

# Metal Complexes Containing Allenylidene and Higher Cumulenylidene Ligands: A Theoretical Perspective

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RECEIVED ON JANUARY 18, 2011

## CONSPECTUS

Transition metal complexes containing unsaturated carbenes have enjoyed a recent surge in research interest. In addition to showing potential as molecular wires and as components of opto-electronic materials, they provide multifaceted reactive sites for organic synthesis. In this Account, we describe results of recent theoretical studies that delineate the main features of electronic structure and bonding in allenylidenes and higher cumulenylidene complexes,  $[L_nM]=C(=C)_n=CR^1R^2$  (where L represents the ligand, M the metal, and  $n \geq 1$ ).

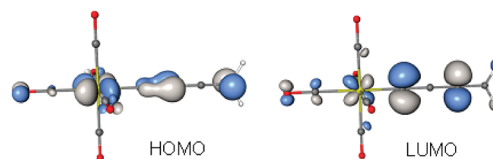
Although free cumulenylidene ligands,  $:C(=C)_n=CR^1R^2$ , are extremely unstable and reactive species, they can be stabilized by coordination to a transition metal. The  $\sigma$ -donation of the electron lone pair on the terminal carbon atom to an empty metal d-orbital, together with the simultaneous  $\pi$  back-donation from filled metal d $_{\pi}$ -orbitals to empty cumulene  $\pi^*$  system orbitals, leads to the formation of a strong M=C bond with multiple character. Density functional theory studies on the model systems  $[(CO)_5Cr(=C)_nCH_2]$  and  $[trans-CI(PH_3)_4Ru(=C)_nCH_2]^+$  (where  $n = 1-9$ ) have been useful in interpreting the structural and spectroscopic properties and the reactivity of this class of complexes.

Geometry optimizations significantly contributed to the generalization of the sparse structural data available for allenylidene, butatrienylidene, and pentatetraenylidene complexes to higher cumulenylidene complexes (with up to eight carbon atoms in the chain), which show a clear structural trend. In particular, the geometries of all even-chain cumulenes are consistent with an almost purely cumulenic structure, whereas the geometries of odd-chain cumulenes present a significant polyene-like carbon-carbon bond length alternation.

The calculated bond dissociation energies (BDEs) of the cumulenylidene ligand remain almost constant on lengthening the cumulene chain. These BDEs indicate that there is no thermodynamic upper limit to the cumulene chain length and suggest that the synthetic difficulties in preparing higher cumulenylidenes are due to an increase in reactivity. The calculated charges on the carbon atoms show no significant polarization along the cumulene chain, indicating that charge distribution is not important in determining the regioselectivity of either electrophilic or nucleophilic attack, which is instead determined by frontier orbital factors.

The breakdown of the contributions from the metal and the carbon atoms along the chain to the HOMO and LUMO shows that the HOMO has contributions mainly from the metal and the carbon atoms in even positions along the chain ( $C_2, C_4, C_6$ , and higher). In contrast, the LUMO has contributions mainly from the carbon atoms in odd positions along the chain ( $C_1, C_3, C_5$ , and higher), thus explaining the experimentally observed regioselectivity of electrophilic and nucleophilic attacks, which are directed, respectively, to even and odd positions of the cumulenylidene chain.

The study of the electronic structure of cumulenylidenes has allowed us not only to give a consistent rationale for the main structural and spectroscopic properties and for the reactivity of this emerging class of compounds but also to predict the effect of ancillary ligands on the metal center or substituents on the carbon end. The result is a useful guide to new developments in the still-underexplored fields of this fascinating class of compounds.



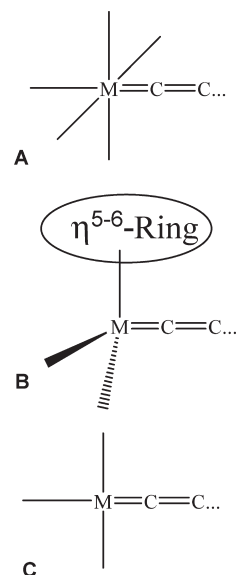
## 1. Introduction

The chemistry of transition metal complexes containing a highly unsaturated carbon chain is a field of intense current activity in organometallic chemistry. Among them, the unsaturated carbene complexes  $[L_nM]=C(=C)_n=CR^1R^2$  with  $n \geq 1$  have recently received much attention,<sup>1–8</sup> because they can be of potential interest in the field of molecular wires and novel opto-electronic materials<sup>9</sup> and can also provide multifaceted reactive sites of interest in organic synthesis.<sup>10,11</sup> These cumulenylidene metal complexes can be formally considered as derived from organic cumulenes  $R^3R^4C=C(=C)_n=CR^1R^2$  where a terminal carbon moiety,  $=CR^3R^4$ , is replaced by a double-bonded transition metal fragment  $[L_nM]$ .

Most of these cumulenylidene complexes are based on octahedral (**A**), half-sandwich (**B**), or square planar (**C**) metal fragments of group 6, 7, 8, and 9 with  $d^6$  and  $d^8$  electron counts,<sup>1–8</sup> see Scheme 1.

The shortest members of this series, transition metal allenylidenes,  $[L_nM]=C=C=CRR'$ , were first prepared in 1976,<sup>12</sup> but their chemistry developed only in the 1980s after the discovery of a simple synthetic route through the activation of suitably substituted propargylic alcohols.<sup>13</sup> A wide range of allenylidene complexes has been synthesized and characterized since then, with a variety of metals, among which those with Ru(II) constitute the most extended group.<sup>5,6</sup> While a large number of allenylidene complexes are known,<sup>1,2,5,6</sup> only few cumulenylidene complexes have been reported with four or more carbon atoms.<sup>2–4,7,8,15–24</sup> Indeed, their high reactivity makes their synthesis and isolation a difficult task. The first pentatetraenylidene metal complexes have been prepared and isolated in 1994 by Dixneuf et al.,<sup>15</sup> and a few pentatetraenylidenes have been synthesized and characterized since then.<sup>9,16–19</sup> Higher cumulenylidene complexes with an even number of carbon atoms are less stable: for several years butatrienylidene complexes have been generated in solution without being isolated or spectroscopically detected, but only trapped with nucleophiles.<sup>14,20</sup> The first butatrienylidene complex was isolated and structurally characterized in 2000, and since then very few butatrienylidenes have been prepared and characterized by X-ray methods.<sup>21,22</sup> Any attempt to prepare and isolate hexapentatrienylidene complexes failed so far, and these species have only been proposed as reactive intermediates.<sup>23</sup> Heptahexaenylidene complexes of chromium and tungsten pentacarbonyl were recently isolated by Fischer and co-workers and are up to now the longest known metal cumulenylidene complexes.<sup>24</sup>

**SCHEME 1.** Most Common Metal Fragments in Allenylidene and Cumulenylidene Complexes

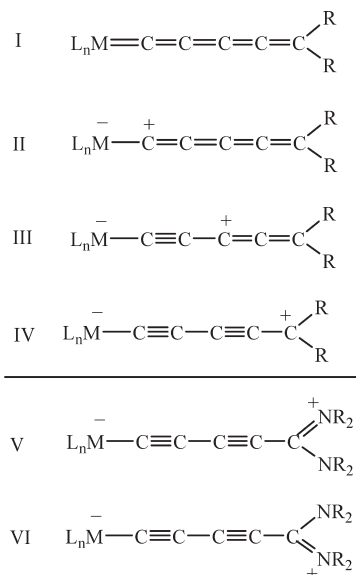


Several comprehensive reviews have already summarized the chemistry of allenylidene and higher cumulenylidene complexes,<sup>1–8</sup> and we refer to them for the main aspects of these systems. In this Account, we will limit to the description of theoretical studies that provide a sound basis for the interpretation of their structural and spectroscopic properties and of their reactivity. Moreover, we will focus on the work of our group on the electronic structure, bonding, and reactivity of higher cumulenylidene complexes, although results obtained by other groups will be reported and discussed whenever appropriate.

## 2. Selected Structural, Spectroscopic, and Electrochemical Aspects of Allenylidene and Cumulenylidene Complexes

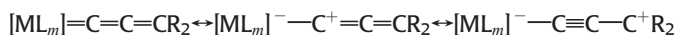
As molecular entities, cumulenylidene ligands,  $:C(=C)_n=CR^1R^2$ ,  $n \geq 1$ , are extremely unstable and reactive species that can be most conveniently generated and detected by special gas-phase techniques.<sup>25</sup> They are, however, stabilized by coordination to a transition metal through the  $\sigma$ -donation of the electron lone pair on the terminal carbon atom to an empty metal  $d$  orbital and the simultaneous  $\pi$  back-donation from filled metal  $d_{\pi}$  orbitals to empty cumulene  $\pi^*$  system orbitals, leading to the formation of a strong  $M=C$  bond with a multiple-bond character. Therefore, as ligands, allenylidene and cumulenylidene species exhibit both  $\sigma$ -donor and  $\pi$ -acceptor properties, which, in addition, can be suitably tuned by varying the substituent on the terminal C atom. Useful clues on the  $\sigma$ -donating and



**SCHEME 2.** Possible Resonance Structures for Pentatetraenylidene Complexes

geometry, electronic structure, bonding, and reactivity of cumulenylidenes with a critical analysis of the available experimental data.

**3.1. Geometries.** Structural parameters are available from the X-ray diffraction analysis of several metal allenylidene complexes<sup>1,2</sup> and are all consistent with a linear metallacumulene structure with extensive contributions from metal alkynyl resonance forms:



Relatively short M–C bond lengths are found, with values in the upper range of metal carbon double bonds (see previous section), whereas for the allenylidene ligand, the C1–C2 bond lengths are significantly shorter (1.20–1.27 Å) than the C2–C3 lengths (1.33–1.41 Å). Only few structural parameters are available for higher metal cumulenylidenes, limited to butatrienylidenes<sup>21,22</sup> and pentatetraenylidenes.<sup>15–19</sup> Analogous to what was observed for allenylidenes, pentatetraenylidenes show an essentially linear carbon chain with a significant short–long–short–long alternation of C–C bond lengths, which has been attributed to the extensive contribution of metal alkynyl resonance forms, III–IV in Scheme 2. Such a bond length alternation depends on the substituent on the terminal C atom and is particularly pronounced for  $\pi$ -donor substituents such as  $-NR_2$  or  $-OR$ , which stabilize the alkynyl resonance forms with a positive charge on the cumulenylidene terminal carbon atom, through the further contribution of mesomers as V–VI in Scheme 2. A different situation is observed for the two structurally resolved

butatrienylidene complexes, which show M–C and C–C bond lengths consistent with an almost purely metallacumulenic description.

The geometry optimizations carried out at DFT level on the  $[(CO)_5Cr(=C)_nH_2]$  ( $n = 2–9$ ) and  $[trans\text{-}Cl(PH_3)_4Ru(=C)_nH_2]^+$  ( $n = 1–8$ ) series of metal cumulenylidenes gave an important contribution to generalize the sparse structural data available for allenylidene, butatrienylidene, and pentatetraenylidene to higher cumulenylidene complexes, indicating a clear structural trend.

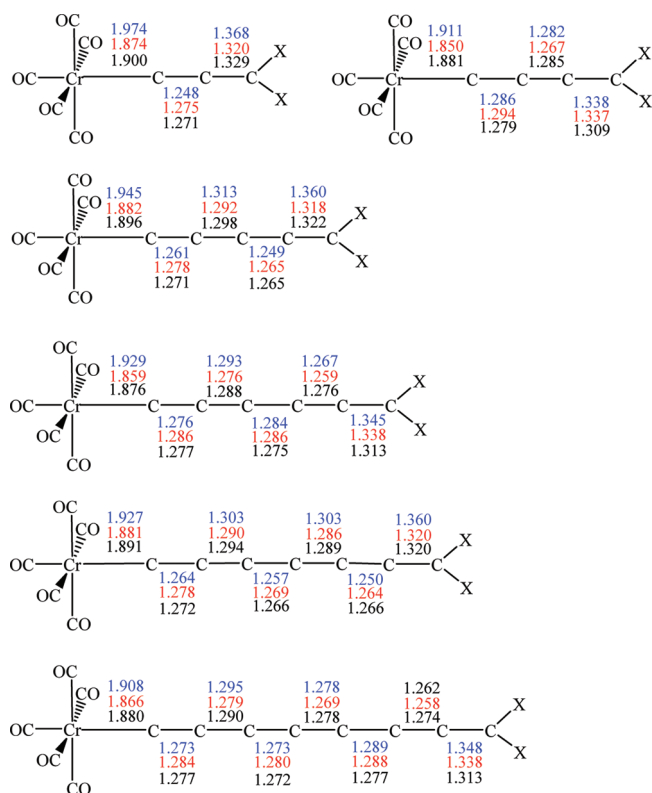
Our results for the  $[(CO)_5Cr(=C)_nH_2]$  series showed for the geometries of all odd chain cumulenes a significant polyyne-like carbon–carbon bond length alternation perturbing an average cumulenic structure with two slightly different types of C–C bond lengths, falling in the ranges 1.26–1.27 and 1.29–1.33 Å, see Figure 1. The geometries of even chain cumulenes are consistent with a purely cumulenic structure, the C–C bond lengths ranging from 1.27 to 1.29 Å, except for the terminal C–C bond, which is markedly longer, 1.32–1.34 Å, as expected for an  $sp^2$  hybridization of the terminal carbon atom. Relatively short Cr–C distances are calculated, in the range 1.86–1.90 Å, with significant chromium–carbon double bond character,<sup>32</sup> slightly shorter for even  $n$  chains.

Similar structural trends were obtained by Saillard and co-workers in their DFT calculations on the  $[trans\text{-}Cl(PH_3)_4Ru(=C)_nCH_2]^+$  series, with only minor differences in the M–C and C–C bond lengths due to the different metal fragment.

**3.2. Electronic Structure and Bonding.** The electronic structure and bonding in metal cumulenylidene complexes can be conveniently described by the Chatt–Dewar–Duncanson model, according to which the bonding in  $[L_nM(=C)_nH_2]$  arises from the  $\sigma$  electron donation from the  $C_nH_2$  lone pair on the first carbon atom to an empty  $d_\sigma$  metal orbital and the simultaneous  $\pi$  back-donation from filled  $d_\pi$  metal orbitals to the lowest empty  $\pi^*$  orbitals of  $C_nH_2$ . This fragment approach was applied to higher cumulenylidene complexes for the  $[(CO)_5Cr(=C)_nH_2]$  series and then to the  $[trans\text{-}Cl(PH_3)_4Ru(=C)_nH_2]^+$  species giving similar results.

The results for the  $[(CO)_5Cr(=C)_nH_2]$  series in terms of the interaction between the  $[(CO)_5Cr]$  and the  $C_nH_2$  fragments, exploiting the  $C_{2v}$  symmetry of the complex, exemplify this approach, and the orbital interaction diagrams for  $[(CO)_5Cr(=C)_4H_2]$  and  $[(CO)_5Cr(=C)_5H_2]$  reported in Figures 2 and 3 illustrate the behavior of metallacumulenes with  $n$  even and odd, respectively. The  $[(CO)_5Cr]$  fragment has a pseudo-octahedral geometry lacking one ligand, and its frontier d orbitals are made up by a set of three filled  $t_{2g}$ -like orbitals,



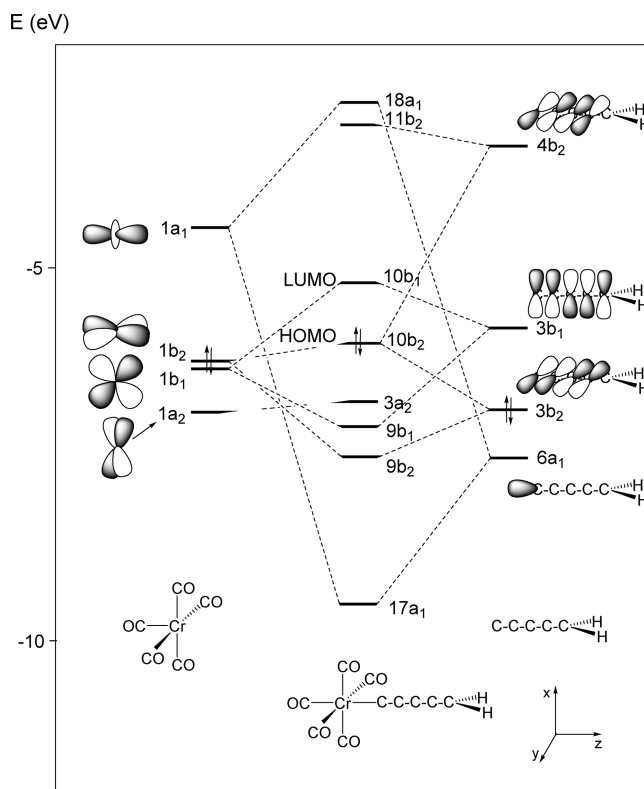


**FIGURE 1.** Optimized bond lengths (Å) in  $[(\text{CO})_5\text{Cr}(\text{=C})_n\text{X}_2]$  complexes,  $n = 3\text{--}8$  and  $\text{X} = \text{H}$  (black),  $\text{NH}_2$  (blue), or  $\text{NO}_2$  (red).

$1a_2$  ( $d_{xy}$ ),  $1b_1$  ( $d_{xz}$ ), and  $1b_2$  ( $d_{yz}$ ), slightly mixed with the  $\pi^*$  orbitals of the CO ligands, and by two empty  $e_g$ -like orbitals,  $1a_1$  ( $d_{z^2}$ ,  $p_z$  hybrid) and the high-lying  $2a_1$  ( $d_{x^2-y^2}$ ).

All cumulene carbenes  $\text{C}_n\text{H}_2$  have a closed shell ground state with a lone pair on the first carbon atom corresponding to a high-lying doubly occupied orbital of  $a_1$  symmetry. They present a characteristic  $\pi$  system made up of two sets of orbitals, lying either in the molecular plane ( $\pi_{||}$ ) or perpendicular to it ( $\pi_{\perp}$ ). The former set consists of  $n - 1$  in-plane  $\pi_{||}$  orbitals (of  $b_2$  symmetry), and the latter of  $n$  perpendicular  $\pi_{\perp}$  orbitals (of  $b_1$  symmetry), and they are occupied by a total of  $2n - 2$  electrons. A different occupation pattern is observed depending on whether  $n$  is odd or even:  $\text{C}_n\text{H}_2$  cumulenylienes with  $n$  even have a  $\pi_{\perp}$  HOMO and a  $\pi_{||}$  LUMO, while those with  $n$  odd have a  $\pi_{||}$  HOMO and a  $\pi_{\perp}$  LUMO, as illustrated in Scheme 3 for  $\text{C}_4\text{H}_2$  and  $\text{C}_5\text{H}_2$ . The main  $\pi$  accepting properties of these unsaturated ligands are determined by the LUMO and, to a lesser extent, by the LUMO + 1.

Figures 2 and 3 show three main orbital interactions between the  $[(\text{CO})_5\text{Cr}]$  metal fragment and the  $\text{C}_4\text{H}_2$  or  $\text{C}_5\text{H}_2$  moiety: (i) the donation from the cumulene lone pair orbital into the metal  $d_{z^2}$  forming the metal–carbon  $\sigma$  bond;

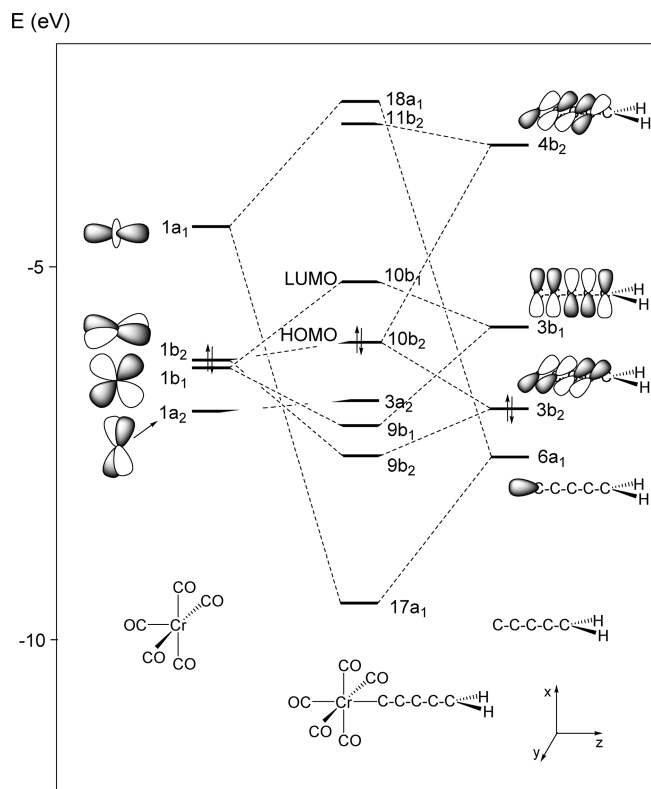
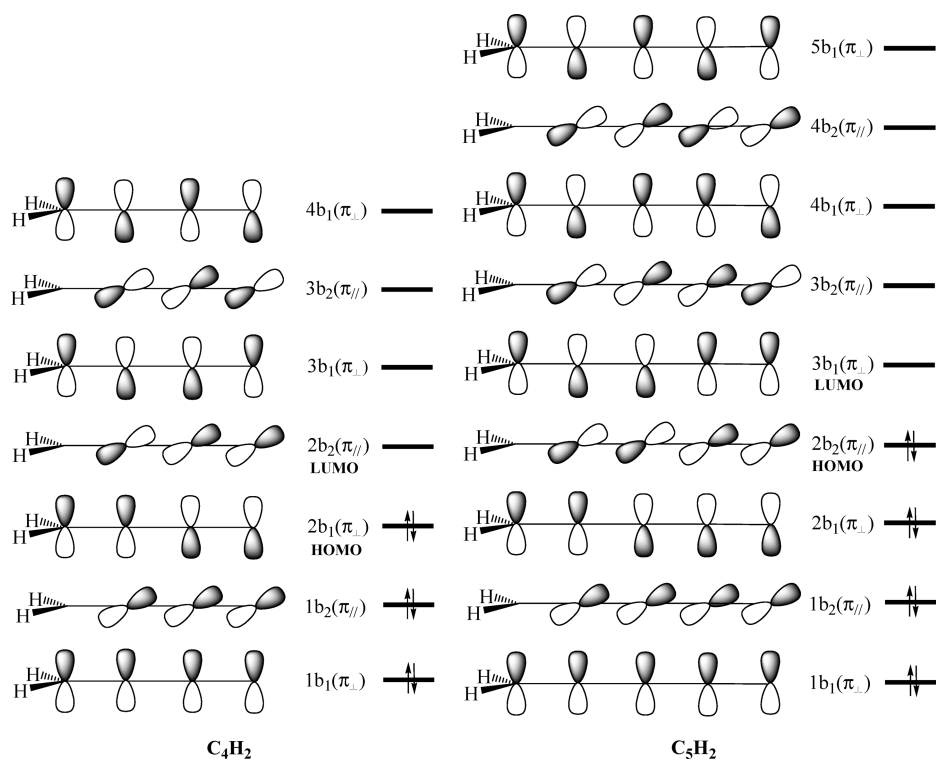
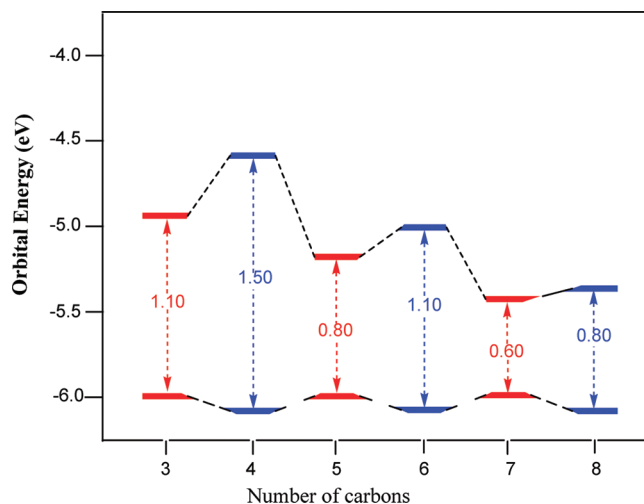


**FIGURE 2.** Orbital interaction diagram for the  $[(\text{CO})_5\text{Cr}(\text{=C})_4\text{H}_2]$  complex.

(ii) a stabilizing back-donation from one of the two filled quasi-degenerate  $d_{\pi}$  metal orbitals into the empty LUMO of the cumulene unit; and (iii) an interaction of the remaining filled  $d_{\pi}$  orbital with the filled HOMO and, to a minor extent, with the empty LUMO + 1 of cumulene corresponding, respectively, to a destabilizing two-orbital, four-electron interaction or to a further stabilizing  $\pi$  back-donation contribution. Two different  $\pi$  back bonding interactions, occurring in two orthogonal planes, can therefore be distinguished: a major contribution coming from the LUMO ( $\pi_{||}$  for  $\text{C}_4$  or  $\pi_{\perp}$  for  $\text{C}_5$ ) and a minor contribution from the LUMO + 1 ( $\pi_{\perp}$  for  $\text{C}_4$  or  $\pi_{||}$  for  $\text{C}_5$ ).

On lengthening the cumulene chain from  $\text{C}_2$  to  $\text{C}_9$ , the HOMO–LUMO gap decreases although with a superimposed odd/even alternation (Figure 4) in agreement with the UV/vis spectra of  $[(\text{CO})_5\text{Cr}(\text{=C})_n\text{C}(\text{NR}_2)_2]$  ( $n = 1, 2, \text{ or } 3$ ) showing a bathochromic shift on increasing the chain length from  $\text{C}_3$  to  $\text{C}_7$ .<sup>7</sup> The decrease is mainly due to a lowering of the LUMO energy consistent with electrochemical studies on Rh complexes evidencing a significant decrease of the reduction potential on increasing the chain length.<sup>26</sup>

Interesting information on the thermodynamic stability of metal cumulenylienes and on its dependence on the

SCHEME 3.  $\pi$ -System for  $C_4H_2$  and  $C_5H_2$  CumulenesFIGURE 3. Orbital interaction diagram for the  $[(CO)_5Cr(=C)_5H_2]$  complex.FIGURE 4. HOMO and LUMO energies for  $[(CO)_5Cr(=C)_nH_2]$  complexes,  $n = 3-9$ .

carbon chain length comes from the bond dissociation energies of the cumulenylidene ligand calculated for the  $[(CO)_5Cr(=C)_nH_2]$  series of complexes. The results obtained are given in Table 1 and show relatively high bonding energies (260–285  $\text{kJ mol}^{-1}$ ) with slightly larger values for metal cumulenylidenes with  $n$  odd. One of the main results was that the chromium–cumulene bond dissociation

energies remain almost constant on lengthening the cumulene chain showing only a very slight decrease. This indicates that there is no thermodynamic upper limit to the cumulene chain length, suggesting that the synthetic difficulties to prepare higher cumulenylidenes are not due to thermodynamic reasons.

The contributions from  $\sigma$  donation and  $\pi$  back-donation to the metal–cumulene bond dissociation energy have been separated into a steric term,  $E_{\text{ster}}$ , and an orbital interaction term,  $E_{\text{orb}}$ , which can be further broken up into contributions from the various irreducible representations of the overall symmetry group of the system. This decomposition scheme is particularly useful in the considered complexes of  $C_{2v}$  symmetry because it allows one to separate the energy contributions corresponding to  $\sigma$  donation and to  $\pi$  back-donation taking place, respectively, into the  $A_1$  and the  $B_1$  ( $\pi_{\perp}$ ) and  $B_2$  ( $\pi_{\parallel}$ ) representations.

The results of this energy decomposition are reported in Table 1 and show that (i) the overall contribution to the orbital interaction term from  $\pi$  back-donation,  $E_{B_1} + E_{B_2}$ , is slightly higher than that from  $\sigma$  donation,  $E_{A_1}$ , and (ii) on

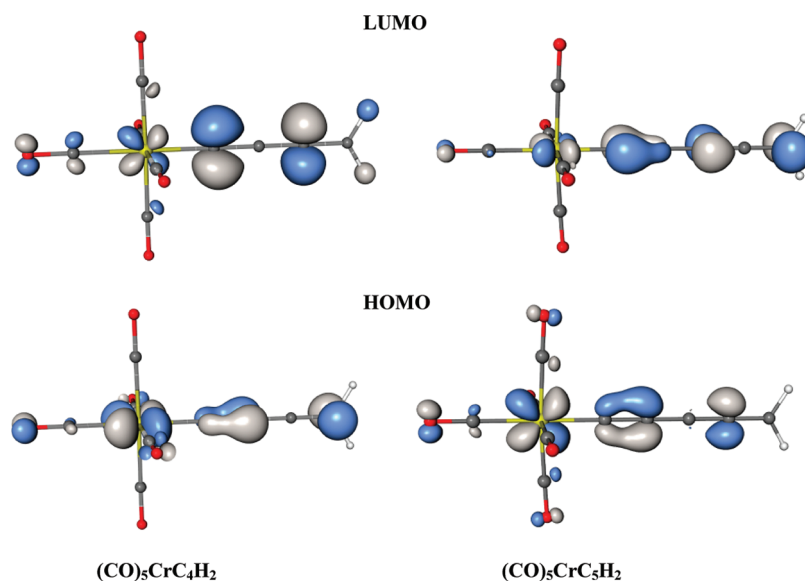
**TABLE 1.** Metal–Cumulene Bond Dissociation Energies ( $\text{kJ mol}^{-1}$ ) and Their Decomposition for the  $[(\text{CO})_5\text{Cr}(\text{=C})_n\text{CH}_2]$  Complexes with  $n = 3-9$

$n$	$D_e$	$E_{\text{ster}}$	$E_{\text{orb}}$	$E_{A_1}$	$E_{B_1}$	$E_{B_2}$	$E_{B_1} + E_{B_2}$
3	283	113	-407	-197	-157	-54	-211
4	276	130	-415	-196	-75	-147	-222
5	282	116	-410	-196	-148	-68	-216
6	275	137	-423	-197	-86	-145	-231
7	280	122	-414	-197	-145	-77	-222
8	259	150	-421	-196	-90	-140	-230
9	278	125	-418	-197	-143	-850	-228

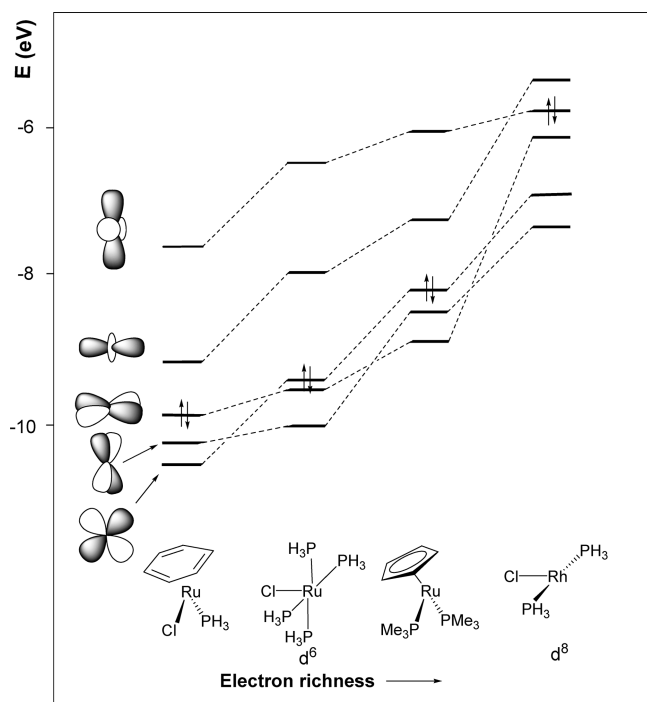
lengthening the cumulene chain the  $\sigma$  contribution ( $E_{A_1}$ ) and the  $\pi$  contribution ( $E_{B_1} + E_{B_2}$ ) remain essentially constant, apart for a small odd/even oscillation, which is responsible for the slightly larger bonding energies for the odd chains.

**3.3. 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 allenylidene metal complexes.<sup>1-3,5-8</sup> In particular, their reactivity is mainly governed by the electron-deficient character of the  $C_1$  and  $C_3$  carbon atoms, which are therefore subject to nucleophilic attack, whereas the electron-rich character of the  $C_2$  carbon atom makes it susceptible to electrophilic attack.<sup>1-3</sup> The preference of nucleophilic addition for  $C_1$  versus  $C_3$  depends on the nature of the metal center and on the steric and electronic properties of the ancillary ligands and of the  $C_3$  substituents and has been only recently addressed.<sup>35</sup>

Much less is known on the reactivity of higher metallacumulenes. The data available for the few known butatrienylidene, pentatetraenylidene, hexapentaenylidene, and heptahexaenylidene complexes give evidence that the cumulenylidene chain consists of alternating arrays of electrophilic and nucleophilic sites. Nucleophiles preferably add to the odd carbon atoms of the chain, whereas electrophiles add to even carbon atoms, although the first and last positions may be disfavored by the steric protection of ancillary ligands or of the substituents on the carbon end, depending also on the nature of the nucleophiles.<sup>10</sup>



**FIGURE 5.** Orbital decomposition of HOMO and LUMO for  $[(\text{CO})_5\text{Cr}(\text{=C})_n\text{H}_2]$  complexes,  $n = 4$  and  $5$ .



**FIGURE 6.** Frontier orbital energies for  $d^6$  and  $d^8$  metal fragments with increasing electron richness.

The rationalization of the reactivity trends of metal cumulenylidenes has been one of the main goals of all theoretical studies on these systems. The first semiempirical studies in the late 1970s and early 1980s already pointed out the alternating electron-poor/electron-rich character of the carbon atoms along the allenylidene chain with  $C_1$  and  $C_3$  being electrophilic and  $C_2$  nucleophilic,<sup>29,30</sup> in agreement with the observed regioselectivity, and later DFT studies better quantified these results.<sup>31</sup>

We have first generalized these results to higher cumulenylidenes within our study on the  $[(CO)_5Cr(=C)_nH_2]$  series.<sup>32</sup> For all the considered metallacumulene complexes, the calculated Mulliken atomic charges show no significant polarization of the carbon atoms of the cumulene chain indicating that charge distribution is not important in determining the regioselectivity of either electrophilic or nucleophilic attack.

The molecular orbital diagrams of all considered cumulenylidenes (see Figures 2 and 3 for  $n=4$  and 5) show a high-lying HOMO and a low-lying LUMO, both quite isolated from the remaining orbitals, suggesting that the reactivity of these complexes is determined by frontier orbital factors and that these two orbitals play the main role in determining the regioselectivity of, respectively, the electrophilic and nucleophilic attack. The breakdown of the contributions from the metal and the carbon atoms along the chain to the HOMO

and LUMO of all  $[(CO)_5Cr(=C)_nH_2]$  complexes shows that the HOMO has contributions mainly from the metal and the carbon atoms in even positions along the chain, that is,  $C_2$ ,  $C_4$ ,  $C_6$ , etc., whereas the LUMO has contributions mainly from the carbon atoms in odd positions along the chain, that is,  $C_1$ ,  $C_3$ ,  $C_5$ , etc., thus explaining the experimentally observed regioselectivity of the nucleophilic and electrophilic attacks, see Figure 5 for the  $C_4H_2$  and  $C_5H_2$  complexes. The LUMO contribution from the terminal carbon atom is usually somewhat larger,<sup>32,33</sup> suggesting its preferential attack by nucleophiles, but this can be easily overcome by electronic and steric effects of substituents.

It is noteworthy that an increase of the chain length causes a lowering of the LUMO energy, which determines a higher reactivity toward nucleophilic attacks and is probably the reason for the difficulties to synthesize and isolate higher metallacumulenes.

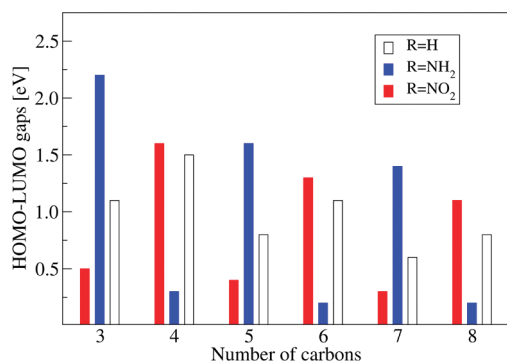
### 3.4. Effects of Metal Termini and of Substituents on the Carbon End. 3.4.1. Metal Termini Effects.

In the last 20–30 years a large number of allenylidenes and several cumulenylidenes have been synthesized and characterized involving mainly group 6, 7, and 8 metals, *vide supra*. To give a full rationale of the effect of the metal termini on the properties of metallacumulenes, we recently investigated a large series of  $L_nM(=C)_nH_2$  complexes,  $n=4$  and 5, based on several  $ML_m$  metal fragments, including the  $d^6$   $[(CO)_5Cr]$ ,  $[(CO)_5Mo]$ ,  $[(CO)_5W]$ ,  $[Cp(CO)_2Mn]$ ,  $[Cp(dppe)Fe]^+$ ,  $[trans-CI(dppe)_2Ru]^+$ ,  $[Cp(PMe_3)_2Ru]^+$ , and  $[BzCl(PH_3)_2Ru]^+$ , ranging from electron-poor to electron-rich character, and the  $d^8$   $[trans-CI(PH_3)_2Rh]$  and  $[trans-CI(PH_3)_2Ir]$ .<sup>36</sup>

For all these isolobal  $d^6$  and  $d^8$  complexes, which include the vast majority of experimentally characterized cumulenylidenes, the optimized bond lengths show the same qualitative pattern calculated for the  $[(CO)_5Cr(=C)_nCH_2]$  series with a purely cumulenic structure for even chain cumulenes and a significant polyynyl C–C bond length alternation for odd chain cumulenes. The nature of the metal fragment affects only the odd chain cumulenes, and we found that an increase of the electron richness of  $d^6$  metal fragments causes a decrease of the polyynyl-like bond length alternation and the same effect is observed for  $d^8$  metals. This result is a consequence of the destabilization of the zwitterionic polyynyl resonance forms where a formal negative charge is located on the metal, see Scheme 2, and is consistent with essentially all the available structural data.

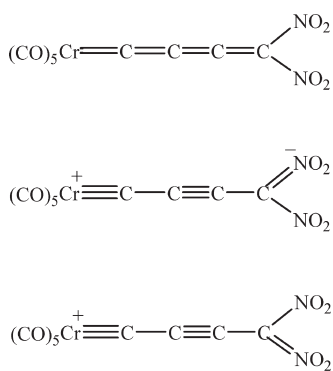
For all  $d^6$  and  $d^8$  complexes, the qualitative features of the electronic structure were found to be independent of the nature of the metal termini and show the same type of





**FIGURE 7.** HOMO–LUMO gaps (eV) for  $[(\text{CO})_5\text{Cr}(=\text{C})_n\text{X}_2]$  complexes with  $n = 3–8$  and  $\text{X} = \text{H}, \text{NH}_2,$  or  $\text{NO}_2$ .

**SCHEME 4.** Possible Resonance Structures for Nitro-Substituted Butatrienylidene Complexes



orbital interactions. The nature of the metal and of its ligands mainly causes an energy shift of the metal frontier orbitals, which reflects in the extent of their interactions with the cumulenylidene orbitals thus affecting the various bonding components. The direction and the magnitude of these shifts are in principle predictable on the basis of the metal configuration and the electron-donating or -withdrawing nature of the ligands. In particular, an increase of the electron richness or a shift from a  $d^6$  to a  $d^8$  configuration causes a rise of all metal frontier orbitals, see Figure 6. As a consequence, the  $d_\pi$  orbital rises closer to the cumulenylidene LUMO and  $\pi$ -back-donation increases, whereas the  $d_\sigma$  orbital rises farther from the cumulenylidene lone pair and  $\sigma$ -donation decreases. These two effects have been quantified by calculating the bonding energies and their separation in  $\sigma$  and  $\pi$  components: the increase of  $\pi$ -back-donation prevails leading to an overall increase of the metal–cumulene bond energy, which is more evident for  $d^8$  configuration. This increase of the metal–cumulene bonding energy with the electron richness of the metal fragment reflects the destabilization of the polyynyl resonance forms showing single

M–C bond character, see Scheme 2, and is consistent with the results of geometry optimization, *vide supra*.

The effects of the metal termini on the reactivity were considered through an analysis of the energies of both HOMO and LUMO and their breakdown into atomic contributions. The results indicate that the energy of the LUMO significantly increases with the electron richness of the metal termini leading to a reduced reactivity toward the nucleophilic attack. This is in agreement with the experimental data, which show a high stability of allenylidene complexes with the most electron-rich metal fragments, such as  $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PR}_3)_2]^+$ , and a low stability of complexes with electron-poor metal fragments, such as  $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{PMe}_3)\text{Cl}]$  or  $[\text{M}(\text{CO})_5]$  ( $\text{M} = \text{Cr}, \text{Mo},$  or  $\text{W}$ ). The localization of the HOMO and LUMO on even/odd carbon atoms is essentially unaltered by variations in the metal electron count from  $d^6$  to  $d^8$  or in the electron richness, and therefore, no significant change in the regioselectivity of electrophilic or nucleophilic additions is foreseen.

**3.4.2. Substituent Effects.** Most of the synthesized allenylidene and cumulenylidene complexes bear sterically hindered alkyl and aryl groups on the terminal carbon atom, which stabilize these reactive species through steric and electronic effects. The effect of the substitution of the carbon end on the physical and chemical properties of allenylidene and the cumulenylidene complexes has substantially paralleled their synthesis and characterization. The attention has been focused on electron-donating heteroatom substituents  $\text{ER}_n$  ( $-\text{OR}$  or  $-\text{NR}_2$ ), which were found to stabilize the most reactive longer chain cumulenylidene complexes, and their effects have been investigated by X-ray crystallography, IR, UV–vis, and NMR spectroscopies and electrochemical techniques.

We carried out a systematic study on the effect of several terminal substituents on the geometry, electronic structure, and reactivity of metal cumulenylidenes by performing DFT calculations on the  $[(\text{CO})_5\text{Cr}(=\text{C})_n\text{CX}_2]$  ( $n = 2–9$ ;  $\text{X} = \text{F}, \text{SiH}_3, \text{CH}=\text{CH}_2, \text{NH}_2,$  or  $\text{NO}_2$ ) series<sup>37</sup> and comparing the results with those previously obtained for the unsubstituted complexes.<sup>32</sup> The optimized bond lengths within the cumulene unit are significantly affected only by  $\pi$ -donor ( $-\text{NH}_2$ ) and  $\pi$ -acceptor ( $-\text{NO}_2$ ) substituents, which lead to different effects depending on whether the complex has an even or odd chain, see Figure 1. In particular, for  $\text{NH}_2$  substituents the characteristic polyynyl alternation of odd cumulenylidenes is significantly enhanced, consistent with the stabilization of zwitterionic polyynyl resonance structures by these  $\pi$ -donor amino substituents, see Scheme 2, and in agreement with all

X-ray structural data. On the other hand, in the presence of NO<sub>2</sub> substituents, the characteristic cumulenenic structure of even chain cumulenylidenes shows a significant carbon–carbon bond length alternation. However, this alternation pattern is different from that observed for odd chain cumulenes, involves a shortening of the Cr–C bond rather than its lengthening, and can be explained by invoking the contribution of zwitterionic resonance structures with an alkylidyne character stabilized by the  $\pi$ -acceptor nitro substituent, see Scheme 4.

The electronic structure of the cumulenylidene complexes was found essentially independent of the terminal substituents and shows the same kinds of orbital interactions. The extent of these interactions is affected by the substituents, in particular by the  $\pi$ -donating (–NH<sub>2</sub>) and the  $\pi$ -accepting (–NO<sub>2</sub>) groups, through a shift of the frontier orbitals of the cumulenylidene ligands.  $\pi$ -Donor substituents raise the cumulenylidene LUMO and LUMO + 1 ( $\pi^*$ ) orbitals farther from the metal  $d_{\pi}$  orbital and cause a decrease of  $\pi$ -back-donation, whereas  $\pi$ -acceptors stabilize the cumulenylidene LUMO and LUMO + 1 ( $\pi^*$ ) orbitals closer to the metal  $d_{\pi}$  orbital leading to an increase of  $\pi$ -back-donation. A smaller effect is observed on the lone pair localized on the initial carbon atom, and the  $\sigma$  interaction is less affected. The calculated bonding energies and their analysis in terms of the  $\sigma$  and  $\pi$  components confirm this picture showing that  $\pi$ -donor groups lead to a decrease of the metal–cumulenylidene bond energy, which mainly affects odd chains, agreeing with the increased weight of the polyynyl resonance forms showing single M–C character, see Scheme 2, whereas  $\pi$ -acceptor groups lead to an increase of the dissociation energies, which is more evident for even chains, consistent with the increased weight of the polyynyl resonance forms showing triple M≡C character, see Scheme 4.

When reactivity is considered, the results indicate that the localization of the HOMO and LUMO on even/odd carbon atoms is essentially unaltered by the terminal substituents and, therefore, no significant changes in the regioselectivity of additions are foreseen. However, HOMO and LUMO energies are strongly affected by the amino and nitro substituents, which cause a striking oscillation of the HOMO–LUMO gap. In particular,  $\pi$ -donor amino substituents cause an increase of the HOMO–LUMO gap for odd-chain and a decrease for even-chain cumulenes, while  $\pi$ -acceptor nitro substituents cause an increase of the HOMO–LUMO gap for even-chain and a decrease for odd-chain cumulenes, see Figure 7. Moreover, amino groups lead to a destabilization

and nitro groups to a stabilization of LUMO whose energy determines the reactivity toward nucleophiles. For  $\pi$ -donor-substituted odd-chain metallacumulenes, these two effects add suggesting a significant decrease of their reactivity toward nucleophilic attack, in agreement with experimental evidence indicating a high stability of amino-substituted allenylidenes and pentatetraenylidenes.<sup>7,9</sup> For  $\pi$ -acceptor-substituted even-chain metallacumulenes, the large increase of the HOMO–LUMO gap and the increase of M–C bond energy are expected to overcome the modest decrease of the LUMO energy suggesting a decrease of their reactivity. Higher even-chain metallacumulenes, whose synthesis is particularly elusive, are therefore expected to be stabilized by the presence of  $\pi$ -acceptor substituents such as NO<sub>2</sub>, CN, COOR, or C<sub>6</sub>H<sub>4</sub>–NO<sub>2</sub>, a prediction that has not yet been experimentally investigated.

#### 4. Concluding Remarks

The theoretical understanding of the electronic structure of allenylidenes and higher cumulenylidenes has reached a remarkable level. A consistent rationale is now possible for the main structural, spectroscopic, and reactivity properties of this growing class of compounds.

DFT calculations have emerged not only as a reliable interpretative guide to the experimental behavior of known cumulenylidenes but also as a powerful predictive tool capable of guiding new developments in this still underexplored field of fascinating compounds, such as higher even-chain and early transition metal cumulenylidenes.

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#### BIOGRAPHICAL INFORMATION

**Cecilia Coletti** received her Ph.D. degree in 1997 at the University of Perugia. After a postdoctoral appointment at Copenhagen University, she has worked at the University of Chieti where she is now Associate Professor.

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#### FOOTNOTES

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## REFERENCES

- Bruce, M. I. Organometallic chemistry of vinylidene and related unsaturated carbenes. *Chem. Rev.* **1991**, *91*, 197–257. Werner, H. Allenylidenes: Their multifaceted chemistry at rhodium. *Chem. Commun.* **1997**, 903–910.
- Bruce, M. I. Transition metal complexes containing allenylidene, cumulenylidene, and related ligands. *Chem. Rev.* **1998**, *98*, 2797–2858.
- Cadierno, V.; Gamasa, M. P.; Gimeno, J. Recent developments in the reactivity of allenylidene and cumulenylidene complexes. *Eur. J. Inorg. Chem.* **2001**, 571–591.
- Bruce, M. I. Metal complexes containing cumulenylidene ligands  $\{L_nM\}C(=C)_n=CRR'$  ( $n \geq 2$ ). *Coord. Chem. Rev.* **2004**, *248*, 1603–1625.
- Rigaut, S.; Touchard, D.; Dixneuf, P. H. Ruthenium-allenylidene complexes and their specific behaviour. *Coord. Chem. Rev.* **2004**, *248*, 1585–1601.
- Winter, R. F.; Zálaiš, S. Allenylidene complexes of ruthenium: Synthesis spectroscopy and electron transfer properties. *Coord. Chem. Rev.* **2004**, *248*, 1565–1583.
- Fischer, H.; Szesni, N.  $\pi$ -Donor-substituted metallacumulenes of chromium and tungsten. *Coord. Chem. Rev.* **2004**, *248*, 1659–1677.
- Cadierno, V.; Gimeno, J. Allenylidene and higher cumulenylidene complexes. *Chem. Rev.* **2009**, *109*, 3512–3560.
- Roth, G.; Fischer, H.; Meyer-Friedrichsen, T.; Heck, J.; Houbrechts, S.; Persoons, A. Synthesis and nonlinear optical properties of new heptapentaenylidene complexes: Study on the second harmonic generation efficiencies of amino-substituted group 6 cumulenylidenes. *Organometallics* **1998**, *17*, 1511–1516.
- Metal Vinylidenes and Allenylidenes in Catalysis: From Reactivity to Applications in Synthesis; Bruneau, C., Dixneuf, P. H., Eds.; Wiley-VCH: Weinheim, Germany, 2008.
- Bruneau, C.; Dixneuf, P. H. New vinylidenes and allenylidenes in catalysis: applications in anti-Markovnikov additions to terminal alkynes and alkene metathesis. *Angew. Chem., Int. Ed.* **2006**, *45*, 2176–2203.
- (a) Fischer, E. O.; Kalder, H. J.; Frank, A.; Köhler, F. H.; Huttner, G. 3-Dimethylamino-3-phenylallenylidene, a novel ligand at the pentacarbonyl-chromium and -tungsten skeleton. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 623–624. (b) Berke, H. Simple synthesis of dicarbonyl( $\eta^5$ -cyclopentadienyl)-(3,3-di-tert-butylallenylidene)-manganese. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 624–624.
- Selegue, J. P. Synthesis and structure of  $[Ru(C_3Ph_2)(PMe_3)_2(Cp)]PF_6$ , a cationic diphenylallenylidene complex. *Organometallics* **1982**, *1*, 217–218.
- Winter, R. F.; Klinkhammer, K.-W.; Zálaiš, S. Ruthenium-aminoallenylidene complexes from butatrienylidene intermediates via an aza-Cope rearrangement: Synthetic, spectroscopic, electrochemical, spectroelectrochemical, and computational studies. *Organometallics* **2001**, *20*, 1317–1333.
- Touchard, D.; Haquette, P.; Daridor, A.; Toupet, L.; Dixneuf, P. H. First isolable pentatetraenylidene metal complex containing the  $Ru=C=C=C=C=CPh_2$  assembly. A key intermediate to provide functional allenylidene complexes. *J. Am. Chem. Soc.* **1994**, *116*, 11157–11158.
- Lass, R. W.; Steinert, P.; Wolf, J.; Werner, H. Synthesis and molecular structure of the first neutral transition-metal complex containing a linear  $M=C=C=C=C=CR_2$  chain. *Chem.—Eur. J.* **1996**, *2*, 19–23.
- Kovacik, I.; Laubender, M.; Werner, H. A new rhodium(I) hexapentaene complex prepared from a precursor containing a  $RhC_5$  chain. *Organometallics* **1997**, *16*, 5607–5609.
- Roth, G.; Fischer, H. Complexes with diamino-substituted unsaturated  $C_3$  and  $C_5$  ligands: First group 6 pentatetraenylidenes and new allenylidene complexes. *Organometallics* **1996**, *15*, 1139–1145.
- Szafert, S.; Haquette, P.; Fallon, S. B.; Gladysz, J. A. Synthesis and properties of chiral rhenium pentatetraenylidene complexes of  $[(\eta^5-C_5H_5)Re(NO)(PPh_3)(=C=C=C=C=CAr_2)]^+[BF_4]^-$  ( $CAr_2 = 9$ -fluorenylidene). *J. Organomet. Chem.* **2000**, *604*, 52–58.
- Bruce, M. I.; Ellis, B. G.; Skelton, B. W.; White, A. H. Further chemistry of butatrienylidene complexes. *J. Organomet. Chem.* **2005**, *690*, 1772–1783.
- (a) Ilg, K.; Werner, H. The first structurally characterized metal complex with the molecular unit  $M=C=C=C=CR_2$ . *Angew. Chem., Int. Ed.* **2000**, *39*, 1632–1634. (b) Ilg, K.; Werner, H. Closing the gap between  $MC_3$  and  $MC_5$  metallacumulenes: the chemistry of the first structurally characterized transition metal complex with  $M=C=C=C=CR_2$  as the molecular unit. *Chem.—Eur. J.* **2002**, *8*, 2812–2820.
- Venkatesan, K.; Blacque, O.; Fox, T.; Alfonso, M.; Schmalte, H. W.; Berke, H. Synthetic access to half-sandwich manganese  $C_4$  cumulenylidene complexes. *Organometallics* **2004**, *23*, 4661–4671. Semenov, S. N.; Blaque, O.; Fox, T.; Venkatesan, K.; Berke, H. Self-coupling of a 4-H-butatrienylidene tungsten complex. *Angew. Chem., Int. Ed.* **2009**, *48*, 5203–5206.
- Rigaut, S.; Olivier, C.; Costuas, K.; Choua, S.; Fadhel, O.; Massue, J.; Turek, P.; Saillard, J.-Y.; Dixneuf, P. H.; Touchard, D.  $C_7$  and  $C_9$  carbon rich bridges in diruthenium systems: Synthesis, spectroscopic, and theoretical investigations of different oxidation states. *J. Am. Chem. Soc.* **2006**, *128*, 5859–5876.
- Dede, M.; Drexler, M.; Fischer, H. Heptaheptaenylidene complexes: Synthesis and characterization of the first complexes with a  $M=C=C=C=C=C=CR_2$  moiety ( $M = Cr, W$ ). *Organometallics* **2007**, *26*, 4294–4299.
- Stang, P. J. Unsaturated carbenes. *Chem. Rev.* **1978**, *78*, 383–405.
- Kovacik, I.; Gevert, O.; Werner, H.; Schmittel, M.; Söllner, R. Study of the  $\pi$ -acceptor ability of unsaturated ligands:  $-C(=C)_nPh_2$  ( $n = 0, 1, 2$  and 4) based on cyclic voltammetry of complexes  $trans-[RhCl(L)(PPr_3)_2]$  ( $L = -C(=C)_nPh_2, C_2H_4$  and  $CO$ ). *Inorg. Chim. Acta* **1998**, *275–276*, 435–439.
- Rigaut, S.; Touchard, D.; Dixneuf, P. H. New paramagnetic ruthenium complexes via one-electron reduction of metallacumulenes. *J. Chem. Soc., Chem. Commun.* **2001**, 373–374.
- Pombeiro, A. J. L. Electron-donor/acceptor properties of carbynes, carbenes, vinylidenes, allenylidenes and alkynyls as measured by electrochemical ligand parameters. *J. Organomet. Chem.* **2005**, *690*, 6021–6040.
- Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L.  $CpM(CO)_2$ (ligand) complexes. *J. Am. Chem. Soc.* **1979**, *101*, 585–591.
- Kostić, N. M.; Fenske, R. F. Molecular orbital study of bonding, conformations, and reactivity of transition-metal complexes containing unsaturated organic ligands. Electrophilic and nucleophilic additions to acetylidene, vinylidene, vinyl, and carbene ligands. *Organometallics* **1982**, *1*, 974–982.
- (a) Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Modrego, J.; Oñate, E.; Vela, N. Synthesis and characterization of hydride-alkynyl, allenylidene, carbyne, and functionalized-alkynyl complexes containing the  $[Os(\eta^5-C_5H_5)(PPr_3)_2]^+$  fragment: the complex  $[Os(\eta^5-C_5H_5)(=C=C=CPh_2)(PPr_3)_2]PF_6$ , a new type of allenylidene derivative from the reactivity point of view. *Organometallics* **2000**, *19*, 2585–2596. (b) Rigaut, S.; Costuas, K.; Touchard, D.; Saillard, J.-Y.; Golhen, S.; Dixneuf, P. H. Bis-allenylidene metal complex and unique related radical with delocalization of one electron over both trans carbon-rich chains. *J. Am. Chem. Soc.* **2004**, *126*, 4072–4073.
- Re, N.; Sgamellotti, A.; Floriani, C. Density functional study of metallacumulene complexes. *Organometallics* **2000**, *19*, 1115–1122.
- Auger, N.; Touchard, D.; Rigaut, S.; Halet, J.-F.; Saillard, J.-Y. Electronic structures of ruthenium cumulene complexes  $[Cl(PPh_3)_4RuC_nH_{2n}]^+$  ( $n = 1–8$ ) and of their reduced states. Bonding and properties of the cationic, neutral, and anionic series with respect to the cumulenyl chain length. *Organometallics* **2003**, *22*, 1638–1644.
- Creati, F.; Coletti, C.; Re, N. A density functional study of butadiyne to butatrienylidene isomerization in  $[Ru(HC\equiv C\equiv CH)(PMe_3)_2(Cp)]^+$ . *Organometallics* **2009**, *28*, 6603–6613.
- Coletti, C.; Gonsalvi, L.; Guerriero, A.; Marvelli, L.; Peruzzini, M.; Reginato, G.; Re, N. Rhenium allenylidenes and their reactivity towards phosphines: A theoretical study. *Organometallics* **2010**, *29*, 5982–5993.
- Marrone, A.; Coletti, C.; Re, N. Metal fragment modulation of metallacumulene complexes: A density functional study. *Organometallics* **2004**, *23*, 4952–4963.
- Marrone, A.; Re, N. Effects of terminal substituents on metallacumulene complexes: A density functional study on  $(CO)_5Cr(=C)_nX_2$  ( $X = F, SiH_3, CH_2, NH_2, NO_2$ ). *Organometallics* **2002**, *21*, 3562–3571.