ion pair. Other mixed fluoroborates are feasible in this system; the spectral data do not provide a means for positive identification, and indeed that was not the intent of this study.

Conclusions

The present study has provided the first spectroscopic evidence for the existence, although limited, of the $CO_2F_2^{2-}$ anion. The spectra also suggest that TlF elimination to form the Tl^+ CO_2F^- is very facile, even at the very low temperatures employed. By comparison, no evidence was found for a discrete BF_3O^{2-} anion, casting serious doubt on reports of the room-temperature synthesis of this species. Beyond these findings, this study demonstrates that the competing pathway of TlF elimination is sufficiently favored that the stabilization of mixed oxyfluoride anions of a 2− charge is difficult and in many cases not feasible. By comparison, those systems where the oxide-transfer technique was most effective in producing a distinct anionic species were those where electron delocalization could occur through a π-bonding network.[7-9]

Acknowledgment. The authors gratefully acknowledged support of this research by the National Science Foundation under Grant CHE 8400450. B.S.A. also acknowledges the Dreyfus Foundation for a Teacher-Scholar Grant.

Contribution from the Istituto di Chimica e Tecnologia dei Radioelementi del CNR, Padova, Italy,
Istituto di Chimica Generale ed Inorganica, University of Padova, 35100 Padova, Italy,
and Istituto di Chimica Generale ed Inorganica, University of Torino, Torino, Italy

Electronic Structure of Ferracyclopentadienyl Derivatives. UV PES and ab Initio Study of $Fe_2(\mu\text{-}CO)(CO)_5(C_4R_4)$ and $Fe_3(\mu\text{-}CO)_2(CO)_6(C_4R_4)$

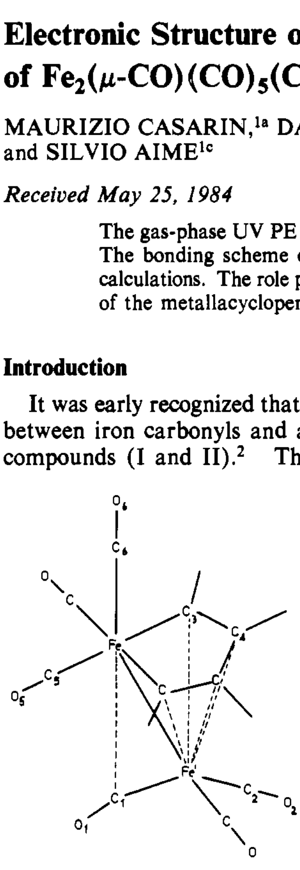
MAURIZIO CASARIN,[1a] DAVID AJÒ,[1a] GAETANO GRANOZZI,*[1b] EUGENIO TONDELLO,[1b]
and SILVIO AIME[1c]

Received May 25, 1984

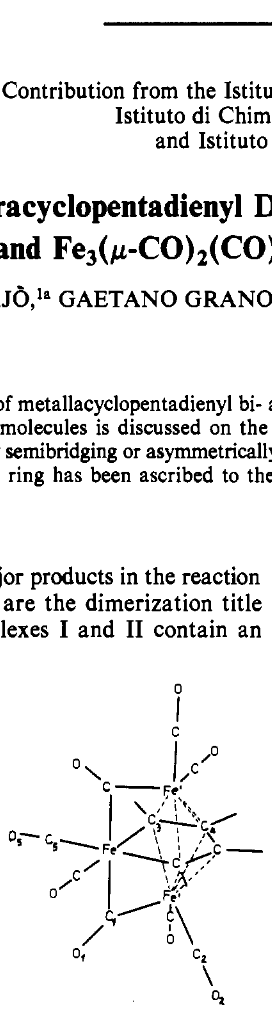
The gas-phase UV PE spectra of metallacyclopentadienyl bi- and trinuclear derivatives of Fe and Ru are reported and discussed. The bonding scheme of these molecules is discussed on the basis of theoretical results obtained by pseudopotential ab initio calculations. The role played by semibridging or asymmetrically bridging carbonyl groups has been clarified. The very high stability of the metallacyclopentadienyl ring has been ascribed to the presence of a very strong M–C interaction, only σ in character.

Introduction

It was early recognized that the major products in the reaction between iron carbonyls and alkynes are the dimerization title compounds (I and II).[2] The complexes I and II contain an identical structural arrangement of the metallacyclopentadienyl FeC_4 system, and compound II can be envisaged as the result of the addition of an $Fe'(CO)_3$ unit to the type I compound. The X-ray structure determination of $Fe_2(CO)_6[C_4(CH_3)_2(OH)_2]$, reported by Hock and Mills in 1961,[3] revealed the first example of a molecule containing a semibridging carbonyl group; it was shown that one of the CO groups exhibits an anomalous behavior since the $Fe'–C_1–O_1$ angle (see structures I and II) is only 168° and the distance between the ring Fe atom and C_1 amounts to 2.48 Å, which is rather low for two nonbonded atoms. Subsequent X-ray investigations on similar compounds showed the same peculiarity.[4] Cotton[5] proposed to interpret this behavior on the basis of electronic arguments: adopting the validity of the EAN rule, he suggested a Fe′→Fe dative bond and the consequent relief of the charge excess of Fe by back-donation to $\pi^*_{\parallel}$ of $C_1–O_1$ (hereafter ∥ and ⊥ symbols refer to the plane passing through metal atoms and bridging or semibridging carbonyls).[6] The agreement on this explanation, however, is not general since very recently[4g] some authors proposed to ascribe the bending of $Fe'–C_1–O_1$ to steric hindrance. The presence of two different types of iron atoms was also assessed by Mössbauer spectroscopy,[7] and the fluxional behavior of the $Fe'(CO)_3$ group was investigated by VT ^{13}C NMR spectroscopy.[8] It was shown that the "frozen" structure containing the semibridging carbonyl can be detected only at low temperature.



I



II

An X-ray determination of a type II structure was reported by Dodge et al.[9] for $Fe_3(CO)_8(C_4Ph_4)$; the metallic frame corresponds to an open triangle whose two edges are asymmetrically bridged by CO groups and the metallacycle is perpendicularly crossing the Fe_3 plane. Furthermore, the VT ^{13}C NMR spectra showed that a localized CO exchange at each $Fe'(CO)_3$ unit is occurring in the reported range of temperature.[10]

These interesting features prompted us to seek new theoretical and spectroscopic evidence in order to obtain a more detailed

---

(1) (a) CNR of Padova. (b) University of Padova. (c) University of Torino.

(2) (a) Hübel, W.; Braye, E. H. *J. Inorg. Nucl. Chem.* **1959**, *10*, 250. (b) Braye, E. H.; Hübel, W. *J. Organomet. Chem.* **1965**, *3*, 25.

(3) Hock, A. A.; Mills, O. S. *Acta Crystallogr.* **1961**, *14*, 139.

(4) (a) Epstein, E. F.; Dahl, L. *J. Am. Chem. Soc.* **1970**, *92*, 493. (b) Degrêve, P. Y.; Meunier-Piret, J.; Van Meerssche, M.; Piret, P. *Acta Crystallogr.* **1967**, *23*, 119. (c) Prince, S. R. *Cryst. Struct. Commun.* **1976**, *5*, 451. (d) Todd, L. J.; Hickey, J. P.; Wilkinson, J. R.; Huffman, J. C.; Folting, K. *J. Organomet. Chem.* **1976**, *112*, 167. (e) Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 5068. (f) Noda, I.; Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1983**, *250*, 447. (g) Astier, A.; Daran, J. C.; Jeannin, Y.; Rigault, C. *J. Organomet. Chem.* **1983**, *241*, 53.

(5) Cotton, F. A. *Progr. Inorg. Chem.* **1976**, *21*, 1.

(6) (a) In 1965 Kettle proposed on the basis of symmetry arguments that the deviation from a linear M–C–O structure is a function of the difference in occupation of the two π* orbitals.[6b] (b) Kettle, S. F. A. *Inorg. Chem.* **1965**, *4*, 1661.

(7) Emerson, G. F.; Mahler, J. E.; Pettit, R.; Collins, R. *J. Am. Chem. Soc.* **1964**, *86*, 3590.

(8) Aime, S.; Milone, L.; Sappa, E. *J. Chem. Soc., Dalton Trans.* **1976**, 838.

(9) Dodge, R. P.; Schomaker, V. *J. Organomet. Chem.* **1965**, *3*, 274.

(10) Aime, S.; Milone, L.; Sappa, E. *Inorg. Chim. Acta* **1976**, *16*, L7.

0020-1669/85/1324-1241$01.50/0

Table I. Pseudopotential Parameters for Iron, Carbon, and Oxygen Atoms[a]

atom	l	α	n_i	a_i
Fe	0	2.639 18	0	34.070 27
			2	−13.600 79
			4	48.267 84
	1	0.769 38	0	16.303 32
			2	−6.561 82
			4	0.707 34
	2	2.344 58	−1	−11.420 62
			0	15.421 12
			2	−15.239 66
C	0	5.330 46	−1	1.369 25
			0	21.035 11
	1	14.061 16	0	−6.052 01
O	0	10.373 87	−1	1.647 68
			0	45.078 23
	1	25.320 09	0	−7.790 73

[a] See text for definitions.

Table II. Orbital Exponents and Coefficients of the Minimal Gaussian Basis Set for Iron, Carbon, and Oxygen Atoms

atom	orbital	exponent	coeff
Fe	4s	0.537 72	−0.422 45
		0.164 92	0.727 13
		0.063 22	0.558 14
	4p	0.917 07	−0.112 05
		0.221 57	0.578 22
		0.083 53	0.535 96
	3d	21.589 62	0.071 56
		6.151 47	0.275 55
		1.896 23	0.502 70
		0.587 53	0.399 51
		0.163 25	0.099 71
C	2s	2.382 01	−0.242 14
		1.443 06	0.185 26
		0.405 85	0.591 28
		0.138 43	0.454 70
	2p	8.609 57	0.043 65
		1.943 55	0.209 50
		0.542 80	0.502 76
		0.152 50	0.469 54
O	2s	5.799 12	−0.137 73
		1.298 34	0.292 95
		0.547 30	0.531 22
		0.226 13	0.302 85
	2p	12.655 16	0.068 20
		2.953 70	0.274 40
		0.886 19	0.482 32
		0.259 96	0.416 02

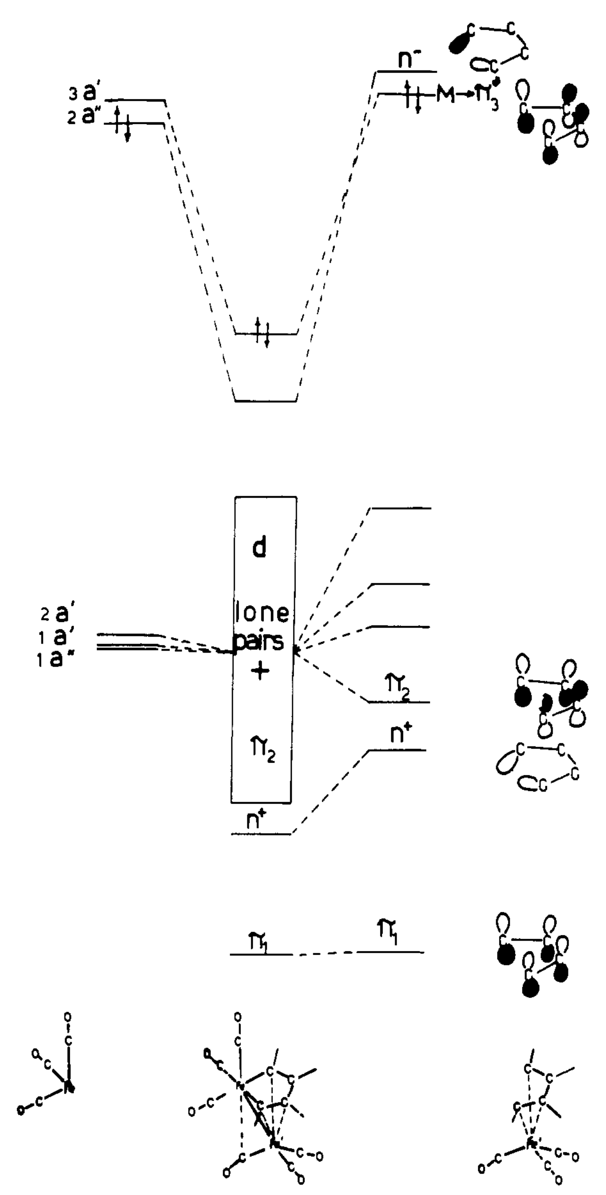


Figure 1. EHT orbital interaction diagram for $Fe_2(CO)_6(HC_2H)_2$.

picture of the metallacycle bonding mechanism and to assess the role played by the semibridging and asymmetrically bridging carbonyl groups. We report here the gas-phase UV photoelectron (PE) spectra of compounds I and II together with the results of quantum-mechanical calculations. In order to obtain theoretical results at ab initio quality level for such complex molecules, we have adopted the valence-only pseudopotential method[11] with a minimal basis set. This method has received a preliminary testing on iron tricarbonyl butadiene comparing our results with all-electron literature results.[12]

Experimental Section

Compounds $Fe_2(CO)_6(C_4R_4)$ (I), $Fe_3(CO)_8(C_4R_4)$ (II), and $Ru_3(CO)_8(C_4R_4)$ (III) (where R = H (I), C_2H_5 (I′, II, III)) were prepared according to the methods detailed in the literature.[13]

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 1 s^{-1} self-ionization. A heated inlet probe system was adopted at 40–60 °C for compounds of type I and 110–130 °C for types II and III. The IE's reported in the figures are the mean values over several distinct runs.

The ab initio LCAO–MO–SCF calculations were performed with the introduction of pseudopotentials to deal with all core electrons on each atom. The Barthelat et al. formalism[14] has been chosen, 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 are reported in Table I. A minimal basis set was optimized for each valence shell by a pseudopotential version of the ATOM program[15] (Table II). The standard Huzinaga[16] Gaussian basis set was used for hydrogen atoms. The reliability of both pseudopotentials and basis sets was checked[17] against the all-electron ab initio calculation (minimal basis set) on $Fe(CO)_3C_4H_6$ published by Connor et al.[12] All the molecular calculations were carried out by running the PSHONDO program[18] on a VAX-11/780

---

(11) See, for example: Kahn, L. R.; Baybutt, P.; Truhlar, D. G. *J. Chem. Phys.* **1976**, *65*, 3826.

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

(13) Hübel, W. In "Organic Synthesis via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Interscience: New York, 1968; Vol. 1.

(14) Barthelat, J. C.; Durand, P.; Serafini, A. *Mol. Phys.* **1977**, *33*, 159.

(15) Roos, B.; Salez, C.; Veillard, A.; Clementi, E. "A General Program for Calculation of Atomic SCF Orbitals by the Expansion Method", Technical Report RJ518; IBM: Armonk, NY, 1968.

(16) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(17) Lorenzoni, E.; Granozzi, G., unpublished work.

Table III. Pseudopotential ab Initio Results for $Fe_2(CO)_6(HC_2H)_2$[a]

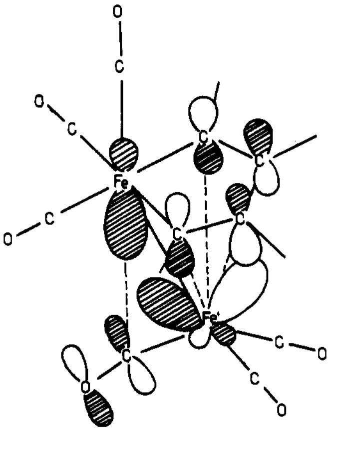
MO	eigenvalue, eV	population, % Fe	Fe′	$2\,C_3$	$2\,C_4$	4 H	C_1O_1	5 CO	dominant character
29a′ (HOMO)	−7.61	17	24	25	9		17	8	Fe-Fe′ bond + π^*_3 + $\pi^*_{\parallel}$ (C_1O_1)
19a″	−9.90	6	15	52	22		2	3	π_2
18a″	−11.69	17	4	60	7	9		3	n^-
28a′	−12.18	7	42	27	7	7	1	9	3d t_{2g}-like MO's + n^+
27a′	−12.58	33	16	15	14	4	6	12	
26a′	−13.41	60	13	6	7	5	1	8	3d t_{2g}-like MO's
17a″	−13.64	1	66	8	6	4	9	6	
25a′	−13.95	47	29	7	5		4	8	
16a″	−14.50	80	1	5	1		1	12	
24a′	−14.55	12	13	18	48			9	π_1
23a′	−14.95	12	62	7	6	4		9	3d t_{2g}-like MO

[a] See structure in the text for atom numbering.

computer (running time for I ca. 12 h). Extended Hückel type (EHT) calculations have been performed with adoption of the literature parameters.[19] The geometrical parameters used in the calculation were taken from the X-ray structural determinations of related compounds.[3,9] Actual calculations were performed for molecules in which R = H. The molecular symmetry of I and II refers respectively to C_s and C_{2v} point groups. Gross atomic charges and bond overlap populations were obtained by Mulliken's population analysis.[20]

Results and Discussion

A first qualitative picture of the interaction mechanism in I can be obtained from Figure 1, where an EHT interaction diagram is reported. The whole molecule has been built up from the two $Fe(CO)_3$ (Ia) and $Fe'(CO)_3C_4H_4$ (Ib) fragments, which maintain the same geometry (C_s symmetry) of I. The choice of these fragments, different from that adopted by Thorn and Hoffmann,[19] where the $Fe_2(CO)_6$ moiety interacts with C_4H_4, allows us to detect the perturbations induced by Ia on the "biradical" Fe′–butadiene fragment levels. The orbitals of Ia are grouped in two sets (3a′ + 2a″ and 1a′ + 2a′ + 1a″ in Figure 1), which are reminiscent of e_g-like and t_{2g}-like MO's of the symmetric C_{3v} iron tricarbonyl fragment. The energy levels of Ib are the well-known levels of iron tricarbonyl butadiene (i.e. $Fe' \rightarrow \pi^*_3,\pi_2,\pi_1$ and t_{2g}-like metallic MO's)[21] perturbed by the absence of two hydrogen atoms; as a consequence we find two further MO's, representing respectively the in-phase occupied (n^+) and out-of-phase empty (n^-) linear combinations of the "radical lobes" pointing toward the incoming Fe atom. This n^- empty orbital interacts with the 2a″ orbital of Ia while the HOMO of Ib is strongly mixed with the LUMO of Ia; the resulting HOMO for the whole molecule is highly delocalized and it represents at the same time Fe′→Fe, $Fe' \rightarrow \pi^*_3$, and $Fe \rightarrow \pi^*_{\parallel}$ C_1–O_1 interactions:



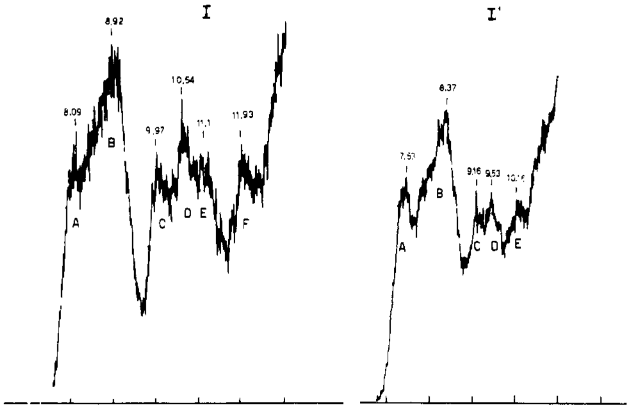


Figure 2. He I excited PE spectra of $Fe_2(CO)_6(HC_2H)_2$ (I) and $Fe_2(CO)_6(EtC_2Et)_2$ (I′).

The above EHT scheme has been of value in the analysis of the quantitative results obtained through the ab initio method. In Table III the eigenvalues and the population percentage analysis of the 11 outermost MO's are listed. The 29a′ HOMO describes the same type of interactions already anticipated by the EHT results: note the high C_1–O_1 contribution (17%) in accordance with the back-donation mechanism involving the semibridging carbonyl. Furthermore, the direct metal–metal interaction is predicted to be rather bent: the contribution of 29a′ to the total Fe–Fe′ overlap population is 0.06 e (rather high for a first-transition-series metal–metal bond). According to the ab initio results, the 18a″ (n^-) and 28a′ and 27a′ MO's (both having n^+ character) contribute to the bonding of Fe with the organic part of Ib. The 28a′ MO, however, carries also a significant nonbonding 3d character from the Fe′ atom. In contrast with the EHT results for the whole molecular system I, the 19a″ MO (π_2) lies at higher energy with respect to 18a″ (n^-). As far as the π interaction between Fe′ and C_4H_4 is concerned, no significant difference with respect to the usual iron–butadiene bonding scheme is found (29a′, 19a″, and 24a′ MO's). The remaining MO's maintain an iron-like character (3d lone pairs) with a large degree of localization. However, one has to recall for the discussion that follows the well-known limitation of the Koopmans theorem[22] arising from larger relaxation effects during the ionization processes for 3d metal-like MO's with respect to the delocalized ones.[23] For this reason the above ab initio results are used only for the description of the neutral ground state and for the discussion of the PE spectra but no attempt to use the numerical values from the calculations to reproduce the experimental IE's will be made.

We can now relate the interpretation of the PE spectra of I and I′ reported in Figure 2, where bands are alphabetically labeled. Only the IE region below 11.5 eV is reported in the figure since

---

(18) A version of the HONDO program (Dupuis, M.; Rys, J.; King, M. F. Quantum Chemistry Program Exchange, Indiana University; Program 336) including pseudopotentials modified by J. P. Daudey.

(19) Thorn, D. L.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 126.

(20) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1823.

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

(22) Koopmans, T. *Physica* **1933**, *1*, 104.

(23) For a recent discussion, see: Bohm, C. M. *Theor. Chim. Acta* **1982**, *61*, 539.

Table IV. Pseudopotential ab Initio Results for $Fe_3(CO)_8(HC_2H)_2$[a]

MO	eigenvalue, eV	population, %							dominant character
		Fe	2 Fe′	2 C_3	2 C_4	4 H	2 C_1O_1	6 CO	
$22a_1$ (HOMO)	−7.73	21	8				56	15	$Fe \rightarrow \pi^*_\parallel (C_1O_1)$
$15b_2$	−8.93	7	25	24	10		27	7	$Fe' \rightarrow \pi^*_3 + \pi^*_\parallel (C_1O_1)$
$10a_2$	−11.82	10	24	46	18		1	1	π_2
$14b_2$	−11.98	29	40	1	10		8	12	3d t_{2g}-like MO
$15b_1$	−12.11	10	18	56	6	7		3	n^-
$21a_1$	−12.34		66	11	3	2	3	15	3d t_{2g}-like MO's
$13b_2$	−13.33	40	32	2			13	13	
$20a_1$	−13.48	40	16	21		7	4	12	
$14b_1$	−13.76	1	53	8		3	33	2	3d t_{2g}-like MO's + $\pi_\perp (C_1O_1)$
$9a_2$	−13.87	33	21		1		44	1	
$19a_1$	−14.25	30	50	1	2	1	4	12	3d t_{2g}-like MO's
$8a_2$	−14.58	26	47	10	9			8	
$12b_2$	−14.64	1	77	1	2		4	15	
$18a_1$	−15.40	21	26	24	11	5	6	7	n^+ + 3d
$13b_1$	−15.74	1	19	4		2	58	16	$\pi_\perp (C_1O_1)$
$7a_2$	−16.18	20	12	1			45	22	
$11b_2$	−16.43	1	15	12	52		7	13	π_1

[a] See structure in the text for atom numbering.

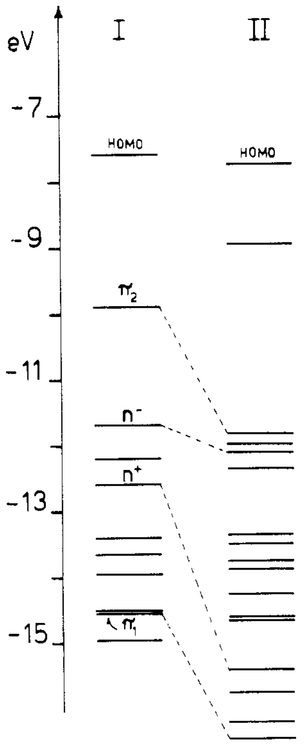
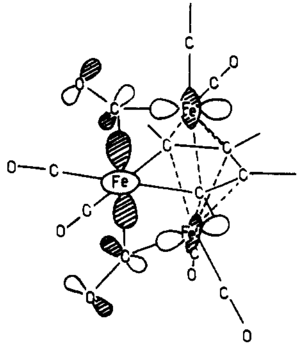


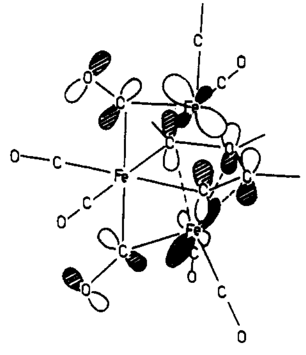
Figure 3. Comparison between ab initio eigenvalues for $Fe_2(CO)_6(HC_2H)_2$ (I) and $Fe_3(CO)_8(HC_2H)_2$ (II).

the higher IE region consists of very ill-resolved structures primarily due to ionization from iron–CO σ-bonding MO's and 1π and 4σ CO-localized levels. The analysis of this region is unproductive and is out of the scope of this paper.

No doubt exists in relating bands C–F of I and bands C–E of I′ to ionizations deriving from C_4R_4-localized MO's because of their dramatic intensity decrease in the He II spectra.[24] In the case of I we propose to assign these bands respectively to π_2 (19a″), n^- (18a″), n^+ (27a′), and π_1 (24a′) ionizations; the broad band B is to be related, in turn, to ionization from the six iron-like 3d pairs. The band A is then related to the ionization from the 29a′ HOMO. Two experimental evidences confirm these hypothesis: (i) the comparison with the literature spectra of many other systems containing the $Fe_2(CO)_6$ subunit[26] and (ii) the $\Delta IE(\pi_2 - \pi_1)$ value, which agrees with data on iron butadiene complexes.[27] Furthermore, the comparison with the spectrum of I′ gives a support to the proposed assignments. In fact, it is very interesting to point out the very large shift of the bands assigned to ionizations from the MO's localized on the organic moiety (1.5–2 eV) with respect to that associated to metallike ionizations (ca. 0.5 eV), as a consequence of the electron-releasing effect of the ethyl groups. In particular, the bands assigned to π ionizations (C and F in I) are the most shifted so that the spectral pattern of I′ is easily rationalized if we admit that the π_2 ionization is hidden under the broad band B while C–E bands are respectively associated to n^-, n^+, and π_1 ionizations. Band A is again assigned to ionization from the HOMO (29a′ in I) although the increase of relative intensity of band A with respect to band B on passing from I to I′ suggests contribution also from one of the t_{2g}-like MO's.



22 a_1(HOMO)



15 b_2

The pseudopotential ab initio results for II are reported in Table IV, and the levels are compared with those of I in the diagram reported in Figure 3. The nature of two outermost $22a_1$ and $15b_2$ MO's reflects the changed role of the two bridging carbonyls. The $22a_1$ MO represents a concerted strong back-bonding interaction[28] from all iron atoms toward the $\pi^*_\parallel$ MO's of bridging carbonyls, not involving at all the organic moiety. In contrast, the inner $15b_1$ MO is more similar to the HOMO of I since it involves mainly

---

(24) In fact, on the basis of the Gelius model,[25] we expect a marked decrease in the cross-section ratio σ(C 2p)/σ(Fe 3d) on passing from the He I to the He II excitation source.

(25) Gelius, U. In "Electron Spectroscopy"; Shirley, D. A., Ed.; North-Holland: Amsterdam, 1972; p 311.

(26) (a) De Kock, R. L.; Baerends, E. J.; Oskam, A. *Inorg. Chem.* **1983**, *22*, 4158. (b) Granozzi, G.; Casarin, M.; Aime, S.; Osella, D. *Inorg. Chem.* **1982**, *21*, 4073.

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

(28) (a) Bénard, M. *Inorg. Chem.* **1979**, *18*, 2782. (b) Granozzi, G.; Tondello, E.; Bénard, M.; Fragalà, I. *J. Organomet. Chem.* **1980**, *194*, 83.

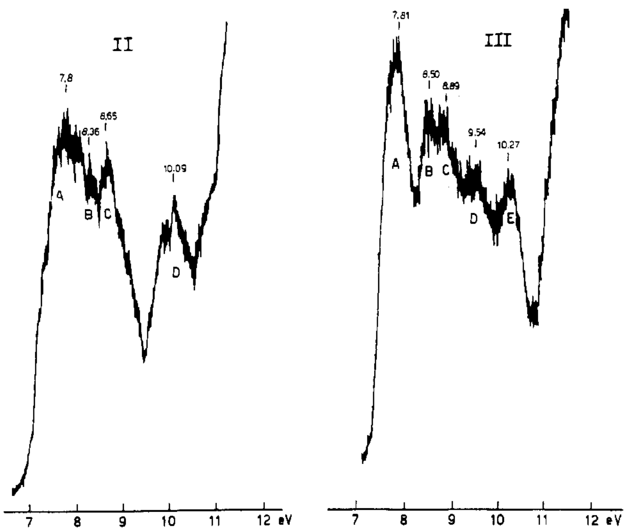


Figure 4. He I excited PE spectra of $Fe_3(CO)_8(EtC_2Et)_2$ (II) and $Ru_3(CO)_8(EtC_2Et)_2$ (III).

Fe′ atoms in the $Fe' \to \pi_3^*$ interaction. Neither of the two MO's shows significant direct Fe′–Fe bonding character.

Both π_2 ($10a_2$) and π_1 ($11b_2$) MO's of the metallacycle are strongly stabilized (by a similar extent) in II with respect to I (see Figure 3) because of the presence of the second interacting Fe′ atom. One unexpected difference between I and II is the larger stabilization of the n^+ ($18a_1$) orbital with respect to n^- ($15b_1$) one (see Figure 3). The different geometrical disposition of the ligands around the Fe atom in II (with respect to that in I) is responsible for this fact since an Fe d pair is now forced to mix with the n^+ combination. The nine t_{2g}-like MO's localized on the three iron atoms (see Table IV) lie in the same energy region of the corresponding ones in I (see Figure 3); among them, however, the $14b_1$ and $9a_2$ MO's show a relevant contribution from inner filled $\pi_\perp$ MO's of the two bridging carbonyls. This is not a peculiar feature of this molecule since it is common for molecular systems containing highly negative bridging carbonyls.[28,29] The bonding counterparts of these interactions are the inner $13b_1$ and $7a_2$ MO's, which lie in the same energy region as the π_1 $11b_2$ MO.

The experimental PE data of compounds II and III are reported in Figure 4. Obviously, the high number of ionization events occurring in the range of a few electron volts does not allow us to propose a detailed assignment of each of them. We can just suggest some rational assignments on the basis of the discussed theoretical trends, profiting from the comparison between PE data of II and III. In fact, often the analysis of PE spectra of complexes with same ligand and different isoelectronic metal atoms is a powerful tool for the assignments since one can use well-known trends in the properties of the metal atoms (such as photoionization cross-section and *n*d orbital energies). On the theoretical basis we suggest that π_1 and n^+ ionizations are hidden under the broad band beyond 11 eV (see Figure 4). Consequently, band D of II is related to both the n^- and π_2 MO's (it corresponds to band E in the Ru analogue), while the broad bands A–C contain the 11 ionizations from nine t_{2g}-like pairs and from $22a_1$ and $15b_2$ MO's. The same 11 ionization events span over four well-resolved bands in the Ru compound. Furthermore, band D of III gains intensity under the He II radiation source, indicating a high 4d metal character of the corresponding MO's. If we assume that the atomic percentage populations of Table IV are valid also for the Ru compound and that the differences in the relaxation energies of t_{2g}-like MO's are small, we can tentatively suggest the assignments of band D in III to ionization from $19a_1$, $3a_2$, and $12b_2$ MO's. Furthermore, we may suggest with confidence that band A contains ionization from the $22a_1$ HOMO and $15b_2$ MO.

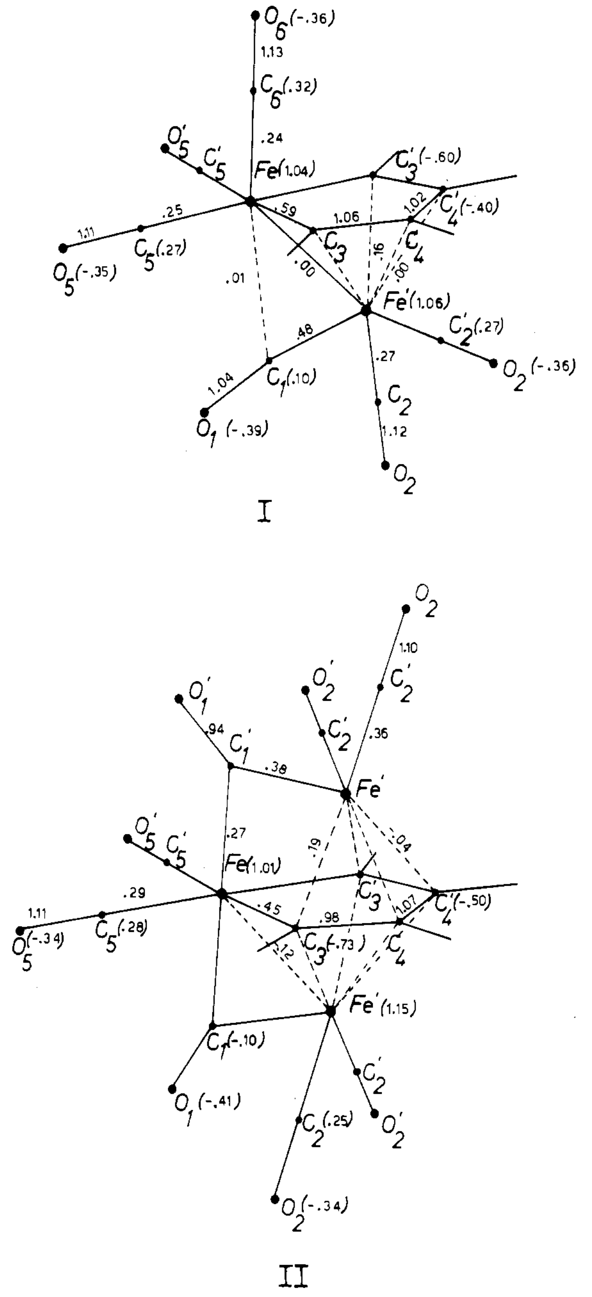


Figure 5. Ab initio gross atomic charges (in parentheses) and overlap populations of $Fe_2(CO)_6(HC_2H)_2$ (I) and $Fe_3(CO)_8(HC_2H)_2$ (II).

A deeper insight into the charge distribution and bonding interactions of the studied molecules can be obtained from the examination of Figure 5, where the gross atomic charges and overlap populations (OP's) obtained by the Mulliken population analysis[20] of the ab initio eigenvectors are reported. Most of these data are self-explainatory, but some of them warrant outlining.

The Fe and Fe′ gross atomic charges are very similar in both I and II despite their different chemical environments. This points to an efficient charge redistribution mechanism over the whole molecule primarily due to the presence of the σ/π-bonded organic moiety. However, the role played by the semibridging carbonyl in compound I is not negligible, as clearly shown by the high electron density residing on C_1. As a matter of fact, in a calculation carried out with an idealized sawhorse geometry[19] the charge unbalance between the iron atoms amounts to 0.2 e and the total energy is higher by about 4 kcal/mol. The two bridging carbonyls in compound II draw even more charge from metallic atoms (see Figure 5), so preventing any direct Fe–Fe′ interaction (OP(Fe–Fe′)

---

(29) The $\pi_\perp$ and $\pi_\parallel$ MO's peculiar to a bridging carbonyl have different behavior with respect to the interaction with the metal atoms. The $\pi_\parallel$ filled MO acquires a partial σ character and is stabilized with respect to the $\pi_\perp$ one. As a consequence the corresponding $\pi^*_\parallel$ virtual level is a better acceptor than the $\pi^*_\perp$ one.

= −0.12 e). The C_4H_4 moiety is more negatively charged in II (−1.78 e) than in I (−1.45 e), as expected for the presence of the second Fe′ atom. Furthermore, it is very interesting to compare the OP's of the metallacycles: in II we note an OP(C_4–C_4') value larger than OP(C_3–C_4) in contrast with the same quantities in I. Bearing in mind the bonding scheme between Fe′ and the organic moiety (see Figure 1), this is indicative that the π_3^* orbital is highly populated due to the back-bonding interactions with the two Fe′ atoms. Finally, we want to point out the very high value for the OP(Fe–C_3) both in I and in II even larger than the Fe–CO OP's. An accurate analysis of the eigenvectors shows that the π contributions to the Fe–C_3 interaction are negligible and that both n^+ and n^- combinations of the two radical lobes contribute to the bonding.

Concluding Remarks

The present paper points out the capability of the pseudopotential method to calculate, with relatively low computational efforts, the valence electronic structure at ab initio levels for molecules containing two or more transition metals. The theoretical results furnished a detailed picture of the bonding scheme in both I and II type molecules, clarifying the role played by the semibridging or asymmetrically bridging carbonyl groups.[30] In the dinuclear derivative the semibridging carbonyl contributes to the charge transferring from the iron atom in the ring, in accordance with Cotton's proposal.[5] In the trinuclear derivative direct metal–metal interactions are forbidden by the conversion of the semibridging into asymmetrically bridging carbonyl. The theoretical data also predict a high stability for the ferracyclopentadienyl ring due to a very strong Fe–C interaction only σ in nature. This is confirmed by the well-known chemical behavior of II, which decomposes at 150 °C to give I, where the ferracyclopentadienyl ring is preserved.

Acknowledgment. Thanks are due to the Ministero della Pubblica Istruzione (Grant MPI 12/2/15) and to the CNR of Rome for generous financial support of this study. We thank also Dr. J. P. Daudey for a copy of the PSHONDO program.

Registry No. I, 59447-66-4; I′, 95120-71-1; II, 95120-69-7; III, 95120-70-0.

---

(30) Very similar conclusions on the nature of the bonding of semibridging carbonyl groups have been reached recently by: Bénard, M.; Dedieu, A.; Nakamura, S. *Nouv. J. Chim.* **1984**, *8*, 149.

Contribution from the Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Tokyo 113, Japan

Reactions of $[W(N_2)_2(dpe)_2]$ with $HFeCo_3(CO)_{12}$ in Aqueous and Halogenated Solvents To Form Hydrazido(2−) Hydroxo Complexes of Tungsten(IV) and Dihalo Complexes of Tungsten(III). Crystal Structure of $[WCl_2(dpe)_2]BF_4\cdot{}^1/_3CH_2Cl_2$

MINORU IMAEDA, HIROSHI NISHIHARA, KOJI NAKANO, HIKARU ICHIDA, AKIKO KOBAYASHI, TARO SAITO,*[1] and YUKIYOSHI SASAKI

Received July 3, 1984

Reactions of $[W(N_2)_2(dpe)_2]$ (dpe = 1,2-bis(diphenylphosphino)ethane) with $HFeCo_3(CO)_{12}$ in water–tetrahydrofuran formed $[W(OH)(NNH_2)(dpe)_2][FeCo_3(CO)_{12}]$. Treatment of an anion-exchanged derivative $[W(OH)(NNH_2)(dpe)_2]PF_6$ with acetone in the presence of $HFeCo_3(CO)_{12}$ afforded $[W(OH)(NNCMe_2)(dpe)_2]PF_6$. No hydrazido(2−) complex formed in dichloromethane, and $[WCl_2(dpe)_2][FeCo_3(CO)_{12}]$ was obtained. This complex and its anion-exchanged derivatives showed the NMR spectra characteristic of paramagnetic ($\mu_{\text{eff}} \simeq 1.5\ \mu_B$) complexes. The X-ray crystal structure of $[WCl_2(dpe)_2]BF_4\cdot{}^1/_3CH_2Cl_2$ (**10**) was determined. Complex **10** crystallized in the trigonal $P\bar{3}$ space group, with a = 21.027 (3) Å, c = 11.091 (2) Å, V = 4246.8 (15) Å^3, and Z = 3. With 3208 unique reflections, R converged to 0.079 (R_w = 0.091). The Mo–Cl distance was 2.312 (5) Å.

Introduction

There have been significant advances in the chemistry of dinitrogen complexes of molybdenum and tungsten[2] since the first report on the protonation of coordinated dinitrogen in $[W(N_2)_2(dpe)_2]$,[3] notably in mechanistic elucidation of the protonation reactions.[4]

We reported in a previous paper that coordinated dinitrogen could be protonated by acidic hydridometal carbonyls such as $HFeCo_3(CO)_{12}$, $HCo(CO)_4$, or $H_2Fe(CO)_4$.[5] These hydride complexes have counteranions that do not coordinate to the metal center, in contrast to X^- in simple acids HX,[2] and we isolated hydrazido(2−) complexes $[W(OR)(NNH_2)(dpe)_2]A$ (A = $FeCo_3(CO)_{12}$, $Co(CO)_4$, $Co_3(CO)_{10}$,[5] $HFe_3(CO)_{11}$, $HFe_4(CO)_{13}$.[6] They contained an alkoxide ligand from solvent alcohols, and participation of alcohols in the protonation reaction was suggested.[5] In this paper, we describe the results of similar reactions in water–tetrahydrofuran, benzene, toluene, dichloromethane, dibromomethane, or dichloroethane. The purpose of the present work was to study the role of solvents in protonating the coordinated dinitrogen. We have found the formation of a new hydrazido(2−) complex coordinated with a hydroxide anion in water–tetrahydrofuran and new tungsten(III) halide complexes in halogenated solvents.

Experimental Section

The preparation and workup were carried out in nitrogen atmosphere. Tetrahydofuran (THF) and diethyl ether were distilled from $LiAlH_4$,

---

(1) Present address: Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan.

(2) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.

(3) Chatt, J.; Heath, G. A.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1972**, 1010.

(4) (a) Chatt, J.; Richards, R. L. *J. Organomet. Chem.* **1982**, *239*, 65. (b) Anderson, S. N.; Fakley, M. E.; Richards, R. L.; Chatt, J. *J. Chem. Soc., Dalton Trans.* **1981**, 1973. (c) Baumann, J. A.; George, T. A. *J. Am. Chem. Soc.* **1980**, *102*, 6154. (d) Bassard, G. E.; George, T. A.; Howell, D. B.; Koczon, L. M.; Lester, R. K. *Inorg. Chem.* **1983**, *22*, 1968. (e) George, T. A.; Koczon, L. M. *J. Am. Chem. Soc.* **1983**, *105*, 6334. (f) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1980**, *102*, 7461. (g) Henderson, R. A. *J. Chem. Soc., Dalton Trans.* **1982**, 917.

(5) Nishihara, H.; Mori, T.; Tsurita, Y.; Nakano, K.; Saito, T.; Sasaki, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4367.

(6) Saito, T. 2nd China-Japan-USA Symposium on Organometallic and Inorganic Chemistry, Shanghai, 1982; Abstract B31J.

0020-1669/85/1324-1246$01.50/0