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Reactivity of (Mono-*tert*-butyloxiranyl)lithium: A Theoretical Ab Initio Study

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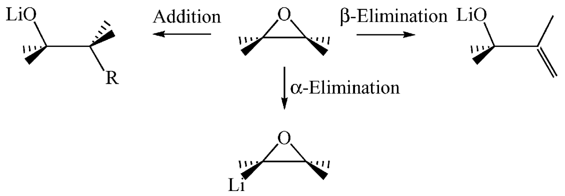
The reactivity of the lithiated *tert*-butyloxiranyl anion has been studied by means of ab initio calculations at the CCSD(T)//MP2 level of theory. Four reaction paths have been studied (three ring-opening reactions and one addition reaction). All extrema were located and characterised. The effects of solvation by one or two MeLi molecules were studied for each reaction path by reoptimising the various extrema. It was found that the addition reaction path becomes competitive when at least two MeLi molecules are taken into account. This shows the catalytic effect of alkyllithium on this reaction path. In no case could a free carbene be characterised as a reaction intermediate.

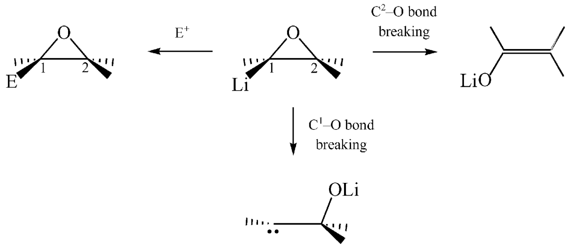
Introduction

The reaction of strong bases with oxirane derivatives may lead to the well-known addition reaction. In some cases, proton removal is observed, and it may occur either from the α- or β-position. In the case of β-elimination, an allylic alcohol is obtained; this is an efficient way to synthesise such an alcohol.[1] The use of chiral bases leads to an enantioselective reaction.[2] When deprotonation of the epoxide ring occurs at the α-position, an oxiranyl anion is obtained, generally as a lithiated species (Scheme 1).[3]



Scheme 1.

The oxiranyllithium may be trapped by a great variety of electrophiles (Scheme 2):[4] again, the use of chiral bases leads to enantiocontrol of the reaction.[5] The oxiranyl species may also rearrange through C–O bond-breaking. When the C^2–O bond is broken, an enolate–lithium complex is obtained and gives an aldehyde or ketone as the product.[6]



Scheme 2.

Breaking of the C^1–O bond leads to a carbene intermediate (Scheme 2). Although it has not been characterised as an isolated species, many reactions characteristic of a carbene have been observed. The R^2 group may migrate towards the unsaturated centre (Scheme 3).[7] The final product is a ketone (or an aldehyde). The migratory ability of the R^2 group has been studied in detail, and the following order was found: H > Me > *n*Bu > aryl > *t*Bu.[8] The carbene species may also insert into a C–H bond. As described by Cope et al.,[9] a transannular insertion of the carbene moiety leads to the formation of a bicyclic product. This reaction has been widely used for the synthesis of bicyclic compounds.[10] The intermediate carbene may also add to a C=C double bond to give a cyclopropane. First discovered by Crandall and Lin,[11] in the case of 1,2-di-*t*Bu-oxirane, this reaction has had numerous synthetic applications.[12] Among them, it has recently been used in an intramolecular fashion for the synthesis of bicyclic compounds.[13] Insertion into a C–Li bond has also been observed, generally when the alkyllithium used for deprotonation is present in excess.[14] Elimination of Li_2O from the primary adduct leads to the formation of an ethylene species. When bulky amides are used for addition to the alkyllithium, highly stereoselective reactions are observed.[15] Finally, dimerisation of the carbene has also been observed[16]

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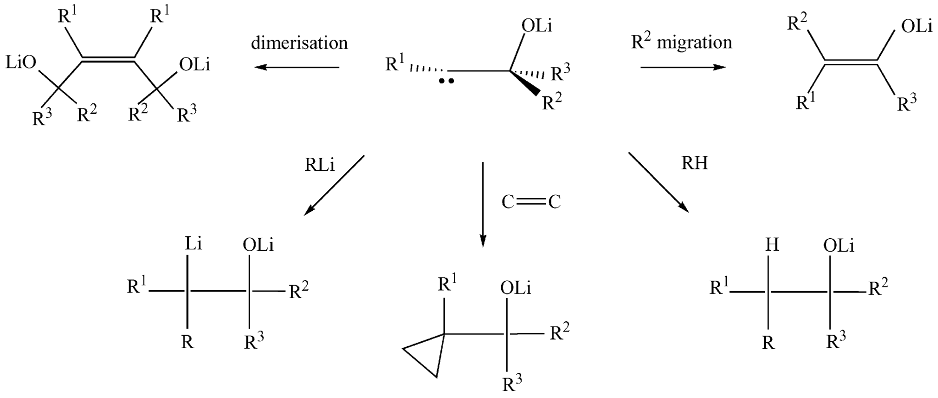


Scheme 3.

and leads to the formation of diols. The reactivity of the intermediate carbene is summarised in Scheme 3.

In most cases, several competing reactions are observed; the competition between the different reaction pathways has been the subject of numerous studies.[17] During the last 15 years, the reactivity of oxiranyllithium has been described in five reviews.[18]

Theoretical studies on oxiranyl species are by far less abundant. To the best of our knowledge, the first report of ab initio calculations on these species[19] describes a study of the reaction of methyloxirane with OH^-. It was shown that the β-elimination is preferred to the addition reaction. Similar results on the reactivity of methylthiirane with OH^- and SH^- have also been presented. Later studies have dealt with the enantioselectivity of the β-elimination from cyclohexene oxide[20,21] and of the oxiranylcarbaldimine rearrangement.[22] Experimental and theoretical studies have also been presented on cyclopentene and cyclohexene reactivities in nonpolar solvents.[23] In two papers,[21,23] α-elimination has been shown to be less favourable than β-elimination. Finally, the aggregation of oxiranyllithium has been studied by means of DFT calculations.[24]

The aim of this paper is to present a theoretical study of the reactivity of a lithiated α-oxiranyl anion with alkyllithium. Among the numerous oxiranyllithium compounds that have been experimentally studied, we have chosen the (mono-*t*Bu-oxiranyl)lithium for two reasons. First, this species has been studied in detail by Crandall and Lin,[25] and the experimental results are available. Secondly, this is the simplest alkyl-substituted oxiranyllithium compound in which there is no hydrogen atom at the β-position. Competing routes such as β-elimination are therefore not possible and will not disrupt the studied reaction paths. The alkyllithium (*n*-, *sec*- and *tert*-butyllithium in the paper by Crandall and Lin)[25] will be modelled by using methyllithium.

Three reaction pathways will be considered: both C^2–O and C^1–O bond-breaking will be studied first. In the latter case, addition to the Me–Li bond or R^2 migration will also be studied. Our goal is, on one hand, to describe some competing reaction paths,[26] and on the other hand, to understand the exact role of the alkyllithium. Experimental results show that the formation of the ethylene product is observed only when RLi is present in excess (3 equiv.). One molecule is needed for proton removal and the second adds to the oxiranyl species. The role of the third molecule is therefore under question.

Three sets of calculations will be presented. First, the ring-openings of the oxiranyl ring (C^1–O or C^2–O bond-breaking) will be studied. In a second set of calculations, an additional molecule of MeLi is taken into account in our computation. The addition reaction path is computed and the ring-opening reaction paths are recomputed in the presence of this additional molecule of MeLi. In the third set of calculations, two MeLi molecules are taken into account and the various pathways are recomputed.

Method of Calculation

The Gaussian set of programs has been used throughout.[27] First, the potential energy surface (PES) will be explored at the MP2/6-31G** level of calculation. All stationary points are located at this level. Frequency calculations will be carried out to identify these extrema: a minimum and a transition state (TS) are characterised by zero and only one imaginary frequency, respectively. To obtain more reliable results, the correlation energies of the various extrema will be recalculated at the more sophisticated CCSD(T) level. Only single-point calculations will be calculated at this CCSD(T)/6-31G**//MP2/6-31G** level. As suggested by a referee, the influence of diffuse functions (6-31++G** basis set) will be tested in the first set of calculations.

Results and Discussion

Oxiranyllithium

Oxiranyl Species

The oxiranyl species has been optimised with the anionic site in a *trans* position with respect to the *t*Bu substituent. The main optimised geometrical parameters are given in Figure 1 together with those of the *t*Bu-epoxide.

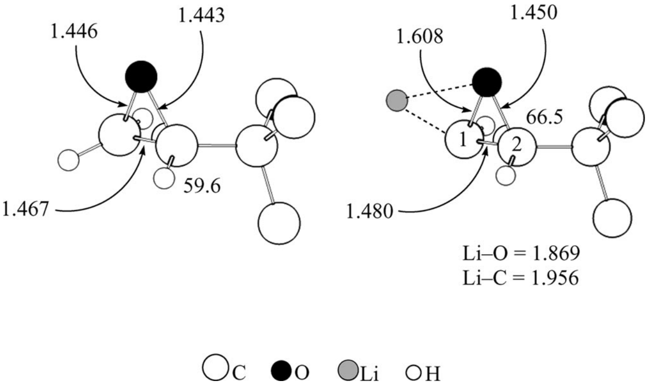


Figure 1. Selected geometrical parameters [Å, °] for *t*Bu–oxirane (left) and *t*Bu–oxiranyllithium (right). For the sake of clarity the hydrogen atoms on the *t*Bu substituent have been omitted.

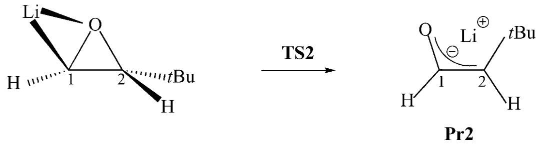
On the whole, the geometrical results are similar to those previously found by Pratt and Ramachandran.[24] Two features are worth noting in this structure. First, the lithiated carbon atom is far from being tetrahedral: the C–C–Li and O–C–Li angles are equal to 98.4 and 62.4°, respectively. This strong distortion may be explained by the Li^+ cation interacting with both the anionic carbon atom (C–Li = 1.956 Å) and the oxygen atom (O–Li = 1.869 Å) at this position (Figure 1). The second important point is the large deformation of the epoxide cycle: the carbanionic C^1–O bond is dramatically lengthened to 1.608 Å, whereas the C^2–O bond length increases to 1.450 Å (C^2–O = 1.443 Å in the non-lithiated epoxide). This geometrical deformation should indicate a dramatic weakening of the C^1–O bond in the lithiated epoxide.

Ring-Opening of the Oxiranyl Species

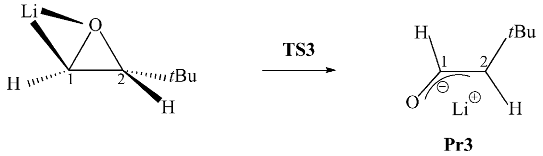
In a first set of calculations, three ring-opening reaction paths were calculated. First, breaking of the carbanionic C^1–O bond should lead to the carbene. This species may evolve towards an Li^+–enolate complex through a hydrogen migration from C^2 to C^1 (Scheme 4).

Breaking of the C^2–O bond directly leads to the Li^+–enolate complex. However, due to the partial C=C double bond in the product, two isomers may be expected depending on the relative positions [*cis* (Scheme 5) or *trans* (Scheme 6)] of the oxygen atom and the *tert*-butyl substituent.

These three reaction paths have been studied. In each case, only one transition state (TS) was found. All extrema (minima and transition states) were fully optimised and characterised by frequency calculations. The results are given in Table 1.



Scheme 5.



Scheme 6.

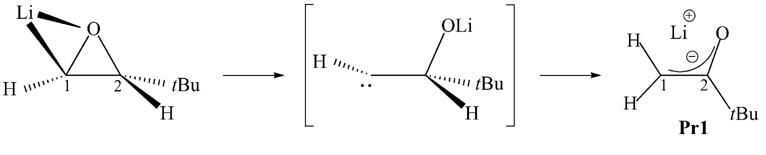
Table 1. Relative energies [kcal/mol] of the stationary points located on the various reaction paths [obtained with the 6-31G** and 6-31++G** basis sets at the MP2 and CCSD(T) levels]. The origin of the energies is that of the *trans*-oxiranyllithium.

		TS1	**TS2**	**TS3**	**Pr1**	**Pr2**	**Pr3**
MP2	6-31G**	35.3	33.7	29.4	–54.6	–49.0	–49.0
CCSD(T)	6-31G**	29.2	32.6	28.2	–53.6	–48.0	–48.0
MP2	6-31++G**	34.2	33.6	27.5	–55.1	–49.5	–49.4
CCSD(T)	6-31++G**	28.2	32.5	26.5	–54.1	–48.4	–48.3

The three reactions are strongly exothermic (by about 50 kcal/mol), which reflects the large cyclic strain in the reactant. As expected, the C^2-disubstituted Li^+–enolate complex (**Pr1**) is found to be the most stable product (ΔE = –54.6 kcal/mol).

The energetic ordering of the TS is found to be opposite to that of the products: the lowest transition state is **TS3** (ΔE = 29.4 kcal/mol) and the highest one is **TS1** (ΔE = 35.3 kcal/mol). The energy difference between **TS2** and **TS3** may originate from geometrical constraints: in **TS2**, the oxygen atom moves towards the *t*Bu substituent. The distances between the methyl carbon atoms of the *t*Bu substituent and the oxygen atom are rather small and may generate steric repulsion. These distances are substantially larger in **TS3** (Figure 2).

Another geometrical effect may explain the differences in the TS energies: in **TS3**, the H^1 atom lies almost in the H^2–C–C plane (dihedral angle H^1–C–C–H^2 = 176.6°). This is not the case in **TS2** in which H^1 has to move to the other side of the C–C–O plane of the oxiranyl species. As a conse-



Scheme 4.

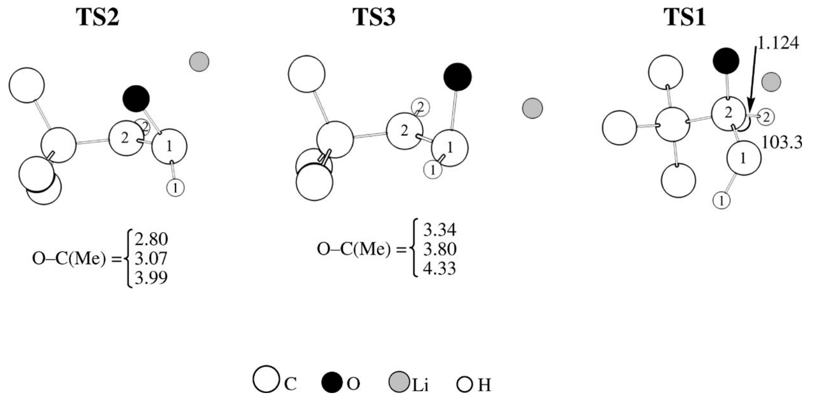


Figure 2. Selected geometrical parameters [Å, °] for the three transition states.

quence, the H^1–C–C–H^2 moiety (dihedral angle H^1–C–C–H^2 = 118.5°) is far from being planar, which may destabilise this structure.

The most puzzling result in Table 1 is the high energy of **TS1**: breaking of the long C^1–O bond (1.608 Å) is expected to be less costly in energy terms than breaking of the shorter C^2–O bond (1.450 Å). This is not the case as **TS1** (35.3 kcal/mol) is higher in energy than **TS2** (33.7 kcal/mol) and **TS3** (29.4 kcal/mol). The high energy of **TS1** is a result of the H^2 migration which is concerted with the C^2–O bond-breaking. This point is illustrated by the lengthening of the C–H^2 bond from the reactant (1.095 Å) to **TS1** (1.124 Å) and the H^2–C^2–C^1 angle decreasing (from 117.5° in the reactant to 103.3° in **TS1**, Figure 2). On the whole, the geometry of **TS1** resembles the carbene structure that has been postulated as a reaction intermediate (see Scheme 4).

CCSD(T) Calculations

The seven stationary points characterised at the MP2/6-31G** level were recomputed at a higher correlation level (CCSD(T)/6-31G**) by using the MP2-optimised geometries. The results are given in Table 1.

From Table 1, it can be seen that the relative energies of the products (**Pr1**, **Pr2** and **Pr3**) are almost unaffected by increasing the calculation level: they are all destabilised by 1 kcal/mol. Similarly, **TS2** and **TS3** are stabilised by about 1 kcal/mol. The only noticeable difference is observed for **TS1**, which is found to be more stable by 6.1 kcal/mol at the CCSD(T) level. This stabilisation upon increase of the correlation calculation level is not surprising as two bonds (C^1–O and C^2–H^2) are broken in this transition state, whereas only one (C^2–O) is broken in both **TS2** and **TS3**.

In order to test the influence of diffuse functions in the basis set, six stationary points were reoptimised at the MP2 level by using the 6-31++G** basis set. Single-point calculations were performed at the CCSD(T) level (Table 1). On the whole, the energy differences between the 6-31G** and 6-31++G** results are less than 2 kcal/mol at both levels of calculation. Consequently, the smaller 6-31G** basis set will be used in the following.

Oxiranyllithium + MeLi

In the following, we have considered the reaction of the Li^+–oxiranyl species with an additional methyllithium molecule. Four reaction paths were calculated. The three ring-opening reaction paths described in the preceding section were recalculated in the presence of one MeLi molecule. The addition of MeLi to the oxiranyl species leading to olefin formation has also been studied. This last reaction path will be discussed first after describing the complexed reactant.

Reactant

The optimised geometrical parameters for the complex between MeLi and the lithiated oxiranyl species are given in Figure 3 (for the sake of comparison, the geometry of the uncomplexed oxiranyllithium is also given).

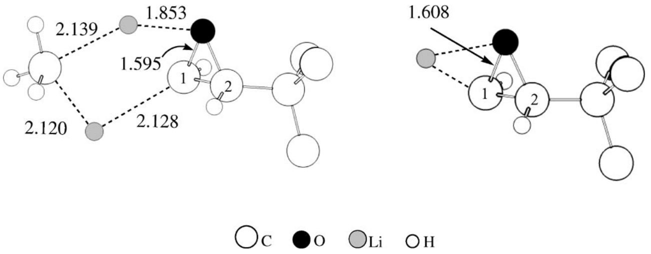
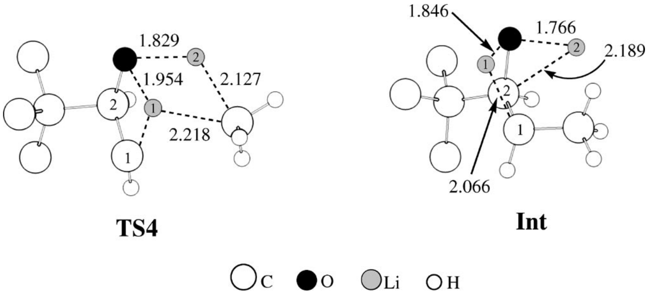


Figure 3. Selected geometrical parameters [Å] for complexed *t*Bu–oxiranyllithium and noncomplexed species.

In the complexed oxiranyllithium, a five-membered ring is found, and each lithium cation interacts with only two atoms. One important point is that the geometry around the carbanionic carbon atom is less distorted than in the uncomplexed species. If one excepts the intracyclic O–C–C angle (O–C–C = 55.8°), all angles around the carbanionic carbon atom are in the range 103.8–126.7°. The C^1–O bond length is 1.595 Å, a value shorter than that in the uncomplexed species (1.608 Å). On the whole, this complexed species looks less distorted than in the preceding case. From an energetic point of view, the interaction energy between MeLi and the lithiated oxiranyl species is equal to –51.2 kcal/mol.

Addition Reaction Path

Starting from the reactant (**Rea**), two transition states (**TS4** and **TS5**), one intermediate minimum (**Int**) and the final product (**Pr4**) have been characterised on this reaction path. In the first TS (**TS4**, located 35.7 kcal/mol above the reactant, Table 2), the MeLi molecule lies above the unsaturated carbon atom (Figure 4). The two lithium atoms are bound to the oxygen atom and to the carbon atom C^{Me} of the methyl group; the C^{Me}LiOLi four-membered ring is nearly planar (C^{Me}–Li^1–O–Li^2 = 14.8°). The Li^1–O–C^2–C^1 atoms are coplanar (Li–O–C^2–C^1 = 1.3°), the methyl substituent being in an *anti* position with respect to the *t*Bu group.[28] In this transition state, the C^1–C^{Me} distance is long (2.964 Å), whereas the Li–O and Li–C^{Me} bonds are near their equilibrium distances.

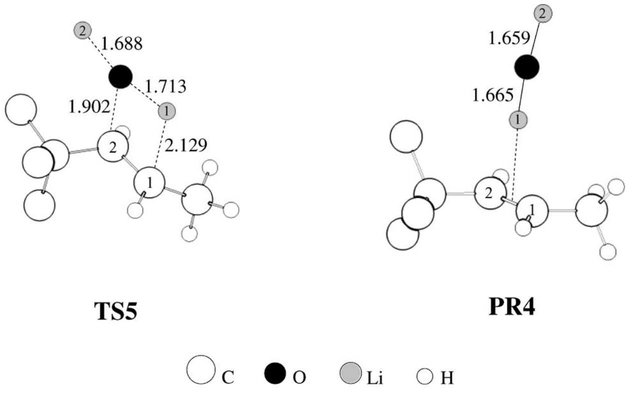


TS4 **Int**

Figure 4. Selected geometrical parameters [Å] for the transition state **TS4** and the relative minimum **Int**.

In the secondary minimum **Int**, which is located 31.6 kcal/mol below the reactant, the methyl group is bound to the C^1 atom (C^1–C^{Me} = 1.523 Å, Figure 4). The geometry around the C^1 carbon atom is nearly standard (C^1–H = 1.090 Å; C^2–C^1–C^{Me} = 108.5°; C^2–C^1–H = 112.0°) except for the lithium substituent (C^2–C^1–Li^1 = 75.4°). As in the lithiated epoxide, the lithium cation chelates the C^1 and O atoms (C^1–Li^1 = 2.066 Å; O–Li^1 = 1.846 Å). The C^2–C^1 distance is close to that of a C–C single bond (1.513 Å). The geometry around the C^2 atom is roughly tetrahedral (C^1–C^2–O = 108.4°; C^1–C^2–C^{tBu} = 117.7°; C^1–C^2–H = 109.9°). The second lithium cation (Li^2) interacts with the O and C^2 atoms (O–Li^2 = 1.766 Å; C^2–Li^2 = 2.189 Å).

The second transition state (**TS5**) on this reaction path corresponds to the elimination of Li_2O from the secondary intermediate **Int**. It is located 20.4 kcal/mol below the reactant (Table 2). In this structure, the C^1–C^2 bond (1.407 Å) is intermediate between a single and a double C–C bond (Figure 5). The C^1 and C^2 carbon atoms are pyramidalised in the same half-plane; the Li_2O moiety is slightly bent (Li–O–Li = 166.4°) and the four-membered ring O–Li^1–C–C is almost planar (O–Li^1–C^1–C^2 = 2.6°).



TS5 **PR4**

Figure 5. Selected geometrical parameters [Å] for the transition state **TS5** and the product **Pr4**.

The final product **Pr4** may be described as a *trans*-disubstituted alkene (C^1–C^2 = 1.349 Å) in weak interaction with Li_2O. This molecule is almost linear (Li–O–Li = 173.0°); the two Li–O bond lengths are slightly different due to the interaction with the alkene (Figure 5). The reaction is exothermic by 42.0 kcal/mol (Table 2).

Ring-Opening Reactions

All the extrema characterised in the first section were reoptimised in the presence of a MeLi molecule. The geometries of these various extrema are similar to those found previously. The relative energies of these extrema are given in Table 2 together with those obtained without the MeLi molecule.

Addition of a MeLi molecule has little effect on the thermodynamics of the ring-opening reactions: the largest change (1.5 kcal/mol) was observed for **Pr3**. This result indicates that the reactant and the products enjoy similar stabilisation upon complexation by a MeLi molecule. This is not the case for transition structures: taking into account one MeLi molecule lowers the **TS1** relative energy and destabilises the **TS2** and **TS3** structures (Table 2). **TS1** becomes slightly favoured by 1.7 kcal/mol with respect to **TS3**, **TS2** being higher in energy. All these transition-state energies are close to each other and close to that (35.7 kcal/mol) of the transition state for the addition reaction (**TS4**). On the whole, the four reaction paths should be competitive.

Table 2. Relative energies [kcal/mol] of the various extrema complexed by a MeLi molecule [MP2: Entry 2; CCSD(T): Entry 3]. The results without MeLi (MP2 level) are also given (Entry 1) for the sake of comparison.

		Rea	TS1	TS2	TS3	Pr1	Pr2	Pr3	TS4	TS5	Int	Pr4
0 MeLi	MP2	0	35.3	33.7	29.4	–54.6	–49.0	–49.0	–	–	–	–
1 MeLi	MP2	0	33.1	37.4	34.8	–55.3	–48.3	–50.5	35.7	–20.4	–31.6	–42.0
1 MeLi	CCSD(T)	0	27.3	35.3	33.0	–54.8	–48.0	–50.0	31.0	–16.5	–29.6	–37.5

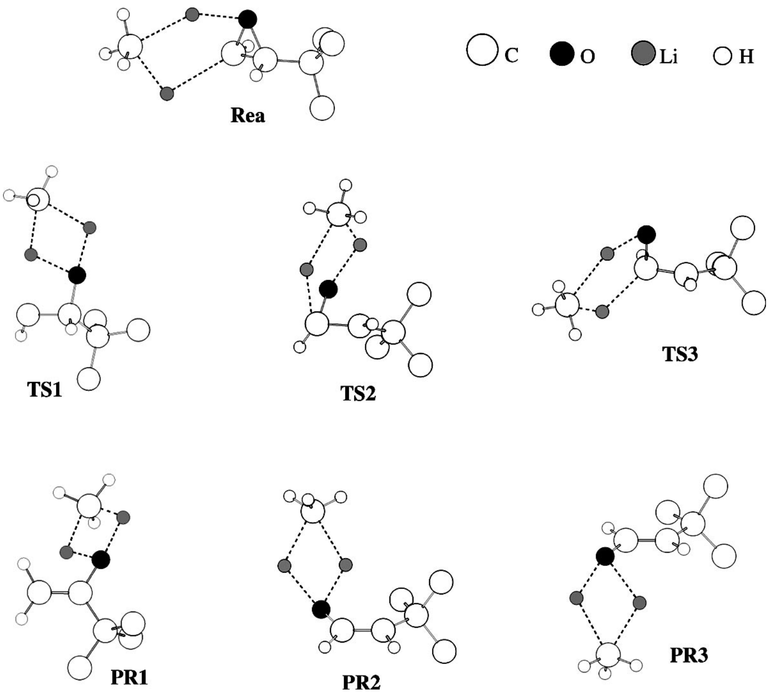


Figure 6. Geometries of the extrema complexed with MeLi.

Discussion

The stabilisation energies upon complexation were calculated, and the results are given in Table 3. The optimised geometries of the reactant, transition states and products are given in Figure 6. Schematically, two types of geometries are found in the Li^+–oxiranyl complexes with MeLi. In the first one, a nearly planar four-membered Li–O–Li–C^{Me} ring is found. Such a geometry is found in **Pr1**, **Pr2**, **Pr3** and **TS1**. These four-membered rings are all geometrically similar to each other (C^{Me}–Li = 2.12–2.17 Å; O–Li = 1.78–1.79 Å; O–Li = 1.93–1.98 Å).[29] In each case, the stabilisation energy is larger than 50 kcal/mol (Table 3), and the four values are close to each other (50.5–53.4 kcal/mol).

Table 3. Complexation energies [kcal/mol] of the various extrema.

Rea	**TS1**	**TS2**	**TS3**	**Pr1**	**Pr2**	**Pr3**
51.2	53.4	47.4	45.7	51.9	50.5	52.7

In the second geometry, a five membered-ring is found: the oxygen atom and the carbanionic carbon atoms are directly bound to only one lithium atom, and the methyl group bridges the two lithium cations. This geometry is found in the reactant (**Rea**), in which the two electronegative sites are vicinal, which leads to a large stabilisation energy (ΔE = 51.2 kcal/mol). This geometry is also found in the transition states **TS2** and **TS3**, in which the two electronegative sites are not vicinal. The four-membered ring formation is probably forbidden because of steric repulsion with the *t*Bu group. Consequently, the stabilisation energies upon complexation are smaller for **TS2** (ΔE = 47.4 kcal/mol) and for **TS3** (ΔE = 45.7 kcal/mol).

CCSD(T) Calculations

As in the preceding case, CCSD(T) single-point calculations were performed on the various extrema. The results are given in Table 2. As in the case without the complexing MeLi, the thermodynamics of ring-opening of the oxiranyl anion are almost unchanged from MP2 to CCSD(T) levels: in each case, the energy variation is less than 1 kcal/mol. Again, **TS2** and **TS3** are slightly stabilised (by about 2 kcal/mol); **TS1** is stabilised more (by 5.8 kcal/mol). This difference probably comes from the number of bonds that are broken (two in **TS1** vs. one in **TS2** and **TS3**). The energetics of the addition reaction path change when the calculation level is improved. The two minima, **Int** and **Pr4**, as well as the interconnecting TS (**TS5**) are destabilised by 2–5 kcal/mol. In contrast, **TS4**, which leads to the intermediate **Int**, is stabilised by 4.7 kcal/mol. At this calculation level, it is more stable than **TS2** and **TS3**.

Oxiranyllithium + 2 MeLi

Extrema Location

All stationary points on the various reaction paths were reoptimised and recharacterised in the presence of a second MeLi molecule. The results are given in Table 4 and show that three of the transition states (**TS1**, **TS3** and **TS4**) have almost the same energy (24.3–25.1 kcal/mol) at the MP2 level. Only **TS2** (33.4 kcal/mol) is significantly higher in energy. For the ring-opening reactions, the complexation by a second MeLi molecule roughly lowers the relative energies of almost all the extrema (**TS1**, **TS3**, **Pr1**, **Pr2**, **Pr3**) by about 10 kcal/mol (compare Entries 1 and 2). The only ex-

Table 4. Relative energies (ΔE) and complexation energies (*Solv*; calculated with respect to the monosolvated species) of the extrema complexed by two MeLi molecules. The relative energies for the complexation by one MeLi are given for the sake of comparison.

		Rea	**TS1**	**TS2**	**TS3**	**Pr1**	**Pr2**	**Pr3**	**TS4**	**TS5**	**Int**	**Pr4**
ΔE (1 MeLi) [kcal/mol]	MP2	0	33.1	37.4	34.8	–55.3	–48.3	–50.5	35.7	–20.4	–31.6	–42.0
ΔE (2 MeLi) [kcal/mol]	MP2	0	25.1	33.4	24.3	–64.5	–59.0	–60.0	24.9	–39.0	–48.2	–66.3
Solv (2 MeLi) [kcal/mol]	MP2	36.8	44.8	40.8	47.3	45.9	47.5	46.3	47.6	55.4	53.4	61.1
ΔE (2 MeLi) [kcal/mol]	CCSD(T)	0	19.6	30.7	23.2	–63.7	–58.4	–59.3	20.1	–35.3	–45.9	–62.6

ception is for **TS2**, which is stabilised by only 4.0 kcal/mol. In the case of the addition reaction path, the various extrema are increasingly stabilised along the reaction path: 10.8, 16.6, 18.6 and 24.3 kcal/mol for **TS4**, **Int**, **TS5** and **Pr4** respectively.

Discussion

The geometries of the various extrema are depicted in Figure 7. In five extrema located on the ring-opening reaction paths (**Pr1**, **Pr2**, **Pr3**, **TS1** and **TS3**), a nearly planar six-membered Li–Me–Li–Me–O is found. No noticeable difference appears among these structures, and the interaction energies with MeLi are similar (44.8–47.5 kcal/mol, Table 4). Model calculations on $H_3COLi(MeLi)_2$ indicate that such a six-membered ring actually corresponds to the most stable geometry. A slightly different geometry (two fused four-membered rings) is found in the **TS2** case and leads to a weaker (40.8 kcal/mol) stabilisation.

In the reactant case (**Rea**), the two electronegative sites (O and carbanionic carbon atom) have to interact with the Li^+ cation and the two MeLi molecules. This should lead to a seven-membered ring, which is expected to be unfavourable. In fact we found a structure in which a five-membered ring (C–Li–Me–Li–O) is fused with a four-membered ring (O–Li–Me–Li). This geometry does not seem to be optimal, and the associated stabilisation energy (36.8 kcal/mol, Table 4) is found to be noticeably less than those of the extrema discussed above.

On the addition pathway, complexations of **Int**, **TS5** and **Pr4** are found to be stabilising by more than 53 kcal/mol, values that are larger than that found for the six-membered ring formation. Examination of the **Pr4** case gives a rationale for this difference. In **Pr4**, the interacting species is Li_2O, which is more polar than the species previously involved. Calculations on the (Li_2O–MeLi) complex give an interaction energy of 60.2 kcal/mol, a value close to that found in the **Pr4** case (61.1 kcal/mol). Similar but less effective interactions between MeLi and the Li_2O moiety are found in the **TS5** (55.4 kcal/mol), **Int** (53.4 kcal/mol) and, to a lesser extent, **TS4** species.

CCSD(T) Calculations

Finally, CCSD(T) calculations were performed on the optimised geometries. The results are displayed in Table 4. As in the case of the interaction with only one MeLi molecule, the energies of the extrema located on the ring-opening reaction paths are slightly modified when the correlation level is increased, except for the energy of **TS1**, which is lowered by 5.5 kcal/mol. Again, the addition reaction path is disturbed more by the increase of the correlation level: all extrema are destabilised by 2–4 kcal/mol except for **TS4**, which is stabilised by 4.8 kcal/mol (Table 4).

At our best level of calculation, we found all the reaction paths to be exothermic by about 60 kcal/mol, **Pr1** and **Pr4** being the most stable products. From a kinetic point of view, the lowest-energy transition states are **TS1** and **TS4**, the energies of which only differ by 0.5 kcal/mol. These two pathways are therefore expected to be competitive. The reaction path leading to **Pr3** is disfavoured by more than 3 kcal/mol, whereas the reaction path passing through **TS2** is strongly disfavoured by more than 10 kcal/mol.

Discussion

The various results [obtained at the CCSD(T) level] with 0, 1 or 2 MeLi molecule(s) are brought together in Table 5. The energetic ordering of the various extrema depends on the number of MeLi molecules taken into account in the calculations. Without any solvating MeLi molecules, the ring-opening reaction leading to **Pr3** is the most favourable pathway.

Complexation by one MeLi molecule has almost no effect on the thermodynamics of the ring-opening reactions. Conversely, the energetic ordering of the transition states changes; with one MeLi, **TS1** is the lowest-energy transition state, whereas it is **TS3** when MeLi is not included in the calculations. The addition reaction path (through **TS4**) is moderately disfavoured, its activation energy being larger by 3.7 kcal/mol than that associated with the preferred ring-opening reaction.

Complexation by a second MeLi molecule noticeably changes the various energy profiles. First, the relative energies of the three ring-opening products are stabilised by 10 kcal/mol because of the weak stabilisation of the reactant. Additional stabilisation up to 25 kcal/mol is found in addition intermediate and product cases (**Int** and **Pr4**), because complexation involves Li_2O. Secondly, of the transition states, **TS3** and **TS4** enjoy stabilisation of about 10 kcal/mol, similar to that of **Pr1**, **Pr2** and **Pr4** and for the same reasons. Weaker stabilisations are found for **TS2**, because of steric repulsion, and **TS1**. In this last case, the smaller stabilisation comes from the large stabilisation energy (8 kcal/mol, Table 5) found by complexation with the first MeLi molecule. As a result the addition reaction becomes competitive with the first ring-opening reaction only when two MeLi molecules are taken into account. This re-

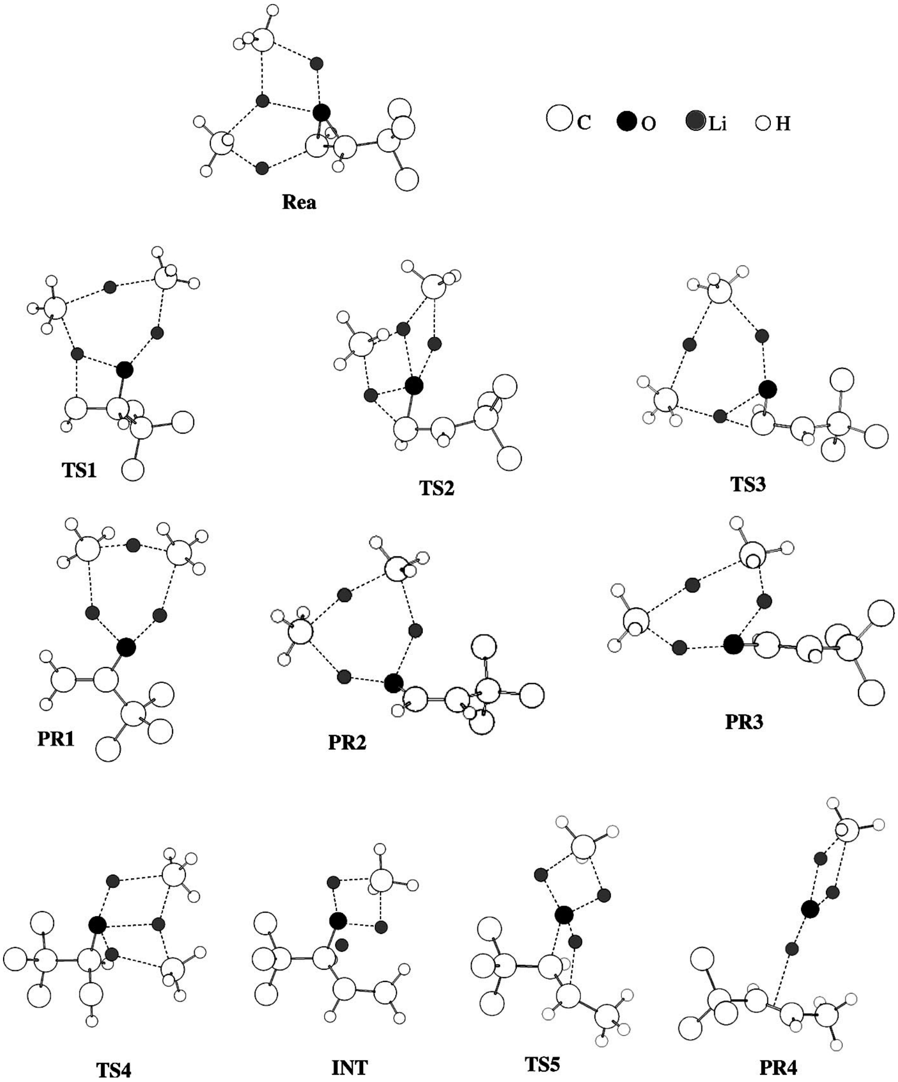


Figure 7. Geometries of the extrema complexed with two MeLi molecules.

Table 5. Relative energies [kcal/mol] of the various extrema at the CCSD(T) level depending on the number of MeLi molecules taken into account.

	Rea	TS1	TS2	TS3	Pr1	Pr2	Pr3	TS4	TS5	Int	Pr4
0 MeLi	0	29.2	32.6	28.2	–53.6	–48.0	–48.0	–	–	–	–
1 MeLi	0	27.3	35.3	33.0	–54.8	–48.0	–50.0	31.0	–16.5	–29.6	–37.5
2 MeLi	0	19.6	30.7	23.2	–63.7	–58.4	–59.3	20.1	–35.3	–45.9	–62.6

sult clearly shows the catalytic effect of the second (third if the MeLi molecule used to give the oxiranyl species is taken into account) MeLi molecule in the addition reaction.

Conclusions

In our study, the ring-opening of the lithium–oxiranyl anion and MeLi addition to this species have been studied at the CCSD(T)//MP2 level with the 6-31G** basis set. Three cases have been considered depending on the number (0, 1 or 2) of MeLi molecules explicitly taken into account in the calculations. In each case, the various minima and transition states have been located and characterised. It has been found that one ring-opening reaction path is favoured when zero or one MeLi molecule is taken into account. The addition reaction path becomes competitive when two MeLi molecules are present in the calculation. Clearly, the second MeLi molecule acts as a catalyst in the addition reaction.

A last comment concerns the intermediacy of a carbene species in the oxiranyl ring-opening. In no case could a reaction intermediate resembling a carbene be located as a secondary minimum. However, transition states such as

TS1 (or **TS4**) present a geometry close to that expected for such species. A similar conclusion has recently been reached[30] in a study of the mechanism of cyclopropanation with metallated carbenoids.

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