Mechanism of the Allylic Rearrangement of Allyloxo Metal Oxo Complexes: An Ab Initio Theoretical Investigation

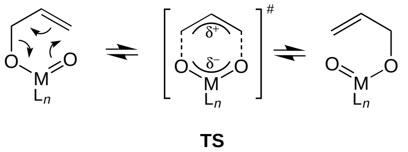
Stéphane Bellemin-Laponnaz,[b] Jean Pierre Le Ny,[b] and Alain Dedieu*[a]

Abstract: The mechanism of the isomerization of allyl alcohols by the 1,3-transposition of a hydroxy group, which is catalyzed by transition metal complexes in a high oxidation state, has been investigated by ab initio quantum chemical calculations for a trioxorhenium catalyst. The calculations point to a cyclic transition state that consists of a perrhenate anionic moiety and an allylic cationic group. This is similar to the transition state found for the [3,3] sigmatropic rearrangement in allyl formate. The energy barrier is lower in the organometallic case. The calculations also suggest that the kinetic discrimination that is observed experimentally for the catalyzed *cis*–*trans* isomerization of hex-1-en-3-ol is due to microsolvation effects of the corresponding transition states by the alcohols that are present in the reaction medium. All these features are explained in terms of orbital interactions present in the transition state.

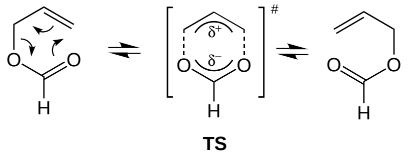
Keywords: ab initio calculations · allyl alcohols · homogeneous catalysis · rhenium · solvent effects

Introduction

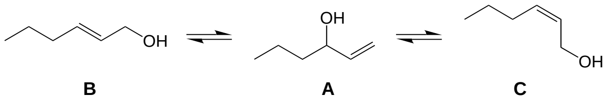
An allylic rearrangement that involves a cyclic transition state akin to that of a Claisen-type rearrangement and which incorporates a metal oxo unit (Scheme 1) has been recently proposed[1] (on the basis of an original proposal of Charbardes et al.[2]) in order to account for the isomerization of allyl alcohols by the 1,3-transposition of a hydroxy group catalyzed by trioxorhenium complexes and other metal oxo catalysts.[1, 3] Since two metal–oxo bonds are supposed to participate in the rearrangement, the closest organic analogue to the organometallic mechanism is not the Claisen rearrangement but the 1,3-acyloxy shift in allyl esters (Scheme 2). Despite this close similarity, the organometallic reaction is much more efficient: enthalpies of activation of 13.3 ± 0.3 kcal mol^{-1} and 20.9 ± 0.4 kcal mol^{-1} have been measured[1c] for the formation of *trans*-hex-2-en-1-ol (**B**) and *cis*-hex-2-en-1-ol (**C**), respectively, in the catalyzed isomerization of hex-1-en-3-ol (**A**) (Scheme 3), whereas barriers for the organic reaction range between 35 and 45 kcal mol^{-1} in the gas phase,[4] depending on the acyl moiety. Recent calculations for the 1,3-acyloxy shift in the parent allyl formate also yield high barriers (ranging



Scheme 1. Proposed organometallic cyclic transition state for the allylic rearrangement.



Scheme 2. Organic analogue to the organometallic mechanism proposed in Scheme 1.



Scheme 3. Isomerization of hex-1-en-3-ol.

---

[a] Prof. A. Dedieu
Laboratoire de Chimie Quantique
UMR 7551 CNRS and Université Louis Pasteur
4 rue Blaise Pascal, 67000 Strasbourg (France)
Fax: (+33) 3-88-61-20-85
E-mail: dedieu@quantix.u-strasbg.fr

[b] S. Bellemin-Laponnaz, Dr. J. P. Le Ny
Laboratoire de Chimie des Métaux de Transition et de Catalyse
UMR 7513 CNRS and Université Louis Pasteur
4 rue Blaise Pascal, 67000 Strasbourg (France)
Fax: (+33) 3-88-41-61-71

0947-6539/99/0501-0057 $ 17.50+.50/0

between 40 and 50 kcal mol^{-1}, depending on the method used).[5a,b] It has been tentatively suggested[1c] that a second oxo group, which serves as a spectator ligand, could help to stabilize the negative charge developed on the metal in the transition state, thereby lowering the activation barrier. It was also suggested,[1c] in line with the known mechanistic data on the Claisen rearrangement,[6] that in the catalyzed isomerization of **A** the greater activation enthalpy for the formation of the *cis* isomer **C** might be accounted for by a greater difference in charge and/or separation (distance effect) in the corresponding transition state. This increase in charge separation, which would correspond to a quasi-ionic pair TS, would also be consistent with the unexpected observation of a positive entropy of activation.[1c]

In an effort to increase our understanding of these reaction mechanisms we have now undertaken a theoretical study based on ab initio calculations at the HF-SCF and MP2 levels. Our goal was twofold: i) to shed more light on the similarities and differences between the organometallic and organic reactions (geometry and electronic structure of the transition state, energetics of the process) and ii) to rationalize on more theoretical grounds the kinetic discrimination observed for the formation of isomers **B** and **C**. To this end, calculations were first carried out for the rearrangements of the parent systems $OC(H)OCH_2CH{=}CH_2$ (**1**) and $[Re(O_3)OCH_2CH{=}CH_2]$ (**2**). Subsequently, calculations were performed on the methyl derivatives in order to mimic the experimental systems more closely; that is, the propyl derivatives **A**, **B**, and **C**. Thus, in the organic case the two processes which started from the $OC(H)OCHCH_3CH{=}CH_2$ system (**3a**) and led to the *cis*- and *trans*-$OC(H)OCH_2CH{=}CHCH_3$ isomers **3c** and **3b**, respectively, were investigated. Similarly, in the organometallic case we considered $[Re(O_3)OCHCH_3CH{=}CH_2]$ (**4a**) and the *cis*- and *trans*-$[Re(O_3)OCH_2CH{=}CHCH_3]$ isomers, **4c** and **4b**, as models of **A**, **C**, and **B**, respectively. Finally, the study was extended to another transition metal by comparison of the rhenium system **2** with the $[Ta(O)(OH)_2OCH_2CH{=}CH_2]$ system (**5**).

Computational Methods

The calculations were carried out with the Gaussian 94 program system.[7] The geometries of the organometallic systems were optimized at the HF level by the gradient technique, with the LANL2DZ basis set and additional polarization functions on the carbon and oxygen atoms. In this basis set the innermost core electrons of the rhenium atom (up to 4d) are described by the relativistic pseudopotential of Hay and Wadt[8] and the remaining outer core and valence electrons by a (5,6,4) < 3,3,2 > basis set.[8] The first-row atoms are described by the Dunning–Hay (9,5) contracted into < 4,2 > basis set.[9] The exponents of the polarization functions are 0.75 and 0.85 for carbon and oxygen, respectively. Single-point calculations at the MP2 level were then performed to evaluate the relative energies of the various structures. For the organic systems, the geometry optimizations were carried out at both the HF and MP2 levels, using the same basis set as for the organometallic systems. The transition states **TS1** and **TS2** for the rearrangement of **1** and **2** were characterized by a numerical frequency analysis. In both cases a single imaginary frequency was found (634*i* cm^{-1} and 346*i* cm^{-1} for **TS1** for **TS2**, respectively). For the transition states corresponding to the rearrangement of the methyl-substituted derivatives and of the tantalum system, the optimized geometries are close to those of **TS1** and **TS2** (see Figures 1 and 2). Therefore, we did not perform a frequency analysis for these transition states. The standard notation level of energy calculation//level of geometry optimization is used throughout the article.

Results and Discussion

The optimized geometries of the reactants and transition states for the organic and organometallic systems are shown in Figure 1 for the unsubstituted systems **1**, **2**, and **5**, and in Figure 2 for the corresponding methyl derivatives of the organic system **3** and of the rhenium system **4**. For the alkyl-substituted systems, either organic or organometallic, there are of course many conformers that are quite close in energy and that were not differentiated experimentally.[1c] The structures that are reported here have been obtained by a downhill optimization from a geometry generated by a small displacement from the transition state geometry. Thus, **3a** and **3a′** correspond to **TS3a** and **TS3b** respectively; **3a** is more stable than **3a′** by 3.6 kcal mol^{-1} (MP2 values). Similarly **4a** and **4a′** correspond to **TS4a** and **TS4b**; **4a** is more stable than **4a′** by only 0.9 kcal mol^{-1}. The computed rearrangement barriers are presented in Tables 1–3,[10] together with the recently reported results obtained for **1** with a 6-31G* basis.[5]

Although the HF- and the MP2-optimized geometries of the organic systems are slightly different, especially for the

Table 1. Energy barriers (in kcal mol^{-1}) computed at various levels of theory for the 1,3-rearrangement in **1**, **2**, and **5**.

Level	TS1	TS2	TS5
HF//HF	55.5	31.8	46.1
MP2//HF	47.4	23.7	29.0
MP2//MP2	46.1	–	–
B3LYP//B3LYP	–	19.5	–
MP4/6-31G*//MP2/6-31G*[a]	46.1	–	–
B3LYP/6-31G*//B3LYP/6-31G*[b]	41.4	–	–
MP2/6-31G*//B3LYP/6-31G*[b]	47.4	–	–

[a] Ref. [5a]; difference in the zero-point vibrational energy taken into account. [b] Ref. [5b]; difference in the zero-point vibrational energy not taken into account. At the B3LYP/6-31G* level the corresponding correction is computed to be only −1.4 kcal mol^{-1}.

Table 2. Reaction energies and barriers (in kcal mol^{-1}) computed at various levels of theory for the isomerization of **3**.

Level	**3a** → **3b**		**3a′** → **3c**	
	ΔE	$\Delta E^{\neq}$	ΔE	$\Delta E^{\neq}$
HF//HF	−0.3	+51.3	−2.8	+50.3
MP2//HF	+1.2	+48.6	−1.3	+44.9
MP2//MP2	+1.2	+44.5	−1.4	+43.0

Table 3. Reaction energies and barriers (computed and experimental, in kcal mol^{-1}) for the isomerization of **4** (experimental values are enthalpy of reactions and activation enthalpies for the $[Re(O_3)OCH(C_3H_7)CH{=}CH_2]$ system **A**).

Level	**4a** → **4b**		**4a′** → **4c**	
	ΔE	$\Delta E^{\neq}$	ΔE	$\Delta E^{\neq}$
HF//HF	+0.4	+27.5	+0.6	+28.7
MP2//HF	+2.0	+24.7	+2.9	+25.2
Exp	+0.9	+13.3	−4.0	+20.9

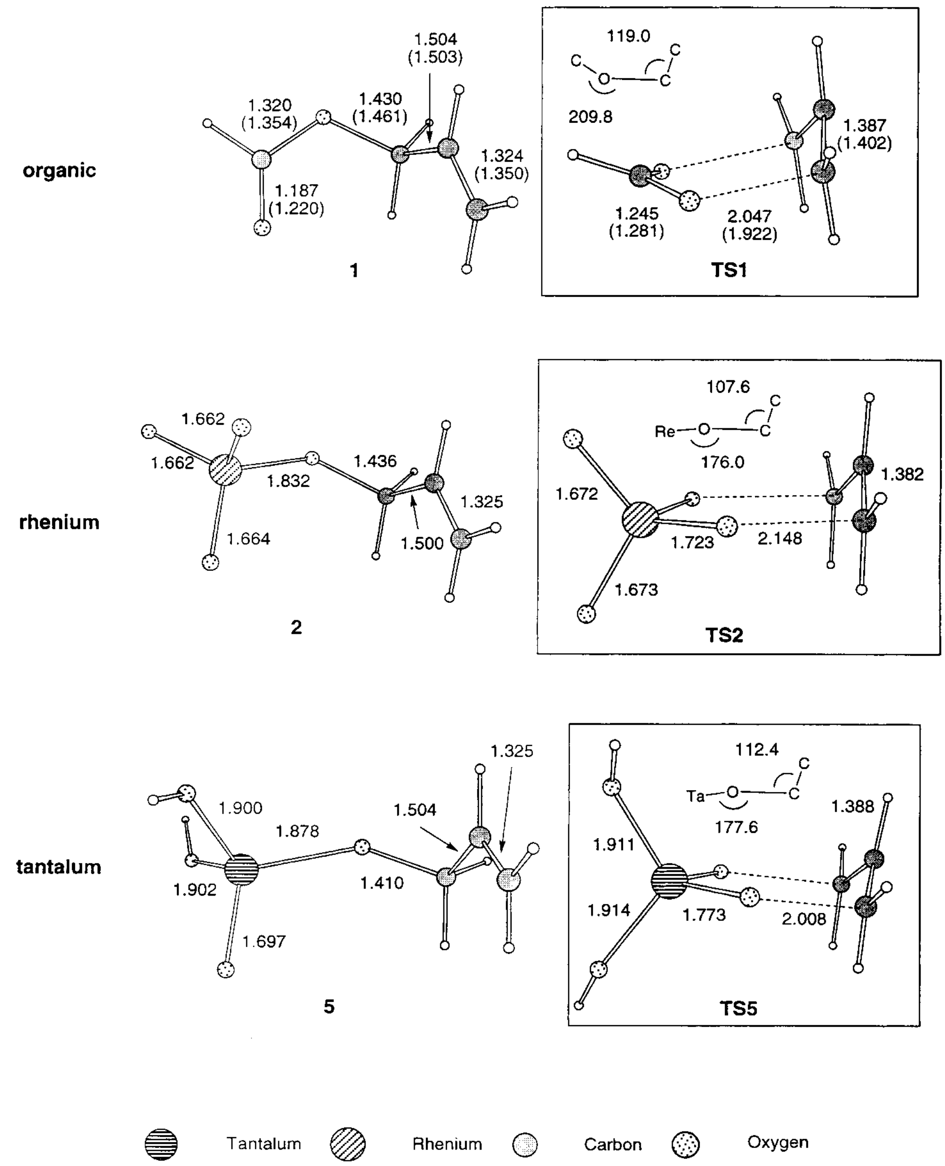


Figure 1. Optimized geometries of the reactant and corresponding transition state for the allylic rearrangement in the systems: [OC(H)OCH$_2$CH=CH$_2$] (**1**), [Re(O$_3$)OCH$_2$CH=CH$_2$] (**2**), and [Ta(O)(OH)$_2$OCH$_2$CH=CH$_2$] (**5**) together with selected bond lengths [Å] and angles [°]. HF and MP2 results; MP2 values for **1** and **TS1** are given in parentheses.

O···C distances in the transitions states, the MP2//MP2 and MP2//HF energies are similar. This justifies our choice of the MP2//HF level for our investigations of the organometallic systems.[11] Moreover, previous theoretical studies carried out for [RReO$_3$] complexes (X = H, F, CH$_3$, η^1-C$_3$H$_5$) have shown that the HF level of theory is adequate for the structure determination of systems in which Re is in the formal +VII oxidation state.[12] Indeed, our computed Re=O bond lengths are within the range of those found experimentally.[13] The Re–O single bond length computed for **2**, **3**, and **4** (1.83 Å) is also in good agreement with the experimental value (ca. 1.85 Å) obtained recently for [ReO$_3$(OCMe$_2$CMe$_2$OR)] (R = H, Me).[14] The studies on the 1,3-acyloxy shift in allyl formate[5] or similar studies on the Claisen rearrangement[15] also led to the conclusion that the results are more sensitive to the level of the energy calculation than to the level of geometry optimization. They showed in particular that energy barrier *differences* were correctly reproduced once electron correlation had been taken into account, either at the MP2, QCI, or DFT level.[5, 15]

An initial result that emerges from Figures 1 and 2 is that the structure of the transition states is of a *single* type, either boatlike only for the organic systems, or chairlike only for the organometallic systems. All our attempts to obtain the alternative structure, that is the chair structure in the organic case or the boat structure in the organometallic case, were unsuccessful. This is in contrast to the Cope and Claisen rearrangements where *both* chairlike and boatlike structures have been found.[5, 15] For the allyl formate rearrangement the B3LYP/6-31G* optimization of Zipse[5b] also resulted in only one concerted structure for the transition state (boat-type), which is at variance with the MP2/6-31G* optimization performed by Pascal et al.[5a] where both structures were found; the boat structure was slightly more stable. However, the location of a chair-type transition state may be very sensitive to the basis set used: with the 6-31G basis set the chairlike transition state has a second imaginary frequency and is therefore not a true transition state.[5a]

The most salient feature of Figures 1 and 2 is the rather flat geometry of the reacting unit in all transition structures: the out-of-plane bending angle between the formyl group and the plane made of the forming and breaking bonds amounts to 29.8° in the organic system **TS1**. In the organometallic system **TS2** the structure is chairlike and the corresponding angle for the ReO$_2$ unit is even smaller, 4.0°. Moreover, a test calculation on **TS1** in which the bending angle was set to 0° instead of 29.8° yielded a destabilization of only 3.5 kcal mol^{-1} (MP2//HF value). Similar features have been already noticed by Zipse; he ascribed them to the strong involvement of the σ-lone pairs of the oxygen atoms instead of the π-lone pairs.[5b] The methylene groups that are involved in the Claisen or in the Cope rearrangement are devoid of such σ-lone pairs, which precludes the possibility of a planar or almost planar reacting unit in these rearrangements. In fact, as clearly pointed out by Zipse,[5b] these oxy rearrangements in the allyl

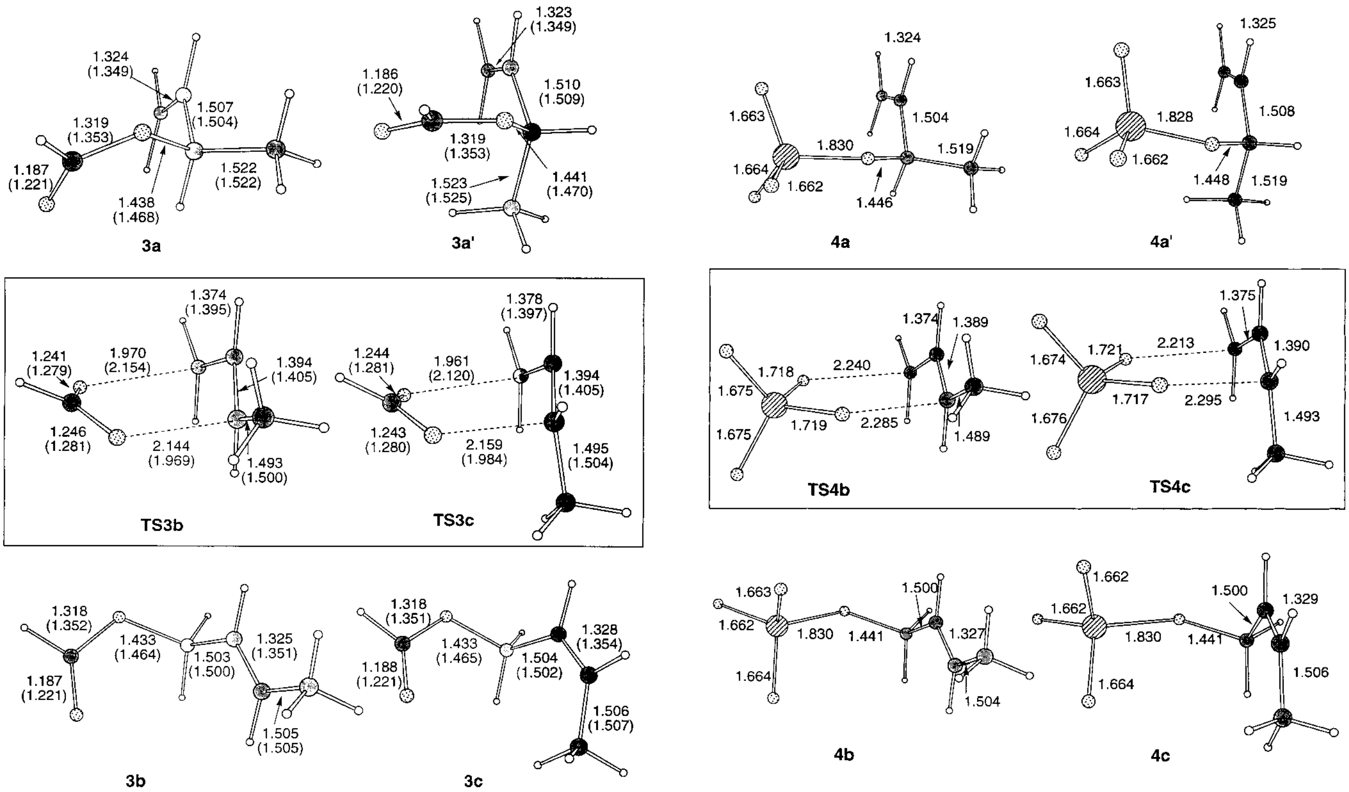


Figure 2. Left: HF- and MP2-optimized geometries of the reactant, transition state, and product for the allylic rearrangement in the two structural isomers **3a** and **3a'** of the methyl-substituted organic system [OC(H)OCHCH$_3$CH=CH$_2$]. MP2 values are given in parentheses. Right: HF-optimized geometries of the reactant, transition state, and product for the allylic rearrangement in the two structural isomers **4a** and **4a'** of the methyl-substituted organometallic system [Re(O$_3$)OCHCH$_3$CH=CH$_2$]. Selected bond lengths [Å] and angles [°] are also given.

esters are best understood as "intramolecular nucleophilic substitution reactions (S$_N$2'), in which the carbonyl lone pair features as the nucleophile, and the C–O bond adjacent to the allyl group takes the role of the leaving group." The same holds for the organometallic system in which the two oxygen atoms of the ReO$_4$ unit also bear σ-lone pairs, thus accounting for the similarity of the geometry of the organic and organometallic transitions states. Alternatively, as suggested by one referee, both the organic and organometallic reactions can be described as pseudopericyclic.[16] Such reactions have been studied in the past few years,[17, 18] including, in particular, sigmatropic rearrangements of esters.[18]

As far as their electronic structures are concerned, these transition states correspond to an allyl cation interacting either with a perrhenate ReO$_4^-$ or with a formate HCO$_2^-$ moiety: the overall charge of the ReO$_4$ unit (as given by the Mulliken population analysis) is −0.75 e in **TS2**, −0.81 e in **TS4b** and **TS4c** (with opposite values for the overall charge of the allyl cationic moiety). There is less zwitterionic character in the organic analogues: the formate unit has a charge of −0.61 e in **TS1**, and of −0.67 e and −0.66 e in **TS3b** and **TS3c**, respectively. We must note, however, that the *increase* in the negative charge on going from the reactant to the transition state is only slightly greater for ReO$_4$ (0.35 e, from −0.40 e in **2** to −0.75 e in **TS2**) than for HCO$_2$ (0.31 e from −0.30 e in **1** to −0.61 e in **TS1**).

There is one important difference, however, between the organic and the organometallic reactions: the computed energy barriers range between 23 and 25 kcal mol^{-1} (MP2//HF level) for the rhenium complexes (29 kcal mol^{-1} for the tantalum complex), that is much less than in the organic analogues for which a barrier of more than 45 kcal mol^{-1} is computed. This difference can best be rationalized by considering the four-electron repulsive interactions between the orbitals of the allylic cationic fragment and the orbitals of either the ReO$_4^-$ or the HCO$_2^-$ fragment that are responsible for the barrier.[19] In particular, one finds in the organometallic system a four-electron repulsive interaction between the π-allyl orbital and the orbital **6** of the ReO$_4$ moiety (see the left side of Figure 3); there is also some antibonding contribution

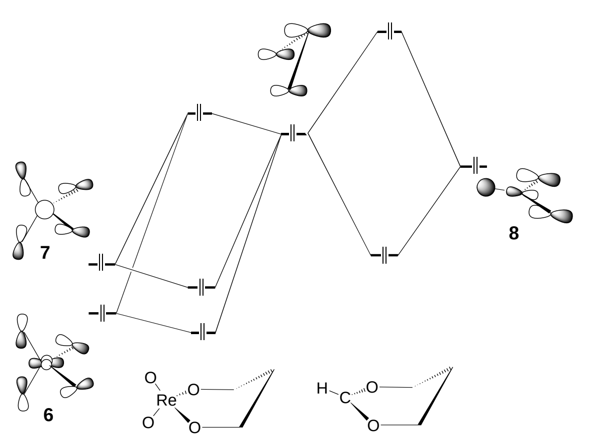


Figure 3. Schematic interaction diagram between the occupied π-allyl orbital of (C$_3$H$_5$)$^+$ and the interacting orbitals of either ReO$_4^-$ (left) or HCO$_2^-$ (right) for the transition state of the allylic rearrangement.

from the orbital **7** and some bonding contribution from the empty π*-orbital of the allyl. Its analogue in the organic system is the interaction between the π-allyl orbital and **8** (see the right side of Figure 3). However, the energy of **6** (as **7**) is much lower than that of **8** on account of its mixing with the formally empty metal orbitals (either $5\,d_{x^2-y^2}$ or 6s). The result is a much smaller repulsion in the organometallic system. Thus the combination of *two* oxo termini and of a central atom bearing orbitals that can stabilize the oxygen lone pairs (here a transition metal in a high oxidation state) accounts for the relative ease of the oxy rearrangement process in the organometallic system. It is interesting to recall at this stage that in calculations carried out for the Claisen rearrangement, a decrease of the energy barrier has been found on substituting the oxyallyl unit with electron-withdrawing atoms.[21e] Here too, one of the effects exerted by these substituents is certainly to lower the energy of the orbitals of the oxyallyl unit that interact with the orbitals of the facing allyl cation. One should finally note that, at variance with results obtained for various organic pseudopericyclic organic reactions,[17b,e, 18] the geometries are apparently *less* favorable in the lower transition state **TS1**: the C⋯C distance between the allylic carbon termini, 2.33 and 2.38 Å in **TS1** and **TS2**, respectively, matches the O⋯O distance more closely in **TS1** (2.23 Å) than in **TS2** (2.72 Å).

For the isomerization process of **4a** or **4a′** into **4b** or **4c**, the computed energy barriers are somewhat greater than the experimental activation enthalpies (Table 3) and more for **4b** than for **4c**. As a result, the *difference* in the computed barriers is much smaller than the difference in the experimental activation enthalpies, 0.5 $\text{kcal}\,\text{mol}^{-1}$ at the MP2//HF level instead of 7.6 $\text{kcal}\,\text{mol}^{-1}$ experimentally. There is also a small difference in the organic system, especially at the HF//HF and MP2//MP2 levels (Table 2; that a reverse order is found may be attributed to the greater difference in the stability of **3a** with respect to **3a′**, 3.6 $\text{kcal}\,\text{mol}^{-1}$ instead of 0.9 $\text{kcal}\,\text{mol}^{-1}$ for **4a** versus **4a′**). Thus at this stage the computed energies of the above model systems do not account for the selectivity in the isomerization that is observed experimentally so that some additional features need to be investigated.

These features can be either of computational or of chemical nature: the lack of zero-point energy corrections, the use of CH_3 to mimic the propyl substituent, as well as solvation effects[21] arising from the bulk solvent or from interactions between the organometallic system and the alcohols that are present in the reaction mixture. A precise determination of the zero-point energy corrections cannot be performed because we did not perform a frequency calculation for the methyl-substituted systems. However, for the rearrangement of **1**, a small zero-point energy (ZPE) correction was obtained by Zipse.[5b] We also computed (at the HF level) a small ZPE correction to the energy difference between **TS2** and **2**: $-1.2\,\text{kcal}\,\text{mol}^{-1}$. Therefore, one can reasonably expect a small influence of the ZPE correction on the computed energy barriers for **TS4b** and **TS4c**, and an even smaller influence on the difference. The replacement of CH_3 by an alkyl substituent with a longer chain should also not alter greatly the difference in the energy barriers. The fact that the geometry of both **TS4b** and **TS4c** is that of an allylic cation sitting almost perpendicularly to a rather flat $[C_2O_2Re]$ unit (and not a cyclohexane chairlike geometry) prevents any strong and differential steric interaction between an oxo ligand and the propyl substituent. Finally, a great discrimination between **TS4b** and **TS4c** by the solvent is not expected (here the noncoordinating dichloromethane CH_2Cl_2): Since both transition states have similar charges (vide supra) and dipole moments (10.4 D and 10.2 D respectively) the Kirkwood–Onsager dielectric effects should be similar. Self-association effects of the solvent,[22] if any, should also be similar for both isomerization processes. Therefore, it must be considered how the free alcohol that is present in the reaction mixture can interfere with the process taking place in the rhenium coordination sphere, either by coordination to the rhenium atom or by the formation of hydrogen bonds with the oxygen atoms.

In order to shed some light on this point, up to four water molecules were added successively to the transition state **TS2** and its geometry reoptimized.[23] The validity of the use of H_2O to model the hydrogen bonding or the coordinative properties of the alcohol was checked by means of a calculation with one CH_3OH molecule instead of one H_2O molecule. The corresponding optimized geometries of **TS2(H$_2$O)**, **TS2(2H$_2$O)**, **TS2(3H$_2$O)**, **TS2(4H$_2$O)**, and of **TS2(CH$_3$OH)** are shown in Figures 4 and 5, respectively.

The optimization procedure with either one or two water molecules started from a geometry in which one H_2O was coordinated to Re in the axial position of a trigonal bipyramidal $[Re(O)_4(H_2O)]$ unit. However, in both cases the optimization ended with structures in which water is hydrogen-bonded to the ligands rather than coordinatively linked through its oxygen atom to the Re center. Thus, the coordinating properties of the alcohol should not come into play. Interestingly, the geometry of **TS2(CH$_3$OH)** is very similar to the geometry of **TS2(H$_2$O)**. This shows the validity of the use of H_2O as a model for CH_3OH in our present investigations.

In **TS2(H$_2$O)** one water molecule is hydrogen-bonded to one spectator oxo ligand (through one of its hydrogen atoms) and to two hydrogen atoms of the allylic cation (through its oxygen atom). In **TS2(3H$_2$O)** the two additional water molecules are hydrogen-bonded to the oxo ligands that participate in the rearrangement. They also interact with the equatorial hydrogen atoms of the C_3H_5 unit through their oxygen atom; the corresponding O⋯H distances are 2.24 and 2.23 Å. This dual interaction leads to a lengthening of the O⋯C distance by ≈0.3 Å (it has also been found that the transition state has more dissociative character upon solvation in the case of the Claisen rearrangement[21e–h]). The binding of an extra water molecule in **TS2(2H$_2$O)** and in **TS2(4H$_2$O)** does not interfere with the structure: one hydrogen atom of the extra water molecule interacts with the second oxo spectator ligand; however, this hardly changes the geometry of the system.[24] The most salient feature shown by the various structures of **TS2(*n*H$_2$O)** is that the chair character of the transition state increases as successive H_2O molecules are added: the folding angle varies from 176° in **TS2** to ≈164° in

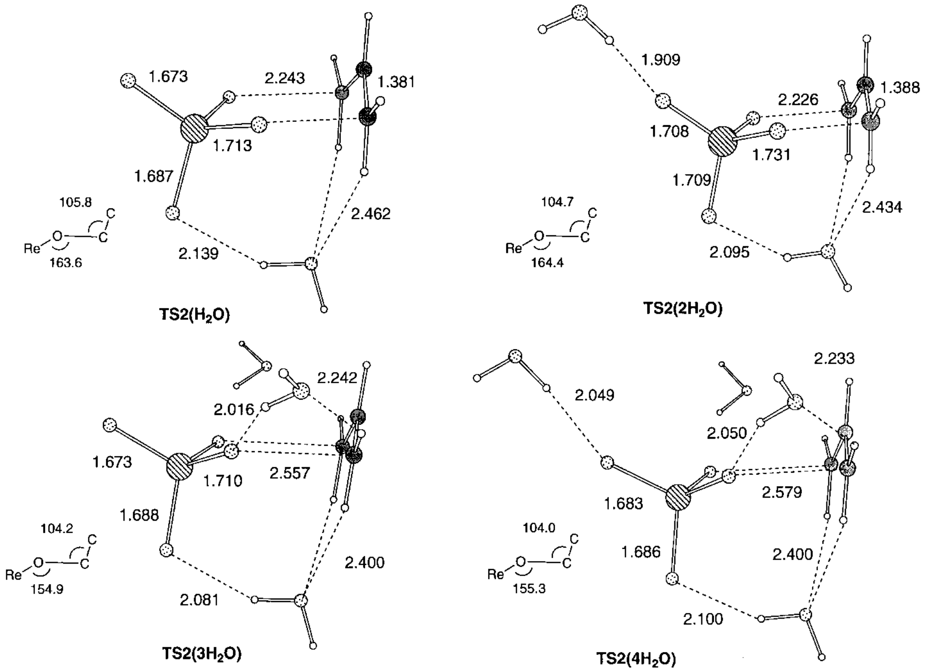


Figure 4. HF-optimized geometries of the transition state and product for the allylic rearrangement in the $[Re(O_3)OCH_2CH{=}CH_2]$ (**2**) in the presence of one, two, three, or four water molecules. Selected bond lengths [Å] and angles [°] are also given.

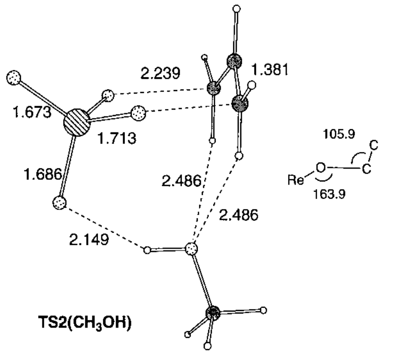


Figure 5. HF-optimized geometries of the transition state and product for the allylic rearrangement in the $[Re(O_3)OCH_2CH{=}CH_2]$ (**2**) in the presence of one methanol molecule. Selected bond lengths [Å] and angles [°] are also given.

TS2(H$_2$O) and **TS2(2 H$_2$O)**, and to ≈155° in **TS2(3 H$_2$O)** and **TS2(4 H$_2$O)** (Figure 4). The increased folding results from the necessity of the two oxo ligands that are participating in the rearrangement to interact simultaneously with the two carbon atoms of C_3H_5 and with the two hydrogen atoms of the hydrogen-bonded water molecules.[27]

Therefore, the discrimination observed when the allylic moiety has an alkyl (e. g. propyl) substituent can be tentatively attributed to the interference of the free alcohol molecules in the rearrangement process. These free alcohol molecules should wrap around the perrhenate moiety, while retaining—through their oxygen atom—some interaction with the hydrogens of the allylic cation, as exemplified by the structures of **TS2(*n* H$_2$O)**, $n = 1-4$. Thus, the transition state would be akin to a solvent-shared ion-pair.[28] As a result of this wrapping, the transition state adopts a chairlike geometry. The precise location of the alcohol molecules should depend on their size and on the position of the alkyl substituent. However, one can reasonably expect more congestion and more steric repulsion—and therefore a higher energy barrier—when the alkyl group substitutes for the axial hydrogen (as in **TS4c**) rather than when it substitutes for the equatorial hydrogen (as in **TS4b**).

In order to place this proposal on a firmer basis we computed the transition state structures for the bismethyl-substituted systems $[Re(O_3)OCHCH_3CH{=}CHCH_3]\cdot 3H_2O$. In this system the two methyl substituents are symmetrically placed either in the equatorial (**TS$_{eq}$**) or in the axial position (**TS$_{ax}$**), and three water molecules can participate in the interaction (Figure 6).[29] As in **TS2(*n* H$_2$O)**, the water molecules in **TS$_{eq}$** and **TS$_{ax}$** arrange themselves in order to maximize the number of hydrogen bonds, which produces a more congested structure for **TS$_{ax}$**: the $O\cdots C_{allyl}$ distance is 2.851 Å instead of 3.030 Å in **TS$_{eq}$**.[30] Moreover, in **TS$_{ax}$** the allyl group is almost perpendicular to the plane of the forming and breaking bonds, instead of producing a folding angle of 114.4°, as in **TS$_{eq}$**. Simultaneously, the folding angle of the ReO_4 unit is larger: 162.7° as compared to 143.3° in **TS$_{eq}$**. These variations in the folding angles both lead to an increased overlap of the orbitals **6** and **7** with the π-orbital of the allyl group and hence contributes to a greater four-electron repulsive orbital interaction in **TS$_{ax}$**. It is therefore not surprising that the stability of **TS$_{ax}$** is less than that of **TS$_{eq}$** by 8.6 kcal mol^{-1}.[31]

In fact, the destabilization of **TS$_{ax}$** can be totally attributed to the deformation imposed on the $[ReO_2C_3]$ skeleton by the interacting H_2O molecules, and not to a differential effect in the stabilization provided by the H_2O molecules. The stabilization provided by the H_2O molecules is equal for both **TS$_{ax}$** and **TS$_{eq}$**, that is 34.6 kcal mol^{-1}.[32] On the other hand, the $[Re(O_3)OCHCH_3CH{=}CHCH_3]$ unit is less stable in the structure corresponding to **TS$_{ax}$** than in the structure corresponding to **TS$_{eq}$** by 8.5 kcal mol^{-1}, which is the difference in energy between **TS$_{ax}$** and **TS$_{eq}$**. Thus all our results strongly suggest that microsolvation effects of the alcohols present in the reaction medium are at the origin of the selectivity that is experimentally observed.

For the rearrangement involving the tantalum system **5**, the overall shape of the corresponding transition state is very similar to that of **TS2** (see Figure 1). The Ta–O bond distances are slightly longer: 1.773 Å instead of 1.723 Å. The greatest difference is found for $O\cdots C$, which amounts to 2.008 Å instead of 2.148 Å. Therefore, **TS5** appears to be tighter than **TS2**. A greater energy barrier is computed for **TS5**, as expected from experiments carried out either with

0947-6539/99/0501-0062 $ 17.50+.50/0

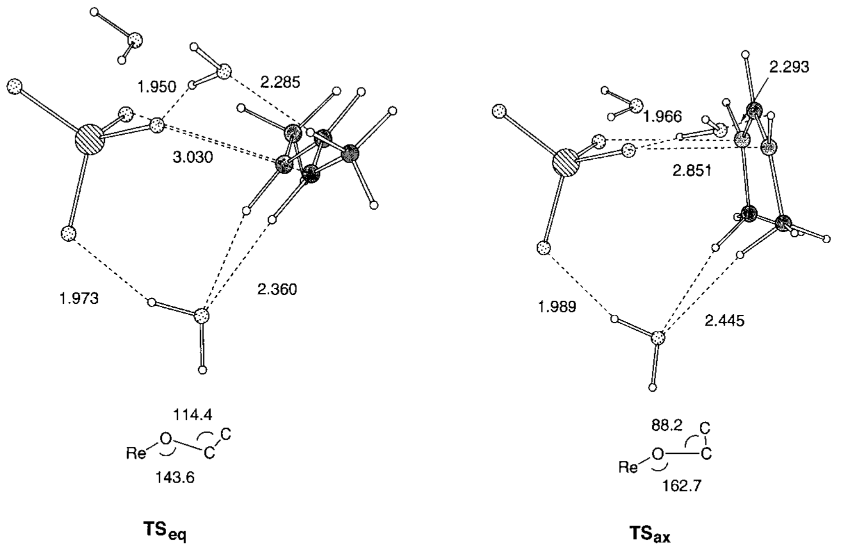


Figure 6. HF-optimized geometries of the transition states for the allylic rearrangement in the bismethyl-substituted system $[Re(O_3)OCHCH_3CH{=}CHCH_3] \cdot 3\,H_2O$ which contained two methyl substituents, placed either in the equatorial (**TS$_{eq}$**) or in the axial position (**TS$_{ax}$**), and three interacting water molecules. Selected bond lengths [Å] and angles [°] are also given.

$[MoO_2(OR)_2]$ or $[VO(OR)_3]$ catalysts.[1a,b] One factor that accounts for this feature is the smaller charge separation in the Ta system compared to the Re system: in **TS5** the $[TaO_2(OH)_2]$ unit has an overall charge of -0.59 e, the allyl cation bears a $+0.59$ e charge, whereas in **TS2** the calculated values are -0.75 e and $+0.75$ e for TaO_4 and C_3H_5, respectively. A more careful decomposition reveals that this difference arises almost entirely from the difference in the charges of the $[Ta(OH)_2]$ and $[ReO_2]$ spectator groups with respective charges of $+1.23$ e and $+1.03$ e. This is in agreement with the earlier proposal that the two spectator oxo ligands in the Re system can be more effective in the accommodation of the excess negative charge.[1c] The smaller charge separation in **TS5** results in a smaller electrostatic attraction between the two units: a calculation which used the atomic point charges of the two transition states (as obtained from a Mulliken population analysis) yielded an attraction of 39.6 kcal mol^{-1} for **TS5** instead of 54.9 kcal mol^{-1} in **TS2**. This is somewhat counterbalanced by a smaller repulsive interaction between the π-orbital of the allylic moiety and the orbital corresponding to **6** in **TS5**, which is also due to this reduced charge separation.[33] Finally, as far as the effects of the alcohols that are present in the reaction medium are concerned, we can use the results from previous theoretical studies that have related the acceleration of the Claisen rearrangement in aqueous solution to the transition state geometry. In particular, it has been found that a loose (tight) transition state structure leads to a rate increase (decrease).[21c,e] Since **TS5** is tighter than **TS2** (it has also a smaller charge separation) one expects a rate enhancement by the alcohols to be smaller in the tantalum systems than in the rhenium systems.

Conclusions

Our calculations confirm the original proposal[1, 2] of the involvement of a cyclic transition state in the allylic rearrangement catalyzed by a trioxorhenium complex that leads to the isomerization of allyl alcohols by 1,3-transposition of a hydroxy group. This transition state has a structure very similar to that of the transition state found in 1,3-acyloxy shifts in allyl esters.[34] However, the corresponding energy barrier is much lower as a result of a smaller repulsion between the oxo lone pairs and the π-allyl orbitals. This repulsion is highly dependent on the folding angles in the chair structure of the $[ReO_2C_3]$ skeleton. These angles can be strongly affected by microsolvation effects of the alcohols present in the reaction medium. We have suggested that such effects on the angles, rather than a variation in the charge difference and/or separation of the transition state, account for the kinetic discrimination (in terms of activation enthalpies) that is observed for the catalyzed *cis–trans* isomerization of hex-1-en-3-ol. At present we have no clear-cut explanation of the entropy effects.[1c] Hydrophobic effects of the allylic cation might well come into play. They certainly warrant the further theoretical studies that are currently in progress.[36]

Acknowledgements

Calculations were carried out on the IBM RS6000 workstations of our laboratory. We are grateful to Dr. L. Padel and Mrs. Fersing for their help and technical assistance.

---

[1] a) J. Belgacem, J. Kress, J. A. Osborn, *J. Am. Chem. Soc.* **1992**, *114*, 1501; b) J. Belgacem, J. Kress, J. A. Osborn, *J. Mol. Cat.* **1994**, *86*, 267; c) S. Bellemin-Laponnaz, H. Gisie, J. P. Le Ny, J. A. Osborn, *Angew. Chem.* **1997**, *109*, 1011; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 976.
[2] P. Chabardes, E. Kuntz, J. Varagnat, *Tetrahedron* **1977**, *33*, 1775.
[3] a) T. Hosogai, Y. Fujita, Y. Ninagawa, T. Nishida, *Chem. Lett.* **1982**, 357; b) S. Matsubara, T. Okazoe, K. Oshima, K. Takai, H. Nozaki, *Bull. Chem. Soc. Jpn.* **1985**, *58*, 844.
[4] E. S. Lewis, J. T. Hill, E. R. Newman, *J. Am. Chem. Soc.* **1968**, *90*, 662.
[5] a) Y. L. Pascal, J. Levisalles, J. -M. Normant, *Tetrahedron*, **1993**, *49*, 7679; b) H. Zipse, *J. Chem. Soc. Perkin Trans 2*, **1996**, 1797.
[6] F. E. Ziegler, *Chem. Rev.* **1988**, *88*, 1423.
[7] a) Gaussian94, Revision B.2: M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Reploge, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales, and J. A. Pople, Gaussian Inc., Pittsburgh PA, **1995**; b) The calculations used 5 functions with true d character; c) The MP2 calculations were carried out with a frozen core.
[8] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270.
[9] T. H. Dunning, Jr., P. J. Hay in *Modern Theoretical Chemistry* (Ed.: H. F. Schaefer, III), Plenum, New York **1977**, p. 1.

[10] Zero-point energies are not taken into account. The corresponding total energies (in Hartrees) are: **1**: HF//HF −304. 7233; MP2//HF −304.5496; MP2//MP2 −304.5551; **TS1**: HF//HF −304. 6348; MP2//HF −305.4741; MP2//MP2 −305.4815; **2**: HF//HF −494.3135; MP2//HF −495.8029; B3LYP//B3LYP −497.4682; **TS2**: HF//HF −494.2628; MP2//HF −495.7652; B3LYP//B3LYP −497.4371; **3a**: HF//HF −343.7668; MP2//HF −344.7227; MP2//MP2 −344.7285; **TS3b**: HF//HF −343.6850; MP2//HF −344.6453; MP2//MP2 −344.6576; **3b**: HF//HF −343.7672; MP2//HF −344.7208; MP2//MP2 −344.7266; **3a′**: HF//HF −343.7603; MP2//HF −344.7169; MP2//MP2 −344.7227; **TS3c**: HF//HF −343.6801; MP2//HF −344.6453; MP2//MP2 −344.6541; **3c**: HF//HF −343.7648; MP2//HF −344.7189; MP2//MP2 −344.7249; **4a**: HF//HF −533.3590; MP2//HF −534.9787; **TS4b**: HF//HF −533.3152; MP2//HF −534.9394; **4b**: HF//HF −533.3583; MP2//HF −534.9754; **4a′**: HF//HF −533.3560; MP2//HF −534.9772; **TS4c**: HF//HF −533.3103; MP2//HF −534.9370; **4c**: HF//HF −533.3550; MP2//HF −534.9726; **5**: HF//HF −474.5969; MP2//HF −475.9092; **TS5**: HF//HF −474.5234; MP2//HF −475.8630.

[11] We have also carried out a few test calculations at the DFT-B3LYP level for **2**, **TS2**, **TS4b**, and **TS4c**. Although the optimized geometries differ slightly from the those optimized by HF calculations (especially for the O⋯C distance which is optimized to be 1.967, 2.055, and 2.059 Å in **TS2**, **TS4b**, and **TS4c**, respectively), the energies are similar to those from MP2//HF calculations: the energy barrier for **TS2** is computed to be 19.5 kcal mol^{-1} at the DFT-B3LYP level and 23.7 kcal mol^{-1} at the MP2//HF level. Similarly, **TS4b** and **TS4c** are found to be very close in energy (as found at the MP2//HF level, see the Results and Discussion section): the energy of **TS4b** is only 2.3 kcal mol^{-1} lower than that of **TS4c**.

[12] a) G. Frenking, I. Antes, M. Böhme, S. Dapprich, A. W. Ehlers, V. Jonas, A. Neuhaus, M. Otto, R. Stegmann, A. Veldkamp, S. Vyboishchikov, in *Reviews in Computational Chemistry*, *Vol. 8* (Eds.: K. B. Lipkowitz, D. B. Boyd,), VCH, New York, **1996**, p. 63.; b) S. Köstlmeier, G. Pacchioni, W. A. Herrmann, N. Rösch, *J. Organomet. Chem.* **1996**, *514*, 111;

[13] a) W. A. Herrmann, P. Kiprof, K. Rypdal, J. Tremmel, R. Blom, R. Alberto, J. Behm, R. Albach, H. Bock, B. Solonki, J. Mink, D. L. Lichtenberger, N. E. Gruhn, *J. Am. Chem. Soc.* **1991**, *113*, 6527; b) W. A. Hermann, W. Scherer, R. Fischer, J. Blümel, M. Kleine, W. Mertin, R. Gruehn, J. Mink, H. Boysen, C. C. Wilson, R. M. Ibberson, L. Bachman, M. Mattner, *J. Am. Chem. Soc.* **1995**, *117*, 3231; c) P. Wikrent, B. J. Drouin, S. G. Kukolich, J. C. Lilly, M. T. Ashby, W. A. Hermann, W. Scherer, *J. Chem. Phys.* **1997**, *107*, 2187.

[14] W. A. Hermann, W. A. Wojtczak, G. R. J. Artus, F. E. Kühn, M. M. Mattner, *Inorg. Chem.* **1997**, *36*, 465.

[15] a) R. L. Vance , N. G. Rondan, K. N. Houk, F. Jensen, W. T. Borden, A. Komornicki, E. Wimmer, *J. Am. Chem. Soc.* **1988**, *110*, 2314; b) O. Wiest, K. A. Black, K. N. Houk, *J. Am. Chem. Soc.* **1994**, *116*, 2314; c) M. M. Davidson, I. H. Hillier, R. J. Hall, N. A. Burton, *J. Am. Chem. Soc.* **1994**, *116*, 9294; d) H. Y. Yoo, K. N. Houk, *J. Am. Chem. Soc.* **1994**, *116*, 12 047.

[16] J. A. Ross, R. P. Seiders, D. M. Lemal, *J. Am. Chem. Soc.* **1976**, *98*, 4325.

[17] See for instance: a) S. Ham, D. M. Birney, *Tetrahedron Lett.* **1994**, *35*, 8113; b) D. M. Birney, *J. Org. Chem.* **1996**, *61*, 243; c) S. Ham, D. M. Birney, *Tetrahedon Lett.* **1997**, *38*, 5925; d) D. M. Birney, X. Xu, S. Ham, X. Huang, *J. Org. Chem.* **1997**, *62*, 7114; e) D. M. Birney, S. Ham, G. R. Unruh, *J. Am. Chem. Soc.* **1997**, *119*, 4509.

[18] D. M. Birney, X. Xu, S. Ham, *Angew. Chem.* in press.

[19] Electron–electron repulsions have been found to contribute rather strongly to the barriers of pericyclic reactions.[20]

[20] a) K. N. Houk, R. W. Gandour, R. W. Strozier, N. G. Rondan, L. A. Paquette, *J. Am. Chem. Soc.* **1979**, *101*, 6797; b) R. D. Bach, G. J. Wolber, H. B. Schlegel, *J. Am. Chem. Soc.* **1985**, *107*, 2837; c) R. D. Bach, J. J. W. McDouall, H. B. Schlegel, G. J. Wolber, *J. Org. Chem.* **1989**, *54*, 2931.

[21] For theoretical studies of solvation effects on the Claisen rearrangement see ref. [14c] and: a) D. L. Severance, W. L. Jorgensen, *J. Am. Chem. Soc.* **1992**, *114*, 10966; b) C. J. Cramer, D. G. Truhlar, *J. Am. Chem. Soc.* **1992**, *114*, 8794; c) J. W. Storer, D. J. Giesen, G. D. Hawkins, G. C. Lynch, C. J. Cramer, D. G. Truhlar, D. A. Liotard, *ACS Symp. Ser.* **1994**, *568*, 24; d) J. Gao, *J. Am. Chem. Soc.* **1994**, *116*, 1563; e) A. Sehgal, L. Shao, J. Gao, *J. Am. Chem. Soc.* **1995**, *117*, 11 337; f) R. J. Hall, M. M. Davidson, N. A. Burton, I. H. Hillier, *J. Phys. Chem.*, **1995**, *99*, 921; g) M. M. Davidson, *J. Phys. Chem.* **1995**, *99*, 6748; h) J. M. Guest, J. S. Craw, M. A. Vincent, I. H. Hillier, *J. Chem. Soc. Perkin Trans 2*, **1997**, 71;

[22] J. J. Gajewski, *Acc. Chem. Res.* **1997**, *30*, 219.

[23] Note that **TS2(H$_2$O)**, **TS2(2H$_2$O)**, and **TS2(CH$_3$OH)** were optimized through a transition-state search algorithm (i.e. looking for one imaginary frequency) and without any symmetry constraint. Since the structures of **TS2(H$_2$O)** and **TS2(2H$_2$O)** turned out to be of C_s symmetry, this symmetry was imposed for **TS2(3H$_2$O)**, **TS2(4H$_2$O)**, **TS$_{eq}$**, and **TS$_{ax}$**. Thus, by the use of the principle of microscopic reversibility, the geometry optimization could be performed by the search for a global minimum with symmetry constraints. This procedure was applied to **TS2** and indeed led to a single imaginary frequency (see text). The same might be expected for **TS2(3H$_2$O)**, **TS2(4H$_2$O)**, **TS$_{eq}$**, and **TS$_{ax}$**.

[24] It is of interest here that in polymeric methyltrioxorhenium(vii), hydrogen bridges are formed between the water molecules of the water layer and the terminal oxo groups of the double layer of the corner-sharing [CH$_3$ReO$_5$] octahedra.[25] On the other hand, in $[(\eta^5\text{C}_5\text{Me}_5)_2\text{Re}_2^{\text{V}}\text{O}_4\cdot\text{H}_2\text{O}]_\infty$ the water molecules are hydrogen-bonded to the oxo bridges.[26]

[25] W. A. Herrmann, W. Scherer, R. W. Fischer, J. Blümel, M. Kleine, W. Mertin, R. Gruehn, J. Mink, H. Boysen, C. C. Wilson, R. M. Ibberson, L. Bachmann, M. Mattner, *J. Am. Chem. Soc.* **1995**, *117*, 3231.

[26] W. Herrmann, M. Flöel, J. Kulpe, J. K. Felixberger, E. Herdtweck, *J. Organomet. Chem.* **1988**, *355*, 297.

[27] This feature is best seen from the fact that one gets similar out-of-plane bending angles for **TS2(H$_2$O)** and **TS2(2H$_2$O)** on one hand, and for **TS2(3H$_2$O)** and **TS2(4H$_2$O)** on the other.

[28] a) Y. Marcus, *Ion Solvation*, Wiley, Chichester, **1985**. See also b) G. Boche, *Angew. Chem.* **1992**, *104*, 742; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 731.

[29] The bismethyl-substituted system was chosen in order to retain the C_s symmetry in the calculations. Because of computer limitations we restricted ourselves to the consideration of only three water molecules; this is justified on the basis of the similarity between **TS2(3H$_2$O)** and **TS2(4H$_2$O)**.

[30] The calculation of the volume of an ellipsoidal cavity which envelopes all the van de Waals spheres centered on the atoms led to values of 718 and 762 Å^3 for **TS$_{ax}$** and **TS$_{eq}$**, respectively.

[31] HF//HF value; in the light of the results obtained for the difference between **TS4b** and **TS4c** (Table 3), the MP2//HF value is expected to be quite similar. DFT(B3LYP) calculations yield a value of 6.3 kcal mol^{-1}, which is also in good agreement with the HF//HF value.

[32] These values are also HF//HF values and do not take into account the basis set superposition error (BSSE). However, correction for correlation effects and BSSE are expected to be quite similar for **TS$_{ax}$** and **TS$_{eq}$**.

[33] The decrease in the negative charge of the metallic unit leads to a lowering of the orbitals of this unit, while the decrease of the positive charge of the allylic unit leads to a rise of the π orbitals of this unit. As a result, the energy gap between the two sets of orbitals becomes larger and the corresponding four-electron repulsions smaller.

[34] After submission of this article, a study of the 1,3-transposition of allylic alcohols catalyzed by methyltrioxorhenium was reported.[35] Since no incorporation of ^{18}O was observed in the rearranged allyl alcohol, an alternative mechanism has been suggested which involves a 1,3-sigmatropic shift of the [ReO$_3$(OH)(CH$_3$)] unit (via one of its oxo ligands) across the allylic moiety. We have checked that in our case such a 1,3-sigmatropic is unlikely: the corresponding barrier is, at the DFT-B3LY level, higher by 25.1 kcal mol^{-1} than the barrier for the [3,3] rearrangement.

[35] J. Jacob, J. H. Espenson, J. H. Jensen, M. S. Gordon, *Organometallics*, **1998**, *17*, 1835.

Note added in proof (19.11.98): The MP2//MP2 value for the energy barrier for the 1,3 rearrangement in **2** has now been determined. Its value of 20.9 kJ mol^{-1} is close to the MP2//MP2 and B3LYP//B3LYP value.

Received: March 31, 1998 [F 1078]