THEORETICAL INVESTIGATION ON HYDROFORMYLATION REACTIONS

II*. HYDROCARBONYLIRON INTERMEDIATES IN REPPE SYNTHESIS

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Summary

Extended Hückel theory calculations have been carried out to investigate the possible formation of stable π and σ complexes between olefins and some hydrocarbonylirons postulated as active catalysts in Reppe synthesis. It was found that $H_2Fe(CO)_4$ and $HFe(CO)_4^-$ do not coordinate ethylene, unlike the corresponding CO deficient species $H_2Fe(CO)_3$ and $HFe(CO)_3^-$, which interact with the olefin to give stable π complexes. Moreover ethylene—$H_2Fe(CO)_3$ is more stable than ethylene—$HFe(CO)_3^-$, in line with the conclusions based on the experimental results. Stable alkyl intermediates are predicted starting from the coordinatively saturated hydrocarbonyls.

Introduction

In the conventional hydroformylation process [1] an olefin is converted into the next higher homologous aldehyde or alcohol through reaction with carbon monoxide and hydrogen using carbonyl transition metal compounds as catalysts. Reppe's modification of this process leads to the same products from carbon monoxide and water [2,3], following the equation:

$$RCH{=}CHR' + CO + H_2O \overset{cat}{\to} RCH_2CH(CHO)R' + RCH(CHO)CH_2R'$$
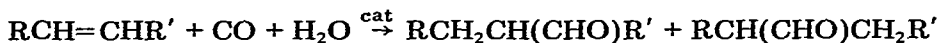
In this case complexes of transition metals such as Fe, Rh, Ru, Os, Ir, and Pt can be employed as catalytic precursors with a Brønsted or a Lewis base. The most widely used precursor in the industrial processes is $Fe(CO)_5$, while $HFe(CO)_4^-$, $H_2Fe(CO)_4$ and other parent hydrocarbonyls were detected in the basic reaction medium, or were used directly as precursors in the investigations of the reaction mechanism [4]. From an economic view point, a very impor-

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* For part I see Ref. 6.

tant feature of Reppe's reaction is that a cheap catalyst such as $Fe(CO)_5$ is active under relatively mild conditions [5] whereas the same complex is a poor catalyst for the hydroformylation reaction when molecular hydrogen is used.

In the course of a theoretical investigation of the structure of the transition metal complexes most usually employed in the hydroformylation of olefins, we previously [6] considered a series of carbonyl- and hydrocarbonyl-cobalt compounds. A preliminary study on the structure of π and σ intermediates, postulated by the experimentalists in order to rationalize the oxo-mechanism, was also undertaken [7]. In the case of the bridged octacarbonyl dicobalt, particular attention was then devoted to the effect of substituents on the flap angle of the inner carbonyl ring [8].

In this paper we present a theoretical investigation of the interaction between olefins and some of the carbonyl- and hydrocarbonyl-iron compounds, thought to be active catalysts in Reppe synthesis. Our goal is to obtain information on the nature, geometry and stability of the actual intermediates in the process.

The semiempirical Extended Hückel Theory (EHT) [9] was employed in order to permit a total energy minimization process with respect to the largest possible number of variables in each system considered. The justification for this choice has been discussed previously [6—8].

The geometries for the iron complexes were determined by optimizing a convenient number of angular variables. In particular no symmetry constraints were applied, so that the symmetries are themselves a result of the calculations. In order to check the ability of the method to predict reliable structures, the energy minimization was performed with three different parametrizations. The results have been analyzed by comparison with the experimental data and the results of ab initio calculations available in the literature.

Method of calculation

EHT was used in its standard formulation [9]. Calculations at the single and double zeta level were performed by using three different sets of parameters

TABLE 1

PARAMETERS USED IN THE EHT CALCULATIONS [a]

|	Double ζ [b] A			Single ζ [c] B		C
	ζ_i	c_i	H_{ii} (eV)	ζ_i	H_{ii} (eV)	H_{ii} (eV)
C 2s	1.625		−21.4	1.62	−23.0	−23.0
2p	1.625		−11.4	1.62	−13.4	−13.4
O 2s	2.275		−32.3	2.28	−33.9	−33.9
2p	2.275		−14.8	2.28	−16.4	−16.4
H 1s	1.3		−13.6	1.3	−13.6	−13.6
Fe 3d	5.35	0.5366	−12.2	2.7	−17.3	−11.0
	1.8	0.6678				
4s	1.9		−8.86	1.6	−10.0	−10.0
4p	1.9		−5.12	1.6	−8.0	−8.0

[a] $K = 1.8$. [b] Ref. 12. [c] Ref. 13.

(A, B, and C, collected in Table 1). Off-diagonal elements H_{ij} were computed from the Wolfsberg—Helmholtz equation [10]. Powell's method [11] was employed for an automatic optimization of the geometrical parameters: the number and the type of variables taken into consideration in the energy minimization process will be specified and discussed for each system separately.

Results and discussion

Catalytic precursors

We started by examining the geometries and the relative stabilities in a series of carbonyl- and hydrocarbonyl-irons implied in Reppe synthesis, either as catalysts or as intermediates.

Fe(CO)₅. This compound has been widely investigated by several authors concerned with rationalization of transition metal pentacoordination [14—16] and the study of carbonylmetals [17—19]. Its ground state geometry (here referred to as IA) was shown by X-ray diffraction to be a bipyramid structure (D_{3h} symmetry) with bondlengths of 1.827 and 1.807 Å for FeC_{eq} and FeC_{ax} respectively [20]. The total energy minimization process performed using the three sets of parameters ($A—C$ in Table 1) always predicted the correct symmetry. A C_{4v} isomer with square pyramid structure (IB) was also predicted by EHT calculations, which well reproduce the bondangle $C_{eq}\hat{F}eC_{ax}$ (105°) calculated from ab initio using gaussian basis sets [16].
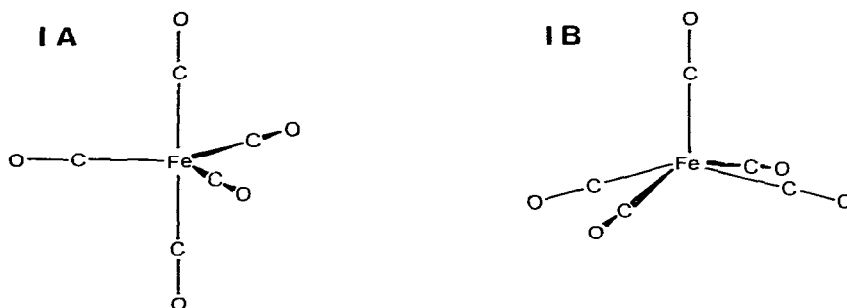
The inversion barrier for the molecular rearrangement between the two structures of Fe(CO)₅ was estimated to be 1 kcal mol⁻¹ by Spiess and his colleagues [21] from spin-lattice relaxation time and line-shape measurements in the ¹³C NMR spectra of solid Fe(CO)₅. Our EHT calculations reproduce this value very satisfactorily, as do those of the ab initio calculations, as shown in Table 2, in which the most relevant results obtained by the two methods are compared. It should also be noted that the symmetries of the last HOMO's calculated using EHT with parametrization A (double zeta basis set) coincide with those predicted by ab initio computations [16].

HFe(CO)₄⁻, H₂Fe(CO)₄, Fe(CO)₄²⁻. The geometrical structures of these isoelectronic compounds have been determined by electron diffraction or by IR spectroscopy. HFe(CO)₄⁻ (II) is a distorted trigonal bipyramid with the hydride in axial position [23]; H₂Fe(CO)₄ (III) has C_{2v} symmetry, with two carbonyls and two H atoms in the equatorial plane [24]; Fe(CO)₄²⁻ (IV) is a tetrahedral

pyramid [25].
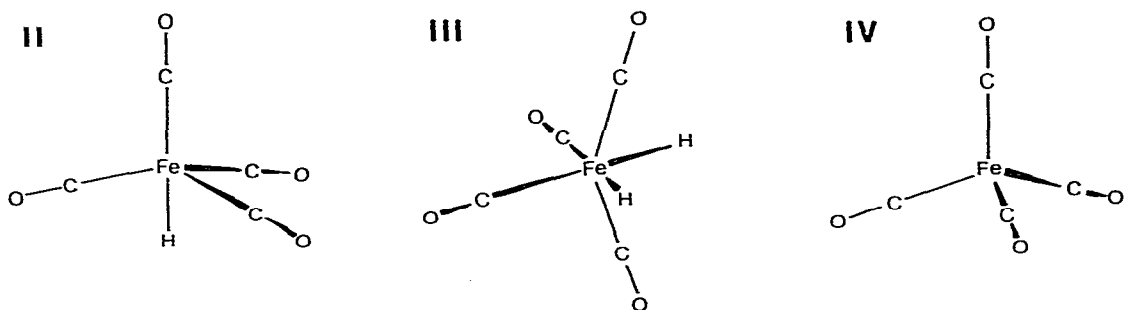
EHT calculations predict the correct symmetry and lead to optimized geo-metrical parameters which well reproduce the experimental data for each of the three compounds. For $H_2Fe(CO)_4$, however, the agreement with spectroscopic results is less accurate, and, in this case, parametrization B is the most satis-factory. The optimized energies and geometrical parameters, together with the charges on the Fe atom are shown in Table 3. In general it appears that the computational technique can be confidently used to predict the geometries of such iron-complexes.

[HFe$_3$(CO)$_{11}$]$^-$. The structure of the anion [HFe$_3$(CO)$_{11}$]$^-$ has been deter-mined by X-ray diffraction [27] shown to have C_s symmetry (VA) with an isosceles triangle of metal atoms, in which one of the edges is bridged by one carbonyl and the H atom. The only geometrical parameters reported are the Fe—Fe distances.
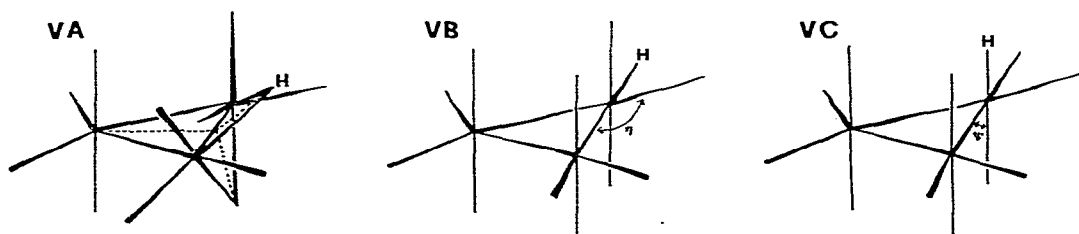
We deduced the other bond lengths and the bond angles from the structure of the parent complex Fe$_3$(CO)$_{12}$ [28], and the metal—hydride distance was assumed equal to 1.68 Å by analogy with HRu$_3$(CO)$_{10}$(CNMe$_2$) [29]. The geometrical parameters taken into consideration in the energy minimization process were the dihedral angles γ and δ formed by the plane containing the iron atoms and the planes defined by the H bridge and the bridging carbonyl, respectively. The values optimized in the framework of the double ζ parame-trization, are γ 107.0° and δ 106.1° and agree very well with the value of 110° determined by X-ray diffraction for Fe$_3$(CO)$_{12}$ [28].

NMR studies [30] on [HFe$_3$(CO)$_{11}$]$^-$ showed a dynamical scrambling of car-bonyls, which was interpreted as a two-center or a multi-center process taking place at about 40°C via a non-bridged intermediate state bearing the hydride in a terminal position [30,31]. Thus we considered two possible open forms of [HFe$_3$(CO)$_{11}$]$^-$, in which the hydride occupies an equatorial (VB) or an axial

TABLE 2

AB INITIO AND EHT OPTIMIZED GEOMETRICAL PARAMETERS AND ENERGIES OF $Fe(CO)_5$

| | ab initio [a] | EHT [b] | | |
		A	B	C
IA (D_{3h})				
Energy (eV)	−49591.485	−1103.735	−1241.064	−1193.211
Charge on Fe [c]	1.039 [d]	0.47	−2.18	2.24
Symmetry of HOMO's [e]	e'', e'	e'', e'	a_2'', e'	e'', e'
IB (C_{4v})				
C_{ax} FeC_{eq} [f]	105.0	103.5	104.5	106.3
Energy (eV)	−49591.458	−1103.689	−1240.991	−1193.159
Charge on Fe [c]		0.49	−2.18	2.28
Symm. of HOMO's [e]	b_2, e, a_1	b_2, e, a_1	b_2, e, a_1	b_2, a_1, e
ΔE (kcal mol^{-1}) [g]	0.6	1.1	1.7	1.2

[a] Ref. 16. [b] Present work; assumed bond lengths: FeC 1.82, CO 1.145 Å. [c] a.u. [d] Ref. 22. [e] Orbitals ordered by increasing energies. [f] In degrees. [g] Experimental value ~1 kcal mol^{-1} [21].

(VC) position respectively. EHT calculations predict comparable energies for the two isomers, as given in Table 4, in which the optimized geometrical parameters are also shown.

Hydrocarbonyliron complexes with olefins

Relatively little has been published on the catalytic activity of iron complexes in Reppe's synthesis. The first proposed reaction mechanism mainly

TABLE 3

EXPERIMENTAL AND EHT OPTIMIZED GEOMETRIES OF $HFe(CO)_4^-$, $H_2Fe(CO)_4$ AND $Fe(CO)_4^{2-}$

| | Experimental | EHT [a] | | |
		A	B	C
$HFe(CO)_4^-$ (II)				
Symmetry	C_{3v} [b]	C_{3v}	C_{3v}	C_{3v}
$HFeC_{eq}$ [c]	81.3 [b]	84.7	81.1	81.9
Energy (eV)		−933.496	−1053.645	−1005.156
Charge on Fe [d]		0.32	−2.33	1.75
$H_2Fe(CO)_4$ [e] (III)				
Symmetry	C_{2v} [f]	C_{2v}	C_{2v}	C_{2v}
$C_{ax}FeC_{ax}$ [c]	148.5 [f]	171.6	151.7	162.9
$C_{eq}FeC_{eq}$ [c]	96.0 [f]	94.9	97.5	89.3
$HFeH$ [c]	100.0 [f]	83.2	86.2	82.5
Energy (eV)		−939.589	−1056.633	−1008.401
Charge on Fe [d]	1.34 [g]	0.59	−2.16	2.01
$Fe(CO)_4^{2-}$ [e] (IV)				
Symmetry	T_d [h]	T_d	T_d	T_d
Energy (eV)		−924.501	−1049.471	−998.450
Charge on Fe [d]		−0.42	−3.02	1.25

[a] Present work. [b] Ref. 23, from which the assumed bond distances for EHT calculations were deduced: FeC_{eq} 1.75, FeC_{ax} 1.72, $C_{eq}O_{eq}$ 1.15, $C_{ax}O_{ax}$ 1.18, FeH 1.57 Å. [c] In degrees. [d] a.u.; [e] Assumed bond lengths: FeC 1.82, CO 1.145, FeH 1.556 Å. [f] Ref. 24. [g] Ref. 26 (calculated from binding energies using the potential model). [h] Ref. 25.

TABLE 4

OPTIMIZED GEOMETRIES AND ENERGIES FOR [HFe$_3$(CO)$_{11}$]$^-$

Isomer		EHT [a]	
		A	B
VA (C_s) [b]	γ [c]	107.0	102.5
	δ [c]	106.1	107.9
	Energy (eV)	−2538.814	−2877.751
VB (C_s) [d]	FeFeH	88.7	100.0 [e]
	η [f]	100.0	100.0 [e]
	Energy (eV)	−2538.542	−2877.486
VC (C_s) [d]	FeFeH	83.6	88.9
	ψ [f]	99.0	90.0 [e]
	Energy (eV)	−2538.464	−2877.200

[a] Present work. [b] Assumed bond lengths (Å): FeFe 2.577, 2.69, 2.69, FeH 1.68, FeC$_B$ 2.05, FeC$_T$ 1.82, CO 1.13. [c] Dihedral angles defined in the text, in degrees. [d] Assumed bond lengths (Å): FeFe 2.69, FeH 1.56, FeC 1.82, CO 1.13. [e] Assumed value. [f] See the scheme for structures VB and VC.

involved di- or trinuclear iron complexes [4 and refs. therein], while, in the last few years, monomeric species, formed from Fe(CO)$_5$ in the reaction:

$$Fe(CO)_5 + OH^- \xrightarrow{-CO_2} HFe(CO)_4^- \rightarrow H_2Fe(CO)_4$$

have been implicated as the actual catalysts in the reaction [3].

In our investigation we chose H$_2$Fe(CO)$_4$ and HFe(CO)$_4^-$ as the hydrocarbonylirons interacting with the olefin, and, for the sake of simplicity, ethylene was adopted as the model system for the organic moiety in the catalytic reaction.

As for the computational details, the double ζ parametrization (A) is used from now on; from a comprehensive comparison among A, B and C parameter sets, the first gave the best overall results in the prediction of orbital symmetries, charges and geometries.

Complexes of ethylene with H$_2$Fe(CO)$_4$ and HFe(CO)$_4^-$

The formation of complexes from ethylene and hydrocarbonylirons was thoroughly investigated. The optimized geometries for the isolated systems (III and II) were assumed as starting conformations for the hydrocarbonylirons, while the experimental geometry was adopted for ethylene [32].

No stable intermediates were obtained in spite of an accurate energy minimization performed with respect to the most relevant angular variables at several values of the Fe—olefin distance. The hydrocarbonyl and the olefin tend to separate progressively along a monotonic trend.

In spite of this finding, the formation of alkyl- complexes was studied starting from the same fragments in which an H atom was migrated from Fe to the organic moiety. Stable complexes were formed with both H$_2$Fe(CO)$_4$ (VI) and HFe(CO)$_4^-$ (VII), and they are shown in Fig. 1; in the caption of the same figure the geometrical variables in the energy minimization process are shown
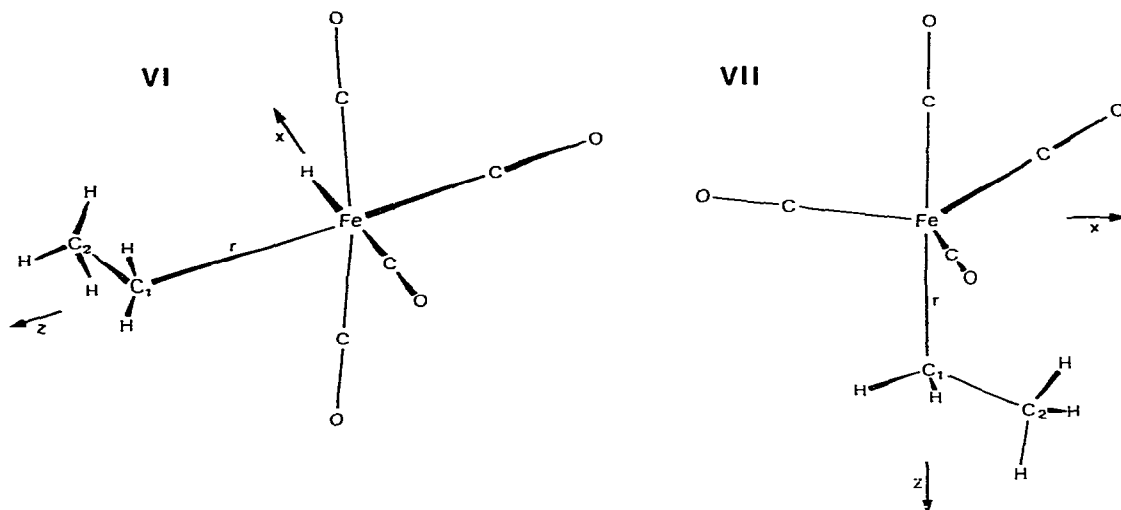
Fig. 1. EHT optimized geometries of σ complexes: VI: $HFe(CO)_4 \cdot CH_2CH_3$. FeC(1) 2.20 Å, $HFeC_{eq}$ 89.3, $C_{eq}FeC_{eq}$ 94.5, $C_{ax}FeC_{ax}$ 171.6, HFeC(1) 86.5, FeC(1)C(2) 116.1, HC(1)C(2) 112.8, HC(1)H 106.3 Å. Total energy: —1154.516 eV; charge on Fe: 0.57 a.u.; charge on ethyl: —0.26 a.u. VII: $Fe(CO)_4^- \cdot CH_2CH_3$. FeC(1) 2.25 Å, $C_{eq}FeC_{ax}$ 95.3, dihedral angle $C_{eq}FeC_{ax}C_{eq}$ 120.0, FeC(1)C(2) 117.3, $C_{ax}FeC(1)$ 179.5, HC(1)C(2) 112.8, HC(1) 107.6. Total energy: —1148.469 eV; charge on Fe: 0.30 a.u.; charge on ethyl: —0.19 a.u. Thr assumed bond lengths in the Fe hydrocarbonyls VI and VII are the same as in $H_2Fe(CO)_4$ and $HFe(CO)_4^-$ respectively; model geometry for ethyl: CC 1.42 Å, CH 1.09 Å, tetrahedral CH_3 group.

together with their optimized values. The trends of total energies vs. r = Fe—C(H₂), chosen as the reaction coordinate, are shown in Fig. 2. In the case of $HFe(CO)_4 \cdot CH_2CH_3$ the interfragment distance corresponding to the energy minimum is 2.20 Å. The conformation of the complex is nearly the same as that of $H_2Fe(CO)_4$, from which it differs in the substitution of an hydrogen atom by the ethyl fragment. As shown in Fig. 1 the organic moiety lies in the equatorial plane of the hydrocarbonyliron, with the methyl oriented towards the Fe bound hydrogen. A charge transfer of 0.26 electrons towards the organic moiety is calculated.

For $Fe(CO)_4^- \cdot CH_2CH_3$ the optimized value of r was 2.25 Å. Fig. 1 shows that the Fe—C(H₂) bond is lined up with the FeC_{ax} one, i.e. it merely takes the place of the FeH bond in $HFe(CO)_4^-$. Moreover the projection of the CC bond on the plane of the equatorial carbons is symmetric with respect to two of them, so that the complex retains C_s symmetry. A charge transfer of 0.19 electrons is predicted for complex VII, and is less than that found for VI. The stabilization energies of the σ complexes VI and VII, calculated with respect to the energies of the transition metal radicals and ethyl *, are about 58 and 39 kcal mol⁻¹, respectively. While conscious of the inaccuracy of the absolute values of the stabilization energies, we note that the complex with $H_2Fe(CO)_4$

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* Isolated ethyl energy: —231.522 eV; $HFe(CO)_4$ and $Fe(CO)_4^-$ optimized energies: —920.487 and —915.234 eV.
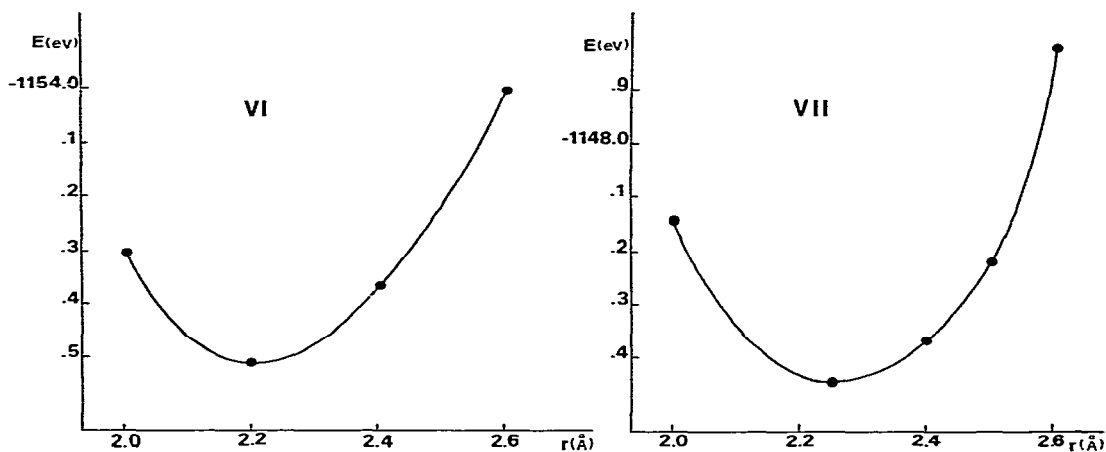
Fig. 2. Variation of optimized EHT energy with r = Fe—C(H$_2$) for HFe(CO)$_4$ · CH$_2$CH$_3$ (VI) and Fe(CO)$_4^-$ · CH$_2$CH$_3$ (VII).

is about 20 kcal mol^{-1} more stable than the other.

The bond between the organic moiety and the hydrocarbonylirons is depicted in Fig. 3, where the plots of the 31° MO (HOMO) of VI and the inner 29° MO of VII are shown. In each case it appears that the stability of the complex is due to the overlap of d_{z^2} and p_z orbitals of Fe and the p_z orbital of the carbon atom in the CH$_2$ group.
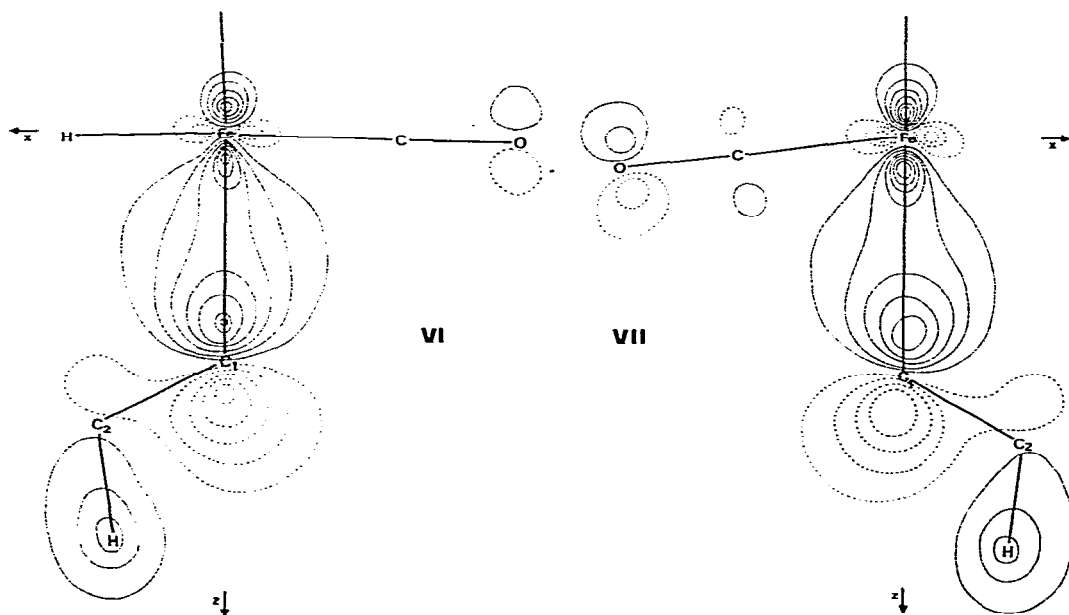

Fig. 3. Contour maps of the 31° MO of HFe(CO)$_4$ · CH$_2$CH$_3$ (VI) and of the 29° MO of Fe(CO)$_4^-$ · CH$_2$CH$_3$ (VII). The plots are in the xz plane (see Fig. 1); the contour levels correspond to ψ = ±0.05, 0.10, 0.15, 0.20, 0.25, 0.30 a.u.

Complexes of ethylene with $H_2Fe(CO)_3$ and $HFe(CO)_3^-$

As reported in the preceding section, no stable complexes are predicted by EHT when ethylene interacts directly with $H_2Fe(CO)_4$ or $HFe(CO)_4^-$.

In order to identify a species which is able to coordinate the olefin, we turned our attention to possible coordinatively unsaturated moieties not reported by the experimentalists. In the hydroformylation reaction catalyzed by cobalt complexes such as $Co_2(CO)_8$ and $HCo(CO)_4$, the formation of intermediates involving the CO deficient species $HCo(CO)_3$ and the olefin was proposed from kinetic [33], spectroscopic [34] and in mechanicistic [35] studies and was considered in theoretical investigations [6,7,36]. Moreover it was observed that the reaction rate decreases with increasing CO pressure both in hydro-formylation and in Reppe reaction [1,4]. For these reasons we decided to examine a possible species derived from $H_2Fe(CO)_4$ or $HFe(CO)_4^-$ by removal of one carbonyl. As with $H_2Fe(CO)_3$, EHT calculations predict the existence of two energetically comparable isomers obtained by the removal either of an axial (VIIIA in Fig. 4) or of an equatorial carbonyl (VIIIB). The energy required for the CO elimination is about 80 kcal mol^{-1}.

Of the two equivalent structures, we adopted VIIIA as the model fragment which is approached by ethylene along the axial direction of the removed carbonyl. A stable complex was formed without any barrier and the olefin was
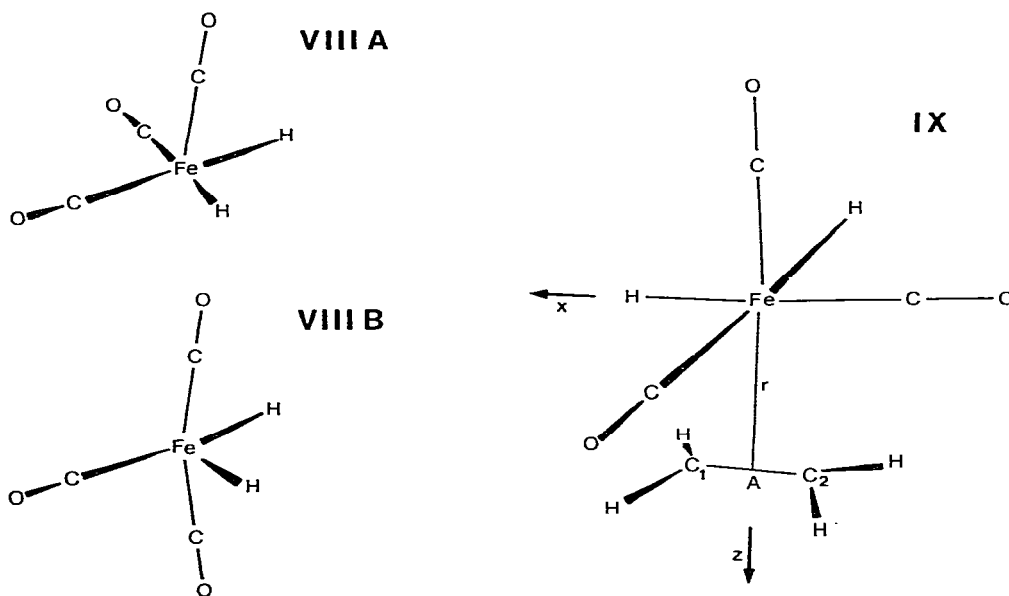

Fig. 4. Optimized geometries of the two isomers of $H_2Fe(CO)_3$ and of the π complex $H_2Fe(CO)_3$ · CH_2CH_2. VIIIA: obtained by removal of an axial carbonyl from $H_2Fe(CO)_4$ · $C_{eq}FeC_{eq}$ 95.3, $C_{ax}FeC_{eq}$ 92.8, HFeH 82.5, $C_{eq}FeH$ 91.0. Total energy: -738.615 eV, charge on Fe: 0.73 a.u.. VIIIB: obtained by removal of an equatorial carbonyl from $H_2Fe(CO)_4$ · $C_{ax}FeC_{ax}$ 175.5, $C_{ax}FeC_{eq}$ 91.6, HFeH 87.3, $C_{eq}FeH$ 93.2, 179.5. Total energy: -738.622 eV; charge on Fe: 0.53 a.u. IX: $H_2Fe(CO)_3$ · CH_2CH_2. r 2.18 Å, $C_{eq}FeC_{eq}$ 94.9, $C_{ax}FeC_{eq}$ 92.1, HFeH 83.2, $C_{eq}FeA$ 93.5, FeAC(1) 88.5, HCH 112.7, 112.4, CCH 122.5, dihedral angle $C_{eq}FeAC(1)$ 4.4. Total energy: -954.862 eV; charge on Fe: 0.65 a.u.; charge on ethylene: 0.07 a.u. Assumed bond lengths are the same as in $H_2Fe(CO)_4$ (see Table 3). Experimental geometry assumed for isolated ethylene [32]: energy: -215.725 eV.

coordinated to the iron atom. The trend of the energy vs. the distance r between Fe and the mid point of the C=C-double bond is shown in Fig. 5. The value of r corresponding to the minimum is 2.18 Å and the stabilization energy with respect to the component fragments is 12 kcal mol^{-1}. Ethylene places itself perpendicular to the approaching direction, and its structure loses its planarity by few degrees while the EHT optimized C=C value is 1.331 Å. Also the hydrocarbonyl $H_2Fe(CO)_3$ rearranges slightly and one of the equatorial hydrogens is eclipsed by the double bond.

The structure of this intermediate (IX) is shown in Fig. 4, in which the optimized energy and geometrical parameters are listed in the caption. The stability of the complex is due mainly to the mixture of the π orbital of ethylene with the d_{z^2} of Fe, and of the π^* of ethylene with the d_{xz} of Fe, as shown by the plots of the two most significant occupied MO's (Fig. 6).

Starting from the stable π complex just described, we investigated its possible conversion into a σ intermediate by migration of an H atom from the hydrocarbonyl to the olefin. The complex thus obtained was not stable, since it tends to rearrange to the starting π conformation without any energy barrier.

We considered in the same way the coordinatively unsaturated species $HFe(CO)_3^-$ deriving from $HFe(CO)_4^-$. Two isomers are obtained when either an equatorial or the axial carbonyl is removed (XA and XB in Fig. 7), the former being about 21 kcal mol^{-1} more stable than the latter. The formation of a complex with ethylene was investigated by allowing the organic moiety to approach XA along an equatorial direction and chosing the Fe-double bond distance r as the reaction coordinate. The two fragments are repulsive until they are 2.6 Å apart, then they give a complex (XI) with minimum energy corresponding to r 1.86 Å. The structure of XI has C_s symmetry, with ethylene on the equatorial plane of the hydrocarbonyliron, and is shown in Fig. 7. Optimized energies and angular variables for XA, XB and XI are given in the caption. The
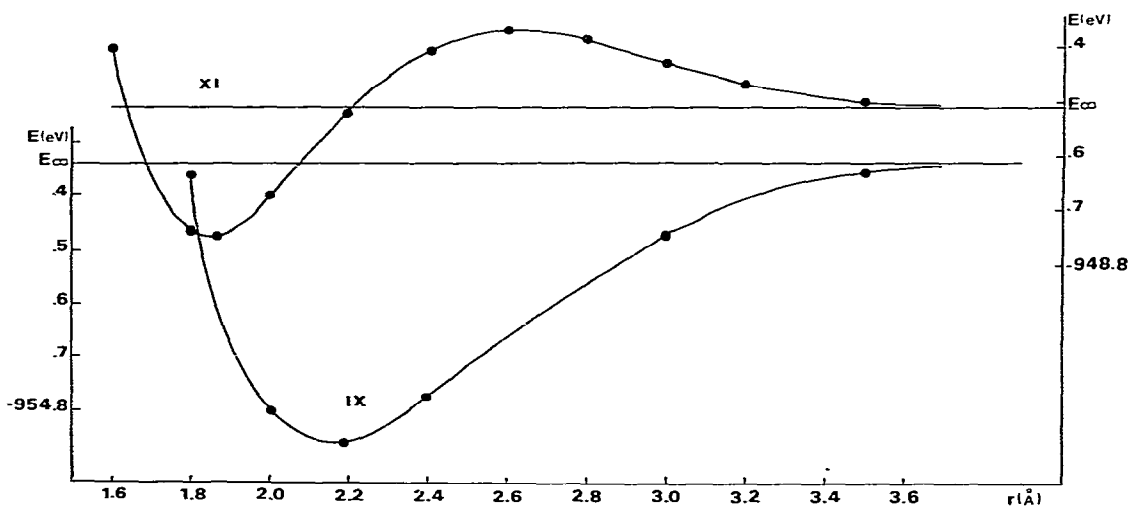

Fig. 5. Variation of optimized EHT energy with $r = $ Fe—A for the π complexes $H_2Fe(CO)_3 \cdot CH_2CH_2$ (IX) and $HFe(CO)_3^- \cdot CH_2CH_2$ (XI).
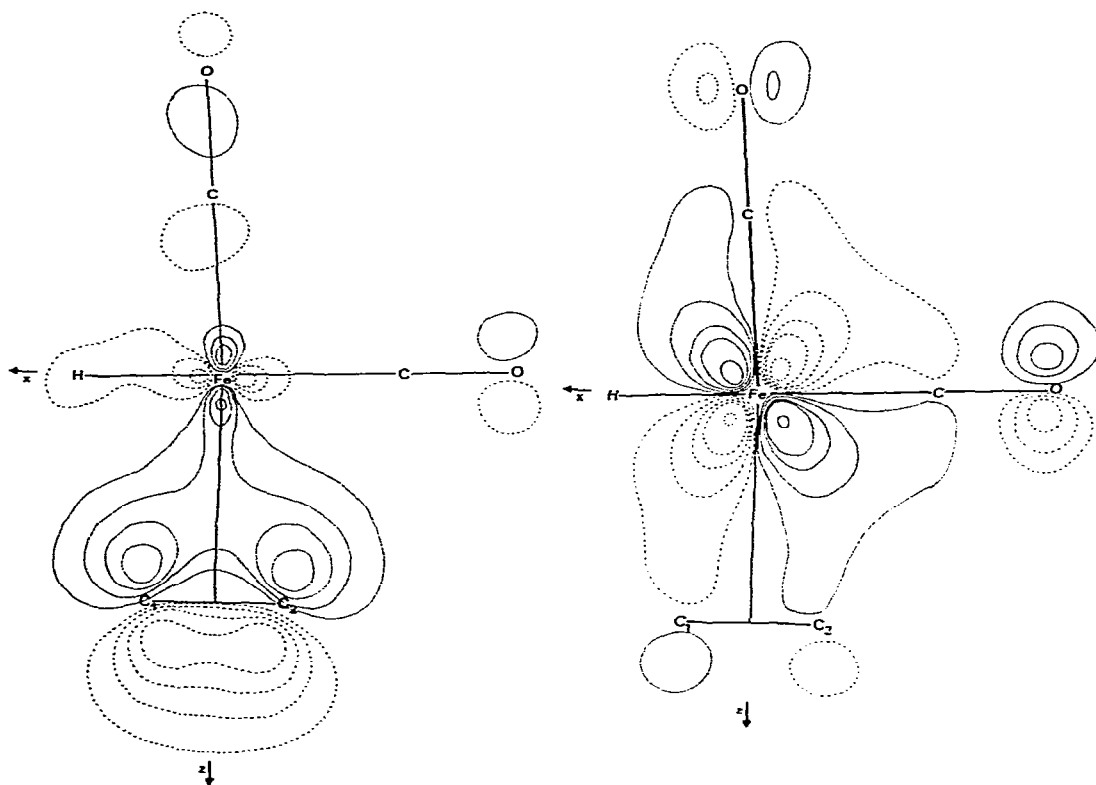
Fig. 6. Contour maps of the 23° and 24° MO of $H_2Fe(CO)_3 \cdot CH_2CH_2$ (IX). The plots are in the xz plane (see Fig. 4) and the contour levels correspond to $\psi = \pm 0.05, 0.10, 0.15, 0.20, 0.50$ a.u.
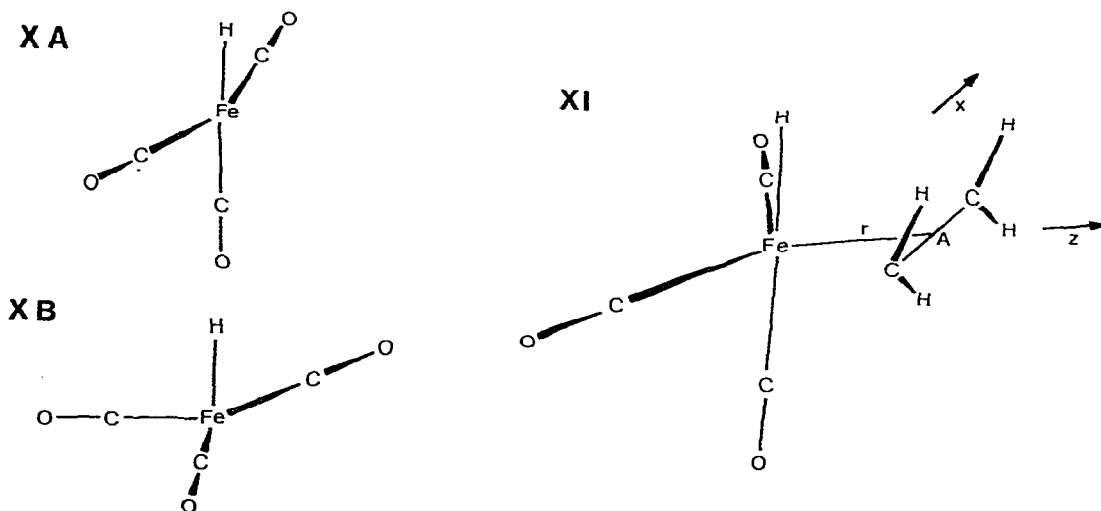
Fig. 7. EHT optimized geometries of two isomers of $HFe(CO)_3^-$ and of π complex $HFe(CO)_3^- \cdot CH_2CH_2$. XA: obtained by removal of an equatorial carbonyl from $HFe(CO)_4^-$. $HFeC_{ax}$ 178.0, $HFeC_{eq}$ 85.8, $C_{eq}FeC_{eq}$ 160.2. Total energy: —732.886 eV; charge on Fe: —0.38 a.u. XB: obtained by removal of the axial carbonyl from $HFe(CO)_4^-$. $HFeC_{eq}$ 89.1. Total energy: —731.980 eV; charge on Fe: 0.18 a.u. XI: $HFe(CO)_3^- \cdot CH_2CH_2$. C_s symmetry, r 1.87 Å, $C_{eq}FeC_{eq}$ 113.4, $HFeC_{eq}$ 86.0, $HFeC_{ax}$ 178.2, HFeA 84.0, FeAC 90.0, HCH 111.3, CCH 121.6. Total energy: —948.848 eV; charge on Fe: 0.41 a.u.; charge on ethylene: —0.40 a.u. Assumed bond lengths in Å: FeC 1.75, FeH 1.57, CO 1.15, CC 1.335, CH 1.09.
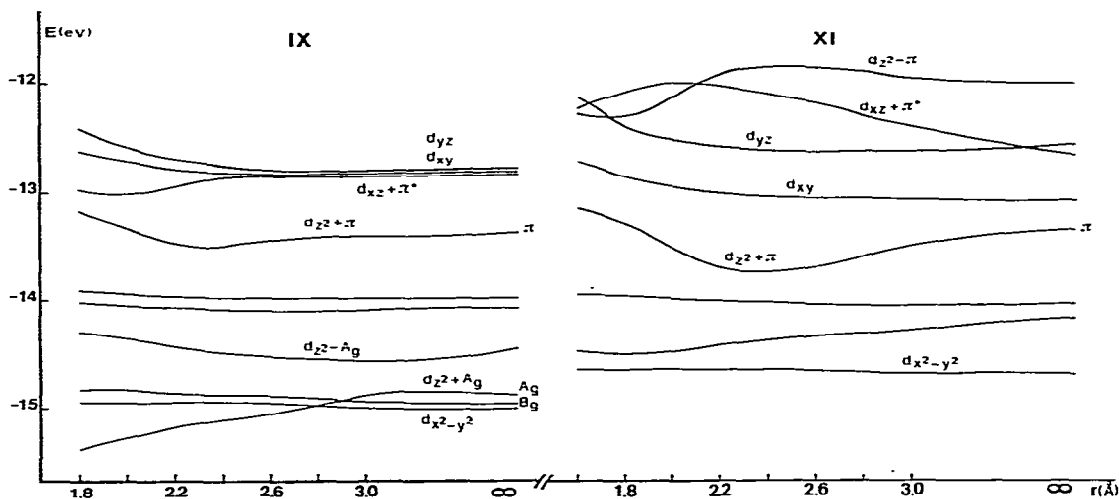
Fig. 8. Variation of the energies of the highest occupied MO's with the reaction coordinate r = FeA for the formation of π complexes $H_2Fe(CO)_3 \cdot CH_2CH_2$ (IX) and $HFe(CO)_3^- \cdot CH_2CH_2$ (XI).

barrier found along the formation path of XI is 3.6 kcal mol^{-1}, and the stabilization energy with respect to the component moieties is 5 kcal mol^{-1}, as shown in Fig. 5. The curves relating to IX and XI show that the former is more stable than the latter, even if its equilibrium distance is significantly larger, and its formation takes place without a barrier. The trends of the highest occupied MO's of the two π intermediates as r is varied are shown in Fig. 8. The dominant feature of the rather low stability of XI is the antibonding character of the d_{z^2}–π MO from infinity to r 2.2 Å. At shorter distances the interaction between the d_{z^2} orbital of Fe and the π orbital of ethylene decreases, and at about 1.86 Å the total energy reaches a minimum. In contrast the antibonding d_{z^2}–π is a high energy empty MO (not reported in Fig. 8) of the complex with $H_2Fe(CO)_3$, thus justifying its higher stability.

Selfconsistent procedure for bond lengths

It is well known that while EHT gives satisfactory results in the prediction of bond angles through a total energy minimization process, it is generally unable to give good estimates of bond lengths, with a few special exceptions. In the present paper Fe—ethylene and Fe—ethyl distances were chosen as reaction coordinates; as for the remaining bonds, experimental or model values were assumed during the calculations. The reliability of the adopted Fe—CO distances was verified through a selfconsistent iterative procedure, based on a quadratic correlation between EHT overlap populations (n) and the bond distances (r), following the parabolic equation:

$$r = a + bn + cn^2 \qquad (1)$$

in line with that used by Hoffmann for CC bond lengths [37].

The coefficients a, b, c were obtained through a least squares fitting from the

TABLE 5

SELFCONSISTENCY ON FeC AND CC BOND LENGTHS

Complex [a]	n [b]	FeC$_{ax}$ [c]		FeC$_{eq1}$ [c]		FeC$_{eq2}$ [c]		CC [d]	
		r_i [e]	r_f	r_i	r_f	r_i	r_f	r_i	r_f
VI	4	1.82	1.848	1.82	1.834	1.82	1.847	1.420	1.493
VII	10	1.72	1.844	1.75	1.654	1.75	1.642	1.420	1.492
VIII A	4	1.82	1.809	1.82	1.810	—	—	—	—
IX	5	1.82	1.857	1.82	1.849	1.82	1.791	1.335	1.377
X A	5	1.75	1.769	1.75	1.789	—	—	—	—
XI	5	1.75	1.778	1.75	1.736	—	—	1.335	1.411

[a] See Figs. 1, 4 and 7. [b] Number of iterations required for selfconsistency. [c] Eq. 1 employed. [d] Hoffmann's equation employed. [e] r_i = initial value, r_f = final value in Å.

experimental FeC bond lengths in $Fe(CO)_5$ [20], $HFe(CO)_4^-$ [23], $H_2Fe(CO)_4$ [24], $Fe(CO)_4C_2H_4$ [38], $Fe_2(CO)_9$ [39], $Fe_3(CO)_{12}$ [28], and the corresponding EHT overlap populations, calculated with A parametrization. The best parabolic fitting of these points gave a 2.2400, b —0.4917, c —0.1256, with a standard deviation of 0.0324.

For the CC bond lengths in the organic moieties Hoffmann's equation [37] was used. The values lengthen significantly, as reported in Table 5, and this is consistent with the fission of the CC bond when the organic fragment interacts with the hydrocarbonyliron (see e.g. the experimental CC-value of 1.46 Å in a stable complex such as $Fe(CO)_4C_2H_4$ [38]). A few iterations were sufficient to reach self-consistency within 0.001 Å, and the differences between initial and final values of FeC are less than 0.04 Å, with the exception of complex VII. In fact, this intermediate required 10 iterations with a variation of FeC of about 0.1 Å, and the same behaviour was observed in $HFe(CO)_4^-$. The results of the iterative procedure are listed in Table 5. Overall equation 1 seems to reproduce satisfactorily the bonding in this kind of iron carbonyl complex.

Concluding remarks

In this investigation of the structure of possible intermediates which may be formed under the conditions of the Reppe synthesis when the hydrocarbonyl interacts with the olefin, a remarkable result is the lack of formation of stable π complexes involving $H_2Fe(CO)_4$ and $HFe(CO)_4^-$. In contrast the EHT computations predict the formation of stable intermediates (IX and XI) when CO deficient species such as $H_2Fe(CO)_3$ and $HFe(CO)_3^-$ are considered. This is not surprising, since in the hydroformylation reaction catalyzed by $HCo(CO)_4$ the existence of a $HCo(CO)_3$-olefin complex has been proposed by the experimentalists. The complex involving $H_2Fe(CO)_3$ is more stable than that derived from $HFe(CO)_3^-$, consistent with the conclusions drawn by Pettit et al. [3], who suggested $H_2Fe(CO)_4$ as the species which is able to coordinate the olefin in Reppe synthesis. IX does not give a stable alkyl complex, but it tends to revert to a π structure. The described behaviour might be a starting point for investigation of the isomerization processes of olefins which occur as side reactions. On the

other hand, stable alkyl complexes are predicted by the EHT calculations when $H_2Fe(CO)_4$ or $HFe(CO)_4^-$ are involved, suggesting that the formation of stable σ intermediates requires the re-attachment of a carbonyl ligand.

Acknowledgment

References

1 P. Pino, F. Piacenti and M. Bianchi, in I. Wender and P. Pino (Eds.), Organic Syntheses via Metal Carbonyls, Vol. II, Wiley, New York, 1977, p. 43.
2 W. Reppe and H. Wetter, Justus Liebigs Ann. Chem., 582 (1953) 133.
3 H.C. Kang, C.H. Mauldin, T. Cole, W. Slegeir, K. Cann and R. Pettit, J. Am. Chem. Soc., 99 (1977) 8323.
4 See ref. 1, p. 199.
5 N. von Kutepow and H. Kindler, Angew. Chem., 72 (1960) 802.
6 V. Bellagamba, R. Ercoli, A. Gamba and G.B. Suffritti, J. Organometal. Chem., 190 (1980) 381.
7 V. Bellagamba, P. Demontis, R. Ercoli, A. Gamba and G.B. Suffritti, Istituto Lombardo (Rend. Sc.), A113 (1979) 301.
8 V. Bellagamba and A. Gamba, J. Organometal. Chem., 212 (1981) 125.
9 R. Hoffmann, J. Chem. Phys., 39 (1963) 1397.
10 M. Wolfsberg and L. Helmholtz, J. Chem. Phys., 20 (1952) 837.
11 M.J.D. Powell, Computer J., 7 (1964) 155.
12 H. Berke and R. Hoffmann, J. Am. Chem. Soc., 100 (1978) 7224.
13 L.L. Lohr Jr. and W.N. Lipscomb, Inorg. Chem., 3 (1964) 22.
14 (a) A.R. Rossi and R. Hoffmann, Inorg. Chem., 14 (1975) 365; (b) M. Elian and R. Hoffmann, Inorg. Chem., 14 (1975) 1058.
15 J.K. Burdett, J. Chem. Soc. Faraday Trans. II, 70 (1974) 1599.
16 J. Demuynck, A. Strich and A. Veillard, Nouv. J. Chim., 1 (1977) 217.
17 E.J. Baerends and P. Ros, Mol. Phys., 30 (1975) 1735.
18 A.B. Anderson, Inorg. Chem., 15 (1976) 2598.
19 D.A. Pensak and R.J. McKinney, Inorg. Chem., 18 (1979) 3407.
20 B. Beagley and D.G. Schmidling, J. Mol. Struct., 22 (1974) 466.
21 H.W. Spiess, R. Grosescu and U. Haeberlen, Chem. Phys., 6 (1974) 226.
22 E.J. Baerends and P. Ros, J. Electron. Spectrosc. Relat. Phenom., 7 (1975) 69.
23 M.B. Smith and R. Bau, J. Am. Chem. Soc., 95 (1973) 2388.
24 E.A. McNeill and F.R. Scholer, J. Am. Chem. Soc., 99 (1977) 6243.
25 W.F. Edgell, J. Huff, J. Thomas, H. Lehman, C. Angell and G. Asato, J. Am. Chem. Soc., 82 (1960) 1254.
26 H.W. Chen, W.L. Jolly, J. Kopf and T.H. Lee, J. Am. Chem. Soc., 101 (1979) 2607.
27 L.F. Dahl and J.F. Blount, Inorg. Chem., 4 (1965) 1373.
28 F.A. Cotton and J.M. Troup, J. Am. Chem. Soc., 96 (1974) 4155.
29 M.R. Churchill, B.G. DeBoer and F.J. Rotella, Inorg. Chem., 15 (1976) 1843.
30 (a) A. Forster, B.F.G. Johnson, J. Lewis, T.W. Matheson, B.H. Robinson and W.G. Jackson, J. Chem. Soc. Chem. Commun., (1974) 1042; (b) J.R. Wilkinson and L.J. Todd, J. Organometal. Chem., 118 (1976) 199.
31 E. Band and E.L. Muetterties, Chem. Rev., 78 (1978) 639.
32 K. Kuchitsu, J. Chem. Phys., 44 (1966) 906.
33 F. Ungváry and L. Markó, J. Organometal. Chem., 219 (1981) 397.
34 P. Wermer, B.S. Ault and M. Orchin, J. Organometal. Chem., 162 (1978) 189.
35 M. Orchin and W. Rupilius, Catal. Rev., 6 (1972) 85.
36 J.Ph. Grima, F. Choplin and G. Kaufmann, J. Organometal. Chem., 129 (1977) 221.
37 R. Hoffmann, Tetrahedron, 22 (1966) 521.
38 M.I. Davis and C.S. Speed, J. Organometal. Chem., 21 (1970) 401.
39 F.A. Cotton and J.M. Troup, J. Chem. Soc. Dalton Trans., (1974) 800.