Dinuclear PhosphoiminoBINOL-Pd Container for Malononitrile: Catalytic Asymmetric Double Mannich Reaction for Chiral 1,3-Diamine Synthesis

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A phosphoiminoBINOL ligand was designed to form a dinuclear metal complex that could hold a malononitrile molecule. The dinuclear bis(phosphoimino)binaphthoxy-Pd2(OAc)2 complex catalyzed a double Mannich reaction of N-Boc-imines with malononitrile to give chiral 1,3-diamines with high enantioselectivity. The rational asymmetric catalyst, which smoothly introduces the first coupling product to the second coupling reaction while avoiding the reverse reaction, facilitates the over-reaction into a productive reaction process.

The importance of catalysts with high catalytic activity in achieving "green" or sustainable chemistry has been well documented1. The benefit of high catalytic activity is not limited to reducing the amount of catalyst used. Catalysts with superior activity have the potential to promote unprecedented chemical transformations. As shown in Fig. 1, in the reaction of a nucleophile (Nu) with an electrophile (E), conventional catalysts are used for the synthesis of the 1:1 coupling adduct Nu−E (eq. 1).

If the first coupling product (Nu−E) can be made to react subsequently with further electrophiles through catalysis, 1:2 and/or 1:3 adducts (i.e. Nu−E2, Nu−E3) can be obtained. Although reactions of this type can be seen as over-reactions (eq. 2), such multicomponent coupling reactions are fascinating due to their potential as a direct approach toward highly functionalized advanced materials. List et al. reported an outstanding example: the condensation of acetaldehyde with two molecules of N-Boc imine using 20 mol% proline as a catalyst, which was originally developed for a single condensation reaction2. In order to utilize the double condensation reaction as a rational asymmetric catalytic reaction, new concepts for the design of highly active catalysts are required, and the first coupling product must be smoothly introduced to the second coupling reaction while avoiding the reverse reaction. Here, we report the design and development of a dinuclear palladium catalyst that enables a novel double Mannich reaction.

In this study, malononitrile was selected as a nucleophile with two acidic protons to be directed toward a double Mannich reaction3–6. In the interactions of nitriles with late transition metal salts, malononitrile can bind to two metal atoms7. For example, for the 5th-period elements, the two metal centers should be around 7.5 Å from each side of the malononitrile unit (Fig. 2A). In order to achieve a dinuclear reaction in one asymmetric reaction sphere while retaining the same geometry, a novel phosphoiminoBINOL ligand was designed, as shown in Fig. 2B. The phosphoimino moiety is designed to capture soft metals such as Pd, Rh, Au, Ag, and Cu, and the soft dinuclear complex binds strongly to malononitrile (or an anion of malononitrile generated during the reaction). The phenol functions in the ligand contribute by stabilizing the intermediate through hydrogen bonding. If the phenols incorporate a hard metal such as Li, Mg, or Zn, the resulting metal phenoxide acts as a Brønsted base, enhancing the catalytic activity. The hard Lewis acidity of the metal phenoxide is also characteristic.

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The synthesis of phosphoiminoBINOLs L1-L4 can be readily achieved through imine formation between 3,3′-formyl BINOL and the corresponding aminophosphine (Fig. 2C). The isopropyl-substituted phosphoiminoBINOL (L1) was stable to handling under air, and showed a high affinity with various soft metal salts. When 2 mol equiv. of Pd(OAc)2 was added to L1, the formation of a dinuclear palladium complex took place, as demonstrated by ESI-MS: an ion peak was detected at m/z = 1117.1705 in CH2Cl2, and this was attributed to [L1(−2H)+Pd2(OAc)]+. Fine crystals were obtained from a CH2Cl2 solution, and the structure of phosphoiminoBINOL- Pd2(OAc)2 was determined by X-ray crystallographic analysis (Fig. 3).

Based on this structure, one of the acetoxy anions of Pd(OAc)2 was replaced with L1 to make a palladium acetoxy phenoxide. The distance between two palladium cations is 6.907 Å, which is suitable for binding malononitrile (or a generated anion of malononitrile), and there is one H2O molecule positioned at the center of the asymmetric sphere. L1-Pd2 reacted smoothly with malononitrile. The 1H NMR spectrum of free malononitrile in CDCl3 shows a single methylene peak at 3.60 ppm. When malononitrile is added to 1 equiv. of L1-Pd2, the peak was shifted to 2.43 ppm 1H NMR (see details in Supplementary Information). ESI-MS analysis of a 1:1 mixture of malononitrile with L1-Pd2 showed a clear new peak at m/z = 1123.1764, attributed to [L1(−2H)+Pd2+NCCHCN]+.

With this fascinating container for malononitrile (L1-Pd2) in hand, the optimum catalyst for the conventional single Mannich reaction was examined before we attempted the challenge of the double Mannich reaction (Table 1). Although the Mannich reaction was smoothly catalyzed by the simple use of L1-Pd2, the Mannich product 2a was obtained with only 8% ee. As we expected cooperative effects due to the phenoxy unit of L1-Pd2 (Fig. 2B), the addition of several hard metal salts was examined (Entries 2–8). Several metal acetates were effective in improving asymmetric induction. With assistance from Zn(OAc)2 or Mg(OAc)2, L1-Pd2 smoothly catalyzed the Mannich reaction to give 2a with 68% ee and 74% ee, respectively. The structure-activity relationship of the ligands is also shown in Table 1. The equivalent catalyst using the methyl analog of L1 ((L2)-Pd2) gave 2a with only 11% ee (entry 9).

Although the t-Butyl analog L4-Pd2 gave 2a with 77% ee, the catalyst activity was reduced (entry 11). The diastereomeric ligand L5 synthesized from (S)-BINOL, and L6 and L7 for constructing mono-nuclear palladium complex resulted in low levels of asymmetric induction. For L1-Pd2 with a Zn(OAc)2 catalyst system, when the N-Boc imine 1a was added slowly, the Mannich adduct 2a was obtained with 91% ee in 5 mol % catalyst use (entry 15).
Figure 3. X-ray structure of L1-Pd2 (CCDC 1543349).

Figure 4. Dinuclear phosphoiminoBINOL-Pd catalyzed asymmetric Mannich reaction using malononitrile.

1 eq slow addition over 4 h
1.5 eq

2a: 70% conv. amine/diamine = 73/27 91% ee
2b: 50% conv. amine/diamine = 66/34 81% ee
2c: 66% conv. amine/diamine = 76/24 94% ee
2d: 60% conv. amine/diamine = 87/13 96% ee
2e: 95% conv. amine/diamine = 66/34 81% ee
2f: 84% conv. amine/diamine = 49/51 94% ee
2g: 85% conv. amine/diamine = 49/51 91% ee
2h: 97% conv. a) Conversion yield (determined as same as Table 1). b) Carried out in CHCl₃.
The results of the L1-Pd2-catalyzed asymmetric Mannich reaction under the optimized conditions are summarized in Fig. 4. Aromatic imines with various substituents were smoothly converted to the Mannich products with high enantioselectivity.

Using monobenzylated malononitrile, the chiral amine 2h having adjacent quaternary carbon center was obtained in 97% yield with 93% ee. This suggests the strong catalyst activity of the dinuclear L1-Pd2 complex. We assumed that the highly active dinuclear L1-Pd2 catalyst would facilitate the conversion of the Mannich adducts (2a–d) to the second Mannich reaction for giving the 1,3-diamines 3. Actually, the use of L1-Pd2 with a Zn(OAc)2 catalyst system resulted in the production of a significant amount of the 1:2 adduct 3, as desired. For the synthesis of 2f and 2g, co-production of the same amount of diamines was observed even when 1.5 equiv. of malononitrile was applied to the imine substrate24,25. For the double Mannich reaction, the reaction conditions were modified

Figure 5. Catalytic asymmetric double Mannich reaction.

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so that 2.5 equiv. of N-Boc imine were used with respect to the malononitrile. L1-Pd2 with Zn(OAc)2 catalyzed the double Mannich reaction quite smoothly to give the 1,3-diamine 3a in quantitative yield with high diastereoselectivity (dl/meso = 93/7)\(^{26-43}\). The major dl-isomer was obtained in 99% ee. The results of 1,3-diamine synthesis by the double Mannich reaction are summarized in Fig. 5.

For N-Boc-imines derived from both electron-donating and electron-deficient benzaldehydes, chiral 1,3-diamines were obtained in a highly enantioselective manner. A chiral bisfuryl-1,3-diamine(3i) was obtained with 86% ee, and a bisnaphthyl-1,3-diamine(3j) was also obtained successfully with 91% ee. When the second Mannich reaction was examined using rac-2a with N-Boc-imine, 3a was obtained in 73% ee with increasing co-production of the meso-form in dl/meso = 1:1. This result suggests that the second Mannich reaction is catalyzed independently from the first Mannich reaction, and the enantiomeric excess of 3a is improved due to the meso-trick\(^{44}\).

The formation of the (R)-enriched Mannich adduct using L1 can be explained using the working model described in Fig. 6.

The dinuclear L1-Pd\(_2\) complex binds to malononitrile at both nitrogen atoms of the nitrile moieties. Although the formation of palladium enolate by simple mixing of malononitrile with L1-Pd\(_2\) is suggested by the detection of an ion peak for [L1(−2H) + Pd\(_2\) + NCCHCN]\(^+\) at m/z = 1123.1764, the addition of Zn(OAc)\(_2\) also assists the smooth formation of the palladium enolate. The low asymmetric induction and catalyst activity of the mono-nuclear palladium complex using L6 and L7 suggest the effective role of the dinuclear palladium complex for converting 2a to 3a (Table 1, entries 13, 14) Moreover, because asymmetric induction of the Mannich adducts 2a and 3a is strongly influenced by the selection of hard metal salts, as shown in Table 1, a Zn(OAc)\(_2\)-driven reactant is incorporated in the asymmetric reaction sphere\(^{45-53}\). When the hard zinc atom is captured by the two hard phenoxy oxygens of L1-Pd\(_2\), the zinc atom can act as a Lewis acidic site for activating Boc-imines. During nucleophilic attack by the Pd-enolate malononitrile of the zinc-activated N-Boc imine, the approach shown in model A (Fig. 6) involves serious steric repulsion between a benzene ring from the phosphine in L1 and the

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### Table 1. Development of dinuclear phosphoiminoBINOL-metal catalyst for Mannich reaction using malononitrile.

| Entry | Ligand | Additive | Yield (%)\(^a\) | 2a/3a | ee of 2a (%) |
|-------|--------|----------|-----------------|------|-------------|
| 1     | L1     | —        | 99              | 83/17| 8           |
| 2     | L1     | LiOAc    | 86              | 84/16| 10          |
| 3     | L1     | NaOAc    | 99              | 72/28| 26          |
| 4     | L1     | Mg(OAc)\(_2\) | 91         | 57/43| 74          |
| 5     | L1     | Ca(OAc)\(_2\) | 94       | 74/26| 30          |
| 6     | L1     | Zn(OAc)\(_2\) | 93       | 60/40| 68          |
| 7     | L1     | ZnCl\(_2\) | 88              | 92/8 | 7           |
| 8     | L1     | Zn(OTf)\(_2\) | 66         | 93/7 | 18          |
| 9     | L2     | Zn(OAc)\(_2\) | 46       | 96/4 | 11          |
| 10    | L3     | Zn(OAc)\(_2\) | 72       | 85/15| 37          |
| 11    | L4     | Zn(OAc)\(_2\) | 78       | 68/32| 77          |
| 12    | L5     | Zn(OAc)\(_2\) | 73       | 78/22| 6           |
| 13\(^b\) | L6   | Zn(OAc)\(_2\) | 75     | 90/10| 10          |
| 14\(^b\) | L7   | Zn(OAc)\(_2\) | 65     | 92/8 | rac         |
| 15\(^c\) | L1   | Zn(OAc)\(_2\) | 70     | 73/27| 91          |

\(^a\)Conversion yield (see details for the determination in SI). \(^b\)10 mol % of Pd(OAc)\(_2\) were used. \(^c\)5 mol % of PhosphoiminoBINOL, 10 mol % of Pd(OAc)\(_2\), and 5 mol % of Zn(OAc)\(_2\) were used. Imine 1a was slowly added over 4 h.

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The formation of the (R)-enriched Mannich adduct using L1 can be explained using the working model described in Fig. 6.
N-Boc imine. By flipping the face of the N-Boc imine, as shown in Model B, the steric repulsion can be released, and nucleophilic attack of the Re-face of the N-Boc imine gives the (R)-enriched Mannich product.

In conclusion, the dinuclear bis(phosphoimino)binaphthoxy-Pd$_2$(OAc)$_2$ complex described herein facilitated a double Mannich reaction of N-Boc-imine with malononitrile to give chiral 1,3-diamines in a highly enantioselective manner. This demonstrates that over-reaction need not always be useless and undesired: well managed over-reaction can open up novel synthetic processes.

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