Theoretical ab Initio and UV–PES Study of the $M(CO)_3$–Butadiene Interaction in Bicyclic Polyene Complexes

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The gas-phase ultraviolet photoelectron spectra of several mono- and bimetallic $M(CO)_3$ complexes of 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene (M = Fe, Ru) have been recorded in order to investigate the possible dependence of the $M(CO)_3$–butadiene interactions on the stereochemistry (different endo and exo isomers). Actually, the endo/exo isomers show remarkable spectral differences. In order to elucidate the origin of such differences, minimal basis set ab initio calculations have been carried out on the endo/exo $Fe(CO)_3$ complexes. From the theoretical study it turns out that the bonding mechanism in both isomers is similar. However, the calculations show differences in the molecular energy levels that can be traced back to long-range electrostatic effects due to the $M(CO)_3$ moiety.

Introduction

Unsaturated bonds of cyclic polyolefins are readily coordinated to metal carbonyl groups,[2] and the resulting complexes often show high stability.

In recent years several polyene carbonyl complexes have been synthesized and characterized. For example, metal carbonyl complexes of 2,3,5,6-tetramethylidenebicycloalkanes (Ia–d) have been prepared and their structures determined by X-ray diffraction studies.[3] The two exocyclic *s-cis*-butadiene units are able to coordinate one or two $M(CO)_3$ d^8 groups, and in the case of Ia, by virtue of the further endocyclic double bond, they can coordinate one $M(CO)_3$ d^6 group. The resulting complexes are particularly interesting from the theoretical point of view due to an unusual case of isomerism. Actually in these ligands Ia–d, the exo and endo faces (with respect to the rigid "roof-shaped" skeleton) are distinguishable, and consequently two different mononuclear isomeric complexes have been isolated.[3] That the $M(CO)_3$–butadiene bonding mechanism in the two isomers is not "a priori" identical is suggested by their NMR spectra.[3]

Ia Z=CH=CH
Ib Z=CH_2–CH_2
Ic Z=CH_2
Id Z=O

In order to seek more evidence for such endo/exo inequivalence, we have recorded the gas-phase UV photoelectron (PE) spectra of a series of mono- and bimetallic $M(CO)_3$ derivatives (M = Fe, Ru) of 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene (Ia) (Figure 1). The present investigation is the development of a previous study where the PE spectra of $Fe(CO)_3$ complexes of Id have been reported.[4]

Ab initio quantum mechanical calculations have been also carried out in order to elucidate the nature of the exo/endo bonding differences. Due to the large molecular complexity, the valence-only pseudopotential method[5] with a minimal basis set has been adopted.

Experimental Section

The preparation of the following compounds (see Figure 1) has been reported elsewhere: Ia,[6] IIx, IIn, IVnx, IVxx, and VIIx,[3a–c] IIIx, IIIn, Vnx, VInx, and VIxx.[3d]

He I and He II excited PE spectra were measured on a Perkin-Elmer PS-18 spectrometer modified for He II measurements by inclusion of a hollow cathode discharge lamp which gives a high photon flux at He II wavelengths (Helectros Developments). The ionization energy (IE) scale was calibrated by reference to peaks due to admixed inert gases (Xe–Ar) and to the He $1s^{-1}$ self-ionization. A heated inlet probe system was adopted at 40–60 °C for monometallic compounds and 100–120 °C for bimetallic ones. The IEs together with the proposed assignments are reported in Table I. The ab initio LCAO–MO–SCF calculations were performed with the introduction of pseudopotentials to deal with all core electrons on each atoom. The Barthelat et al. formalism[7] has been choosen where for a given atom, C, the local operator for each l value has the form

$$w_{l,c}(r) = \sum_i a_i r^{n_i} \exp(-\alpha r^2)$$

The a_i, n_i, and α parameters adopted for Fe, O, and C atoms and the minimal basis set optimized for each valence shell by a pseudopotential version of the ATOM program[8] are reported elsewhere.[9] The standard Huzinaga[10] Gaussian basis set was used for hydrogen atoms. All the molecular calculations were carried out by running the PSHONDO program[11] on a VAX-11/780 computer. The geometrical parameters used in the calculations were taken from the X-ray structural determinations.[3] Gross atomic charges and bond overlap populations were obtained by Mulliken's population analysis.[12]

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[1] (a) University of Padova. (b) University of Lausanne. (c) University of Toulouse. (d) CNR of Padova.

[2] Deganello, G. In "Transition Metal Complexes of Cycic Polyolefins"; Academic Press, New York, 1979.

[3] (a) Pinkerton, A. A.; Chapuis, G.; Vogel, P.; Hanisch, U.; Narbel, Ph.; Boschi, T.; Roulet, R. *Inorg. Chim. Acta* **1979**, *35*, 197. (b) Narbel, Ph.; Boschi, T.; Roulet, R.; Vogel, P.; Pinkterton, A. A.; Schwarzenbach, D. *Inorg. Chim. Acta* **1979**, *36*, 161. (c) Meier, E.; Cherpillod, O.; Boschi, T.; Roulet, R.; Vogel, P.; Mahaim, C.; Pinkerton, A. A.; Schwarzenbach, D.; Chapuis, C. *J. Organomet. Chem.* **1980**, *186*, 247. (d) Narbel, Ph.; Roulet, R.; Tagliaferri, E.; Vogel, P. *J. Organomet. Chem.* **1980**, *194*, 103. (e) Meier, E.; Pinkerton, A. A.; Roulet, R.; Vogel, P.; Schwarzenbach, D. *J. Organomet. Chem.* **1981**, *220*, 341. (f) Boschi, T.; Narbel, P.; Vogel, P.; Roulet, R. *J. Organomet. Chem.* **1977**, *133*, C39. (g) Roulet, R.; Tagliaferri, E.; Vogel, P.; Chapuis, G. *J. Organomet. Chem.* **1981**, *208*, 353.

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[9] Casarin, M.; Ajo', D.; Granozzi, G.; Tondello, E.; Aime, S. *Inorg. Chem.*, in press.

[10] Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

[11] Daudey, J. P. PSHONDO: a modified version of HONDO program (Dupuis, M.; Rys, T.; King, H. F. *J. Chem. Phys.* **1976**, *65*, 383) including pseudopotentials.

[12] Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1823.

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Table I. Ionization Energy Data (eV) and Assignments of the PE Spectra of the Studied Complexes[a]

complex	label A	 B	 C	 D	 E
VIIx	7.68 (M → π_3*)	8.47 (d + π_2^f)	9.30 (π_2^c)	10.81 (π_1^f + π_1^c)	11.75 (σ)
IIx	7.90 (M → π_3*)	8.54 (d + π_2^f)	9.30 (π_2^c + π_b)	10.60 (π_1^f + π_1^c)	11.50 (σ)
IIn	7.79 (M → π_3*)	8.46 (d + π_2^f)	9.40 (π_2^c + π_b)	10.30 (π_1^f)	11.10 (π_1^c)
IIIx	7.78 (M → π_3*)	8.65 (d + π_2^f)	9.42 (π_2^c + π_b)	10.68 (π_1^f + π_1^c)	11.39 (σ)
IIIn	7.77 (M → π_3*)	8.76 (d + π_2^f)	9.43 (π_2^c + π_b)	10.28 (π_1^f)	11.27 (π_1^c)
IVnx	7.62 (d)	8.50 (d)	9.54 (π_2^c + π_b)	10.76 (π_1^c)	11.66 (σ)
Vnx	7.49 7.90 (M → π_3*)	8.80 (d)	9.46 (π_2^c + π_b)	10.88 (π_1^c)	11.59 (σ)
VInx	8.03 (d)	8.76 (d)	9.14 9.55 (π_2^c + π_b)	10.84 (π_1^c)	11.67 (σ)
VIxn	7.96 (d)	8.79 (d)	9.27 9.59 (π_2^c + π_b)	10.82 (π_1^c)	11.56 (σ)
VIxx	7.62 (d)	9.03 (d)	9.64 (π_2^c + π_b)	10.84 (π_1^c)	11.69 (σ)
IVxx	7.43 (M → π_3*)	8.40 (d)	9.33 9.65 ($\pi_2^c(a_2 + b_1) + \pi_b$)	10.62 ($\pi_1^c(b_2)$) 11.00 ($\pi_1^c(a_1)$)	11.66 (σ)

[a] See Figure 1 for the nomenclature of the complexes.

Table II. Minimal Basis Set Pseudopotential ab Initio MOs of (Butadiene)tricarbonyliron[a]

MO	eigenvalue	Fe	2 C_i	2 C_t	3 CO	6 H	descript
18a′ (31a′)	−7.97 (−8.07)	28 (41)	14 (9)	44 (34)	12 (14)	2 (1)	M → π_3*
12a″ (18a″)	−11.18 (−10.78)	13 (13)	20 (21)	63 (62)	4 (4)	0 (1)	π_2
17a′ (30a′)	−13.13 (−12.57)	58 (52)	14 (20)	9 (12)	16 (15)	3 (2)	3d(a_1)
11a″ (17a″)	−14.26 (−13.77)	58 (66)	11 (8)	14 (11)	8 (9)	9 (6)	3d(e^a)
16a′ (29a′)	−14.66 (−14.09)	35 (35)	48 (48)	13 (12)	2 (2)	2 (3)	π_1
15a′ (28a′)	−15.07 (−14.69)	55 (65)	7 (5)	14 (10)	11 (7)	13 (7)	3d(e^s)

[a] The all-electron results of ref 14 are reported in parentheses for comparison. C_i = internal carbon; C_t = terminal carbon.

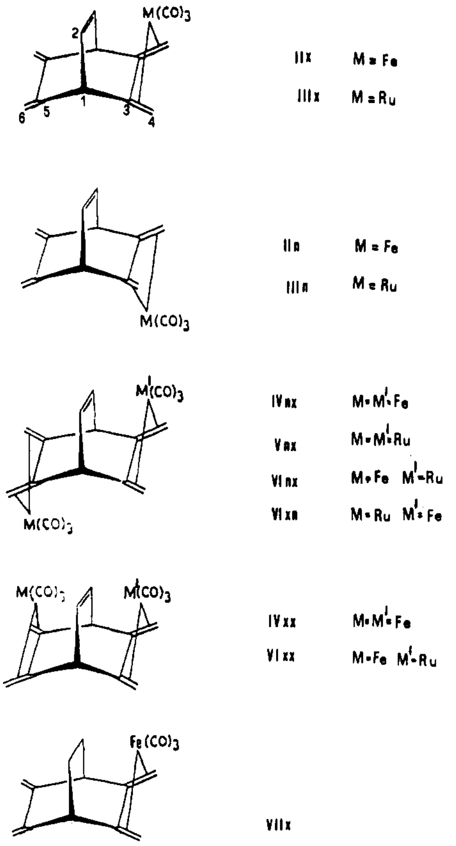

Figure 1. Complexes investigated by UV–PE spectroscopy in this paper.

Results and Discussion

A detailed analysis of the following PE and theoretical data requires a preliminary description of the M(CO)$_3$–butadiene interaction and of the electronic structure of Ia. For this reason the results of the ab initio pseudopotential calculations on (butadiene)tricarbonyliron and Ia will be first examined. This will also provide a test of the quality of the theoretical results obtained by the adopted computational method.

Fe(CO)$_3$–Butadiene Interaction. A qualitative description of the Fe(CO)$_3$–butadiene interaction based on published EHT results[13] is reproduced in Figure 2. This bonding scheme involves both ligand → metal donation (mainly through the mixing between the butadiene π_2 and the Fe(CO)$_3$ 2e^a levels) and metal → ligand back-donation into the π_3* virtual level. In figure 2 we have labelled the resulting MOs according to their predominant character (i.e., M → π_3*, π_2, π_1, and 3d(a_1), 3d(e^s), 3d(e^a) metal-based MOs).

In Table II we report the pseudopotential ab initio results for (butadiene)tricarbonyliron. The eigenvalues and populations are compared with the corresponding literature all-electron ones[14] which were obtained with a similar minimal valence basis set. The very good agreement between the two sets of theoretical data is evidence of the validity of the pseudopotential approach.

The reported ab initio MOs are easily associated (Table II) with the levels of Figure 2. As a whole the ab initio results confirm the EHT qualitative bonding scheme, even if a minor discrepancy is present in the 16a′ and 15a′ MOs whose predominant character is reversed with respect to the EHT results. This probably reflects an underestimation of the 1e^s − π_1 interaction by the EHT method and an effectively better energy matching between the π_1 and 1e fragment orbitals.

Electronic Structure of Ia. Simple qualitative symmetry arguments indicate that the four π orbitals of Ia arising from the π_1 and π_2 orbitals of the two *cis*-butadiene groups have different symmetry representations in the C_{2v} point group ($\pi_2(a_2)$, $\pi_2(b_1)$, $\pi_1(b_2)$, and $\pi_1(a_1)$). Further-

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(13) (a) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058. (b) Albright, T. A.; Hoffmann, R.; Hofmann, P. *Chem. Ber.* **1978**, *111*, 1591.

(14) Connor, J. A.; Derrick, L. M. R.; Hall, M. B.; Hillier, I. H.; Guest, M. F.; Higginson, B. R.; Lloyd, D. R. *Mol. Phys.* **1974**, *28*, 1193.

Table III. Minimal Basis Set Pseudopotential ab Initio MOs of Olefin Ia

MO	eigenvalue	2 C_1	2 C_2	4 C_3	4 C_4	12 H	descript	IE[a]	IE[b]
$5a_2$	−11.56	0	0	33	67	0	π_2	8.44	8.38
$8b_1$	−11.68	2	4	31	62	1	π_2	8.53	8.58
$7b_2$	−12.82	2	78	11	8	1	π_b	9.36	9.16
$6b_2$	−14.27	4	4	54	34	4	π_1	10.41	10.29
$10a_1$	−14.56	5	7	53	32	3	π_1	10.63	10.70
$9a_1$	−15.93	19	5	39	16	21	σ		

[a] Calculated rescaling by 27% the Koopmans' value. [b] Reference 16.

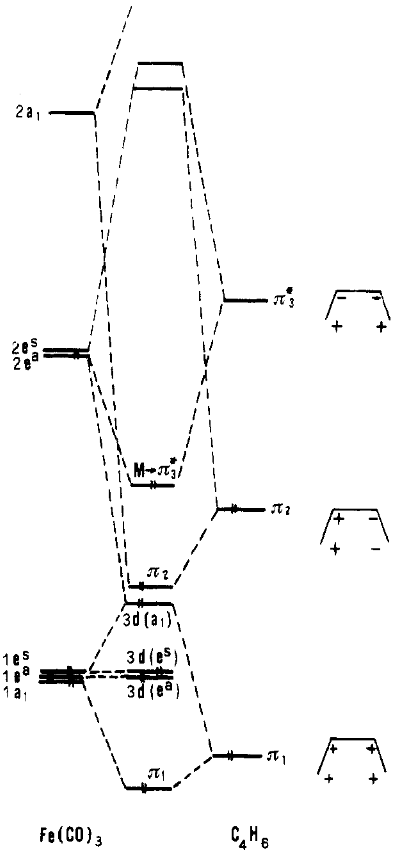

Figure 2. Qualitative interaction diagram of $Fe(CO)_3$–butadiene based on published EHT results.[13]

more, $a_2 - b_1$ and $b_2 - a_1$ splittings are predicted by operation of "through-bond" and "through-space" interactions.[15]

The PE spectrum of Ia has been already reported.[16] The pseudopotential ab initio results reported in Table III are in full agreement with the published PE assignments.[16] A linear correlation between computed and experimental IEs is obtained by adopting the Koopmans' theorem;[17] in particular, an empirical rescaling by 27% gives an excellent numerical agreement with the experimental IEs (see the corrected values in Table III).

The $7b_2$ MO (Table III) mostly represents the endocyclic π_b bond with some out-of-phase mixing with the inner $\pi_1(6b_2)$ MO. A similar mixing between the π_2 butadiene MOs and the π_b one is ruled out by symmetry.

PE Spectra of $M(CO)_3$ Complexes of Ia. The He I excited spectra of some mono- and bimetallic complexes of Ia are shown in Figures 3–6 where the bands are alphabetically labeled. The corresponding vertical IEs and

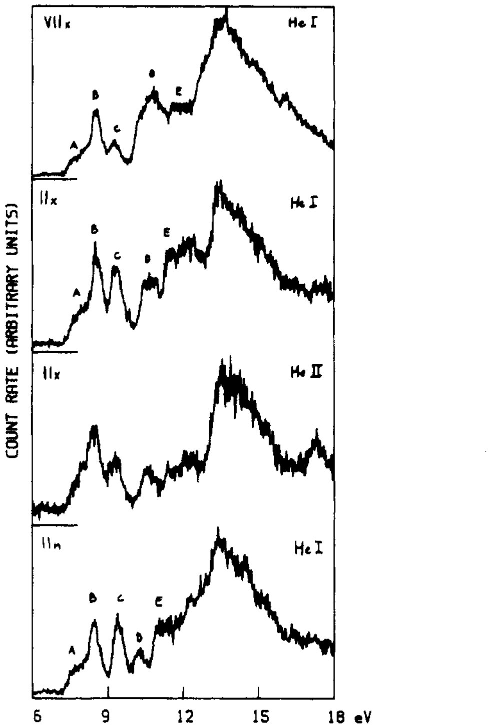

Figure 3. He I PE spectra of IIx, IIn, and VIIx complexes. The He II PE spectrum of IIx is also reported.

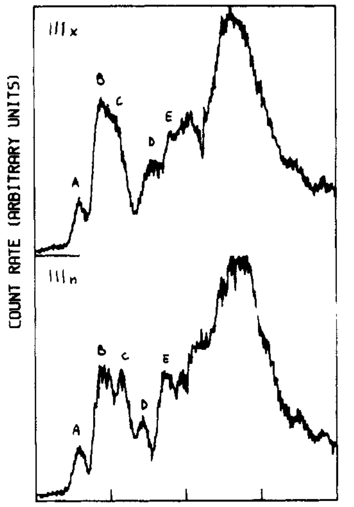

Figure 4. He I PE spectra of IIIx and IIIn complexes.

the proposed assignments are reported in Table I.

On the basis of the PE data of several (diene)tricarbonyliron complexes, Worley et al.[18] have derived empirical complexation perturbation values for π_1 and π_2 diene MOs; in particular, they have found that both π_1 and π_2 MOs are stabilized by complexation with respect to the

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[15] (a) Hoffmann, R.; Imamura, A.; Here, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. (b) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. (c) Gleiter, R. *Angew. Chem.* **1974**, *86*, 770.

[16] Mohraz, M.; Batich, C.; Heilbronner, E.; Vogel, P.; Carrupt, P. A. *Recl. Trav. Chim. Pay-Bas* **1979**, *98*, 361.

[17] Koopmans,. T. C. *Physica (Amsterdam)* **1933**, *1*, 104.

[18] Worley, S. D.; Webb, T. R.; Gibson, H.; Ong, T. S. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *18*, 189.

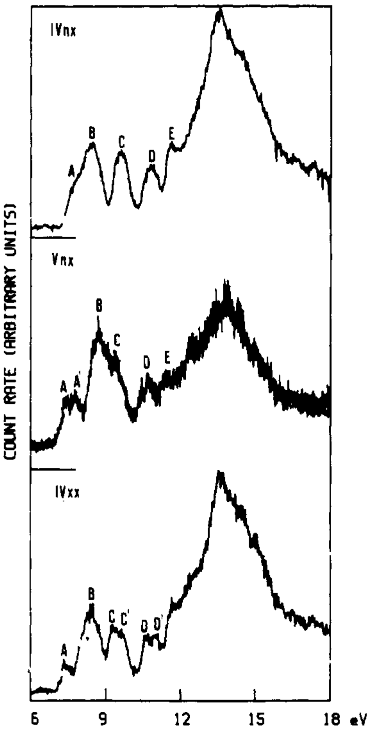

Figure 5. He I PE spectra of IVnx, Vnx, and IVxx omobimetallic complexes.

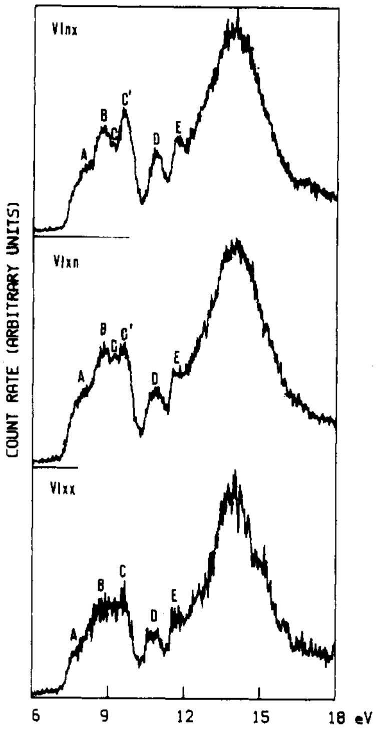

Figure 6. He I PE spectra of VInx, VIxn, and VIxx heterobimetallic complexes.

free diene and that $\Delta\pi_1$ (IE(π_1^c) – IE(π_1^f)) and $\Delta\pi_2$ (IE(π_2^c)– IE(π_2^f)) are fairly constant along the studied series ($\Delta\pi_1 = 0.22 \pm 0.06$ eV; $\Delta\pi_2 = 0.89 \pm 0.07$ eV[18]).

As a starting point for the following discussion of our PE data, we will adopt Worley's model. Some minor criticism to this approach will be proposed, however, when the theoretical results reported in the next paragraph will be considered. On this basis it is assumed that in the mononuclear complexes the ionizations from the π_2^f and π_1^f MOs (i.e., from MOs mainly localized on the uncomplexed butadiene group) lies near to the middle of the energy range spanned by the corresponding ionizations of the free ligand[19] whereas those from the π_2^c and π_1^c MOs are expected at higher IEs.

Let us examine first the data of the iron complex IIx (Figure 3). We propose to assign the ionizations from π_2^f and π_2^c MOs to the B and C bands, respectively, and analogously ionizations from π_1^f and π_1^c MOs to the broad band D. Furthermore, intensity considerations on IIx and VIIx spectra (the latter not having a π_b MO) (Figure 3) and comparison with the free ligands Ia and Ib[16] lead us to assign also π_b ionization to band C. Band A and part of band B are to be related to the metal-based 3d ionizations (one M → π_3* and three "d" lone-pair orbitals). The high "d" contributions to these bands is confirmed by the examination of the He II excited PE spectrum (Figure 3) which shows a remarkable increase of the relative intensities of these bands with respect to the higher IE ones.[20]

The proposed assignments for the iron complex IIn (Figure 3) are reported in Table I. The more marked difference between the spectra of isomers IIx and IIn is the intensity decrease and the lower IE shift of band D. We tentatively (vide infra) assign band D of IIn to ionization from π_1^f MO while the ionization from π_1^c is assumed to be hidden under the subsequent broad band E. The corresponding $\Delta\pi_2$ and $\Delta\pi_1$ parameters for IIx and IIn are $\Delta\pi_1^n = 0.80$ eV, $\Delta\pi_1^x < 0.20$ eV, $\Delta\pi_2^n = 0.94$ eV, and $\Delta\pi_2^x = 0.76$ eV. Only the $\Delta\pi_1^n$ value is substantially different from the parameters derived by Worley et al.[18]

The assignment proposed for the corresponding Ru(CO)$_3$ IIIx and IIIn complexes are reported in Table I.[22,23] With respect to the iron analogues, the intensity of the band associated with metal-based "d" ionization (band B in Figure 4) is increased as a consequence of the "heavy metal effect".[24] Furthermore, it is now possible to resolve band A that we associate to the M → π_3* back-bonding interaction.

The larger energy separation between band A and the band associated with the "d" ionizations in the Ru complexes can be explained in term of a decrease of the relaxation contribution for the 4d orbitals compared to the 3d ones.[25] As a whole, however, the same endo/exo differences found in the iron analogues are also found in the ruthenium isomers.

The spectra of the bimetallic trans complexes (Figures 5 and 6) can be easily interpreted as a superimposition of those of the endo and exo monometallic isomers. The bands associated with metal "d" based MOs will increase in intensity with respect to the ligand-based ionizations (due to the presence of two metal atoms), and the bands associated with π_1^f and π_2^f MOs will dissapear (Table I). For example, the spectrum of IVnx can be interpreted by assigning band C and D to ionization from the π_2^c and π_1^c MOs of both butadiene units, respectively. The cis hetero complex VIxx has a lower symmetry than the analogous omobinuclear complex IVxx, and it belongs to the C_s group

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(19) It is assumed that the symmetry lowering due to the Fe(CO)$_3$ group cancels the splitting originated by the "through-space" and "through-bond" interactions.

(20) In fact, on the basis of the Gelius model[21] we expect a marked decrease in the photoionization cross-section ratio $\sigma(C_{2p})/\sigma(Fe_{3d})$ on passing from the He I to He II excitation source.

(21) Gelius, U. In "Electron Spectroscopy"; Shirley, D. A., Ed.; North Holland Publishing Co.: Amsterdam, 1972.

(22) The He I PE spectrum of (butadiene)tricarbonylruthenium has been reported in ref 23. Contrary to the proposed assignments we prefer to associate just one M → π_3* ionization to the lowest IE band.

(23) Worley, S. D.; Webb, T. R.; Ou, T. Y. *J. Electron Spectrosc. Relat. Phenom.* **1982**, *28*, 129.

(24) Evans, S.; Green, M. L. M.; Jewitt, B.; Orchard, A. F.; Pigall, C. F. *J. Chem. Soc., Faraday Trans. 2* **1972**, 1847.

(25) Wong, K. S.; Dutta, K. T.; Fehlner, T. P. *J. Organomet. Chem.* **1981**, *215*, C48.

Table IV. Minimal Basis Set Pseudopotential ab Initio MOs of IIn

MO	eigenvalue	Fe	2 C_1	2 C_2	2 C_3	2 C_4	2 C_5	2 C_6	3 CO	12 H	descript
29a′	−8.09	24	0	1	17	43	0	3	11	1	$M \rightarrow \pi_3^*$
20a″	−11.51	10	1	0	14	57	5	10	3	0	π_2^c
19a″	−11.85	2	2	3	4	9	25	53	1	1	π_2^f
28a′	−12.64	5	2	75	5	3	5	3	1	1	π_b
27a′	−13.64	45	2	9	16	10	4	1	12	1	$d(a_1)$
26a′	−14.39	18	5	0	16	6	29	21	3	2	$\pi_1^{f,c}$
18a″	−14.75	66	4	0	6	8	2	1	10	3	$d(e^a)$
25a′	−15.23	39	3	6	14	5	18	10	3	2	$\pi_1^{f,c}$
24a′	−15.34	59	3	3	7	5	7	3	10	3	$d(e^s)$
23a′	−15.76	1	18	6	24	12	13	5	1	20	σ

Table V. Minimal Basis Set Pseudopotential ab Initio MOs of IIx

MO	eigenvalue	Fe	2 C_1	2 C_2	2 C_3	2 C_4	2 C_5	2 C_6	3 CO	12 H	descript
29a′	−8.03	24	0	1	18	43	1	1	11	1	$M \rightarrow \pi_3^*$
20a″	−11.30	2	1	1	2	8	27	58	0	1	π_2^f
19a″	−11.62	11	1	2	15	57	4	6	3	1	π_2^c
28a′	−12.98	2	2	70	4	3	10	8	0	1	π_b
27a′	−13.38	38	4	6	16	11	9	5	8	3	$d(a_1)$
26a′	−14.44	21	1	6	4	0	39	25	4	0	π_1^f
18a″	−14.84	66	4	2	6	9	1	0	9	3	$d(e^a)$
25a′	−14.89	24	9	3	31	11	10	3	2	7	π_1^c
24a′	−15.32	78	0	0	1	4	1	0	13	3	$d(e^s)$
23a′	−15.77	6	14	7	25	15	11	5	1	16	σ

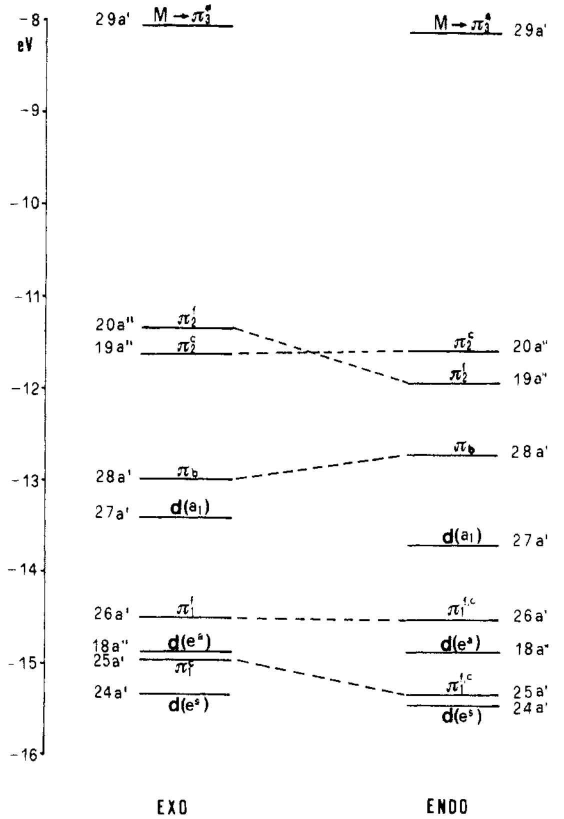

Figure 7. Comparison between the ab initio computed eigenvalues of IIx and IIn complexes.

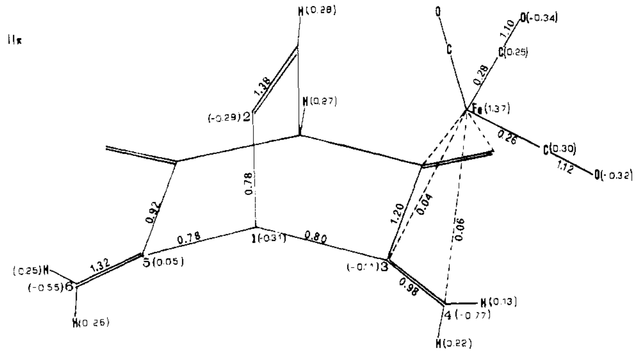

Figure 8. Ab initio gross atomic charges (in parentheses) and overlap populations of IIx complex obtained by Mulliken's population analysis.

as the trans complexes examinated above; thus its spectrum (Figure 6) can be interpreted following the same method as for the trans complexes (Table I).

On the contrary, the PE spectrum of IVxx cannot be interpeted as being derived from two independent Fe–butadiene systems. Band A is shifted toward lower IE and bands C and D are separated into two components (Figure 5). The origin of these differences is the high symmetry (C_{2v}) which is typical of the free ligand. By analogy with the interpretation invoked for the free ligand, we will find the π_1^c and π_2^c components split by operation of "through-bond" and "through-space" interactions.[15] Therefore, band C is to be related to the ionization of π_b and $\pi_2^c(a_2)$ MOs, shoulder C′ is to be related to $\pi_2^c(b_1)$ MO, and bands D and D′ are to be related to $\pi_1^c(b_2)$ and $\pi_1^c(a_1)$ MOs, respectively. Bands A and B are again associated to the metal "d" based MOs.

Ab Initio Results for Exo and Endo Fe(CO)$_3$ Complexes. The reported analysis of the PE data reveals significant differences in the spectra of endo and exo isomers. In order to elucidate the origin of such differences, we have carried out ab initio calculations for IIn and IIx (Tables IV and V). Due to the well-known importance of the reorganization contributions for the calculations of IEs of metal complexes (breakdown of Koopmans' theorem[26]) and of the quality of the basis set employed (minimal), we will only use the ab initio results in a comparative manner (exo/endo ground-state comparison) and no attempt to compare the theoretical data with the experimental PE ones will be ventured.

The MOs mainly describing the π system of the ligand can be clasified as π^f or π^c according to their localization degree on the free or complexed butadiene moieties. However, from an examination of Tables IV and V it appears that such a discriminatory criterion is usable only in the case of IIx (Table V). In the case of IIn the 26a′ and 25a′ MOs are both delocalized over the free and complexed butadiene groups (Table IV). It is interesting to

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(26) See, for example, the discussion of: Böhm, M. C. *Theor. Chim. Acta* **1982**, *61*, 539.

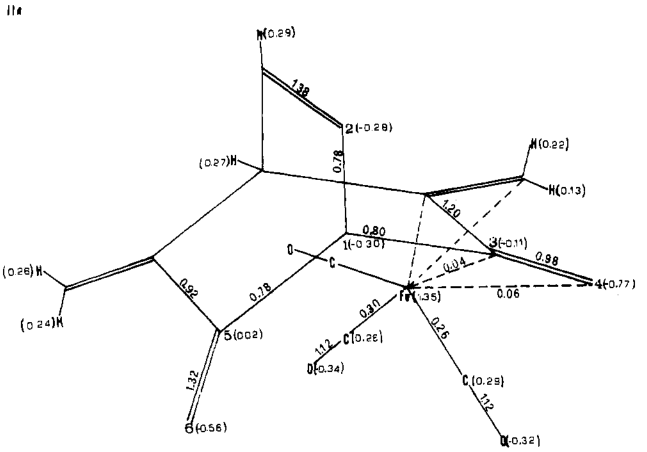

Figure 9. Ab initio gross atomic charges (in parentheses) and overlap populations of IIn complex obtained by Mulliken's population analysis.

note that such behavior is exhibited by those MOs whose corresponding PE bands were not in agreement with the expectations based on Worley's model (see previous paragraph). Since this mixing is present only for the π_1 MOs of the endo isomer, we may suggest some active role of the $Fe(CO)_3$ group in the endo position. The reason why such a mixing is evident only in the π_1 and not in the π_2 orbitals could be ascribed to the larger localization of the π_1 orbitals on the internal C_3 and C_5 atoms of the two butadiene moieties (which are close to the $Fe(CO)_3$ group).

The outermost occupied levels of the two isomers are compared in Figure 7. Remarkable differences are found although the gross features of $Fe(CO)_3$–butadiene bonding is similar in both cases. These differences do not result in significant differences in the net atomic charges and total overlap populations of the two complexes (see Figures 8 and 9). Hence we interpret the aforesaid differences in the eigenvalues (Figure 7) as reflecting minor long-range electrostatic effects. In fact, assuming the $Fe(CO)_3$ group as a positively charged group, we can interpret qualitatively the stabilization of $\pi_2{}^f$ and the destabilization of $\pi_b{}^{27}$ on going from IIx to IIn as an electrostatic energy shift, visible only for those MOs not directly involved into the bonding with the $Fe(CO)_3$ group.

As a final consideration derived from these theoretical results, we would like to comment on the model used to interpret the complexation shifts of the PE bands assigned to ligand-based MOs. Worley et al.[18] derived such complexation shifts comparying the PE spectra of the free and complexed ligands; caution is needed in extrapolating those shifts and their significance to molecules containing two ligating groups (one free and one complexed). In fact, the present theoretical results show that to assign band D in the PE spectrum of IIn to the $\pi_1{}^f$ MO is an unaccettable oversimplification due to the mentioned mixing between the $\pi_1{}^c$ and $\pi_1{}^f$ MOs.

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Registry No. Ia, 95017-43-9; IIx, 72983-28-9; IIn, 72984-40-8; IIIx, 72924-38-0; IIIn, 75597-78-3; IVnx, 63945-85-7; IVxx, 63976-22-7; Vnx, 75528-84-6; VInx, 75528-83-5; VIxn, 75597-80-7; VIxx, 75597-79-4; VIIx, 71520-86-0; $Fe(CO)_3$–butadiene, 12078-32-9.

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(27) According to the results of the Mulliken's population analysis, no direct interaction of π_b with the $Fe(CO)_3$ groups is to be claimed.

Synthesis of Five- and Six-Membered Ylide–Chelate Complexes by the Reaction of Pentacarbonyl(dimethyloxosulfonium methylide)chromium(0) with Bis(arsines) of the Type $(R_2As)_2X$ (X = C=PPh$_3$, NMe, O, S) and 1,2-Ethylenebis(phosphines) and -bis(arsines)[1]

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The reaction of $(R_2As)_2X$ (X = C=PPh$_3$, NMe, O; R = Me, Ph) with $Cr(CO)_5[CH_2S(O)Me_2]$ in toluene at 45 °C results in the formation of a series of arsonium ylide–chelate complexes $(CO)_4\overline{CrCH_2AsR_2XAsR_2})$. The complex derived from $(Ph_2As)_2O$ is converted into $(CO)_4\overline{CrCH_2As(Ph)_2SAsPh_2}$ by treatment with gaseous hydrogen sulfide. The reactions of $R^1{}_2E^1CH_2CH_2E^2R^2{}_2$ (E = P, As; R = Me, Ph) with $Cr(CO)_5[CH_2S(O)Me_2]$ afford novel six-membered ylide–chelate complexes of the type $(CO)_4\overline{CrCH_2E^1R^1{}_2(CH_2)_2E^2}R^2{}_2$ as well as the known five-membered chelates $(CO)_4\overline{CrE^1R^1{}_2(CH_2)_2E^2}R^2{}_2$. The novel coordination compounds have been characterized by elemental analysis and infrared, proton, and phosphorus NMR spectroscopy.

Introduction

The work reported here is a result of our continuing interest in the synthesis and reactivity of transition metal–sulfur ylide complexes.[2] Thus recently we reported the preparation of five-membered metallaheterocycles of the type $(CO)_4\overline{CrCH_2ER_2CH_2E}R_2$ by treatment of the sulfur ylide complex $Cr(CO)_5[CH_2S(O)Me_2]$ (**1**) with methylenebis(phosphines) and $(Ph_2As)_2CH_2$ (**2a**) (eq 1).[3,4] These

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(1) Transition Metal Complexes of Unstable Ylides. 6. For part 5, see: Weber, L.; Wewers, D. *Chem. Ber.* **1985**, *118*, 541.

(2) Weber, L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 516.

(3) Weber, L.; Wewers, D.; Meyer, W.; Boese, R. *Chem. Ber.* **1984**, *117*, 732.