Mechanistic Models

A DFT Study on Hetero-Diels–Alder Reactions Catalyzed by Cobalt Complexes: Lewis Acidity Enhancement as a Consequence of Spin Transition Caused by Lewis Base Coordination

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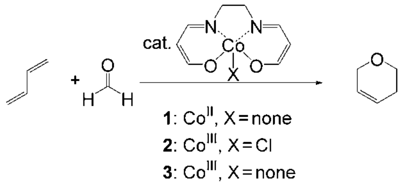
Among the various chiral Schiff base transition-metal complexes, the cobalt complexes with acacen- and salen-type ligands have been successfully employed as chiral Lewis acid catalysts, for example, for the enantioselective hetero-Diels–Alder reaction,[1] the carbonyl-ene reaction,[2] 1,3-dipolar cycloaddition of nitrones,[3] and ring opening of epoxides.[4] For these enantioselective catalyses, high efficiency and high stereoselectivity were realized, and specific catalytic activity of the cobalt complexes was achieved. Recently, theoretical analyses of reactions catalyzed by Schiff base complexes have attracted considerable attention,[5] but few analyses of the reaction pathways catalyzed by the Schiff base complexes as Lewis acids were performed. During our study on the catalyis of enantioselective cycloadditions and ene reactions by 3-oxobutylideneaminatocobalt complexes,[1a,b,2,3] we found that the enantioselectivity and reaction rate were improved when cationic Co^{III} complexes were used instead of Co^{II} complexes. Here we report on a theoretical analysis of cobalt-catalyzed hetero-Diels–Alder reactions, which revealed the crucial effect of aldehyde coordination as an axial ligand on the spin states and Lewis acidity of the cobalt complexes.

The hetero-Diels–Alder reaction catalyzed by the cobalt complex is depicted in Scheme 1; Danishefsky's diene[6] was replaced by a simple butadiene, and formaldehyde was adopted as the representative aldehyde. For the cobalt catalysts, complexes **1**–**3** were adopted as models. The unrestricted Becke three-parameter hybrid exchange functional combined with the Lee–Yang–Parr correlation functional (B3LYP)[7] was used with the LANL2DZ,[8] 6-31G(d), and 6-311G(d,p) basis sets for geometry optimizations and vibrational analyses.[9,10] Results with these basis sets were qualitatively quite consistent with our previous experimental results.[5d–f] The BP86 and BLYP methods were also examined at the 6-31G(d) level to check the validity of conclusions obtained by the B3LYP method.[10] For the cobalt(II) complexes, the doublet and quartet states were calculated, and for the cobalt(III) complexes, the singlet, triplet, and quintet states were examined. Reasonable rotational isomers were fully optimized, and the obtained energies were compared.[11] The total energy profiles for the catalytic cycle (single-point energies at B3LYP/6-31G(d)//B3LYP/6-31G(d)) are shown in Figures 1–3.[10]



Scheme 1. Model system for hetero-Diels–Alder reaction.

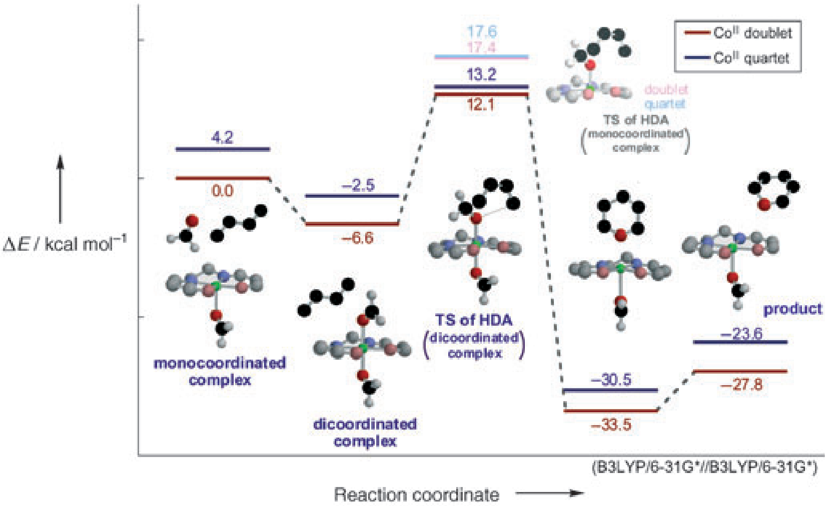


Figure 1. Energy profile for the catalytic cycle of the hetero-Diels–Alder reaction catalyzed by cobalt(II) complex **1**. Co green; N blue; O red, pink.

Calculation of the ground states of model complexes **1**–**3** revealed that Co^{II} complex **1** is in the doublet state, while Co^{III}-Cl complex **2** and cationic Co^{III} complex **3** are in the triplet state.

The effect of coordination of the aldehyde to cobalt complexes **1**–**3** was then examined. The structures of monocoordinated complexes Co^{II}-H_2CO and Co^{III}-H_2CO and dicoordinated complexes Co^{II}-$2H_2CO$, Co^{III}-Cl-H_2CO, and Co^{III}-$2H_2CO$ were optimized. The Co^{II}-H_2CO and Co^{II}-$2H_2CO$ complexes are in the doublet state, and the Co^{III}-H_2CO and Co^{III}-$2H_2CO$ complexes in the triplet state, though for the dicoordinated Co^{III}-$2H_2CO$ complex, the energy difference between the triplet and singlet states was very small for some of the employed basis sets. On the other hand, Co^{III}-Cl-H_2CO is in the singlet state. This indicates that the spin transition is caused by coordination of the aldehyde for Co^{III}-Cl complex **2**. The dicoordinated complexes are more stable than the corresponding monocoordinated com-

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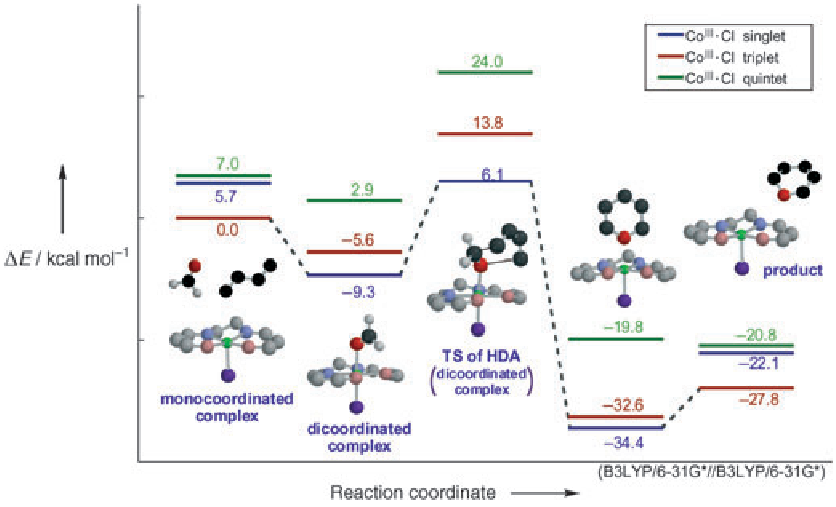

Figure 2. Energy profile for the catalytic cycle of the hetero-Diels–Alder reaction catalyzed by cobalt(III)-Cl complex **2**. Co green; N blue; O red, pink.

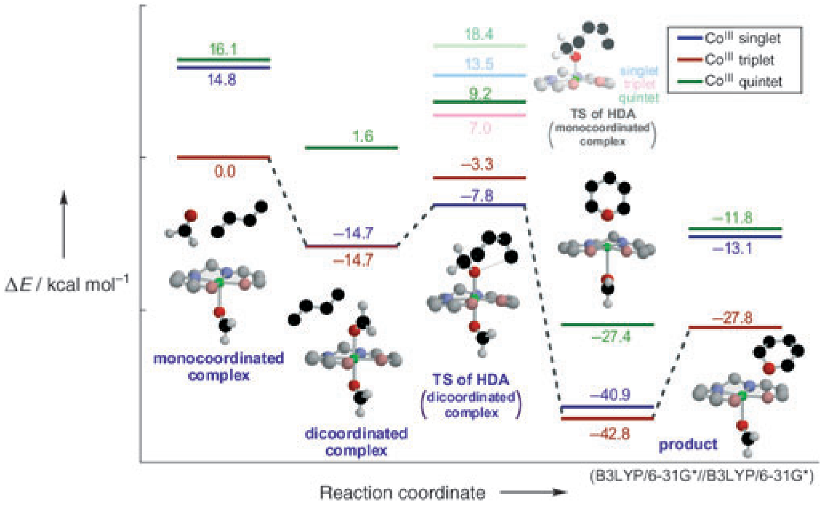

Figure 3. Energy profile for the catalytic cycle of the hetero-Diels–Alder reaction catalyzed by cobalt(III) complex **3**. Co green; N blue; O red, pink.

plexes.[12] For all the coordinated complexes, only structures in which a formaldehyde ligand is found on the same side as the O atoms of the ligand plane were obtained. It is reasonable to assume that the aldehydes should be located in a direction that negates the dipole moment of the cobalt complex. These results are well supported by the X-ray structure analysis of the salen cobalt(III) complex with two coordinated molecules of benzaldehyde.[1c]

By using all the coordinated complexes, the transition states (TS) of the hetero-Diels–Alder reaction with butadiene were calculated. Although the question of a concerted or stepwise process in Diels–Alder reactions has often been controversial, the present calculation concludes that the concerted pathway is more favorable than the stepwise pathway in the cobalt-complex-catalyzed hetero-Diels–Alder reaction.[13] These results are quite consistent with a recent analysis of the hetero-Diels–Alder reaction of butadiene and formaldehyde by CASSCF calculations[14] and with our experimental results.[1a,b]

Many rotational isomers involved in the direction of approach of the butadiene were obtained for the concerted pathway. The TSs with the attack of butadiene towards the two nitrogen atoms were higher in energy, though the energy differences of the other rotational isomers, in which butadiene approaches over the oxygen atom or bisects the two oxygen atoms, are small. All the obtained TS structures in the concerted pathway are very asynchronous, but the structures were not significantly affected by the cationic character (Table 1). In particular, the distance between the aldehyde oxygen and diene carbon atoms is very long (2.32–2.78 Å), while that between the aldehyde carbon and diene carbon atoms is relatively short (1.69–1.91 Å). For the TSs of the aldehyde Co complex with butadiene, the doublet and quartet states are close in energy for Co^{II} complex **1**, and the singlet states are the most stable for dicoordinated Co^{III}-Cl complex **2** and Co^{III} complex **3**. After the TS, the product is coordinated to the cobalt complex, and the calculation indicates that the singlet state is stable for the Co^{III}-Cl-product complex, while the stable spin state is a triplet for the Co^{III}-H_2CO-product complex. The ligand-exchange reaction of such types of Schiff base cobalt complexes proceed in a dissociative manner to release the product.[15] The monocoordinated cobalt complex is regenerated and the catalytic cycle completed. It has been concluded that the spin transition between the triplet and singlet states is caused by axial coordination of the aldehyde[16] in the cobalt(III) catalytic cycle by comparison with the monocoordinated cobalt(III) pathway.

Activation energies, representative bond lengths, and bond orders of the TSs are summarized in Table 1. The

Table 1: Activation energies [kcal mol^{-1}], bond lengths [Å], and bond orders of the transition states.[a]

Complex	Spin state	ΔE	Co−O$_{aldehyde}$	C$_{aldehyde}$−C$_{diene}$[c]	O$_{aldehyde}$−C$_{diene}$[c]
Co^{II}-H_2CO	doublet	17.4[b]	2.191	1.856 (0.66)	2.357 (0.62)
Co^{II}-2 H_2CO	doublet	18.7	2.289	1.906 (0.65)	2.315 (0.62)
Co^{III}-Cl-H_2CO	singlet	15.3	1.974	1.766 (0.61)	2.617 (0.61)
Co^{III}-H_2CO	triplet	7.0[b]	2.004	1.793 (0.76)	2.784 (0.57)
Co^{III}-2 H_2CO	singlet	6.8	1.903	1.685 (0.79)	2.566 (0.63)

[a] At the B3LYP/6-31G(d)//B3LYP/6-31G(d) level. [b] Activation energy for the monocoordinated Co^{II}-H_2CO and Co^{III}-H_2CO complexes, though these species are less stable than the dicoordinated complexes. [c] Bond orders in parentheses.

activation energy clearly decreases in proportion to the cationic character of the cobalt complex ($\mathrm{Co^{II}}$ **1** > $\mathrm{Co^{III}}$-Cl **2** ≫ $\mathrm{Co^{III}}$ **3**). These tendencies are quite consistent with previously reported experimental observations.[1a,b] It is noteworthy that by comparison with the ground states of the dicoordinated complexes, the $\mathrm{Co{-}O_{aldehyde}}$ distance is shortened in the TS. (For the $\mathrm{Co^{III}\text{-}2\,H_2CO}$ complex, the $\mathrm{Co{-}O_{aldehyde}}$ distance changes from 1.93 to 1.90 Å in the singlet state and from 2.26 to 2.06 Å in the triplet state, while for the $\mathrm{Co^{III}\text{-}Cl\text{-}H_2CO}$ complex, it is shortened from 2.04 to 1.97 Å in the singlet state.) Since a diene is more electron rich than an aldehyde, delocalization of the electron from the diene to the aldehyde is favored in the TS, and this leads to stronger coordination of the aldehyde to the cobalt atom. Accordingly, the lower spin states are more favorable in the TS than in the ground states.

The length of the bond between the cobalt atom and the aldehyde indicates the Lewis acidity of the cobalt complex. It is generally considered that axial coordination of a Lewis base such as an aldehyde would decrease the Lewis acidity of complex catalysts. The present study conforms well with this hypothesis for the $\mathrm{Co^{II}}$ complex catalysts; the distance between the cobalt and aldehyde oxygen atoms in the TS is elongated from 2.19 to 2.29 Å by coordination of the aldehyde, since delocalization of an electron occurs from the lone pair of the oxygen atom into the antibonding orbital of the $\mathrm{Co{-}O_{aldehyde}}$ bond. In contrast, spin transition from triplet to singlet for the $\mathrm{Co^{III}}$ complex overcomes the deactivation due to the coordination of the Lewis base, because there is no electron in the d_{z^2} orbital in the singlet state and the coordinative interaction between cobalt atom and aldehyde is stronger. Therefore, the distance is shortened from 2.00 to 1.90 Å (Figure 4).[17] It is generally considered that the closer the substrate approaches the metal center, the greater the enantioselectivity. Thus, in the $\mathrm{Co^{III}}$ complexes coordination of the aldehyde causes the $\mathrm{Co{-}O_{aldehyde}}$ distance to shrink owing to the spin transition from the triplet to singlet in the TS, and hence the enantioselectivity is improved.

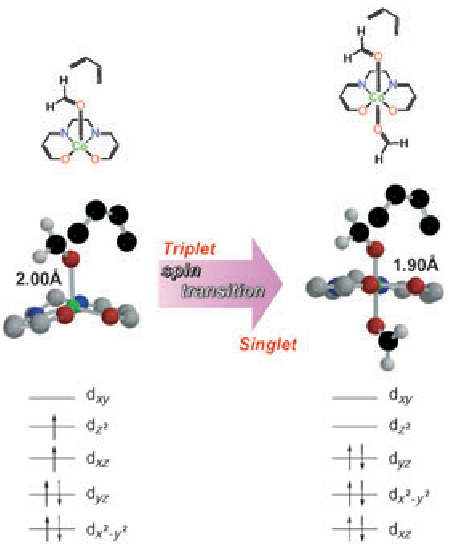

Figure 4. Coordination effect of aldehyde.

In summary, a theoretical analysis of the hetero-Diels–Alder reaction catalyzed by cobalt(II) and cobalt(III) complexes reveals the following results: 1) with increasing cationic character of the cobalt atom, the activation energy decreases; 2) spin transition between the triplet and singlet states occurs in the cobalt(III) catalytic cycle; and 3) axial coordination of an aldehyde plays a crucial role in the spin transition that enhances the Lewis acidity of the cobalt complex and improves the enantioselectivity.

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[10] In this manuscript, single-point energies at the B3LYP/6-31G(d) level are shown in Figures 1–3 and Table 1. The energy profiles (single-point energies, energies including ZPE corrections, and Gibbs energies) at the BLYP/6-31G(d), BP86/6-31G(d), B3LYP/LANL2DZ, B3LYP/6-31G(d), B3LYP/6-311G(d,p), B3LYP/6-311G(d,p)//B3LYP/6-31G(d), and B3LYP/6-311+G(d,p)//B3LYP/6-311G(d,p) levels are given in the Supporting Information. The Gibbs energies were calculated at 195 K (−78 °C) with a simple correction ($RT \ln V_{sol}/V_{gas}$: $T = 195$ K, $V_{gas} = 16$ L mol^{-1}, $V_{sol} = 1$ L mol^{-1}) from the gas phase to solution (1 mol L^{-1}). a) A. Ben-Naim, Y. Marcus, *J. Chem. Phys.* **1984**, *81*, 2016–2027; b) B. O. Leung, D. L. Reid, D. A. Armstrong, A. Rauk, *J. Phys. Chem. A* **2004**, *108*, 2720–2725. All the methods and basis sets led to the same conclusions.

[11] All structures of the rotational isomers around the Co–O axis (B3LYP/LANL2DZ and 6-31G(d)) are shown in the Supporting Information.

[12] After the BSSE correction, the complexation energies of Co^{II}-H_2CO, Co^{III}-Cl, and Co^{III}-H_2CO with H_2CO are 1.1, 4.8, and 11.0 kcal mol^{-1}, respectively. Since the stabilization of the second coordination of the aldehyde to Co^{II}-H_2CO was very small, both mono- and dicoordinated TSs would be possible.

[13] The TSs of the stepwise pathway are shown in the Supporting Information.

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[17] In the TS, the distance between the cobalt atom and the aldehyde in the triplet state of the Co^{III}-2H_2CO complex is 2.063 Å, which is longer than that of the Co^{III}-H_2CO complex.