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Proposal for the Metallacycle Pathway during the Cyclopropanation Catalyzed by Cobalt–Schiff Base Complexes

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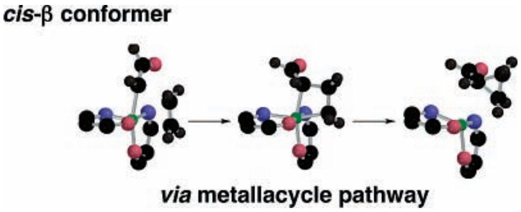
ABSTRACT



The density functional study of the cobalt(II) complex-catalyzed cyclopropanation revealed that the cobalt(II)–Schiff base complex without an ethylene bridge would be flexible enough to transform into the cis-*β* conformer while approaching the olefin; consequently, the metallacycle pathway would be preferred, while the ethylene bridge would stabilize the planar conformer to allow reaction via the concerted mechanism.

Since the dioximatocobalt(II) complexes were reported to catalyze the enantioselective cyclopropanation by Nakamura et al., salen cobalt(II) complexes and ketoiminato cobalt(II) complexes have been reported to achieve high enantio- and diastereoselectivities in the reaction of diazoacetates with styrene derivatives. Nevertheless, few reports on the detailed mechanism have been published, and several speculative transition states consistent with their stereoselectivities have been proposed: e.g., a mechanism via a metallacycle intermediate for the glyoximatocobalt(II) complex **1** catalysis[1] and the concerted mechanism for the salen[2] **2** and ketoiminatocobalt(II)[3] **3** complex catalysis.

In this communication, we describe that the ethylene bridge of these ligand systems has a crucial effect on the reaction pathways of the cobalt(II) complex-catalyzed cyclopropanation. The density functional study on the cobalt(II)−Schiff base complex-catalyzed cyclopropanation revealed that the cobalt(II) complex without an ethylene bridge would be flexible enough to transform into the cis-*β* conformer while approaching the olefin. Consequently, the metallacycle pathway would be preferred, while the ethylene bridge would stabilize the planar conformer to allow the reaction via the concerted mechanism.

The cobalt−carbene intermediate is considered to be generated from the starting cobalt(II) complex with diazoacetate and then react with an alkene to afford the resulting cyclopropane. As model structures for the DFT calculation, the complex **4** without an ethylene bridge was adopted corresponding to the dioximatocobalt(II) complex **1**, and the complex **5** with an ethylene bridge was adopted corresponding to the salen **2** and ketoiminatocobalt(II) **3** complexes. Diazoacetaldehyde and ethylene were employed as representatives of the diazoacetates and alkenes, respectively. The density functional calculation was performed using UB3LYP.[4] 6-31G* basis sets were used for optimization, and single-point calculations were performed with the same basis sets and the higher 6-311G** basis set.[5] Throughout this work,

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(1) (a) Nakamura, A.; Konishi, A.; Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3443−3448. (b) Nakamura, A.; Konishi, A.; Tsujitani, R.; Kudo, M.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3449−3461. (c) Nakamura, A. *Pure Appl. Chem.* **1978**, *50*, 37−42.

(2) (a) Fukuda T.; Katsuki, T. *Synlett* **1995**, 825−826. (b) Fukuda, T.; Katsuki, T. *Tetrahedron* **1997**, *53*, 7201−7208. (c) Niimi, T.; Uchida, T.; Irie, T.; Katsuki, T. *Tetrahedron Lett.* **2000**, *41*, 3647−3651.

(3) (a) Ikeno, T.; Sato, M.; Sekino, H.; Nishizuka, A.; Yamada, T. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 2139−2150. (b) Ikeno, T.; Iwakura, I.; Yamada, T. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 2151−2160. (c) Ikeno, T.; Iwakura, I.; Yabushita, S.; Yamada, T. *Org. Lett.* **2002**, *4*, 517−520. (d) Ikeno, T.; Iwakura, I.; Yamada, T. *J. Am. Chem. Soc.* **2002**, *124*, 15152−15153.

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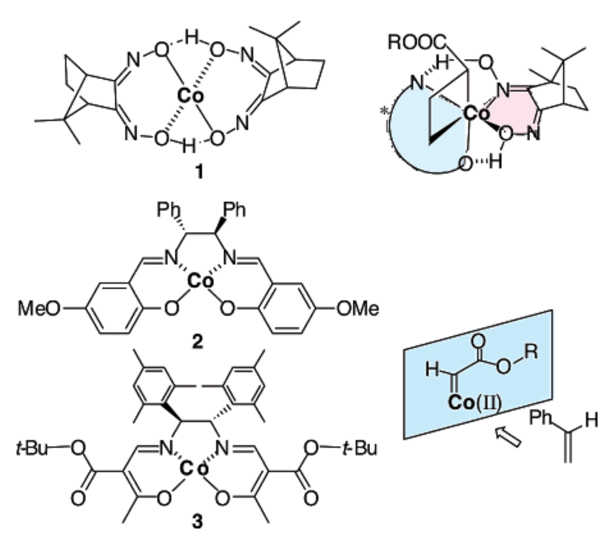


Figure 1. Proposed TS for cobalt-catalyzed cyclopropanation.

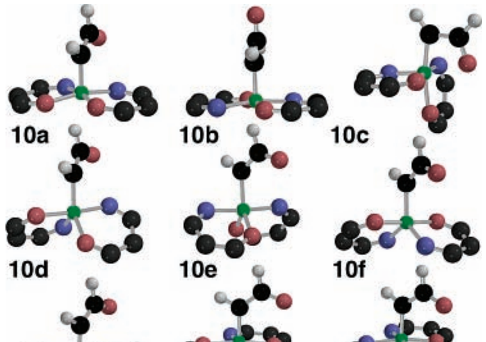
the results at UB3LYP/6-31G*//UB3LYP/6-31G* were described. The obtained overall energy profiles are shown in Figures 2 and 3 after the ZPE correction.

The investigation of the ground states of the unbridged complex **4** afforded three conformers, of which the most stable one, **4d**, was in the quartet state and the others, **4a** and **4b**, were in the doublet states, slightly higher in energy. Also, for the ethylene-bridged complex **5**, the planar structure **5a** was obtained in the doublet state and the bent structure **5b** in the quartet state. These results are summarized as follows: for the four-coordinated d^7 cobalt complex, the tetrahedral structure was favored in the quartet states, while the square planar structure was favored in the doublet states. The ethylene bridge could hold the cobalt complex planar to stabilize the doublet state **5a** although the bent structure **5b** in the quartet would be labile.

Throughout the cyclopropanation reaction catalyzed by the ethylene-bridged complex **5**, the intermediates were estimated to be in the doublet states (Figure 2). The cobalt complex **5a** reacted with diazoacetaldehyde to generate the cobalt carbene complex **7a**, which reacted in a concerted manner with ethylene to produce the corresponding cyclopropane and the starting cobalt complex **5a**. As shown in Figure 2, throughout the reaction, all the structures of the complexes in the quartet state deviated from a planar structure to be sufficiently higher in energy. Because the ethylene bridge would restrict the flexibility of the ligand plane, it is assumed that the quartet states could not be mixed with the doublet states.[6]

The transition state (TS$_1$) for generation of the cobalt carbene complex from the unbridged cobalt complex **4** and diazoacetaldehyde was examined (Figure 3).[7] The planar structures **9a** and **9b** were found to be stable transition states, and the TS$_1$ in the doublet states were more stable than those in the quartet states.[8]

After TS$_1$, the resulting carbene complexes were obtained as planar structures in the doublet states **10a** and **10b**, the cis-β structure was obtained in the doublet **10c** and the bent structure in the quartet states **10d**, **10e**, and **10f**. For all the obtained cobalt carbene complexes, the doublet states were more stable than the quartet states.[9]



While investigating the reaction pathway of these carbene complexes with ethylene, it was found that the coordination

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(4) (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revisions A.6 and A.11; Gaussian, Inc.: Pittsburgh, PA, 1998. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785−789.

(5) These basis sets afforded the same results. Possible rotational isomers were fully optimized, and the energies were compared with each other. See Supporting Information.

(6) S2 values are shown. **5a**, S2 = 0.763; **5b**, S2 = 3.759; **6a**, S2 = 0.820; **6b**, S2 = 3.832; **7a**, S2 = 0.769; **7b**, S2 = 3.786; **8a**, S2 = 0.792; **8b**, S2 = 3.751.

(7) A number of the rotational isomers in the carbene moiety were omitted for clarity. S2 values are shown. **4a**, S2 = 0.764; **4b**, S2 = 0.765; **4d**, S2 = 3.761; **9a**, S2 = 0.826; **9b**, S2 = 0.821; **9d**, S2 = 3.784; **9e**, S2 = 3.784; **9f**, S2 = 3.787; **10a**, S2 = 0.766; **10b**, S2 = 0.765; **10c**, S2 = 0.762; **10d**, S2 = 3.783; **10e**, S2 = 3.782; **10f**, S2 = 3.787; **10g**, S2 = 0.764; **10h**, S2 = 0.776; **11a**, S2 = 0.813; **11b**, S2 = 0.814; **11c**, S2 = 0.773; **11d**, S2 = 3.801; **11e**, S2 = 3.801; **11f**, S2 = 3.805; **11g**, S2 = 0.786; **12**, S2 = 0.795; **13**, S2 = 0.773.

(8) Unbridged cobalt(II) complex is in the quartet state on the basis of the magnetic susceptibility measurement. However, the transition state (TS$_1$) **9** and carbene complex **10** were both in the doublet states and were stable. It was experimentally observed that the green-colored [bis(salicylidene-*N*-phenethyl)]cobalt(II) complex turned red during the reaction with a diazo compound. The spin crossing could be considered during this process, though not mentioned. (a) Punniyamurthy, T.; Bhatia, B.; Iqbal, J. *J. Org. Chem.* **1994**, *59*, 850−853.

(9) Energy differences between the doublet and quartet states in the bridged complexes were much greater than those in the unbridged complexes. These results would also support the fact that the ethylene bridge could retain the planarity of the complex to stabilize the low-spin state.

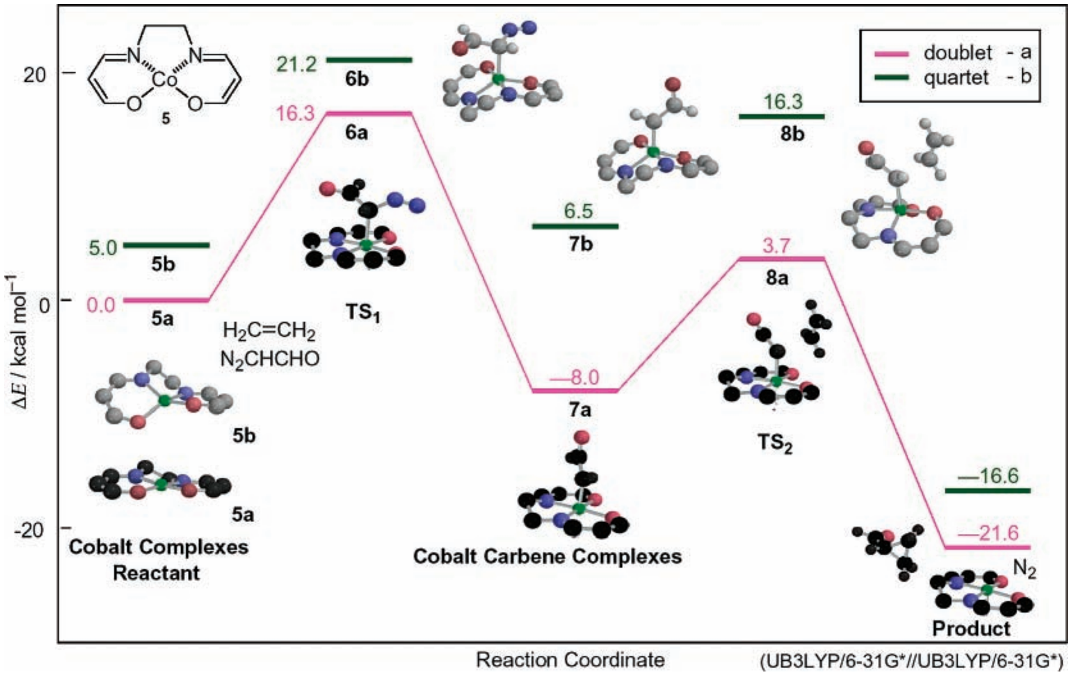

Figure 2. Reaction pathway of cobalt complex **5**-catalyzed cyclopropanation.

of ethylene to the doublet conformer has a crucial effect on the pathways to TS$_2$ and that the cyclopropanation reaction could proceed via the metallacycle intermediate. From the cobalt carbene complexes, the transition states (TS$_2$s) for the concerted cyclopropanation were examined to obtain the respective TS$_2$s **11a**−**f** affording the cyclopropane. Additionally, the stable transition state **11g** for the cobaltacyclobutane intermediate **12** was obtained. The IRC analysis from the TS$_2$ **11g** to the reactant afforded the carbene complex **10g** coordinated by ethylene.[10] The energy surface of the reaction from the cobalt carbene complex **10c** decreased to the ethylene complex **10g**; therefore, the ethylene complex **10g**

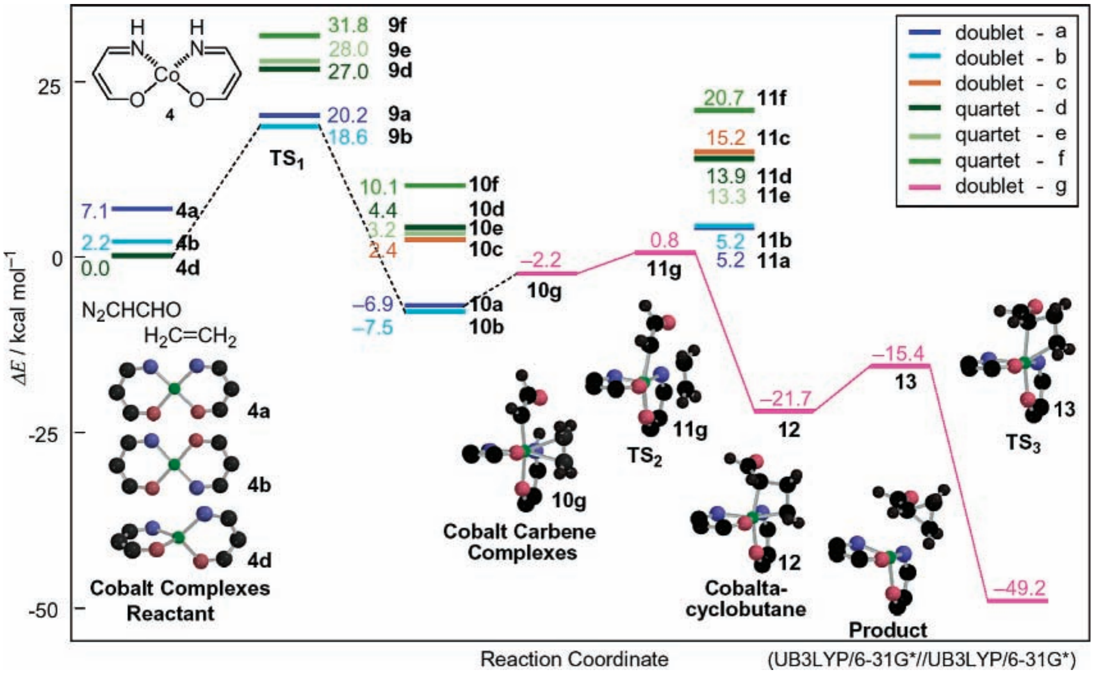

Figure 3. Reaction pathway of cobalt complex **4**-catalyzed cyclopropanation.

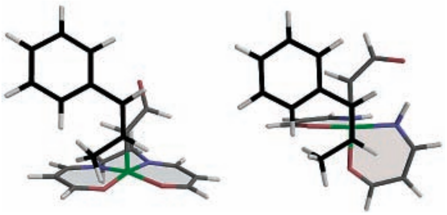

Figure 4. Probable TS of cis-β-methylstyrene in the concerted (left) and metallacycle (right) mechanisms.

could be the transient species on the pathway between the carbene complex **10c** and the TS$_2$ **11g**.[11] From the TS$_2$ **11g**, the cobaltacyclobutane **12** was obtained as an intermediate, and then from the TS$_3$ **13**, the corresponding cyclopropane was produced by the reductive elimination of the starting cobalt complex **4**. The mechanism via cobaltacyclobutane should be reasonable on the basis of a comparison of the activation energies with the concerted mechanism.

It was reported in the literature[2a] that the ethylene-bridged complexes did not work as catalysts for the cyclopropanation reaction of β-methylstyrenes due to steric reasons. On the contrary, the present work proposed that the cobalt complex without an ethylene bridge would be flexible enough to transform into the cis-β structure and could be capable of catalyzing the cyclopropanation of β-methylstyrene via a metallacycle intermediate without any steric repulsion (Figure 4). The reaction of cis-β-methylstyrene with ethyl diazoacetate was actually catalyzed by the unbridged [bis(salicylidene-*N*-phenethyl)]cobalt(II) complex[8a] to afford the corresponding cyclopropane but not by ethylene-bridged complexes.[12] These experimental observations would suggest the possibility that the reaction proceeded via the metallacycle intermediate.

It was concluded that the metallacycle pathway is preferred for the cyclopropanation reaction catalyzed by the cobalt(II) complex without an ethylene bridge, while the concerted mechanism is dominated by the complex with an ethylene bridge. Concerted and metallacycle mechanisms have been proposed for the cyclopropanation catalyzed by copper[13] and cobalt[1−3] complexes. The present work revives the possibility that the cobaltacyclobutane intermediate can provide a practical strategy for designing the complex catalysis.

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Supporting Information Available: Structures of all the rotational isomers and results from the other basis sets. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Ethylene complexes coordinated on the equatorial position parallel to the cobalt−carbene carbon bond **10g** and perpendicular in **10h**, and the axial positions of **10i** and **10j** were also optimized. The complexes **10i** and **10j** were found to be much less stable than complexes **10g** and **10h**.

(11) In the reaction pathway described by the Gibbs free energy, the carbene complex **10c**, the ethylene complex **10g**, and the TS$_2$ **11g** were observed to be 7.3, 14.6, and 18.3 kcal/mol, respectively. It should be considered that the ethylene complex structure could be just a transient structure on the reaction pathway. The activation energy of the TS$_2$ **11g** and **11b** were $\Delta G = 21.0$ and 23.8 kcal/mol, respectively. The mechanism via the cobaltacyclobutane was supported by these results and also on the basis of the Gibbs free energy.

(12) In the presence of the 0.1 mmol cobalt(II) complex, the mixture of ethyl diazoacetate (0.3 mL) and cis (or trans) β-methylstyrene (0.3 mL) was heated at 90 °C for 5 h. Only for the unbridged-complex-catalyzed reaction was the corresponding cyclopropane obtained and identified by TLC, GC, and NMR.

(13) Proposals of mechanisms based on the experimental results: (a) Aratani, T.; Yoneyoshi, Y.; Nagase, T. *Tetrahedron Lett*. **1975**, 1707−1710. (b) Aratani, T. *Pure Appl. Chem.* **1985**, *57*, 1839−1844. (c) Fritschi, H.; Leutenegger, U.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl*. **1986**, *25*, 1005−1006. (d) Fritschi, H.; Leutenegger, U.; Pfaltz, A. *Helv. Chim. Acta* **1988**, *71*, 1553−1565. Proposals of mechanisms based on the theoretical analysis: (e) Fraile, J. M.; García, J.-I.; Martínez-Merino, V.; Mayoral, J. A.; Salvatella, L. *J. Am. Chem. Soc.* **2001**, *123*, 7616−7625. (f) Rasmussen, T.; Jensen, J. F.; Østergaard, N.; Tanner, D.; Ziegler, T.; Norrby, P.-O. *Chem.−Eur. J.* **2002**, *8*, 177−184.