Journal of Organometallic Chemistry, *443* (1993) 191–197

JOM 23026

Easy cleavage of the C=O double bond in W^{II} (η^2-OCH_2) complexes. A molecular orbital analysis

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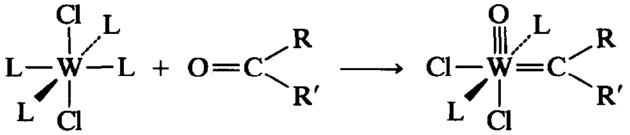
(Received March 16, 1992)

Abstract

A molecular orbital analysis based on extended Hückel calculations shows that the transformation of (η^2-formaldehyde)tungsten complexes into six-coordinate oxo-alkylidene complexes $[WCl_2L_2(O)CH_2]$ is symmetry-forbidden. Nevertheless, the transformation occurs readily because the highest occupied molecular orbitals (HOMO) of the starting materials are metal non-bonding orbitals and because the products are very stable with a WO multiple bond. The facile C=O cleavage is not a general reaction of η^2-aldehyde or ketone complexes: it requires the oxo-alkylidene product.

1. Introduction

It was recently shown that the oxidative addition of carbon–oxygen double bonds to $[WCl_2(PR_3)_4]$ results in the formation of oxo-alkylidene complexes following eqn. (1) [1].



(1)

$L = PR_3$

The oxidative addition of heterocumulenes to $[WCl_2(PR_3)_4]$ also involves the insertion of tungsten into a double bond (O=C=O and RN=C=O [2] or ArP=C=O [3]). These reactions are of special interest owing to the unusual ease of double-bond cleavage. The mechanism suggested for eqn. (1) is the initial formation of an intermediate η^2-complex by substitution of a phosphine ligand. Then, with loss of a second phosphine, this complex adds another OCRR′ or decomposes to an oxo-alkylidene complex (Scheme 1). The bis(ketone) complex can also decompose to give the same complex depending on the nature of the ketone.

In connection with our work on molecular complexes of aldehydes and ketones [4] we have attempted to study this mechanism by means of extended Hückel calculations. The converse reaction, the reductive coupling of two unsaturated ligands to give a multiple bond coordinated to the metal, has already been studied theoretically (as in the coupling of carbenes or carbynes [5], the coupling of carbonyls with isocyanides [6] and the transformation between ketene and carbene carbonyl complexes [7]). The coupling of two carbenes is allowed for a d^2 six-coordinate metal and forbidden for a d^4 [5]. The reaction can become allowed in the latter case if the carbene carbon is replaced by a more electropositive atom. In contrast, for seven-coordination in the capped trigonal prism geometry the d^4 case is the most favoured [6].

If the reaction of Scheme 1 proceeds by loss of a second phosphine, a six-coordinate metal is obtained with a carbene ligand and an electronegative ligand, the oxygen atom. It follows that the reaction must be forbidden. Nevertheless, the fact that the bis(ketone) reacts similarly supports this mechanism. If, on the other hand, C=O breaking precedes the loss of the second phosphine, a seven-coordinate oxo-alkylidene complex is obtained and this reaction is allowed. We have therefore investigated the two pathways described

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0022-328X/93/$6.00

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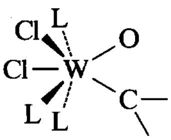
$$\begin{tikzcd}
{[WCl_2L_4] + O{=}CRR'} \arrow[r, "-L"] & {[L_3Cl_2W(\eta^2\text{-}O{=}CRR')]} \arrow[r, "-L", "+O{=}CRR'"'] \arrow[d, "-L"] & {[L_2Cl_2W(\eta^2\text{-}O{=}CRR')_2]} \arrow[dl, "-O{=}CRR'"] \\
& {[L_2Cl_2W(O)CRR']} &
\end{tikzcd}$$

Scheme 1.

in Scheme 2, where the phosphines are replaced by PH_3 and R, R' by H.

The bond lengths used are taken from X-ray structures [1]. Complex **1** can contain an η^2 ligand because tungsten is very electropositive [4]. The ligands coplanar with the CO bond must be bent away from this bond by 10°.

Complex **2** is a d^0 seven-coordinate complex, if the oxo group is considered as O^{2-} and the carbene as $CH_2{}^{2-}$, as is usual. Several geometries can be envisaged [8]: the pentagonal bipyramid (PB), the capped octahedron (CO), and the capped trigonal prism (CTP). Most d^0 complexes have a PB or a CTP structure, with a preference for the PB when the ligands are different. We have therefore considered first a PB structure for **2**. The search for the best geometry leads to equal angles between the ligands in the pentagonal plane (72°). During the transformation **1** → **2**, only the angles of the bonds to the axial ligands, Cl and L, change from 10° to 18°. The CTP structure **5** has also been examined, since it is the geometry studied by Hoffmann and the reaction is allowed. In agreement with experimental and theoretical data, the ligands are bent away from the oxo and carbene ligands by 15°. An interesting feature is the OWC angle which has been optimized at 75°. Such a small angle is common in seven-coordinate complexes with π-acid ligands [6]. This is essentially due to a decrease in ligand–ligand four-electron repulsions through metal orbitals. Complex **5** is easily obtained from **2** by rotation and bending of the ligands, but it is 10 kcal mol^{-1} less stable.



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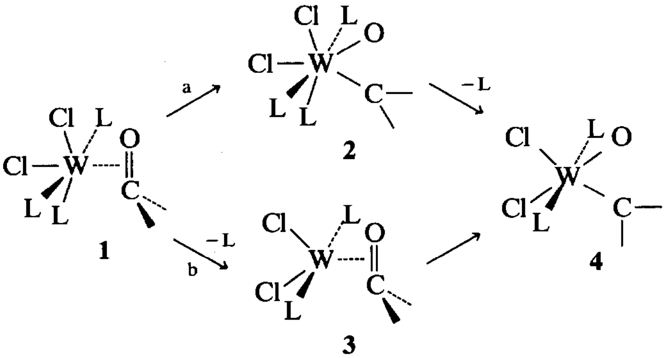
Complex **3** is a d^4 ML_5 complex. Its preferred geometry has been calculated to be a trigonal bipyramid in agreement with previous studies [4,9]. Finally, complex **4** is a classical octahedral d^0 complex with OWC = 90°.

2. Molecular orbital analysis

2.1. *Aldehyde complexes 1 and 3*

Each molecule has been divided into a metallic moiety (WCl_2L_3 or WCl_2L_2) and an organic moiety (OCH_2). The frontier orbitals of a ML_5 or a C_{2v} ML_4 fragment have been described previously [10]. Their shapes are shown in Figs. 1 and 2. In each case, three of them are close in energy and the four electrons of the d^4 metallic fragments are shared between them, giving either two doubly occupied orbitals and one vacant orbital or one doubly occupied orbital and two singly occupied orbitals. The interaction analysis is the same in both cases. In the WCl_2L_2 fragment the five d orbitals appear on the diagram. In the WCl_2L_3 frag-



Scheme 2.

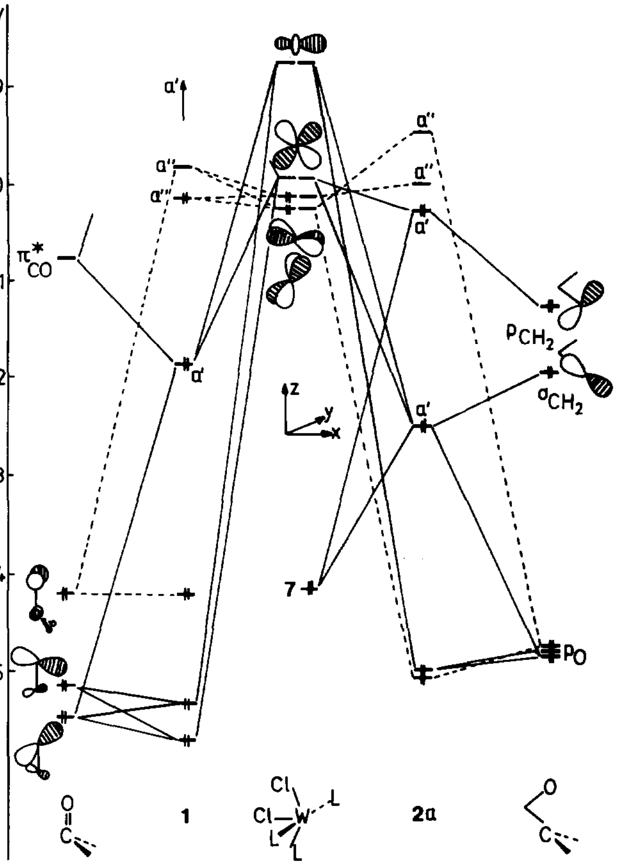


Fig. 1. Interaction diagrams between WCl_2L_3 and formaldehyde CH_2O (on the left) or oxo+carbene ligands (on the right). In solid lines, interactions of a' symmetry. In dashed lines, interactions of a'' symmetry.

ment the $d_{x^2-z^2}$ orbital has been considerably raised by interaction with the Cl ligand along the x axis.

The hydrogen of H_2CO are bent back in **1** and **3**, so that π-CO and the p_z lone pair of oxygen mix together to give two new occupied orbitals [4] (see Figs. 1 and 2). As in all η^2 complexes of aldehydes, the main interaction brings π^*-CO into play, the role of the other frontier orbitals being small. Since the d orbitals of tungsten are high in energy, this interaction is very strong. The result is a long C–O bond (1.38 Å experimentally [1] instead of 1.32 Å, typically found in η^2 complexes [4]). The highest occupied molecular orbital (HOMO) of the metallic fragment remains unchanged and at high energy, very close to the lowest unoccupied molecular orbital (LUMO). The low-lying occupied orbitals of the metallic fragment are not shown in the diagram. They give only small four-electron interactions with the orbitals of H_2CO.

The small HOMO–LUMO gap induces two possible situations. Either the complexes exist in a triplet state and are paramagnetic, or they remain in a singlet state and are unstable towards distortion or rearrangement which would lower the HOMO (Jahn–Teller). The first situation has been experimentally found for the related ethylene complex $[WCl_2(PMe_3)_3(C_2H_4)]$ [1]. The method used does not allow us to compare singlet and triplet states. Since experimentally a reaction occurs with these complexes yielding a complex which is apparently not to be paramagnetic, the singlet state has been assumed.

2.2. The oxo-carbene complexes 2, 4 and 5

The orbital interactions of the oxo ligand with a metallic fragment have already been described [11–13] on the basis of extended Hückel type calculations. The carbene complexes are also well documented from a theoretical point of view [14]. To our knowledge only two theoretical studies have appeared on oxo-carbene complexes [15]. The calculations on octahedral oxo-complexes explain why a π-ligand (carbyne, carbonyl, ethylene) is always *cis* to the oxo-ligand owing to the

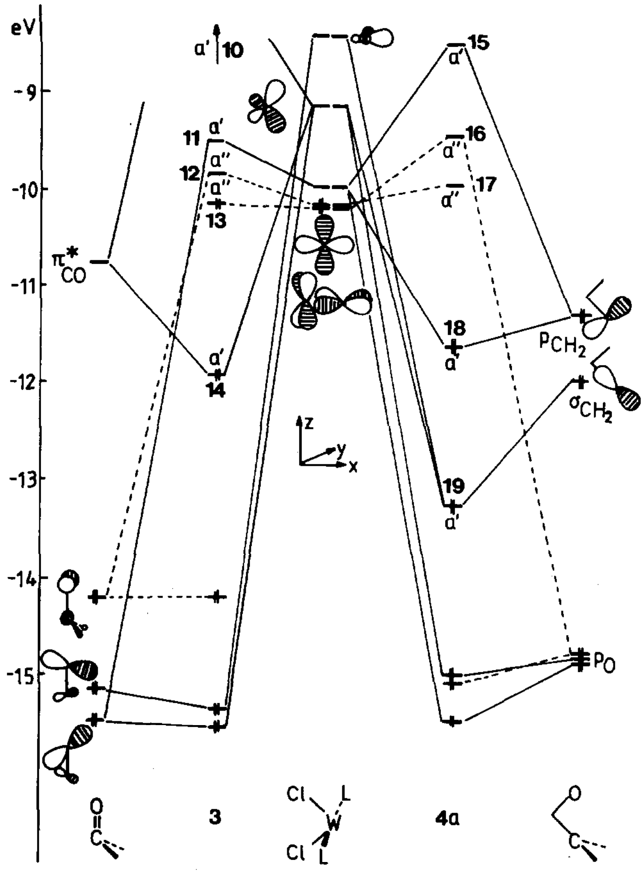
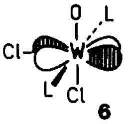


Fig. 2. Interaction diagrams between WCl_2L_2 and formaldehyde CH_2O (on the left) or oxo+carbene ligands (on the right). In solid lines, interactions of a' symmetry. In dashed lines, interactions of a'' symmetry.

shape of the HOMO. For example, the HOMO of the d^2 $W(O)Cl_2(PR_3)_2$ fragment is represented in **6**.



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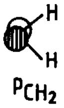
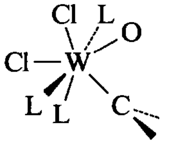


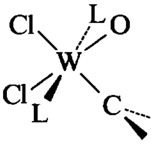
p_{CH_2}

The carbene ligand has only one orientation that allows favourable overlap of this HOMO **6** with the vacant p_{CH_2} orbital. In this orientation, called "in plane" below, the hydrogen atoms are in the CWO plane. This is in agreement with the structural data [1] and with the orientation of ethylene in $[W(O)Cl_2(PR_3)_2(CH_2{=}CH_2)]$ [13] owing to the fact that ethylene and carbene have symmetrically comparable orbitals [8] (π^* with p_{CH_2} and π with σ_{CH_2}, respectively). In tetrahedral oxo-alkylidene complexes the CH_2 group is in the plane of the oxo ligand [15b]. The reason suggested is the existence in the perpendicular conformation of a repulsive interaction between the p_{CH_2} component and a lone pair on the oxygen.

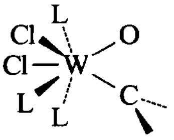
In complexes **2**, **4** and **5**, the in-plane conformation is more stable than the perpendicular by 30, 13 and 10 kcal mol^{-1}, respectively. However, in order to apply symmetry arguments for the transformations **1** → **2** and **3** → **4**, the perpendicular conformations **2a**, **4a** and **5a** must be considered. The symmetry of the carbene hydrogen atoms is maintained during the reaction.



2a



4a

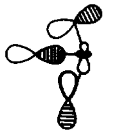


5a

As before, each complex has been divided into a metallic fragment and an organic, considered as O^{2-} and CH_2^{2-}. In these conditions, the metallic fragment is d^0 so that all d orbitals are empty. The two carbene orbitals σ_{CH_2} and p_{CH_2} and the three oxygen lone pairs are doubly occupied. The interaction diagrams are shown in Figs. 1 and 2 (on the right). Let us analyse first the interactions in **4a** (Fig. 2). Owing to the fact that OWC = 90°, the orbitals of the metallic fragment WCl_2L_2 are directed towards the O and CH_2 ligands, so that the interactions are strongly stabilizing. The d^0 WCl_2L_2 fragment possesses five vacant orbitals capable of interacting with the five occupied orbitals of CH_2^- and O_2^-. This gives multiple bonds, a W–O triple bond and a W–C double bond, as shown in Fig. 2. In the perpendicular conformation **4a** a second-order destabilizing interaction with p_z-O reduces the stabilization of p_{CH_2} in agreement with the argument of Nakamura and Dedieu [15b]. Such an interaction cannot occur in the in-plane conformation **4**. In this latter conformation, the p_{CH_2} orbital is in the *yz* plane (a'' symmetry) and interacts with the highest of the two a'' d orbitals, which is very near to $d_{x^2-z^2}$. Since the overlaps are roughly the same in the two cases, the stabilization obtained for p_{CH_2} is similar in the two conformations, the small energy difference between them arising essentially from the destabilizing interaction of p_z-O. There are also numerous four-electron destabilizing interactions between low-lying orbitals of WCl_2L_2 and H_2CO, but these are not shown in the diagrams.

The comparison of the diagrams for **3** and **4a** shows that the interaction of H_2CO with WCl_2L_2 is far more favourable in the oxo-carbene complex.

Let us consider now complex **2a** (Fig. 1). The interaction of σ_{CH_2} looks very similar to that in **4a** but p_{CH_2} is strongly destabilized. As stated above, the $d_{x^2-z^2}$ orbital in WCl_2L_3 is at very high energy and no d orbital has a good overlap with p_{CH_2}. Only destabilizing interactions exist, with p_z-O on the one hand and with low-lying orbitals like **7** on the other. These orbitals are localized essentially on the ligands but have some d_{z^2} character. They also destabilize σ_{CH_2}.



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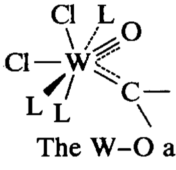
This notion of ligand–ligand through-metal interaction has already been described for the aldehyde complexes [4]. In the in-plane conformation **2**, the p_{CH_2} orbital is of a'' symmetry and the destabilizing interactions disappear. Moreover there is one d orbital of the same symmetry which interacts with it in a stabilizing manner. The diagram for **2** looks very similar to that of **4**. This explains why the energy difference between **2** and **2a** is larger than that between **4** and **4a** (30 *vs.* 13 kcal mol^{-1}).

The comparison of the diagrams in Fig. 1 shows again that the oxo-carbene complex **2a** is more stable than **1**. However, the energy difference is smaller than in the preceding case. The d^0 WCl_2L_3 fragment has only four accessible vacant orbitals. Therefore, four bonds only can be made with O and CH_2. That means that in the seven-coordinate complex **2**, the W–O bond is not a pure triple bond and the W–C bond is not a pure double bond. In such complexes in fact, only two π bonds can be formed to maintain an electron count of 18, and **2** can be represented as the resonance form **2b**. Similar arguments have been made for di-imido complexes [16].

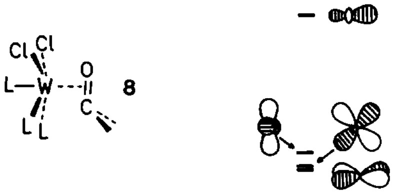


2b

The W–O and W–C overlap populations reflect this diminution of the bond orders. The W–O overlap population decreases from 0.67 in **4** to 0.53 in **2** and the W–C overlap population from 0.83 to 0.71.

3. Breaking of the C=O bond

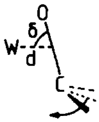
The four complexes **1**, **2a**, **3** and **4a** have C_s symmetry. In both **1** and **3** there is one more occupied orbital of a'' symmetry than in **2a** and **4a**. Therefore, one occupied orbital of **1** or **3** must correlate with a vacant orbital of **2a** or **4a** and the transformations **1** → **2a** and **3** → **4a** must be both forbidden in the Woodward Hoffmann sense. The difference with the seven-coordinate case studied by Hoffmann is due to the orbital symmetry of the WCl_2L_3 fragment in **8**, as shown in Scheme 3.



Scheme 3.

When the WCl_2L_3 fragment rotates from its conformation in **1** to that in **8**, the d_{yz} orbital of a'' symmetry is pushed up and the $d_{z^2-y^2}$ orbital of a' symmetry comes down. Thus, the WCl_2L_3 fragment in **8** has two a' orbitals and one a'' orbital. As in **1** or **3**, the a'' orbital is destabilized by the p_y lone pair on oxygen and the HOMO of **8** is of a' symmetry. In the corresponding oxo-carbene complex, the two highest orbitals coming from p_{CH_2} and σ_{CH_2} have the same symmetry as in **2a** or **4a** (a'). Consequently **8** and its corresponding oxo-carbene complex have the same number of occupied orbitals of each symmetry. The reaction is allowed.

The reaction paths have been calculated in each case by varying linearly the C–O distance, d, δ and the CH_2 pyramidalization as shown in **9**. Ten points have been calculated. The evolutions of the highest orbitals are drawn in Fig. 3 for the transformation **3** → **4a**.



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The level correlations are obvious in Fig. 2. Orbitals 12 and 13 are little perturbed by interaction with H_2CO and correlate to **16** and **17** respectively. Orbital **11** might also correlate to **15** in the same manner. However the high-lying orbital **10** which is located part on d_{xz} and part on π^*-CO goes down when the C–O length increases and might correlate to an orbital having a large contribution on CH_2, for example **18**. A avoided crossing exists between **10** and **11**, as shown in Fig. 3, and **10** correlates to **15** and **11** to **18**. Orbital **14**, which is also largely located on π^*-CO goes down when the C=O bond breaks and when O and C approach the metal. It evolves smoothly to **19** which is essentially metal–CH_2 bonding. Orbital **18** corresponds to the $2b_2$ ligand–ligand antibonding orbital described in ref. 5 which correlates with a high-lying π^* orbital and is responsible for forbidding the reaction. The other low-lying occupied orbitals do not play an important role in the description of the reaction. Their evolutions are smooth owing to numerous avoided crossings.

Therefore the vacant orbital **11** correlates to the occupied orbital **18** and the reaction is forbidden, as assumed.

The evolution of the orbitals during the transformation **1** → **2a** are shown in Fig. 4. They look very similar to the previous case with one exception. The disappearance of the $d_{x^2-z^2}$ orbital of a' symmetry suppresses the avoided crossing that existed between **10** and **11** in Fig. 3 and the high-lying vacant orbital decreases sharply to the HOMO of **2a**. In conclusion, both reactions are forbidden. Nevertheless they are facile. There is no energy barrier for the transformation **3** → **4a** and only a small barrier for the transformation **1** → **2a**. This can be explained in two ways. First in each case, the HOMO of the η^2-aldehyde complex is a metallic non-bonding orbital which is not affected by the movement of the organic part and remains at the same energy during the reaction. Secondly, owing

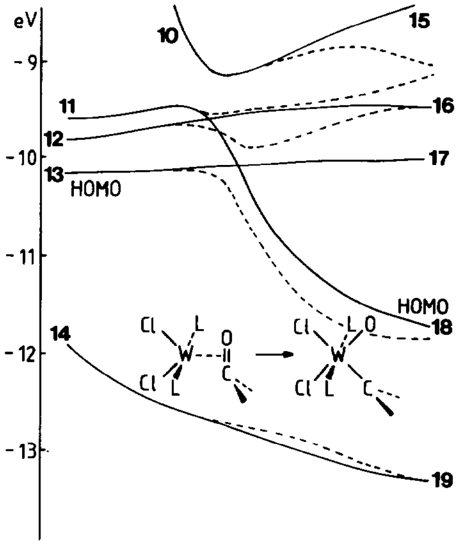

Fig. 3. Evolution of the main orbitals during the reaction path leading from **3** to **4a** (solid lines) and from **3** to **4** (dashed lines).

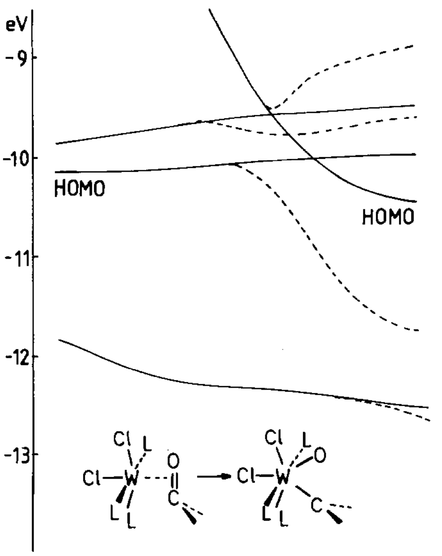

Fig. 4. Evolution of the main orbitals during the reaction path leading from **1** to **2a** (solid lines) and from **1** to **2** (dashed lines).

to the strength of the W–O and W–C bonds in the oxo-carbene complexes, the energy gain is huge, more for **4a** than for **2a**, since the WO bond is stronger in the former.

Finally, the reaction path starting from complex **8** has also been calculated; it shows no vacant–occupied level crossing and the reaction is allowed, as supposed. The energy barrier is smaller than for the reaction **1** → **2a**.

The reaction paths considered until now maintain C_s symmetry along the reaction. However the oxo-carbene complexes obtained in these reactions are those in which the CH_2 groups lie in the plane containing the oxo ligand, *i.e.* **2** or **4**. The carbene group must rotate by 90° during the reaction. If this rotation begins far along the reaction path, the reaction is easier, the total energy decreases more quickly for **3** → **4** and the barrier is reduced for **1** → **2**. The same conclusion has been drawn by Morokuma [7]: his transition state is late and asynchronous in the sense that the double bond is nearly totally broken before the CH_2 rotates.

An important consequence of the CH_2 rotation is that the symmetry is broken during the reaction. That means that all orbital crossings become avoided and the reactions become allowed. The evolutions of the orbitals when the rotation is added are plotted in dashed lines in Figs. 3 and 4. This time the HOMOs correlate together.

Cleavage of the double C=O bond in an η^2-aldehyde complex of W^{II} is easy, the most favoured path being through complex **3**. However the transformation of **3** to **1** requires the loss of one PH_3. For this loss a barrier of 15 kcal mol^{-1} has been experimentally estimated and our calculations give a similar value. Although the EHT method cannot give quantitative values, our calculations show that the breaking of the C=O bond in **1** is easier than the loss of a phosphine. This means that path a in Scheme 2 would be preferred. Then the loss of one PH_3 from **2** to give **4** does not require any barrier, owing to the greater stability of **4** relative to **2** (triple WO bond). In fact, in order to avoid the barrier of the PH_3 loss, one can imagine a reaction path in which the C=O breaking is concerted with the departure of PH_3. The large energy gain obtained during the C=O breaking to give **4** cancels the barrier of the PH_3 loss. Effectively there is no barrier for the path leading directly from **1** to **4**.

4. Conclusion

This study shows that the monoketone complex $[WCl_2L_3(\eta^2\text{-}OCH_2)]$ transforms easily to the oxo-alkylidene complex $[WCl_2L_2(O)CH_2]$ without an energy barrier. This explains the mild experimental conditions needed to break the C=O double bond at room temperature, in non-polar solvents, without forcing conditions or additional reagents [1].

The molecular orbital analysis performed in this work enables us to understand why the cleavage of the C=O double bond is so easy in this complex, despite the fact that the reaction is intrinsically forbidden. The HOMO and LUMO of the η^2-aldehyde complexes **1** and **3** are very close in energy. That means that these molecules are unstable with respect to a distortion or a rearrangement which would lower the HOMO. This lowering is obtained in the oxo-carbene complexes **2** and **4** whose HOMOs are largely stabilized. Even though the reaction is forbidden, this does not result in any barrier. Effectively, the HOMO of the η^2-complex (**1** or **3**) and the LUMO of the oxo-carbene complex (**2** or **4**) which correlate together, lie at the same energy since they are the same non-bonding metal orbital. Finally, the large energy gain obtained when the C=O bond breaks to give the oxo and carbene ligands balances any possible energy barrier. In particular, it cancels the energy needed to lose a phosphine, so that the best reaction path consists in a C=O cleavage synchronous with the PH_3 loss in the monoketone complex $[WCl_2L_3(\eta^2\text{-}OCH_2)]$ **1**.

Such a cleavage is not a general reaction of the η^2-aldehyde or ketone complexes since a lot of these complexes have been isolated and characterized [4,17]. Where does the peculiarity of complexes $[W^{II}Cl_2L_3(\eta^2\text{-}OCH_2)]$ come from? Consider for example d^8 $[ML_4(OCH_2)]$ complex. It looks like **3** with four additional electrons. In Fig. 2, two more orbitals are occupied and the number of orbitals of the same symmetry becomes equal in the two parts of the diagram. Therefore the breaking of the C=O bond to give an oxo-carbene complex might be allowed. Why does it not occur experimentally?

The answer lies in the possible or impossible existence of the final oxo-carbene complex. Terminal mono-oxo ligands are common in the chemistry of the higher oxidation states of metals from vanadium to osmium [18]. They have generally strong multiple metal oxygen bonds and therefore require empty metal d orbitals. A carbene ligand also needs empty orbitals to interact with. Therefore, the presence of both an oxo and a carbene ligand excludes the late transition metal complexes and requires high oxidation states. Furthermore, the number of other ligands around the metal must be consistent with the 18-electron rule. This is the reason why the known oxo-alkylidene complexes contain Mo^{VI}, W^{VI} or Re^{VII}. They are of the type $[WCl_2(PR_3)_2(O)(CRR')]$ [1,19] or $[WCl_2PR_3(O)(CRR')]$ [20] and $[ReCl_3(O)(CRR')]$ [15]. Therefore the cases where C=O breaking can occur in η^2-aldehyde complexes are very limited.

Acknowledgment

The author thanks Dr. O. Eisenstein for her advices.

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Appendix A

All calculations were performed by using the extended Hückel method with weighted H_{ij} values [21]. The values for H_{ii} and exponents are taken from previous work [5b,22]. The following bond lengths were used: W–Cl 2.5 Å; W–P 2.56 Å; W–O(OCH_2) 1.94 Å; W–O(oxo) 1.708 Å; W–C(OCH_2) 2.18 Å; W–C(carbene) 1.98 Å; C–O(OCH_2) 1.38 Å; C–H 1.08 Å.