CALCULATIONS OF TRANSITION METAL COMPOUNDS USING AN EXTENSION OF THE CNDO FORMALISM

III *. APPLICATION TO THE CO INSERTION REACTION AS AN EXAMPLE FOR MECHANISTIC STUDIES

D. SADDEI, H.-J. FREUND and G. HOHLNEICHER *

Lehrstuhl für Theoretische Chemie der Universität zu Köln, Köln (F.R.G.)

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Summary

An extended version of the CNDO formalism is used to study the mechanism of the CO insertion as an example of intra-molecular insertion reactions which take place in-the ligand sphere of a transition metal atom. It is shown that charge density and bond order arguments can explain the experimental facts on a whole class of compounds:

$Mn(CO)_5R$ with $R = H, CH_3, C_2H_5, CHO, CH_2F, CF_3$.

The mechanism is predicted to be an R migration. The sequence of the reaction rates is correctly given, and especially the strong inhibition of the reaction by increasing fluorination of the substituent. The reversibility of the reaction is also considered. In the case of $Mn(CO)_5C_2H_5$ a possible side reaction by abstraction of β-hydrogen instead of alkyl migration is expected, and actually found experimentally.

I. Introduction

Since basic steps in chemical reactions can often be rationalised in terms of electrophilic or nucleophilic attack, the theoretical calculation of charge densities and bond orders has contributed a lot to the evaluation and understanding of reaction paths in organic chemistry. In organometallic chemistry, however, little use has been made of this type of approach. This is mainly due to the fact that the explicit consideration of electron—electron repulsion is necessary to obtain reasonable charge distributions. Semiempirical methods of the

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* For part II see ref. 4.

Hückel and Extended Hückel type widely used in transition-metal chemistry to explain bonding abilities [1], usually do not lead to useful charge distributions. On the other hand, the CNDO formalism introduced by Pople et al. [2], which in organic chemistry has proved to be very successful in predicting charge distributions relevant to reaction mechanisms, has not been widely applied to transition metal compounds. In our opinion this is due to some shortcomings in the proposed extensions of the CNDO formalism to transition elements [3], mainly, the use of equal Slater exponents for different types of atomic orbitals. If a completely decoupled set of s, p and d orbitals is used for the metal atom, together with the correct Hamiltonian [3], such an extended CNDO formalism is not only well suited for investigating bonding abilities in transition-metal compounds [3,4] and related surface cluster models [5,6], but also for studying many body effects in connection with photoemission [7]. The obtained charge distributions and bond orders are in good agreement with results of the few available non-empirical calculations (ab initio LCAO-SCF and SCF-X_α-SW) and with information derived from vibrational spectroscopy [5].
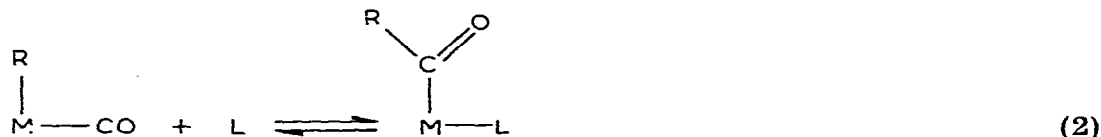
Recently it has been demonstrated that the extended version of the CNDO formalism can also be applied successfully to excited states and even photochemical behaviour [8]. In the present paper we study the applicability of our extended CNDO formalism to the discussion of reactions which take place in the ligand sphere of a transition-metal complex. As an example we have choosen a type of reaction which has been studied in detail experimentally [9,10] and to some extent also by other theoretical methods [17].

II. The insertion reaction

The insertion reaction follows the general scheme

$$M-X + Y \rightleftharpoons M-Y-X \tag{1}$$

where M is a metal and X and Y are monoatomic or polyatomic species. X and Y can differ with respect to their donor and acceptor qualities. Technically important examples for this type of reaction are the Ziegler-Natta catalysis in polymerization of α-olefins or the metal complex catalysed hydroformylation of alkenes. In the light of the proposed mechanisms [9,10,12,13] the key step in both of these reactions is an intramolecular process. The group Y is initially incorporated in the ligand sphere and then inserted into the M—X bond, leading to an intermediate complex with an incomplete ligand shell. In a subsequent step the full coordination is restorted by addition of a new ligand. For the hydroformylation reaction, e.g., the key step is the intramolecular CO insertion into a metal—carbon σ-bond,

$$
\begin{array}{ccccc}
R & & & & \overset{R}{\underset{\diagdown}{}}C\overset{O}{\underset{\diagup}{}} \\
| & & & & | \\
M & \!\!-\!\!-\!\!CO & + & L & \rightleftharpoons & M\!-\!-\!L
\end{array}
\tag{2}
$$

R = alkyl

leading to the so called acyl-product. In many cases this reaction is reversible. Two mechanism are considered for this reaction [10], which may be looked upon as 1,1-addition (compare Fig. 1), namely a CO insertion (mechanism A) and a methyl-group migration (mechanism B).

The class of compounds which is most frequently used in studies of this reaction is $Mn(CO)_5R$, with for example $R = -H, -CH_3, -CFH_2, -CF_3, -C_2H_2$. If L in equation 2 is again CO, the product is $Mn(CO)_5COR$.

Two important experimental features of these systems are:

i) Using ^{13}C labelling techniques, Noack and Calderazzo [10] have found that mechanism B is the most probable for $Mn(CO)_5CH_3$.

ii) The rate of reaction strongly depends on the nature of the ligand R. It increase in the order

$$-CF_3 < -CFH_2 < -CH_3 < -C_2H_5$$
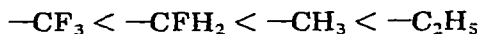
For $R = CF_3$ the reaction is immeasurably slow [14].

From the second result it seems probable that electron releasing substituents enhance the rate whereas electron withdrawing substituents reduce it. For the first three members of the above series it has been claimed [12] that replacement of H by F strengthens the metal—carbon bond, but this is a purely phenomenological description.

Theoretical investigations of the mechanism of the intramolecular CO insertion are rather scarce. Fonnesbech et al. [11], for instance, tackled this problem in connection with the hydroformylation of alkenes. From charge densities and bond orders obtained from ab initio calculations these authors concluded that in the case of $CH_3Co(CO)_4$ the first step is an electrophilic addition of CO to CH_3 (mechanism A). As a general result this would clearly contradict
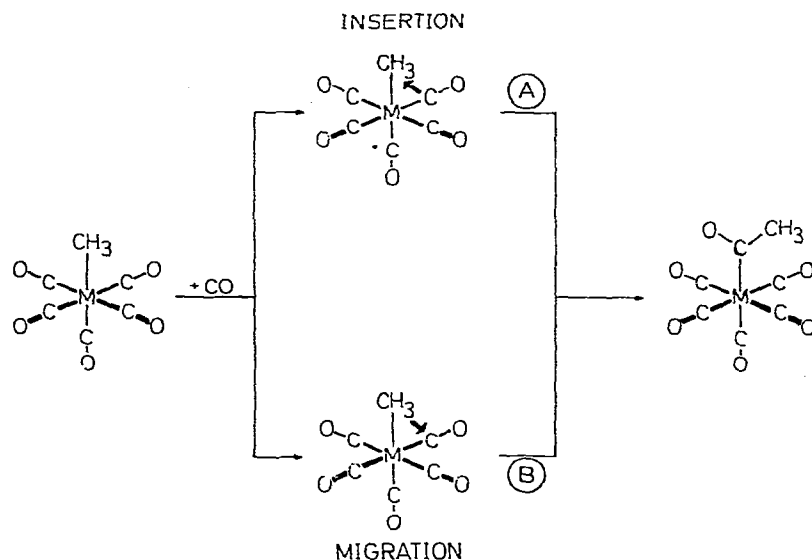

Fig. 1. Two possible reaction mechanisms which have been proposed [12] to describe the CO insertion for a methyl-substituted complex.

what has been found experimentally, especially for $Mn(CO)_5CH_3$.

As the most reliable experimental information is available for $Mn(CO)_5R$ we concentrated our own theoretical investigations on this group of compounds. Three main questions have to be answered:

i) Which mechanism is indicated by the theory?

ii) Can we interpret the influence of the substituent R on the reaction rate?

iii) Is the metal—alkyl bond really strengthened by successive replacement of H by F in R?

Before we try to answer these questions by looking at charge densities and bond orders (Section IV), we briefly discuss the bonding in the relevant compounds (Section III). All calculations were performed using the method suggested in Part I of this series [3]. The same formalism and the same parametrization is used as in this paper.

III. Bonding in $Mn(CO)_5R$

The fragment which is common to all the molecules under consideration is $Mn(CO)_5$. It is assumed to have C_{4v} symmetry with metal—carbon (carbon—oxygen) bond length 1.853 Å (1.134 Å) in the equatorial plane and 1.822 Å (1.134 Å) in the axial position [15]. For the calculation all bond angles have been set at $180°$ or $90°$. We do not use the experimentally observed umbrella structure [16], since we use $Mn(CO)_5$ only as a reference system. Moreover, we have found that , as long as it is not too great, such a deformation has only a small influence on the calculated charge densities and bond orders. The metal—ligand interaction is well described for CO by the Dewar-Chatt-Duncanson model [17], with about equally important σ-donor and π-acceptor effects. The highest occupied orbital of CO (5σ) is well characterized as a lone pair at the carbon atom. This lone pair acts as a σ-donor and by interaction with it the metal d-orbitals of appropriate symmetry (compare Fig. 2) are somewhat destabilized, but retain their predominant metal d-character. With respect to the metal—carbonyl bond these orbitals are σ-antibonding (σ_a).

Because of the large difference in electronegativity between C and O, the occupied 1π-orbital of CO has larger coefficients at the oxygen atom whereas the 2π-orbital contains stronger carbon character. Together with the appropriate energy differences this means that the interaction of the π-system of CO with the metal atom is dominated by 2π, leading to a stabilization of d-orbitals of proper symmetry. If these orbitals which are π-bonding (π_b) with respect to the metal—carbonyl bond are occupied in the final complex, the 2π-orbital of CO acts as an acceptor level. From our previous investigations of transition-metal carbonyls [3,4,6] we know that the interaction of 2π with the metal atom d-orbitals is not strong enough to stabilize these orbitals below the highest occupied orbital with strong ligand character. The spectrum of the occupied states is therefore well separated into a region with predominant metal and a region with predominant ligand character.

These qualitative arguments are in complete agreement with the result of our calculations (Fig. 3). With respect to C_{4v} symmetry the d-orbitals of the metal atom belong to representations a_1, b_1, b_2 and e. The five 5σ-orbitals of the CO ligands yield symmetry adapted combinations which belong to the representa-
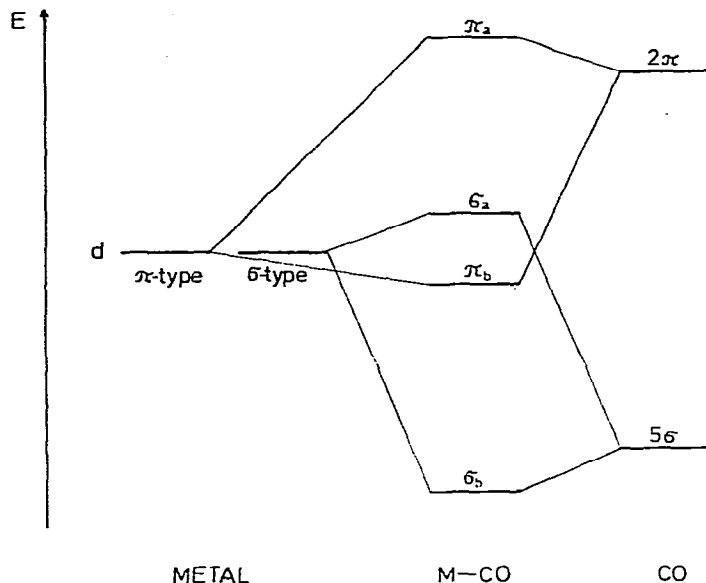
E axis (vertical, left). Diagram labels: π_a, 2π, σ_a, π_b, 5σ, σ_b, π-type, σ-type, d. Bottom axis: METAL, M—CO, CO.

Fig. 2. Schematic MO-representation of the metal—CO interaction in linear geometry, where σ—π separation is possible.

tions a_1, b_1 and e. However, only the orbitals a_1 and b_1 can interact with the metal atom d-orbitals because of local symmetry constrains (the importance of local symmetry constrains is discussed in detail in Part II of this series [4]) thereby yielding two destabilized levels of predominant metal d-character which are σ-antibonding with respect to the metal—carbon bond ($a_1^{\sigma a}$ and $b_1^{\sigma a}$). The shape of the corresponding orbitals is indicated in Fig. 4. The e-orbital which results from the 5σ orbitals does not have the proper local symmetry to interact directly with one of the metal d-orbitals. From the orbitals of the pure ligand sphere which are formed from 2π of CO only the lowest e and the b_2 have appropriate local symmetry to yield first order interactions with the d-orbitals of the metal atom. The resulting stabilized combinations which are metal—carbon π-bonding ($e^{\pi b}$ and $b_2^{\pi b}$) are again predominantly of metal d-character (compare Fig. 4). Thus we find four levels which can be assigned as "metal d-states" ($e^{\pi b}$, $b_2^{\pi b}$, $a_1^{\sigma a}$ and $b_1^{\sigma a}$). Those four levels have to be considered if we now introduce the substituent R which has to occupy the second axial position.

The simplest substituent is the hydrogen atom. From the metal d-states only $a_1^{\sigma a}$, which is mainly d_{z^2} in the representation used, can interact with the 1s-orbital of the hydrogen atom. This σ-type interaction leads to a stabilized a_1-orbital which on our calculation is situated somewhat below $b_2^{\pi b}$ in Mn-(CO)$_5$H. Schematically this is shown on the left hand side of Fig. 4. Eight electrons (seven from the Mn(CO)$_5$ fragment and one from the substituent) are available to occupy the orbitals a_1, $b_2^{\pi b}$ and $e^{\pi b}$. The latter is well separated from a_1^* which is mainly the $a_1^{\sigma a}$-orbital of the Mn(CO)$_5$ fragment. We therefore, expect a stable closed shell configuration for the ground state of Mn(CO)$_5$H.
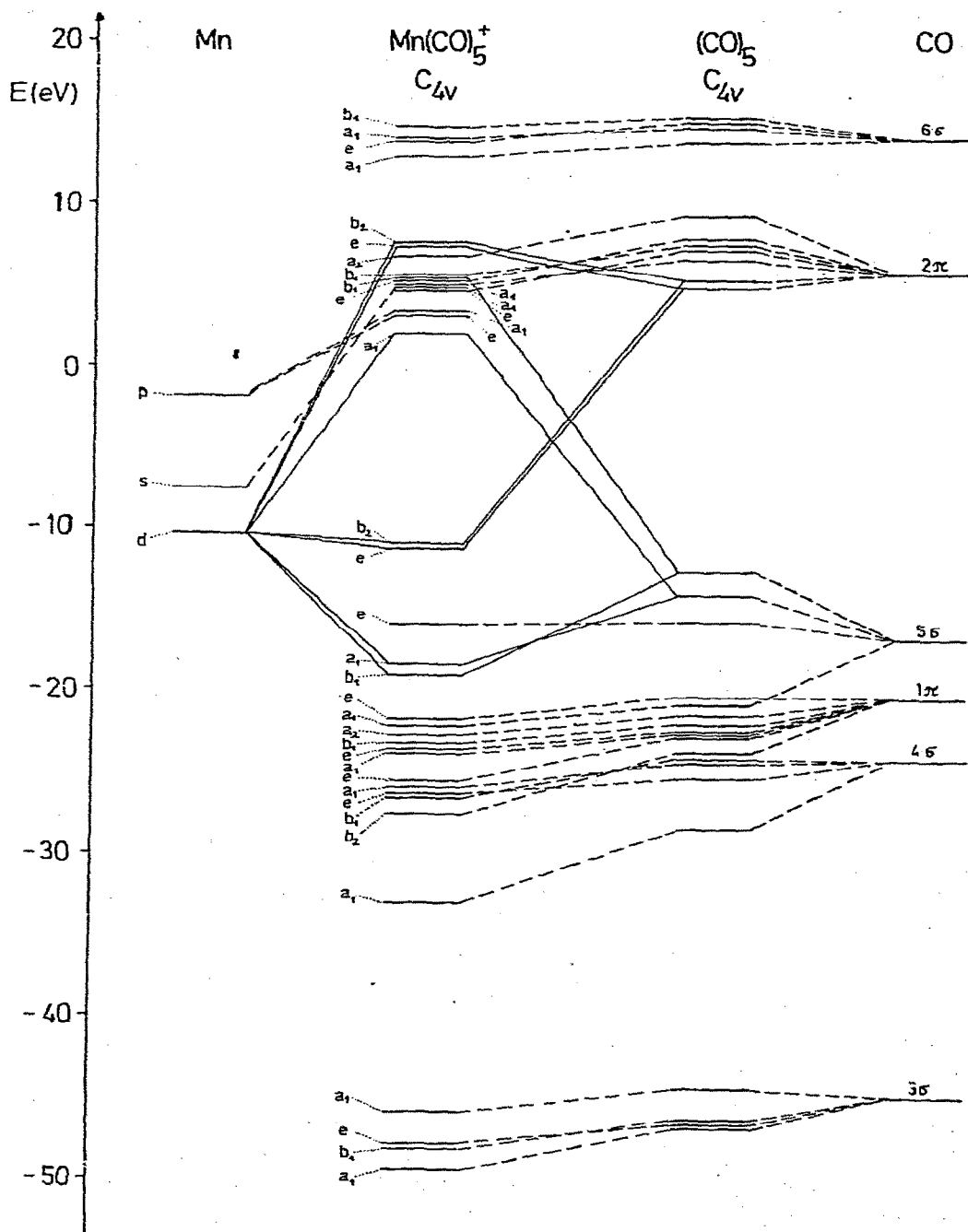
Fig. 3. Calculated MO diagram for the $Mn(CO)_5^+$ fragment and the corresponding ligand arrangement. The eigenvalues spectrum of $Mn(CO)_5^+$ is shifted by +5 eV to account for the electrostatic stabilization. Interactions which correspond to those in Fig. 1 are indicated by full lines.
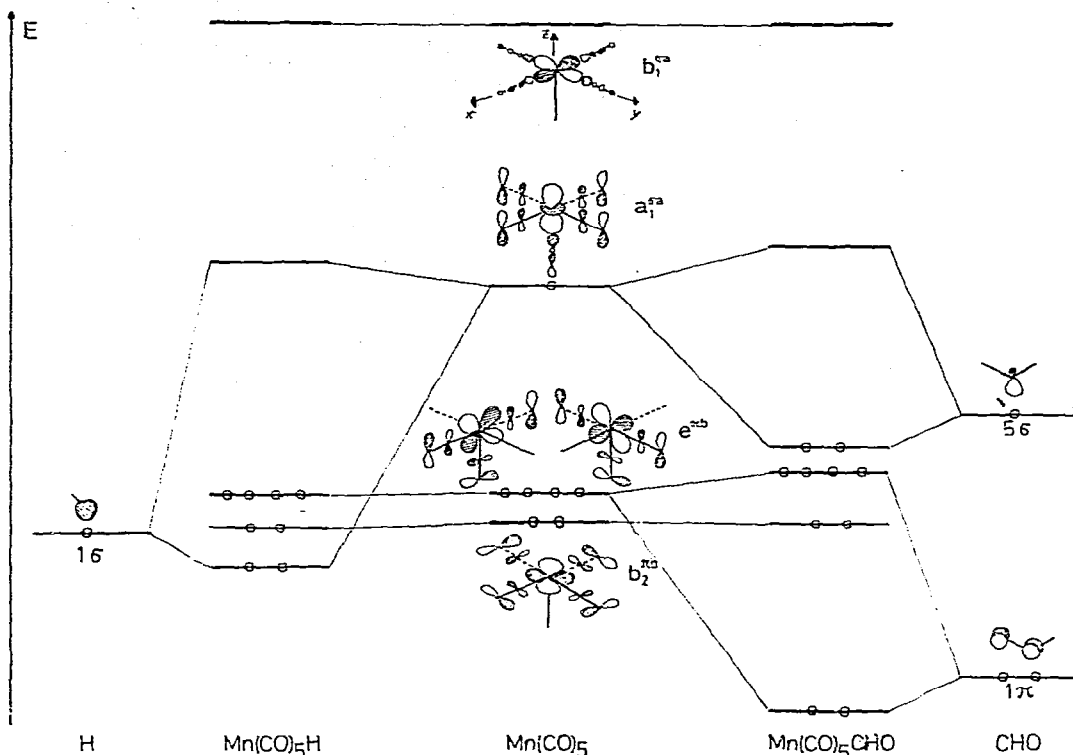
Fig. 4. Schematic MO representation for the interaction of H and CHO radicals with a Mn(CO)$_5$ radical.

If the hydrogen atom is replaced by a methyl group the situation becomes somewhat more complex (left hand side of Fig. 5). The highest orbital ($3a_1$) which is singly occupied in the methyl radical is of σ-character with respect to the newly forming bond, while the second highest orbital ($1e$) which is strongly C—H bonding has π-character. We therefore, find a strong σ-type interaction between $3a_1$ and $a_1^{\sigma a}$ of the Mn(CO)$_5$ fragment and a much smaller but not negligible π-type interaction between $1e$ and $e^{\pi b}$. To a first order approximation the orbitals $b_1^{\sigma a}$ and $b_2^{\pi b}$ are not affected, because of their local δ-symmetry. These orbitals can only interact with d-orbitals at the substituent, as for instance in the case of R = Cl. Again the orbital which results from $e^{\pi b}$ is the highest occupied one, and the correct closed shell ground state is obtained.

If we now proceed to R = C$_2$H$_5$ things become somewhat more complicated due to the loss of local symmetry. Fortunately, this loss does not influence the overall symmetry very much. It is therefore still possible to classify the orbitals with predominant metal d-character with respect to C_{4v} symmetry. The result of our calculation is shown on the right hand side of Fig. 5. The situation is much the same as for R = CH$_3$. Only the metal—ligand σ-bonding orbital, which is mainly of the ligand type, now lies somewhat above the two slightly split components evolving from $e^{\pi b}$.

We finally come to Mn(CO)$_5$CHO as a prototype for the acyl products. The two uppermost occupied orbitals in the free ligand are 5σ and 1π. Because of

TABLE 1

CALCULATED CHARGE DENSITIES FOR $Mn(CO)_5R$ COMPOUNDS AND FOR A QUASI C_{3v} STRUCTURE OF $Mn(CO)_4COCH_3$

Atom

R	H	CH_3	CH_3 [a]	CFH_2	CF_3	C_2H_5	$COCH_3$	$Mn(CO)_4COCH_3$
Mn	0.61	0.00	1.23	0.61	0.51	0.53	0.48	0.36
C_{eq}	0.09	0.09	0.20	0.11	0.1	0.10	0.10	0.06
O_{eq}	-0.10	-0.07	-0.35	-0.11	-0.06	-0.08	-0.05	-0.13
C_{ax}	0.05	0.03	0.17	0.05	0.00	0.05	0.07	0.10
O_{ax}	-0.20	-0.17	-0.35	-0.15	-0.17	-0.20	-0.16	-0.24
α-C		-2.7	-0.88	-0.02	0.27	-0.42	0.09	-0.20
β-C						-0.13	0.19	0.09
α-H	-0.43	-0.05	0.13	-0.11		0.06		
β-H						-0.07	-0.20	-0.01
F				-0.23	-0.27			
α-O							-0.05	-0.06

[a] Ab-initio results from ref. 15.

TABLE 2

WIBERG INDICES FOR $Mn(CO)_5R$ COMPOUNDS AND $Mn(CO)_4COCH_3$ (QUASI C_{3v})

Bond

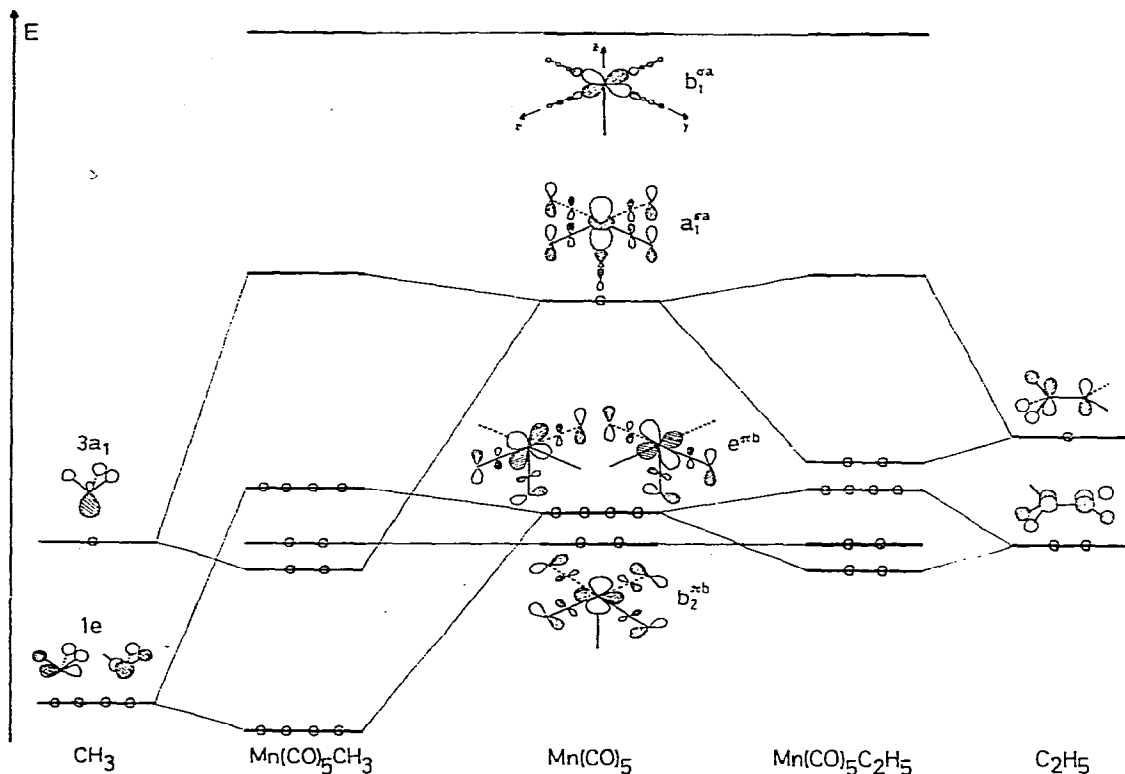| R	H	CH_3	CFH_2	CF_3	C_2H_5	$COCH_3$	$Mn(CO)_4COCH_3$
$W_{Mn-C_{eq}}$	0.73	0.71	0.70	0.70	0.71	0.87	0.77
$W_{Mn-\pi-C_{eq}}$	0.32	0.30	0.30	0.29	0.30	0.28	—
$W_{Mn-C_{ax}}$	0.85	0.79	0.80	0.84	0.82	0.85	0.96
$W_{Mn-\pi-C_{ax}}$	0.50	0.46	0.46	0.46	0.48	0.44	
W_{Mn-R}	0.60	0.65	0.59	0.54	0.59	0.58	0.83
$W_{Mn-\pi-R}$	0.00	0.03	0.02	0.03	0.02	0.11	
W_{C-F}				0.91			
W_{C-C}					0.86	0.84	0.66
$W_{\alpha C-H}$		0.97			0.89		
$W_{\beta C-H}$					0.76	0.63	
W_{C-O}						1.34	

Fig. 5. Schematic MO representation for the interaction of CH_3 and C_2H_5 radicals with a $Mn(CO)_5$ radical.

the strong electronegativity of oxygen, 1π lies not only below 5σ but also below the d-orbitals of the metal atom. $e^{\pi b}$ is therefore destabilized to some extent in $Mn(CO)_5CHO$. The HOMO of the CHO radical forms a σ-bond mainly by interaction with $a_1^{\sigma a}$ of the $Mn(CO)_5$ fragment as shown on the right hand side of Fig. 4.

In connection with reaction mechanisms the most important feature of the above discussion of bonding abilities in $Mn(CO)_5R$ compounds is that the orbital diagrams of Figs. 4 and 5 clearly reveal that empty substituent orbitals of local π-symmetry are of little importance for the bonding. This is in full agreement with the usual assumption of poor π-acceptor qualities of alkyl groups. The metal—R bond has thus to be considered as a nearly pure σ-bond. For σ-bonds, however, the main factor which determines the charge distribution in the bond is the electronegativity difference. Electronegativity arguments should therefore be well applicable in analysing the influence of different substituents. This is discussed on a more qualitative basis in the next section.

IV. Charge densities and bond orders

Charge densities and bond orders obtained from our calculations are summarized in Tables 1 and 2, respectively. For comparison we also show in Table 1 charge densities obtained by Guest et al. [15] from an ab-initio calculation of

$Mn(CO)_5CH_3$. These values are about twice as large as those derived from the corresponding CNDO calculation, but the relative distribution is quite similar.

To split the bond orders into σ- and π-contributions we extended Wiberg's definition [18]:

$$W_{AB} = \sum_{\substack{\nu \in A \\ \mu \in B}} P^2_{\mu\nu}$$

to the corresponding σ- and π-parts:

$$W^{\pi}_{AB} = \sum_{\substack{\nu^{\pi} \in A \\ \mu^{\pi} \in B}} P^2_{\mu^{\pi}, \nu^{\pi}}$$

$$W^{\sigma}_{AB} = \sum_{\substack{\nu^{\sigma} \in A \\ \mu^{\sigma} \in B}} P^2_{\mu^{\sigma}, \nu^{\sigma}}$$

Here ν^{π} and μ^{π}, for example, are those components of the atomic orbitals ν and μ which have local π-symmetry with respect to the AB bond. From the definition it follows that

$$W_{AB} = W^{\sigma}_{AB} + W^{\pi}_{AB}$$

For the prototype molecule, $Mn(CO)_5CH_3$, the combined information of Tables 1 and 2 leads to the result which is visualized in Fig. 6. Because of the different signs of charge on the carbon of the equatorial CO group and on the carbon of the methyl group the situation is well suited for a polar attack. The lower value of the Wiberg index of the Mn—CH$_3$ bond compared to the Mn—CO bond is well in accordance with the idea that the methyl group is the substituent which migrates. Contrary to Fonnesbech et al. [11] who predict mechanism A in the case of cobalt compounds we find mechanism B to be the most probable for the methyl substituted manganese carbonyl, and this is in agreement with the experimental findings of Noack and Calderazzo [10]. As the Wiberg indices are similar for all the investigated substituents R, this result should hold for the whole series.

If we now inspect the charge distribution in the other compounds under consideration we find that the charge at the carbon atom of the equatorial CO ligands is nearly independent of R. The negative charge at the α-C atom of the substituent, however, decreases in the order $C_2H_5 > CH_3 > CFH_2 > CF_3$. This is exactly the order which has been found experimentally for the decrease in the reaction rate. In the case of the CF_3 ligand the charge on R has become positive, thus a nucleophilic attack to CO is no longer probable.

Our results on charge densities are supported by the experimental ESCA shifts of gaseous $Mn(CO)_5CH_3$ and $Mn(CO)_5CF_3$ [19]. In the first case the C1s ionization of the alkyl substituent is found on the lower binding energy side of the C1s ionization of the complexed CO. In the second case the C1s ionization of the CF_3 group appears at higher binding energies than CO—C1s. From the work of Gelius [20] and of Davis and Shirley [21] it is generally accepted that experimental shifts can be well correlated with theoretical shifts obtained from

charge densitiy distributions. Such an analysis indicates that the electron density at the C atom is considerably higher in CH_3 than in CO, and that the reverse is true for CF_3.

Turning back to mechanistic considerations we find that our results support the phenomenological interpretation that electron withdrawing groups at the carbon atom, which participates in the metal—R bond, reduce the reaction rate. We do not, however, agree with the idea [12] that this decrease is due to an increase in the strength of the metal—carbon bond. The corresponding Wiberg indices become somewhat smaller if we proceed from CH_3 to CF_3. This clearly shows, that the decrease in reaction rate is not connected with a strengthening of the metal—C bond but with the change in charge distribution which reduces the possibility of nucleophilic attack.

In this connection it is necessary to comment on the widely held opinion that the general instability of alkyl substituted carbonyls is due to a specific instability of the metal—alkyl bond. From our results we cannot accept this line of argumentation. The Wiberg indices for the metal—alkyl bonds are not much smaller than those for the equatorial CO ligands although the latter contain a considerable (about 40%) amount of π-contribution. (It should be mentioned that the larger Wiberg index of the axial M—CO bond results mainly from a larger π-contribution). We therefore have to conclude that the observed instability of the metal—alkyl bond is rather due to kinetic effects, in accordance with the indications of the ab-initio calculations by Guest et al. [15].

As mentioned in the introduction, CO insertion reactions are often reversible. According to the concept of microscopic reversibility the decarboxylation should follow the reverse of the path for the CO insertion. To study how far this is consistent with our calculations, we have investigated the postulated transition state of quasi C_{3v} symmetry which, in the foreward reaction is reached after methyl migration. The relevant charge densities and bond orders are shown in Fig. 7 together with the same numbers for the final alkyl product.

From these results we deduce that the back reaction is much more probable in the quasi C_{3v} transition state. In the final product, charge densities and Wiberg indicies are unfavourable for a back reaction by alkyl migration. It is
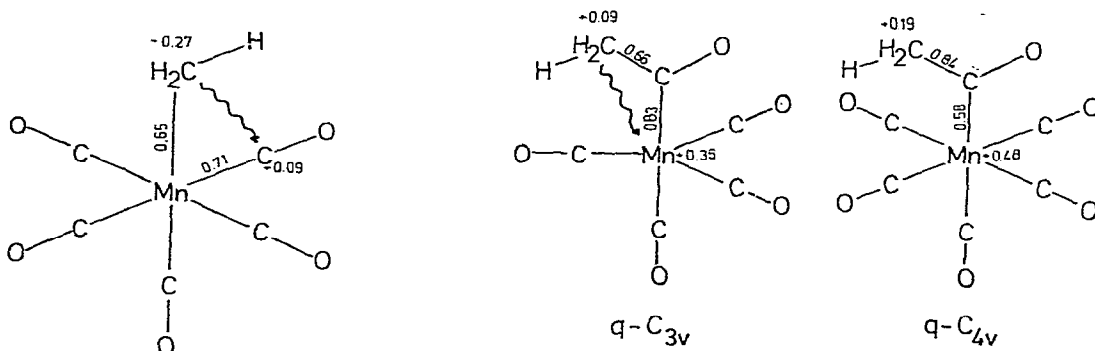

Fig. 6. Charge distribution and bond orders in $Mn(CO)_5CH_3$. The arrow indicates the nucleophilic attack.

Fig. 7. Charge distribution and bond orders in $Mn(CO)_4COCH_3$ and $Mn(CO)_5COCH_3$.

therefore most probable that they key step for the back reaction with respect to the end product (alkyl product) is the cleavage of one of the metal—CO bonds in the equatorial plane, leading to the quasi C_{3v} transition state. This possible alternative path, i.e. an alkyl migration resulting in a 7-fold coordinated metal atom followed by removal of a CO ligand is unfavourable on electronic and steric grounds.

We finally consider a side reaction which is possible for alkyl substituents which carry a β-hydrogen. As shown in Table 1 the charge density at this hydrogen in the ethyl substituted complex is slightly negative, whereas it is positive at the α-hydrogen as in the case of the methyl group. The β-H atoms are therefore disposed to a nucleophilic attack at the metal atom, leading to a second reaction path:

$$Mn(CO)_5C_2H_5 \rightleftharpoons Mn(CO)_5H + C_2H_4$$

Inspection of Table 2 confirms that the Wiberg indicies of those bonds which have to be cleaved in this reaction actually have the lowest values. That this reaction is experimentally found in association with CO insertion is therefore explicable in the framework of our calculations.

V. Conclusion

We have shown in this paper that an extended version of the CNDO formalism which we have introduced in Part I [3] of this series yields a valuable basis for the discussion of mechanistic problems in transition metal chemistry. For the special case of the CO insertion in $Mn(CO)_5R$ it was not only possible to rationalize the correct mechanism and the dependance of the reaction rate on the substituent R, but also the possible paths of back- and side-reactions. As reaction mechanisms are usually explained in terms of nucleophilic and electrophilic elementary processess, it is most important that any theoretical method which is used as a guideline for such a discussion leads to reliable charge densities and bond orders. The success of the application outlined in this paper, and especially the good correspondence with observed ESCA shifts, seems to show that a properly handled CNDO type method is well suited to yield well balanced charge densities and bond orders for transition-metal compounds also. If this turns out to be true for a larger amount of examples, CNDO type calculations could become as important a tool for mechanistic studies in transition-metal chemistry as they are in organic chemistry.

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