Studies of the Oxidative Addition of Some Substrates containing Carbon–Heteroatom Bonds to Some Tungsten and Platinum Complexes†

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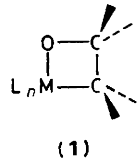
The oxidative addition of some substrates containing carbon–heteroatom bonds to some tungsten and platinum complexes is analysed from a frontier orbital point of view. For the tungsten complexes the main attention is focused on $[WCl_2(PR_3)_4]$ and for the platinum complexes on $[Pt(PR_3)_4]$. The tungsten complex is able to cleave carbon–heteroatom bonds giving two fragments of the substrate which add to the tungsten complex, whereas with the platinum complex the carbon–heteroatom bond adds to the metal. It is suggested that the first step in the reaction of the d^4 tungsten complex with the substrates is a nucleophilic attack of the heteroatom in the substrate at the tungsten atom, an end-on interaction, followed by a side-on co-ordination. The oxidative addition is proposed to take place by electron transfer from a tungsten *d* orbital to the antibonding carbon–heteroatom orbital leading to cleavage of this bond. In the case of the platinum complex the first part of the reaction is also suggested to be an end-on interaction of the heteroatom in the substrate at the platinum atom followed by side-on co-ordination leading to the product.

The transfer of an oxygen atom to and from a transition-metal centre [equations (1) and (2)] is a fundamental and a widespread reaction;[1] the oxygen donor system (DO) donates an oxygen atom to the transition-metal complex (M) which can transfer the oxygen atom either back to D, equation (1), or to a new acceptor A, equation (2). A variety of oxygen donors are available, ranging from systems with a very labile oxygen as *e.g.* iodosylbenzene to systems with a strong bound oxygen such as carbon dioxide.[1] Reactions (1) and (2) are not only restricted to oxygen systems as molecules having carbon–nitrogen and carbon–sulphur bonds also undergo reactions in which the carbon–heteroatom bond is cleaved. The transition-metal systems which are involved in these reactions can be simple ions, organometallic complexes, clusters, and even surfaces.[1]

$$\mathrm{DO + M \rightleftharpoons D + MO} \qquad (1)$$

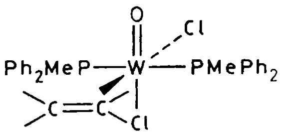
$$\mathrm{MO + A \rightleftharpoons M + AO} \qquad (2)$$

The reactions outlined in equations (1) and (2) could be the transition metal-catalysed oxidation of an organic compound, a field which has been in intensive development during the last decade. A lot of attention has been devoted to the mechanism of these transition metal-catalysed oxidations[1a,d,e,2] and one of the most intriguing and often invoked involves four-membered metallacyclo-oxetanes, (**1**),[1a,e,2a–d,m,3] as crucial intermediates. However, only a small number of such metallacyclo-oxetanes, (**1**), have been prepared and characterized.[4] The first step in the formation of (**1**) is often suggested to be co-ordination of an alkene to the metal centre followed by the addition of the alkene across an oxo–metal bond.[2a]

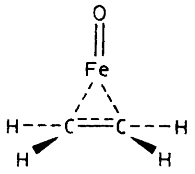


(**1**)

Recently two transition-metal complexes, (**2**)[5] and (**3**),[4f] containing both an oxo–metal bond and an alkene co-ordinated to the metal centre have been characterized. Both (**2**) and (**3**) might be examples of complexes by which an addition of the co-ordinated alkene to the oxo–metal bond could lead to the metallacyclo-oxetane, (**1**), and hence the formation of *e.g.* an epoxide.



(**2**)



(**3**)

A complex with carbon monoxide as ligand instead of the alkene in (**2**) has also been reported.[6] However, both alkene complexes, (**2**) and (**3**), and the one containing carbon monoxide, (**5**), as ligand do not rearrange to epoxides, carbon dioxide, or other products of ligand oxidation.[4f,6,7] However, in the case of the tungsten complex $[WCl_2(PMePh_2)_4]$ (**4**) the reverse reaction takes place: epoxides, carbon dioxide, as well as other compounds containing carbon–heteroatomic bonds undergo oxidative addition to (**4**) as outlined in Scheme 1.[6]

The deoxygenation of epoxides [Scheme 1, equation (3)] has also been observed for some other Group 6 and 4 transition-metal complexes.[2a,8,9] However, the reaction of (**4**) with epoxides is the first example in which both the oxygen and alkene remain bound to the metal centre. The other reactions outlined in Scheme 1 take place in a similar way with the two substrate fragments bound to the metal centre in the product.

If the transition metal is changed to a more electron-rich metal a different reaction course takes place. Atomic iron and ethylene oxide react in a matrix at low temperature to give an iron cyclo-oxetane which undergoes a photochemical rearrangement to the oxoiron–π-ethylene complex, (**3**),[4f] and $[Pt(PPh_3)_4]$, (**8**) reacts with tetracyanoethylene oxide to give a platinum cyclo-oxetane, (**9**) [Scheme 2, equation (7)], and with carbonyl sulphide to give a platinum η^2-COS complex, (**10**) [Scheme 2, equation (8)].[4a–d] The same behaviour is also

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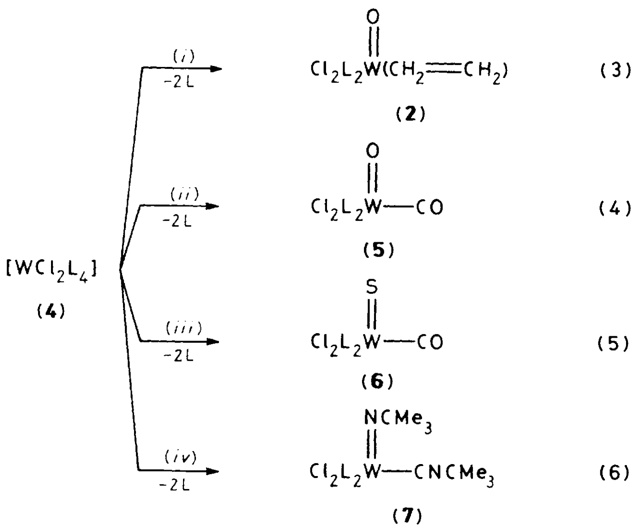
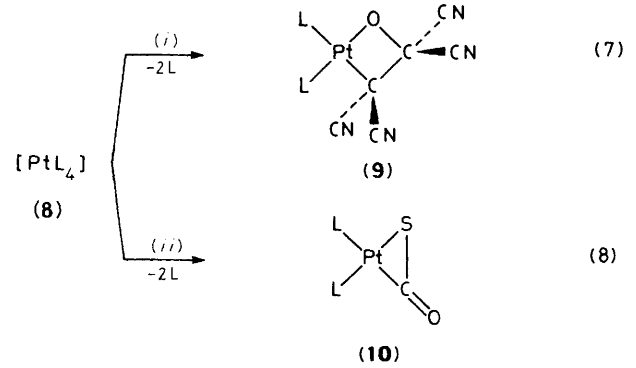
† *Non-S.I. unit employed:* eV ≈ 1.60×10^{-19} J.



Scheme 1. L = PMePh$_2$. (*i*) Etylene oxide; (*ii*) CO$_2$; (*iii*) COS; (*iv*) Me$_3$CN=C=NCMe$_3$



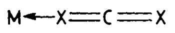
Scheme 2. (*i*) Tetracyanoethylene oxide; (*ii*) COS

observed when CO$_2$ reacts with [Ni(PPh$_3$)$_4$] and CS$_2$ reacts with [ML$_4$] (M = Pd or Pt).[2c]

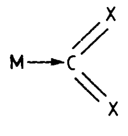
The deoxygenation of epoxides leading to the alkene and the oxometal complex has been suggested to take place *via* a metallacyclo-oxetane, (**1**).[1a,2a] It appears from the text and the reactions in Schemes 1 and 2 that some transition-metal complexes are able to cleave carbon–heteroatomic bonds, while others add to such bonds.

In this paper we throw some light on the mechanism of these reactions, the electronic structure of the complexes, and why especially (**4**), involving a d^4 metal, cleaves carbon–heteroatomic bonds, whereas with complex (**8**), involving a d^{10} metal, the reaction stops at the cyclic complex. For these purposes we will use extended-Hückel calculations[10] in combination with the fragment orbital formalism.[11]

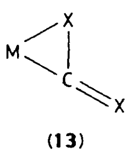
Approach of CX$_2$ *to a Metal Centre.*—Several theoretical investigations of the co-ordination of CX$_2$ (X = O or S) to a transition-metal centre have been performed:[12] it can co-ordinate in three different ways, end-on (**11**), *via* C (**12**), and side-on (**13**), respectively, of which the latter is the most frequently observed. It has been argued that a CX$_2$ molecule can start to approach an electronically unsaturated transition-metal centre end-on followed by interconversion to side-on co-ordination.[12b]



(**11**)



(**12**)



(**13**)

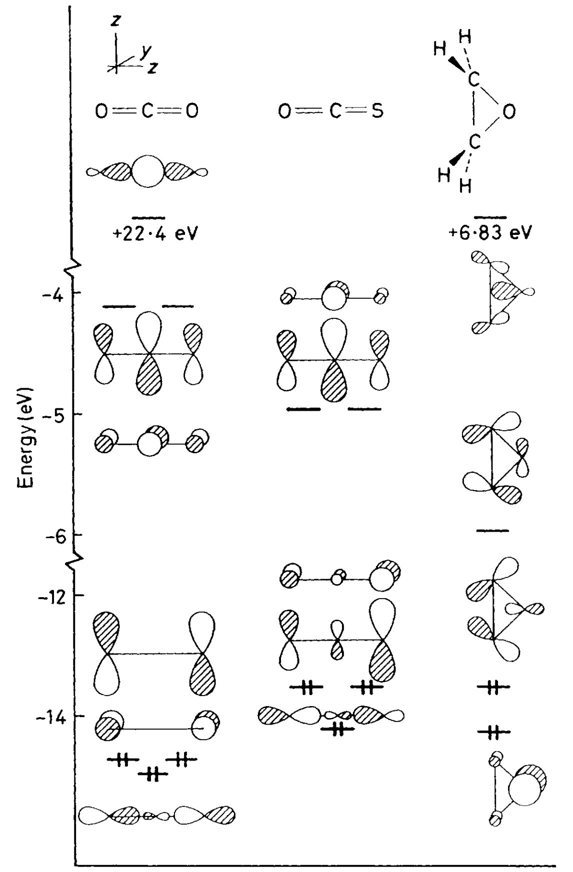


Figure 1. The frontier orbitals of carbon dioxide, carbonyl sulphide, and ethylene oxide

Results and Discussion

The tungsten complex (**4**) reacts with a variety of different substrates (Scheme 1) and we have chosen to investigate its reaction with ethylene oxide and carbon dioxide and for the platinum complex (**8**), its reaction with ethylene oxide and carbonyl sulphide. Although these substrates are seemingly very different some similarities appear when the reactions are analysed from a frontier orbital point of view. The frontier orbitals of carbon dioxide, carbonyl sulphide, and ethylene oxide are shown in Figure 1.

The frontier orbitals of carbon dioxide are shown to the left in Figure 1; extended-Hückel calculation gives the π_g orbitals as the highest-occupied-molecular orbital (h.o.m.o.) with the σ(C–O) orbital below. The lowest-unoccupied-molecular orbitals (l.u.m.o.s) of carbon dioxide are the π^*(C–O) of p_y and p_z character, and several eV above the l.u.m.o. is σ^*(C–O). The frontier orbitals of carbonyl sulphide are shown in the middle of Figure 1 and are similar to those of carbon dioxide. For ethylene oxide the frontier orbitals are shown to the right in Figure 1. The h.o.m.o. of ethylene oxide is a combination of p_x and p_z orbitals at the two carbons mixed in with a small part of p_x at oxygen showing C–C as well as C–O bonding. The second h.o.m.o. is of p_y character at the oxygen. The l.u.m.o. of ethylene oxide is the antibonding counterpart to the h.o.m.o. Several eV above the l.u.m.o. is located an orbital which is mainly antibonding between the oxygen and the two carbons. It appears from the h.o.m.o. and l.u.m.o. of ethylene oxide that the

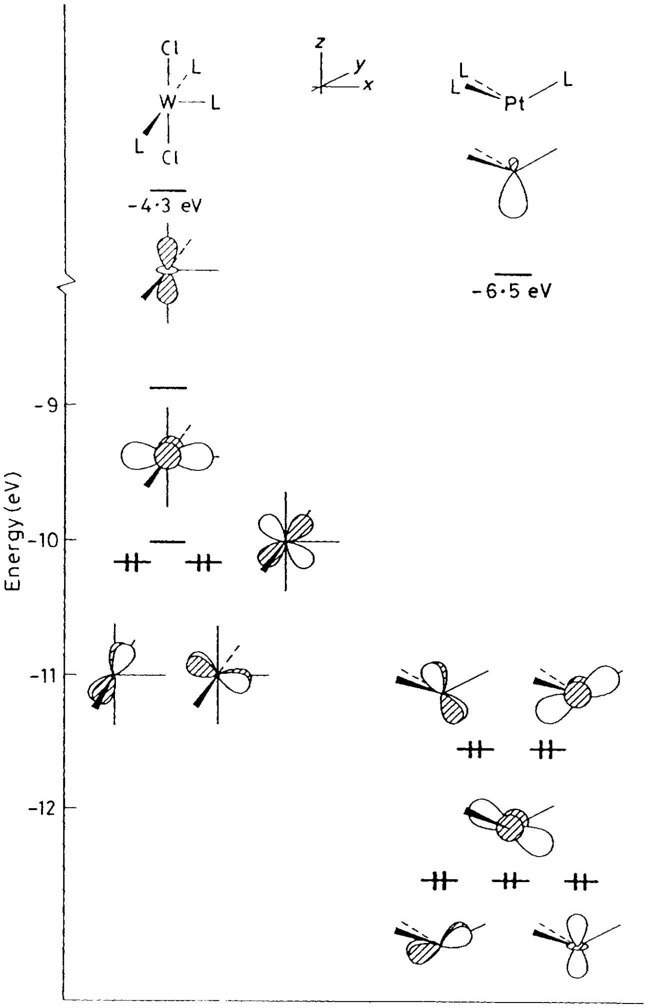
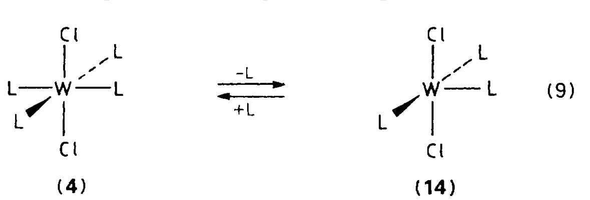


Figure 2. The frontier orbitals of *trans*-[WCl_2L_3] (to the left) and [PtL_3] (to the right)

part of the orbital located at the carbons is the distorted π and π^* orbital of ethylene.

Let us continue with the transition-metal complexes involved in the reactions. In the tungsten complex (**4**) the two chlorine ligands are placed *trans*, whereas in the products (**2**) and (**5**)—(**7**) a *cis* geometry of the chlorine ligands is found. Complex (**4**) is a 16-electron system, but co-ordination saturated, indicating that the first step in the reaction probably is a loss of a phosphine ligand leading to the more reactive five-co-ordinated 14-electron species (**14**) [equation (9)]. This statement is supported by experimental results.[13] First a steric factor of the phosphine ligands can be observed, the overall reaction rate increasing with bulkier phosphine groups. Secondly, the reaction rate decreases when phosphines are added to the solution, indicating that the equilibrium (9) is shifted to the left. The five-co-ordinated intermediate is assumed to be the reactive species. The frontier orbitals of *trans*-[WCl_2L_3] are shown to the left in Figure 2.

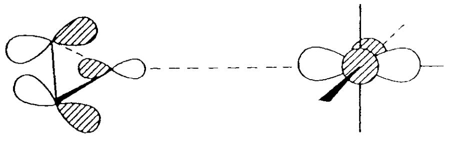


(**4**) (**14**)

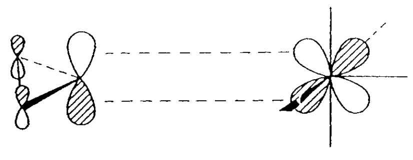
The h.o.m.o. of (**14**) comprises the degenerate *d* orbitals of mainly d_{xy} and d_{yz} character, the l.u.m.o. is d_{xz}, and the remaining two *d* orbitals, $d_{x^2-y^2}$ and d_{z^2}, are found at higher energies. With the small h.o.m.o.–l.u.m.o. gap for (**14**) a high-spin state is also possible for the complex which the present calculations do not take into account, and the ordering of the orbitals is also very dependent on geometry changes.[14]

The frontier orbitals of ethylene oxide and carbon dioxide show some similarities, among the h.o.m.o.s are orbitals mainly located at the oxygen and the l.u.m.o. of both systems is mainly located at the carbons.

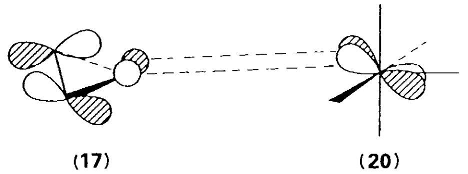
Because (**14**) is a 14-electron complex nucleophilic co-ordination of carbon dioxide and ethylene oxide, respectively is favoured.[12b] The initial rendezvous between the tungsten atom and carbon dioxide or ethylene oxide is an attack of the oxygen at the tungsten atom. Orbital reasons for this co-ordination are shown below for the interaction of ethylene oxide with complex (**14**).



(**15**) (**18**)

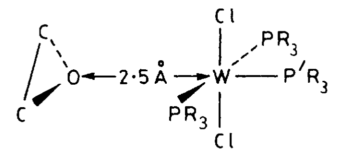


(**16**) (**19**)



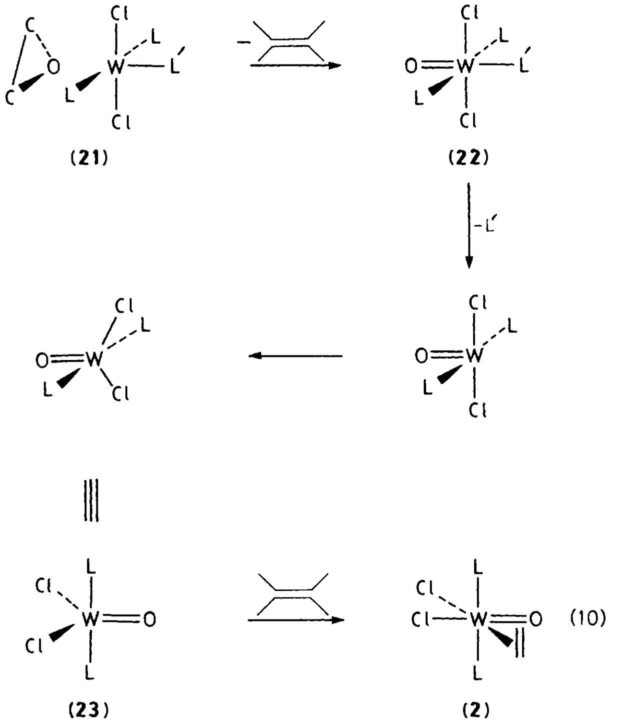
(**17**) (**20**)

Two of the occupied m.o.s of ethylene oxide, (**15**) and (**16**), have the right symmetry to interact with the l.u.m.o.s of (**14**), (**18**), and (**19**), respectively. The l.u.m.o. of ethylene oxide, (**17**), is also set up for interaction with the h.o.m.o. of (**14**). Similar arguments can also be used for carbon dioxide as well as the other substrates. Let us start with an approach of ethylene oxide as outlined in (**21**). Moving ethylene oxide towards the tungsten complex (**14**) to an oxygen–tungsten distance of 2.5 Å as shown in (**21**) leads to several electronic changes in both systems: the W–P′R_3 overlap population is reduced from 0.58 in (**14**) to 0.51 in (**21**) and an W–O overlap population is formed [0.21 in (**21**)]. In the epoxide the C–C overlap population increases from 0.70 in the free ethylene oxide to 0.76 in (**21**), while the C–O overlap population decreases from 0.52 to 0.49. The changes in overlap populations indicate that the approach of the oxygen in



(**21**)

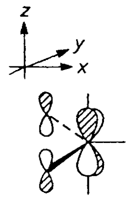
ethylene oxide towards the tungsten atom as outlined in (**21**) leads to formation of an O–W bond, while the W–P′R$_3$(=L′) bond is weakened. In ethylene oxide the C–C bond is changed towards the C–C bond in ethylene, while the C–O bonds are beginning to be broken. Besides the interactions shown in (**15**)—(**20**), the unoccupied m.o. located at +6.83 eV is lowered in energy by the interaction (we will return to this interaction later). The approach of ethylene oxide as outlined in (**21**) can thus lead to the formation of an oxotungsten complex (**22**) and an alkene in which the stereochemistry of the epoxide is maintained (*cis*-epoxides give *cis*-alkenes and *trans*-epoxides give *trans*-alkenes).



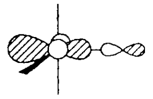
(**21**) (**22**)

(**23**) (**2**) (10)

Calculation of the overlap populations between tungsten and the ligands reveals that the ligand placed *trans* to oxygen in (**22**) is most weakly bound (L′). For that reason we assume that it is this ligand which undergoes ligand substitution with the alkene. The frontier orbitals of the intermediate (**23**) are shown below:



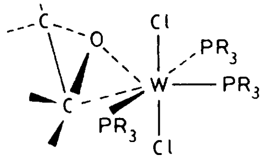
(**24**)


(**25**)

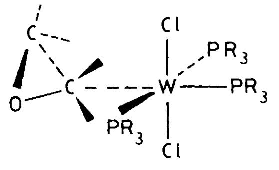
(**24**) is the h.o.m.o., and is set up for interaction with the π^* orbital of the alkene; the l.u.m.o. is d_{xz} and is not involved in interaction, whereas the second l.u.m.o., (**25**), located 0.6 eV above the l.u.m.o. can interact with the π orbital of the alkene. The frontier orbitals of (**23**) are thus set up for interaction with the alkene leading to the product of the reaction, (**2**).

The deoxygenation step, (**21**), by which the alkene is formed with maintained stereochemistry is in accordance with the experimental results for these deoxygenation reactions.[8c]

Approach of the C–O bond in ethylene oxide to the tungsten atom as outlined in (**26**) could lead to a tungsten cyclo-oxetane; but it appears from the frontier orbitals of ethylene oxide that these are not directly set up for an interaction with tungsten, and furthermore the total energy of such an approach is several eV less favourable compared with the approach shown in (**21**). The same results are found for approach of one of the carbons in ethylene oxide to tungsten as outlined in (**27**).



(**26**)



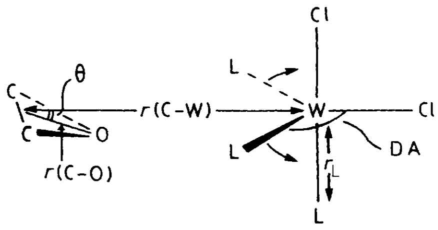
(**27**)

An approach of carbon dioxide in a similar way as ethylene oxide as depicted in (**28**) leads to a similar qualitative picture of the reaction.

(**28**)

The reactions of the different substrates with the tungsten complex shown in Scheme 1 lead to a binding of both fragments of the substrate to the tungsten atom. We have just described a reaction path where the first step was an abstraction of the oxygen atom from the substrate followed by an addition of the remaining part of the substrate to the metal. In the following we will show how the reaction can take place by a mechanism where both fragments become bound to tungsten in one step. To simplify the reaction path we will as a starting point assume that it is the *cis* form of [WCl$_2$L$_3$] which is the reactive species, but the reaction is also possible with the *trans* form (see later). The *cis* form could *e.g.* be formed by a double Berry pseudorotation.[14,15]

Let us start with the oxidative addition of ethylene oxide to complex (**4**); we will analyse the reaction by extending the end-on approach in (**21**) to a reaction path where ethylene oxide starts out with an end-on followed by a side-on approach.[12b] We are aware of the fact that the quantitative results obtained by extended-Hückel calculations cannot be sufficiently trusted in studies where the formation and cleavage of several bonds are simultaneously involved. However, as our intention is to give a qualitative description of the reactions, extended-Hückel calculations should be able to provide us with useful trends. The reaction co-ordinates needed in the end-on to side-on reaction are shown in (**29**).



(**29**)

The tilting of ethylene oxide is formed by moving the oxygen atom towards the phosphine ligand and at the same time the

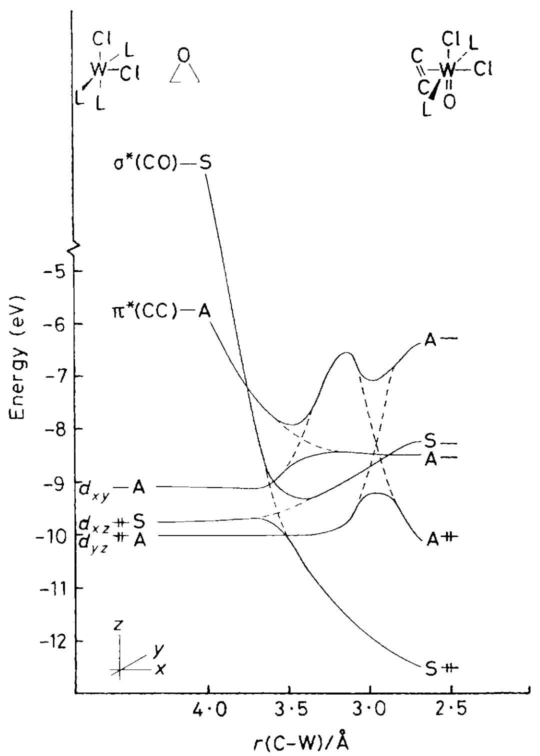


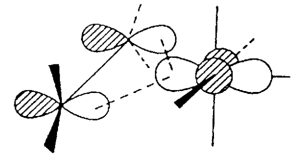
Figure 3. Energy correlation diagram for the reaction of ethylene oxide with [WCl$_2$L$_3$]

C–C part approaches the tungsten atom. The variables in (**29**) are: r(C–W) the distance from the tungsten atom to the centre of the C–C bond in ethylene oxide, θ the turning over of ethylene oxide from the end-on to the side-on mode, r(C–O) the distance from the oxygen atom to the centre of the C–C bond in ethylene oxide, and r_L the bond length from tungsten to the axial phosphine ligand. In an attempt to reduce the calculations we have reduced the four basis co-ordinates to two main co-ordinates X and Y, where X is the distance between the centre of the C–C bond and the tungsten atom, r(C–W) coupled to the tilting angle, θ [$d\theta/dr$(C–W)], and Y is the ligand dissociation co-ordinate r_L coupled to r(C–O) [dr(C–O)/dr_L = 0.25 Å/0.30 Å]. With the starting co-ordinates as X, $Y \approx$ 6.0, 2.55 a reaction path has been calculated which ends in (**2**) and a phosphine ligand.

Using fragment molecular orbital analysis it is possible to decompose the reaction path into orbital interactions between the tungsten complex and ethylene oxide. There are a lot of mixings and crossings of the molecular orbitals during the reaction so we will focus attention only on the main interactions. At the beginning of the reaction course where the end-on co-ordination of ethylene oxide at the tungsten complex is dominant, the main interactions are between the h.o.m.o. and second h.o.m.o. of ethylene oxide and the empty d_{xz} and $d_{x^2-y^2}$ orbitals at tungsten, respectively. When ethylene oxide approaches tungsten and begins to tilt the interaction pattern changes. It is now mainly acceptor orbitals at ethylene oxide and donor orbitals at tungsten which are involved in the interaction.

Figure 3 shows a correlation diagram for the reaction path, constructed for different geometries along the reaction path but with a slightly changed structure of the starting tungsten complex as the bonding angles between the equatorial ligands are 120°. To the left the orbitals are classified as symmetric (S) or antisymmetric (A) with respect to the mirror plane (xz).

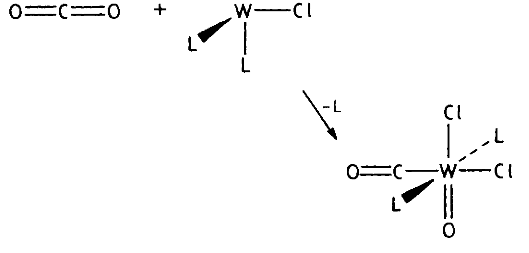
Because of the slight change in initial structure of *cis*-[WCl$_2$L$_3$] the ordering of the d orbitals in Figure 3 differs from those shown in Figure 2. The most conspicuous difference is the large stabilization of the m.o. which originates from σ*(C–O) in ethylene oxide. Along the reaction path σ*(C–O), symmetric with respect to the xy plane, mixes with tungsten $d_{x^2-y^2}$, also symmetric with respect to the same plane and at about X, $Y \approx$ 3.50, 4.65 an avoided crossing between this unoccupied orbital and the h.o.m.o. of the system, the tungsten d_{xz} takes place. This avoided crossing leads to a decrease in population of the d_{xz} orbital from 1.97 to 0.54 e. The accepting orbitals in this electron flow are p_x orbitals located at the carbons and the oxygen of ethylene oxide. Their population increases by 0.54 e for each carbon and 0.38 e for the oxygen. The overlap population of the C–C bond in ethylene oxide increase at the same time from 0.78 to 1.14, whereas it decreases for the C–O bond from 0.30 to −0.10, indicating that the C–C bond is strengthened and that C–O bond is weakened. The oxidative addition has now occurred as two electrons have been transferred from the metal to ethylene oxide. In the product the original σ*(C–O) orbital is mainly a combination of the π(C–C) and tungsten $d_{x^2-y^2}$, (**30**). The two electrons transferred from the metal to ethylene oxide cause first cleavage of the C–O bonds and then co-ordination of the alkene to the tungsten atom. After the cleavage of the C–O bonds the non-bound alkene can either leave the scenario or it can continue the reaction path to become co-ordinated to the tungsten atom. Here we will force the alkene towards the tungsten atom.



(**30**)

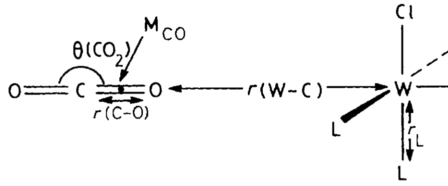
Two other avoided crossings are observed in Figure 3, one between an orbital of ethylene oxide which in the product is the π*(C–C) orbital and tungsten d_{xy}, the other between two tungsten orbitals d_{xy} and d_{yz}. The latter avoided crossing is important, as two electrons are transferred from d_{yz} to the d_{xy} orbital, making the d_{xy} orbital available for back donation to the π*(C–C) orbital in the ethylene part of ethylene oxide, and the d_{zy} orbital available for interaction with an occupied orbital at the oxygen.

The end-on to side-on approach can also be extended to the reaction of carbon dioxide with the tungsten complex shown in equation (11). In this reaction there are also at least four



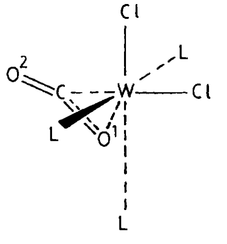
(11)

independent geometrical deformations, which means four basis internal co-ordinates for the reaction. The variables are the distance between the tungsten atom and the carbon dioxide, r(W–C), which is decreased, and the turning over of the carbon dioxide from the end-on to a side-on mode, θ(CO$_2$). Furthermore, the carbon–oxygen bond, r(C–O), in carbon dioxide has to be increased (to break the bond) and the axial phosphine ligand has to dissociate, r_L. The four reaction co-ordinates are shown in (**31**) (M_{CO} is the middle of the carbon–oxygen bond).



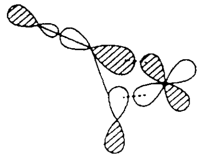
(**31**)

The variables are also here reduced to two X and Y where $dX = d\theta/dr(C\text{–}W) = 7°/-0.25$ Å and $dY = dr(C\text{–}O)/dr_L = 0.20$ Å$/0.25$ Å. With the starting co-ordinates $X, Y = 2.50, 4.00$ a reaction path for equation (11) can then be calculated. The interaction trends between carbon dioxide and the tungsten complex are the same as those found for ethylene oxide and the tungsten complex. Let us here try to discuss the reaction path more in terms of orbital interactions. Along the reaction path an interacting system is formed where both carbon and oxygen in carbon dioxide interact with the metal as shown in (**32**).

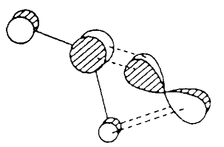


(**32**)

One of the geometrical changes needed when going from carbon dioxide and the tungsten complex to (**5**) is cleavage of one of the carbon–oxygen bonds [C–O^1 in (**32**)] in carbon dioxide. This can be traced to a population of σ*(C–O) of carbon dioxide, but also the interaction of the π* orbital of carbon dioxide with tungsten d_{xy} as depicted in (**33**) and (**34**), respectively.



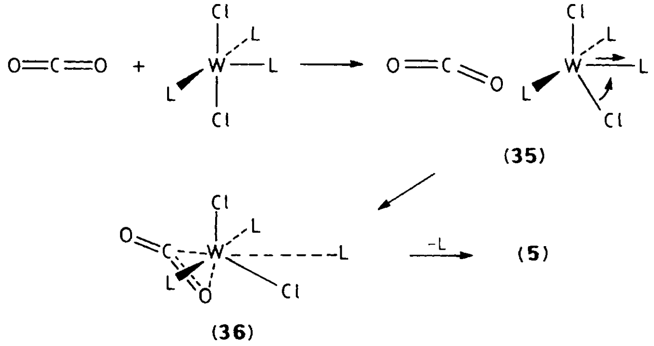
(**33**)



(**34**)

The σ*(C–O) orbital in carbon dioxide undergoes significant stabilization by the interaction with the tungsten complex. The energy of this orbital is 22.4 eV in carbon dioxide (Figure 1), but during the reaction course the energy decreases to −13.0 eV. The σ*(C–O) orbital also changes composition during the reaction from $D_{\infty h}$ to C_{2v} as some p character is mixed in the atomic orbital on carbon, by which it becomes C–O^2 bonding and C–O^1 antibonding. At $X, Y \approx 2.65, 3.35$ the l.u.m.o. of the system, which at this point is the σ*(C–O) mixed with some d_{xz}, (**34**), crosses the h.o.m.o., a combination of tungsten d_{xy} and d_{yz}, and the oxidative addition takes place. This h.o.m.o.–l.u.m.o. crossing causes a change in overlap population for C–O^1 in carbon dioxide from +0.47 to −0.30 indicating that this bond in carbon dioxide has been broken. The population of the d orbitals at tungsten changes too; the major difference is found for the d_{xy} orbital for which the population changes from 1.92 to 0.77 e and d_{yz} which donates 0.62 e to carbon dioxide in going from 1.93 to 1.31 e. When the σ*(C–O) orbital of carbon dioxide becomes populated the overlap between tungsten and O^1 increases; before the population of the σ*(C–O) orbital the W–O^1 overlap was 0.37, becomes 0.57 afterwards. The fragment m.o. analysis at about $X, Y \approx 2.65, 3.35$ indicates that a W–(η^2-CO_2) complex, (**32**), does not exist over a wide range of X, Y.

The reaction mechanism outlined above for the addition of carbon dioxide to *cis*-[WCl_2L_3] accounts also for the addition to *trans*-[WCl_2L_3] as shown in Scheme 3. As the carbon dioxide begins to tilt from an end-on to side-on co-ordination at tungsten the axial chlorine starts moving up towards the equatorial position pushing the phosphine ligand out as shown in (**35**) and (**36**) in Scheme 3. The present results for the reaction of carbon dioxide with [WCl_2L_3] indicate thus that the first step is an oxygen abstraction from carbon dioxide followed by a ligand substitution (exchange) of one of the phosphine ligands with carbon oxide.



Scheme 3.

The above analysis indicates that the oxidative addition of ethylene oxide and carbon dioxide to the tungsten complex can be formulated in the same way. The first part of the reaction is an approach of the heteroatom in the substrate towards the tungsten atom, the heteroatom acting as a nucleophile. There are now two possibilities, a direct oxygen abstraction from the substrate, or the incoming molecule tilts to a side-on mode and the electrophilic character of carbon becomes dominant. The tungsten atom acts in both types of the reactions as an electron donor and donates electron density into the antibonding carbon–oxygen bond leading to cleavage of this bond and addition of oxygen to the tungsten atom. The remaining part of the substrate may add to the metal later, or, by the end-on to side-on mode, in a concerted way along with the binding of the oxygen to the metal.

Reactions of [PtL_4].—Let us now turn to the oxidative addition of [PtL_4] with ethylene oxide and carbonyl sulphide. We use carbonyl sulphide instead of carbon dioxide because the expected product of carbon dioxide addition is according to our knowledge unknown experimentally, whereas the carbonyl sulphide product [$PtL_2(COS)$] has been identified, but is very labile.[4c,d] The addition of epoxides to [PtL_4] is possible if the epoxide is substituted with electron-withdrawing groups. In the reaction between tetracyanoethylene oxide and [PtL_4] it has been possible to obtain the crystal structure of the product [$PtL_2\{C_2(CN)_4O\}$].[4a,b] This structure is planar according to the theory that four-co-ordinated 16-electron complexes are square planar.[4a–d,15] Oxidative additions of [PtL_4] are known to proceed *via* PtL_3.[16] Furthermore it is known that [PtL_3] can dissociate another ligand before reaction (12). It is well known that the second ligand dissociation is very slow compared with the first one, so we will assume a [PtL_3] structure for the reaction. The frontier orbitals of [PtL_3] are shown to the right

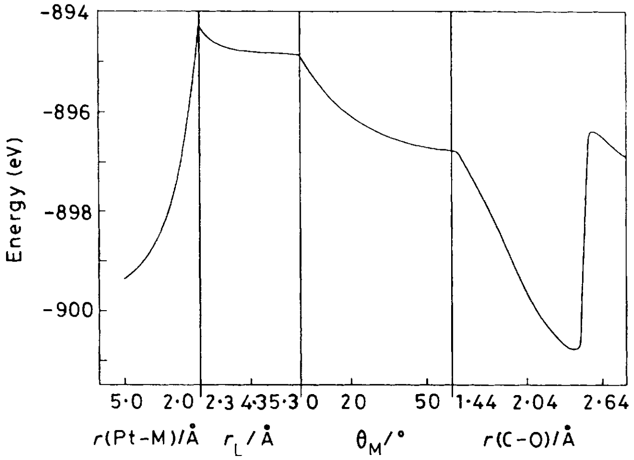
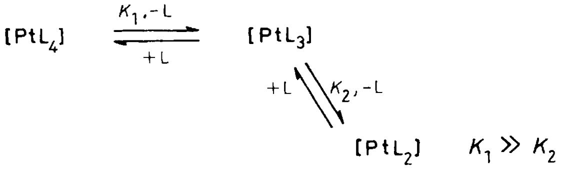


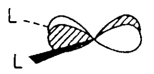
Figure 4. Energy variation for the addition of ethylene oxide to [PtL$_3$]



(12)

in Figure 2 and show the expected three below two splitting as we have chosen a C_{3v} geometry of [PtL$_3$] formed from ligand dissociation of tetrahedral [PtL$_4$].

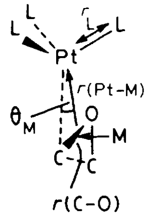
If two ligands dissociate before the platinum complex reacts a rather simple reaction path can occur. The h.o.m.o. of [PtL$_2$] with C_{2v} symmetry is a b_2 orbital, (**37**), which is set up for interaction with the l.u.m.o. of both ethylene oxide and carbonyl sulphide leading to the oxidative addition.



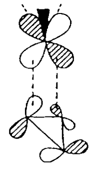
(**37**)

Let us start with the oxidative addition of ethylene oxide, which we have used as a model for tetracyanoethylene oxide, to [PtL$_3$]. From the frontier orbitals of ethylene oxide (Figure 1) and [PtL$_3$] (Figure 2) it appears that several approaches are possible: one is a nucleophilic type of attack of platinum at the one or both carbons,[4b] but we have found that the steric repulsion between the substituents of the epoxide, especially when tetracyanoethylene oxide is considered, and the phosphine ligand of the platinum complex is too large to favour this reaction path, although we cannot exclude that the reaction takes place in this way. Another possibility is an interaction of platinum with one of the carbon–oxygen bonds in ethylene oxide. A third approach, the end-on to side-on, is orbital energetically more favourable that the interaction of platinum with one of the carbon–oxygen bonds in ethylene oxide. This approach takes place *via* an initial interaction between the l.u.m.o. of [PtL$_3$] and the h.o.m.o. of ethylene oxide. An approach of ethylene oxide to [PtL$_3$] leading to an oxo-platinum complex is from an energetic point of view a very unrealistic reaction as a lot of antibonding oxoplatinum character is found in such a complex,[17] but by changing the end-on to side-on approach slightly from that used in the reactions of the substrates with the tungsten complex it is possible to construct a reaction path which leads to the product.

The parameters to be varied to obtain a platinum cyclo-oxetane from [PtL$_3$] and ethylene oxide are shown in (**38**). We have calculated the change in energy for the different variables shown in (**38**) in an attempt to get a very qualitative picture about this reaction path. The one-dimensional energy variation is shown in Figure 4. It appears that the driving force in the reaction is the cleavage of the carbon–oxygen bond, r(C–O), whereas the end-on approach is rather repulsive because of electron–electron repulsion between the *d* electrons at platinum and the lone-pair electrons at oxygen. The minimum in energy is obtained for a carbon–oxygen distance of about 2.45 Å which is in good agreement with the distance obtained from the structural data for [PtL$_2${C$_2$(CN)$_4$O}] where it is 2.3 Å.[4a] The most important orbital interaction in the oxidative-addition reaction between ethylene oxide and [PtL$_3$] is the l.u.m.o. of ethylene oxide interacting with the h.o.m.o. of [PtL$_3$], (**39**).



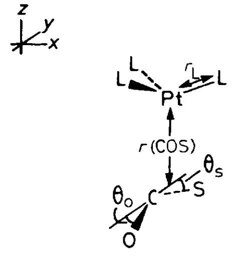
(**38**)



(**39**)

Let us turn the attention to the reaction of carbonyl sulphide with [PtL$_3$]; here again we have chosen an end-on followed by a side-on co-ordination of the sulphur in carbonyl sulphide at platinum in [PtL$_3$].

The approach of carbonyl sulphide to [PtL$_3$] is shown in (**40**). This approach has been chosen in the *zy* direction rather than a more *xz*-oriented approach in an attempt to reduce the steric repulsion between the ligand and the incoming substrate. The four initial basis co-ordinates shown in (**40**) are r_L the ligand dissociation, r(COS) the distance from platinum to the middle of the carbon–sulphur bond, and $θ_S$ and $θ_O$ which are changes in angles in carbonyl sulphide. Two more parameters are needed because the two remaining phosphine ligands have to end up in the same plane as the approaching carbonyl sulphide. To reduce the calculation procedure we have also coupled the variables to two main co-ordinates *X* and *Y*: r_L and the dihedral angle of the phosphine ligands are coupled to r(COS) to comprise the *X* co-ordinate; the *Y* co-ordinate is then the two COS angles, $θ_S$ and $θ_O$, and the bond angle of the two phosphine ligands. An investigation of the orbital changes along



(**40**)

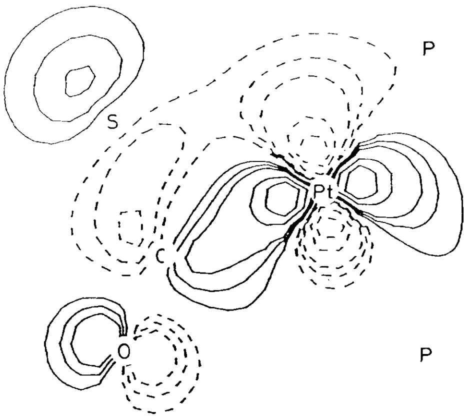


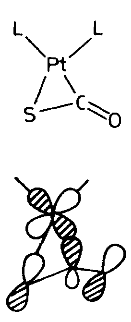
Figure 5. Contour plot of the orbital leading to co-ordination of the C–S bond to platinum plotted in the *yz* plane. The contour levels of ψ are 0.04, 0.07, 0.10, 0.20, and 0.30

Table. Parameters used in extended-Hückel calculations

Orbital	H_{ii}/eV	ζ_1[a]
H 1*s*	−13.6	1.3
C 2*s*	−21.4	1.625
2*p*	−11.4	1.625
O 2*s*	−32.3	2.2750
2*p*	−14.8	2.2750
P 3*s*	−18.6	1.60
3*p*	−14.0	1.60
S 3*s*	−20.0	1.817
3*p*	−13.3	1.817
Cl 3*s*	−30.0	2.033
3*p*	−15.0	2.033
W 6*s*	−8.26	2.3410
6*p*	−5.17	2.309
6*d*	−10.37	4.982 (0.668 53)[b]
Pt 6*s*	−9.077	2.5540
6*p*	−5.475	2.5350
6*d*	−12.59	6.0130 (0.633 07)[c]

[a] Coefficients and exponents in a double ζ expansion. [b] $\zeta_2 = 2.0680$ (0.542 44). [c] $\zeta_2 = 2.6960$ (0.551 61).

such a reaction path for the platinum complex and carbonyl sulphide gives a simple picture of the interaction compared with those found in the $[WCl_2L_3]$ case. The interaction leading to reaction is mainly between the π^* of carbonyl sulphide and the d_{yz} orbital of platinum as shown in (**41**).



(**41**)

A contour plot of the orbital leading to the η^2 co-ordination of carbon and sulphur to platinum is shown in Figure 5. As platinum has no vacant *d* orbitals the main interaction between carbonyl sulphide and $[PtL_2]$ is the π back donation from the d_{yz} to the π^* of carbonyl sulphide, whereas only a low donation from the carbon–sulphur bond to platinum is possible, because of the lack of available *d*-acceptor orbitals at platinum. The π back bonding weakens the C–S bond because of the donation of elections into the π^* orbital, but not enough to break it. The overlap population of the carbon–sulphur bond decreases from 1.24 to 1.17 upon π back bonding.

An experimentally well established effect shows up from the calculations on (**9**) and (**10**). The platinum–phosphorus bond *trans* to the oxygen (sulphur) has a slightly larger overlap population than the platinum–phosphorus bond *trans* to carbon indicating that the former should be slightly shorter than the latter in agreement with the *trans* effect observed for these types of compounds.

At this point it might be appropriate to draw attention to the difference between the tungsten and platinum complexes. In the case of the tungsten complex the substrates start as nucleophiles in an O-on (end-on) approach and good acceptor orbitals at the metal complex are required to afford a stabilization of the system. From Figure 2 it is obvious that both the l.u.m.o. and second l.u.m.o. of (**14**) and the l.u.m.o. of $[PtL_3]$ are electron acceptors, but the l.u.m.o. of $[PtL_3]$, an *sp* orbital, is located 3.6 eV higher in energy than the l.u.m.o. of (**14**). There are three unoccupied *d* orbitals in (**14**), whereas all the *d* orbitals in $[PtL_3]$ are occupied resulting in stabilization in the former case, but mainly a destabilizing two-orbital four-electron interaction in the latter case. These considerations might favour the initial nucleophilic approach of the substrates in the case of the tungsten complex.

The main part of the reaction path takes place with a side-on mode of the substrates and the electrophilicity of the substrates is dominant. This part of the reaction needs good metal donor orbitals to proceed. Although the tungsten complex is electron poor compared with the platinum complex, it is a better donor than the latter as the h.o.m.o. energy of (**14**) is located higher in energy than in $[PtL_3]$. The observed difference in the reaction course between the tungsten and platinum complexes and a molecule containing a carbon–heteroatom bond might then be traced to the occupancy and energies of the frontier orbitals of the two metal complexes. The tungsten complex, (**14**), is both a good donor as well as a good acceptor, whereas $[PtL_3]$ is a poorer donor and acceptor.

Appendix

All calculations were performed using the extended-Hückel method.[12] The orbital parameters along with the H_{ij} values are summarized in the Table. The bond lengths and angles were taken from refs. 4—6. Standard bond lengths and angles were used for the different substrates and PH_3 was used as a model for the phosphines in the metal complexes.

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