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Title: Bis(imidazolidine)pyridine-CoCl₂: A Novel, Catalytically Active Neutral Complex for Asymmetric Michael Reaction of 1,3-Carbonyl Compounds with Nitroalkenes

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Bis(imidazolidine)pyridine-$CoCl_2$: A Novel, Catalytically Active Neutral Complex for Asymmetric Michael Reaction of 1,3-Carbonyl Compounds with Nitroalkenes

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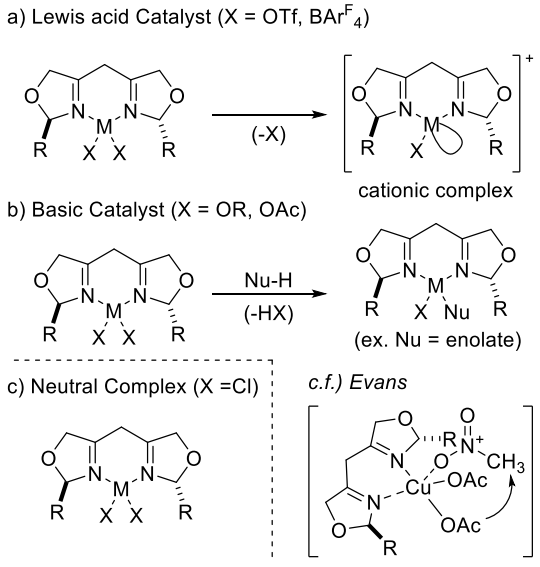
Abstract. A neutral bis(imidazolidine)pyridine (PyBidine)-$CoCl_2$ complex showed catalytic activity for the Michael reaction of malonates with nitroalkenes. The results indicated that a weak amine base aided enolate formation from the neutral complex, in which the N-H proton of the imidazolidine ligand played a significant role.

Keywords: Asymmetric catalysis**;** Michael addition**;** Cobalt**;** Enolates**;** Imidazolidine

Chiral metal complexes have been applied extensively in acid- or base-promoted asymmetric chemical transformations. Some pivotal bis(oxazoline)-metal catalyses are representative examples (Scheme 1).[1]

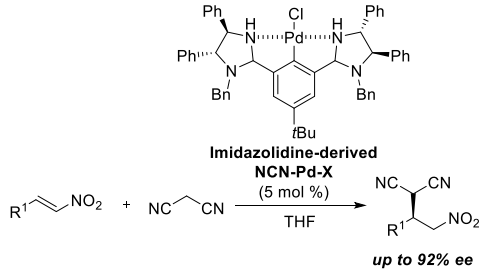


Scheme 1. Classification of bis(oxazoline)-metal catalyses.

In the bis(oxazoline)-Lewis acid catalysis, non-coordinating anions (*e.g.*, OTf^- and tetrakis[3,5-bis(trifluoromethyl)phenyl]borate: $[BAr^F_4]^-$) are used for making cationic metal complexes with an unsaturated coordination sphere (Scheme 1a).[2] For basic catalysts, the counter anion acts as the conjugate base for eliminating an acidic proton from the substrate (Scheme 1b).[3] The combination of a Lewis acidic metal center with the basic anion is also interesting, and Evans' bis(oxazoline)-$Cu(OAc)_2$-catalyzed nitroaldol (Henry) reaction[4] is a good example.[4d] In this case, a weakly Lewis acidic copper center increases the acidity of the coordinating nitroalkanes, which allows the generation of copper nitronate using the moderately basic acetate anion as a prelude to the nitroaldol reaction.

These studies can explain the stability of the metal-halide complex as well (Scheme 1c). Because the halide strongly connects to the metal center, the metal-halide complex, referred to as the "neutral complex," only shows low Lewis acidity. In addition, because the halide anion cannot provide meaningful basicity for promoting catalysis, typically the metal-halide complex is stable and catalytically inactive.

However, in 2013, a unique asymmetric reaction catalyzed by a neutral pincer NCN-palladium-Cl complex (Scheme 2) was reported.[5]



Scheme 2. Neutral pincer bis(imidazolidine)-derived NCN-PdCl complex for Michael addition of malononitrile with nitroalkenes.

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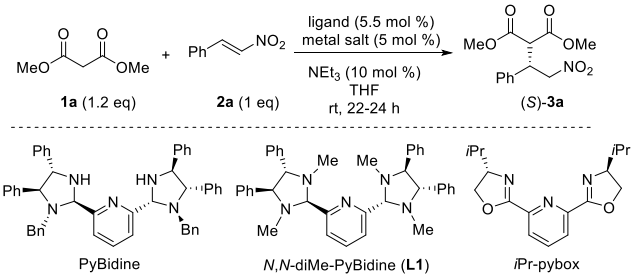
The bis(imidazolidine)-derived NCN-PdCl complex showed catalyst activity in Michael addition of malononitrile with nitroalkenes to give products in good yields with up to 92% ee.[5a] The comparable catalytic activity of the neutral catalyst with the cationic form of this catalyst is remarkable. For example, using the neutral NCN-PdCl catalyst gave the product in 82% yield and 80% ee, while the cationic NCN-PdOTf catalysis resulted in 75% yield with 77% ee. Although focus has been on activation mode using a hydrogen-bond managed by the NH-proton of imidazolidine ligand on the metal complex, the origin of the catalytic activity observed in the neutral complex was unknown.

Prompted by discovery of the catalytically active bis(imidazolidine)-derived NCN-PdCl complex, a detailed study was conducted on the catalytic activity of a metal chloride complex using bis(imidazolidine)pyridine ligand (PyBidine), which easily forms a complex with a wide range of metal salts.[6] Results from screening asymmetric catalyses using the PyBidine-metal chloride complexes revealed that the PyBidine-$CuCl_2$ and PyBidine-$CoCl_2$ complexes possessed catalyst activity in the Michael reaction using malonate (Table 1, entries 2 and 4).[7]

Table 1. Catalytic activity of PyBidine-metal salt complexes.

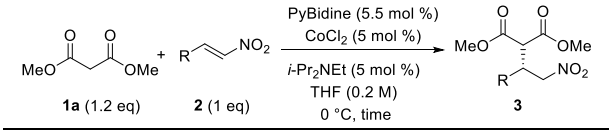


Entry	Ligand	Metal salt	Yield (%)	Ee (%)[e]
1	PyBidine	$Cu(OTf)_2$	93	81
2	PyBidine	$CuCl_2$	64	53
3	PyBidine	$Co(ClO_4)_2$[a]	88	83
4	PyBidine	$CoCl_2$	95	87
5[b]	PyBidine	$CoCl_2$	>99	89
6[b,c]	PyBidine	$CoCl_2$	>99	91
7[d]	PyBidine	$CoCl_2$	6	89
8	PyBidine	$CoCl_2$[a]	63	86
9	**L1**	$CoCl_2$	trace	-
10	*i*Pr-pybox	$CoCl_2$	trace	-

a) Hexahydrate, b) iPr_2NEt was used instead of NEt_3. c) At 0 °C. d) Without base. e) Absolute configuration was determined by ref. 7a and 7e.

When 5 mol % PyBidine-$CoCl_2$ complex was applied to a mixture of dimethylmalonate with nitrostyrene in THF, the reaction accelerated smoothly with the aid of Et_3N (10 mol %) to give the product in 95% yield with 87% ee. The results were comparable using the cationic PyBidine-$Co(ClO_4)_2$ complex (88% yield, 83% ee, entry 3). For the PyBidine-$CoCl_2$-catalyzed Michael reaction, reaction at 0 °C using iPr_2NEt was found to be the best set of conditions. Under the optimized conditions, the scope and limitations were examined, and the results are shown in Table 2. Not only simply substituted nitrostyrenes, but also 1-naphthyl nitroalkene, 2-thienyl nitroalkene, and aliphatic nitroalkenes were successfully used to give enantioselective products. When 298 mg (2 mmol) of **2a** was used, 504 mg of **3a** was obtained in 90% yield with 85% ee.

Table 2. Catalytic enantioselective Michael reaction.



Entry	R	Time (h)	Yield (%)	Ee (%)
1	Ph (**3a**)	24	>99	91
2	*p*-ClC_6H_4 (**3b**)	24	66	90
3	*p*-MeC_6H_4 (**3c**)	28	48	79
4	*m*-$NO_2C_6H_4$ (**3d**)	54	60	91
5	1-naphthyl (**3e**)	30	52	74
6	2-thienyl (**3f**)	30	67	78
7	PhCH=CH- (**3g**)	53	31	93
8[a]	*i*Pr (**3h**)	24	33	89
9[b]	Ph (**3a**)	48	90	85

a) At rt. b) 2 mmol scale.

To determine the reason for the catalytic activity, a single crystal of the PyBidine-$CoCl_2$ complex was obtained from PyBidine with $CoCl_2$-$6H_2O$. X-ray crystallographic analysis revealed that the tridentate PyBidine ligand was coordinated meridionally to the cobalt center in a trigonal bipyramidal configuration, and no H_2O was coordinated to the cobalt center, even when the complex was prepared from $CoCl_2$-$6H_2O$ (Figure 1).[8] This clearly indicates that the Lewis acidity of PyBidine-$CoCl_2$ complex is extremely low. Note that the PyBidine-$CoCl_2$ complex prepared from $CoCl_2$-$6H_2O$ was catalytically active and gave the Michael adduct in 63% yield with 86% ee (Table 1, entry 8).

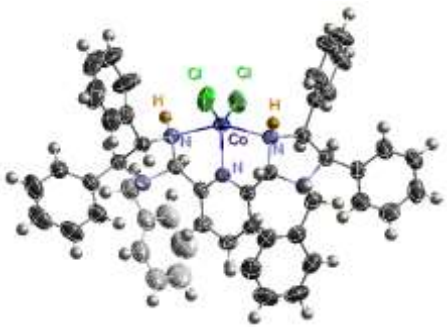


Figure 1. X-ray structure of the PyBidine-$CoCl_2$ complex (CCDC 1906366). Solvent was omitted to clarify (See details in SI).

Formation of the cobalt-enolate complex PyBidine-$CoCl_2$ was examined using ESI-MS (Figure 2), which provided a peak at 797.2676 corresponding to $[PyBidine\text{-}CoCl]^+$ (calcd. for $C_{49}H_{45}ClCoN_5$: 797.2690). When the PyBidine-$CoCl_2$ was mixed with dimethyl malonate, no obvious change was observed. However, addition of 1 mol eq. of TEA to the PyBidine-$CoCl_2$-dimethyl malonate mixture resulted in detection of a new peak at 893.3338, which was assigned to the cobalt-enolate of $[PyBidine\text{-}Co\text{-}MeO_2CCHCO_2Me]^+$ (calcd. for $C_{54}H_{52}CoN_5O_4$: 893.3351). Although the same ESI-MS study was conducted on the pybox-$CoCl_2$ complex, no peak was observed, suggesting enolate formation. Importantly, *N*,*N*-dimethyl pybidine-$CoCl_2$ complex and pybox-$CoCl_2$ and could not promote the Michael reaction, even in the presence of *i*Pr_2NEt (Table 1, entry 9 and 10).

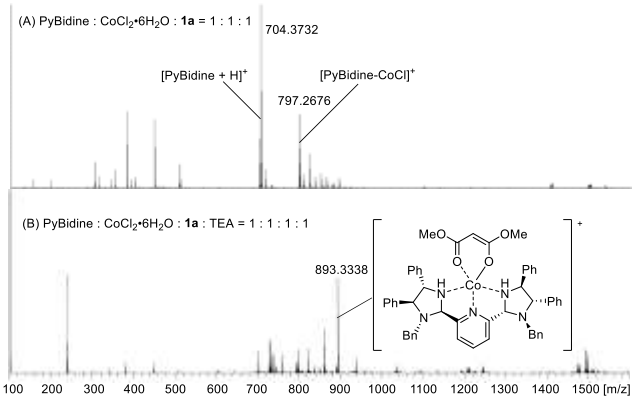
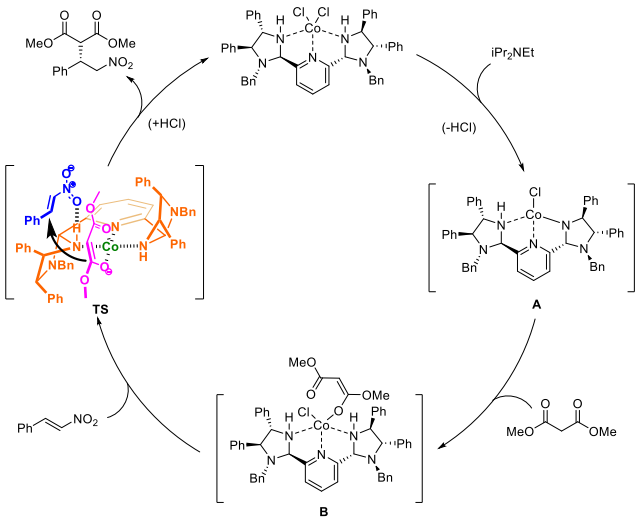


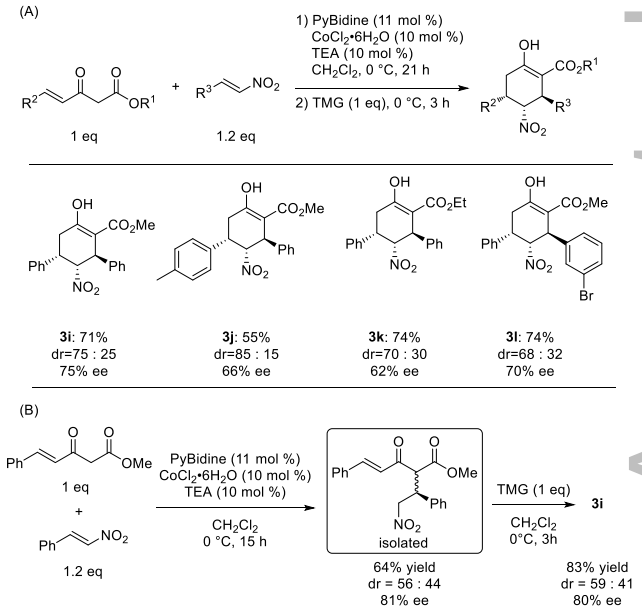
Figure 2. ESI-MS analysis of PyBidine-Co-enolate formation.



Scheme 3. Proposed reaction mechanism of PyBidine-$CoCl_2$-catalyzed asymmetric Michael reaction.

These mechanistic studies demonstrated that enolate formation from PyBidine-$CoCl_2$ was much easier than that from pybox-$CoCl_2$ as explained in Scheme 3. For the PyBidine-$CoCl_2$ complex, the N-H proton of the imidazolidine ligand should be acidic and easily deprotonated by a weak base of *i*Pr_2NEt to enhance release of chloride anion from the cobalt center. Although generation of the PyBidine-CoCl intermediate (**A**) was unclear in formation of cobalt enolate **B** from the dimethyl malonate, the N-H proton would regenerate on the imidazolidine ligand (*i.e.*, these processes can be explained as a type of anion exchange). In the subsequent Michael addition, the recovered N-H proton would act as a Brønsted acid for enhancing the reactivity of nitrostyrene. The proposed **TS** model in Scheme 3, which can be generated by an analogy of previously reported TS for the PyBidine-Cu catalyzed [3+2] cyclization of iminoester with nitrostyrene,[6f] explains the production of (*S*)-enriched Michael adduct using (*S*,*S*)-diphenylethylenediamine-derived PyBidine-$CoCl_2$ complex.

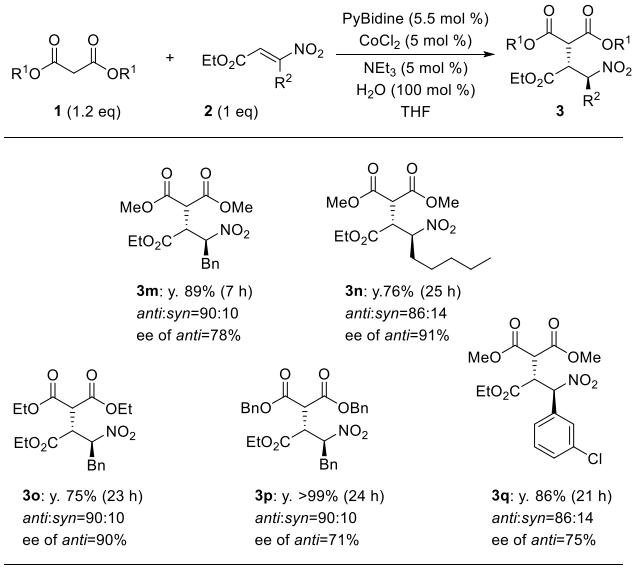
The PyBidine-$CoCl_2$ catalyst system was applied to sequential reactions. In Scheme 4, a sequential Michael/Michael reaction was examined using γ,δ-unsaturated β-ketoesters.[9] PyBidine-$CoCl_2$ the catalyst prepared from $CoCl_2$-$6H_2O$, smoothly catalyzed the first step of Michael reaction (reaction optimization detailed in Supporting Information). Based on a protocol developed by Takemoto[10] and Feng,[11] subsequent treatment with 1,1,3,3-tetramethylguanidine (TMG) gave the penta-substituted cyclohexenes with enantioselectivity, although the stereoselectivities were somewhat lower than those found for the reaction using malonate (Scheme 4A).



Scheme 4. Catalytic asymmetric Michael/Michael reaction using the PyBidine-$CoCl_2$ catalyst. The diastereomeric ratio of products were determined by ^{1}H-NMR.

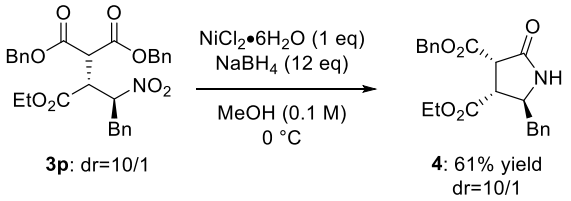
However, when the first Michael product was isolated, it was 81% ee, which was confirmed after conversion to the cyclohexene **3j** using TMG (Scheme 4B). These results suggest that the PyBidine-$CoCl_2$ catalyst also promoted the second Michael cyclization, although the resolution was negative.

The PyBidine-$CoCl_2$ catalyst was also applied to the Michael/protonation reaction.[12] Use of the substrate with an electron-withdrawing group at the β-position resulted in a high yield of product. Because the diastereoselectivity should be determined in the protonation step, the reaction conditions were re-investigated by focusing on the proton source, and the addition of H_2O improved the diastereoselectivity. The results of catalytic Michael/protonation reaction using (*E*)-3-nitro-3-substituted acrylate is summarized in Scheme 5.



Scheme 5. Catalytic asymmetric Michael/protonation reaction using PyBidine-$CoCl_2$ catalyst. The diastereomeric ratio of products were determined by ^{1}H-NMR.

Stereochemistry of the major diastereomer was determined after converting the cyclic compounds (Scheme 6).



Scheme 6. Chemical transformation of **3p**.

In conclusion, neutral PyBidine-$CoCl_2$ catalyst possessed activity in reaction to produce PyBidine-Co-enolate. This enolate formation was dramatically accelerated by an imidazolidine ligand, which is a new function of N-H protons, in addition to their action as a hydrogen-bonding donor.

Experimental Section

General procedure of asymmetric Michael addition reaction

PyBidine (0.011 mmol) and $CoCl_2$ (0.010 mmol) were added to a two-necked round flask containing a stir bar under Air. THF (1.00 ml) was added to the flask and the mixture was stirred overnight. To the resulting mixture, dialkylmalonate (0.24 mmol) and *i*-Pr_2NEt (0.010 mmol) were added subsequently at room temperature, and then nitroalkene (0.20 mmol) was added at 0 °C. After being stirred for appropriate time, the reaction mixture was quenched by adding aqueous HCl. The aqueous layer was extracted with dichloromethane, and the combined organic layers were dried over Na_2SO_4. After removing the solvent under reduced pressure, the resulting residue was purified by silica gel column chromatography to afford product. The enantiomeric excesses of the products were determined by chiral stationary phase HPLC.

General procedure of asymmetric sequential Michael addition reaction

PyBidine (0.011 mmol) and $CoCl_2 \cdot 6H_2O$ (0.010 mmol) were added to a two-necked round flask containing a stir bar under Ar. THF (1.00 ml) was added to the flask and the mixture was stirred for six hours. After removal the solvent under reduced pressure, dichloromethane (1.00 ml) was added. To the resulting solution, γ,δ-unsaturated-β-ketoester (0.10 mmol) and NEt_3 (0.010 mmol) were added subsequently at room temperature, and then nitroalkene (0.12 mmol) were added at 0 °C. After being stirred for 21 hours, tetramethyl guanidine (0.10 mmol) was added. After being stirred for additional three hours, reaction mixture was quenched by adding water. The aqueous layer was extracted with dichloromethane, and the combined organic layers were dried over Na_2SO_4. After removing the solvent under reduced pressure, the resulting residue was purified by silica gel column chromatography to afford product. The enantiomeric excesses of the products were determined by chiral stationary phase HPLC.

General procedure of asymmetric sequential Michael addition reaction

PyBidine (0.011 mmol) and $CoCl_2$ (0.010 mmol) were added to a two-necked round bottom flask containing a stir bar under Air. Solvent mixture (THF:H_2O = 1000:3.6, 1.00 ml) was added to the flask and the mixture was stirred overnight. To the resulting mixture, dialkylmalonate (0.24 mmol), NEt_3 (0.010 mmol) and nitroalkene (0.20 mmol) were added subsequently at room temperature. After being stirred for appropriate time, the reaction mixture was quenched by adding aqueous HCl. The aqueous layer was extracted with dichloromethane, and the combined organic layers were dried over Na_2SO_4. After removing the solvent under reduced pressure, the resulting residue was purified by silica gel column chromatography to afford product. The enantiomeric excesses of the products were determined by chiral stationary phase HPLC.

Acknowledgements

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[8] CCDC 1906366 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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