Manganese and cobalt 3-oxobutylideneaminato complexes: Design and application for enantioselective reactions

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Received 1 September 2005; received in revised form 1 November 2005; accepted 1 November 2005

Abstract

The optically active 3-oxobutylideneaminato transition-metal complexes have been developed as efficient catalysts for a variety of enantioselective reactions; e.g. the corresponding manganese(III) complexes catalyzed the enantioselective aerobic epoxidation of unfunctionalized olefins, and the corresponding cobalt complexes have been developed for the enantioselective borohydride reduction of various carbonyl compounds. The cobalt complexes could also be employed for the catalytic enantioselective cyclopropanation with diazoacetates and the Lewis acid catalyses such as the hetero Diels–Alder reaction, carbonyl–ene reaction, and 1,3-dipolar cycloaddition of nitrones. In the presence of the cobalt complex, the Henry reaction proceeded with a high enantioselectivity, and the enantioselective chemical fixation of carbon dioxide to obtain the optically active cyclic carbonate. In these Lewis acid catalyses, the valence of cobalt and the counter anion have significant effects on the reaction rate and stereoselectivity.

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Keywords: Enantioselective reaction; Manganese; Cobalt; Schiff base; Lewis acid; Aerobic oxidation; Borohydride reduction; Carbon dioxide

1. Introduction

Since transition-metal Schiff base complexes were originally developed as a model system of the transition-metal porphyrin complexes, various salen–metal complexes have been employed as one of the most privileged chiral catalysts [1] for a variety of enantioselective reactions. In our laboratory, on the basis of the examination of the 1,3-diketonatocobalt complexes catalyses [2], the optically active 3-oxobutylideneamine derivatives have been developed as efficient ligands for various transition-metal complexes. Treatment of the corresponding 1,3-dicarboxyl compounds, prepared by the reported method [3], with dimethylformamide dimethylacetal, and successive hydrolysis afforded the formylated 1,3-dicarboxyl compounds, which were then treated with optically active diamines to obtain the 3-oxobutylideneamine ligands. Finally, the
complexation with manganese or cobalt salts afforded the complexes according to Scheme 1.

In the 3-oxobutylideneaminato metal complexes, their side chains, chiral 1,2-ethylenediamine unit, center metal, its valence, and counter anion could be designed readily, therefore, the optimization of the complex catalyst for various reactions could be accomplished smoothly. As these manganese and cobalt complexes are fairly stable and easily prepared on a multi-gram scale, their structures can be defined by X-ray crystal analysis (Fig. 1) [4]. By using these kinds of complex catalysts, several enantioselective reactions have been reported by our laboratory. In this review, some examples and overview of the complexes are described.

2. Enantioselective aerobic epoxidation

Although molecular oxygen is one of the most environmentally benign and ultimate oxidants, there are few reports on the

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Fig. 1. Crystal structures of 3-oxobutylideneaminato manganese and cobalt complexes.
widely applicable aerobic oxidation in the fine chemicals industries. For example, the enantioselective epoxidation of various alkenes are so far performed using other oxidants, such as iodosylbenzene [5–7], sodium hypochlorite [8], and peracid [9], to afford the corresponding epoxides with high-to-excellent enantioselectivities in the presence of salen–Mn(III) complex catalysts. By the combined use of molecular oxygen and secondary alcohols, the terminal alkenes were converted to the corresponding hydrated products in the presence of cobalt(II) complexes having 1,3-diketone-type ligands. During this hydration reaction, both oxidation (oxygenation) and reduction (hydrogenation from 2-propanol) occurred, thus it was called the ‘oxidation–reduction hydration’ [2,10,11].

Similar to the coexistence of an aldehyde, the effective aerobic epoxidation of alkenes catalyzed by such metal complexes as nickel(II) [12–14], iron(III) [15], vanadium(IV) [16,17], and manganese(III) [18] coordinated by the 1,3-diketone ligand have been developed. In the presence of pivalaldehyde and a catalytic amount of the optically active 3-oxobutylideneaminitomanganese(III) complex, molecular oxygen was captured efficiently to generate the highly oxidized manganese intermediate, which epoxidized various unfunctionalized olefins into the epoxides with good-to-high enantioselectivities (Table 1) [19–23]. By the addition of N-methylimidazole, the

| Entry | Olefin | Yield (%)<sup>a</sup> | ee (%)<sup>b</sup> |
|-------|-------|-----------------|-----------------|
| 1     |       | 70              | 64              |
| 2     |       | 43              | 70              |
| 3     |       | 52              | 84              |

<sup>a</sup> Isolated yield.

<sup>b</sup> Determined by GC analysis (ChiralDEX B-DA).

Table 2

| Entry | Ketone | Catalyst | ee (%)<sup>a</sup> |
|-------|--------|----------|-----------------|
| 1     |        | 1        | 91<sup>b</sup>   |
| 2     |        | 2        | 90              |
| 3     |        | 3        | 95<sup>b</sup>   |
| 4     |        | 3        | 97              |

<sup>a</sup> Determined by HPLC analysis.

<sup>b</sup> Using MeOH instead of EtOH.

**Reaction conditions.** Olefin 0.8 mmol, 2,2-dimethylpropanal 2.8 mmol, Mn(III) catalyst 0.104 mmol (13 mol%) in benzene 2 mL, 30 °C, 1 atm O₂ 1 h.

**Table 1**
Aerobic enantioselective epoxidation of unfunctionalized olefins

**Table 2**
Enantioselective reduction of various ketones

**Reaction conditions.** 0.50 mmol of substrate, 0.005 mmol of Co catalyst, 0.75 mmol of NaBH₄, 2.25 mmol of EtOH, 10.3 mmol of THFA, in CHCl₃ (10 mL), at −20 °C, 12 h, quantitative yield.
enantiofacial selection was reversed [24,25]. It might be ascribed to the fact that the acylperoxo-Mn intermediate, that was generated from molecular oxygen, pivalaldehyde, and the Mn(III) complex catalyst, could be effectively converted into the Mn-oxo species. The mechanism of the effect was recently analyzed by DFT calculations [26].

3. Enantioselective borohydride reduction

Optically active alcohols are some of the most important compounds for fine chemicals, such as medicinal compounds and functional materials. In order to obtain these chiral compounds, various methods for the enantioselective reduction of ketones have been proposed. Asymmetric hydrogenation is one of the most promising procedures for this purpose, and various efficient catalysts have been developed [27–29]. Transfer hydrogenolysis, catalyzed by similar complexes, are also effective for the enantioselective reduction of ketones to obtain the optically active alcohols [30–32]. Although sodium borohydride is commercially available, easily handled, and widely used in the laboratory and industry, the enantioselective borohydride reduction of ketones has not been developed [33–35]. We discovered that the cobalt complexes with 3-oxobutylideneaminato ligands were efficient catalysts for the enantioselective borohydride reduction of ketones [36], imines [37], and \(\alpha,\beta\)-unsaturated carbonyl compounds [38] to afford the corresponding secondary alcohols, amines and saturated carbonyl compounds with high enantioselectivities (Tables 2–4) [39–41].

In the presence of a catalytic amount (0.1–5 mol%) of the optically active cobalt(II) complex, the enantioselective reduction of various aryl ketones proceeded using borohydride modified with tetrahydrofurfuryl alcohol (THFA). A preliminary investigation suggested that the addition of an alcohol was indispensable for achieving a high enantiomeric excess. Without ethanol, the reduced product was obtained in less than a 10% yield and its enantiomeric excess was only 5%, whereas in the presence of ethanol, it was improved to 83% ee. In the presence of the tetrahydrofurfuryl alcohol, a higher enantioselectivity as well as a faster reaction rate were realized [42]. It is noted that a suitable cobalt(II) complex catalyst should be chosen corresponding to the substrates to achieve high enantioselective excesses [43]. More than several hundred TONs were

Table 3

| Entry | Imine | Catalyst | Yield (%)a | ee (%)b |
|-------|-------|----------|------------|---------|
| 1     | 2     | 85       | 98         |
| 2     | 3     | 97       | 90         |
| 3     | 2     | 86       | 91         |
| 4     | 2     | 97       | 99         |

Reaction conditions. 0.50 mmol of substrate, 0.005 mmol (1 mol%) of Co catalyst, 0.75 mmol of modified NaBH₄ (0.75 mmol of NaBH₄, 0.75 mmol of EtOH, and 10.3 mmol of THFA), in CHCl₃, at 0 °C, 4 h.

\(^a\) Isolated yield.
\(^b\) Determined by HPLC analysis.
Table 4
Enantioselective 1,4-reduction of α,β-unsaturated carboxamides

| Entry<sup>a</sup> | Unsaturated carboxamide | Yield (%) | ee (%)<sup>b</sup> |
|-------------------|-------------------------|-----------|-------------------|
| 1<sup>c</sup>     | ![Image](image1)         | 92        | 70                |
| 2                 | ![Image](image2)         | 98        | 83                |
| 3                 | ![Image](image3)         | 97        | 85                |
| 4                 | ![Image](image4)         | 98        | 86                |

<sup>a</sup> Reaction conditions: 0.5 mol% Co complex, 4.0 equiv. NaBH₄, 8.0 equiv. THFA, in CH₂Cl₂, RT, 2 h.
<sup>b</sup> Determined by HPLC analysis.
<sup>c</sup> Reaction time 4 h.

Table 5
Highly chemo-, diastereo-, and enantioselective reduction of various 2-alkyl-1,3-diketones

| Entry | 3-Hydroxy ketones | Yield (%)<sup>a</sup>/conversion (%)<sup>a</sup> | Selectivity |
|-------|-------------------|-----------------------------------------------|-------------|
|       |                   |                                               | Chemo- (%)<sup>b</sup> | Anti- (%)<sup>b</sup> | Enantio- ee (%)<sup>c</sup> |
| 1     | ![Image](image5)  | 46/48                                         | 99          | 99               | 96           |
| 2     | ![Image](image6)  | 47/55                                         | 95          | 98               | 96           |
| 3     | ![Image](image7)  | 47/54                                         | 96          | 98               | 96           |
| 4     | ![Image](image8)  | 45/52                                         | 93          | 94               | 98           |

Procedure. Four portions of the 0.1 equiv. of the pre-modified borohydride were successively added at 2 h intervals to the solution of the cobalt catalyst and the substrate; 0.25 mmol of substrate, 0.0125 mmol (5 mol%) of cobalt catalyst, 0.1 mmol of NaBH₄, 0.1 mmol of EtOH, 1.4 mmol of tetrahydrofurfuryl (THFA) CHCl₃ (total 12.8 mL) at −20 °C.

<sup>a</sup> Isolated yield.
<sup>b</sup> Determined by <sup>1</sup>H NMR analysis.
<sup>c</sup> Determined by HPLC analysis.
achieved and some of the efficient cobalt(II) complex catalysts are now available commercially[44].

The catalytic and enantioselective reduction were successfully applied to the preparation of various optically active 2-substituted-3-hydroxycarbonyl compounds from the corresponding 1,3-dicarbonyl compounds [45,46]. As kinetic resolution should be considered for the unsymmetrical 2-substituted-1,3-diketone, 2,4-dimethyl-1-phenyl-1,3-pentanedione, 0.5 equiv. of the pre-modified borohydride was employed in the presence of the optically active cobalt complex to obtain the corresponding aldol compound, 3-aryl-3-hydroxyketone, in 46% yield with 99% chemoselectivity (arylketone vs alkylketone), 99% anti-selectivity, and 96% ee (Table 5, entry 1) [47]. Also, the recovered 2-methyl-1,3-diketone was found to be 99% ee. The addition of the appropriate base caused a racemization equilibrium during the enantioselective reduction. In the presence of 4 mol% of the cobalt complex catalyst, the enantioselective reduction of the 2-methyl-3-(2-naphthyl)-3-oxopropionic acid ethyl ester afforded 3-hydroxy-2-methyl-3-(2-naphthyl)propionate in 91% yield with 92% anti-selectivity and 95% ee (Table 6, entry 1) [48].

4. Enantioselective cyclopropanation

In the presence of the 3-oxobutyldieneaminatocobalt complex, it was reported that the cyclopropanation reaction of diazoacetate and styrene derivatives proceeded in high yield with a high trans and enantioselectivity (Table 7) [49,50]. The steric demand of the chiral diamine unit of the complexes influenced the enantioselectivity, and the ester groups on their side chains somewhat influenced the trans-selectivity. The addition of a catalytic amount of N-methylimidazole significantly accelerated the reaction and enhanced the enantioselectivity due to its coordination to the center cobalt atom of the complex as an axial ligand [51]. Alcoholic or aqueous alcoholic solvents were also particularly effective for the cyclopropanation of 1-substituted 1-phenylethylenes in order to achieve a high enantioselectivity (entry 4) [52].

Table 6
Dynamic kinetic resolution of enantioselective reduction for anti-aldol compounds

| Entry | 3-Hydroxyester | Yield (%)a | Anti-selectivity (%)b | ee (%)c |
|-------|----------------|------------|------------------------|---------|
| 1     |                | 91         | 92                     | 95d     |
| 2     |                | 91         | 89                     | 93c      |
| 3     |                | 93         | 87                     | 94f     |
| 4     |                | 84         | 87                     | 95f     |

*Modified borohydride: NaBH₄ (113.5 mg, 3.0 mmol) in CHCl₃ (20.0 mL), EtOH (176 µL, 3.0 mmol), tetrahydrofurfuryl alcohol (4.07 mL, 42.0 mmol), 0 °C, 3 h. Reaction conditions: cobalt catalyst (5.7 mg, 0.01 mmol), sodium methoxide (13.5 mg, 0.25 mmol), 2-alkyl 3-ketoester (0.25 mmol), CHCl₃ (12.0 mL), pre-modified NaBH₄ (2.4 mL, 0.30 mmol), 15 h, −10 °C.

a Isolated yield.

b Determined by 1H NMR analysis.

c Determined by HPLC analysis (2-propanol/hexane).

d Using Daicel Chiralpak AD-H.

e (2S,3R)-product was obtained corresponding to (R,R)-cobalt catalyst.

f Using Daicel Chiralcel OB-H.
spectroscopic analyses of the reaction pathway and the reaction intermediates have been limited until recently. We performed a semiempirical analysis using the PM3 method on the 3-oxobutylideneaminocobalt(II) complex catalyzed cyclopropanation to reveal that the enantioselectivity occurred due to the repulsion between the aryl group of the diamine unit and the ester moiety, and that diastereoselectivity was controlled by the repulsion between the ester moiety and the approaching olefin [54]. On the basis of the DFT analysis, we also revealed two prominent effects caused by the axial ligand [55,56]. One is that the activation energy for the formation of the cobalt carbene intermediate was reduced and that the activation energy for the cyclopropanation step was increased. The other is that the distance of the carbene carbon above the ligand plane was shortened during the cyclopropanation step. The DFT and time-resolved FT-IR analyses of the reaction pathway and intermediates revealed that the active intermediate of the cobalt catalyzed cyclopropanation is the paramagnetic cobalt carbene complex with a single cobalt–carbene carbon bond, in spite of the fact that the usual metal–carbene complexes are diamagnetic and have a double bond character (Fig. 2) [57,58].

| Entry | Alkene | Yield (%) | trans/cis | ee (trans) (%) |
|-------|--------|-----------|-----------|---------------|
| 1     |        | 97        | 90:10     | 96            |
| 2     |        | 95        | 87:13     | 96            |
| 3     |        | 47        | 47:53     | 99 (93)       |
| 4d    |        | 99        |           | 90            |

*a Reaction conditions. Five mole percent of Co complex and 10 mol% (2.0 equiv. vs Co(II) complex) of N-methylimidazole in THF at 40–50 °C for 4.5–30 h.
*b 5.0 equiv. vs t-butyl diazoacetate were employed.
*c ee of the cis-isomer is shown in parenthesis.
*d Reaction was performed in MeOH-5% H2O without N-methylimidazole.

5. Cobalt complex as a Lewis acid catalyst

The optically active 3-oxobutylideneaminocobalt complexes were designed for the enantioselective Lewis acid catalyzes, such as the hetero Diels–Alder reaction [59–61] and the carbonyl–ene reaction [62,63]. It was found that the cationic cobalt complex was highly active for the hetero Diels–Alder reactions to afford the corresponding dihydropyran-4-one with high performance and high enantioselectivities. Varieties of counter anions of cationic cobalt(III) complexes were screened for the carbonyl–ene reaction, and hexafluorooantimonate was found to be the most effective. In the presence of the cobalt(III) hexafluoroantimonate complex, the enantioselective carbonyl–ene reaction of various alkenes with glyoxal derivatives was carried out to afford the corresponding homoallylic alcohols in high yields with high enantioselectivity. Even in the presence of 0.2 mol% cobalt complexes, the reaction proceeded in high yield and maintained a high enantioselectivity (Tables 8 and 9).

The 1,3-dipolar cycloaddition reactions of nitrones with alkenes are some of the useful and reliable strategies for...
Table 8
Enantioselective hetero Diels–Alder reaction of various aldehydes

| Entry | Aldehyde | Time (h) | Yield (%) | ee (%) |
|-------|----------|----------|-----------|--------|
| 1     |          | 3        | 89        | 87     |
| 2     |          | 3        | 81        | 81     |
| 3     |          | 7        | 94        | 94     |
| 4     |          | 59       | 83        | 90     |
| 5c    |          | 96       | 69        | 90     |
| 6d    |          | 96       | 89        | 88     |

*a Reaction conditions. 0.025 mmol (5.0 mol%) Co(III)-OTf catalyst, 0.5 mmol aldehyde, 150 mg MS 4A, and 1.0 mmol diene in CH₂Cl₂ (2.5 mL).
*b Isolated yield after the treatment with CF₃COOH.
*c 9.0 mol% Co(III)-OTf complex 4 and 200 mg MS 4A were employed.
*d 8.0 mol% complex 4 was employed.

Table 9
Enantioselective carbonyl-ene reaction of various alkenes and glyoxals

| Entry | R | Alkene | Yield (%) | ee (%) |
|-------|---|--------|-----------|--------|
| 1     | Ph |        | 93        | 93     |
| 2     |    |        | 81        | 91     |
| 3     |    |        | 75        | 94     |
| 4c    | OBn|        | 91        | 85     |
| 5c    |    |        | 93        | 85     |

*a Reaction conditions. Co(III)-SbF₆ catalyst 0.025 mmol (5.0 mol%), glyoxal derivative 1.0 mmol, and alkene 0.5 mmol in CHCl₃ (2.5 mL) at -20 °C.
*b Isolated yield.
*c Reaction was carried out at -60 °C.
preparing isoxazoline derivatives and have been widely investigated. The remarkable feature of this cycloaddition reaction is the concerted $[4\pi + 2\pi]$ supra-facial process like the Diels–Alder reaction to simultaneously construct three new chiral centers. Various chiral Lewis acids have been developed for the catalytic and enantioselective versions of electron-deficient alkenes, such as $\alpha,\beta$-unsaturated carbonyl compounds, of which the LUMO energy could be lowered by coordination to a Lewis acid to accelerate the reaction. However, the competitive coordination of nitrones should be considered over the coordination of monodentate carbonyl compounds. The chelation of alkenoyl oxazolidinone was, therefore, preferred for the cycloaddition reactions with nitrones [64,65]. Recently, the 1,3-dipolar cycloaddition of the monodentate $\alpha,\beta$-unsaturated aldehyde has ultimately been achieved using chiral DBFOX/Ph–Zn or Ni catalysts [66,67], CpRu-BIPHOP-F or Fe catalysts [68], and efficient organocatalysts [69].

The cationic 3-oxobutylideneaminatocobalt complexes with hexafluoroantimonate as a counter anion can effectively activate monodentate $\alpha,\beta$-unsaturated aldehydes and catalyze the 1,3-dipolar cycloaddition reaction. The corresponding isoxazolines from the various $\alpha,\beta$-unsaturated aldehydes and nitrones were obtained in high yield and with high regio-, endo-, and enantioselectivities (Table 10) [70–72].

The result indicated that even in the presence of a relatively strong Lewis base, the 3-oxobutylideneaminatocobalt complexes could act as effective Lewis acid catalysts. The

| Entry | Aldehyde | R$^1$ | R$^2$ | Yield (%)$^a$ | Rs (a/b)$^b$ | endo/exo$^b$ | ee (endo) (%)$^c$ |
|-------|----------|------|------|--------------|------------|------------|---------------|
| 1     | H C=O   |     |      | Quant        |            |            |               |
| 2     | H C=O   |     |      | 90          | 89/11      |            |               |
| 3     | CH$_3$  | H    |      | 94          | >99/1      | 98/2       | 63            |
| 4     | H C=O   | CH$_3$|      | 91          | 5/95       |            | 82            |
| 5     | H C=O   | C$_6$H$_5$CH$_2$| 93| 1/99 | >99/1      | 92            |

$^a$ Isolated after the reduction with NaBH$_4$.

$^b$ Determined by $^1$H NMR analysis.

$^c$ Determined by HPLC analysis using Daicel Chiralpak AD-H or Chiralcel OD-H.

$^d$ Reaction temperature: $-78^\circ$C.

$^e$ Eight mole percent complex 5 was employed at $-60^\circ$C and five portions of nitrone was added at 24 h intervals.

$^f$ Complex 5 was employed.

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**Table 10**

1,3-Dipolar cycloaddition of nitrone and various $\alpha,\beta$-unsaturated aldehydes

![Chemical structure](image.png)

Reaction time: 24–144 h. Reaction temperature: $-40^\circ$C.
DFT calculation of the hetero Diels–Alder reaction catalyzed by the cationic ketoiminatocobalt(III) complexes revealed that the axial coordination of aldehydes as a Lewis base induces a spin transition in the catalytic cycle to increase the Lewis acidity of the catalyst [73].

Further studies along this line will head to the enantioselective Henry reaction and enantioselective chemical fixation of CO₂.

In the presence of a catalytic amount of a tertiary amine, such as diisopropylethylamine and triethylamine, and the 3-oxobutylideneaminatocobalt(II) complex, the enantioselective Henry reaction of nitromethane and aldehydes proceeded to afford the β-nitroalcohols in high yield and with high enantioselectivity (Table 11) [74,75]. It was found that the ortho-halo substitution improved the enantioselectivity; e.g. the reactions of o-chlorobenzaldehyde, o-fluorobenzaldehyde, and o-trifluoromethylbenzaldehyde were effectively catalyzed to afford the corresponding β-nitro alcohols with high yields and high enantioselectivities up to 92% ee.

Carbon dioxide has drawn much attention as an environmental problem [76–78] as well as C₁ chemical feedstock [79]. The preparation of cyclic carbonate and polycarbonate from CO₂ and oxirane is one of the most valuable processes for chemical fixation in industries. Severe reaction conditions have been used for the chemical fixation of stable carbon dioxide with oxirane to form the cyclic carbonate; e.g. high-pressure [80,81], high-temperature [82,83], supercritical conditions [84], and electrochemical reactions [85,86]. The presence of an amine and a Lewis acid is important for the reaction. The use of well-defined complex catalysts is expected to be one of the most promising procedures for chemical fixation [87]. It was proposed that the chemical fixation reaction of carbon dioxide into a five-membered cyclic carbonate would be cocatalyzed by a Lewis base amine and Lewis acids. The mechanism of the reaction is considered as follows. The Lewis acid activates oxirane by coordination to the oxygen atom and Lewis base cooperatively attacks the oxirane to generate the alkoxide intermediate, which will capture carbon dioxide, and recyclization with the release of an amine base will afford the corresponding five-membered cyclic carbonate. Consequently, amine bases are indispensable for this reaction and the optically active Lewis acid that can operate even in the presence of Lewis bases is expected to achieve the enantioselective fixation of carbon dioxide. Under kinetic reaction conditions, the carbonate from N,N-diphenylaminomethyloxirane was enantiomerically formed by the cooperative

![Scheme 2.](image)
The reaction and improved the enantioselectivity. The present axial ligand, 3-oxobutylideneaminatocobalt complexes, the electron-donating axial ligand of the alkylcobalt complex, whereas in cyanocobalamine, the nitrogen-containing heterocyclic moiety acted as a photoreceptor to induce electron transfer for CO2 fixation in the photosynthetic system of plants. Although the enantioselective fixation of carbon dioxide catalyzed by the 3-oxobutylideneaminatocobalt complexes did not involve an electron transfer system, their function for CO2 fixation can be assimilated to that of the chlorophyll catalyzed system. It is noted that the enantioselective reactions catalyzed by the 3-oxobutylideneaminatomanganese and 3-oxobutylideneaminatocobalt complexes are the abstracted and mimic systems from nature as well as the artificial applications to synthetic organic syntheses. Further studies for the development of a complex catalyst system are now underway in order to exceed the natural catalytic systems.

Acknowledgements

This work was supported by a Grant-in-Aid for the 21st century COE program ‘KEIO LCC’ from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The authors thank the Research Center for Computational Science, Okazaki National Institute, for their support of the ab initio calculations.

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