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PII: S0022-328X(20)30338-7

DOI: https://doi.org/10.1016/j.jorganchem.2020.121436

Reference: JOM 121436

To appear in: Journal of Organometallic Chemistry

Received Date: 21 May 2020

Revised Date: 10 July 2020

Accepted Date: 10 July 2020

Please cite this article as: W. Taniguchi, J.-i. Ito, M. Yamashita, CNC-pincer iron complexes containing a bis(N-heterocyclic carbene)Amido ligand: Synthesis and application to catalytic hydrogenation of alkenes, *Journal of Organometallic Chemistry* (2020), doi: https://doi.org/10.1016/j.jorganchem.2020.121436.

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# CNC-pincer Iron Complexes Containing A Bis(N-Heterocyclic Carbene)Amido Ligand: Synthesis and Application to Catalytic Hydrogenation of Alkenes

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# Keywords

Pincer complexes

Iron

N-Heterocyclic carbene

Alkene hydrogenation

DFT calculations

#### Abstract

This work studied preparation and catalytic application of CNC-pincer Fe complexes containing a bis(NHC)amido ligand (NHC: N-heterocyclic carbene). Deprotonation of bis(3-isopropylimidazoliumyl)amine salt  $[(CNC^{iPr})H_3]^{2+}[\Gamma]_2$  (**1a**) with lithium

hexamethyldisilazide (LiHMDS) afforded the corresponding bis(NHC)amido-Li complex **2a**. Treatment of *in-situ* generated **2a** with FeI<sub>2</sub>(thf)<sub>2</sub> gave a CNC-pincer Fe(II) iodide complex Fe(CNC<sup>*i*Pr</sup>)I (**3a**) and a cationic homoleptic Fe(III) complex [Fe(CNC<sup>*i* $Pr</sup>)_2]^+T^-$  (**4a**). Reaction of *in-situ* generated **2a** with Fe[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> produced the corresponding amido complex Fe(CNC<sup>*i*Pr</sup>)[N(SiMe<sub>3</sub>)<sub>2</sub>] (**5a**). Similarly, deprotonation of a less hindered methyl analogue  $[(CNC<sup>Me</sup>)H_3]_2^+[\Gamma]_2$  (**1b**) with LiHMDS followed by treatment of Fe[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> gave an amido complex Fe(CNC<sup>Me</sup>)[N(SiMe<sub>3</sub>)<sub>2</sub>] (**5b**). Molecular structures of **3a**, **5a** and **5b**, which were confirmed by X-ray diffraction study, showed a distorted tetrahedral geometry. Complexes **3a** and **5b** were found to be active in hydrogenation of alkenes. Reaction mechanism was investigated by density functional theory (DFT) calculations.

#### 1. Introduction

Fe complexes have been extensively studied for the development of homogeneous catalysis, since Fe is abundant natural resource and its low toxicity.[1] Among homogeneous catalytic reactions using Fe complexes, hydrogenation of unsaturated hydrocarbons and carbonyl compounds has been extensively studied in terms of replacement of precious metals, such as Ru and Ir.[2-4] In 2004, Chirik reported seminal work for the development of highly active catalysts based on NNN-pincer Fe complexes I having a bis(imino)pyridine ligand (Fig. 1).[5] In the same year, Peters reported tris(phosphino)borate ligated Fe complexes II as a hydrogenation catalyst.[6] After these reports, a variety of iron complexes having a pincer ligand such as bis(NHC)pyridine (III, NHC: N-heterocyclic carbone),[7] bis(phosphino)carbazolide

(IV),[8] bis(phosphino)amide (V),[9] and bis(phosphino)silyl (VI)[10] have been developed for catalytic hydrogenation of alkenes. In addition to tridentate ligands, bidentate ligands were also effective in Fe catalysts.[11] Nagashima and co-workers reported disilaferracyclic complex VII as an effective catalyst for hydrogenation of polysubstituted alkenes.[12] Bis(anthracene) ferrate complex VIII was also found as a catalyst for hydrogenation.[13] Recently, Fe<sub>4</sub>, Fe<sub>6</sub>, and Fe<sub>7</sub> nanoclusters were developed as effective catalysts.[14]



**Fig. 1.** Reported structurally well-defined Fe complexes used as catalysts for hydrogenation.

NHCs have been used as excellent ancillary ligands for transition metals arising from their strong electron-donating ability and formation of a thermodynamically strong metal-ligand bond to resist toward decomposition.[15] In this context, a number of Fe complexes with NHC ligands were reported as highly active catalysts for cross-coupling, hydrosilylation, and aziridination.[16] Introduction of NHC into a pincer ligand scaffold have been studied for design of robust and versatile ancillary ligands.[17] Recently, Danopoulos[18] and Fout[19] reported CNC and CCC-pincer Fe complexes with bis(NHC) scaffold, in which the central pincer donors, such as phenyl and pyridyl groups, significantly affected both coordination geometry and spin multiplicity at the Fe center. Luo and Kunz reported bis(NHC) pincer ligands with diarylamide and carbazolide backbones, respectively.[20,21] These CNC ligands have been used to synthesize various transition metal complexes including groups 3 and 8–10 metals.[20-24] Although those ligands would serve as a highly strong electron donor, introduction of Fe has not been reported. Related PNP- and NNN-pincer ligands containing anionic nitrogen donors offered efficient Fe catalysts for polymerization, hydrogenation, nitrogen reduction, and asymmetric reactions.[8,25] Thus, we expect that the bis(NHC)amide ligands can construct highly active Fe catalysts arising from their strong electron-donating ability and thermo-dynamic stability. In this work, we report synthesis of CNC-pincer Fe complexes and their application for catalytic hydrogenation of alkenes. A catalytic cycle was proposed based on density functional theory (DFT) calculations.

#### 2. Results and discussion

In this work, we used bis(imidazoliumyl)amine salt  $[(CNC^R)H_3]^{2+}[\Gamma]_2$  {R = <sup>*i*</sup>Pr, bis[2-(3-isopropylimidazolium)-4-methylphenyl]amine diiodide (**1a**); R = Me, bis[2-(3-isopropylimidazolium)-4-methylphenyl]amine diiodide (**1b**)} for ligand precursors, which were reported by Luo.[20] According to the previously reported deprotonation of bis(imidazoliumyl)carbazole by alkyllithium to give the corresponding lithium bis(NHC)carbazolide,[21e] we examined deprotonation of **1a** (Scheme 1). Reaction of **1a** with 3.2 equiv. of lithium hexamethyldisilazide (LiHMDS) in THF at

room temperature smoothly proceeded to give (CNC<sup>*i*Pr</sup>)Li (**2a**). The <sup>1</sup>H NMR spectrum of **2a** in THF-*d*<sub>8</sub> showed the disappearance of the signals of imidazolium and N–H protons observed in **1a**. In the <sup>13</sup>C NMR spectrum, the signal of carbenes was observed at  $\delta$  202.0 ppm. This chemical shift is comparable to that of the lithium bis(NHC)carbazolide ( $\delta$  206.1 ppm).[21c,d]



Scheme 1. Synthesis of  $(CNC^{iPr})$ Li (2a) and reaction of *in-situ* generated 2a or 2b with FeI<sub>2</sub>(thf)<sub>2</sub> and Fe[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>.

Reaction of *in-situ* generated **2a** in THF with 1 equiv. of  $FeI_2(thf)_2[26]$  resulted in the formation of a mixture of a  $Fe(CNC^{iPr})I$  complex **3a** and a cationic homoleptic complex **4a**. Extraction of the crude mixture with toluene and recrystallization of the toluene extract afforded red crystals of **3a** in 34% yield. To the residue, THF was added to give

a green suspension. After the filtration of the suspension, recrystallization from the resulting green solution yielded green crystals of **4a**. (See Fig. S8 for a preliminary result on the crystal structure of **4a**). As another Fe precursor, we used  $Fe[N(SiMe_3)_2]_2$ , which has high solubility to common organic solvents.[27] Reaction of  $Fe[N(SiMe_3)_2]_2$  with *in-situ* generated **2a** at room temperature resulted in the formation of an amido Fe complex  $Fe(CNC^{iPr})[N(SiMe_3)_2]$  (**5a**). Complex **5a** was isolated in 37% yield by crystallization form toluene solution.

In contrast to the isopropyl-substituted ligand precursor **1a**, the reaction of FeCl<sub>2</sub> or FeI<sub>2</sub>(thf)<sub>2</sub> with *in-situ* generated **2b** did not allow an introduction of Fe atom to the methyl analogue **1b**. On the other hand, the reaction of Fe[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> with **2b** generated by a treatment of **1b** with LiHMDS (3.2 equiv) at room temperature produced the desirable amido Fe complex Fe(CNC<sup>Me</sup>)[N(SiMe<sub>3</sub>)<sub>2</sub>] (**5b**). Complex **5b** was obtained in 68% yield as yellow crystals by recrystallization with toluene and *n*-pentane solution.

Molecular structures of **3a**, **5a** and **5b** were confirmed by X-ray diffraction study (Fig. 2-4). The Fe center of **3a** is described as a distorted tetrahedral geometry with geometry factor  $\tau_4 = 0.77$  (where  $\tau_4 = 1$  shows a tetrahedral structure and  $\tau_4 = 0$  shows a square planar structure).[28] The molecular structures of **5a** and **5b** showed distorted tetrahedral geometry [ $\tau_4 = 0.80$  (**5a**) and 0.78 (**5b**)] with the CNC ligand and N(SiMe<sub>3</sub>)<sub>2</sub> ligand. This structural feature is similar to that of the four-coordinated Fe(II) complexes with a PNP tridentate ligand.[25b] The Fe1–N1 bond lengths [1.975(3) Å (**3a**), 1.9963(14) Å (**5a**), 2.0168(17) Å (**5b**)] are close to those of anionic PNP-pincer Fe complexes.[25a-d] The Fe–CNHC bond lengths [2.072(3), 2.059(3) Å] in **3a** are slightly shorter than that of bis(NHC) pyridine Fe(II) complex Fe(CNC)Br<sub>2</sub> (2.16-2.19 Å).[18a]

In **5a** and **5b**, the Fe1–N6 bond lengths [1.9870(14) Å (**5a**), 1.9911(19) Å (**5b**)] are in the range of those of other Fe–N(SiMe<sub>3</sub>)<sub>2</sub> complexes (1.94-1.98 Å).[29]



**Fig. 2.** Molecular structure of **3a** (thermal ellipsoid at 50% probability; hydrogen atoms and co-crystallized toluene molecule are omitted for clarity). Selected bond distances (Å) and angles (deg): Fe1-N1 1.975(3), Fe1-C8 2.072(3), Fe1-C21 2.059(3), Fe1-I1 2.6468(5), C21-Fe1-C8 126.82(13), N1-Fe1-I1 124.06(8).



Fig. 3. Molecular structure of 5a (thermal ellipsoid at 50% probability; hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): Fe1-C8

2.0436(17), Fe1-C21 2.0969(17), Fe1-N1 1.9963(14), Fe1-N6 1.9870(14), Si1-N6 1.7137(15), Si2-N6 1.7033(15), C8-Fe1-C21 113.86(7), N6-Fe1-N1 123.48(6).



**Fig. 4.** Molecular structure of **5b** (thermal ellipsoid at 50% probability; hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): Fe1-C8 2.109(2), Fe1-C19 2.066(2), Fe1-N1 2.0168(17), Fe1-N6 1.9911(19), C8-Fe1-C19 123.26(8), N1-Fe1-N6 126.31(7)

The properties in solution of **3a**, **5a** and **5b** were studied by NMR spectroscopy and electrochemistry. The <sup>1</sup>H NMR spectrum of **3a** showed broad signals in the range of -62 to +73 ppm (Figure S4 in Supporting Information). The Evans method [30] provided solution magnetic moments of 5.0  $\mu_B$  for **3a**, 5.0  $\mu_B$  for **5a**, and 4.7  $\mu_B$  for **5b** in THF-*d*<sub>8</sub> at room temperature. These values are close to the spin-only magnetic moment for the S = 2 spin system (4.90  $\mu_B$ ) [31] and are comparable to that of the (PNP)Fe(II) complex **IV** (4.8-4.9  $\mu_B$ ).[8] Cyclic voltammogram of **3a** measured in THF at room temperature showed an irreversible oxidation response at E = -0.56 V (vs. Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup>) which could be assigned to the Fe(II)/Fe(III) redox couple (Fig. S5 in Supporting Information), according to the previously reported oxidation of pyrrole-based (PNP)Fe(II) complex (E<sub>1/2</sub> = -0.41 V)[25c] and bis(NHC)Fe(II) complexes ( $E_{1/2} = -0.37 - +0.42$  V).[32]

Catalytic activity of CNC-Fe complexes 3a, 5a, and 5b was evaluated in hydrogenation of styrene **6a** (Table 1). The catalytic hydrogenation of **6a** quantitatively proceeded by using 1 mol% of **3a** and 2 mol% of LiBEt<sub>3</sub>H at 30 °C under 1.0 MPa of H<sub>2</sub> (Entry 1). Decreasing the amount of LiBEt<sub>3</sub>H reduced the yield of 7a (Entry 2). The catalytic reaction was also completed with 0.5 mol% of 3a although a slightly longer reaction time was required (Entry 3). No reaction was observed without addition of LiBEt<sub>3</sub>H (Entry 4). The amido complex **5a** was found to be less active in hydrogenation (Entry 5). In contrast, the amido complex 5b with the methyl-substituted ligand exhibited catalytic activity without additives to give 7a quantitatively (Entry 6). The formation of HN(SiMe<sub>3</sub>)<sub>2</sub> was confirmed by GC analysis. This result suggested that **5b** underwent heterolytic splitting of  $H_2$  by the Fe–N(SiMe<sub>3</sub>)<sub>2</sub> bond. Initial turnover frequency (TOF) was estimated to be 90 h<sup>-1</sup> (Entry 7, 30 min.). This value was lower than that of I (TOF = 1344  $h^{-1}$ , 22 °C, 4 atm, 16 min.).[5] Catalytic reaction proceeded with 0.1 mol% of **5b** to give **7a** in 24% yield (Entry 8). To enhance the reaction rate, the additives effect of examined. Consequently, HBpin was (4,4,5,5-tetramethyl-1,3,2-dioxaborolane) was found to be a suitable additive to increase the yield of 7a with turnover number (TON) of 850 (Entry 9), which was lower than those of I (TON = 2500, 1-hexene)<sup>[5]</sup> and VII (TON = 2000, 1-octene).[12] According to reports about reaction of Fe[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and [CpFe[N(SiMe<sub>3</sub>)<sub>2</sub>] with HBpin,[33] reaction of **5b** with HBpin might generate a hydride species as a catalytically active intermediate.

	Fe cat. (1.0 mol	Fe cat. (1.0 mol%)		
Ph' 🔍 🕇 6a	H <sub>2</sub> THF, 30 ℃	Ph <sup>r</sup> S 7a		
Entry	Fe cat.	Additive	Time (h)	Yield $(\%)^c$
	(mol%)	(mol%)		
1	<b>3a</b> (1.0)	LiBHEt3 (2.0)	1	95
2	<b>3a</b> (1.0)	LiBHEt3 (1.0)	3	77
3	<b>3a</b> (0.50)	LiBHEt3 (1.0)	3	92
4	<b>3a</b> (1.0)	-	3	0
5	<b>5a</b> (1.0)	-	3	3
6	<b>5b</b> (1.0)	- ~ ~	3	99
7	<b>5b</b> (1.0)		0.5	45
8 <sup>[b]</sup>	<b>5b</b> (0.10)	-	48	24
9 <sup>[b]</sup>	<b>5b</b> (0.10)	HBpin (0.20)	12	85

Table 1. Hydrogenation of styrene catalyzed by 3a, 5a, or 5b<sup>[a]</sup>

[a] Reaction condition: 6a (1.0 mmol), Fe cat. (0.010 mmol), H<sub>2</sub> (1.0 MPa). [b] 6a (10.0 mmol), 5b (0.010 mmol), H<sub>2</sub> (3.0 MPa). c Determined by GC.

Next, hydrogenation of other alkenes **6b-e** was tested (Table 2). Catalytic reaction was conducted with 1 mol% of **3a** or **5b** under 1.0 MPa of H<sub>2</sub>. Hydrogenation of 1,1and *cis*-disubstituted alkenes,  $\alpha$ -methylstyrene (**6b**) and cyclooctene (**6c**), proceeded at 30-50 °C to give the corresponding alkane in moderate to high yield (Entries 1-4). In these reactions, catalytic activity of **5b** was higher than that of **3a**. In contrast, hydrogenation of *trans*-disubstituted and trisubstituted alkenes did not proceed at 50-80 °C, probably due to the steric effect (Entries 5,6).

Entry	Alkenes	Cat	Temp (°C) / Time (h)	Yield $(\%)^{[d]}$
1[a]	Ph	<b>3</b> a	40 / 24	47
2[b]	00	5b	30 / 6	71
3[a]		<b>3</b> a	30 / 24	38
4[b]	6c	5b	50 / 6	85
5[c]	Ph 6d	5b	50 / 24	0
6[c]	Ge	5b	80 / 24	0

Table 2. Hydrogenation of alkenes 6b-e catalyzed by 3a or 5b

[a] Reaction condition: 6 (1.0 mmol), 3a (0.010 mmol), LiBHEt<sub>3</sub> (0.020 mmol), H<sub>2</sub> (1.0 MPa).
[b] 6 (1.0 mmol), 5b (0.010 mmol), H<sub>2</sub> (1.0 MPa).
[c] 6 (1.0 mmol), 5b (0.010 mmol), H<sub>2</sub> (1.0 MPa).
[d] Determined by GC.

In the hydrogenation of alkenes, we assume two reaction mechanisms based on monohydride and dihydride intermediates (Scheme 2).[34] In the monohydride mechanism, insertion of an alkene into the Fe-H bond of the monohydride intermediate gives a corresponding alkyl intermediate, which undergoes hydrogenolysis to give a product (Scheme 2a). In the dihydride mechanism, the reaction of  $H_2$  with the monohydride intermediate produces the dihydride intermediate with a concomitant formation of protiated ligand (Scheme 2b). Subsequent insertion of an alkene followed by reductive elimination gives a product. Another issue in the catalytic reaction is spin multiplicity. Recently, DFT calculation for hydrogenation of styrene with complex **II** 

shown in Figure 1 reveled that the reaction proceeds via the triplet.[35a] In contrast, hydrogenation of 1-butene by complex **I** was proposed to involve the open-shell singlet state.[35c] To distinguish two mechanisms and spin multiplicity, we performed stoichiometric reactions and DFT calculations.



Scheme 2. Proposed mechanism of hydrogenation of alkene.

First, we conducted stoichiometric reactions to generate hydride and alkyl species. However, reaction of **3a** with LiBEt<sub>3</sub>H (1.0 equive.) at room temperature gave unidentified products and reaction of **5b** with 1.0 MPa of H<sub>2</sub> at room temperature resulted in no reaction. Although, reaction of **3a** with MeLi (1.8 equiv.) or reaction **3a** with LiBEt<sub>3</sub>H in the presence of styrene (1.0 equiv.) was performed to synthesize an alkyl complex, the products were not currently identified.

To obtain insights into the reaction mechanism of the present hydrogenation catalyzed by **5b**, DFT calculations were conducted by using a model complex **9** containing a slightly simplified CNC ligand (methyl groups on the benzene rings were removed) on quintet and triplet states (Figure 5 and see Supporting Information for details). First, we calculated the reaction of H<sub>2</sub> with the amido complexes <sup>5</sup>**9** on quintet state (where the superscript number denotes their spin multiplicity,

Figure 5a).[36] Hydrogenolysis of the quintet <sup>5</sup>9, which corresponds to the experimentally observed structure, with H<sub>2</sub> occurs in a concerted fashion without an  $\eta^2$ -H<sub>2</sub> intermediate to give hydridoiron-amine complex <sup>5</sup>10 via <sup>5</sup>TS1. This step is endergonic by 20.1 kcal/mol with relatively high energy barrier of 33.4 kcal/mol. The subsequent dissociation of the amine from <sup>5</sup>10 leads to formation of tetracoordinate hydride intermediate <sup>5</sup>11. In contrast, the triplet amido complex <sup>3</sup>9 is higher in energy than the quintet <sup>5</sup>9 by 19.8 kcal/mol. The subsequent hydrogenolysis of the triplet state <sup>3</sup>9 proceeds as a stepwise process involving an  $\eta^2$ -H<sub>2</sub> intermediate <sup>3</sup>12. The energy barrier (19.7 kcal/mol) through <sup>3</sup>TS1 in the triplet state is smaller than that in the quintet state. The resulting similar hydride intermediate <sup>3</sup>11 is more stable than <sup>5</sup>11 in the quintet state by 3.4 kcal/mol. These results suggest a spin-crossover process between triplet and quintet states should take place during the hydrogenolysis.[35a,37]



Fig. 5. Gibbs free energy profiles (kcal/mol) for (a) hydrogenolysis of model amido complexes <sup>5</sup>9 and <sup>3</sup>9 with H<sub>2</sub>, (b) migratory insertion of styrene to hydride intermediates <sup>5</sup>11 and <sup>3</sup>11, and (c) hydrogenolysis of 1-phenylethyl intermediates <sup>5</sup>15 and <sup>3</sup>15 with H<sub>2</sub>

(Superscript <sup>5</sup> and <sup>3</sup> in the compound number denote their spin multiplicity. The model CNC ligand structure is shown in the top).

Next, migratory insertion reactions of styrene into hydride intermediates <sup>3</sup>11 and <sup>5</sup>11 were investigated (Fig. 5b).[35] In this process, 2,1-insertion to a hydride intermediate is more favorable than 1,2-insertion (Fig. S15 and S17 in Supporting Information). Coordination of styrene to <sup>3</sup>11 gives a  $\eta^2$ -styrene intermediate <sup>3</sup>13. Subsequent migratory insertion of styrene into the Fe-H bond in <sup>3</sup>13 leads to a 1-phenylethyl intermediate <sup>3</sup>14, which has a  $\beta$ -agnostic interaction between the 1-phenylethyl ligand and the Fe atom.[35a,e] The energy barrier of transition state <sup>3</sup>TS2 is 8.4 kcal/mol and the formation of <sup>3</sup>14 is endergonic by 6.6 kcal/mol. Isomerization of <sup>3</sup>14 breaks the  $\beta$ -agnostic interaction via <sup>3</sup>TS3, leading to a 1-phenylethyl intermediate <sup>3</sup>15 with an energy gain of 5.1 kcal/mol in comparison with <sup>3</sup>11. In contrast to the triplet state, the coordination of styrene to the quintet <sup>5</sup>11 giving a styrene-adduct <sup>5</sup>13 is an endergonic reaction. Subsequent migratory insertion through <sup>5</sup>TS2 with the energy barrier of 13.3 kcal/mol gives 1-phenylethyl intermediate <sup>5</sup>15, which is more stable than the triplet state state.

The subsequent hydrogenolysis of the triplet 1-phenylethyl complex <sup>3</sup>15 contains a stepwise process, consisting of the formation of a  $\eta^2$ -H<sub>2</sub> intermediate <sup>3</sup>16 through a coordination of H<sub>2</sub> and  $\sigma$ -bond metathesis leading to the product **7a**, to reproduce the hydride complex <sup>3</sup>11 via <sup>3</sup>TS4 with an energy barrier of 15.9 kcal/mol (Fig. 5c). This activation energy is higher than that for <sup>3</sup>TS2. In contrast, hydrogenolysis of the quintet <sup>5</sup>15 proceeds via <sup>5</sup>TS4 with the energy barrier of 27.5 kcal/mol, which is higher than

that of the triplet state. Currently, we propose that the catalytic reaction proceeds via a triplet state and hydrogenolysis of  $^{3}15$  is the rate limiting step.

For the dihydride mechanism, we calculated the heterolytic cleavage of  $H_2$  with the Fe-N bond of hydride intermediates <sup>3</sup>11 and <sup>5</sup>11 to afford dihydride intermediates <sup>3</sup>17 and <sup>5</sup>17, respectively (Fig. 6a). However, the formation of <sup>3</sup>17 and <sup>5</sup>17 is a highly endergonic process and energy barriers of transition states <sup>3</sup>TS5 and <sup>5</sup>TS5 are very large.

.. of <sup>3</sup>15 or transition states <sup>3</sup>TS:



**Fig. 6.** Gibbs free energy profiles (kcal/mol) for (a) reaction of  $H_2$  with <sup>3</sup>**11** and <sup>5</sup>**11**, (b) subsequent hydrogenation of styrene, and (c) oxidaitive addition of  $H_2$ .

Next, migratory insertion of styrene into the Fe-H bond and subsequent reductive elimination of ethylbenzene were calculated (Fig. 6b). In the quintet <sup>5</sup>17, coordination of styrene affords a styrene-adduct <sup>5</sup>18. The following migratory insertion proceeds via <sup>5</sup>TS6 with the energy barrier of 9.7 kcal/mol to form intermediate <sup>5</sup>19. However, transition state <sup>5</sup>TS7 for reductive elimination giving an ethylbenzene-adduct <sup>5</sup>20 has a relatively high energy barrier of 40.0 kcal/mol. Then, dissociation of ethylbenzene produces <sup>5</sup>21. In the triplet <sup>3</sup>17, migratory insertion of styrene occurs with a lower energy barrier to afford <sup>3</sup>19. The subsequent reductive elimination proceeds via <sup>3</sup>TS6 with lower energy barrier compared to that of the quintet <sup>5</sup>TS6.

Finally, generation of dihydride intermediates <sup>3</sup>17 and <sup>5</sup>17 via oxidative addition of  $H_2$  were investigated (Fig 6c). Although we attempted to optimize a reaction pathway on the triplet surface, we could not find transition state for oxidative addition of  $H_2$ . In contrast, coordination of  $H_2$  to the quintet <sup>5</sup>21 affords an  $\eta^2$ - $H_2$  intermediate <sup>5</sup>22, which undergoes oxidative addition through <sup>5</sup>TS8 to give <sup>5</sup>17.

To compare with monohydride and dihydride mechanisms, the dihydride intermediates  ${}^{3}17$  and  ${}^{5}17$  are much higher in energy than the monohydride intermediates  ${}^{3}11$  and  ${}^{5}11$ . Energy barriers of  ${}^{5}TS5$  and  ${}^{3}TS5$  for the formation of  ${}^{3}17$  and  ${}^{5}17$  are also higher than that of  ${}^{3}TS4$ , which is the rate limiting step in the monohydride mechanism. Those results suggest that the monohydride mechanism involving  ${}^{3}11$  and  ${}^{5}11$  is favored.

### 3. Conclusion

We synthesized a series of CNC pincer-Fe complexes with bis(NHC) amido ligands. Those Fe complexes exhibited catalytic activity for hydrogenation of alkenes. DFT calculations suggested that the monohydride mechanism involving the migratory insertion step and the hydrogenolysis through triplet-states is more favorable than that the dihydride mechanism.

#### 4. Experimental Section

#### 4.1. General Information.

All manipulations of air- and moisture-sensitive compounds were carried out under Ar atmosphere by using Schlenk and glove box technique. Et<sub>2</sub>O, THF, toluene and *n*-hexane were purified by passing through a solvent purification system (Grass Contou). THF-*d*<sub>8</sub> was purified by distillation over sodium benzophenone. Compounds **1a** and **1b**,[20] and FeI<sub>2</sub>(thf)<sub>2</sub>[26] were prepared according to the literature methods. NMR spectra were recorded on JEOL ECA (400 MHz for <sup>1</sup>H, 100 MHz for <sup>13</sup>C, and 155 MHz for <sup>7</sup>Li) spectrometer. Chemical shifts were reported in  $\delta$  (ppm) relative to the residual signals at  $\delta_{\rm H}$  1.72 and  $\delta_{\rm C}$  25.3 ppm for THF-*d*<sub>8</sub> and LiCl in D<sub>2</sub>O at  $\delta_{\rm Li}$  0 ppm. Elemental analysis were recorded on a Perkin Elmer 2400II. Melting points (mp) were determined with an MPA100 OptiMelt instrument (Tokyo Instruments, Inc.) and are uncorrected. GC analysis were recorded on SHIMAZU GC-2014 with GL Sciences InertCap 5MS/Sil capillary column (0.25 mm LD. × 30 m, df = 0.25  $\mu$ m).

#### 4.2. Preparation of iron complexes

4.2.1. Preparation of  $Fe(CNC^{iPr})I(3a)$ 

To a solution of LiHMDS (267.8 mg, 1.6 mmol) in THF (10 mL) was added **1a** (334.5 mg, 0.5 mmol). After being stirred at room temperature for 1 h, a solution of FeI<sub>2</sub>(thf)<sub>2</sub> (226.9 mg, 0.5 mmol, 1.0 eq.) in THF (15 mL) was added. The brown solution was stirred at room temperature for 12 h. After removal of the solvent in vacuo, the residue was washed with *n*-hexane. The crude product was extracted with toluene and the extract was filtered through a pad of Celite. Crystallization of the concentrated solution at room temperature gave red crystals of **3a** (102.9 mg, 0.172 mmol, 34%). To the residue obtained by extraction with toluene, THF was added to give a green suspension. After the filtration of the suspension, recrystallization from the resulting green solution yielded **4a**. **3a**: Mp. 129 ° (dec.); <sup>1</sup>H MMR (400 MHz, THF-*d*<sub>8</sub>):  $\delta = 73.88, 53.37, 42.49, 30.66, -1.63, -34.39, -62.38 ppm; <math>\mu_{eff} = 5.0 \ \mu_B$  (Evans method, THF-*d*<sub>8</sub>); elemental analysis calcd for C<sub>26</sub>H<sub>30</sub>FeIN<sub>5</sub>·C<sub>7</sub>H<sub>8</sub>: C 57.66, H 5.57, N 10.19; found: C 57.73, H 5.41, N 10.12.

# 4.2.2. Preparation of Fe(CNC<sup>*i*Pr</sup>)[N(SiMe<sub>3</sub>)<sub>2</sub>] (**5a**)

To a solution of LiHMDS (160.6 mg, 0.96 mmol) in Et<sub>2</sub>O (6 mL) was added **1a** (200.7 mg, 0.30 mmol). After being stirred at room temperature for 17 h, the solvent was removed in vacuo. The residue was suspended in toluene and a solution of  $Fe[N(SiMe_3)_2]_2$  (113.0 mg, 0.30 mmol) in toluene was added. The orange suspension was stirred at room temperature for 34 h. Insoluble materials was removed by centrifugation and the solvent was removed in vacuo. The residue was removed in vacuo. The residue was added with *n*-hexane and was extracted with toluene. The extract was filtered through a pad of Celite and the solvent was removed in vacuo. Crystallization of the crude product with a mixture of toluene and *n*-pentane gave yellow crystals of **5a** (58.6 mg, 0.093 mmol).

Mp. 127 ° (dec.); <sup>1</sup>H MMR (400 MHz, THF- $d_8$ )  $\delta$  = 74.00, 69.81, 61.36, 55.47, 44.34, 32.02, 29.66, 23.26, 20.14, 18.55, 12.55, -4.19, -10.87, -13.99, -82.75 ppm;  $\mu_{eff}$  = 5.0  $\mu_B$  (Evans method, THF- $d_8$ ); elemental analysis calcd for C<sub>32</sub>H<sub>48</sub>FeN<sub>6</sub>Si<sub>2</sub>: C 61.13, H 7.69, N 13.37; found: C 61.14, H 7.74, N 13.40.

# 4.2.3. Preparation of $Fe(CNC^{Me})[N(SiMe_3)_2]$ (5b)

To the solution of LiHMDS (80.3 mg, 0.48 mmol) in Et<sub>2</sub>O (6 mL) was added **1b** (92.0 mg, 0.15 mmol). After being stirred at room temperature for 17 h, the solvent was removed in vacuo. The residue was suspended in toluene and a solution of Fe[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (56.5 mg, 0.15 mmol) in toluene was added. The orange suspension was stirred at room temperature for 20 h. Insoluble materials in toluene was removed by centrifugation and the solvent was removed in vacuo. The residue was washed with *n*-hexane and was extracted with toluene. The extract was filtered through a pad of Celite and the solvent was removed in vacuo. Crystallization of the crude product with a mixture of toluene and *n*-pentane gave yellow crystals of **5b** (70.6 mg, 0.12 mmol). Mp. 139 ° (dec.); <sup>1</sup>H MMR (400 MHz, THF-*d*<sub>8</sub>)  $\delta$  = 62.39, 45.23, 30.32, 23.38, 17.11, -26.27 ppm;  $\mu_{eff}$  = 4.7  $\mu_{B}$  (Evans method, THF-*d*<sub>8</sub>); elemental analysis calcd for C<sub>28</sub>H<sub>40</sub>FeN<sub>6</sub>Si<sub>2</sub>: C 58.72, H 7.04, N 14.68; found: C 58.74, H 6.69, N 14.61.

#### 4.3. General procedure of catalytic hydrogenation of alkenes.

All alkenes were dried by  $CaH_2$  and purified by distillation. Alkene (1.0 mmol) was added to the solution of iron complex (0.10 mmol) and additive in THF (1.0 mL). The mixture was transferred to a 5 mL autoclave. Then,  $H_2$  gas was introduced to the autoclave. After the reaction, internal standard (*n*-dodecane) was added to the reaction mixture, which was analyzed by GC.

#### 4.4. X-ray diffraction analysis.

Details of the crystal data and collection parameters are listed in Table S4. The crystals were coated with immersion oil and put on a MicroMountTM (MiTeGen, LLC), and then mounted on diffractometer. Diffraction data were collected on a Rigaku XtaLAB Synergy-R diffractometer equipped with a HyPix-6000HE HPC detector using MoKα radiation. The Bragg spots were integrated using CrysAlisPro program package.<sup>[38]</sup> Absorption corrections were applied. All the following procedure for analysis were performed using Yadokari-XG 2009<sup>[39]</sup> as a graphical interface. The structure was solved by a direct method with programs of SHELEXT<sup>[40]</sup> and refined by a full-matrix least squares method with the program of SHELXL-2018.<sup>[40]</sup> Anisotropic temperature factors were applied to all non-hydrogen atoms. The hydrogen atoms were put at calculated positions and refined applying riding models. Deposition Number CCDC 1982151 (**3a**), 1982152 (**4a**), 1982153 (**5a**) and 1982154 (**5b**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre.

## 4.5. DFT calculations.

Calculations were performed with the Gaussian 16 program package.<sup>[41]</sup> Geometries of the ground state and the transition state were optimized by using B3PW91-D3<sup>[42]</sup> functional with D3 dispersion correction in gas phase. Lanl2dz<sup>[43]</sup> with the effective core potentials was used for Fe and the 6-31G(d) basis set was used for C, H, N and Si atoms (BS1). The vibrational frequencies and zero-point energy were calculated at the

same level of theory. Transition states was confirmed by intrinsic reaction coordinate (IRC) computation to connect to relevant minima. Single-point energies for each optimized geometry were performed with the SDD (Fe)<sup>[44]</sup> and 6-311+G(d,p) (C, H, N, and Si) basis sets (BS2). The solvent effect was evaluated using the conductor-like polarizable continuum model (CPCM)<sup>[45]</sup> for all calculations of single-point energies.

#### Acknowledgements

This work was supported by Grants-in-Aid for Scientific Research from JSPS (KAKENHI 2717H01191). Financial sup-port was also received from JST CREST 14529307. Theoretical calculations were carried out using resources of the Re-search Center for Computational Science (Okazaki, Japan) and the Information Technology Center of Nagoya University (Nagoya, Japan).

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CNC-pincer Fe complexes containing a bis(NHC)amido ligand were synthesized and characterized by X-ray diffraction study.

CNC-pincer Fe complexes were found to be active in hydrogenation of alkenes.

DFT calculations suggested the monohydride mechanism involving the migratory insertion and the subsequent hydrogenolysis on the triplet surface.

n i ret surface

#### **Declaration of interests**

 $\boxtimes$  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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