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Molecular Structure and Bond Characterization of the Fischer-Type Chromium−Carbene Complexes $(CO)_5Cr{=}C(X)R$ ($X = H, OH, OCH_3, NH_2, NHCH_3$ and $R = H, CH_3, CH{=}CH_2, Ph, C{\equiv}CH$)

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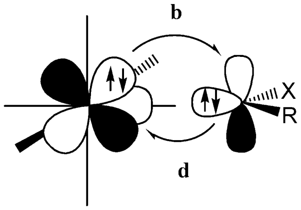
In this work we have examined a series of 25 different Fischer carbene complexes of the type $(CO)_5Cr{=}C(X)R$ with $X = H$, OH, OCH_3, NH_2, and $NHCH_3$ and $R = H$, CH_3, $CH{=}CH_2$, Ph, and $C{\equiv}CH$, to analyze the influence of each substituent on the molecular structure and bonding of these complexes. Energy and charge decomposition analysis of the interaction between the chromium pentacarbonyl and the carbene fragments reveal that for the metal−carbene bond donation is quantitatively more important than back-donation. However, it is the back-donation rather than donation that correlates with most geometrical and electronic parameters of the complexes studied. The reasons for the larger influence of back-donation on the molecular structure of Fischer carbene complexes are discussed.

1. Introduction

The use in organic synthesis of complexes of the type $(CO)_5M{=}C(X)R$ ($M = Cr$, Mo, W; X = a π-donor substituent; and R = a saturated alkyl or unsaturated alkenyl, alkynyl, or aryl group), which are known as Fischer carbene complexes after their discoverer,[1] is relatively recent and, despite that, it has already produced impressive synthetic results.[2] These versatile organometallic reagents have an extensive chemistry, and they are probably one of the few systems that undergo cycloadditions of almost any kind. For instance, [1+2], [2+2], [3+2], [3+3], [4+1], [4+2], [4+3], and [6+3] cycloadditions and multicomponent cycloadditions such as [1+1+2], [1+2+2], [3+2+1], [4+2+1], or even [4+2+1−2] and [2+2+1+1] to Fischer carbenes have been reported.[3]

In Fischer carbene complexes, the central carbene carbon atom is linked through a formal metal−carbon double bond to a low-valent group VI to VIII transition metal. This multiple bond between the metal and the carbene carbon atom is of great interest in organometallic chemistry because breaking of this bond is a key step in a number of Fischer carbene reactions. The metal−carbene bond of Fischer carbene complexes is usually[4] discussed in terms of the familiar Dewar−Chatt−Duncanson (DCD) model[5] considering that the two synergistic main bonding interactions are σ donation from the carbon lone pair orbital of the carbene into the empty d(σ) orbital of the metal, and π back-donation from an occupied d(π) metal atomic orbital to the formally empty p(π) orbital of the carbene (see Scheme 1). Typically, in these complexes one carbene substituent acts as a π donor, allowing for an electronic stabilization of the electron-deficient carbene carbon atom, whereas the other carbene substituent may be either a saturated or unsaturated group. The low-valent metal center is stabilized by π-acceptor substituents such as carbon monoxide, phosphine, or cyclopentadienyl ligands.

Scheme 1



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The nature of the metal−carbene bond has been the subject of several theoretical studies. Most of the earlier works on carbene complexes in which the transition metal possesses a full coordination sphere were carried out by means of semiempirical,[6,7] Hartree−Fock (HF),[8−11] and post-HF methods,[12−15] while most of the recent works have been performed through density functional theory (DFT).[15−25] Using ab initio calculations with limited configuration interaction, Hall and Taylor differentiated between the electronic structures of Fischer-type and Schrock-type carbene complexes.[12] This and additional[8,9,21,23] theoretical comparisons between Fischer and Schrock carbene complexes have shown that Schrock carbenes result from the coupling of a triplet carbene ligand to a triplet transition metal moiety, leading to nearly covalent σ and π bonds. These carbene complexes have nucleophilic character at the carbene carbon atom. On the contrary, Fischer carbenes have electrophilic character at this atom and they are formed by coordination of a singlet carbene ligand to a singlet transition metal through a dative carbene to metal σ donation and a dative metal to carbene π back-donation. The analysis of the metal−carbene bonding has shown that both σ donation and π back-donation are significant.[17,18,22,23] Furthermore, a dominant influence of the metal fragment on the metal−carbene bond has also been put forward by Cundari and Gordon.[11] Finally, it is worth noting that naked transition metal carbenes $M{=}CH_2$ have also been analyzed in a variety of theoretical studies.[26]

In Fischer-type chromium−carbene complexes of the type $(CO)_5Cr{=}C(X)R$, the electronic characteristics of the carbene substituents X and R control the electrophilicity of the complex and therefore have a great influence on its chemical reactivity. Indeed, it has been proposed that the π bond character of a metal carbene can be best represented by a Cr−C−X three-center four-electron bond, the X group having a large effect on the nature of the chromium−carbene bond.[6,15] As an example of the importance of substituents on the chemical reactivity of Fischer carbenes, let us consider the Dötz benzannulation reaction.[27] This is an efficient synthetic method that starting from aryl- or alkenyl-substituted alkoxycarbene complexes of chromium affords *p*-alkoxyphenol derivatives by successive insertion of the alkyne and one CO ligand in an α,β-unsaturated carbene and subsequent electrocyclic ring closure.[28] For this reaction, it is found that in general phenol is the major reaction product. Substitution of alkoxycarbene by aminocarbene complexes modifies the outcome of the reaction. Aminocarbene complexes give indanones **4** as the major product due to failure to incorporate a carbon monoxide ligand from the metal, while alkoxycarbenes tend to favor phenol products **3** (see Scheme 2)[28,29] with some exceptions.[30] This is referred to as the heteroatom effect, generally believed to be attributable to the better donor capacity of the nitrogen over oxygen. In line with these results, theoretical calculations by Gleichmann, Dötz, and Hess[31] indicated that phenol formation is significantly more exothermic for hydroxycarbenes than for aminocarbenes. Another interesting example showing the key influence of the groups attached to the carbon carbene atom concerns the kinetic and thermodynamic acidity of Fischer carbene complexes.[32] Bernasconi and co-workers found that a weaker π-donor substituent in the carbene strongly increases the thermodynamic

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Scheme 2

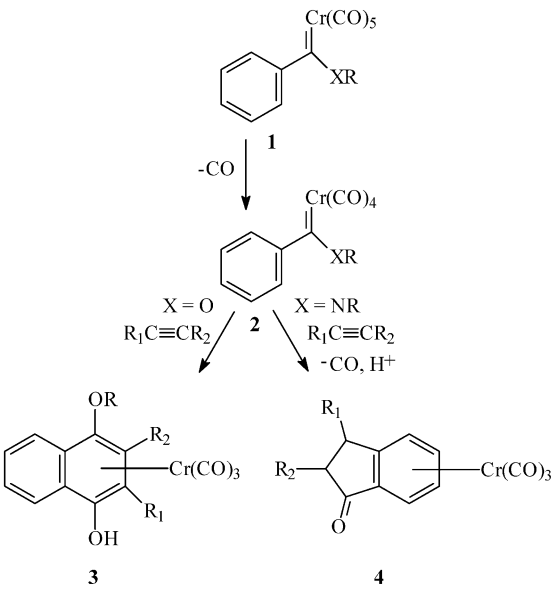

Table 1. Labels for the 25 Fischer-Type Chromium−Carbene Complexes Studied

$(CO)_5Cr{=}C(X)R$	H	CH_3	$CH{=}CH_2$	Ph	C≡CH
OCH_3	A	F	K	P	U
OH	B	G	L	Q	V
$NHCH_3$	C	H	M	R	W
NH_2	D	I	N	S	X
H	E	J	O	T	Y

acidity of Fischer carbene complexes. Remarkably, a study on the kinetics and mechanism of hydrolysis of $(CO)_5MC(X)Ph$ complexes found important differences relative to complexes with different X groups.[33] A similar result has been reported in connection with the kinetics of the reversible cyclization of Fischer carbene complexes.[34] Thus, the character of the substituents directly connected to the carbene carbon atom has a large effect on the reactivity of Fischer carbenes. Consequently, it is possible to electronically tune Fischer carbene complexes by using specific X and R carbene substituents to get the desired chemical response.[35]

Considering the importance of the Fischer carbene complexes as well as the relevant effects of carbene substituents on their chemical reactivity, it seems worthwhile to carry out a systematic study of a series of pentacarbonyl chromium−Fischer carbene complexes varying in a systematic manner the substituents attached to the carbene carbon atom. To perform such a study, we have chosen the $(CO)_5Cr{=}C(X)R$ (X = H, OH, OCH_3, NH_2, and $NHCH_3$ and R = H, CH_3, $CH{=}CH_2$, Ph, and C≡CH) Fischer-type carbene complexes having carbene substituents of diverse degrees of σ- and π-donor character. To identify each complex studied, we have labeled them with a capital letter (see Table 1). It is worth noting that a systematic comparative study of a series of Fischer carbene complexes differing in the substituents of the carbene moiety has not been carried out yet. With this study, we hope to provide answers to the changes in the nature of the chromium−carbene bond and to the origin of the different reactivity of some carbene complexes after modification of carbene substituents. In particular, the relative strength of σ donation and π back-donation as a function of the nature of the different substituents in the carbene will be discussed.

2. Methods

The reported calculations were carried out using the Amsterdam Density Functional (ADF) package developed by Baerends et al.[36] and vectorized by Ravenek.[37] The adopted numerical integration procedure was due to te Velde et al.[38] A set of auxiliary s, p, d, f, and g STO functions, centered on all nuclei, were introduced in order to fit the molecular density and Coulomb potential accurately in each SCF cycle.[39] An uncontracted triple-ς basis set was used for describing the 3s, 3p, 3d, 4s, and 4p orbitals of the chromium atom. For carbon, nitrogen, oxygen, and hydrogen, use was made of a double-ζ basis set augmented by an extra polarization function.[40] The fully occupied inner shells of chromium (1s2s2p), as well as of carbon, nitrogen, and oxygen (1s), were assigned to the cores and treated by the frozen-core approximation.[41] All the geometries and frequencies were calculated using a generalized gradient approximation (GGA) that includes the nonlocal exchange correction of Becke[42] and the nonlocal correlation correction of Perdew[43] (BP86 functional). The geometry optimization procedure was based on an analytical gradient scheme developed by Ziegler and co-workers.[44] The harmonic vibrational frequencies were computed from the force constants obtained by numerical differentiation of the energy gradients.[45] Kinetical relativistic effects are unimportant for an accurate calculation of chromium complexes[16] and were neglected in our calculations.

To analyze the nature of the metal−carbene bond, we have carried out energy and charge decomposition analysis. As far as the energy decomposition is concerned,[46] the total bond

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energy of singlet C(X)R carbene to the singlet ground state of the $(CO)_5Cr$ fragment[19] in the $(CO)_5Cr{=}C(X)R$ complex has been divided into deformation energy and interaction energy ($\Delta E = \Delta E_{def} + \Delta E_{int}$). The deformation energy is the energy needed to modify the geometry of the free fragments to attain the geometry that they have in the complex. The interaction energy is the energy released when the two free deformed fragments are brought to the position that they have in the complex, and it has been, in turn, split into electrostatic, Pauli repulsion, and orbital interaction terms ($\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{oi}$). The term ΔE_{elstat} corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the prepared fragments and is usually attractive. The Pauli repulsion ΔE_{Pauli} comprises the destabilizing interactions between occupied orbitals and is responsible for the steric repulsion. The orbital interaction ΔE_{oi} accounts for charge transfer (interaction between occupied orbitals on one moiety with unoccupied orbitals of the other, including the HOMO−LUMO interactions) and polarization (empty/occupied orbital mixing on one fragment due to the presence of another fragment). ΔE_{oi} can be decomposed according to the extended transition-state method (ETS)[46b−d] into the contributions from each irreducible representation Γ of the interacting system.[46] In systems with a clear σ, π separation (e.g., Fischer carbenes with a plane of symmetry) this symmetry partitioning proves to be quite informative.

For the charge decomposition analysis (CDA) we have used the method by Dapprich and Frenking[47] as implemented in the CDA 2.1 program.[48] In the CDA method the molecular orbitals (canonical, natural, or Kohn−Sham) of the complex are expressed in terms of the molecular orbitals of appropriately chosen fragments. In the present case, the Kohn−Sham (KS) orbitals of the Fischer carbene complex are formed in the CDA calculations as a linear combination of the KS orbitals of the carbene and those of the $Cr(CO)_5$ fragment. The orbital contributions are separated into four parts:[47] (a) the mixing of the occupied KS orbitals of the carbene and the unoccupied KS orbitals of the $Cr(CO)_5$ fragment (carbene → $Cr(CO)_5$ donation); (b) the mixing of the occupied KS orbitals of the $Cr(CO)_5$ fragment and the unoccupied KS orbitals of the carbene ($Cr(CO)_5$ → carbene back-donation); (c) mixing of the KS occupied orbitals of carbene and $Cr(CO)_5$ fragments (carbene ↔ $Cr(CO)_5$ repulsive polarization); (d) the residue term arising from the mixing of the unoccupied KS orbitals, which in all systems reported in this work are very close to zero. The CDA calculations of Fischer carbene complexes have been performed using approximate BP86 wave functions constructed from KS orbitals calculated by means of the Gaussian 98 program[49] at the ADF optimized geometries. The standard basis set combination suggested by Frenking et al.,[50] which has small-core effective core potentials (ECP) and (441/2111/41) for Cr atom in conjunction with all-electron 6-31G(d) basis sets for the main group elements, has been used for CDA computations.

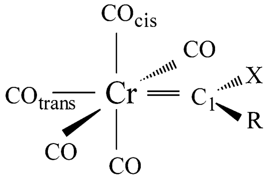

Figure 1. Schematic representation of a Fischer-type chromium−carbene complex.

3. Results and Discussion

This section is organized as follows. First, we report the geometries and bond dissociation energies of the Fischer carbene complexes analyzed. Second, we discuss the nature of the chromium−carbene bond through charge and energy decomposition analysis. Finally, the electrophilicity of these complexes as defined by Parr and co-workers[51] is analyzed.

3.1 Geometries and Bond Dissociation Energies. Table 2 gathers the values of the most relevant geometrical parameters (see Figure 1) for each complex together with the corresponding chromium−carbene bond dissociation energy and the frequency corresponding mainly to the $C-O_{trans}$ bond. We have incorporated in Table 2 previous data collected from experimental and other theoretical studies. Comparison between our theoretical and the experimental bond distances for the five complexes for which experimental results are available (the H, L, N, P, and Q complexes) shows that the theoretical $Cr-C_{carbene}$ bond lengths are somewhat underestimated, the largest error being 0.048 Å. The differences between the experimental and theoretical $Cr-CO_{trans}$ and $C-O_{trans}$ bond lengths are even smaller, indicating that in general there is a good agreement between theoretical and experimental bond lengths. It is worth noting that previous results from Ziegler and co-workers for the carbene complex E (R and X = H) collected in Table 2 show that relativistic effects do not play an important role in the optimization of the geometry,[16] all metal−ligand distances remaining almost unchanged when relativistic effects are included in the Hamiltonian. For $Cr(CO)_6$, Ziegler and co-workers also reported that the BP86 method affords estimates of the same accuracy as the CCSD(T) method.[52]

Substitution of an amino X group at the carbene carbon atom by a hydroxy substituent results in a shortening of the $Cr-C_{carbene}$ bond length by about 0.05 Å, reflecting the stronger π-electron-donating character of the amino group.[6,53] The shortest $Cr-C_{carbene}$ bond length for a given R substituent corresponds always to the complex having X = H, the weakest π-electron-donor substituent. Larger $Cr-C_{carbene}$ bond lengths go with shorter $Cr-CO_{trans}$ and larger $C-O_{trans}$ bond distances

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Table 2. Bond Dissociation Energies (kcal·mol^{-1}), the Most Important Bond Distances (Å), and Dihedral Angles α (in deg) as Shown in Figure 1, and Vibrational Frequencies of the C−O$_{trans}$ Mode (cm^{-1})

	D_e	d(Cr−C$_1$)	d(Cr−CO$_{trans}$)	d(C−O$_{trans}$)[a]	ν(C−O$_{trans}$)	d(Cr−CO$_{cis}$)	d(C−O$_{cis}$)	α(C$_{cis}$CrC$_1$ X)
A	76.4	1.965	1.909	1.158	1987.7	1.897	1.157	23.7
B	77.8	1.949	1.915	1.157	1968.1	1.902	1.156	51.3
		2.000[b]	1.870[b]	1.130[b]		1.870[b]	1.130[b]	
C	73.9	2.029	1.892	1.160	1972.5	1.878	1.165	3.9
D	68.7	2.006	1.897	1.159	1951.1	1.885	1.162	33.0
E	97.9	1.914	1.937	1.154	1959.4	1.906	1.155	43.3
		1.884[c]	1.892[c]			1.892[c]		
		1.933[d]	1.954[d]			1.954[d]		
		1.930[e]	1.954[e]			1.954[e]		
F	73.4	2.010	1.899	1.159	1954.5	1.898	1.158	21.4
		1.93/1.98[f]	1.88/1.94[f]			1.86/1.92[f]		
		2.02[g]						
G	71.4	1.990	1.904	1.158	1961.4	1.899	1.157	23.3
H	72.4	2.075	1.885	1.161	1944.8	1.880	1.165	17.9
		2.090[h]	1.870[h]			1.870[h]		
I	69.9	2.053	1.888	1.160	1950.3	1.881	1.164	17.1
		2.081[i]	1.884[i]			1.884[i]		
		2.16[g]						
J	90.6	1.941	1.927	1.156	1974.8	1.902	1.157	40.0
K	70.6	2.007	1.901	1.159	1957.6	1.897	1.158	20.7
L	72.0	1.999	1.906	1.158	1963.6	1.902	1.157	46.1
		1.990[f]	1.950[f]	1.160[f]		1.920[f]	1.160[f]	
		1.993[j]	1.899[j]	1.167[j]		1.893[j]	1.166[j]	
		2.030[k]	1.890[k]	1.160[k]		1.890[k]	1.160[k]	
		2.040[l]	1.870[l]	1.130[l]		1.890[l]	1.160[l]	
M	67.4	2.070	1.886	1.169	1948.9	1.879	1.165	18.6
N	67.5	2.046	1.891	1.160	1953.7	1.881	1.164	21.3
		2.080[l]	1.880[l]	1.160[l]		1.890[l]	1.160[l]	
O	94.7	1.960	1.924	1.156	1967.9	1.904	1.157	43.6
P	72.2	1.999	1.902	1.159	1946.5	1.895	1.158	16.8
		2.02[g]	1.870[m]			1.890[m]		
		2.040[m]						
Q	70.2	2.004	1.903	1.158	1963.7	1.898	1.157	42.4
		2.052[m]	1.866[m]	1.160[l]		1.908[h]	1.160[l]	
		2.040[l]	1.870[l]			1.890[l]		
R	68.4	2.061	1.888	1.161	1967.3	1.876	1.166	17.5
S	66.8	2.039	1.892	1.160	1955.0	1.874	1.166	4.6
		2.16[g]	1.853[i]			1.882[i]		
		2.057[i]						
T	87.5	1.974	1.916	1.157	1969.3	1.905	1.157	48.2
U	70.1	1.999	1.905	1.158	1961.8	1.896	1.158	32.8
V	71.8	1.978	1.911	1.157	1973.7	1.902	1.156	48.8
W	64.7	2.067	1.886	1.160	1953.6	1.875	1.166	3.4
X	64.5	2.048	1.891	1.159	1957.7	1.875	1.165	5.8
Y	81.4	1.963	1.922	1.155	1980.0	1.905	1.156	46.2

[a] The experimental bond length in free CO is 1.128 Å.[58] [b] Ab initio closed-shell HF.[8] [c] LDA.[19] [d] BP86.[16] [e] BP86+QR.[16] [f] LDA.[16] [g] Semiempirical calculations.[6] [h] Exp.[59] [i] LDA.[17] [j] BP86.[22] [k] BP86.[31] [l] Exp.[60] [m] Exp.[61]

and also smaller C−O$_{trans}$ frequencies, as expected from the DCD mechanism[5] applied to metal−carbene and metal−CO bond formation. Thus, all Fischer carbene complexes with NH_2 or $NHCH_3$ as the X substituent have Cr−CO$_{trans}$ bond lengths ranging from 1.886 Å (complex M) to 1.897 Å (complex D), while all complexes carrying the OH or OCH_3 substituents are found with bond distances varying from 1.899 Å (complex F) to 1.915 Å (complex B). Finally, bond distances from 1.916 Å (complex T) to 1.937 Å (complex E) are associated with complexes having a H atom as the X substituent.

The last column in Table 2 lists the ∠C$_{cis}$CrC$_{carbene}$X dihedral angles for each complex as defined in Figure 1. At least two arrangements can be in principle differentiated for the studied Fischer carbene complexes, namely, the staggered conformation *S* (the plane of carbene bisects two carbonyls' plane), and the eclipsed conformation *E*. These conformations are related by a rotation of the carbene ligand around the Cr−C$_{carbene}$ bond. Previous studies have shown that, in Fischer carbene complexes, this rotation is essentially free,[8,14,17,19] with rotational barriers of <1 kcal mol^{-1}. The preference for an *E* or *S* arrangement is determined by the substituents of the carbene ligand as well as by the Cr−C$_{carbene}$ bond length. Thus, when the carbene ligand adopts an *S* conformation, the steric repulsion is reduced (vide infra). Moreover, a small reduction in the orbital interaction is also observed due to the decrease in the overlap between the HOMO of Cr(CO)$_5$ and the LUMO of carbene. As pointed out by Jacobsen and Ziegler,[17] the preference for the *E* or *S* conformation depends on the balance of these two effects, steric repulsion and orbital interaction. Values in Table 2 point out that the Cr−C$_{carbene}$ bond length has a larger influence on the ∠C$_{cis}$CrC$_{carbene}$X dihedral angles than the size of the carbene substituents. Actually, it is generally found that smaller Cr−C$_{carbene}$ bond lengths result in larger ∠C$_{cis}$CrC$_{carbene}$X dihedral angles, while bulkier R groups, such as the phenyl substituent, do not have ∠C$_{cis}$CrC$_{carbene}$X dihedral angles differing significantly from other smaller R substituents. Remarkably, all Fischer carbenes with X = H, having small Cr−C$_{carbene}$ bond distances, possess ∠C$_{cis}$CrC$_{carbene}$X dihedral angles close to 45.0°, corresponding to a perfect *S* conformation, while those with X = NHR′ (R′ = H and CH_3) have in general large Cr−C$_{carbene}$ bond distances and small ∠C$_{cis}$CrC$_{carbene}$X dihedral angles.

Table 3. Charge Donation, Back-Donation, Back-Donation/Donation Ratio, and Repulsive Polarization Terms Obtained in the CDA Analysis (in electrons)

	donation	back-donation	back-donation/ donation	repulsive polarization
A	0.528	0.244	0.462	−0.319
B	0.499	0.255	0.511	−0.342
C	0.511	0.218	0.427	−0.299
D	0.501	0.214	0.427	−0.317
E	0.501	0.284	0.567	−0.358
F	0.536	0.218	0.407	−0.327
G	0.525	0.227	0.432	−0.334
H	0.524	0.190	0.363	−0.299
I	0.527	0.207	0.393	−0.295
J	0.518	0.267	0.515	−0.325
K	0.522	0.206	0.395	−0.334
L	0.507	0.215	0.424	−0.328
M	0.502	0.191	0.380	−0.309
N	0.499	0.198	0.397	−0.313
O	0.508	0.240	0.472	−0.348
P	0.513	0.243	0.474	−0.344
Q	0.503	0.249	0.495	−0.335
R	0.486	0.214	0.440	−0.315
S	0.480	0.229	0.477	−0.324
T	0.492	0.263	0.535	−0.365
U	0.391	0.205	0.524	−0.323
V	0.469	0.222	0.473	−0.339
W	0.404	0.205	0.507	−0.306
X	0.391	0.193	0.494	−0.307
Y	0.496	0.258	0.520	−0.268

Finally, a direct relationship between the bond dissociation energies and the chromium−carbene bond length is not observed, although commonly a larger distance between the carbene and the pentacarbonyl chromium fragments is connected to a smaller bond energy dissociation value, as expected. For a series of $(CO)_5Cr{=}C(X)R$ complexes having the same R substituent, it is found that the complex with X = H has a larger dissociation energy than complexes with X = OR′, which, in turn, have larger dissociation energies than those with X = NHR′. Not surprisingly, the stronger π-electron-donating character of the amino group reduces the back-donation to carbene, resulting in smaller dissociation energy. For a given X group, the complex with R = H substituent always has the largest dissociation energy. In the following sections, the nature of the chromium−carbene bond is analyzed by means of charge and energy decomposition analysis. The results that have been obtained provide a rationale for the above-mentioned relations.

3.2. Charge Decomposition Analysis. To analyze the metal−carbene bonding in the $(CO)_5Cr{=}C(X)R$ complexes, we have carried out CDA calculations. This method is employed here as a quantitative tool for the analysis of the $(CO)_5Cr{=}C(X)R$ complexes in terms of charge donation and back-donation between $(CO)_5Cr$ and C(X)R closed-shell fragments. Since CDA calculations provide the amount of electronic charge transfer in the carbene → metal donation and the metal → carbene back-donation,[47] values from the CDA can be used to quantify the DCD model.[5]

Table 3 collects the donation, back-donation, and repulsive polarization[62] contributions, as well as the back-donation/donation ratio, for each Fischer carbene complex studied with the CDA method. For most of the systems, the carbene → metal donation values are over 2 times larger than metal → carbene back-donation (see back-donation/donation ratio in Table 3).[19,23] Larger overlaps (by a factor of about 2) and reduced energy gaps (by ca. 3 eV) for the main orbital interaction involved in the σ donation as compared to that of the π back-donation justify the larger relevance of σ donation with respect to π back-donation in the metal−carbene bond. An opposite behavior was found for the metal−CO and metal−CN bonds,[18,52,53] for which the π back-donation is about twice as important as σ donation.

The values obtained for σ charge donation are relatively constant, ranging from 0.528 to 0.480 electrons (similar overlaps and energy gaps for the orbitals most involved in σ donation for all complexes), except for systems with R = $C{\equiv}CH$, for which lower values of donation are obtained as a result of the important σ-withdrawing character of this substituent.[54] Conversely, complexes with R = CH_3 exhibit the largest values of σ donation as expected from the σ electron-donating character of the methyl group. Unlike donation, values of charge back-donation are more spread over a broad range of values, varying from 0.284 to 0.190. For a given R, back-donation increases in the order H > OH > OCH_3 > NH_2 > $NHCH_3$; that is, it becomes more intense with the decrease of the π-donor character of the X group. Since the phenyl substituent is a π electron donor,[55] one should expect a reduction of back-donation for systems with R = Ph, which in fact is not observed because the noncoplanarity of the phenyl group within the carbene ligand impedes π electron donation from the phenyl group. The low back-donation values of Fischer carbene complexes with R = $C{\equiv}CH$ are somewhat unexpected given the π-acceptor nature of this group and are attributed to the reduced σ donation that in these systems partially blocks the synergetic mechanism that favors back-donation.

It is instructive to plot the obtained charge donation and back-donation values as a function of the $Cr-C_{carbene}$, $Cr-CO_{trans}$, and $C-O_{trans}$ bond distances. Charge donation values lead to poor correlations. On the other hand, satisfactory correlations are achieved when charge back-donation values are employed, as shown in Figure 2. In particular, it is found that the $(CO)_5Cr{=}C(X)R$ complexes with X substituents having higher π-donor character show smaller back-donation values, larger $Cr-C_{carbene}$ and $C-O_{trans}$ bond lengths, and shorter $Cr-CO_{trans}$ bond distances. The greater influence of back-donation on the structural properties of the complexes may be attributed to the fact that donation values are almost uniform for all complexes analyzed, whereas charge back-donation numbers are more dispersed over a wide range of values. Actually, most complexes failing to agree with the correlations presented in Figure 2 are those having R = $C{\equiv}CH$ that, as above-mentioned, have charge donation values lower than the common transfer of ca. 0.5 electron. It is worth noting that a previous CDA study of complexes $TM(CO)_5L$ (TM = Cr, Mo, W; L = CO, SiO, CS, N_2, NO^+, CN^-, NC^-, HCCH, CCH_2, CH_2, CF_2, H_2) showed also that the TM → L back-donation correlates quite well with the change of the $TM-CO_{trans}$ bond length, while the TM ← L donation does not.[18]

One may probably expect a good correlation between the energies of the HOMO and the LUMO of the carbene

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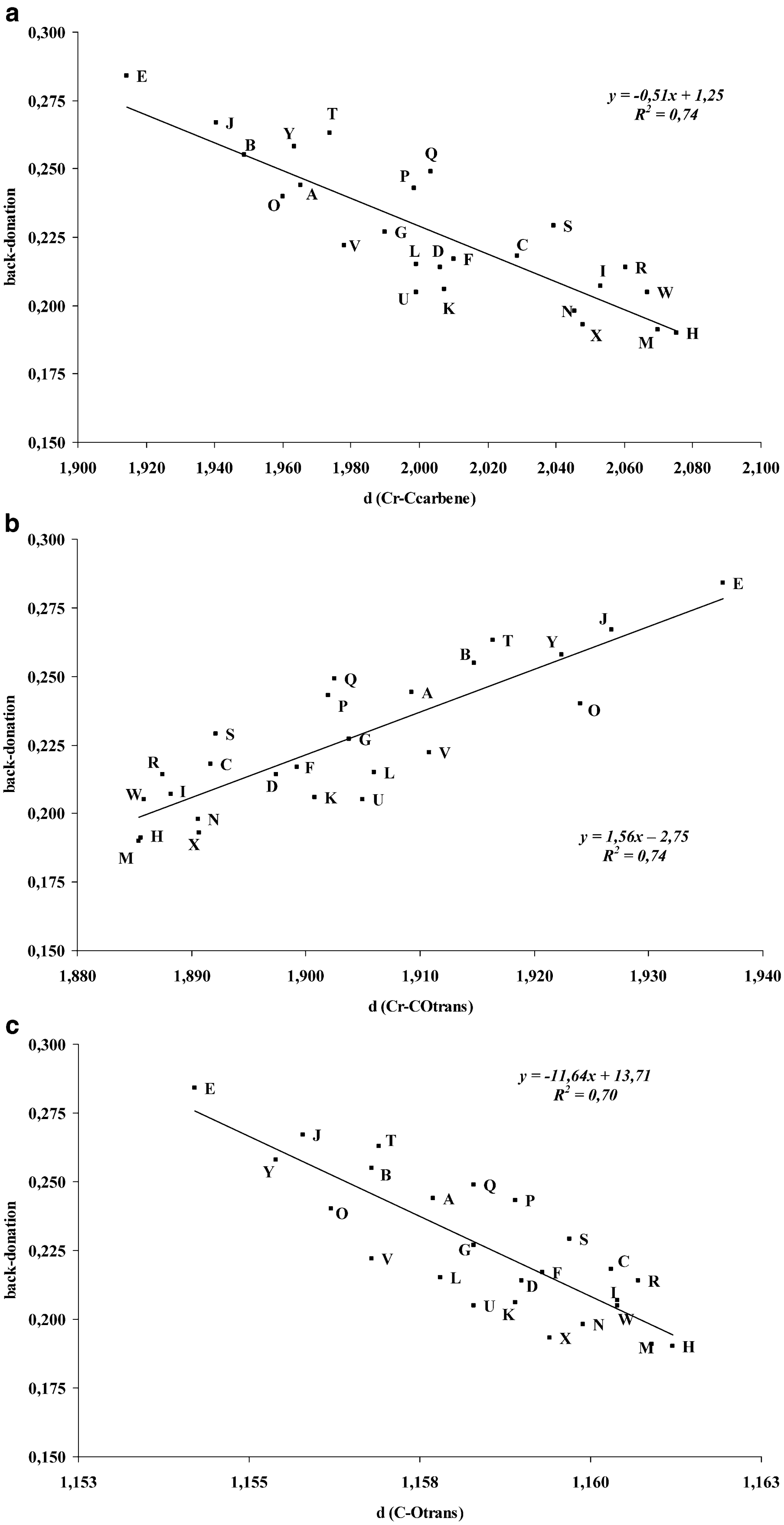

Figure 2. (a) Back-donation values vs the chromium−carbene bond distance (Å). (b) Back-donation values vs the Cr−CO$_{trans}$ bond distance (Å). (c) Back-donation values vs the C−O$_{trans}$ bond distance (Å).

and charge donation and back-donation, respectively. However, the correlations obtained in these cases are rather poor because other factors such as the Cr−C$_{carbene}$ bond length and the overlaps between frontier orbitals

Table 4. Results of the Energy Decomposition Analysis for the $(CO)_5CrC(X)R$ Complexes Studied (in kcal·mol^{-1})

	ΔE_{int}	$\Delta E_{\mathrm{Pauli}}$	$\Delta E_{\mathrm{elstat}}{}^{a}$	$\Delta E_{\mathrm{oi}}{}^{a}$	$\Delta E_{\sigma}{}^{b}$	$\Delta E_{\pi}{}^{b}$	ΔE_{def}	$\Delta E(=-D_e)$
A	−79.8	168.3	−153.3 (61.8)	−94.8 (38.2)	−66.7 (70.0)	−28.6 (30.0)	3.4	−76.4
B	−81.0	175.7	−158.0 (61.5)	−98.7 (38.5)	−67.8 (68.2)	−31.7 (31.8)	3.2	−77.8
C	−76.5	154.0	−148.8 (64.6)	−81.7 (35.4)	−66.5 (78.6)	−18.1 (21.4)	2.7	−73.9
D	−76.1	161.7	−152.9 (64.3)	−84.9 (35.7)	−67.2 (76.9)	−20.2 (23.1)	2.9	−68.7
E	−102.6	199.6	−175.4 (58.0)	−126.8 (42.0)	−72.3 (57.2)	−54.1 (42.8)	4.7	−97.9
F	−75.9	161.3	−149.2 (62.9)	−88.0 (37.1)	−64.1 (73.1)	−16.7 (26.9)	2.5	−73.4
G	−74.9	164.8	−148.7 (62.0)	−91.0 (38.0)	−65.8 (71.6)	−26.0 (28.4)	3.5	−71.4
H	−75.2	147.8	−144.5 (64.8)	−78.5 (35.2)	−63.6 (80.6)	−15.3 (19.4)	2.8	−72.4
I	−72.6	151.4	−144.0 (64.3)	−80.0 (35.7)	−64.8 (79.5)	−16.7 (20.5)	2.7	−69.9
J	−96.0	195.8	−176.4 (60.5)	−115.4 (39.5)	−72.9 (62.5)	−43.8 (37.5)	5.5	−90.6
K	−73.6	159.2	−142.0 (61.0)	−90.8 (39.0)	−66.6 (73.2)	−24.4 (26.8)	3.0	−70.6
L	−75.6	161.7	−143.8 (60.6)	−93.5 (39.4)	−66.3 (70.1)	−28.4 (29.9)	3.6	−72.0
M	−70.0	143.2	−133.8 (62.8)	−79.4 (37.2)	−64.9 (79.8)	−16.5 (20.2)	2.6	−67.4
N	−70.0	148.7	−137.0 (62.6)	−81.7 (37.4)	−66.6 (77.9)	−18.9 (22.1)	2.5	−67.5
O	−98.0	189.4	−174.0 (60.5)	−113.4 (39.5)	−68.8 (63.4)	−37.7 (36.6)	3.3	−94.7
P	−74.8	160.7	−142.7 (60.6)	−92.8 (39.4)	−66.1 (70.8)	−27.3 (29.2)	2.6	−72.2
Q	−73.5	157.7	−140.6 (60.8)	−90.6 (39.2)	−65.2 (69.5)	−28.7 (30.5)	3.3	−70.2
R	−70.9	143.9	−133.6 (62.2)	−81.2 (37.8)	−65.5 (78.7)	−17.7 (21.3)	2.5	−68.4
S	−70.9	149.6	−136.3 (61.8)	−84.2 (38.2)	−67.1 (81.5)	−15.3 (18.5)	4.0	−66.8
T	−91.8	186.2	−169.7 (61.0)	−108.3 (39.0)	−68.3 (58.9)	−47.7 (41.1)	4.3	−87.5
U	−73.1	153.4	−135.3 (59.7)	−91.2 (40.3)	−64.8 (70.7)	−26.9 (29.3)	3.0	−70.1
V	−74.7	160.2	−138.8 (59.1)	−96.1 (40.9)	−66.5 (68.6)	−30.4 (31.4)	2.9	−71.8
W	−66.9	135.7	−125.5 (61.1)	−77.1 (38.1)	−64.3 (79.2)	−16.9 (20.8)	2.3	−64.7
X	−67.2	140.7	−128.1 (61.6)	−79.8 (38.4)	−62.6 (76.8)	−18.9 (23.2)	2.7	−64.5
Y	−85.3	165.2	−139.4 (55.6)	−111.1 (44.4)	−69.0 (61.8)	−42.7 (38.2)	3.9	−81.4

[a] In parentheses, percentage of the total attractive interactions $\Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{oi}}$. [b] In parentheses, percentage of the total orbital interactions ΔE_{oi}.

of the carbene and the $Cr(CO)_5$ fragment also have a great influence on charge donation and back-donation.

3.3. Energy Decomposition Analysis. To gain a deeper insight into the nature of the Cr−C$_{\mathrm{carbene}}$ bond, we have performed an energy decomposition analysis[46] of the chromium−carbene bond dissociation energy. Table 4 contains the results obtained from the energy decomposition analysis of the Fischer carbene complexes studied.

We have divided the bond dissociation energy into the deformation energy term (ΔE_{def}) and the interaction energy term (ΔE_{int}). For the 25 Fischer carbene complexes studied, the ΔE_{def} value ranges from 2.3 (complex X) to 5.5 (complex J) kcal·mol^{-1}, and the ΔE_{int} term takes values from −66.9 (complex W) to −102.6 (complex E) kcal·mol^{-1}. From these numbers, it is clear that the key to understanding the differences between the Fischer carbene complexes must be found in the ΔE_{int} term, and not in the ΔE_{def} energy value. The interaction energy term can be further partitioned into the Pauli repulsion energy ($\Delta E_{\mathrm{Pauli}}$), the electrostatic interaction ($\Delta E_{\mathrm{elstat}}$), and the orbital interaction (ΔE_{oi}) energy terms. There is a relation with the Cr−C$_{\mathrm{carbene}}$ bond length and the different components of the interaction energy. Thus, in general a larger Cr−C$_{\mathrm{carbene}}$ bond distance goes with smaller (in absolute value) $\Delta E_{\mathrm{Pauli}}$, $\Delta E_{\mathrm{elstat}}$, and ΔE_{oi} energy terms. For instance, the highest values (in absolute value) of these three terms correspond to the same complex, complex E, which has the smaller Cr−C$_{\mathrm{carbene}}$ bond length. For a given R, the $\Delta E_{\mathrm{Pauli}}$, $\Delta E_{\mathrm{elstat}}$, and ΔE_{oi} energy terms increase in absolute value following the order of decreasing π-donor character of the X substituent: H > OR′ > NHR′.

The first two terms, $\Delta E_{\mathrm{Pauli}}$ and $\Delta E_{\mathrm{elstat}}$, are often added to a single term $\Delta E°$, sometimes called "steric energy", which has no relation with the loosely defined steric interaction used to refer to repulsive interactions of bulky substituents.[25] In our systems, Pauli repulsion and electrostatic terms more or less tend to cancel each other. For this reason, the analysis of the bonding interactions can be performed by looking at the orbital interaction energy term (ΔE_{oi}). This energy term exhibits a good correlation with the chromium−carbene bond distance as shown in Figure 3. It is worth noting that stronger orbital interactions and shorter bonds do not always translate into higher bond dissociation energies, because the electrostatic attraction and the Pauli repulsion also play a role when differences in ΔE_{oi} are small. For example, complex D has a shorter Cr−C$_{\mathrm{carbene}}$ bond distance (see Table 2) and stronger orbital interactions (see Table 4) than complex C, but the total interaction energy and the bond dissociation energy of complex C are larger than those of complex D.

To analyze further the orbital interaction energy term, we have slightly modified the geometry of the optimized complexes (by changing only dihedral angles and freezing the rest of the geometrical parameters) in order to attain C_s symmetry. In this geometrical arrangement, it is possible to separate the interaction energy into the σ and π orbital interaction components. Because of the geometry changes, the two σ and π terms added do not sum exactly the ΔE_{oi} gathered in Table 4. In most cases, the changes needed to get the plane of symmetry increase in absolute value the Pauli repulsion, the orbital interaction, and the electrostatic terms. From the results in Table 4, we can see that, first, the component connected with donation (ΔE_{σ}) is more than twice as large as the term associated with back-donation (ΔE_{π}), and second, ΔE_{π} values are more scattered over a broad range of values, whereas ΔE_{σ} values are more uniform. We have also found that the geometrical parameters correlate quite well with ΔE_{π} values (see

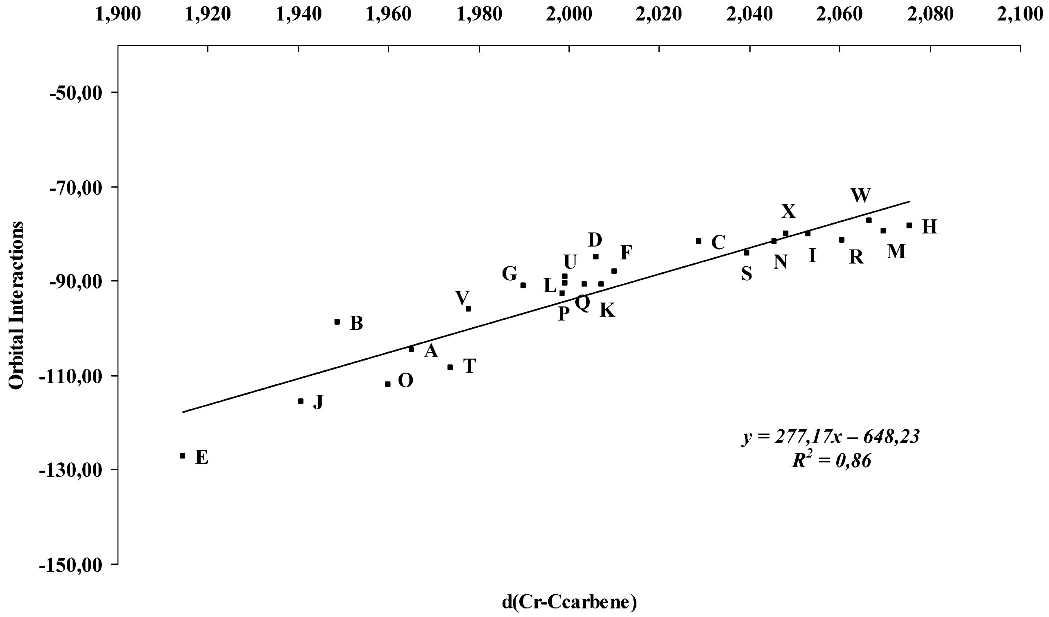

Figure 3. Orbital interaction energy values (kcal·mol^{-1}) vs the metal–carbene bond distance (Å).

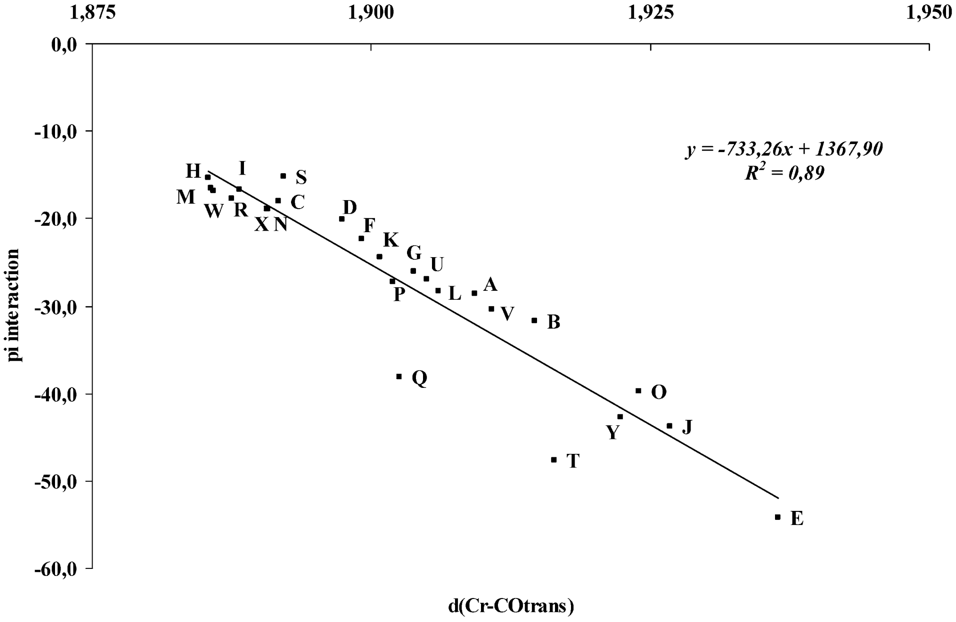

Figure 4. π contribution to the orbital interaction energy values (kcal·mol^{-1}) vs the Cr–CO$_{\mathrm{trans}}$ bond distance (Å).

Figure 4) and not so clearly with ΔE_σ energies. All these results are in perfect qualitative agreement with the conclusions obtained from the CDA calculations. In general, correlations of ΔE_π energies versus Cr–C$_{\mathrm{carbene}}$, Cr–CO$_{\mathrm{trans}}$, or C–O$_{\mathrm{trans}}$ bond lengths are quantitatively somewhat better than those generated using the charge back-donation values obtained from the CDA calculations. Qualitatively, however, correlations of Figure 2b and Figure 4 are quite similar. We find the same grouping of complexes in the two representations, and, in particular, it is found that for a fixed R substituent the π component of the charge or the energy decomposition analysis decreases (in absolute value) when we have a stronger π-donor substituent, i.e., in the order H > OH > OCH_3 > NH_2 > $NHCH_3$.

3.4. Electrophilicity. An important property of Fischer carbene complexes is their electrophilic character. Formally, as a result of the donation being larger than back-donation, these carbene complexes have a $[(CO)_5Cr^{\delta-}\leftarrow C^{\delta+}]$ charge separation, which indicates a lack of charge on the carbene carbon atom and suggests an electrophilic reactivity of the carbene site.[56] To evaluate the electrophilicity of these complexes, we have calculated the electrophilicity index, ω, for each complex measured according to Parr, Szentpály, and Liu[51] using the expression

$$\omega \equiv \mu^2/2\eta \qquad (1)$$

where μ is the chemical potential (the negative of the electronegativity) and η is the hardness.[57] Chemical

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[56] (56) Elschenbroich, Ch.; Salzer, A. In *Organometallics: A Concise Introduction*, 2nd ed.; VCH: Weinheim, Germany, 1992; p 214.

[57] (57) (a) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989. (b) Pearson, R. G. *Chemical Hardness*; Wiley-VCH: Oxford, 1997.

Table 5. Electrophilicity Index, ω (eV), of the Different Fischer Carbene Complexes Analyzed

$(CO)_5Cr{=}C(X)R$	H	CH_3	$CH{=}CH_2$	Ph	$C{\equiv}CH$
OCH_3	4.595	4.050	5.221	4.606	7.109
OH	4.814	4.377	7.613	5.967	7.367
$NHCH_3$	3.250	3.059	3.763	3.538	5.422
NH_2	3.682	3.262	4.349	3.651	5.793
H	7.721	6.332	10.399	9.184	10.487

potential and hardness can be calculated from the HOMO and LUMO orbital energies using the following approximate expressions:[57]

$$\mu = (\epsilon_{\mathrm{LUMO}} + \epsilon_{\mathrm{HOMO}})/2 \tag{2}$$

$$\eta = \epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}} \tag{3}$$

The values of the electrophilicity index in Table 5 show clearly that π-donor substituents reduce the electrophilicity of the complex, as a result of the acceptor orbital in carbene becoming occupied by π donation. Thus, for a fixed R, the electrophilicity increases following the order H > OH > OCH_3 > NH_2 > $NHCH_3$, which is the same order of increasing back-donation. For a given X, the complex with R = CH_3 has smaller electrophilic character because of the donating properties of the methyl group. On the contrary, Fischer carbenes with R = $C{\equiv}CH$ have the largest electrophilicities, in line with the acceptor character of the $C{\equiv}CH$ group.

4. Summary and Conclusions

In this work, we have carried out a DFT study of a series of pentacarbonyl chromium−Fischer carbene complexes of the type $(CO)_5Cr{=}C(X)R$ with X = H, OH, OCH_3, NH_2, and $NHCH_3$ and R = H, CH_3, $CH{=}CH_2$, Ph, and $C{\equiv}CH$ to analyze the influence of the carbene substituents on their molecular and electronic structure. For a series of $(CO)_5Cr{=}C(X)R$ complexes having the same R substituent, we have found that stronger π electron donors lead to larger $Cr{-}C_{\mathrm{carbene}}$ bond lengths, shorter $Cr{-}CO_{\mathrm{trans}}$ and larger $C{-}O_{\mathrm{trans}}$ bond distances, and smaller chromium−carbene bond dissociation energies.

Charge and energy decomposition analyses show that the donation from the carbene fragment to the $Cr(CO)_5$ fragment is stronger than back-donation. However, it is back-donation rather than donation that correlates with most geometrical and electronic parameters of the complexes studied. The reason for the larger influence of back-donation is that charge back-donation values and π orbital interaction energies are more scattered over a large range of values, while charge donation values and σ orbital interaction energies are more constant. Thus, the main differences among the Fischer carbenes chosen arise from the different degree of metal to carbene back-donation. For a given R, back-donation increases in the order H > OH > OCH_3 > NH_2 > $NHCH_3$; that is, it becomes larger with the decrease in the π-donor character of the X group. In general, the electrophilic character of the Fischer carbene complex follows the same trend. The X substituent has a larger effect on the $Cr{-}C_{\mathrm{carbene}}$ bonding than the R group.

It remains to investigate how a variation of the substituents in the carbene fragment influences the chemical reactivity of Fischer carbene complexes by examining the thermodynamics and the kinetics of a series of typical Fischer carbene-mediated reactions. We will address this problem in forthcoming studies.

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Supporting Information Available: A listing containing the optimized and C_s modified geometries in *xyz* format of the 25 Fischer carbene complexes studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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(62) One reviewer objected against the name "repulsive polarization", because the term "polarization" indicates attractive interactions that arise from the excited configurations in one fragment that are caused by the electric field of the other fragment. Thus, a better name would be "exchange repulsion" or "Pauli repulsion". We agree with the reviewer. Nevertheless, we prefer to keep the name "repulsive polarization" because it has been introduced and defined as a repulsive term that arises from the interactions of filled orbitals in the first paper about the CDA[47] and in subsequent papers.[18,20,21,23,24]