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Dimethylberyllium + CO$_2$ $\rightarrow$ Fire!
A DFT and *ab initio* Study into the photon emission observed in a gas phase carbon dioxide activation reaction.

Ross Fairlie and Götz Bucher*

WestCHEM, School of Chemistry, University of Glasgow, Joseph-Black-Building, University Avenue, Glasgow G12 8QQ, United Kingdom

goetz.bucher@glasgow.ac.uk

Abstract

Dimethylberyllium, Me$_2$Be, is known to ignite when the neat compound is reacted with CO$_2$. In this contribution, we present evidence from DFT and *ab initio* calculations demonstrating that while the two-stage gas phase carboxylation of Me$_2$Be to yield beryllium acetate is strongly exothermic, it is not sufficiently so to result in the formation of excited states, as required by a combustion process. The reaction, however, will liberate sufficient heat to drive endothermic unimolecular decomposition reactions. In the case of the reaction of diethylberyllium Et$_2$Be, this results in the formation of beryllium hydride via a β-hydride elimination reaction, and potentially of Be atoms. Pyrolysis of Me$_2$Be, which lacks β-hydrogen atoms, is predicted to give the extremely reactive methyleneberyllium CH$_2$=Be, a ground-state triplet species. All reactive intermediates generated by pyrolysis of either Me$_2$Be or Et$_2$Be are calculated to react with CO$_2$ in exothermic reactions. With one possible exception, however, none of the carboxylation reactions is predicted to be sufficiently exothermic to yield a product in an excited state. The photon emission observed experimentally is rationalized via the oligomerization of monomeric BeO, which was studied up to two different tetramers. Formation of (BeO)$_2$, (BeO)$_3$, and (BeO)$_4$ ring structures was found to be so intensely exothermic that even relatively high-lying (5.6 eV) excited states will be populated with ease. Finally, the reaction of Be atoms with CO$_2$, previously studied by matrix isolation spectroscopy (Andrews, L.; Tague, T. T., Jr., *J. Am. Chem. Soc.* **116**, 1994, 6856-9), was found to proceed via initial formation of a four-membered ring carbene-type structure, which had not been taken into account in the earlier experimental work.

Introduction

Beryllium, the fourth element in the periodic table, shows a fascinating chemistry, which - due to toxicity issues - is underexplored, with very few experimental studies nowadays taking place in academic research.[1] It is neglected in spite of a variety of potential applications. E.g., thin films of beryllium oxide BeO have promise in fabricating metal oxide semiconductor devices (CMOS). For that reason, a number of reports on using volatile organoberyllium compounds in the generation of BeO thin films have appeared very recently. [2,3]

The fact that neutral covalent Be compounds have only four electrons at the Be atom results in numerous interesting bonding situations. In many cases, the electron demand is satisfied via three-centre-two-electron bonds. Thus, dimethylberyllium, as the simplest diorganoberyllium compound, in the solid state has a chain structure involving Be-C-Be three-centre-two-electron bonds,[4] whereas the compound is monomeric in the gas phase.[5,6] Diorganoberyllium compounds in principle show a reactivity similar to organolithium or diorganomagnesium compounds or Grignard reagents. Hence, reaction with ketones would result in formation of tertiary alcohols or in reduction of the ketone,[7] and reaction with carbon dioxide in formation of carboxylic acids.[7] Neat dimethylberyllium, however, has been reported to give a fire upon contact with CO_2.[7] While CO_2 fire extinguishers are known to be unsuitable for extinguishing metal fires, as the thermally activated metals would reduce CO_2,[8] this type of reactivity is not generally known for organometallic reagents. Organolithium reagents, Grignard reagents, organoaluminium compounds will undergo an exothermic reaction with CO_2, but have not been reported to ignite. Due to the inherently very low reactivity of carbon dioxide, it is *a priori* unlikely to undergo reactions that are sufficiently exergonic to result in formation of excited states. Hence, the photon emission reported for the reaction of Me_2Be with CO_2 requires the presence of unusually reactive intermediates, and thus warrants a detailed investigation.

This work will employ modern density functional theory, CASSCF theory and coupled cluster calculations in investigating the mechanisms operative in the gas phase reaction of Me_2Be with CO_2, and will seek an explanation for the photon emission observed in this gas phase reaction. For comparison, we will also investigate the reaction of the closely related diethylberyllium Et_2Be with CO_2.

Computational Methods

All DFT calculations were performed using the *Gaussian09* suite of programs.[9] All stationary points optimised were fully characterised as minima or transition structures by performing a vibrational analysis. DFT methods employed include the B3LYP,[10] M06,[11] and M06-2X[11] functionals, in combination with 6-31G(d),[12] cc-pVTZ[13] or cc-pVQZ[13] basis sets. As the system Me_2Be + CO_2 is fairly small, single point energy calculations at the CCSD(T) level of theory were performed,[14] employing ORCA version 2.9.[15] For some open-shell species, CASSCF[16] calculations were performed, again employing ORCA 2.9, in combination with an SVP basis set.[17]

Results and Discussion

Reactions of dialkylberylliums and alkylacyloxyberylliums with CO_2. As monomeric Me_2Be **1** is a Lewis acid, it is anticipated to complex with the weakly Lewis-basic oxygen atoms of the CO_2 molecule. The resulting complex **3**, however, is weak, with a binding enthalpy between 0 and 2 kcal mol^{-1}, depending on the level of theory employed. At ambient temperature or above, the Gibbs free energy of formation of **3** with respect to free **1** and CO_2 is positive, implying that it is not likely to play a significant role in a combustion process. The gas phase reaction of **1** with CO_2 takes place with a modest activation enthalpy around $\Delta H^{\ddagger} \sim 12$ kcal mol^{-1}, it is considerably exothermic with $\Delta H \sim -30$ kcal mol^{-1}. Methylberyllium acetate **5** can react with a second equivalent of carbon dioxide to yield beryllium diacetate **7**. The thermodynamic driving force for this 2nd step is predicted to slightly exceed ΔH for the first step. The reaction parameters for the analogous reactions of diethylberyllium **2** are similar; with slightly smaller barriers and being very slightly more exothermic, the reactions of **2** and **6** should be even faster than the reactions of **1** and **5**. Scheme **1** shows the

reactions of **1** and **2** with CO_2, Table S1 (see Supporting Information) gives the calculated energies and entropies of activation and reaction, and Figure 1 displays a set of results obtained for the reaction of **1** in graphical fashion.
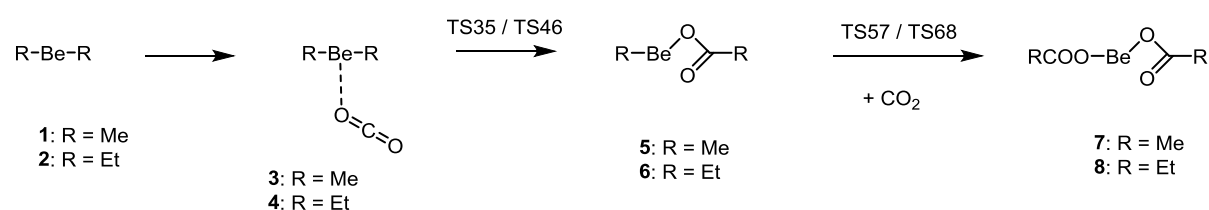
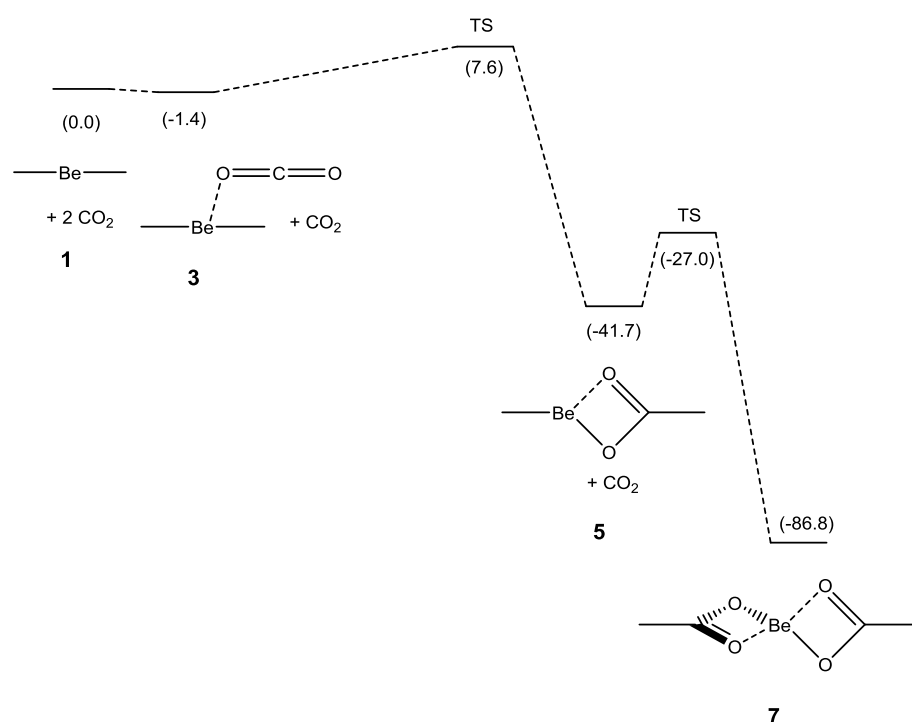**Scheme 1: reactions of 1 and 2 with CO₂.**

Figure 1: Calculated potential energy hypersurface for the reaction of **1** with two equivalents of carbon dioxide (M06-2X/cc-pVQZ). Enthalpies in kcal mol^{-1}, relative to **1** + 2 CO_2 = 0.0 kcal mol^{-1}.

The results clearly demonstrate that the two-stage reaction of dimethyl- and diethylberyllium with two equivalents of CO_2 is considerably exothermic and occurs with small barriers. The results obtained using different DFT methods and basis sets agree qualitatively, and the inexpensive B3LYP/6-31G(d) method fares reasonably well, when the results obtained by the much more expensive M06-2X/cc-pVQZ and CCSD(T) methods are taken as benchmark. However, the energy released does not differ significantly between **1** and **2** (in fact, reactions of **2** and **6** are slightly more exothermic), and it is insufficient to generate excited states resulting in the photon emission observed in a combustion process. The lowest excited states of **5** or **6** are triplet excited states with excitation energies (B3LYP/6-311++G(d,p)//B3LYP/6-31G(d)) of 5.2 eV (**5**) or 4.7 eV (**6**), which is far larger than the energy released in the reactions of **1** or **2** with CO_2 (less than 2 eV). The second stage of carboxylation of **1** or **2** is even more unlikely to result in photon emission, as both monomeric beryllium diacetate **7** and monomeric beryllium dipropionate **8** have still higher calculated excitation energies.[18] Moreover, the reaction sequence results in a significantly negative change in entropy and

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will therefore be progressively disfavoured as the temperature of the system increases.[19] Hence, alternative reaction pathways need to be investigated. As the reactions of **1** / **2** and **5** / **6** with CO_2 are significantly exothermic, these reaction pathways can well be endothermic and have significant activation enthalpies, provided the reaction entropies are favourable.

Figure 2 shows optimized geometries of stationary points in the sequential twofold carboxylation of **1**. In agreement with its very weakly exothermic enthalpy of formation, the weak complex of **1** with CO_2 shows only a slight deviation from the geometry of monomeric **1**, with a close to linear C-Be-C unit. The reaction proceeds in a concerted fashion via a highly asynchronous transition state. The first new bond to be formed is between the beryllium atom and oxygen, whereas the new C-C bond is formed only much later on the reaction coordinate. In the resulting methylberyllium acetate **5**, the Be atom is coordinated in an almost symmetric fashion to both oxygen atoms of the acetate moiety. The following transition state of the reaction of **5** with a 2nd equivalent of CO_2 again is highly asynchronous, the new Be-O bond being formed first. The geometries of stationary points in the analogous reactions of **2** are similar, see the SI for Cartesian coordinates.
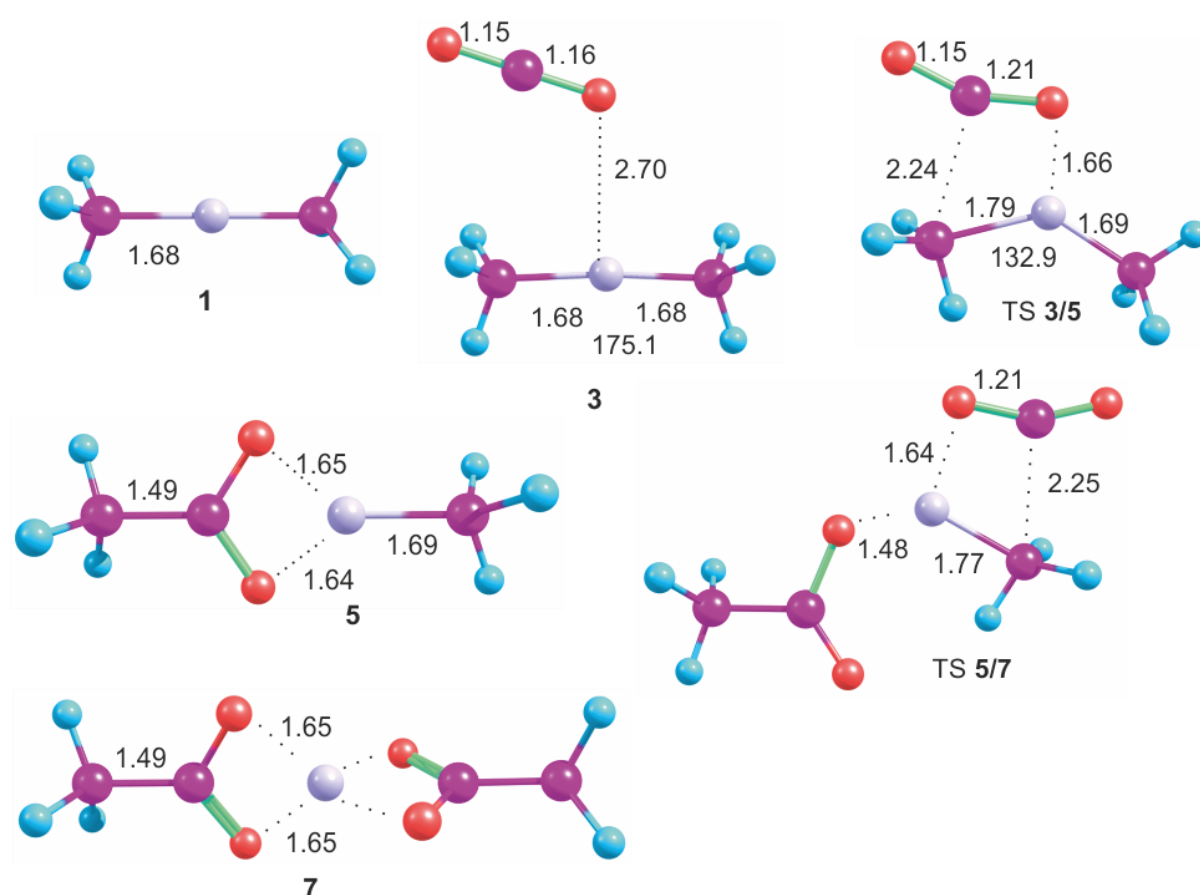

Figure 2: Optimized geometries (M06-2X/cc-pVQZ) of stationary points in the reaction of dimethylberyllium **1** with two equivalents of CO_2. Bond lengths in Å, angles in °. Top left: dimethgylberyllium **1**. Top centre: complex of **1** with CO_2 (**3**). Top right: transition state for reaction of **1** with CO_2. Middle left: monomeric methylberyllium acetate **5**. Middle right: transition state for reaction of **5** with CO_2. Bottom left: monomeric beryllium acetate **7**.

Thermal reactions of dialkylberyllium compounds. At elevated temperatures, dialkylberyllium compounds bearing a β-hydrogen atom have been known to undergo a β-hydride elimination

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reaction. In case of diethylberyllium **2**, this reaction would initially yield ethylberyllium hydride **9** and ethylene, and, in a second step, beryllium dihydride **10** plus another equivalent of ethylene. Hydride **10**, finally, could fragment into a BeH radical **11** and a hydrogen atom, or into a beryllium atom **12** and a dihydrogen molecule. Similarly, **9** could also yield Be and ethane, and **2** could fragment in a Be atom and *n*-butane. Dimethylberyllium **1** does not have β-hydrogen atoms, and therefore cannot undergo the β-hydride elimination reaction. It can, hovever, transfer an α-hydrogen atom, eliminating methane to yield methyleneberyllium **13**, which would be in equilibrium with metallocarbene **14**. Alternatively, **1** could undergo fragmentation into a CH₃Be radical **15** and a methyl radical, or it could fragment into a Be atom and ethane. The α-hydrogen transfer reaction is also available to **2**, yielding ethylideneberyllium **16** and ethane. Carbene complex **16** could both rearrange to metallocarbene **17**, or undergo a β-hydrogen shift yielding vinylberyllium hydride **18**. The latter, finally, could eliminate acetylene to give beryllium dihydride **10**. Scheme **2** shows the reaction pathways outlined here, Table S2 (see Supporting Information) displays the calculated energies and entropies of activation and reaction, and Figure 3 shows selected result in graphic fashion.
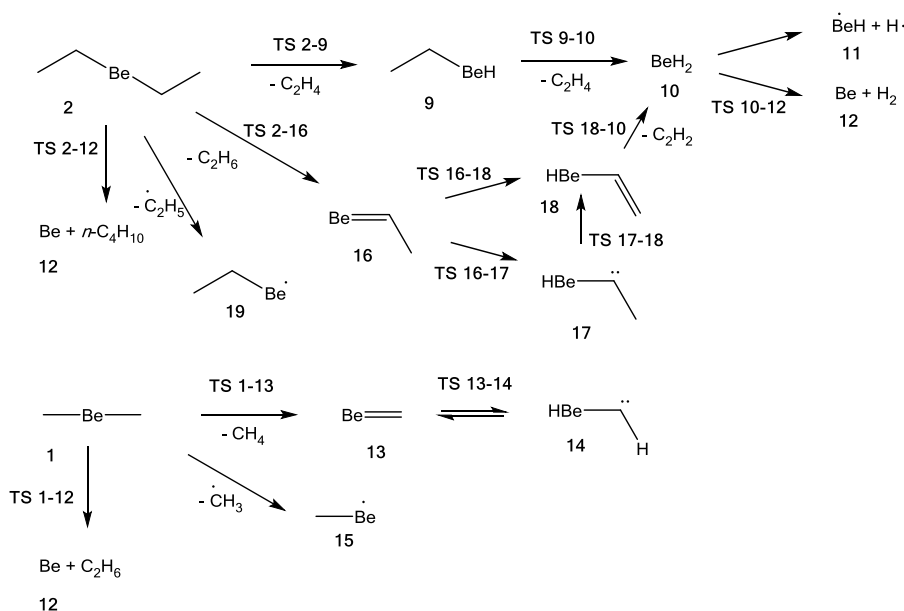
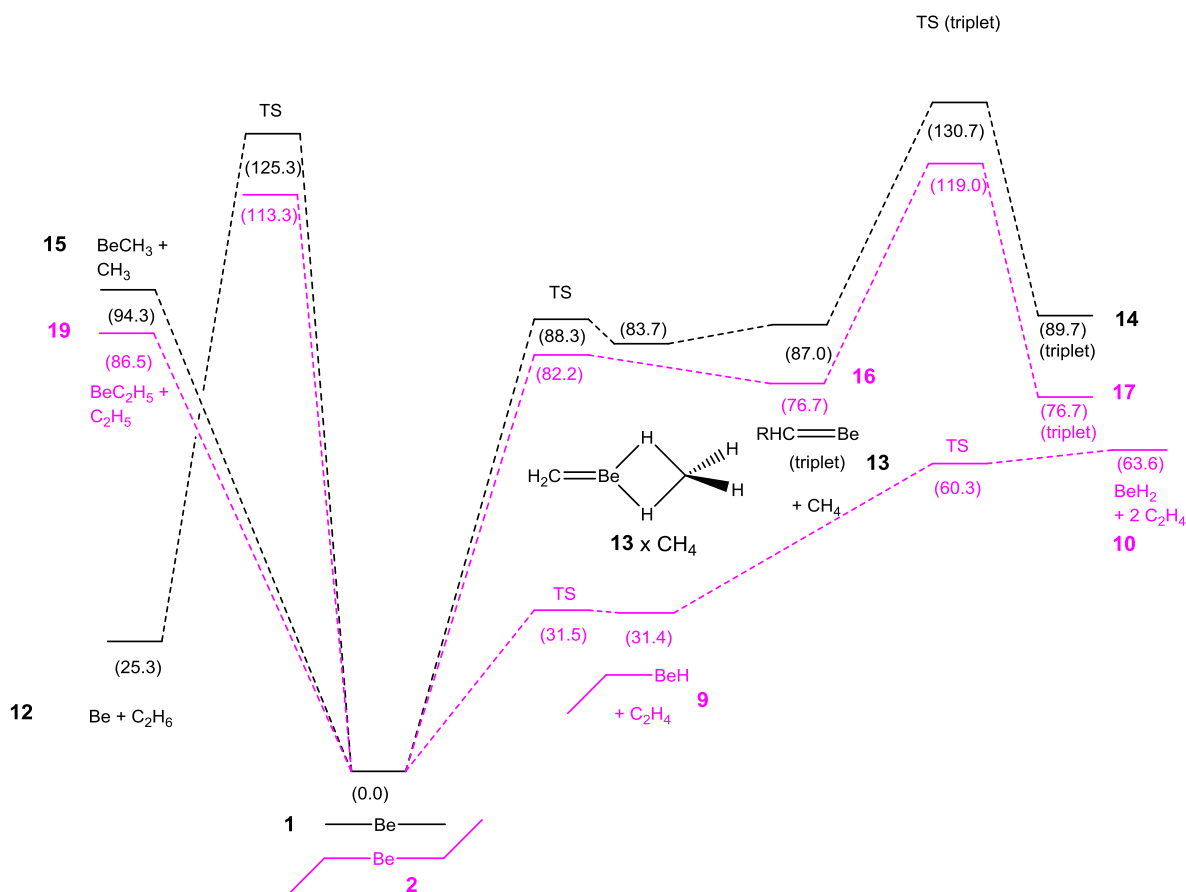**Scheme 2: thermal fragmentation pathways of 2 and 1.**

Figure 3: calculated potential energy hypersurfaces for pyrolysis reactions of dimethylberyllium **1** (black) and diethylberyllium **2** (magenta). Enthalpies in kcal mol^{-1}, relative to **1** or **2** = 0.0 kcal mol^{-1}. Results obtained at the M06-2X/cc-pVQZ level of theory, except for the stationary points involving atomic beryllium (CASSCF(4,6)/SVP).

While the transition states for the reactions **1** → Be + C_2H_6 and **2** → Be + C_4H_{10} could be optimized at the DFT levels employed, the formation of a beryllium atom, which is a species well known for requiring multireference treatment,[20] renders the results questionable. Unfortunately, full-valence CASSCF calculations (which would correspond to an active space of 16 electrons in 18 orbitals for **1**) proved impracticable. As a model reaction we consider the reaction BeH_2 (**10**) → Be + H_2. At the CASSCF(4,6)/SVP (corresponding to a full valence active space) level of theory, this reaction (yielding a complex of a beryllium atom and a dihydrogen molecule) is calculated to be endothermic by ΔH = 13.9 kcal mol^{-1}, with an activation enthalpy $\Delta H^{\ddagger}$ = 82.7 kcal mol^{-1}. At the M06-2X/cc-pVQZ levels of theory, these parameters are obtained as ΔH = 41.6 kcal mol^{-1} and $\Delta H^{\ddagger}$ = 88.7 kcal mol^{-1}. While the energy of the transition state therefore is at most slightly overestimated by the DFT method, the energy of the Be + H_2 complex, with a severe multireference character, is strongly ($\Delta\Delta H$ = 27.7 kcal mol^{-1}) overestimated by DFT. We conclude that the barriers calculated by DFT for the analogous reactions **1** → Be + ethane and **2** → Be + *n*-butane are probably overestimated by up to 6-8 kcal mol^{-1}, which would make them unlikely to compete with the other fragmentation reactions available to **1** and **2**.

The calculations indicate that Me$_2$Be **1** should be far more stable thermally than Et$_2$Be **2** that has the β-hydride elimination pathway available for its decay, which **1** has not. Formation of beryllium hydride **10** from **2**, with stepwise elimination of two molecules of ethene, occurs with a barrier of ca. 33 -35 kcal mol^{-1} per elimination step. The competing formation of ethylideneberyllium **16** is predicted to have a far higher barrier of around 82 kcal mol^{-1}. As the entropies of reaction in both cases are governed by the increase of the number of degrees of freedom in the system, they are comparable. It can be concluded that beryllium alkylidenes will not be formed from **2** in a thermal process (and very likely not from any dialkylberyllium containing β-hydrogen atoms). In case of the thermal decay of dimethylberyllium **1**, the elimination of methane, yielding methyleneberyllium **13**, is predicted to be less energetically costly (ΔG = 79 kcal mol^{-1}, ΔG‡ = 89 kcal mol^{-1}) than homolytic cleavage of the C-Be bond, with ΔG = 85 kcal mol^{-1}. Nevertheless, the values are close enough that at the temperatures required to induce these reactions, both will probably take place, and free radical reaction pathways may also play a role. Rearrangement of methyleneberyllium **13** to berylla-carbene **14**, on the other hand, is unlikely to occur, as this species is slightly higher in energy than **13**, less favorable entropically, and is formed via a very high-energy transition state.
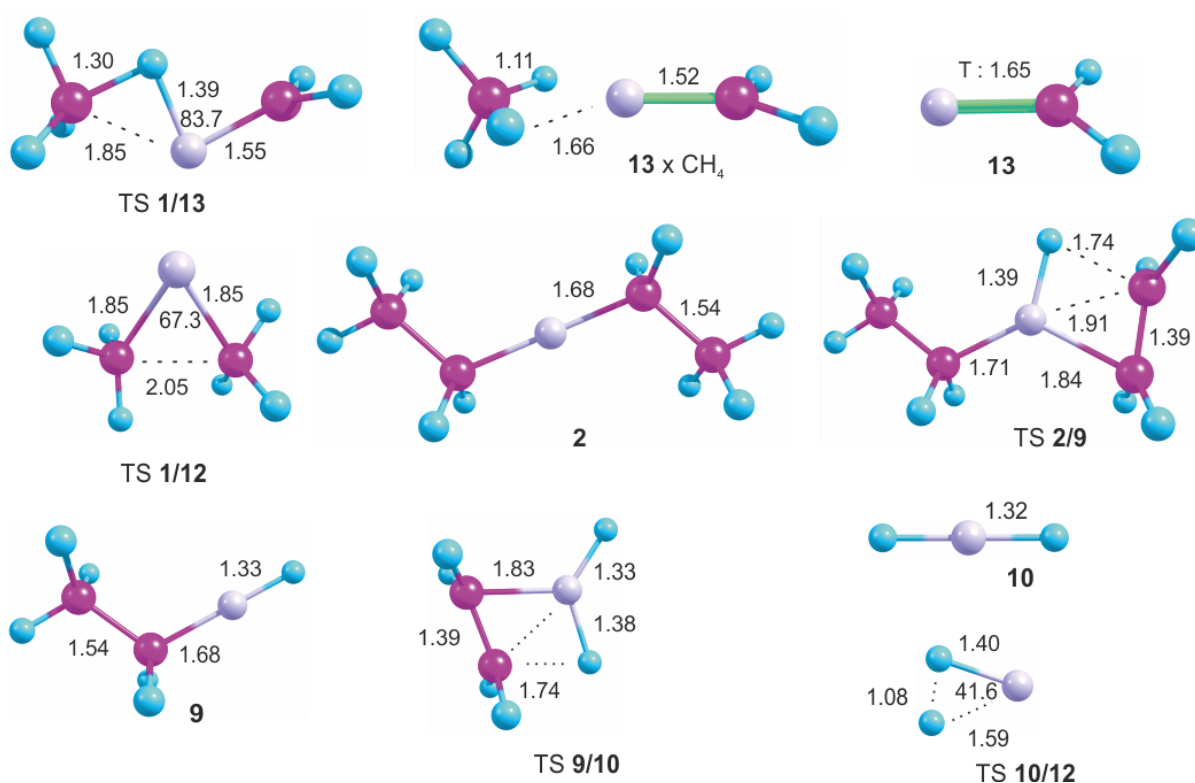

Figure 4: Calculated geometries (M06-2X/cc-pVQZ) of selected stationary points in the pyrolysis reactions of **1** and **2**. Bond lengths in Å, angles in °. Top left: TS **1** → **13**. (For the geometry of **1**, see Figure 1, bottom right). Top centre: complex of **13** with CH$_4$ (singlet state). Top right: **13** (triplet ground state). Middle left: TS **1** → Be + ethane. Middle centre: **2**. Middle right: TS **2** → **9** + ethene. Bottom left: 9. Bottom centre: TS **9** → **10** + ethene. Bottom right top: **10**. Bottom right bottom: TS **10** → **12** + H$_2$ (CASSCF(4,6)/SVP).

As shown in Figure 4, the transition state for rearrangement of **1** into a complex of singlet **13** with methane has significant Be-H bonding character. One of the new C-H-Be three-center two-electron bonds is largely formed at the stage of this TS, with a Be-H distance of only 1.39 Å. In the resulting

complex of singlet **13** with methane, the Be-H distances are significantly larger (1.66 Å). The TS for elimination of ethane from **1** to yield a Be atom has a typical C-C distance of 2.05 Å. Its structure, a Be-C-C triangle, is similar to the structure of the TS for elimination of H_2 from beryllium hydride **10**. The transition states for the two β-hydride elimination reactions of **2** and **9**, finally, again are late transition states of asynchronous concerted reactions. The new Be-H bonds form first, whereas the Be-C bonds significantly cleave only late on the reaction coordinate. Our value for the Be=C bond length in triplet **13**, finally, are in agreement with the results of both early[21,22] and recent, very high-level[23] calculations.

Reactions of thermal fragmentation products with CO_2. Among the species formed in the thermal fragmentation reactions of **1** and **2**, several can also react with CO_2. Beryllium dihydride **10** can undergo a twofold carboxylation, yielding beryllium formate (Scheme 3). Likewise, ethylberyllium hydride **9** can undergo a twofold carboxylation, resulting in a mixed beryllium formate / propionate monomer. As with the formation of **5**-**8**, these reactions are not expected to be sufficiently exothermic to result in the emission of light.[19] With the exception of the beryllium atom **12**, the reaction intermediates predicted to be formed in the thermal fragmentation of **1** lie far higher in energy and therefore have more potential to react with CO_2 in a reaction producing an excited state capable of photon emission. Reaction of methyleneberyllium **13** with CO_2 is predicted to yield a strained beryllacyclobutanone **29**, followed by reaction with a second equivalent of CO_2 to yield monomeric beryllium malonate **30** (Scheme 4). The reaction of Be atoms **12** with CO_2 and part of the potential energy hypersurface of this reaction had already been described in previous publications.[24,25] In addition to the minima previously observed experimentally and described computationally (**26** and **27**), we have identified the cyclic isomers **24** and **25** as stationary points.
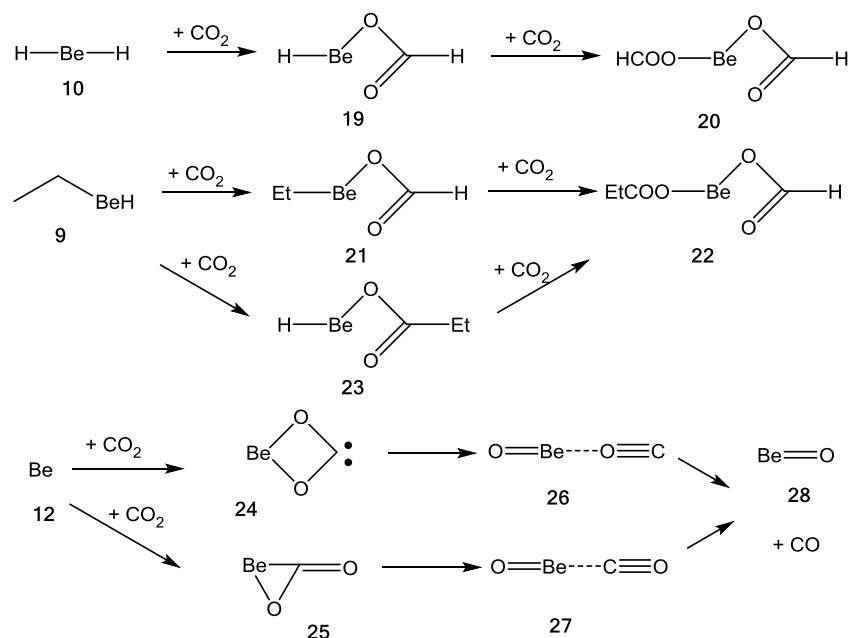
Scheme 3: **Reactions of fragmentation products of 2 with CO_2 and possible follow-up reactions.**
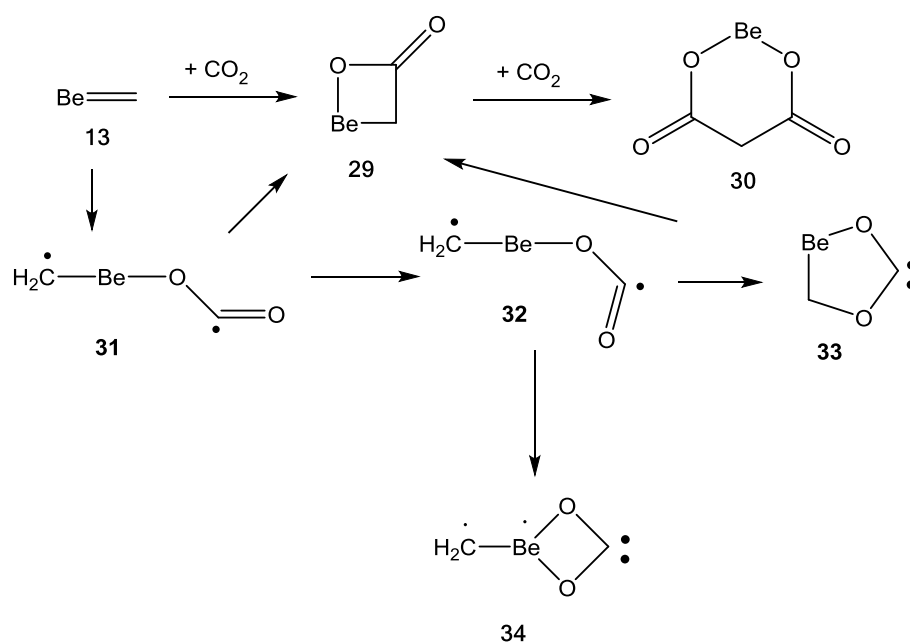
Scheme 4: Reactions of 13 with CO_2 and possible follow-up reactions
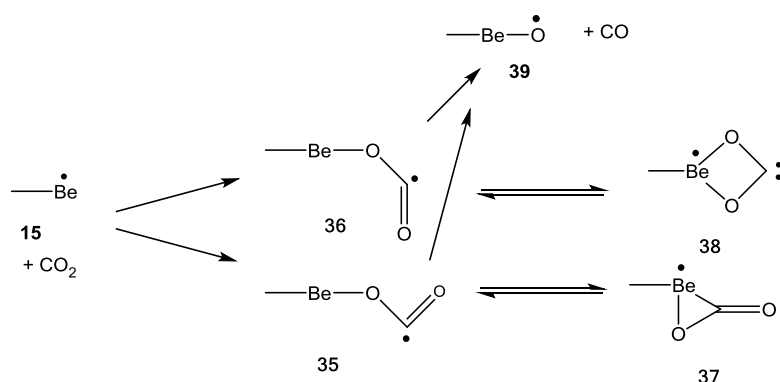
Scheme 5: Reactions of 15 with CO_2 and possible follow-up reactions.

It is noted that intermediates such as **16**, **17**, **18**, **19**, or **14**, although likely to undergo a facile reaction with CO_2 once formed, are not considered here, as they are not likely to be formed in the first place due to competing fragmentation reactions of **1** and **2** that are more favorable in terms of both enthalpy and entropy. Table S3 (see Supporting Information) lists the calculated electronic energies, enthalpies, entropies, and free energies of reaction.

The results shown in Table S3 indicate that any reactive beryllium species formed by pyrolysis of either **1** or **2** will readily react with CO_2. In case of **2**, where thermal decay of the precursor will preferentially result in the generation of beryllium hydride **10**, the formation of hydridoberylliumformate **19** and beryllium formate **20** will liberate ca. 40 -50 kcal mol^{-1} of energy per carboxylation step, similar to the analogous reactions of **1** and **2**. More interesting is the reaction of methyleneberyllium **13** with CO_2, see Figure 5. This reaction initially yields a triplet biradical **31/32**. Depending on its conformation, it can undergo a strongly exothermic cyclization to berylla-β-lactone **29**, which will be followed by a second strongly exothermic carboxylation step to yield beryllium malonate monomer **30**. Other possible intermediates like biradical **34** or carbene **33** are

higher in energy and therefore unlikely to play a role in the reaction. Starting from **13**, formation of **30** is calculated to be exothermic by ca. 120 kcal mol^{-1}. Even formation of **29**, which - judging from its significantly exothermic complex formation with CO_2 - still is a very high-energy intermediate, is very strongly exothermic. In fact, the energy liberated in this step is likely sufficient to generate at least part of the **29** formed in an excited state, thus offering the potential for release of photons.[26]
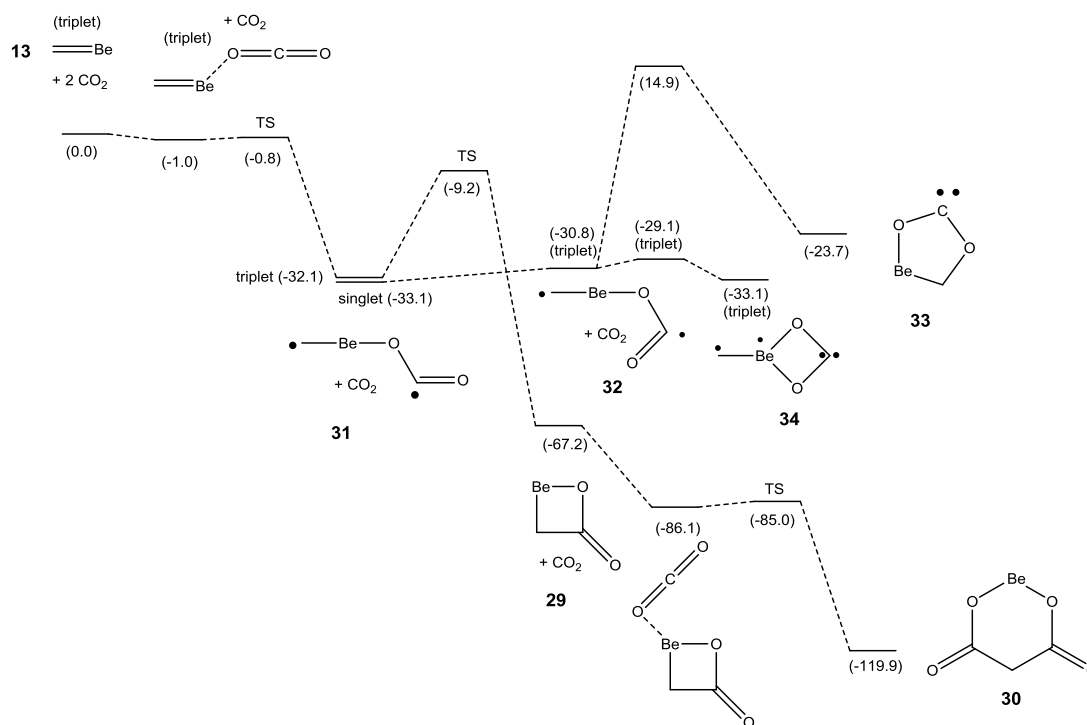

Figure 5: calculated potential energy hypersurface for the reaction of **13** with two equivalents of carbon dioxide (M06-2X/cc-pVQZ). Enthalpies in kcal mol^{-1}, relative to **13** + 2 CO_2 = 0.0 kcal mol^{-1}.
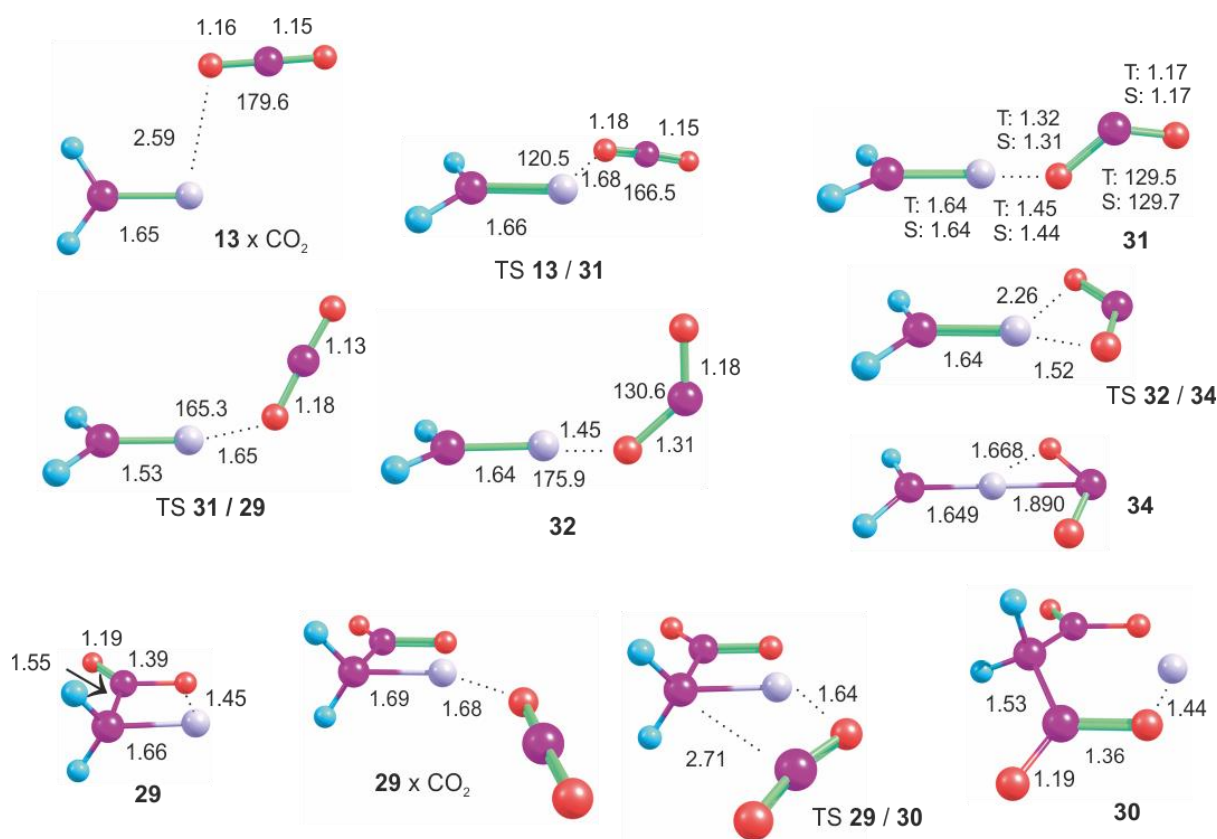
Figure 6: Calculated geometries (M06-2X/cc-pVQZ) of selected stationary points in the carboxylation of methyleneberyllium **13**. Top left: complex of triplet **13** with CO_2. Top middle: transition state (triplet) for formation of *trans* biradical **31**. Top right: *trans* biradical **31**, geometric parameters given for both the singlet and triplet state. Center left: transition state for formation of berylladioxetanone **29**. Center middle: *cis* triplet biradical **32**. Center right top: transition state for formation of triplet biradical **34**. Center right bottom: triplet biradical **34**. Bottom left: berylladioxetanone **29**. Bottom 2nd from the left: complex of **29** with CO_2. Bottom 2nd from the right: transition state for formation of beryllium malonate **30**. Bottom right: beryllium malonate **30**.

Triplet **13** only forms a very weak, van-der-Waals type complex with CO_2. However, the potential energy hypersurface (PES), even on the triplet spin manifold, is extremely shallow, and an approach of one of the CO_2 oxygen atoms from 2.59 Å to 1.68 Å, as in the TS for the formation of **31**, requires almost no activation energy. On the singlet PES, a weak complex between **13** and CO_2 is no minimum structure, and singlet **31** is predicted to be formed without barrier. Depending on the amount of HF exchange, singlet **31** is found to have a non-planar C_S-symmetric geometry (B3LYP and M06-2X, as shown in Figure 6), or a planar C_S symmetric geometry (CO_2 moiety in the plane of the CH_2Be unit, M06) No transition state could be localized for interconversion of the *trans*- (**31**) and *cis*- (**32**) conformers of the CH_2Be-OCO biradical. The *cis*-conformer **32** is predicted to be a minimum structure only on the triplet spin manifold, whereas an attempted optimization on the singlet spin manifold converged to the *trans*-biradical **31**. Biradical **32** can undergo two reactions, yielding either the arrow-shaped triplet biradical **34**, or the singlet carbene **33**. Neither of these reactions is significantly exothermic. *Trans*-biradical **31** can cyclize to yield beryllaoxetanone **29**. The transition state of this concerted, yet extremely asynchronous reaction essentially amounts to a slight loosening of the Be-O bond in singlet **31**, coupled with a slight approach of the carbon atom in CO_2

towards the methylene carbon of **13**. After the TS, the reaction coordinate follows a path of C-C approach until **29** is formed.[27] Four-membered ring **29** forms a very strong complex with CO_2, with a very close Be-O contact calculated as only 1.68 Å. To reach the TS for formation of beryllium malonate **30**, only a very small degree of Be-O approach is still required, whereas the newly forming C-C bond is almost undeveloped in this TS.

Atomic beryllium, formed from **2** via beryllium hydride **10**, or from **1** by concerted elimination of ethane or stepwise loss of two methyl radicals, has long been known to react with CO_2. Laser-ablated Be atoms, matrix isolated in Ar, were demonstrated to react with carbon dioxide to yield oxoberyllium carbonyls **26** and **27**.This reaction probably takes place in the condensation zone, and may involve excited states of Be atoms.[24,25] In addition to these species, we identified the beryllacyclic carbene **24** and the berylla-α-lactone **25** as minima which had not yet been described in the literature, see Scheme 3. Importantly, it is not the known **26** or **27** that are predicted to be the lowest-energy species on the $BeCO_2$ potential energy hypersurface, but rather the four-membered ring carbene **24**. The infrared spectrum of **24** is calculated (by all three DFT methods employed, see SI) to only show bands at wavenumbers below 1300 cm^{-1}. In the original publication on the characterization of **26/27** by matrix isolation spectroscopy,[24] however, experimental data were only shown above this range. The sequences Be + $CO_2 \rightarrow$ **24** $\rightarrow$ **26** and Be + $CO_2 \rightarrow$ **25** $\rightarrow$ **27** represent logical pathways for formation of the oxoberyllium carbonyls. We therefore suggest that **24** and **25** were indeed formed upon reaction of Be with CO_2 in Ar matrix, but had not been identified in the original work. We note that four-membered ring carbenes similar to **24**, containing a magnesium instead of a beryllium ring atom, have been observed in mass spectrometry experiments,[28-30] and that there is also evidence for formation of magnesium-CO_2 adducts similar to **25**.[29]Figure 7 shows a graphical representation of some of the thermochemical data, and Figure 8 calculated geometries.
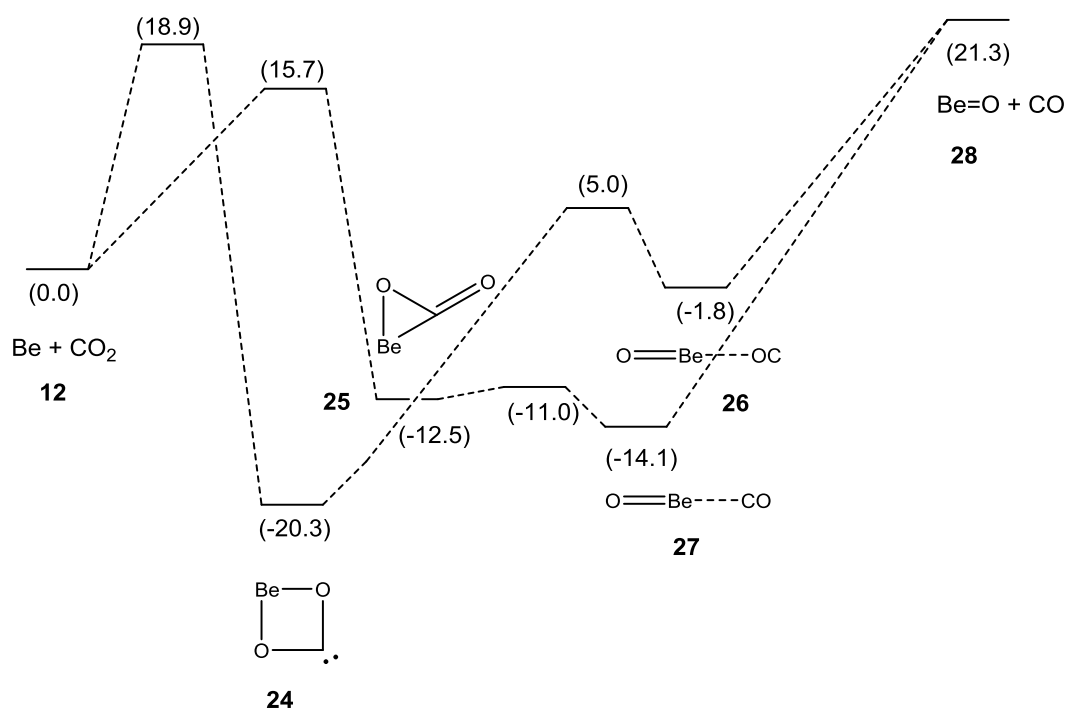

Figure 7: calculated potential energy hypersurface (M06-2X/cc-pVQZ) for the reaction of atomic beryllium **12** with CO_2. Enthalpies in kcal mol^{-1}, relative to **12** + CO_2 = 0.0 kcal mol^{-1}. Please note the

cautionary remark below concerning the validity of the reference energy for the system of a separate Be atom / CO_2 molecule.

As far as the data in Figure 7 as well as in Table S3 are concerned, we note that the energy of the reference point (atomic beryllium + CO_2) cannot reliably be calculated at the DFT level of theory employed. Due to its multireference character, the energy of a Be atom is overestimated by DFT, possibly by as much as ca. 28 kcal mol^{-1} (see above). The results shown above also indicate that the energies of the transition states for its two reactions with CO_2 might also be overestimated by DFT, but to a significantly lesser degree. In spite of these limitations, the results presented clearly indicate that the beryllium-carbene **24** is the global minimum on the $BeCO_2$ potential energy hypersurface. Formation of the three-membered ring **25** is predicted to be thermodynamically less favorable, but should be kinetically favored due a smaller activation enthalpy involved in its formation.
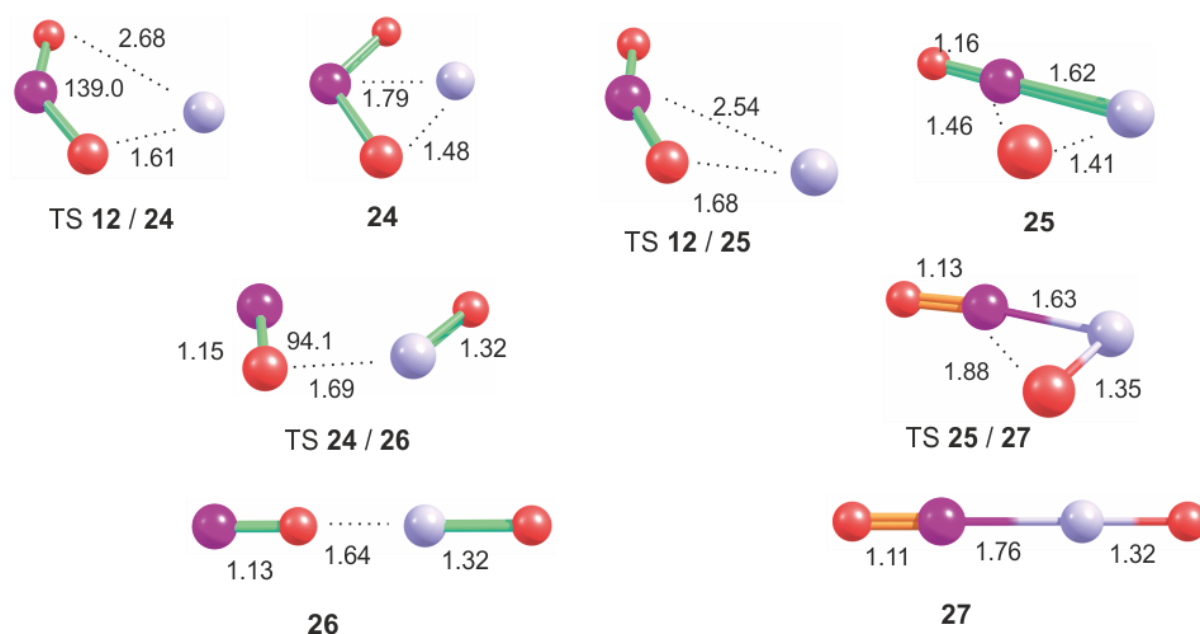

Figure 8: Calculated geometries (M06-2X/cc-pVQZ) of stationary points in the carboxylation of atomic beryllium **12**. Top left: transition state for formation of carbene **24**. Top 2nd from the left: carbene **24**. Top 2nd from the right: transition state for formation of berylla-α-lactone **25**. Top right: berylla-α-lactone **25**. Middle left: transition state for formation of CO-BeO **26**. Bottom left: CO-BeO **26**. Middle right: transition state for formation of OC-BeO **27**. Bottom right: OC-BeO **27**.

Two distinct transition states could be localized for formation of four-membered ring **24** and three-membered ring **25**. Both transition states occur rather late on the reaction coordinate, with significant bonding between beryllium and oxygen already present. Formation of four-membered ring carbene **24** is predicted to be favored both kinetically and thermodynamically. The calculated structure of **24** is remarkable in that the cross-ring distance between beryllium and carbon is very short (r_{Be-C} = 1.79 Å), which is below the van-der-Waals radius of carbon alone. Very likely, the structure is stabilized by interaction of the back lobe of the carbon lone pair with an empty orbital present at the beryllium atom.

The methylberyllium radical **15** is less likely to be formed from **1** than triplet methyleneberyllium **13**. However, **15** (plus methyl) and **13** (plus methane) are sufficiently close in energy to warrant an

investigation of the reaction of **15** with CO_2. In analogy with the reaction of **13**, reaction of **15** with CO_2 is predicted to initially yield a free radical **35/36** (see Scheme 5). These species can then undergo a cyclization to **37** or **38**, or lose carbon monoxide to yield methylberylliumoxy **39**. We note that there is a discrepancy between the calculated stabilities of **35/36** vs. **37/38**, if the results of DFT calculations are compared with the CCSD(T) single point energies, with CCSD(T) predicting a far larger relative stability of the ring-closed isomers. In addition, the DFT methods give differing results about the minimum structure nature of the ring-closed isomers. At the M06-2X/cc-pVQZ level of theory, only the four-membered ring isomer **38** is predicted to be a minimum structure, wheras the closely related M06/cc-pVQZ methods predicts the three-membered ring structure **37** to be an energy minimum, but not **38**. This indicates that the use of CCSD(T) optimizations might be required in this system, which however was beyond the scope of the current investigation. In any event, under pyrolysis conditions, the entropically highly favorable formation of **39** will very likely prevail.[31] Figure 9 shows a graphical representation of thermochemical data, and Figure 10 shows optimized structures.
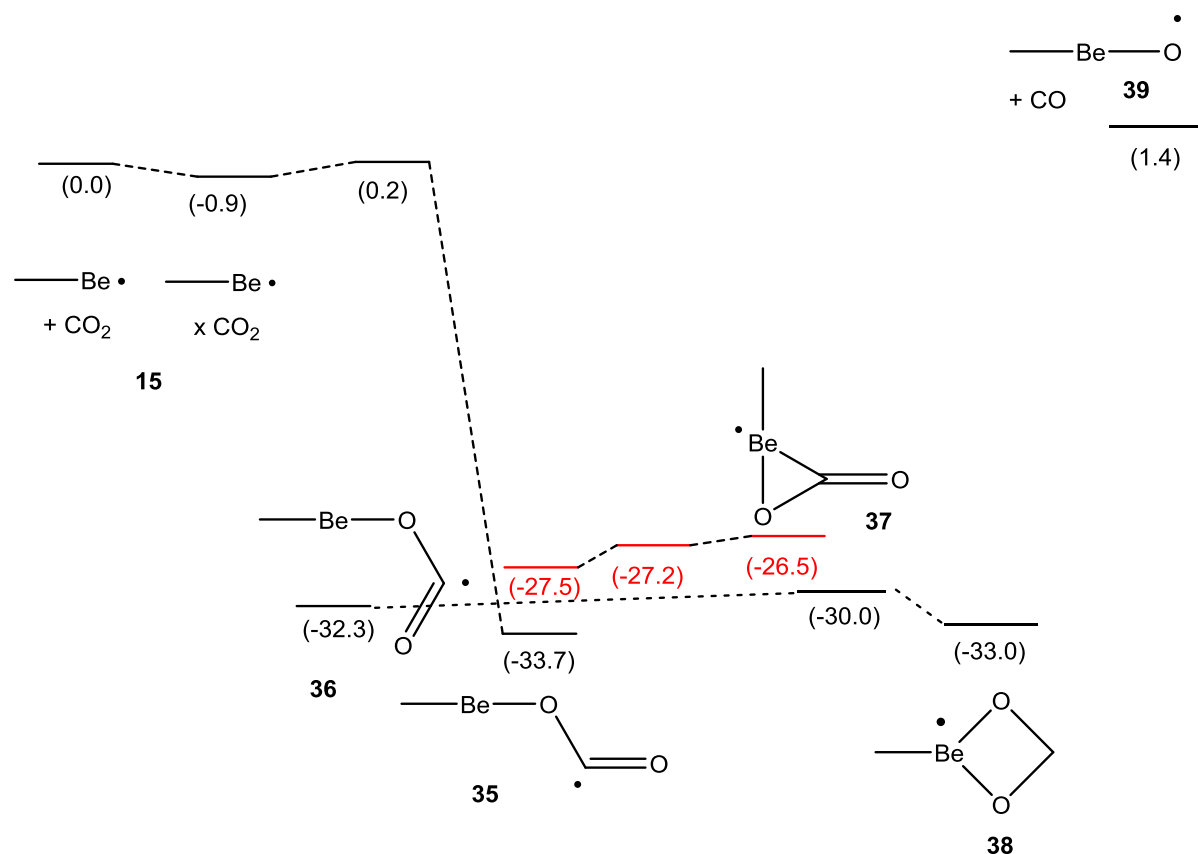

Figure 9: calculated potential energy hypersurface (black: M06-2X/cc-pVQZ, red: M06/cc-pVQZ) for the reaction of methylberyllium radical **15** with CO_2. Enthalpies in kcal mol^{-1}, relative to **15** + CO_2 = 0.0 kcal mol^{-1}.
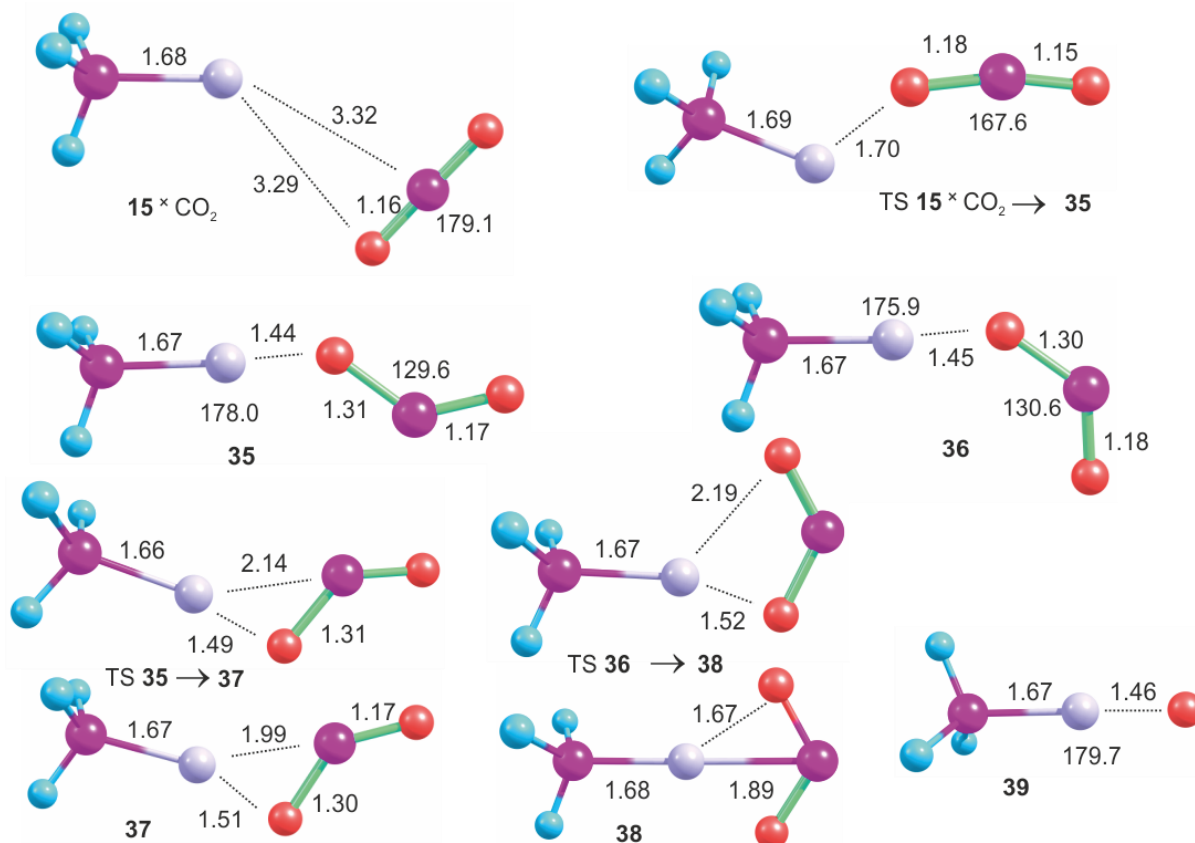
Figure 10: Calculated geometries (all M06-2X/cc-pVQZ, unless indicated otherwise) of stationary points in the carboxylation of methylberyllium radical **15**. Top left: complex of **15** with CO_2. Top right: transition state for the formation of **35**. 2nd Row left: s-*trans* CO_2 adduct **35**. 2nd Row right: s-*cis* CO_2 adduct **36**. 3rd Row left: transition state for the formation of **37** (M06/cc-pVQZ). 3rd Row middle: transition state for the formation of **38**. Bottom left: 3-membered ring **37** (M06/cc-pVQZ). Bottom middle: 4-membered ring **38**. Bottom right: methylberylliumoxy radical **39**.

The calculations indicate that the initially formed complex of **15** with CO_2, in agreement with its extremely weakly negative enthalpy of formation, only shows very little interaction between the two fragments. The Be-O bond is already fairly short (R_{Be-O} = 1.70 Å) in the very low-energy transition state for formation of s-*trans* adduct radical **35**, indicating a very shallow PES with respect to this parameter. The s-*cis* adduct radical **36**, which is predicted to be slightly higher in energy than **35**, differs from the latter essentially only in the Be-O-C-O dihedral angle. It is noted that we have been unable to locate transition structures for the formation of **36** from **15** and CO_2, or from **35** by isomerization. Given the very small calculated barriers for the ring-closing reactions **35** → **37** and **36** →**38**, the geometric changes required to reach the transition structures for these reactions are quite substantial, with significant changes in bond angles required. This again is evidence for the very shallow (caldera-type) nature of the **15** + CO_2 PES.

To summarize this section, reaction of both **1** and **2** with CO_2 is calculated to be sufficiently exothermic to strongly heat up the reaction mixture, in particular in the absence of a solvent acting as a heat sink. The energy released is predicted to be sufficient to drive strongly endothermic thermal breakdown of the precursor molecules. As a result, highly reactive intermediates such as beryllium hydride **10**, atomic beryllium **12**, methylene beryllium **13**, or methylberyllium radical **15**

will be formed that all can undergo further highly exothermic reaction with CO_2. With the possible exception of the berylla-β-lactone **29**, however, none of the carboxylation products formed will carry sufficient excess energy to be formed in an excited state, as required for photon emission. Therefore, another chemical reaction must be responsible for the combustion processes observed experimentally.

Oligomerization of BeO: the driving force of the combustion process. Monomeric beryllium oxide BeO **28** is an extraordinarily reactive species and probably the strongest existing Lewis acid. It will form Lewis acid / base complexes even with the light noble gases, and readily reacts with CO_2 or methane.[32,33,25b] In line with its extreme reactivity, its formation, e.g. by loss of CO from **26** or **27** or of a methyl radical from **39**, is calculated to be endothermic in all reactions considered here. At high temperatures, however, the entropic gain associated with the dissociation of its adducts will outweigh their enthalpic stabilisation, and **28** will be formed. Figure 11 shows some representative data.
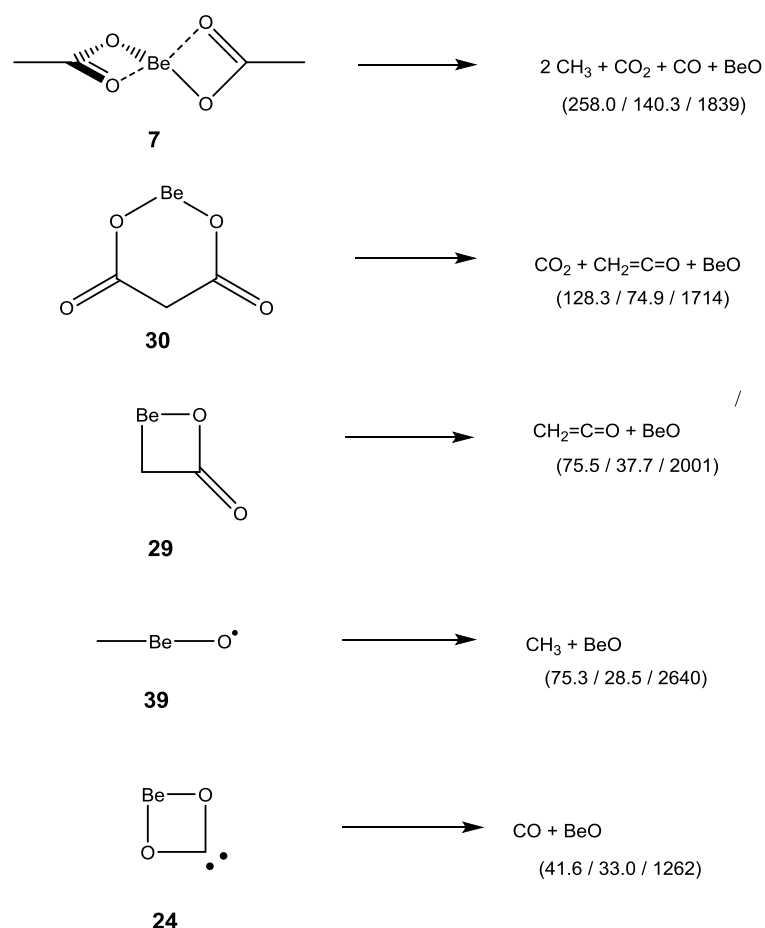

Figure 11: Fragmentation reactions yielding monomeric BeO **28**. In brackets: (enthalpy change / entropy change / temperature at which ΔG of the reaction = 0 kcal mol^{-1}). Enthalpies in kcal mol^{-1}, entropies in cal mol^{-1} K^{-1}, temperatures in K.

The data shown in Figure 11 suggest that initially, it should be species like **24** or **30** that will act as source of **28**. However, given sufficiently high temperatures, essentially all species dealt with here that contain a Be-O bond will yield **28**.

Once **28** is formed, its oligo- and polymerization, eventually yielding bulk crystalline beryllia $(BeO)_n$, will liberate an enormous amount of energy in form of heat and photons. The published lattice energy of beryllia is a huge 1079 kcal mol^{-1}.[34] Even the formation of small fragments of the BeO lattice, such as its dimer Be_2O_2 **40** and its trimer Be_3O_3 **41** can thus be expected to occur in reactions that are highly exothermic. In this work, we have studied the dimerization of **28** to yield **40**, the subsequent addition of a third equivalent of **28** to yield six-membered ring **41**, and the addition of a fourth equivalent of **28** to yield either the eight-membered ring **42** or the cubane-type cluster **43** (Scheme 5). The dimerization of **28** to yield the four-membered ring **40** is calculated (M06-2X/cc-pVQZ) to be exothermic by $\Delta H = -172.2$ kcal mol^{-1}. The S_1 state of **40** is calculated (TD-B3LYP/6-311++G(2df,p)//M06-2X/cc-pVQZ) to have an energy of 3.3 eV above S_0, which is less than half of the energy liberated in the reaction, meaning that **40** will very likely be formed in an excited state.[33b] Unsurprisingly, dimerization of **28** is found to be barrierless. Addition of a further molecule of **28** to **40** yields the cyclic trimer **41**, again in a barrierless and even more exothermic (M06-2X/cc-pVQZ: $\Delta H = -202.6$ kcal mol^{-1}) reaction. This reaction also is more than exothermic enough for **41** to be formed in an excited state (TD-B3LYP, as above: S_1: 5.6 eV). The final step of the sequence considered here is the reaction of **41** with a fourth equivalent of **28** to yield either **42** or **43**. At the same level of theory, formation of **42** is calculated to be exothermic by $\Delta H = -140.7$ kcal mol^{-1}, which is still sufficient to populate the lowest excited singlet state of **42** (S_1: 5.9 eV or 135.7 kcal mol^{-1}). Formation of the cubane-type cluster **43** is predicted to be less favorable ($\Delta H = -105.5$ kcal mol^{-1}, S_1: 5.5 eV or 126.5 kcal mol^{-1}). Bulk beryllia BeO is known to crystallize in a wurtzite structure, with a tetrahedral coordination sphere around both Be and O, maximizing Be-O interaction. In case of larger BeO clusters, therefore, it is anticipated that three-dimensional structures will be favored over ring structures, probably already for clusters not much larger than the ones treated here.[35]
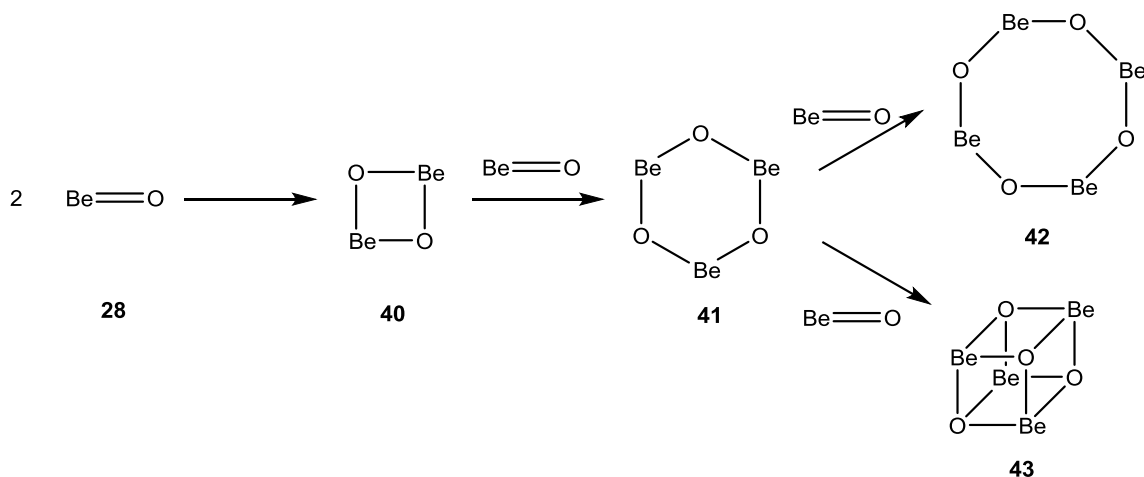
Scheme 5: reactions in the oligomerization of **28**.

Conclusion

The gas-phase reaction of both dimethylberyllium **1** and diethylberyllium **2** with carbon dioxide is predicted to be sufficiently exothermic to significantly heat up the system, while it should not result in formation of products in excited states. In a high temperature regime, both **1** and **2** will undergo unimolecular decomposition reactions. In case of **2**, the pyrolysis will preferentially yield beryllium

hydride via β-hydride elimination reactions, and eventually atomic beryllium. In case of the pyrolysis of **1**, where β-hydride elimination is not an option, the extremely reactive beryllium carbene **13**, a triplet ground state molecule, is predicted to be formed. Simple Be-C bond homolysis, resulting in formation of the $BeCH_3$ radical **15**, also represents a viable pathway for decomposition of **1** at high temperatures. All reactive intermediates formed in the thermal decomposition of both **1** and **2** are predicted to react with CO_2 in highly exothermic reactions. However, with the possible exception of the formation of the beryllaoxetanone **29**, none of them are calculated to supply sufficient excess energy for the product to be formed in an excited state. Photon emission, however, is predicted to result from the oligomerization of monomeric beryllium oxide **28**. Formation of dimer **40**, trimer **41**, and cyclic tetramer **42** in each case is sufficiently exothermic for excited states to be populated, rationalizing the photon emission experimentally observed in the gas phase reaction of **1** with CO_2.

Acknowledgement

Supporting Information:

Tables S1-S3 containing calculated thermochemical data of stationary points investigated, Cartesian coordinates of stationary points optimized, energies.

Footnotes and References:

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