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Effects of Terminal Substituents on Metallacumulene Complexes: A Density Functional Study on $(CO)_5Cr(=C)_nX_2$ ($X=F$, SiH_3, $CHCH_2$, NH_2, NO_2)

Alessandro Marrone and Nazzareno Re*

Facoltà di Farmacia, Università G. D'Annunzio, I-66100 Chieti, Italy

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Density functional calculations have been carried out on the series of metallacumulene complexes $[(CO)_5Cr(=C)_nX_2)]$ ($X = F$, SiH_3, $CHCH_2$, NH_2, NO_2; $n = 2-8$) to study the effects of the terminal substituents on electronic structure, bonding, and reactivity of these complexes based on d^6 transition metal fragments. Optimized geometries have been calculated for all complexes and found in good agreement with the available X-ray experimental data. The calculated dissociation energies for the metal−cumulene bond are significantly affected mainly by the NH_2 and NO_2 substituents acting by resonance effect. In particular the π-donor amino substituents cause a decrase while the π-acceptor nitro substituents cause an increase of the bonding energies which are more evident for cumulenes with an odd or an even number of carbon atoms, respectively. The electronic structure has been analyzed in terms of the synergistic σ donation π back-donation model and the contribution from π back-donation was found much more sensitive to the nature of the substituents. The perturbational theory of reactivity has been employed to explain the effect of the substituents on reactivity patterns of these complexes.

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1. Introduction

Metallacumulene complexes have recently received much attention, due to the broad interest in long unsatured carbon chains and to their intermediancy in several catalytic reactions.[1−11] While several lower homologues with two (vinylidene complexes) and three (allenylidene complexes[12−15]) carbon atoms are well-known, only a few examples have been reported with more than three carbon atoms.[4−9] A butatrienylidene metal complex has been isolated recently and structurally characterized by X-ray methods[8a] although such species were already suggested as plausible intermediates in the synthesis of some functionalized allenylidenes.[8b,c] Very few pentatetraenylidene metal complexes have been synthesized and fully characterized in the last years.[4−7,9] Complexes with $n > 5$ thus far have not been isolated or spectroscopically characterized. Heptahexaenylidene species have been suggested as plausible intermediates in the synthesis of some functionalized allenylidenes but not isolated.[9a]

Most metallacumulene complexes bear carbon substituents, mainly aryl groups which protect the terminal sp^2 carbon atom and thus stabilize expecially the most reactive higher homologues. Many synthesized metallacumulenes bear heteroatom substituents, mainly amino and alkyloxo groups, which are expected to stabilize these complexes through polyynil resonance structures such as those shown in Scheme 1.[1] However, despite the interest for the effects of the terminal substituents on the structural and spectroscopic properties of metallacumules, no series of complexes have been characterized consisting of the same metal fragment and a wide variety of substituent with different electronic effects allowing an empirical correlation between the metallacumulene properties and the nature of the substituents. In particular, essentially no experimental

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* Address correspondence to this author. Fax: +39 0871 3555267. E-mail: nre@unich.it.

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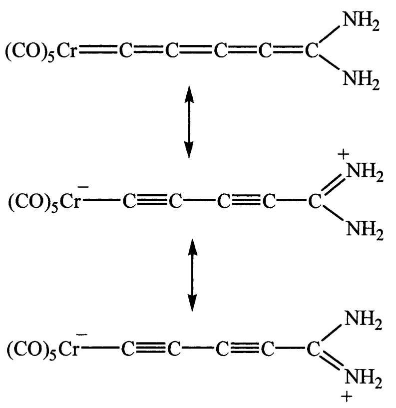
Scheme 1



data are available for complexes containing cumulenylidene ligands with electron-withdrawing substituents although this area is considered an interesting synthetic challenge and is expected to give more surprises in the future.[1]

Only a few theoretical investigations have been performed on the simplest metallacumulene complexes[17−22] and, except for vinylidenes,[17] at mainly the semiempirical level.[19−22] In a recent work we have analyzed the electronic properties of $(CO)_5Cr({=}C)_nH_2$ metallacumulene complexes of various lengths ($n = 2$, 9).[23] In particular, we found the following: (i) the geometries of even-chain cumulenes are consistent with a purely cumulenic structure, while the geometries of odd-chain cumulenes show a small but significant polyynyl carbon−carbon bond length alternation; (ii) the dissociation energies for the metal−cumulene bond are essentially independent of chain length, suggesting that there is no thermodynamic upper limit to the cumulene chain length and that the synthetic difficulties to prepare metallacumulene with carbon chains longer than three carbon atoms are due only to the high reactivity of these species; (iii) the regioselectivity of both electrophilic and nucleophilic attack are frontier orbital controlled with the LUMO mainly localized on the odd-carbon atoms (C_1, C_3, C_5, ...) and the HOMO on the even-carbon atoms (C_2, C_4, C_6, ...) determining respectively their electrophilic or nucleophilic character.

In this paper we perform Density Functional Theory (DFT) calculations on a series of $(CO)_5Cr({=}C)_nX_2$ (X = F, SiH_3, $CHCH_2$, NH_2, NO_2; $n = 2-8$) complexes to study the effects of the terminal substituents on electronic structure, bonding, and reactivity of these metallacumulene complexes based on d^6 transition metal fragments. The $[(CO)_5Cr]$ metal fragment has been used as representative of d^6 Cr(0), Mo(0), W(0) metal systems which are quite common in the chemistry of metal allenylidenes and vinylidenes[1,12] and is also implied in some stable pentatetraenylidene metal complexes recently synthesized.[7,9b] We considered substituents X with a range of electronic properties, i.e., electron-withdrawing groups acting through either inductive (F) or resonance (NO_2) effect and electron-donating groups acting again through inductive (SiH_3) or resonance (NH_2) effect; the vinyl group has been employed to simulate phenyl substituents which are quite common in allenylidene[1] and pentatetraenylidene[7,9] complexes.

We have carried out geometry optimizations and studied the stability of these complexes and the nature of π conjugation along the metal and carbon atoms and their dependence on the nature of the substituents. We have also made use of the perturbational theory of reactivity, examining the charge distribution and the energies and localization of the frontier orbitals, to study the reactivity patterns of these complexes and their dependence on the nature of the substituents.

2. Computational Details

The calculations reported in this paper are based on the ADF (Amsterdam Density Functional) program package.[24] The molecular orbitals were expanded in an uncontracted double-ζ Slater-type orbital (STO) basis set for all main group atoms. For Cr orbitals we used a double-ζ STO basis set for 3s and 3p and a triple-ζ STO basis set for 3d and 4s. As polarization functions, we used one 4p function for Cr, one 3d for C and O, and one 2p for H. The inner shell cores have been kept frozen.

The LDA exchange correlation potential and energy were used, together with the Vosko−Wilk−Nusair parametrization,[25] for homogeneous electron gas correlation, including the Becke's nonlocal correction[26a] to the local exchange expression and the Perdew's nonlocal correction[26b] to the local expression of correlation energy. Molecular structures of all considered complexes were optimized at this nonlocal (NL) level in C_{2v} symmetry.

There can be two different limit orientations of the $[(CO)_5Cr({=}C)_nX_2)]$ complexes with the C_nX_2 plane arranged eclipsed or staggered with the cis carbonyl ligands. Since previous calculations on the unsubstituted vinylidene complex[23] gave the two orientations very close in energy (ca. 1 kJ mol^{-1}), indicating an essentially free rotation around the M−C bond, we considered only eclipsed conformations which allow a simpler bonding analysis.

The coordinate system has been chosen so that the z axis is in the Cr−C(chain) direction and the cumulene plane lies in the xz plane.

3. Results and Discussion

Geometry Optimization. All the considered complexes have been optimized and showed a $^1A_1$ singlet ground state. The optimized bond lengths within the cumulene unit are reported in Figure 1 together with those for the unsubsituted complexes taken from ref 23, while the bond lengths between the terminal carbon atom and the substituent heteroatoms are reported in Table 1.

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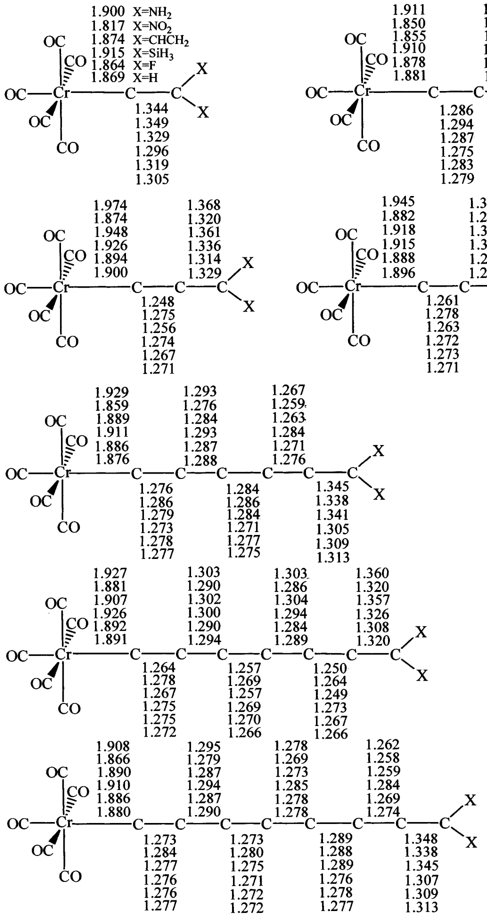


Figure 1. Optimized parameters within the cumulene unit for $(CO)_5Cr(=C)_nX_2$ complexes. Bond lengths in angstroms and bond angles in degrees.

Table 1. Optimized Bond Lengths between the Terminal Carbon Atom and the Substituents Heteroatoms in $(CO)_5Cr(=C)_nX_2$ Complexes[a]

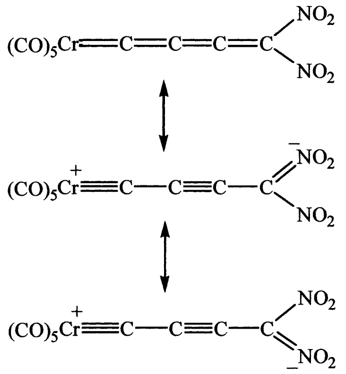
	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$
R(C−NH$_2$)	1.390	1.354	1.379	1.357	1.371	1.359	1.370
R(C−NO$_2$)	1.446	1.508	1.447	1.501	1.447	1.493	1.445
R(C−SiH$_3$)	1.906	1.912	1.907	1.912	1.910	1.914	1.910
R(C−F)	1.341	1.325	1.334	1.329	1.331	1.333	1.331

[a] Bond lengths in angstroms.

A different substituent effect on the geometry of the cumulene unit is observed for complexes with even- and odd-carbon chains. In essentially the same way found for the unsubstituted complexes,[23] the geometries of all odd-chain cumulenes show a polyynyl carbon−carbon bond length alternation superimposed on an average cumulenic structure for all substituents. However, for NH$_2$-substituted cumulenes, the polyynyl alternation is significantly enhanced, the two distinct types of C−C bond lengths falling in the ranges 1.26−1.28 and 1.29−1.34 Å for X = H, F, SiH$_3$, and NO$_2$ and in the ranges 1.24−1.26 and 1.29−1.37 Å for X = NH$_2$. This is consistent with the stabilization of zwitterionic polyynyl resonance structures, responsible for C−C bond lengths alternation, by the amino substituents; see Scheme 1.

On the other hand, the geometries of even-chain cumulenes with F, SiH$_3$, and NH$_2$ substituents, analogously to those of the unsubstituted complexes,[23] are consistent with a purely cumulenic structure with C−C bond lengths ranging from 1.27 to 1.29 Å, except for the terminal C−C bond which is marketely longer, 1.31−1.34 Å, as expected for sp^2 hybridation of the terminal carbon atoms. However, the geometries of NO$_2$-substituted cumulenes show a significant superimposed carbon−carbon bond length alternation. It is worth noting that such alternation is different from that observed for odd-chain cumulenes and involves a shortening of the Cr−C bonds rather than its lengthening. This peculiar alternate pattern can be explained by invoking the contribution of zwitterionic resonance structures with an alkylidyne character; see Scheme 2.

Scheme 2



The importance of the zwitterionic resonance structures in Schemes 1 and 2 in the description of respectively amino odd-chain and nitro even-chain cumulenes is illustrated by the terminal C−N bond lengths reported in Table 1. Indeed, in the amino complexes the C−N bond lengths are significantly shorter for the odd-chain cumulenes and fall in the range 1.35−1.36 Å being much shorter than the *N*-alkyl bonds in amines and indicating a double bond character. Analogously, in the nitro complexes the C−N bond lengths are significantly shorter for the even-chain cumulenes and fall in the range 1.44−1.45 Å, being shorter than in nitroalkanes and still indicating a double bond character.

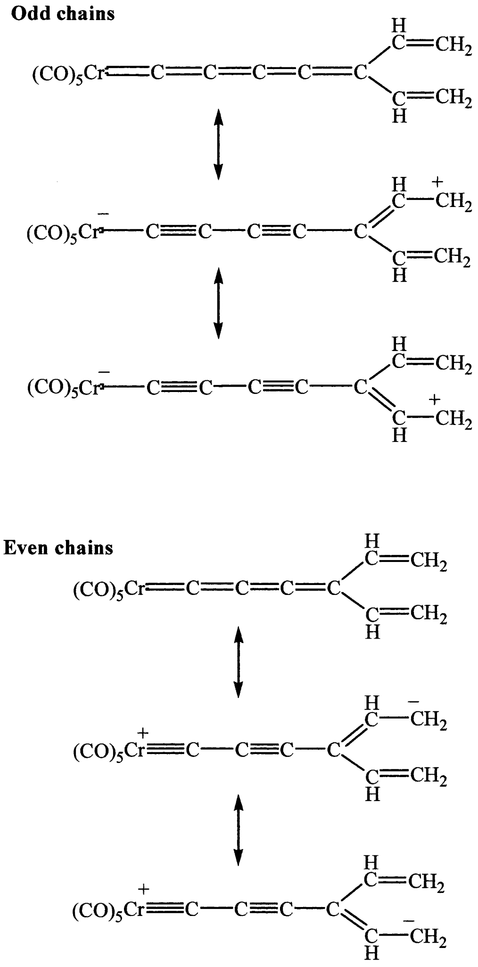
The Cr−C distance, which in unsubstituted metallacumulenes falls in the range 1.87−1.90 Å [23] and is typical of the chromium−carbon double bond, is significantly affected by the presence of terminal substituents. In particular, a lengthening of this distance is observed for the π-donor group NH$_2$ and is more pronounced in odd-chain cumulenes, while a shortening is observed for the π-acceptor group NO$_2$ and is more pronounced in even-chain cumulenes. This trend can be explained with respectively a minor or major metal-to-cumulene π back-donation driven by the π-donor or π-acceptor properties of these substituents and is consistent with the contribution of the zwitterionic resonance structures in Schemes 1 and 2, respectively.

A particular behavior is observed for the vinyl-substituted cumulenes which show a carbon−carbon bond length alternation in both odd- and even-chains similar, although less pronounced, to those shown by amino- and nitro- substituted cumulenes, respectively. These alternate geometries are probably related to the stabilization by zwitterionic resonance structures with polyynyl or alkylidyne character respectively for odd and even chains, such as those reported in Scheme 3. Indeed, the vinyl group has both a high-lying filled π and a low-lying vacant π^* orbital and can therefore behave as a

Table 2. Experimental M−C and C−C Distances (Å) for Some Allenylidene, Butatrienylidene, and Pentatetraenylidene Complexes

molecule	M−C$_1$	C$_1$−C$_2$	C$_2$−C$_3$	C$_3$−C$_4$	C$_4$−C$_5$
$(CO)_5Cr({=}C)_3Ph_2$[27]	1.931(2)	1.249(3)	1.358(3)		
$(CO)_5Cr({=}C)_3PhNMe_2$[13]	2.015(2)	1.236(2)	1.342(2)		
$Cp(PMe_3)_2Ru({=}C)_3Ph_2$[16]	1.884(5)	1.255(8)	1.329(9)		
$Cp(PMe_3)_2Ru({=}C)_3MeNPh_2$[8b]	1.97(1)	1.18(2)	1.41(1)		
trans-$Cl(PPr^i{}_2)_2Ir({=}C)_4Ph_2$[8a]	1.816(6)	1.283(8)	1.275(8)	1.339(8)	
$(CO)_5Cr({=}C)_5NEt_2CMe{=}C(NMe)_2$[9b]	2.041(6)	1.219(8)	1.379(8)	1.209(9)	1.433(8)
$(CO)_5W({=}C)_5(NMe_2)_2$[7]	2.144(6)	1.223(9)	1.361(9)	1.192(9)	1.399(9)
trans-$[Cl(dppe)_2Ru({=}C)_5Ph_2]^+$[5a]	1.891(9)	1.25(1)	1.30(1)	1.24(1)	1.36(1)

Scheme 3



π-donor in odd-chain and as a π-acceptor in even-chain cumulenes.

A comparison between theoretical and experimental geometries is difficult as most of the observed structures refer only to aryl-, alkyl-, or amino-substituted cumulenes and different metal fragments. In particular, the experimental data in Table 2 refer to some representative allenylidene[8b,13,16,27] and pentatetraenylidene[5a,7,9b] complexes with d^6 metal fragments and to the only structurally characterized butatrienylidene complex, *trans*-$Cl(PPr^i{}_2)_2Ir({=}C)_4Ph_2$, with a d^8 metal fragment.[8a] A reasonable comparison can be made between the calculated geometries for $(CO)_5Cr({=}C)_3(CHCH_2)_2$, $(CO)_5Cr({=}C)_3(NH_2)_2$, and $(CO)_5Cr({=}C)_5(NH_2)_2$ with the X-ray data for respectively $(CO)_5Cr({=}C)_3Ph_2$,[27] $(CO)_5Cr({=}C)_3PhNMe_2$,[13] and $(CO)_5Cr({=}C)_5NEt_2CMe{=}C(NMe_2)_2$,[9b] which, however, differ from our models for the presence of methyl, ethyl, and phenyl instead of hydrogen or vinyl groups and eventually for the presence of only one amino substituent instead of two. The calculated values are in reasonably good agreement with the experimental data, although the bond alternation is slightly underestimated by ca. 0.02−0.04 Å; however, this could be due to the presence of the methyl, ethyl, phenyl, or alkenyl groups in the experimental complexes which are expected to stabilize the polyynyl resonance structures enhancing the bond alternation. Moreover, the comparison between the X-ray data for phenyl- and amino-substituted allenylidenes and pentatetraenylidenes in Table 2 confirms the trend, showed by our calculations, for the effects of amino substituents with a more pronounced carbon−carbon bond length alternation.

It is also worth comparing the geometries of the C_nX_2 units in the considered complexes with those for the corresponding free cumulene carbenes to study (i) the effect of the terminal substituents on the free cumulene geometries and (ii) the distortion of the substituted cumulenes upon coordination. The unsubstituted C_nH_2 molecules have been proposed by radioastronomy to be constituents in interstellar gas and those with $n = 3$ and 4 have been spectroscopically identified.[28]

Theoretical calculations at the MP2[29] or the DFT[23] level have been recently performed on C_nH_2 cumulenes, showing a closed shell ground state for all molecules and essentially cumulenic geometries with only a small polyyne-like carbon−carbon bond alternation for odd-numbered chains. We performed DFT calculations at the same level of theory employed for the complexes on the C_nX_2 cumulenes up to $n = 8$ and found singlet ground states for all considered species. The calculated main geometrical parameters are reported in Figure 2 together with those for the unsubstituted C_nH_2 species taken from ref 23.

A comparison between the C−C bond lengths of the $[(CO)_5Cr({=}C)_nX_2)]$ complexes (Figure 1) and those of the corresponding free cumulene carbenes (Figure 2) shows that the geometries of the free C_nX_2 are quite similar to those of the corresponding coordinated species, with an enhanced polyyne-like alternation in amino-substituted odd-numbered cumulenes and in nitro-substituted even-numbered cumulenes. These two carbon−carbon bond length alternations differ in that the former ends with a shorter C_1−C_2 bond while the latter ends with a longer C_1−C_2 bond and can be explained by the contribution of zwitterionic resonance polyyne-like structures analogous to those proposed for the corresponding metallacumulenes, see Scheme 4. As for metallacumu-

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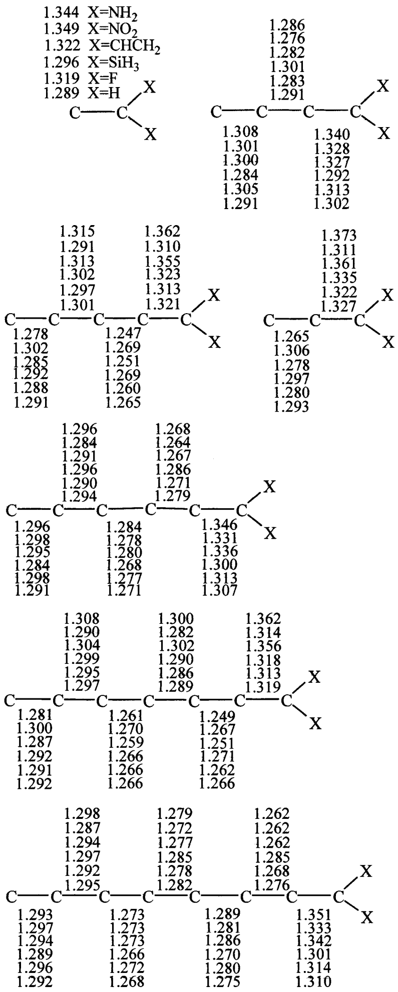


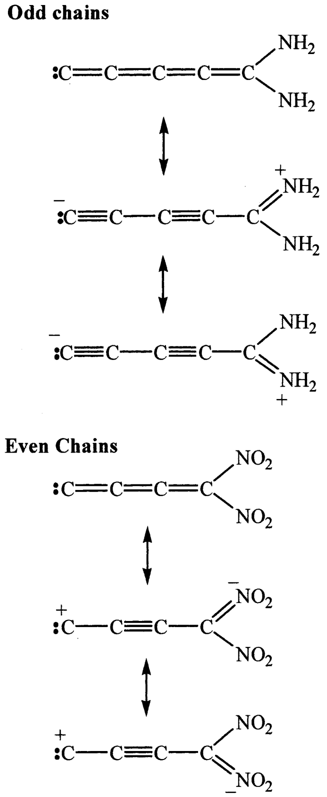
Figure 2. Optimized parameters of the carbene cumulene molecules $:C(=C)_{n-1}X_2$. Bond lengths in angstroms and bond angles in degrees.

lenes, vinyl-substituted cumulenes show similar but less pronounced carbon–carbon bond length alternations in both odd- and even-chains.

Some small but significant distortions of these cumulene moieties upon coordination are yet observed, probably due to the population of the two lowest unoccupied orbitals (see below) upon metal-to-cumulene back-donation.

Electronic Structure. The electronic structure of these $[(CO)_5Cr(=C)_nX_2)]$ complexes is illustrated by Figures 3 and 4 which report the orbital interaction diagram for $[(CO)_5Cr(=C)_4X_2)]$ and $[(CO)_5Cr(=C)_5X_2)]$ ($X= NH_2, NO_2$) and are representative of the behavior of these substituted metallacumulenes with even- and odd-chain, respectively. The frontier orbitals of the pseudooctahedral $[(CO)_5Cr]$ fragment are well-known[23] while those of the free cumulenes C_nH_2 are described in ref 23 and are made up of a set of n out-of-plane π orbitals (hereafter called $\pi_\perp$, all of b_1 symmetry) and a set of $n - 1$ in-plane π orbitals (hereafter called $\pi_\parallel$, all of b_2 symmetry), occupied by $2n - 2$ electrons. In these figures we report on the right the orbital levels of both unsubstituted and substituted free cumulenes to illustrate the effect of the terminal substituents on the cumulene MOs and thus on the orbital interactions. In particular, for cumulene carbenes C_nX_2 with π-donor or π-acceptor substituents ($X = NH_2, NO_2$) the out-of-plane π system includes one more nitrogen p orbital, filled for NH_2 and empty for NO_2, and as a consequence, the $\pi_\perp$ orbitals (b_1) are more strongly destabilized by the amino group and more strongly stabilized by the nitro group than the $\pi_\parallel$ ones (b_2).

Scheme 4



As for the unsubstituted complexes,[23] besides the donation from the cumulene lone pair into the metal d_{z^2}, two different π back-bonding interactions, occurring in two orthogonal planes, can be distinguished: a major contribution coming from the LUMO ($\pi_\parallel$ for C_4 or $\pi_\perp$ for C_5) and a minor contribution coming from the LUMO+1 ($\pi_\perp$ for C_4 or $\pi_\parallel$ for C_5). However, a stronger back-donation from the filled d_π metal orbitals is observed for the nitrosubstituted complexes, because of the energy lowering of both LUMO and LUMO+1, while a weaker back-donation is observed for the amminosubstituted complexes, because of the energy rise of the LUMO and LUMO+1.

Moreover, a small HOMO-LUMO gap is observed for the nitro odd-chain and the amino even-chain metallacumulenes, so that going from C_2 to C_8, the HOMO-LUMO gap of these complexes shows a striking oscillation, being small for odd-chain and large for even-chain in nitro cumulenes and large for odd-chain and small for even-chain in amino cumulenes; see Figure 5. This result suggests a low stability for odd-chain metallacumulenes with π-acceptor substituents and for even-chain metallacumulenes with π-donor substituents in agreement with a large body of evidence in the synthesis of vinylidene (C_2), allenylidene (C_3), and pentatetraenylidene (C_5) complexes. Indeed, while allenylidene and pentatetraenylidene complexes with π-donor substituents (NR_2, OR, ...) or vinylidene complexes with π-acceptor substituents (CN, CO_2R, ...) are quite common,[1,12] essentially no allenylidene or pen-

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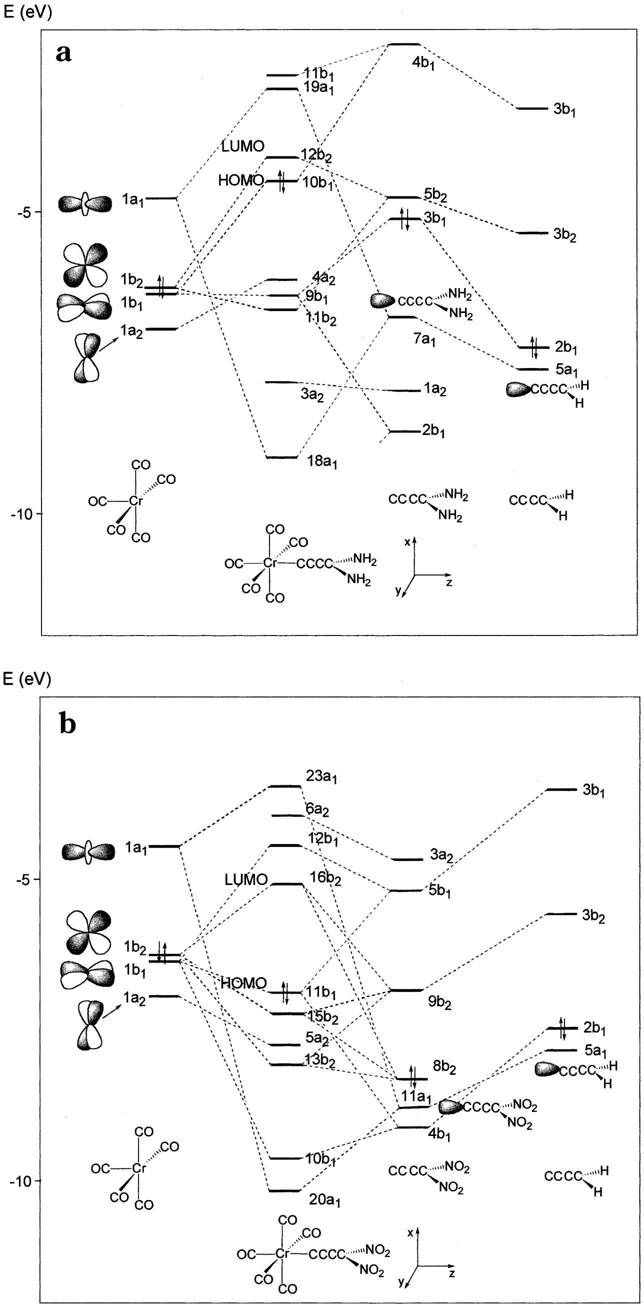

Figure 3. Orbital interaction diagram for (a) $(CO)_5Cr(=C)_4(NH_2)_2$ and (b) $(CO)_5Cr(=C)_4(NO_2)_2$. On the extreme right the energy levels of the unsubstituted $:C(=C)_3H_2$ cumulene are reported.

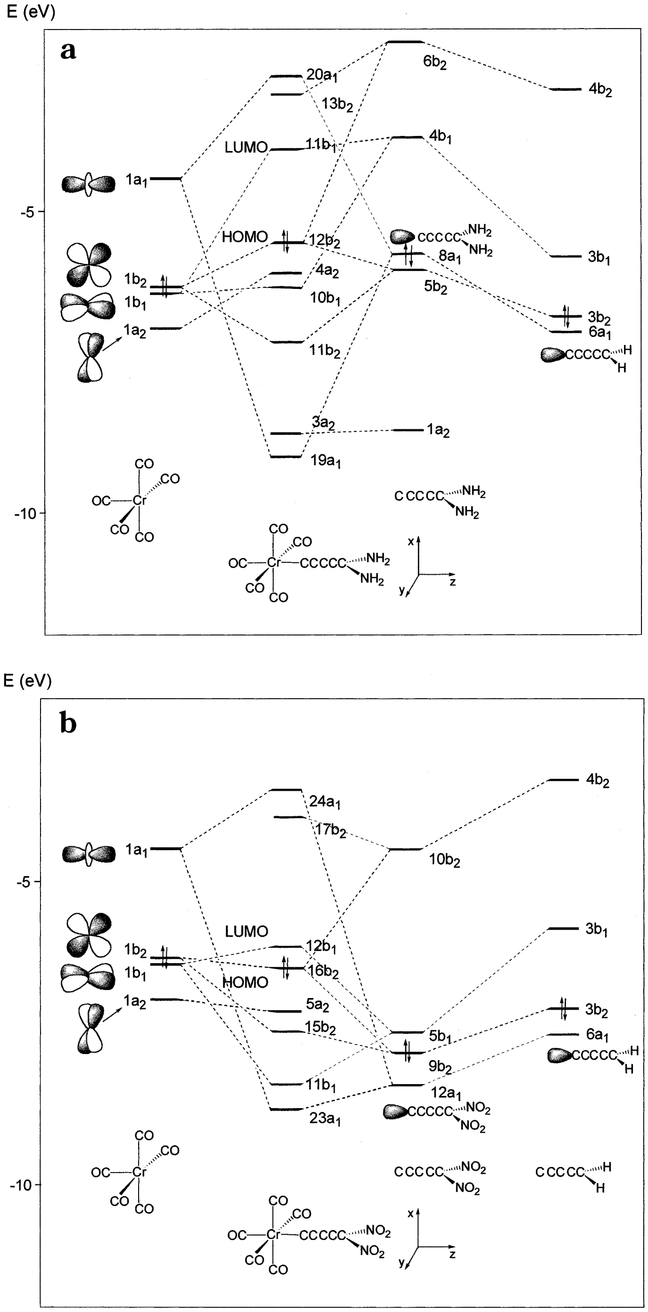

Figure 4. Orbital interaction diagram for (a) $(CO)_5Cr(=C)_5(NH_2)_2$ and (b) $(CO)_5Cr(=C)_5(NO_2)_2$. On the extreme right the energy levels of the unsubstituted $:C(=C)_4H_2$ cumulene are reported.

tatetraenylidene complex with π-acceptor substituents or vinylidene complexes with π-donor substituents have been characterized to the best of our knowledge. An intermediate HOMO-LUMO gap is observed for the vinyl-substituted cumulenes with both odd- and even-chains similar; see Figure 5. This behavior is related to the electronic nature of the vinyl group which leads to (i) a minor destabilization of the cumulene $\pi_\perp$ orbitals and thus to a decrease of the HOMO with respect to amino-substituted even-chains and (ii) to a minor stabilization of the $\pi_\perp$ and thus to an increase of the LUMO with respect to nitro-substituted odd-chains.

Our results thus suggest that odd-chain metallacumulenes are stabilized by π-donor substituents (such as NR_2, OR, ...) while even-chain metallacumulenes are stabilized by π-acceptor substituents (such as NO_2, CO_2R, CN, ...); aryl substituents, with combined π-donor and -acceptor properties, stabilize both odd- and even-chain metallacumulenes but to a minor extent.

On lengthening the cumulene chain of the same parity, i.e. $C_4 \rightarrow C_6 \rightarrow C_8$ or $C_3 \rightarrow C_5 \rightarrow C_7$, the HOMO-LUMO gap decreases (see Figure 5) in agreement with the UV/vis spectra of $[(CO)_5Cr(=C)_n(NR_2)_2]$ ($n = 3, 5$) which show a bathochromic shift from C_3 to C_5.[7]

Bonding Energies. The bond dissociation energies between the $Cr(CO)_5$ and C_nX_2 fragments, $D(Cr-C_nX_2)$, have been calculated according to the following scheme:

$$[(CO)_5Cr(=C)_nX_2)] \rightarrow (CO)_5Cr + C_nX_2$$

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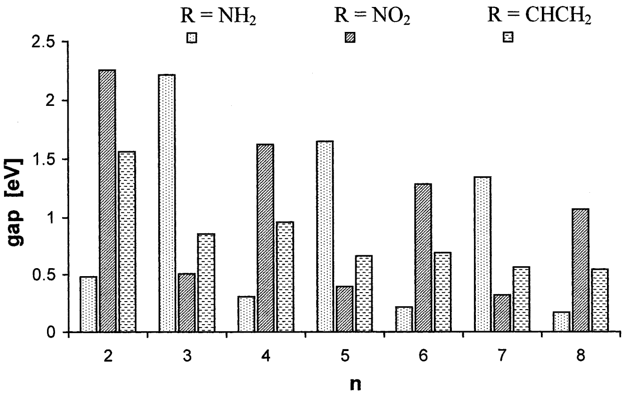

Figure 5. HOMO-LUMO gaps (eV) of $(CO)_5Cr(=C)_n(NH_2)_2$, $(CO)_5Cr(=C)_n(NO_2)_2$, and $(CO)_5Cr(=C)_n(CHCH_2)_2$ complexes.

where both the cumulene complex and the two fragments have been considered in their ground-state equilibrium geometries. By using the fragment-oriented approach of the DFT computational scheme implemented in the ADF program, the above bond dissociation energies are computed in two steps. First we calculate the "snapping energies", $E^*(Cr-C_nX_2)$, i.e. the energies gained when snapping the metal−cumulene bond, obtained by building $[(CO)_5Cr(=C)_nX_2)]$ from the fragments with the conformation they assume in the equilibrium geometry of the overall complex. Then we compute the energies $E^R_{C_nX_2}$ and $E^R_{(CO)_5Cr}$ gained when the isolated fragments relax to their equilibrium geometries. Corrections for the zero-point vibrations were not included since they are expected to be quite small. Indeed, the vibrational zero-point corrections to metal−ligand bonding energy have been calculated to be ca. 4−18 kJ mol^{-1} for $(CO)_5W=CR_2$ carbene complexes[30] and are expected to be smaller for chromium complexes and longer chains. A recent investigation of the effects of the basis set incompleteness on the bond dissociation energies of some metal−ligand and metal−metal bonds has led to the conclusion that double-ζ plus polarization basis sets give reasonably accurate bond energies for organometallic systems with sufficiently small BSSE corrections to warrant its neglect in most situations.[31]

The results obtained are given in Table 3 for $X = NH_2$, NO_2 and in Table S1 for all other substituents, and show relatively high bonding energies (210−334 kJ mol^{-1}) which strongly depend on the nature of the terminal substituents and on the parity of the carbon chain. A comparison with experimental data is not possible since, to the best of our knowledge, no bonding energy has been measured for vinylidene or higher cumulene complexes.

Table 3 confirms the main trend observed for unsubstituted metallacumulenes, i.e., chromium−cumulene bond dissociation energies do not show any significant decrease on lengthening the cumulene chain. Therefore, the presence of terminal substituents does not change the conclusion of our previous work that there is no thermodynamic upper limit to the cumulene chain length and that the synthetic difficulties to prepare metallacumulene with carbon chains longer than three carbon atoms is due to the high reactivity of these species.

Table 3. Calculated Bond Dissociation Energies for the $(CO)_5Cr(=C)_n(NH_2)_2$ and $(CO)_5Cr(=C)_n(NO_2)_2$ Complexes (kJ mol^{-1})

(a) $(CO)_5Cr(=C)_n(NH_2)_2$

n	E^*	$E^R_{Cr(CO)_5}$	$E^R_{Cn(NH_2)_2}$	D_e
2	302	9	1	292
3	261	5	1	255
4	294	9	1	284
5	265	4	1	259
6	277	7	1	268
7	247	6	1	240
8	218	7	2	210

(b) $(CO)_5Cr(=C)_n(NO_2)_2$

n	E^*	$E^R_{Cr(CO)_5}$	$E^R_{Cn(NO_2)_2}$	D_e
2	340	18	7	315
3	353	18	5	330
4	327	14	1	311
5	339	15	3	322
6	326	16	1	309
7	351	15	2	334
8	343	13	1	328

Tables 3 and S1 (see Supporting Information for Table S1) also show that the chromium−cumulene bond dissociation energies are more strongly affected by the amino and nitro substituents with π-donor and π-acceptor properties, respectively. In particular the amino substituents cause a decrease of the Cr−C bond dissociation energies, which is more evident for odd-chain cumulenes, while the nitro substituents lead to an increase of the dissociation energies, which is more evident for even-chain cumulenes. These results are consistent with the calculated geometries showing a Cr−C bond lengthening for odd-chain cumulenes with terminal amino groups and a Cr−C bond shortening for even-chain cumulenes with terminal nitro groups (see above) and can be explained by a minor or major metal-to-cumulene π back-donation driven by respectively the π-donor or π-acceptor properties of these substituents. The same broad effect, but to a much minor extent and minor even−odd alternation, can be observed also for the Cr−C bond dissociation energies of metallacumulenes with inductive electron-donor (SiH_3) or electron-withdrawing (F) substituents. On the other hand, no significant change of the chromium−cumulene bond dissociation energies is caused by vinyl substituents, probably due to the compensation of the π-donor or π-acceptor effects of these substituents.

Bonding Analysis. The bonding of an unsatured σ,π-ligand coordinated to a transition metal fragment is usually described by a synergistic σ donation π back-donation, i.e., the Dewar−Chatt−Duncanson model.[32] According to this model, the bonding in metallacumulenes arises from the σ electron donation from the filled a_1 orbital of C_nX_2, describing the lone pair on the initial carbon atom, to the empty metal $a_1(d_{z^2})$ orbital, and the simultaneous π back-donation from the filled $b_1(d_{xz})$, $b_2(d_{yz})$ metal orbitals to the two lowest empty π^* orbital of C_nX_2 of $b_1(\pi_\perp)$ and $b_2(\pi_\parallel)$ symmetry. For odd n the LUMO is of b_1 symmetry and is responsible for most of

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[30] Vyboishchikov, S. F.; Frenking, G. *Chem. Eur. J.* **1998**, *4*, 1428.

[31] Rosa, A.; Ehlers, A. W.; Baerends, E. J.; Snijders, J. G.; te Velde, G. *J. Phys. Chem.* **1996**, *100*, 5690.

[32] Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71. Chatt, J.; Ducanson, L. A. *J. Chem. Soc.* **1953**, 2939.

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the accepting properties of the organic fragment while the LUMO+1 is of b_2 symmetry and, being higher in energy, shows minor accepting properties; see Figure 4. For even n the LUMO is b_2 while the LUMO+1 is of b_1 symmetry; see Figure 3.

To separate the contributions from σ donation and π back-donation we employed an analysis of the metal−cumulene bond dissociation energies based on the extended transition state method.[33a] The bond dissociation energy is decomposed into a number of contribution:

$$D(\mathrm{Cr{-}C}_n\mathrm{X}_2), = -[E_{\mathrm{prep}} + E_{\mathrm{ster}} + E_{\mathrm{orb}}]$$

The first term, E_{prep}, is the energy necessary to convert the fragments from their equilibrium geometries to the conformation they assume in the optimized structure of the overall complex and corresponds to the sum of the fragment relaxation energies, $E^{\mathrm{R}}{}_{\mathrm{C_nX_2}} + E^{\mathrm{R}}{}_{\mathrm{Cr(CO)_5}}$. E_{ster} represents the steric repulsion between the two fragments and consists of two components: (i) the electrostatic interaction of the nuclear charges and the unmodified electronic charge density of one fragment with those of the other fragment and (ii) the four-electron destabilizing interactions between occupied orbitals (Pauli repulsion). E_{orb}, known as the orbital interaction term, represents the attracting orbital interactions which give rise to the energy lowering upon coordination. This term may be broken up into contributions from the orbital interactions within the various irreducible representations Γ of the overall symmetry group of the system, according to the decomposition scheme proposed by Ziegler.[33b]

This decomposition scheme is particularly useful in the considered complexes as it allows one to separate the energy contributions corresponding to σ donation (E_{A1}) and to π back-donation ($E_{\mathrm{B1}} + E_{\mathrm{B2}}$). Indeed, the ligand-to-metal donation takes place into the A_1 representation, while the metal-to-ligand back-donation takes place into the B_1 and B_2 representations. In particular for the odd-chain E_{B1} is the energy contribution from the back-donation into the LUMO (b_1) while E_{B2} is the contribution from back-donation into the LUMO+1 (b_2) and is therefore expected to be smaller; on the other hand, for the even-chain the roles of the two contributions are exactly exchanged.

The results of this energy decomposition for the amino- and nitro-substituted metallacumulene complexes are reported in Table S2. The results for X = F, SiH_3, and $CHCH_2$ are very similar to those observed for the unsubstituted cumulene complexes: (i) the A_1 contribution is essentially constant and (ii) the E_{B1} and E_{B2} contributions oscillate on increasing the chain length being respectively the major and the minor contribution from back-donation in odd-chain or the minor and the major in even-chain cumulenes. However, while the σ contribution, E_{A1}, is essentially unaffected by the presence of the substituents the overall contribution from π back-donation, $E_{\mathrm{B1}} + E_{\mathrm{B2}}$, is slightly decreased or increased (10−20 kJ mol^{-1}) by inductive electron-donor (SiH_3) or electron-withdrawing (F) substituents, respectively.

On the other hand, the energy contributions from π back-donation, E_{B1} and E_{B2}, are strongly affected by the amino and nitro substituents with π-donor and π-acceptor properties. Indeed, our results show a strong decrease of E_{B1} (by 20−90 kJ mol^{-1}) and a smaller decrease of E_{B2} (5−20 kJ mol^{-1}) in the amino cumulenes and parallelly a strong increase of E_{B1} (by 30−80 kJ mol^{-1}) and a smaller increase of E_{B2} (10−30 kJ mol^{-1}) in the nitro cumulenes. This is explained by noting that the empty π orbitals responsible for the back-donation from the metal (the LUMO and the LUMO+1) are destabilized by π-donor and stabilized by π-acceptor substituents which then determines respectively a decrease or an increase of back-donation; however, since the out-of-plane $\pi_{\perp}$ orbitals (of b_1 symmetry) are more strongly destabilized by the amino group and more strongly stabilized by the nitro group than the in-plane $\pi_{\|}$ orbitals (of b_2 symmetry), both effects are higher for the B_1 contribution. The overall contribution from the π back-donation, $E_{\mathrm{B1}} + E_{\mathrm{B2}}$, is strongly decreased in the amino cumulenes (30−100 kJ mol^{-1}) and strongly increased in the nitrocumulenes (50−90 kJ mol^{-1}) and, since the σ contribution, E_{A1}, is almost unaffected, it accounts for the whole effect of the NH_2 and NO_2 substituents on the bond dissociation energy.

Reactivity. Metallacumulenes may undergo both electrophilic and nucleophilic attack allowing for further transformations and functionalization. Considerable knowledge has been achieved in the chemistry and the reactivity of vinylidene and allenylidene metal complexes.[1,12,15] In particular, metal vinylidenes are highly reactive and susceptible to nucleophilic attack at the C_1 carbon and electrophilic attack at the C_2 carbon[1,12] while metal allenylidenes undergo nucleophilic attack on the C_1 or C_3 carbons, and electrophilic attack at the C_2 carbon.[1,12,15] On the other hand, little is known about the reactivity of higher metallacumulenes. The recently isolated *trans*-$\mathrm{Cl(PPr^i{}_3)_2Ir({=}C)_4Ph_2}$ butatrienylidene complex undergoes nucleophilic attack at the C_3 and electrophilic attack at the C_2 carbon while ruthenium cationic butatrienylidene intermediates undergo only nucleophilic attack at C_3. The available data for the few known pentatetraenylidene complexes give evidence for regioselective nucleophilic attack at the C_1, C_3, or C_5 and electrophilic attack at the C_2.[5−7,9] Finally the chemistry of heptahexaenylidenes,[9a] never isolated but only hypothesized as intermediates in the synthesis of some funtionalized allenylidenes and pentatetraenylidenes, has been interpreted in terms of nucleophilic attack at the C_5 atom. The nature of the substituents does not change the regioselectivity of nucleophilic or electrophilic attack to metallacumulene complexes which is essentially the same for both carbon and heteroatom substituents. However, the nature of the substituents may change the overall reactivity of the cumulene chain; in particular π-donor substituents have been found to stabilize allenylidene and pentatetraenylidene complexes toward nucleophilic attack as witnessed by the high stability of $\mathrm{(CO)_5M({=}C)}_n\mathrm{NR_2}$ (M = Cr, W; n = 3, 5) complexes.[7]

In a recent work we have studied the reactivity and regioselectivity of unsubstituted $\mathrm{(CO)_5Cr({=}C)}_n\mathrm{H_2}$ metallacumulene complexes of various lengths (n = 2, 9) toward nucleophilic and electrophilic additions.[23] In this paper we have theoretically studied the effects of terminal substituents on the reactivity and regioselec-

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[33] (a) Ziegler T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1. (b) Ziegler, T.; *NATO ASI*, **1986**, *C176*, 189.

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tivity of metallacumulene complexes toward nucleophilic and electrophilic additions following the approach of Fukui,[34] further generalized by Klopman,[35] which distinguish between charge-controlled and frontier-controlled reactions.

For all the considered substituted metallacumulene complexes we performed a Mulliken population analysis calculating the gross atomic charges on the metal, the carbonyls, and the various carbon atoms of the cumulene ligand. The results for the fluoro- and silyl-substituted cumulenes, the species with the most and least electronegative atoms attached to the terminal chain carbon, are reported in Table S3 (Supporting Information) and show no significant charge differences among the central carbon atoms of the cumulene chains indicating that charge distribution is not important in determining the regioselectivity of either electrophilic or nucleophilic attack, as already observed for the unsubstituted metallacumulenes.[23] An analysis of MOs energies shows that all substituted homologues present relatively high-lying HOMOs and low-lying LUMOs, suggesting that the reactivity of these complexes toward both electrophilic and nucleophilic attack is again determined by frontier orbital factors. Moreover, since the HOMOs are quite isolated in energy from the other highest occupied MOs and the LUMOs are even better isolated from the other lowest unoccupied orbitals, these two orbitals play the main role in determining the regioselectivity of respectively the electrophilic and nucleophilic attack.

The breakdowns of the contribution from the metal and the carbon atoms along the chain to the HOMO and LUMO of [$(CO)_5Cr(=C)_nX_2$)] cumulenes with X = $CHCH_2$, NH_2, and NO_2, listed in Table S4 (Supporting Information), show essentially the same peculiar pattern observed for unsubstituted complexes;[23] the HOMO has contributions mainly from the metal and the carbon atoms in even positions along the chain (C_2, C_4, C_6, ...) while the LUMO has contributions mainly from the carbon atoms in odd positions along the chain (C_1, C_3, C_5, ...) determining the regioselectivity of respectively the nucleophilic and electrophilic attack to these atoms in agreement with the known reactivity patterns of all known carbon- and heteroatom-substituted metalacumulenes.[1,5−7,8−912,15] There is, however, one significant difference: the HOMO of the even-chain amino-substituted cumulenes has major contributions from the carbon atoms in odd positions along the chain, i.e., C_1, C_3, C_5, and C_7, and this would determine the regioselectivity of an electrophilic attack to these atoms rather than to the metal and the carbon atoms in even positions along the chain, i.e., C_2, C_4, and C_6, as observed for unsubstituted and all other substituted complexes. However, a comparison of this peculiar theoretical result with experimental data is not possible, since no amino-substituted butatrienylidene or vinylidene complexes have been characterized, consistent with our prediction that even-chain metallacumulenes with π-donor substituents are quite unstable (see above).

As for the unsubstituted cumulenes, on increasing the chain length there is an energy raise of the HOMO and a lowering of the LUMO which determines an increase of the reactivity toward both electrophilic and nucleophilic attacks and is responsible of the synthetic difficulties in preparing higher metallacumulenes. The presence of the terminal substituents, however, may significantly change the energies of the HOMO and LUMO orbitals thus affecting the reactivity of the higher cumulogs. The HOMO and LUMO energies are more strongly affected by the amino and nitro substituents with π-donor and π-acceptor properties, respectively. Particularly important is the effect on the LUMO whose energy determines the reactivity toward nucleophilic attack which is responsible for the high reactivity of these metallacumulenes. In particular the amino substituents cause an increase of the LUMO energies that is much more pronounced for odd-chain cumulenes (1.3−1.7 eV) while the nitro substituents cause a decrease of the LUMO energies that is less pronounced for even-chain cumulenes (0.7−1.2 eV). Therefore π-donor substituents leads to a significant decrease of the reactivity of odd-chain metallacumulenes toward nucleophilic attack in agreement with experimental evidence indicating a high stability of amino-substituted allenylidenes and pentatetraenylidenes.[7,9] On the other hand, π-acceptor substituents lead to an increase of the reactivity of metallacumulenes toward nucleophilic attack; however, this increased reactivity is less important for even-chain metallacumulenes whose Cr−C bonding energy is foreseen to be increased by the presence of these substituents (see above). Higher even-chain metallacumulenes, whose synthesis is particularly elusive, are therefore expected to be stabilized by the presense of π-acceptor substituents such as NO_2, CN, COOR, $C_6H_4NO_2$, etc.

4. Conclusions

Density functional calculations have been carried out on the series of metallacumulene complexes [$(CO)_5Cr(=C)_nX_2$)] (X = F, SiH_3, $CHCH_2$, NH_2, NO_2; $n = 2-8$) to study the effects of the terminal substituents on electronic structure, bonding, and reactivity of these metallacumulene complexes based on d^6 transition metal fragments. Optimized geometries have been calculated for all complexes and found in good agreement with the available X-ray experimental data. The calculated chromium−cumulene bond dissociation energies are more strongly affected by the amino and nitro substituents with π-donor and π-acceptor properties, respectively. In particular the amino substituents cause a decrease of the Cr−C bond dissociation energies that is more evident for odd-chain cumulenes while the nitro substituents lead to an increase of the dissociation energies that is more evident for even-chain cumulenes. These results are consistent with the calculated geometries showing a Cr−C bond lengthening for odd-chain cumulenes with terminal amino groups and a Cr−C bond shortening for even-chain cumulenes with terminal nitro groups.

The electronic structure has been analyzed in terms of the synergistic σ donation π back-donation model and

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(34) Fukui, K.; Yonezawa, T.; Nagata, C. *J. Chem. Phys.* **1957**, *27*, 1247. Fukui, K.; Yonezawa, T.; Nagata, C. *J. Chem. Phys.* **1959**, *31*, 550. Fukui, K. *Theory of Orientation and Stereoselection*; Springer: Berlin, Germany, 1975.

(35) Klopman, G.; Hudson, R. F. *Theor. Chim. Acta* **1967**, *8*, 1965. Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223. Klopman, G. In *Chemical Reactivity and Reaction Paths*; Klopman, G., Ed.; Wiley: New York, 1974; pp 59−67.

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the contribution from π back-donation was found much more sensitive to the nature of the substituents and particularly affected by those with π-donor and π-acceptor properties.

The perturbational theory of reactivity has shown essentially no effect of the substituents on the regioselectivity of both electrophilic and nucleophilic attack. Indeed, the LUMO is mainly localized on the odd-carbon atoms (C_1, C_3, C_5, ...) while the HOMO is localized on the even-carbon atoms (C_2, C_4, C_6, ...) thus determining respectively their electrophilic and nucleophilic character.

π-Donor substituents cause an increase of the LUMO energies which is much more pronounced for odd-chain metallacumulenes and therefore leads to a significant decrease of the reactivity of these complexes toward nucleophilic attack in agreement with experimental evidence indicating a high stability of amino-substituted allenylidenes and pentatetraenylidenes. On the other hand, higher even-chain metallacumulenes, whose synthesis is particularly elusive, are expected to be stabilized by the presense of π-acceptor substituents, such as NO_2, CN, COOR, $C_6H_4NO_2$, etc.

These results not only shed light on the well-known stabilizing effect of electron-donating substituents on metallacumulene complexes but also allow us to foresee the thermodynamic and kinetics properties of the more elusive metallacumulene complexes with electron-withdrawing substituents which are considered an interesting synthetic challenge and are expected to give more surprises in the future.

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Supporting Information Available: Tables of bond dissociation energy, bond dissociation energy decomposition, Mulliken charges, and breakdowns of the orbital contributions. This material is available free of charge via the Internet at http://pubs.acs.org.

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