

On the structure and stability of electron deficient species derived from $[\text{Cr}(\text{CO})_3(\text{arene})]$

John E. McGrady*, Paul J. Dyson

Department of Chemistry, The University of York, Heslington, York YO10 5DD, UK

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Dedicated to Professor Martin Bennett on the occasion of his retirement.

Abstract

Electron impact ionisation mass spectrometry has been used to study $[\text{Cr}(\text{CO})_3(\text{arene})]$, arene = C_6H_6 , $\text{C}_6\text{H}_4\text{Me}_{2-1,4}$, $\text{C}_6\text{H}_2\text{Me}_{4-1,2,4,5}$ and C_6Me_6 . Successive loss of CO ligands results in the production of electron-deficient complexes $[\text{Cr}(\text{CO})_{3-x}(\text{C}_6\text{H}_6)]^+$ (where $x = 0$ to 3). Analysis of these species using approximate density functional theory indicates that the loss of CO ligands stabilises high-spin states, the effect being more marked in the cationic species than in their neutral counterparts. The high-spin states also tend to have more symmetric structures than their low-spin counterparts. The calculated value of the second CO dissociation energy is lower than either the first or third, consistent with gas-phase data obtained by electron impact ionisation mass spectrometry, which consistently show more intense peaks for the $[\text{Cr}(\text{CO})(\text{C}_6\text{H}_6)]^+$ than for $[\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_6)]^+$. The loss of the second CO ligand results in a transition from a doublet to a sextet ground state, and the resultant substantial structural rearrangements may be responsible for the anomalously low dissociation energy. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The structure of electron-deficient transition metal complexes continues to attract a great deal of attention in the literature, largely because of the important role they play as intermediates in organometallic reactions [1]. Their extreme instability, however, means that highly specialised techniques are required to isolate and characterise them. Matrix isolation of photochemically produced species is perhaps the best known of the techniques, and has been used for the study of unstable compounds for almost 50 years [2]. In conjunction with vibrational spectroscopy, the technique has provided insight into the bonding in a wide range of reactive intermediates [2b]. More recently, mass spectrometry, often in conjunction with the use of ion traps, has offered a new dimension to the study of electron-deficient species [3]. The two techniques are complementary in the sense that while matrix isolation gives information on neutral species, mass spectrometry detects only

the positively or negatively charged analogues. A combination of the two allows analysis of the effect of increasing electron deficiency, either through removal of electrons individually, through ionisation or electron attachment, or pairwise, via ligand dissociation. The major limitation of both experimental techniques is that they are unable to provide detailed structural information. This is a particular problem in electron-deficient species, where coordinative unsaturation leads to many possible arrangements of the remaining ligands. The development of approximate density functional theory over the past 10 years has filled this void to some extent [4]. The technique has been remarkably successful in reproducing experimentally observed structural parameters, giving experimentalists the confidence to apply the same methodology to transient species. In recent years, the products of ligand loss from numerous mono- and bimetallic species have been studied [5–7], notable contributions coming from the groups of Ziegler, Bursten and Poli. The latter has been particularly prominent in establishing the importance of non-singlet spin states in organometallic chemistry.

* Corresponding author. Fax: +44-1904-432516.

In this paper we report the results of mass spectrometric experiments on complexes of general formula $[\text{Cr}(\text{CO})_3(\text{arene})]$, and then use approximate density functional theory to investigate the structures and stabilities of the various species observed. The photochemistry of the title compounds has been extensively studied over the past 25 years [8]. The primary photo-product has been shown to be the dicarbonyl, $[\text{Cr}(\text{CO})_2(\text{arene})]$, although significant quantities of the monocarbonyl are formed, as well as various bimetallic products. The aim of this paper is to compare and contrast the calculated structures and stabilities of the charged compounds observed in the mass spectra with their neutral, photochemically generated counterparts.

2. Experimental

2.1. Sample preparation and mass spectrometry

The samples used in the mass spectrometry study, $[\text{Cr}(\text{CO})_3(\text{arene})]$ (arene = C_6H_6 , $\text{C}_6\text{H}_4\text{Me}_{2-1,4}$, $\text{C}_6\text{H}_2\text{Me}_{4-1,2,4,5}$ and C_6Me_6) were prepared using the Strohmeier reflux method [9]. The compounds were recrystallised from $\text{Et}_2\text{O}-\text{CH}_2\text{Cl}_2$ solutions at 4°C and

Table 1
Relative intensities of the peaks observed in the positive-ion mass spectra of $[\text{Cr}(\text{CO})_3(\text{arene})]$

	Arene			
	C_6H_6	$\text{C}_6\text{H}_4\text{Me}_2$	$\text{C}_6\text{H}_2\text{Me}_4$	C_6Me_6
$[\text{Cr}(\text{CO})_3(\text{arene})]^+$	65	66	41	100
$[\text{Cr}(\text{CO})_2(\text{arene})]^+$	4	14	0	2
$[\text{Cr}(\text{CO})(\text{arene})]^+$	10	18	16	65
$[\text{Cr}(\text{arene})]^+$	100	100	100	48

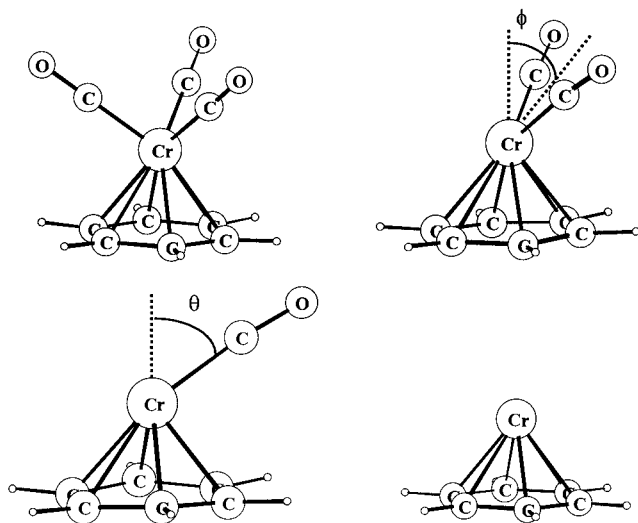


Fig. 1. Generic structures for $[\text{Cr}(\text{CO})_x(\text{C}_6\text{H}_6)]^+$, $x = 0-3$.

characterised by IR spectroscopy based on the $\nu(\text{CO})$ stretches. Mass spectra were recorded in positive mode using electron impact ionisation on a micromass autospec instrument operating in positive ion mode.

2.2. Density functional calculations

All calculations described in this paper are based on approximate density functional theory. Calculations were performed using the Amsterdam Density Functional (ADF99) package [10]. A double- ζ Slater-type basis set, extended with a single polarization function, was used to describe the main group atoms, while the chromium was modelled with a triple- ζ basis set. Electrons in orbitals up to and including $1s$ {C,O} and $3p$ {Cr} were considered to be part of the core and were treated in accordance with the frozen core approximation. The local density approximation was employed in all cases [11], along with the local exchange-correlation potential of Vosko, Wilk and Nusair [12] and gradient corrections to exchange (Becke [13]) and correlation (Perdew [14]). All structures were optimized using the gradient algorithm of Versluis and Ziegler [15].

3. Results

3.1. Mass spectrometry

The compounds $[\text{Cr}(\text{CO})_3(\text{arene})]$ (arene = C_6H_6 , $\text{C}_6\text{H}_4\text{Me}_{2-1,4}$, $\text{C}_6\text{H}_2\text{Me}_{4-1,2,4,5}$ and C_6Me_6) were analysed by electron impact ionisation mass spectrometry in positive mode. The relative intensities of the peaks for the resulting singly charged cations are listed in Table 1. For all compounds the dominant peaks correspond to the parent cation, $[\text{Cr}(\text{CO})_3(\text{arene})]^+$, and the fully decarbonylated species, $[\text{Cr}(\text{arene})]^+$. In between these two limits, smaller peaks are observed for the di- and monocarbonyls, $[\text{Cr}(\text{CO})_2(\text{arene})]^+$ and $[\text{Cr}(\text{CO})(\text{arene})]^+$, the latter being the more intense of the two in each case. For the hexamethylbenzene system, the intensity of the monocarbonyl peak is sufficiently large that it dominates both the dicarbonyl and the fully decarbonylated species. Whilst the conditions within a mass spectrometer may be far from equilibrium, it seems reasonable to seek a thermodynamic origin for these trends in terms of the relative stabilities of the species involved, especially when others have noted a similar trend [16].

3.2. Density functional calculations

Generic structures for the four different stoichiometries are shown in Fig. 1. Optimised bond lengths and angles for all spin states of $[\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)]^{0/+}$, $[\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_6)]^{0/+}$, $[\text{Cr}(\text{CO})(\text{C}_6\text{H}_6)]^{0/+}$

Table 2
Structural parameters for $[\text{Cr}(\text{CO})_x(\text{arene})]^{0/+}$

	2S+1	Energy (kcal mol ⁻¹)	Cr–CO (Å)	Cr–C (Å)	C–O (Å)	ϕ (°)	θ (°)
[Cr(CO) ₃ (C ₆ H ₆)]	1	–2994.7	1.865	2.237	1.166		
	5	–2927.2	1.989	3.119	1.162		
[Cr(CO) ₂ (C ₆ H ₆)]	1	–2603.9	1.863	2.205	1.171	35.0	
	3	–2604.0	1.894	2.245	1.167	3.2	
	5	–2570.9	1.987	2.581	1.163	0.0	
[Cr(CO)(C ₆ H ₆)]	1	–2215.3	1.866	2.147	1.176		53.6
	3	–2218.1	1.871	2.198	1.176		49.8
	5	–2218.3	1.992	2.263	1.163		1.8
[Cr(C ₆ H ₆)]	1	–1823.7		2.092			
	5	–1830.7		2.249			
[Cr(CO) ₃ (C ₆ H ₆) ⁺]	2	–2810.3	1.925	2.257	1.147		
	6	–2778.1	2.147	2.997	1.138		
[Cr(CO) ₂ (C ₆ H ₆) ⁺]	2	–2433.4	1.939	2.239	1.149	15.6	
	4	–2441.0	1.954	2.355	1.152	5.0	
	6	–2428.8	2.128	2.754	1.140	0.0	
[Cr(CO)(C ₆ H ₆) ⁺]	2	–2057.2	1.890	2.217	1.154		53.8
	4	–2063.8	1.970	2.277	1.147		55.6
	6	–2082.3	2.043	2.540	1.141		0.0
[Cr(C ₆ H ₆) ⁺]	2	–1676.6		2.114			
	6	–1711.7		2.519			
CO	1	–339.2			1.139		

and $[\text{Cr}(\text{C}_6\text{H}_6)]^{0/+}$ are summarised in Table 2. The angles θ and ϕ defined in the figure provide a measure of the distortion of the mono- and dicarbonyl species away from their most symmetric structures (C_{6v} and C_{2v} , respectively). From the data collected in Table 2, it is possible to identify three distinct trends.

(i) In both neutral and cationic species, the progressive stripping of CO ligands results in a stabilisation of the higher spin states. Thus whilst the ground state of $[\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)]$ is a singlet, that of $[\text{Cr}(\text{C}_6\text{H}_6)]$ is a quintet. Between these two limits, the singlet and triplet are almost isoenergetic in $[\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_6)]$, as are the singlet, triplet and quintet in $[\text{Cr}(\text{CO})(\text{C}_6\text{H}_6)]$. It is interesting to note that Fu and co-workers have shown that the rate constant for the recombination of $[\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_6)]$ with CO lies approximately midway between values typical of spin-allowed (singlet–singlet) and spin-forbidden (singlet–triplet) reactions [8c]. This intermediate behaviour could be explained by the presence of approximately equal concentrations of singlet and triplet $[\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_6)]$ in the gas phase, consistent with their almost identical energies.

(ii) For the mono- and dicarbonyl species, the states of higher multiplicity tend to have more symmetric structures. For example, the singlet state of $[\text{Cr}(\text{CO})(\text{C}_6\text{H}_6)]$ is strongly bent ($\theta = 53.6^\circ$), while the quintet has almost perfect C_{6v} symmetry ($\theta = 1.8^\circ$). Similarly, the singlet state of $[\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_6)]$ ($\phi = 35.0$) is far more distorted than the quintet ($\phi = 0.0$).

(iii) The transition from low- to high-spin states occurs earlier in the cationic species than their neutral

analogues. Thus whilst the singlet and triplet states of $[\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_6)]$ are very similar in energy, the quartet is very much more stable than the doublet in $[\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_6)]^+$. Likewise, the singlet, triplet and quintet of $[\text{Cr}(\text{CO})(\text{C}_6\text{H}_6)]$ lie within 3 kcal mol⁻¹ of each other, but the sextet state of $[\text{Cr}(\text{CO})(\text{C}_6\text{H}_6)]^+$ is over 18 kcal mol⁻¹ lower than any other spin state. This distinction between neutral and cationic species may have very important implications in terms of the complementary nature of mass spectrometric and matrix-isolation experiments alluded to in Section 1. Whilst we can be confident that $[\text{Cr}(\text{CO})(\text{C}_6\text{H}_6)]^+$ has a C_{6v} -symmetric structure, we cannot eliminate the possibility that the neutral species has a strongly bent structure. Thus the symmetry of species inferred from vibrational spectroscopy on matrix-isolated species cannot necessarily be extrapolated directly to the structures of charged species observed in the mass spectrum.

4. Discussion

Observation (i), the stabilisation of higher spin states in electron deficient compounds, has been noted by other authors [5–7], and so only a brief description of the essential points is presented here. The important features are summarised in Fig. 2, which shows molecular orbital diagrams for the singlet ground state of $[\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)]$ and the isoenergetic singlet and triplet states of $[\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_6)]$. The metal-based orbitals of the stable tricarbonyl are typical of an 18-electron compound, with a substantial splitting between the

weakly π -bonding occupied orbitals and the vacant, degenerate, σ -antibonding pair. The loss of one CO ligand strongly stabilises one of the pair of antibonding orbitals, bringing it closer to the occupied manifold. If this stabilisation is sufficiently large, then promotion of an electron becomes favourable, giving triplet or quartet states in the neutral or cationic species, respectively. The figure also reveals the origin of the preference for a more symmetric structure in the triplet: reduction of ϕ from 35.2 to 0° further stabilises the singly occupied 3a' orbital by moving the CO ligands onto its nodal plane. Similar arguments can be used to rationalise the shift from bent to symmetric structures associated with the triplet–quartet transition in $[\text{Cr}(\text{CO})(\text{C}_6\text{H}_6)]$.

The electronic origin of the third trend, the earlier transition to high spin states for the cations relative to neutral species, is more subtle. In coordination chemistry, the balance between high- and low-spin states is usually discussed in terms of a competition between two factors, the ligand field splitting and the exchange energy, favouring low- and high-spin configurations, respectively [5],7]. In making a comparison between isostructural neutral and cationic species, we make the

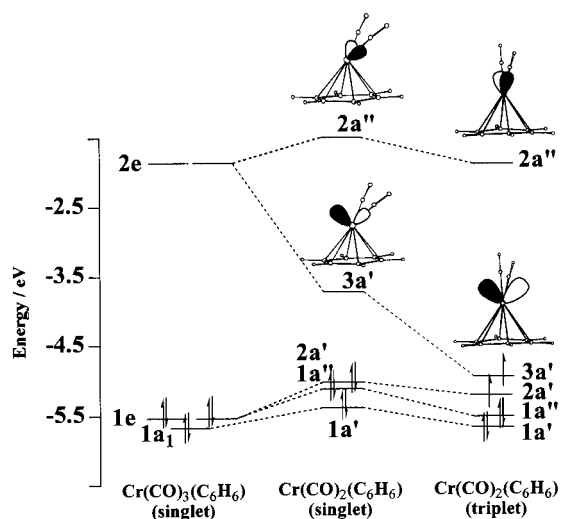


Fig. 2. Molecular orbital diagrams for spin-singlet state of $[\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)]$ and the singlet and triplet states of $[\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_6)]$ (for the triplet, only the spin- α orbitals are shown; those in the spin- β manifold have similar relative energies, but are shifted upwards by approximately 0.8 eV).

Table 3
CO dissociation energies for $[\text{Cr}(\text{CO})_x(\text{C}_6\text{H}_6)]^{z+}$

	ΔE (kcal mol ⁻¹)	
	$z = 0$	$z = 1$
$[\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)]^{2+} \rightarrow \text{CO} + [\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_6)]^{2+}$	51.5	30.1
$[\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_6)]^{2+} \rightarrow \text{CO} + [\text{Cr}(\text{CO})(\text{C}_6\text{H}_6)]^{2+}$	46.5	19.5
$[\text{Cr}(\text{CO})(\text{C}_6\text{H}_6)]^{2+} \rightarrow \text{CO} + [\text{Cr}(\text{C}_6\text{H}_6)]^{2+}$	48.4	31.4

assumption that the relatively small changes in structure mean that changes in the ligand field splitting will not play a dominant role. We therefore focus attention on changes in the exchange energy associated with the spin-state transitions. The exchange energy is proportional to the number of pairwise interactions between electrons of the same spin, given by $n(n-1)/2$, where n is the number of spin- α or spin- β electrons. Thus within the manifold of metal-based electrons, the three spin- α electrons in the singlet state contribute $(3 \cdot 2)/2 = 3$ units of exchange energy (denoted K), as do their three spin- β counterparts, giving a total of 6 K. In the triplet state, promotion of one spin- β electron to a spin- α orbital increases the exchange energy within the α manifold to $(4 \cdot 3)/2 = 6$ K and decreases that in the β manifold to $(2 \cdot 1)/2 = 1$ K, giving 7 K in total. By similar logic, promotion of a second electron to form the quintet gives a total exchange energy of $(5 \cdot 4)/2 + (1 \cdot 0)/2 = 10$ K. In a similar manner, the doublet, quartet and sextet states in the cationic species can be shown to be stabilised by 4, 6 and 10 K, respectively. As far as the transition between spin states is concerned, however, the crucial parameters are the differences in exchange energy. In the neutral species, the singlet–triplet and triplet–quintet transitions result in an increase of 1 and 3 K, respectively, whilst in the cations, the corresponding increments for doublet–quartet and quartet–sextet transitions are 2 and 4 K, respectively. This simple analysis is consistent with the third observation, suggesting that high-spin states are more accessible in odd electron species than in their even-electron counterparts.

4.1. Successive CO dissociation energies

In the description of the mass spectra of $[\text{Cr}(\text{CO})_3(\text{arene})]$, we noted that the peak for the monocarbonyl species was always more intense than that for the dicarbonyl. The successive CO dissociation energies, defined as the difference in energy between $[\text{Cr}(\text{CO})_x(\text{C}_6\text{H}_6)]^{0/+}$ and $[\text{Cr}(\text{CO})_{x-1}(\text{C}_6\text{H}_6)]^{0/+} + \text{CO}$ are summarised in Table 3. Values for the cationic species are universally smaller than those for their neutral counterparts, consistent with much reduced Cr–CO backbonding in the ionised species. Significantly, the second dissociation energy for the cation is over 10 kcal mol⁻¹ lower than the first or third, consistent with the observed ratio of peak intensities for $[\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_6)]^+$ and $[\text{Cr}(\text{CO})(\text{C}_6\text{H}_6)]^+$. The facile loss of the second CO ligand coincides with a change from a spin doublet ground state to a sextet, and therefore a substantial rearrangement of the ligand sphere. The stabilising effect of this rearrangement may therefore be responsible for the anomalously low second dissociation, and therefore the low intensity of the $[\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_6)]^+$ peak in the mass spectra.

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