ferent types of bridging ligands, namely μ_3-OH and μ_3-OC_2H_5, may well be present in the species formed in 95% EtOH, however infrared mull samples do not indicate the presence of a bridging hydroxide ligand.[23]

A few mechanistic comments can be made regarding the synthesis of $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-}$ from $Cr(CO)_6$. Little effect on product yield was observed when the hydroxide ion concentration was varied in the range 2.5–5.0 mol of OH^- per mol of $Cr(CO)_6$. Infrared analysis of the reaction solution revealed the presence of $[(\mu\text{-}H)Cr_2(CO)_{10}]^-$.[24] Indeed, $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-}$ can be directly prepared from a methanolic alkaline solution containing only the bridging hydride.

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Registry No. 1, 81097-71-4; 2, 88729-66-2; $Cr(CO)_3(NH_3)_3$, 14974-11-9; $Cr(CO)_3(CH_3CN)_3$, 16800-46-7; $[Et_4N][Cr(CO)_5Br]$, 14780-93-9.

Supplementary Material Available: Tables of anisotropic and isotropic temperature factors for all atoms, tables of bond lengths and angles for the cations, figures of the ordered cation and disordered cation in each conformation, and structure factor tables (9 pages). Ordering information is given on any current masthead page.

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A Study of σ and π Bonding in Iron Tetracarbonyl Complexes

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Core electron binding energies have been measured for a series of monosubstituted iron carbonyls of the formula $Fe(CO)_4L$, where L = pyridine, trimethylphosphine, acrolein, methyl acrylate, dimethyl maleate, 1,1-dichloroethylene, and *trans*-1,2-dichloroethylene. The core binding energies have been used in conjunction with available valence orbital ionization potentials to compare the bonding properties of the ligands L with carbon monoxide. The method led to the following conclusions: (1) The Fe $d_{x^2-y^2}$, d_{xy} orbitals of the axially coordinated pyridine and trimethylphosphine complexes do not interact with the axial ligands, whereas the Fe d_{xy}, d_{yz} orbitals in these complexes are destabilized by about 0.3 eV relative to $Fe(CO)_5$ because of the loss of the strongly back-bonding CO ligand. (2) The replacement of CO in the equatorial plane with an olefin having electron-withdrawing substituents causes the Fe $d_{x^2-y^2}$, d_{xy} orbitals to be stabilized by 0.2–0.4 eV relative to $Fe(CO)_5$, whereas the Fe d_{xz}, d_{yz} orbitals are destabilized by about 0.3 eV because of their orthogonality to the olefin π^* orbitals. (3) The olefin π orbitals are stabilized by about 0.6 eV by coordination to the $Fe(CO)_4$ fragment, indicating significant σ interaction.

Introduction

We have previously compared the ligand properties of carbon monoxide and ethylene in a study of the photoelectron spectra of $Fe(CO)_4C_2H_4$ and $Fe(CO)_5$.[1] In that study we used both gas-phase core binding energies from X-ray photoelectron spectroscopy (XPS) and valence ionization potentials from ultraviolet photoelectron spectroscopy (UPS). The XPS data were used to correct the UPS data for changes in charge and relaxation energy so that the nature and extent of the molecular orbital interactions accompanying complex formation could be determined unambiguously. We now wish to report the extension of this method to a series of iron tetracarbonyl complexes.

The iron tetracarbonyl complexes which we have chosen for this study are well characterized, and their ultraviolet photoelectron spectra have been previously reported.[2-6] The $Fe(CO)_4L$ compounds fall into two basic classes: those in which the ligand L is a strong σ donor, occupying an axial position of the trigonal bipyramid, and those in which L is an olefin, occupying an equatorial position with the C=C bond in the equatorial plane.

Results

The iron $2p_{3/2}$, carbon 1s, and oxygen 1s binding energies of the $Fe(CO)_4L$ compounds determined in this study and of $Fe(CO)_5$ and $Fe(CO)_4C_2H_4$, determined previously,[1] are presented in Table I. The assignment of the spectra is discussed below.

L = Acrolein, Methyl Acrylate, Dimethyl Maleate. The carbon 1s spectra of all three complexes contain a broad peak at 293.5 eV and a well-resolved narrower peak at 290.4 eV. The area ratios of the higher binding energy peak to the lower binding energy peak are acrolein, 5:2; methyl acrylate, 6:2; dimethyl maleate, 8:2. No appreciable

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Table I. Core Binding Energies (eV) of Fe(CO)$_4$L Compounds[a]

L	Fe $2p_{3/2}$		C 1s		O 1s	
	E_B	fwhm[b]	E_B	fwhm	E_B	fwhm
CO[c]	715.79 (4)	1.25 (9)	293.71 (5)	1.27 (13)	539.96 (2)	1.38 (5)
ethylene[d]	715.40 (2)	1.39 (7)	293.53 (3)[e]	1.41 (7)	539.81 (2)	1.62 (7)
			290.32 (3)[f]	1.32 (11)		
acrolein	715.63 (2)	1.31 (6)	293.63 (3)[g]	1.65 (9)	539.97 (3)	1.57 (7)
			290.44 (3)[f]	1.30 (10)	537.20 (6)[h]	1.32 (22)
methyl acrylate	715.44 (3)	1.37 (9)	293.49 (4)[i]	2.14 (13)	539.61 (2)[j]	1.76 (6)
			290.34 (4)[f]	1.37 (12)	537.20 (6)[h]	1.43 (37)
dimethyl maleate	715.42 (2)	1.35 (7)	293.59 (8)[i]	2.61 (21)	539.56 (4)[j]	1.83 (15)
			290.52 (10)[f]	1.27 (35)	537.37 (5)[h]	1.25 (15)
trans-1,2-dichloroethylene	715.62 (2)	1.28 (6)	293.83 (3)	1.49 (7)	540.13 (2)	1.48 (5)
			291.57 (3)[f]	1.26 (8)		
1,1-dichloroethylene	715.63 (2)	1.28 (5)	293.78 (4)	1.36 (12)	540.10 (2)	1.50 (6)
			292.73 (12)[k]	1.22 (15)		
			290.36 (4)[l]	1.24 (14)		
pyridine	714.64 (4)	1.39 (12)	291.92 (3)[m]	2.84 (43)	538.82 (2)	1.72 (16)
trimethylphosphine	714.74 (2)	1.25 (6)	292.42 (5)	1.66 (15)	538.81 (2)	1.52 (7)
			290.77 (4)[n]	1.16 (11)		

[a] Incertainty in last digit indicated parenthetically. [b] Full width at half maximum. [c] Reference 9. [d] Reference 1. [e] Metal carbonyl carbon. [f] Olefin carbon. [g] Metal carbonyl and organic carbonyl carbon. [h] Organic carbonyl oxygen. [i] Metal carbonyl, organic carbonyl, and methoxy carbon. [j] Metal carbonyl and methoxy oxygen. [k] CCl_2 carbon of olefin [l] CH_2 carbon of olefin. [m] All carbons. [n] Methyl carbons.

shake-up was observed in any of the spectra, so the area ratios may be used in the assignment of the peaks. It may be reasonably concluded that the peak at lower binding energy is due to the olefinic C═C carbon atoms and that the peak at higher binding energy is due to the metal carbonyl carbon atoms and to olefin carbon atoms attached to oxygen atoms.

The oxygen 1s spectrum of the acrolein complex shows two peaks of area ratio 4:1, with the metal carbonyl oxygen peak at higher binding energy. The oxygen 1s spectra of the methyl acrylate and dimethyl maleate complexes are similar in appearance to that of the acrolein complex, but the methoxy oxygen peaks overlap the metal carbonyl oxygen peaks so that the area ratio is 5:1 in the case of the methyl acrylate complex and 6:2 in the case of the dimethyl maleate complex.

L = *trans*-1,2-Dichloroethylene, 1,1-Dichloroethylene. The assignment of these complexes was straightforward. The deconvoluted carbon 1s spectrum of the 1,1-dichloroethylene complex is shown in Figure 1. The chlorine 2p spectra were deconvoluted assuming the theoretical 2:1 area ratio for the $2p_{3/2}$ and $2p_{1/2}$ peaks. The $2p_{3/2}$ binding energies are given at the end of the Experimental Section.

L = Trimethylphosphine, Pyridine. The carbon 1s spectrum of the trimethylphosphine complex contains two well-resolved peaks with the expected 4:3 area ratio. The carbon 1s spectrum of the pyridine complex is broad and essentially featureless, and could not be meaningfully deconvoluted. The O 1s spectra of both compounds are distinctly asymmetric, with extra intensity on the low binding energy sides of the peaks. This low binding energy intensity is probably due to the trans carbonyl oxygens, which have more negative charges than the equatorial oxygens. The iron $2p_{3/2}$ binding energies of these two compounds are a full electronvolt lower than those of the other compounds in Table I. This result is consistent with the strong donor ability of the trimethylphosphine and pyridine ligands, which causes a significant increase in negative charge on the iron atom.

Analysis of UPS Data Using XPS Results

It has been shown that shifts in strictly nonbonding valence ionization potential are proportional to the corresponding shifts in core binding energy of the atom or atoms on which the molecular orbital is localized.[7] Shifts in core binding energy are due to changes in charge and electronic relaxation, and, in the absence of changes in bonding interactions, valence ionization potential shifts have similar causes. However, shifts in valence ionization potential are about eight-tenths of the corresponding core binding energy shifts. This approximation can be applied to the analysis of molecular orbital interactions even when the orbitals of the reference compound are not strictly nonbonding.[8] Core binding energies are used to correct the valence ionization potentials of the reference compound for differences in potential and relaxation energy for each molecule under study. The corrected ionization potentials are called "localized orbital ionization potentials" (LOIPs). If the bonding characters of the molecular orbitals of the reference compound and the compound of interest are identical, then the experimental ionization potential of the compound of interest and the corresponding LOIP will be equal. If the experimental ionization potential is greater than the LOIP, an increase in bonding character relative to the reference compound is indicated. If the experimental ionization potential is less than the LOIP, a decrease in bonding character is indicated.

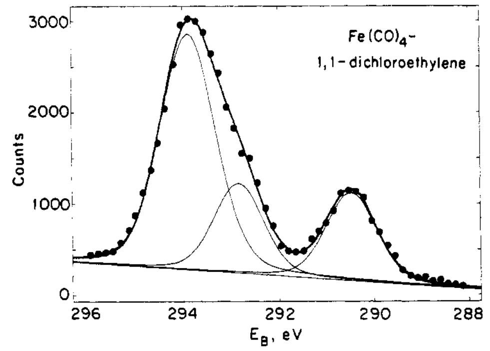

Figure 1. Carbon 1s spectrum of tetracarbonyl(1,1-dichloroethylene)iron. See Table I for peak assignments.

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Table II. Experimental Ionization Potentials and Calculated Localized Orbital Ionization Potentials (eV) of $Fe(CO)_4L$ Compounds

	$d_{x^2-y^2}$, d_{xy}			d_{xz}, d_{yz}		
L	IP	LOIP	IP − LOIP	IP	LOIP	IP − LOIP
CO[a]	8.6	(8.6)		9.9	(9.9)	
ethylene[b]	8.38	8.3	0.1	9.23	9.6	−0.4
acrolein[c]	8.69	8.5	0.2	9.42	9.8	−0.4
methyl acrylate[c]	9.50	8.3	0.2	9.28	9.6	−0.3
dimethyl maleate[c]	8.68	8.3	0.4	9.31	9.6	−0.3
trans-1,2-dichloroethylene[c]	8.72	8.5	0.2	9.49	9.8	−0.3
1,1-dichloroethylene[c]	8.82	8.5	0.3	9.51	9.8	−0.3
pyridine[d]	7.65	7.7	0.0	8.65	9.0	−0.4
trimethylphosphine[d]	7.77	7.8	0.0	8.85	9.1	−0.3

[a] Reference 10. [b] Reference 2. [c] Reference 3. [d] Reference 4.

Table III. Experimental Ionization Potentials and Calculated Localized Orbital Ionization Potentials (eV) of the C=C π Orbital in $Fe(CO)_4$-Olefin Compounds

olefin	E_B(C 1s) of the free ligand	IP of the free ligand[a]	IP of the complex[b]	LOIP	IP(Complex) - LOIP
ethylene	290.88[c]	10.51	10.56	10.1	0.5
acrolein	291.32[d]	10.94	10.76	10.2	0.5
methyl acrylate	290.99[d]	10.74	10.80	10.2	0.6
trans-1,2-dichloroethylene	292.41[c]	9.8	9.7-9.9	9.1	~0.7
1,1-dichloroethylene	292.28[c,e]	9.96	9.98	9.4	0.6

[a] Reference 11. [b] Reference 2. [c] Reference 12. [d] Reference 13. [e] Average of CCl_2 and CH_2 binding energies.

All of the complexes in this study show two principal ionizations in the region 8–10 eV. The band at lower ionization potential is due to the Fe $d_{x^2-y^2}$, d_{xy} orbitals. The reference compound in this study is the parent iron carbonyl $Fe(CO)_5$, therefore we can directly compare the bonding characteristics of CO and the ligands (L) of the $Fe(CO)_4L$ complexes. The method is illustrated here for the metal orbitals of $Fe(CO)_4P(CH_3)_3$. The iron core binding energy difference between $Fe(CO)_4P(CH_3)_3$ and $Fe(CO)_5$ is −1.05 eV. The correction term is thus −0.8(1.05), or −0.8 eV. The first ionization potential of $Fe(CO)_5$ is 8.6 eV, so that the LOIP value of the Fe $d_{x^2-y^2}$, d_{xy} orbital of $Fe(CO)_4P(CH_3)_3$ is 0.8 eV lower, or 7.8 eV. The experimental ionization potential, 7.77 eV, is in excellent agreement with the LOIP value. Indeed, these values should be the same because the replacement of an axial CO with a $P(CH_3)_3$ should not have any effect on the equatorial $d_{x^2-y^2}$, d_{xy} orbitals beyond the effects of changes in charge and relaxation energy. The LOIP value for the Fe d_{xz}, d_{yz} orbitals of $Fe(CO)_4P(CH_3)_3$ is 9.1 eV. The experimental ionization potential is 8.85 eV, corresponding to a destabilization of approximately 0.3 eV. This destabilization is quite reasonable, because $P(CH_3)_3$ is a poorer back-bonder than the CO it replaces. The results of similar analyses for all of the $Fe(CO)_4L$ compounds are presented in Table II.

The results for the axially coordinated pyridine complex are essentially identical with those obtained for the trimethylphosphine complex. It is important to note that, although the core binding energy differences are large for these axially coordinated ligands, the method of analysis nevertheless correctly predicts the ionization potentials of the equatorial orbitals. In the case of the olefin complexes, the binding energy differences are smaller, and any error associated with the correction term will be even smaller.

In our previous study[1] of the bonding in iron tetracarbonyl ethylene, we concluded that the total $\sigma + \pi$ orbital interaction in the equatorial plane is the same in $Fe(CO)_4C_2H_4$ as in $Fe(CO)_5$. This indicates that ethylene and carbon monoxide stabilize the Fe $d_{x^2-y^2}$, d_{xy} orbitals to essentially the same extent. On the other hand, the Fe d_{xz}, d_{yz} orbitals of $Fe(CO)_4C_2H_4$ are destabilized relative to $Fe(CO)_5$ because of a decrease in back-bonding of these orbitals caused by their orthogonality to the ethylene π^* orbital. We can similarly analyze the data for the substituted olefins. In the case of the acrolein and methyl acrylate complexes, the substitution of an electron-withdrawing group causes the equatorial orbitals to be stabilized by ~0.2 eV. It would appear that an aldehyde group and a methyl ester group have approximately the same stabilizing effect. The sustitution of two methyl ester groups, as in the dimethyl maleate complex, causes the stabilization to increase to ~0.4 eV.

The stabilization of the equatorial orbitals in the dichloroethylene complexes is about the same as in the acrolein and methyl acrylate complexes. This is contrary to the CNDO results of Van Dam and Oskam,[2] which indicated that dihalogenated olefins should be better electron acceptors than olefins with aldehyde and ester groups. Notice that a naive interpretation of the Fe 3d orbital ionization potentials, ignoring the effects of charge, leads to the conclusion that the dichloroethylene ligands stabilize the metal orbitals to a greater extent than does dimethyl maleate.

For all the olefin complexes, the Fe d_{xz}, d_{yx} orbitals are destabilized by ~0.3 eV. This was also the amount of destabilization observed in the axially coordinated compounds. This value of ~0.3 eV would appear to be the amount of destabilization attributable to the loss of one CO ligand.

The same method of analysis can also be applied to the C=C π orbital. The results of this analysis are presented in Table III. If one were to compare the C=C π ionization potentials of the free olefins with those of the coordinated

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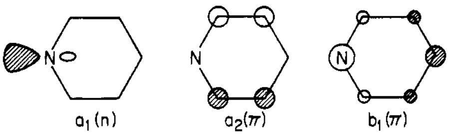
olefins, without considering core binding energies, it might be concluded that this orbital is essentially unaffected by complex formation. This line of reasoning ignores the fact that, in the complex, the olefin acquires a negative charge because of its attachment to an electropositive metal center. On the other hand, by comparing the ionization potential of the complex with the LOIP value, it is found that the C=C π orbital is stabilized to the extent of ~0.6 eV by complexation to the metal carbonyl fragment, corresponding to significant σ donation by this orbital.

The stabilization of the C=C π orbitals can be compared to the stabilization of the lone pair orbitals of the axially coordinating ligands. Using the phosphorus core binding energy difference[14] and the lone pair ionization potential of trimethylphosphine,[15] we calculate an LOIP of 9.6 eV for this orbital in $Fe(CO)_4P(CH)_3$. The actual ionization potential of this orbital in the complex is 10.45 eV, indicating a stabilization of ~0.9 eV—a somewhat greater stabilization than that observed in the olefin complexes.

In the case of the pyridine complex, a similar analysis is complicated by conflicting assignments of the free ligand ultraviolet photoelectron spectrum[16,17] and conflicting assignments of the spectrum of the complex.[3,6] The three lowest ionization potentials of pyridine are 9.7, 9.8, and 10.5 eV, and we shall accept the assignment advocated by Heilbronner et al.,[17] i.e., that these ionization potentials correspond to the $a_1(n)$, $a_2(\pi)$, and $b_1(\pi)$ orbitals, respectively. These orbitals are depicted schematically below.



Three ligand ionizations are observed in the complex: 10.39, 11.33, and 11.70 eV (by Daamen and Oskam),[6] or 10.53, 11.50, and 11.80 eV (by Flamini et al.).[3] The $a_1(n)$ and $b_1(\pi)$ orbitals are substantially localized on the pyridine nitrogen atom, so that LOIPs may be calculated for these orbitals. Eight-tenths of the pyridine nitrogen core binding energy difference[18] is 1.2 eV, corresponding to LOIPs of 10.9 and 11.7 eV for the $a_1(n)$ and $b_1(\pi)$ orbitals, respectively. The $a_1(n)$ orbital should be significantly stabilized on complex formation because it is donating electron density to an unfilled Fe σ orbital. The $b_1(\pi)$ orbital should be very slightly stabilized or unaffected by complex formation, because it is interacting with higher-lying filled iron π orbitals. Clearly, the ionization at 10.4 eV cannot be assigned to either the $a_1(n)$ orbital or to the $b_1(\pi)$ orbital as this would indicate destabilization. The $b_1(\pi)$ orbital must be assigned to the the ionization at ~11.8 eV because the alternative ionization at ~11.4 eV would indicate significant destabilization of this orbital. The conclusion that there is little or no stabilization of this orbital on complex formation is consistent with the lack of destabilization of the Fe d_{xz}, d_{yz} orbitals beyond that attributable to the loss of a back-bonding carbon monoxide. The band at 11.4 eV is due to the Fe–N σ orbital, indicating a stabilization of ~0.5 eV upon complex formation. This assignment of these two orbitals is the reverse of the assignment of Daamen and Oskam.

We were unable to obtain the C 1s binding energies necessary to calculate an LOIP for the $a_2(\pi)$ orbital, but we believe that the ionization at 10.4 eV corresponds to this orbital. This orbital is not expected to participate in complex formation, so that the observed shift of 0.6 eV from the free ligand is due primarily to changes in the carbon atom charges. The change in charge on complex formation should be considerably less for the carbon atoms than for the nitrogen atom, and the observed shift supports this argument.

The above examples illustrate the utility of the LOIP method in studying the nature of orbital interactions that occur on complex formation and show that the valence photoelectron spectra of organometallic molecules can be much more reliably interpreted when core binding energy data are available. We believe that the method has general applicability in organometallic chemistry.

Experimental Section

The $Fe(CO)_4$ complexes of acrolein, methyl acrylate, and dimethyl maleate were prepared by the method of Murdoch[19] et al. The $Fe(CO)_4$ complexes of *trans*-1,2-dichloroethylene and 1,1-dichloroethylene were prepared by the method of Gravels and von Gustorf,[20] and $Fe(CO)_4C_5H_5N$ was prepared by the method of Schubert and Sheline.[21] These preparations utilize the reaction of $Fe_2(CO)_9$ with the appropriate ligand. Iron tetracarbonyl trimethylphosphine was prepared by the sealed-tube reaction of equimolar amounts of $Fe(CO)_5$ and $P(CH_3)_3$. The tube was held at 70 °C for 48 h, and the unreacted material was pumped off at 0 °C. The residue was sublimed at 30 °C under vacuum to give the desired product. All of the complexes were further purified by vacuum sublimation prior to the obtaining of spectra. In all cases, the melting points and infrared spectra agreed with those reported in the literature.

Vapor-phase X-ray photoelectron spectra were obtained with a GCA/McPherson ESCA 36 spectrometer by a method described previously.[9] All of the compounds had sufficient room temperature vapor pressure to obtain spectra. Spectra were calibrated by using the N_2 1s, Ne 1s, and Ne 2s reference peaks. Peak positions, half-widths, areas, and their uncertainties (2σ) were determined by using the computer program CURVY.[22]

The following binding energies were measured but are not listed in Table I: $Fe(CO)_4C_5H_5N$, 406.30 eV (N 1s); $Fe(CO)_4P(CH_3)_3$, 137.21 eV (P $2p_{3/2}$); $Fe(CO)_4$(*trans*-HClC=CHCl), 205.86 eV (Cl $2p_{3/2}$); $Fe(CO)_4(Cl_2CCH_2)$, 205.93 eV (Cl $2p_{3/2}$).

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Registry No. $Fe(CO)_4L$ (L = acrolein), 88852-56-6; Fe(CO)L (L = methyl acrylate), 52646-70-5; $Fe(CO)_4L$ (L = dimethyl maleate), 12287-97-7; $Fe(CO)_4L$ (L = *trans*-1,2-dichloroethylene), 52646-80-7; $Fe(CO)_4L$ (L = 1,1-dichloroethylene), 52613-75-9; $Fe(CO)_4L$ (L = pyridine), 53317-88-7; $Fe(CO)_4L$ (L = trimethylphosphine), 18475-02-0.

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