Dalton Transactions

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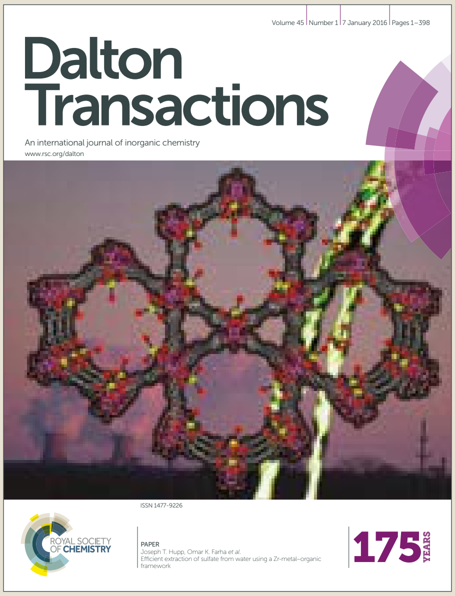

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Dalton Transaction

PAPER

Bis(silylenyl)-substituted ferrocene-stabilized η^6-arene iron(0) complexes: synthesis, structure and catalytic application†

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Reaction of $FeX_2(thf)_n$ (X = Cl n = 1.5, Br n = 2) with the chelating 1,1'-bis(silylenyl)-substituted ferrocene ligand ***Si*****Fc*****Si*** **A** (Fc = ferrocendiyl, ***Si*** = $PhC(NtBu)_2Si$:) furnishes the corresponding dihalido Fe(II) complexes [(***Si***Fc***Si***)FeX_2] (X = Cl, **1** and X = Br, **2**) in high yields. Reduction of the latter with an excess of KC_8 in the presence of benzene and toluene leads to the unprecedented bis(silylene) stabilized Fe^0 complexes [(***Si***Fc***Si***)Fe-$\eta^6(C_6H_6)$] **3** and [(***Si***Fc***Si***)Fe-$\eta^6(C_7H_8)$] **4**, respectively. The ^{57}Fe Mössbauer spectrum of **3** at 13 K exhibits parameters ($\sigma = 0.3676\ mm\cdot s^{-1}$; $\Delta E_Q = 1.334\ mm\cdot s^{-1}$) which are consistent with the presence of a pentacoordinated Fe^0 atom in a *pseudo* trigonal-bipyramidal coordination environment, with two dative Si→Fe bonds and three coordination sites occupied by the η^6-coordinated arene ligand. Results from DFT calculations, ^{57}Fe Mössbauer parameters and the diamagnetic NMR spectra confirm the redox-innocent nature of these ligands and the zero oxidation state of the iron center. The catalytic ability of **3** was investigated with respect to ketone hydrogenation. In all cases, good to excellent yields to the corresponding alcohols were obtained at 50 °C and 50 bar H_2 pressure. Electron-donating as well as -withdrawing substituents were tolerated with excellent to good yields. Conversions of bulkier ketones and unactivated aliphatic ketones lead merely to moderate yields. This represents the first example of a silylene-iron metal complex which has been utilized as a highly active precatalyst in the hydrogenation of ketones. The results underline the powerful ability of chelating bis(N-heterocyclic silylene) ligands acting as strong σ-donor ligands in stabilizing a new generation of low-valent, electron-rich transition metal complexes for catalytic transformations.

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Introduction

After the discovery of an isolable *N*-heterocyclic carbene (NHC) by Arduengo *et al*. in 1991,[1] Denk and West *et al.* isolated the first *N*-heterocyclic silylenes (NHSis) a few years later.[2] The electronic nature of divalent Si^{II} with a singlet electronic ground state enables NHSis to act as strong σ-donor (Si(3s)→TM) and π-acceptor (TM→Si(3p)) ligands in NHSi-TM complexes (TM = transition metal). To date, a variety of NHSi-TM complexes have been isolated and demonstrated to be active in small molecule activation reactions[3,4] and a variety of catalytic transformations.[5,6] For the first time, the ability of an NHSi to act as supporting ligand in a catalytically active reaction was first demonstrated in Suzuki cross-coupling reaction of aryl boronic acids with bromoarenes by Fürstner *et al.*[7] Due to its stronger σ-donor ability compared to already broadly established phosphines and NHCs as supporting ligands in catalysis,[8] some of us showed that mono- and bidentate NHSis (Chart 1) can be utilized as powerful steering ligands in homogeneous catalysis.[6,9] Experimental data indicated that the σ-donor strengths of this novel bidentate ligands can be adjusted by modification of the heterocyclic backbone (Figure 1: **A**, **B**).[10]

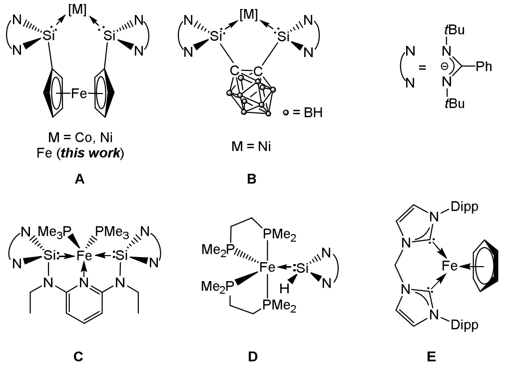

Chart 1 Examples of catalytically active mono- and bi-dentate metallylene-transition metal complexes.

Recently, the synthesis of a new bis(silylenyl)-substituted ferrocene ligand (***Si***Fc***Si***) **A** (Fc = ferrocendiyl, ***Si*** = $PhC(N^tBu)_2Si$:) was reported. This ligand is one of the strongest σ-donor ligand, as shown by isolation of a bis(silylene)-η^5-cyclopentadienyl Co(I) complex.[11] The catalytic abilities of the Co(I) complex were probed in [2+2+2] cycloaddition reaction of phenyl acetylene and acetonitrile. Moreover, our group could show that a bis(silylene)-substituted

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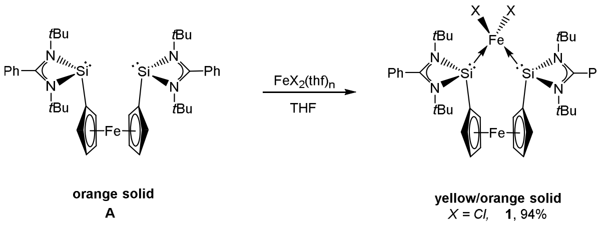
ortho-carborane Ni complex **B** complex can serve as superior ligand in the nickel-catalyzed amination of arenes.[12]

In the past few years, iron-based catalysis has gained considerable attention as an alternative to established catalysts based on noble metals due to its greater abundance, low-cost and low toxicity.[13] The synthesis of the highly electron-rich monodentate hydrido silylene Fe^0 complex **D**,[14] and pincer-type iron complex **C**,[15] isolated in our group, are the first examples of catalytically active silylene-iron(0) complexes in hydrosilylation of ketones. Also, complex **C** exhibit the highest electron density on the iron center for pincer-type complexes with an additional intramolecular dative (pyridine)N→Fe bond. Following the isolation of the first bis(NHC)-stabilized η^6-arene Fe(0) complex **E** in 2013 and its application in catalytic organic amide reduction,[16] we were highly interested in the isolation and reactivity of the analogous bis(NHSi)-stabilized η^6-arene Fe^0 complexes. Herein, we report the first η^6- arene bis(NHSi) Fe^0 complexes **3** and **4** which are stabilized by the bidentate ***Si***Fc***Si*** chelate ligand **A**. Complex **3** has been successfully applied as first example of a silylene-TM complex for the hydrogenation of unsaturated organic substrates.

Results and Discussion

Starting from **A**, [11] we first targeted the isolation of the dihalido Fe^{II} complexes $[(\textbf{\textit{Si}}\text{Fc}\textbf{\textit{Si}})FeX_2]$ **1** (X = Cl) and **2** (X = Br) as suitable Fe^0 precursors. Dehalogenation of **1** and **2** wit KC_8 should give access to a series of new ***Si***Fc***Si***-stabilized η^6-arene Fe^0 complexes. A stoichiometric mixture of **A** and $FeX_2(thf)_n$ (X = Cl n = 1.5; Br n = 2) were dissolved in benzene, resulting in an intense yellow solution at room temperature. Monitoring the reaction progress by ^1H NMR spectroscopy (see Fig. S1 in ESI) shows the formation of paramagnetic species with broad signals and chemical shifts in the range of σ = 1 to 14 ppm. Crystallization from concentrated benzene solutions resulted in orange-yellow crystals in high yields (ca. 70 %) at room temperature, which were suitable for X-ray diffraction analysis (Fig. 1).



Scheme 1 Synthesis of the dihalido (*Si***Fc***Si*) Fe^{II} complexes **1** and **2**.

When the reactions were carried out in THF, **1** and **2** can be isolated in higher yields of 94 % (**1**) and 87 % (**2**) on multi gram scale (up to 3 g), respectively. The complexes **1** and **2** are very air sensitive and degrade to a black powder within a couple of minutes in air. Complexes **1** and **2** are well soluble in benzene, toluene and THF without decomposition. Their compositions were confirmed by elemental analysis. Their ^{57}Fe-Mössbauer spectra were recorded at 13 K: The isomer shift (σ) and quadrupole splitting (ΔE_Q) values for the bis-Si^{II}-coordinated Fe center (σ [$mm\cdot s^{-1}$] = 0.6619; 0.6562 and ΔE_Q [$mm\cdot s^{-1}$] = 3.2667; 3.459 for X = Cl; Br) are in accordance with the expected values for distorted high-spin Fe^{II} complexes in a tetrahedral environment (S = 2) (see Fig. S2 in ESI).[15,17] This is also in agreement with the observed paramagnetic ^1H NMR spectra in solutions. Complex **1** crystallizes in the orthorhombic space group *Pbca*; the dibromido Fe^{II} complex **2** crystallizes in the triclinic space group *P*-1. The molecular structures (Fig. 1) of **1** and **2** exhibit a distorted-tetrahedral geometry (Σ∡: **1**: 436.15 °, **2**: 436.31 °), in which the iron atom is coordinated by the bidentate chelating bis(NHSi) ligand **A** and two halides. Both complexes **1** and **2** show similar Fe-Si, Si-N and Si-C bond lengths and an average Si-Fe-Si angle of 100.60 °. The Fe-Si distances in **1** (2.4923(4); 2.4823(4) Å) are akin to the previously reported bond lengths in the paramagnetic bis(silylene) pincer-type dichlorido Fe^{II} complex with d(Fe-Si) of 2.5256(7) and 2.5110(7) Å.[15]

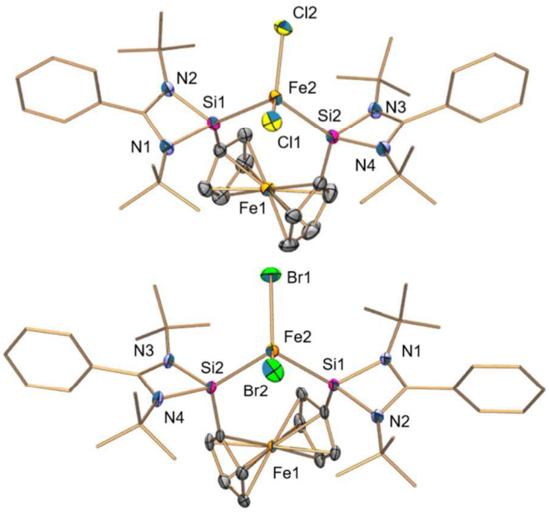
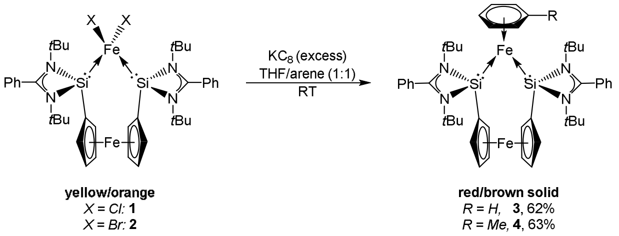


Fig. 1 Molecular structures of **1** (top) and **2** (bottom) at 50 % probability level. Hydrogen and solvent atoms are omitted for clarity. **1**: Selected bond lengths [Å]: Fe2-Cl1 2.255(6), Fe2-Cl2 2.2553(4), Si1-Fe2 2.4923(4), Si2-Fe2 2.4823(4), Si2-N3 1.8438(11), Si2-N4 1.8543(11), Si1-N2 1.8490(11), Si1-N1 1.856(12). Selected bond angle [°]: Cl1-Fe2-Cl2 119.94(2), Si1-Fe2-Si2 100.341(13), Cl2-Fe2-Si1 109.481(14), Cl1-Fe2-Si1 108.269(14), Cl2-Fe2-Si2 107.609(15), Cl1-Fe2-Si2 109.442(15). **2**: Selected bond lengths [Å]: Fe2-Br1 2.402(5), Fe2-Br2 2.397(5), Si1-Fe2 2.498(8), Si2-Fe(2) 2.504(8), Si2-N3 1.850(2) , Si2-N4 1.863(2), Si1-N2 1.853(2), Si1-N1 1.859(2). Selected bond angle [°]: Br1-Fe2-Br2 117.04(2), Si1-Fe2-Si2 100.90(3), Br2-Fe2-Si1 108.40(2), Br1-Fe2-Si1 109.82(2), Br2-Fe2-Si2 109.97, Br1-Fe2-Si2 109.48(2).

Reduction of **1** and **2** (Scheme 2) with an excess of KC_8 in presence of benzene or toluene (in THF, 1:1) gives the desired 18 electron η^6-arene *Si***Fc***Si* Fe^0 complexes **3** and **4** in moderate yields (≈ 60 %) after workup. The reduction, followed by ^1H NMR spectroscopy, reveals the formation of a new diamagnetic species. Using **2**, the dehalogenation is faster (3h) compared to **1** (5h) at room temperature. After removal of all volatiles in vacuum, **3** and **4** could be extracted with diethylether and isolated as red-brown, air sensitive solids which decompose above 145 °C (**3**, arene = benzene) and 143 °C (**4**, arene = toluene) without melting, respectively**.**



Scheme 2. Synthesis of **3** and **4** through dehalogenation of **1** and **2** in the presence of benzene and toluene, respectively.

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The composition of the isolated complexes **3** and **4** were confirmed by elemental analysis and ESI-MS spectrometry (see Fig. S4 in ESI). The ^{1}H-NMR spectra of the diamagnetic complexes in deuterated benzene (C_6D_6) exhibit resonances in accordance with the molecule structure. The resonance signal of the protons of the coordinate benzene in **3** appears as a singlet with a chemical shift of $\delta = 5.16$ ppm which is shifted to lower field in comparison with other known η^6(benzene) Fe^0 complexes (see Fig. S3 in ESI), bearing bis(NHC) **E**,[16] or bis(phosphine) ligands ($\sigma = 4.56 - 4.91$ ppm).[18] Because of their relatively low solubility of **3** and **4** in deuterated solvents such as C_6D_6 and THF-d_8, the respective ^{13}C- and ^{29}Si-NMR spectra could not be recorded.

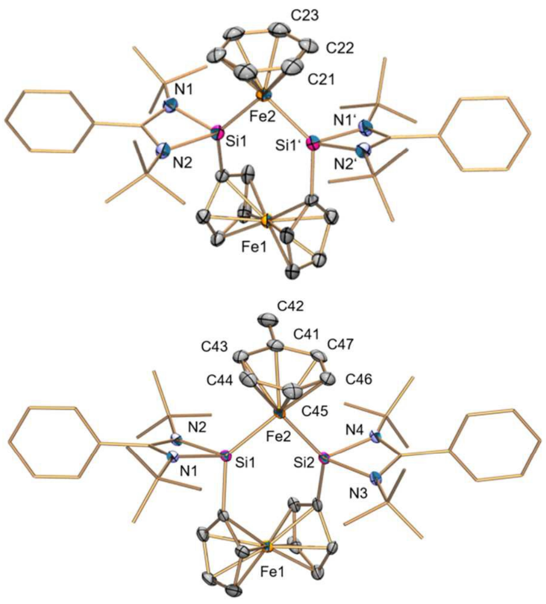

Fig. 2 Molecular structures of **3** (top) and **4** (bottom) at the 50 % probability level. Hydrogen and solvent atoms are omitted for clarity. **3**: Symmetry transformations used to generate equivalent atoms (`): 1-x, -y,z. Selected bond lengths [Å]: Fe2-Si1 2.1782(16), Fe2-C22 2.084(5), Fe2-C23 2.089(6), Fe2-C21 2.089(6), C21-C22 1.426(9), Si1-C16 1.899(5), Si1-N1 1.917(4), Si1-N2 1.914(4). Selected bond angle [°]:Si1-Fe2-Si1` 89.31(8), N1-Si1-N2 68.16(7). **4**: Selected bond lengths [Å]: Fe2-Si2 2.1752(8), Fe2-Si1 2.1707(8), Si1-C31 1.890(3), Si1-N1 1.913(2), Si1-N2 1.912(2), Fe2-C44 2.078(3), Fe2-C46 2.079(3), Fe2-C45 2.085(3), Fe2-C43 2.096(3), Fe2-C47 2.103(3), Fe2-C41 2.130(3).C41-C42 1.505(4). Selected bond angle [°]: C41-C43 1.408(4). Si1-Fe2-Si1` 89.52(3), N1-Si1-N2 68.11(9).

Red rhombohedral crystals suitable for X-ray diffraction analysis (Fig. 2) were obtained in the case of **3** in saturated benzene solutions and for **4** in diethyl ether at room temperature. **3** crystallizes in the orthorhombic space group *Fdd2* with one co-crystallized benzene molecule in the unit cell. Compound **4** co-crystallizes with two diethyl ether molecules in the unit cell in the monoclinic space group C12/*c*1 and exhibits almost identical metric parameters. Both η^6-arene Fe complexes **3** and **4** have the same Si-Fe-Si bond angle of virtually 90 ° (**3** 89.27(8) °; **4** 89.52(3) °). The $Si^{II} \rightarrow Fe$ bond lengths (**3**, 2.1782(16) Å; **4**, 2.1707(8), 2.1752(8) Å) are shorter compared to those of **1** (2.486(6) Å) and **2** (2.499(8) Å), because of π-back donation from the electron-rich Fe^0 center to the Si^{II} atoms of the chelating bis(NHSi) ligand **A**. The Si-Fe bond lengths are shorter compared to $[(NHSi)Fe(CO)_4]$ (2.234(2) Å) [19], but indeed comparable to other reported silylene- or bis(silylene) stabilized Fe^0 complexes like $[(NHSi)Fe(dmpe)_2]$ **D** (2.184(2) Å, dmpe = 1,2 bis(dimethylphosphanyl)ethane),[14] and tridentate pincer-type (***Si***N***Si***) iron(0) complex **C** (2.1637(15); 2.1695(13) Å) with σ-donating ligands (dmpe; PMe_3).[15]

Cyclic voltammetry was performed for **3** and **4** in THF showing one reversible redox event at $E^{1/2} = -1.56$ V (*vs* Fc/Fc^+) for **3** and at $E^{1/2} = -1.58$ V (*vs* Fc/Fc^+) for **4** (cyclic voltammogram, see Fig. S6 in ESI). These redox waves have been assigned to a respective Fe^0/Fe^{+1} electron transfer process since the HOMO is metal centered as confirmed by DFT calculations (see below Fig 5). Irreversible reduction processes occur in the cationic region, which are overlapping with the reversible electron transfer process of the ferrocene in the bis(NHSi) ligand **A,** which is assumed to result from irreversible reduction processes of this ligand.

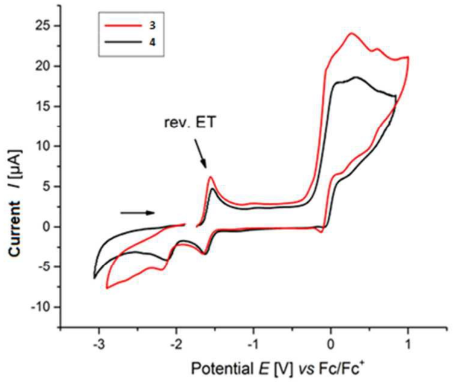

Fig. 3 CV of **3** (red) and **4** (black) (1mM in THF/ 0.1M $TBAPF_6$) recorded at a scan rate $v = 100\ mV{\cdot}s^{-1}$ showed one reversible redox event for both complexes.

To gain further insights into the electronic features, both **3** and **4** were additionally characterized by ^{57}Fe Mössbauer spectroscopy (see Fig. S5 in ESI). The ^{57}Fe Mössbauer parameters of **3** exhibit two doublets, shown in Fig. 4; one for the Fe^{II} center in the ferrocene backbone ($\sigma = 0.5301\ mm{\cdot}s^{-1}$; $\Delta E_Q = 2.3012\ mm{\cdot}s^{-1}$) and one for the bis(NHSi)-stabilized Fe^0 site with an isomeric shift of $\sigma = 0.3676\ mm{\cdot}s^{-1}$ and quadrupole splitting of $\Delta E_Q = 1.334\ mm{\cdot}s^{-1}$. The ^{57}Fe Mössbauer parameters for both complexes are summarized in Table 1 together with previously reported penta-coordinated Fe^0 complexes for comparison.[15,16]

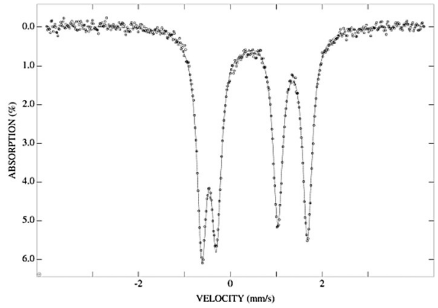

Fig. 4 ^{57}Fe Mössbauer spectrum of **3** in the solid state at 13 K. Circles are the experimental data, lines the simulated data with parameters: $\sigma = 0.3604\ mm{\cdot}s^{-1}$; $\Delta E_Q = 1.334\ mm{\cdot}s^{-1}$ for the Fe^0 core.

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Table 1 ^{57}Fe-Mössbauer parameter of pentacoordinated Fe^{0} complexes.

Complex	σ [mm·s^{-1}]	ΔE$_Q$ [mm·s^{-1}]	Ref.
[***Si***Fc***Si***]Fe(η^6-C_6H_6) **3**	0.36	1.33	***this work***
[***Si***Fc***Si***]Fe(η^6-C_7H_8) **4**	0.41	1.27	***this work***
[bis(NHC)]Fe(η^6-C_6H_6) **E**	0.43	1.37	[16]
[***Si***N***Si***]Fe(PMe_3)$_2$ **C**	0.24	1.66	[15]

The ^{57}Fe Mössbauer parameters strongly depend on the nature of the donors and the coordination symmetry around the iron atom. The σ-value is directly related to the s-electron density at the iron center, giving insights into the oxidation state of the Fe center when compared with other pentacoordinate Fe complexes. If compared with previously reported pentacoordinate Fe^{0} complexes (Table 1), the isomeric shift of **3** and **4** (σ = 0.36 ; 0.41 mm·s^{-1}) lies in the range between 0.24 and 0.43 mm·s^{-1}.[15,16] Interestingly, by changing from toluene to benzene as stabilizing ligand, a reduced σ-value was observed, indicating a stronger interaction between the Fe center and the coordinated benzene versus toluene. This is in agreement with the observed Fe-Arene distances in **3** (1.535 Å) and **4** (1.549 Å) by structural analysis where an elongation could be observed, going from benzene to toluene. DFT calculations (see details in ESI) show that the exchange of toluene coordinated in **4** by benzene, forming **3**, is slightly exergonic (**4** + benzene → **3** + toluene; -ΔG = - 2.1 kcal·mol^{-1}) which is experimentally confirmed when **4** was exposed to benzene at room temperature. The bis(NHC) analoguos complex **E** [16] has a notably higher σ-value (0.43 mm·s^{-1}) which is assumed to be related to the reduced σ-donor strength of C^{II} versus Si^{II}.[15] The structure of **3** and **4** can be described as a penta-coordinated Fe^{0} complex by comparing their quadrupole splitting (ΔE$_Q$) with the previously reported values for the complexes **C** and **E**. The ^{57}Fe Mössbauer parameter are consistent with a penta-coordinate Fe^{0} atom in a *pseudo*-trigonal bipyramidal coordination environment, with two coordinative Si→Fe bonds and three coordination sites occupied by the η^6-coordinated arene ring, which is in agreement with the results of the structural analysis of both complexes. In addition, to gain further insights into the electronical structure of the iron core and the bonding situation, DFT calculations were performed for **3** and **4** and additionally for the bis(NHC) complex **E**. The metric parameters of the calculated structures are in very good agreement with the experimental values (Tab. 2).

Table 2 Comparison of DFT-calculated and experimental distances and angles for **3** and **4**.

complex	**3**		**4**	
	Exp.	**Calc.**	**Exp.**	**Calc.**
Fe-Si [Å]	2.177	2.164	2.175	2.171
	2.177	2.164	2.171	2.172
Si-Fe-Si [°]	89.3	89.2	89.5	89.7
Fe-Arene [Å]	1.535	1.540	1.549	1.547

Both complexes show identical frontier orbitals, with very few differences in the absolute energies of the LUMO + 1, LUMO, HOMO and HOMO - 1 molecular orbitals as shown in Fig. 5 (see details in chapter 4 ESI).

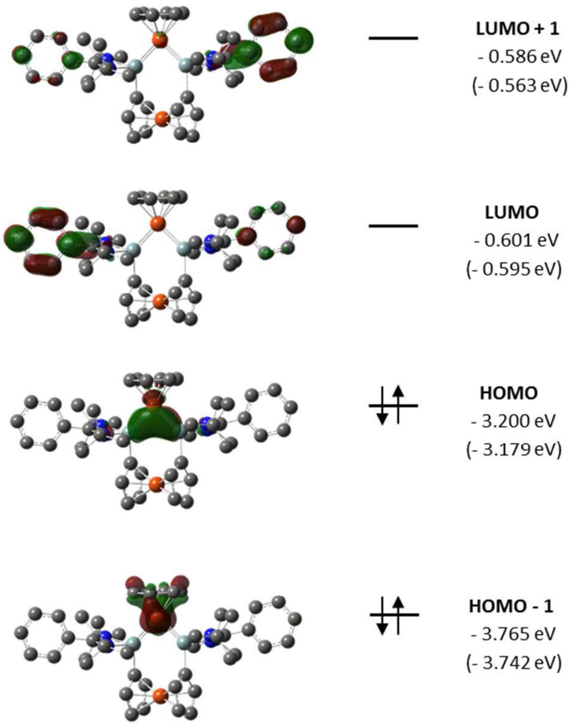

Fig. 5 Frontier molecular orbitals in **3** calculated at the B3LYP-D3 level with s6-31G* basis set for Fe and 6-31G* basis set for all other atoms. The energies in bold parentheses are the calculated energies for **4** (red = iron, blue = nitrogen, green = silicon).

The LUMO + 1 and LUMO of both complexes are located at the phenyl groups of the coordinated *N*-heterocyclic silylene moieties in ligand **A**, which corresponds to a π*-orbital. The π backdonation from the Fe^{0} center into the 3p-orbital of the Si^{II} atoms is reflected in the HOMO. The HOMO - 1 orbital reflects the ***π***(arene) interaction between the coordinated arene ring (benzene/toluene) and the bis(NHSi) stabilized Fe^{0} center. The HOMO-LUMO gap is nearly identical in both complexes with 2.599 eV (3) and 2.584 eV (4, see Fig. S17 in ESI) and smaller when compared with the bis(NHC) complex E with a HOMO-LUMO gap of 2.710 eV.[16] Overall, the results from DFT calculations of **3** and **4** confirm the redox-innocent behavior of the ligands with a zero oxidation state of the Fe atom.

Furthermore, the complex **5** was synthesized (Scheme 3) by arene→CO ligand exchange under a CO atmosphere and by direct access through reduction of the precursor complex **1** in the presence of CO. When solutions of **3** and **4** in THF are exposed to CO (1 atm), an immediate color change from red to yellow is observed at room temperature. The IR spectra of the identical products were recorded after removal of the solvent (see Fig. S14 in ESI) resulting in three strong stretching frequencies (υ_{CO} = 1941, 1900, 1862 cm^{-1}), which are typical for cis-$L_2M(CO)_3$ complexes with 2A` und 1A`` IR active modes. This provided further evidence of an authentic zero oxidation state of the iron center in **3** and **4**. As expected for **5**, the CO stretching frequencies are bathochromic shifted compared to monodentate [(NHSi)Fe(CO)$_4$] complexes due to the bis(NHSi) coordination.[5,20] Surprisingly, when compared to a bis(NHC) carbonyl Fe^{0} complex,[16] the IR stretching frequencies (υ_{CO} = 1968, 1890, 1865 cm^{-1}) are very similar.

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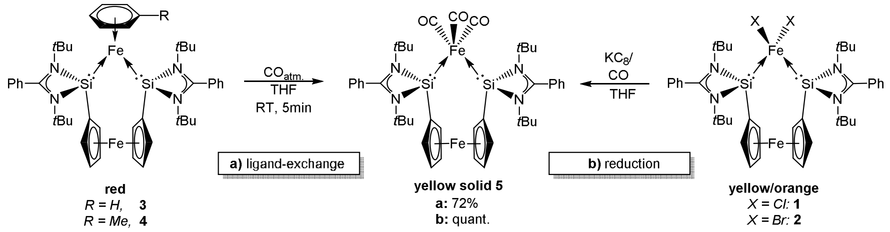
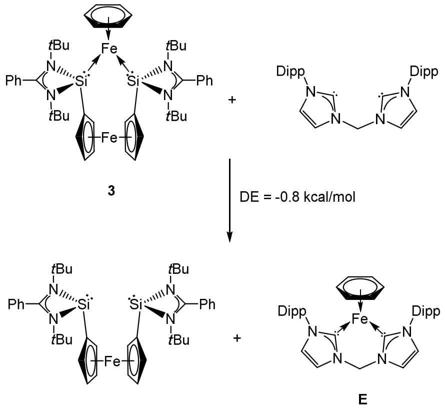


Scheme 3 Synthesis of **5** via a) ligand exchange reaction and b) reduction.

By changing from NHC to NHSi as ligand, the υ_{CO} values of **5** are practically identical with those of the corresponding carbonyl complex of **E**. The affinity of the free bis(NHC) ligand relatively to the bis(NHSi) ligand towards Fe^0 center in **3** has been calculated (Scheme 4), resulting in a negligible ΔG value of -0.8 kcal mol^{-1}, which is a suitable explanation for the identical CO stretching frequencies in the IR spectra.

By reduction of the precursor complex **1** in presence of a CO atmosphere, **5** can also be isolated in good yields (72 %) as an orange solid. Complex **5** is stable under reduced pressure and shows no decomposition in solutions after several hours. Several attempts to crystallize **5** in benzene, THF and diethyl ether were not successful. The recorded ^{1}H and ^{13}C{^{1}H} NMR spectra in C_6D_6 show a very symmetric pattern, where a single resonance signal at σ = 225 ppm could be assigned to the three equivalent CO ligands through a DEPT-135 NMR experiment. The composition of **5** was confirmed by ESI-MS spectrometry where the $[M]^+$ peak could be observed (calc. for $[C_{43}H_{54}N_4Si_2Fe_2O_3]^+$ (m/z): 842.2428; found: 842.2430 (see Figs. S12, S13 in ESI).



Scheme 4 DFT calculations of the affinity of the free bis(carbene) ligand towards the iron(arene) center in **3**.

Catalytic hydrogenation

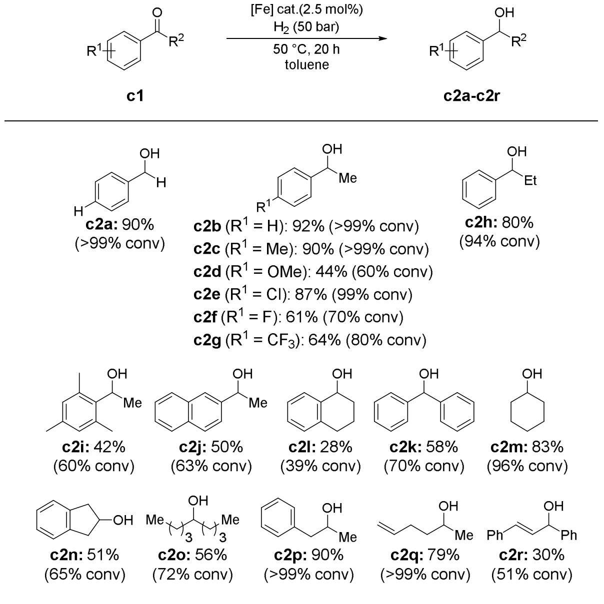
To probe the utility of the novel Fe complex **3**, we performed the catalytic hydrogenation of various ketones and an aldehyde for comparison (Scheme 5). Screening of the reaction parameters such as pressure, temperature and solvent (Table 3) revealed that 2.5 mol% of **3** allow the hydrogenation of acetophenone in toluene at 50 °C under a dihydrogen pressure of 50 bar (entry 6). Notably, any deviation from this catalytic setup in terms of catalyst loading, solvent or temperature led to lower conversions. To further expand the substrate scope, we subjected benzaldehyde and several electronically modified ketones to our optimized setup (Scheme 5).

Table 3 Optimization of the acetophenone hydrogenation.[a]

Entry	Solvent	T [°C]	p(H_2) [bar]	Conv (%)[b]
1	THF	RT	20	30
2	Toluene	RT	20	66
3	THF	RT	50	50
4	Toluene	RT	50	70
5	THF	50	50	55
6	Toluene	50	50	>99
7	Toluene	50	50	80[c]

[a] All reactions were performed on a 0.10 mmol scale. [b] Determined by GLC analysis with respect to starting material. [c] Conversion measured after 10 h.

This afforded clean reduction of the aldehyde to the corresponding alcohol (**c1a** → **c2a**). Likewise, acetophenone also underwent reduction to afford 1-phenylethan-1-ol in near quantitative yield (**c1b** → **c2b**). Ketones with electron-donating (**c1c/c1d** → **c2c/c2d**) as well as -withdrawing (**c1e–c1g** → **c2e–c2g**) substituents in the *para* position of the aryl group were also tolerated with excellent to moderate isolated yields. Similarly, ethyl phenyl ketone could also be reduced affording the corresponding alcohol with 80% isolated yield (**c1h** → **c2h**).



Scheme 5 Fe(0)-η^6(arene) complex **3** catalyzed reduction of various Ketones. All reactions were performed on a 0.10 mmol scale. Isolated yields were calculated after flash column chromatography. Conversions are determined by GLC analysis with respect to starting material.

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Bulkier substituents were detrimental to reactivity, resulting in moderate yields (**c1i–c1k** → **c2i–c2k**). Various cyclic and linear aliphatic ketones were also tested. Cyclohexanone underwent smooth reduction (**c1m** → **c2m**) while indan-2-one gave low conversion and diminished isolated yield (**c1n** → **c2n**). Acyclic ketones could also be reduced with moderate to excellent isolated yields (**c1o**/**c1p** → **c2o**/**c2p**). Hydrogenation of allylacetone and chalcone were also carried out, and we are pleased to observe the high chemoselectivity of our catalytic system favoring carbonyl reduction over C=C bonds (**c2q**/**c2r** → **c2q**/**c2r**).

Conclusions

In summary, the first ferrocene bis(NHSi)-stabilized (**Si**Fc**Si**, ligand **A**) η^6(arene) Fe^0 complexes **3** and **4** were synthesized by facile reduction of the corresponding Fe^{II} precursors **1** (X = Cl) and **2** (X = Br) in the presence of benzene or toluene. The latter were synthesized by direct coordination of the corresponding Fe^{II} dihalides with **A** as a η^2-chelating ligand, yielding **3** and **4**. Complexes **3** and **4** were fully characterized: Their structural analysis, ^{57}Fe Mössbauer spectra, and DFT calculations confirm the redox-innocent behavior of the bis(NHSi) ligand **A** and of the arene ligands (benzene, toluene). When **3** and **4** were exposed to a CO, the related carbonyl Fe^0 complex **5** could be obtained as sole product by arene→CO ligand exchange. Complex **5** was also obtained in good yields from the reduction of **1** in the presence of CO. As a primary example in $Si^{II} \rightarrow Fe^0$ chemistry, the catalytic hydrogenation of ketones with **3** (2.5 mol%) could be achieved, resulting in good to excellent yields for ketones with electron-donating as well as -withdrawing substituents. Moderate yields were only obtained for sterically demanding and less activated aliphatic ketones. We are currently investigating the coordination ability of ligand **A** towards other first-row transition metals and the application of the resulting complexes in metal-mediated catalytic transformations.

Conflict of Interest

There are no conflicts of interest to declare.

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