Synthesis of N-Heterocycle Substituted Silyl Ligands within the Coordination Sphere of Iron

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Supporting Information

ABSTRACT: N-Heterocycle-substituted silyl iron complexes have been synthesized by nucleophilic substitution at trichlorosilyl ligands bound to iron. The homoleptic (triprolyl)- and tris(3-methylindolyl)silyl groups were accessed from (Cl3Si)CpFe(CO)2 (Cl3SiFp) by substitution of chloride with pyrrolide or 3-methylindolide, respectively. Analogously, nucleophilic substitution of Cl with pyrrolide on the anionic Fe(0) synthon Cl3SiFe(CO)3 + generates the (triprolyl)silyl ligand, bound to the iron tetracarbonyl fragment. The bulkier 2-mesitylpyrrolide substitutes a maximum of 2 chlorides on Cl3SiFp under the same conditions. The tridentate, trionic nucleophile tmim (tmimH3 = tris(3-methylindol-2-yl)methane) proves reluctant to perform the substitution in a straightforward manner; instead, ring-opening and incorporation of THF occurs to form the tris-THF adduct tmim(C4H8O)3SiFe(CO)4. The bidentate, monoanionic nucleophile 2-(dipp-iminomethyl)pyrrolide (DippIMP, dipp = 2,6-diisopropylphenyl) shows chloride displacement and addition of a second DippIMP moiety on the imine backbone. The heterocycle-based silyl ligands were shown to be sterically and electronically tunable, moderately electron-donating ligands. The presented approach to new silyl ligands avoids strongly reducing conditions and potentially reactive hydrosilane intermediates.

INTRODUCTION

Low-valent silicon(II) compounds are attracting considerable attention as strongly donating, tunable ligands for transition metals.1 While free silylenes were initially observed as highly reactive intermediates,2 the use of nitrogen substituents has given access to a number of persistent silylenes following the first N-heterocyclic silylene (NHSi) reported in 1994 by Denk et al.3 Similarly to N-heterocyclic carbenes (NHC), stable silylenes bind a variety of transition metals.4–6 However, owing to the lower electronegativity and larger size of silicon, they conserve a higher Lewis acidity than their carbon-based congeners and they are often stabilized by coordination of a Lewis base, resulting in a 4-coordinate Si(II) center in the metal complex.6,7 The coordination chemistry of Si(II) ligands has now been well established, and their use as supporting ligands in catalysis is emerging as a promising area of research.8–16

In contrast with their neutral congeners, anionic Si(II) ligands (silyl anions or silanides) have seen less applications as supporting ligands.17–20 Their use being mostly limited to multidentate architectures,21 including a recently reported PSiP pincer system featuring indolyl linkers.22 This presumably arises from the high reactivity of the metal–silyl bond, exemplified by the role of metal–silyl complexes as reactive intermediates in catalytic hydrosilylation.8,23–25 A possible approach toward stable silanides is the use of electron-withdrawing substituents to tame the reducing strength of the Si-centered lone pair. Encouragingly, this approach has allowed for the isolation of free silanides bearing trimethylsilyl and aromatic26–30 moieties, and more recently fluorobenzyl31 and pyrazole moieties.32 In this context, silyl ligands bearing electron-withdrawing N-heterocyclic substituents such as N-pyrrolyl or N-indolyl represent an attractive yet undereveloped ligand class, with only a handful of representatives known to date.33

The three classical approaches for the synthesis of silanides are deprotonation of an Si−H bond, nucleophilic cleavage of a Si−Si bond with an alkoxide, and reduction of (1) a silicon-halogen, (2) a disilane, or (3) a Si−Ar bond.27,30,32,34 Relatively harsh reaction conditions are possible side reactions, e.g., substitution at Si by strong bases limit the scope of these reactions. Therefore, many compounds containing metal–silicon bonds are not prepared by coordination of a free silanide but rather by oxidative addition of an Si−H bond to a reduced metal precursor.38–40 In particular, the only tris(N-pyrrolyl)silyl complexes known prior to this work have been synthesized by oxidative addition of tris(N-pyrrolyl)silane...
been used for simple silyl group transformations on Ni46 and IR spectroscopy. The electronic properties can be incorporated around silicon in this way, and we characterize the corresponding neutral Fe(II) hydride (\( \text{Cl}_3\text{Si} \text{Fe}\text{Cp}(\text{CO})_2 \)) for penta-tertiary amines to obtain \( \text{trans-Cl}\text{Pt}(\text{PET})_2\text{SiH}_2\text{NMMe}_2 \), this methodology was previously applied to the exchange of Cl on \( \text{Cp}(\text{CO})_2\text{Fe}\text{SiCl}_3 \) (FpSiCl3) for pentafluorophenyl43 and amido (\( \text{R'N} \))44,45 substituents (Scheme 1). It has also been used for simple silyl group transformations on Ni46 and other group 6–8 transition metals.46–54

### RESULTS AND DISCUSSION

#### Nucleophilic Substitution

Here we investigate the synthesis of a range of unusual silyl ligands incorporating pyrrolyl and indolyl substituents by nucleophilic substitution on the Fe-bound SiCl3 fragment. Constructing complex silyl ligands in the coordination sphere of the metal avoids the intermediacy of hydrosilanes—which can be subject to undesired rearrangements55 and reactive silanides. We show that such substitution reactions are possible both on the neutral Fe(II) complex \( \text{Cl}_3\text{Si} \text{Fe}\text{Cp}(\text{CO})_2 \) (1) and on the Fe(0) anion \( \text{Cl}_3\text{Si} \text{Fe}\text{Cp}(\text{CO})_2^- \) (2), the latter being conveniently generated by deprotonation of the corresponding neutral Fe(II) hydride (3, Chart 1). Steric bulk can be incorporated around silicon in this way, and we characterize two more complex reactions occurring with multidentate nucleophiles to form cyclic silyl derivatives. The electronic properties of the obtained silyl ligands are discussed on the basis of NMR and IR spectroscopy.

#### Chart 1. Chlorosilyl Iron Complexes Used as Precursors for Nucleophilic Substitution

Scheme 1. Nucleophilic Substitution of \( \text{Cl}^- \) with \( \text{C}_6\text{F}_5\text{N}^- \) and \( \text{R'}\text{N}^- \) in \( \text{(Cl}_3\text{Si})\text{Fe}\text{Cp}(\text{CO})_2 \)

Here we investigate the synthesis of a range of unusual silyl ligands incorporating pyrrolyl and indolyl substituents by nucleophilic substitution on the Fe-bound SiCl3 fragment. Constructing complex silyl ligands in the coordination sphere of the metal avoids the intermediacy of hydrosilanes—which can be subject to undesired rearrangements and reactive silanides. We show that such substitution reactions are possible both on the neutral Fe(II) complex \( \text{Cl}_3\text{Si} \text{Fe}\text{Cp}(\text{CO})_2 \) (1) and on the Fe(0) anion \( \text{Cl}_3\text{Si} \text{Fe}\text{Cp}(\text{CO})_2^- \) (2), the latter being conveniently generated by deprotonation of the corresponding neutral Fe(II) hydride (3, Chart 1). Steric bulk can be incorporated around silicon in this way, and we characterize two more complex reactions occurring with multidentate nucleophiles to form cyclic silyl derivatives. The electronic properties of the obtained silyl ligands are discussed on the basis of NMR and IR spectroscopy.

#### Scheme 2. Nucleophilic Substitution of Chloride with Pyrrolide on Compound 1

#### Scheme 3. Nucleophilic Substitution of Chloride with Pyrrolide on the Iron Tetracarbonyl Complex

393.9943 au, calc’d \( m/\zeta = 393.9947 \) au. The absence of an Fe–H resonance in the \( ^1\text{H} \) NMR spectrum indicates that deprotonation has taken place, i.e. the fourth equiv of pyrrolide functions as a sacrificial base for deprotonation of 3 to Na-2. Additionally, the disappearance of the three distinct \( ^{13}\text{C} \) NMR resonances around 200 ppm for 3 and appearance of a single resonance at 217.9 ppm for Na-5 is consistent with the formation of a fluxional 5-coordinate structure with fast axial-equatorial exchange. The independently synthesized ammonium salt \( \text{NET}_{2} \) readily undergoes substitution under the same conditions, showing that nucleophilic substitution is feasible on Cl3Si bound to Fe(0) and may take place after deprotonation of 3. From a practical point of view, however, reactions involving \( \text{NET}_{2} \) are less well-behaved because the counterion is susceptible to Hoffmann degradation, i.e. 1,2-elimination to give \( \text{NET}_{3} \), ethylene, and pyrH.

Crystals of Na-5 suitable for X-ray crystallography were grown by slow diffusion of hexane into a solution of the complex in the presence of benzo-15-crown-5 in THF. The X-ray crystal structure reveals a trigonal bipyramidal (TBP) geometry with the –SiPyr3 moieties in the apical positions, as commonly found for analogous phosphine73 (base stabilized) silylene7,75 and silyl59,95,96 iron tetracarbonyl complexes (Figure 1). The Si–Fe distance in 5 (2.2576(8) Å) is well in between the extremes, close to the mean for silyl and silylene iron
tetracarbonyl complexes (2.1960<sup>86</sup> < Si–Fe < 2.3630<sup>93</sup> Å) and more generally, of Si–Fe bonds. The single precedent of a structurally characterized pyrSi-containing complex is Os(SiPyr<sub>3</sub>)<sub>2</sub>(CO)<sub>4</sub>(Ph<sub>3</sub>P)·H<sub>2</sub>O reported by Hübler et al.<sup>11</sup> In this complex, both the N–Si–N angles and the Si–M distance are very similar to those in Na–S (see ESI Table S1). The difference in Si–M distance between the two complexes (0.117 Å) is the same as the difference in covalent radius of iron and osmium (0.12 Å).<sup>97</sup>

The generality of this substitution for other monodentate heterocycles was investigated. The substitution of chloride with the bulkier 2-mesitylpyrrolide (right) on 1 afforded the trisubstituted 6 (Scheme 4), as indicated by a 3:1 ratio of the 1<sup>H</sup> NMR resonance integrals of MI with those of the Cp ligand. In contrast, substitution of chloride with the bulkier 2-mesitylpyrrolide (MP) on 1 affords the disubstituted 7 (Scheme 4), the structure of which was further confirmed by X-ray crystal structure determination (Figure 2). The solid-state structure reveals a piano-stool complex with the silyl ligand as one of the legs. Compared to Na–S, the Si–Fe distance is slightly longer (Δd = 0.0145(13) Å) and the angle sum of the substituents on silicon is significantly bigger (314.21(19) vs 303.58(18)<sup>°</sup>). In solution, compound 7 exhibits three 1<sup>H</sup> NMR resonances in a 1:1:1 ratio for the individual methyl-groups on the equivalent mesityl moieties, arising from slow rotation around the C<sub>aryl</sub>–C<sub>pyr</sub> bonds. The energy barriers for interchanging the methyl groups through rotation around the Si–Fe bond and the C<sub>aryl</sub>–C<sub>pyr</sub> bonds were calculated in the gas phase by DFT potential energy surface scan (PES) calculations (see ESI Figures S1–S4).<sup>38</sup> These calculations show a maximum energy difference of about 8 kcal/mol upon 360° rotation around the Si–Fe bond and of at least 33 kcal/mol upon 180° rotation around either C<sub>aryl</sub>–C<sub>pyr</sub> bond. This corroborates the interpretation of the NMR spectrum in terms of a fast rotation around the Si–Fe bond, rendering the mesityl groups equivalent on the NMR timescale, with magnetically inequivalent methyl groups within a mesityl moiety.

The series of complexes described herein provides an opportunity to study the effect of substitution on the properties of silyl ligands (Table 1). Formal substitution of three chlorides in compound 1 with three pyrrolyls in 4 results in a slight shift of the IR bands £(CO) and £(CO) to lower energies by 12 and 15 cm<sup>−1</sup>, respectively, indicating that the pyrSi– ligand is slightly more electron donating than the ClSi– analogue. Similarly, the three IR bands associated with CO stretch modes of the Fe(CO)<sub>4</sub> moiety shift slightly from 2026, 2041, and 1917 cm<sup>−1</sup> in the ClSi– complex 2 to 2019, 1934, and 1906 cm<sup>−1</sup> in the PyrSi– complex 5. The IR absorptions in the tris(3-methylindolyl)silyl complex 6 are within 1 cm<sup>−1</sup> of those of the tris-pyrylolsilyl complex 4, indicating that the net electronegativity of pyr and MI is virtually the same. The £(CO) bands of the dipyrrolyl, monochloro complex 7 (2027, 1977 cm<sup>−1</sup>) are found between those of 1 (2033, 1985 cm<sup>−1</sup>) and 4 (2021, 1970 cm<sup>−1</sup>), consistent with intermediate electronic properties between ClSi– and PyrSi–. More generally, the heterocyclic silyl ligands in 4, 6, and 7 are less donating than Ph<sub>3</sub>Si– and Me<sub>3</sub>Si– (2001, 1994 cm<sup>−1</sup>, respectively) and more donating than (C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>Si– (2047, 2057 cm<sup>−1</sup>, respectively) in the corresponding CpFe(CO)<sub>2</sub> complexes (Figure 3).

As was observed from the effect on £(CO), substitution of chloride with pyrrolyls increases the overall donor strength of the ligand, which generally arises from a combination of increased σ-basicity and/or decreased π-acidity. Interestingly, the stronger donor PyrSiCl displays a longer Si–Fe(CO)<sub>4</sub> bond in compound Na–S than ClSi in 2 by 0.021(3) Å. This lengthening indicates a slightly weaker bond, suggesting that π-acidity is important to the Fe–Si bonding in this series of compounds.

The sum of the R–Si–R substituent angles around silicon is found to be less sensitive to the electronegativity of the substituent. Generally speaking, these angles provide a measure for...
the extent of hybridization of the bonding orbitals: smaller R–Si–R angles indicate more p-character in the Si–R bonding orbitals and consequently more s-character in the Si–M bonding orbital, according to Bent’s rule.99 In the ideal case, the sum of angles is 328.5° for sp³ hybridization and 270° for the nonhybridized extreme. The sums of the E–Si–E angles in Na-5 (303.58(18)°) and 2 (304.8(2)°) are virtually equal but significantly lower than that of the C–Si–C angles in Me₃SiFe(CO)₄ (310.8(15)°), indicating that electron withdrawing substituents on silicon result in a higher s-character of the σ-bonding orbital. Interestingly, the angles between the substituents on silicon in Fp-based 4 are slightly larger (103–106°) than those in Fe(CO)₄-based Na-5 (100–103°), suggesting more p-character in the Si–M bonding orbitals and, hence, a less ionic Si–M bond, likely because of the stronger electron-accepting character of the Fe(II) fragment compared to the Fe(0) fragment in Na-5.

The ²⁹Si NMR signals in Table 1 generally shift toward high field upon substitution of chloride with pyrrolide. Interestingly, the high-field shift observed upon trisubstitution is almost identical on the Fp and Fe(CO)₄ fragments: 24 ppm difference between 1 and 4 vs 23 ppm difference between 2 and 5. However, the series of Fp complexes (4, 6, 7) exhibit no straightforward correlation with the donor strength of the ligand: the difference in chemical shift between trisubstituted 4 and disubstituted 7 (Δδ = 3.5 ppm) is smaller than that between 4 and the tris-indolyl substituted 6 (Δδ = 6.7 ppm), whereas 4 and 6 exhibit indistinguishable donor properties according to 〈ɛ(CO)〉. Such nonlinearity was also observed by Leis et al.79 for a range of HMPA stabilized silylene metal carbonyl complexes (M = Fe, Cr, Ru; R in SiR₂ = tBuO, tBuS, Me, Cl, 1-AdaO, 2-AdaO, NeopO, TritO, Ph). This behavior has been attributed to a combined influence of diamagnetic and paramagnetic effects on the silicon shift.100

Overall, the spectroscopic data consistently indicate that pyrrolide and indolide substituents on silicon are electron withdrawing, only slightly less so than chloride, resulting in moderately donating silyl groups. Furthermore, their effect on the electronic properties of the silyl ligand is approximately the same for an anionic Fe(0) and a neutral Fe(II) supporting metal. This suggests that such heterocycles might be used to construct tunable analogues of the SiCl₄ ligand by varying the substitution patterns on the heterocycles.

## MULTIDENTATE N-DONORS

Having established the substitution at silicon for simple pyrrolide derivatives, the reactivity of multidentate nucleophiles was investigated, starting with the trisodium salt of tris(3-methylindol-2-yl)methane (tmimNa₃, 8, Scheme 5). The tmim scaffold has previously been shown to form stable phosphine ligands that can be bound to Fe(CO)₄.73 Additionally, we recently showed that the tmim³⁻ trianion can fully substitute the Si(II) center in (Idipp)SiCl₄ (Idipp = 2,3-dihydro-1,3-bis(2,6-diisopropylphenyl)-1H-imidazol-2-ylidene) to form the naked silanide (tmim)Si.³³ Scaffold tmimH₃ was synthesized according to the literature procedure,101 followed by deprotonation using NaH. The reaction of 8 with NEt₄-2 was initially conducted in THF at 60 °C. Under these conditions, the targeted trisubstitution product could not be detected. In contrast, analysis of the reaction mixture by ESI-MS indicates the presence of an anionic complex incorporating three additional THF molecules at M⁻ = 812.2437 au (Figure 4).

![Scheme 5. Nucleophilic Substitution of Chloride and Incorporation of THF on 2](image)

Interestingly, signals corresponding to the incorporation of one or two THF molecules were not observed, whereas the unsubstituted complex is still present, suggesting that the second and third incorporation of THF are much faster than the first. The corresponding product could unfortunately not be fully isolated but could be sufficiently enriched to a purity of approximately 70% to be analyzed by multinuclear NMR (vide infra), confirming its identity as the product of triple ring-opening and insertion of THF, compound 9 (Scheme 5). In other solvents, the reaction of NEt₄-2 and 8 gave unresolved complex mixtures. Additionally, reaction between the neutral precursor 1 and 8 afforded an intractable mixture of products.

The tmim moiety of crude product 9 in CD₃CN gives rise to four resonances in ¹H NMR for the aromatic protons, indicating local 3-fold symmetry (see Supporting Information Figure S15). Furthermore, the spectrum of the reaction mixture of 9 displays four multiplet signals at δ = 3.66, 3.73, 4.00, and 4.10 ppm which couple in HMQC with two signals in ¹³C NMR at 44.5 and 61.9 ppm, originating from the diastereotopic protons of C–CH₂ and O–CH₂. An additional set of three multiplets with a 1:2:1 ratio at δ = 1.60, 1.77, and 2.34 ppm, corresponding to four protons, and coupling with two signals in ¹³C NMR at 29.1 and 30.7 ppm, originates from the central CH₂ moieties.

We propose that 9 forms through a ring-opening reaction of THF by nucleophilic attack of 8 on the THF α-carbon, presumably preceded by coordination of THF to silicon, making its α-carbon more prone to nucleophilic attack. A related ring opening and incorporation of THF has previously been observed by Okazaki et al.¹⁰² in the reaction between C(SiMe₂)₂NR₂ and the Fp-anion to form Fp(CH₂)₄OSiMe₂NR₂. They explain this by initial coordination of THF to the silane, followed by nucleophilic attack of F⁻ on the α-carbon. Similarly, Dufour et al.¹⁰⁰ observed ring opening and incorporation of THF in a reaction between the chlorosiilyliron complex

![Figure 4. ESI-MS of 9 in THF after reaction for 65 h at 60 °C in THF, calculated (top), experimental (bottom). Insets: enlarged isotope patterns of the designated peaks.](image)
ClSiR₂F₀₆ (R₂ = –CH₂CH = CHCH₂–) and the Fp anion, resulting in a FpSiR₂O(CH₂)₄F₀₆ complex. They suggest substitution of chloride in FpSiR₂Cl with THF to give an oxonium species followed by nucleophilic attack of Fp⁺ on the α-carbon. The transformation of 8 to 9 shows that multiple insertions are also possible with a suitable multidentate organic nucleophile.

Finally, the monoanionic bidentate iminopyrrolide substituent DippIMP was investigated as a nucleophile (Scheme 6).

Scheme 6. Reaction of DippIMP with 1 in THF at –78 °C → r.t., Including Proposed Reaction Pathway

As the imine functionality in DippIMP is susceptible to intramolecular hydrosilylation, the corresponding hydrosilanes are unsuitable precursors for silyl complexes via either deprotonation or oxidative addition. DippIMPH was synthesized according to the literature procedure, followed by deprotonation using NaHMDS. Reaction of either two or three equiv of DippIMPNa with 1 formed the same compound 10, while reaction of 1 equiv of DippIMPNa with 1 afforded a mixture of compounds containing both 1 and 10. The ²⁹Si NMR resonance of 10 is found at δ = 39.4 ppm, similar to complexes 4, 6, and 7 (Table 1), consistent with substitution at Si taking place. ¹H NMR analysis of 10 indicates that two DippIMP molecules have been incorporated and that the reaction is more complex than simple disubstitution at silicon. The ¹H NMR spectrum displays five distinct signals for the pyrrole moieties. A COSY spectrum indicates the presence of two distinct pyrrole rings, one with a 3H spin system (J(H,H) = 2.8 Hz, J(H,H) = 1.3 Hz) and one with a 2H spin system (broad singlets). The weak coupling in the latter suggests at least J(H,H)-coupling between them. Moreover, both spin systems are in a 1:1 ratio with the Cp group, indicating the presence of 2 pyrrole moieties for one metal center. Interestingly, the presence of a resonance at δ = 9.63 ppm suggests that the product contains an N–H bond. Finally, a singlet resonance in ¹H NMR at δ = 5.75 ppm accounting for 1H and coupling with an sp³-carbon at δ = 61.9 ppm indicates the presence of an sp³–CH₃ fragment. The data outlined above collectively support the assignment of 10 as the C–C coupled structure depicted in Scheme 6. The ipr residues give rise to 3 septets in a 1:1:2 ratio and 5 doublets in a 1:1:1:1:4 ratio, suggesting hindered rotation around the Cₙimine–Nₐimin bond and free rotation around the Cₐimin–Nₐimin bond. In ¹³C NMR two resonances appear for the carbonyl carbons, which suggests that the substituent is bound to silicon in a bidentate fashion, rendering the silicon atom chiral and hence the carbonyls diastereotopic. The structure inferred from NMR was confirmed by the crystal structure (Figure 5). Crystals suitable for X-ray crystallography were grown by slow diffusion of hexane into a THF solution. The N–Si distance is smaller for the former imine (N21–Si) than for the pyrrole substituent (N11–Si), likely due to hyperconjugation of the N21 lone pair into Si, as opposed to N11, where the lone pair is delocalized in the aromatic system. The sum of E–Si–E angles (304.44(13))° is small compared to 7, due to the 5-membered ring system. As a result, the amount of s-character in the Si–Fe bond is higher, resulting in a shorter distance (10: 2.2456(7), 7: 2.2721(10) Å).

The formation of complex 10 is consistent with initial substitution of two chlorides by one DippIMP, forming an overall cationic complex bearing an iminopyrrolide chlorosilyl benzene ligand (Scheme 6). Activation of the imine through coordination to the electron-poor silicon would then facilitate nucleophilic attack of a second DippIMP anion. The preference for the 4-position is likely sterically driven. The formation of 10 is kinetically competitive with that of the intermediate, preventing isolation of the latter.

**CONCLUSIONS**

A series of unusual silyl-iron complexes with N-heterocyclic substituents was synthesized by nucleophilic substitution of the chlorides of a metal-bound trichlorosilyl ligand. This method affords homoleptic silyl ligands with unencumbered substituents such as pyrrol-1-yl (pyr, Si–) and 3-methylindol-1-yl ((M1),Si–), and the heteroleptic silyl ligand (MP)_₂ClSi– with the bulkier 2-mesitylpyrrol-1-yl. The ligands were found to be slightly more electron-donating than Cl, Si–, which makes them moderately electron donating and electronically and sterically tunable. Attempts to expand this methodology to multidentate nucleophiles (tmim, DippIMP) led to more complex reactivity pathways. These results demonstrate that on-metal synthesis can be applied to the preparation of silyl ligands of increased complexity, allowing for fine-tuning of their steric and electronic properties.

**EXPERIMENTAL SECTION**

All reactions involving silicon-containing compounds were conducted under an N₂ atmosphere by using standard glovebox or Schlenk techniques. Diethyl ether, n-hexane, toluene, and acetone were dried with an MBRAUN MB SPS-79 system, degassed by bubbling
with N₂ for 30 min, and stored over molecular sieves in a glovebox. THF was distilled from benzophenone/Na, degassed by bubbling with N₂ for 30 min, and stored over molecular sieves in a glovebox. All chemicals were obtained commercially and used as received unless stated otherwise. All NMR chemical shifts are reported relative to TMS with the residual solvent signal as internal standard. All NMR experiments involving silicon-containing compounds were conducted in J-Young NMR tubes under an N₂ atmosphere. IR spectra were recorded on a PerkinElmer Spectrum Two FT-IR spectrometer. ESI-MS measurements were performed on a Waters LCT Premier XE KE317 spectrometer. Elemental analysis was conducted by the Mikroanalytisches Laboratorium Kolbe. Ph₂PCl₂ was dried according to the method described in purification of laboratory chemicals. The following compounds were synthesized according to literature procedures: Cl₆SiFe(CO)₃, Cl₅SiFe(CO)₄, Cl₄SiFe(CO)₅, Cl₃SiFe(CO)₆, Cl₂SiFe(CO)₇, ClSiFe(CO)₈, (SiMe₃)₃Al, and toluene (1 mL) and the solution added to the mixture, which was allowed to warm to r.t. over 20 h. The solvent was evaporated, toluene (2 mL) was added to the residue, and the solvent was evaporated again to remove most of the residual THF. The mixture was extracted with toluene (2 × 2 mL) and the solvent was removed in vacuo. Analytically pure material (44 mg, 0.11 mmol, 87%) was obtained by precipitation from toluene (2 mL) with hexane (12 mL), storage at −35 °C for 2 h and removal of the supernatant. H NMR (400 MHz, CD₅C₅, 25 °C) δ = 6.80 (t, J(H,H) = 2.0 Hz, J(H,C) = 2.0 Hz), 2H, Ar-C), 2.04 ppm (s, 6H, Ar-C); ²⁹Si NMR (79 MHz, CD₅C₅, 25 °C) δ = 39.1 ppm; IR (THF): ν = 2100, 1970 cm⁻¹. Anal. Calc’d C₂₃H₂₃FeN₃O₄Si: C 68.57, H 4.91, N 7.06%; found C 68.22, H 2.57, N 6.74%.

### Synthesis of [(IM)₃SiCl]Fe(CO)₂ (IM = 3-methylindolyl). 6.
A precooled THF (1 mL) solution of IM (52 mg, 0.17 mmol) was added to a precooled THF (4 mL) solution of sodium 3-methylindolide (M₆N, 111 mg, 0.500 mmol) at −78 °C. The flask was rinsed with THF (1 mL) and the solution added to the mixture, which was allowed to warm to r.t. and stirred for 20 h. The solvent was evaporated, toluene (2 mL) was added to the residue, and the solvent was evaporated again to remove most of the residual THF. The mixture was extracted with toluene (2 × 2 mL) and the solvent was removed in vacuo. ¹H NMR (400 MHz, CD₅C₅, 25 °C): δ = 7.54 (ddd, J(H,H) = 7.8 Hz, J(H,I) = 1.3 Hz, J(H,F) = 0.8 Hz, 3H, indole-H7), 7.46 (dt, J(H,H) = 8.3 Hz, 3J(H,F) = 0.9 Hz, 3H, indole-H4), 7.19 (q, J(H,H) = 7.0 Hz, J(H,F) = 1.0 Hz, 3H, indole-H2), 7.10 (ddd, J(H,H) = 7.9 Hz, J(H,F) = 7.1 Hz, J(H,I) = 1.0 Hz, 3H, indole-H6), 6.98 (ddd, J(H,H) = 8.4 Hz, J(H,F) = 7.1 Hz, J(H,I) = 1.3 Hz, 3H, indole-H5), 3.79 (s, 9H, Cp), 2.81 ppm (d, J(H,H) = 1.2 Hz, 9H, CH₃). ¹³C NMR (100 MHz, CD₅C₅, 25 °C): δ = 213.5 (CO), 141.0, 133.2, 128.2, 121.1, 119.6, 115.8, 115.1, 84.9 (Cp), 10.0 ppm (CH₃); ²⁹Si NMR (79 MHz, CD₅C₅, 25 °C) δ = 32.4 ppm; IR (THF): ν = 2020, 1969 cm⁻¹; Anal. Calc’d C₂₃H₂₃FeN₃O₄Si: C 68.57, H 4.91, N 7.06%; found C 68.22, H 2.57, N 6.74%.

### Synthesis of [(MP)₃SiCl]Fe(CO)₂ (MP = 2-mesitylpyrrolidyl). 7.
A precooled THF (1 mL) solution of IM (72 mg, 0.23 mmol) was added to a precooled THF (4 mL) solution of sodium 2-mesitylpyrrolidide (M₆P, 96 mg, 0.46 mmol) at −78 °C. The flask was rinsed with THF (1 mL) and the solution added to the mixture, which was allowed to warm to r.t. over 20 h. The solvent was evaporated, toluene (1 mL) was added to the residue, and the solvent was evaporated again to remove most of the residual THF. The mixture was extracted with toluene (2 × 2 mL) and the solvent was removed in vacuo. Analytically pure material (85 mg, 0.14 mmol, 60%) was obtained by trituration of the solid with hexane (2 × 1 mL). Crystals suitable for X-ray crystallography were grown by slow diffusion of hexane into a concentrated solution of S in THF in the presence of benzo-15-crown-5. H NMR (400 MHz, CD₅C₅, 25 °C): δ = 7.13 (t, J(H,H) = 2.0 Hz, J(H,C) = 2.0 Hz, 6H, pyrrole-H5), 6.36 ppm (t, J(H,H) = 2.0 Hz, J(H,C) = 2.0 Hz, 6H, pyrrole-H3); ¹³C NMR (101 MHz, CD₅C₅ + C₆H₆, 25 °C) δ = 217.9 (CO), 125.5 (pyrrole), 110.5 ppm (pyrrole); ²⁹Si NMR (79 MHz, CD₂Cl₂, 25 °C) δ = 45.0 ppm; ESI-MS: M⁺: m/z = 393.9943 au, calc’d m/z = 393.9947 au; IR (THF): ν = 2019m, 1946s, 1906 cm⁻¹. The presence of solvation THF in the solid hampered the determination of anal., which was therefore determined on the crystallized (benzo-15-crown-5)-Na salt: Anal. Calc’d C₂₃H₂₃FeN₃O₄Si·Na: C 55.41, H 5.50, N 4.41%; found C 55.12, H 5.61, N 4.51%.

### X-Ray Crystal Structure Determination of Na₅·[(C₆H₅)₆O₄]₃·[C₆H₅Fe(N₃)₂]: [C₆H₅Fe(N₃)₂]F, Fw = 953.81, colorless needle, 0.40 × 0.10 × 0.06 mm, monoclinic, P2₁/c (no. 14), a = 14.3159(8), b = 10.3810(4), c = 30.8666(18), β = 90.911(1), V = 4545.0(6) Å³, Z = 4, Dₖ = 1.394 g/cm³, μ = 0.44 mm⁻¹. The diffraction experiment was performed on a Bruker Kappa Apex II diffractometer with sealed tube and Triphotomonochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/2θ)max = 0.65 Å⁻¹. The crystal appeared to be twinned with a 2-fold rotation about hkl=(0,0,1) as twin operation. Consequently, two orientation matrices were used for the integration with the Eval15 software. This resulted in a total of 90621 measured reflections. A multiscan absorption correction and scaling was performed with TWINABS (correction range 0.53–0.75). 10544 Reflections were unique (Rint = 0.076), of which 8267 were observed [I > 2σ(I)]. The structure was solved with Patterson superposition methods using SHELXTL. 724 independent reflections were observed with SHELXL-2014. All structure factor calculations were performed with the SHELXL program.
(sin $\theta$)/$\lambda_{\text{max}}$ = 0.65 Å$^{-1}$. The Eval1S software$^{110}$ was used for the intensity integration. A multiscan absorption correction and scaling was performed with SADABS$^{111}$ (correction range 0.61–0.75). 6750 Reflections were unique ($R_{e,\text{ex}}$ = 0.081), of which 3828 were observed ($1 > 2\sigma(I)$). The structure was solved with Patterson superposition methods using SHELXT.$^{112}$ Least-squares refinement was performed with SHELXL-2014$^{113}$ against F2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model.$^{367}$ Parameters were refined with no restraints. R1/wR2 [1 > 2σ(I)]: 0.0529/0.1085. R1/wR2 [all refl.]: 0.1177/0.1311. S = 1.010. Residual electron density between −0.30 and 0.57 eÅ$^{-3}$. Geometry calculations and checking for higher symmetry was performed with the PLATON program.$^{114}$

**Synthesis of (tmim)Na$_3$ (Na-8).** A solution of 8 (4.95 g, 12.3 mmol) in THF (10 mL) was added to prewashed (hexane 3 × 5 mL and THF 5 mL) NaH (60% in oil, 2.07 g, 52 mmol) under THF (101 MHz, CD$_3$CN, 25 °C) to obtain Na-8 (4.18 g, 82%).$^{115}$ The solution was added to the mixture, which was allowed to warm to r.t. Evaporation of the solvent in vacuo, titration with hexane, and drying in vacuo yielded the product (10 mg, 13 mmol, 35%)$^{110}$ in 96% purity.

**Synthesis of (tmim)Na (Na-9).** A solution of 766 mg, 3.01 mmol) was added to a precooled THF (1 mL) solution of NaH (60% in oil, 12.1 mg, 0.30 mmol) in THF (10 mL) at 0 °C. Filtration, and the orange (green luminescent) solid was washed with hexane (3 × 5 mL and THF 5 mL) NaH (60% in oil, 2.07 g, 52 mmol) under THF (101 MHz, CD$_3$CN, 25 °C) to yield Na-9 (4.18 g, 82%).$^{115}$ The solution was added to the mixture, which was allowed to warm to r.t. Evaporation of the solvent in vacuo, titration with hexane, and drying in vacuo yielded the product (10 mg, 13 mmol, 35%) in 96% purity.

**Synthesis of (tmim)Na 3 (Na-8).** A solution of 8 (4.95 g, 12.3 mmol) in THF (10 mL) was added to prewashed (hexane 3 × 5 mL and THF 5 mL) NaH (60% in oil, 2.07 g, 52 mmol) under THF (10 mL) over 15 min and stirred for 2.7 h. The excess NaH was removed by filtration, and the orange (green luminescent) filtrate was freed of solvent in vacuo, yielding a yellow powder (8.46 g, quantitative). Analysis by $^{1}$H NMR showed only (tmim)Na$_3$ and THF (−30 w%). A titration with HCl (0.1 M in H$_2$O) on a sample (100.4 mg) in a mixture of THF (4 mL) and water (1 mL) was performed to determine the base content, which was consistent with 8.4 w% (tmim)Na$_3$. This value was used for stoichiometry calculations in subsequent experiments.$^{115}$ $^{1}$H NMR (400 MHz, CD$_3$CN, 25 °C): δ = 7.19 (m, 6H, ArH), 6.62 (m, 6H, ArH), 6.25 (s, 1H, R$_3$CH), 2.41 ppm (s, 9H, CH$_3$).$^{116}$ 11138 Re fl. was performed with SHELXT.$^{111}$ Least-squares refinement was performed with SHELXL-2014$^{113}$ against F2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model.$^{367}$ Parameters were refined with no restraints. R1/wR2 [1 > 2σ(I)]: 0.0529/0.1085. R1/wR2 [all refl.]: 0.1177/0.1311. S = 1.010. Residual electron density between −0.30 and 0.57 eÅ$^{-3}$. Geometry calculations and checking for higher symmetry was performed with the PLATON program.$^{114}$
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