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Diazoalkanes in Low-Coordinate Iron Chemistry: Bimetallic Diazoalkyl and Alkylidene Complexes of Iron(II)

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Abstract

Addition of trimethylsilyldiazomethane and its conjugate base to β -diketiminate-iron precursors gives novel dinuclear complexes in which the bridges are either diazomethane derivatives or an alkylidene. One product is an unusual bridging alkylidene complex containing two three-coordinate iron(II) centers. On the other hand, syntheses using the deprotonated diazomethane give two bridging diazomethyl species with binding modes that have not been observed in iron complexes previously. In the presence of coordinating THF solvent, a diiron(II) compound with μ -N bridges rearranges to a more stable isomer with μ -N,C bridges, a process that is accompanied by a 1,3-shift of a silyl group.

Synopsis

Trimethylsilyldiazomethane leads to low-coordinate alkylidene and diazomethyl complexes of iron(II) that have been characterized by crystallography, spectroscopy, and calculations.

Diazoalkane complexes have a variety of possible coordination modes: terminal or bridging, σ - or π -bound, or some combination thereof.^{1, 2} Though most studies have focused on their role as precursors to metal alkylidene complexes,³ diazoalkanes have also been studied with respect to their redox activity, and as N₂ surrogates for evaluation of mechanisms for cleaving N-N triple bonds.⁴ Since β -diketiminate-iron(I) precursors have led to redox-active ligands,^{5–8} N₂ binding and cleavage,^{9–13} and Fe-N multiple bonds,^{14–16} the behavior of

Supporting Information

General information, experimental procedures, spectroscopic data and X-ray crystallographic data in CIF format are available free of charge via the Internet at <http://pubs.acs.org>.

diazoalkanes in this system was expected to lead to novel coordination chemistry. Here we report the use of trimethylsilyldiazomethane to prepare new products, including a β -diketiminato-supported diiron alkylidene with two highly unsaturated iron centers and an Fe-Fe distance under 3 Å, as well as two isomers of dimeric species including the first example of *C*-coordination of the trimethylsilyldiazomethyl anion to a transition metal. This is the first system in which complexes have been isolated with both bridging modes of the NNC unit, and the ability to isolate both of them enables us to compare their stabilities.

Treating the known^{17–19} $[\text{LFe}(\mu\text{-Cl})]_2$ with just over 2 molar equivalents of KC_8 at low temperature followed by the addition of trimethylsilyldiazomethane forms the diiron alkylidene complex $[\text{LFe}]_2\text{C}(\text{H})\text{SiMe}_3$ (**1**) where $\text{L} = \text{MeC}[\text{C}(\text{Me})\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)]_2$ (Scheme 1). There are few examples in which addition of trimethylsilyldiazomethane to a first-row transition metal complex results in loss of N_2 and formation of an alkylidene complex.^{1, 2, 20–23} Compound **1** is distinctive because it does not have additional bridging ligands between the two metal centers like other bridging alkylidene complexes.²⁴

Two X-ray crystal structures of **1** have been solved, and the structures have different co-crystallized solvents but very similar metrical parameters. One is shown in Figure 1, and the other is in Figure S20. The results clearly show that the diazoalkane has lost N_2 and formed a bridging alkylidene. The Fe-C bond lengths range from 1.956(6) to 1.973(6) Å, and are only slightly shorter than reported bridging iron(II) alkylidene complexes (ave. 2.02(6) Å in the CCSD).^{25–27} The iron sites are trigonal planar, each having a sum of angles $> 359^\circ$. The Mössbauer spectrum of **1** at 80 K shows two quadrupole doublets with identical isomer shifts but different quadrupole splittings ($\delta_1 = 0.62$ mm/s, $|E_{\text{Q}1}| = 1.27$ mm/s; $\delta_2 = 0.62$ mm/s, $|E_{\text{Q}1}| = 2.01$ mm/s; Figure S6). The isomer shifts are very similar to those of other high-spin, three-coordinate iron(II) complexes.^{6, 8, 28} The large difference in quadrupole splittings may appear surprising for the similar sites, but previous work has shown that the quadrupole splitting of planar three-coordinate iron sites is very sensitive to even slight geometric variations.²⁸ The solution magnetic moment from the Evans method at room temperature is 4.77(4) BM per dimer, which is lower than the spin-only uncoupled value of 6.9 BM and suggests antiferromagnetic coupling between high-spin d^6 ions.

The Fe-Fe bond distances of 2.93(2) Å in the structures of **1** suggest the possibility of a weak Fe-Fe bond, as the FSR (Formal Shortness Ratio)²⁹ is 1.25. The Fe-Fe distance is shorter than twice the canonical covalent radius for high-spin Fe (1.52 Å),³⁰ but is longer than most Fe-Fe single bonds (ave. 2.62(11) Å in Cambridge Structural Database).²⁵ We considered the hypothesis that there is a Fe-Fe bond, but that the steric bulk from the diketiminato aryl groups elongates the Fe-Fe bond, weakening the bonding interaction. In order to evaluate this hypothesis, we used DFT (Density Functional Theory) calculations and NBO (Natural Bond Orbital) analysis.

Geometry optimization of a full model of **1** with the M06 functional gave excellent agreement with the crystallographic geometry. The optimized structure reproduced the Fe-Fe distance as well as the 0.02 Å difference between the two Fe-C bond lengths (see Supporting Information). NBO analysis of a broken-symmetry model identified no formal bond between the two Fe centers. Figure 2 shows the two highest-energy bonding orbitals as well as the

nonbonding d -orbitals. No substantial direct Fe-Fe interaction is evident (the lowest energy orbital shown in Figure 2 is the superposition of two Fe-C bonding orbitals). Finally, we performed scans of different Fe-Fe distances for a truncated model **1^{trunc}** that lacks aryl groups, in order to evaluate the influence of sterics on the energy. The calculated energy of **1^{trunc}** had a shallow minimum with Fe-Fe = 2.59 Å. Stretching the Fe-Fe distance in **1^{trunc}** to the distance observed in **1** caused an increase in energy of only 2 kcal/mol, which is small enough that it can hardly be considered a bond. The energy gain increased to 15 kcal/mol with extension of the Fe-Fe distance to 3.6 Å (Figure S26), at which point the lengthening of Fe-C bonds to 2.06 Å in the strained structure explains the destabilization. Thus, the combination of NBO analysis, the lack of direct bonding/antibonding interactions between the Fe atoms in the frontier orbitals, and the muted dependence of the energy on the Fe-Fe distance all argue against any significant Fe-Fe "bond" existing in **1**.

The alkylidene complex **1** was stable for 3 days at 80 °C in C₆D₆, as judged by ¹H NMR spectroscopy. Attempts to remove the silyl group using fluoride sources such as Bu₄NSiPh₃F₂, Bu₄NF, and Me₃SnF led to no reaction or to loss of the diazoalkane. Attempts to form a bridging alkylidyne complex through deprotonation of the alkylidene C-H with KO^tBu, PhLi, and KH led to decomposition.

Further attempts toward synthesis of an alkylidyne complex used the lithium salt of trimethylsilyldiazomethane ([Li][CN₂(SiMe₃)N₂]), and the reactions are shown in Scheme 2. Addition of [Li][CN₂(SiMe₃)N₂] to [LFe(μ-Cl)]₂ in Et₂O gave a dimeric complex **2**, in which the N terminus coordinates to Fe (Figure 3). The C-N distance of 1.15(3) Å indicates a triple bond, and thus we suggest the bond orders shown in Figure 3. These indicate that the diazomethyl ligand has transferred charge from C to the terminal N. This coordination mode has previously been seen in a Ga complex.³¹ In contrast, when the same reaction is performed in THF, the trimethylsilyl group migrates to the terminal N, leading to a CNN bridging dimer, [LFe(μ-CNN(SiMe₃))]₂ (**3**, Figure 3). The C-N distance is again short at 1.173(7) Å, indicating a triple bond. This type of isomerization to a bridging diazoalkyl ligand is unknown for transition metal systems, though it has been seen with lanthanides and uranium.^{32–35} The known aluminum complex [(CH(SiMe₃)₂)Al(μ-NNC(SiMe₃))]₂ has the same CNN bridging core, but its trimethylsilyl group is coordinated to carbon.³¹

Using 2,5-dimethyltetrahydrofuran as a solvent led to exclusive formation of **2**. Therefore, the differentiation between formation of **2** and formation of **3** appears to be a kinetic phenomenon that is dependent on the coordinating ability of the solvent. Monitoring a mixture of [LFe(μ-Cl)]₂ and [Li][CN₂(SiMe₃)N₂] in THF at 25 °C over time through ¹H NMR aliquots dissolved in C₆D₆ shows that **2** is formed first in the THF reaction mixture but over the course of 30 minutes, **3** is ultimately formed (Figure S5). Further, **2** isomerizes to **3** upon standing in THF for 3 hours at 25 °C. However, leaving **3** at RT as a solution in diethyl ether or 2,5-dimethyltetrahydrofuran for two days did not lead to the formation of any **2**. This evidence supports the assignment of **2** as the kinetic product and **3** as the thermodynamic product, which can be accessed through a pathway involving coordination of THF.

The isomers of $[\text{Li}][\text{C}(\text{SiMe}_3)\text{N}_2]$ have been reported to be in equilibrium, with a preference for *N*- or *C*-lithiation that is similarly dependent on the coordinating ability of the solvent.^{36–39} Computations suggest that the *N*-lithiated species is thermodynamically favored but solvation of the metal diminishes this preference until in pure THF, the *C*-lithiated species is favored (Figure 4).³⁶ This is the same preference we observed in the iron complexes **2** (favored in Et₂O) and **3** (favored in THF), though we also observe a silyl shift. Importantly, we have characterized both C- and N-bound isomers crystallographically in the same system for the first time.

We have also characterized **2** and **3** spectroscopically. The Mössbauer spectra of **2** and **3** indicate that there is only one type of iron environment within each dimer (**2**: $\delta = 0.77$ mm/s, $|E_Q| = 1.94$ mm/s; **3**: $\delta = 0.76$ mm/s, $|E_Q| = 2.17$). These parameters are typical for tetrahedral high-spin iron(II) systems.^{6, 8, 28} Free diazoalkanes have characteristic $\nu(\text{C}=\text{N}=\text{N})$ stretches in the infrared spectrum near 2100–2200 cm^{−1}.^{1, 2} When bound to a metal center, the frequency shifts to lower energy as the N–N bond order decreases and the C–N bond order increases.^{1, 2} Diazoalkyl complexes are characterized by lower stretching frequencies $\nu(\text{C}=\text{N}=\text{N})$ in the range of 1950–2035 cm^{−1} (Table 1).^{31–34} As expected, complex **1** has no bands in the 1700–2500 cm^{−1} region. Complexes **2** and **3** do exhibit stretching frequencies in the 1950–2100 cm^{−1} range (Table 1). Overall, the $\nu(\text{C}=\text{N}=\text{N})$ stretching frequencies and core bond lengths and angles of **2** and **3** are comparable to literature examples.²²

In summary, three novel iron β -diketiminate complexes have been synthesized and characterized: a diiron alkylidene with two three-coordinate iron sites, as well as two isomeric diazoalkyl complexes. The latter highlight the ability of silyl groups to shift position readily between positions on an NNC bridge.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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ABBREVIATIONS

THF tetrahydrofuran

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Figure 1.

Two views of the solid-state molecular structure of $[\text{LFe}]_2\text{C}(\text{H})\text{SiMe}_3$ (1). Thermal ellipsoids are displayed at 50% probability. The aryl groups of the β -diketiminate ligands and solvent of crystallization are omitted for clarity.

Figure 2. Frontier orbitals in $[\text{LFe}]_2\text{C}(\text{H})\text{SiMe}_3$ (1). S represents the overlap between correlated orbitals. The bottom two orbitals are doubly occupied, and have Fe-C bonding character.

Figure 3.

Solid state molecular structures of **2** (left) and **3** (right). Thermal ellipsoids are displayed at 50% probability and the aryl groups of the β -diketimate ligands have been omitted for clarity.

Figure 4.
Isomers of [Li][CN₂(SiMe₃)N₂]^{36–39}

Scheme 1.
Synthesis of $[\text{LFe}]_2\text{C}(\text{H})\text{SiMe}_3$

Scheme 2.
Syntheses of Iron Diazoalkyl Complexes

Table 1
Comparison of $\nu(\text{C}=\text{N}=\text{N})$ stretching frequencies, C-N and N-N bond lengths in compounds 2 and 3

	Metal	IR (cm^{-1}) $\nu(\text{C}=\text{N}=\text{N})$	C-N bond ^a (Å)	N-N bond ^a (Å)	Ref.
2	Fe	2063, 1984	1.15(3)	1.25(3)	this work
	Ga	2120	1.16(1)	1.25(1)	31
3	Fe	2077, 1989	1.173(7)	1.319(6)	this work
	U	2121	1.176(3)	1.308(3)	34
	Sm	2057, 1974	1.169(4)	1.328(3)	33
	La	2063, 1970	1.162(2)	1.335(2)	33
	Y	2058, 1983	1.159(5)	1.338(3)	32
	Yb	2087	1.178(9)	1.326(6)	32

^aIn some cases, inequivalent bond distances have been averaged.