

Density functional calculations of the structures and bond energies of $\text{Cr}(\text{CO})_6$ and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{CX})$ ($\text{X} = \text{O}, \text{S}$) complexes

E. Furet, J. Weber

Département de Chimie Physique, Université de Genève, 30 quai Ernest-Ansermet, 1211 Genève 4, Suisse; Fax: 41-(22)-702-65-18

Received May 9, 1994/Final revision received August 3, 1994/Accepted August 11, 1994

Summary. Quantum chemical calculations based on density functional theory have been performed on $\text{Cr}(\text{CO})_6$, $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{CS})$ at the local and nonlocal level of theory using different functionals. Good agreement is obtained with experiment for both optimized geometries and metal–ligand binding energies. In particular, a comparison of metal–arene bond energies calculated for the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{CS})$ complexes correlates well with kinetic data demonstrating that substitution of one CO group by CS leads to an important labilizing effect of this bond, which may be primarily attributed to a larger π -backbonding charge transfer to the CS ligand as compared with CO.

Key words: Density functional theory – Metal–ligand bond energies – Chromium – Arene complexes – Chalcocarbonyls

1 Introduction

The structure and reactivity of (arene) $\text{Cr}(\text{CO})_3$ systems have been the subject of intensive investigation in organometallic chemistry [1–4]. It is indeed well known that these complexes are readily prepared by ligand displacement from $\text{Cr}(\text{CO})_3\text{L}_3$ precursors or via arene exchange from labile (arene) $\text{Cr}(\text{CO})_3$ complexes, with, e.g., arene = naphthalene [5]. The investigation of arene labilization in such compounds has proven to be a point of considerable interest, as evidenced by numerous experimental studies which have been carried out in the last ten years [6–10]. Indeed, arene displacement may be used as a convenient procedure to obtain novel chromium organometallic systems with catalytic properties or to synthesize (poly)functional arene derivatives such as chiral, nonracemic, cyclohexadienes [11].

It is therefore of interest to perform theoretical investigations of the thermochemical properties of these systems so as to provide reliable values of key parameters such as metal–arene binding energies. Such studies would indeed allow to predict which substituents on the $\text{Cr}(\text{CO})_3$ tripod favor arene displacement and, consequently, lead to reaction products obtained under mild conditions. As far as carbonyl systems are concerned, Ziegler et al. have recently shown that density

functional theory (DFT) is able to lead to good results for the calculation of bond energies of $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ [12]. It was therefore interesting to use DFT so as to calculate the structural and thermochemical properties of compounds such as (arene) $\text{Cr}(\text{CO})_2\text{L}$ ($\text{L} = \text{CO}, \text{CS}$) derivatives. We report here the results of such a study, by concentrating on key structural parameters and on the metal–arene bond energy. For test purposes, we also report similar results obtained for $\text{Cr}(\text{CO})_6$.

2 Computational details

The linear combination of Gaussian-type orbitals-density functional (LCGTO-DF) method [13,14] and its corresponding deMon package [15] have been used. Preliminary geometry optimizations employed the Vosko–Wilk–Nusair (VWN) local spin density exchange-correlation potential [16]. In a second stage, nonlocal gradient correction terms were added to the VWN potential, and the geometries were recomputed. We have used two different nonlocal (NL) corrections to the exchange and correlation functionals. In calculations labeled BP, the gradient-corrected functional of Becke [17] was used for exchange and that of Perdew [18] for correlation. In calculations labeled PP, both nonlocal gradient-corrected exchange and correlation functionals suggested by Perdew and Wang have been included [19,20]. An “all electron” basis set of double-zeta quality augmented by two polarization functions for chromium and of double-zeta plus polarization quality for the other heavy atoms have been employed [21]. For the hydrogens, no polarization function has been considered. The contraction pattern of these basis sets is: Cr (63321/5211/41), C (631/31/1), O (631/31/1), S (6321/521/1), H (41). The electron density and exchange-correlation potential were fitted using the following auxiliary bases: Cr (5,5;5,5), C (4,3;4,3), O (4,3;4,3), S (5,4;5,4), H (4,2;4,2). Our convergence criterion on the total energy for the SCF part of the computations was 10^{-6} Hartree. For geometry optimizations, the Broyden–Fletcher–Golfarb–Shanno algorithm has been chosen with a requested accuracy on the norm of the gradient of 10^{-3} au.

The $\text{Cr}(\text{CO})_6$ compound has been considered to have the O_h point group symmetry. For $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$, C_{3v} symmetry has been used, as suggested by both neutron diffraction and X-ray crystallographic studies [22,23], where as $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{CS})$ has been optimized under the constraint of C_s symmetry.

The binding energies reported in this work are calculated using the following formula:

$$\Delta E = E_{\text{molecule}} - \sum E_{\text{fragment}},$$

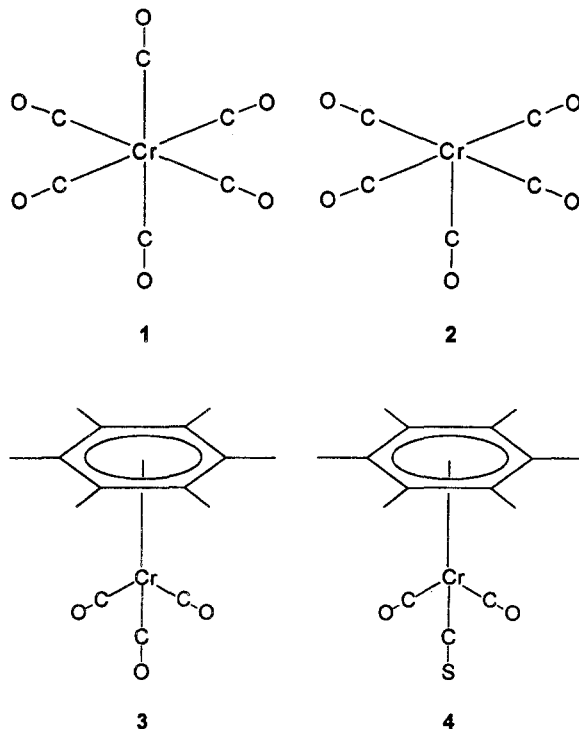
where E_{molecule} is the total energy of the complex at the optimized geometry, and E_{fragment} is the total energy of the relaxed fragment. The basis set superposition error (BSSE) has been corrected using the Boys–Bernardi technique [24]. In view of the computational effort required, no calculation of the zero-point energy (ZPE) correction has been made. In any case, Ehlers and Frenking have recently shown that, for transition metal carbonyls, ZPE and thermal corrections at 298 K compensate to within 1 kcal/mol [25].

3 Results and discussion

In recent years, sophisticated *ab initio* methods such as modified coupled-pair functional (MCPF), coupled-cluster methods (CCSD, CCSD(T)), local (LDA) and nonlocal (NLDA) density functional approximation theory have been applied to $\text{Cr}(\text{CO})_6$ in order to determine its electronic structure, bond energies and vibrational spectrum [12, 25–30]. This compound was therefore an ideal test case to calibrate our calculations.

The LCGTO-DF results of our full geometry optimizations of $\text{Cr}(\text{CO})_6$ (1), $\text{Cr}(\text{CO})_5$ (2) (Scheme 1) and CO are presented in Table 1. As expected, it is seen that the local spin density approximation underestimates the metal to ligand bond length in 1, the difference between the calculated and experimental value reported by both Jost et al. [31] and Rees et al. [32] being 0.046 Å. This is in agreement with previous studies carried out using other density functional versions [28, 29, 33–36]. The introduction of nonlocal corrections leads to a significant improvement of the Cr–C distance, the difference with the experimental value decreasing to 0.009 Å (BP case) and 0.015 Å (PP case). A very similar result has been obtained by Ziegler et al. on $\text{Cr}(\text{CO})_6$ using nonlocal density functional theory with a metal to carbon bond equal to 1.909 Å [34]. These results are slightly better than those provided by the MCPF (1.940 Å), CCSD (1.949 Å) and CCSD(T) (1.939 Å) methods [27].

The C–O bond in the $\text{Cr}(\text{CO})_6$ complex exhibits the same trend when going from local to nonlocal calculations, i.e. it undergoes a lengthening. However, in



Scheme 1.

Table 1. Optimized geometries of the compounds investigated^a

	VWN	BP	PP	Exp.
Cr(CO) ₆ (1)	d(Cr-C)	1.905	1.899	1.914 ^{b,c}
	d(C-O)	1.162	1.161	1.140
	E _{tot}	-1724.70366	-1724.35708	
Cr(CO) ₅ (2)	d(Cr-C _{eq})	1.902	1.890	
	d(Cr-C _{ax})	1.830	1.824	
	d(C _{eq} -O _{eq})	1.165	1.163	
	d(C _{ax} -O _{ax})	1.170	1.169	
	∠C _{ax} -Cr-C _{eq}	91.0	91.0	
	∠Cr-C _{eq} -O _{eq}	179.6	179.3	
	E _{tot}	-1604.54585	-1611.31520	-1611.00942
Cr(CO) ₅ CS	d(Cr-C _{eq} (O))	1.908		
	d(Cr-C _{ax} (O))	1.929		
	d(Cr-C _{ax} (S))	1.874		
	d(C _{eq} -O _{eq})	1.161		
	d(C _{ax} -O _{ax})	1.161		
	d(C _{ax} -O _{ax})	1.566		
	∠(O)C _{ax} -Cr-C _{eq} (O)	90.0		
	∠Cr-C _{eq} -O _{eq}	180.0		
	E _{tot}	-2047.63464		
	d(C-O)	1.140	1.146	1.128
	E _{tot}	-112.41890	-113.31739	-113.27179
CO	d(C-S)	1.561		1.535
	E _{tot}	-436.22160		
(η ⁶ -C ₆ H ₆)Cr(CO) ₃ (3)	d(Cr-ring)	1.709	1.701	1.724 ^{d,e}
	d(Cr-C _{benz})	2.223	2.214	2.223-2.243
	d(Cr-C(O))	1.815	1.836	1.845
	d(C _{benz} -C _{benz})	1.402	1.413	1.406
		1.418	1.431	1.422
	d(C-O)	1.165	1.173	1.158
	d(C _{benz} -H)	1.096	1.092	
	∠(O)C-Cr-C(O)	89.3	89.1	86.4-89.1
	∠Cr-C-O	179.7	179.6	177.9-178.5
	∠(C ₆ H ₆)plane-H ^f	2.7	2.0	1.7
E _{tot}	-1609.77760	-1616.90369	-1616.57774	

Cr(CO) ₃	<i>d</i> (Cr-C(O))		1.805
	<i>d</i> (C-O)		1.180
	⟨O⟩C-Cr-C(O)		90.3
	⟨Cr-C-O		178.6
	<i>E</i> _{tot}		-1384.54119
(η ⁶ -C ₆ H ₆)Cr(CO) ₂ CS (4)	<i>d</i> (Cr-ring)	1.653	1.735
	<i>d</i> (Cr-C _{benz})	2.190	2.257
		2.167	2.234
		2.164	2.236
	<i>d</i> (Cr-C(O))	1.822	1.851
	<i>d</i> (Cr-C(S))	1.782	1.805
	<i>d</i> (C _{benz} -C _{benz})	1.401	1.410
		1.421	1.431
		1.404	1.414
		1.417	1.426
		1.163	1.171
		1.572	1.586
		1.096	1.093
		88.9	89.6
		179.0	179.0
		87.5	88.1
	Cr(CO) ₂ CS	⟨C ₆ H ₆ ⟩plane-H ^f	3.0/2.7/3.6
<i>E</i> _{tot}		-1931.84710	-1939.84066
<i>d</i> (Cr-C(O))			1.821
<i>d</i> (Cr-C(S))			1.742
<i>d</i> (C-O)			1.176
		1.587	
		91.8	
		88.9	
		177.7	
		177.4	
		-1707.48858	

^a Total energies in Hartrees, distances in Å, angles in degrees

^b Ref. [31], ^cRef. [32], ^dRef. [22], ^eRef. [23]

^f The hydrogen atoms are tilted towards chromium

both cases this parameter is overestimated as compared to the experimental value (1.140 Å): 1.154 Å (VWN), 1.162 Å (BP). The same calculations performed on free carbonyl lead to the following values: 1.140 Å (VWN) and 1.148 Å (BP). It is immediately seen that coordination leads to an increase of the CO distance of 0.014 Å in both cases, reflecting the weakening of the C–O bond due to π back-donation to the carbonyls.

The full geometry optimization of **2** has been carried out under the constraint of C_{4v} symmetry in agreement with previous calculations [37, 38]. We thus obtained a $\langle C_{ax}CrC_{eq}$ angle equal to 91.0° for the two nonlocal calculations, this value being 1.5° less than that found by Barnes et al. at the SCF level of theory [27], and 2° less than the experimental result reported for matrix isolated $Cr(CO)_5$ [39]. On the other hand, Frenking et al. have optimized the structure of the $Cr(CO)_5$ fragment at both the SCF and MP2 levels of theory [25]. From their results, they conclude that the $\langle C_{ax}CrC_{eq}$ angle is larger than 90° at the SCF level of theory in agreement with the work of Barnes et al. and smaller than 90° at the MP2 level. This is at variance with our result where the more sophisticated NLDA calculations lead to an angle larger than 90° , whereas the LDA result shows this angle to be smaller than 90° . It is generally accepted that the local density approximation gives results of nearly MP2 quality [40]. A closer look at the distances shows that the equatorial bonds for Cr–C and C–O are very close to the values found in $Cr(CO)_6$ at the same level of approximation. On the other hand, the removal of one of the "axial" CO's is reflected in **2** by the shortening of the Cr– C_{ax} bond length (1.830 Å, BP) and the increase of the C–O distance (1.170 Å, BP). This result, which is due to be well-known *trans* effect in organometallic chemistry, parallels the findings of Barnes et al., who conclude to a similar Cr– C_{ax} bond distance shortening when going from **1** to **2**.

Considering the quality of the structural results obtained with the nonlocal approximation, the investigation of the first CO binding energy has been performed at this level of theory (BP only). Table 2 presents the total energies calculated for $Cr(CO)_6$ and its fragments. Our calculated binding energy ΔE is equal to 44.6 kcal/mol. In a previous DFT study, Ziegler et al. found a significantly lower value (35.1 kcal/mol). However, their calculation differs from the present one on the following points: they calculated ΔE at the experimental geometry and using a different functional for correlation [12]. On the other hand, Delley et al. obtained 36 kcal/mol for the first dissociation energy of $Cr(CO)_6$ using the same nonlocal exchange term but a correlation functional derived from that of Lee–Yang–Parr (LYP) [41]. As pointed out by Ziegler [42], the NL correction for exchange tends to lengthen bond distances, whereas the NL correction for correlation shows the opposite trend. The largest effect is due to the NL correction for exchange. As a consequence, the inclusion of the Becke correction alone should lead to too long bond distances and therefore to too low bond energies. This exemplified by the 1.942 Å value found by Delley et al. for the Cr–C distance. Further support for our results is provided by two independent studies carried out at the CCSD(T) level of theory by Barnes et al. [27] and Frenking et al. [25], which lead to dissociation energies very close to our value. Barnes et al. indeed reported a value of 42.7 kcal/mol calculated using a small basis set, whereas Frenking et al. found 45.8 kcal/mol using the effective core potentials (ECP) method. In addition, Ziegler et al. have recently redetermined the first dissociation energy of $Cr(CO)_6$ using nonlocal corrections and obtained 46.2 kcal/mol [30]. Therefore, these results obtained using both high-level *ab initio* methods and DFT give further support to the reliability of our calculations. Our final binding energy corrected for

Table 2. Binding energies^a for Cr(CO)₆, Cr(CO)₅CS, (η^6 -C₆H₆)Cr(CO)₃ and (η^6 -C₆H₆)Cr(CO)₂CS calculated at the nonlocal level of theory (BP)

	L = CO	L = CS
Cr(CO) ₅ L	- 1724.70366	- 2047.63464
L _{free}	- 113.31739	- 436.22160
L _{in complex}	- 113.31699	- 436.22156
L + Cr(CO) _{5ghost}	- 113.32049	- 436.22583
BSSE	350.10 ⁻⁵ 2.2 kcal/mol	427.10 ⁻⁵ 2.7 kcal/mol
Cr(CO) _{5free}	- 1611.31520	- 1611.31520
Cr(CO) _{5in complex}	- 1611.31418	- 1611.31326
Cr(CO) ₅ + CO _{ghost}	- 1611.31763	- 1611.31561
BSEE	345.10 ⁻⁵ 2.2 kcal/mol	235.10 ⁻⁵ 1.5 kcal/mol
E _{binding} (L)	7107.10 ⁻⁵ 44.6 kcal/mol	9784.10 ⁻⁵ 61.4 kcal/mol
E _{binding} - BSSE	6412.10 ⁻⁵ 40.2 kcal/mol	9122.10 ⁻⁵ 57.2 kcal/mol
Exp	37 kcal/mol	
(η^6 -C ₆ H ₆)Cr(CO) ₂ L	- 1616.90369	- 1939.84066
C ₆ H _{6free}	- 232.26285	- 232.26285
C ₆ H _{6in complex}	- 232.26090	- 232.26066
C ₆ H ₆ + Cr(CO) ₂ L _{ghost}	- 232.26253	- 232.26291
BSSE	163.10 ⁻⁵ 1.0 kcal/mol	225.10 ⁻⁵ 1.4 kcal/mol
Cr(CO) ₂ L _{free}	- 1384.54119	- 1707.48858
Cr(CO) ₂ L _{in complex}	- 1384.54066	- 1707.48734
Cr(CO) ₂ L + C ₆ H _{6ghost}	- 1384.55084	- 1707.49382
BSSE	1018.10 ⁻⁵ 6.4 kcal/mol	648.10 ⁻⁵ 4.1 kcal/mol
E _{binding} η^6 -C ₆ H ₆)	9965.10 ⁻⁵ 62.5 kcal/mol	8923.10 ⁻⁵ 56.0 kcal/mol
E _{binding} -BSSE	8784.10 ⁻⁵ 55.1 kcal/mol	8050.10 ⁻⁵ 50.5 kcal/mol
Exp	53 kcal/mol	

^a Energies are in Hartress, unless specified

BSSE is 40.2 kcal/mol, this value being 3.1 kcal/mol larger than that found by Barnes et al. using CCSD(T) (37.1 kcal/mol) and 3.2 kcal/mol larger than the experimental value (37 kcal/mol at 298 K [43, 44]). Our BSSE corrections for the two fragments are relatively small (2.2 kcal/mol for each) which suggests that the orbital basis sets used are adequate for such calculations.

It is also seen in Tables 1 and 2 and that the CS ligand is much more strongly bonded than CO to the chromium atom in the Cr(CO)₅ system: the Cr-C(S) bond distance in Cr(CO)₅CS is smaller by 0.031 Å than the Cr-C(O) distance in Cr(CO)₆, whereas the corresponding bond energies are 57.2 and 40.2 kcal/mol, respectively. This feature, which may be attributed to a better π -backbonding

capability of CS as compared to CO, is also observed in the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{CX})$ compounds (see below).

The DFT results obtained for $\text{Cr}(\text{CO})_6$ show that this method is able to lead to accurate geometries and binding energies for organometallics. We can confidently turn to the study of the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2\text{L}$ ($\text{L} = \text{CO}$ (**3**), CS (**4**)) complexes (Scheme 1). The optimized bond distances and angles for the two compounds are reported in Table 1. As for $\text{Cr}(\text{CO})_6$, it is seen that for **3** all the M-ligand distances are smaller than the experimental ones at the local level of approximation. This is especially true for the M-ring bond, the difference being as large as 0.079 Å. Clearly, the calculation of this parameter needed to be improved in order to obtain accurate binding energies. From the two NLDA calculations, it is seen in Table 1 that the best agreement is achieved with Becke exchange-Perdew correlation functionals. Several interesting features can be noted from the result of geometry optimization. First, an alternance of short and long distances is clearly observed in the benzene ring, which is in agreement with the experimental study of **3** performed by Rees and Coppens using both X-ray and neutron diffraction at low temperature [22]. Secondly, the C–O distance is larger in **3** than in **1** by about 0.011 Å, whereas the Cr–C(O) bond length is shorter by about 0.060 Å. This suggests that carbonyls are more tightly bound in **3** than in **1** which is in agreement with the conclusion deduced by Butler et al. from a study of the vibrational spectra and potential constants of benzenetricarbonylchromium derivatives [45]. Finally, the hydrogen atoms of the benzene ring are tilted towards chromium by an angle of about 2.0°, in good agreement with the value found by Rees and Coppens (cf. Table 1).

The geometry optimization of compound **4** has been carried out at the LDA and NLDA levels of theory. No X-ray nor neutron diffraction data are available to elucidate the structure of this complex. However, we may compare our results with those obtained on $(\text{CH}_3\text{CO}_2)(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_2(\text{CX})$ ($\text{X} = \text{O}, \text{S}, \text{Se}$) complexes for which X-ray diffraction studies have been performed [46–49]. For both the LDA and NLDA calculations, four inequivalent C–C distances are found in the benzene ring, the shortest bond being located in the trans position with respect to the chalcocarbonyl ligand. The position of the projection of chromium on the C_6H_6 ring and the center of mass of the six carbon atoms of the arene are not significantly different. Thus, the variation in M-ring distances does not reflect a slippage of the metal center, but presumably a distortion of the benzene ring. Actually, whereas the four carbon atoms nearest to the CS ligand form almost a perfect plane, the remaining two in the trans position are located out of this plane by about 0.02 Å, leading to a somewhat folded benzene ring. A similar observation has been made on $(\text{CH}_3\text{CO}_2)(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_2(\text{CS})$, for which the eclipsed conformation of the tripod is preferred [49]. The M–C distance for the atom in the trans position with respect to CX is longer in $(\text{CH}_3\text{CO}_2)(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_2(\text{CS})$ than in $(\text{CH}_3\text{CO}_2)(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3$. From Table 1, one can also observe that the hydrogen atoms are tilted towards chromium as in **3**. In addition, it is seen that the local approximation overestimates this angle with respect to the NL case, which was already the case in **3**. The average M-ring distance in compound **4** gives a first clue to the change in the M-ring bond strength as compared with **3**. Table 1 shows that the M-ring distance is longer by 0.026 Å (NLDA) in **4** than in **3**, suggesting a weaker metal–ring bond. The experimental results obtained for $(\text{CH}_3\text{CO}_2)(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_2(\text{CS})$ and $(\text{CH}_3\text{CO}_2)(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3$ display a similar trend, as going from the tricarbonyl to thiocarbonyl substituted complex leads to a lengthening of 0.016 Å of this bond distance, the respective bond lengths being 1.714 Å for the latter and 1.730 Å for the former. The results of the

vibrational study of Butler et al. on $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{CX})$ ($\text{X} = \text{O}, \text{S}, \text{Se}$) [45] also corroborate our calculations. They obtained a continuous decrease of the M-ring stretching force constant when going from $\text{X} = \text{O}$ ($1.19 \text{ mdyn. \AA}^{-1}$) to $\text{X} = \text{Se}$ ($0.897 \text{ mdyn. \AA}^{-1}$, $1.01 \text{ mdyn. \AA}^{-1}$). For compound **4** they report 1.04 and $1.12 \text{ mdyn. \AA}^{-1}$.

As to the geometry of the tripod, it is seen that the $(\text{O})\text{C}-\text{Cr}-\text{C}(\text{X})$ angles are very close to 90° . The NLDA calculations lead to a $(\text{O})\text{C}-\text{Cr}-\text{C}(\text{S})$ angle smaller by 1.5° than the $(\text{O})\text{C}-\text{Cr}-\text{C}(\text{O})$ one, and smaller by 1° than the $(\text{O})\text{C}-\text{Cr}-\text{C}(\text{O})$ angle in complex **3**. In the case of the $(\text{CH}_3\text{CO}_2)(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_2(\text{CX})$ complexes, these differences exhibit the same trend, being larger than 2° (5.2° , 2.3°). If we compare the M-CO distances between **3** and **4**, a small increase of 0.006 \AA is noticed. On the other hand, the M-C(S) distance is significantly shorter than the M-C(O) one in the two complexes (1.805 \AA vs. 1.851 \AA , 1.845 \AA **3**). This suggests that the CS ligand is more tightly bound than the carbonyls, and also that it weakens the M-C(O) bond in **4**. To confirm this particular feature due to the CO substitution by CS, we have carried out an additional calculation on the $\text{Cr}(\text{CO})_5(\text{CS})$ compound using the BP functional (Table 1). The M-C(S) and the CS bonds are then found to be equal to 1.874 and 1.566 \AA , respectively. It is thus seen that we have for this complex a larger M-C(S) distance and a smaller CS one as compared to **4** (BP), $+0.069 \text{ \AA}$ and -0.020 \AA respectively. As previously observed in the case of $\text{Cr}(\text{CO})_6$ and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$, M-C(X) bonds are stronger in the arene complexes, while the CX bonds are weaker. The stretching force constants reported by Butler et al. confirm this conclusion [45], the values being $k(\text{M}-\text{CS}) = 3.26 \text{ mdyn. \AA}^{-1}$ in **4**, $2.45 \text{ mdyn. \AA}^{-1}$ in $\text{Cr}(\text{CO})_5(\text{CS})$ and $k(\text{M}-\text{C}) = 2.40 \text{ mdyn. \AA}^{-1}$ in **3**, $2.10 \text{ mdyn. \AA}^{-1}$ in **1**.

The geometry optimizations on **3** and **4** enabled us to derive a qualitative picture of the relative strength of the bond between benzene and the chromium atom. We shall now discuss this point from a quantitative point of view. Examination of the results obtained for the geometry optimization of **1**, **3** and **4**, and for the first dissociation energy of CO in **1**, prompted us to calculate the bond energy between benzene and the $\text{Cr}(\text{CO})_2\text{CX}$ tripod at the BP level of theory. Table 2 presents the total energies, the BSSE corrections for the various fragments, as well as the binding energies determined for compounds **3** and **4**. The benzene molecule has been optimized under the constraint of D_{6h} symmetry. The $\text{Cr}(\text{CO})_2\text{L}$ fragments have been constrained to the symmetry point group of complexes **3** and **4**, i.e. C_{3v} for $\text{Cr}(\text{CO})_3$ and C_s for $\text{Cr}(\text{CO})_2(\text{CS})$. Additional calculations performed by releasing these constraints did not lead to lower energy minima. The M-ring binding energy determined for **3** is 55.1 kcal/mol without ZPE correction. This value is very close to that determined by Hoff et al. (53 kcal/mol) [50]; this "experimental" result being only an upper limit due to the use of an estimate for the enthalpy of formation of the $\text{Cr}(\text{CO})_3$ fragment. However, the actual value should be close to this energy as suggested by the good agreement with our calculations. For the thiocarbonyl substituted complex, the M-ring binding energy is 50.5 kcal/mol , a value smaller by 4.6 kcal/mol than the one found for **3**. The inclusion of BSSE corrections in both calculations leads to a decrease of the binding energy difference of 1.9 kcal/mol , which shows the influence of such corrections. It appears that in **4** the benzene ring is less tightly bonded than in **3** as could be expected from the results of geometry optimization, which is in total agreement with the kinetic data of Butler and Ismail [10]. The weaker M-ring bond in the thio-substituted complex has to be attributed to the better π -backbonding capability of CS as compared to CO. This feature should be reflected by the charges

borne by the ligand atoms. For both complexes, the formal oxidation number of chromium is 0. According to a Mulliken population analysis performed using the BP results, the chromium atom bears a positive charge of + 0.275 in **4**, while in compound **3** the positive charge on chromium is equal to + 0.122, which confirms the results of our preliminary analysis. Surprisingly, the global charge on the arene does not vary in the same proportion when going from **3** and **4** (+ 0.078 and **3** and + 0.100 in **4**). The main difference between the two complexes is observed for the significant negative charge borne by the CS ligand (− 0.297) as compared to the one of the carbonyls (− 0.066 in **3** and − 0.039 in **4**). The comparison of the atomic charges in these two systems leads to the conclusion that the withdrawing effect of the CS ligand is responsible for the larger positive charge on metal in **4**.

As a conclusion, the present theoretical results show that undoubtedly CO substitution by CS in (η^6 -C₆H₆)Cr(CO)₂(CX) systems leads to a significant labilization effect of the metal–arene bond, as previously noted by Butler et al. [10]. This statement, which is mainly based on an accurate DFT calculation of the M–ring bond energies in these systems, is confirmed by an examination of the results of both geometry optimization and electron population analysis. The present work shows therefore that DFT calculations are able to provide valuable quantitative results on organometallic systems.

Acknowledgements. The authors are grateful to Pr. D. R. Salahub for providing a copy of the deMon program and to Dr. A. Goursot for fruitful discussions. Financial support by the Federal Office for Education and Science, acting as Swiss COST office, is gratefully acknowledged. This work is also part of Project 20-36131.92 of the Swiss National Science Foundation.

References

1. Semmelhack MF, Clark GR, Garcia JL, Harrison JJ, Thebtaranonth Y, Wulff W, Yamashita A (1981) *Tetrahedron* 37:3957
2. Muetterties EL, Bleeke JR, Wucherer EJ, Albright TA (1982) *Chem Rev* 82:499
3. Solladié-Cavallo A (1985) *Polyhedron* 4:901
4. Kündig EP (1985) *Pure Appl Chem*. 57:1855
5. Kündig EP, Perret C, Spichiger S, Bernardinelli G (1985) *J Organomet Chem* 286:183
6. Gower M, Kane-MacGuire LAP (1979) *Inorg Chim Acta* 37:79
7. Zimmerman CL, Shaner SL, Roth SA, Willeford RB (1980) *J Chem Res, Synop* 108
8. Traylor TG, Stewart KJ (1984) *Organometallics* 3:325
9. Howell JAS, Dixon DT, Kola JC, Ashford NF (1985) *J Organomet Chem* 294:C1
10. Butler IS, Ismail AA (1986) *Inorg Chem* 25:3910
11. Bernardinelli G, Cunnigham A, Dupré C, Kündig EP, Stussi D, Weber J (1992) *Chimia* 46:126
12. Ziegler T, Tschinke V, Ursenbach C (1987) *J Am Chem Soc* 109:4825
13. Andzelm J, Radzio E, Salahub DR (1985) *J Chem Phys* 83:4573
14. Salahub DR (1987) *Adv Chem Phys* 69:447
15. Salahub DR, Fournier R, Mlynarski P, Papai I, St-Amant A, Ushio J (1991) In: Labanowski JK and Andzelm JW (eds) *Density functional methods in chemistry*. Springer, New York, p 77
16. Vosko SH, Wilk L, Nusair M (1980) *Can J Phys* 58:1200
17. Becke AD (1988) *Phys Rev A* 38:3098
18. Perdew JP (1986) *Phys Rev B* 33:8822; (1986) erratum: 34:7406
19. Perdew JP (1991) In: Ziesche P and Eschrig H (eds) *Electronic structure of solids* 91. Akademie Verlag, Berlin.
20. Perdew JP, Chevary JA, Vosko SH, Jackson KA, Pederson MR, Singh DJ, Fiolhais C (1992) *Phys Rev B* 46:6671

21. Godbout N, Andzelm J, to be published
22. Rees B, Coppens P (1973) *Acta Crystallogr* B29:2515
23. Bailey MF, Dahl LF (1965) *Inorg Chem* 4:1314
24. Boys SF, Bernardi F (1970) *Mol Phys* 19:553
25. Ehlers AW, Frenking G (1994) *J Am Chem Soc* 116:1514
26. Barnes LA, Rosi M, Bauschlicher CW (1991) *J Chem Phys* 94:2031
27. Barnes LA, Liu B, Lindh R (1993) *J Chem Phys* 98:3978
28. Baerends EJ, Rozendaal A (1986) In: Veillard A (ed) *Quantum chemistry: the challenge of transition metals and coordination chemistry*, NATO ASI series C, Reidel, Dordrecht, Vol. 176, p 159
29. Delley B, Wrinn M, Lüthi HP (1994) *J Chem Phys* 100:5785
30. Li J, Schreckenbach G, Ziegler T (1994) *J Phys Chem* 98:4838
31. Jost A, Rees B, Yelon WB (1975) *Acta Crystallogr* B31:2649
32. Rees B, Mitschler A (1976) *J Am Chem Soc* 98:7918
33. Delley B (1991) *J Chem Phys* 94:7245
34. Fan L, Ziegler T (1991) *J Chem Phys* 95:7401
35. Fan L, Ziegler T (1991) *J Chem Phys* 94:6057
36. Sosa C, Andzelm J, Elkin BC, Wimmer E, Dobbs KD, Dixon DA (1992) *J Phys Chem* 96:6630
37. Hay PJ (1978) *J Am Chem Soc* 100:2411
38. Demuynck J, Kochanski E, Veillard A (1979) *J Am Chem Soc* 101:3467
39. Burdett JK, Graham MA, Perutz RN, Poliakov M, Rest AJ, Turner JJ, Turner RF (1975) *J Am Chem Soc* 97:4805
40. Andzelm J, Wimmer E (1992) *J Chem Phys* 96:1280
41. Lee C, Yang W, Parr RG (1988) *Phys Rev* B37:785
42. Ziegler T (1991) *Chem Rev* 91:651
43. Lewis KE, Golden DM, Smith GP (1984) *J Am Chem Soc* 106:3905
44. Bernstein M, Simon JD, Peters KS (1983) *Chem Phys Lett* 100:241
45. English AM, Plowman KR, Butler IS (1982) *Inorg Chem* 21:338
46. Carter OL, McPhail AT, Sim GA (1967) *J Chem Soc A*:1619
47. Saillard JY, Grandjean D (1976) *Acta Cryst* B32:2285
48. Saillard JY, Leborgne G, Grandjean D (1975) *J Organomet Chem* 94:409
49. Saillard JY, Grandjean D (1978) *Acta Cryst* B34:3772
50. Mukerjee SL, Lang RF, Ju T, Kiss G, Hoff CD, Nolan SP (1992) *Inorg Chem* 31:4885