13 alkyl halide–sodium reactions except that MR_3 is formed instead of $NaMR_4$ when excess sodium is used. Additional reactions will have to be investigated for us to realize the successful synthesis of an organogallium(I) derivative.

Acknowledgment. This work was supported in part by the National Science Foundation through Grant CHE-81-3316 and by the Office of Naval Research. We also thank Professor J. L. Atwood and his students at University of Alabama, University, AL, for attempting the X-ray structural study of $Ga(C_5Me_5)_3$.

Registry No. $Ga(C_5Me_5)_3$, 105121-75-3; $Na(C_5Me_5)$, 40585-51-1; $Ga(C_5Me_5)_2Cl$, 105121-76-4; $Ga(C_5Me_5)Cl_2$, 105139-46-6; $GaCl_3$, 13450-90-3; C_5Me_5H, 4045-44-7.

Molecular Orbital Study of Olefin Homologation by Bimetallic Complexes. 1. The C–C Bond Formation Step

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A molecular orbital analysis of the formation of the metallacyclopentane $Fe_2(CO)_8C_3H_8$ from the bimetallic carbenic complex $Fe_2(CO)_8CH_2$ and ethylene (C_2H_4) is presented. Various mono-, di-, and tribridged isomers of the complexes $Fe_2(CO)_8C_3H_8$ and $Fe_2(CO)_8CH_2$ are considered. Two types of reaction paths have been studied. The first one is a two-step process. It involves the precoordination of C_2H_4 before the so-called insertion occurs. The second one is the direct insertion of C_2H_4 into the carbene–metal bond with or without a previous opening of the bridging structure. From the present study that is based on extended Hückel calculations, the direct insertion is the favored reaction path. The differences of regioselectivity experimentally observed for mono- and tribridged complexes are rationalized within this model.

I. Introduction

The formation of the C–C bond over heterogeneous transition-metal catalysts is an active field of fundamental research due to its major importance in industrial synthesis.[1] In recent years, several experimental studies helped in the understanding of its still obscure mechanism. In 1980–1981, Brady and Pettit[2] showed that CH_2N_2/H_2 or CO/H_2 maintained in identical temperature and pressure conditions over Fischer–Tropsch catalysts gives identical distributions of hydrocarbon products. In the same conditions, results favor the classical Fischer–Tropsch proposal[3] for the C–C bond formation mechanism in which metallic carbene surface species are involved. They are inconsistent with the two other major alternatives proposed on the one hand by Anderson and Emmet[4] (condensation between hydroxymethylene groups) and on the other hand by Pichler and Schlutz[5] (insertion of CO into a metal–alkyl bond). In 1983–1984, Basset et al.[6] and Strehlow et al.[7] showed that, over the same Fischer–Tropsch catalysts, a C_n olefin is homologated to higher C_{n+p} and lower C_{n-p} parent hydrocarbons ($p = 1, 2, ...$). They suggested that the homologation of olefin and Fischer–Tropsch reactions proceed by the same elementary step of C–C bond formation. Further, they have shown that the homologation is a C_1 addition step. These studies confirmed the role played by the carbene intermediate on the metallic surfaces in C–C bond formation. With the assumption of carbene involvement, two mechanisms have been considered.[6] The first one is a carbene insertion into a metal–alkyl bond; the second one is a coupling of carbene and olefins to yield metallacycles with three carbon atoms. The latter hypothesis is supported by the findings of Pettit[7] and Norton[8] which showed that the homologation of ethylene and propene into propene and butene, respectively, is made over bimetallic complexes of osmium and iron. In the case of osmium, a metallacyclopentane complex has been isolated.[8] The fact that identical distributions of products are obtained over various heterogeneous and bimetallic catalysts of C–C bond formation with various feed composition (C_2N_2/H_2, CO/H_2, C_2H_{2n}/H_2) suggests that all the catalysts involve a common mechanism with a metallacyclopentane intermediate. The present study intends to analyze the electronic factors that govern such a mechanism on the basis of molecular orbital considerations supported by extended Hückel technique (EHT) calculations.[9] Quantitative thermodynamic values for the reactions cannot be obtained since this method is unsuitable to give reliable determination of energetics in problems involving large structure reorganization. However, the trends we observe and the reasons behind them that are based on orbitals considerations remain valuable

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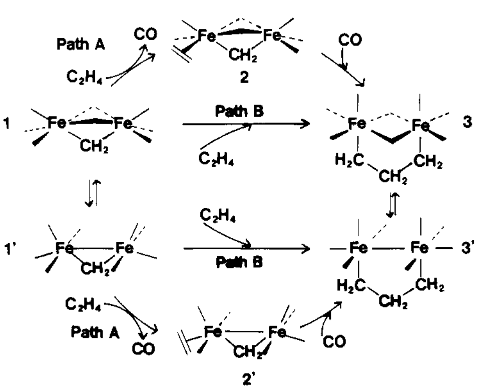


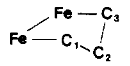
Figure 1. Description of the reactants and products with their interconversion reaction paths presently studied (the carbonyl ligands are not represented).

at more accurate levels. The chemical system under scrutinity is $Fe_2(CO)_8CH_2 + C_2H_4$. It has been experimentally studied by Pettit et al.[7] It serves here as a model for the various catalytic systems so far reported.

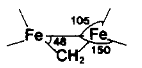
In Figure 1, the various reaction paths which are studied in this report are depicted. The starting carbenic species is either a tribridged (1) or a monobridged (1′) bimetallic complex. Both structures have been experimentally identified for the complex $Fe_2(CO)_8CH_2$; the former structure has been identified in the solid state by X-ray cristallography[10] and the later, in solution by IR spectroscopy.[7] Two types of mechanism have been considered to yield the metallacycle 3 or 3′. The first one (path A) is a two-step procedure which has been proposed by Pettit et al.[7] It involves an elimination of CO which is followed by the addition of ethylene on a metal center. Then, the insertion of the unsaturated ligand in the metal–carbene bond yields C–C bond formation. The second one (path B) is a one-step mechanism. It involves the direct insertion of ethylene into the $Fe-CH_2$ bond.

II. Relative Stability of the Potential Reactants 1 and 1′ and Products 3 and 3′

The four species 1, 1′, 3, and 3′ are depicted in Figure 1. The Fe–Fe bond length of 1 has been fixed to its experimental value (2.51 Å).[10] This bond is stretched by 0.2 Å when 1 rearranges to 1′. The same stretching has been reported for similar structure changes.[11] It leads to the same bond length as in 3′. The Fe–Fe bond length in 3 is assumed to have the intermediate value of 2.6 Å. In all the species 1, 1′, 3, and 3′, the metal atoms can be considered as being in an octahedral environment. The octahedron is mainly distorded in 1′, due to the three-membered ring requirements. The optimal structure 1′ is indicated below. The conformation of the five-membered ring in 3 and 3′ is similar to that determined experimentally in $Co_2Cp_2(\mu\text{-}CO)_2(\mu\text{-}C_3H_6)$.[12] The ring is nonplanar.



3 or 3′



1′

The optimal bending corresponds to dihedral angles between the $C_1-C_2-C_3$ and $Fe-Fe-C_1-C_3$ planes of 131° and 140°, respectively.[12b] Such a bending allows the carbon atoms to be in a tetrahedral environment.

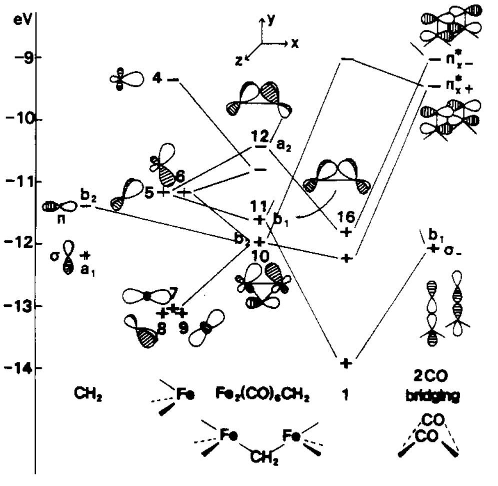


Figure 2. Interaction diagram between two $Fe(CO)_3$, a CH_2, and two bridging CO fragments to yield complex 1. Energies are in electronvolt.

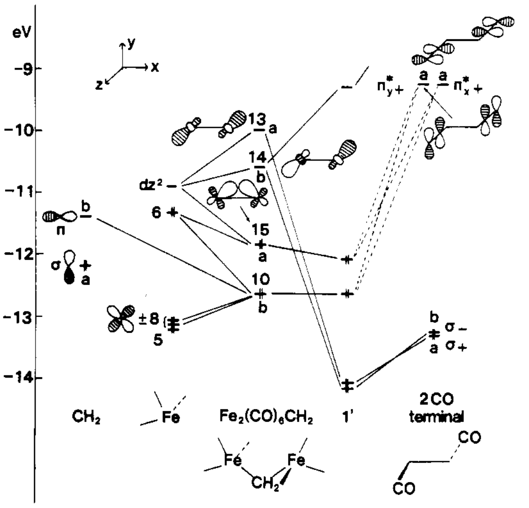


Figure 3. Interaction diagram between two $Fe(CO)_3$, a CH_2, and two terminal CO fragments to yield complex 1′. Energies are in electronvolt.

In bimetallic ligand-bridging complexes, important questions concern the existence and the nature of metal–metal bonds. Experimentally, it has been found that the electron density between the metal atoms is insignificant in the isoelectronic complex $Fe_2Cp_2(CO)_2(\mu\text{-}CO)_2$.[13] Some ab initio or extended Hückel calculations have been performed to investigate the nature of the metal–metal bond,[14,15] in this class of carbonyl-bridged complexes. The overlap populations calculated in the present study (−0.002 in 1, 0.004 in 3, 0.155 in 1′, 0.213 in 3′) agree with those obtained for similar compounds by Benard.[15] These results mean that there is no metal–metal bond in 1 or 3 contrary to the situation found in 1′ and 3′. An understanding of the structure of 1, 1′, 3, and 3′ can be obtained by analyzing them with the fragment decomposition method.

The corresponding molecular interaction diagrams for 1 and 1′ are depicted in Figures 2 and 3. For both complexes, the molecular fragments that have been considered are $(CO)_3Fe-CH_2-Fe(CO)_3$ and two CO's. In a first ap-

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(13) Mitschler, A.; Rees, B.; Lehmann, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 3390–3397.

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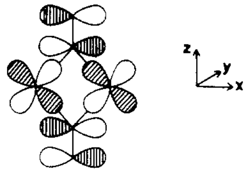
proximation, the $(CO)_3Fe$–CH_2–$Fe(CO)_3$ fragments of 1 and 1′ differ only by some conformational moves of the $Fe(CO)_3$ fragments around the Fe–CH_2 bonds. Both $(CO)_3Fe$–CH_2–$Fe(CO)_3$ fragments can be analyzed as being made of two $Fe(CO)_3$ subunits interacting with a common CH_2 entity. The shape of the frontier orbitals of the $Fe(CO)_3$ fragments has been reported elsewhere.[16] They are depicted in Figures 2 and 3 as well as their interaction with a CH_2 and two CO fragments. The HOMO 16 of complex 1 has Fe–Fe antibonding and metal–bridging ligand bonding character. Thus, the metal–metal relationship in 1 does not correspond to a direct bond but to an undirect delocalized multicentered bond. The small value of the Fe–Fe overlap population confirms this analysis which is applicable also to the tribridged complex 3.



16

As shown in Figure 3, it is worth noting that the out of phase combination 14 of the d_{z^2} fragment orbitals lies below the in-phase combination 13. The reason behind is that there is a second-order perturbation mixing between 13 and the Fe–Fe bonding orbital 15. The latter is the HOMO of 1′.

The energy separation between the interacting orbitals of the CO and $Fe_2(CO)_6CH_2$ fragments involved in the formation of 1 or 3 is smaller than that found for the formation of 1′ or 3′. It explains the better stability of 1 over 1′ (0.9 eV) and of 3 over 3′ (1.3 eV).

Let us now consider the interconversion between 1 and 1′ and between 3 and 3′. This type of fluxional interconversion between monobridged and tribridged carbonyl species is well-documented.[11,17] For example, the easy cis–trans isomerization of $Cp_2Fe_2(CO)_4$ is explained by this property.[18] In some complexes such as $Cp_2Ru_2(CO)_4$, it has been shown that the interconversion involved no significant energy barrier. The energy barrier associated with the transformation of 1 into 1′ or of 3 into 3′ is computed to be 1.3 eV.

At the EHT level, the formation reaction of the dimetallacycles 3 or 3′ from the carbenic complexes 1 or 1′ and ethylene is computed to be endothermic by 1.9 and 2.4 eV, respectively. The same endothermicity has been found by Hoffman et al. in an EHT study of the olefin metathesis;[19] the metallacyclobutane is less stable than the olefin–methylidene complex. However, recent work based on ab initio calculations gives the opposite conclusion.[20] The EHT method, due to the lack of repulsive terms, makes the double bonds too stable when they are compared to the single bonds. It results that the first member of eq 1 is too stablized relative to the second one. The

$$Fe_2(CO)_8CH_2 + C_2H_4 \rightarrow Fe_2(CO)_8(C_3H_6) \quad (1)$$

overstabilization can be roughly evaluated by the comparison of the energies of three ethylene and two propene molecules at both the EHT level and the ab initio level (3-21G basis set). The energy difference between the two systems is equivalent to the difference between a C=C double bond and two C—C single bonds. All the C–H bonds are assumed to have the same energy. This difference corresponds to that between the metallacycle and the C_2H_4 + carbene complex: a C=C double bond disappears and two new C—C single bonds are formed. At the EHT level, the double bond is more stable than two single bonds by 0.97 eV. On the contrary, at the ab initio level, it is less stable by 1.2 eV. Hence, one can estimate the overstabilization of the first member of eq 1 to be ca. 2.2 eV at the EHT level. With the assumption of this correcting value, the formation of the dimetallacycles would be found quasi-isoenergetic at ab initio calculations level.

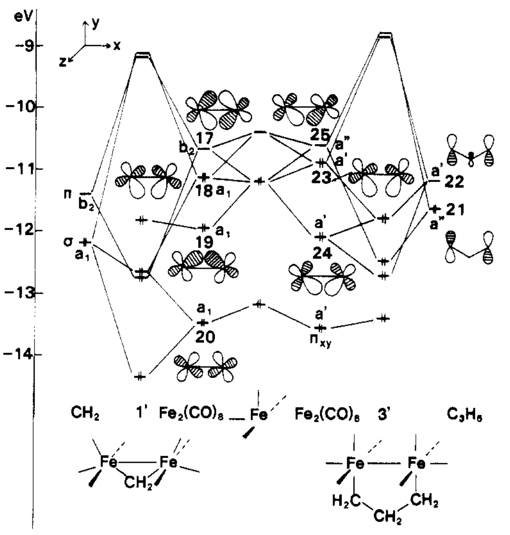


Figure 4. Interaction diagrams between $Fe_2(CO)_8$ and CH_2 (on the left part) or C_3H_6 (on the right part) to yield 1′ and 3′, respectively. Energies are in electronvolt.

An interesting point is to compare the interaction of the $Fe_2(CO)_8$ fragments with a carbene CH_2[21] and with a trimethylene C_3H_6 substituent. The interaction diagrams for 1′ and 3′ are given in Figure 4.

These diagrams can be built as follows: the interaction of two $Fe(CO)_4$ fragments (symmetry C_{2v}) leads to a $Fe_2(CO)_8$ system which then interacts with CH_2 or C_3H_6. Some interesting features are worth noting. In the C_3H_6 fragment, the antisymmetric orbital 21 (a″) has a lower energy than the symmetric orbital 22 (a′). This counter intuitive order has already been observed by Hoffmann[22] and explained by the mixing of the symmetric combination with the σ_{CH_2} and $\sigma^*_{CH_2}$ orbitals associated with the central methylene group. When the two parts of Figure 4 are compared, one sees that the main difference between them comes from the existence of a very low-lying orbital of a_1 symmetry in the left part. The reason is a better orientation of the parts of the orbitals of the $Fe_2(CO)_8$ fragment able to interact favorably with the organic fragment. It is concluded that the interaction of the $Fe_2(CO)_8$ fragment is more stabilizing with a carbene than with a trimethylene fragment.

III. The Two-Step Process (Path A). An Elimination–Addition Reaction Followed by the C_2H_4 Insertion

As it was proposed by Pettit et al., we looked at a mechanism involving the loss of a CO ligand. The Fe–CO

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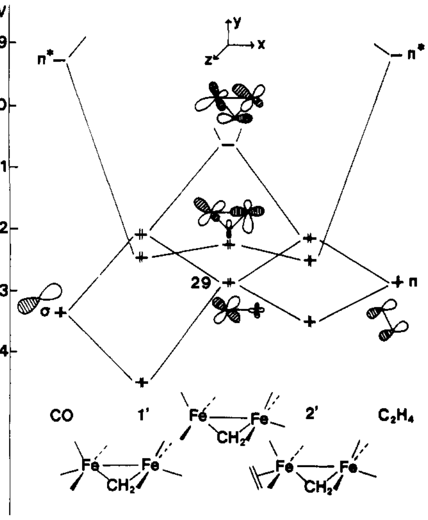
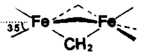


Figure 5. Interaction diagrams between a $Fe_2(CO)_7CH_2$ fragment and CO (on the left part) or C_2H_4 (on the right part) to yield 1′ and 2′, respectively. Energies are in elctronvolt.

bond that breaks can be axial or equatorial. In 1, both positions are energetically equivalent (the loss of an equatorial CO is favored by 0.1 eV only). In 1′, the loss of the equatorial CO cis to the carbene is favored by 0.3 eV relative to the axial CO and by 0.4 eV relative to the equatorial CO trans to the carbene. This can be explained by considering the HOMO of 1′. Apart from its clearly dominant metal contribution, it has contributions on the carbonyls. The axial CO and the equatorial CO trans to CH_2 interact through their π^* orbitals in a bonding way and hence favor the stabilization of the HOMO. On the contrary, the equatorial CO cis to CH_2 interacts through its lone pair in an antibonding way and hence destabilizes the HOMO. Consequently, the loss of the latter ligand stabilizes the HOMO and the loss of the former destabilizes it. After the departure of CO, the other carbonyls move to yield the more stable structure of the unsaturated complexes. If the bridges are kept, we obtain structures **26** and **27** which both have metal atoms in a trigonal



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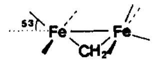
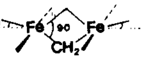


27

pyramid coordination. **26** is computed to be 0.7 eV below **27** (in agreement with the energetic difference between **1** and **1′**). The CO loss costs in both cases about 3 eV. This EHT value is more than twice the experimental value[23] (1.23 eV). A similar value is found by Hoffmann et al.[24] The iron atoms in **26** and **27** are unsymmetrically coordinated. One can wonder whether the restauration of the symmetry would lead to complexes more stable than **26** or **27**. Various opened structures have been considered such as **28** or **28′** in order to explore such possibilities.



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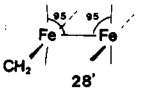

28′

They all have been found to be less stable than **27**. For example, **28** and **28′** are both less stable than **27** by 0.77 and 0.14 eV, respectively.

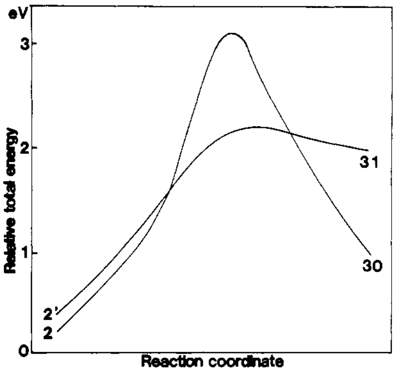

Figure 6. Total energy variations along the reaction paths from $Fe_2(CO)_7(C_2H_4)CH_2$ (**2** or **2′**) to $Fe_2(CO)_7C_3H_6$ (**30** or **31**). Energies are in electronvolt.

Let us consider now the coordination of ethylene on **26** and **27** to yield complexes **2** and **2′**. The C=C bond of ethylene has been elongated to 1.46 Å, and the hydrogen atoms bent back by 15°.[25] It is the experimental geometry[26] in iron complexes. The distance between Fe and the middle of the C=C bond is 2.12 Å. The coordination of C_2H_4 relative to the coordination of CO is in fact an unfavorable process as it can be seen in Figure 5. In the left part is represented the interaction of $Fe_2(CO)_7CH_2$ with CO to give 1′ and in the right part, the interaction of the same fragment with C_2H_4 to give 2′. In both cases the HOMO is slightly stabilized by interaction with the π^*_{CO} or the π^*_{CC}. The main difference lies in the interaction of the orbital **29** with the CO lone pair or the π_{cc}. The overlap between **29** and the CO lone pair is larger than the overlap with the π_{cc} because the CO lone pair is directed exactly toward **29**. Despite the larger energy gap, a stronger interaction results with the CO lone pair than with π_{cc} and hence a low-lying orbital in the case of 1′. One would expect also a more destabilized orbital. However, a second-order stabilizing interaction with the LUMO of $Fe_2(CO)_7CH_2$ intervenes. It is stronger for 1′ than for 2′, and consequently, the HOMO's of 1′ and 2′ have roughly the same energy. The existence of a very stabilized orbital in 1′ explains that CO is a better ligand than ethylene. The same diagrams are obtained for $Fe(CO)_5$ and $Fe(CO)_4C_2H_4$; they confirm the experimental results:[26,27] $Fe(CO)_5$ is known to be stable and $Fe(CO)_4C_2H_4$ to be thermally unstable.

The problem of the rotational barrier and of the conformational preferences of ethylene complexes has been widely studied.[25b,28] In both species **2** and **2′**, the ethylene prefers to be in the equatorial plane, the rotational barrier being 9.4 kcal/mol for **2** and 8.7 kcal/mol for **2′**. The analogy between the orbitals of the ML_3 and ML_5 fragments[25b] leads us to conclude that the orbital interactions favor the in-plane conformation. This theoretical result is contradictory with the experimental results found for $ML_3(C_2H_4)$ complexes where the perpendicular orientation is obtained. This discrepancy is due to steric effects as it is confirmed by the experimental in-plane conformation of the ML_3–carbene complexes[16,29] where the same orbital

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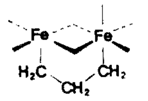
(28) Demuynck, J.; Strich, A.; Veillard,A. *Nouv. J. Chim.* **1977**, *1*, 217–228.

interactions are involved, but not the same steric effects.

The formation of the metallacyclopentanes **3** and **3′** from **2** and **2′** involves the coupling of the carbene with the ethylene. In **2** and **2′**, the carbene is negatively charged (−0.284 and −0.357, respectively) and thus acts as a nucleophile on the ethylene which is slightly positively charged. This reaction looks like the olefin insertion reaction into a M–H bond which has been studied by Thorn et al.[25a] They show that the best way for the insertion is the "end-on" coplanar approach which allows for good overlap. In **2′**, the most stable conformation corresponds to the situation where the ethylene and the carbene are coplanar. In **2**, the conformation convenient for the reaction is the less stable one and needs 9.4 kcal/mol to be reached. The reaction of an olefinic complex with a nucleophile has already been studied theoretically.[30] Thus, we will only give here (Figure 6) the energy profile of the reaction leading to the metallacyclopentanes $Fe_2(CO)_7C_3H_6$ (**30** and **31**) which by further recoordination of CO would give **3** and **3′**. The activation energies are high (2.6 eV for **2** and 1.8 eV for **2′**) although both reactions are symmetrically allowed (no HOMO–LUMO crossing). They would be explained in part by the better description of the double bond relative to the single bond, as it was already discussed. Another reason why this process is not favored is that the necessary movements of the CO's which must follow the first step is more difficult in **2** than in **2′**.



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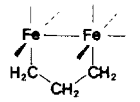

31

In summary, mechanism A seems to be unfavorable for both theoretical and practical reasons. Orbital considerations have shown that the coordination of ethylene is not a favorable process relative to the coordination of CO (see Figure 5). The experimental reasons are the following: the departure of CO usually occurs at high temperature (for example, the decomposition of the iron–pentacarbonyl complex begins only above 120 °C.[27] The experimental conditions of Pettit et al. (55 °C)[7] does not correspond to this range of temperature. The loss of CO followed by the coordination of an olefin or an alkyne has already been invoked for the reaction of a carbenic complex with an unsaturated organic species, but the reaction was photochemically induced[31] (for example, $Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)Cp_2$). Secondly, the metallacyclopentanes obtained experimentally by the coupling of the carbenic complexes with ethylene are the symmetrical $Fe_2(CO)_8C_3H_6$ (**3** or **3′**) complexes (such a metallacyclopentane has been isolated in the case of a diosmium carbenic complex[8]) and not **30** or **31**. The experiences of Pettit et al.[7] or Norton et al.[8] are made with an excess of ethylene and without CO. Thus, it is unlikely that CO could recoordinate on **30** or **31** to give **3** or **3′**. The foregoing considerations have lead us to consider another mechanism consisting of a direct attack of ethylene on the carbenic complex without changing the coordination sphere of the metals.

Table I. σ and π Populations of the Carbene Fragment, σ and π Transfers, and Total Charge in the Bimetallic Complexes 1, 1′, 32, 33, 34, and 35

	pop.		transfer		
complex	σ	π	σ	π	total charge
1	5.25	0.98	0.75	−0.98	−0.23
1′	5.29	1.08	0.71	−1.08	−0.37
32	5.29	0.80	0.71	−0.80	−0.09
33	5.32	0.59	0.68	−0.59	0.09
34	5.31	0.89	0.69	−0.89	−0.20
35	5.30	0.43	0.70	−0.43	0.27

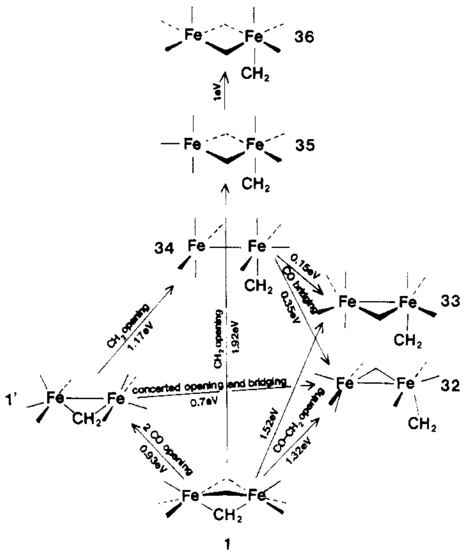

Figure 7. Various bridged and nonbridged bimetallic carbenic species involved in the different studied reaction paths. The CO ligands are not depicted. The energies reported in electronvolt are energy differences.

IV. Study of the Opening of the Carbene Complexes

The population analysis of **1** shows (Table I) that the carbene is negatively charged (−0.23 au) with 0.98 au in the p_x orbital of the carbon. The p_x orbital is split between an occupied orbital and the LUMO with coefficients of 0.43 and 0.57, respectively. There are also significant contributions on the metal atoms in these two orbitals and on the bridged carbonyls in the LUMO (C_{2p_x}, 0.40; O_{2p_x}, 0.23). Thus, no frontier orbital has large coefficients on the p_x orbital of the carbene. The same situation occurs for **1′**.

Ab initio calculations have clearly established[32] that the electrophilic or nucleophilic reactions on metal carbene complexes are frontier orbital controlled. Consequently, if **1** acts as an electrophile as it is expected with ethylene, the attack would be unselective and difficult since the LUMO is shared between the carbene, the iron atoms, and the bridged carbonyls. If, after activation of ethylene, it acts as a nucleophile, the site of attack will be rather the metal atoms than the carbene since the d_{xy} orbitals of the Fe atoms have the largest coefficients in the HOMO. Thus, the direct attack of C_2H_4 on **1** or **1′** to yield **3** or **3′** looks unfavorable. The foregoing analysis led us to search for other derived carbenic species which could be more favorable for the attack of ethylene. Such species are produced by the opening of the bridging carbene; this process has already been considered by other authors[33] to

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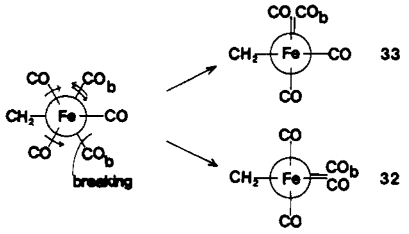
[29] Butler, W. M.; Enemark, J. H. *Inorg. Chem.* **1973**, *13*, 540. Anderson, O. P.; Packard, A. B. *Ibid.* **1978**, *17*, 1333. Cardin D. J.; Cetinkaya, B.; Lappart, M. F.; Manojlovic-Muir, L. J.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1971**, 400.

[30] Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308–4320.

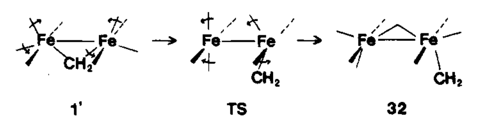
[31] Colborn, R. E.; Dyke, A. F.; Knox, S. A. R.; Macpherson, K. A.; Mead, K. A.; Orpen, A. G.; Roue, J.; Woodward, P. *Philos. Trans. R. Soc. London, Ser. A* **1982**, *308*, 67–73. Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 803.

[32] (a) Block, T. F.; Fenske, R. F.; Casey, C. P. *J. Am. Chem. Soc.* **1976**, *98*, 441–443. (b) Nakatsuji, H.; Ushio, J.; Han, S.; Yonezawa, T. *Ibid.* **1983**, *105*, 426–434. (c) Ushio, J.; Nakatsuji, H.; Yonezawa, T. *Ibid.* **1984**, *106*, 5892–5901.

explain the cis–trans isomerization of bridged carbenic complexes. Cotton et al.[18] show that, in some tribridged species, two bridges open together. These considerations led us to study the structures depicted in Figure 7. The opening of the two bridged CO's which transforms 1 into 1′ has already been considered in the first section. The openings that lead to 32 and 33 correspond to the different



movements of the bridged CO's shown above with the help of a Newman projection. They both require 2.3 eV. These energies are due to the necessary rearrangement of the ligands. Their magnitude prevents the reaction path to go through 32 or 33. The simultaneous opening of the carbene and bridging of a CO from 1′ lead directly to 32 with a barrier of 0.7 eV. It is interesting to note that the



transition state prefers to have a square-planar $Fe(CO)_4$ fragment than a trigonal-bipyramidal one (see the structure 28′). The nonconcerted pathway that gives the nonbridged carbene 34 first and then 32 requires the same amount of energy. It is thus competitive with the concerted pathway.

The most interesting species of Figure 7 are the bridged carbenes 1 and 1′ and the corresponding nonbridged species 34, 35, and 36. In the nonbridged carbenes, a value of 1.79 Å for the Fe–C bond length has been assumed in agreement with some experimental values of electron-deficient complexes.[34] 34 is stable and does not dissociate. This is shown by the orbital energy variations when the Fe–Fe bond is elongated. The bonding orbitals rise in energy while the antibonding orbitals decrease in agreement with the existence of a Fe–Fe bond.[35] The $Fe(CO)_4$ moiety prefers to have a square-pyramidal geometry rather than a trigonal-bipyramidal one.

As illustrated in the Figure 7, the carbene prefers to be bridged rather than opened in both cases 1 and 1′. The interaction diagrams of the $Fe_2(CO)_8$ and CH_2 fragments to yield 1 (on the right) or 35 (on the left) are depicted in Figure 8. In the right diagram, the symmetry is C_{2v}. They are large overlaps between the σ,π_{CH_2} orbitals and the orbitals of the $Fe_2(CO)_8$ fragment of the same symmetry. Strong stabilizing interactions result. In the left diagram, the symmetry is lower (C_s) and the σ_{CH_2} and π_{CH_2} orbitals are of the same symmetry and interact both with the same orbitals of the $Fe_2(CO)_8$ fragment.

The comparison of the two diagrams shows that the difference of stability between 1 and 35 comes essentially from the position of the HOMO's which are in fact the HOMO's of the two $Fe_2(CO)_8$ fragments. The HOMO's of 35 and 1 (Figure 2) result from the strong interaction of a vacant orbital of the $Fe_2(CO)_6$ fragment (12 in Figure 2) with a combination of the π^*_{co} of the bridged carbonyls. However, in 35, the orbitals of the two $Fe(CO)_3$ fragments that interact to form $Fe_2(CO)_6$ are not at the same energy level as was for 1. It explains why the resulting vacant orbital is higher in 35 than in 1 (see scheme I). The interaction of these orbitals with the π^*_{co} of the bridged carbonyls has roughly the same strength in 1 and in 35. It results that the energy positions of the HOMO of 35 and of 1 are identical with that of the respective $Fe_2(CO)_6$ fragments. The stability difference between 1′ and 34 is explained by similar diagram.

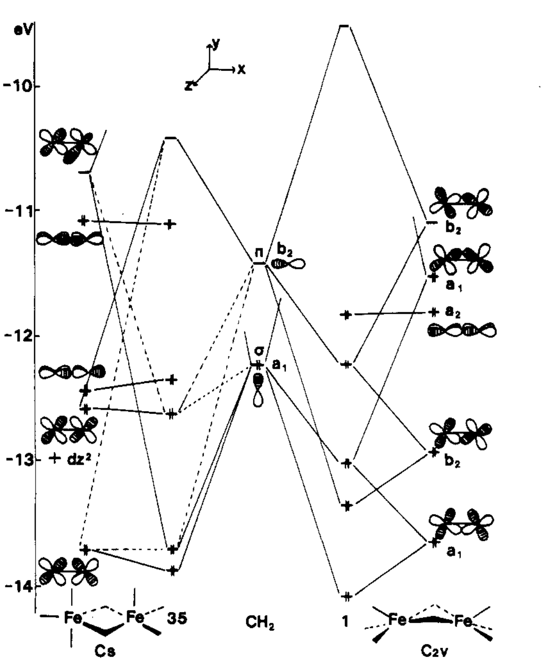
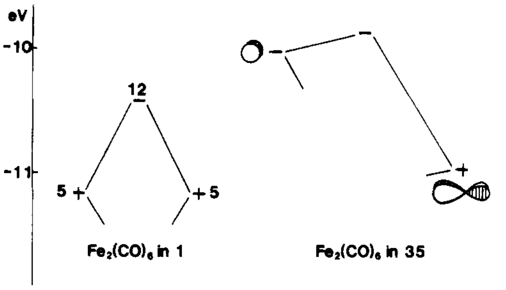


Figure 8. Interaction diagrams between $Fe_2(CO)_8$ and CH_2 to yield the nonbridged 35 (on the left part) or bridged 1 (on the right part) carbenic complex, respectively. Energies are in eV.

Scheme I



Let us compare new the population analysis of the various carbenic species above studied (see Table I). The σ transfer is roughly the same for all complexes. These complexes differ by the amount of π transfer (the back-donation). The smaller the π transfer, the smaller the negative charge on the carbene. This charge can even become positive as in 33 or 35. The amount of π transfer is easily understood by the consideration of the same diagrams as before (Figures 2, 3, and 8). For example in 1 and 1′, the large π transfer (0.98 ua and 1.08 ua) is explained by the strong interaction between the π_{CH_2} orbital and the occupied orbitals of the $Fe_2(CO)_6$ fragments. For 35 we have seen in Figure 8 that the interactions of the π_{CH_2} orbital with the other fragment are weak. A small π transfer (0.43 ua) is computed, and a positively charged carbene results. The distribution of the π_{CH_2} orbital be-

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(33) Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 861–862.

(34) (a) Taylor, T. E.; Hall, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 1576–1584. (b) Pangler, D. S.; Wendoloski, J. J.; Dupuis, M.; Chen, M. M. L.; Schaeffer, H. F. *Ibid.* **1981**, *103*, 3985–3990.

(35) Shaik, S.; Hoffmann, R.; Fisel, C. R.; Summerville, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4555–4572.

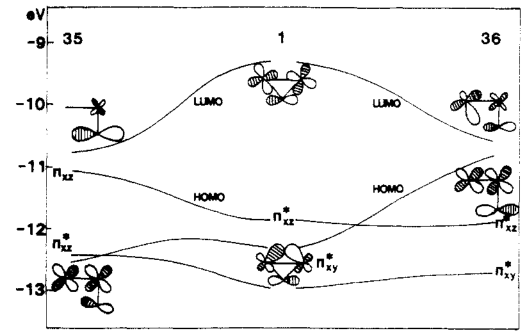
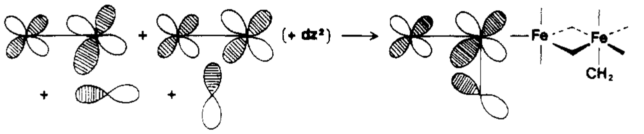


Figure 9. Energy variations of the frontier orbitals along the reaction paths that yield to **35** and **36** from bridged complex **1**.

Scheme II

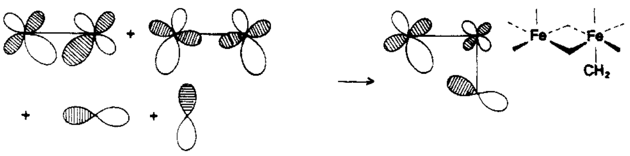


tween the molecular orbitals is in relation with the charge of the carbene. In the complexes where the carbene is negatively charged (**1**, **1′**, and **34**), the π_{CH_2} orbital is shared between the LUMO and an occupied orbital which is either the HOMO (in **34**) or the first orbital (in **1**) or second orbital (in **1′**) below the HOMO. In these cases, both the LUMO and the occupied orbital have important coefficients on the iron atoms too. On the contrary, in the complexes where the carbene is positively charged (**35**) or not charged (**32** and **33**), the π_{CH_2} orbital is mainly on the LUMO with a coefficient equal to 0.84, 0.72, or 0.81, respectively. The metallic atomic orbitals of these complexes are involved in the occupied orbital essentially. Thus, in these cases, the carbene acts as an electrophile via the LUMO of the complexes. Such a situation is favorable for the attack of the ethylene.

Before this direct reaction between the bimetallic carbene and ethylene was studied, we will point out the interesting behavior of **36**. In **36**, the energy potential curve associated with the Fe–C bond length is very flat; when the Fe–C bond is elongated from 1.8 to 2 Å, the energy changes by 0.03 eV only, but the charge on the carbene varies from a positive value (0.19) to a highly negative one (−1.05). This corresponds to a crossing of the frontier orbitals as shown by the analysis of the orbital evolutions during the opening of **1** into **35** or **36** (Figure 9). When **1** opens to give **35**, no symmetry plane is preserved. This reduction of symmetry allows the mixing of the two high occupied π^*_{xz} and π^*_{xy} orbitals. The HOMO of **1** is the out of phase combination and rises in energy. By mixing with p_z, it rearranges to π^*_{xz}. The next orbital (π^*_{xy}) that is bonding between the carbene and the left iron atom should be destabilized when the corresponding bond is broken without the in phase complementary interaction with π^*_{xz}. In the final product **35**, we have seen (Figure 8) that, via the π_{CH_2} and the σ_{CH_2} orbitals, a mixing between two orbitals of the $Fe_2(CO)_8$ fragment occurs as shown in Scheme II. This mixing explains the change in the phase of this orbital in the transformation **1** → **35**. A bonding character appears between the right iron atom and the carbene.

On the contrary in **36**, the symmetry is conserved during the opening. The mixing between π^*_{xz} and π^*_{xy} is not allowed. π^*_{xz} has a constant energy. The π_{xy} energy increases sharply since there is no mixing to cancel the destabilizing effect of the breaking of the Fe–CO bond. This orbital becomes the HOMO and is mainly on the carbene.

Scheme III

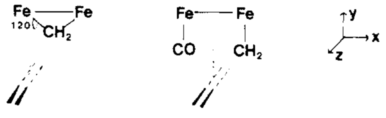


The LUMO of **1** is antibonding between the left iron atom and the carbene. So the breaking of the bond which yields **35** or **36** from **1** stabilizes this orbital. We see in Figure 8 that the LUMO of **35** becomes predominantly π_{CH_2}. The LUMO results from the mixing of two orbitals of the $Fe_2(CO)_8$ fragment with the σ_{CH_2} and π_{CH_2} orbitals as shown in Scheme III. The two orbitals described in Schemes II and III have roughly the same shape although they result from the combination of different orbitals of the $Fe_2(CO)_8$ fragments (two orbitals with π^*_{xy} character in Scheme II, one with the same π^*_{xy} character, and one with dominant σ character in scheme III). Due to the presence of two CO ligands along the x and y directions on the left iron atom in **35**, the latter is destabilized and thus cannot intervene in the mixing as it does in **36**.

Finally, we have in **36** two frontier orbitals that are very close in energy. The LUMO is bonding between the right iron atom and the carbene and the HOMO is antibonding between them. Thus when the Fe–CH_2 bond length is shortened, the energy of the HOMO continues to rise and that of the LUMO to decrease. This explains that they cross and that the π_{CH_2} initially concentrated in the HOMO and consequently partially filled becomes concentrated in the LUMO and empty, inducing the change in the charge on the carbene.

V. Direct Reaction of Ethylene on the Carbenes. Reaction Path B

Various directions of approach of C_2H_4 in various orientations were examined. The horizontal orientation (the C=C lies in the symmetry plane Fe–Fe–CH_2) has been compared to the vertical orientation (the C=C bond is orthogonal to the symmetry plane). For the different approachs that have been considered, the first one yields a slightly better overlap between ethylene and the carbene, but the reaction path is unfavorable energetically due to a large steric hindrance. The vertical approach involves a reduced overlap, but the accessibility is better. It is slightly preferred in all cases although the energy difference is very small. On the bridged carbenes **1** and **1′**, the preferred direction of attack is the midlle of the Fe–CH_2 bond with an angle of 120° as shown.



This angle is determined by the steric hindrance of the ligand cis to the carbene. The approach of C_2H_4 is accompanied by a linear opening of the carbene and movement of the other ligands. On the opened carbenes **32**–**35**, the direction of attack is the middle of the Fe–Fe bond with an angle of 90°. In all cases, the variations of the orbital energies along the reaction path were studied and plotted. Two cases can be distinguished: the first one is an allowed reaction (**32**, **33**, **35**) and the second is a forbidden reaction (**1**, **1′**, **34**) in the sense of Woodward–Hoffmann rules.[36] A curve representative of each case is

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[36] Hoffmann, R.; Woodward, R. B. *J. Am. Chem. Soc.* **1965**, *87*, 2046–2048; *Angew. Chem.* **1969**, *81*, 797–869.

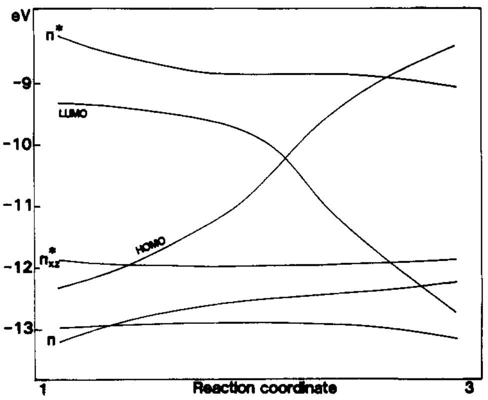


Figure 10. Energy variations of the frontier orbitals during the reaction of C_2H_4 on complex 1 to yield 3 directly.

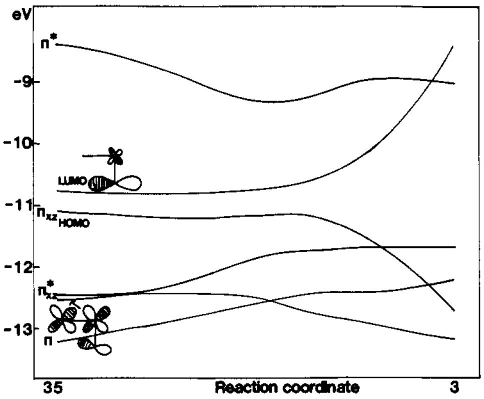
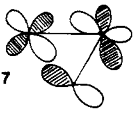


Figure 11. Energy variations of the frontier orbitals during the reaction of C_2H_4 on complex 35 to yield 3 directly.

plotted in Figures 10 (attack on 1) and 11 (attack on 35). In Figure 10, a crossing between the frontier orbitals clearly occurs. For the initial product 1, the two orbitals concerned are described in Figure 9. When C_2H_4 approaches, the carbene opens. It gives the two orbitals **37** and **38**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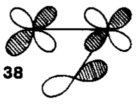
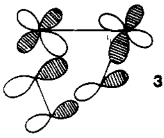

38

similar to those described in Figure 9 for **36**. One sees that **37** has a large overlap with the π^* orbital of C_2H_4 and **38** a large overlap with the π orbital.

However, as the coefficients and shapes of the atomic orbitals located on the left iron atom and on the carbene atom are not equal, the overlaps of **37** with π and of **38** with π^* are not zero. Through the π and π^* orbitals of C_2H_4, **37** and **38** will mix when the reaction proceeds. It yields two orbitals, the in phase and the out of phase combinations of **37** and **38** which become respectively the HOMO **39** and the LUMO **40** of the product. In the transition state we obtain the following combination: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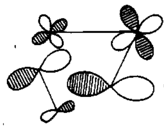
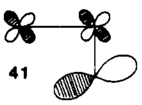

40

$$(39) = 0.51\ (37) + 0.74\ (38) - 0.47\ (\pi) \quad \text{(HOMO)}$$

$$(40) = 0.70\ (37) - 0.32\ (38) + 0.53\ (\pi^*) + 0.32\ (\pi)\text{(LUMO)}$$

Thus, the HOMO is the antibonding combination of the bimetallic carbene fragment with the π orbital of C_2H_4 and the LUMO, the bonding combination with the π^* orbital. The HOMO rises and the LUMO decreases sharply when C_2H_4 approaches. This explains why these two orbitals cross. If the metallacyclopropane ring is assimilated to a double bond, as it is often made for cyclopropane reactivity in organic chemistry, thus the reaction of 1 or 1′ with C_2H_4 can be compared to the 2 + 2 cyclodimerization of ethylene (a thermally forbidden reaction).[36] Let us now consider the reaction of **35** with C_2H_4. The HOMO of **35** is initially π_{xz} (see Figure 9). When the reaction proceeds, the arrangement of the CO's around the left iron atom transforms from a trigonal bipyramid to a square-planar pyramid as in **36**. In this transformation, no symmetry plane is preserved. We find a phenomenon similar to that observed for the transformation of 1 to **35**: the π_{xz} orbital mixes with the π^*_{xy} orbital and hence the HOMO becomes more and more π^*_{xy}. We observe then the same mixing as before of the LUMO **41** and of the HOMO **42** of **35** via the interaction of the π and π^* orbitals of C_2H_4. At the transition state, we have the following combinations: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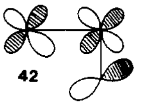
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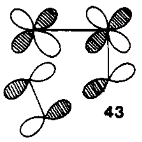
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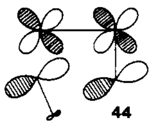

44

$$(43) = 0.45\ (41) + 0.85\ (42) + 0.22\ (\pi^*) \quad \text{(HOMO)}$$

$$(44) = 0.60\ (41) - 0.49\ (42) + 0.47\ (\pi^*) - 0.43\ (\pi)\text{(LUMO)}$$

The coefficient of the π_{CH_2} orbital in **41** is so large compared to **42** that it dominates in the resulting orbital **43**. The combination $d_{xy}-\pi_{CH_2}$ is bonding in **43** while it was antibonding in **42**. This is the clear-cut difference with the preceding case (compare **39** and **43**). Now the HOMO can no longer mix with the π orbital of C_2H_4 when this molecule approaches the complex but only with the π^* orbital in a bonding way. It explains that the HOMO has a decreasing energy when the reaction proceeds. On the contrary, the LUMO **44** combines with C_2H_4 in an antibonding way explaining its energy rises. In this case, the HOMO and LUMO do not cross and the reaction is allowed. For all studied complexes, the frontier orbitals have the same form as in 1 or in **35** and the same explanation can be considered. Consequently, the key factor for the reaction to be allowed is that the coefficient of the π_{CH_2} orbital is sufficiently large in the LUMO of the initial complex to assure the bonding combination of the carbene orbitals with those of C_2H_4 in the HOMO of the transition state. This is the case for **32**, **33**, and **35**.

Let us consider now how the reaction proceeds. First, we notice that the overlap population between C_2H_4 and the carbene increases quicker than the overlap population between C_2H_4 and the iron atoms. This signifies that the carbon–carbon bond is made before the carbon–iron bond. This was already noted by Hoffmann et al.[24] as consistent with the energetics of the C–C and C–metal bond formation. To study the electron shift during the reaction, we have compared the population analyses of the same $Fe_2(CO)_8CH_2$ complexes with or without C_2H_4 along the reaction path. For **35**, we observe first a transfer from the

Table II. Energies of the Transition States Obtained from the Various Complexes 1, 1′, 32, 33, 34, 35, and 36 for the Ethylene Insertion into the Fe–Carbene Bond (see Figures 1 and 7)[a]

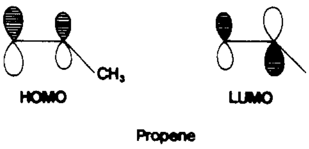
	1	1′	32	33	34	35	36
ΔE	4.8	5.7	5.0	5.1	4.7	4.3	3.9
E^*	4.8	4.8	3.8	3.6	2.7	2.1	1.1

[a] The energy reference is the most stable complex 1 for ΔE. It is the corresponding complex for E^* (ΔE and ϵ^* are in eV).

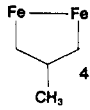
π orbital of the ethylene to the empty p orbital of the carbene. The iron atoms and the carbonyls are roughly unaffected. After the transition state, there is a transfer from the $d_{x^2-y^2}$ of the left iron atom to the π^* orbital of ethylene. This scheme is consistent with a nucleophilic attack of C_2H_4 on the carbene. For 1, the electron shift is more complicated. We saw that the LUMO of 1 is partly on the carbene, partly on the iron atom, and on the bridged carbonyls (Figure 2). The π_{CH_2} orbital of the carbene is partially filled. The orbital mixing in the LUMO has a clear consequence for the electron transfers as the reaction proceeds. First, we observe a transfer from C_2H_4 to the p_y, $d_{x^2-y^2}$, and d_{xy} orbitals of the left iron atom and to the p_x orbital of the carbon of the bridged carbonyls. Next, there is a subsequent transfer from the π_{CH_2} orbital to ethylene. Then, the reaction evolves as above, i.e., with a back transfer from the iron atom to C_2H_4. Thus, the initial transfer from C_2H_4 to the metallic skeleton allows the nucleophilic attack of the carbene on the ethylene. It is a kind of a Lewis acid catalized nucleophilic addition on ethylene. The best transition state found so far is obtained from **35**. But to reach **35**, we have first to open the bridged bimetallic carbene **1**. One can wonder whether it is necessary to reach **35** before attacking C_2H_4 or whether it would not be preferable to attack during the opening. Indeed, when **1** opens to yield **35**, the carbenic center becomes more and more positive and its π_{CH_2} orbital more and more empty and concentrated in the LUMO. Consequently, we have studied the approach of C_2H_4 at an intermediate point of the opening with the π_{CH_2} orbital already empty. The energy of the transition state is only slightly improved (0.12 eV). One can also wonder whether it would not be preferable to do the reaction on **36** in which the carbonyls are already in the final arrangement and in which there is a vacant site in the adequate position on the left iron atom. Effectively, in spite of the reduced stability of **36** relative to **35** (ca. 1 eV), the transition state found for the reaction on **36** is the best one. Its energy is still high (3.9 eV above **1**). This value has no absolute meaning since the EHT method is not particularly reliable for reactions involving bond forming. Only comparison can tentatively be made. So we could conclude from this study that, if the reaction proceeds by direct attack of C_2H_4 on the bimetallic carbene, it will prefer to pass through complex 36. In Table II, activation energies obtained for the various carbenic species studied are listed. With **32** and **33**, the activation energy is surprisingly large since in both cases, the reaction is allowed. These values are due to steric hindrance which involves the incoming C_2H_4 and the bridged carbonyl (the passage from **35** to **33** in the absence of C_2H_4 occurs without any barrier). Thus, it is preferable to start from a species where the carbonyls are already bridged. The comparison of the activation energies for 1, **35**, and **36** or 1′ and **34** shows that the ethylene prefers to attack the complexes after the opening of the carbene.

VI. Conclusion

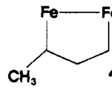
We have seen in section III that mechanism A is not favorable from energetical and orbital considerations. Further, the obtention of the $Fe_2(CO)_7C_3H_6$ complexes **30** and **31** from 1 and 1′ requires respectively 5.6 and 4.8 eV. These values have to be compared with the activation energies involved by 1 and 1′ in the second mechanism (3.9 eV for both of them) via the open intermediates **36** and **34**. If we can trust the method for comparisons, we can therefore conclude that the reaction prefers to occur via a direct attack of C_2H_4 on the bimetallic carbene. This conclusion seems in agreement with the experimental data since it is unlikely that a CO ligand could coordinate on **30** or **31** under the conditions of pressure which are used. Mechanism B accounts well for the variations of the regioselectivity of the reaction with the experimental conditions. In solution, Pettit et al. obtained a large proportion of isobutene when the starting species was propene. On the contrary, in surface chemistry, Basset et al. obtained almost exclusively *n*-butene from propene. From an IR study of the solution, Pettit et al. concluded that the starting species is the monobridged bimetallic carbene 1′. We found that in this case the reaction involves the nucleophilic attack of the carbene on C_2H_4. The starting species is 1′ or better its open isomer **34** (see Table II). The frontier orbitals of the propene are polarized as follows:



The nucleophilic addition of the carbene involves the substituted carbon preferrentially and leads to a symmetrical metallacycle, **45**, which further decomposes into



45



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isobutene. The reaction of Basset et al. on metallic iron can be represented by the reaction of the organometallic complex **1** (which has been identified in solid state) or better its open form **35** or **36**. In this case, the reaction involves the nucleophilic addition of C_2H_4 onto the electrophilic carbene. Therefore, the propene will attack the carbene by way of the unsubstituted carbon, giving a disymmetrical metallacycle, **46**, which decomposes into *n*-butene. In this work, we have tried to understand the mechanism of formation of the metallacycle which could be involved in the homologation of olefins. In a further report, we will study the decomposition of this metallacycle into an olefin and a metallic residue.