Table IX. Vibrational Frequencies of the Species Involved in the Reaction $HOC^+ \rightarrow HCO^+$ [a]

		LDA	HF[b]			LDA	HF[b]
HOC^+	σ	3119	3463	HCO^+	σ	3142	3317
	σ	1968	1997		σ	2238	2288
	π	317	620		π	786	1051
TS	A′	2102	2208				
		1896	2056				
		1278i					

[a] The unit is cm^{-1}. [b] Reference 41. HF/5-31G//MP3/6-31G** calculations.

in Table VIII. Geometries optimized by the LDA and the NL agree with experiment fairly well. The discrepancies are within 0.005 Å. The geometries for the transition state obtained by the LDA and the NL are similar, but the latter is closer to the MP3/6-31G** geometry, as shown in Table VIII.

Nobes et al.[41] studied the basis set and CI effects on the theoretical energy barriers. The results obtained by different ab initio calculations ranged from 77.0 kcal/mol at the HF/4-31G level to 39.4 kcal/mol for MP3/6-311G***//MP3/6-31G**. The study revealed that a larger basis set and a higher level of theory always decreased the barrier. The value of 42.8 kcal/mol listed in Table VIII was obtained[41] by MP3/6-31G**//MP3/6-31G**. Being corrected by the zero-point energy, the best result that Nobes et al.[41] has obtained is 35.9 kcal/mol. Our calculations by LDA generate a lower barrier of 27.2 kcal/mol. The nonlocal corrections slightly raise this barrier to 27.5 kcal/mol. The influence of the nonlocal corrections to the energy barrier for the isomerization reaction E is thus negligible. The zero-point energy corrected barrier for the NL is 26.0 kcal/mol, which is 9.9 kcal/mol lower than the value of 35.9 kcal/mol obtained by MP3/6-311G***. It is possible that such a discrepancy will be reduced when more extensive CI is included in the ab initio calculations. The vibrational frequencies calculated by the LDA are given in Table XI.

IV. Concluding Remarks

We have studied the hydrogen abstraction reactions A and B. The local density functional theory predicted lower energy barriers than the experimental observations, but the nonlocal corrections successfully rectified the underestimated barriers yielding remarkable agreement with the experiment. The reaction mechanisms proposed by the LDA and NL schemes are qualitatively different, and it is suggested that the double-well reaction profile introduced by LDA with two intermediates is incorrect and is an artifact of the local approximation, which is known to overestimate bonding between atoms. The nonlocal corrections, on the other hand, seem to represent the experimental findings and should be used in studies on reactions involving a transition state with a three-center, three-electron bond.

The dissociation reaction C is appropriately described by the LDA scheme. The influence of the nonlocal corrections is much smaller for reaction C than for either A or B. It is encouraging to see that DFT-based methods are able to handle "symmetry-forbidden" reactions with a high barrier, where interactions between two or more configurations are of importance, Figure 6. More work is needed to understand how DFT-based methods are able to treat this category of processes.

The isomerization reactions D and E are also described well by the DFT-based methods, and the nonlocal approximations provide a small but significant improvement. It can be concluded that the nonlocal method due to Becke[33] and Perdew[20c] demonstrates considerable promise as a practical tool in kinetic studies on organic reactions.

Acknowledgment. This investigation was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). We also acknowledge access to the IBM-6000 installations at the University of Calgary.

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Catalysis of the Ring-Opening and Isomerization of Cyclopropane by Complexation with Metal Radical Cations: An ab Initio Study

Alexander Alex and Timothy Clark*

Contribution from the Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Federal Republic of Germany.

Received July 30, 1992

Abstract: The ring opening and isomerization of cyclopropane are shown by ab initio calculations to be catalyzed by complexation with $Be^{\bullet+}$. The reactions proceed via a common metallacyclobutane radical cation intermediate formed in a reaction that is endothermic by 12.3 kcal mol^{-1} relative to the cyclopropane–$Be^{\bullet+}$ complex. From this intermediate, three alternative reaction paths were examined, two isomerizations to give a propene–$Be^{\bullet+}$ complex and a C–C bond cleavage forming a carbene–ethylene–$Be^{\bullet+}$ species. These reactions are found to be exothermic by 5.4 and 5.2 kcal mol^{-1} relative to the cyclopropane–$Be^{\bullet+}$ complex, respectively. The isomerization of cyclopropane to give propene is calculated to be exothermic by 8.0 kcal mol^{-1} (exptl 7.9 kcal mol^{-1}). Remarkable parallels to transition-metal catalyzed reactions were found for all the reactions examined.

Introduction

The ability of transition-metal complexes to effect structural changes in organic substrates is widespread in organometallic chemistry, examples are the metal-assisted rearrangements of strained-ring molecules, particularly the reactions of cyclopropanes to olefins, and the metal promoted isomerization of olefins.[1] In this paper we focus our attention on the conversions of cyclopropanes. The related isomerization of olefins will be the subject of further work.

The gas-phase thermal isomerization and ring-opening of cyclopropane require activation energies of 60–61 and 64–65 kcal mol^{-1}, respectively.[2] Yamaguchi et al.[3a] and Getty et al.[3b] found

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Table I. Activation Energies (in kcal mol^{-1}) for the Reactions Examined[b]

	PUHF (UHF)	PMP2 (MP2)	PMP3 (MP3)	PMP4 (MP4(SDTQ))	QCISD(T) (QCISD)	+ZPE[a]
E_{a2}	31.3 (31.9)	38.0 (38.4)	35.5 (35.8)	33.6 (33.9)	31.2 (31.1)	29.0
E_{a3}	21.8 (20.4)	33.3 (32.4)	32.2 (31.6)	32.1 (31.5)	31.6 (27.6)	30.7
E_{a5}	2.5 (3.9)	−0.7 (0.4)	0.4 (1.0)	−0.8 (−0.2)	−0.2 (0.8)	−0.7
E_{a7}	24.3 (24.3)	32.7 (32.7)	30.8 (30.8)	30.5 (30.5)	30.2 (30.3)	29.0
E_{a8}	22.6 (22.6)	25.0 (25.0)	24.5 (24.5)	24.6 (24.6)	24.4 (24.1)	24.1
E_{a9}	30.1 (30.1)	26.8 (26.8)	26.7 (26.7)	26.4 (26.4)	26.3 (26.4)	24.9
E_{a10}	32.4 (34.4)	43.8 (45.2)	40.5 (41.3)	40.7 (41.5)	40.0 (39.1)	36.8
E_{a11}	19.8 (20.4)	24.1 (24.4)	23.8 (24.0)	24.0 (24.3)	24.2 (23.9)	22.7
E_{a12}	33.6 (27.9)	13.4 (8.6)	15.3 (11.8)	13.9 (10.4)	13.1 (14.6)	14.4

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

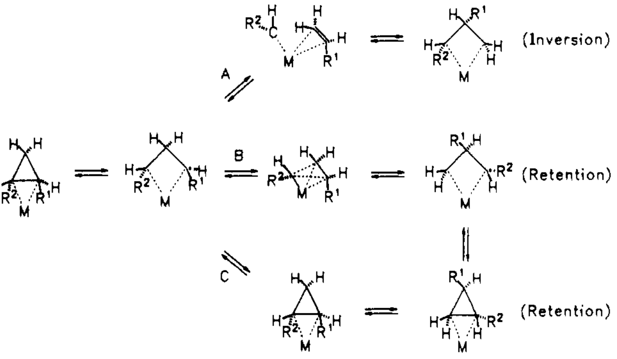
Table II. Reaction Energies (in kcal mol^{-1}) for the Reactions Examined[b]

	PUHF (UHF)	PMP2 (MP2)	PMP3 (MP3)	PMP4 (MP4(SDTQ))	QCISD(T) (QCISD)	+ZPE[a]
ΔE_1	−46.9 (−46.9)	−57.2 (−57.2)	−56.9 (−56.9)	−58.2 (−58.2)	−58.2 (−56.8)	−57.3
ΔE_2	12.8 (14.2)	18.3 (19.3)	15.1 (15.8)	15.1 (15.7)	14.4 (14.1)	12.3
ΔE_3	−24.7 (−25.9)	−19.3 (−20.1)	−18.5 (−19.0)	−18.7 (−19.3)	−18.7 (−18.9)	−17.7
ΔE_4	50.9 (50.7)	54.0 (53.8)	54.9 (54.8)	55.5 (55.3)	55.5 (54.9)	54.7
ΔE_5	−24.3 (−24.6)	−14.4 (−14.7)	−16.9 (−17.2)	−16.1 (−16.4)	−16.2 (−16.9)	−17.5
ΔE_6	62.7 (62.7)	65.8 (65.8)	66.0 (66.0)	65.7 (65.8)	65.2 (64.8)	63.2
ΔE_{11}	−32.3 (−26.1)	−19.5 (−14.2)	−19.8 (−16.1)	−20.2 (−16.4)	−18.6 (−18.7)	−21.1
ΔE_{12}	7.6 (0.1)	0.2 (−5.8)	1.3 (−3.0)	1.4 (−2.8)	−0.1 (−0.2)	3.4

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

an activation energy of 61.6 kcal mol^{-1} in ab initio calculations. Trimethylene has been ruled out as a stable intermediate by high level ab initio calculations.[4] The electrophilic ring-opening of cyclopropane has been studied extensively experimentally[5] and theoretically.[5a,b,h,6] The ring opening of the cyclopropane radical cation has also been studied both experimentally[7] and theoretically.[8] The activation energy for this reaction was calculated by Borden et al.[9] to be 36.1 kcal mol^{-1}. In semiempirical calculations on the ring-opening of substituted cyclopropane radical anions, formation of a stable trimethylene radical anion intermediate with an activation energy of 4–5 kcal mol^{-1} was found.[10] These radical anion intermediates are also known experimentally.[11] Because the activation energies for the ring openings of the radical cation and the radical anion are much lower than that of the neutral reaction, they should be catalyzed by complexation with a group 2 metal radical cation such as Be$^{\bullet+}$. In a previous paper, we investigated the catalysis of the dimerization of ethylene by group 2 metal radical cations[12] and found a major catalytic effect compared to the neutral reaction.

Scheme I. Proposed Mechanisms for the Ring-Opening and Isomerization of Metallacyclobutanes and Cyclopropanes by Transition-Metal Ions[15a,b]



We now report model ab initio molecular orbital calculations[13] on the ring-opening and isomerization of cyclopropane and the

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Table III. Absolute Energies (in au) of **1–17**[c]

	PUHF (UHF)[a]	PMP2 (MP2)	PMP3 (MP3)	PMP4 (MP4sdtq)	QCISD(T) (QCISD)	ZPE[b]	NIMAG
1	−78.03172	−78.28435	−78.30536	−78.31870	−78.32095 (78.31238)	34.37	0
2	−117.05887	−117.44820	−117.47640	−117.49407	−117.49569 (−117.48342)	54.76	0
3	−117.07147	−117.45472	−117.48496	−117.50436	−117.50687 (−117.49404)	53.62	0
4	−131.40918 (−131.40905)	−131.81468 (−131.81478)	−131.84266 (−131.84260)	−131.86240 (−131.86234)	−131.86395 (−131.84943)	55.71	0
5	−131.35925 (−131.35820)	−131.75432 (−131.75358)	−131.78608 (−131.78556)	−131.80889 (−131.80837)	−131.81430 (−131.79994)	53.27	1
6	−131.38882 (−131.38643)	−131.78564 (−131.78404)	−131.81853 (−131.81746)	−131.83839 (−131.83732)	−131.84093 (−131.82703)	53.34	0
7	−131.35411 (−131.35389)	−131.73253 (−131.73239)	−131.76719 (−131.76710)	−131.78719 (−131.78710)	−131.79060 (−131.78300)	52.38	1
8	−131.42817 (−131.42777)	−131.81635 (−131.81603)	−131.84803 (−131.84781)	−131.86824 (−131.86802)	−131.87074 (−131.85709)	54.47	0
9	−131.38483 (−131.38028)	−131.78679 (−131.78346)	−131.81794 (−131.81590)	−131.83967 (−131.83763)	−131.84128 (−131.82579)	52.80	1
10	−131.42757 (−131.42571)	−131.80862 (−131.80754)	−131.84541 (−131.84483)	−131.86405 (−131.86346)	−131.86673 (−131.85388)	51.87	0
11	−53.29586 (−53.29401)	−53.41946 (−53.41839)	−53.43482 (−53.43422)	−53.44058 (−53.43997)	−53.44138 (−53.43830)	15.26	0
12	−131.37316 (−131.37302)	−131.77495 (−131.77487)	−131.80359 (−131.80353)	−131.82314 (−131.82308)	−131.82506 (−131.81103)	55.32	1
13	−131.36127 (−131.36106)	−131.77222 (−131.77210)	−131.80009 (−131.80000)	−131.82033 (−131.82024)	−131.82210 (−131.80734)	54.20	1
14	−131.37041 (−131.37026)	−131.76277 (−131.76267)	−131.79351 (−131.79345)	−131.81372 (−131.81366)	−131.81576 (−131.80109)	54.35	1
15	−131.35749 (−131.35428)	−131.74485 (−131.74278)	−131.77807 (−131.77683)	−131.79747 (−131.79623)	−131.80025 (−131.78713)	52.13	1
16	−131.35723 (−131.35390)	−131.74730 (−131.74508)	−131.78064 (−131.77923)	−131.80008 (−131.79867)	−131.80234 (−131.78898)	51.67	1
17	−131.44022 (−131.42797)	−131.81671 (−131.80673)	−131.85010 (−131.84310)	−131.87051 (−131.86352)	−131.87065 (−131.85681)	50.56	0
18	−131.38669 (−131.38350)	−131.79537 (−131.79307)	−131.82577 (−131.82437)	−131.84840 (−131.84701)	−131.84984 (−131.83358)	52.04	1

[a] *1–3* were calculated at the RHF/6-31G* level. [b] The QCISD(T)/6-31G*//6-31G* calculated energy corrected for the zero-point energies calculated at UHF/6-31G*//6-31G*. [c] All calculations used 6-31G* basis set on the UHF/6-31G* optimized geometries.

isomerization of a metallacyclobutane on the $[BeC_3H_6]^{\cdot+}$ potential energy surface. This work is intended to provide a further example of catalysis of organic reactions by a group 2 metal radical cation, $Be^{\cdot+}$. A part of this study is the reexamination of the $Be^{\cdot+}$-catalyzed unimolecular 1,3-hydrogen shift in propene at a higher level than that used previously.[14]

Experimental studies both in the gas phase and in solution have revealed several different products for the reaction of metal cations with cyclopropane. These include metallacycles,[15e–h] carbene–olefin species,[16a,c,d,f] η^3-allyl–metal–hydride complexes,[16e] or $[MC_3H_6]^+$ adducts.[16a] These species are proposed to be intermediates in catalytic processes such as olefin metathesis.[17] Of special interest are the carbene species because of their use in cyclopropane synthesis.[18] The carbene-transfer reaction was studied theoretically at the GVB level by Rappé and Goddard[19a] and by Upton and Rappé[19b,c] with a $TiCl_2$–cyclopropane species and by Anslyn and Goddard[19d] with $MoCl_4$ and $MoCl_3^+$ as model systems. Their results will be compared to ours below. Several theoretical studies on cyclopropane–metal complexes have been published in the past decade.[20] In the study most relevant to this work, Siegbahn et al.[20e,f] examined the ring-opening of cyclopropane by various Pd species. Corner attack was calculated to be favorable for Pd^0 and edge attack for $PdCl^+$.$PdCl_2$ and $PdCl_4^{2-}$ seem to be inactive under normal conditions. The ring-opening of cyclopropane by Cl^+ and Br^+ has also been examined by ab initio theory[6f] and was found to proceed via a "zigzag" reaction path. The metallacyclobutane species for Li^+ and Na^+ were also optimized in C_{2v} symmetry but characterized to be second order stationary points.[6f] Recently, Bauschlicher, Freiser, Hill, and Langhoff[21] examined the bonding of, for example, C_3H_6 isomers to the singly charged and dipositive ions of Sc, Y, and La theoretically and experimentally. They found that the dipositive ions

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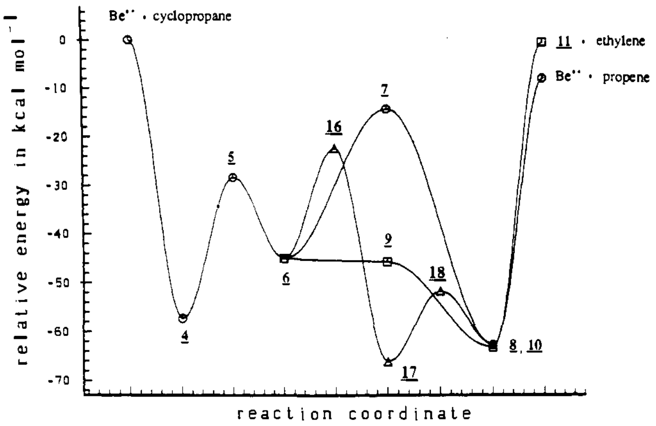

Figure 1. Energy diagram for the isomerization of cyclopropane to propene and the abstraction of ethylene catalyzed by complexation with a $Be^{\bullet+}$ radical cation. Starting point is $Be^{\bullet+}$ + cyclopropane; end points are $Be^{\bullet+}$ + propene and **11** + ethylene.

bind only electrostatically to olefins, whereas the singly charged ions insert into a C–C π-bond to form a three-membered ring.

In a series of experimental studies, Puddephatt et al.[15a,b] and Casey et al.,[15c] among others, have proposed a mechanism for the ring-opening of cyclopropane by platinum complexes. This mechanism (shown in Scheme I) forms the basis of our investigation and will be compared to our results and discussed in detail below. As will be shown, there are significant parallels between experimental results and our calculations that suggest the simple prototype system $[BeC_3H_6]^{\bullet+}$ to be a far better model for transition-metal catalyzed open-shell processes than might be expected, as we also found for ethylene dimerization.[12]

Results and Discussion

The energy profile calculated for the $Be^{\bullet+}$-catalyzed isomerization pathways of cyclopropane to propene and the alternative reaction via a carbene-olefin species to give ethylene is shown in Figure 1. It is quite similar to those found in general for gas phase reactions of metal cations with neutral molecules.[22] The activation energies are listed in Table I and the reaction energies in Table II. The absolute energies for 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 $Be^{\bullet+}$ to cyclopropane (**2**) to form species **4** with C_1 symmetry. The corresponding C_{2v} species has the same total energy within 10^{-5} au but is a transition state. The complexation energy is calculated to be -57.3 kcal mol^{-1} (ΔE_1). The Be is edge-bound to the cyclopropane. The following ring-opening reaction requires an activation energy of 29.0 kcal mol^{-1} (E_{a2}) via transition state **5** (C_1) in a reaction that is endothermic by 12.3 kcal mol^{-1} (ΔE_2) to give the metallacycle[15g,h] **6** (C_s), which we reported in an earlier paper.[14] **4** and **6** were also optimized in C_{2v} symmetry at the MP2/6-31G* level and were characterized to be minima on the MP2 potential energy surface by diagonalization of the MP2 force constant matrix. Symmetry breaking in such complexes appears to be common at UHF/6-31G*. The reaction energy changes from +12.3 (ΔE_2, UHF/6-31G*) to +23.0 kcal mol^{-1} at MP2/6-31G*; the MP2-optimized atomic distances are given in parentheses. The correlation effect for species **4** is very small, for **6** it is more significant. We note that the local minima calculated with UHF are also present on the MP2 potential energy surface. In both cases **6** is a reactive intermediate. Therefore the more economical UHF calculations should also give reasonable results. The spin-contamination of the wave functions of all species is small, but we nevertheless report the PUHF[23] total energies. PUHF has been shown to reproduce experimental data well.[24] However, the influence of spin-contamination on the geometries is expected to be small.[25]

The ring-opening catalyzed by $Be^{\bullet+}$ proceeds via a "corner-attack", as previously calculated by Siegbahn et al.[20e] for $PdCl^+$. The second step is a 1,2-hydrogen shift from **6** via transition state **7** (C_1) with an activation energy of 30.7 kcal mol^{-1} (E_{a3}) to give the propene complex **8** (C_1) in a reaction that is exothermic by 17.7 kcal mol^{-1} (ΔE_3). The complexation energy of propene (**3**) to $Be^{\bullet+}$ is calculated to be 54.7 kcal mol^{-1} (ΔE_4). The isomerization path has no point higher in energy than the starting point $Be^{\bullet+}$ + cyclopropane. The total reaction is calculated to be exothermic by 8.0 kcal mol^{-1}; the experimental value[26] is 7.9 kcal mol^{-1}.

An alternative reaction is the C–C cleavage to give ethylene (**1**) and a $Be^{\bullet+}$–carbene species. This was observed experimentally by Armentrout and Beauchamp[16a] for Co^+ and by Byrd and Freiser[16c] for the Rh^+–cyclopropane system. It is fairly common for the transition-metal cations of Cr–Cu[16g] and is denoted as reaction path A in Scheme I. The metallacyclic ring is opened in a reaction via transition state **9**; the calculated activation energy (E_{a5}) decreases from 3.9 kcal mol^{-1} (UHF/6-31G*//6-31G*) to -0.7 kcal mol^{-1} (QCISD(T)/6-31G* + ZPE). The reaction energy to form the carbene–olefin species **10** is -17.5 kcal mol^{-1} (ΔE_5). However, Upton and Rappé found titanacyclobutane to be 11.5 kcal mol^{-1} more stable than the metal–carbene–olefin species.[19b,c] Anslyn and Goddard[19d] found a similar result for $MoCl_4$, but calculated the metallacycle to be more stable in the case of $MoCl_3^+$. The energy required for the decomplexation of ethylene to give the carbene complex **11** is 63.2 kcal mol^{-1} (ΔE_6). The ring-opening reaction from cyclopropane and $Be^{\bullet+}$ to give **11** and ethylene is calculated to be 0.8 kcal mol^{-1} endothermic, according to gas-phase experiments for Co^+.[16a] Carbene complexes of transition-metal ions such as Cr^+ or Ru^+ were studied extensively by the Goddard group.[27] They found low-lying excited states for these species. The QCI calculation for **11** shows that it can be described well by the UHF single determinant approach. This was also found for the methylene species **9** and **10**.

Experimentally, the isomerization of platinacyclobutanes was found to occur with retention of configuration on the ring.[15a,c] This is only possible if the rotation of the carbene group and the olefin occur simultaneously. Olefin rotation in Pt complexes has been examined experimentally[28] and theoretically[29] and was found to be more favorable than the rotation around the metal–carbene bond.[30] Additionally, no olefin is found as product in experimental studies on Pt complexes.[15b,c] However, in our model system, there is little or no activation energy for formation of the olefin–carbene–complex, suggesting that $Be^{\bullet+}$ is not a good model for Pt complexes. Inversion on metallacyclobutanes does, however, occur for other metals, and olefins were found as products.[16a,c]

Mechanism B is described in the literature as a "concerted" mechanism, in which the metal interacts directly with the β-carbon atom[15a] to give retention on the ring. This type of rearrangement could not be found in our calculations. Species **12**, a transition state for a metal-assisted rotation of a methylene group in cy-

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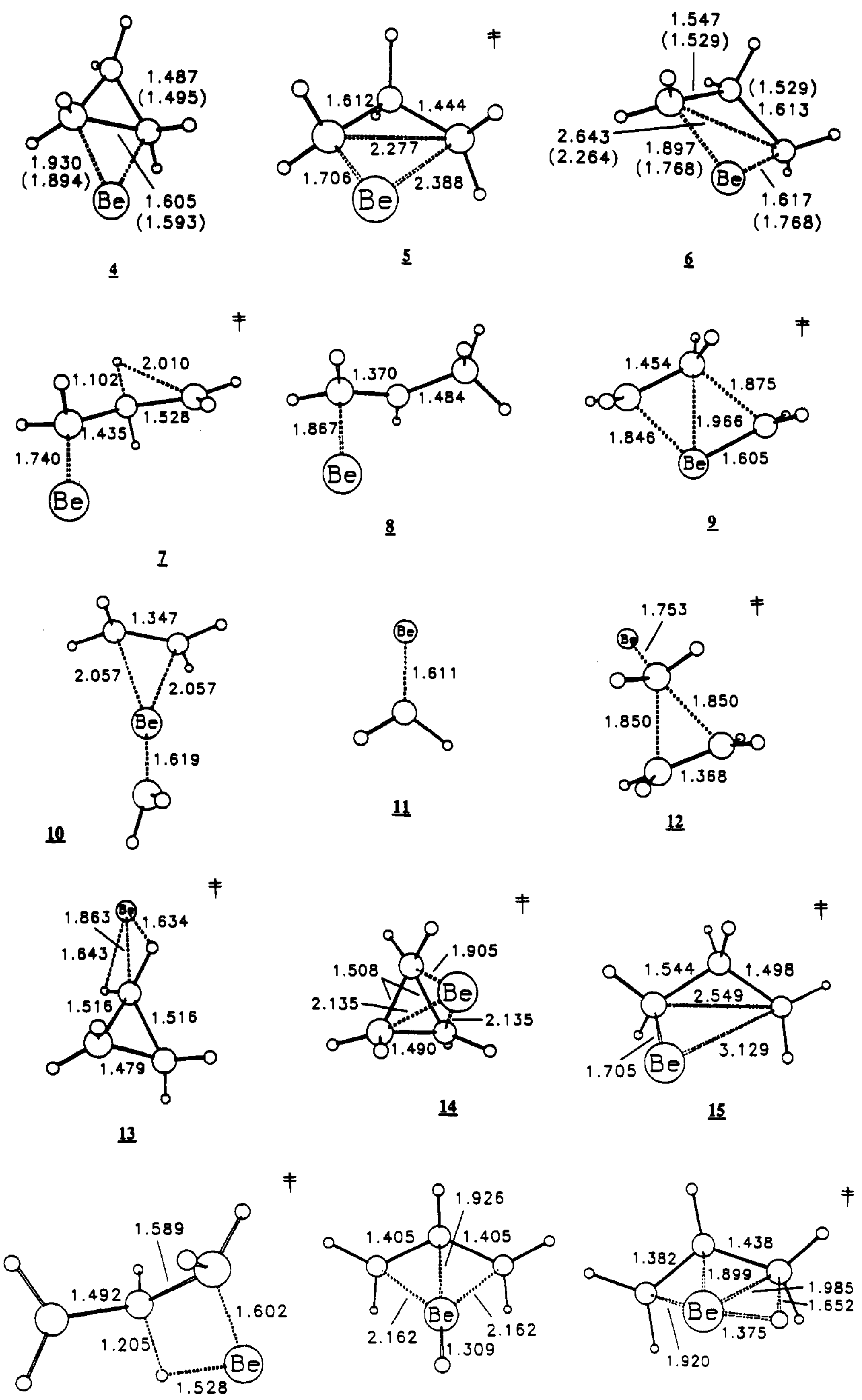
Chart I



clopropane is found to be 29.0 kcal mol^{-1} (E_{a7}) higher in energy than **4**. The interaction with the β-carbon atom is very strong. Inversion on the ring should occur. There is a strong catalytic effect for the isomerization of cyclopropane. The neutral reaction[2] is activated by more than 60 kcal mol^{-1}. A species similar to **12** was calculated by Schleyer et al.[6e] to be a transition state for rotation of a methyl group in $C_3H_7^+$.

Mechanism C includes an "edge to edge" isomerization of the metallacyclic species. The ring recloses to **4** and the $Be^{\bullet+}$ migrates over the hydrocarbon ring. There are two possible modes of rearrangment. In the first possibility, a transition state (**13**, C_s) with the $Be^{\bullet+}$ "corner-bound" to the ring is calculated to be 24.1 kcal mol^{-1} (E_{a8}) less stable than **4**. The alternative path is via a "face-bound" $Be^{\bullet+}$ (**14**, C_s) with an activation energy of 24.9

kcal mol^{-1} (E_{a9}). When the ring is reopened, both processes give retention on the ring, in accord with experimental results.[15a–d]

We also found another transition state (**15**) for the direct cis–trans isomerization of the metallacycle. In contrast to the isomerization mechanisms shown before, no ring-closure to cyclopropane is required. The activation energy of 36.8 kcal mol^{-1} (E_{a10}) is 7.8 kcal mol^{-1} higher than that calculated for reaction path A. Therefore we conclude that the cis–trans isomerization of the metallacycle proceeds via transition state **12**.

Another reaction mechanism for the isomerization of cyclopropane includes β-hydrogen shift to form a η^3-allyl–metal–hydride complex as an intermediate. For Ir a crystal structure for such a species is known[16e] and for Fe[31] and Rh[16c,32] allylic species have been observed in the gas phase. Several theoretical investigations of the β-hydride shift have been published in the past decade.[33] Recently, Bauschlicher et al. have calculated the symmetrically bridged $HMC_3H_5{}^{n+}$ species (M = Sc, Y, La; n = 1, 2).[21a] This type of structure was also reported for the MC_3H_5 species (M = Li–Cs)[34a] and allylborane.[34b] We found a similar geometry for the Be$^{\cdot+}$ system, a η^3-allyl–metal–hydride complex **17** (C_s) that is surprisingly the most stable species calculated in this work. The activation energy from **6** via transition state **16** is 22.7 kcal mol^{-1} (E_{a11}), and the reaction is exothermic by 21.1 kcal mol^{-1} (ΔE_{11}). Note that the metallacyclobutane ring is opened in the transition state to give the 0° BeCCH dihedral angle required for a β-hydride shift. The ring reclosure gives the allyl-hydride species. The final step is a 1,2-hydrogen shift from **17** via transition state **18** to give the product **8**, the propene complex of Be$^{\cdot+}$. The activation energy is 14.4 kcal mol^{-1} (E_{a12}), and the reaction is endothermic with 3.4 kcal mol^{-1} (ΔE_{12}).

Following the model used to treat the dimerization of ethylene,[12] both reductive and oxidative catalysis should be possible. Oxidative catalysis was not found in the reactions examined. The NBO charges[35] on the metal for all species calculated were in the range of +0.9 to +1.6 indicating a charge transfer from the metal radical cation to the organic moiety. For the ring-opening of **4** to give the metallacyclobutane **6**, the NBO charge on Be in the cyclopropane complex **4** is 0.96 but increases from the transition state **5** (1.08) to the product **6** (1.55). Species **6** can thus be written as $[Be^{2+}{:}C_3H_6{}^{\cdot-}]$. Reductive catalysis is found for the reaction examined, analogously to our previous results.[12] The general scheme for redox-catalysis presented previously[12] is also found to be valid in the present work.

Summary

Only corner attack by Be$^{\cdot+}$ was found in the ring-opening of cyclopropane. The formation of a reactive metallacyclic intermediate is suggested. A facile reaction path for the catalysis of the ring-opening and isomerization of cyclopropane with group 2 metal radical cations clearly exists. Again we find remarkable analogies to the experimentally observed transition-metal catalyzed processes. We also find an energetically reasonable reaction path involving a β-hydride shift for Be$^{\cdot+}$. This type of reaction is usually thought of as a typical transition metal reaction. There are two energetically equivalent pathways for isomerization of cyclopropane to propene with and without direct involvement of the metal cation, but there is no doubt that involvement of the metal is more favorable for transition-metal cations. The most remarkable point is the redox catalysis from **4** to **8**, the isomerization of cyclopropane to propene. The metal charges in educt and product are nearly equal (0.96 and 0.91, respectively) but increase in the reactive intermediate **6** to 1.55, indicating that Be plays a true catalytic role as a one-electron reductive catalyst.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Volkswagen Stiftung. We thank Professors C. Casey and H. Schwarz for helpful discussions.

Supplementary Material Available: Gaussian archive entries for the QCISD(T)/6-31G*//UHF/6-31G* single points on the reactants, transition states, and products (4 pages). Ordering information is given on any current masthead page.

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