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Selective hydrosiloxane synthesis *via* dehydrogenative coupling of silanols with hydrosilanes catalysed by Fe complexes bearing a tetradentate PNNP ligand†

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A well-defined iron complex system was established using PNNP-R (R = Ph and Cy) as a strong σ-donating ligand with a rigid meridional tetradentate structure. Reactive Fe(0) complexes [{Fe(PNNP-R)}$_2$(μ-N$_2$)] were synthesized by a reaction of the corresponding iron dihalide with NaBEt$_3$H and structurally characterized. The reaction proceeded *via* the iron dihydride intermediate [Fe(H)$_2$(PNNP-R)], which underwent H$_2$ reductive elimination, supporting the hemilabile behavior of PNNP-R. [{Fe(PNNP-R)}$_2$(μ-N$_2$)] catalyzed the dehydrogenative coupling of silanols with silanes to selectively form various hydrosiloxanes, which are important building blocks for the synthesis of a range of siloxane compounds. This system exhibited higher catalytic efficiency than the previously reported precious-metal-catalyzed systems.

Introduction

Iron complexes with low toxicity and high terrestrial abundance have recently drawn increasing attention as a new class of catalyst precursors in an attempt to develop environmentally benign and sustainable methods for organic synthesis.[1] Intensive studies on Fe complexes have been conducted to date; however, examples of well-defined reactions remain scarce compared with those of 4d or 5d metal complexes. A main reason for this is the diverse and changeable reactivity of Fe complexes, which is often attributed to the paramagnetism of the Fe metal with a high spin state.[1d]

In this context, we focus on tetradentate PNNP-R ligands,[2] 2,9-bis((diphenylphosphino)methyl)-1,10-phenanthroline (R = Ph)[2a] and 2,9-bis((dicyclohexylphosphino)methyl)-1,10-phenanthroline (R = Cy),[2c,d] which connect with a metal centre through a rigid meridional coordination mode with four σ-donating moieties. The strong electron-donating ability of PNNP-R allows it to act as a strong-field ligand that effectively stabilizes Fe complexes with a low-spin state. Thus, we expected that PNNP-R supported-Fe complexes behave as stable diamagnetic species and are potentially useful as inexpensive and nontoxic surrogates for precious-metal catalysts.

In this study, various PNNP-R-supported-Fe complexes including reactive Fe(0) complexes coordinated with a labile ligand were synthesized and structurally characterized. Using this complex system as a catalyst precursor, selective hydrosiloxane formation by catalytic dehydrogenative coupling of silanols and silanes was achieved with high efficiency.

Results and discussion

Synthesis and characterization of PNNP-R-supported Fe complexes

Complexation of an Fe precursor with a PNNP-R ligand was performed by heating a solution of FeCl$_2$ and PNNP-Ph ligand in THF under reflux. After 6 h, PNNP-Ph-supported iron dichloride [FeCl$_2$(PNNP-Ph)] (**1a**) was obtained as a red solid (82% yield) (Scheme 1). The reaction of PNNP-Cy and FeCl$_2$ was similarly performed; however this resulted in the formation of a complicated mixture. Thus, the reaction of FeBr$_2$ with PNNP-Cy was performed following the previous report[2d] to selectively form [FeBr$_2$(PNNP-Cy)] (**1b**). Single-crystal X-ray diffraction studies revealed two different solid-state structures: a pentacoordinate distorted trigonal–bipyramidal structure of **1a** (τ = 0.50)[3] and a hexacoordinate octahedral structure of **1b** with the more donating PNNP-Cy ligand, both of which exhibit paramagnetic broad signals in the ^{1}H NMR spectra.

Several Fe(II) complexes were reported as being convertible into catalytically active Fe(0) species by treatment with a suit-

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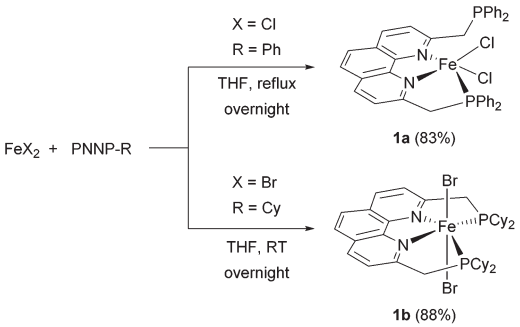
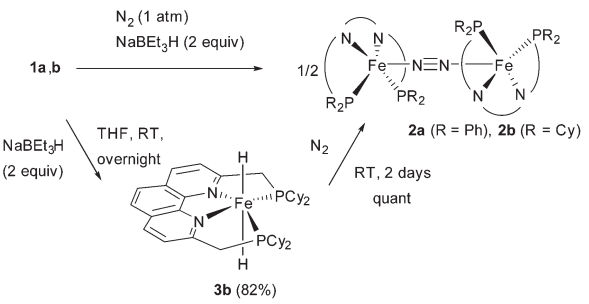


Scheme 1 Synthesis of **1a** and **1b**.

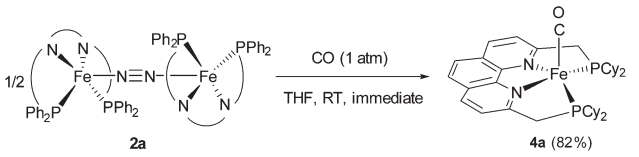
able reducing agent.[4,5] Motivated by these observations, we aimed to demonstrate the reduction pathway of Fe(II) complexes in an attempt to isolate active Fe(0) species by utilizing a rigid PNNP-R ligand. Treatment of **1a** with $NaBEt_3H$ (2 equiv.) under an Ar atmosphere resulted in the formation of a complex mixture. On the other hand, when the reaction was performed under a N_2 atmosphere, Fe(0) dinitrogen complex **2a** was obtained as the sole product (Scheme 2). In contrast, the reaction of **1b** with $NaBEt_3H$ resulted in the formation of a dihydrido complex [Fe(H)$_2$(PNNP-Cy)] (**3b**) in 82% yield. Complex **3b** was confirmed to be gradually converted into **2b**, which was obtained as a mixture containing several unidentified compounds. Therefore, **2a** is likely formed *via* intermediary dihydrido complex **3b**, which undergoes H_2 reductive elimination.

Notably, two hydride ligands in **3b**, which locate in *trans* positions, underwent reductive elimination reaction. Therefore, the occurrence of phosphine side-arm dissociation is strongly indicated in this step. This is also supported by the reluctant step-wise reduction of **1b** *via* **3b**, which has the more donating PNNP-Cy ligand than the PNNP-Ph ligand.

Complexes **2a** and **2b** easily decomposed under 1 atm of N_2 pressure even in the solid state because of the facile liberation of the N_2 ligand. Thus, it was difficult to isolate **2a** and **2b**, and they were prepared *in situ* and identified by NMR spectroscopic analysis. Fortunately, when the THF/hexane solution of the reaction mixture was cooled to −40 °C, single deep-red crystals of **2a** or **2b** were obtained and quickly subjected to a single-crystal X-ray analysis under a cold N_2 stream, which supports the N_2-bridged dinuclear Fe structure of **2a** and **2b** (*vide infra*).



Scheme 2 Synthesis of **2a**, **2b** and **3b**.



Scheme 3 Synthesis of **4a**.

Since **2a** and **2b** are supported by the electron-donating PNNP-R ligand, they are expected to possess a highly electron-rich Fe(0) center. However, the ν_{N_2} was not detected either by IR or Raman.[6] To evaluate the π-back-bonding ability of the Fe(0)(PNNP-Ph) moiety, the Fe(0) carbonyl complex [Fe(CO)(PNNP-Ph)] (**4a**) was synthesized by the ligand exchange of **2a** with CO. Reaction of **2a** with CO (1 atm) immediately proceeded at room temperature to form **4a** quantitatively (Scheme 3). The latter exhibits a strong ν_{CO} band at a rather lower field of 1866 cm^{-1} than structurally similar Fe(0) complexes bearing a bipyridine or a phosphinomethyl(bipyridine) ligand.[7]

Complexes **2a**, **2b**, and **4a** adopt a square-pyramidal geometry [τ = 0.099 (**2a**), 0.143 (**2b**), and 0.143 (**4a**)],[3] in which the N_2 or CO ligands are located at the axial position. The core structure around the Fe atom is comparable to those of previously reported Fe(0) analogous complexes (Fig. 1).[8] The bond lengths of N–N bonds in **2a** and **2b** of 1.135(4) and 1.134(6) Å, respectively, are in the range of normal N–N triple bond lengths. The phenanthroline ligands are reported to act as redox-active ligands and exhibit shortened C11–C12 and elongated N–C11/C12 bond lengths in their reduced form.[9] Indeed, the C11–C12 bonds in **2a**, **2b**, and **4a** (1.390–1.396 Å) are slightly shorter than those in Fe(II) complexes **1a** and **1b** (1.41–1.44 Å), whereas N–C11/C12 bonds are slightly longer in **2a**, **2b**, and **4a** (1.382–1.391 Å) than in **1a** and **1b** (1.354–1.367 Å) (Table 1). Thus, the occurrence of the electron transfer from the Fe(0) atom to the PNNP-R ligand is indicated in **2a**, **2b**, and **4a**.

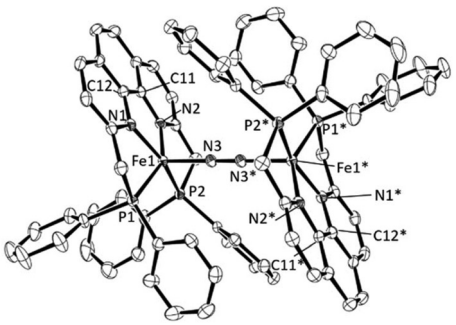


Fig. 1 ORTEP diagram of **2a** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1 Selected bond lengths and angles of **1a**, **1b**, **2a**, **2b**, **4a** and **5a**

Complex	C11–C12	N2–C12	N1–C13
1a	1.438(2)	1.364(2)	1.360(2)
1b	1.426(9)	1.354(8)	1.367(8)
2a	1.392(4)	1.382(3)	1.387(3)
2b	1.390 (av.)	1.387 (av.)	1.384 (av.)
4a	1.390(4)	1.375(4)	1.384(4)
5a	1.407(5)	1.387(4)	1.381(4)

Dehydrogenative coupling of silanols with hydrosilanes

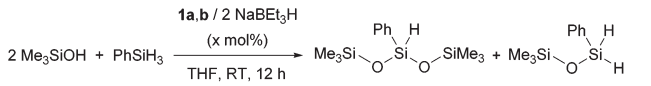
Interestingly, complexes **1a** and **1b** can be successfully applied as a catalyst to the dehydrogenative coupling reaction of hydrosilanes with silanols to form various hydrotrisiloxanes. Hydrosiloxanes containing a reactive Si–H terminus are important building blocks for the precise synthesis of various siloxane compounds (silicones),[10] and thus their efficient syntheses have recently received much attention. However, the number of examples that afford high reaction selectivity is extremely limited.[11] One reason for this is the complicated reactivity of silanols; *i.e.* silanols easily undergo dehydrative condensation to form a homo-coupling product. In addition, the by-product, H_2O further reacts with unreacted hydrosilanes to generate various silanol molecules, which are also quickly converted to homo-coupled-siloxanes. In this study, selective formation of various hydrotrisiloxanes has been achieved with high efficiency using **1a** as a catalyst precursor. In the presence of **1a** (0.1 mol%) and $NaBEt_3H$ (0.2 mol%), $PhSiH_3$ reacted with 2 equiv. of Me_3SiOH to form hydrotrisiloxane $(Me_3SiO)_2(SiHPh)$ in an excellent yield (Table 2, entry 1). Notably, neither disiloxane $(Me_3SiO)(SiH_2Ph)$ nor tetrasiloxane $(Me_3SiO)_3(SiPh)$ was obtained in the reaction. It was also confirmed that hydrotrisiloxane $(Me_3SiO)_2(SiHPh)$ was selectively obtained in the reaction of $PhSiH_3$ with 3 equiv. of Me_3SiOH as the sole product even at a higher catalyst loading, **1a** (1 mol%) and $NaBEt_3H$ (2 mol%).

Since complex **1a** was partially converted to **2a** upon treatment with 1 equiv. of $NaBEt_3H$, the combination of **1a** (0.1 mol%) and $NaBEt_3H$ (0.1 mol%) exhibited a lower catalytic performance.[11]

The catalyst loading could be reduced to 0.01 mol% to give $(Me_3SiO)_2(SiHPh)$ in a highly selective manner (89% yield) accompanied by the formation of disiloxane $(Me_3SiO)(SiH_2Ph)$ (8% yield) as a minor product (Table 2, entry 2). The reaction suggests a much higher turnover number (TON) of >18 000 than those of the previous reports, which are catalysed by precious-metal complexes (TON 1000–4000).[7a,12a,b] Complex **1b** reacts with $NaBEt_3H$ at a slower rate to form active **2b** (*vide supra*) and thus exhibited less activity, resulting in the formation of $(Me_3SiO)_2(SiH_2Ph)$ (28%) and $(Me_3SiO)(SiH_2Ph)$ (28%) in the presence of **1b** (0.01 mol%) and $NaBEt_3H$ (0.02 mol%) (Table 2, entry 3). It was alternatively confirmed that **1a** did not catalyse the reaction in the absence of $NaBEt_3H$ (Table 2, entry 4). The reaction catalysed by $NaBEt_3H$ was also performed, leading to the formation of a mixture of disiloxane $(Me_3SiO)(SiH_2Ph)$ (55%) and trisiloxane $(Me_3SiO)_3(SiPh)$ (30%), accompanied by the homo-coupling product $Me_3SiOSiMe_3$ (4%) (Table 2, entry 5).

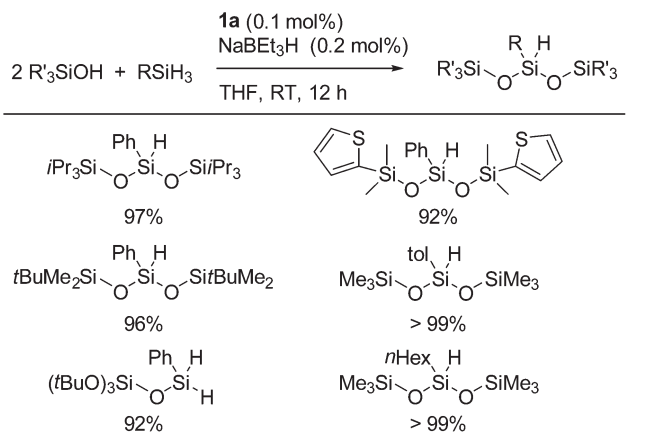
With the optimized conditions using 0.1 mol% of the **1a**/2$NaBEt_3H$ combination, we next examined the substrate scope of the dehydrogenative coupling of silanols with primary silanes (Scheme 4). $PhSiH_3$ reacted with various aliphatic silanols. When using iPr_3SiOH and tBuMe$_2$SiOH, the corresponding trisiloxanes $(R_3SiO)_2(SiHPh)$ were formed in excellent yields. Reaction of $PhSiH_3$ with bulky $(t\text{BuO})_3SiOH$ resulted in the selective formation of hydrodisiloxane $((t\text{BuO})_3SiO)(SiH_2Ph)$ in 92%. Interestingly, the silanol with a coordinating thiophenyl substituent, Me$_2$(2-thiophenyl)SiOH was also applicable in the reaction to furnish the corresponding hydrotrisiloxane in 92% yield. 4-Me$C_6H_4SiH_3$ and nHexSiH_3 were also

Table 2 Dehydogenative coupling of Me_3SiOH with $PhSiH_3$ catalysed by **1a** and **1b**[a]



Entry	Cat. (× mol%)	Product yields by NMR[b]
1	**1a** + 2$NaBEt_3H$ (0.1 mol%)	$(Me_3SiO)_2(SiHPh)$ >99 $(Me_3SiO)(SiH_2Ph)$ —
2	**1a** + 2$NaBEt_3H$ (0.01 mol%)	$(Me_3SiO)_2(SiHPh)$ 89 $(Me_3SiO)(SiH_2Ph)$ 8
3	**1b** + 2$NaBEt_3H$ (0.01 mol%)	$(Me_3SiO)_2(SiHPh)$ 28 $(Me_3SiO)(SiH_2Ph)$ 28
4	**1a** (1.0 mol%)	$(Me_3SiO)_2(SiHPh)$ — $(Me_3SiO)(SiH_2Ph)$ 5
5	$NaBEt_3H$ (0.1 mol%)	$(Me_3SiO)_2(SiHPh)$ — $(Me_3SiO)(SiH_2Ph)$ 55 $(Me_3SiO)_3SiPh$ 30 $Me_3SiOSiMe_3$ 4

[a] Reaction conditions: $PhSiH_3$ (32.4 mg, 0.30 mmol) and Me_3SiOH (56.8 mg, 0.63 mmol) in THF (5 mL) at room temperature for 12 h. [b] Yields are determined by ^1H NMR with mesitylene as an internal standard.



Scheme 4 Reaction of silanols with primary silanes catalyzed by **1a**/$NaBEt_3H$.

subjected to the reaction, leading to the quantitative formation of the corresponding hydrotrisiloxane $(Me_3SiO)_2(SiHR)$ (R = 4-MeC_6H_4, *n*Hex).

The combination of **1a**/2$NaBEt_3H$ also catalysed the coupling of Me_3SiOH with secondary silanes. In the presence of **1a** (0.1 mol%) and $NaBEt_3H$ (0.2 mol%), Me_3SiOH reacted with Ph_2SiH_2 and $PhMeSiH_2$ to selectively form the corresponding hydrotrisiloxanes in good yields, $(Me_3SiO)SiHPh_2$ (77%) and $(Me_3SiO)SiHPhMe$ (84%), respectively (Scheme 5).

Stoichiometric reactions were conducted to shed light on the reaction mechanism. Complex **2a** slowly reacted with Me_3SiOH at ambient temperature to give a complicated mixture, which exhibited extremely suppressed catalytic activity.[13] In contrast, complex **2a** smoothly underwent ligand exchange with $PhSiH_3$ to form the Fe(0) silane complex **5a** as the sole product in 76% yield (Scheme 6). In the ^1H NMR spectrum, the agostic Si–H signal was observed in a high-field region, δ = –8.06 ppm as a triplet ($^2J_{PH}$ = 36.8 Hz) and SiH_2 protons are equivalently observed at δ = 4.75 ppm as a singlet signal. The silyl signal was observed at δ = 12.2 ppm in the $^{29}Si\{^1H\}$ NMR spectrum.

X-ray diffraction studies revealed a highly distorted square-pyramidal structure of **5a** (τ = 0.11) (Fig. 2).[3] The agostic proton H1, which was detected by difference Fourier synthesis, locates at the bridging position between the Si and the Fe atoms.

The Si1–H1 bond length is slightly elongated (1.711 Å), which is indicative of the agostic coordination mode of the Si1–H1 moiety.[14] The C11–C12 and N–C11/C12 bond lengths exhibit similar values to those in **2a**, **2b**, and **4a**, again indicating the electron transfer from the Fe(0) centre to the PNNP-Ph ligand in **5a**.

It was confirmed that **5a** catalysed the dehydrogenative coupling of Me_3SiOH with $PhSiH_3$ to the same level as **1a**/2$NaBEt_3H$.[15] Thus, we postulate that **5a** is a potential catalytic intermediate. Although a mechanistic study is still underway in our laboratory, one possible mechanism including an Fe(0)/Fe(II) cycle is postulated following the dehydrogenative coupling reactions of silanes with alcohols;[16] *i.e.* the reaction initiates with the oxidative addition of $PhSiH_3$ to form a silyl hydrido intermediate, which successively reacts with silanol, resulting in the formation of siloxanes, H_2 and the active Fe(0) species. Alternatively, the activated $PhSiH_3$ of **5a** is directly attacked by silanol to form siloxane, in which step, the Si–H bond cleavage and the Si–O bond formation proceeded in a concerted fashion. This mechanism is also demonstrated in the transition-metal-catalysed dehydrogenative coupling of hydrosilanes with alcohols.[17]

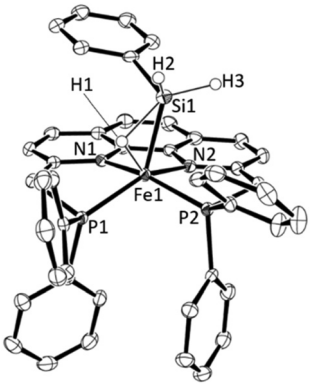
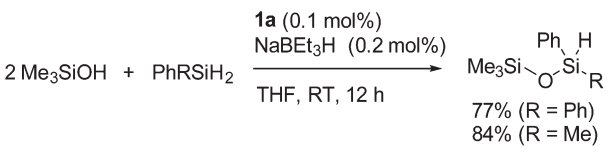
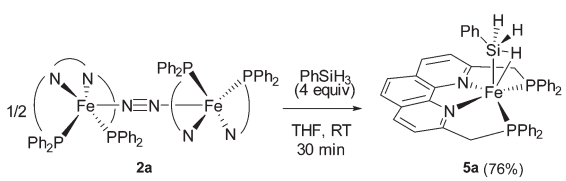


Fig. 2 ORTEP diagram of **5a** with 50% probability elipsoids. Hydrogen atoms except those attached to the Si atom are omitted for clarity.



Scheme 5 Reaction of Me_3SiOH with secondary silanes catalysed by **1a**/$NaBEt_3H$.



Scheme 6 Synthesis of **5a**.

Conclusions

In summary, the PNNP-R ligands with strong σ-donating ability successfully enabled us to isolate various Fe complexes as stable low-spin species. Notably, efficient hydride reduction of Fe(II) complexes to reactive Fe(0) complexes **2a** and **2b** was demonstrated to support the formation of dihydrido complexes **3a** and **3b** as intermediates. It was also confirmed that **3b** underwent H_2 reductive elimination reaction, which possibly initiated with the dissociation of the phosphine side-arm of the PNNP-Cy ligand. Thus, the hemilabile behaviour of the PNNP-R ligands was indicated.

Selective formation of hydrotrisiloxanes was achieved through dehydrogenative coupling of silanols with silanes using **1a** as the catalyst precursor. The reaction proceeded with high efficiency with good reaction selectivity.

Experimental

General considerations

All experiments were performed under a nitrogen atmosphere using Schlenk techniques or a glove box unless otherwise noted. *n*-Hexane, tetrahydrofuran, toluene and dichloromethane were purified by a solvent purification system (MBraun SPS-800 or a Glass Contour Ultimate Solvent System). C_6D_6 was dried over sodium benzophenone ketyl and distilled.

CD_2Cl_2 was dried over CaH_2 and distilled. Neocuproine was recrystallized by C_6H_6 from neocuproine hemihydrate. All other reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. ^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H}, and ^{31}P{^{1}H} NMR spectra (^{1}H, 600 MHz; ^{13}C, 150 MHz; ^{29}Si, 119 MHz; ^{31}P, 243 MHz) were recorded on a Bruker AVANCE III HD 600 spectrometer. Chemical shifts are reported in δ (ppm) and referenced to the residual solvent signals for ^{1}H and ^{13}C, 1,4-bis(trimethylsilyl)benzene for ^{29}Si, and 85% H_3PO_4 as an external standard for ^{31}P. The high-resolution ESI mass spectra were obtained on a Bruker microTOF II. Column chromatography was performed with silica gel (Kanto Chemical CO., INC. Silica gel 60 N, 100–210 μm).

Synthesis of 2,9-bis((diphenylphosphino)methyl)-1,10 phenanthroline (PNNP-Ph)[2a]

PNNP-Ph was prepared according to the modified procedure of the reported mehod.[2b] To a THF solution of neocuproine (0.500 g, 2.4 mmol) was added a THF solution of LDA (1 M in THF, 14.4 ml, 9.84 mmol) at −30 °C. PPh_2Cl (1.05 g, 4.81 mmol) was added to the solution at 0 °C and the solution was slowly warmed to room temperature and stirred overnight. The solution was quenched with H_2O (0.5 mL) and stirred for 1 h. After removal of solvent *in vacuo*, the residue was dissolved in CH_2Cl_2 (10 mL) and washed with H_2O (5 mL). The organic layer was corrected, dried over Na_2SO_4 and filtered. After evaporation, the residue was dissolved in CH_2Cl_2 (10 mL) and subjected to silica gel column chromatography (THF/hexane = 1/2). Crystallization of the obtained orange solid from CH_2Cl_2/Et_2O (1 : 50 v/v) afforded PNNP-Ph as a white crystalline solid (1.24 g, 82.4%). ^{1}H NMR (600 MHz, C_6D_6): δ 7.67 (t, 8H, J = 16.2 Hz, PPh-*H*), 7.40 (d, 2H, J = 8.16 Hz, Phen-*H*), 7.14–7.11 (m, 10H, Ar–*H*), 7.07 (d, 2H, J = 8.16 Hz, Phen-*H*), 7.04 (t, 4H, J = 7.85 Hz, PPh-*H*), 4.00 (s, 4H, PCH_2) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 159.05 (d, ^2J_P = 8.7 Hz), 146.6, 139.7, 135.7, 133.7 (^1J_P = 18.7 Hz), 128.8, 128.7, 128.7, 128.2, 125.6, 123.3, 123.2, 40.4 (^1J_P = 17.9 Hz) ppm. ^{31}P{^{1}H} NMR (243 MHz, C_6D_6): δ −10.2 ppm.

Synthesis of 2,9-bis((dicyclohexylphosphino)methyl)-1,10 phenanthroline (PNNP-Cy)

PNNP-Cy (1.31 g, 2.18 mmol, 78.0%) was prepared following the same procedure as that for PNNP-Ph using neocuproine (0.600 g, 2.8 mmol), LDA (1 M in THF, 11.5 ml, 11.5 mmol) and $PClCy_2$ (1.34 g, 5.8 mmol). ^{1}H NMR (600 MHz, C_6D_6): δ 7.62 (d, 2H, J = 8.22, Phen-*H*), 7.57 (d, 2H, J = 8.28, Phen-*H*), 7.26 (s, 2H, Phen-*H*), 3.44 (s, 4H, PCH_2), 1.94–1.92 (m, 8H, Cy-*H*), 1.80–1.70 (m, 12H, Cy-*H*), 1.62–1.61 (m, 4H, Cy-*H*), 1.46 (qt, 4H, J = 12.30, 7.23, Cy-*H*), 1.33–1.16 (m, 16H, Cy-*H*) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 161.7 (d, ^2J_P = 9.9 Hz), 146.5, 135.7, 127.1, 125.5, 123.5 (d, ^3J_P = 7.3), 34.2 (d, ^1J_P = 16.2 Hz), 33.8 (d, ^1J_P = 23.1 Hz), 30.5 (d, ^2J_P = 14.3 Hz), 29.6 (d, ^3J_P = 9.1 Hz), 27.8 (d, ^2J_P = 17.6 Hz), 27.7, 27.0 ppm. ^{31}P{^{1}H} NMR (243 MHz, C_6D_6): δ 2.6 ppm.

Synthesis of [$FeCl_2$(PNNP-Ph)] (1a)

A Schlenk tube equipped with a Teflon valve was charged with a THF solution (10 mL) of PNNP-Ph (0.200 g, 0.34 mmol) and $FeCl_2$ (0.045 g, 0.35 mmol). The solution was stirred at 60 °C overnight. After cooling to room temperature, the red solids were filtered and evaporated. The residue was extracted with CH_2Cl_2 and dried *in vacuo* to give **1a** as a red solid (0.201 g, 82.3%). Single crystals of **1a** were obtained from a cold CH_2Cl_2/Et_2O solution. ^{1}H NMR (600 MHz, C_6D_6): δ 51.36 (br), 24.81 (br), 15.49 (br), 11.07 (br), 7.32 (s), 4.95 (br), 2.58 (br), −8.78 (br).

Anal. calcd for $C_{38}H_{30}Cl_2FeN_2P_2$: C 64.89; H 4.30; N 3.98%. Found: C 64.91; H 4.48; N 4.07%.

Synthesis of [$FeBr_2$(PNNP-Cy)] (1b)

Complex **1b** was synthesized by the modified procedure of the previous report.[2d] A Schlenk tube equipped with a Teflon valve was charged with a THF solution (10 mL) of PNNP-Cy (0.500 g, 0.83 mmol) and $FeBr_2$ (0.180 g, 0.84 mmol). The solution was stirred at room temperature overnight. After removal of the volatiles, the residue was washed with toluene (10 ml × 3) and dried. The resulting red solids were extracted with THF and filtered. Volatiles were removed to give **1b** as a red solid (0.598 g, 88.1%). Single crystals of **1b** were obtained from CH_2Cl_2/Et_2O solution at room temperature. ^{1}H NMR (600 MHz, C_6D_6): δ 64.02 (br), 30.77 (br), 26.80 (br), 9.85 (br), 8.68 (br), 7.32 (s), 4.86 (br), 1.89–0.85, −2.54 (br), −12.84 (br) ppm.

Synthesis of [Fe(PNNP-Ph)]$_2$(μ-N_2) (2a)

1a (5.0 mg, 7.1 μmol) was suspended in C_6D_6 (0.4 mL) and $NaBEt_3H$ (1 M in THF, 14.2 μl, 14.2 μmol) was added. The resulting deep red solution was filtered and ^{1}H and ^{31}P NMR spectra were obtained to confirm the quantitative formation of **2a** as the sole product. Alternatively, preparation of a single crystal of **2a** is as follows. To a THF suspension (5 mL) of **1a** (0.030 g, 43 μmol) was added $NaBEt_3H$ (1 M in THF, 86 ml, 86 μmol) under a N_2 atmosphere. The solution was stirred at room temperature for 30 minutes and filtered. After adding hexane (5 ml), the solution was kept at −40 °C for 2 days to give **2a** as deep red crystals, which easily decompose at room temperature. ^{1}H NMR (600 MHz, C_6D_6): δ 7.51 (d, 2H, J = 6.72 Hz, Phen-*H*), 7.37 (d, 2H, J = 6.28 Hz, Phen-*H*), 7.23 (s, 2H, Phen-*H*), 6.94 (t, 2H, J = 6.78 Hz, PPh-*H*), 6.61–6.66 (m, 8H, PPh-*H*), 6.57 (t, 2H, J = 13.7 Hz, PPh-*H*), 6.41–6.38 (br, 8H, PPh-*H*), 4.27 (d, 2H, J = 15.61 Hz, PCH_2), 4.16 (d, 2H, J = 14.58 Hz, PCH_2) ppm. ^{31}P{^{1}H} NMR (243 MHz, C_6D_6): δ 93.0 ppm. The ^{13}C NMR spectrum of **2a** was obscured due to the significant overlap with $NaBEt_3H$/THF signals.

Synthesis of [Fe(PNNP-Cy)]$_2$(μ-N_2) (2b)

2b was prepared following the same procedure as that for **2a**. ^{1}H NMR (600 MHz, C_6D_6): δ 7.61 (d, 2H, J = 6.48 Hz, Phen-*H*), 7.50 (d, 2H, J = 5.30 Hz, Phen-*H*), 7.16 (s, 2H, Phen-*H*), 3.68 (d, 2H, J = 14.71 Hz, PCH_2), 3.41 (d, 2H, J = 15.03 Hz, PCH_2), 1.90–0.31 (44H, PCy-*H*) ppm. ^{31}P{^{1}H} NMR (243 MHz, C_6D_6):

δ 94.1 ppm. The ^{13}C NMR spectrum of **2b** was obscured due to the significant overlap with $NaBEt_3H$/THF signals.

Synthesis of [Fe(H)$_2$(PNNP-Cy)] (3b)

To a C_6H_6 suspension (5 mL) of **1b** (0.030 g, 37 μmol) was added $NaBEt_3H$ (1 M in THF, 74 μl, 74 μmol) under a N_2 atmosphere. The solution was stirred at room temperature for 30 minutes and filtered. Removal of the solvent gave **3b** as a green solid (0.0201 g, 31 μmol, 82.4%). **3b** was crystallized from THF/*n*-hexane in −40 °C for 1 day to form green block crystals. ^{1}H NMR (600 MHz, C_6D_6): δ 7.36 (s, 2H, Phen-*H*), 7.32 (d, 2H, J = 7.32 Hz, Phen-*H*), 7.16 (d, H, J = 7.31 Hz, Phen-*H*), 3.63–3.62 (m, 4H, PCH_2), 2.26 (d, 4H, J = 7.26 PC*H*), 1.87–1.64 (m, 24H, PCy-*H*), 1.37–1.16 (m, 16H, PCy-*H*), −8.45 ppm (t, 2H, ^2J_P = 68.9 Hz, FeH_2) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 160.0, 142.2, 129.5, 125.3, 116.9, 111.6, 38.8 (d, ^1J_P = 23.8 Hz), 37.8 (d, ^1J_P = 14.0 Hz), 31.6, 28.1, 27.5, 27.3, 22.6 ppm. ^{31}P{^{1}H} NMR (243 MHz, C_6D_6): δ 93.0 ppm. Complex **3b** easily decomposed and its elemental analysis was not available.

Synthesis of [Fe(PNNP-Ph)(CO)] (4a)

In a Schlenk tube, **2a** was *in situ* generated by the reaction of **1a** (0.050 g, 0.071 mmol) with 2 equiv. of $NaBEt_3H$ (1 M in THF, 86 μl, 86 μmol). After freeze–thaw–pump cycles (×3), CO (1 atm) was introduced into the reaction vessel. After stirring at room temperature for 30 minutes, all the volatiles were evaporated. The residue was dissolved in C_6H_6 (5 mL) and filtered with an alumina pad. After evaporation, **4a** was obtained as a deep green solid (0.038 g, 82.2%). Single crystals of **4a** were obtained from cold THF/hexane solution. ^{1}H NMR (600 MHz, C_6D_6): δ 7.60–7.51 (m, 8H, PPh-*H*), 7.15–7.12 (m, 10H, Phen-*H* + PPh-*H*), 6.84 (d, 2H, J = 6.84 Hz, Phen-*H*), 6.78–6.76 (m, 4H, PPh-*H*), 6.65 (t, 2H, J = 7.02 Hz, Phen-*H*), 6.49 (t, J = 7.62 Hz, PPh-*H*), 4.32 (d, 2H, J = 14.58 Hz, PCH_2), 4.08–4.03 (m, 2H, PCH_2) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 216.3, 156.4, 139.3, 139.0, 132.7, 130.8, 130.5, 129.2, 125.8, 117.5, 112.1, 46.5 ppm. ^{31}P{^{1}H} NMR (243 MHz, C_6D_6): δ 108.6 ppm. IR (ATR) ν_{CO} 1866 cm^{-1}. Anal. calcd for $C_{39}H_{30}FeN_2OP_2$: C 70.92; H 4.58; N 4.24%. Found: C 70.99; H 4.69; N 4.07%.

Synthesis of [Fe(η^2-HSiH$_2$Ph)(PNNP-Ph)] (5a)

To a THF suspension of **1a** (0.030 g, 43 μmol) (3 mL) was added $NaBEt_3H$ (1 M in THF, 86 μl, 86 μmol) at room temperature. The mixture was stirred for 30 minutes, added phenylsilane (18.4 mg, 171 μmol), and further stirred for 30 minutes at room temperature. The solution was concentrated to dryness under vacuum, and the resulting solid was washed with hexane (1 mL × 3) and dried. The resulting compound was extracted with C_6H_6 and filtered. After evaporation, **5a** was obtained as a black solid (0.024 g, 76%). **5a** was crystallized from cold Et_2O/*n*-hexane to form block crystals. ^{1}H NMR (600 MHz, C_6D_6): δ 7.54 (br, 4H, PPh-*H*), 7.20 (s, 2H, Phen-*H*), 7.13–7.05 (m, 8H, Ar–*H*), 6.93 (d, 2H, J = 7.26 Hz, Phen-*H*), 6.83 (t, 1H, J = 7.26, SiPh), 6.71–6.69 (m, 6H, Ar–*H*), 6.61 (t, J = 7.32 Hz, 2H), 6.51–6.49 (m, 6H), 4.75 (s, 2H, SiH_2), 4.26 (d, 2H, J = 15.84 Hz, PCH_2), 3.81 (dt, 2H, J = 16.5, 5.28 Hz, PCH_2), −8.06 ppm (t, 1H, J = 36.8 Hz, agostic-*H*). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 155.9, 140.8, 140.6, 133.1, 132.9, 132.8, 131.3, 131.2, 129.5, 128.3, 126.7, 126.0, 118.8, 114.6, 47.1 ppm. ^{31}P{^{1}H} NMR (243 MHz, C_6D_6): δ 106.22 ppm.^{29}Si{^{1}H} NMR (119 MHz, C_6D_6): δ −12.2 ppm. Complex **5a** easily decomposes *via* $PhSiH_3$ dissociation even at −35 °C and elementary analysis is not available.

Catalytic dehydrogenation of silanes with silanols

A typical procedure (Table 1, entry 1) is as follows. All reactions were carried out under a nitrogen atmosphere. To a vial were added a THF solution (0.5 mL) of $PhSiH_3$ (32.4 mg, 0.30 mmol) and a 0.1 M stock solution of **1a**/2$NaBEt_3H$ (30 μl, 0.030 μmol).[18] After stirring for 5 minutes, Me_3SiOH (56.0 mg, 0.62 mmol) was added, and the mixture was stirred at room temperature for 12 h. Mesitylene (36.0 mg, 0.30 mmol) as an internal standard was added to the reaction mixture, and ^{1}H NMR spectra were recorded to determine the NMR yield of $(Me_3SiO)_2(SiHPh)$ (>99%).

For compound characterization data, please see the ESI.†

Conflicts of interest

There are no conflicts to declare.

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