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Preparation, Characterization, and Catalytic Reactions of NCN Pincer Iron Complexes Containing Stannyl, Silyl, Methyl, and Phenyl Ligands

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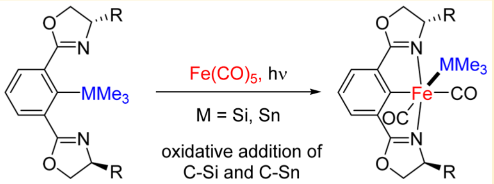
Supporting Information



ABSTRACT: Preparation and reactivity of chiral and achiral NCN pincer Fe complexes containing bis(oxazolinyl)phenyl (abbreviated as phebox) ligands with $SnMe_3$, $SiMe_3$, Me, and Ph ligands were investigated. Irradiation of (phebox)$SnMe_3$ (**2**) with 1 equiv of $Fe(CO)_5$ led to oxidative addition to give NCN pincer stannyl complex (phebox)$Fe(CO)_2(SnMe_3)$ (**3**). Similarly, oxidative addition of (phebox)$SiMe_3$ (**4**) with $Fe(CO)_5$ resulted in the formation of silyl complex (phebox)$Fe(CO)_2SiMe_3$ (**5**). Me and Ph complexes (phebox)$Fe(CO)_2R$ (**7**, R = Me; **8**, R = Ph) were synthesized by transmetalation of the bromide complex (phebox)$Fe(CO)_2Br$ (**1**) with $ZnMe_2$ and $ZnPh_2$, respectively. These phebox Fe complexes served as catalysts for hydrosilylation of a ketone and C−H silylation of *N*-methylindole.

INTRODUCTION

Transition metal complexes containing meridional-type ligands have been applied to catalytic and stoichiometric reactions of organic and inorganic molecules.[1] Since nonprecious metal catalysts are considered to be a significant research area toward environmentally friendly processes,[2] Fe complexes containing pyridine-based meridional ligands and related nitrogen ligands have been extensively developed as efficient catalysts in polymerization, oligomerization, cycloaddition, hydrosilylation, and hydrogenation, as well as asymmetric transformations.[3−7] In contrast to neutral meridional pyridine ligands, NCN and PCP pincer ligands based on phenyl and alkyl scaffolds are expected to exhibit different properties arising from the anionic ligand framework with a Fe−C σ-bond. In addition, the presence of two metallacycles contributes to the robust structure. Since the early studies of $[C_6H_3(CH_2NMe_2)_2]FeCl_2$[8a,b] and $\{[C_6H_3(CH_2PMe_2)_2]FeCl_2\}_n$,[8c] NCN and PCP pincer Fe complexes have been developed by several research groups for stoichiometric and catalytic reactions.[8,9] In particular, C−H bond activation of PCP ligand precursors with $Fe(PMe_3)_4$ and $Fe(Me)_2(PMe_3)_4$ was used to form unique Fe hydride complexes, which served as efficient catalysts in hydrosilylation of carbonyl compounds and dehydrogenation of ammonia borane.[8d−i] However, examples of chiral and achiral NCN-Fe complexes remain to be explored compared to second- and third-row metals, such as Rh and Pd, likely due to their instability.

Reactivity of metal complexes is also affected by other ligands besides the spectator ancillary ligand. In that sense, group 14 elements, such as silyl, stannyl, alkyl, and aryl ligands, are considered to be important species for transition metal complexes.[10−12] The characteristic aspects of silyl and stannyl complexes would be their strong *trans* effect and σ-donating characters.[13] Since $CpFe(CO)_2SiMe_3$ was reported,[14] various silyl transfer reactions mediated by Fe silyl species have been developed.[15] Concurrently, Si−H and Sn−H oxidative addition and salt metathesis between an anionic complex and a silyl halide or a silyllithium and a metal halide were reported as common synthetic strategies for the preparation of silyl and stannyl complexes.[10] In contrast, oxidative addition of Si−C and Sn−C is rare in Fe complexes, and examples are limited to reactions of cyclosilabutane or $Ph_3Sn(CH_2)_2PPh_2$ with Fe(0) carbonyl complexes.[16]

Recently, we described chiral NCN-Fe complexes (phebox)-$Fe(CO)_2Br$ (**1**) and their application to asymmetric hydrosilylation of ketones.[9a] In the catalysis, the addition of Na(acac) (acac = acetylacetonate) enhanced reactivity and enantioselectivity, suggesting that the exchange of the Br ligand afforded a catalytically active species. We hypothesized that introduction of group 14 elements into the phebox-Fe framework might modify reactivity. In this context, oxidative addition of Si−C and Sn−C bonds of the phebox ligand precursor (phebox)-MMe_3 (M = Si, Sn) could be a versatile method.

Here, we report the preparation of NCN pincer Fe stannyl and silyl complexes, which was achieved by oxidative addition of $SiMe_3$- and $SnMe_3$-substituted ligand precursors. Structurally related alkyl and phenyl complexes are also described that were synthesized by transmetalation of the bromide complexes with organozinc reagents. Catalytic activities of these Fe complexes were evaluated in the hydrosilylation of ketones and C−H silylation of indole derivatives.

RESULTS AND DISCUSSION

Following the preparation of (phebox-*dm*)$Fe(CO)_2Br$ (**1**),[9a] we examined oxidative addition of the stannyl precursor

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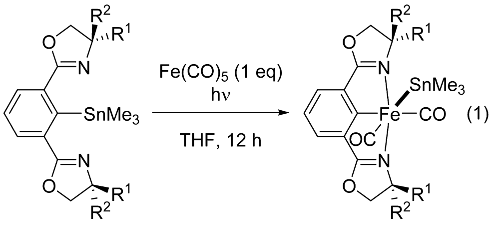
(phebox-*dm*)$SnMe_3$ (**2a**)[17] to Fe(0) carbonyl complexes. When thermal reaction of **2a** with $Fe_2(CO)_9$ was carried out in THF at 50 °C for 12 h, the desired stannyl Fe complex (phebox-*dm*)$Fe(CO)_2SnMe_3$ (**3a**) was obtained in 21% yield after purification by silica gel column chromatography (eq 1).



2a: $R^1 = R^2 = Me$
2b: $R^1 = i Pr$, $R^2 = H$

3a: $R^1 = R^2 = Me$ (57%)
3b: $R^1 = i Pr$, $R^2 = H$ (62%)

However, the formation of unidentified byproducts decreased the yield of **3a**. In contrast, the reaction of **2a** with $Fe(CO)_5$ did not proceed under heating at 50 °C. Oxidative addition requires a coordinatively unsaturated precursor $Fe(CO)_4$, which can be generated by the fragmentation of $Fe_2(CO)_9$.[18] Thus, we examined the irradiation reaction of $Fe(CO)_5$ to generate a $Fe(CO)_4$ species. As a result, irradiation of a THF solution of **2a** and $Fe(CO)_5$ by a Xe lamp (250−385 nm) at room temperature for 12 h resulted in the formation of **3a** in 57% yield (eq 1). The use of a similar procedure provided the chiral complex (phebox-*ip*)$Fe(CO)_2SnMe_3$ (**3b**) in 62% yield. Notably, **3a** and **3b** are stable in air and light in the solid state. When a C_6D_6 solution of **3b** was irradiated by a Xe lamp for 15 h, decomposition of **3b** was not observed.

The ^1H NMR spectrum of **3a** measured in C_6D_6 showed a signal from the $SnMe_3$ group at δ −0.08 ppm with satellite peaks (J_{SnH} = 38 Hz). The methyl groups on the oxazolines were observed as two singlet peaks at δ 0.96 and 0.97 in the integral ratio of 6H:6H. This spectral feature suggests that **3a** has C_s symmetric geometry. In the ^{13}C NMR spectrum, the signal of the $SnMe_3$ group appeared at δ −7.1 ppm with satellite peaks (J_{SnC} = 169 Hz). The IR spectrum showed CO stretching vibrations at 1988 and 1907 cm^{-1}. These peaks of **3a** were shifted to lower frequency compared to those of **1a** (2020 and 1969 cm^{-1}), suggesting enhanced back-donation. In the ^1H NMR spectrum of **3b**, signals of the *i*Pr groups on the oxazolines were observed as four independent peaks due to an unsymmetrical structure. The ^1H and ^{13}C NMR spectra of **3b** exhibited signals of the $SnMe_3$ at δ −0.02 and −7.1 ppm, respectively.

Crystals of **3a** were obtained by cooling a CH_3CN solution at −20 °C. The ORTEP diagram obtained by X-ray analysis is shown in Figure 1. The structure around the Fe center is described as a pseudo-octahedron with a meridionally coordinated phebox ligand. The Fe1−C1 bond length of 1.9226(19) Å is comparable to those of neutral NCN Fe complexes, **1a** [1.930(2) Å],[9a] (phebox)Fe(CO)(CN*t*Bu)Br [1.923(7) Å],[9b] and $[C_6H_3(CH_2NMe_2)_2]FeCl_2$ [1.937(2) Å],[8a] and shorter than those of the PCP-Fe complexes $[C_6H_3(OP i Pr_2)_2]$-$Fe(H)L_2$ [L = PMe_3, CO; Fe−C = 1.995(2)−2.001(2) Å].[8h,i] The $SnMe_3$ ligand is attached at a position vertical to the NCN ligand plane. This feature is a consequence of oxidative addition of the C−Sn bond of **2a** to the Fe(0) center. The Sn−Fe bond length of 2.5930(3) Å is slightly longer than in CpFe(CO)-$(SnMe_3)_2(H)$ [2.558(1), 2.569(1) Å].[19] The Fe1−C10 bond length [1.806(2) Å] is longer than the Fe1−C11 bond length [1.790(2) Å] due to the *trans* influence of the $SnMe_3$ ligand. Another structural feature is that the equatorial CO ligand deviates significantly from linearity with the C1−Fe1−C11 bond angle of 164.54(9)°, compared to that of **1a** (175.82°).

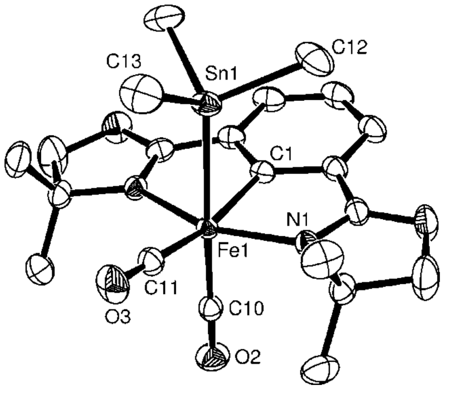
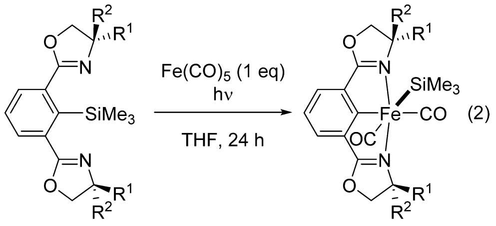


Figure 1. ORTEP diagram of **3a** at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Fe1−C1 = 1.9226(19), Fe1−C10 = 1.806(2), Fe1−C11 = 1.790(2), Fe1−N1 = 2.0088(12), Fe1−Sn1 = 2.5930(3), C10−O2 = 1.137(3), C11−O3 = 1.153(3), Sn1−C12 = 2.1657(19), Sn1−C13 = 2.172(3). Selected angles (deg): N1−Fe1−N1 = 156.42(7), C1−Fe1−C11 164.54(9), Sn1−Fe1−C10 = 177.02(6), C1−Fe1−Sn1 = 78.55(6).

Next, we studied oxidative addition of a C−Si bond of the organosilane precursor (phebox-*dm*)$SiMe_3$ (**4a**)[20] to synthesize a silyl complex (eq 2). The irradiation reaction of **4a** with $Fe(CO)_5$ for 24 h led to the formation of the silyl complex (phebox-*dm*)$Fe(CO)_2(SiMe_3)$ (**5a**). The purification of the crude product by silica gel column chromatography afforded **5a** in 60% yield. Similarly, chiral complexes **5b**−**d**, containing isopropyl, phenyl, and benzyl groups on the oxazolines, were also obtained in 70−76% yields in a similar manner. Oxidative addition of the C−Si bond took longer compared to that of the C−Sn bond. As mentioned earlier, a C−Si bond cleavage by metal complexes was promoted by coordination of a phosphine ligand or the ring opening of distorted cyclosilabutane.[16,21] In our case, coordination of the nitrogen atom on the oxazoline ring could act as a directing group for the C−Si bond cleavage.



4a: $R^1 = R^2 = Me$
4b: $R^1 = i Pr$, $R^2 = H$
4c: $R^1 = Ph$, $R^2 = H$
4d: $R^1 = Bn$, $R^2 = H$

5a: $R^1 = R^2 = Me$ (60%)
5b: $R^1 = i Pr$, $R^2 = H$ (76%)
5c: $R^1 = Ph$, $R^2 = H$ (70%)
5d: $R^1 = Bn$, $R^2 = H$ (75%)

Complexes **5a**−**d** were identified on the basis of ^1H and ^{13}C NMR, IR spectra, and elemental analysis. In the ^1H NMR spectrum of **5a**, two singlet signals of methyl groups on the oxazolines were observed at δ 0.97 and 1.02 ppm due to the C_s symmetry. The methyl signal of the $SiMe_3$ group appeared at δ 0.04 ppm and 3.9 in the ^1H and ^{13}C NMR spectra, respectively. In the IR spectrum, two CO absorptions were observed at 1982 and 1902 cm^{-1}, which were similar to those of **3a**.

Crystals of **5a** and **5b** were obtained by cooling a pentane solution to −20 °C. The ORTEP diagrams are shown in Figures 2 and 3. The complexes **5a** and **5b** were described as pseudo-octahedrons with meridional coordination of the phebox ligand and *cis* arrangement of the CO ligands. The $SiMe_3$ ligand was perpendicularly coordinated to the phebox plane as described in the $SnMe_3$ ligand of **3a**. In **5a**, the Fe1−C1 bond length [1.920(2) Å] is comparable with those of other phebox Fe complexes.[9] The Fe1−Si1 bond length of 2.4006(10) Å is slightly longer than those of (C_5H_5)Fe and (C_5Me_5)Fe silyl complexes (2.26−2.34 Å)[15g,22a] and $(CO)_2$(dppe)Fe(H)$SiMe_3$ [2.360(2) Å].[22b] The Fe1−C10 bond length of 1.823(2) Å is slightly longer than the Fe1−C11 bond length of 1.789(2) Å, suggesting a *trans* influence of the silyl group as observed in the stannyl complex **3a**.

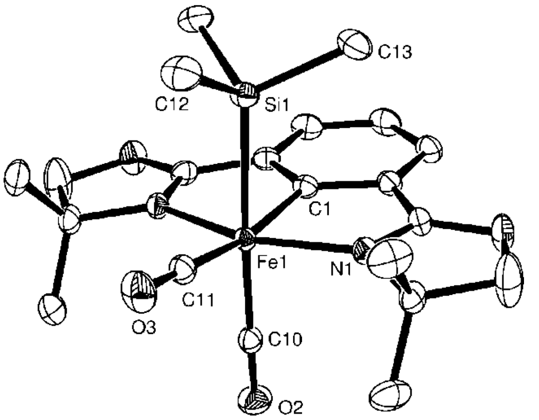


Figure 2. ORTEP diagram of **5a** at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Fe1−C1 = 1.920(2), Fe1−N1 = 2.0121(13), Fe1−Si1 = 2.4006(10), Fe1−C10 = 1.823(2), Fe1−C11 = 1.789(2), C10−O2 = 1.134(3), C11−O3 = 1.156(3). Selected angles (deg): N1−Fe1−N1 = 156.87(7), C1−Fe1−C11 = 167.79(8), Si1−Fe1−C10 = 175.12(6).

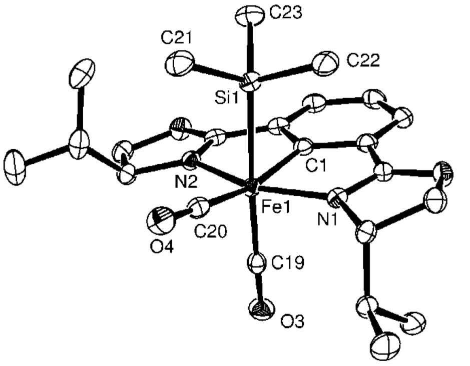
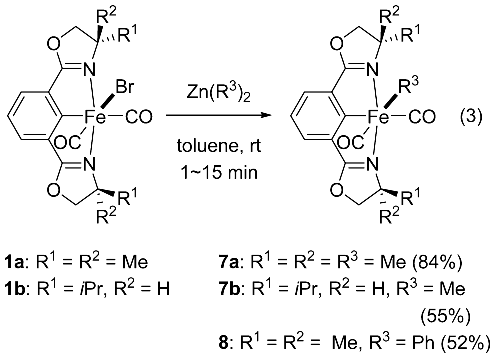


Figure 3. ORTEP diagram of **5b** at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): F1−C1 = 1.9145(13), Fe1−C19 = 1.8176(14), Fe1−C20 = 1.7847(15), Fe1−N1 = 1.9915(11), Fe1−N2 = 2.0115(11), Fe1−Si1 = 2.4237(5), C19−O3 = 1.1414(17), C20−O4 = 1.1516(18), N1−Fe1−N2 = 156.90(5), C1−Fe1−C20 = 165.78(6), Si1−Fe1−C19 = 176.92(4).

We were interested in comparing the methyl and phenyl complexes to the stannyl and silyl complexes. Thus far, $CpFe(CO)_2R$ has been prepared by oxidative addition of MeI to $[CpFe(CO)_2]^-$ or transmetalation of $CpFe(CO)_2X$ with organometallic reagents.[23] In this regard, we examined transmetalation of **1a** and **1b** with several organometallic reagents. As a result, reaction of **1a** with 2 equiv of $ZnMe_2$ at room temperature for 15 min resulted in the formation of methyl complex **7a**, which was isolated in 84% yield by column chromatography (eq 3). Similarly, reaction of **1b** with $ZnMe_2$ afforded the methyl complex **7b** in 55% yield. On the other hand, the use of MeLi and MeMgBr resulted in decomposition with a free phebox ligand. Unfortunately, irradiation of (phebox-*dm*)Me with $Fe(CO)_5$ in THF-d_8 did not afford **7a**.



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In the ^1H NMR spectrum of **7a**, two singlets assigned to the methyl groups on the oxazolines were observed at δ 0.91 and 0.98 ppm. The characteristic singlet signal of the methyl ligand appeared at δ −0.02 ppm. This chemical shift was in the range of other iron methyl complexes.[24] The ^{13}C NMR spectrum of **7a** showed a signal for the methyl ligand at δ 13.6 ppm. The IR spectrum of **7a** revealed two CO absorptions at 1982 and 1927 cm^{-1}, which were shifted to higher wave numbers compared to **3a** and **5a**.

The phenyl complex **8** was also synthesized by treatment of **1a** with an excess amount of $ZnPh_2$ in 52% yield (eq 3). The ^{13}C NMR spectrum of **8** showed the signal assigned to the *ipso*-carbon of the phenyl ligand at δ 165.0 ppm.

Crystals of **7a** and **8** were obtained by cooling a pentane solution to −20 °C. The geometry around the Fe atom is pseudo-octahedral, and the methyl and phenyl ligands are coordinated to the vertical position of the phebox plane (Figures 4 and 5). In **7a**, the Fe−Me bond length (Fe1−C17 = 2.071(3) Å) is in the range of other Fe methyl complexes (Fe−Me = 2.00−2.18 Å).[25] The Fe−Ph bond in **8** of 2.0619(19) Å was also found to be similar to those of other iron phenyl complexes (Fe−Ph = 1.99−2.09 Å).[26]

In comparing structures of **3a**, **5a**, **7a**, and **8**, the Fe−CO bond *trans* to the stannyl, silyl, methyl, and phenyl ligands was significantly affected by these ligands. The longest distance of the Fe−CO bond was observed in the silyl complex **5a**. This trend likely follows the strength of the *trans* influence of these ligands.[13]

In order to evaluate the catalytic activity of this series of phebox Fe complexes with stannyl, silyl, and alkyl ligands, asymmetric hydrosilylation of ketone **9** was examined.[7a−e,27] The catalytic reaction of **9** with 1.5 equiv of **11a** was performed in the presence of 2 mol % of the Fe complexes at 50 °C for 24 h (Table 1). The silyl complex **5b** was found to show the highest reactivity among **3b**, **5b**, and **7b** to give the corresponding (*R*)-alcohol **10a** in 98% yield with 32% ee (entries 1−3). Low reactivity of the stannyl complex **3b** was probably due to its high stability.[28] In the case of **7b**, decomposition of the phebox-Fe framework might lead to the decrease in yield and enantioselectivity. We previously reported

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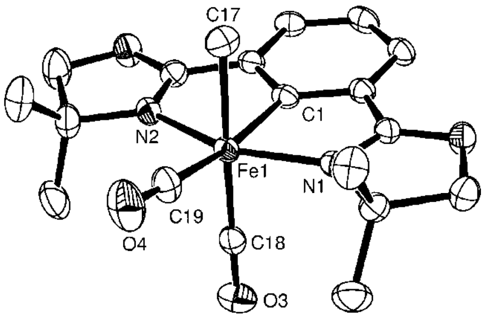


Figure 4. ORTEP diagram of **7a** at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Fe1−C1 = 1.924(2), Fe1−N1 = 2.007(2), Fe1−N2 = 2.004(2), Fe1−C17 = 2.071(3), Fe1−C18 = 1.802(3), Fe1−C19 = 1.789(3), C18−O3 = 1.143(3), C19−O4 = 1.149(3). Selected angles (deg): N1−Fe1−N2 = 156.84(8), C1−Fe1−C19 = 169.158(11).

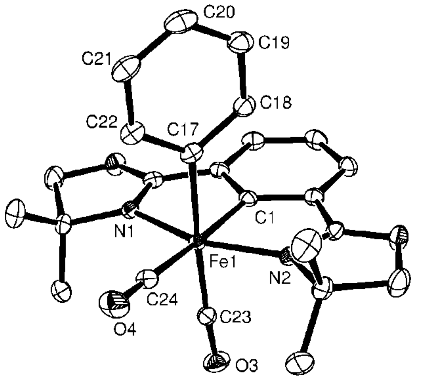
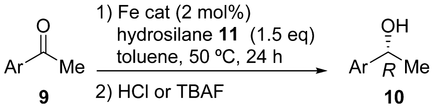


Figure 5. ORTEP diagram of **8** at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Fe1−C1 = 1.9236(18), Fe1−N1 = 2.0046(16), Fe1−N2 = 2.0059(16), Fe1−C17 = 2.0619(19), Fe1−C23 = 1.8031(19), Fe1−C24 = 1.802(2), C23−O3 = 1.138(2), C24−O4 = 1.149(2). Selected angles (deg): N1−Fe2−N2 = 156.85(6), C1−Fe1−C24 = 175.32(8).

Table 1. Asymmetric Hydrosilylation of Ketones[a]

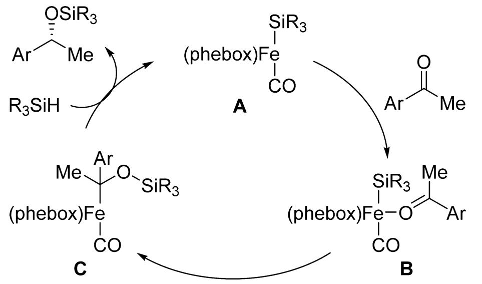


Ar = 4-PhC$_6$H$_4$ (**9a**), 4-ClC$_6$H$_4$ (**9b**), 3-MeOC$_6$H$_4$ (**9c**) 4-MeO$_2$CC$_6$H$_4$ (**9d**), 2-naphthyl (**9e**)

entry	cat.	ketone	HSiR$_3$[b]	solvent	yield (%)	ee (%)
1	**3b**	**9a**	**11a**	hexane	8	4
2	**5b**	**9a**	**11a**	hexane	98	32
3	**7b**	**9a**	**11a**	hexane	56	12
4	**5b**	**9a**	**11a**	toluene	99	34
5	**5b**	**9a**	**11a**	THF	17	8
6	**5b**	**9a**	**11a**	MeCN	0	
7[c]	**5c**	**9a**	**11a**	toluene	90	21
8[c]	**5d**	**9a**	**11a**	toluene	99	3
9	**5b**	**9a**	**11b**	toluene	85	15
10	**5b**	**9a**	**11c**	toluene	66	6
11	**5b**	**9a**	**11d**	toluene	2	0
12[d]	**3b**	**9a**	**11a**	toluene	29	2
13[d]	**5b**	**9a**	**11a**	toluene	31	8
14	**5b**	**9b**	**11a**	toluene	90	18
15	**5b**	**9c**	**11a**	toluene	81	16
16	**5b**	**9d**	**11a**	toluene	82	9
17	**5b**	**9e**	**11a**	toluene	88	10

[a]Reaction condition: **9** (0.5 mmol), **11** (0.75 mmol), Fe catalyst (0.01 mmol), 50 °C, 24 h. [b](EtO)$_2$MeSiH (**11a**), PhSiH$_3$ (**11b**), Ph$_2$SiH$_2$ (**11c**), (Me$_3$SiO)$_2$MeSiH (**11d**). [c]48 h. [d]Irradiation by Xe lamp at room temperature for 24 h.

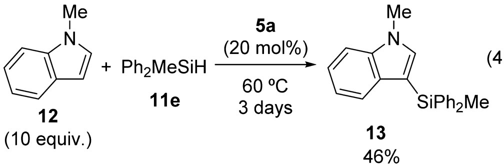
Scheme 1



that the bromide complex **1b** required a base, Na(acac), to facilitate the hydrosilylation of **9**.[9a] In contrast, the silyl complex **5b** underwent the catalytic reaction in the absence of bases, indicating that **5b** served as an efficient precursor. The use of nonpolar solvents promoted the catalytic reaction, while THF and MeCN resulted in a decrease in the yield (entries 4−6). Silyl complexes **5c** and **5d** with phenyl and benzyl groups required longer times to complete the reaction probably due to the presence of bulky substituents (entries 7 and 8). Regarding the hydrosilanes, **11a** was found to be the best reducing agent (entries 4, 9−11). Catalytic reaction under irradiation of a Xe lamp at room temperature resulted in low yields (entries 12, 13). Other aromatic ketones **9b−e** gave high yields, but modest enantioselectivity (entries 14−17). Notably, the absolute configuration of **10a** was the same as that obtained by **1b**.[9a]

A proposed mechanism is shown in Scheme 1, following the mechanism of Rh-catalyzed hydrosilylation of ketones proposed by Ojima and co-workers.[29] We propose the silyl intermediate **A** as the active species. Insertion of a C=O bond into the Fe−Si bond of **B** forms a silyloxyalkyl intermediate **C**.[30] Reaction of **C** with hydrosilane gives the product and regenerates **A**. In this regard, oxidative addition of a Si−H bond and reductive elimination of the product might proceed following the proposed mechanism of the formation of CpFe(CO)$_2$SiR$_3$ from CpFe(CO)$_2$Me.[15e,f,n,31] We previously reported that the coordination number of the phebox ligand was flexible.[9b] A change in coordination between NCN-tridentate and NC-bidentate modes might promote the final exchange process.

We also examined the silyl transfer reaction using the phebox Fe complexes. In this context, direct C−H silylation of aromatic compounds with hydrosilane is an attractive transformation to silyl compounds.[32] Recently, developments of C−H silylation of indole derivatives with hydrosilane catalyzed by Ir, Ru, and Fe have been reported.[33] When the mixture of 10 equiv of *N*-methylindole (**12**) and Ph$_2$MeSiH (**11e**) in the presence of the silyl complex **5a** (0.2 equiv) was heated at 60 °C for 3 days, the corresponding *β*-silylated indole **13** was obtained in 46% yield (eq 4).[34] In this reaction, the *α*-silylated product was



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not detected as reported by Ru and Fe catalysts,[33c,d] nor was incorporation of the $SiMe_3$ group observed. We are tentatively assuming that a Fe-$SiPh_2Me$ intermediate as described in **A** of Scheme 1 was formed by reaction of **5a** and Ph_2MeSiH.[35] Electrophilic substitution with *N*-methylindole then produced the silylated compound **13**.

CONCLUSION

We described the preparation and characterization of a series of NCN pincer Fe complexes containing stannyl, silyl, methyl, and phenyl ligands. The silyl and stannyl complexes were successfully obtained by oxidative addition of C−Si and C−Sn bonds in the ligand precursors by $Fe(CO)_5$ under irradiation conditions. The methyl and phenyl complexes were synthesized by transmetalation of the bromide Fe complex with $ZnMe_2$ and $ZnPh_2$, respectively. The phebox Fe complexes adopted similar pseudo-octahedral geometry, containing the meridionally NCN-coordinated phebox ligand with the η^1-stannyl, silyl, methyl, and phenyl ligands at the apical position. The catalytic activity of pincer Fe complexes was evaluated in the hydrosilylation of a ketone, where the silyl complex was found to be the most suitable catalyst. The silyl complex also catalyzed the C−H silylation of *N*-methylindole with hydrosilane to give the β-silylated indole compound.

EXPERIMENTAL SECTION

General Procedures. All air- and moisture-sensitive compounds were manipulated using standard Schlenk and vacuum line techniques under an argon atmosphere. ^{1}H and ^{13}C NMR spectra were obtained at 25 °C on a Varian Mercury 300 spectrometer. ^{1}H NMR chemical shifts are reported in δ units, in ppm, relative to the singlet at 7.26 ppm for $CDCl_3$ and 7.16 ppm for C_6D_6. ^{13}C NMR spectra are reported in terms of chemical shifts relative to the triplet at 77.0 ppm for $CDCl_3$ and 128.0 ppm for C_6D_6. Infrared spectra were recorded on a JASCO FT/IR-230 spectrometer. Elemental analyses were recorded on a YANACO MT-6. Photoreaction was performed by using an ASAHI SPECTRA MAX-303 with a xenon lamp. Column chromatography was performed with a silica gel column (Kanto Kagaku Silica gel 60N). (Phebox)$SnMe_3$[17] and (Phebox)$SiMe_3$[20] were prepared by the literature methods.

Reaction of (Phebox)$SnMe_3$ with $Fe(CO)_5$. To a THF solution (6 mL) of (phebox-*dm*)$SnMe_3$ (**2a**) (130 mg, 0.30 mmol) was added $Fe(CO)_5$ (45 μL, 0.33 mmol) under an argon atmosphere. The mixture was stirred under irradiation for 12 h. After removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:5) to give (phebox-*dm*)$Fe(CO)_2SnMe_3$ (**3a**) (94.7 mg, 0.17 mmol, 57%). A similar procedure using (phebox-*ip*)$SnMe_3$ (**2b**) (139 mg, 0.30 mmol) gave (phebox-*ip*)$Fe(CO)_2SnMe_3$ (**3b**) (106.8 mg, 0.19 mmol, 62%). **3a:** ^{1}H NMR (300 MHz, C_6D_6, rt): δ −0.08 (J_{SnH} = 38 Hz, 9H, SnMe_3), 0.96 (s, 6H), 0.97 (s, 6H), 3.66 (d, J = 8.4 Hz, 2H), 3.73 (d, J = 8.4 Hz, 2H), 7.03 (t, J = 7.4 Hz, 1H), 7.73 (d, J = 7.4 Hz, 2H). ^{13}C NMR (75 MHz, C_6D_6, rt): δ −7.1 (J_{SnC} = 169 Hz, SnMe_3), 27.0, 28.6, 65.8, 82.2, 121.7, 124.8, 131.2, 168.1, 208.6, 214.7, 219.4. IR (KBr): ν 2973, 2901, 1988 (ν_{CO}), 1907 (ν_{CO}), 1605, 1541, 1484, 1397, 1335, 981, 728 cm^{-1}. Anal. Calcd for $C_{21}H_{28}FeN_2O_4Sn$: C, 46.11; H, 5.16; N, 5.12. Found: C, 46.02; H, 5.27; N, 5.01. **3b:** ^{1}H NMR (300 MHz, C_6D_6, rt): δ −0.02 (J_{SnH} = 38 Hz, 9H, SnMe_3), 0.42 (d, J = 7.2 Hz, 3H), 0.46 (d, J = 6.9 Hz, 3H), 0.54 (d, J = 6.6 Hz, 3H), 0.58 (d, J = 6.6 Hz, 3H), 2.21−2.32 (m, 2H), 3.22−3.32 (m, 2H), 3.69−4.01 (m, 4H), 7.01 (t, J = 7.6 Hz, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 7.8 Hz, 1H). ^{13}C NMR (75 MHz, C_6D_6, rt): δ −7.1 (J_{SnC} = 170 Hz, SnMe_3), 14.4, 15.2, 19.2, 20.3, 29.4, 30.2, 70.1, 71.0, 71.2, 71.4, 121.6, 125.0, 125.2, 130.1, 131.3, 169.7, 170.5, 208.7, 216.0, 218.2. IR (KBr): ν 2960, 2909, 1981 (ν_{CO}), 1903 (ν_{CO}), 1603, 1543, 1487, 1388, 1334, 1144, 968, 734 cm^{-1}. Anal. Calcd for $C_{23}H_{32}FeN_2O_4Sn$: C, 48.04; H, 5.61; N, 4.87. Found: C, 48.45z; H, 5.88; N, 4.87.

Reaction of (Phebox)$SiMe_3$ with $Fe(CO)_5$. To a THF solution (6 mL) of (phebox-*dm*)$SiMe_3$ (**4a**) (103 mg, 0.30 mmol) was added $Fe(CO)_5$ (45 μL, 0.33 mmol) under an argon atmosphere. The mixture was stirred under irradiation for 24 h. After removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:5) to give (phebox-*dm*)$Fe(CO)_2SiMe_3$ (**5a**) (83 mg, 0.18 mmol, 60%). A similar procedure using (phebox-*ip*)$SiMe_3$ (**4b**) (74.5 mg, 0.20 mmol), **4c** (44.1 mg, 0.10 mmol), and **4d** (46.9 mg, 0.10 mmol) gave (phebox-*ip*)$Fe(CO)_2SiMe_3$ (**5b**) (74.3 mg, 0.152 mmol, 76%), **5c** (38.7 mg, 0.070 mmol, 70%), and **5d** (43.5 mg, 0.075 mmol, 75%), respectively. **5a:** ^{1}H NMR (300 MHz, C_6D_6, rt): δ 0.04 (s, 9H, SiMe_3), 0.97 (s, 6H), 1.02 (s, 6H), 3.69 (s, 4H), 7.03 (t, J = 7.5 Hz, 1H), 7.72 (d, J = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, C_6D_6, rt): δ 3.9, 26.4, 29.0, 66.2, 82.1, 121.6, 124.3, 131.8, 168.1, 208.2, 216.6, 219.2. IR (KBr): ν 2969, 2903, 1982 (ν_{CO}), 1902 (ν_{CO}), 1606, 1543, 1486, 1396, 1337, 1204, 978, 828, 736 cm^{-1}. Anal. Calcd for $C_{21}H_{28}FeN_2O_4Si$: C, 55.27; H, 6.18; N, 6.14. Found: C, 55.28; H, 6.24; N, 6.15. **5b:** ^{1}H NMR (300 MHz, C_6D_6, rt): δ −0.03 (s, 9H, SiMe_3), 0.49 (d, J = 7.2 Hz, 6H), 0.55 (d, J = 6.6 Hz, 3H), 0.62 (d, J = 6.9 Hz, 3H), 2.20−2.35 (m, 2H), 3.24−3.38 (m, 2H), 3.72−3.98 (m, 4H), 7.01 (t, J = 7.8 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H). ^{13}C NMR (75 MHz, C_6D_6, rt): δ 4.0, 14.5, 16.1, 19.3, 20.8, 29.3, 30.1, 70.1, 71.1, 71.4, 71.7, 121.4, 124.6, 124.8, 130.0, 131.7, 169.5, 170.8, 208.1, 217.8, 218.2. IR (KBr): ν 2952, 1979 (ν_{CO}), 1901 (ν_{CO}), 1604, 1489, 1387, 1335, 1145, 966, 827, 732 cm^{-1}. Anal. Calcd for $C_{23}H_{32}FeN_2O_4Si$: C, 57.02; H, 6.66; N, 5.78. Found: C, 57.13; H, 6.80; N, 5.76. **5c:** ^{1}H NMR (300 MHz, C_6D_6, rt): δ 0.29 (s, 9H, SiMe_3), 3.93−4.26 (m, 6H), 6.96−7.16 (m, 11H), 7.81 (d, J = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, C_6D_6, rt): δ 3.6, 70.0, 70.8, 77.5, 78.7, 121.3, 124.6, 124.7, 128.7, 129.0, 129.1, 129.5, 130.3, 131.5, 137.9, 140.4, 169.7, 170.1, 206.9, 216.3, 220.3. IR (KBr): 2962, 1981 (ν_{CO}), 1923 (ν_{CO}), 1483, 1390, 1261, 1142, 1089, 971 cm^{-1}. Anal. Calcd for $C_{29}H_{28}FeN_2O_4Si$: C, 63.05; H, 5.11; N, 5.07. Found: C, 63.20; H, 4.93; N, 4.92. **5d:** ^{1}H NMR (300 MHz, C_6D_6, rt): δ 0.00 (s, 9H, SiMe_3), 2.17 (t, J = 12.8 Hz, 1H), 2.38 (t, J = 12.8 Hz, 1H), 3.66−3.94 (m, 8H), 6.79−7.07 (m, 11H), 7.74 (d, J = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, C_6D_6, rt): δ 4.2, 41.7, 41.9, 67.1, 68.0, 75.8, 76.7, 121.7, 124.8, 124.9, 127.0, 127.1, 129.06, 129.1, 129.4, 130.6, 131.3, 137.25, 137.27, 170.0, 170.3, 207.3, 218.3, 218.6. IR (KBr): 2960, 1980 (ν_{CO}), 1912 (ν_{CO}), 1485, 1392, 1260, 1090, 970, 801, 732 cm^{-1}. Anal. Calcd for $C_{31}H_{32}FeN_2O_4Si$: C, 64.14; H, 5.56; N, 4.83. Found: C, 64.08; H, 5.57; N, 4.68.

Reaction of 1a with $ZnMe_2$. To a toluene solution (10 mL) of (phebox-*dm*)$Fe(CO)_2Br$ (**1a**) (231 mg, 0.5 mmol) was added a hexane solution of $ZnMe_2$ (1 M, 1 mL, 1 mmol) under an argon atmosphere. The mixture was stirred at room temperature for 15 min. After removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:6) to give (phebox-*dm*)$Fe(CO)_2Me$ (**7a**) (170.6 mg, 0.42 mmol, 84%). A similar procedure using (phebox-*ip*)$Fe(CO)_2Br$ (**1b**) (245 mg, 0.50 mmol) gave (phebox-*ip*)$Fe(CO)_2Me_3$ (**7b**) (117.7 mg, 0.28 mmol, 55%). **7a:** ^{1}H NMR (300 MHz, C_6D_6, rt): δ −0.02 (s, 3H, *Me*), 0.91 (s, 6H), 0.98 (s, 6H), 3.56 (d, J = 8.3 Hz, 2H), 3.63 (d, J = 8.3 Hz, 2H), 7.06 (t, J = 7.5 Hz, 1H), 7.71 (d, J = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, C_6D_6, rt): δ 13.6 (*Me*), 27.3, 27.9, 65.7, 82.1, 122.0, 124.9, 131.1, 168.5, 207.7, 219.9, 226.1. IR (KBr): ν 2971, 2931, 2870, 1982 (ν_{CO}), 1927 (ν_{CO}), 1610, 1485, 1394, 1338, 1206, 1140, 979, 734 cm^{-1}. Anal. Calcd for $C_{19}H_{22}FeN_2O_4$: C, 57.30; H, 5.57; N, 7.03. Found: C, 56.59; H, 5.80; N, 6.85. Correct elemental analysis could not be obtained after several attempts. **7b:** ^{1}H NMR (300 MHz, C_6D_6, rt): δ 0.09 (br, 3H, *Me*), 0.44 (d, J = 6.9 Hz, 3H), 0.46 (d, J = 7.2 Hz, 3H), 0.55 (d, J = 6.3 Hz, 3H), 0.59 (d, J = 7.2 Hz, 3H), 2.19 (br, 2H), 3.19 (br, 2H), 3.60−3.90 (br, 4H), 7.03 (br, 1H), 7.68 (br, 2H). ^{13}C NMR (75 MHz, C_6D_6, rt): δ 12.2 (*Me*), 14.5, 15.0, 19.2, 19.8, 29.5, 29.9, 68.7, 71.0, 71.1, 71.4, 122.0, 125.1, 125.2, 130.4, 130.5, 170.1, 170.5, 207.7, 218.3, 226.2. IR (KBr): ν 2961, 2873, 1987 (ν_{CO}), 1921 (ν_{CO}), 1651, 1611, 1556, 1487, 1386, 1335, 1250, 1145, 968, 733 cm^{-1}. Anal. Calcd for $C_{21}H_{26}FeN_2O_4$: C, 59.17; H, 6.15; N, 6.57. Found: C, 58.01; H, 6.33; N, 6.29. Correct elemental analysis could not be obtained after several attempts.

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Reaction of 1a with $ZnPh_2$. To (phebox-*dm*)Fe(CO)$_2$Br (**1a**) (185 mg, 0.4 mmol) and $ZnPh_2$ (351 mg, 1.6 mmol) was added toluene (8 mL) under an argon atmosphere. After being stirred at room temperature for 1 min, the reaction mixture was quickly purified by column chromatography on silica gel with ethyl acetate/hexane (1:6) to give (phebox-*dm*)Fe(CO)$_2$Ph (**8**) (96.6 mg, 20.8 mmol, 52%). **8:** ^{1}H NMR (300 MHz, C_6D_6, rt): δ 0.85 (s, 6H), 0.92 (s, 6H), 3.42 (d, J = 8.4 Hz, 2H), 3.55 (d, J = 8.4 Hz, 2H), 6.94 (t, J = 6.6 Hz, 1H), 7.01−7.07 (m, 4H), 7.41 (d, J = 7.2 Hz, 2H), 7.65−7.72 (m, 2H). ^{13}C NMR (75 MHz, C_6D_6, rt): δ 27.1, 28.3, 66.2, 81.9, 122.5, 122.9, 125.6, 126.5, 130.2, 132.0, 132.3, 139.6, 165.0 (Fe-C_{ipso}), 169.5, 209.2, 216.1, 221.1. IR (KBr): ν 2963, 2005 (ν_{CO}), 1935 (ν_{CO}), 1611, 1549, 1486, 1397, 1261, 1094, 1022, 803 cm^{-1}. Anal. Calcd for $C_{24}H_{24}FeN_2O_4$: C, 62.62; H, 5.26; N, 6.09. Found: C, 62.09; H, 5.29; N, 5.81. Correct elemental analysis could not be obtained after several attempts.

Hydrosilylation of 9a. To a solution of Fe catalyst (0.01 mmol) and **9a** (0.5 mmol) was added hydrosilane (0.75 mmol) by a syringe under an argon atmosphere. After being stirred at 50 °C for 24 h, a HCl solution was added at 0 °C. The mixture was extracted with EtOAc. The extract was washed with brine and saturated $NaHCO_3$ and dried over Na_2SO_4. After removal of the solvent, the residue was purified by silica gel column chromatography with ethyl acetate/hexane to give **10a**.

Reaction of 12 with Ph_2MeSiH. To a solution of Fe catalyst (0.06 mmol) and **12** (3 mmol) was added Ph_2MeSiH (0.3 mmol) by a syringe under an argon atmosphere. The mixture was stirred at 60 °C for 3 days. The crude product was purified by column chromatography on silica gel to give **13**.

X-ray Diffraction. The diffraction data for **3a**, **5a**, **5b**, **7a**, and **8** were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). An empirical absorption correction was applied by using SADABS. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located on calculated positions and refined as rigid groups. Crystallographic data are summarized in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedure and characterization of **13**, crystallographic data and CIF files for **3a**, **5a**, **5b**, **7a**, and **8**, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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