Journal of Organometallic Chemistry, 288 (1984) 79–88
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

He(I) AND He(II) PHOTOELECTRON SPECTRA OF 1-AZA-1,3-BUTADIENE-TRICARBONYLIRON COMPLEXES: [$Fe(CO)_3(R^1N{=}CHCH{=}CHR^2)$]

R.R. ANDRÉA, P.C.J. BEENTJES, D.J. STUFKENS and A. OSKAM *

Anorganisch Chemisch Laboratorium, J.H. van 't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)

(Received November 28th, 1984)

Summary

He(I) and He(II) photoelectron spectra are reported for the 1-aza-1,3-butadienes ($R^1N{=}CHCH{=}CHR^2$, denoted by R^1,R^2-ABD) t-Bu,Me-ABD and i-Pr,Ph-ABD and their tricarbonyliron complexes [$Fe(CO)_3$(R^1,R^2-ABD)]. Assignments of ionizations from the iron *d* and ligand orbitals have been made with the aid of He(I)/He(II) intensity ratios and some semi-empirical molecular orbital calculations on the model ligand Me,H-ABD (MNDO) and on the model complex [$Fe(CO)_3$(H,H-ABD)] (CNDO/S).

A remarkable feature is the lowering of the ionization energy from the Fe $d^2_{xz/yz}$ orbital with respect to the other *d* orbitals $(d_{xy}/d_{x^2-y^2}/d_{z^2})^6$ by about 0.9 eV, an effect which has not been found for the related [$Fe(CO)_3$(1,3-butadiene)] complexes. The involvement of the nitrogen lone pair in the bonding between the R^1,R^2-ABD and $Fe(CO)_3$ moieties is discussed.

Introduction

There is much interest in the chemical, structural and bonding properties of π-complexes formed by olefinic organic molecules with transition metals [1–5]. Because of their unusual bonding modes [6,7] the complexes [$Fe(CO)_3(\eta^4\text{-}C_4H_6)$] ($\eta^4\text{-}C_4H_6$ = 1,3-butadiene) and [$Fe(CO)_3(\eta^4\text{-}C_4H_4)$] ($\eta^4\text{-}C_4H_4$ = cyclobutadiene) have been the subject of many studies and discussions. These two species still provide model compounds for understanding the bonding properties and chemistry of organometallic π-complexes [8,9].

One of the most direct methods of elucidating the electronic structure is ultraviolet photoelectron spectroscopy (UPS), and many UPS studies have already been performed on these compounds [10,11]. Green [12], Cowley [13] and Oskam [14]

---

* To whom correspondence should be addressed.

0022-328X/85/$03.30

have reviewed the UPS data and molecular orbital (MO) diagrams have been presented by Hoffmann and coworkers [5,9] and by others [10,11]. The MO calculations on $[Fe(CO)_3(C_4H_6)]$ and $[Fe(CO)_3(C_4H_4)]$, however, were correlated to UP spectra which were complicated by strong overlap of bands in the iron *d* ionization region.

Until now, very little has been known about the electronic properties of the 1-aza-1,3-butadienes (η^4-$R^1N{=}CHCH{=}CHR^2$, denoted by R^1,R^2-ABD [15]) bonded to an $Fe(CO)_3$ moiety. The chemistry of these compounds has mostly been studied by Otsuka et al. [17]. The bonding mode of the R^1,R^2-ABD ligand has been established by an X-ray study [18] and found to be $\eta^4(\eta^2$-C=N and η^2-C=C). The structure is therefore more or less the same as that for $[Fe(CO)_3(\eta^4\text{-}C_4H_6)]$, without involvement of the nitrogen lone pair in the bonding [18].

We present here the results of a detailed UPS study of the 1-aza-1,3-butadienetricarbonyliron complexes $[Fe(CO)_3$(t-Bu,Me-ABD)] and $[Fe(CO)_3$(i-Pr,Ph-ABD)]. The results are of importance for the understanding of the (photo-) chemical properties of these complexes [19], just as in the case of the recently investigated σ,σ-bonded 1,4-diaza-1,3-butadiene (R-DAB [15]) complexes [16,20].

Experimental

Syntheses

The free ligands t-Bu,Me-ABD and i-Pr,Ph-ABD were prepared by the method of Cardaci et al. [21]. After several recrystallizations from pentane/ether, the purity of the ligands was checked with ^1H NMR spectroscopy. The tricarbonyliron complexes with these R^1,R^2-ABD ligands were prepared by the method of Otsuka et al. [17]. All reactions and manipulations involving the complexes were carried out under nitrogen. All the organic solvents used were freshly distilled from Na wire. The compounds were identified by ^1H NMR and FT-IR spectroscopy and elemental analyses. The thermal stabilities of the complexes in the gas phase were checked by thermoanalyses under high vacuum.

Photoelectron spectra

The UP spectra were recorded using a Perkin–Elmer PS-18 photoelectron spectrometer, modified with a Helectros Developments hollow cathode He(I)/He(II) light source. The spectra were calibrated with reference to internal He, Ar and Xe. No correction was made for analyzer dependence, and the resolution throughout the experiments was better than 30 meV for the Ar doublet.

Results and discussion

Free ligands

The He(I) and He(II) photoelectron (PE) spectra of the free ligands t-Bu,Me-ABD and i-Pr,Ph-ABD are shown in Figs. 1 and 2. The observed vertical ionization energies (IE) are listed in Table 1.

Semi-empirical MNDO MO calculations [22] were performed on the model ligand Me,H-ABD and its rotation barrier from the *E-s-trans-E* to the *E-s-cis-E* conformation was calculated as described for Me-DAB [15] using both NDDO [23] and MNDO [20] schemes. A barrier of 5 kJ/mol for the chelating conformation of the

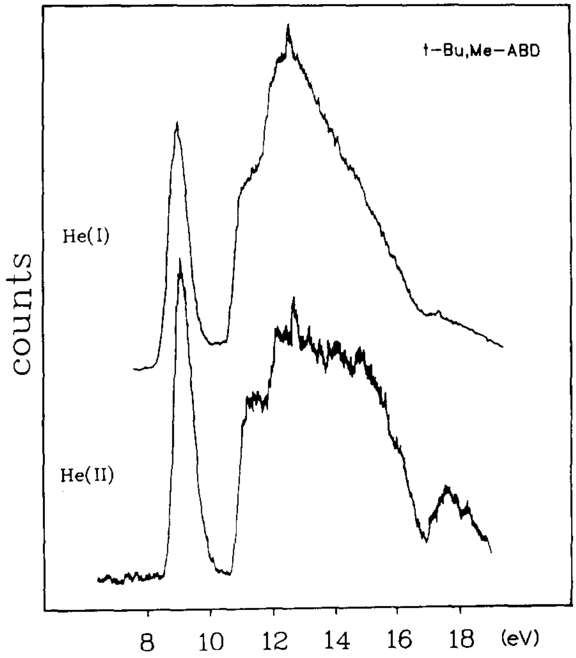

Fig. 1. He(I) and He(II) photoelectron spectra of t-Bu,Me-ABD.

Me,H-ABD ligand has been calculated, and this is 16 kJ/mol less than that for Me-DAB [23].

The calculated and observed orbital sequence of the R^1,R^2-ABD ligands is more or less the same as previously suggested for R-DAB [20] ligands (R = alkyl). There is near coincidence of the nitrogen lone pair n and the highest occupied π-orbital

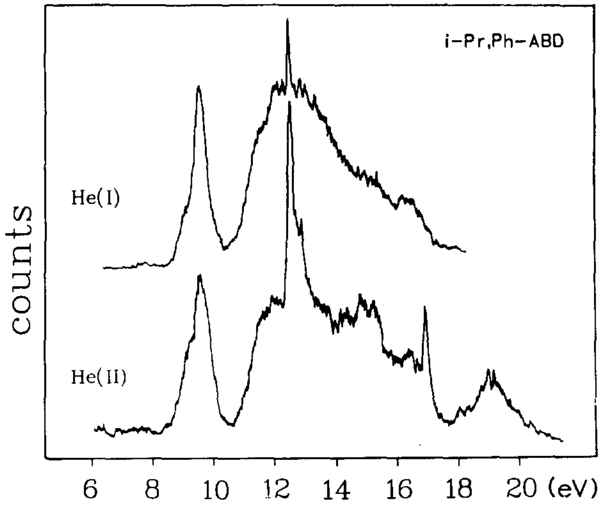

Fig. 2. He(I) and He(II) photoelectron spectra of i-Pr,Ph-ABD.

$\pi_2(-)$. An *IE* of 9.03 eV for these two orbitals (in the approximation of Koopmans' theorem [24]) is in agreement with earlier He(I) investigations on conjugated hetero-butadienes [25], and comparable with values reported for free R-DAB [20].

The He(II) PE spectrum (Fig. 1) provides no evidence for any separation between the *IE*'s of these two orbitals. However, as can be seen from its large He(II) cross-section relative to the other bands, the band at 9.03 eV has N_{2p} and C_{2p} [26] character, corresponding to ionizations from the nitrogen pair orbital and the highest occupied π orbital. The *IE* value of 11.35 eV for the $\pi_1(+)$ orbital of t-Bu,Me-ABD is also more or less the same as for the related 1,3-butadiene systems [27].

The UP spectra of the aryl substituted i-Pr,Ph-ABD are complicated by the presence of ionizations from the phenyl π-system. Because free rotation of the phenyl ring with respect to the planar N=C–C=C skeleton is expected in the gas phase, the *IE* values of the *n* and $\pi_2(-)$ orbitals should not differ much from those of t-Bu,Me-ABD.

For the broad band at ca. 9.5 eV we assign the shoulder at 9.18 eV to ionizations from the *n* and $\pi_2(-)$ orbitals and the maximum of the band at 9.65 eV to phenyl π("e_{1g}") orbitals. An argument for this assignment is that the shoulder at 9.18 eV exhibits a larger cross-section in He(II) spectrum than the centre of the band (Fig. 2).

Complexes

Before discussing the UP spectra of the complexes it is useful to consider the

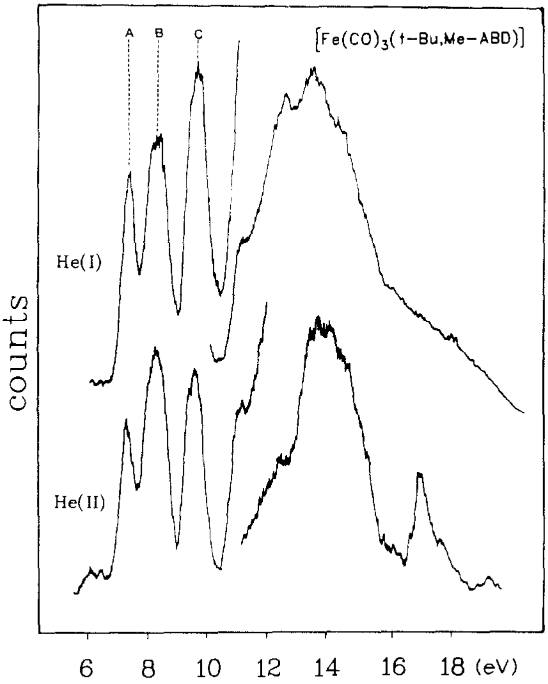

Fig. 3. Full He(I) and He(II) photoelectron spectra of [Fe(CO)$_3$(t-Bu,Me-ABD)].

influence of complexation on the ordering of the orbitals in R^1,R^2-ABD ligands.

It is to be expected that in [Fe(CO)$_3$(R^1,R^2-ABD) the $\pi_2(-)$ and $\pi_1(+)$ ligand orbitals will be stabilized because of mixing with empty metal frontier orbitals $2e$ and $2a_1$, respectively. Apart from π-bonding there will also be π-backbonding from a filled Fe d-orbital ($d_{xz/yz}$) into an empty low-lying $\pi^\star$ orbital of the ligand. This bonding model is generally accepted for [Fe(CO)$_3$(C_4H_6)] [9,10,11a]. For this latter complex the presence of three non-bonding d-orbitals and one $d+\pi_3{}^\star$ MO is supported by its UP spectrum [11b]. Although only one broad band is observed for the ionizations from the nearly coinciding metal d orbitals, He(I)/He(II) cross section differences within this band show the presence of a MO with mixed ($d+\pi_3^\star$) character [11a]. In Figs. 3 and 4 the He(I) and He(II) PE spectra of [Fe(CO)$_3$(t-Bu,Me-ABD)] are shown, and the observed vertical *IE* values are listed in Table 1 together with their assignments, which are discussed below.

From comparison of the data for the related [Fe(CO)$_3$(R-DAB)] and [Fe(CO)$_3$(C_4H_6)] complexes, bands **A** and **B** at 7.4 and 8.3 eV respectively are assigned to ionizations from the iron metal d orbitals. The **A**/**B** intensity ratio in the He(I) PE spectrum (1/3) is in agreement with an assignment of band **A** to ionization from the mixed $d_{xz/yz}+\pi_3^\star$ orbital and band **B** to that from the three non-bonding and nearly coinciding $d_{x^2-y^2}/d_{xy}/d_{z^2}$ orbitals. This assignment is supported by the observation that the intensity of band **A** decreases with respect to band **B** on going from He(I) to He(II) excitation, which is consistent with participation of C_{2p} [26] in the $d_{xz/yz}+\pi_3^\star$ orbital.

Band **C** at 9.63 eV is assigned to ionizations from the n and $\pi_2(-)$ orbitals of the complexes t-Bu,Me-ABD. Consideration of the UP data for other $4e$ donor olefin

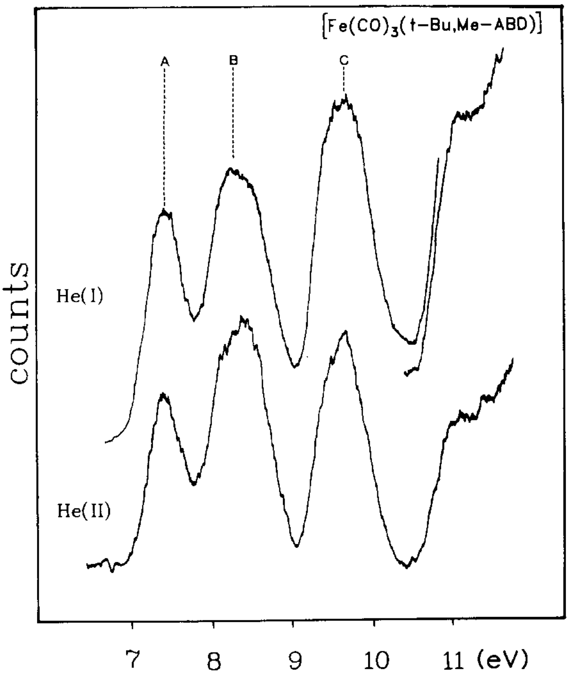

Fig. 4. Expanded low *IE* region He(I) and He(II) photoelectron spectra of [Fe(CO)$_3$(t-Bu,Me-ABD)].

TABLE 1

OBSERVED VERTICAL IONIZATION ENEGIES (*IE*) OF TWO 1-AZA-1,3-BUTADIENES (t-Bu,-Me-ABD and i-Pr,Ph-ABD) AND THEIR TRICARBONYLIRON COMPLEXES [Fe(CO)$_3$(R^1,R^2-ABD)]

Ligand	*IE* (eV) (±0.05 eV)						
t-Bu,Me-ABD	9.03	–	11.35				
i-Pr,Ph-ABD	9.18 [a]	9.65	11.73				
Assignment	$\pi_2(-)$ n	π(Ph) "e_{1g}"	$\pi_1(+)$				
Complex	***IE* (eV) (±0.05 eV)**						
[Fe(CO)$_3$(t-Bu,Me-ABD)]	7.40	8.35	–		9.63 [b]		11.41
[Fe(CO)$_3$(i-Pr,Ph-ABD)]	7.44	8.31	9.12	9.86		10.38	–
Bandindex	**A**	**B**	**X**	**C**		**D**	
Assignment	$d+\pi_3^{\star}$	d_{Fe}	π(Ph)	n	$\pi_2(-)$		$\pi_1(+)$
T_i	$2e$	$1a_1+1e$	"e_{1g}"				

[a] Shoulder. [b] No splitting has been observed.

tricarbonyliron complexes [12,14] suggests that the band at 11.41 eV belongs to ionizations from the $\pi_1(+)$ orbital of the ligand.

The $\pi_2(-)$ and $\pi_1(+)$ orbitals in [Fe(CO)$_3$(t-Bu, Me-ABD)] are less stabilized with respect to the free t-Bu,Me-ABD ligand (ΔIE's are 0.55 and 0.04 eV respectively) than the corresponding orbitals of C_4H_6 in [Fe(CO)$_3$(C_4H_6)] (ΔIE's are 0.74 and 0.09 eV respectively).

This decrease of stabilization (perturbation energy as defined by Worley et al. [28]) and the decrease of the first *IE* of the HOMO ($d+\pi_3^{\star}$) point to a weakening of both the metal–ligand π-bonding and π-back-bonding in [Fe(CO)$_3$(R^1,R^2-ABD)] with respect to [Fe(CO)$_3$(C_4H_6)], although the change of π-back-bonding is much larger. Such an effect has also been observed for [Fe(CO)$_3$(norbornadiene)] with respect to [Fe(CO)$_3$(C_4H_6)] [28]. This decrease of π-backbonding may be due to asymmetry of the R^1,R^2-ABD ligand induced by the nitrogen atom. The C=N bond is shorter than the C=C bond, and the atomic orbitals coefficients are changed due to the greater electronegativity of N than of C.

The π-back-bonding may, however, also be weakened as the result of a bonding interaction between the nitrogen lone-pair and the central metal atom. This interaction is evident from a shortening of the Fe–N bond length by 0.1 Å [18] and from the stabilization of the nitrogen lone pair orbital by 0.6 eV with respect to the free ligand (see Table 1). As the results of this decrease of π-back-bonding and the interaction with the nitrogen lone pair, the electron density at the metal atom in [Fe(CO)$_3$(R^1,R^2-ABD)] is increased with respect tot that in [Fe(CO)$_3$(C_4H_6)]; this increase is evident from the lower *IE*'s of the three non-bonding ($e+a_1$) iron *d* orbitals.

The involvement of the nitrogen atom in the bonding of [Fe(CO)$_3$(R^1,R^2-ABD)] is also suggested by MO calculations and by photochemical investigations of these complexes in noble gas matrices in which the bonding mode changes from η^4 to σ-N [19]; the experimental results agree well with the UP data.

With these assignments based on empirical criteria, such as He(I)/He(II) cross

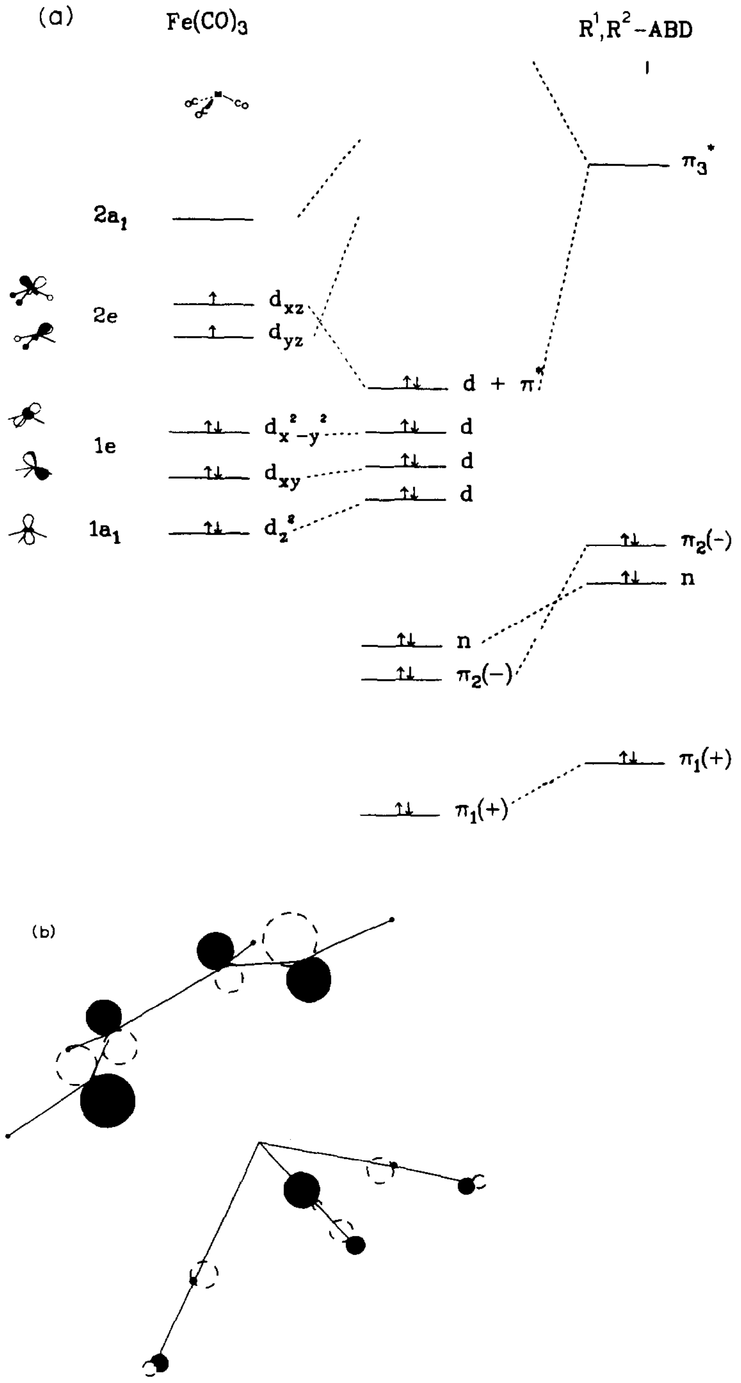

Fig. 5. (a) Molecular orbital diagram of $[Fe(CO)_3(R^1,R^2\text{-ABD})]$. (b) A PICTOR plot of the HOMO in $[Fe(CO)_3(H,H\text{-ABD})]$.

section differences, intensity ratios, molecule-in-molecule approach and data of related compounds, it is possible to construct a qualitative MO interaction diagram. This scheme was confirmed by semi-empirical MO calculations on the free ligand in its *E-s-cis-E* conformation (MNDO [22]) and on the model complex [Fe(CO)$_3$(H,H-ABD)] (CNDO/S method in the parametrization of Del Bene and Jaffé [30], in which the repulsion integrals were approximated by the method of Nishimoto and Mataga [31]). A picture of the HOMO was constructed from the eigenvectors of the CNDO/S calculations on the model complex.

The related complex [(Fe(CO)$_3$(i-Pr,Ph-ABD)], with an aromatic R group on the C=C unit, was also studied, because some differences were observed between the photochemical behaviour of alkyl and aryl R^1,R^2-ABD complexes [19]. As mentioned before, the UP spectra of the i-Pr,Ph-ABD compound are more complicated than these of dialkyl-ABD due to the presence of ionization from phenyl π-orbitals. The He(I) and He(II) PE spectra are shown in Fig. 6 and the observed vertical *IE*'s are listed in Table 1.

In these UP spectra five bands are observed in *IE* region below 12 eV marked with indices **A**–**D** and **X**. Band **A** and **B** exhibit a relatively large He(II) cross-section with respect to **X**, **C** and **D**.

From a comparison with *IE* values of [Fe(CO)$_3$(t-Bu,Me-ABD)] it is obvious that band **A** and **B** belong to ionizations from orbitals with Fe 3*d* character. Assignment of **A** to $d_{xz/yz} + \pi_3^\star$ and **B** to $d_{x^2-y^2/xy}$ and d_{z^2} orbital is estabished by the 1/3 He(I) intensity ratio for the four expected metal *d* ionizations (iron d^8 complex).

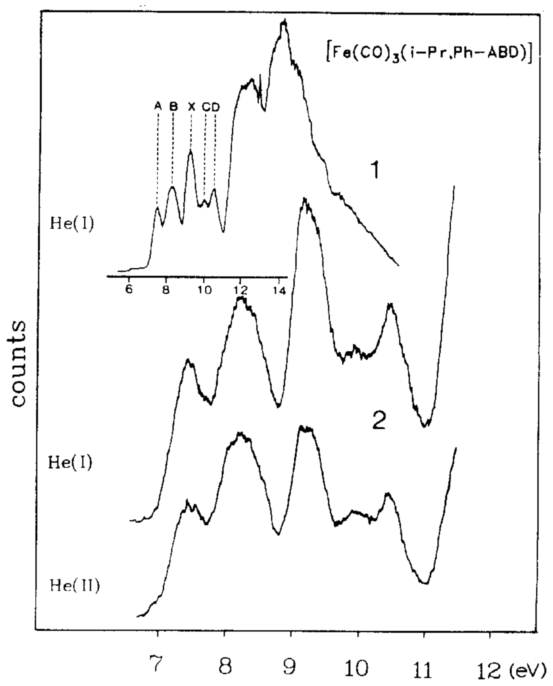

Fig. 6. Full He(I) (part **1**) and expanded He(I) and He(II) photoelectron spectra (part **2**) of [Fe(CO)$_3$(i-Pr,Ph-ABD)].

The *IE* value of the $d+\pi_3^\star$ orbital at 7.44 eV is hardly shifted with respect to that of the t-Bu,Me-ABD complex, which implies the same degree of π(back-)bonding.

The bands **X** (9.12 eV), **C** (9.86 eV) and **D** (10.38 eV) arise respectively from ionizations of the phenyl π ring electrons, the nitrogen lone pair, and $\pi_2(-)$ of the ligand. This sequence is tentative and mainly based on intensity ratio differences, which can be seen in the expanded part of Fig. 6, and on comparison with the free i-Pr,Ph-ABD ligand (vide supra).

The *IE* value of 9.12 eV, assigned to phenyl ("e_{1g}") ionization, indicates that the electron density on the phenyl ring of i-Pr,Ph-ABD is increased on complexation with $Fe(CO)_3$. This cannot be explained in terms of conjugation since such an effect is not apparent in the X-ray structure of $[Fe(CO)_3(Ph,Ph\text{-}ABD)]$ [18]. It is, however, obvious from the UP data that some charge is shifted from the N=C–C=C skeleton ($\pi_2(-)$) into the phenyl ring. This shift of charge provides a reasonable explanation for the larger stabilization of the $\pi_2(-)$ orbital at 10.38 eV than for the nitrogen lone pair at 9.86 eV. The latter *IE* value, which was not observed as a separate ionization band for the $[Fe(CO)_3(t\text{-}Bu,Me\text{-}ABD)]$ complex, is stabilized by the same amount with respect to the free ligand.

References

1 R. Mason, Nature, 217 (1968) 543.
2 M.R. Churchill and R. Mason, Adv. Organomet. Chem., 5 (1967) 93.
3 O.S. Mills and G. Robinson, Proc. Chem Soc., (1960) 421 and Acta Cryst., 16 (1963) 758.
4 (a) R.P. Dodge and V. Schomaker, Acta Cryst., 18 (1965) 614; (b) A. De Cian, P.M.L. Huillier and R. Weiss, Bull. Soc. Chim. Fr., (1973) 451.
5 R. Hoffmann, Angew. Chem., 94 (1982) 725 and references herein.
6 M.J.S. Dewar, Bull. Soc. Chim. Fr., 18 (1951) C71.
7 J. Chatt, J. Chem. Soc., (1963) 2939.
8 F.A. Cotton and G. Wilkinson, Adv. Inorg. Chemistry, Wiley, New York, 1973.
9 M. Elian and R. Hoffmann, Inorg. Chem., 14 (1975) 1058.
10 M.C. Böhm and R. Gleiter, J. Comp. Chem., 1 (1980) 407.
11 (a) 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; (b) M.B. Hall, I.H. Hillier, J.A. Connor, M.F. Guest and D.R. Lloyd, ibid., 30 (1975) 839.
12 J.C. Green, Structure and Bonding, 43 (1981) 37.
13 A.H. Cowley, Prog. Inorg. Chem., 26 (1979) 46.
14 H. van Dam and A. Oskam, Trans. Met. Chem., 9 (1984) 125, Marcel Dekker Inc.
15 Most 1-aza-1,3-butadienes that are known have the general formula $R^1N{=}CR^3CR^4{=}CR^5R^2$, but the ligands used in this paper are of formula $R^1N{=}CHCH{=}CHR^2$ and this will be abbreviated to R^1,R^2-ABD. This is in line with the nomenclature for 1,4-diaza-1,3-butadienes RN=CHCH=NR (abbr. as R-DAB) and their complexes [16]. Other important abbreviations for the R-groups used throughout this paper are Me = methyl, i-Pr = iso-propyl, t-Bu = tert. butyl and Ph = phenyl.
16 G. van Koten and K. Vrieze, Adv. Organomet. Chem., 21 (1982) 151.
17 S. Otsuka, T. Yoshida and A. Nakamura, Inorg. Chem., 6 (1967) 20.
18 A. De Cian and R. Weiss, Acta Cryst., B28 (1972) 3264.
19 M.W. Kokkes, P.C.J. Beentjes, D.J. Stufkens and A. Oskam, manuscript in preparation.
20 R.R. Andréa, J.N. Louwen, M.W. Kokkes, D.J. Stufkens and A. Oskam, J. Organomet. Chem., 281 (1985) 273.
21 G. Bellachioma and G. Cardaci, J. Chem. Soc., Dalton Trans., (1976) 1735.
22 M.J.S. Dewar and W. Thiel, J. Amer. Chem. Soc., 99 (1977) 4899; L.P. Davies, R.M. Guidry, J.R. Williams, M.J.S. Dewar and H.S. Rzepa, J. Comp. Chem., 2 (1981) 433.
23 R. Benedix, P. Birrer, F. Birnstock, H. Hennig and H.-J. Hoffmann, J. Mol. Struct., 51 (1979) 99.
24 T. Koopmans, Physica (Utrecht), 1 (1934) 104.

25 D. Vocelle, A. Dargelos, R. Pottier and C. Sandorfy, J. Chem. Phys., 66 (1977) 2860.
26 A. Schweig and W. Thiel, J. Chem. Phys., 60 (1974) 951.
27 M. Beez, G. Bieri, H. Bock and E. Heilbronner, Helv. Chim. Acta, 56 (1973) 1028.
28 S.D. Worley, T.R. Webb, D.H. Gibson and T.-S. Ong, J. Electron Spectrosc. Relat. Phenom., 18 (1980) 189.
29 K. Noack, Helv. Chim. Acta, 45 (1962) 1847.
30 J. Del Bene and H.H. Jaffé, J. Chem. Phys., 48 (1968) 1807.
31 K. Nishimoto and N. Mataga, Z. Phys. Chem., 12 (1977) 325.