Iron(II) Complex with a Silacycle-Bridged Biaryl-Based Ligand
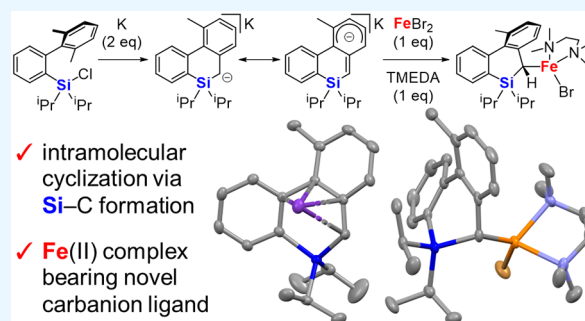
Yuto Suga and Yusuke Sunada*

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ABSTRACT: Treatment of 2,6-dimethyl-1,1′-biphenyl-substituted chlorosilane with potassium followed by FeBr₂/TMEDA led to the formation of an iron(II) monobromide complex supported by a TMEDA ligand and a carbanion-based ligand containing a six-membered silacycle-bridged biphenyl skeleton. The obtained complex crystallized as a racemic mixture of (Sa, S) and (Ra, R) forms, in which the dihedral angle of the two phenyl rings of the biphenyl moiety was ~43°.

✓ intramolecular cyclization via **Si**–C formation

✓ **Fe**(II) complex bearing novel carbanion ligand

INTRODUCTION

In order to better align contemporary organic synthesis with the pressing global demand for environmental sustainability, the use of Earth-abundant transition metals such as iron as catalysts has received much attention.[1] The synthesis of iron complexes that feature well-designed auxiliary ligands leads directly to the development of highly active iron catalysts. For instance, the use of noninnocent ligands for iron complexes has produced a series of characteristic catalytic transformations mediated by homogeneous iron-based catalysts.[2] This strategy has led to iron-based catalysts that function as alternatives to conventional precious-metal-based catalysts and to develop extraordinary transformations mediated by these iron catalysts. In recent years, development of catalytic systems based on iron that enable catalytic asymmetric reactions has been desired. In this context, iron catalysts combined with chiral ligands, which have proven to be useful in precious-metal-based catalyst systems, have been developed, and various iron-catalyzed asymmetric reactions have been reported.[3] However, it is known that common chiral ligands, e.g., bidentate phosphine-based ligands, often dissociate from the iron center, which prevents the rapid and effective survey of iron-catalyzed asymmetric reactions. For instance, Chirik and co-workers have reported the synthesis of iron complexes that bear chiral bidentate phosphine ligands and their application as catalysts for the asymmetric hydrogenation of alkenes, albeit that no enantioselectivity was induced using the isolated $(P^*)_2Fe$-$(CH_2SiMe_3)_2$-type complexes.[4] The lack of observed enantioselectivity was attributed to the dissociation of the bidentate phosphine ligands from the iron center.

Against this background, we envisioned that the establishment of a new strategy to design iron catalysts with a new type of auxiliary ligand that could potentially function as a chiral ligand could contribute to the exploration of iron-catalyzed

asymmetric reactions. Thus, we focused on the use of a monoanionic ligand and the introduction of a biaryl moiety to develop a strongly coordinating auxiliary ligand that could potentially exhibit axial chirality in the ligand skeleton. In this study, we found that treatment of 2,6-dimethyl-1,1′-biphenyl-substituted chlorosilane with potassium led to the formation of an anionic six-membered silacycle-bridged biphenyl-based ligand. This ligand framework was then introduced on an iron(II) center by subsequent treatment with $FeBr_2$, giving new iron monobromide complex **3** in moderate yield. An X-ray diffraction analysis of single crystals of **3** revealed that **3** bears a unique six-membered silacycle-bridged biphenyl-based ligand, which was formed via an intramolecular Si−C bond-forming cyclization reaction.

RESULTS AND DISCUSSION

Synthesis of the Ligand Consisting of the Six-Membered Silacycle-Bridged Biphenyl-Based Framework. To prepare the ligand precursor, we introduced a 2,6-dimethyl-1,1′-biphenyl moiety, along with two ^iPr groups as the bulky substituents, on the silicon center of a mono-(chloro)silane moiety. Mono(chloro)silane **1** was synthesized according to a slightly modified literature method.[5] First, 2,6-dimethyl-2′-bromobiphenyl was treated with one equivalent of ^nBuLi at 0 °C in Et_2O. Subsequent addition of dichlorodiiso-propylsilane led to the formation of **1** in 82% yield (Scheme 1). In the proton nuclear magnetic resonance (^1H NMR)
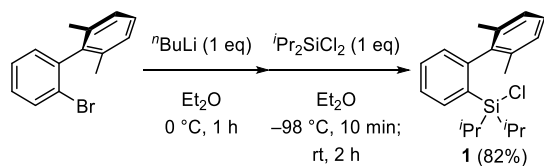
Scheme 1. Preparation of 1

spectrum of **1**, two doublets derived from the methyl groups of the ^{i}Pr moieties were observed at 1.01 and 0.98 ppm, and the methyl group on the 2,6-dimethyl-1,1′-biphenyl moiety appeared at 2.00 ppm. In addition, one singlet was observed at 25.88 ppm in the ^{29}Si NMR spectrum.

Chlorosilane **1** was then treated with two equivalents of potassium in THF at 35 °C for 26 h, from which the potassium salt of six-membered silacycle-bridged biphenyl-based compound **2** was obtained as dark red crystals in 71% isolated yield (Scheme 2). In the ^{29}Si NMR spectrum of **2** in THF-d$_8$, a

Scheme 2. Preparation of 2 from the Reaction of 1 with Potassium
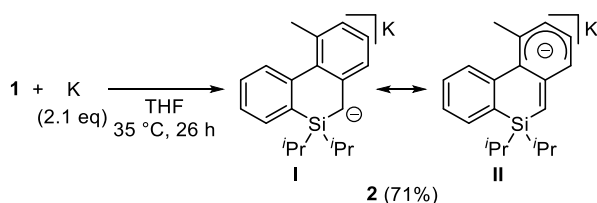
singlet was observed at −13.33 ppm. The signals of the methyl group of the ^{i}Pr moiety appeared at 0.88 and 0.90 ppm in the ^{1}H NMR spectrum of **2** in THF-d$_8$, whereas the protons assignable to the phenyl group appeared in the range of 5.58−7.59 ppm which are shifted to higher field compared with those found in **1**. The ^{1}H NMR signal observed at 2.86−2.87 ppm was assignable to the benzylic proton in the six-membered silacycle, and the corresponding carbon resonated at 50.26 ppm in the ^{13}C NMR spectrum.

A single-crystal X-ray diffraction analysis of the obtained dark red crystals revealed that they consist of the potassium salt of the six-membered silacycle-bridged biphenyl-based framework. The thermal-ellipsoid plot of potassium salt **2** is provided in Figure 1. The C (8)−C (9) bond distance of 1.525 (3) Å is within the range of typical carbon−carbon single bond, whereas the C (1)−C (3) bond length is found to be
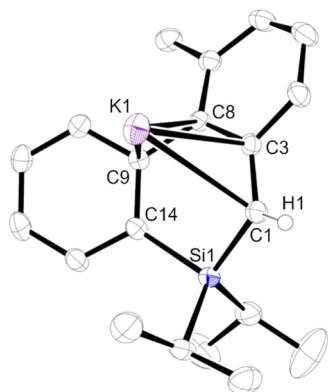

Figure 1. Molecular structure of **2** with thermal ellipsoids at 50% probability; all hydrogen atoms except H (1) are omitted for clarity.

1.449 (3) Å which is significantly shorter than C (8)−C (9) bond separation. In addition, the C (3)−C (4) and C (3)−C (8) bond distances were found to be 1.477 (3) and 1.501 (3) Å, respectively, these are also shortened compared with the C (8)−C (9) bond. These bond distances suggest the presence of significant contribution of a canonical form **II** shown in Scheme 2 in the structure of **2**. Furthermore, the short intermolecular bond distances (3.03−3.38 Å) between K (1) and four carbon atoms (C (3), C (4), C (5) and C (6)) imply the partial anionic character of the aryl ring; this might also support the contribution of canonical structure **II**.

The dihedral angle between the two phenyl rings in the biaryl moiety and the Si−C (1) bond distance was found to be ca. 38° and 1.865 (2) Å, respectively. One structural feature of **2** is that the potassium atom in **2** is coordinated to four carbon atoms of the silicon-containing six-membered ring to form an η^4-coordinated sila-cyclohexadienyl framework, with K−C bond distances ranging from 3.019 (3) to 3.255 (3) Å. Moreover, two potassium atoms derived from the neighboring molecules in the unit cell are coordinated to the phenyl ring of **2**; namely, one potassium atom is coordinated to the phenyl ring of the 2,6-dimethylphenyl moiety, whereas the other potassium interacts with the C$_6$H$_4$ moiety in **2** (see the Supporting Information). The five carbon atoms comprising an η^4-sila-cyclohexadienyl moiety form a nearly planar skeleton, wherein the deviation of the atoms from the least-squares plane ranges from 0.023 to 0.148 Å. For comparison, a related molecular structure of a lithium-coordinated sila-cyclohexadienyl compound has been reported by Tokitoh and co-workers, in which all the carbon atoms derived from the sila-cyclohexadienyl skeleton lie on a plane with deviations ranging from 0.001 to 0.011 Å.[6]

Although the minute details have not been explored yet, a tentative reaction mechanism for the generation of **2** via the reaction of **1** with potassium is proposed in Scheme 3. First, a

Scheme 3. Proposed Reaction Mechanism for the Generation of the Potassium Salt of the Biaryl-Based Compound 2
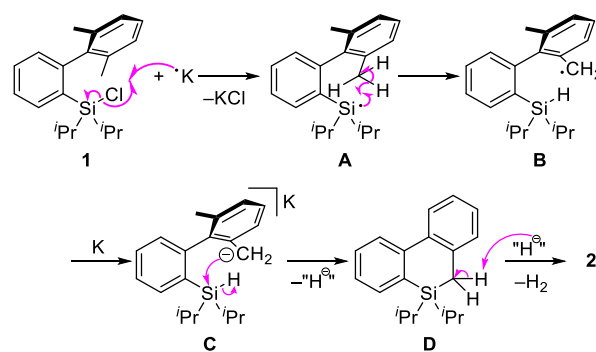
one-electron reduction of the Si−Cl moiety in **1** via contact with potassium occurs to form a silyl-radical intermediate **A**.[7] The subsequent abstraction of one of the three H atoms of the nearby methyl group on the 2,6-dimethylphenyl moiety would then induce the formation of intermediate **B** bearing a benzyl-radical moiety. Similar abstraction of one of the three H atoms of the methyl group by the silyl radical was previously reported by Shiina and Kumada.[8] Then, following reduction by potassium proceeded to generate the benzyl-anion species **C**. Subsequent intramolecular Si−C bond formation took place to

give the six-membered silacycle intermediate **D**. It should be mentioned here that Urabe and co-workers have described the related Si−C bond formation reaction involving PhCH₂MgBr and Ph₃SiH to afford Ph₃SiCH₂Ph.[9] Because the silyl-substituted benzylic proton was known to be abstracted by treatment with a strong base, cleavage of one of the two benzylic C−H bonds in **D** followed to form **2**.[10]

Synthesis of the Iron(II) Complex Bearing the Six-Membered Silacycle-Bridged Biphenyl-Based Ligand. Then, potassium salt **2** was treated with the iron precursor to produce the corresponding iron complex. Namely, chlorosilane **1** was treated with two equivalents of potassium in THF at 35 °C for 19 h to form **2**, followed by the treatment with a 1:1 mixture of FeBr₂ (one equivalent relative to **1**) and N,N,N',N'-tetramethylethylenediamine (TMEDA) in THF. After the work up and recrystallization (for details, see the Supporting Information), complex **3** was isolated in 53% yield as yellow crystals (Scheme 4). The molecular structure of **3** (Figure 2) was determined via a single-crystal X-ray diffraction analysis.
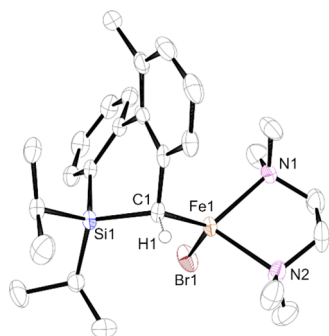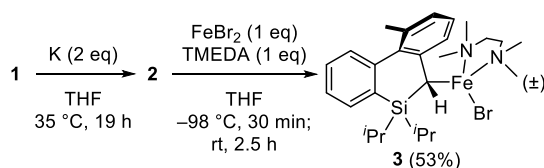
Scheme 4. Synthesis of 3

Figure 2. Molecular structure of **3** with thermal ellipsoids at 50% probability; all hydrogen atoms except H (1) are omitted for clarity.

Complex **3** crystallizes in the monoclinic space group $P2_1/c$, and the unit cell consists of a racemic pair of **3**, i.e., (S_a, S)-**3** and (R_a, R)-**3**. The iron center in **3** displays a tetrahedral coordination geometry and is surrounded by two nitrogen atoms derived from TMEDA, one Br atom, and one carbon atom. A striking feature of the molecular structure of **3** is that the benzylic position derived from **2** coordinated to the iron center with an Fe−C (1) bond length of 2.091 (3) Å. This bond distance is comparable to those in iron(II)−benzyl complexes.[11] The dihedral angle between the two phenyl rings in the biaryl moiety was ~43° with a Si−C (1) bond distance of 1.862 (3) Å; these values are comparable to those in the previously reported, structurally similar 10-methyl-5-phenyl-5,6-dihydrodibenzo[b,d]siline (dihedral angle: ~39°; Si−C = 1.866 (2) Å).[12] It is noteworthy that the reactions of anionic sila-cyclohexadienyl reagents with transition-metal precursors generally lead to the formation of metal complexes in which the sila-cyclohexadienyl skeleton is coordinated to the metal center in an η^5-fashion;[6a,13] thus, to the best of our knowledge,

3 is the first example of a complex that features an η^1(C)-coordinated silacyclohexadienyl framework.

Complex **3** is paramagnetic and affords broad peaks over a wide range from 155.50 to −63.72 ppm in the ¹H NMR spectrum in C_6D_6 at room temperature. The solution magnetic moment measured using the Evans method[14] (μ_{eff} = 4.93 ± 0.02) is consistent with an open-shell S = 2 ground state, which is commonly observed in Fe(II) complexes with tetrahedral coordination geometry. In fact, a similar value of magnetic moment was observed in previously reported four-coordinate Fe(II) complexes having either TMEDA or benzyl ligands such as $(TMEDA)Fe[CH_2C(CH_3)_3]_2$ (μ_{eff} = 4.8),[15a] (bis-NHC)-$Fe(CH_2Ph)_2$ (μ_{eff} = 4.7 (1)) (NHC = N-heterocyclic carbene)[15b] and $[PhB(CH_2PPh_2)_3]Fe(CH_2Ph)$ (μ_{eff} = 5.04).[15c] Complex **3** is relatively sensitive to air and moisture, albeit that the results of the elemental analysis are consistent with the theoretical values of the molecular formula of **3** (for details, see the Supporting Information).

As silicon-containing aromatic compounds are known to show unique chemical properties, several reports dealing with the synthesis of a six-membered silacycle-bridged biaryl framework have already been published.[9,16] Among these, it should be emphasized here that the six-membered silacycle-bridged biaryl framework has been reported to exhibit conformationally stable axial chirality when prepared as a chiral compound.[9] Although complex **3** was obtained as a racemic mixture of (S_a, S)-**3** and (R_a, R)-**3** at this stage, it is feasible to expect that further optical resolution of **3** will provide a novel iron complex featuring unprecedented chiral ligands. Another structural feature of **3** is that the silacycle-bridged biaryl based ligand functions as a monoanionic carbanion-type ligand. As described in a review by Power, sterically demanding carbanion-type ligands can function as thermally stable auxiliary ligands when introduced to base-metal centers such as iron(II).[17] Given that the silicon center in **3** bears two ^{i}Pr groups as well as a six-membered silacycle-bridged biaryl framework, this biphenyl-based ligand exhibits high levels of steric demand around the iron center. It should be noted here that no precedents for the construction of transition-metal complexes featuring carbanion-coordinated six-membered silacycle-bridged biaryl ligands were found, despite the fact that iridium-[18] and iron-based[19] complexes with silyl-coordinated analogous ligands have been reported.[20] Thus, it is expected that further research to improve these structural characteristics of **3** might contribute to the discovery of novel iron-based catalysts suitable for catalytic asymmetric reactions.

■ CONCLUSIONS

In this study, we effectively constructed a six-membered silacycle-bridged biaryl-based ligand that was subsequently coordinated to an iron(II) center via the sequential reaction with FeBr₂/TMEDA. Because the six-membered silacycle-bridged biaryl framework reportedly to exhibit conformationally stable axial chirality, complex **3** could be positioned as a new entry of iron complex that features a novel ligand which potentially functions as the chiral ligand after optical resolution. Efforts to develop new organoiron catalysts that bear such unique chiral ligands that realize effective catalytic asymmetric reactions are currently in progress in our laboratories, and the results will be reported in due course elsewhere.

◼ ASSOCIATED CONTENT

🄪 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c03161.

> Full experimental details and methods, computational methods, and additional crystallographic information (PDF)

Accession Codes

CCDC 2248818 and 2248819 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

◼ ACKNOWLEDGMENTS

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