Catalysis of Ethylene Dimerization by Complexation with Metal Radical Cations: An ab Initio Study

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Abstract: The 2s + 2s cycloaddition of ethylene, a forbidden Woodward–Hoffmann type closed-shell reaction, is illustrated by ab initio calculations to be catalyzed by complexation with Be$^{\bullet+}$. The reaction path calculated proceeds via a metallacyclopentane radical cation intermediate and two successive 1,2-hydrogen shifts to form the isomeric butenes. The possible reaction to cyclobutane by formation of a second carbon–carbon bond from the metallacyclopentane has also been examined. The complexed dimerization reaction is found to be exothermic for all products (26.3 kcal mol^{-1} for 1-butene, 27.9 kcal mol^{-1} for cis-2-butene, 29.5 kcal mol^{-1} for trans-2-butene, and 21.3 kcal mol^{-1} for cyclobutane) with no point on any of the reaction paths higher in energy than the starting point, Be$^{\bullet+}$ + 2C$_2$H$_4$. Remarkable parallels to transition-metal-catalyzed dimerizations are found.

Introduction

Among others, Bauld,[1] Haselbach,[2] Roth,[3] and Dinnocenzo[4] have recently demonstrated that one-electron oxidation can accelerate a variety of Woodward–Hoffmann type reactions remarkably. Recent reviews by Bally[5] and Chanon et al.[6] give further examples. Ab initio molecular orbital calculations[7,8] have been used widely to investigate these reactions. The electronic flexibility gained by the presence of a singly occupied orbital often leads to low activation energies, as found in many neutral radical reactions,[9] and the inclusion of a charge, which favors one- and three-electron bonding,[10] often leads to even more facile reactions. This latter effect was recently demonstrated theoretically for the addition of the methyl radical to ethylene[11] and for the 1,2-halogen shift in β-halogenoalkyl radicals[12] by complexation of one reactant to a lithium cation. The calculated barriers are lowered significantly, an effect that is expected to be general for radical reactions involving odd-electron bonds in the transition state.[13] Additionally, this effect has recently been observed experimentally.[14] It has also been shown by ab initio calculations that triplet reactions such as these involving ground-state dioxygen, ^{3}O$_2$, can be catalyzed by complexation of the oxygen molecule with a lithium cation.[15] However, this type of catalysis is not limited to introducing charge into a radical reaction. In principle, it is also possible to introduce both charge and radical character into a closed-shell reaction by complexation with a doublet metal cation. We have used ab initio calculations on the 1,3-hydrogen shift in propene,[16] to show that

Scheme I^a
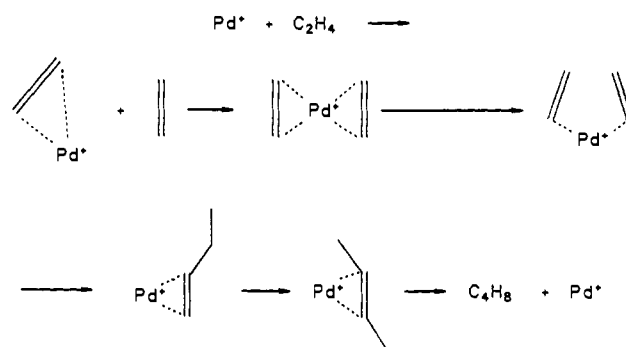
^{a}Schematic representation of the proposed reaction mechanism for the ethylene dimerization by Pd$^+$ cation.[26]

difficult or forbidden closed-shell neutral reactions that proceed easily in the corresponding radical cation can be catalyzed by complexation with a group II metal monocation.

The dimerization of ethylene, a 2s + 2s cycloaddition process and forbidden Woodward–Hoffmann type reaction, requires an activation energy[17a,b] of about 43.0–43.8 kcal mol^{-1}. The activation energy for the cycloreversion reaction[17b,c] is 61.8–62.5 kcal mol^{-1}. Some theoretical studies on this reaction have been published in the past decade.[18] A non-concerted pathway with calculated activation energies for dimerization of ethylene in the range of 42.4–50.5 kcal mol^{-1} and activation energies for the cycloreversion reaction[18a,b] of 52.8–77.7 kcal mol^{-1} was found. In addition, a tetramethylene intermediate has been ruled out by high-level ab initio studies.[18c]

However, Fujisawa et al.[19] reported the reaction of ethylene with its radical cation in a freon matrix to give the 1-butene radical cation. Gas-phase experimental studies by Gross et al. on, for example, the reaction of styrene radical cation and styrene show that the reaction does not proceed through a classical cyclic intermediate, but instead an acyclic 1,4-distonic radical cation is produced.[20] Pabon and Bauld[8] examined the dimerization reaction

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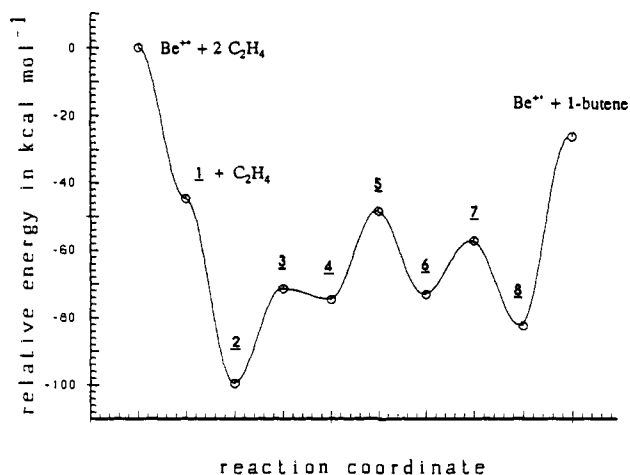
2s + 2s Cycloaddition of Ethylene

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Figure 1. Energy diagram for the dimerization of ethylene to 1-butene catalyzed by complexation with a Be^{*+} cation. Starting point is Be^{*+} + $2C_2H_4$, end point is Be^{*+} + 1-butene.

of the ethylene radical cation with ethylene theoretically and found it to be slightly exothermic and to require an activation energy of only 7 kcal mol^{-1} to form a cyclobutane radical cation. The dimerization of ethylene, a hole-catalyzed reaction, should therefore be catalyzed by a group II metal radical cation.

We now report ab initio molecular orbital calculations[21] on the dimerization of ethylene. This work is designed to provide an example of catalysis of a bimolecular reaction by a group II metal radical cation, Be^{*+}, analogous to the unimolecular 1,3-hydrogen shift in propene.[16] The various mechanistic possibilities for this reaction were shown by a computational study of Barone and Chanon,[22] but not all of them will be discussed in this work. For examples of uneven catalysis with organometallic radicals see the work of Chanon[23a] and of Trogler.[23b]

Experimental analogies to the proposed process are known. Ghosh, Michalik, Lee, and Kevan[24] recently identified a Pd^+-ethylene complex as the intermediate precursor for ethylene dimerization on NaPd–X and CaPd–X zeolites by ESR studies. Bonneviot et al.[25] and Ghosh and Kevan[26] have proposed the mechanism shown in Scheme I. Pd^{3+} ions formed by pretreatment of the zeolite catalyst with oxygen at high temperature are reduced by ethylene to Pd^+. These Pd^+ ions migrate through the zeolite lattice into the supercage, where two ethylene molecules are bound successively to the metal ion to form a bis-ethylene complex. This intermediate undergoes a geometric isomerization before di-
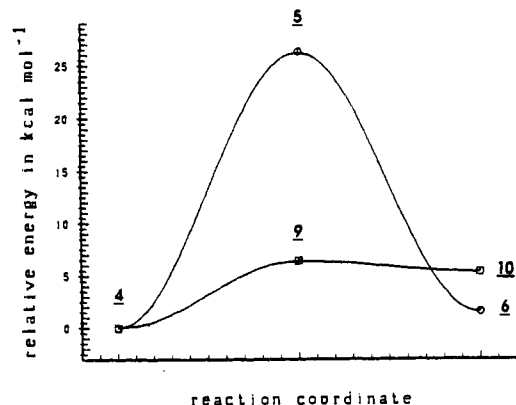

Figure 2. Comparison of the energy diagrams of the first 1,2-hydrogen shift from 4 to 8 (upper curve) to the ring closure of 4 to give 10.
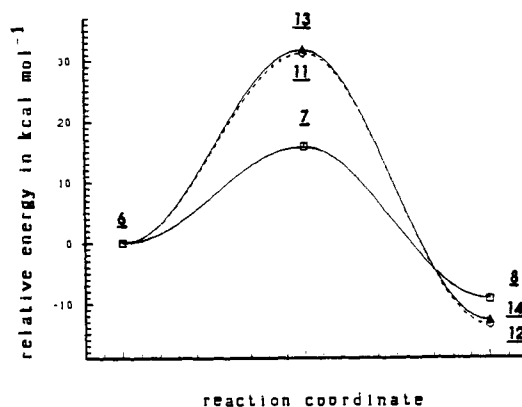

Figure 3. Comparison of the energy diagram of the second 1,2-hydrogen shifts from 6 to 8 (lower curve), 12 (dashed), or 14.

Table I. Activation Energies (kcal mol^{-1}) for the Reactions 2 → 8 (E_{a3}–E_{a5}), 2 → 10 (E_{a7}), 6 → 12 (E_{a8}), and 6 → 14 (E_{a9})[a]

	UHF	MP2	MP3	MP4(sdtq)	+ZPE[b]
E_{a3}	28.5	28.8	29.2	28.3	28.2
E_{a4}	37.5	28.9	30.1	29.3	26.7
E_{a5}	7.6	17.5	17.2	17.2	15.8
E_{a7}	8.3	1.7	4.8	4.6	6.4
E_{a8}	35.6	31.5	34.5	32.9	31.2
E_{a9}	36.5	32.2	35.2	33.5	31.9

[a] All calculations used the 6-31G* basis set at the UHF/6-31G*-optimized geometries. [b] The MP4(sdtq)/6-31G*//6-31G*-calculated energy corrected for the zero-point energies calculated at UHF/6-31G*//6-31G*.

Table II. Reaction Energies (kcal mol^{-1}) for the Reactions 2 → 8 (ΔE_3–ΔE_5), 2 → 10 (ΔE_7), 6 → 12 (ΔE_8), and 6 → 14 (ΔE_9)[a]

	UHF	MP2	MP3	MP4(sdtq)	+ZPE[b]
ΔE_1	−41.7	−44.9	−45.8	−46.0	−44.8
ΔE_2	−40.4	−57.3	−56.5	−56.4	−54.8
ΔE_3	+18.4	+23.8	+23.4	+23.8	+24.9
ΔE_4	+3.6	+1.9	+2.1	+1.9	+1.5
ΔE_5	−19.1	−11.3	−10.3	−10.4	−9.3
ΔE_6	+52.4	+55.5	+56.4	+57.1	+56.2
ΔE_7	+7.2	+0.5	+3.4	+3.2	+5.4
ΔE_8	−20.4	−15.7	−14.4	−14.3	−13.6
ΔE_9	−19.5	−15.0	−13.7	−13.7	−12.8

[a] All calculations used the 6-31G* basis set at the UHF/6-31G*-optimized geometries. [b] The MP4(sdtq)/6-31G*//6-31G*-calculated energy corrected for the zero-point energies calculated at UHF/6-31G*//6-31G*.

(21) All calculations used the Convex, Cray, and IBM versions of the Gaussian 88 program (Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Kahn, L.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A., Gaussian Inc., Pittsburgh, PA, **1988**) on Convex C210s, Cray YMP 8/16 and IBM 3090-120 and the Convex and Cray versions of Cadpac 4.0 (Amos, R. D.; Rice, J.; CADPAC: The Cambridge Analytical Derivatives Package, Issue 4.0, Cambridge, **1987**). Geometry optimizations were performed at the unrestricted Hartree-Fock level using the 6-31G* basis set (Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654) for C, H, and Be. Optimized structures were characterized by diagonalization of the UHF/6-31G* force constant matrix. The energies given in the text and the figures refer to the fourth order Møller–Plesset correction for electron correlation including single, double, triple, and quadruple excitations (MP4(sdtq: Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. Binkley, J. S.; Pople, J. A. *Int. J. Quant. Chem.* **1975**, *9*, 229 and references therein. Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quant. Chem. Suppl.* **1976**, *10*, 1 and references therein. Frisch, M. J.; Krishnan, R.; Pople, J. A. *Chem. Phys. Lett.* **1980**, *75*, 66). The core orbitals were not included in the calculation of the MP4 correction.
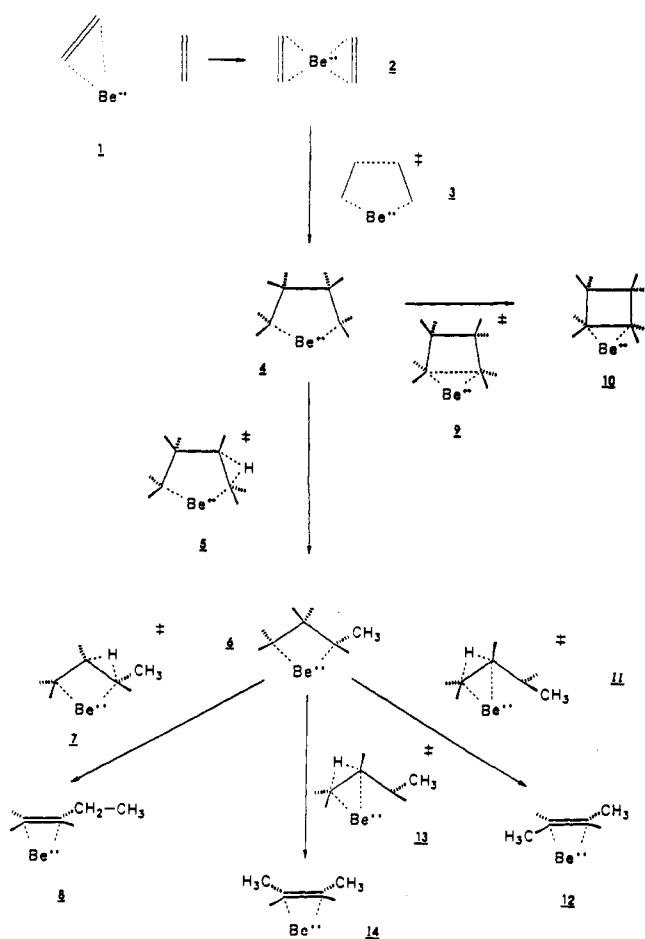
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merization. The first product is 1-butene, which is further isomerized to the 2-butenes. This proposed mechanism has been compared with the results of our ab initio molecular orbital study on the Be^{*+}-catalyzed reaction. As will be shown, there are significant parallels that suggest the simple prototype system to

Scheme II[a]

[a] Schematic representation of the reactions examined. The numbers correspond to those used in the text and in the figures and tables.

Table III. Absolute Energies (au) of 1–14[a]

	UHF	MP2	MP3	MP4(sdtq)	ZPE[b]	N[c]
1	−92.37365	−92.63141	−92.65387	−92.66753	35.70	0
2	−170.46967	−171.00710	−171.04924	−171.07605	71.88	0
3	−170.42428	−170.96124	−171.00264	−171.03103	71.82	1
4	−170.44039	−170.96916	−171.01196	−171.03819	73.14	0
5	−170.38061	−170.92308	−170.96404	−170.99145	70.14	1
6	−170.43466	−170.96617	−171.00863	−171.03519	72.73	0
7	−170.42260	−170.93828	−170.98115	−171.00785	71.22	1
8	−170.46510	−170.98423	−171.02500	−171.05168	73.96	0
9	−170.42725	−170.96641	−171.00425	−171.03083	75.14	1
10	−170.42892	−170.96835	−171.00662	−171.03302	75.52	0
11	−170.37797	−170.91603	−170.95364	−170.98279	70.89	1
12	−170.46723	−170.99121	−171.03152	−171.05804	73.61	0
13	−170.37655	−170.91486	−170.95256	−170.98185	71.01	1
14	−170.46579	−170.99006	−171.03039	−171.05695	73.66	0

[a] All calculations used the 6-31G* basis set on the UHF/6-31G*-optimized geometries. The total energies of C_2H_4 were taken from ref 27; the geometries of 1-butene, cis-2-butene, trans-2-butene, and cyclobutane were optimized at the 6-31G* level; the total energies (au) are as follows. 1-Butene: HF −156.10608, MP2 −156.62021, MP3 −156.65964, MP4(sdtq) 156.68524, ZPE 72.98. cis-2-Butene: HF −156.10786, MP2 −156.62247, MP3 −156.66186, MP4(sdtq) −156.68750, ZPE 72.74. trans-2-Butene: HF −156.11041, MP2 156.62495, MP3 156.66429, MP4(sdtq) 156.68988, ZPE 72.61. Cyclobutane: HF −156.09720, MP2 −156.61721, MP3 156.65532, MP4(sdtq) 156.67956, ZPE 74.55. [b] The zero-point energy calculated at UHF/6-31G*//6-31G* in kcal mol⁻¹. [c] The number of imaginary frequencies calculated at UHF/6-31G*//6-31G*.

be a far better model for transition-metal-catalyzed open-shell processes than we had expected. Although the analogy with hole catalysis was the original rationalization for this work, the calculations revealed that the electron-transfer during catalysis actually occurs in the opposite direction (i.e. $M^{•+} + C_2H_4 \rightarrow M^{2+} + C_2H_4^{•-}$) to that proposed[16] as a mechanistic concept in our original work. However, the same principles should apply to a one-electron-reduction catalysis as to hole catalysis, so that the general picture remains the same.

Results and Discussion

The complete reaction mechanism calculated for the $Be^{•+}$-catalyzed dimerization of ethylene is shown in Scheme II. The energy profile of the reaction leading to 1-butene is shown in Figure 1 and those leading to cyclobutane and to 2-butenes in Figures 2 and 3, respectively. The activation energies are listed in Table I and the reaction energies in Table II. The absolute energies of all stationary points characterized are summarized in Table III. The numbering used for activation energies corresponds to that used for reaction energies.

The first step in the mechanism is the complexation of an ethylene to $Be^{•+}$ to form species 1 with C_s symmetry. The complexation energy is calculated to be 44.8 kcal mol⁻¹ (ΔE_1). The carbon–carbon distance is 1.350 Å, about 0.033 Å longer than in free ethylene.[27] The C_{2v} species, 1a, is the transition state for a 1,2-$Be^{•+}$-shift and is only 0.10 kcal mol⁻¹ less stable than 1. The dynamics of an ethylene molecule adsorbed in NaY-[28a] and

NaX-zeolite[28b] have been examined by ^2H NMR spectroscopy. Ethylene was found to be π-bound to cations and to rotate around the cation/ethylene axis. The lack of C_{2v} symmetry for 1 at the UHF level was checked by optimizing at MP2/6-31G* and by diagonalization of the MP2 force constant matrix. The C_{2v} species was found to be a minimum on the MP2 potential energy surface (the MP2 values for 1a are given in parentheses). The UHF and MP2 potential energy surfaces are therefore significantly different in this case. Complexation of a second ethylene to 1 gave 2, a bis-ethylene complex with C_1 symmetry. The complexation energy for the second ethylene is about 0.7 kcal mol⁻¹ lower than for the first one at UHF/6-31G* but, surprisingly, 10.0 kcal mol⁻¹ (54.8 kcal mol⁻¹, ΔE_2) higher at the MP4(sdtq)/6-31G* level. This again indicates a large correlation effect for these $Be^{•+}$–ethylene species. The $BeC_4H_8^{•+}$ systems calculated here are probably more correctly described at the MP2 level than at UHF. Nevertheless, the more economical UHF calculations should be adequate to give a general picture of the metal-ion catalysis in this system. The exact nature of these ethylene:$M^{•+}$ complexes will be discussed in a future publication.

The third step in the dimerization is the formation of a carbon–carbon bond via transition-state 3 to give the metallacyclopentane species 4. This reaction requires an activation energy of 28.2 kcal mol⁻¹ (E_{a3}) and is endothermic by 24.9 kcal mol⁻¹ (ΔE_3). The big energy difference between 2 and 4 would be a problem in a catalytic cycle because it would never turn over catalytically. This is a known problem in theoretical studies of catalytic cycles such as, for example, the work of Morokuma's group on the olefin hydrogenation by the Wilkinson catalyst.[29] Larger metals, such as Mg and Ca, show smaller energy differences between 2 and 4. The high barrier is a result of the extreme stability of 2, a geometrical arrangement of two ethylene molecules that cannot occur in catalytically active zeolite sites because of steric interactions.[30] The calculated barrier should therefore be taken as the upper limit for this process. Any other arrangement of ethylene molecules around a metal cation should be less stable than 2. In principle, the second ethylene may interact with the first before it is bound to the metal ion. High-level ab initio calculations show that tetramethylene is not a stable intermediate in the neutral dimerization reaction of ethylene.[18c] We did not

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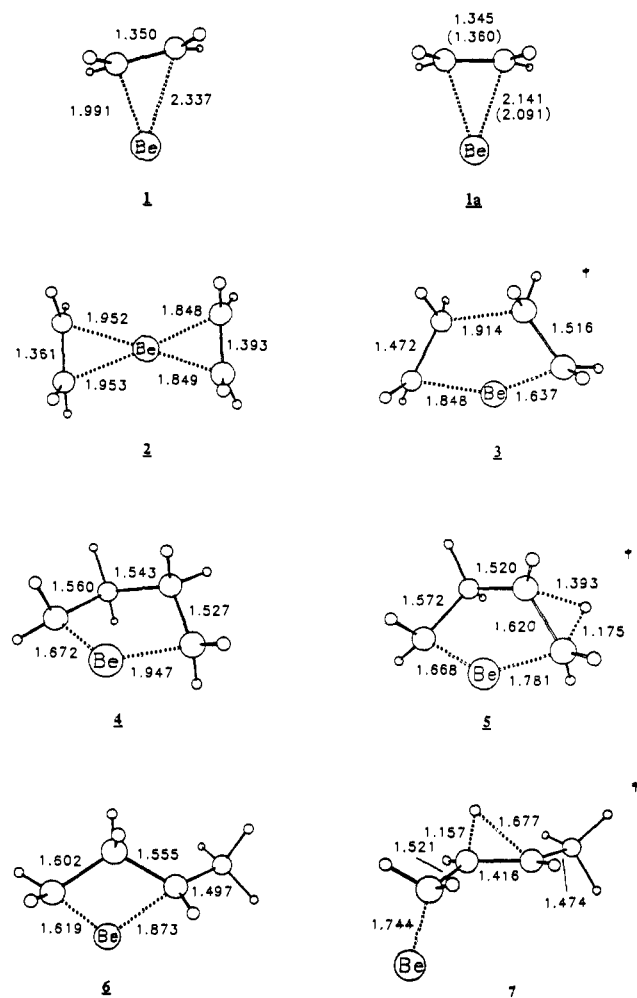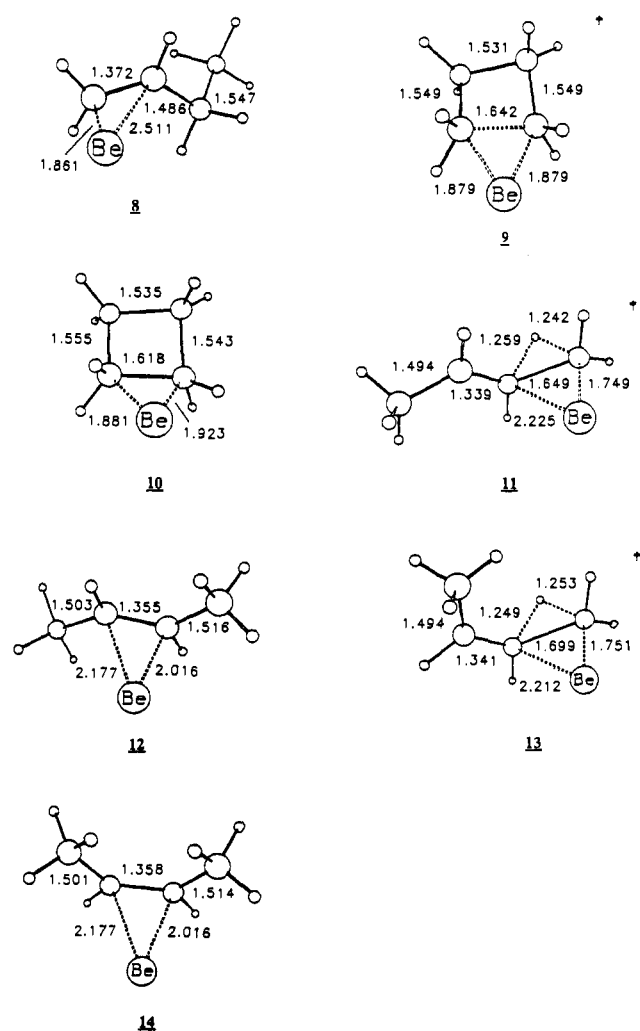2s + 2s Cycloaddition of Ethylene

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Chart I

1.350
2.337
1.991
Be

1

1.345
(1.360)
2.141
(2.091)
Be

1a

1.952 1.848
1.361 Be 1.393
1.953 1.849

2

1.472 1.914 1.516
1.848 Be 1.637

3

1.560 1.543
1.672 Be 1.527
1.947

4

1.520 1.393
1.572 1.620 1.175
1.668 Be 1.781

5

1.602 1.555
1.619 Be 1.497
1.873

6

1.157 1.677
1.521 1.416
1.474
1.744
Be

7

Chart II

1.372 1.547
1.486 1.861 2.511
Be

8

1.531
1.549 1.642 1.549
1.879 Be 1.879

9

1.535
1.555 1.543
1.618
1.881 Be 1.923

10

1.242
1.494 1.259
1.339 1.649 1.749
2.225 Be

11

1.503 1.355
2.177 Be 1.516
2.016

12

1.253
1.494 1.249
1.341 1.699 1.751
2.212 Be

13

1.501 1.358
2.177 Be 1.514
2.016

14

find such a species with a new carbon–carbon bond to be stabilized by complexation with a Be[•+].

Metallacycles[31] like **4** are well-known species in the gas-phase chemistry of transition-metal ions such as Fe, Co, and Ni.[32,33] X-ray crystal structures are also available for metallacyclopentane complexes of Re,[34] Ir,[35] Pt,[36] and Co.[37] These structures differ depending on the metal ion, but have features like the local C_2 symmetry of the metallacycle species and their surprising thermal stability[38] in common. The process of decomposition of metallacyclopentanes has also been studied theoretically.[39]

There are two ways possible to form 1-butene from **4**. The dominant reaction for most of the acyclic transition-metal alkyl complexes is cis-elimination of the metal and a β-hydrogen.

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However, this reaction is postulated to be suppressed torsionally in four-, five- and six-membered cyclic species.[38] More recent results of Schrock et al.[40] suggest β-hydrogen elimination, but other mechanims could not be excluded. Wreford et al.[4] have reported the catalysis of the dimerization reaction of ethylene by a titanium complex to give 1-butene. In this case, the authors point out that β-hydrogen elimination is not the only possible way; intramolecular hydrogen transfer as well as α-elimination could also occur. β-Hydrogen elimination and other alternative reaction mechanisms are still under investigation and will be discussed in detail in a following paper.

If the metal is not directly involved in the following isomerizations, only two sequential 1,2-hydrogen shifts to 1-butene or formation of a second carbon–carbon bond to cyclobutane remain possible. The first 1,2-hydrogen shift forms a "ring-opened" methyl cyclopropane species **6** via transition-state **5**. The barrier is high (26.7 kcal mol^{-1}, E_{a4}) but the reaction is nearly thermoneutral (+1.5 kcal mol^{-1}, ΔE_4). The second 1,2-hydrogen shift via transition-state **7** forms **8**, the Be[•+] complex of 1-butene, directly. This reaction has a low activation energy (15.8 kcal mol^{-1}, E_{a5}) and is exothermic by 9.3 kcal mol^{-1} (ΔE_5). The energy then required to separate the product 1-butene from the metal is 56.2 kcal mol^{-1} (ΔE_6). The energy profile for this reaction leading to 1-butene is shown in Figure 1.

The high activation energy for the first hydrogen shift suggests that cyclobutane formation may compete. The thermal decom-

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ΔE_{ET} = electron transfer energy

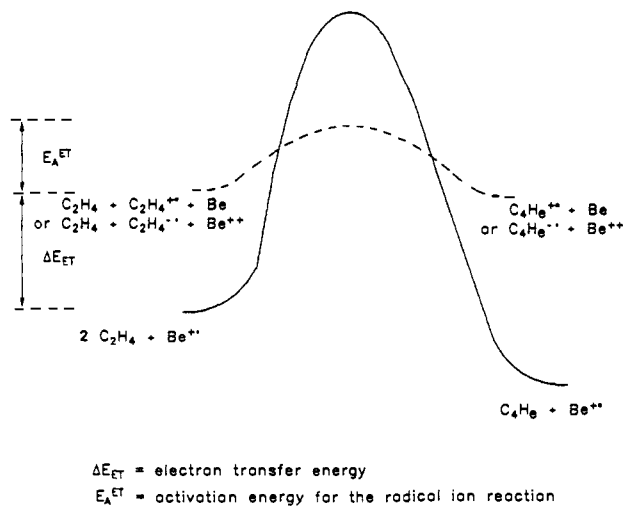E_A^{ET} = activation energy for the radical ion reaction

Figure 4. Schematic representation of the energy profile for the metal radical cation catalyzed dimerization of ethylene.

position of, for example, 1,4-tetramethylenebis(tri-*n*-butylphosphine)platinum(II) in solution gives predominantly cyclobutane as product[38] and cyclobutane derivatives are easily synthesized in preparative yield.[42] In contrast, the formation of cyclobutane was not reported for the gas-phase dimerization of ethylene[24] catalyzed by Pd$^+$. Ring closure of **4** via transition-state **9** to form the cyclobutane complex of Be$^{\bullet+}$, **10**, requires an activation energy of only 6.4 kcal mol^{-1} (E_{a7}) but is endothermic by 5.4 kcal mol^{-1} (ΔE_7). This suggests that the ring-closure is reversible with the equilibrium strongly favoring the metallacycle species. Armentrout and Beauchamp have shown that the ring-opening of cyclobutane in the gas phase by Co$^+$ is exothermic,[32a] in agreement with our results for Be$^{\bullet+}$. The process of ring-closure of **10** for our system is thus kinetically favored but thermodynamically unfavorable compared to the first 1,2-hydrogen shift to form **6**. The energy diagram for this reactions is shown in Figure 2.

We have therefore shown that feasible paths for formation of 1-butene or cyclobutane exist in a metal-ion-catalyzed reaction that does not necessarily involve transition metals.

The formation of 2-butenes could in general proceed on the active metal center, on acidic sites in the zeolite lattice, or on both. The experimentally observed isomerization rate of 1-butene over CaPd–X zeolite is much faster than the ethylene dimerization rate and does not differ much from the isomerization rate over Ca–X zeolite,[43] indicating that palladium is not an active site for isomerization.[24] The acidic hydroxyl groups polarized by calcium ions have been proposed as catalytically active sites for 1-butene isomerization over Ca–X zeolites. Because Ca–X zeolite is inactive for ethylene dimerization, a two-step mechanism was proposed[24] in which the dimerization of two ethylene molecules to form 1-butene[44] is followed by an acid-catalyzed olefin isomerization on acidic sites in the zeolites.

These experimental results suggest that the formation of 2-butenes via a common intermediate **6** for all the butene isomers remains possible but unlikely. Nevertheless, we have also taken

possible reaction paths from **6** to the 2-butenes into account in order to consider all possible mechanisms. There is an energetically feasible reaction path to the 2-butenes from intermediate **6** via a 1,2-hydrogen shift in the direction opposite to that leading to 1-butene. These are examples of dyotropic rearrangements.[45] The calculated activation energies via transition-states **11** and **13** to give **12** and **14**, the complexes of *trans*-2-butene and *cis*-2-butene, respectively, with Be$^{\bullet+}$, are 31.2 (E_{a8}) and 31.9 kcal mol^{-1} (E_{a9}). The reactions are exothermic by 13.6 (ΔE_8) and 12.8 kcal mol^{-1} (ΔE_9), respectively. *trans*-2-Butene is thus the kinetically and thermodynamically preferred product relative to *cis*-2-butene, but it is only favored thermodynamically relative to 1-butene. The differences in activation energies between the 1,2-hydrogen shifts to 1-butene or trans-2-butene and *cis*-2-butene are 15.4 and 16.1 kcal mol^{-1}. We can therefore rule out 1,2-hydrogen shifts from a common intermediate **6** as a pathway to the 2-butenes in the Be$^{\bullet+}$-catalyzed ethylene dimerization. The energy profile for these reactions is shown in Figure 3.

Our original idea for the type of catalysis presented here[16] was that electron transfer from the organic moiety to the metal occurs in the region of the transition state and that a radical cation reaction occurs. We now find that an NBO[46] analysis of the points on the reaction path reveals the reverse electron transfer (i.e. M$^{\bullet+}$ + C$_2$H$_4$ → M^{2+} + C$_2$H$_4^{\bullet-}$) and that the reaction involves radical anions. Thus, the process considered here is a reductive, rather than oxidative, catalysis. The details of such processes have been considered for the alkali metals[47] and further work[48] shows that the ET reaction in the complex $^2A_1$[Be$^{\bullet+}$:C$_2$H$_4$] → $^2B_2$-[Be^{2+}:C$_2$H$_4^{\bullet-}$] is calculated (6-31G*//6-31G*) to be 16.7 kcal mol^{-1} endothermic, so that the general scheme given for catalysis[16] (see Figure 4) remains valid.

Summary

We have presented a feasible reaction path for the catalysis of the dimerization of ethylene with a group II metal radical cation. We find remarkable analogies to the experimentally observed transition-metal-catalyzed processes. The resulting reaction paths and products are in agreement with the proposed reaction path (Scheme I) and product distributions found for the transition-metal systems. 1-Butene is found to be the initial dimerization product. The lack of cyclobutane formation can be explained as a result of a thermodynamically unfavorable ring-closure. We also have shown that the formation of 2-butenes on the metal active center is unlikely. Our model reaction suggests that transition metals are not a prerequisite for the ethylene dimerization reaction. Alternative reaction mechanisms involving a metal–carbene complex on β-hydrogen elimination will be presented in a later paper.

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