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Peculiar nucleophilic behavior of some vinylidene complexes: a theoretical study

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Abstract

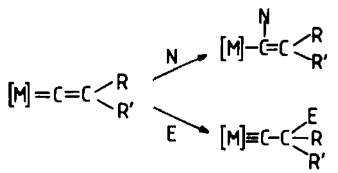
Electrophilic addition to vinylidene complexes of Mn, Fe, Ir and Rh has been studied by means of molecular orbital calculations. For most of the complexes the regioselectivity is controlled by the HOMO. However the complexes CpRhL=C=CHR constitute a special class for which attachment of the electrophile to the central carbon is possible. There is competition between several occupied orbitals and a perturbational analysis has identified the determining factors.

Introduction

Nucleophilic and electrophilic additions to vinylidene complexes have been extensively studied and the following rules have been established: nucleophilic attack occurs at the α-carbon of the vinylidene ligand and electrophilic attack at the β-carbon (Scheme 1). Several such electrophilic additions have been reported for $L_5W{=}C{=}CRR'$ [1], $CpMoBrL_2{=}C{=}CHR$ [2], dinuclear vinylidene complexes [3], and even for the cationic complex $CpFe(CO)(PR_3){=}C{=}CH_2{}^+$ [4].

But recent results of Werner et al. show that exceptions to these rules exist. Firstly in the case of the square-planar $IrCl(PR_3)_2{=}C{=}CHR'$ the electrophile becomes attached to the metal and not to the β-carbon [5a], and a similar result has been observed for $ReCl(dppe)_2{=}C{=}CHPh$ [5b]. Secondly the electrophilic attack on the complex $CpRh(PR_3){=}C{=}CHR'$ occurs at the α-carbon [6].

The purpose of this work is to try to account for these differences in behavior by means of molecular orbital calculations based on the Extended Hückel Theory [7].

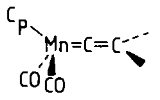


Scheme 1.

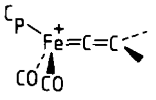
In their theoretical work in the subject [8], Kostic and Fenske showed that: nucleophilic α-attack is frontier-controlled and depends on the shape of the LUMO whereas the site of electrophilic β-attack is less certain and seems to be both frontier- and charge-controlled. The latter assumption was also made by Albright et al. [9], but electrophilic additions on Schrock-type metal carbene have been shown to be frontier-controlled [10].

Orbital interactions analysis

Four complexes, **1** to **4** have been studied:



1



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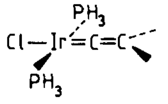

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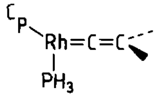

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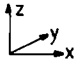


In the comparison a fixed C=C bond length was used (1.32 Å); this corresponds with the experimental value in most such complexes. It was necessary to consider

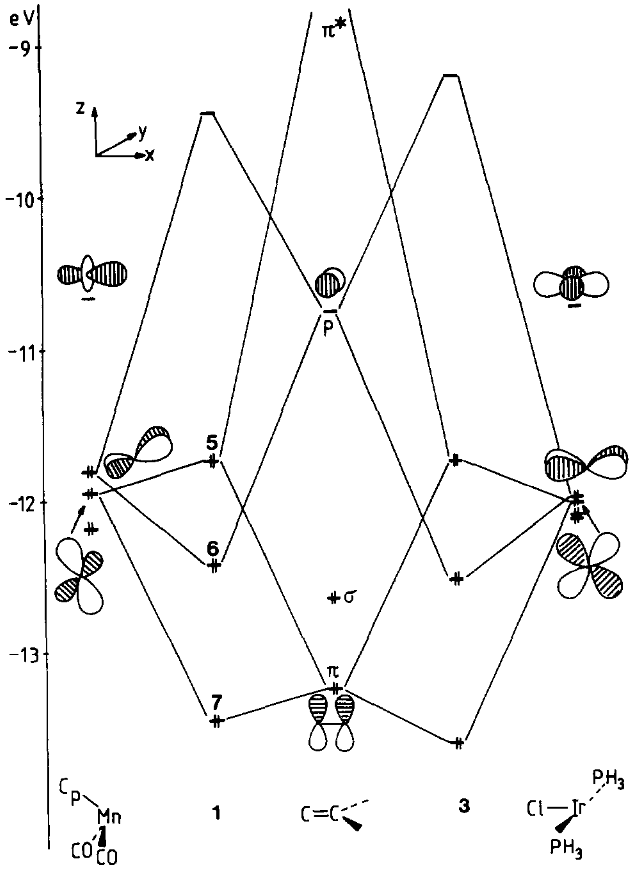


Fig. 1. Most important orbital interactions between the horizontal vinylidene fragment and CpMn(CO_2) (on the left) and IrCl(PH_3)$_2$ (on the right).

complexes **1** and **2**, which have been studied previously [8], in order to make a comparison with the same computational method. For each complex, two conformations have been considered, one with the CH_2 unit in the horizontal plane *xy* and the other with that unit in the vertical plane *xz*. In each case the horizontal conformation is preferred, in agreement with the earlier calculations [8,11] and with the experimental data [12] except that for $IrCl(P^iPr_3)_2{=}C{=}CHCO_2Me$ (**3** with H replaced by substituents) [13]. The energy difference between the conformations is small for **1**, **2** and **3** (respectively 3.2, 3, and 2.5 kcal/mol) in agreement with the earlier results [8] but much larger for **4** (16 kcal/mol). The smallness of the barrier accounts for the preference for the vertical conformation in $IrCl(P^iPr_3)_2{=}C{=}CH$-CO_2Me in which there is steric hindrance between the substituents on the β-carbon and the phosphines $P(^iPr)_3$.

Each complex was broken down into a metallic fragment and the vinylidene fragment CCH_2 and the orbital interactions analysed. The orbitals of the d^6 $CpML_2$ fragment ($CpMn(CO)_2$ and $CpFe^+(CO)_2$) are well known [11,14]: they

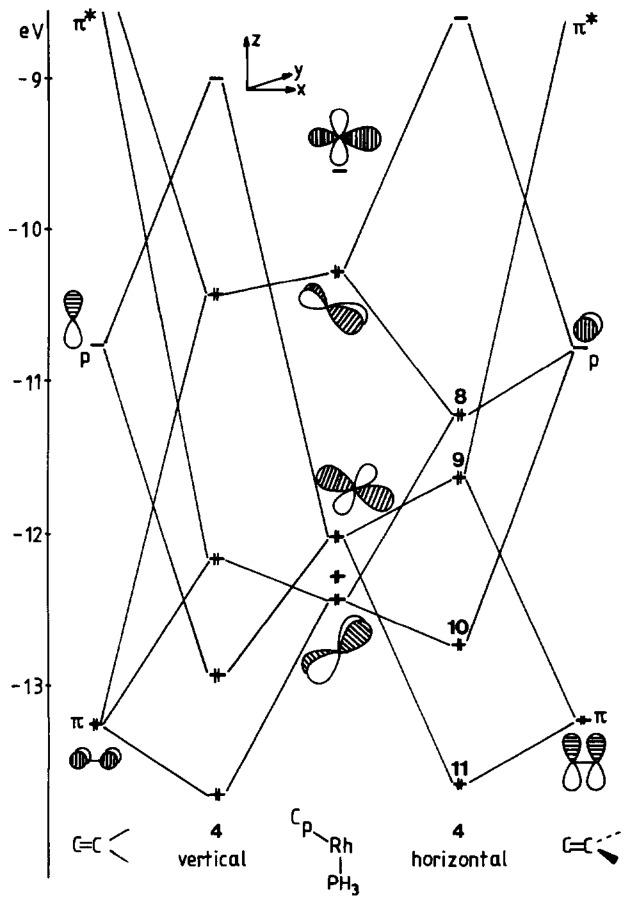


Fig. 2. Most important orbital interactions between $CpRh(PH_3)$ and the horizontal vinylidene fragment (on the right) or the vertical vinylidene fragment (on the left).

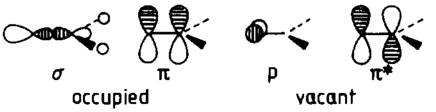
Table 1

Most important coefficients in the LUMO and HOMO of complexes $[M]{=}C_\alpha{=}C_\beta H_2$ **1** to **4**

[M]	LUMO		HOMO	
$CpMn(CO)_2$	Mn d_{xy}	−0.50	Mn d_{xz}	−0.72
			Mn d_{z^2}	0.15
(**1**)	C_α p_y	0.86	C_α p_z	0.11
			C_β p_z	0.50
$CpFe^+(CO)_2$	Fe d_{xy}	−0.42	Fe d_{xz}	−0.62
			Fe d_{z^2}	0.13
(**2**)	C_α p_y	0.89	C_α p_z	0.26
			C_β p_z	0.61
$IrCl(PH_3)_2$	Ir d_{xy}	−0.57	Ir d_{xz}	−0.83
(**3**)	C_α p_y	0.90	C_α p_z	0.12
			C_β p_z	0.54
$CpRh(PH_3)$	Rh d_{xy}	−0.67	Rh p_y	0.18
(**4**)	Rh d_{yz}	0.26	Rh d_{yz}	−0.56
	C_α p_y	0.72	C_α p_y	0.50
			C_β p_y	0.05

consist of a set of relatively low-lying occupied orbitals and a well-separated LUMO (Fig. 1). The orbitals of the d^8 C_{2v} ML_3 fragment ($IrCl(PH_3)_2$) are similar [14]. The d^8 CpML fragment ($CpRhPH_3$) behaves differently [15]: it derives from the $CpML_2$ fragment by loss of a ligand. The LUMO ($d_{x^2-y^2}$–d_{z^2}) that has no contribution from L_2 in $CpML_2$ is raised in CpML by an out-of-phase combination with L along the p_z axis. In contrast the d_{yz} (mixed to some extent with d_{xy}) orbital that is vacant in $CpML_2$ (out-of-phase combination with L_2) no longer has a contribution from L in CpML and is lowered: it becomes the HOMO, with a larger mixing with d_{xy}. As a result the CpML fragment has a HOMO well separated from the other occupied orbitals, lying at high energy not far from the LUMO (Fig. 2).

The vinylidene fragment itself has four interacting orbitals, as shown below:



The interactions in complexes **1** and **3** are compared in Fig. 1, and can be seen to be identical. One occupied orbital of the metallic fragment (d_{xz}), interacts with both π and π^* giving a low-lying orbital and the HOMO of the complex. This accounts for the results listed in Table 1: firstly the HOMO is mostly located on the metal, and secondly this orbital is the out-of-phase combination with the π orbital and the in-phase combination with the π^* orbital. As a result the coefficients cancel on C_α and add on C_β: the HOMO is more localized on C_β than on C_α.

The second important interaction is between the HOMO (d_{xy}) of the metallic fragment and the vacant p orbital to give an occupied orbital and the LUMO of the complex, thus mostly located on C_α. The interaction between the σ lone pair and the LUMO of the metallic fragment which gives rise to the first metal–carbon bond was not considered in this study because it does not contribute to the formation of

Table 2

Electronic transfers in the vacant orbitals of the fragments (in electrons)

	p	π^*	Metal LUMO
1	0.61	0.17	0.68
2	0.49	0.16	0.78
3	0.53	0.20	0.73
4	1.04	0.29	0.63

the frontier orbitals. The interaction diagram for **2** is more complicated, but the main interactions are identical. The low energy difference between the horizontal and vertical conformations is easily explained. By a rotation of 90°, the metallic orbitals which interact respectively with the π system and with the p orbital are inverted, and since they are close in energy and have similar shape, the interactions have nearly the same stabilizing effect in the two conformers.

Table 2 gives the electronic transfers in the vacant orbitals of the considered fragments. They are of the same magnitude for **1**, **2** and **3**, in agreement with the similarity of the interactions. This leads to a similar value for the C–C overlap population (1.33) and therefore to a similar bond length for all the complexes, as is found experimentally.

We now consider complex **4**. Figure 2 depicts the interactions of the metallic fragment CpRh(PH_3) with the horizontal and vertical vinylidene fragment. The horizontal conformer (on the right) is first considered. As in **1**, one occupied orbital of the metallic fragment (d_{xz}) interacts with π and π^* to give two occupied orbitals but not the HOMO of the complex. The p orbital interacts this time with two orbitals of the metallic fragment; the same as in **1** on the one hand and the HOMO on the other hand. Since this latter orbital is high in energy, the resulting orbital becomes the HOMO of the whole complex. Consequently the HOMO of **4** in its horizontal conformation is derived from the p orbital and so has a large coefficient on C_α (see Table 1).

It can be seen from Table 2 that the backdonation to the vinylidene fragment is larger in **4** than in the other complexes, especially the transfer to the p orbital. This arises from the supplementary interaction of the p orbital with the metallic HOMO. The increased transfer into the π^* orbital is due to a better overlap with the metallic orbital which is more hybridized towards the vinylidene fragment than in **1**. A consequence of these larger transfers is a strengthening of the Rh–C bond and a weakening of the C–C bond, reflected in a smaller C–C overlap population for the same C–C distance (1.28 vs. 1.33). This is effectively confirmed by the X-ray data [12b]: the unit cell contains two independent molecules whose RhC distances (1.83 and 1.74 Å) are shorter than in Rh carbene complexes (1.93 to 2 Å), and furthermore one C–C distance is longer than an typical double bond (1.41 Å).

The larger energy difference between the horizontal and the vertical conformers (16 kcal/mol) is well explained by the diagrams of Fig. 2. Since the metallic orbitals which interact with the p orbital or the π system are separated by a very large gap in energy, it is easy to understand that the inversion of their role will give very different interactions. The p orbital has a larger coefficient than the π^* orbital on C_α: its overlap with the metallic orbitals will be better. Secondly it is nearer the metallic orbitals than π^*. Therefore the interactions of the p orbital with the metallic fragment will predominate and the conformation which favors them will be the best. This is the case for the horizontal conformation.

If the vertical conformer could exist, it would behave like **1** and **2** since the diagram in Fig. 2 shows that its HOMO comes from the π system, as it was the case in Fig. 1.

In conclusion the orbital analysis allows a good understanding of the shape of the frontier orbitals of complexes **1** to **4**, as described in Table 1. It demonstrates and accounts for the different behavior of the HOMO of **4**.

Electrophilic attack

Frontier orbitals and charges

If the reaction is frontier-controlled, the shape of the HOMO will indicate the site of attack. The data in Table 1 are again considered. For all the complexes, the HOMO is divided between the metal and one carbon (C_β in **1**–**3**, C_α in **4**). This means that the metal can be a competitive site for the electrophilic attack. This is effectively the case for **3** where H^+ attaches to Ir, but not for the other complexes where the attachment is on the carbon chain. Consideration of the HOMO alone is not sufficient to account for this difference in behavior.

To explain the experimental results we must also consider the charges (Table 3). It is known that the Extended Hückel method is not suitable for quantitative charge evaluation, and so the emphasis will be not on the values themselves but rather on the relative signs. The metal is positively charged in **1**, **2** and **4** and so is not a good site for electrophilic attack. The negatively charged sites are C_β in **1** and **2** and both C_α and C_β in **4**. In contrast, in **3** the metal is negatively charged and so can add an electrophile. This reversal in the charge sign comes from the metallic fragment. It can be seen from Table 3 that the metal in the fragment $IrCl(PH_3)_2$ is strongly negative. This is due to the strongly electron-donating ability of the phosphines. The negative charge on the metal is not compensated by the back-donation to the vinylidene fragment since the transfer to the metallic LUMO balances it (see Table 2). If the phosphines were replaced for example by CO, which is a good π-acceptor, the complex $IrCl(CO)_2{=}C{=}CH_2$ would behave like **1** and **2**; the calculated charges for this complex are 0.26, 0.20, and -0.28 on Ir, C_α, and C_β, respectively. On the other hand, if CO were replaced by PH_3 in **1**, complex $CpMn(PH_3)_2{=}C{=}CH_2$ would behave like **3** and take up the electrophile at the metal. This is confirmed by our calculations, which show that Mn is much more negatively charged than the β carbon (-0.91 compared with -0.05 on C_α and -0.31 on C_β).

Table 3

Charges on the metal, on C_α and C_β in the complexes $[M]{=}C_\alpha{=}C_\beta H_2$ **1** to **4**. In parentheses are given the charges in the fragments [M] and CCH_2

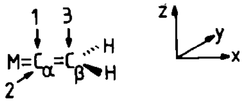
[M]	Metal	C_α	C_β
$CpMn(CO)_2$ (**1**)	0.04 (−0.04)	0.02 (−0.20)	−0.28 (−0.02)
$CpFe^+(CO)_2$ (**2**)	0.6 (0.41)	0.17	−0.29
$IrCl(PH_3)_2$ (**3**)	−0.37 (−0.44)	0.10	−0.29
$CpRh(PH_3)$ (**4**)	0.49 (−0.19)	−0.43	−0.41

Owing to the presence of one PH_3, the metal in the fragment $CpRhPH_3$ is also negatively charged but less so than in the previous case. In this case the large back-donation into the vinylidene fragment prevails over the electronic transfer into the metallic LUMO (Table 2) and consequently the metal is positively charged in the whole complex **4**.

Thus, consideration of both the shape of the HOMO and the charges indicates that the nucleophilic site is C_β in **1** or **2**, C_α in **4** and the metal in **3**.

Perturbational treatment

One way of studying the regioselectivity of a reaction is to place a model reactant at the same distance from the different sites of attack and examine the overlap populations. This has been done already for the attack by nucleophilic reaction [16]. The largest overlap population corresponds to the preferential site (strongest created bond). Of course, the sites to be considered must be of the same nature, and so only the attack on C_α and C_β can be compared, the attack on the metal being excluded. The model electrophile is H^+. The energy of its vacant orbital is taken at -10 eV, a value intermediate between the HOMO's and LUMO's of the complexes. H^+ is placed at 2 Å away from C_α and C_β in three different geometries corresponding to the π and p orbitals of the vinylidene fragment, as shown below:



The resulting overlap populations are listed in Table 4. For complex **1**, they indicate that the preferred carbon is C_β, in agreement with the shape of the HOMO. For complex **4**, the overlap population point to electrophilic attack on C_β, in contradiction with the previous arguments and with the experiment. This result seems to indicate that the occupied orbital **9** lying just below the HOMO **8** (Fig. 2) plays a more important role than the HOMO itself. The energy gap between them is relatively small (0.4 eV) and the coefficient p_z on C_β in **9** is larger than the coefficient p_y on C_α in **8** (0.62 vs. 0.50), inducing a stronger interaction with H^+. Such a competition does not exist in the case of complex **1** because the energy gap between orbitals **5** and **6** is larger (0.7 eV) and because the coefficient p_y on C_α in **6** is smaller than the coefficient p_z on C_β in **5** (0.43 vs. 0.50).

A more detailed analysis is necessary. A simple perturbational treatment allows the $2e^-$ interaction energies to be expressed as a function of the electrophile orbital energy without taking into account the precise nature of the electrophile. Only the coefficients on the carbon atoms in the interacting orbitals of the complex and their energies are needed [17,16c].

Table 4

Overlap population in the complexes $[M]=C_\alpha=C_\beta H_2$ between H^+ ($H_{ii} = -10$ eV) and the carbon C_α or C_β in the three possible directions

[M]	$C_\alpha(1)$	$C_\alpha(2)$	$C_\beta(3)$
$CpMn(CO)_2$ (**1**)	0.077	0.077	0.132
$CpRh(PH_3)$ (**4**)	0.083	0.139	0.154

A function $f(x)$ is calculated for each carbon, x being the electrophile orbital energy $f(x)$ is proportional to the stabilization energy obtained by interaction of the electrophile orbital and the occupied orbitals of the complex. Its expression (eq. 1) is deduced from the Perturbation Theory.

$$f(x) = \sum_i f_i(x) = \sum_i \frac{\left(\frac{k}{2}(x + E_i) - E_i\right)^2 C_i^2}{x - E_i} \tag{1}$$

where E_i is the energy of the orbital i, C_i is the coefficient on the considered carbon in this orbital and k has the usual value of 1.75.

Complexes **1** and **4** are now compared with this method. Firstly the comparison of the $f_i(x)$ terms gives the relative contribution of each occupied orbital of the complex. In complex **1**, attack 2 on C_α depends only on orbital **6**. For attack 3 on C_β, the HOMO **5** plays the major role but orbital **7** has a non-negligible contribution (between 30 and 50% of the HOMO's contribution depending on x) which reinforces the regioselectivity in favor of C_β. In complex **4**, lower occupied orbitals (**10** and **11**) also play a role in both $C_\alpha(2)$ and $C_\beta(3)$ attack, but in each case their contribution is less than 25% of the contribution of **8** or **9**, which remains determining for the regioselectivity. For both complexes attack 1 on C_α depends only on the low lying orbitals **7** and **11**, which have mainly π_{cc} character and a slightly greater coefficient on C_α than on C_β.

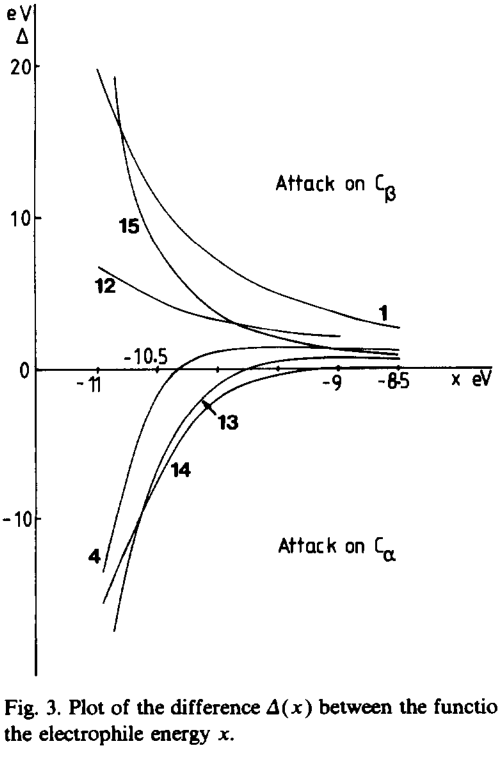


Fig. 3. Plot of the difference $\Delta(x)$ between the functions $f(x)$ for the attack 2 on C_α and 3 on C_β against the electrophile energy x.

Secondly, for a given x, attack occurs at the carbon giving the largest $f(x)$ value. As stated above, attack 1 on C_α is never preferred, because of the low energy of the interacting orbitals. The interesting comparison is between attack 2 on C_α and attack 3 on C_β. The difference $\Delta(x) = f(x)\ C_{\beta(3)} - f(x)\ C_{\alpha(2)}$ is plotted in Fig. 3. A positive value means that attack 3 on C_β is preferred.

For complex **1** $\Delta(x)$ is positive whatever the electrophile energy, and therefore the electrophile attack will always occur at C_β, in agreement with the experimental data. For complex **4**, $\Delta(x)$ changes its sign for a given value of $x (\approx -10.3$ eV). For electrophiles having a low-lying vacant orbital, attack will occur at C_α. This is the case for H^+. For electrophiles having a high-lying LUMO, attack will occur at C_β, but with a low selectivity since $\Delta(x)$ is small.

Factor controlling the regioselectivity

The orientation of the electrophilic addition toward $C_\alpha(2)$ or $C_\beta(3)$ for complex **4** depends essentially on two factors: the energy gap between orbitals **8** and **9** and, to a greater extent, the relative weight of coefficients p_y on C_α and p_z on C_β, which are involved through their squares. Let us see now how to vary these factors. Two ways of changing the orbital energies as possible. One involves changing the orbitals of the metallic fragment by replacing, for example, PH_3 by another ligand L, or by changing the metal. The other involves replacing it on C_β by an electron-donating or electron-accepting group R. This replacement also has an influence on the coefficients. Therefore four new complexes **12**–**15** are considered:

$CpRh(CO){=}C{=}CH_2$ $L = CO$ (**12**)
$CpRh(NH_3){=}C{=}CH_2$ $L = NH_3$ (**13**)
$CpRh(PH_3){=}C{=}CHCN$ $R = CN$ (**14**)
$CpRh(PH_3){=}C{=}CHOH$ $R = OH$ (**15**)

The effect of the ligand L is first considered. If L lowers the HOMO of the metallic fragment CpRhL, the HOMO **8** of the whole complex will be also lowered (Fig. 2). The consequence is a smaller energy gap between **8** and **9** or even an inversion of these orbitals. The result is unfavourable for attack 2 on C_α. This is the case for $L = CO$, where the $\pi^\star_{CO}$ orbital stabilizes the HOMO of CpRhCO. Effectively $\Delta(x)$ remains positive for complex **12** whatever the electrophile energy (Fig. 3). It means that **12** behaves like **1** toward an electrophile.

In contrast, if L raises the HOMO of the metallic fragment CpRhL, the gap between **8** and **9** increases. The result will be an enhanced tendency for attack at $C_\alpha(2)$. This is the case for $L = NH_3$ which is a better donor than PH_3. A small increase in the coefficient ratio $p_y\ C_\alpha / p_z\ C_\beta$ is also observed. The $\Delta(x)$ curve for complex **13** (Fig. 3) looks like that for complex **4**, but the $C_\alpha(2)$ attack is preferred for a larger range of electrophiles.

The effect of the substitution at C_β is now considered. The electron-withdrawing group CN has an effect only on the $\pi^\star_{CC}$ orbital, the energy of which is lowered (with a lowering of **9** as a consequence) and the coefficient p_z on C_β reduced. These two effects combine to favor attack 2 on C_α. Effectively Δx for complex **14** always remains negative. The electron-donating group OH raises both the π_{CC} and $\pi^\star_{CC}$ orbitals by mixing of the p_z oxygen lone pair. It lowers the $p_z\ C_\beta$ coefficient in the π_{CC} orbital and increases it in the $\pi^\star_{CC}$ orbital. As a result orbital **9** is destabilized and its p_z coefficient on C_β is not changed significantly. The OH group has also an effect on the p orbital of the vinylidene fragment: this orbital is lowered owing to the removal of the out-of-phase mixing with the π_{CH_2} orbital that existed in the unsubstituted vinylidene fragment. The principal effect of the OH group is therefore to invert orbitals **8** and **9** in complex **15**, which favors electrophilic attack on C_β: $\Delta(x)$ for **15** is always positive and **15** behaves like **1**.

What happens now when the metal is changed? To first approximation, this can be simulated by a variation in the energy of d orbitals. The CpML fragment still has a high HOMO well separated from the others, with a translation relative to CpRhL. Therefore the energy gap between **8** and **9** does not vary much. If the d orbitals are lowered, the interaction with the p vinylidene orbital is weaker and therefore the coefficient p_y on C_α in **8** in decreased. This enhances the regioselectivity toward C_β. On the contrary, if the d orbitals are higher, the interaction with the p orbital is stronger and the coefficient p_y on C_α in **8** increases. This leads to preferred attack on C_α as was verified by calculations on $CpIr(PH_3)=C=CH_2$.

To complete the study it is necessary to check whether the changes in the ligand and the nature of the substituent do or do not have an influence on the behavior of complex **1**. The effect of replacing the CO's by two PH_3 in **1** is studied first (complex $CpMn(PH_3)_2=C=CH_2$ has already been considered previously in respect of the charges). The effect of $\pi^\star_{CO}$ is to lower the two highest occupied orbitals of the $CpMn(CO)_2$ fragment, the second one more than the HOMO. When PH_3 replaces CO, these orbitals are both raised and inverted. The energy gap between **5** and **6** is therefore increased and the HOMO **5** always controls the regioselectivity. We have seen that the effect of an OH group is to lower the p orbital and to raise the π and $\pi^\star$ orbitals of the vinylidene fragment. Here too, the result is an increased gap between **5** and **6**. The effect of a CN group is to lower the $\pi^\star_{CC}$ orbital and to reduce the p_z coefficient on C_β which remains however greater than p_y on C_α in **6**. Therefore, although the energy gap between **5** and **6** is reduced, there is no change in the selectivity. We conclude that, whatever the ligand L or the substituent R, the electrophilic attack will always occur on C_β in complex **1**, and that the selectivity is controlled in this case by the HOMO and the charges.

The mechanistic study described above shows that for some vinylidene complexes a more elaborate analysis is necessary to interpret the experimental results.

Conclusion

The molecular orbital calculations presented here allow a good understanding of the electrophilic additions to the vinylidene complexes. It appears that most of them show the same behavior, i.e. they are attacked at the terminal carbon C_β by an electrophile, or exceptionally at the metal. For these complexes, the HOMO arises from the interaction of the metallic fragment with the π system of the vinylidene fragment and has a large p_z coefficient on C_β and on the metal. The orbital coming from the p vinylidene orbital is much lower and has a smaller p_y coefficient on C_α. Thus in these cases, the regioselectivity is controlled both by the shape of the HOMO and by the relative charges on the metal and on C_β. In most cases, the metal is positively charged and cannot take up an electrophile. However, if the ligands are strong electron-donors (such as phosphines), the metal can be more negatively charged than the carbons, in spite of the back-donation. Then the electrophile will attack to the metal, as found experimentally for $ClIr(PH_3)_2{=}C{=}CH_3$ (3) and as can be predicted for $CpMn(PH_3)_2{=}C{=}CH_2$.

The $CpML{=}C{=}CHR$ species constitute a special class of vinylidene complexes. This is because there is a large gap between the HOMO and the other occupied orbitals in the metallic fragment d^8 CpML. This means that the orbital coming from the p vinylidene orbital can now be the HOMO of the complex. However its energy difference from the orbital arising from the π system is small, and its p_y coefficient on C_α is always smaller than the p_z coefficient on C_β in the latter orbital. Therefore, these two orbitals are in competition and the site of the electrophilic attack is highly dependent on the nature of the ligand L, of the substituent R, and of the metal M, which can reduce or increase the energy gap and the p_y coefficient on C_α. It depends also on the energy of the electrophile. A perturbational analysis is thus necessary to determine the addition site. The following features are revealed: electrophilic attack at the central carbon C_α is favored by a low-lying electrophile orbital, a donor ligand ($NH_3 > PH_3$), an electron-withdrawing substituent, and high metal d orbitals. These considerations account for the H^+ attack on C_α in $CpRh(PH_3){=}C{=}CH_2$ (4) and allow the prediction that $CpRh(PH_3){=}C{=}CHR$. where R is electron-attracting or $CpRh(NH_3){=}C{=}CH_2$ will behave similarly for a larger range of electrophiles. We can also predict that, in contrast either $CpRh(CO){=}C{=}CH_2$ or $CpRh(PH_3){=}C{=}CHR$ in which R is electron-donating will undergo attachment of the electrophile at C_β whatever the electrophile, and thus behave like the majority of the vinylidene complexes.

Appendix

All calculations were performed by the extended Hückel method [18] with weighted H_{ij}s. The values for the H_{ii}s and exponents were taken from previous studies [19]. The following bond lengths were used (Å): M–C : 1.8; C=C : 1.32; M–C (Cp): 2.08 (Fe), 2.25 (Rh), 2.12 (Mn); M–CO: 1.8; C–O: 1.15; Ir–P: 2.40; Ir–Cl: 2.40; Rh–P: 2.27; C–N: 1.16; C–CN: 1.45; C–OH: 1.36.

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