Electron pairing analysis of the Fischer-type chromium–carbene complexes (CO)$_5$Cr=C(X)R (X = H, OH, OCH$_3$, NH$_2$, NHCH$_3$ and R = H, CH$_3$, CH=CH$_2$, Ph, C≡CH)

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Abstract

The electron-pair density distributions of a series of 25 Fischer carbene complexes of the type (CO)$_5$Cr=C(X)R (X = H, OH, OCH$_3$, NH$_2$, NHCH$_3$ and R = H, CH$_3$, CH=CH$_2$, Ph, C≡CH) are analyzed using the Atoms in Molecules theory. Localization and delocalization indices are used to characterize the electron pairing taking place in the Cr=C–X moiety in these complexes. Electron delocalization between the Cr and C atoms and between the C atom and the X group are related to the π-donor strength of the X group and the degree of back-donation between the chromium pentacarbonyl and the carbene fragments. The results obtained with the Atoms in Molecules theory complement those obtained in a previous study by means of energy and charge decomposition analyses. Electron delocalization between the Cr atom and the X group is consistent with the hypothesis of a weak 3-center 4-electron bonding interaction in the Cr=C–X group of atoms. Except for X = H, δ(Cr,X) increases with the decrease of the π-donor character of the X group.
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1. Introduction

Since the discovery of Fischer carbene complexes [1], these versatile organometallic reagents

have showed an extensive chemistry. They participate in a large number of organic and inorganic synthetic reactions [2–19]. The general molecular structure definition of these compounds is (CO)$_5$M=C(X)R, where the central carbene carbon atom is linked to a low-valent transition metal of group VI–VIII. One substituent of the carbene acts as a π-donor (X) allowing for an electronic stabilization of the electron-deficient carbene carbon atom, whereas the other carbene substituent may be either a saturated alkyl or an unsaturated

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alkenyl, alkynyl, or aryl group (R). The low-valent metal center is stabilized by π-acceptor substituents such as carbon monoxide, phosphine, or cyclopentadienyl ligands.

The metal–carbene bond of Fischer carbene complexes is usually [2] discussed in terms of the familiar Dewar–Chatt–Duncanson (DCD) model (see Scheme 1) [20,21], considering that the two main synergistic bonding interactions are σ donation from the carbon lone pair orbital of the carbene into the empty d(σ) orbital of the metal, and π back-donation from an occupied d(π) metal atomic orbital to the formally empty p(π) orbital of the carbene. It has been proposed that the π bond character of a metal–carbene can be better represented by a M─C─X 3-center 4-electron (3c–4e) bond [22,23], and then it is understandable that the X group has a large effect on the nature of the chromium–carbene bond.

Several studies have shown that the chemical reactivity of the Fischer-type chromium–carbene complexes $(CO)_5Cr=C(X)R$ depends mainly on the electronic characteristics of the carbene substituents, X and R, which seem to have a remarkable control on the electrophilicity of the complex [24–26]. From these experimental results one can consider the possibility of electronically tuning Fischer carbene complexes by using specific X and R carbene substituents to get the desired chemical response [27]. An amount of theoretical studies about the nature of the metal–carbene bond have been done to analyze these kind of structures. The earliest works on carbene complexes were carried out by means of semiempirical

Scheme 1.

[23,28–30], Hartree–Fock (HF) [31–36], and post-HF methods [22,37–39], while most of the recent works have been performed through density functional theory (DFT) [22,40–49]. Several of these calculations [31,34–36,47,49] have focused on the theoretical comparison between Fischer and Schrock carbene complexes. Schrock carbenes result from the coupling of a triplet carbene ligand (carbene fragment) to a triplet transition metal (metal fragment) moiety, leading to nearly covalent σ and π bonds. These carbene complexes have nucleophilic character at the carbene carbon atom. On the contrary, Fischer carbenes have electrophilic character at this atom and are formed by coordination of a singlet carbene ligand to a singlet transition metal through a dative carbene to metal σ donation and a dative metal to carbene π back-donation. The analysis of the metal–carbene bonding has shown that both σ donation and π back-donation are significant [42,46,47].

Theoretical studies on the energetics, geometry and electronic structure of these kind of compounds could be the key to have a predictable criteria for the Fischer carbene complex chemical reactivity. Furthermore, this kind of studies should afford a detailed characterization of the interaction between the two fragments (metal fragment $((CO)_5Cr)$ and carbene fragment $(C(X)R)$). In a previous work [50], we calculated the relative strength of σ donation and π back-donation as a function of the nature of different X and R substituents in a series of 25 Fischer carbene complexes, using charge decomposition analysis (CDA) [51,52] and energy decomposition analysis (EDA) [53–57]. We found that donation from the carbene fragment to the $Cr(CO)_5$ fragment is stronger than back-donation. However, it is back-donation rather than donation that correlates with most geometrical and electronic parameters of the complexes studied. The reason for the larger influence of back-donation is that charge back-donation values and π orbital interaction energies are more scattered over a large range of values, while charge donation values and σ orbital interaction energies are more constant. We also found that the smaller the π-donor character of X, the largest the back-donation. In general, it was found that back-donation, as defined in the CDA or EDA methods,
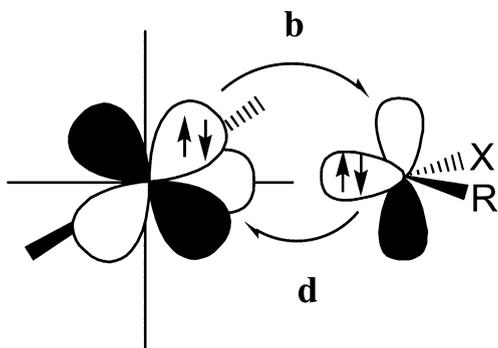
is proportional to the $Cr–CO_{(trans)}$ distance, and inversely proportional to the $Cr–C_{carbene}$, and $C–O_{(trans)}$ distances.

The present work analyzes the same series of Fischer carbene complexes using the Atoms In Molecules (AIM) theory [58]. According to this theory, the topology of the electron density, $\rho(\mathbf{r})$, determines which atoms are bonded in a molecule, and allows to divide the real space into disjoint regions (basins). Usually, each basin is associated to an atom. Integration of $\rho(\mathbf{r})$ within an atomic basin yields the number of electrons associated to the corresponding atom. Moreover, knowledge of the electron-pair density, $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$, allows to analyze the pairing of the electrons in a molecule [59]. Some years ago, Bader and MacDougall [60] have reported an AIM analysis for a series of triatomic carbenes, discussing the differences between the singlet and triplet states of these molecules in terms of $\rho(\mathbf{r})$. Recently, Tafipolsky et al. [61] have used the AIM theory to analyze the electronic structure of acyclic and N-heterocyclic carbenes, both free and coordinated to a Cr atom. They calculated a series of topological properties of theoretical charge densities along a full bond path, concluding that there exists a significant π-electron delocalization in these aminocarbenes. In the present paper, the emphasis is on the electron-pair structure of a series of 25 Fischer carbenes. The aim is to relate chemical concepts such as electron sharing, σ- and π-donation to the electron-pair density distributions of these systems, using the AIM theory. An additional goal is to investigate the hypothesis of a 3c–4e bonding interaction between the Cr—C—X atoms. The 25 complexes analyzed in this paper have been labelled as in [50] (see Table 1 and Fig. 1). Note that the X and R substituents attached to the carbene C atom have different degrees of σ- and π-donor character. In
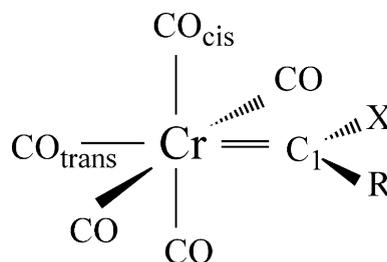

Fig. 1. Schematic representation of a Fischer-type chromium–carbene complex.

particular, the π-donor character of the X group increases in the order $H < OH < OCH_3 < NH_2 < NHCH_3$.

2. Methods

For the present work, wavefunctions and electron densities, needed to carry out the AIM topological analysis that concerns us, have been obtained by means of the Gaussian 98 program [62], at the B3LYP/6-311G** level of theory [63,64]. Furthermore, molecular geometries and results of the EDA analysis [53–57] have been taken from [50], in which all calculations were performed with the ADF [65–67] package, using a generalized gradient approximation that includes the non-local exchange correlation of Becke and the non-local correlation correction of Perdew (BP86 functional) [68–70]. A double-zeta basis set augmented with a polarization function was used for H, C, N and O atoms, while an uncontracted triple-zeta basis set was used for the Cr atom [71,72]. Molecular geometries were fully optimized for all carbene complexes. Additional calculations were performed enforcing C_s symmetry for each molecule. More details can be found in [50].

Table 1
Labels for the 25 Fischer-type chromium–carbene complexes studied

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

For each of the molecules, a topological analysis of $\rho(\mathbf{r})$ has been performed, and electron populations have been obtained for each atom, using the AIMPAC package [73]. Furthermore, localization and delocalization indices have been also calculated. The localization index (LI), $\lambda(A)$, is the number of electrons which are completely localized in an atom A, while the delocalization index (DI), $\delta(A, B)$ is the number of electrons delocalized or shared between two atoms A and B [59]. In fact, this delocalization index can be regarded as the AIM generalization of the well-known concept of bond order or 2-center bond index. For instance, at the HF level of theory the localization and delocalization indices reduce to Wiberg indices [74] if the integrations over atomic basins are replaced by a Mulliken-like partitioning in Hilbert space, or to the more recently introduced effective pair populations [75–78].

The calculation of LIs and DIs is based on $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$, which is not available in DFT. As an approximation, we considered a non-interacting electron-pair density obtained from the Kohn–Sham (KS) orbitals [79]. Within this approximation, LIs and DIs at a DFT level of theory can be calculated as

$$\lambda(A) = 2 \sum_{i,j} (S_{ij}(A))^2, \qquad (1)$$

$$\delta(A, B) = 4 \sum_{i,j} S_{ij}(A) S_{ij}(B), \qquad (2)$$

where $S_{ij}(A)$ is the overlap of the molecular orbitals (MO) i and j in the basin of atom A, and the summations run over all the occupied MOs. LIs and DIs calculated using this approximation do not account explicitly for electron correlation effects between electrons of different spin. A previous study has shown that approximated DFT indices are very close to the HF ones [79]. Taking into account that Coulomb electron correlation generally decreases electron delocalization between bonded atoms, approximate DIs can be considered as upper bounds to the correlated ones.

Some years ago, a series of authors introduced the multicenter bond indices, being the 3-centre bond index the most relevant [80–83]. Later, Ponec and co-workers [84,85] reported an AIM general-

ization of the 3-center DI, which depends on the third-order electron density. At the HF (or approximate KS-DFT) level, this 3-center DI can be expressed for $A \neq B \neq C$ as

$$\delta(A, B, C) = 12 \sum_{i,j,k} S_{ij}(A) S_{jk}(B) S_{ki}(C). \qquad (3)$$

Ponec has used this DI to detect 3-center bonding in several molecules. Positive $\delta(A, B, C)$ values are characteristic of 3-center 2-electron (3c–2e) bonds, while negative values correspond to 3c–4e bonds. $\delta(A, B, C)$ is close to zero when no 3c-bonding between the three atoms is present [84,86,87]. At this point, it is worth to remark that the topological analysis of $\rho(\mathbf{r})$ only defines bonds between pairs of atoms, and the concept of 3c-bonding is not considered in the context of the AIM theory [58]. However, $\delta(A, B, C)$ can be used to justify the use of 3-center bonding models in molecules difficult to describe with classical 2-center bonds of the Lewis model [84].

The numerical accuracy of the AIM calculations has been assessed using two criteria: (i) The integration of the Laplacian of the electron density ($\nabla^2 \rho(\mathbf{r})$) within an atomic basin must be close to zero. (ii) The number of electrons in a molecule must be equal to the sum of all the electron populations of a molecule, and also equal to the sum of all the LIs and half of the DIs in the molecule. For all the atomic calculations, integrated absolute values of $\nabla^2 \rho(\mathbf{r})$ were always less than 0.001. For all the molecules, errors in the calculated numbers of electrons were always less than 0.01.

3. Results and discussion

The main goal of the paper is to analyze the bonding interactions between the Cr atom, the C atom of the carbene moiety, and the atoms of the X and R groups which are bonded to the carbene C atom. Therefore, when discussing electron populations, LIs and DIs, we will use C to denote the central atom in the carbene group, and X and R to denote the two atoms bonded to the C atom, besides Cr.

Table 2 gathers electron populations, $N(Cr)$, $N(C)$, and $N(X)$, and LIs, $\lambda(Cr)$, $\lambda(C)$, and $\lambda(X)$,

Table 2
Selected atomic populations (N), localization (λ) and delocalization (δ) indices for the Fischer carbenes at the totally optimized geometry

	N(Cr)	N(C)	N(X)	λ(Cr)	λ(C)	λ(X)	δ(Cr,C)	δ(C,X)	δ(C,R)	δ(Cr,X)	δ(Cr,R)	δ(Cr,C,X)
A	22.858	5.579	9.022	19.856	3.834	7.787	0.844	1.113	0.905	0.112	0.041	−0.028
B	22.817	5.605	9.053	19.828	3.854	8.001	0.880	1.100	0.922	0.118	0.044	−0.029
C	22.861	5.627	8.126	19.865	3.853	6.357	0.705	1.332	0.908	0.095	0.031	−0.018
D	22.851	5.629	8.122	19.862	3.857	6.503	0.732	1.323	0.919	0.102	0.035	−0.024
E	22.829	6.257	0.978	19.840	4.353	0.421	1.124	0.976	0.976	0.051	0.051	0.041
F	22.836	5.575	9.030	19.849	3.799	7.787	0.752	1.081	1.017	0.099	0.038	−0.010
G	22.871	5.592	9.047	19.883	3.808	7.974	0.788	1.078	1.019	0.100	0.038	−0.013
H	22.867	5.613	8.128	19.876	3.805	6.361	0.628	1.302	1.009	0.080	0.029	0.002
I	22.884	5.615	8.126	19.890	3.811	6.496	0.658	1.289	1.006	0.086	0.031	−0.005
J	22.824	6.210	0.991	19.831	4.259	0.429	1.009	0.956	1.095	0.046	0.050	0.034
K	22.817	5.569	9.021	19.833	3.771	7.774	0.736	1.089	1.058	0.097	0.043	−0.012
L	22.836	5.612	9.040	19.855	3.824	7.953	0.824	1.059	1.086	0.100	0.039	−0.014
M	22.872	5.621	8.128	19.880	3.790	6.355	0.623	1.303	1.045	0.081	0.035	−0.004
N	22.898	5.624	8.116	19.902	3.790	6.478	0.664	1.283	1.055	0.089	0.035	−0.011
O	22.831	6.227	1.007	19.835	4.248	0.434	0.910	0.944	1.282	0.040	0.047	0.030
P	22.859	5.570	9.021	19.864	3.777	7.775	0.758	1.090	1.006	0.100	0.038	−0.014
Q	22.840	5.611	9.049	19.855	3.818	7.962	0.752	1.069	1.061	0.093	0.034	−0.009
R	22.879	5.622	8.122	19.894	3.795	6.345	0.637	1.306	1.002	0.084	0.030	−0.007
S	22.874	5.614	8.121	19.884	3.792	6.484	0.668	1.300	0.992	0.088	0.031	−0.012
T	22.820	6.221	1.003	19.826	4.255	0.432	0.910	0.947	1.212	0.040	0.043	0.030
U	22.850	5.486	9.005	19.862	3.676	7.761	0.757	1.056	1.145	0.102	0.052	−0.018
V	22.856	5.506	9.015	19.867	3.688	7.941	0.795	1.057	1.153	0.106	0.052	−0.020
W	22.856	5.547	8.091	19.870	3.703	6.311	0.644	1.260	1.140	0.092	0.043	−0.016
X	22.853	5.542	8.095	19.873	3.706	6.461	0.664	1.253	1.143	0.093	0.043	−0.017
Y	22.829	6.128	0.946	19.848	4.164	0.393	0.934	0.931	1.318	0.040	0.065	0.028

for the Cr, C, and X atoms, as well as DIs relevant to the description of the Cr—C—X bonds: $\delta(Cr,C)$, $\delta(C,X)$, $\delta(C,R)$, $\delta(Cr,X)$, $\delta(Cr,R)$, and $\delta(Cr,C,X)$, for the 25 Fischer carbene complexes studied.

According to the AIM analysis, the electron population in the Cr atom is practically constant for the molecular series studied. Indeed, $N(Cr)$ values for these compounds are between 22.8 and 22.9 electrons, which correspond to atomic charges between +1.1 and +1.2. For the C atom, the population takes values between 5.5 and 6.3, corresponding to charges between +0.5 and −0.3. Indeed, negative $N(C)$ populations are found only for complexes with H as the substituent X, while complexes with π-donor substituents have C atoms with positive charges (+0.4 to +0.5). In general, the positive charge in the Cr atom is partially compensated with negative charges in the carbonyl groups. In average, CO groups have charges of ca. −0.2 each, with little differences between *cis* and *trans* carbonyls or between carbonyls in different complexes (data not reported). LIs for the Cr and C atoms follow closely the trends found for the corresponding populations. For all the carbenes, $\lambda(Cr)$ takes values between 19.8 and 19.9, which means that ca. 3 of the electrons associated to Cr are shared with other atoms. $\lambda(C)$ values are between 4.2 and 4.4, when X = H and between 3.7 and 3.9, for the rest of X groups.

DIs provide additional information on the characteristics of the Cr—C bond. $\delta(Cr,C)$ decreases with increasing π-donor character of the X group and increasing back-donation. Thus, for a given R, $\delta(Cr,C)$ decreases in the order H > OH > OCH₃ > NH₂ > NHCH₃, with the only exception of complex P ($\delta^P(Cr,C)$ is slightly larger than $\delta^Q(Cr,C)$). For instance, complexes with X = H have $\delta(Cr,C)$ values between 0.91 and 1.12, while those with X = NHCH₃ have $\delta(Cr,C)$ values between 0.62 and 0.71. Although the Cr—C bond in these complexes is formally a double bond, $\delta(Cr,C)$ values within this range (0.6–1.1) are characteristic of single covalent bonds, or bonds with little double bond character [59]. However, bond polarization does also have an influence on electron delocalization between bonded atoms. In particular, the positive charges in the Cr and C atoms in most of the complexes can explain the

relatively low values of $\delta(Cr,C)$. Thus, further analysis is required to establish the bond order of the Cr—C bond (see below). It is worth noting that, although maximal Cr—C delocalization is found for complexes with negative C charges due to stronger back-donation, there is no significant correlation between $\delta(Cr,C)$ and $N(Cr)$ or $N(C)$ for the rest of the series.

Both $\delta(C,X)$ and $\delta(C,R)$ take values between 0.9 and 1.3, which are typical of single bonds with partial double bond character. In general, $\delta(C,X)$ increases with the π-donor strength of the group X. Thus, an increase in the transfer of π electrons from X to C increases the double bond character in the C—X bond. The resulting partial double bond character between the heteroatom and the C is manifested by a shortening of the C—X bond. Thus, all complexes with X = OCH₃ and NHCH₃ have C—X bond lengths shorter than systems with X = OH and NH₂, respectively. At the same time, the π back-donation from Cr is reduced and $\delta(Cr,C)$ decreases, as discussed above. For a given X, as a general trend, $\delta(C,R)$ decreases in the direction CCH > CHCH₂ > CH₃ ⩾ Ph > H. The larger $\delta(C,R)$ values for R = CCH is in agreement with the σ and π withdrawing character of this substituent [88].

The Cr—CO$_{trans}$ and C=O bonds in these complexes are formally single and double, respectively. This agrees with the values for $\delta(Cr, C_{CO})_{trans}$, which are between 0.8 and 0.9, and $\delta(C,O)_{trans}$, which is ca. 1.6 for all the complexes (data not reported). Although these indices present little variation along the carbene series, they have a good correlation with $\delta(Cr,C)$: the larger $\delta(Cr,C)$, the smaller $\delta(Cr,C_{CO})_{trans}$ and the larger $\delta(C,O)_{trans}$. Although we have found that for X = N, $\delta(C,O)_{trans}$ is slightly smaller and $\delta(Cr, C_{CO})_{trans}$ is somewhat larger than for X = O, our results do not support a major change in the Cr—CO$_{trans}$ bond when going from X = N to X = O complexes as derived from the CASSCF results of Wang et al. [22].

Electron delocalization between non-bonded atoms is generally small, but can be of chemical significance [89]. In the present study, it is of interest to analyze the non-bonded electron delocalization between the Cr, X and R atoms (see

Table 2). $\delta(Cr,R)$ values are rather small (between 0.03 and 0.06), while $\delta(Cr,X)$ values are significantly larger (between 0.08 and 0.12), except when $X = H$. In the latter case, $\delta(Cr,X)$ is generally lower than $\delta(Cr,R)$. This relatively large DI between the chromium and the X group might imply a 3c–4e interaction. Indeed, this is the case of the FHF^- and FFF^- systems having 3c–4e bonding interaction [86,90]. In addition, molecules such as CO_2, SO_2 and SO_3 also exhibit significant non-bonded delocalization between O atoms [59,79]. Going deeper into the $\delta(Cr,X)$ values, for a given R, the larger the π-donor character of the X group, the smaller the electron delocalization between the Cr and X groups, except when $X = H$. Thus, despite amino substituents are stronger π-donors than hydroxy substituents, we have found somewhat unexpectedly that $\delta(Cr,X)$ is larger for $X = O$ than for $X = N$. This result is consistent with Fermi hole density contours [22] showing that when a reference electron is placed on the Cr atom, the electron delocalization on the heteroatom is larger for $X = O$ systems than for $X = N$ species. We attribute the larger $\delta(Cr,X)$ for $X = O$ as compared to $X = N$ to the fact that hydroxy substituents have one more electron pair to be delocalized. Also, it is important to note that the stronger π-electron donating character of the amino group leads to larger chromium–carbene bond distances (by about 5 pm as compared to $X = O$) and smaller back-donations. These two effects also act in the direction of reducing the $\delta(Cr,X)$ delocalization. As far as the R group is concerned, for a given X $\delta(Cr,X)$ increases in the order $CH_3 \approx Ph \approx CH_2CH < CCH < H$.

Additional insight on the nature of the $Cr–C–X$ interaction can be gained by examining the associated 3c-DI (Eq. (3)) (see Table 2). As a general trend, $\delta(Cr,C,X)$ values are very close to zero and present a small variation, so it really becomes very difficult to speak about the existence of 3c–4e bonds in these systems. Nevertheless, some insight into these values can help in order to complement the rest of the work. First, $\delta(Cr,C,X)$ is negative, except for the carbenes with $X = H$, and is minimal (ca. -0.03) for the carbenes A and B, which are also the ones with the largest $\delta(Cr,X)$ index. These results might indicate some degree of

3c–4e delocalization in these carbenes. In contrast, carbenes E, J, O, T, and Y exhibit $\delta(Cr,C,X)$ values between 0.03 and 0.04, and cannot be considered to have 3c–4e delocalization. The extent of the 3-center delocalization in all carbenes in this series may be considered low, in comparison to molecules which are usually attributed to have 3c–4e bonding interactions (e.g., N_3^-: -0.36; N_2O: -0.20) [84,91]. Furthermore, one must be aware that non-bonded electron delocalization or 3-center delocalization have been found in many different molecules [84,89]. For instance, this analysis also detects a low 3-center delocalization between the Cr atom and the carbonyl groups in this carbene series. Thus, it may be concluded that these systems present a weak 3c–4e bonding interaction character, which is incremented with the decrease of the π-donor character of the X group, except for $X = H$, and for $R = H$ and CCH.

Further analysis of the molecular structure of these complexes can be achieved by analyzing separately the localization and delocalization patterns of the σ and π electrons. In order to carry out this kind of analysis, we modified slightly the geometry of the optimized complexes (by changing only the $Cr–C$ torsion and freezing the rest of the geometrical parameters) in order to attain C_s symmetry (see [50]). This approach is justified because the energy barrier associated to rotation around the $Cr–C$ bond is quite small [31,39,41,43]. Table 3 presents values of the most relevant DIs calculated at the C_s geometry, together with the σ and π contributions to these indices. Note that DIs calculated at the C_s and totally optimized geometries are very similar.

The symmetry analysis reveals that both the σ and π contributions to $\delta(Cr,C)$ and $\delta(Cr,X)$ are important. For the complexes with $X = H$ (E, J, O, T, Y), the AIM analysis is totally consistent with a $Cr=C–H$ bonding pattern. For instance, the σ contribution to $\delta(C,H)$ is close to 1 for these complexes, with no significant π contribution. Accordingly, the $C–H$ bond can be considered as a single non-polar bond, with an electron-pair equally shared between the two atoms. Essentially, these $C–H$ bonds are equivalent to those found for instance in ethene [59]. In contrast, the σ contributions to $\delta(Cr,C)$ are in the range 0.6–0.7,

Table 3
Selected delocalization indices (δ) for the Fischer carbenes at the C_s geometry

	δ(Cr,C)			δ(C,X)			δ(C,R)			δ(Cr,X)		
	Total	σ	π	Total	σ	π	Total	σ	π	Total	σ	π
A	0.861	0.574	0.286	1.099	0.760	0.338	0.912	0.903	0.009	0.118	0.047	0.070
B	0.893	0.590	0.304	1.103	0.775	0.328	0.927	0.917	0.010	0.122	0.049	0.074
C	0.723	0.536	0.187	1.331	0.844	0.487	0.919	0.911	0.009	0.103	0.043	0.060
D	0.741	0.544	0.196	1.338	0.857	0.481	0.931	0.922	0.008	0.108	0.045	0.063
E	1.151	0.674	0.477	0.972	0.960	0.012	0.972	0.961	0.012	0.050	0.035	0.015
F	0.768	0.536	0.232	1.083	0.754	0.329	1.030	0.939	0.091	0.098	0.042	0.056
G	0.783	0.540	0.244	1.081	0.762	0.319	1.035	0.943	0.092	0.103	0.045	0.058
H	0.658	0.503	0.154	1.302	0.837	0.465	1.024	0.939	0.085	0.087	0.039	0.048
I	0.671	0.511	0.160	1.313	0.847	0.466	1.028	0.944	0.085	0.091	0.040	0.050
J	1.033	0.626	0.407	0.957	0.947	0.010	1.108	0.997	0.111	0.045	0.031	0.014
K	0.766	0.549	0.217	1.039	0.744	0.295	1.110	0.926	0.185	0.094	0.043	0.051
L	0.790	0.552	0.238	1.067	0.768	0.299	1.086	0.928	0.158	0.100	0.044	0.056
M	0.667	0.514	0.153	1.253	0.835	0.418	1.102	0.935	0.168	0.089	0.040	0.049
N	0.697	0.528	0.169	1.270	0.844	0.426	1.078	0.933	0.145	0.095	0.041	0.054
O	0.931	0.601	0.330	0.942	0.929	0.013	1.223	0.981	0.242	0.038	0.029	0.010
P	0.774	0.531	0.243	1.078	0.745	0.332	1.005	0.949	0.057	0.103	0.043	0.060
Q	0.773	0.531	0.242	1.095	0.763	0.332	1.016	0.957	0.058	0.102	0.044	0.058
R	0.656	0.497	0.159	1.313	0.839	0.474	1.010	0.956	0.054	0.090	0.040	0.050
S	0.680	0.503	0.177	1.305	0.845	0.461	1.012	0.958	0.054	0.096	0.040	0.056
T	1.007	0.596	0.410	0.945	0.934	0.011	1.101	1.026	0.074	0.043	0.029	0.014
U	0.750	0.523	0.227	1.050	0.744	0.306	1.163	0.985	0.178	0.100	0.043	0.058
V	0.816	0.554	0.262	1.043	0.759	0.284	1.178	0.995	0.183	0.113	0.047	0.066
W	0.630	0.483	0.147	1.270	0.832	0.438	1.161	0.997	0.163	0.087	0.039	0.049
X	0.665	0.495	0.169	1.274	0.843	0.431	1.173	1.009	0.163	0.096	0.039	0.058
Y	0.939	0.586	0.353	0.935	0.922	0.013	1.332	1.072	0.260	0.039	0.028	0.011

and the π contributions range from 0.3 to 0.5. This means that the Cr—C bond has some degree of double bond character, with two pairs of electrons being unequally shared between the two atoms. When π-donor substituents are considered instead of H, both the σ and π components decrease in δ(Cr,C). This effect is stronger for δ^π(Cr,C), which is less than 0.2 when X is NH_2 or $NHCH_3$, in agreement with the decrease in Cr—C back-donation for strong π-donor substituents. At the same time, δ^π(C,X) increases with the decrease in back-donation (up to ca. 0.5 for X = NH_2, $NHCH_3$). δ^σ(C,X) depends mainly on the nature of the X atom bonded to C: it is ca. 0.75 for C—O bonds, ca. 0.85 for C—N bonds and ca. 0.95 for C—H bonds. As for the C—R bond, δ^σ(C,R) is between 0.9 and 1.0 for all the complexes. The π component is small (less than 0.1) except for the CCH and CHCH$_2$ substituents (δ^π(C,R) between 0.16 and 0.26), which is due to some conjugation with the C=C double bonds of these substituents.

The work by Cases et al. [50] revealed that there is a correlation between several geometrical parameters and the degree of back-donation from Cr to C, as defined in the EDA method. In this study, the orbital interaction energy obtained from a Morokuma-like EDA for C_s symmetry systems was separated into the σ and π interaction components (ΔE_σ and ΔE_π, respectively), and ΔE_π was used as a quantitative measure of back-donation. Using this criterion, several relationships between back-donation and relevant DIs indices can be found. Thus, Fig. 2 depicts back-donation in front of δ(Cr,C), δ(C,X) and δ(Cr,X), as well as the π components of these indices. Figs. 2(a) and (b) reveal that back-donation is directly proportional to δ(Cr,C) and inversely proportional to δ(C,X). Note that the relationship between δ(Cr,C) and back-donation is specially strong. Moreover, there is also a good correlation between back-donation and δ(Cr,X), if complexes with X = H are not considered, which do not have π electrons to de-
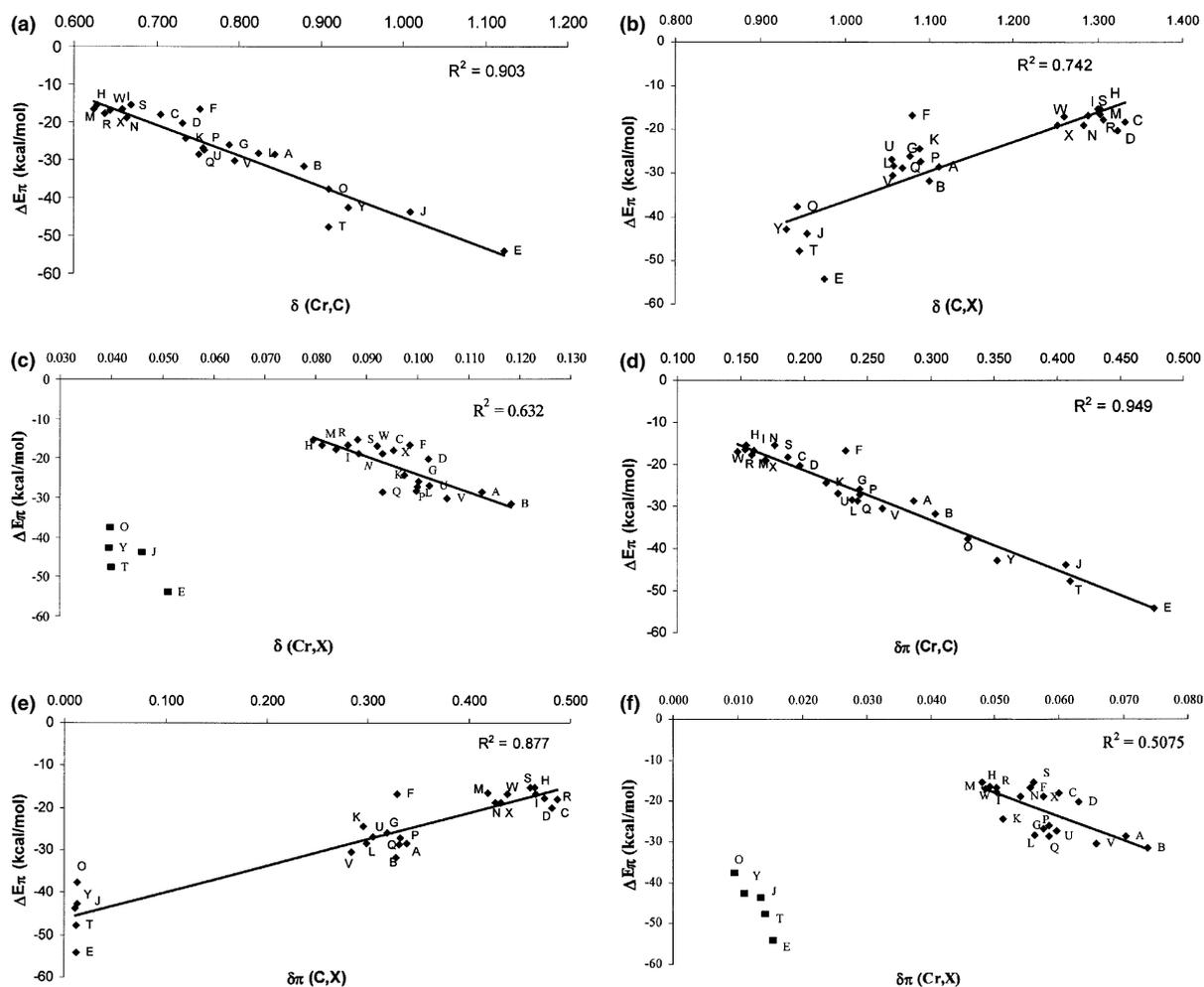
Fig. 2. Back-donation vs. several delocalization indices: (a) back-donation vs. $\delta(Cr,C)$; (b) back-donation vs. $\delta(C,X)$; (c) back-donation vs. $\delta(Cr,X)$; (d) back-donation vs. $\delta^\pi(Cr,C)$; (e) back-donation vs. $\delta^\pi(C,X)$; (f) back-donation vs. $\delta^\pi(Cr,X)$.

localize (Fig. 2(c)). It is interesting to remark that most of the variance in these three DIs is related to the π electrons. Indeed, except for $\delta(Cr,X)$, the π components show a better correlation with back-donation than the total DIs (see Figs. 2(d) and (e)). This is not surprising, since back-donation in the EDA method is also related to the π interactions.

4. Summary and conclusions

We have analyzed the electron pairing patterns in a series of pentacarbonyl Cr–Fischer carbene complexes of the type $(CO)_5Cr=C(X)R$, $(X = H,$

OH, OCH_3, NH_2, and $NHCH_3$; R = H, OH, OCH_3, NH_2, and $NHCH_3$). We have paid special attention to the $Cr=C$ and $C-X$ bonds, and the effect of the X and R substituents on the character of these bonds. The possibility of a 3-center interaction has also been considered for the $Cr=C-X$ moiety.

According to the LIs and DIs as defined in the AIM theory, both the $Cr=C$ and the $C-X$ bond can be considered as covalent bonds, with two sets of electrons (of σ and π type, respectively) being partially shared between each pair of atoms. C–R and Cr–CO bonds were characterized as single covalent bonds, except for complexes with

R = CCH and CHCH$_2$. In these cases, the C—R bond has some double bond character, especially for R = CCH. Finally, C=O bonds were characterized as double covalent bonds with a high degree of polarization.

The π-donor character of the substituent X has the largest impact on the electron delocalization between the Cr, C, and X atoms. Substituents with a high π-donor character lead to a decrease in electron sharing between Cr and C, while increasing electron sharing between C and X. For all the molecules, the σ component in $\delta(Cr,C)$ and $\delta(C,X)$ is more important than the π component. However, the π component exhibits a larger variation along this series. Indeed, $\delta^{\pi}(Cr,C)$ is clearly related to the degree of back-donation from Cr to C.

Finally, the fact that the DI between the non-bonded Cr and X atoms is relatively high in most of these carbenes gives some support to the concept of a 3-center bonding interaction in the Cr=C—X moiety. According to the DIs for these atoms, the bonding is susceptible to be of the 3c–4e type for X = OH, OCH$_3$, NH$_2$, and NHCH$_3$. The 3c–4e character seems to be more important for X = O than for X = N complexes. For these complexes, there is a good correlation between $\delta(Cr,X)$ and back-donation, increasing $\delta(Cr,X)$ with the decrease of the π-donor character of X. As a whole, we can consider that these compounds present a weak 3c–4e interaction that increases with the decrease of the π-donor character of the X substituent.

Acknowledgements

References

[1] E.O. Fischer, A. Maasböl, Angew. Chem. Int. Ed. Engl. 3 (1964) 580.
[2] K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreissl, U. Schubert, K. Weiss, Transition Metal Carbene Complexes, VCH, Weinheim, 1983.
[3] K.H. Dötz, Angew. Chem. Int. Ed. Engl. 23 (1984) 587.
[4] L.S. Hegedus, in: Comprehensive Organometallic Chemistry II, vol. 12, Pergamon Press, Oxford, 1995.
[5] W.D. Wulff, in: Comprehensive Organic Synthesis, vol. 5, Pergamon Press, Oxford, 1991.
[6] W.D. Wulff, Comprehensive Organometallic Chemistry II, Pergamon Press, Oxford, 1995.
[7] D.F. Harvey, D.M. Sigano, Chem. Rev. 96 (1996) 271.
[8] A. de Meijere, Pure Appl. Chem. 68 (1996) 61.
[9] J. Barluenga, J. Pure Appl. Chem. 68 (1996) 543.
[10] R. Aumann, H. Nienaber, Adv. Organomet. Chem. 41 (1997) 163.
[11] K.H. Dötz, P. Tomuschat, Chem. Soc. Rev. 28 (1999) 187.
[12] M.A. Sierra, Chem. Rev. 100 (2000) 3591.
[13] M.W. Davies, C.N. Johnson, J.P.A. Harrity, J. Org. Chem. 66 (2001) 3525.
[14] J. Barluenga, A.L. Suárez-Sobrino, M. Tomás, S. García-Granda, R. Santiago-García, J. Am. Chem. Soc. 123 (2001) 10494.
[15] J. Barluenga, J. Pure Appl. Chem. 71 (1999) 1385.
[16] H.-G. Schmalz, Angew. Chem. Int. Ed. Engl. 33 (1994) 303.
[17] H.-W. Frühauf, Chem. Rev. 97 (1997) 523.
[18] J. Barluenga, S. Martínez, A.L. Suárez-Sobrino, M. Tomás, J. Am. Chem. Soc. 123 (2001) 11113.
[19] J. Barluenga, M. Tomás, E. Rubio, J.A. López-Pelegrin, S. García-Granda, M.P. Priede, J. Am. Chem. Soc. 121 (1999) 3065.
[20] M.J.S. Dewar, Bull. Soc. Chim. Fr. 18 (1951) C79.
[21] J. Chatt, L.A. Duncanson, J. Am. Chem. Soc. (1953) 2929.
[22] C.-C. Wang, Y. Wang, H.-J. Liu, K.-J. Lin, L.-K. Chou, K.-S. Chan, J. Phys. Chem. A 101 (1997) 8887.
[23] T.F. Block, R.F. Fenske, J. Am. Chem. Soc. 99 (1977) 4321.
[24] K.H. Dötz, Angew. Chem. Int. Ed. Engl. 14 (1975) 644.
[25] C.F. Bernasconi, G.S. Perez, J. Am. Chem. Soc. 122 (2000) 12441.
[26] C.F. Bernasconi, M. Ali, F. Lu, J. Am. Chem. Soc. 122 (2000) 1352.
[27] W.Q. Jiang, M.J. Fuertes, W.D. Wulff, Tetrahedron 56 (2000) 2183.
[28] T.F. Block, R.F. Fenske, C.P. Casey, J. Am. Chem. Soc. 98 (1976) 441.
[29] R.J. Goddard, R. Hoffmann, E.D. Jemmis, J. Am. Chem. Soc. 102 (1980) 7667.

[30] F. Volatron, O. Eisenstein, J. Am. Chem. Soc. 108 (1986) 2173.

[31] H. Nakatsuji, J. Ushio, S. Han, T. Yonezawa, J. Am. Chem. Soc. 105 (1983) 426.

[32] J. Ushio, H. Nakatsuji, T. Yonezawa, J. Am. Chem. Soc. 106 (1984) 5892.

[33] D.S. Marynick, C.M. Kirkpatrick, J. Am. Chem. Soc. 107 (1985) 1993.

[34] T.R. Cundari, M.S. Gordon, J. Am. Chem. Soc. 113 (1991) 5231.

[35] T.R. Cundari, M.S. Gordon, J. Am. Chem. Soc. 114 (1992) 539.

[36] T.R. Cundari, M.S. Gordon, Organometallics 11 (1992) 55.

[37] T.E. Taylor, M.B. Hall, J. Am. Chem. Soc. 106 (1984) 1576.

[38] E.A. Carter, W.A. Goddard, J. Am. Chem. Soc. 108 (1986) 4746.

[39] A. Márquez, J. Fernández Sanz, J. Am. Chem. Soc. 114 (1992) 2903.

[40] H. Jacobsen, G. Schreckenbach, T. Ziegler, J. Phys. Chem. 98 (1994) 11406.

[41] H. Jacobsen, T. Ziegler, Organometallics 14 (1995) 224.

[42] A.W. Ehlers, S. Dapprich, S.F. Vyboishchikov, G. Frenking, Organometallics 15 (1996) 105.

[43] H. Jacobsen, T. Ziegler, Inorg. Chem. 35 (1996) 775.

[44] N. Fröhlich, U. Pidun, M. Stahl, G. Frenking, Organometallics 16 (1997) 442.

[45] G. Frenking, U. Pidun, J. Chem. Soc. Dalton Trans. (1997) 1653.

[46] M. Torrent, M. Duran, M. Solà, Organometallics 17 (1998) 1492.

[47] S.F. Vyboishchikov, G. Frenking, Chem. Eur. J. 4 (1998) 1428.

[48] A. Beste, O. Krämer, A. Gerhard, G. Frenking, Eur. J. Inorg. Chem. (1999) 2037.

[49] G. Frenking, J. Organomet. Chem. 635 (2001) 9.

[50] M. Cases, G. Frenking, M. Duran, M. Solà, Organometallics 21 (2002) 4182.

[51] S. Dapprich, G. Frenking, CDA 2.1, Marburg, 1994.

[52] S. Dapprich, G. Frenking, J. Phys. Chem. 99 (1995) 9352.

[53] F.M. Bickelhaupt, N.M.M. Nibbering, E.M. van Wezenbeek, E.J. Baerends, J. Phys. Chem. 96 (1992) 4864.

[54] T. Ziegler, A. Rauk, Inorg. Chem. 18 (1979) 1755.

[55] T. Ziegler, A. Rauk, Inorg. Chem. 18 (1979) 1558.

[56] T. Ziegler, A. Rauk, Theor. Chim. Acta 46 (1977) 1.

[57] K. Kitaura, K. Morokuma, Int. J. Quantum Chem. 10 (1976) 325.

[58] R.F.W. Bader, Atoms in Molecules: A Quantum Theory, Clarendon Press, Oxford, 1990.

[59] X. Fradera, M.A. Austen, R.F.W. Bader, J. Phys. Chem. A 103 (1999) 304.

[60] P.J. MacDougall, R.F.W. Bader, Can. J. Chem. 64 (1986) 1496.

[61] M. Tafipolsky, W. Scherer, K. Öfele, G. Artus, B. Pedersen, W.A. Herrmann, G.S. McGrady, J. Am. Chem. Soc. 124 (2002) 5865.

[62] M.J. Frisch et al., Gaussian 98, Rev. A11, Pittsburgh, PA, 1998.

[63] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[64] W.J. Hehre, R. Ditchfield, J.A. Pople, J. Chem. Phys. 56 (1972) 2257.

[65] E.J. Baerends, D.E. Ellis, P. Ros, Chem. Phys. 2 (1973) 41.

[66] C. Fonseca Guerra, O. Visser, J.G. Snijders, G. te Velde, E.J. Baerends, in: E. Clementi, G. Coringiu (Eds.), Methods and Techniques for Computational Chemistry, STEF, Cagliari, 1995, p. 305.

[67] G. te Velde, F.M. Bickelhaupt, E.J. Baerends, C. Fonseca Guerra, S.J.A. Van Gisbergen, J.G. Snijders, T. Ziegler, J. Comput. Chem. 22 (2001) 931.

[68] A.D. Becke, J. Chem. Phys. 84 (1986) 4524.

[69] A.D. Becke, Int. J. Quantum Chem. 23 (1983) 1915.

[70] J.P. Perdew, Phys. Rev. B 33 (1986) 8822.

[71] J.G. Snijders, E.J. Baerends, P. Vernooijs, At. Nucl. Data Tables 26 (1982) 483.

[72] P. Vernooijs, J.G. Snijders, E.J. Baerends, Slater Type Basis Functions for the Whole Periodic System. Internal Report, Vrije Universiteit of Amsterdam, Amsterdam, 1981.

[73] F.W. Biegler-König, R.F.W. Bader, T.-H. Tang, J. Comput. Chem. 3 (1982) 317.

[74] K.B. Wiberg, Tetrahedron 24 (1968) 1083.

[75] R. Ponec, M. Strnad, Int. J. Quantum Chem. 50 (1994) 43.

[76] R. Ponec, F. Uhlik, J. Mol. Struct. (Theochem) 391 (1997) 159.

[77] R. Bochicchio, R. Ponec, L. Lain, A. Torre, J. Phys. Chem. A 104 (2000) 9130.

[78] R. Ponec, R. Carbó-Dorca, Int. J. Quantum Chem. 72 (1999) 85.

[79] J. Poater, M. Solà, M. Duran, X. Fradera, Theor. Chem. Acc. 107 (2002) 362.

[80] A.B. Sannigrahi, T. Kar, Chem. Phys. Lett. 173 (1990) 569.

[81] A.B. Sannigrahi, P.K. Nandi, L. Beherea, T. Kar, J. Mol. Struct. (Theochem) 276 (1992) 259.

[82] K.C. Mundim, M. Giambiagi, M.S. de Giambiagi, J. Phys. Chem. 98 (1994) 6118.

[83] M. Giambiagi, M.S. de Giambiagi, K.C. Mundim, Struct. Chem. 1 (1990) 123.

[84] R. Bochicchio, R. Ponec, A. Torre, L. Lain, Theor. Chem. Acc. 105 (2001) 292.

[85] R. Bochicchio, L. Lain, A. Torre, R. Ponec, J. Math. Chem. 28 (2000) 83.

[86] T. Kar, E. Sánchez Marcos, Chem. Phys. Lett. 192 (1992) 14.

[87] R. Ponec, I. Mayer, J. Phys. Chem. A 101 (1997) 1738.

[88] R.D. Topsom, Acc. Chem. Res. 16 (1983) 292.

[89] X. Fradera, J. Poater, S. Simon, M. Duran, M. Solà, Theor. Chem. Acc. 108 (2002) 214.

[90] J. Molina Molina, J.A. Dobado, Theor. Chem. Acc. 105 (2001) 328.

[91] T. Kar, J.G. Ángyán, A.B. Sannigrahi, J. Phys. Chem. A 104 (2000) 9953.