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Characterization of Ferrocene and (η^6-Benzene) Tricarbonylchromium Complexes by X-ray Photoelectron Spectroscopy

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Abstract

The X-ray photoelectron spectra of the two series of ferrocene (η^5-$C_5H_5)_2$Fe and (η^6-benzene)-chromium tricarbonyl complexes have been investigated. The binding energies of the 2p electrons indicate that the actual oxidation states of the metals are close to zero. The metal core electron levels are insensitive to changes in the substitution of the cyclopentadienyl and benzene rings.

Introduction

The cyclopentadienyl anion, $C_5H_5^-$ (Cp^-), forms a wide range of stable π-bonded complexes with transition metals. The best known example is ferrocene (Cp_2Fe). Benzene can also form a variety of such complexes, e.g. $BzCr(CO)_3$ ($Bz = \eta^6$-C_6H_6). Both molecules are neutral and contain metals in the formal oxidation states of Fe(II) and Cr(0). The ground-state electronic configuration in both cases is predicted to be a singlet (closed shell) by a standard, qualitative, linear combination of atomic and molecular orbitals model.

Ferrocene is particularly well known for its redox behaviour, readily forming the ferrocinium cation [1]:

$$Cp_2Fe \rightleftharpoons Cp_2Fe^+ + e^- \qquad (1)$$

For this reason, the effect of adsorbed ferrocene and its derivatives on electrode properties has been extensively studied [2–6]. It has been shown that reaction (1) is stable over several redox cycles when fixed to a graphite electrode suggesting that it may prove a useful basis for electrocatalytic applications.

X-ray photoelectron spectroscopy (XPS) is a convenient, non-destructive method for studying the chemical state of surface adsorbed species. It has been used to confirm the presence of ferrocinium [1] and chromium species [7] on modified graphite electrodes.

It was our intention, therefore, in the work presented in this paper to extend the range of ferrocene-type materials that have been characterized by XPS in order to facilitate future electrode studies. The compounds examined include several arene derivatives of chromium because not only is their electrode behaviour of interest, but also because of their importance in the development of polymer-supported organometallic hydrogenation catalysts. The latter studies will also require the characterization of surface-active metal species.

Experimental

The organometallic complexes listed in Scheme 1 were generous gifts from Professor Tirouflet (Université de Dijon, France) and were used without further purification.

The XPS spectrometer used was a Kratos Instruments model ES200B operating in the fixed-analyser transmission mode. Electrons produced by Al Kα radiation (1486.6 eV) were pre-retarded to the pass energy of the hemispherical analyser at 65 eV and detected by a single channel electron multiplier (Channeltron). Calibration of the spectrometer was achieved using the gold $4f_{7/2}$ line at 84.0 eV. Samples were mounted on double-sided Lomacol tape and introduced in the spectrometer under an argon atmosphere using a fast-insertion probe. The probe was cooled in some cases to -100 °C in order to prevent the more volatile compounds such as ferrocene subliming at 10^{-8} torr. Any charging of the

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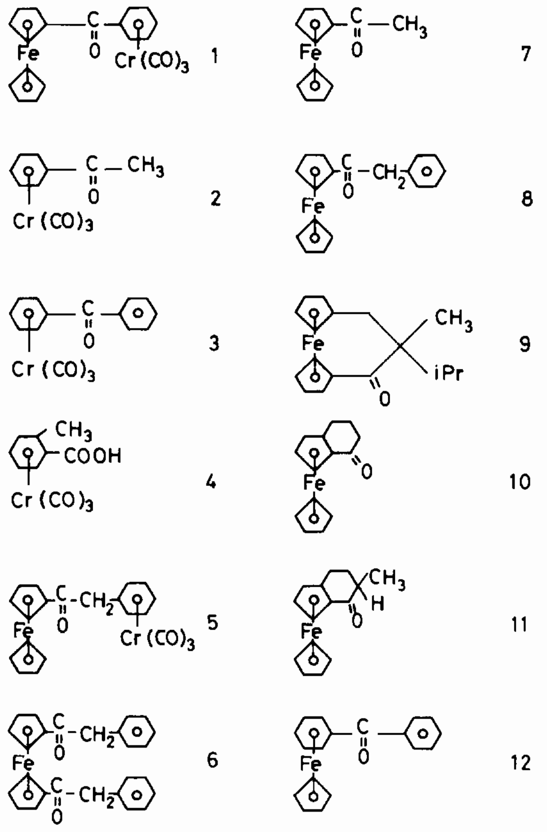

Scheme 1. Key to the structures of the molecules studied in this paper.

non-conducting samples, which could be up to 2 eV, was corrected by fixing the binding energy of the carbon 1s level at 285.0 eV. This procedure afforded an internally consistent set of ionization potential data accurate to approximately ± 0.2 eV. High-resolution scans were recorded from the iron and chromium 2p, 3s and 3p electron levels together with those from the oxygen and carbon 1s regions of the X-ray photoelectron spectra.

Results and Discussion

The measured binding energies for chromium, iron, and oxygen referenced against the carbon 1s photoelectron line at 285.0 eV are given in Table I. Also listed are the spin–orbit splittings in the Cr and Fe 2p levels and the full-width at half-maximum height (FWHM) of the oxygen 1s line. Typical iron and chromium 2p ionization bands are shown in Fig. 1 for the mixed ferrocene–(η^6-benzene) chromium tricarbonyl derivative (compound 5).

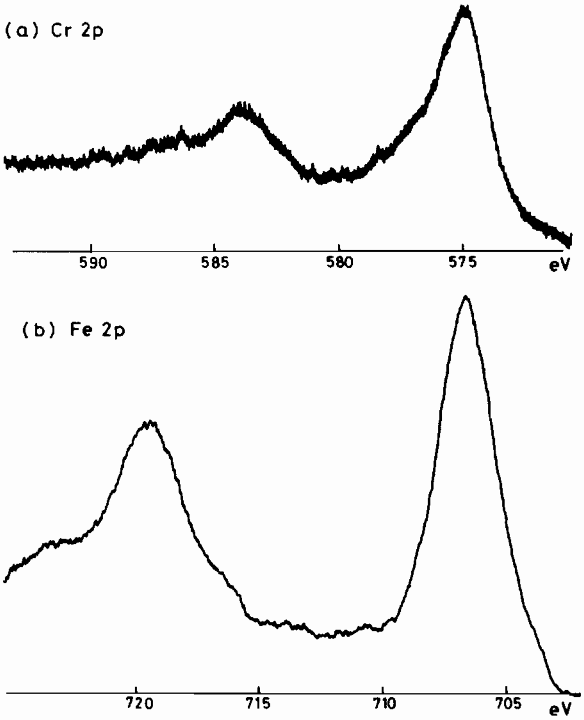

Fig. 1. Typical spectra of the metal 2p regions for the mixed ferricinium–(η^6-benzene) chromium tricarbonyl compound (5). (a) the Cr 2p photoelectron region, (b) the Fe 2p photoelectron region.

TABLE I. Ionization Potential Data (eV) for the π-bonded Organometallic Complexes Studied[a]

	Cp_2Fe[b]	1	2	3	4	5	6	7	8	9	10	11	12
O 1s		532.1	532.2	532.0	531.9	531.8	531.4	532.3	532.1	531.8	532.3	532.1	531.6
FWHM		2.4	2.7	2.6	2.5	3.0	3.0	2.4	2.6	2.3	1.9	2.0	2.1
Fe $2p_{3/2}$	707.9	706.9				706.7	707.6	707.3	708.2	707.5	707.7	707.7	706.9
$2p_{1/2}$		719.8				719.5	720.3	720.0	721.0	720.1	720.4	720.2	719.5
$3s_{1/2}$	92.7	92.2					92.6	92.1	93.1	92.5	91.1		
$3p_{3/2,\,1/2}$		54.2				55.5	54.6	54.1	54.8	54.5	54.1	54.7	53.6
Cr $2p_{3/2}$		574.8	575.1	575.6	574.6	574.9							
$2p_{1/2}$		584.0	584.0	584.6	583.7	584.0							
$3s_{1/2}$						76.5							
$3p_{3/2,\,1/2}$		44.2				44.7							
ΔFe 2p[c]		12.9				12.8	12.7	12.7	12.8	12.6	12.7	12.5	12.6
ΔCr 2p[c]		9.2	8.9	9.0	9.1	9.1							

[a] Carbon 1s peak set at 285.0 eV. [b] Ref. 12. [c] Spin-orbit splitting for Fe 2p and Cr 2p states.

Taking an average of all the formally iron(II) compounds studied here, the Fe $2p_{3/2}$ and $2p_{1/2}$ photoelectron peaks appear at 707.4 and 720.1 eV, respectively. These values are almost identical with those recorded from the surface of a sample of α-iron (707.3 and 720.3 eV) [8] indicating that the actual metal oxidation state is close to zero in the complexes under investigation. Moreover the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ photoelectron levels measured from characteristic iron(II) and iron(III) compounds generally appear at binding energies some 3.5 eV higher. The average spin-orbit splitting as assessed from the $2p_{3/2}$–$2p_{1/2}$ doublet separation is also in good agreement with the values for α-iron and other zerovalent compounds of iron.

For the oxides of iron, coupling between the single unpaired 2p core electrons which results from the process of photoelectron production in this level, and the outer unpaired 3d electrons, leads to a manifold of states with similar energies. The resulting $2p^{-1}$ ionization thus consists of broad peaks with ill-defined maxima due to multiplet splitting. This is not seen for the ferrocene derivatives. The peaks are sharp (FWHM = 2.0 eV) and clearly separated. Another important observation in the photoelectron spectra of transition-metal compounds is the presence of additional peaks from shake-up processes. Such peaks are often relatively weak features which are considered to occur via ligand-to-metal charge transfer into an empty metal d orbital [9]. For the present compounds which have a closed shell configuration and effectively, a filled 3d shell, such processes would not be expected to occur and, in fact, no satellites can be identified in the X-ray photoelectron spectra recorded.

In some of the spectra, the $2p_{3/2}$ ionization exhibited a shoulder to higher-binding energy (710.9 eV). The intensity of this shoulder was seen to grow during an observation and has therefore been assigned to decomposition caused by the X-rays and/or the electron flux at the sample. It is most likely to be due to iron oxides, or possibly, to ferricinium-type oxidized complexes similar to those found on the modified graphite electrodes described earlier.

The chromium $2p^{-1}$ ionization comprised a well-resolved doublet with an average spin–orbit splitting of 9.1 eV. The mean $2p_{3/2,\,1/2}$ binding energies (575.0 and 584.1 eV) are spanned by the range found previously for chromium(0) compounds [10]. This is in agreement with the predicted formal oxidation state. There was a small chemical shift (1.2 eV) to higher binding energy compared to chromium metal indicating a small residual positive charge on the chromium atom. The shifts were half that observed for $Cr(CO)_6$ (2.2–2.6 eV) suggesting that charge balance is maintained in these molecules by a small negative charge on the three coordinated carbonyl groups and the effect of each CO group on the central metal was additive. Pignataro *et al.* [11] also noted a drift of electrons to the CO ligands in $BzCr(CO)_3$ and $Cr(CO)_6$.

Substitution in the arene ring by electron withdrawing groups such as the carbonyl moiety was expected to result in the stabilization of negative charge on the ligand and hence increased positive charge on the metal ion. However, the effects were small and, as Table I indicates, the range of Cr 2p ionization values showed no definite correlation with expected arene ring charge distributions. Similarly, no additional effects were observed due to conjugation between arene moieties on different metal centres.

High-energy shoulders were sometimes observed on the Cr $2p_{3/2}$ peak with up to 20% of the intensity of the main peak. As discussed previously for iron, these shoulders were taken to indicate decomposition products formed by X-irradiation and the electron flow from the X-ray gun. Again, it was the central metal which had been oxidized in the decomposition products.

The measured mean binding energy for the oxygen 1s level remained remarkably constant across the group of compounds studied. Differences due to changes in relative numbers of ketone and carbonyl group oxygen atoms were absent. It would appear that this region of the spectrum was complicated by adsorbed moisture despite careful handling of the samples under an argon atmosphere and, possibly, by a contribution from the Lomacoll mounting tape also.

Conclusions

It has been shown that a formal metal oxidation state of zero is a good description of the complexes studied here and that the metal 2p core levels are sensitive to the changes in their oxidation state brought about by decomposition or reaction. They serve therefore as a simple probe for the study of redox reactions at electrode surfaces. Not surprisingly the metal core levels were insensitive to changes in substitution on the ligand ring. These groups can therefore be changed in order to study their effect on electron-transfer processes or be used as markers for complementary spectroscopic techniques such as micro-Raman spectroscopy. The results of a micro-Raman study of the same group of complexes have already been reported [13].

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