



Dalton
Transactions

**Four- and Three-coordinate Planar Iron(II) Complexes
Supported by Bulky Organosilyl Ligands**

Journal:	<i>Dalton Transactions</i>
Manuscript ID	DT-ART-07-2023-002219.R1
Article Type:	Paper
Date Submitted by the Author:	09-Sep-2023
Complete List of Authors:	Ishii, Reon; The University of Tokyo, Department of Applied Chemistry Nakagawa, Minesato; The University of Tokyo, Department of Applied Chemistry Wada, Yoshimasa; The University of Tokyo, Institute of Industrial Science Sunada, Yusuke; The University of Tokyo, Institute for Industrial Science

SCHOLARONE™
Manuscripts

ARTICLE

Four- and Three-coordinate Planar Iron(II) Complexes Supported by Bulky Organosilyl Ligands

Reon Ishii,^a Minesato Nakagawa,^a Yoshimasa Wada^{a,b} and Yusuke Sunada^{*a,b,c}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

The ligand exchange reaction of $(\text{THF})_2\text{Fe}[\text{Si}(\text{SiMe}_3)_3]_2$ with 2 equivalents of an *N*-heterocyclic carbene (NHC) led to the formation of the square-planar iron(II) complex with *trans*-oriented $-\text{Si}(\text{SiMe}_3)_3$ ligands. Conversely, the introduction of a *cis*-coordinate bidentate organosilyl ligand instead of $-\text{Si}(\text{SiMe}_3)_3$ furnished the formation of square planar iron(II) complex supported by *cis*-coordinate bidentate organosilyl ligand. A three-coordinate planar iron(II) bis(silyl) complex was also synthesized using a *cis*-coordinate bidentate organosilyl ligand and a cyclic (alkyl)(amino)carbene auxiliary ligand. Investigating the catalytic performance of these complexes in the hydrosilylation of acetophenone revealed that the square-planar iron(II) complex with *trans*-oriented $-\text{Si}(\text{SiMe}_3)_3$ ligands exhibits superior reactivity relative to its tetrahedral precursor.

Introduction

The tetrahedral coordination geometry is the most common configuration in mononuclear four-coordinate iron(II) complexes. The tetrahedral configuration is generally sterically preferred in iron(II) complexes and typically observed when large auxiliary ligands are present. However, it has been reported that the use of appropriate auxiliary ligands, for example, macrocyclic chelating ligands such as porphyrins, facilitates the formation of square-planar iron(II) complexes.¹ Other auxiliary ligands that form square-planar four-coordinate iron(II) complexes are strongly electron-donating ligands, and thus strong field ligands.² In these ligands, electronic stabilization due to the presence of a high-energy, empty, antibonding $d_{x^2-y^2}$ orbital overcomes any competing steric effects. *N*-heterocyclic carbenes (NHC)³ and phosphine ligands are good representative examples of such auxiliary ligands, and selected examples are summarized in Figure 1. For instance, Ohki *et al.* have reported that a *trans*-bis(NHC) iron(II) complex with two methyl groups at the iron center adopts a square-planar coordination geometry, whereas the equivalent complex with the methyl ligands substituted by two chloride ligands adopts the more conventional tetrahedral coordination geometry. The *trans*-bis(NHC)Fe(Me)₂ complex was found to be a good catalyst for transfer hydrogenation and the hydrosilylation of 2'-acetonaphthone.^{2b} Chirik and co-workers

have conducted a systematic investigation on the coordination geometry of $(\text{P})_2\text{Fe}(\text{aryl})_2$ (aryl = mesityl, C_6Cl_5 ; P = phosphine) iron(II) complexes. They observed that bis(monodentate phosphine) iron(II) complexes prefer to adopt the square-planar coordination geometry, whereas the introduction of a bidentate phosphine ligand gave rise to the formation of both square-planar and tetrahedral complexes, depending on the particular steric influence of the ligand.^{2c} In addition, several examples of square planar iron(II) complexes supported by pincer-type ligands were also reported.^{2m-q}

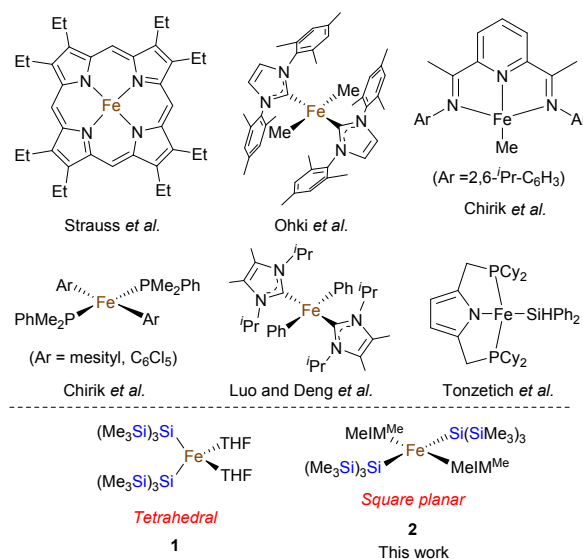


Figure 1. Selected examples of previously reported four-coordinate square-planar iron(II) complexes.

We have recently focused on the synthesis of reactive iron(II) and manganese(II) complexes supported by bulky organosilyl ligands of the type $-\text{Si}(\text{SiMe}_3)_3$.⁴ For instance, we have reported that bis(silyl)-iron(II) complex $(\text{THF})_2\text{Fe}[\text{Si}(\text{SiMe}_3)_3]_2$ (**1**) can be

^a Department of Applied Chemistry, School of Engineering, The University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153-8505, Japan.

^b Institute of Industrial Science, The University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153-8505, Japan.

^c JST PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012 Japan.

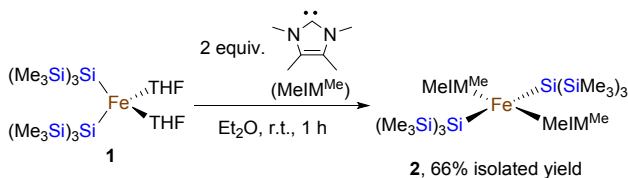
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

easily synthesized in one step by the reaction of FeBr_2 with 2 equivalents of $\text{K}[\text{Si}(\text{SiMe}_3)_3]$. A single-crystal X-ray diffraction analysis of **1** revealed that the iron center in **1** adopts a tetrahedral configuration, whilst **1** was also shown to be a good catalyst for the hydrosilylation of ketones. In addition, the two THF ligands in **1** could be easily replaced by two other electron-donating ligands, and thus $(\text{pyridine})_2\text{Fe}[\text{Si}(\text{SiMe}_3)_3]_2$ was formed instantly upon addition of 2 equivalents of pyridine to **1** at room temperature.^{4a} Given that organosilyl ligands generally act as the strong electron-donating ligands as well as strong field ligands,⁵ we hypothesized that it could be possible to construct square-planar iron(II) complexes from **1** by ligand exchange with the appropriate auxiliary ligands. In this paper, we report that a ligand-exchange reaction of **1** with the NHC MeIM^{Me} ($\text{MeIM}^{\text{Me}} = 1,3\text{-dimethyl-4,5-dimethylimidazol-2-ylidene}$) efficiently produces the square-planar iron(II) complex $\text{trans}-(\text{MeIM}^{\text{Me}})_2\text{Fe}[\text{Si}(\text{SiMe}_3)_3]_2$ (**2**) in good yield. The molecular structure of **2** was unequivocally determined via single-crystal X-ray diffraction analysis. The structural characterization and synthesis, by introduction of a six-membered bidentate organosilyl ligand to the iron(II) center, of an analogous iron(II) complex (**3**), which exhibits an unprecedented square-planar $\text{cis}-(\text{MeIM}^{\text{Me}})_2\text{Fe}(\text{silyl})_2$ configuration, is also reported. In addition, a planar three-coordinate Fe(II)-bis(silyl) complex (**4**) was obtained when a sterically bulky cyclic (alkyl)(amino)carbene (CAAC) ligand was used instead of MeIM^{Me} . The performance of **2**, **3** and **4** as catalysts for the hydrosilylation of acetophenone was examined, and square-planar complex **2** was found to be a better catalyst than tetrahedral precursor **1**.

Results and discussion

Synthesis of $\text{trans}-(\text{MeIM}^{\text{Me}})_2\text{Fe}[\text{Si}(\text{SiMe}_3)_3]_2$ (**2**).

As described in the introduction, the two THF ligands in **1** can be easily replaced with electron-donating ligands. Here, the NHC ligand MeIM^{Me} , in which electron-donating methyl groups are attached to the two nitrogen centers was used. The reaction of **1** with 2 equivalents of MeIM^{Me} in diethyl ether at room temperature for 1 h generated $\text{trans}-(\text{MeIM}^{\text{Me}})_2\text{Fe}[\text{Si}(\text{SiMe}_3)_3]_2$ (**2**) in the form of red crystals in 66% yield after recrystallization from diethyl ether at $-30\text{ }^\circ\text{C}$ (Scheme 1). Although **2** is highly sensitive toward air and moisture, the results of the elemental analysis were consistent with the theoretically expected values.



Scheme 1. Synthesis of **2**.

A single-crystal X-ray diffraction analysis of **2** revealed that the iron center adopts a four-coordinate square-planar coordination geometry (Figure 2). The crystallographic analysis

also revealed that the *trans*-oriented MeIM^{Me} and $-\text{Si}(\text{SiMe}_3)_3$ ligands are related by an inversion center. In other words, the iron center in **2** is surrounded by two MeIM^{Me} ligands as well as two $-\text{Si}(\text{SiMe}_3)_3$ ligands, and the two MeIM^{Me} ligands are located *trans* to each other. The iron center and the four surrounding atoms create a plane where none of the atoms deviate from the least-square plane defined by these atoms. The Okuniewski parameter, τ , was estimated to be ~ 1.26 , which corroborates a square-planar configuration.⁶ The five-membered rings of the MeIM^{Me} ligands are oriented around iron center in direction perpendicular to the least-square plane, and their dihedral angle was found to be 83.05° . This orientation is likely induced by the desire to avoid steric repulsion between the MeIM^{Me} ligands and the $-\text{Si}(\text{SiMe}_3)_3$ ligands. The Fe–C bond lengths in **2** ($1.9563(15)\text{ \AA}$) are comparable to those found in previously reported four-coordinate square-planar iron(II) complexes that contain two *trans* NHC ligands analogous to the MeIM^{Me} ligands. The following is a list of representative examples: *trans*-(MeIM^{H})₂ $\text{Fe}(\text{SnBu}_3)_2$ (Fe–C = $1.942(3)\text{ \AA}$)⁷; *trans*-($^i\text{PrIM}^{\text{H}}$)₂ $\text{Fe}(\text{mesityl})_2$ (Fe–C = $2.016(3)\text{ \AA}$)⁷ and *trans*-($^i\text{PrIM}^{\text{Me}}$)₂ $\text{Fe}(\text{mesityl})_2$ (Fe–C = $1.973(4)$ and $1.980(4)\text{ \AA}$)^{2d}, where $\text{MeIM}^{\text{H}} = 1,3\text{-dimethyl-4,5-imidazol-2-ylidene}$, $^i\text{PrIM}^{\text{H}} = 1,3\text{-diisopropyl-4,5-imidazol-2-ylidene}$, and $^i\text{PrIM}^{\text{Me}} = 1,3\text{-diisopropyl-4,5-dimethylimidazol-2-ylidene}$. In contrast, the Fe–C bond lengths are significantly shorter than those of previously reported bis(NHC) complexes with a tetrahedral coordination geometry such as $(\text{MeIM}^{\text{H}})_2\text{Fe}(\text{mesityl})_2$ (Fe–C = $2.164(2)$ and $2.153(2)\text{ \AA}$)⁷. It should be noted here that despite the difference in the coordination geometry around the iron center, the Fe–Si bond lengths ($2.5385(4)\text{ \AA}$) are comparable to those found in precursor **1** ($2.5445(8)\text{ \AA}$)^{4a} as well as those in the iron(II) bis(silyl) complex $[(\text{SiMe}_3)_2\text{SiSiMe}_2\text{OSiMe}_2\text{Si}(\text{SiMe}_3)_3]\text{Fe}(\text{THF})_2$, which has recently been reported by Marschner *et al.* (2.494 \AA)⁸. In addition, a cobalt complex, *trans*-(NHC)₂ $\text{Co}[\text{Si}(\text{H})\text{Ph}_2]_2$, of which structure is relevant to complex **2** was recently reported by Deng and co-workers.⁹

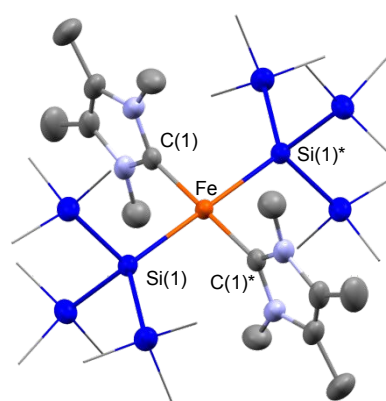


Figure 2. Molecular structure of **2** with thermal ellipsoids at 50% probability; methyl groups on the silicon atoms are shown in wireframe style; all hydrogen atoms are omitted for clarity.

Complex **2** is paramagnetic, and its ^1H NMR spectrum in C_6D_6 at room temperature exhibits a signal at 5.00 ppm for SiMe_3 as

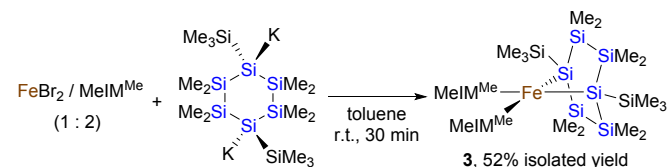
well as resonances at -46.24 and 16.10 ppm for the methyl group of the MeIM^{Me} ligands. The theoretical magnetic moment in solution for a square-planar iron(II) complex with an open-shell intermediate spin $S = 1$ ground state with a d^6 electronic configuration and high-energy, empty, antibonding $d_{x^2-y^2}$ orbital is $\mu_{\text{eff}} = 2.83$. The magnetic moment of **2** in C₆D₆ solution was measured using the Evans method at room temperature,¹⁰ and found to be slightly higher than the theoretical value ($\mu_{\text{eff}} = 3.75$). This larger μ_{eff} value in **2** might be ascribed to a significant contribution from spin-orbit coupling in the planar structure as observed in the square planar cobalt complexes reported by Chirik and co-workers.¹¹

It should be noted here that Luo and Deng *et al.* have reported the synthesis of an iron(II) diphenyl complex supported by two ⁱPrIM^{Me} ligands, (ⁱPrIM^{Me})₂FePh₂. The single-crystal X-ray diffraction analysis of (ⁱPrIM^{Me})₂FePh₂ revealed the presence of both the *trans* square-planar isomer and the tetrahedral isomer.^{2d} In addition, the magnetic susceptibility of this complex was estimated to be $\mu_{\text{eff}} = 4.2$ in solution. DFT calculations conducted on the (ⁱPrIM^{Me})₂FePh₂ complex revealed that the tetrahedral and *trans* square-planar isomers have similar energies, whereby the tetrahedral isomer is by 1.5 kcal/mol lower in enthalpy than the square-planar isomer in the gas phase. Based on these experimental and theoretical results, the authors suggested that the large magnetic moments of iron(II) diphenyl complex might be due to the contributions of spin-orbit coupling in the planar structure and/or the presence of the high-spin tetrahedral isomer together with the square-planar isomer.

The above mentioned Luo and Deng's results prompted us to estimate the relative stability of square planar isomer (**2**_{s-opt}) relative to its tetrahedral isomer (**2**_{t-opt}). The geometry of (MeIM^{Me})₂Fe[Si(SiMe₃)₃]₂ was optimized using DFT calculations with the B3PW91 functional and the 6-31G** basis set for H, C, N, and Si atoms, and with the B3PW91 functional and the SDD basis set, which uses the Stuttgart-Dresden effective core potentials, for Fe. The results showed that the energy minima for the $S = 1$ and $S = 2$ electronic configurations refer to the **2**_{s-opt} and **2**_{t-opt}, respectively. Although the estimated Fe–Si bond lengths in **2**_{s-opt} (2.6285 Å) are slightly longer than those determined crystallographically, the Fe–C separation (1.9736 Å) and the bond angles found in **2**_{s-opt} agree well with the experimental results (for details, see the Supporting Information). The theoretical calculations revealed that both **2**_{s-opt} and **2**_{t-opt} have similar energies, and that **2**_{t-opt} is by 5.5 kcal/mol lower in enthalpy. This small enthalpy difference is similar to that reported for (ⁱPrIM^{Me})₂FePh₂ reported by Luo and Deng *et al.* It should be noted here that the subtle energy preference of **2**_{t-opt} with tetrahedral geometry is inconsistent with the experimental observation in which the square planar isomer **2** was obtained as the sole product. This might be due to the inherent uncertainty tolerances of DFT calculations on the transition metal complexes with open-shell electronic configuration. Similar discussion was also made on the Luo and Deng's complexes.^{2d}

Synthesis of square-planar iron(II) complex **3**, which bears a *cis*-oriented bidentate organosilyl ligand.

Next, we attempted to introduce a *cis*-coordinate bidentate organosilyl ligand onto the iron center to examine whether the orientation of the two silicon atoms of the organosilyl ligand affects the coordination geometry around the iron center. Thus, a potassium salt of the six-membered cyclic oligosilanide shown in Scheme 2 was generated according to a previous report by Marschner *et al.*¹² This ligand was then treated with a 1:2 mixture of FeBr₂ and MeIM^{Me} in toluene at room temperature, from which complex **3** was obtained as red crystals in 52% isolated yield.



Scheme 2. Synthesis of **3**.

The solid-state structure of **3**, which was determined using single-crystal X-ray diffraction, is shown in Figure 3. Similar to complex **2**, the iron center in **3** exhibits a square-planar coordination geometry; however, in contrast to the *trans* configuration in **2**, the two MeIM^{Me} ligands occupy the *cis* positions and the Okuniewski parameter ($\tau \approx 1.21$) is comparable to that of **2**.⁶ The coordination geometry around the iron center was found to be slightly distorted compared to that in **2**, where the silicon and carbon atoms deviate from the least-square plane defined by the two carbon and two silicon atoms by ~ 0.16 and ~ 0.18 Å, respectively. The dihedral angles between the FeSi₂C₂ plane and the five-membered rings of the MeIM^{Me} ligands ($\sim 80.2/\sim 82.0^\circ$) are comparable to those in **2**. The Si(1)–Fe–Si(2) angle ($85.997(14)^\circ$) is considerably narrower than that in tetrahedral complex **1** ($135.23(3)^\circ$). The Fe–Si bond lengths (Fe–Si(1) = 2.4091(4) Å; Fe–Si(2) = 2.4259(4) Å) are considerably shorter than those in **2** (2.5445(8) Å), reflecting the lower *trans* influence of the MeIM^{Me} ligands compared to that of the organosilyl ligands. Similarly, the Fe–C bonds in **3** (Fe–C(1) = 1.9800(13) Å; Fe–C(2) = 1.9873(14) Å) are slightly longer than the equivalent bonds in **2**, presumably due to the strong *trans*-influence arising from the organosilyl ligands, rather than the MeIM^{Me} ligands, located at the *trans*-position.

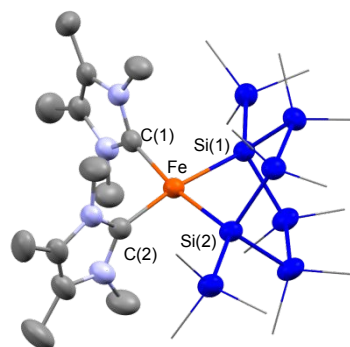


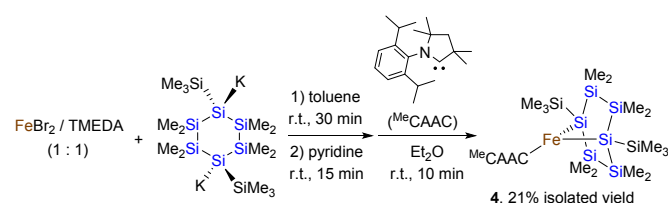
Figure 3. Molecular structure of **3** with thermal ellipsoids at 50% probability. The methyl groups on the silicon atoms are shown in wireframe style; all hydrogen atoms are omitted for clarity.

In the ^1H NMR spectrum of **3** in C_6D_6 at room temperature, five resonances are observed at -78.37, -31.32, -1.40, 11.98 and 15.87 ppm, which were in good agreement with the molecular structure of **3**. The magnetic susceptibility of **3** in C_6D_6 solution at room temperature was measured using the Evans method. The estimated effective magnetic moment ($\mu_{\text{eff}} = 4.13$) is slightly higher than the theoretical value ($\mu_{\text{eff}} = 3.75$), this could be attributed to the significant contributions of spin-orbit coupling in the planar structure.

To confirm whether the choice of functional and basis sets for the calculation of complex **2** was appropriate or not, geometry optimization of complex **3** was performed with the same level of theory for the calculation of **2**. It was found that the optimized structural parameters of **3**_{opt} are in good agreement with the data obtained from the XRD analysis (see Supporting Information for details). Thus, we concluded that the choice of functional and basis sets for the calculation of iron complexes was appropriate.

Synthesis of three-coordinate planar iron(II) complex **4**.

As mentioned above, the use of MeIM^{Me} ligands in iron(II) bis(silyl) complexes supported by sterically demanding organosilyl ligands facilitates the construction of four-coordinate square-planar iron(II) complexes. We next focused on the introduction of other types of carbenes at the iron center, and, due to their differing electronic properties compared to NHCs, a cyclic (alkyl)(amino)carbene (CAAC) was chosen as the ligand to use. CAACs, which consist of nitrogen- and a carbon-based moieties flanking the carbene center, are better σ -donors/ π -acceptors than conventional NHCs.¹³ Unfortunately, despite several attempts to produce an iron(II) bis(silyl) complex supported by both $^{\text{Me}}\text{CAAC}$ and $-\text{Si}(\text{SiMe}_3)_3$ ligands, no identifiable products were formed in the reaction of **1** with $^{\text{Me}}\text{CAAC}$ ($^{\text{Me}}\text{CAAC} = 1-(2,6\text{-di-isopropylphenyl})-3,3,5,5\text{-tetramethyl-pyrrolidin-2-ylidene}$). Therefore, a 1 : 1 mixture of FeBr_2 and TMEDA (TMEDA = N,N,N',N' -tetramethylethylenediamine) was treated with the potassium salt of a six-membered cyclic oligosilanide in toluene followed by the addition of pyridine to generate the iron(II) bis(silyl) complex *in situ*. Then, 1 equivalent of $^{\text{Me}}\text{CAAC}$ was added, from which ($^{\text{Me}}\text{CAAC}$)Fe(II) bis(silyl) complex **4** was obtained as dark purple crystals in 21% yield.



Scheme 3. Synthesis of **4**.

The molecular structure determined using single-crystal X-ray diffraction is shown in Figure 4. The iron center in **4** adopts a

three-coordinate planar structure with two silicon atoms derived from the bidentate organosilyl ligand and the carbon atom of the $^{\text{Me}}\text{CAAC}$ ligand. These three surrounding atoms are positioned on a plane, and the iron center in **4** resides on this plane with a deviation of 0.049 Å. The five-membered ring in $^{\text{Me}}\text{CAAC}$ also lies on this plane, and C(2) and N(1) deviate from this plane by 0.149 and 0.141 Å, respectively. It should also be noted here that the two Fe–Si bonds (Fe–Si(1): 2.4886(6) Å; Fe–Si(2): 2.5110(7) Å) are considerably longer than those found in **3**, which probably reflects the high spin ($S = 2$) induced by the planar three-coordinate structure (*vide infra*). These Fe–Si bond lengths are comparable to those found in the planar three-coordinate anionic complex $(\text{NET}_4)\{\text{FeCl}[\text{Si}(\text{SiMe}_3)_3]_2\}$ (Fe–Si = 2.488(6)/2.491(6) Å), which has been reported by Tilley *et al.*¹⁴

Complex **4** is paramagnetic and affords broad peaks over a wide range from -40.07 ppm to 50.63 ppm in the ^1H NMR spectrum in C_6D_6 at room temperature. The magnetic moment of **4** in C_6D_6 solution at room temperature was measured using the Evans method. Although the observed value for **4** ($\mu_{\text{eff}} = 5.83$) is slightly higher than that expected for an open-shell $S = 2$ ground state with a three-coordinate planar structure ($\mu_{\text{eff}} = 4.89$), this result is consistent with the fact that **4** adopts a coordination geometry that is different from those of **2** and **3**. Although **4** is highly sensitive to air and moisture, the results of the elemental analysis were consistent with the theoretically expected values.

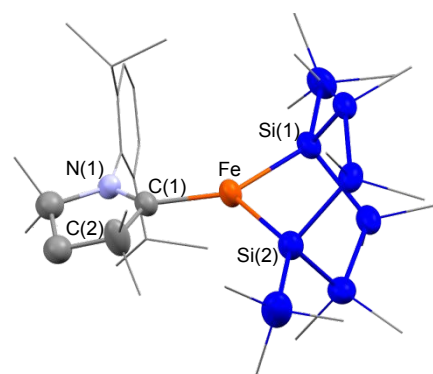


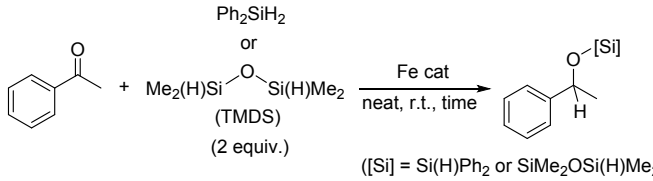
Figure 4. Molecular structure of **4** with thermal ellipsoids at 50% probability; carbon atoms of the 2,6-diisopropylphenyl group and all methyl groups are shown in wireframe style; all hydrogen atoms are omitted for clarity.

Catalytic performance of planar iron(II) complexes **2**, **3**, and **4**.

The development of highly reactive iron catalysts has attracted much attention recently due to the increasing desire for cheap and environmentally friendly catalytic reactions.¹⁵ Especially, the development of iron-catalyzed hydrosilylation reactions is currently a hot topic in synthetic chemistry¹⁶, and hydrosilylation of ketones is often used to evaluate the catalytic performance of newly synthesized iron complexes. For instance, as described in Introduction, Ohki *et al.* have demonstrated the catalytic performance of their *trans*-(NHC)₂FeMe₂^{2b} complex toward hydrosilylation of acetophenone. Iron(II) complexes with tetrahedral coordination geometry and an $S=2$ electronic configuration are often unreactive, despite their 14-electron structure, presumably due to the lack of low-lying empty

molecular orbitals available for substrate binding.¹⁷ We have examined the catalytic activity of planar iron(II) bis(silyl) complexes **2**, **3**, and **4**, and their tetrahedral precursor **1** in the catalytic hydrosilylation of acetophenone. Notably, **2** and **4** exhibit good catalytic performance for the hydrosilylation of acetophenone with Ph₂SiH₂ under neat conditions, i.e., the quantitative formation of the hydrosilylated product was confirmed within 1 h at room temperature in the presence of 0.1 mol% of **2** or **4** (Table 1, entries 2 and 5). A slightly decreased catalytic performance was observed for **3**, where an 85% conversion of acetophenone was observed in the presence of 0.1 mol% of **3** under otherwise identical reaction conditions (entry 4). In contrast, 0.5 mol% of **1** was required for the complete consumption of acetophenone under otherwise identical reaction conditions, as reported in our previous paper (entry 1)^{4a}. Thus, we concluded that the planar iron(II) bis(silyl) complexes show superior catalytic performance than their tetrahedral counterpart. It is noteworthy that the amount of catalyst used could be decreased to 0.05 mol% when the hydrosilylation of acetophenone was mediated by **2**, and the formed silyl ether was isolated in 89% yield after distillation (entry 3).

Table 1. Hydrosilylation of acetophenone catalyzed by iron complexes **1**, **2**, **3**, and **4**.^a



entry	cat	hydrosilane	Cat. loading (mol%)	Time (h)	Conv. (%) ^b
1 ^c	1	Ph ₂ SiH ₂	0.5	1	> 99
2	2	Ph ₂ SiH ₂	0.1	1	> 99
3	2	Ph ₂ SiH ₂	0.05	1	> 99 (89) ^d
4	3	Ph ₂ SiH ₂	0.1	1	85
5	4	Ph ₂ SiH ₂	0.1	1	> 99
6	1	TMDS	0.5	24	30
7	2	TMDS	0.5	24	85
8	3	TMDS	0.5	24	22
9	4	TMDS	0.5	24	75

^a Reactions were performed using 3 mmol of acetophenone and Ph₂SiH₂ (6.6 mmol) 1 mmol of acetophenone with TMDS (2.2 mmol) in the presence of a catalytic amount of the iron catalyst under neat conditions at room temperature.

^bThe conversion was determined using ¹H NMR spectroscopy in the presence of an internal standard (1,4-dioxane). ^cFor details, see ref. 4a. ^dValue in bracket indicates the isolated yield of the formed silyl ether.

As noted by Larson *et al.*,¹⁸ 1,1,3,3-tetramethyldisiloxane (TMDS) is considered to be one of the most practical reagents for hydrosilylations in terms of its cost and availability, and therefore, we decided to examine the hydrosilylation of acetophenone with TMDS using iron-based catalysts **1**, **2**, **3**, and **4**. When the reaction was mediated by 0.5 mol% of **1** at room temperature for 24 h under neat conditions the conversion only reached 30%. However, the conversion of acetophenone

increased to 85% when using 0.5 mol% of **2** under otherwise identical reaction conditions. Similarly, **4** showed good catalytic performance for the hydrosilylation of acetophenone with TMDS, providing 75% of the hydrosilylated product (entry 9). The catalytic performance of **3** was also investigated under the same reaction conditions, from which the corresponding hydrosilylated product was obtained with a 22% conversion (entry 8). Given these results, the catalytic performance of square-planar iron(II) complex **2** can be considered the best of those examined in this study.

Conclusions

In conclusion, two square-planar iron(II) bis(silyl) complexes have been synthesized by introducing two *N*-heterocyclic carbene (NHC) ligands onto an “Fe(silyl)₂” species. The arrangement of the auxiliary ligands around the iron center changed depending on the structure of the organosilyl ligands. For example, the mono-coordinated ligand, –Si(SiMe₃)₃, gave rise to the formation of *trans*-configured complex **2**, whereas the use of a *cis*-coordinate bidentate organosilyl ligand provided *cis*-oriented complex **3**. In addition, the introduction of a cyclic (alkyl)(amino)carbene (CAAC) ligand furnished planar three-coordinated iron(II) bis(silyl) complex **4**. An investigation of the catalytic performance of the obtained complexes in the hydrosilylation of acetophenone revealed that **2** is a superior catalyst compared to tetrahedral precursor **1**. Efforts to synthesize iron silyl complexes with higher reactivity based on the introduction of appropriate organosilyl ligands as well as auxiliary ligands are currently in progress in our laboratories.

Author Contributions

Y. Sunada designed the project. R. Ishii and M. Nakagawa carried out the experiments together. Y. Wada performed the theoretical calculation. R. Ishii, Y. Wada and Y. Sunada analyzed the data and wrote the paper. All authors discussed the results and made comments and edits to the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by JST (Japan) in the form of PRESTO grant JPMJPR20A9, and Grant in Aid for Scientific Research (B) (20H02751) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The synchrotron radiation experiments to collect the preliminary X-ray diffraction data for **4** were performed at the BL02B1 of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2022B1592).

Notes and references

- 1 (a) J. Kirner, W. Dow, W. Scheidt, *Inorg. Chem.* 1975, **15**, 1685-1690; (b) S. Strauss, M. Silver, K. Long, R. Thompson, R. Hudgens, K. Spartialian, J. Ibers, *J. Am. Chem. Soc.* 1985, **107**, 4207-4215; (c) S. Strauss, M. Silver, J. Ibers, *J. Am. Chem. Soc.* 1983, **105**, 4108-4109; (d) D. Riley, J. Stone, D. Busch, *J. Am. Chem. Soc.* 1977, **99**, 767-777; (e) B. Liu, Q. Xia, W. Chen, *Angew. Chem. Int. Ed.* 2009, **48**, 5513-5516.
- 2 (a) M. Ingleson, R. Layfield, *Chem. Commun.* 2012, **48**, 3579-3589; (b) T. Hashimoto, S. Urban, R. Hoshino, Y. Ohki, K. Tatsumi, F. Glorius, *Organometallics* 2012, **31**, 4474-4479; (c) E. Hawrelak, W. Bernskoetter, E. Lobkovsky, G. Yee, E. Bill, P. J. Chirik, *Inorg. Chem.* 2005, **44**, 3103-3111; (d) Y. Liu, L. Luo, J. Xiao, L. Wang, Y. Song, J. Qu, Y. Luo, Y. Deng, *Inorg. Chem.* 2015, **54**, 4752-4760; (e) S. Zlatogorsky, C. Muryn, F. Tuna, D. Evans, M. Ingleson, *Organometallics* 2011, **30**, 4974-4982; (f) Z. Ouyang, L. Deng, *Organometallics* 2013, **32**, 7268-7271; (g) D. Prokopchuk, E. Wiedner, E. Walter, C. Popescu, N. Piro, W. Kassel, R. Bullock, M. Mock, *J. Am. Chem. Soc.* 2017, **139**, 9291-9301; (h) K. Ray, A. Begum, T. Weyhermüller, S. Piligkos, J. van Slageren, F. Neese, K. Wieghardt, *J. Am. Chem. Soc.* 2005, **127**, 4403-4415; (i) B. Hakey, J. Darmon, Y. Zhang, J. Petersen, C. Milsman, *Inorg. Chem.* 2019, **58**, 1252-1266; (j) C. Thompson, H. Arman, Z. Tonzetich, *Organometallics* 2019, **38**, 2979-2989; (k) M. Bouwkamp, S. Bart, E. Hawrelak, R. Trovitch, E. Lobkovsky, P. J. Chirik, *Chem. Commun.* 2005, 3406-3408; (l) J. Chatt, B. Shaw, *J. Chem. Soc.* 1961, 285-290. (m) C. V. Thompson, H. D. Arman, Z. J. Tonzetich, *Organometallics* 2019, **38**, 2979-2989; (n) C. V. Thompson, H. D. Arman, Z. J. Tonzetich, *Organometallics* 2017, **36**, 1795-1802; (o) S. Zhang, J. P. Krogman, *Organometallics* 2021, **40**, 1926-1933; (p) M. W. Bouwkamp, S. C. Bart, E. J. Hawrelak, R. J. Trovitch, E. Lobkovsky, P. J. Chirik, *Chem. Commun.* 2005, 3406-3408; (q) I. Fernández, R. J. Trovitch, E. Lobkovsky, P. J. Chirik, *Organometallics* 2008, **27**, 109-118.
- 3 (a) M. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* 2014, **510**, 485-496; (b) P. Bellotti, M. Koy, M. Hopkinson, F. Glorius, *Nat. Rev. Chem.* 2021, **5**, 711-725; (c) S. Díez-González, N. Marion, S. Nolan, *Chem. Rev.* 2009, **109**, 3612-3676; (d) W. Herrmann, C. Kocher, *Angew. Chem. Int. Ed. Engl.* 1997, **36**, 2162-2187; (e) W. Herrmann, *Angew. Chem. Int. Ed.* 2002, **41**, 1290-1309; (f) P. Arnold, S. Pearson, *Coord. Chem. Rev.* 2007, **251**, 596-609; (g) T. Weskamp, V. Böhm, W. Herrmann, *J. Organomet. Chem.* 2000, **600**, 12-22; (h) S. C. Sau, P. K. Hota, S. Mandal, M. Michele Soleilhavoup, G. Bertrand, *Chem. Soc. Rev.* 2020, **49**, 1233-1252.
- 4 (a) S. Arata, Y. Sunada, *Dalton Trans.*, 2019, **48**, 2891-2895; (b) Y. Kobayashi, Y. Sunada, *Catalysts* 2020, **10**, 29-40; (c) K. Saito, T. Ito, S. Arata, Y. Sunada, *ChemCatChem* 2021, **13**, 1152-1156; (d) S. Arata, K. Suzuki, K. Yamaguchi, Y. Sunada, *Dalton Trans.* 2020, **49**, 17537-17541; (e) Y. Kobayashi, Y. Sunada, *ACS Sustainable Chem. Eng.* 2022, **10**, 1078-1082; (f) Y. Kobayashi, Y. Sunada, *Chem. Sci.* 2023, **14**, 1065-1071.
- 5 (a) J. Corey, *Chem. Rev.* 2016, **116**, 11291-11435; (b) J. Corey, *Chem. Rev.* 2011, **111**, 863-1071; (c) J. Corey, J. Braddock-Wilking, *Chem. Rev.* 1999, **99**, 175-292.
- 6 A. Okuniewski, D. Rosiak, J. Chojnacki, B. Becker, *Polyhedron* 2015, **90**, 47-57.
- 7 H. Schneider, D. Schmidt, A. Eichhöfer, M. Radius, F. Weigend, U. Radius, *Eur. J. Inorg. Chem.* 2017, 2600-2616.
- 8 A. Pöcheim, R. Zitz, J. Hönigsberger, C. Marschner, J. Baumgartner, *Inorg. Chem.* 2022, **61**, 17527-17536.
- 9 L. Zhou, D. Wang, C. Yang, L. Deng, *Chin. Chem. Lett.* 2023, in press (DOI: 10.1016/j.ccl.2023.108682).
- 10 (a) E. Schubert, *J. Chem. Educ.* 1992, **69**, 62; (b) C. Piguet, *J. Chem. Educ.* 1997, **74**, 815-816; (c) G. Bain, J. Berry, *J. Chem. Educ.* 2008, **85**, 532-536.
- 11 (a) S. P. Semproni, C. Milsman, P. J. Chirik, *J. Am. Chem. Soc.* 2014, **136**, 9211-9224; see also (b) P. D. W. Boyd, D. A. Buckingham, R. T. McMeeking, S. Mitra, *Inorg. Chem.* 1979, **19**, 3585-3591
- 12 (a) M. Haas, M. Leypold, L. Schuh, R. Fischer, A. Torvisco, H. Stueger, *Organometallics* 2017, **36**, 3765-3773; (b) A. Wallner, M. Hölbling, J. Baumgartner, C. Marschner, *Silicon Chem.* 2005, **3**, 175-185.
- 13 (a) R. Jazzar, M. Soleilhavoup, G. Bertrand, *Chem. Rev.* 2020, **120**, 4141-4168; (b) M. Soleilhavoup, G. Bertrand, *Acc. Chem. Res.* 2015, **48**, 256-266; (c) S. Kundu, S. Sinhababu, V. Chandrasekhar, H. Roesky, *Chem. Sci.* 2019, **10**, 4727-4741; (d) S. C. Kushvaha, A. Mishra, H. Roesky, K. C. Mondal, *Chem. Asian J.* 2022, **17**, e202101301.
- 14 D. Roddick, T. D. Tilley, A. Rheingold, S. Geib, *J. Am. Chem. Soc.* 1987, **109**, 945-946.
- 15 (a) B. Plietker, In *Iron Catalysis in Organic Chemistry*, Ed.; B. Plietker, Wiley-VCH, Weinheim, Germany, 2008; (b) I. Marek, Z. Rappoport, In *The Chemistry of Organoiron Compounds*, Eds.; S. Patai, Z. Rappoport, Wiley and Sons: New York, 2014; (c) D. Wei, C. Darcel, *Chem. Rev.* 2019, **119**, 2550-2610; (d) J. V. Obligacion, P. J. Chirik, *Nat. Rev. Chem.*, 2018, **2**, 15-34; (e) A. Fürstner, *ACS Cent. Sci.* 2016, **2**, 778-789; (f) I. Bauer, H. -J. Knölker, *Chem. Rev.* 2015, **115**, 3170-3387; (g) C. -L. Sun, B. -J. Li, Z. -J. Shi, *Chem. Rev.*, 2011, **111**, 1293-1314; (h) E. Nakamura, N. Yoshikai, *J. Org. Chem.*, 2010, **75**, 6061-6067.
- 16 (a) D. S. Mérel, M. L. T. Do, S. Gaillard, P. Dupau and J. -L. Renaud, *Coord. Chem. Rev.* 2015, **288**, 50-68; (b) R. H. Morris, *Chem. Soc. Rev.* 2009, **38**, 2282-2291; (c) K. Junge, K. Schröder and M. Beller, *Chem. Commun.* 2011, **47**, 4849-4859.
- 17 (a) N. Shirasawa, T. T. Nguyet, S. Hikichi, Y. Moro-oka, M. Akita, *Organometallics* 2001, **20**, 3582-3598; (b) S. C. Bart, E. J. Hawrelak, A. K. Schmisser, E. Lobkovsky, P. J. Chirik, *Organometallics* 2004, **23**, 237-246.
- 18 J. Pesti, G. Larson, *Org. Process Res. Dev.* 2016, **20**, 1164-1181.