angles in degrees.

TABLE 1: Energy Decomposition Analysis and Hirshfeld Partial Charges q of $TM-C_2H_x^+$ at BP86/TZP (kcal/mol) Using Closed Shell Fragments $TM^+(d^{10})$ and C_2H_x

	Cu^+				Ag^+				Au^+			
	C_2H_4		C_2H_2		C_2H_4		C_2H_2		C_2H_4		C_2H_2	
ΔE_{int}	−63.5		−62.0		−40.8		−35.9		−79.1		−70.8	
ΔE_{Pauli}	98.9		103.6		61.8		56.4		157.2		161.0	
ΔE_{elstat}	−90.6	(55.8%)	−94.6	(57.1%)	−59.8	(58.3%)	−54.8	(59.4%)	−134.7	(57.0%)	−134.1	(57.8%)
ΔE_{orb}	−71.8	(44.2%)	−71.1	(42.9%)	−42.8	(41.7%)	−37.5	(40.6%)	−101.6	(43.0%)	−97.8	(42.2%)
$\Delta E(a_1)\sigma$	−42.6	(59.4%)	−39.5	(55.7%)	−29.6	(69.2%)	−25.6	(68.4%)	−68.0	(67.0%)	−63.1	(64.6%)
$\Delta E(a_2)\delta$	−2.2	(3.1%)	−0.9	(1.3%)	−1.6	(3.7%)	−0.3	(0.8%)	−2.6	(2.6%)	−1.3	(1.4%)
$\Delta E(b_1)\pi_\perp$	−5.1	(7.1%)	−6.9	(9.7%)	−2.7	(6.4%)	−3.4	(9.0%)	−5.5	(5.4%)	−6.9	(7.0%)
$\Delta E(b_2)\pi_\parallel$	−21.9	(30.5%)	−23.7	(33.4%)	−8.8	(20.6%)	−8.2	(21.8%)	−25.5	(25.0%)	−26.5	(27.1%)
E_{prep}	3.5		3.7		2.0		1.8		6.2		5.8	
$-D_e$	−60.0		−58.3		−38.8		−34.1		−72.9		−64.9	
$-D_0$	−58.5		−57.7		−37.5		−33.6		−71.2		−64.3	
q(TM)	0.85		0.88		0.81		0.83		0.73		0.77	
$q(C_2H_x)$	0.15		0.12		0.19		0.17		0.27		0.23	

[a] Values in parentheses give the percentage of attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$. [b] Values in parentheses give the percentage contribution to the total orbital interactions.

elongation of the carbon−carbon bond length of C_2H_x as a consequence of the removal of electron density from its bonding π-orbital and increase of electron density in its antibonding π^* orbital. Another geometrical consequence of the complexation is the partial pyramidalization (ethylene ligand) or bending (acetylene ligand) at the carbon atoms. Figure 1 shows that the C−C distances of the ligands are longer than in free ethylene and acetylene[37] and that there is substantial pyramidalization and bending, respectively, at the carbon atoms (see the Supporting Information for the pyramidalization and bending angles). The energies that are associated with the deformation of the ligands will be discussed below.

Particulary interesting are the geometrical differences of the metal−ligand fragments between the high- and low-valent TM compounds. No data belonging to $Cl_4CrC_2H_x$ are reported because it was not possible to obtain SCF convergence for this system at the BP86/TZP level of theory. In agreement with previous results[5,25,26] we find shortenings of 0.3−0.4 Å in the metal−ligand distances of the high-valent analogues with respect to the low-valent ones. The C_2H_x fragment is also much more distorted in the former compounds. The larger geometrical reorganization of the ligands should be related to a larger electron density distortion with respect to the free fragments which was investigated by us earlier.[5,25,26] The changes of the electronic structure will be discussed in the next section.

Bonding Analysis

(a) Complexes of Group 11 Elements TM^+-C_2H_x (TM = Cu, Ag, Au). The EDA results and the calculated Hirshfeld charges[42] of the ethylene and acetylene complexes of group 11 elements are given in Table 1. The four top entries give the values of the interaction energy (ΔE_{int}) and its decomposition in terms of the electrostatic, Pauli, and orbital (covalent) contributions. The orbital term is further partitioned according to the irreducible representations of the C_{2v} point group, which is shown in the following four entries. The percentage values refer to the contribution of each term to the total orbital term, ΔE_{orb}. Finally, the preparation energy (ΔE_{prep}) and the dissociation energy (D_e and, including the ZPE, D_o) are given. The absolute values of the bond dissociation energies given in Table 1 are too high, but the trend is correctly predicted. The experimental values for the BDEs are $D_o(Cu^+-C_2H_4)$ = 41.5 kcal/mol,[38] $D_o(Ag^+-C_2H_4)$ = 33.7 kcal/mol[39] and $D_o(Au^+-C_2H_4)$ ∼65 kcal/mol.[13c,d]

The calculations predict that the interaction energy for both ethylene and acetylene complexes have the trend for the different metals TM Au > Cu > Ag. The same V-like trend caused by relativistic effects is observed for the BDEs. The marginally larger BDEs of the ethylene complexes with respect to the acetylene ones (with differences increasing downward in the group) are due to the slightly stronger metal−ligand interactions in the former species and are not due to the preparation energies, i.e., the ethylene ligand is always stronger bonded than acetylene. Note that the metal−C(ethylene) bonds are always longer than the metal−C(acetylene) ones although the former bonds are stronger than the latter. It follows that *there is no correlation between the metal−ligand bond length and the bond strength of group 11 complexes* $TM^+-C_2H_x$.

Previous studies on the bonding situation of $(C_2H_4)TM^+$ and $(C_2H_2)TM^+$ complexes suggested that the interaction is mainly electrostatic with only negligible covalent contributions.[13a,14,15a,16] Table 1 shows that, according to the energy decomposition analysis, the character of the C_2H_4/C_2H_2-TM bond is more electrostatic than covalent but the covalent contributions play an important role: the ΔE_{orb} term accounts for 41−44% of the attractive interactions. Notice that the percentage values of ΔE_{elstat} and ΔE_{orb} change very little for the different metals.

A qualitative orbital interaction diagram which illustrates the DCD bonding model for ethylene and acetylene complexes is shown in Figure 2. In ethylene complexes there are two principal bonding components: the metal ← ligand σ donation which involves the d_z2 AO of the metal (Figure 2a) and the metal → ligand $\pi_\parallel$ in-plane back-donation (Figure 2b). Acetylene has an additional out-of-plane $\pi_\perp$ orbital which in principle could also serve as an electron donor. The orbitals that contribute to the metal ← ligand $\pi_\perp$ out-of-plane donation are shown in Figure 2c. Finally, the out-of-plane $\pi_\perp$ orbitals yield metal → ligand back-donation by mixing the occupied d_{xy} AO of the metal and the vacant $\pi_\perp^*$ orbital of the ligand. These orbitals have δ symmetry (Figure 2d). Note that the strength of the interactions shown in Figure 2, parts a−d depends on the occupation of the orbitals. The group 11 metal ions TM^+ have a d^{10} configuration, i.e., the valence (n − 1)d orbitals are fully occupied but the valence (n)s orbital is empty. The molecules have C_{2v} symmetry and therefore, the valence s and d_{z^2} AO of the metal can mix yielding an empty acceptor orbital for the in-plane metal ← ligand σ donation (Figure 2a). In contrast to this there should be no metal ← ligand $\pi_\perp$ out-of-plane donation in the (C_2H_4)-

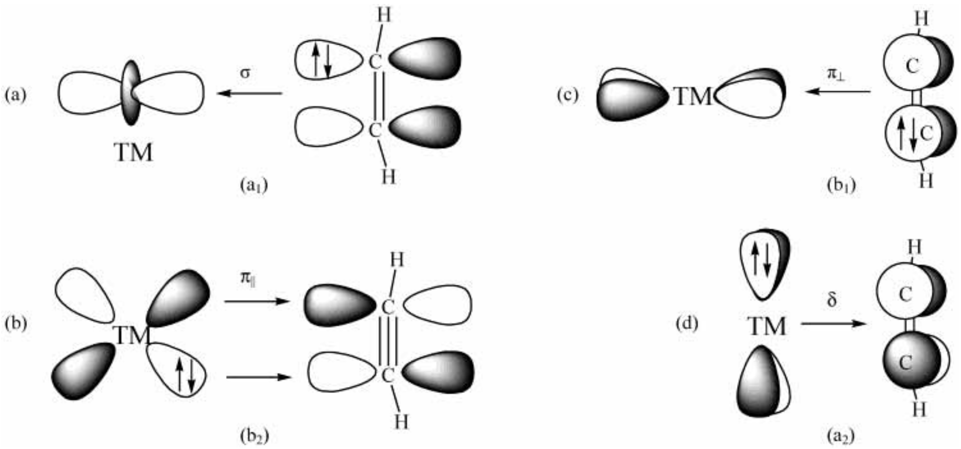

Figure 2. Schematic representation of the most important orbital interactions in TM−alkyne complexes: (a) metal ← ligand in-plane σ donation; (b) metal → ligand in plane $\pi_{||}$ back-donation; (c) metal ← ligand out-of-plane $\pi_{\perp}$ donation; (d) metal → ligand δ back-donation. The symmetry assignments a_1, a_2, b_1, and b_2 are given with respect to overall C_{2v} symmetry.

TM^+ and $(C_2H_2)TM^+$ complexes because the d_{yz} valence AO of the metals is occupied.

As commented in the methods section, the EDA makes it possible to further partition the orbital term in contributions that can be classified according to the irreducible representations of the local symmetry point group of the molecular system which in all the complexes we have studied is C_{2v}. Figure 2 shows that, under the symmetry point group, the four orbital interactions have the symmetries $a_1(\sigma)$, $a_2(\delta)$, $b_1(\pi_{\perp})$, and $b_2(\pi_{||})$. The partitioning of the ΔE_{orb} term gives therefore a quantitative estimate of the strength of the interactions which are schematically shown in Figure 2. The data collected in Table 1 show that the largest contribution to the orbital term comes from the $a_1(\sigma)$ interaction which yields between 59.4 and 69.2% of the total covalent bonding in the ethylene complexes and between 55.7 and 68.4% in the acetylene ones. The $b_2(\pi_{||})$ term contributes less but it is still significant: 20.6−30.5% in (C_2H_4)-TM^+ and between 21.8 and 33.4% in $(C_2H_2)TM^+$. Note that the relative contribution of the in-plane $b_2(\pi_{||})$ back-donation has the trend Cu > Au > Ag for both classes of compounds. The contribution of the metal ← ligand out-of-plane $b_1(\pi_{\perp})$ donation is much smaller and it is probably mainly caused by orbital relaxation effects rather than genuine charge donation. The contribution of the $a_2(\delta)$ back-donation is negligible.

The $a_1(\sigma)$ interaction is slightly more important in the ethylene complexes than in acetylene complexes: Table 1 shows that, in the cationic complexes of group 11 elements, ethylene is a better σ donor whereas acetylene is a marginally better π acceptor. However, the EDA results show that overall the natures of the metal−ethylene and metal−acetylene bonding in the complexes $(C_2H_x)TM^+$ are very similar to each other.

The calculated charges at the metals TM and the ligands C_2H_x indicate the metals carry most of the positive charge of the complex (Table 1). Note that the acetylene ligand is always slightly less positively charged than the ethylene ligand. This is in agreement with the EDA results which suggest that, in the acetylene complexes, metal ← (C_2H_x) donation ($a_1 + a_2$ orbital interactions) has less weight and metal → (C_2H_x) back-donation ($b_1 + b_2$ orbital interactions) has more weight than in the ethylene complexes.

Complexes of Group 8 Elements $(CO)_4TM$-C_2H_x (TM = Fe, Ru, Os). The nature of the metal−ligand bonding in the group 8 ethylene complexes $(CO)_4TM(C_2H_4)$ has previously been analyzed in a theoretical study by Li et al.[19] The $Fe(CO)_4$-(C_2H_4) complex was also studied by Axe et al.[20] and by Chen et al.[22] Bender et al. analyzed the bonding in $Os(CO)_4(C_2H_4)$.[23] The bonding situation in the group 8 acetylene complexes $(CO)_4TM(C_2H_2)$ has been addressed by Decker and Klobukowski.[21] Chen et al have also studied the $Fe(CO)_4(C_2H_2)$ complex.[22] The complex $Os(CO)_4(C_2H_4)$ has earlier been investigated by means of an energy decomposition analysis[19] while $Fe(CO)_4(C_2H_4)$ was the subject of a recent EDA investigation.[24a]

Table 2 gives the EDA results and the calculated Hirshfeld charges[42] for the ethylene and acetylene complexes of group 8 elements. The calculated data show that the trend of the BDEs as we move down the group displays a characteristic V-shaped curve. Notice, however, that now the first-row TM complexes have slightly larger bond energies than the third-row TM species. This is opposite to the trend observed for cationic complexes of group 11 elements. The reason the dissociation energies of the $Os(CO_4)C_2H_x$ species are smaller than the dissociation energies of $Fe(CO)_4C_2H_x$ is not due to weaker metal−ligand bonding interactions but rather to the significantly higher preparation energies of the former complexes. The role of the deformation energy in bonding and reactivity of olefin complexes $Fe(CO)_4C_2X_4$ (X = H, F, Cl, Br, I, CN) was investigated in a detailed theoretical study by Weitz and co-workers.[24a] The complex $Ru(CO)_4C_2H_2$ has a larger interaction energy ΔE_{int} than $Fe(CO)_4C_2H_2$ (Table 2). The metal−ligand bonds have a slightly more electrostatic than covalent character, the ΔE_{elstat} term yields 51.9−56.3% of the total attractive forces. The metal-acetylene bond has more covalent character than the metal-ethylene bond although the differences are not very large. Notice that the ratio of the ΔE_{orb} and ΔE_{elstat} contributions is very similar to those found in the cationic complexes of group 11 elements. The theoretically predicted bond dissociation energy of $(CO)_4Fe$−C_2H_4, D_o = 30.6 kcal/mol, is slightly lower than the experimental value which is 37 ± 3 kcal/mol.[40]

The decomposition of ΔE_{orb} into contributions from the different symmetry representations of the C_{2v} point group shows that the largest contributor to the covalent bonding is the b_2 $(\pi_{||})$ metal → ligand back-donation which accounts 51.5−55.5% of the total ΔE_{orb} term in the ethylene complexes and 54.7−60.8% in the acetylene ones. The larger contribution of the back-donation in complexes of group 8 elements when compared to those of group 11 cations can be explained with the positive charge carried by the metal fragment in the latter species. Table 2 shows that the ligands C_2H_x in the complexes $(CO)_4TM(C_2H_x)$

TABLE 2: Energy Decomposition Analysis and Hirshfeld Partial Charges q of $(CO)_4TM-C_2H_x$ at BP86/TZP (kcal/mol) Using Closed Shell Fragments $TM(CO)_4$ and C_2H_x

	$Fe(CO)_4$				$Ru(CO)_4$				$Os(CO)_4$			
	C_2H_4		C_2H_2		C_2H_4		C_2H_2		C_2H_4		C_2H_2	
ΔE_{int}	−48.3		−49.6		−41.7		−52.3		−62.2		−70.2	
ΔE_{Pauli}	123.1		128.0		137.1		149.4		180.4		185.5	
ΔE_{elstat}	−91.0	(53.1%)	−92.3	(51.9%)	−100.6	(56.3%)	−107.3	(53.2%)	−133.5	(55.0%)	−134.3	(52.5%)
ΔE_{orb}	−80.4	(46.9%)	−85.3	(48.1%)	−78.2	(43.7%)	−94.4	(46.8%)	−109.2	(45.0%)	−121.5	(47.5%)
$\Delta E(a_1)\sigma$	−35.2	(43.8%)	−34.1	(39.9%)	−31.3	(40.0%)	−32.6	(34.5%)	−46.3	(42.4%)	−45.5	(37.4%)
$\Delta E(a_2)\delta$	−0.9	(1.1%)	−1.1	(1.3%)	−0.8	(1.1%)	−1.0	(1.1%)	−1.1	(1.0%)	−1.3	(1.1%)
$\Delta E(b_1)\pi_\perp$	−2.9	(3.6%)	−3.5	(4.1%)	−2.7	(3.4%)	−3.4	(3.6%)	−3.6	(3.3%)	−4.4	(3.6%)
$\Delta E(b_2)\pi_\|$	−41.4	(51.5%)	−46.7	(54.7%)	−43.4	(55.5%)	−57.4	(60.8%)	−58.2	(53.3%)	−70.3	(57.9%)
E_{prep}	14.9	$(5.3 + 9.6)^c$	18.9	$(6.0 + 12.9)^c$	24.6	$(14.3 + 10.3)^c$	35.7	$(18.2 + 17.5)^c$	32.9	$(17.9 + 15.0)^c$	41.4	$(21.3 + 20.1)^c$
$-D_e$	−33.4		−30.8		−17.1		−16.6		−29.3		−28.8	
$-D_0$	−30.6		−28.8		−15.3		−15.2		−26.9		−27.0	
$q[TM]^d$	0.09		0.14		0.10		0.19		0.12		0.21	
$q(C_2H_x)$	−0.09		−0.14		−0.10		−0.19		−0.12		−0.21	

[a] Values in parentheses give the percentage of attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$. [b] Values in parentheses give the percentage contribution to the total orbital interactions. [c] The values in parentheses give the preparation energies of the metal fragment and ligand, respectively. [d] Partial charge of $TM(CO)_4$.

TABLE 3: Energy Decomposition Analysis and Hirshfeld Partial Charges q of $(CO)_5TM-C_2H_x$ at BP86/TZP (kcal/mol) Using Closed Shell Fragments $TM(CO)_5$ and C_2H_x

	$Cr(CO)_5$				$Mo(CO)_5$				$W(CO)_5$			
	C_2H_4		C_2H_2		C_2H_4		C_2H_2		C_2H_4		C_2H_2	
ΔE_{int}	−29.9		−29.6		−25.6		−26.5		−35.4		−38.1	
ΔE_{Pauli}	83.9		86.2		69.1		74.9		93.0		103.5	
ΔE_{elstat}	−59.5	(52.3%)	−59.8	(51.7%)	−52.0	(55.0%)	−54.5	(53.8%)	−70.0	(54.5%)	−75.0	(52.9%)
ΔE_{orb}	−54.3	(47.7%)	−56.0	(48.3%)	−42.6	(45.0%)	−46.9	(46.3%)	−58.4	(45.5%)	−66.6	(47.1%)
$\Delta E(a_1)\sigma$	−29.0	(53.5%)	−27.1	(48.4%)	−20.4	(47.9%)	−19.8	(42.3%)	−28.8	(49.3%)	−28.4	(42.6%)
$\Delta E(a_2)\delta$	−0.6	(1.2%)	−1.3	(2.3%)	−0.6	(1.5%)	−1.1	(2.2%)	−0.7	(1.3%)	−1.4	(2.1%)
$\Delta E(b_1)\pi_\perp$	−2.2	(4.0%)	−2.5	(4.5%)	−2.1	(5.0%)	−3.0	(6.4%)	−2.7	(4.6%)	−4.1	(6.1%)
$\Delta E(b_2)\pi_\|$	−22.5	(41.4%)	−25.1	(44.9%)	−19.4	(45.6%)	−23.0	(49.0%)	−26.2	(44.9%)	−32.8	(49.2%)
E_{prep}	6.3	$(0.9 + 5.4)^c$	8.4	$(1.0 + 7.4)^c$	4.9	$(1.3 + 3.6)^c$	7.5	$(1.4 + 6.1)^c$	7.5	$(1.9 + 5.6)^c$	11.6	$(2.2 + 9.4)^c$
$-D_e$	−23.6		−21.2		−20.6		−19.0		−27.9		−26.6	
$-D_0$	−20.9		−19.6		−18.8		−18.0		−25.9		−25.3	
$q[TM]^d$	0.03		0.07		0.04		0.08		0.06		0.11	
$q(C_2H_x)$	−0.03		−0.07		−0.04		−0.08		−0.06		−0.11	

[a] Values in parentheses give the percentage of attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$. [b] Values in parentheses give the percentage contribution to the total orbital interactions. [c] The values in parentheses give the preparation energies of the metal fragment and ligand, respectively. [d] Partial charge of $TM(CO)_5$.

are always negatively charged while they are positively charged in $TM(C_2H_x)^+$ (Table 1).

We want to point out that the contribution of the metal ← ligand out-of-plane $b_1(\pi_\perp)$ donation is very small in both the ethylene and acetylene complexes. This is reasonable because the d_{yz} acceptor orbital of the metal is occupied. The contribution of the $a_2(\delta)$ back-donation is negligible. Thus, the EDA results suggest that the nature of the $(CO)_4TM-C_2H_2$ and $(CO)_4TM-C_2H_4$ bonding of group 8 metals is not very different from each other. As in the group 11 complexes $TM(C_2H_x)^+$, the acetylene ligand in $(CO)_4TM-C_2H_2$ is always slightly less positively charged than the ethylene ligand in $(CO)_4TM-C_2H_4$. The EDA results in Table 2 show that, in the acetylene complexes, $(CO)_4TM \leftarrow (C_2H_x)$ donation ($a_1 + a_2$ orbital interactions) has less weight and $(CO)_4TM \rightarrow (C_2H_x)$ back-donation ($b_1 + b_2$ orbital interactions) has more weight than in the ethylene complexes.

The acetylene complexes of group 8 elements have slightly lower BDEs than the ethylene complexes although the instantaneous metal−ligand attraction ΔE_{int} in the former is higher (Table 2). This is because the preparation energies of the acetylene ligand are higher than those of the ethylene ligand.

Complexes of Group 6 Elements $(CO)_5TM$-C_2H_x and Cl_4TM-C_2H_x (TM = Cr, Mo, W). Table 3 gives the EDA results and the calculated Hirshfeld charges[42] for the ethylene and acetylene carbonyl complexes of group 6 elements. The calculated data show that both the BDE and the ΔE_{int} values follow the same trend for the metals Mo < Cr < W. The only compound for which experimental values of the BDE have been reported is $(CO)_5Cr-C_2H_4$.[41] The average value of the experimental 24.8 ± 1.2 kcal/mol is slightly larger than the calculated value $D_o = 20.9$ kcal/mol. In agreement with what was observed for the complexes of group 8 elements, the character of the metal−ligand bond is slightly more electrostatic than covalent. The ΔE_{elstat} term contributes 51.7−55.0% of the total attractive interactions. The bonding in acetylene complexes has again a slightly higher covalent character than in the ethylene complexes. The decomposition of the orbital term shows that the $a_1(\sigma)$ interactions have a comparable strength as the $b_2(\pi_\|)$ interactions while the $a_2(\delta)$ and $b_1(\pi_\perp)$ terms are negligible. The calculated charge distribution indicates that the ligands C_2H_x of the group 6 complexes $(CO)_5TM-C_2H_x$ carry a negative charge which is slightly less than in the group 8 species $(CO)_4TM-C_2H_x$ (Table 2). This is in agreement with the trend

TABLE 4: Energy Decomposition Analysis and Hirshfeld Partial Charges q of $Cl_4TM-C_2H_x$ at BP86/TZP (kcal/mol) Using Triplet Fragments $TMCl_4$ and C_2H_x

	$MoCl_4$				WCl_4			
	C_2H_4		C_2H_2		C_2H_4		C_2H_2	
ΔE_{int}	−126.1		−153.1		−139.7		−169.4	
ΔE_{Pauli}	209.1		268.7		257.9		313.9	
ΔE_{elstat}	−132.6	(39.6%)	−165.9	(39.3%)	−172.8	(43.5%)	−206.8	(42.8%)
ΔE_{orb}	−202.6	(60.4%)	−256.0	(60.7%)	−224.7	(56.5%)	−276.5	(57.2%)
$\Delta E(a_1)\sigma$	−101.9	(50.3%)	−121.4	(47.4%)	−116.0	(51.6%)	−135.0	(48.8%)
$\Delta E(a_2)\delta$	−2.5	(1.2%)	−2.8	(1.1%)	−2.8	(1.2%)	−2.4	(0.9%)
$\Delta E(b_1)\pi_\perp$	−6.9	(3.4%)	−27.4	(10.7%)	−8.4	(3.7%)	−30.0	(10.9%)
$\Delta E(b_2)\pi_{\|\|}$	−91.3	(45.1%)	−104.4	(40.8%)	−97.5	(43.4%)	−109.1	(39.4%)
E_{prep}	133.9	$(44.8 + 89.1)^c$	141.2	$(47.5 + 93.7)^c$	126.8	$(41.0 + 85.8)^c$	131.5	$(41.7 + 89.8)^c$
$-D_e$	7.8		−11.9		−12.9		−37.9	
$-D_0$	9.4		−9.8		−11.4		−35.6	
$q[TM]^d$	0.03		0.07		0.04		0.08	
$q(C_2H_x)$	−0.03		−0.07		−0.04		−0.08	

[a] Values in parentheses give the percentage of attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$. [b] Values in parentheses give the percentage contribution to the total orbital interactions. [c] The values in parentheses give the preparation energies of the metal fragment and ligand, respectively. [d] Partial charge of $TMCl_4$.

of the energy contributions of the orbital interaction terms. Table 3 shows that, in the acetylene complexes, $(CO)_5TM \leftarrow (C_2H_x)$ donation ($a_1 + a_2$ orbital interactions) has now more weight and $(CO)_5TM \rightarrow (C_2H_x)$ back-donation ($b_1 + b_2$ orbital interactions) has less weight than in the group 8 complexes (Table 2).

The theoretically predicted dissociation energies of the ethylene complexes are slightly larger than those of the acetylene complexes which is mainly caused by the larger preparation energies of the latter species. The breakdown of the ΔE_{prep} term into contributions of the metal fragment and the ligand shows (Table 3) that it costs always more energy to deform the acetylene ligand than the ethylene ligand. This holds also for the other complexes except for $(C_2H_x)Ag^+$ and $(C_2H_x)Au^+$ (Table 1) where the differences between the ΔE_{prep} values of the ethylene and acetylene complexes are very small, though. There seems to be a subtle balance between different factors which contribute to the deformation energy. Acetylene has a C−C triple bond which needs more energy to be stretched than the C−C double bond of ethylene. The latter ligand has four C−H bonds which become deformed from the planar equilibrium geometry while acetylene has only two C−H bonds which become bend in the complexes.

One important goal of this study is to address the differences in the bonding situation between a low-valent and a high-valent transition metal compound. We shall now compare the EDA results for $(CO)_5TM-C_2H_x$ with the results for $Cl_4TM-C_2H_x$. Our previous analysis of the electronic structure of $(CO)_5W-C_2H_x$ and $Cl_4W-C_2H_x$ has shown that the latter species should be considered as a metallacylic compound which has two shared-electron bonds between WCl_4 and C_2H_x where each fragment has two unpaired electrons.[5] The EDA study was therefore carried out using the triplet states of $TMCl_4$ and C_2H_x. The results and the calculated Hirshfeld charges[42] are shown in Table 4.

The calculations give much larger interaction energies ΔE_{int} for the high-valent compounds species $Cl_4TM-C_2H_x$ than for the low-valent complexes $(CO)_5TM-C_2H_x$. This is in agreement with the much shorter TM−C distances in the former compounds than in the latter. The bond dissociation energies of the molecules $Cl_4TM-C_2H_x$ are very low, however. The theoretically predicted BDE of $Cl_4Mo-C_2H_4$ is even positive, i.e., the molecule is only kinetically stable. The small bond dissociation energies come from the large preparation energies ΔE_{prep}. The excitation energy of the C_2H_x fragments from the singlet ground state to the triplet reference state is very large. This has been discussed before.[5]

The EDA results suggest that the metal−carbon bonds in the high-valent compounds $Cl_4TM-C_2H_x$ have a higher covalent character than in the low-valent complexes $(CO)_5TM-C_2H_x$ (Tables 3 and 4). The breakdown of the ΔE_{orb} term into contributions from orbitals having different symmetry shows that, in $Cl_4TM-C_2H_x$, the $a_1(\sigma)$ interactions have a comparable strength as the $b_2(\pi_{\|})$ interactions and that the $a_2(\delta)$ term is negligible. The same result was found for $(CO)_5TM-C_2H_x$. A significant difference between the high-and low-valent species is found for the $b_1(\pi_\perp)$ term. The contribution of the b_1 orbitals in the ethylene complexes $Cl_4TM-C_2H_4$ is very small, only 3.4% and 3.7% of the total ΔE_{orb} term, but it becomes three times larger in the acetylene complexes $Cl_4TM-C_2H_2$ (Table 4). This means that the metal−carbon bonds in the latter species are additionally stabilized by out-of-plane π bonding, which contribute ~11% of the total covalent bonding. The enhanced metal ← ligand out-of-plane $\pi_\perp$ donation in $Cl_4TM-C_2H_2$ can be explained with the electron configuration d^0 of the metal in the high-valent compound. On the other hand, a contribution of ~11% is still not very large. The calculated strength of the metal ← ligand out-of-plane $\pi_\perp$ donation is not sufficient to classify the acetylene as a four π-electron donor in $Cl_4TM-C_2H_2$.

The calculated charge distribution show that the ligands C_2H_x in the compounds $Cl_4TM-C_2H_x$ carry small negative charges which have similar absolute values as in the complexes $(CO)_5TM-C_2H_x$. This is in agreement with the EDA results which indicate that the $[TM] \leftarrow (C_2H_x)$ donation ($a_1 + a_2$ orbital interactions) has nearly the same weight as the $[TM] \rightarrow (C_2H_x)$ back-donation ($b_1 + b_2$ orbital interactions) in both classes of compounds (Tables 3 and 4).

So what is the major difference between the bonding situations in $(CO)_5TM-C_2H_x$ and $Cl_4TM-C_2H_x$? Is it justified to use two different bonding models, i.e., donor−acceptor interactions and metallacyclic compound for the two classes of compounds? The EDA results given in Tables 3 and 4 show that the major difference lies in the *absolute* values of the calculated energy terms. The total interaction energies ΔE_{int} but also the energy contributions of ΔE_{elstat}, ΔE_{orb}, and ΔE_{Pauli} of the high-valent compounds $Cl_4TM-C_2H_x$ are much larger than in the low-valent $(CO)_5TM-C_2H_x$ complexes. The electron-sharing (covalent) metal−carbon binding forces in the former molecules yield shorter bond lengths and thus, larger Pauli repulsion and stronger electrostatic attraction. Of course, it is arbitrary to pick out one bonding component to be responsible for the short interatomic distance. A plausible reason for this is the fact that the interacting fragments in $Cl_4TM-C_2H_x$ are open-shell species while the fragments in $(CO)_5TM-C_2H_x$ complexes are closed-shell molecules. The classification of the molecules into two different categories, i.e., donor−acceptor complexes and metallacyclic compounds, is therefore reasonable because it establishes a helpful ordering scheme for compounds which have π-bonded ligands. We want to point out, however, that there is no fundamental difference in the nature of the binding interactions, i.e., the ratio of covalent and electrostatic bonding and the percent contributions of σ and π bonding in the high- and low-valent ethylene and acetylene complexes are not very different from each other. The two bonding models can be considered as sketches of two extreme situations where the real molecules have bonds which are between the two poles. Molecules will exist whose bonding situation may be considered as a borderline case between the two models. In fact, in our previous analysis of the electronic structure of $Cl_5W(C_2H_2)^-$, it was found that the molecule is such an example of a borderline case which may either be considered as donor−acceptor complexes or as a metallacylic compounds.[5c]

Summary

We have carried out a theoretical study on the bonding situation of ethylene and acetylene transition metal complexes by means of an energy decomposition analysis. The results of this study can be summarized as follows.

The metal−ligand bonds of the cationic complexes of group 11 elements $TM-C_2H_x^+$ have more electrostatic than covalent character. However, the covalent contributions to the bonding is quite large (40.6−44.2%) in variance with previous predictions based on orbital and density partitioning schemes. The covalent bonding in these complexes comes mainly from the metal ← ligand σ donation (55.7−69.2%). The contributions of the metal → ligand $\pi_{\|}$ in-plane back-donation are much smaller (20.6−33.4%) because the transition metal carries a positive charge. The metal ← ligand $\pi_{\perp}$ donation is much smaller. The contribution of the $a_2(\delta)$ back-donation is negligible. The ethylene ligand is slightly stronger bonded to TM^+ and the BDE values are also slightly higher compared with acetylene.

For the carbonyl complexes of group 8 elements $(CO)_4TM-(C_2H_x)$ the EDA results show that the electrostatic/covalent character of the metal−ligand bond is very similar to that found in the complexes of group 11 cations. However, the metal → ligand $\pi_{\|}$ in-plane back-donation becomes more important in the latter complexes where it is the largest contributor to the covalent interactions (51.5−60.8%). The metal ← ligand σ donation (34.5−43.8%) is clearly weaker. The metal ← ligand $\pi_{\perp}$ donation and the $a_2(\delta)$ back-donation are negligible. The acetylene ligand has slightly larger interaction energies than the ethylene ligand but the latter has higher bond dissociation energies because the ligand preparation energy of acetylene is higher.

The low-valent complexes of group 6 elements have metal−ligand bonds that are also slightly more electrostatic (51.7−55.0%) than covalent. In the ethylene complexes and in $(CO)_5CrC_2H_2$ the covalent forces come mainly from the metal ← ligand σ donation (47.9−53.5%) whereas in the molybdenum and tungsten acetylene complexes the metal → ligand $\pi_{\|}$ in-plane back-donation plays the most important role (49.0−49.2%). The metal ← ligand $\pi_{\perp}$ donation and the $a_2(\delta)$ back-donation are negligible. The BDEs are marginally larger for the ethylene complexes due to the larger preparation energies of the acetylene ligand but the differences are not very big.

The analysis of the metal−ligand interactions in the high-valent complexes of group 6 elements $Cl_4TM-C_2H_x$ was carried out using the fragments between $TMCl_4$ and C_2H_x in the triplet states. The interaction energies $Cl_4TM-C_2H_x$ are very large but the bond dissociation energies are rather small and in the case of $Cl_4Mo-C_2H_4$ the BDE is even positive. The low BDEs of the high-valent complexes are due to the high preparation energies required to excite C_2H_x from the singlet ground state to the triplet state. The metal−carbon bonds in $Cl_4TM-C_2H_x$ have more covalent than electrostatic character. The $a_1(\sigma)$ interactions have a comparable strength as the $b_2(\pi_{\|})$ interactions while the $a_2(\delta)$ term is negligible. The $b_1(\pi_{\perp})$ orbital interactions of the out-of-plane π orbitals in the acetylene complexes $Cl_4TM-C_2H_2$ contribute ~11% to the total orbital term while they are negligible in the ethylene complexes $Cl_4TM-C_2H_4$.

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Supporting Information Available: A table with the coordinates and energies of the calculated molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Posting. This article was published ASAP on 2/18/2004. In Tables 2−4, the labels for the ligands C_2H_4 and C_2H_2 were incorrect in some column heads. The entries for ΔE_{int} and ΔE_{Pauli} (top two rows) and for $-D_e$, $-D_0$, q[TM], and $q(C_2H_x)$ (bottom four rows) in Table 3 were shifted. The corrected version was posted 3/5/2004.

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