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Re–C Bond Homolysis in Alkyl- and Arylrhenium Trioxides: A Qualitative MO Interpretation[1]

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In many cases, the decomposition of methyltrioxorhenium (CH_3ReO_3, MTO) and other alkyl and aryl derivatives appears occur through the homolytic cleavage of the Re–C bond. Under these circumstances, the already deficient metal [Re(VII)] gives up half of the electron pair donated by the alkyl anion, and the ensuing Re(VI) species has a finite lifetime as a free radical. The problem is tackled from the viewpoint of qualitative MO theory. From a detailed examination of all the orbital interactions between metal and the coordinated atoms in pseudotetrahedral MTO, it is established that the metal receives up to nine electron pairs from the oxygen atoms and CH_3. Accordingly, the complex is better formulated as an 18- rather than the widely accepted 14-electron species. The study of the dynamics of the most critical frontier MOs on elongating the Re–C bond provides significant chemical information. Particularly relevant for the one-electron transfer from carbon to the metal atom is the *avoided crossing* between the HOMO and the LUMO. With the flattening of both separating fragments taken into account, the two levels converge to the accidentally quasi-degenerate σ-CH_3 and ReO_3 z^2 orbitals. In the model, the effects of substituting groups such as phenyl or *tert*-butyl for methyl are also pointed out.

Introduction

A most remarkable case of homolytic cleavage of a metal–carbon bond occurs in coenzyme B_{12}. The biological activity of the system is attributable to the easily generated $Co(II)/CH_3^{\bullet}$ diradical from the Co(III) pseudooctahedral complex.[3]

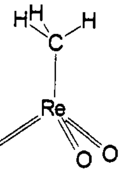
Now, there is reported experimental evidence that the Re–C bond of alkylrhenium trioxide derivatives undergoes homolysis. In fact, the products of the decomposition imply that, in some cases, free alkyl radicals are formed along the pathway.[4] This also implies that the already electron-poor metal [Re(VII)] loses one of the two electrons formerly involved in the Re–C bond.

A few years ago, a qualitative MO description of the homolysis in a model of vitamin B_{12} was presented.[5] Essentially, rather than focusing on the electron distribution in the unperturbed pseudooctahedral Co(III) complex, this study monitored the dynamics of the MOs for a progressive elongation of the Co–C bond (up to 5 Å and over). Importantly, both the Co–C σ and σ^* levels continue to share metal and carbon character even at long separations when the orbital overlap has almost vanished. Eventually, the levels correlated with the two σ hybrids of the separated fragments CH_3 and L_5Co (square pyramidal) that are accidentally quasi-degenerate. It seemed reasonable to conclude that the starting pseudooctahedral d^6 complex, which is diamagnetic, evolves at some point into a triplet species in which the two electrons are shared between the separating metal and carbon centers. It is likely that the system's evolution from triplet to diradical occurs very smoothly. The very important role played by the base *trans* to the alkyl group was also emphasized.

It is now interesting to see if similar concepts, based on the evolving composition of the frontier MOs, can be applied to CH_3-ReO_3 (MTO) and some of its alkyl and aryl derivatives. Other theoretical papers on MTO as well as on the $CpReO_3$ derivative have been reported even at high levels of sophistication.[6] The present semiempirical study, not in contrast with the latter, establishes the major components of the bonding between rhenium and the surrounding atoms in the ground-state structure. Also, it underlines macroscopic trends uniquely emerging when the Re–C bond is elongated.

Results and Discussion

A description of the electronic structure of the pseudotetrahedral MTO molecule is needed in order to interpret its evolution toward a diradical species. The widely accepted VB description (see I) assigns to the metal a total count of 14 electrons. Such a number would be lowered to 13 upon the Re–C homolytic cleavage. By contrast, qualitative MO concepts allow one to assign a more realistic 18-electron count to the $RReO_3$ species.



I

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(1) Multiple Bonds between Main-Group Elements and Transition Metals. 123. Part 122: Herrmann, W. A.; Fischer, R. W.; Scherer, W.; Rauch, M. *Angew. Chem.*, in press.

(2) (a) Istituto CNR. (b) Postdoctoral Fellow of the Spanish Ministerio de Educación y Ciencia. (c) Centro de Tecnologia Química e Bíologica. (d) Technische Universität München.

(3) For leading references, see: Dolphin, D. Ed. *B_{12}*; Wiley: New York, 1982.

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(5) Mealli, C.; Sabat, M.; Marzilli, L. *J. Am. Chem. Soc.* **1987**, *109*, 1593.

(6) (a) Szyperski, T.; Schwerdtfeger, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1228. (b) Wiest, R.; Leininger, T.; Jeung, G.-H.; Bénard, M. *J. Phys. Chem.* **1992**, *96*, 10800.

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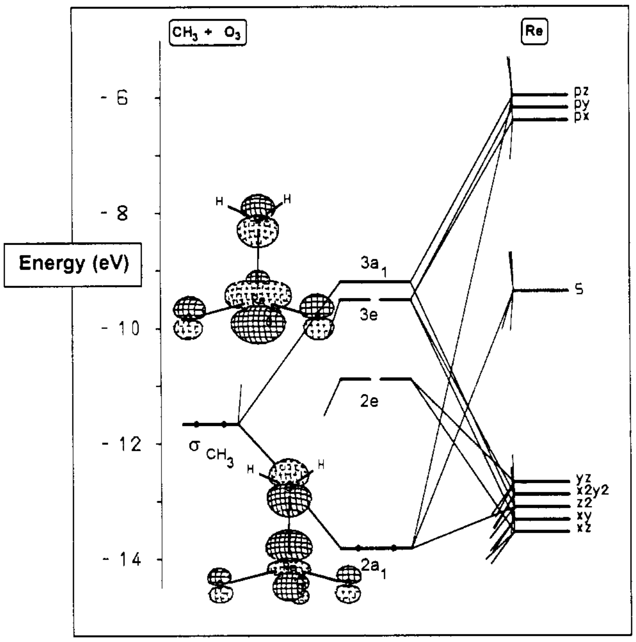
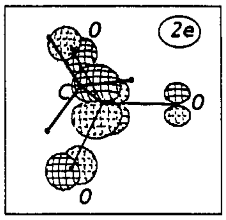


Figure 1. Diagram for the interaction of the rhenium atomic orbitals (right side) with those of the surrounding atoms (oxygen) and fragments (methyl). All of the O_3 symmetry-adapted orbitals are too low in energy and do not appear at the left side of the diagram.

Indeed, it can easily be verified by means of EHMO calculations[7] and fragment orbital analysis[8] (see the diagram of Figure 1) that nine two-center/two-electron interactions are operative between the metal and the coordinated carbon and oxygen atoms (nine bonds of order 1). The metal atomic orbitals (right side) all appear destabilized by appropriate symmetry combinations of radical (oxygen and carbon) and tangential p_π (oxygen) orbitals. None of the oxygen combinations appear at the left side of the diagram because they lie very low in energy. The geometry of the model used is pseudotetrahedral with Re–O distances of 1.71 Å and C–Re–O angles of ca. 106°, close to the experimental values (electron diffraction).[9] The geometry optimization of MTO at the EHMO level gives a best C–Re–O angle of 105°.

More specifically the s, p_x, and p_y orbitals are engaged to form three bonds with three oxygen σ lone pairs (*radial*). The bonding and antibonding levels for the latter interactions are all outside of the energy range of Figure 1. In the C_{3v} point group two sets of d orbitals, namely xz/yz and $xy/x^2\ y^2$ (some hybridization with p_x and p_y is possible), find appropriate combinations of low-lying oxygen σ and p_π orbitals with which to interact. The antibonding MOs for the latter interactions are the levels 2e and 3e of Figure 1. One member from each set is sketched in II and III, respectively.[10] At this point, the metal is already accepting the formal donation of seven electron pairs (14 electrons).

It remains to establish the role of the orbitals p_z and z^2 which belong to the same symmetry (a_1). In a first approximation, p_z can be thought of as the acceptor of the axial methyl lone pair, while z^2 makes a π-type interaction with a totally-symmetric combination of the oxygen p_π orbitals (the π interaction occurs via one axial lobe and the torus of z^2). In reality, some mixing of the p_z and z^2 (and even s) characters occurs, as made evident by the drawings of the MOs $2a_1$ and $3a_1$ of Figure 1. In addition,



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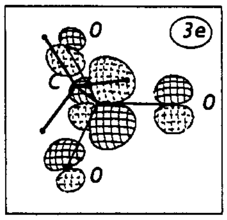

III

another couple of filled and empty a_1 levels has a similar topological distribution but falls outside the energy window of Figure 1. The lower one, bonding between z^2 and the oxygen p_π orbitals, is centered on the oxygen atoms. The one at high energy is predominantly the metal p_z orbital, destabilized by the antibonding interaction with the methyl σ hybrid.

Altogether, the four a_1 MOs [sharing σ(Re–C) and $\pi_\perp$(Re–O) characters] account for two donor/acceptor interactions which raise the total electron count to 18. This qualitative interpretation is consistent with the values of Mulliken population analysis, in particular the metal–ligand reduced overlaps and the populations of the metal orbitals in the molecule. Substantially, no metal orbital is free from interaction with the ligands nor is it affected by a major electron deficiency. On the basis of the latter arguments, one is also tempted to conclude that each Re–O bond in MTO has bond order $2^2/_3$ (there are eight two-center/two-electron interactions between the metal and the three oxygen atoms). The conclusion that in MTO the electron density from the oxygen atoms compensates for the metal deficiency has already been stressed;[9] that statement was clearly supported by a comparison of NMR and IR evidence available for MTO and (η^5-Me_5C_5)ReO_3 species. Our suggestion is that in MTO two additional Re–O bonds with respect to the VB formula I compensate for the reduced number of bonding interactions (from 3 to 1) between the metal and the organic part of the molecule.

An alternative way of performing FMO analysis on MTO is to think of the molecule as being built up from the interaction between the fragments ReO_3 and CH_3. A pyramidal methyl anion is characterized by a doubly populated σ hybrid, which is also the FMO at the left side of Figure 1. As discussed in textbooks,[11] free methyl radicals or cations reorganize toward a planar geometry because some of the filled MOs lying below the frontier σ hybrid follow a stabilizing trend. The latter MO is somewhat destabilized at the planar geometry, but populating it with a single electron is not sufficient to alter the overall energy balance.

Also, an "isolated" pyramidal ReO_3^+ fragment (in the gas phase) would rearrange to planarity upon the addition of one or two electrons to Re(VII). This fact, already pointed out,[6] is based on the following qualitative considerations. The three oxygen atoms have been shown to donate up to eight lone pairs (of σ and π type) to as many metal orbitals. In particular, p_z and z^2 are competing to receive one of these, with an important role being played by the amount of fragment pyramidalization. While the p_z-centered FMO destabilizes on flattening because of the larger antibonding interaction with oxygen p_π orbitals [compare IV with V], the z^2-centered FMO stabilizes. Although $\pi_\perp{}^*$ converts into an equatorial σ^* MO (compare VI with VII), the corresponding energy decreases because of the different contributions from the oxygen atoms.

As expected, the bonding between the fragments CH_3 and ReO_3 is most effective if the latter is sufficiently pyramidalized. The metal has two empty FMOs of a_1 symmetry which can potentially accept the σ lone pair assigned to CH_3. At higher

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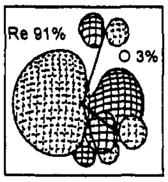
[7] (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179. (c) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2872.

[8] (a) Hoffmann, R.; Fujimoto, H.; Swenson, J. R.; Wan, C. C. *J. Am. Chem. Soc.* **1973**, *95*, 7644. (b) Hoffmann, R.; Fujimoto, H. *J. Phys. Chem.* **1974**, *78*, 1167.

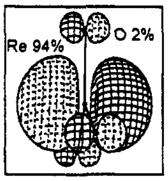
[9] Herrmann, W. A.; Kiprof, P.; Rypdal, K.; Tremmel, J.; Blom, R.; Alberto, R.; Behm, J.; Albach, R. W.; Bock, H.; Solouki, B.; Mink, J.; Lichtenberger, D.; Gruhn, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 6527.

[10] MO drawings were prepared with the program CACAO: Mealli, C.; Proserpio, D. M. *J. Chem. Educ.* **1990**, *67*, 399.

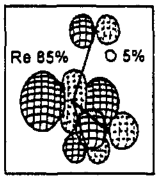
[11] See for example: (a) Gimarc, B. M. *Molecular Structure and Bonding*; Academic Press: New York, 1979. (b) Albright, T. A., Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.



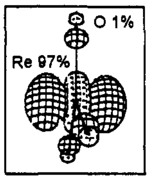
IV



V

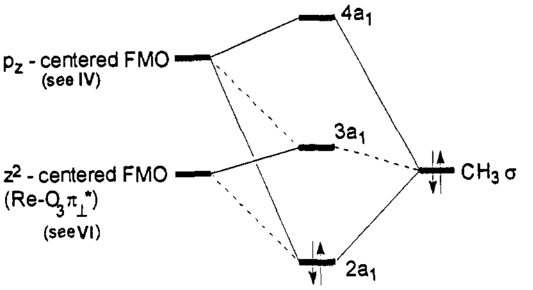


VI



VII

energy, the FMO shown in IV has a well-hybridized lobe (25%, 64% p_z, and 2% z^2) which is most suited to make a good overlap with the CH_3 analog. On the other hand, the z^2-centered FMO (VI) energy almost matches the energy of the CH_3 σ hybrid, but it cannot be properly considered its σ-bonding partner. Besides the lack of a proper hybridization, VI already represents the antibonding counterpart of the interaction between z^2 and an opportune O_3 combination of p_π orbitals.[12] Actually, there is a significant mixing of the FMOs IV and VI, as schematically shown in VIII, but the distinction made above is, in first approximation, useful for assigning a specific character to the four MOs ($1a_1$–$4a_1$).



VIII

Before illustrating the effects that take place during the progressive separation of the two components of MTO (ReO_3 and CH_3), we wish to point out an important consequence that accompanies the loss of pyramidalization of the isolated ReO_3 unit. As shown, at the planar geometry, the MO VII becomes almost pure metallic in character, except for a residual σ^* interaction with O_3. If one or two electrons populate the latter MO (17- or 18-electron ReO_3 species), the planar geometry is preferred. In fact, not only does the level in question gain some energy (ca. 0.3 eV), but also the metal–O_3 $\pi_\perp$ bonding interaction, involving p_z, becomes more efficient. By virtue of the latter, the three Re–O bonds are strengthened (for fixed Re–O distances, the Re–O overlap population increases from 0.81 to 0.85 for the planar $[ReO_3]^-$ anion and slightly less for the unchanged radical). Another point in favor of the planar geometry for Re(VI) and Re(V) species stems from a larger HOMO–LUMO gap (it becomes as large as ca. 1 eV), so it is likely that the fragment ReO_3 has finite lifetime before the aggregation into the known polymeric network (perovskite structure; see textbooks).

The points raised above regarding the electronic ground-state structure of MTO allowed identification of the main bonding–antibonding interactions between the metal and the surrounding atoms. In particular, these seem to hold irrespective of the precise energy order of the HOMO and the next filled levels. Thus, the known discrepancy[9] between Xα and EHMO results (relative to the order of the oxygen-centered and the σ_{Re-C} frontier MOs)[14] is not misleading for our analytical purposes. In fact, it will be shown that, more than the MO picture of the ground-state structure, the monitoring of the MOs (σ_{Re-C}, in particular) along the pathway of homolysis provides useful pieces of chemical information.

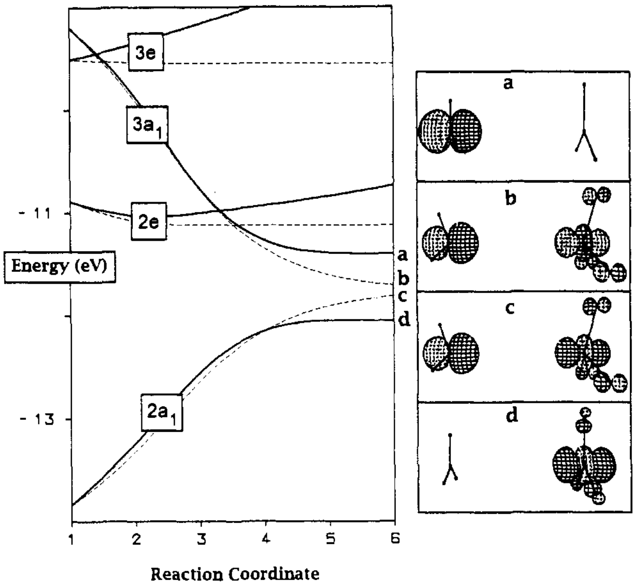


Figure 2. Evolution of the frontier MOs of MTO for increasing Re–C bond length in the range 2.05–4.55 Å. The cleavage of the Re–C bond is accompanied by flattening of both the CH_3 and ReO_3 fragments (solid lines). The MOs $2a_1$ and $3a_1$ acquire (through an *avoided crossing*) pure σ-CH_3 and Re z^2 characters, **a** and **d**, respectively. Conversely, both levels still have mixed contributions if the separating fragments are kept pyramidal (dashed lines and drawings **b** and **c**). In this case, the MOs appear to have distinct characters only when Re–C is >7 Å.

Bearing in mind the above aspects, a Walsh diagram (Figure 2) is constructed to follow the evolution of the MOs on elongating the Re–C bond of MTO from 2.05 to 4.55 Å and beyond. Two different cases are considered: first the geometries of both the ReO_3 and the CH_3 groups are unchanged with respect to the MTO molecule; then the separating fragments are both allowed to become planar (compare dashed and solid lines in the diagram). Since the flattening of the ReO_3 fragment is likely accompanied by the simultaneous shrinking of the Re–O distances, these have been also varied in the range 1.71–1.61 Å.

The most evident feature of the diagram is that the two MOs $2a_1$ and $3a_1$ (recall their original shapes from Figure 1) become closer in energy. The trends relative to the MOs 2e and 3e (antibonding between oxygen and metal d orbitals) are also important, but they will be addressed later in the discussion. At step 6 (Re–C = 4.55 Å), with the fragments constrained to stay pyramidal, the MOs $2a_1$ and $3a_1$ still share the characters from ReO_3 and CH_3 components (see **b** and **c** in Figure 2). In this case, separation of character is only observed when the Re–C distance approaches 7 Å. By referring to the basic rules of perturbation theory and orbital mixing,[13] one sees that the accidental degeneracy of ReO_3 and CH_3 FMOs counterbalances the effects of overlap loss over a long range.

The situation changes significantly if the fragments become planar along the pathway (solid lines). At step 6, the MOs $2a_1$

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(12) A convincing argument that the FMOs σ-CH_3 and the z^2-centered one are not direct bonding partners is given by the fact that the MO $2a_1$ (see VIII) receives a significantly larger contribution from σ-CH_3, which lies higher than z^2. This is true also for the *tert*-butyl model in which σ-$C(CH_3)_3$ is as much as 1 eV above z^2. The apparent contrast with the basic rules governing the interaction between two FMOs[13] is clarified if σ_{alkyl} and metal p_z are taken as the direct bonding partners.

(13) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(14) Xα calculations predict a descending energy order for the MOs $1a_2$, 5e, $5a_1$, whereas the level $5a_1$ is the highest in the present and previous EHMO calculations.[9] Only the σ_{Re-C} bonding MO appears in Figure 2 (*i.e.*, $5a_1$ is there indicated as $2a_1$), while two oxygen-centered levels (already defined as n_O)[9] may lie higher than it. Irrespective of the exact energy sequence, the present analysis suggests different natures for $1a_2$ and 5e. Whereas the former MO is in actuality a nonbonding oxygen combination (no metal atomic orbital has a_2 character in C_{3v} symmetry), the degenerate pair 5e is better described as metal–oxygen π-bonding, whose antibonding counterpart is the set described as 2e in Figure 1 and in the sketch II.

and $3a_1$ (drawings **a** and **d**) are already separated and correspond to the pure carbon p_z and to the metal orbital VII, respectively.

The final composition and energy order of the levels $2a_1$ and $3a_1$ have important implications for the mechanism of the homolytic cleavage. The FMO analysis shows that, in the ground state of the pseudotetrahedral MTO, the Re–C σ-bonding MO ($2a_1$) has predominantly CH_3 character (refer to VIII). Accordingly, the bonding electrons can be assigned to the methyl group. Then, along the pathway, the MOs $2a_1$ and $3a_1$ approach each other and eventually become adjacent in energy (HOMO, LUMO). In principle, a singlet/triplet transition can occur especially if the electron-unpairing energy overcomes the gap between the two MOs. Since the unpaired electrons would populate MOs centered at atoms increasingly separated from each other (see **b** and **c**), the high-spin system could smoothly convert into a diradical.[15] Since the two electrons were initially assigned to the methyl anion, the process must be associated with one *electron jumping* to the metal. The requirement for this type of transfer is an *avoided crossing* that mixes and switches the characters of the levels along the pathway.[16] In the present case, this is substantiated from the observed correlation of the MOs $2a_1$ and $3a_1$ with the *avoided crossing* being most evident on flattening the two AX_3 fragments. Ultimately, the rising $2a_1$ level correlates with a MO of pure methyl character (**a**) while the descending $3a_1$ level correlates with ReO_3 z^2 (**d**). It was pointed out for the models of vitamin B_{12} that the interaction between cobalt and the *trans*-axial base finely tunes the *avoided crossing* (σ-CH_3 above σ-L_5M, when the base is weakly bound).[5] The pyramidal to planar rearrangement of the interacting fragments seems to play an analogous role in the present case of CH_3ReO_3.

The importance of the HOMO–LUMO correlation in the dynamics of the process is also supported by the known behavior of other organometallic rhenium trioxides. For example, on warming of the phenyl derivative (σ-C_6H_5)ReO_3, biphenyl ($C_{12}H_{10}$) forms quantitatively.[4c] The homolysis proceeds at much lower temperature (>45 °C) than for MTO (>200 °C) and is very clean.

Again a Walsh diagram (Figure 3) illustrates a situation somewhat similar to that of Figure 2. However, since the calculated σ hybrid of the isolated C_6H_5 fragment is significantly higher than the σ-CH_3 hybrid (*ca.* 1 eV), already at step 6 (Re–C = 4.55 Å), the levels $2a_1$ and $3a_1$ correspond to the separated σ_{Ph} and z^2 ReO_3 FMOs. Moreover, the trend for $3a_1$ is to remain above 2e, unless the fragment ReO_3 is flattened and the Re–O distances are shortened (compare solid and dashed lines for 2e). Recall that the MOs 2e and 3e are both rhenium/O_3 antibonding (see II and III) and the shorter the Re–O distances, the more destabilized are these levels. Importantly, only if σ_{Ph} ends lower than 2e do the conditions for the Re–C homolysis (*i.e.*, two adjacent σ levels mutually mixing through an *avoided crossing*) appear to be recreated. Unfortunately, neither the strength of the *avoided crossing* nor a quantitative balance between the final gap and the energy gained from spin unpairing can be reliably determined at this computational level.

The impossibility of having at any point two adjacent σ levels seems to be a major complication for alkylrhenium trioxides in which one or more bulky substituents determine a higher energy of the alkyl σ hybrid. In particular, the chemistry of *tert*-butyl seems to be definitely affected as (t-C_4H_9)ReO_3 has escaped isolation as yet.[4a] On a theoretical basis, the σ hybrid of the pyramidal $C(CH_3)_3$ fragment is calculated to be >1 eV higher than that of CH_3. Accordingly, the two evolving $2a_1$ and $3a_1$ levels (Figure 4) cannot become adjacent in energy as in the cases of Figures 2 and 3. Nor can a flattening of the two separating fragments counterbalance this trend.

Although there is still evidence for an *avoided crossing* between

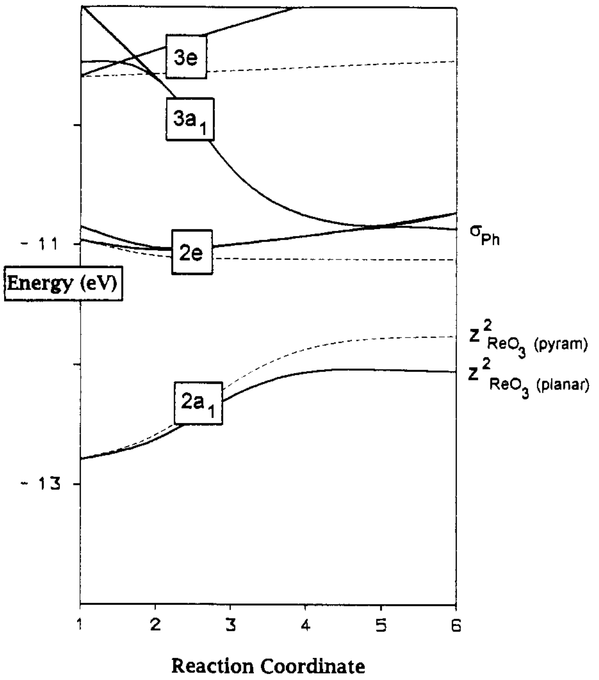

Figure 3. Evolution of the frontier MOs of $PhReO_3$ for increasing Re–C bond length in the range 2.05–4.55 Å. Solid and dashed lines refer to flattening and pyramidal ReO_3 fragments, respectively. The pictorial representations of the levels $z^2_{ReO_3(pyram)}$ and $z^2_{ReO_3(planar)}$ (right side) are analogous to **c** and **d** of Figure 2.

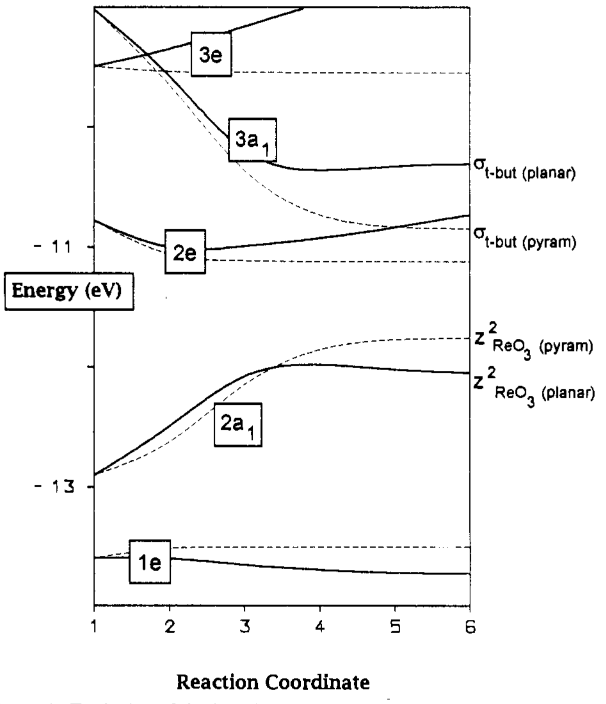

Figure 4. Evolution of the frontier MOs of *tert*-butyl–ReO_3 for increasing Re–C bond length in the range 2.05–4.55 Å. Solid and dashed lines refer to flattening and pyramidal fragments, respectively. The pictorial representations of the levels $z^2_{ReO_3(pyram)}$ and $z^2_{ReO_3(planar)}$ (right side) are analogous to **c** and **d** of Figure 2.

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[15] On a rigorous quantomechanical basis, the homolysis of the covalent M–CH_3 bond, similar to that of H–H or M–M, cannot be described with a single-determinant approach. The dissociation of the fragments CH_3 and ReO_3 implies two electronic states $^{1,3}A_1$ which are described by the two degenerate configurations $(2a_1)^2(3a_1)^0 - (2a_1)^0(3a_1)^2$ and $(2a_1)^1(3a_1)^1$, respectively. The reader must be aware that our simplified description comes from the idea, familiar to chemists, that Δq and spin-pairing energy are the competing factors in fixing the high-spin/low-spin dichotomies.

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$2a_1$ and $3a_1$ (the Re–C σ-bonding orbital correlates with the higher $\sigma_{t\text{-Bu}}$ hybrid), the constantly intermediate 2e levels would be preferentially involved in the formation of a hypothetical triplet state. The consequences for the stability and the geometry of the adduct are not easily predictable, but they should definitely be different from those for the case in which single electrons occupy two levels of σ symmetry.

From an alternative viewpoint, the diagram of Figure 4 provides some hints as to the difficulties encountered in the synthesis of the complex (t-C_4H_9)ReO_3.[4a] It is worth recalling that the known alkyl–ReO_3 complexes are obtained by reaction of Re_2O_7 with tin alkyls.[17] It is difficult to establish whether the mechanism of the formation of $RReO_3$ species is associative or dissociative. However, it is assumed that at some point an alkyl anion forms a solvent cage with the cation ReO_3^+, generated in turn by solvent-induced heterolysis of Re_2O_7.[18] Again, we can refer to the diagrams of Figures 2–4 by looking at the levels in the reverse order (the $RReO_3$ compounds form from the progressive approach of the initially isolated R and ReO_3 fragments). Two electrons, initially in the higher σ hybrid (alkyl anion), must eventually populate the lowest σ MO ($2a_1$) at the left side of each diagram. Only in the case of *tert*-butyl, because of the unavoidable presence of the intermediate 2e level, is there a serious complication for such a two-electron-transferring process.

A potentially different situation may be expected for $RReO_3$ molecules containing an alkyl group with π-acceptor substituents (CH_2NO_2, CH_2CN, enolates, malonates, *etc.*). First, the carbon σ-hybrid, stabilized by the $\pi_\perp$ orbital of the substituent, would interact less with the high-lying metal σ-hybrid IV and more with the FMO VII, which has Re–O $\pi_\perp^*$ character (refer to the diagram in VIII). This causes a partial unsaturation at the metal and a loss of Re–O_3 bonding. Second, even if these adducts are obtainable, they may have more difficulties in undergoing homolysis. In fact, after the Re–C separation, the carbon σ-hybrid is likely to remain below the ReO_3 z^2-centered FMO (VII). Although the energy order of the crucial levels may not be properly evaluated, the arguments based on the MO correlations and the possible lack of an *avoided interlevel crossing* are suggestive of a different chemical behavior for these species.

Finally, we briefly considered the adduct allyl–ReO_3 for which there is experimental evidence for η^1 rather than η^3 coordination.[19] Preliminary EHMO calculations seem consistent with such a result since the total energy is a significant 0.5 eV lower in the ground-state model of the η^1-adduct. In the η^3-allyl coordination, metal unsaturation and loss of Re–O π-bonding are expected. In fact, the η^3-allyl group has only a low-lying overall π-bonding FMO for σ-type interaction and important metal–allyl π-bonding would compete with the Re–O π-bonding.

Conclusions

In this study, we have analyzed the dynamics of the frontier MOs for a progressive elongation of the Re–C bond in selected models of organometallic rhenium trioxides. The EHMO method may appear weak in describing a process involving the transformation of a stable diamagnetic complex into a diradical. How trustworthy are the calculated interactions between the separating rhenium and carbon atoms? If one avoids any emphasis on the energetics of the process, the general trends (*e.g.*, the correlations of bonding/antibonding Re–C MOs, their relative topology and energy order, the presence or absence of intermediate, and interfering levels) can provide useful chemical information.

First, an interpretation of the electronic structure of the pseudotetrahedral MTO species suggests that extrastability is provided by as many as eight bonding interactions between rhenium and the oxygen atoms. The alkyl anion, the donor of two electrons, would thus complete an 18-electron count at the metal. Upon the physical separation of the CH_3 and ReO_3 fragments, the Re(VI) species (*i.e.* the ReO_3 radical) appears to be stabilized in the planar geometry by σ and π interactions with the oxygen atoms. In this case, only the z^2 orbital, hosting the unpaired electron, is unengaged and accidentally quasi-degenerate with the σ hybrid of the CH_3 group (less so with other substituted alkyls). The closer in energy, the longer the two σ orbitals continue to mix (*in-phase* and *out-of-phase* combinations). In spite of the very small overlap, the mixed MO composition persists at very long Re–C separations. This uncommon feature, consistent with perturbation theory arguments, underlies the possible Re–C homolysis. Support of the proposed *electron transfer* or *jumping* comes from the observed interlevel *avoided crossing*, which correlates the original Re–C σ bonding MO with the higher CH_3 σ hybrid. In particular, the latter process seems to be tuned up finely by the structural rearrangement or flattening of the two AX_3 fragments upon their physical separation. An analogous structural role is played by the *trans*-axial base in the models of coenzyme B_{12}.

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Appendix

Calculations of the extended Hückel type were carried out using a modified version of the Wolfsberg–Helmholz formula.[7,8] The parameters for O, C, and H atoms are those routinely used, whereas those of rhenium were taken from ref 20. The selected geometrical parameters used for the initial model (CH_3)ReO_3 are as follows: Re–C, 2.05 Å; Re–O, 1.71 Å; C–H, 1.05 Å; C–Re–O, 106°; Re–C–H, 109.47°. Subsequent geometrical rearrangements are thoroughly indicated in the text.

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