UV PHOTOELECTRON SPECTRA OF IRON TRICARBONYL COMPLEXES OF 2,3,5,6-TETRAKIS(METHYLENE)-7-OXABICYCLO[2.2.1]HEPTANE

GAETANO GRANOZZI *

Istituto di Chimica Generale ed Inorganica, Via Loredan 4, 35100 Padova (Italy)

DAVID AJÒ,

Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Corso Stati Uniti, Padova (Italy)

TRISTANO BOSCHI

Istituto di Chimica, Facoltà di Ingegneria, Roma (Italy)

and RAYMOND ROULET

Institute of Inorganic and Analytical Chemistry, Lausanne (Switzerland)

(Received August 5th, 1981)

Summary

He(I) excited photoelectron spectra of the *endo, exo, endo-exo* and *di-exo* iron tricarbonyl complexes of 2,3,5,6-tetrakis(methylene)-7-oxabicyclo-[2.2.1]heptane have been studied in order to investigate the possible dependence of the Fe—butadiene interactions on the stereochemistry and the additivity of the effects of two $Fe(CO)_3$ groups. The spectral evidence indicates that there is a stronger Fe—butadiene interaction in the *endo* than in the *exo* isomer, and that perturbation of the $Fe(CO)_3$ group on the uncomplexed butadiene is negligible. The perturbations due to the two $Fe(CO)_3$ groups when both the butadiene groups are complexed are additive in the low symmetry *endo-exo* diiron complex, whereas in the high symmetry *di-exo* isomer an extra perturbation is present.

Introduction

Vapour-phase photoelectron spectroscopy (PES) has been used to investigate the interaction between the iron tricarbonyl group and several conjugated dienes by comparing the PE spectra of the complexes with those of the corresponding free ligands [1—3]. The perturbations of the π_1 and π_2 ligand MO's

induced by the complexation were found to be fairly constant along a series of substituted butadiene complexes [3].

The 2,3,5,6-tetrakis(methylene)-7-oxabicyclo[2.2.1]heptane ligand contains two exocyclic *cis*-butadiene moieties, so providing an opportunity of measuring simultaneously the ionization energies (IE's) of both the free and complexed diene systems, and also of detecting long-range effects. Moreover, two inequivalent bonding sites are accessible for the $Fe(CO)_3$ group and, indeed, two different mono-iron (*endo, exo*) and two di-iron complexes (*di-exo, endo-exo*) have been isolated [4]. In the present paper we report the He(I) excited PE spectra of these four complexes with the aim of investigating the possible dependence of the $Fe(CO)_3$—butadiene interaction on the stereochemistry, and studying the effects of the two $Fe(CO)_3$ groups together. Furthermore, the data obtained permit a check of the validity of the interaction parameters derived by Worley et al. [3] for very different butadiene systems.

Experimental

The complexes were prepared and characterized by published methods [4]. PE spectra were measured on a Perkin-Elmer PS-18 spectrometer using a heated probe inlet system in the 40—45°C and 60—65°C temperature ranges for the mono and di-iron complexes, respectively. All the spectra were calibrated by reference to the peaks of Xe and Ar simultaneously introduced into the target chamber.

Results and discussion

The low IE region (up to 12 eV) of the He(I) PE spectra of the *endo, exo, endo-exo* and *di-exo* complexes is shown in Fig. 1. (Higher IE regions have been omitted because they are not relevant for the purposes of this paper.) Bands are labelled alphabetically (in the order of increase in IE) for each spectrum. The experimental correlation diagram for the four complexes is shown in Fig. 2, and the proposed assignments are also given, the f and c superscripts referring to "free" and "complexed" butadiene groups respectively.

Mono-iron complexes
The spectra of both *endo* and *exo* complexes exhibit six bands (Figs. 1a and 1b, respectively) in the reported spectral region, but there are marked differences in the two cases. Band A is well resolved in the *endo* complex whereas it appears as a shoulder in the *exo* one. The opposite is true for band B. The changes in the IE's of all the bands in the two cases are clearly seen in Fig. 2.

The PE spectrum of the free ligand has been already reported [5]. The same assignments have been taken (Fig. 2) as a starting point for the analysis of the spectra of the complexes. In the free ligand the two π_2 MO's, localized in the two butadiene groups and degenerate by symmetry in the 0th order, give rise to two distinct bands ($\pi_2(a_2)$: 8.60 eV; $\pi_2(b_1)$: 9.22 eV) because the "through-bond" and "through-space" interactions mix them and remove their degeneracy. In the mono-iron complexes, where the symmetry is lowered by the Fe-$(CO)_3$ group, it is likely that the ionization from π_2^f lies near to the middle of
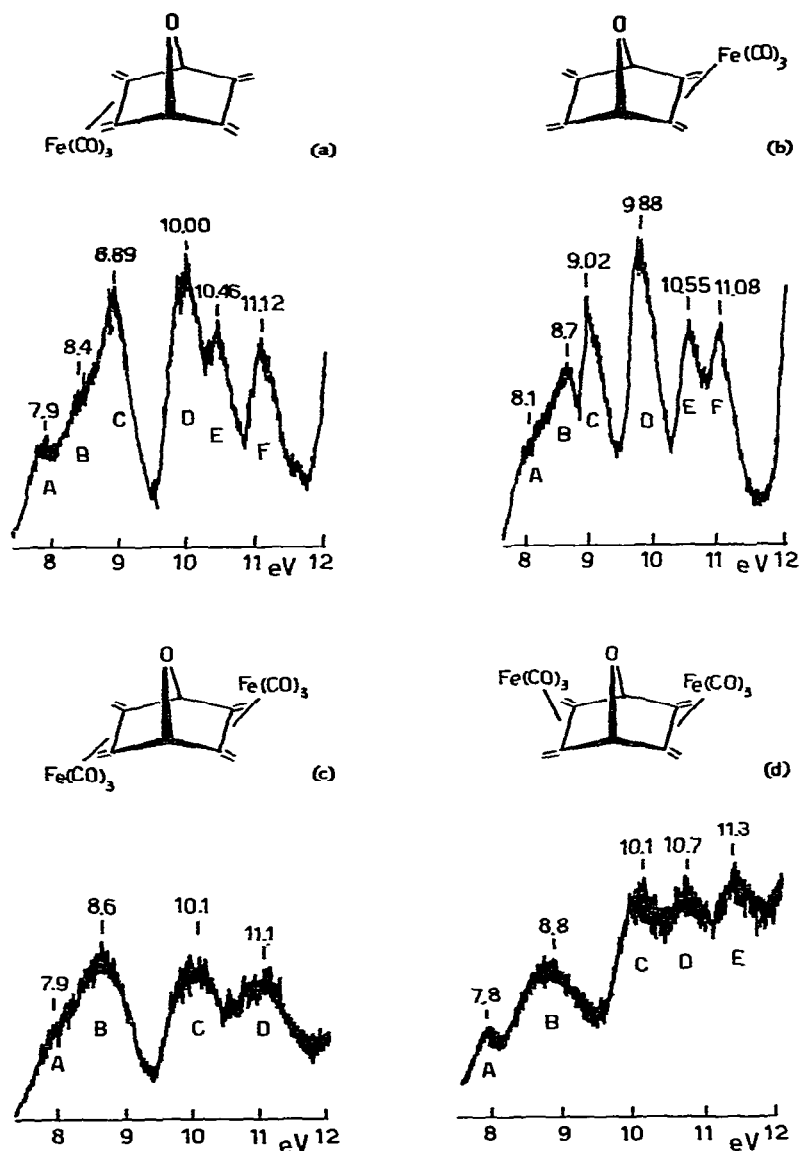
Fig. 1. He(I) excited PE spectra of *endo* (a), *exo* (b), *endo-exo* (c) and *di-exo* (d) iron tricarbonyl complexes of 2,3,5,6-tetrakis(methylene)-7-oxabicyclo[2.2.1]heptane.

the range spanned by π_2 ionizations of the free ligand. Consequently we assign C bands in the spectra of both isomers to the ionizations from π_2^f MO's. By similar arguments, we assign E bands to the π_1^f MO's. The comparison between the π_1^f and π_2^f IE's of the complexes and the corresponding mean value of the free ligand strongly indicates that the perturbation due to Fe(CO)$_3$ on the uncomplexed butadiene is negligible, and that π_1^f and π_2^f ionizations can be satisfactorily taken as internal standards in evaluating the direct Fe—butadiene interaction.
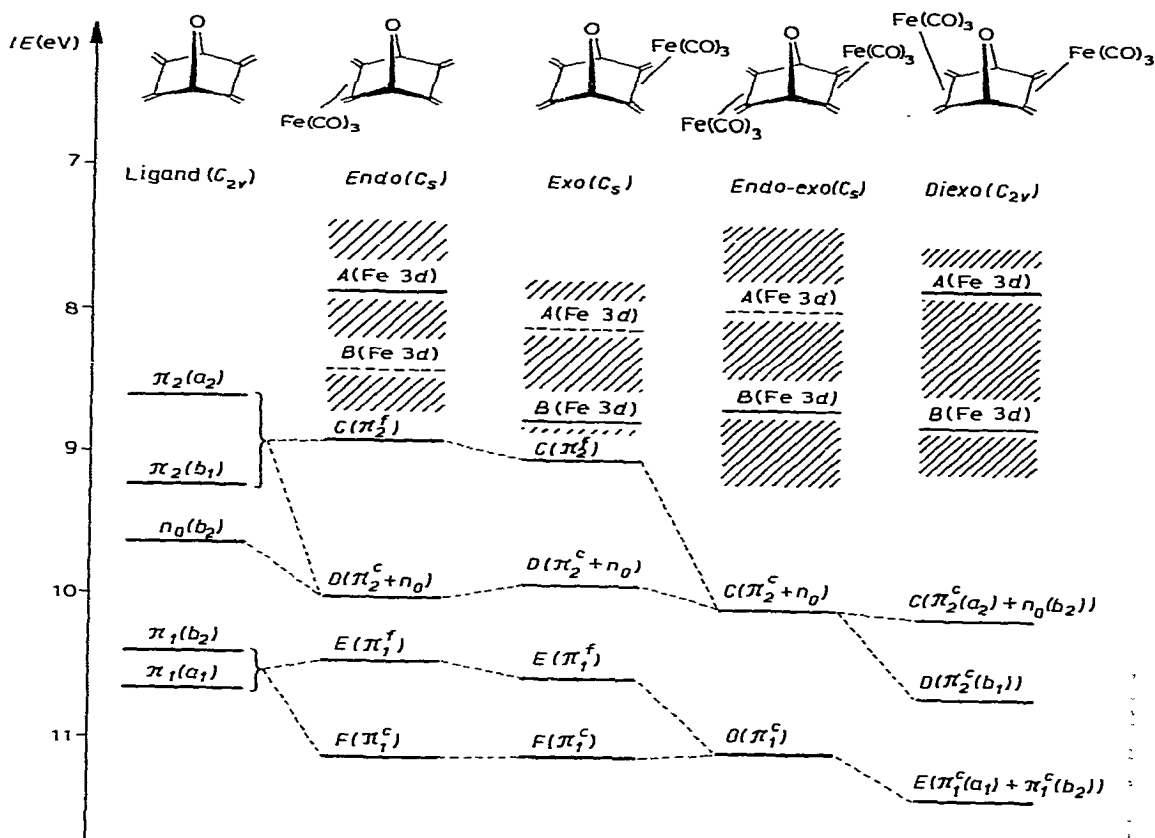
Fig. 2. Experimental correlation diagram for 2,3,5,6-tetrakis(methylene)-7-oxabicyclo[2.2.1]heptane and iron tricarbonyl complexes.

The Fe—butadiene bonding mechanism has been the object of several theoretical treatments [1,6,7] which all point to the importance of the back-donation interaction between an e type (if C_{3v} symmetry is assumed for the Fe-(CO)$_3$ fragment) $3d$ iron AO and the empty π_3^* butadiene MO. The filled π_1 and π_2 ligand MO's are stabilized by bonding interaction with high lying iron AO's of a_1 and e type, respectively. As a result of the donation and back-donation interactions, and according to the PE results of Worley et al. [3], the π_1 and π_2 ligand MO's are both stabilized on complexation. Within this model we feel confident in assigning bands D and F of both isomers to π_2^c and π_1^c ionizations, respectively. It is noteworthy, however, that significantly larger $\Delta\pi_1$ (i.e. $\pi_1^c - \pi_1^f$) values (endo: 0.77 eV; exo: 0.50 eV) are present in these complexes compared with those previously reported (0.22 ± 0.06 eV) [3], but the $\Delta\pi_2$ values lie within the usual range. This indicates the need for caution when the mean $\Delta\pi_1$ and $\Delta\pi_2$ values reported in literature are employed as a predictive tool. The source of this discrepancy could arise from the different references assumed to measure the $\Delta\pi$ values; we use cis-butadiene π MO's as internal standards, while Worley used the π MO's of the free trans-butadiene ligand.

Intensity considerations and comparison with the free ligand strongly indi-

cate the assignment of band D in both spectra to the ionization from the oxygen (O(7)) lone pair (n_0). Band D therefore represents both n_0 and π_2^c ionizations; this prevents the exact evaluation of the IE(n_0) and precise comparison with the corresponding value for the free ligand. However, the non-bonding character of this MO suggests that the slight stabilization of n_0 in both complexes with respect to the free ligand may reflect a small electron withdrawal by the Fe(CO)$_3$ group.

Bands A and B are to be related to ionizations from four MO's which are mainly localized on the Fe(CO)$_3$ group and represent $3d$ metal-like MO's, one of which accounts for the back-donation interaction with the π_3^* butadiene MO. The detailed assignment of these four ionizations in the spectra of all the Fe-butadiene complexes so far reported is still an open question [1—3]. However, the He(I)/He(II) intensity changes found in the PE spectrum of Fe(CO)$_3$(C$_4$H$_6$) [1] seem to us good evidence for excluding the assignment of the low-lying component (band A in our spectra) to the MO involved in the back-donation interaction. By comparing the A—B profiles in the spectra of our *exo* and *endo* complexes some insight into the origin of band A can be gained. This band is better resolved and shifted toward lower IE in the *endo* isomer; this fact, together with the larger $\Delta\pi_1$ value of the *endo* isomer, indicates a larger Fe-butadiene interaction in the *endo* isomer through the totally symmetric MO's (a_1 $3d$ iron AO and ligand π_1 MO). According to this argument, band A must be assigned to the totally symmetric component of iron $3d$ atom-like levels.

We have no firm explanation of the origin of this larger Fe-butadiene interaction in the *endo* isomer, but we think that electrostatic interactions between the oxa bridge and the Fe(CO)$_3$ moiety may be of relevance in explaining such small differences, bearing in mind that significant ionic character has been proposed [1] for the Fe—butadiene interaction.

Di-iron complexes

The PE spectrum of the *endo-exo* di-iron complex (Fig. 1c) can be readily interpreted as a superimposition of those of the *endo* and *exo* mono-iron isomers. In particular, band C represents the coalescence of bands C and D of the mono-iron complexes, and band D originates from the superimposition of bands E and F. The region peculiar to the iron $3d$ ionization does not present any new feature with respect to the mono-iron complexes. These results are in line with the hypothesis of independent butadiene units as far as the complexation is concerned.

In contrast, the PE spectrum of the *di-exo* isomer (Fig. 1d) cannot be interpreted as being derived from two independent Fe-butadiene systems. Band A is significantly shifted toward lower IE when compared to that of all other complexes. Furthermore, the C, D and E bands exhibit a spectral pattern which cannot be related directly to those reported above (Fig. 2). The origin of these differences is the high symmetry (C_{2v}) which is typical of this complex and is the same as that of the free ligand. The effect of this high symmetry can be explained in terms of the mechanism previously invoked for the free ligand [5]. Following this argument, it is straightforward to assign band C to the ionization from n_0 and $\pi_2^c(a_2)$ MO's, and band D to the $\pi_2^c(b_1)$ MO. It is noteworthy that the $\pi_2^c(a_2)$—$\pi_2^c(b_1)$ separation is virtually equal to that for the free ligand, thus

indicating that through-bond and through-space interactions between the two butadiene units are not modified by complexation. Consequently, band E can be assigned to $\pi_1(b_2)$ and $\pi_1(a_1)$ MO's, even if the latter ionization may be hidden under the intense bands at higher IE's. Finally it is noteworthy that, if the free ligand is used as a reference, there is a large downward shift of band A. This seems to indicate that high symmetry requirements are responsible for the perturbation effects of the two distinct $Fe(CO)_3$ groups.

References

1 J.A. Connor, L.M.R. Derrick, M.B. Hall, I.H. Hillier, M.F. Guest, B.R. Higginson and D.R. Lloyd, Mol. Phys., 28 (1974) 1193.
2 J.C. Green, P. Powell and J. van Tilborg, J. Chem. Soc. Dalton, (1976) 1974.
3 S.D. Worley, T.R. Webb, D.H. Gibson and T.-S. Ong, J. Electron Spectrosc. Relat. Phenom., 18 (1980) 189.
4 E. Meier, O. Cherpillod, T. Boschi, R. Roulet, P. Vogel, C. Mahaim, A.A. Pinkerton, D. Schwarzenbach and G. Chapuis, J. Organometal. Chem., 186 (1980) 247.
5 M. Mohraz, C. Batich, E. Heilbronner, P. Vogel and P.A. Carrupt, J. Royal Neth. Chem. Soc., 98 (1979) 361.
6 P.G. Perkins, I.C. Robertson and J.M. Scott, Theor. Chim. Acta, 22 (1971) 299.
7 M. Elian and R. Hoffmann, Inorg. Chem., 14 (1975) 1058.