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Density Functional Study of Metal−Arene Compounds: Mono(benzene)chromium, Bis(benzene)chromium and Their Cations

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To investigate the elementary events of the decomposition of transition metal complexes, a density functional study of the systems $Cr(C_6H_6)_2$ and $Cr(C_6H_6)$ as well as their corresponding cations, has been carried out. The results give a low bond energy (0.36 eV) for the neutral $Cr(C_6H_6)$ compound while the binding energy of the cation $Cr(C_6H_6)^+$ is much higher (1.84 eV), in good agreement with previous theoretical and experimental studies. Concerning the dissociation of $Cr(C_6H_6)_2$, the first process (dissociation of the first ligand) needs much higher energy than the second one, and depends on the intersystem crossing relaxation (ISC) of the intermediate $Cr(C_6H_6)$ compound. Taking into account the ISC process, the three-body decomposition occurs at 3.40 eV, in good agreement with recent experimental results. In the case of the $Cr(C_6H_6)_2{}^+$ dissociation, both processes (with and without ISC) may be available from recent experimental works. Our theoretical results reproduce very well the values corresponding to both ways of decomposition.

1. Introduction

Since its discovery in 1955 by Fischer and Hafner,[1] the parent compound, namely $Cr(C_6H_6)_2$, has been the subject of a massive structural analysis. In gas phase, this compound has a sandwich structure with the benzene rings in an eclipsed configuration. However, there has been a considerable controversy as to whether the molecule possesses a full D_{6h} symmetry,[2−4] a D_{3d} symmetry with alternating long and short C−C bond lengths,[5,6] or D_{3h} with long and short alternating C−C bond lengths.[7] In its singlet ground state, subsequent experimental[8−12] and theoretical[13−19] studies have confirmed finally the D_{6h} symmetry.

The majority of the previous works considered only the simultaneous dissociation of the two benzene ligands from $Cr(C_6H_6)_2$. Penner et al.,[20] from a photodissociation and photoionization experiments, could suggest the possibility of the formation of $Cr(C_6H_6)$, together with benzene, after decomposition of $Cr(C_6H_6)_2$, but without giving a definite confirmation of the existence of the neutral mono(benzene)chromium. A very recent laser vaporization in the gas phase performed by Kurikawa and co-workers,[21] could however measure the ionization energy of $Cr(C_6H_6)$ and thus confirm the production of the mono(benzene)chromium, but in very low abundance.

Obviously, in a mass spectrometer it was easy to obtain the cation compounds, i.e., $Cr(C_6H_6)_2{}^+$ and $Cr(C_6H_6)^+$. Their stabilities are fully discussed either theoretically[13,22−25] or experimentally.[26−30] However, not much attention has been paid in the elucidation of the mechanism of the dissociation of $Cr(C_6H_6)_2$ and its cation. Our interest will emphasize not only the dissociation process, but also the electronic structure change of all fragments involved in the dissociation. In this paper, by using the density functional method including non local gradient-based corrections, we try to give an understanding of the mechanism of the decomposition of $Cr(C_6H_6)_2$ and $Cr(C_6H_6)$ compounds, as well as their corresponding cations, by taking into account the possibly intersystem crossing relaxation (ISC) of the intermediate products.

2. Method of Calculation

For computational consistency, the C_{6v} symmetry was assumed for the all systems considered in all calculations performed, i.e., benzene, mono(benzene)chromium ($Cr(C_6H_6)$), bis(benzene)chromium ($Cr(C_6H_6)_2$), and their respective radical cations. All C−C and C−H bond lengths were optimized as well as the Cr−ring distance. As chromium is a transition metal, it has strongly correlated d electrons. Thus, we choose to do our study by using the density functional approach, which is well adapted to this type of problem.[31] The calculations have been done with the LCGTO-MCP-DF method using the deMon program package.[32,33] The method has been described extensively elsewhere.[34−36] The Dirac formulation for the exchange part associated with the VWN[37] expression for the correlation was used to describe the local potential. Non local gradient-based corrections have been added for exchange[38] and correlation.[39] For chromium we used an all-electron basis set. The (63321/531*/41+) orbital basis set has been employed with the corresponding (5,5;5,5) auxiliary basis set.[36] The carbon orbital basis set was of the type (3111/311) with the corresponding (4,3;4,3) auxiliary basis set.[36] Finally, concerning the hydrogen atoms, the (41/1*) orbital basis set was employed in conjunction with the (5,1;5,1) auxiliary basis set.[36] In each calculation the most stable spin multiplicity was determined by using a spin polarized calculation. Mulliken population analysis, together with ionization potential and binding energies, were thus determined. Finally, the charge-transfer effects arising between the metal atom and the ligands were examined.

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TABLE 1: Absolute Energy (in au), Relative Energy (in eV), Electronic Configuration, Ionization Potential (in eV), and Optimized Cr−Ring Bond Length (in Å) for Bis(benzene)chromium, Mono(benzene)chromium and Their Corresponding Cations

compound	spin mult	absolute energy	relative energy	configuration	ionization potential		Cr−ring distance	
					a	b	a	b
$Cr(C_6H_6)$	7	−1273.692944	0.00	$a_1^1\ e_2^2\ a_1^1\ e_1^2$	6.13	5.13[e]	2.65	2.64[43]
	5	−1273.664168	0.78	$e_2^3\ a_1^1\ e_1^2$			1.80	1.92[43]
	3	−1273.645157	1.30	$e_2^4\ a_1^1\ e_1^1$			1.64	1.62[43]
	1	−1273.672355	0.56	$e_2^4\ a_1^2$			1.57	1.55[43]
$Cr(C_6H_6)^+$	6	−1273.467677	0.00	$e_2^2\ a_1^1\ e_1^2$			2.52	2.11[23]
	4	−1273.429219	1.05	$e_2^3\ a_1^1\ e_1^1$			1.79	
	2	−1273.432222	0.96	$e_2^3\ a_1^2$			1.82	
$Cr(C_6H_6)_2$	1	−1502.918701	0.00	$e_{1g}^4\ a_1^2$	6.02	5.40−5.91[d,e]6.60[22]	1.74	1.54−1.73[c]
	3	−1502.862263	1.54	$e_{1g}^4\ a_1^1\ e_{2u}^1$			1.82	
	5	−1502.828398	2.46	$e_{1g}^3\ a_1^1\ e_{2u}^2$			1.95	
	7	−1502.783803	3.67	$e_{1g}^2\ a_1^1\ e_{2u}^2\ a_1^1$			2.04	
$Cr(C_6H_6)_2^+$	2	−1502.697397	0.00	$e_{1g}^4\ a_1^1$			1.74	
	4	−1502.651103	1.26	$e_{1g}^3\ a_1^1\ e_{2u}^1$	1.88			
	6	−1502.646414	1.39	$e_{1g}^2\ a_1^1\ e_{2u}^2$	2.06			

[a] This work. [b] Other (experimental and theoretical) works. [c] Refs 2, 4, 6, 15, 16, 44−47. [d] Refs 17, 21, 48−54. [e] Ref 21.

3. Results and Discussion

3.1. Electronic Configurations and Electronic States. Absolute and relative energies of $Cr(C_6H_6)$ and $Cr(C_6H_6)_2$ as well as those of the corresponding cations are presented in Table 1 for the lowest spin states of each compound, together with the corresponding molecular configurations of the highest occupied orbitals. It is known that the calculation of the multiplet structure of transition metal complexes is a rather complex procedure.[40] The difficulty arises from the high symmetry of the systems studied (C_{6v} or D_{6h}) which involves degenerate orbitals. Hence, the open-shell configurations cannot be always expressed by a single determinant. It can be seen from Table 1 that each multiplet configuration involves degenerate molecular orbitals. Concerning $Cr(C_6H_6)$, the singlet and septet configurations lead to eigenstates of S^2 and thus, these electronic states can be represented by a single determinant. On the contrary the triplet and quintet configurations have unpaired electrons located on degenerate orbitals (e_1); in that case these configurations cannot be directly related to the corresponding spin multiplet and we choose to calculate their energy by doing a fractional occupation of the degenerate orbitals. The same difficulty arises for the cation where only the sextet state may be represented by a single determinant. For $Cr(C_6H_6)_2$, only the singlet and septet are one-determinantal, as well as the doublet and sextet multiplet states of the cation. It is clear that the one-determinantal approach by using fractional occupations may lead to an erroneous determination of the energy of the corresponding multiplet state. Nevertheless, it will appear below that the various multiplet states which are involved in the different dissociation process have all a one-determinantal form (the singlet state of $Cr(C_6H_6)_2$, the doublet state of its cation, the septet and singlet states of $Cr(C_6H_6)$, as well as the doublet and sextet states of its cation).

Finally, the Cr and Cr^+ are also final products of the dissociation reactions. As explained below, the only multiplet states which will be involved in the process due to the Wigner rules are the septet state for Cr (s^1d^5 configuration corresponding to a ^7S electronic state) and the sextet state of Cr^+ (d^5 configuration corresponding to a ^6S electronic state). They can be thus described by a single determinant. These states are known to be the ground electronic states of both Cr and Cr^+, respectively.[41]

3.2. Optimized Structures and Energies. Absolute and relative energies of $Cr(C_6H_6)$ and $Cr(C_6H_6)_2$ as well as those of the corresponding cations are presented in Table 1 for the lowest spin states of each compound, together with the equilibrium Cr−ring distances and ionization potentials (IPs). The calculated C−C and C−H bond lengths in the case of the bis(benzene)-chromium compare reasonably well with the experimental values determined from an electron diffraction study carried out by Haaland[2] (C−C = 1.423 Å and C−H = 1.090 Å) since no more than 0.010 Å have been noticed.[42]

Selmani et al.[43] were the first to publish theoretical results about the geometry of the $Cr(C_6H_6)$ compound as well as the relative energies of the lowest excited spin states. They found that its ground state has a C_{6v} symmetry with a septet spin multiplicity and an equilibrium Cr−ring distance of 2.64 Å which is in good agreement with our results (see Table 1). Our calculated energies for the excited spin states cannot however be compared with those of Selmani et al because in our case the C_{6v} symmetry was kept constrained and the basis sets used for carbon and hydrogen atoms are different. On the other hand, the calculated Cr−ring distances compare very well in both cases for each excited spin state. In agreement with the results of Selmani et al, the Cr−ring distance is much larger in the septet state, compared to the other spin states, showing that the bond is essentially of dispersive type in the septet state. As will be shown later, such an interaction leads to a small binding energy between the ligand and the metal. In the case of the cation $Cr(C_6H_6)^+$, the optimized minimum energy is found to be obtained in the sextet spin state with an energy of 6.13 eV, which represents the adiabatic ionization potential of the neutral compound which overestimates the reported experimental value[21] by 1 eV (see Table 1). This discrepancy is due essentially to the chromium atomic basis set. In fact when $Cr(C_6H_6)$ is ionized, about 77% of the electron is removed from Cr and it is known that its atomic orbitals in that case contract strongly. Thus a good estimation of the ionization potential would require a much larger basis set. Finally, the comparison of the ionization potential of $Cr(C_6H_6)$ (6.13 eV) to the one of Cr (6.76 eV[41]) shows the partial delocalization of the removed electron (23% on the cycle). Compared to $Cr(C_6H_6)$, the metal−ligand bond length of the cation is smaller by 0.13 Å, showing that the nature of the interaction is not exactly the same and has probably a partial electrostatic character. We may thus expect that the order of magnitude of the binding energy will be higher in the cation than that in the neutral compound.

Our energetic and structural results concerning the bis(benzene)chromium show that the ground state is a singlet with a Cr−ring distance of 1.74 Å, very close to MP2[16] and other

TABLE 2: Mulliken Population Analysis on Various Atoms of ^{7}Cr(C_6H_6), ^{6}Cr(C_6H_6)$^+$, ^{1}Cr(C_6H_6)$_2$, and ^{2}Cr(C_6H_6)$_2$$^+$

	charge		
compound	Cr	C[a]	H[b]
^{7}Cr(C_6H_6)	−0.12	−0.41 (+0.02)[c]	+0.53 (+0.10)
^{6}Cr(C_6H_6)$^+$	+0.65	−0.42	+0.77
^{1}Cr(C_6H_6)$_2$	+0.80	−1.45 (−0.59)	+0.65 (−0.21)
^{2}Cr(C_6H_6)$_2$$^+$	+0.68	−0.96	+1.28

[a] Net charge localized on an individual C atom and multiplied by 6 (or 12). [b] Net charge localized on an individual H atom and multiplied by 6 (or 12). [c] In parentheses are given the variation of the net charge with respect to the isolated molecule of benzene.

TABLE 3: Charge Transfers between the Atomic Orbitals of Cr and Those of C_6H_6 in ^{7}Cr(C_6H_6) and ^{1}Cr(C_6H_6)$_2$; Charge Variation of Atomic Orbitals When Both Compounds Are Ionized

	benzene[a]			chromium[b]	
compound	$2s_C$	$2p_C$	$1s_H$	4s	3d
7Cr(C_6H_6)	−0.05	+0.08	+0.09	−0.12	0.00
^{6}Cr(C_6H_6)$^{+}$[c]	−0.30	+0.28	+0.25	+0.97	−0.20
^{1}Cr(C_6H_6)$_2$	−0.05	−0.55	−0.20	+0.84	−0.04
^{2}Cr(C_6H_6)$_2$$^{+}$[c]	−0.30	+0.80	+0.62	−0.17	+0.05

[a] Charge transfer with respect to the neutral benzene. [b] Only the six valence electrons of the chromiun atom ($4s^1$ $3d^5$) have been considered. [c] Net charge variation with respect to the corresponding neutral compound (^{7}Cr(C_6H_6) and ^{1}Cr(C_6H_6)$_2$).

SCF results[15,47] but larger by about 0.1 Å compared to the known experimental data[2,4,6,44−45] and other MP2,[19] DFT,[17,19] and CCSD(T)[18] results. This shorter Cr−ring distance in the neutral bis(benzene)chromium compound, compared to that in the mono(benzene)chromium (2.65) allows us to expect a larger Cr−ligand binding energy for the former compound. Looking at the bis(benzene)chromium cation, the calculated ionization potential is overestimated by about 0.5 eV compared with recent experimental results[17,21,49,55] but is, nevertheless, in better agreement with experiments than other theoretical calculations.[22] Concerning the geometry of corresponding cation of the latter system, it is similar to that of the neutral compound and we can expect a similar stability of the metal−ligand bond in both systems.

3.3. Mulliken Population Analysis. Atomic Mulliken population analysis for both systems as well as for their respective cations in their most stable spin state are given in Table 2. We see that there is a slight electron transfer from the benzene to the chromium in ^{7}Cr(C_6H_6) leading to a small electrostatic contribution to the metal−ligand binding energy. In agreement with the large chromium−benzene distance given above (2.65 Å), we expect that the binding process is essentially dispersive. Table 3 gives more details about the electron transfer between σ and π type atomic orbitals of both benzene ligands and chromium (the classification refers to the atomic orbitals lying along the symmetry axis for π and perpendicular to this axis for σ). Concerning the electron transfer from the benzene to the chromium in ^{7}Cr(C_6H_6), it arises from both σ and π type orbitals showing that the binding is essentially dispersive and that the global transfer is not due to a donation−back-donation process.

On the other side, the electron transfer is more important in the bis(benzene)chromium ground state from the metal to the ligands (0.80 electron), leading to a significant contribution of the electrostatic interactions. Thus, we may expect that the Cr−benzene binding energy will be higher in this case. The magnitude of the electron transfer compares well with previous MSXα calculations of Weber et al.[22,56] (0.60 or 0.86 electrons) and Osborne et al.[57] (0.94) but deviates somewhat with King et al.[16] results (1.28) who found more pronounced electron migration from the chromium to the ligands. Various XPS[58−60] and NMR[61,62] experiments support this finding and a good agreement has been found with Graves et al.[61] result, who evaluated the electron transfer from the chromium to the ligands by 0.72 electron. Table 3 shows that the migration of the electrons arises essentially from the π type atomic orbitals (AOs) of Cr (d_{xz}, d_{yz}) to the σ and π* orbitals of benzene, with a small back-donation to the σ atomic orbitals of the chromium. This was also shown by Yasuike and Yabushita[19] who indicated that this trend is common to Ti and V too.

The Mulliken atomic populations of the cations are also given in Tables 2 and 3. From Table 3, it is clear that the electron is essentially removed from the chromium in the case of ^{7}Cr(C_6H_6), and that the σ atomic orbitals are the most concerned. On the other side, the fractional charge removed from the benzene comes completely from the π orbitals, while at the same time the σ electrons of the ligand localize on the carbon ring leading to a larger σ-d interaction and thus, undoubtedly, to a larger metal−ligand binding energy. For bis(benzene)chromium, the mechanism is very different because the ionization arises completely from the benzene rings and more precisely from the π orbitals which where overpopulated in the neutral compound. Furthermore, a part of the electrons of the benzene migrates into the σ orbitals of the chromium. The charge on chromium in ^{2}Cr(C_6H_6)$_2$$^+$ (+0.68) is qualitatively in agreement with previous MSXα calculations of Weber et al.[22] (+1.04).

3.4. Binding Energies. The dissociation process of neutral bis(benzene)chromium may be decomposed a priori into two steps:

$$\mathrm{Cr(C_6H_6)_2} \rightarrow \mathrm{Cr(C_6H_6)} + \mathrm{C_6H_6} \qquad (1)$$

which leads to the intermediate product Cr(C_6H_6); the latter dissociates as follows:

$$\mathrm{Cr(C_6H_6)} \rightarrow \mathrm{Cr} + \mathrm{C_6H_6} \qquad (2)$$

leading to the global reaction:

$$\mathrm{Cr(C_6H_6)_2} \rightarrow \mathrm{Cr} + 2\mathrm{C_6H_6} \qquad (3)$$

Taking into account the spin multiplicity, reactants, and products of each reaction must have spin states which satisfy the Wigner-Witmer spin conservation rules.[63] Since Cr(C_6H_6)$_2$ has a singlet ground state, both products in reaction 1 should be in the same spin multiplicity. The most favorable dissociation process can be easily deduced from the absolute energies listed in Table 1 as

$$^1\mathrm{Cr(C_6H_6)_2} \rightarrow {}^1\mathrm{Cr(C_6H_6)} + {}^1\mathrm{C_6H_6} \qquad (4)$$

leading to benzene in its singlet ground state and mono(benzene)chromium in its excited singlet state. The dissociation energy in this case is equal to 3.04 eV. Concerning the second reaction, two possibilities may be envisaged. In the first possibility, the dissociation takes place from the singlet excited state of ^{1}Cr(C_6H_6) into the ground singlet state of benzene plus the excited singlet state of chromium, leading to the scheme:

$$^1\mathrm{Cr(C_6H_6)} \rightarrow {}^1\mathrm{Cr} + {}^1\mathrm{C_6H_6} \qquad (5)$$

This path gives a second dissociation energy of 4.47 eV, much higher than the first one by 1.43 eV. In the second possibility, the excited singlet state ^{1}Cr(C_6H_6) relaxes first to the septet

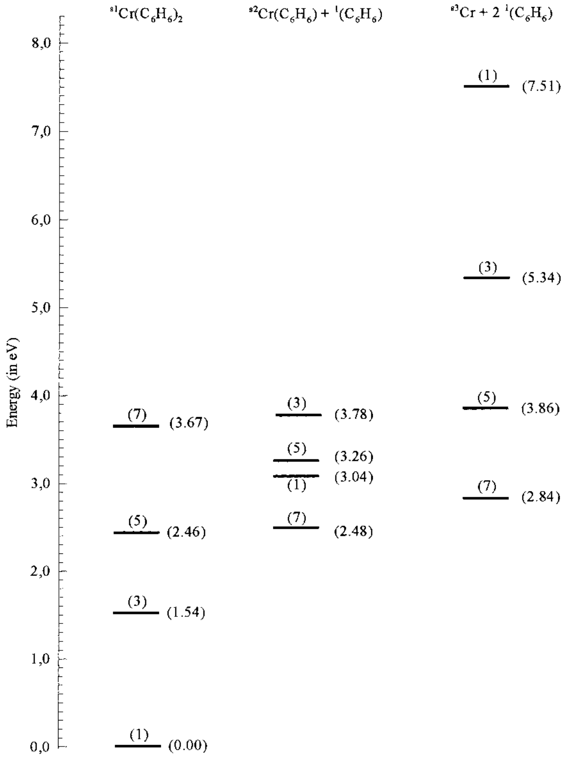

Figure 1. Dissociation diagram of $Cr(C_6H_6)_2$. s1, s2, and s3 are the spin multiplicities of $Cr(C_6H_6)_2$, $Cr(C_6H_6)$, and Cr, respectively. These are indicated in parentheses above each level. The energy of each level is given in parentheses.

ground state and then dissociates to the singlet ground state of benzene plus the septet ground state of chromium. We can summarize this dissociation process as follows:

$$^1Cr(C_6H_6)_2 \rightarrow {}^1Cr(C_6H_6) + {}^1C_6H_6 \xrightarrow{ISC} {}^7Cr(C_6H_6) + {}^1C_6H_6 \rightarrow {}^7Cr + 2{}^1C_6H_6 \quad (6)$$

In this case, the second dissociation energy is much lower, equal to 0.36 eV, showing the dispersive nature of the metal−ligand bond in $^7Cr(C_6H_6)$. This result is to be compared to the value calculated by Pederson et al.[64] (0.69 eV) by using the local density approximation. It is known that local approximations for the exchange and correlation energy typically leads to overbinding;[65] thus we may expect that our results are consistent with those of Pederson et al.[64] No experimental data are yet available, to the best of our knowledge, but recent expectation values from photodissociation experiments[20] estimate that the dissociation energy should be higher than 0.74 eV.

To summarize, the first possibility of the global dissociation process is given by

$$^1Cr(C_6H_6)_2 \rightarrow {}^1Cr + 2{}^1C_6H_6 \quad (7)$$

which leads to a total dissociation energy of 7.51 eV. The second possibility is summarized by

$$^1Cr(C_6H_6)_2 \rightarrow {}^7Cr + 2{}^1C_6H_6 \quad (8)$$

which corresponds to a total dissociation energy of 3.40 eV. In both processes, the dissociation limit is equal to 2.84 eV. Figure 1 shows the diagram of the possible dissociation processes of $^1Cr(C_6H_6)_2$. Experimental data are given in Table 4. They show that the dissociation of $^1Cr(C_6H_6)_2$ is well interpreted by our results if we take into account the ISC relaxation of the intermediate product. More precisely, the total dissociation energy of 3.40 eV reproduces very well recent photodissociation measurements carried out by Penner et al.[20] or the dissociation energies obtained from various thermochemical data.[66−68] Furthermore, relative binding energies of both ligands allow to understand why $Cr(C_6H_6)$ has never been observed by the photodissociation technique. Concerning the calculated dissociation limit (2.84 eV), it is lower than recent calculations performed by King et al.[16] using the Møller−Plesset perturbation theory (3.58 eV). In fact, the single-reference MP2 treatment does not include explicitly intrapair correlation effect which are known to be significant for the first row transition elements.[70]

TABLE 4: Bond Dissociation Energies (in eV) of $Cr(C_6H_6)_2$[a]

compound	Ed1	Ed2	E_{total}	references
$Cr(C_6H_6)_2$	3.04	4.47	7.51[b]	this work
	3.04	0.36	3.40[c]	this work
	2.48	0.36	2.84[d]	this work
			3.48 (0.06)	(66)
			3.42 (0.10)	(67)
			3.40	(68)
		> 0.741	3.39	(20)
			3.582 (MP2)	(16)
		0.003		(42)
		0.69		(64)

[a] Ed1 is the dissociation energy of the first ligand, Ed2 is the dissociation energy of the second ligand, E_{total} is the global dissociation energy. [b] No intermediate ISC process. [c] Intermediate ISC process. [d] Dissociation limit; in parentheses are indicated the error bars.

TABLE 5: Bond Dissociation Energies (in eV) of $Cr(C_6H_6)_2^+$[a]

compound	Ed1	Ed2	E_{total}	references
$Cr(C_6H_6)_2^+$	3.55	3.66	7.21[b]	this work
	3.55	1.84	5.39[c]	this work
	2.59	1.84	4.43[d]	this work
	3.51 (0.35)		3.48 (0.06)	(51)
	2.9	2.00	4.90	(48)
		2.3 (0.39)		(69)
		1.62 (0.22)		(23)
	2.40 (0.19)	1.76 (0.10)	4.16 (0.29)[e]	(26)
	3.26 (0.10)	1.85 (0.09)	5.11 (0.19)[e]	(26)
	2.04 (0.10)	1.70 (0.09)	3.74 (0.19)[e]	(26)
			4.73 (0.13)[f]	(26)
			4.52 (0.58)[f]	(26)

[a] Ed1 is the dissociation energy of the first ligand, Ed2 is the dissociation energy of the second ligand, E_{total} is the global dissociation energy. [b] No intermediate ISC process. [c] Intermediate ISC process. [d] Dissociation limit. [e] Result from a collision-induced dissociation. [f] Results from thermochemical calculations; in parentheses are indicated the error bars.

Our results for the dissociation process of the cation $^2Cr(C_6H_6)_2^+$, as well as experimental and other theoretical results, are presented in Table 5. Taking into account both the Wigner-Witmer rules[63] and the relative ionization potentials of the products listed in Table 1, the first step is as follows:

$$^2Cr(C_6H_6)_2+ \rightarrow {}^2Cr(C_6H_6)^+ + {}^1C_6H_6 \quad (9)$$

where $Cr(C_6H_6)^+$ is obtained in its doublet excited state. Figure 2 shows that the dissociation energy is equal to 3.55 eV. If no spin relaxation (ISC) occurs before the dissociation of the second ligand, the reaction of the latter could be

$$^2Cr(C_6H_6)^+ \rightarrow {}^2Cr^+ + {}^1C_6H_6 \quad (10)$$

which requires 3.66 eV, higher than the first one by 0.11 eV. Thus, the total dissociation energy is equal to 7.21 eV, much

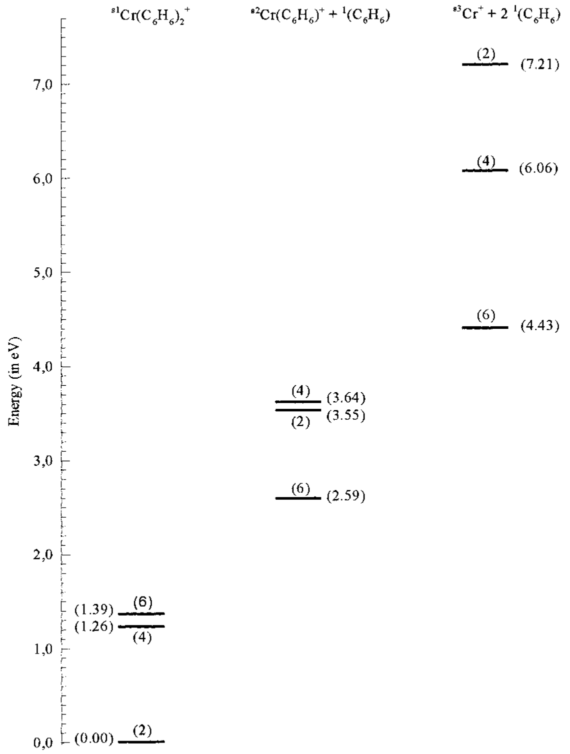

Figure 2. Dissociation diagram of $Cr(C_6H_6)_2{}^+$. s1, s2, and s3 are the spin multiplicities of $Cr(C_6H_6)_2{}^+$, $Cr(C_6H_6)^+$, and Cr^+, respectively. These are indicated in parentheses above each level. The energy of each level is given in parentheses.

higher than all available experimental data reported in Table 5. Now, if an ISC process takes place from the excited doublet ${}^2Cr(C_6H_6)^+$ to the ground sextet state ${}^6Cr(C_6H_6)^+$ before the second dissociation occurs, the process is written:

$$ {}^2Cr(C_6H_6)_2{}^+ \rightarrow {}^2Cr(C_6H_6)^+ + {}^1C_6H_6 \xrightarrow{ISC} {}^6Cr(C_6H_6)^+ + {}^1C_6H_6 \rightarrow {}^6Cr^+ + 2\,{}^1C_6H_6 \quad (11) $$

This second way gives a total dissociation energy of 5.39 eV in much better agreement with various experimental data.[26,48] Looking at the first dissociation energy, its calculated value (3.55 eV) compares satisfactorily with one of the experimental reports of Meyer et al.[26] It corresponds to the case where the effects due to the lifetime of the dissociating ions are ignored in the collision-induced dissociation (CID) threshold; the reported dissociation energy is 3.26 ± 0.10 eV. On the other hand, when these lifetime effects are included, Meyer et al.[26] suggest a dissociation energy of 2.40 ± 0.19 eV which is comparable with our calculated value at the dissociation limit, i.e., 2.59 eV.

Our result concerning the dissociation of the second ligand in ${}^2Cr(C_6H_6)^+$ compares very well with those obtained by Meyer et al.[26] by CID taking into account or not of the lifetime effects on the reaction. Their different results are very close one to each other (1.7 to 1.85 eV) showing that in each case the same electronic spin states of both the reactant and the products are involved. Photodissociation experimental data obtained by Hettich et al.[69] are of the same order of magnitude. Finally, theoretical results of Bauschlicher et al.[23] obtained from a modified coupled pair functional approach are also in good agreement with the present DFT result. As expected from Mulliken population analysis, the chromium−benzene binding energy is higher than in the neutral compound due to a significant σ-d electron transfer from the chromium to the ligand leading to a polar chemical binding.

4. Conclusion

A density functional study of the stability of the $Cr(C_6H_6)_2$ compound as well as its cation has been presented. Calculated binding energies of both ligands compare well with experimental data assuming that an intersystem crossing process takes place on the intermediate compound $Cr(C_6H_6)$ and its cation. Furthermore, it is shown that the cation compound has a dissociation limit energy much higher than the neutral one. It is essentially due to the order of magnitude of the dissociation energy of the second ligand, because of a change of the nature of the chemical bond when going from the neutral to the ionic compound. The first one has a dispersive character due to the high spin multiplicity of the mono(benzene)chromium, while the second one is dominated by electrostatic interactions. Finally, in any case we concluded to a simultaneous dissociation of both ligands; the first process needs a higher energy than the second one.

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(42) We did also optimizations of the Cr−ring distance for all systems considered, i.e., isolated benzene molecule, Cr(C_6H_6) and Cr(C_6H_6)$_2$ as well as their corresponding cations, for the lowest spin states, for which the geometry of the benzene was kept frozen, i.e., the C−C and C−H bonds lengths are those determined experimentally by Haland.[2] The largest deviation found of the Cr−ring does not exceed 0.020 Å. In addition, no significant changes, neither in the Mulliken population analysis nor for the binding energies, have been noticed. These clearly demonstrates a good correlation between the full optimization results with those obtained with only optimizing the Cr−ring distances.

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