



Preparation of a cationic bisoxazolinic nickel pincer catalyst and its applications to Michael addition and Mizoroki–Heck reaction

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ABSTRACT

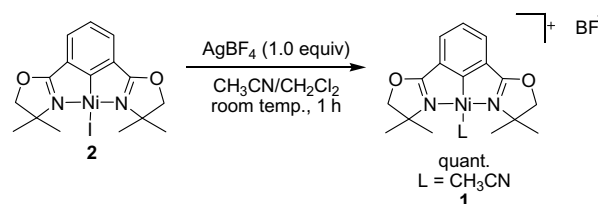
Nickel pincer complex **1** was prepared by the treatment of nickel pincer **2** with AgBF_4 . Cationic nickel pincer complex **1** was air-stable and easy to handle, and was successfully applied to Michael addition and Mizoroki–Heck reaction.

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In recent years, pincer-type palladium catalysts have received remarkable attention because of their high and unique catalytic activities, and several reactions catalyzed by palladium pincer complexes have been reported.¹ On the contrary, there have been rather limited numbers of reports about efficient transformation reactions catalyzed by nickel pincer complexes.²

We have been interested in electrooxidative molecular transformations³ and recently reported an electrooxidative generation of cationic palladium complexes and their application to electrooxidative Wacker-type reactions.^{3b} We extended our interest to the electrochemical properties of cationic transition-metal complexes and the design of new catalytic reactions. From such a point of view, we prepared a novel cationic nickel pincer complex **1** and investigated the electrochemical properties and application to catalytic reactions.⁴ The CV of **1** exhibited one irreversible reduction peak and two sets of redox peaks ascribable to Ni(II)/Ni(III) and Ni(III)/Ni(IV). The nickel center of complex **1** seems to be electron deficient enough to work as an efficient Lewis acid. These considerations prompted us to investigate applications to the catalytic reactions. We, herein, report the synthesis and CV analysis of **1**, and cationic nickel pincer **1**-catalyzed Michael addition and Mizoroki–Heck reaction.⁵

Cationic nickel pincer **1** could be obtained in one-step from nickel pincer **2**.⁶ Treatment of nickel pincer **2** with AgBF_4 (1.0 equiv) in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (1/1) afforded [2,6-bis(4',4'-dimethyl-2'-oxazolanyl)phenyl]nickel tetrafluoroborate (cationic Ni pincer **1**) quantitatively through the exchange of iodide to tetrafluoroborate (Scheme 1). Though the X-ray crystal structure analysis of **1** has not been successful, the structure of **1** was determined by NMR and ESI mass measurements.⁷ Cationic nickel pincer



Scheme 1. Preparation of nickel pincer catalyst **1**.

complex **1** can be handled under atmospheric condition without special care.

First, electrochemical properties of cationic nickel complex **1** were investigated by the comparison of the cyclic voltammetry (CV) of Ni pincer complexes **1** and **2**. CV of Ni pincer complex **2** showed two sets of redox waves in the potential range from -0.4 to 0.7 V, which are similar to the redox waves of iodide (I^-), suggesting that the observed redox peak might be derived from redox of iodide (Fig. 1).⁸ An irreversible reduction peak was observed at -1.1 V, suggesting that a Ni(I) complex might be generated in situ, which would be unstable under the condition and decomposed before the reoxidation to Ni(II).

On the contrary, CV of cationic Ni pincer complex **1** showed two sets of redox waves in the potential range from -0.2 to 0.8 V (Fig. 2), which can be considered as the redox wave of Ni(II)/Ni(III) and Ni(III)/Ni(IV). Similarly to nickel pincer **2**, an irreversible reduction peak was observed in the CV of **1** (-1.2 V). It is interesting to note that dissociation of L ($\text{L} = \text{CH}_3\text{CN}$) from cationic complex **2** would give a highly cationic Ni species which would act as a powerful Lewis acid. Based on the hypothesis, we carried out the Ni pincer **1**-catalyzed Michael addition (Table 1).

In the presence of Ni pincer complex **1** (5 mol %) and diisopropylethylamine ($i\text{-Pr}_2\text{NET}$, 10 mol %), the addition of cyanoacetic acid methyl ester to methyl vinyl ketone (3.0 molar amount) at

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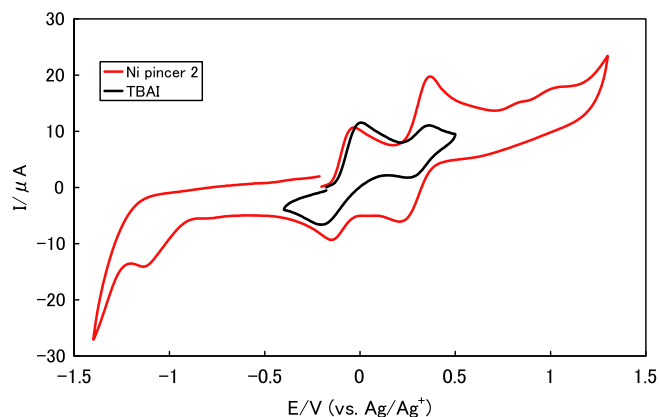


Figure 1. Cyclic voltammograms of nickel pincer complex **2** and Bu_4NI in CH_3CN . 2 mM of **2** and $n\text{-Bu}_4\text{NI}$, 0.1 M of $n\text{-Bu}_4\text{NBF}_4$. Scan rate: 0.1 V/s. Working electrode: Pt. Reference electrode: Ag/Ag^+ . Counter electrode: Pt.

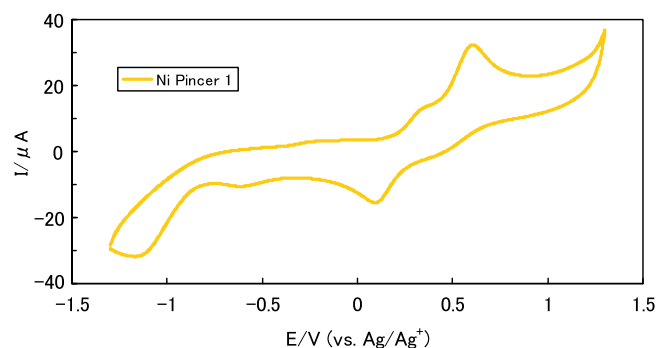
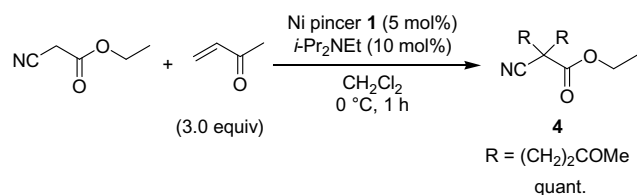


Figure 2. Cyclic voltammogram of cationic Ni pincer complex **1** in CH_3CN . 2 mM of **1**, 0.1 M of $n\text{-Bu}_4\text{NBF}_4$. Scan rate: 0.1 V/s. Working electrode: Pt. Reference electrode: Ag/Ag^+ . Counter electrode: Pt.

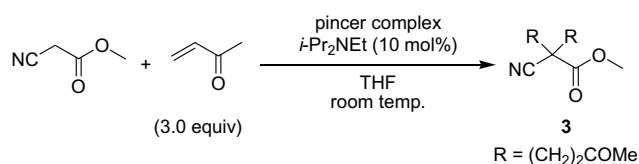
room temperature for 4.5 h afforded **3** quantitatively (entry 1). When 3 mol % of **1** was employed, the yield of **3** decreased slightly (96%, entry 2). With 1 mol % of **1**, only 57% yield of **3** was obtained after 4.5 h (entry 3). Extending the reaction time to 24 h, the reaction was completed with 0.5 mol % of **1** (entry 4). On the contrary, using Ni pincer complex **2** as a catalyst, only 41% yield of **3** was obtained after 4.5 h (entry 5). Without a catalyst, the Michael addition did not proceed (entry 6). The Michael reaction of ethyl cyanoacetate to methyl vinyl ketone was completed in 1 h to give adduct **4** quantitatively⁹ (Scheme 2).

Ethyl 2-cyanoacetate could also be applied to the Michael addition (Scheme 3). The reaction of ethyl 2-cyanoacetate proceeded smoothly under a similar condition to give adduct **5** in 99% yield. The addition of the substrate to acrylonitrile also proceeded, and the corresponding adduct was obtained in 95% yield.



Scheme 2. Nickel pincer **1**-catalyzed Michael addition at 0 °C.

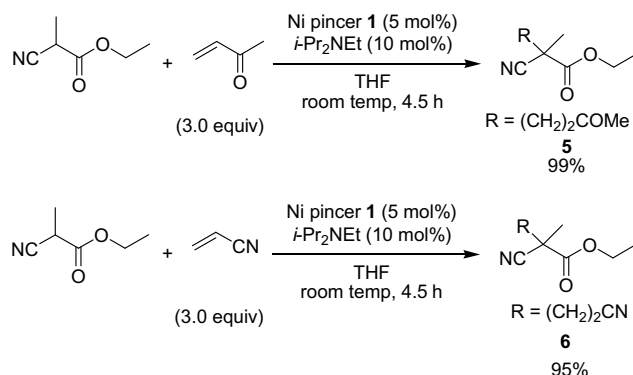
Table 1
Ni pincer **1/2**-catalyzed Michael addition



Entry	Catalyst (mmol)	Time (h)	Yield of 3 ^a (%)
1	1 (5)	4.5	>99 ^b
2	1 (3)	4.5	96
3	1 (1)	4.5	57
4	1 (0.5)	24	>99
5	2 (5)	4.5	41 ^b
6	None	4.5	ND

^a GC yield.

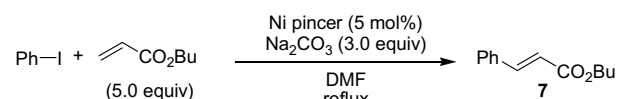
^b Isolated yield.



Scheme 3. Nickel pincer **1**-catalyzed Michael addition of ethyl 2-cyanoacetate.

As mentioned above, the CV of nickel pincer complex **1** exhibited two sets of redox waves, suggesting that the Ni(II) complex can be oxidized to Ni(III) and Ni(IV) species. These observations prompted us to study nickel-catalyzed reactions, and we found that cationic nickel pincer **1** can catalyze Mizoroki–Heck reaction (Table 2). In the presence of Ni pincer complex **1** (5 mol%) and Na_2CO_3 (3.0 equiv), the reaction of iodobenzene and butyl acrylate proceeded at reflux to afford product **7** in 25% yield after 24 h (entry 1), and the yield increased to 82% yield after 48 h refluxing.¹⁰ On the contrary, using nickel pincer catalyst **2**, the yield of **7** was only 24% after 48 h. The drastic acceleration of the **1**-catalyzed reaction after 48 h suggests that a more active catalyst than **1** would be generated in situ and promote the reaction. Using bromobenzene or chlorobenzene instead of iodobenzene, **7** was not obtained at all.

Table 2
Nickel pincer **1/2**-catalyzed Mizoroki–Heck reaction



Entry	Ni pincer	Time (h)	Yield of 7 ^a (%)
1	1	24	25
2	1	48	82
3	2	48	24

^a Isolated yield.

In summary, we synthesized novel cationic nickel pincer catalyst **1** and applied it to Michael addition and Mizoroki–Heck reaction. Scope and limitation of each reaction and further applications are in progress in our laboratory.

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- Ni pincer **2** was prepared according to the literature.^{2d}
- [2,6-Bis(4',4'-dimethyl-2'-oxazolonyl)phenyl]nickel tetrafluoroborate (**1**): yellow solids; ^1H NMR (600 MHz, acetone- d_6): δ 1.36 (s, 12H), 2.40 (s, 3H), 4.67 (s, 4H), 7.29 (d, $J = 7.2$ Hz, 1H), 7.33 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (150 MHz, acetone- d_6): δ 27.6, 28.5, 64.7, 85.0, 126.4, 126.8, 131.2, 167.3, 174.3; IR (KBr) 2976, 2936, 2326, 2296, 1615, 1084 cm^{-1} ; mp 178–183 °C (decomp.); HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{22}\text{N}_3\text{O}_2\text{Ni}(\text{M}^+-\text{BF}_4^-)$: 370.1065, found 370.1043; HRMS (FAB) m/z calcd for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_2\text{Ni}(\text{M}^+-\text{BF}_4^--\text{CH}_3\text{CN})$: 329.0800, found 329.0803.
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- Inamoto and co-workers reported Ni(II) pincer-catalyzed Mizoroki–Heck reaction and found that the addition of Bu_4NI was required for the efficient proceeding of the reaction.^{2e}