Reactivity of a Unique Si(I)-Si(I)-Based η2-Bis(silylene) Iron Complex

He, Z.; Liu, L.; De Zwart, F.J.; Xue, X.; Ehlers, A.W.; Yan, K.; Demeshko, S.; van der Vlugt, J.I.; de Bruin, B.; Krogman, J.

DOI
10.1021/acs.inorgchem.2c01369

Publication date
2022

Document Version
Final published version

Published in
Inorganic Chemistry

License
CC BY

Citation for published version (APA):
Reactivity of a Unique Si(I)−Si(I)-Based η²-Bis(silylene) Iron Complex

Zhiyuan He, Lingyu Liu, Felix J. de Zwart, Xiaolian Xue, Andreas W. Ehlers, KaKing Yan, Serhiy Demeshko, Jarl Ivar van der Vlugt, Bas de Bruin, and Jeremy Krogman

ABSTRACT: In this paper, we report the synthesis of a unique silicon(I)-based metallosilirane and report on its reactivity toward TMS-azide and benzophenone. Metal complexes containing disilylenes (bis)silylenes with a Si−Si bond) are known, but direct ligation of the Si(I) centers to transition metals always generated dinuclear species. To overcome this problem, we targeted the formation of a mononuclear iron(0)−silicon(I)-based disilylene complex via templated synthesis, starting with ligation of two Si(II) centers to iron(II), followed by a two-step reduction. The DFT structure of the resulting η²-disilylene-iron complex reveals metal-to-silicon π-back donation and a delocalized three-center−two-electron (3c−2e) aromatic system. The Si(I)−Si(I) bond displays unusual but well-defined reactivity. With TMS-azide, both the initial azide adduct and the follow-up four-membered nitrene complex could be isolated. Reaction with benzophenone led to selective 1,4-addition into the Si−Si bond. This work reveals that selective reactions of Si(I)−Si(I) bonds are made possible by metal ligation.

INTRODUCTION

Transition metal silylene complexes (Scheme 1a) have attracted significant interest as they have shown interesting electronic structures and reactivity, giving rise to synthetic and catalytic applications that differ significantly from transition metal carbene complexes. Several variants of transition metal silylene complexes have been reported, varying in the oxidation state of the silicon atom and the types of substituents, and among those variants, N-heterocyclic silylenes have been studied most extensively.

Two types of the general class of bis(silylene) compounds have been reported: (1) “bis(silylenes) with a direct Si−Si bond”, wherein the two divalent silicon atoms are adjacent to each other and are connected by a central Si−Si bond (like others in the field, we term these “disilylenes”); (2) “spacer-separated bis(silylenes)”, with the two divalent silicon atoms separated by a spacer. Driess and co-workers recently reported a ferrocene-separated bis(silylene) acting as a bidentate ligand in catalytically active mono- and dicobalt complexes (Scheme 1b).

We consider “disilylenes” to be particularly interesting due to the potential reactivity associated with their Si−Si bond. Compound I, with each Si center bearing an amidinate ligand (Scheme 2), was synthesized by Roesky and co-workers, while Jones et al. reported a bulkier derivative thereof. Additionally, “disilylenes” that are stabilized by an N-heterocyclic carbene (NHC) or an intramolecular phosphine are also reported. Targeting the synthesis of η²-coordinated Si(I)-based “disilylene” complexes seems particularly useful because the altered electronic structure and the lability of the Si−Si bond induced

Received: April 25, 2022
Published: July 20, 2022
Scheme 2. (a) Reported Di- and Multinuclear Disilylene Transition Metal Complexes; (b) Synthesis and Reactivity of a Mononuclear $\eta^6$-Disilylene Iron Complex (This Work)

a. Known Metal Complexes from Coordination to Si(II)-based disilylene

\[ \text{Fe} \quad \text{Rh} \quad \text{Ir} \]

2015

b. This work: $\eta^6$-disilylene Complex Formation by Synthesis-at-the-metal.

Si–Si bond acting as a $\pi$-acceptor moiety, while the three-membered Fe–Si–Si ring shows $2\pi$-aromaticity. It also displays selective Si–Si bond-centered reactivity toward azide activation and ketone addition, giving access to new “spacer-separated bis(silylenes)”.

## RESULTS AND DISCUSSION

### Synthesis of 3.

The amidinate-stabilized silylene iron-halide precursor 1, synthesized from Fe{N(SiMe$_3$)$_2$}$_2$ using a literature procedure,\textsuperscript{10} was characterized with zero-field $^{57}$Fe Mössbauer spectroscopy (Figure 1). The isomer shift $\delta$ (0.61 m/s) and the quadrupole splitting $\Delta E_Q$ (2.81 mm/s) are in agreement with a four-coordinated Fe(II) center.\textsuperscript{11}

Iron-centered reduction of this well-defined Fe(II) species with a slight excess of KC$_8$ in a benzene-THF mixture (1:1 v/v%) generated bis-silylene compound 2, featuring an $\eta^6$-benzene fragment bound to Fe(0).

The $^1$H NMR spectrum of diamagnetic 2 in deuterated benzene exhibits a chemical shift for the $\eta^6$-benzene fragment at $\delta$ 5.15 ppm, which is similar to that seen for the previously reported zero-valent iron complex [(SiFeSi)Fe-$\eta^6$(C$_6$H$_6$)] bearing a ferrocene-bridged bis(silylene) ligand ($\delta$ 5.16 ppm).\textsuperscript{12} The $^{29}$Si NMR spectrum of 2 exhibits two sharp singlets at $\delta$ 45.12 and 42.45 ppm (suggesting chemically inequivalent Si centers), which are close to the reported chemical shift ($\delta$ 43.10 ppm) for an N-heterocyclic silylene iron(0) complex.\textsuperscript{13} Species 2 was also examined using zero-field $^{57}$Fe Mössbauer spectroscopy to confirm the oxidation state of Fe (Figure 1). Indeed, both the isomer shift $\delta$ (0.38 m/s) and quadrupole splitting $\Delta E_Q$ (1.53 mm/s) support reduction to Fe(0).\textsuperscript{14}

Single crystals of 2 that were obtained from pentane at $-30^\circ$C proved suitable for crystallographic analysis by X-ray diffraction at room temperature; loss of crystallinity was observed at 150 K. The molecular structure (Figure 2) shows two different orientations for the Si–Cl bonds with respect to the Fe($\eta^6$-benzene) fragment (one “up” and one “down”), which explains the presence of two chemically inequivalent Si nuclei in the $^{29}$Si NMR spectrum. The Si–Fe–Si angle is nearly 90° ($91.99^\circ$), and the intramolecular Si1…Si2 distance is 3.100(2) Å. The Si–Fe1 bond lengths are 2.162(2) Å (Si1) and 2.148(1) Å (Si2), which are significantly shorter than the corresponding bond lengths in precursor 1 (∼2.445 Å) and slightly shorter than those found in the zero-valent iron silylene
complexes $[(\text{NHSi})\text{Fe(dmpe)}]_2$ (2.184(2) Å) and Fe(0)-[SiNSi] (2.164(15) and 2.170(13) Å).  

Further reduction of this zero-valent Fe species 2 by an excess of KC$_8$ at room temperature yielded the three-membered metallacyclic complex 3, featuring a direct Si–Si bond (Scheme 3). This reaction was also monitored using $^1$H NMR spectroscopy, revealing quantitative conversion (see also Figure S26). The complex was characterized by multinuclear NMR spectroscopy ($^1$H, $^{13}$C, and $^{29}$Si). The $^1$H NMR signal of the Fe-coordinated $^6$-benzene shifts from $\delta$ 5.15 ppm in 2 to $\delta$ 5.34 ppm in 3. The $^{29}$Si NMR spectrum of 3 contains only one singlet at $\delta$ 34.49 ppm, indicating formation of a symmetric molecule.

Dark red single crystals of 3 were collected after storing a pentane solution at $-30$ °C for 1 month. Compound 3 crystallizes in the monoclinic space group $C_{2v}$/$c$, which is in line with the high degree of symmetry observed in the $^1$H NMR spectrum. The Si(1)–Fe–Si(1) three-membered heterocycle forms an equilateral triangle with interatomic distances of 2.217(6) Å (Figure 3); for the Si–Si bond, this value falls in the range observed for Si–Si double bonds (2.120–2.250 Å).  

The isosceles Si–B–Si disilaborirane compound reported by Roeksy and co-workers shows a Si–Si bond length of 2.188(5) Å, while the equilaterial triangular (di-t-butyl(methyl)silyl)bis(tri-t-butylsilyl)cyclotrisilenylium cation has an average Si–Si bond length of 2.217(3) Å.  

**Electronic Structure of 3.** Given the unprecedented nature of the ferracyclic motif found in this species, the bonding of the Si(1)–Si(1) fragment to iron(0) was theoretically investigated at the TZ2P/OPBE level of theory using energy decomposition analysis (EDA). The lowest energy structure with $C_2$ symmetry is analogous to that derived from X-ray diffraction. To facilitate the EDA analysis (for symmetry reasons), the bonding of the disilylene moiety to iron has been analyzed using a $C_3v$ optimized structure, which is only 4.4 kcal mol$^{-1}$ higher in energy. This small energy difference is consistent with the dynamic behavior observed in solution-state NMR spectroscopy, resulting in a single signal for the $^3$Bu substituents at nitrogen.

The Fe($^6$-benzene) fragment has been computed in the singlet state (Fe(0)-$^g$). It has a two-electron occupied $d_{xz}$ orbital (perpendicular to the Si–Fe–Si plane) and an empty $d_{yz}$ orbital. The electronic structure of the Si(1)–Si(1) fragment is best described as having a Si–Si single bond with a lone pair on each silicon atom and an empty p-orbital perpendicular to that plane (Figure S31). The symmetry-adapted linear combinations of the two lone pairs on silicon donate electron density toward the Fe($^6$-benzene) fragment, forming two (delocalized) $\sigma$-bonds of $-30.3$ kcal mol$^{-1}$ (A1) and $-74.4$ kcal mol$^{-1}$ (B1). The iron itself donates electron density back from the occupied $d_{xz}$ orbital into an empty p-orbital formed by the two Si $p_z$ orbitals (B2: $-67.8$ kcal mol$^{-1}$), giving rise to considerable $\pi$-backbonding (Figure 4).

Figure 4. Graphical representation of the Fe-to-(Si–Si) $\pi$-back donation in 3.

To probe the resulting orbital (which is delocalized over the Si–Fe–Si three-membered ring) for aromaticity, we employed the nucleus-independent chemical shift (NICS(0/1)) approach at the B3LYP/6-11+G(d,p) level (negative value of the isotropic magnetic shielding at the center of the Fe–Si–Si three-membered ring and 1 Å perpendicularly above and below, respectively). These are found to be $-47.8$ and $-21.4$ ppm, respectively, corroborating the magnetic aromaticity. For comparison, the NICS(0/1) values at the center of the benzene ring in 3 are calculated to be $-42.8$ and $-18.4$ ppm. Similar values have been reported for other metallacycles. A more refined method by Stanger following the out-of-plane component to the shielding tensor along a trajectory orthogonal to the plane of the ring (NICS$_z$) has been used by Roeksy et al. to assign $\pi$-aromaticity to their disilaborirane species. However, instead of showing the typical off-center minimum for $2\pi$-aromatic systems, the NICS scan of 3 shows a steady and continuous increase to less negative NICS$_z$ values over a value of 3 Å (see Figure S33), which may be caused by anisotropy of the metal center at the ring and/or by $\sigma$-aromaticity.

Therefore, we resorted to the canonical molecular orbital (CMO) analysis of the NICS(0), which separates the total shieldings into contributions from canonical molecular orbitals (C1). Indeed, there is a sizable contribution of $-13.8$ ppm from the Fe $d_{xz}$ orbital (HOMO–5, see Figure S32), which is part of the $\sigma$-framework. More importantly, the major contribution of $-16.6$ ppm originates from the delocalized $\pi$-orbital shown in Figure 4, substantiating the $2\pi$-aromaticity of the Si–Fe three-membered ring in complex 3.

**Reactivity of 3.** The unligated Si(1)-based disilylene species I shows stoichiometry-dependent reactivity toward trimethylsilyl azide, forming either a silazatriene or a silaimine
product.\textsuperscript{24,25} Roesky and co-workers described ring opening of their disilaborirane species VI with TMSN\textsubscript{3}, forming a 1-aza-2,3-disila-4-boretidine derivative (Scheme 4).\textsuperscript{17} We observed

\begin{center}
\textbf{Scheme 4. Synthetic Scheme for the Preparation of Azide Adduct 4 and Final Product 5 upon Reaction of 3 with Trimethylsilyl Azide}
\end{center}

Previous work: Direct nitrene formation by disilylene I.

Previous work: Nitrene incorporation by disilaborirane VI.

This work: Stepwise addition and activation of TMS-azide and nitrene formation using 3.

Inorganic Chemistry

![Image of X-ray structures](image_url)

Selective conversion of 3 with 1 equiv of TMSN\textsubscript{3} to give the unique azide adduct 4 after 1 h at 40 °C in benzene solution. This species was obtained as a single crystalline material by recrystallization from pentane at −30 °C. The molecular structure, as determined by X-ray diffraction, is displayed in Figure 5. It contains a planar four-membered Si-I-Fe-Si heterocycle resulting from the insertion of the azide terminal N-atom in the Si-Si bond, with Fe-Si distance at 80 °C. The two Si-Fe distances are slightly different, 2.1687(6) and 2.1746(7) Å. The intramolecular Si-Si distance is long at 2.504(8) Å.

Prolonged heating of a mixture of 3 with TMSN\textsubscript{3}, or isolated 4 at 80 °C, generated the follow-up trimethyldisilylnitrene complex 5 as the major product, together with small amounts of intermediate 4 (see Figure S17). Single crystals of 5, obtained by recrystallization from benzene at room temperature, were analyzed by X-ray diffraction (Figure 5).

Compound 5 also shows a planar four-membered Si-Fe-Si heterocycle with Fe-Si-N angles of 103(1)° but with a different substitution pattern at N5, i.e., only a TMS group resulting from the insertion of trimethyldisilylnitrene in the Si-Si bond. The two Si-Fe distances are nearly identical, 2.17(4) Å, and so are the Si-Si (1.77(5) Å) bond lengths. The Si-Fe σ-bonds are on average 0.25 Å longer than the Si-N distance in the N-insertion product obtained from disilaborirane,\textsuperscript{18} while the Si-N bond length is similar. The intramolecular Si-Si distance (2.412(2) Å) in 5 is shorter relative to that in 4. Apart from the X-ray crystallographic analysis, reaction monitoring and product identification have also been achieved using NMR spectroscopy. The $^1$H NMR signal of the Fe-bound $\eta^3$-benzene fragment shifts from δ 5.34 ppm (3) to δ 5.26 ppm (4) and 5.12 ppm (5), and the trimethyldisilylnitrene group resulting from the insertion of trimethylsilylnitrene in the reaction mechanism. The initial step involves the nucleophilic attack of the azide onto one of the Si centers, which results in induced nucleophilic character at the second Si center that subsequently attacks the azide in TS1 (Figure 6). As a result, this insertion can be considered to invoke induced FLP reactivity. The energy barrier to afford Int1 (15.4 kcal·mol$^{-1}$) is consistent with the experimentally determined barrier (15.1 kcal·mol$^{-1}$) for formation of 4 (Arrhenius plot, Figure 5). After forming this symmetric azide adduct, the energy barrier for the subsequent dinitrogen release (29.4 kcal·mol$^{-1}$) is high enough to rationalize the successful isolation of 4. Finally, a Staudinger pathway, involving four-membered ring transition state TS3, releases dinitrogen from 4 to afford product 5 (−110 kcal·mol$^{-1}$).

The ambivalent reactivity of the Si(I) centers in the Si-Si bond of 3, able to act either as nucleophile or electrophile, was also apparent during the conversion of species 3 conversion with benzophenone. Disilylene I was previously reported to react with benzophenone to furnish selective C-O cleavage with formation of a cyclodisiloxane (Scheme 5).\textsuperscript{26} Strikingly
different reactivity was observed when complex 3, featuring a “protected” Si–Si bond, was exposed to benzophenone for 1 h at 80 °C. Selective formation of seven-membered ring product 6 was obtained via a formal 1,4-addition of benzophenone, displaying strongly attenuated and controlled reactivity of the Si–Si fragment in complex 3. Complex 6 was characterized in the solid state using single-crystal X-ray diffraction (Figure 7). The structure consists of a nonplanar seven-membered O–Si–Fe–Si–C–C–C ring (angle between the planes O1–C37–C44–C49 and O1–Si1–Fe1–Si2 is 7.20°). The C37–C44 bond length (1.348(5) Å) lies in between that of a typical single carbon bond and a double carbon bond (1.510–1.317 Å). The Si–Fe–Si angle (∠88.21(4)°) is larger than in species 4 and 5 because of increased steric hindrance. One of the phenyl rings has undergone ortho-silylation, concomitant with ring de-aromatization and formation of an enolate-type fragment bound via the oxygen to the second Si center. As a result, overall 1,4-addition of benzophenone has occurred, with no sign of the 1,2-C,O addition product. The 1H NMR signal for the η6-benzene fragment shifts from δ 5.34 ppm (3) to δ 5.07 ppm (6). The C–H hydrogen at the ortho-silylated position resonates at around δ 6.99 ppm according to 2D-COSY NMR spectroscopy, while the other four hydrogens of the de-aromatized ring appear in the range of 4.90–6.20 ppm. The 29Si NMR spectrum of 6 exhibits two sharp singlets at δ...

Figure 6. Computed free energy profile for nitrene formation from trimethylsilyl azide and complex 3 (B3LYP-TZVP and def2-TZVP). Transient bonds in transition states are drawn as dashed lines. The inset shows the Arrhenius plot for the consumption of 3 (for details, see the Supporting Information).

Scheme 5. Synthetic Scheme for the Preparation of 6

Previous work: C–O cleavage of benzophenone by distylene I.

This work: 1,4-dipolar cycloaddition of benzophenone.

Figure 7. X-ray crystal structure of 6 with thermal ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) of 6: Si1–Si2, 3.101(1); Si1–Fe1, 2.146(9); Si2–Fe1, 2.179(9); Si1–O1, 1.688(2); O1–C37, 1.384(3); C37–C44, 1.348(5); C44–C49, 1.503(5); C49–Si2, 1.983(4); Si1–Fe1–Si1, 88.21(4).
CONCLUSIONS

In summary, we have developed an efficient method to synthesize the first example of a mononuclear transition metal complex bearing a ligated Si(I)−Si(I) disilylene fragment, ferrocyclic η3-disilylene complex 3. The electronic structure of this species shows that the Si−Si fragment acts as a four-electron σ-donor to iron, while significant π-back donation from the iron(0) center to the silicon atoms of the disilylene moiety leads to further stabilization of the overall structure. Complex 3 shows well-defined nucleophile-induced FLP reactivity toward TMS-azole and benzophenone, leading to Si−Si bond cleavage by addition of the reagents to the Si2 fragment, generating unexpected four- and seven-membered ring structures. Expanding this unique reactivity to other small molecules is currently being explored within our groups.

EXPERIMENTAL SECTION

Materials and Methods. Unless otherwise stated, all manipulations were performed under a nitrogen atmosphere using Schlenk techniques on a Vigor glovebox maintained at or below 1 ppm of O2 and H2O. All new metal complexes were prepared and handled in the glovebox under a N2 atmosphere. Anhydrous FeCl3 (98%) was purchased from Strem Chemicals. PhC(NBu2)SiCl3,28 LiN(SiMe3)2(Et2O),29 Fe(N(SiMe3)2)2,30 and complex 1 (FeCl2(PhC(NBu2)SiCl3))30 were synthesized according to reported procedures. Other reagents were purchased from J&K Chemical and SCRRC. Glassware was dried at 150 °C overnight. Celite and molecular sieves were dried at 200 °C under vacuum. Benzene, pentane, hexanes, and diethyl ether were degassed with nitrogen, dried over activated molecular sieves, and kept over 4 Å molecular sieves in a N2 atmosphere. Anhydrous FeCl3 (98%) was purchased from Strem Chemicals. PhC(NBu2)SiCl3,28 LiN(SiMe3)2(Et2O),29 Fe(N(SiMe3)2)2,30 and complex 1 (FeCl2(PhC(NBu2)SiCl3))30 were synthesized according to reported procedures. Other reagents were purchased from J&K Chemical and SCRRC. Glassware was dried at 150 °C overnight. Celite and molecular sieves were dried at 200 °C under vacuum. Benzene, pentane, hexanes, and diethyl ether were degassed with nitrogen, dried over activated molecular sieves, and kept over 4 Å molecular sieves in a N2-filled glovebox. NMR data were recorded either on a Bruker 400 or a 500 MHz spectrometer and were internally referenced to residual proton solvent signals in C6D6 (7.16 ppm). Data for 1H NMR are reported as follows: chemical shift (δ ppm) and multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad). IR data were recorded on a Thermo Scientific Nicolet iS5 FTIR, and signal strength is represented as follows: VS = very strong, W = weak, S = strong, VW = very weak, m = middle, w = wide. The UV−Vis spectra were recorded using a StellarNet BLACK Comet C-SR diode array miniature spectrophotometer connected to deuterium and halogen lamp by optical fiber using 1 cm matched quartz cuvettes at room temperature.

Computational Details. Geometries were fully optimized as minima or transition states using the Turbomole program package.31,32

The crystal was kept at 150 K during X-ray Crystallography. Crystals were coated with Paratone-N oil and mounted on a Bruker D8 Venture diffraactometer equipped with an APEX-II CCD diffractometer. The crystal was kept at 150 K during data collection. Using Olex2,30 the structure was solved with the ShelXT31 structure solution program using Intrinsic Phasing and refined with the XL32 refinement package using least squares minimization. CCDC 2157512−2157516 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

 Mössbauer Spectroscopy. Mössbauer spectra were recorded with a 57Co source in a Rh matrix using an alternating constant acceleration Wessel Mössbauer spectrometer operated in transmission mode and equipped with a Janis closed-cycle helium cryostat. Isomer shifts are given relative to the iron metal at ambient temperature. Simulation of the experimental data was performed with the Mfit program (developed by Dr. E. Bill, Max-Planck Institute for Chemical Energy Conversion, Mühlheim/Ruhr, Germany) using Lorentzian line doublings.

Computational Details. Geometries were fully optimized as minima or transition states using the Turbomole program package.31,32
benzene), 53.68 (CMe3), 32.04 (CH3), −0.08 (Si(CH3)3), −1.23 (N3Si(CH3)3). 29Si NMR (99 MHz, benzene-d6, ppm) δ 15.41, 7.05. UV–Vis (THF, λ (nm) (ε, M−1·cm−1)): 485 (2343). IR-ATR (cm−1): 3048 (VW), 2962 (W), 1523 (VW), 1472 (W), 1422 (S), 1391 (W), 1358 (W), 1274 (W), 1237 (W), 1207 (S), 1148 (m), 1078 (W), 1021 (W), 989 (m), 966 (W), 923 (W), 832 (S), 789 (W), 751 (S), 724 (W), 704 (S), 641 (W), 609 (W). Elemental analysis of this species did not yield satisfactory results, which is attributed to the demonstrated thermal instability of this complex, leading to “decomposition” to form species 5.

(PhC(NBu)3)2Fe(C2tBu)(CNSMe3) (5). TMSN3 (7.5 μL, 0.153 mmol) was added by a pipette to a solution of 3 (36 mg, 0.055 mmol) in a J-Young tube or Schlenk tube while stirring at 80 °C. After heating for 90 min, the product was isolated (yield: 20.3 mg, 50%) as a purple-red solid by removing all solvents and other volatile materials under vacuum and washing with cold pentane. At shorter reaction times, this product coexists with complex 4 according to NMR spectroscopy. X-ray quality crystals were collected by dissolving the obtained solid in benzene solution and slow evaporation of the solution at room temperature. 1H NMR (500 MHz, benzene-d6) δ 7.36 (s, 1H, Ar-H), 7.31 (d, 3H, Ar-H), 7.01–6.99 (m, 4H, Ar-H), 6.96 (m, 2H, Ar-H), 5.12 (s, 6H, benzene-H), 1.43 (s, 36H, NtBu-H), 0.39 (s, 9H, Si(CH3)3). 29Si NMR (126 MHz, benzene-d6, ppm) δ 169.61 (NCN), 133.69, 129.24, 128.47, 127.67 (133.69–127.67: Ph), 75.31 (Fe-benzene), 53.61 (CMe3), 31.75 (CH3), 3.79 (NNi(SiMe3)). 29Si NMR (99 MHz, benzene-d6, ppm) δ 7.42, −20.71. UV–Vis (THF, λ (nm) (ε, M−1·cm−1)): 530 (592). IR-ATR (cm−1): 3357 (VW), 2961 (w), 2029 (S), 1597 (W), 1473 (VW), 1419 (S), 1392 (W), 1358 (m), 1237 (W), 1204 (S), 1074 (W), 1019 (S), 924 (VW), 832 (S), 787 (W), 746 (S), 704 (S), 649 (VW), 641 (VW), 609 (W). Anal. calc’d for C83H52FeNiSi3C: 63.30; H, 8.31; N, 9.46. Found: C, 60.19; H, 7.99; N, 8.82.

(PhC(NBu)3)2Fe(C2tBu)(Ph2CO) (6). Benzophenone (437 μL of a 100 mg/ml stock solution in benzene) was added dropwise to a solution of 3 (15.6 mg in benzene (5 mL) in a J-Young tube or Schlenk tube at 80 °C with stirring. Product 6 was isolated as a dark greenish-black solid by washing with cold pentane after removing all solvents and other volatile materials. Yield: 12 mg, 60%. X-ray quality crystals were collected by dissolving the solid in diethyl ether solution and then placing the sample in a −30 °C freezer. 1H NMR (500 MHz, benzene-d6) δ 8.36 (d, 0.5H, Ar-H), 7.76 (d, 2H, Ar-H), 7.52 (d, 1H, Ar-H), 7.31 (d, 0.5H, Ar-H), 7.25 (t, 2H, Ar-H), 7.06–6.95 (m, 9H, Ar-H), 6.98 (d, 1H, de-ArCH), 6.17 (dd, 1H, de-ArCH), 5.86 (m, 1H, de-ArCH), 5.65 (dd, 1H, de-ArCH), 4.90 (d, 1H, de-ArCH), 5.07 (s, 6H, benzene-H), 1.59/1.45/1.31/0.97 (s, 9H, NtBu-H). 13C NMR (126 MHz, benzene-d6, ppm) δ 170.46 (NCN), 167.56 (NCN), 159.33–122.22 (18 signals: 6 C + 18 C; CCCHCHCH + C of 3 Ph), 78.46 (Fe-benzene), 53.23 (CMe3), 53.14 (CMe3), 52.67 (CMe3), 52.38 (CMe3), 32.12 (CH3), 32.01 (CH3), 31.15 (CH3), 31.09 (CH3). 29Si NMR (99 MHz, benzene-d6, ppm) δ 65.57, 33.66. UV–Vis (THF, λ (nm) (ε, M−1·cm−1)): 350 (4785), 435 (2782). IR-ATR (cm−1): 3052 (VW), 2965 (W), 2962 (VW), 1647 (VW), 1596 (VW), 1472 (W), 1421 (S), 1390 (m), 1358 (m), 1264 (m), 1204 (S), 1106 (VW), 1072 (W), 1009 (W), 970 (W), 923 (W), 865 (W), 790 (m), 745 (S), 722 (VW), 699 (VS), 607 (S), 544 (S). Anal. calc’d for C48H29Fe2Ni2O3Si6: C, 70.48; H, 7.48; N, 6.71. Found: C, 65.07; H, 7.09; N, 6.15.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c01369.

General information; synthetic procedures of new compounds, including NMR, IR, and UV–Vis spectra; reaction of 3 with TMS-azide followed by NMR; EDA and DFT calculations; single-crystal X-ray data diffraction (PDF)

Computational details (ZIP)

**Accession Codes**

CCDC 2157512–2157516 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

**AUTHOR INFORMATION**

**Corresponding Authors**

Jarl Ivar van der Vlugt – van’t Hoff Institute for Molecular Sciences, University of Amsterdam, 1098 XH Amsterdam, The Netherlands; Institute of Chemistry, Carl von Ossietzky University, 12629 Oldenburg, Germany; orcid.org/0000-0003-0665-9239; Email: jjarl.livar.van.der.vlugt@uni-oldenburg.de

Bas de Bruin – van’t Hoff Institute for Molecular Sciences, University of Amsterdam, 1098 XH Amsterdam, The Netherlands; orcid.org/0000-0002-3482-7669; Email: b.debruin@uva.nl

Jeremy Krogham – School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China; Email: jkrogham@shanghaitech.edu.cn

**Authors**

Zhiyuan He – School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China; van’t Hoff Institute for Molecular Sciences, University of Amsterdam, 1098 XH Amsterdam, The Netherlands

Lingyu Liu – School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China

Felix J. de Zwart – van’t Hoff Institute for Molecular Sciences, University of Amsterdam, 1098 XH Amsterdam, The Netherlands;
orcid.org/0000-0002-0981-1120

Xiaolian Xue – School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China

Andreas W. Ehlers – van’t Hoff Institute for Molecular Sciences, University of Amsterdam, 1098 XH Amsterdam, The Netherlands; Department of Chemistry, University of Johannesburg, Johannesburg ZA-2006, South Africa

KaKing Yan – School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China;
orcid.org/0000-0001-6963-6099

Serhy Demeshko – Department of Chemistry, Georg August University, 37077 Göttingen, Germany

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.2c01369

**Author Contributions**

*Z.H. and L.L. contributed equally to this work. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors acknowledge the support from the Analytical Instrumentation Center of SPST and ShanghaiTech University (contract no. SPST-AIC1011291). This work was supported by National Natural Science Foundation of China (grant no. 21801166) and start-up funding from ShanghaiTech University. Financial support from the Advanced Research Center for Chemical Building Blocks (ARC-CBBC, project
REFERENCES


(b) Tsipis, A. C.; Depastas, I. G.; Tsigis, C. A. Diagnosis of the σ-, π- and (σ + π)-Aromaticity by the Shape of the NICSscan Curves and Symmetry-Based Selection Rules. *Symmetry 2010*, 2, 284–319.


(c) Heine, T.; van Ragüé Schleyer, P.; Corinnebœuf, C.; Seifert, G.; Revikane, R.; Weber, J. Analysis of Aromatic


(33) TURBOMOLE, Version 7.5.1 (TURBOMOLE GmbH, Karlsruhe, Germany).


---

Recommended by ACS

Silicon Carbamates by CO2 Fixation: Brønsted Acid Labile Precursor of a Lewis Superacid
Deborah Hartmann, Lutz Greb, et al.
SEPTEMBER 16, 2022
INORGANIC CHEMISTRY

Multimetallic Permylentale Nutride Complexes
Duncan A. X. Fraser, Dermot O’Hare, et al.
JULY 25, 2022
INORGANIC CHEMISTRY

Synthesis, Structure, and Reactivity of a Superbulky Low-Valent β-Diketiminate Al(I) Complex
Samuel Grams, Sjoerd Harder, et al.
OCTOBER 04, 2022
ORGANOMETALLICS

Diverse Thermal and Photochemical Reactivity of an Al–Fe Bonded Heterometallic Complex
Soumen Sinhababu and Neal P. Mankad
JULY 08, 2022
ORGANOMETALLICS

Get More Suggestions >